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

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Declaration: I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Resumo

A Ria de Aveiro representa um importante ecossistema em Portugal. Com o objetivo de analisar a distribuição de vários elementos traço (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn) e avaliar a contaminação destes elementos, 119 amostras de sedimentos superficiais (5 cm) foram recolhidas em todos os canais principais. Através de métodos geoestatísticos, foram obtidas as distribuições espaciais para cada elemento para 65 % da área da Ria.

Os resultados demonstraram, através dos hotspots identificados, uma forte associação com fontes antropogénicas, principalmente relacionadas com atividades de transportes marítimos e outras razões como fábricas de fertilizantes, loiças, entre outras. Foram também identificados fatores naturais que influenciam estas distribuições, como as correntes marítimas e as residuais provenientes dos rios, o tempo de residência das partículas e as caraterísticas dos sedimentos como o teor de matéria orgânica e o tipo de partícula.

Através dos resultados obtidos a partir da avaliação do grau de contaminação dos sedimentos, foi possível concluir que aproximadamente 87% das amostras analisadas apresentam estar limpas ou possuir uma contaminação vestigial por elementos traço, não representando perigo. Contudo, as restantes 13.5% das amostras já apresentaram contaminação por As, Pb e Hg. Praticamente todas estas amostras foram recolhidas no canal da Murtosa, tendo sido considerado o local mais contaminado da Ria. No entanto, a partir desta avaliação e dos stocks obtidos em geral (em toneladas: As-61; Cd-0,84; Cr-124; Cu-46; Pb-92; Hg-0,60; Ni-55; Zn-444), a Ria apresentou menos contaminação por elementos traço do que era expetável.

Palavras-chave: Ria de Aveiro, Elementos Traço, Contaminação, Distribuição Espacial, Método Geoestatístico, Fontes Antropogénicas, Correlações

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 and Hg. 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

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Nomenclature

AMA	Advanced Mercury Analyzer
CRM	Certified Reference Materials
GIS	Geografic Information System
GPS	Global Positioning System
$ICP-MS$	Inductively Coupled Plasma Mass Spectrometry
IDW	Inverse Distance Weighting
LOI	Loss On Ignition
$NRCC$	National Research Council Canada
OM	Organic Matter
POP	Persistent Organic Pollutant
PP	Polypropylene
TIN	Triangulated Irregular Network

Chapter 1

Introduction

1.1 Motivation

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 [1, 2]. 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 [3, 4].

Although there are several studies related to this problem in various places, both national and international, the case of Ria de Aveiro and its possible level of contamination by trace elements was never properly studied. Even though, it is a place known for having high anthropogenic activity and at the same time being densely populated [5]. This study becomes extremely important in order to have an environmental assessment of Ria de Aveiro concerning trace elements pollution, evaluating the distribution of these elements, and identifying possible sources. In addition, 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. In this way, it would be possible to give scientific based knowledge for mitigation and remediation implementation measurements, in order to protect this ecosystem from this type of pollution.

1.2 Aim of the study

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 [6]), identify possible anthropogenic sources and other factors responsible for the obtained distributions, and calculate the stocks of each contaminant in the study area. Several studies have already been done regarding trace elements, mainly on Hg due to the historical pollution by this metal in one of the main channels of the Ria (Murtosa) [7]. However, these studies have often not given the same emphasis to the other elements, compared to Hg, and no study has properly assessed their distribution along the Ria de Aveiro. 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 [8]. Therefore, an environmental assessment is also another objective of this study, in terms of the sediment's degree of contamination (Portaria nº 1450/2007) [6], 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.

1.3 Thesis Structure

This thesis is organized into 8 chapters. Chapter one presents the motivation for this study, its objectives, and an explanation of its structure. Chapter two refers to the literature review to understand what is already known about the topic under study. First, a presentation of what heavy metals are and a description of the trace elements under analysis and their possible sources were given. Second, previous studies on heavy metals in the Ria de Aveiro and two case studies that resemble the one done in this thesis were analyzed. Chapter three describes the study area of this work, in this case, the Ria de Aveiro. Chapter four describes the sampling methods. Chapter five explains the various analytical methods used to obtain the organic matter content, to determine the various metals needed for the study, to perform quality control, to obtain the maps of concentration variation, and to calculate the stocks of each of the metals. Chapter six presents the results and discusses them. It focuses on several topics: characterization of the sediment of the Ria de Aveiro, explanation of the distribution of the metal concentrations, suggestion of possible anthropogenic sources and other responsible factors, relation between the metals themselves and also concerning the sediment characteristics, comparison of the results obtained with previous studies in the Ria and studies from other places, presentation of the stocks, and evaluation of the degree of contamination of the sampled sediments. Chapter seven presents the conclusions obtained from this study. Chapter eight presents goals for future work based on this study, thus finalizing the thesis.

Chapter 2

Literature Review

2.1 Estuaries and coastal zones

Coastal zones constitute a wide group of ecosystems, such as beaches, lagoons, estuaries, among others. Given their high ecological, economic and social value, a large part of the world's population resides near these areas, providing a space for large metropolitan areas [9].These ecosystems have a very important environmental role, representing not only areas rich in biodiversity but also areas with essential regulatory functions. With the high oscillations and fluctuations that come from the tidal cycle, the coastal zones are responsible for controlling the effects of these natural events, not allowing their consequences to be felt on the mainland [10].

Among all these examples of coastal zones, estuaries represent a very special type of ecosystem with unique characteristics. The definition for estuary that was best accepted was suggested by Cameron et al. (1963) which consists of the following sentence: ”Estuaries are semi-enclosed coastal water bodies that have a free connection with the sea and in which seawater is measurably diluted with fresh water from land drainage.” Estuaries are complex environments, where freshwater and saltwater mix, which causes a massive variation in salinity, temperature, flow direction, etc [10]. Its area can be defined by three zones: the marine zone, which is directly connected to the sea and where there is basically only saltwater, the medium zone, where there is a mixture of fresh and saltwater and finally, the fluvial zone, where freshwater is predominant, although there is still a tidal influence [12].

Regarding its ecological value, estuaries serve as shelter and reproduction areas for many species of fish, birds, plants, crustaceans, mollusks, among others [10]. Due to the confluence of waters in this ecosystem, its hydrodynamics favors the retention of nutrients, which is crucial to biological activity. Thus, estuaries represent a site responsible for a high level of biodiversity [13]. At the same time, it is also fundamental in terms of regulation, as it acts as a ”buffer system” that prevents the tides from interfering beyond the shores of the estuary [10].

Through its natural features, it is also possible to understand the existence of a high economic and social value associated with estuaries. Because it is a naturally sheltered place, it is conducive to the development of port areas, water sports, and other types of leisure activities. Associated with the high level of biodiversity, it is possible to develop fishing and other activities based on the natural resources that the estuary offers, which is vital to the economy of the riverside communities. Despite the mixture of fresh and saltwater, through the fluvial zones, it is possible to feed the domestic and industrial water supply. Consequently, the estuary also ends up as a receptor of effluents, as it has favorable hydrodynamic characteristics for the dilution and transport of effluents to the sea [13]. However, despite being systems that naturally adapt to environmental and climatic fluctuations, estuaries are also quite fragile areas that, due to all the urban and industrial development around them, often experience severe disturbances caused by man [10].

2.2 Pollution in estuaries and coastal zones

Among the various types of coastal ecosystems, estuaries have been the most explored by man. As previously mentioned, these environments have been used for several purposes, one of which is to serve as a receptor for industrial and municipal effluents, sewage sludge, dredged material and agricultural runoff. Furthermore, accidents such as oil spills and chemical leaks do happen, even if not that often. Although there are hydrodynamic characteristics that favor dilution and dispersion, due to the exponential economic growth and urban development, this type of activity has also increased, becoming a serious problem of environmental pollution and human health [14]. Furthermore, because of these reasons, the hydrodynamic processes only lead to larger areas being subject to contaminants [15].

Several contaminants associated with this type of pollution are, for example, heavy metals, toxic nonmetals, pathogens, petroleum hydrocarbons, and the sediment at the bottom of the estuaries act as sinks for these contaminants. In this way, due to currents, erosion process and others physical-chemical interactions, it is possible to transport these contaminants to other ecosystems. Usually they enter the water body through various processes: direct discharges, ship discharges, river inflow, atmospheric deposition, and runoff from non-point land sources [14, 16, 17].

All of these pollutants are of great concern to marine organisms because of their generally toxic characteristics. There are two pollution pathways, a direct one through water and an indirect one through the food chain [18]. Regarding the second route, bioaccumulation and amplification are capable of leading these contaminants to highly toxic levels. In addition, these processes can carry the contaminants beyond the ecosystem where the pollution started, easily reaching human consumption. The severe consequences result in changes in the vital functions of these organisms, such as at the cellular and tissue level, alterations in behavior and reproduction, often leading to death [18]. Easily over time and through exposure to these pollutants, species abundance and diversity decrease, leading to catastrophic effects on the ecosystems. For these reasons, it is crucial to invest in short and long term monitoring of these aquatic systems, regarding these contaminants, in order to avoid possible negative impacts or even identify the origin of the pollution and be able to implement remediation or mitigation measures[14].

2.3 Trace element contaminants

Trace element contaminants are natural metallic and non-metallic elements components of the earth's crust, that belong mostly to the transition group of the periodic table and have a relatively high density compared to water, more than 5 g/cm3 [19–21]. These elements are known for being non-degradable, persistent, and toxic even in low concentrations [1, 2]. These characteristics make them hazardous due to their bioaccumulation, as they cannot be metabolized by the body and therefore, accumulate easily in the tissues [1]. In this way, it allows them to biomagnify in the food chain.

These trace elements occur in lower concentrations in the environment, but these levels have been highly altered due to anthropogenic activities. As a result of the rapid industrialization and urbanization that has taken place over time, emissions from urban, industrial, mining, and agricultural sources have been released, having an enormous impact in soils, water and sediments [22]. In fact, sediments are sinks of trace elements discharge. Hence this type of pollution has increasingly become a global problem due to the increase in trace elements emissions that cause environmental and public health problems [2].

One of the major problems and target of great study regarding these contaminants is the consequences to the aquatic systems. These ecosystems are complex due to being subject to several inputs, internal and external, over time. They are the ecosystems most subject to contamination, especially freshwater environments, due to the use of water in multiple industrial, urban and agricultural processes and all the proximity to urban and industrial developments, turning the water body into a receptor for effluent discharges [3, 4]. Nevertheless, there are natural and anthropogenic sources and contaminants can enter through, for example, atmospheric deposition, erosion of geological matrix, continental weathering, forest fires, or anthropogenic discharges. Usually, these elements remain either in dissolved or particulate form until settling down at the bottom or be taken up by organisms [1]. Their bioavailability can be influenced by physico-chemical parameters such as pH, temperature, adsorption, among others [19, 23].

2.4 Trace elements and their sources

Most elements are also designated as trace elements due to their low abundance in the environment (µg/kg range to less than 10 mg/kg) [19]. Some trace elements are considered essential from the biological point of view (Cu and Zn), while others are nonessential (the remaining elements of this study), but even the essential ones can be toxic depending on their concentration and availability [24, 25]. That is why many trace elements are considered dangerous or potentially harmful, corresponding a worldwide concern [24]. The trace elements referred in the dredging regulation (Portaria nº 1450/2007) consist of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn) and were used in this study [6].

Arsenic is a ubiquitous metalloid with three allotropic forms [26]. Frequently As is associated with sulfur (S), oxygen (O), and iron (Fe), being rare to find it in free state [27]. Arsenic presents a high health risk, being the inorganic forms the most toxic [28]. Arsenic compounds are a by-product that results from recovery during the smelting process, with Cu and Pb as primary sources [26]. Due to anthropogenic emissions, As can be found in nature through the combustion of fossil fuel, petroleum refining, production of pesticides, mineral fertilizers, metals, drugs, mining, paints, wood preservation, manufacturing of glasses, among other activities [26–30]. Thus, soil and water pollution lead to an accumulation in the food chain, making As the most common cause of acute heavy metal poisoning in adults [28, 29].

Cadmium is an electropositive metal with is divalent form (Cd^{2+}) as the most common. It is a non-essential element, having no biological function in the human body, and ends up being very toxic due to the difficult natural elimination [26, 31, 32]. Cadmium is also a by-product, but in this case mainly of the Zn industry, having a low melting point [26]. Normally is used in Ni-Cd batteries, low-melting alloys, electroplating, PVC plastics, paint pigments, insecticides, commercial fertilizers and fuels. Although Cd exists naturally in nature, it is also emitted into the environment through the activities mentioned above, finding its way easily into the soil and water [26, 29, 33, 34]. For these reasons, food is the main source of human contamination other than smoking or occupational exposure of people during practices with this metal [34].

Chromium (Cr) is a silvery and malleable metal, relatively abundant in the earth´s crust, with high oxidation resistance [26, 35]. There are a lot of controversies involving this metal because, depending on its oxidation state, Cr can range from being an essential trace element, to chemically and biologically inert or even to an environmental and health toxic [26, 35]. However, like any other trace element, concentrations of Cr above the threshold limit represent a threat, regardless of its form. Due to all the dangerous effects, Cr is genotoxic and carcinogenic[35]. This metal has several applications, as it is used in pigments, fertilizers, textile, metal plating, wood preservation, corrosion-resistant alloys, and recently as a catalyst [26, 33, 36–38].

Copper is a reddish and malleable metal and is a good conductor of both heat and electricity [26]. It is abundant in the earth's crust, an essential micronutrient, and takes a significant role in several metabolic processes. Nevertheless, in high concentrations, Cu becomes toxic [39]. That is why preserving the natural concentrations in the environment is important and all the anthropogenic activities related to Cu compromise this balance. Copper is frequently used in the electrical industry, agriculture sector, and health field, being present more specifically in batteries, pigments, alloys, fuels, catalysts, kitchenware, fertilizers, pesticides, antibiotics, drugs, among several other examples [26, 33].

Lead is a soft, bluish-gray metal, highly malleable, a poor conductor of electricity and unlike Cu, exists in small quantities in the earth's crust [26]. Lead is a toxic metal to organisms and ecosystems and is very persistent, making natural elimination difficult [2]. Despite this, some characteristics like low melting point, easy to work with, and durability made this metal a popular choice for some industrial sectors [26]. Anthropogenic activities are the main reason for contact and exposure of living beings to Pb and it is mainly used in pipes, drains, soldering material, batteries, paint pigments, PVC plastics, x-ray shielding, pesticides refiners, and alloys [1, 23, 33]. The well-known leaded gasoline was a worrying source in the past but eventually, the addition of Pb to gasoline was banned [40].

Mercury is a silvery-white glistening metal that exists in organic, inorganic, and elemental forms, being the methylmercury (organic) the most toxic form [26, 41]. Mercury is a persistent toxic substance, which at room temperature is in a liquid state and has unusual high volatility [26, 42]. Is considered as a priority harmful substance, capable of interact with proteins, enzymes and cell membranes [17]. Although there are natural ways of emitting this metal into the environment, such as volcanic emissions, anthropogenic sources have increased over time and have become a strong cause of Hg contamination [1]. Significant producers of Hg are combustion facilities, waste incinerations, mining operations, chlor-alkali plants, paper industries and secondary steel production [43, 44]. Mercury was once added to paintings, but this practice was eventually banned. However, works made with these paints until the prohibition are still exposed and are therefore a possible source [1].

Nickel is a silvery-white, malleable, ferromagnetic metal with high corrosion resistance [26]. It is present in the environment in small concentrations, and can occur in form of sulfide, oxide and silicate minerals. Is also an essential nutrient for the proper functioning of plants, if do not exceed the threshold concentrations [45]. For this reason, the use of this metal in industrial activities accelerates Ni contamination in soils, turning this metal into a pollutant for agricultural environments and consequently leading to health problems [43, 45]. Nickel is commonly used in batteries and electroplating industries, pigments, alloy production, fertilizers, cement industry, as a catalyst in the chemical and food industry, fuels, jewelry, among other examples [26, 33].

Zinc is a bluish-white, relatively soft metal, which represents a nutritionally essential metal, in low concentrations, for biological, metabolic, and immunity functions [26, 46, 47]. Exists in natural concentrations in the environment, being present in the most varied places such as water and soil [43]. For this reason, the concentration of this metal in living beings needs to be regulated, and all the anthropogenic activities that involve Zn can compromise that balance. Most of the Zn comes from ores containing Zn sulfide minerals, which subsequently have various kinds of purposes such as batteries, pigments, alloys production, pesticides, fertilizers, glass, refiners, fuel, wood preservation, and pharmaceuticals [33, 48].

2.5 Previous studies regarding trace element contamination in the Ria de Aveiro

Over the years, the contamination of estuaries and coastal lagoons has increasingly become a topic of study and global concern [49]. Regarding the Ria de Aveiro, which represents an important and well-known aquatic ecosystem in Portugal, as it has a remarkably high focus on anthropogenic activity, it has become an enormous area of study, particularly for trace elements. From 1986 to the 1990s, several aquatic ecosystems gained media and political visibility due to several contaminations, one of them being the Ria de Aveiro, which was the target of frequent discharges [8]. However, most studies often focus only on Hg and the impact of its contamination. This situation is due to the history of the chlor-alkali plant in the Estarreja area, which for many years discharged effluents into the Ria de Aveiro without any controled legislation [50].

In the study conducted by Pereira et al. (1998) [7], concentrations of mercury were measured in surface sediments along the Estarreja channel and Laranjo basin. At the same time, organic matter and granulometry of the samples were determined in order to study possible relations between the metal and the sediment characteristics. It was concluded that the Hg concentrations varied between 0.32 and 343 mg/kg. A correlation was established between sediment granulometry and the metal, in which the highest values were found in muddy sand sediments (near the industrial discharge area), while the lowest values were found in sands. Regarding the role of organic matter, a correlation was also found between this parameter and Hg contents, with usually more Hg levels existing in sediments richer in organic matter. Lastly, a graph relating Hg concentrations with distance to the beginning of the Estarreja channel was obtained, which originated an inverse exponential curve, meaning that concentrations tend to decrease as the distance to that reference point increases.

Among the few studies involving the other trace elements, many of them aim to relate their impact to the life of local organisms and fauna. An example is the study conducted by Martins et al. (2013) [51] that aims to analyze the distribution of trace elements in sediments along the Ria de Aveiro and to evaluate the level of toxicity of these contaminants in benthic foraminifera species. A total of 29 samples were collected in the various channels of the Ria such as the Murtosa , Mira, Ílhavo, City, Aveiro canals and the Aveiro harbor area. Maps of Zn, Pb, Cu, Cr, and Hg concentrations were developed in a size grading format, where the size of the sample circles represent their concentration, in mg/kg. Other trace elements were also studied, although no distribution maps were presented.

Through the results obtained it was observed that similarly to study by Pereira et al. (1998) [7], there is an affinity between trace elements and fine particles, leading to higher concentrations of these contaminants in sediments with these granulometric characteristics. At the same time, organic matter, that is normally found in greater abundance in this type of sediment, acts as sinks for anthropogenic pollutants. It was concluded that there are high concentrations of Zn, Pb and Cu in the Aveiro canals and in the city channel, while there are high concentrations of As, Hg, Zn and Cr in the Murtosa channel. Areas with high residence time and cohesive sediments become sites prone to high levels of contamination, which in this case represent the type of site that these three channels are [51]. These levels of pollution were explained through the various anthropogenic sources existing in these locations such as ceramic, metallurgic, naval shipyard, and chemical industrial activities. Regarding the harbor area and its pollution levels, having a high oceanic influence, the source pointed out as the cause were the commercial and industrial activities that take place on these shores. Finally, it was suggested that the Ílhavo channel was a less contaminated area of the Ria, in comparison [51].

Other study was conducted by Gomes and Delgado (1993) [52] that related metals to clay minerals and possible sources. Samples were collected, both channel sediments and vibrocores in interfluves. It was verified that there is a high level of these contaminants in the sediments, and these are not uniformly distributed along the Ria. As expected, the channels have a higher contamination of metals due to the present physical conditions, such as longer residence time and lower current, and because most industrial activities are concentrated in the north and northwest of the Ria de Aveiro, these areas containing higher concentrations of metals [52]. Only four samples collected correspond to surface sediment, between the first 20 cm, where three were collected in the Ovar channel and the remaining one was collected in the Ílhavo channel. The concentrations of metals recorded from these samples are presented in Table 2.1.

Table 2.1: Obtained results of the study conducted by Gomes and Delgado (1993).

Trace Element	Concentration ranges (mg/kg)
Cd	1.5 - 2
Cr	43 - 51
Cu	33 - 59
Pb	50 - 59
Ni	43 - 63
Zn	277 - 1917

In the end, a relationship between metals and clay minerals has been observed, concluding that sediments with high clay content will lead to a higher concentration of metals.

However, none of the previously presented works provided significant information about the extensive area of the Ria de Aveiro or was focused on the spatial distribution of trace elements, which is crucial for a real assessment of contamination. Only two studies were carried out on the distribution of trace elements along the Ria de Aveiro. In the study conducted by Cachada et al. (2019) [53], 5 cm deep samples were taken at 22 sampling sites in the spring of 2008. Although the objective of the study was a general evaluation of the Ria and therefore to obtain a distribution of trace elements , a more detailed sampling was carried out in the Estarreja and Laranjo areas due to the pollution history. Among the various organic and inorganic contaminants analyzed, the concentrations of trace and major elements were determined through digestion followed by an ICP-MS analysis. Despite this intensive study, this research did not consider a sufficient number of samples for a detailed characterization of the Ria and also did not include Hg in the elements under analysis. Even though, there are several studies exclusively focused on this metal, due to the history of the Ria de Aveiro with Hg and the industrial activities related to it, it is important to take it into account in a complete study like the present one. Furthermore, it does not present a spatial variation, being limited only to the discrete distribution of the sampled points. However, for the present work, the results of this study (Table 2.2) will be useful for temporal and spatial comparison:

Table 2.2: Obtained results of the study conducted by Cachada et al. (2019).

Trace Element	Concentration ranges (mg/kg)
As	4.60 - 256
Cd	0.10 - 3.1
Cr	8.20 - 49.8
Cu	7.00 - 96.1
Pb	8.00 - 76.9
Ni	3.31 - 126
Zn	36.4 - 1270

The study conducted by Martins et al. (2013) [5], was also focused on the distribution of trace elements and a toxicity risk assessment of sediments. A total of 116 sediment samples collected from the main channels of the Ria were analyzed for elements concentrations, including Hg, where a sequential chemical extraction was used for the propose. The granulometry of the sediments was also studied and it was shown that the sediments vary greatly from sand to silt, with a marked distinction between the northern and southern parts of the Ria. The southern zone presented sediments with coarser particles, while the northern zone showed to consist of finer particles [5].

Concerning the trace elements, 5 distribution maps of Zn, Pb, As, Cu, and Hg concentrations in mg/kg were developed, although more elements were analyzed. Through this work, it was concluded that there are several polluted areas such as the end of the Ovar channel, Aveiro City canals, and Murtosa channel. Trace elements contamination such as Zn, Pb, As, Hg, Cu, Ni, and Cd was also identified and highlighted in the Largo do Laranjo area, located in the Murtosa channel known for its history of high anthropogenic activities. Compared to study conducted by Cachada et al. 2019 [53], this study considered a much larger number of sampling points, resulting in a more detailed and useful characterization for temporal and spatial comparisons, but again was limited to the distribution of sampled points, not developing a spatial variation of contaminants in the Ria de Aveiro.

For this reason, the present work is extremely relevant for the study of the actual level of contamination since no work of this type has ever been carried out so far in the Ria de Aveiro. A work which uses geostatistical spatialization methods for this type of assessment, something that has already been proven to be very useful in the evaluation of spatial variability and sources of trace elements in soils [54].

2.6 Spatial distribution studies using geostatistical spatialization methods combined with geographic information systems

The use of geostatistical spatialization methods is increasingly recurrent in several studies due to the additional information that can be obtained since through values obtained by sampling points it is possible to estimate values for unsampled areas. Furthermore, by combining these methods with a geographic information system, it becomes feasible to also create models that explore the correlation between different parameters. Therefore, characteristics such as variation and spatial pattern of the components under analysis can be explored.

One of several studies that have already used this approach is the study conducted by Savignan et al. [23], which aimed to study the spatial distribution of trace elements in the soil of south-western France and to identify possible natural and anthropogenic sources. By combining geostatistics with geographic information systems (GIS), the spatial variations of the various elements over the study area were determined and presented in maps, identifying anomalous concentrations. For this, an interpolation method called ordinary kriging was used through ArcGIS software. Through the maps and crossing them with databases about anthropogenic activities in the study area, it was possible to highlight the potential sources of contamination and understand how these elements got to the soil.

Another study that used maps to analyze spatial variation was conducted by Long et al. [55] which had the purpose of estimating the spatial distribution and health risk by As and other trace elements present in shallow groundwater around the Dongting Lake plain, in China. Using ArcGIS, the sampled points and their respective analyzed concentrations were represented on spatial variation maps, and an interpolation method called inverse distance weighting (IDW) was used.

Compared to study [23], different interpolation methods were used, something that should be suitable for the study area and the parameters that will be used as a basis for interpolation. It was concluded in the end that the maps obtained for the spatial distribution of trace elements, along with the respective parameters calculated as a health risk and pollution index, could be very useful for the construction and implementation of remediation and mitigation strategies, demonstrating the advantages, utilities, and importance of including this type of techniques.

Chapter 3

Study Area

Ria de Aveiro (Figura 3.1), located on the North-Western coast of Portugal, is a complex and irregular system of islands, intertidal zones and several channels, such as Ovar, Mira, Ílhavo, S. Jacinto, Espinheiro and Murtosa. 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 [7, 51]. What joins the many channels together is the big lagoon formed parallel to the coast. Ria de Aveiro extends for 83 km^2 or 66 km^2, depending on whether it is high or low tide, respectively. The water depth is, in average, below 3 meters, although it can reach almost 20 meters between the sea outlet and the entrance to the lagoon [51, 56].

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 [57].

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. Transportation, fishing, shipbuilding, agriculture, water sports and tourism are some of the activities that contribute to multiple effluent discharges [58]. 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 [59]. One of the best known cases is related to mercury contamination into the Laranjo Bay due to discharges of a chlor-alkali plant. This happened between 1950 and 1994, when approximately 33 tons of anthropogenic mercury were discharge into the system [60, 61].

In the present, the area chosen was the entire extension of Ria de Aveiro (Figure 3.1), including all the main channels. Sampling sites were chosen according to areas with a higher probability of contamination due to industrial settlement, recent dredging activities and potentially sedimentation zones.

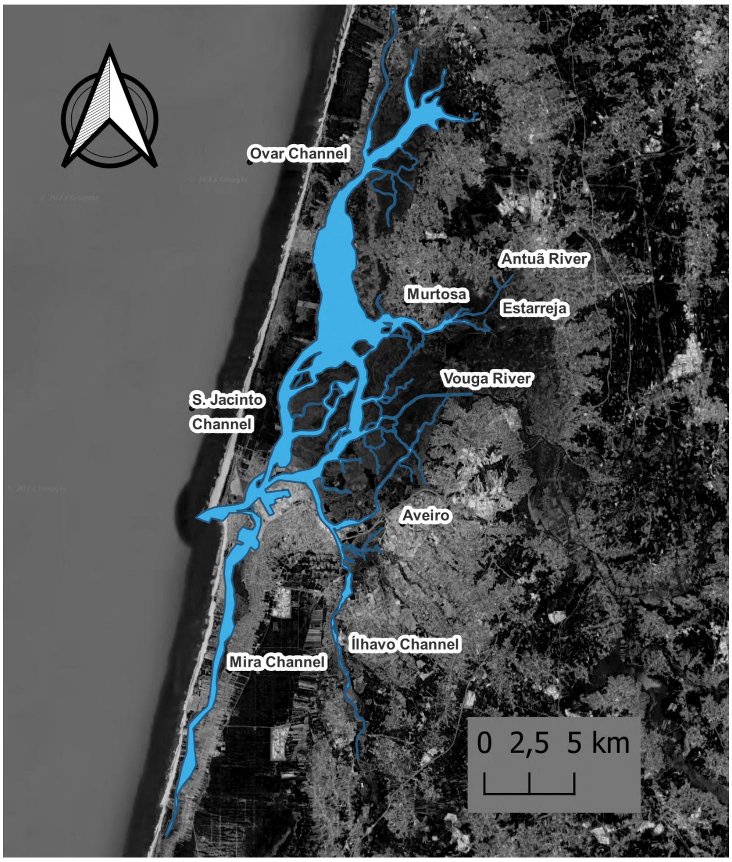


Figure 3.1: Map of the Ria de Aveiro and the area considered for the present study.

Chapter 4

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.

These areas and the suggested number of points in each of them were previously discussed with the University of Aveiro, which helped in the fieldwork due to their excellent knowledge of the Ria. 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 (Table 4.1). After the geographic coordinates of all points were registered, along with their respective ID, to be used in the field with the Global Positioning System (GPS).

Table 4.1: Sampling points per area of the Ria de Aveiro.

Ovar channel to Carregal and Pardilhó (Urban Poles)	**9**
Channel from Murtosa to Chegado; Estarreja/Murtosa/Antuã Industrial Complex	**32**
Vouga River and its Affluents	**5**
Long-distance Fishing Port/Aveiro Shipyards	**10**
Coastal Fishing Port; Aveiro Commercial Port	**15**
Barra Entrance	**3**
Channel of the Central Zone of the Ria; S. Jacinto's Canal	**8**
Aveiro (Urban Poles)	**5**
Mira Channel; Mira/Maçarico S.A (Urban Poles)	**9**
Ílhavo/Rio Boco Channel; Ílhavo and Vagos (Urban Poles)	**11**
Estarreja's Shipyard	**5**
Extra points (Decided in the fieldwork)	**7**
Total Points	**119**

Before field work, all the materials needed for the sampling were prepared. These included plastic zip-lock bags for storing the sediment, spatula for collecting the samples, a refrigerator for storing the samples, a Van Venn dredge of 7 Kg capacity for sediment sampling, the map of the Ria with the marked points for better macroscopic orientation, the list of points with their coordinates, and a GPS. The spatula was previously decontaminated with 20% HNO_3 for two days and then washed three times with milli-Q water.

Sampling was done by boat and was collected surface sediment samples (up to 5 cm depth) with the dredge (Figure 4.1). 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 exact geographic coordinates were registered, because it was not always possible to sample at the previous exact marked location. At times it was impossible to sample at the marked locations, because the currents would hinder the dredging, could have damaged the dredge itself, or even because of obstacles in the water such as branches or other objects that prevented passage. In total, 119 samples were collected.

Figure 4.1: Sampling process during the field work, using a Van Venn dredge of 7 kg capacity.

Chapter 5

Analytical Methods

5.1 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:

$$\%LOI = \frac{m_{drysed(105^{\circ}C)} - m_{drysed(450^{\circ}C)}}{m_{drysed(105^{\circ}C)}} \times 100 \tag{5.1}$$

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

5.2 Digestion and Sample Preparation

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.

Initially, sediment samples were dried at 50°C in an oven. This process took place over a few days, not having a pre-defined period, as it depended on the moisture that each sample contained. After drying, sediments were ground, to make the sample as homogeneous as possible. Therefore, a agate mortar and pestle were used for manual grinding (Figure 5.1). Between grinding each sample, it was necessary to wash the mortar and pestle with milli-Q water to avoid contamination of the samples. Several sediments contained shells and stones that had to be removed by sieving and using a tweezer so that there would be no interference in the elemental analysis of the samples. Finally, the powdered sediment was transferred to plastic zip-lock bags with respective identification.

Figure 5.1: Material used in the grinding process.

After the sediments are dried and ground, samples were ready for the digestion process [62]. This step was divided into 3 rounds of digestions, where each digestion included three blanks, certified reference materials (CRM's) (NRCC - National Research Council Canada - marine sediments: MESS-4 and PACS-2), samples from the Ria de Aveiro, and replicates every 5 samples. Both the blanks and the CRM's were used for the quality control and quality assurance.

Initially, about 100 ± 0.5 mg of sediment sample was weighed for each previously numbered Teflon digestion bomb vessels. Digestion reagents were added to the samples: 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. The digestion vessels were finally closed and placed in the oven at 100°C for 1 hour.

While the digestion bomb vessels were in the oven, 2.8 g of boric acid (H_3BO_3) were weighed into each previously identified 50 mL PP (polypropylene) volumetric tube and diluted in 20 mL of milli-Q water. After samples digestion, the digeston bomb vessels were left to cool, and subsequently, the content of each one was transferred to the respective PP tube and milli-Q water was added to a final volume of 50 mL.

After, the rapid decontamination process was started. The digestion bomb vessels and their lids were placed separately in a tank with distilled water and Tepol detergent to soften the remains of sediments that were stuck to the walls during the digestion. Afterward, they were washed and left to dry. In all the bombs, 1 mL of aqua regia and 3 mL of HF were added, as was done in the blanks. Later, they were placed back in the oven at 100°C for 1 hour. At the end of this process and when cooled, the content of the bombs were transferred to a container suitable for acid waste. Lastly, each one was washed three times with milli-Q water and dried. These steps were always done before the next digestion. After all the digestions were complete, samples were diluted to 15 mL PP volumetric tubes for the trace element analysis. Hence, 1 mL of each sample and 9 mL of milli-Q water containing 2% HNO_3 were pipetted (1:10 dilutions, Figure 5.2) into the respective identified PP tubes. When closing the tubes, they were well shaken to better homogenize the solution.

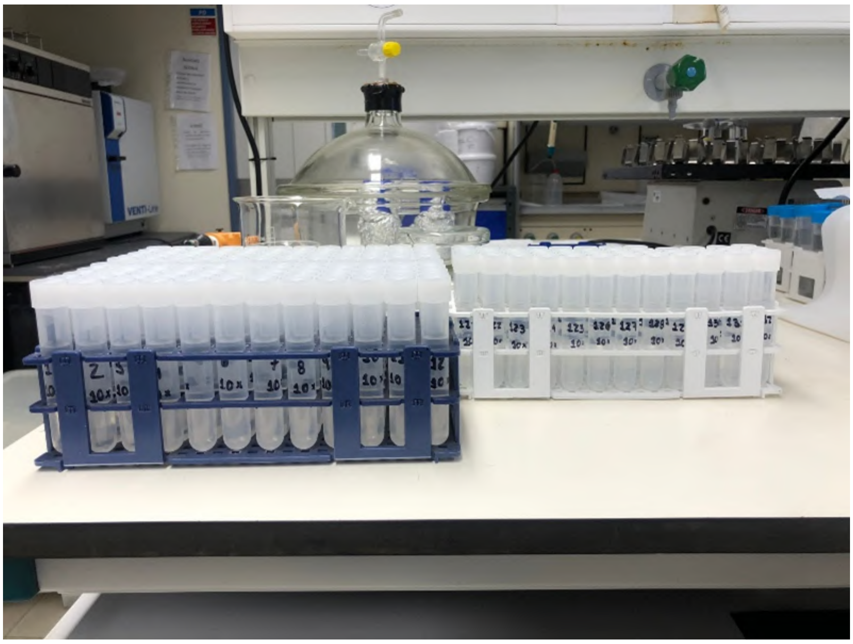


Figure 5.2: 1:10 dilutions in the 15 mL PP tubes after all the digestions.

5.3 Determination of trace and major elements concentrations in sediments

Inductively coupled plasma mass spectrometry (ICP-MS) is an highly sensitive analytical technique that can be used to measure elements at low and ultra low concentrations (µg/L and ng/L, respectively). By separating the ions according to their mass-charge ratio (m/z), the ions are measured in the detector and the concentration of the element under analysis is obtained. This instrument allows to analyze multiple elements simultaneously, perform sensitive measurements due to its low detection limit, and has a large analytical range. It does not require large quantities of samples for analysis, having a high sample throughput. However, it presents some disadvantages such as high equipment costs and the occurrence of interferences that need to be controlled during its use. Usually, the interferences are associated, for example, with isobaric isotopes, i.e. isotopes of different elements having the same mass, which may interfere with the measurement of the elements depending on the relative concentration of these isotopes in the sample. Another option is the rather problematic polyatomic interference, which consists of polyatomic ions that form in the high-temperature plasma derived from the sample matrix or from the reagents used in its preparation, among other possibilities. These having the same m/z ratio as the elements under analysis, end up interfering with the measurement [63].

Once all samples had been subject to the proper dilutions, elemental analysis were performed using an ICP-MS (Figure 5.3). Initially, the sample is inserted as an aerosol form through a nebulizer. Only the smaller aerosol droplets go into the central channel of the argon plasma contained in a quartz tube named torch. The goal is to obtain positive charged ions, so an intense magnetic field is created to obtain the ionization phase. Afterward, the population is extracted into the vacuum system through conical metal plates named interface cones. In this vacuum system exists electrostatic and ion lenses. The first one keeps the ions in a single ion beam, while the second one separates the ions from the photons and residual neutral material, reducing the random background noise when the ions reach the final detector. During the analysis, the type of mass analyzer used was the quadrupole, a sequential mass filter that uses direct and alternating electrical current fields to separate ions based on their mass-charge ratio (m/z). Finally, the electron multiplier detector can create a mass spectrum, through the total signal for each mass. An internal standard was added in constant concentration to all samples reading, in this case, Indium (In), to stabilize the equipment and improve the precision of the ICP-MS during readings [64].

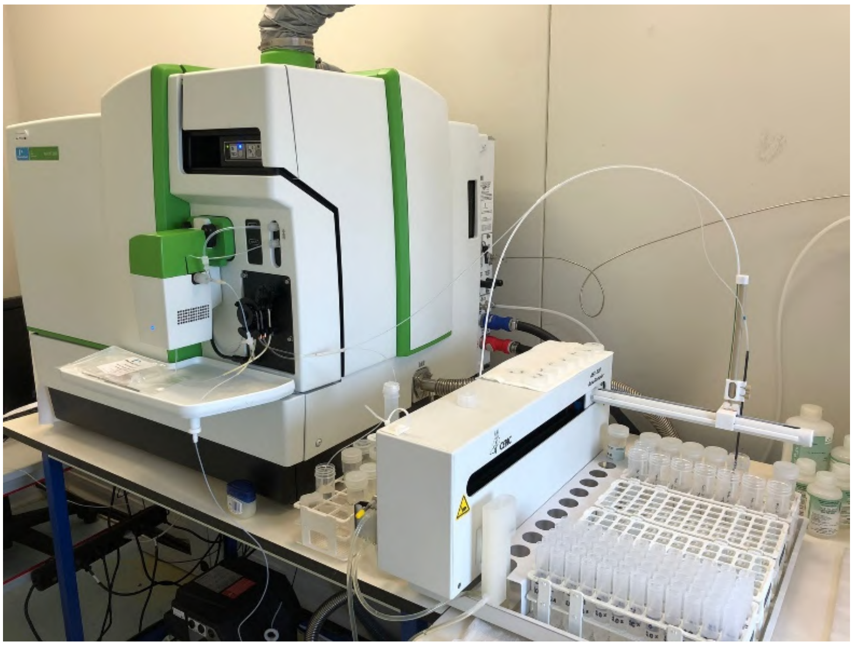


Figure 5.3: 1:10 dilutions in the 15 mL PP tubes after all the digestions.

Regarding the analysis of major elements, which was done after the trace elements analysis, it was necessary to perform dilutions at 1:100. So, 1 mL of the sample diluted (1:10) and 9 mL of milli-Q water with 2% HNO_3 were pipetted into 15 mL PP tubes, properly identified. This dilution was essential since the major elements are not usually analyzed by ICP-MS, precisely because their high concentrations may compromise the proper functioning of the detector of the device.

Although several trace and major elements were analyzed in this work, relatively to trace elements, the results will focus only on the ones taken into account in the National Regulation concerning the dredging materials (Portaria nº 1450/2007) [6], namely arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn).

5.4 Determination of total Mercury (Hg) concentration in sediments

To determine the total mercury content in the samples, an Advanced Mercury Analyzer (AMA-254, Leco) (Figure 5.4) was used. The advantage of using this device is that no sediment pre-treatment is necessary. Thus, the initial ground sediment was used [65].

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. Each sample analysis took approximately 5 minutes, and the process was divided into three different phases: decomposition, pre-concentration, and detection.

The first phase, decomposition, consists of the thermal decomposition of the sample resulting in gas. Therefore, the sample is placed in a combustion tube heated to 750°C.The gas is then transported to the other side of the combustion tube, where any impurities present are removed by the catalyzer.

After, the gas is transferred to the amalgamator, a glass tube containing gold plate ceramics, where the pre-concentration occurs. Afterward, the glass tube is heated to 900°C to release the mercury in vapor form.

In the last phase, detection, the mercury passes through the detection system, a standard atomic absorption spectrometer that uses an element-specific lamp that emits light at a wavelength of 253.7 nm, and a silicon UV diode detector for mercury quantitation. At the end of the process, the software used allows obtaining the mercury concentrations in µg/g.

Figure 5.4: AMA254 analysis.

5.5 Quality Control of Results

Quality control is an essential procedure to validate the obtained results. For this reason, analysis of blanks, CRM's and sample replicates were performed. The two CRM's of marine sediments, MESS-4 and PACS-2, were divided between the 3 batchs of digestions, with MESS-4 used for the first digestion, PACS-2 for the second digestion, and both with replicates for the last digestion.

Initially, it was necessary to ensure that the results obtained from the samples by ICP-MS were within the working range that corresponds to the sediment analysis method for dredge response. Thus, the minimum value corresponds to P1 and the maximum value to P6, for the trace and major elements, as shown in Tables 5.1 and 5.2, respectively.

Table 5.1: Working range for trace elements under analysis.

Working Range	^{52}**Cr**	^{60}**Ni**	^{65}**Cu**	^{66}**Zn**	^{75}**As**	^{111}**Cd**	^{208}**Pb**
P1	1	0.5	0.5	1	0.5	0.005	0.5
P6	80	40	40	80	40	0.4	40

Table 5.2: Working range for major elements under analysis.

Working Range	^{27}**Al**	^{28}**Si**
P1	20	50
P6	1600	4000

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.

After the complete verification, the concentrations of the CRM's in mg/kg were calculated using the following equation:

$$CO = \frac{(ICPV - AB) \times V \times D}{MS} \tag{5.2}$$

Where CO is the concentration in mg/kg, $ICPV$ is the obtained ICP intensity (counts) of the sample, AB is the average value of the intensities of the blanks (not applied always), V is the volume of the solution (mL), D is the dilution that depends on whether it is for trace or major elements, which were 10 and 100 respectively, and MS is the mass of sample that was weighed (mg). The same equation was used to calculate the concentration of the samples later.

Subsequently, it was checked whether the results obtained agreed with the certified value and their respective error range. In addition, an extra quality control method was used for better interpretation of the results, namely Z-score [66]. This method consists of using the following equation:

$$Z = \frac{(Xlab - Xv)}{S} \tag{5.3}$$

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 $|Z| > 3$. The results obtained using the two quality control methods for both MESS-4 and PACS-2 showed the following results:

- For MESS-4, it was possible to conclude that five elements (Al, Cd, Cu, Ni, and Si) had concentrations corresponding to the certified value and its uncertainty range. The remaining elements (As, Cr, Pb, and Zn) had concentrations outside the uncertainty range of the certified material. The elements As, Cr and Zn presented concentrations above the reference value, which may mean some type of contamination at the laboratory level. However, Pb presented a concentration slightly below the reference value, which mean that for this element the digestion may have been insufficient. (Table 5.3)

- Using the Z-score method for MESS-4, it was possible to conclude that four elements (Al, Cd, Cu, and Si) presented satisfactory concentrations, two elements (As and Pb) presented questionable concentrations and three elements (Cr, Ni, and Zn) presented incorrect concentrations. The elements As and Pb that showed questionable concentrations, were the elements that presented concentrations slightly above (As) or below (Pb) the uncertainty range. (Table 5.3)
- Regarding PACS-2, it was possible to conclude that five elements (Al, Cd, Cr, Cu, Ni) obtained concentrations corresponding to the certified value and respective uncertainty interval. The remaining elements (As, Pb, and Zn) had concentrations outside the uncertainty range of the certified material. The elements As and Zn again presented concentrations higher than the reference value, which may mean some type of contamination at the laboratory level, while Pb again presented a concentration slightly lower than the reference value, which may mean that for this element the digestion may have been insufficient. Regarding the Si element, no results could be concluded due to the lack of uncertainty range for the certified material. (Table 5.4)
- Using the Z-score method for PACS-2, it was possible to conclude that five elements (Al, Cd, Cu, Cr, and Ni) presented satisfactory concentrations, and three elements (As, Pb and Zn) presented incorrect concentrations. Regarding the Si element, it was again not possible to conclude any results, due to the lack of uncertainty range for the certified material. (Table 5.4)

Table 5.3: Results from the quality control (ICP-MS: MESS-4) in mg/kg.

MESS-4					
Elements	**Obtained Value**	**Standard Deviation**	**Certified Value**	**± Interval**	**Z-score**
^{52}**Cr**	108.13	7.05	94.30	1.80	7.69
^{60}**Ni**	47.94	5.33	42.80	1.60	3.21
^{63}**Cu**	32.62	0.92	32.90	1.80	-0.16
^{66}**Zn**	182.90	10.75	147.00	6.00	5.98
^{75}**As**	29.58	1.19	21.70	2.80	2.81
^{111}**Cd**	0.25	0.02	0.28	0.04	-0.79
^{208}**Pb**	18.27	1.36	21.50	1.20	-2.69
^{27}**Al**	76217.47	11669.43	79100	2000.00	-1.44
^{28}**Si**	293732.13	44323.53	278000	20000.00	0.79

Table 5.4: Results from the quality control (ICP-MS: PACS-2) in mg/kg.

PACS-2					
Elements	**Obtained Value**	**Standard Deviation**	**Certified Value**	**± Interval**	**Z-score**
^{52}**Cr**	86.07	3.10	90.70	4.60	-1.01
^{60}**Ni**	41.04	1.37	39.50	2.30	0.67
^{63}**Cu**	299.19	9.97	310.00	12.00	-0.90
^{66}**Zn**	471.63	27.33	364.00	23.00	4.68
^{75}**As**	37.71	2.22	26.20	1.50	7.67
^{111}**Cd**	2.29	0.13	2.11	0.15	1.21
^{208}**Pb**	154.05	8.50	183.00	8.00	-3.62
^{27}**Al**	63183.53	6538.89	66200.00	3200.00	-0.94
^{28}**Si**	277652.10	33342.92	280000.00	-	-

For the results obtained by the AMA for mercury, quality control was also performed by checking the results obtained for the CRM's (MESS-4 and PACS-2) according to the certified values and their error ranges. The results of this verification are presented in Table 5.5.

Table 5.5: Results from the quality control (AMA: MESS-4 and PACS-2) in mg/kg.

	MESS-4	**PACS-2**
Obtained Value (Hg)	0.07	2.78
Standard Deviation	0.004	0.04
Certified Value (Hg)	0.09	3.04
± Interval	0.04	0.20
Z-score	-0.54	-1.32

The results showed that for MESS-4 the value obtained is within the error range associated with the certified value, while in the case of PACS-2, the value obtained proved to be slightly below the error range associated with the certified value. However, through the z-score method, it was concluded that for MESS-4 and PACS-2, the Hg concentrations obtained correspond to satisfactory values.

5.6 Spatial distribution and correlations of trace elements

After the quality control and validation of the obtained results, the spatial distribution of the results obtained was performed. 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).

The TIN interpolation method is one of the simplest spatial interpolations and consists of creating a surface composed of non-overlapping, contiguous triangles that connect the nearest neighboring sample points. The resulting surfaces are not smooth. In the IDW interpolation, the unknown point that is meant to be created is formed through the influence of the nearest points, declining the influence with distance. Therefore, is given a certain weight to each point, which is directly related to a parameter called p and is controlled by the user. During the searching process, the Kernel Density Estimation (Heatmap) was also presented as an interpolation tool in Qgis, but even if it looks similar to an interpolation process, the outcome is distinct. The heatmap visualizes hotspots by calculating the density based on the number of points in a location. Hence, this method will not estimate values where no measurement data is available. That is why it was not considered [67].

At the end of the comparison of the two methods, the IDW interpolation was chosen. In this particular study, the number of samples at each location is not regular, leading to less information in certain zones. In such cases, the point density is quite low which usually affects the accuracy of the TIN method [68, 69]. Unfortunately, this spatial irregularity of samples also affects the interpolation process using the IDW method, concluding that there will always be a higher margin of error in zones with more isolated samples, which was initially predicted. However, 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. These differences are beneficial to the accuracy of the results and have led to this choice of method. Spatial distribution maps were determined for trace elements concentrations, for the Si/Al ratio (to be observable what kind of sediments constitute the Ria at the granulometry level) and for organic matter content (%LOI) to get a global view in terms of sediment characteristics.

After the obtained spatial distributions, possible correlations between trace elements and sediment characteristics (Si/Al ratio and OM(%)) were analyzed, as well as the correlations between each trace element itself. In this way, it would be possible to measure the relationships between the variables and understand what this represents. To do this, the Pearson Correlation Coefficient method was used, through excel, more specifically the data analysis tool, and three outputs were obtained for each correlation:

- r, which represents the correlation coefficient that can range from -1 (negative relation) to +1 (positive relation). The interpretation of this coefficient was through the classification made by Shimakura (2006) [70];

- p, which determines whether the correlation coefficient is significant or not. When $p < 0{,}05$ the correlation is statistically significant;

- n, which represents the number of samples used in the correlation study.

5.7 Stocks 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 several diverse samples were initially calculated in the laboratory to be used later in the calculations. It was not possible to calculate the densities of all 119 samples, so four samples were selected, ranging from muds to sands, and these densities were calculated to be used for sediments similar to what was used in the laboratory. Initially, the weight of the beaker in mg and the volume of water in cm^3 corresponding to the same completely filled beaker were measured. Subsequently, the weight in mg of each of the four types of sediment chosen was measured through the exact beaker completely filled. Using the results obtained and in units of kg and m^3, the density of the sediments was calculated using the following equation:

$$D_{Sediment} = \frac{W_{sediment} - W_{beaker}}{V_{water}} \tag{5.4}$$

Where $D_{Sediment}$ is the sediment density in kg/m^3, $W_{sediment}$ is the sediment weight in kg, W_{beaker} is the beaker weight in kg, and V_{water} is the water volume in m^3.

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), certifying that all maps had the same geotransformation, projection, and pixel area. 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:

$$A_T = N_{pixels} \times L_{pixel}^2 \tag{5.5}$$

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:

$$Vol_{sediment} = A_T \times 0.05 \tag{5.6}$$

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:

$$M_{sediment} = Vol_{sediment} \times D_{sediment} \tag{5.7}$$

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:

$$M_{element} = M_{sediment} \times C_{pixel} \tag{5.8}$$

Where $M_{element}$ is the total concentration 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.

Chapter 6

Results and Discussion

6.1 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 6.1).

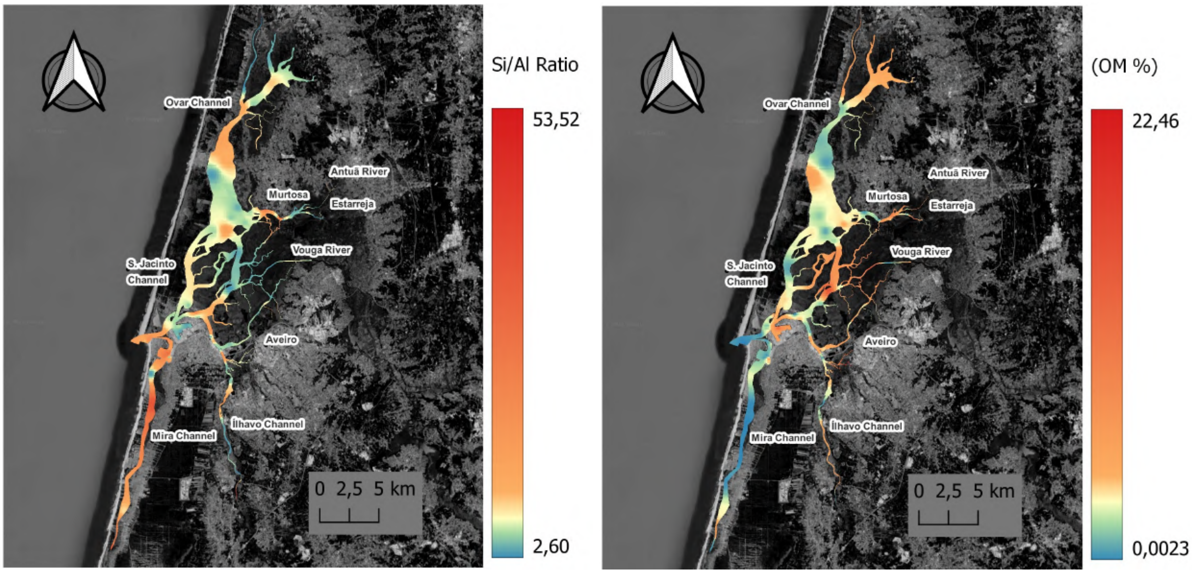


Figure 6.1: Maps of spatial distribution regarding sediment type (Si/Al ratio) and organic matter content (%) along the Ria de Aveiro where a quantile classification was used.

Regarding sediment type, among the 119 samples analyzed the highest Si/Al ratio determined was 53.5, while the lowest was 2.53. The average was 9.76 which shows that although there is a high variability of sediment types in the Ria. A 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, and there were still many areas constituted by sand.

Through a more detailed analysis, it was concluded that the Mira channel presented Si/Al ratios between 3.59 to 36.4. However, the values were mostly high along the entire channel. This was expected because it is a channel connected to the Barra entrance, the only connection to the ocean, which also has a predominantly sandy composition. In the case of the S. Jacinto channel, there appears to be more a mixture of mud and sand, with Si/Al ratios ranging from 5.16 to 15.1. Other areas that stand out are the Ovar and Espinheiro channels (parallel to the S. Jacinto channel), with Si/Al ratios that varied between 2.53 and 21.5, and 3.30 and 20.6, respectively, showed a very diversified sediment distribution. It is possible to identify concentrated areas of sandier sediments while in the remaining areas more mud-like sediments prevail, having been determined at the most upstream area of the Ovar channel the lowest Si/Al ratio (2.53) of the 119 samples analyzed. Regarding the Ílhavo and Murtosa channels, both showed a high mixture of mud and sand along their entire length (ranged from 2.69 to 53.5, and 2.56 to 37.0, respectively). In both channels, more sandy sediments at the most upstream areas of the channels were found, and it was exactly in this same location of the Ílhavo channel that the highest Si/Al ratio was found (53.5).

The marine influence identified by the areas with higher Si/Al ratios can be justified through the tidal currents previously pointed in the study conducted by Lopes and Dias (2007) [57]. This work showed that the currents are stronger in the channels of S. Jacinto and Espinheiro and along narrow channels and entrances. It is therefore observable that in most channel downstream entries, coarser sediments such as sand are present, while along the channels to their upstream ends, there is mostly a mixture of mud and sand. This depends on the velocity of the currents that influence the sedimentation processes. However, there are exceptions because although the tidal current is the greatest drive force, there are other variables such as the current inside the channels, the role of the wind, and the position of the channels regarding the ocean connection. After all, 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) [57] and Martins et al. (2013) [5], which also discussed particle size distribution.

Regarding the organic matter content, the highest value determined was 29.3%, while the lowest was 0.097%. The average was 3.99%, which shows a tendency for low organic matter content among all the analyzed samples. When looking at the organic matter distribution map (Figure 6.1) a tendency towards an opposing pattern to the Si/Al ratio distribution map emerges. It is possible to observe that the Mira channel is poor in organic matter, with levels ranging from 0.097% to 6.65%, and where was recorded the lowest value (0.097%), among all analysed samples, in the middle of the channel. At the same time, the Barra entrance presents similar characteristics, with organic matter varying from 0.25% to 2.12%, which was expected. Concerning the lagoon and Ovar channel, both presented values of organic matter between 0.17% and 15.2%, and 0.12% and 10.01%, respectively, demonstrating a wide range of percentages and again showing a non-homogeneous distribution with well-defined areas. The Murtosa and Ílhavo channels presented a quite irregular distribution of organic matter along with its extension (ranged from 0.24% to 12.2%, and 0.36% to 6.96%, respectively). The highest value of organic matter (29.3%) was observed in one of the Aveiro city canals, connected to the Ílhavo channel.

It can be easily concluded from these observations that there is a tendency pattern between the type of sediment and the organic matter content. Typically, areas that have more coarse materials showed lower 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. A very clear example when looking at the maps (Figure 6.1) is the Mira channel which has been characterized as a sand-rich zone and has a low organic matter content. In opposite, the most upstream end of the Ovar channel showed to be enriched in mud and has a high level of organic matter. This pattern was observed also in the study conducted by Martins et al. [51]. However, it was tested whether there would be a high correlation between these two parameters using the Pearson correlation coefficient. Through the Figure 6.2 and the obtained coefficient ($r=-0.49$, $p<2.273\times10^{-8}$, $n= 119$) it was concluded that there is a moderate inverse correlation (according to the classification by Shimakura (2006) [70]), indicating that local OM sources also have an impact on the distribution

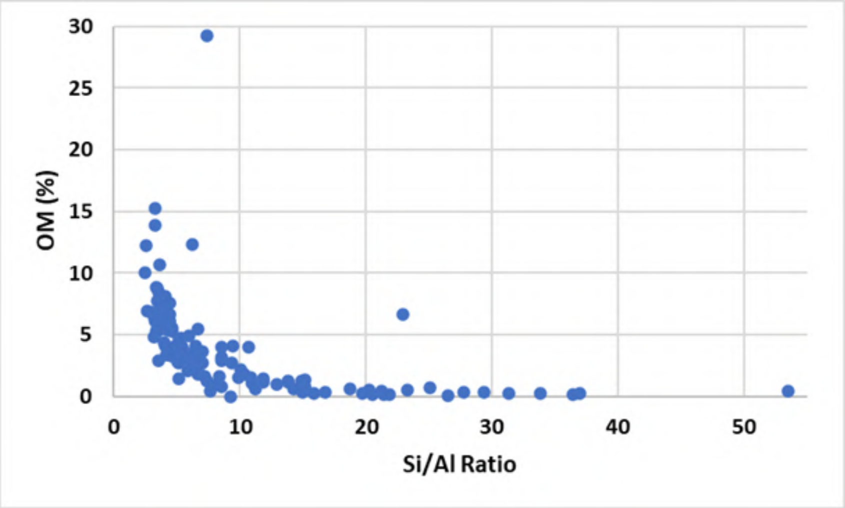


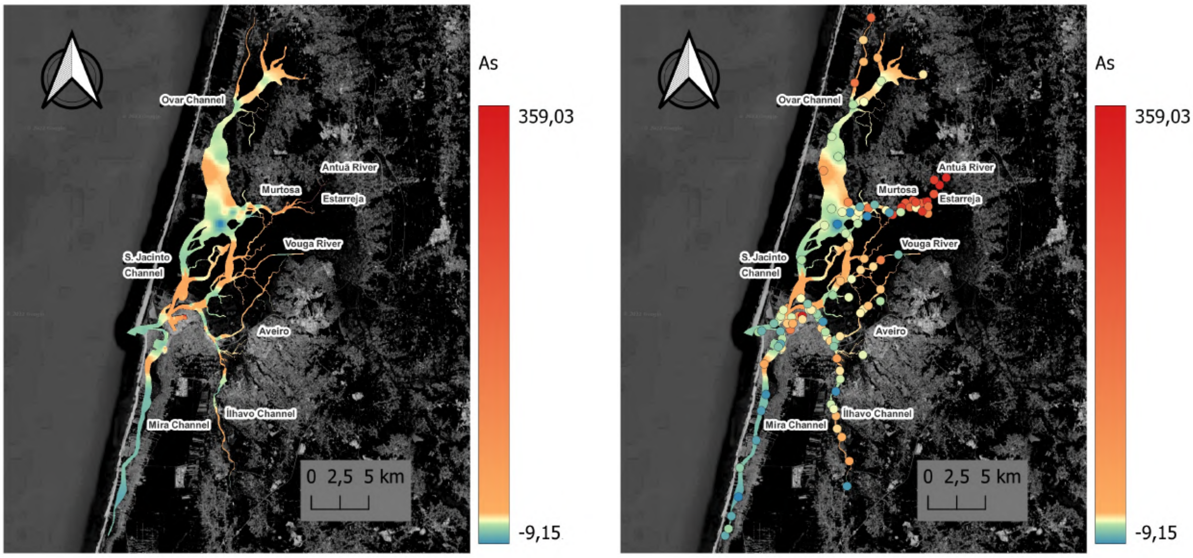
Figure 6.2: Relationship between OM% and Si/Al ratios

6.2 Distribution of trace elements contaminants along the Ria de Aveiro

The main goal of this work was to have a detailed distribution of the analysed trace elements along the Ria de Aveiro. For this reason, possible relations of the elements with sediment type, organic matter, and potential anthropogenic sources were explored. Hydrodynamic factors that may interfere with the distribution were also taken into consideration. Lastly, it is important to compare with values obtained in another study sites for a better perception of the actual level of contamination.

6.2.1 Arsenic

Figure 6.3 presents the spatial distribution of Arsenic (As) concentration (mg/kg) along the Ria de Aveiro.



(a)

(b)

Figure 6.3: (a) Spatial distribution of As concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. Negative values represent values below the ICP-MS detection limit, meaning very low concentrations. A quantile classification was used for the creation of the map.

It can be observed that the As content ranged from 0.19 mg/kg (detectable) to 360 mg/kg, presenting a relatively high range of concentrations. The concentration average was 27.9 mg/kg, showing that most of the sampling sediments have As content below this average concentration. It is observable that the area of the Ria with the highest As concentration is the Murtosa Channel, towards Estarreja, showing at the same time in the channel a maximum of 357 mg/kg and the lowest (detectable) concentration among all the samples, 0.19 mg/kg. However, the area with the highest concentration of As in the entire Ria, 360 mg/kg, was at the commercial port, between the barra entrance and the beginning of the S. Jacinto channel. The lowest concentration recorded was 13.4 mg/Kg, 27 times lower than the maximum concentration in the port, showing a sign of contamination by anthropogenic sources as is also the case of the Murtosa Channel. In the Ílhavo channel As concentrations ranged between 1.53

and 27.6 mg/kg, similarly to the Mira channel where As content varied from 1.71 to 26.7 mg/kg. However, the Mira channel showed low As concentrations in most areas of the channel, while in the case of the Ílhavo channel the distribution was more heterogeneous (Figure 6.3). In summary, the As concentrations determined for the main channels are shown in Table 6.1.

Table 6.1: Arsenic concentration ranges and averages (mg/kg) in the main channels of the Ria de Aveiro

Main Channels	**[As] ranges (mg/kg)**	**[As] averages (mg/kg)**
Ovar	2.29 - 36.6	18.02
Murtosa	0.19 - 357	63.9
S. Jacinto	0.43 - 17.9	9.79
Espinheiro	3.66 - 24.3	12.9
Mira	1.71 - 26.7	5.81
Ílhavo	1.53 - 27.6	14.5

Regarding possible relationships between As and sediment characteristics, correlations were studied using Pearson's correlation coefficient. The results obtained were classified using Table 6.2.

Table 6.2: Categorization of r-values obtained by Pearson's correlation coefficient according to Shimakura (2006).

$\lvert 0-0.19 \rvert$	very weak
$\lvert 0.20-0.39 \rvert$	weak
$\lvert 0.40-0.69 \rvert$	moderate
$\lvert 0.70-0.89 \rvert$	strong
$\lvert 0.90-1 \rvert$	very strong

The obtained coefficient of correlation between As and OM content and Si/Al ratio were r=0.25, $p<0.005$, n=119 and r=-0.24, $p<0.007$, n=119, respectively. Based on the classification by Shimakura (2006) [70], Table 6.2, it is possible to conclude that the correlations are weak. Therefore, these factors are not relevant to consider when justifying the As distribution. Thus, the anthropogenic sources and hydrodynamic factors may be considered as a better explanation for the observed distribution. However, it should be noted that these two parameters, sediment type, and organic matter content are not independent of each other and besides them, more parameters interfere, like the location of the sources, the degradation of organic matter, and the hydrodynamics of the Ria. Hence, the influences of these two parameters concluded in this work are something at the macroscopic level and relative to this specific situation, not covering the concept that there is never a relationship between arsenic and these parameters. The same is valid for the other trace elements.

In order to identify the distribution of the hotspots, the industrial activities surrounding the Ria de Aveiro and the hydrodynamic factors that may help to justify the cause of several high concentrations were studied. The high concentrations of As recorded in the Murtosa channel (with a maximum of 357 mg/kg) appear to be related to the major impact that existed and still persist in the Estarreja area, the industrial plant. This industrial area is responsible for producing, for example, fertilizers and other chemicals that through the effluents released into the Ria, contribute to the high levels of As [5]. In addition, the presence of docks at the beginning of the narrow channel, which can contribute through increased naval activity, that through the currents that increase at this location, carry contaminated particles in the direction of Laranjo and Estarreja. In the case of the commercial port, the observed peak can be justified due to all the shipyard activities that exist in the area, such as boat waste, maintenance, tank cleaning, among others. There is also a Prio Fuel Farm Tank near the port that can contribute to the existing peak of As in the area, as well as to the slight increase at the downstream beginning of the S. Jacinto and Espinheiro channels, compared to the concentrations at the Barra entrance and the downstream beginnings of the Mira and Ílhavo channels, as can be seen in Figure 6.3 [27].

In the Ovar channel, two well-defined areas can be identified where an increase in As concentrations occurs with maximums of 29.9 and 36.6 mg/kg at the downstream beginning and at the end of the channel, respectively. This can be explained by the hydrodynamic of the Ria since it is known that at the ends of the channels there is a higher residence time of particles, which contributes to the accumulation of sediments, and therefore contaminants [57]. In addition, there is a small marina at the northern end of the channel, where the highest concentration was recorded (36.6 mg/kg). Relative to the downstream beginning of the channel, there is a slight increase in As concentrations (the maximum value is 13 times higher than the minimum) that can be justified by two hydrodynamic factors based on the study conducted by Lopes and Dias [57]. It is expected to be a clash of currents at the beginning of the Ovar channel due to the maritime currents coming from the channels of S. Jacinto and Espinheiro and the channel currents coming from the Estarreja channel, supplied by the Antuã river. This clash produces a turbid area that can end up transporting suspended contaminated particles from the Murtosa channel to the Ovar channel. This is due to the strength of the marine currents compared to the river currents. There is then, at the downstream entrance of the Ovar channel, an area where the current velocity decreases, the particles tend to settle, but due to the narrowing of the Ovar channel, a new turbid zone is created due to the increased current velocity, decreasing As concentrations in this narrowing zone. These two factors can justify the slight increase in As concentration in the beginning of the channel, and there is no known concrete anthropogenic source directly related, although on both sides of the channel there are small docks that may also contribute [27].

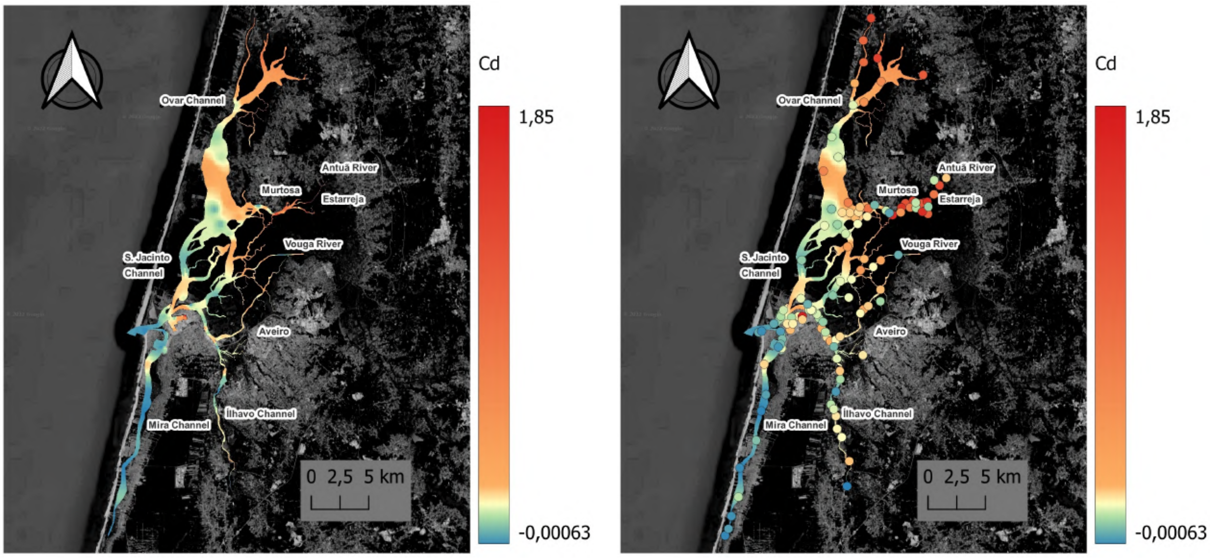
Regarding the two hotspots in the northern part of the Mira channel, the sources appear to be obvious, since the contamination sites correspond to places where there are coastal fishing ports and small marinas, and it is known that one of the possible sources of arsenic is the combustion of fossil fuels, in this case from ships [2]. In the Ílhavo channel, in the northern area, the higher As concentrations correspond mainly to shipyards zone. However, in the southern area, similar higher concentrations are noticeable, probably due to the Vista Alegre factory that produces pieces in porcelain and glass, which possibly contribute to the increase of As concentrations through pigments used in the decoration process [29]. Finally, the highest levels of As content observed in the upper part of the Espinheiro channel appears to have its origin in the Vouga River itself, which through currents helps to disperse contaminants to the north of the channel. The possible source of this As contamination is the pulp mill that discharges its effluents into the Vouga River. Currently, they have treatment mechanisms for their effluents, but in the past, this was not implemented [5]. In addition, there is a bridge that was under reconstruction at the time of sampling, with a small pier near the bridge, indicating nautical activity at the site and perhaps there could be influences from metallurgical factories that exist near the river and release their effluents there. All trace elements are used for alloy production and products that derive from it, so these activities can easily be a type of source for arsenic [1].

Comparing the values obtained in the study conducted by Cachada et al. (2019) [53] that also analyzed several samples along the Ria, all the main channels studied in the present work showed higher maximum As concentrations. In the Murtosa channel, the most contaminated one, the authors showed a maximum of 256 mg/kg of As and this was the channel with the tightest sampling grid [53]. However, the minimums recorded in the past are higher than those recorded currently, which can be justified by the low sampling representativeness in most of the channels. The same can be considered for the maximum concentrations, but the magnitude between past and present, e.g., the maximum concentrations in Murtosa channel of 256 and 357 mg/kg, respectively, seems to be much more similar than for the minimum concentrations. Thus, it is possible to conclude that As concentrations appear to have increased in the last years.

A comparison was also made with the Tagus estuary, conducted by Vale et al. (2008) [71], and an international study, conducted in the Lami estuary, Fiji [72], an ecosystem subjected to various intense trace elements inputs from industrial activities. In the Tagus estuary, As levels ranged from 1.9 to 1022 mg/kg, which is a much higher concentration range than that reported in the Ria de Aveiro. The Lami estuary presented concentration ranges between 1 - 334 mg/kg of As, which were similar to those obtained in the Ria de Aveiro. These data were considered as major concern to the regulatory authorities once they presented very high levels of As in the estuary. For this reason, the study suggested that corrective waste management measures should be implemented immediately, which seems to be something that would fit perfectly in the situation of the Ria de Aveiro.

6.2.2 Cadmium

Figure 6.4 presents the spatial distribution of Cadmium (Cd) concentration (mg/kg) along the Ria de Aveiro.



(a)

(b)

Figure 6.4: (a) Spatial distribution of Cd concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. Negative values represent values below the ICP-MS detection limit, meaning very low concentrations. A quantile classification was used for the creation of the map.

The Cd values ranged from 0.0027 mg/kg (detectable) to 1.86 mg/kg, showing a moderate range of concentrations. The average concentration was 0.27 mg/kg, which indicates that most of the sample concentrations are below this level. Similar to As, the channel with the highest Cd concentrations is the Murtosa channel, where a concentration range between 0.016 and 1.85 mg/kg was determined. The sample analyzed that presented the maximum concentration of As (357 mg/kg) in the Murtosa channel is the same that presented the maximum concentration of Cd (1.85 mg/kg). However, it was not in the Murtosa channel where the highest concentration of Cd in the Ria was recorded, but in the area of the commercial port (1.86 mg/kg). The lowest value obtained in the port was 0.086 mg/kg, up to 21 times lower than the maximum obtained at this site, suggesting that the port is the anthropogenic source of this metal. Regarding the channel with the lowest Cd levels (Figure 6.4), it can be concluded that it is the Mira channel where concentrations varied between the lowest detected value in the entire Ria (0.0027 mg/kg) and 0.23 mg/kg, once again showing hotspots in the north of the channel as it was observed for As. The Ílhavo channel, showed concentrations between 0.0099 and 0.29 mg/kg, a variation very similar to the Mira channel. However, along this channel the distribution is quite heterogeneous, unlike Mira where concentrations are very similar in all samples. A summary of Cd concentrations recorded for the main channels are presented in Table 6.3.

Concerning the possible relationships between cadmium and sediment characteristics, correlations were studied using Pearson's correlation coefficient. The obtained coefficient of correlation between Cd and OM content and Si/Al ratio were $r=0.45$, $p<2.37\text{x}10^{-7}$, $n=119$ and $r=-0.41$, $p<2.79\text{x}10^{-6}$, $n=119$,

Table 6.3: Cadmium concentration ranges and averages (mg/kg) in the main channels of the Ria de Aveiro.

Main Channels	[Cd] ranges (mg/kg)	[Cd] averages (mg/kg)
Ovar	0.055 – 0.83	0.35
Murtosa	0.016 – 1.85	0.54
S. Jacinto	0.068 – 0.28	0.18
Espinheiro	0.027 – 0.32	0.14
Mira	0.0027 - 0.23	0.052
Ílhavo	0.0099 – 0.29	0.15

respectively. Both are considered as moderate correlations, according to Table 6.2. Although there is no well-defined cause-effect, these results indicate a positive tendency to sediments with high OM content have higher Cd concentrations. In opposite to, the negative correlation between Si/Al ratio and Cd concentrations indicated that the coarser particles presented the lower Cd concentrations. Therefore, these factors should be considered in the evaluation of the Cd spatial distribution along the Ria de Aveiro.

Considering the possible sources of Cd in the Ria de Aveiro, many of them correspond to the same as those indicated for As distribution. In the Murtosa channel, the major possible source of Cd is the Estarreja Industrial Park, due to the production of commercial fertilizers, and possible ship activity existing in the channel as evidenced by the docks on the banks may contribute to the increase of this element [5]. In the case of the commercial port, there is again a possible link to sources related to shipyard activities (fuel), in addition to the fuel tanks that complement the area [33]. Concerning the Ovar channel, a pattern similar to the As one can be observed and justified by the hydrodynamic factors, such as the highly turbid zones that contribute to the migration of particles from the Murtosa channel to the Ovar channel, followed by the existence of a higher sedimentation zone at the downstream beginning of this channel that contributes to higher concentrations in this zone relative to other areas of the channel [57]. It is also known that there is a plastics factory that sends its effluent into the Ovar channel, which may contribute to a distribution spread also at the beginning of the channel, with cadmium being used in plastic production [5]. At the same time there are small docks on the sides of the channel that can always contribute to these Cd concentrations. At the end of the Ovar channel, it is possible to identify a rise in the Cd values due to the residence time that increases considerably at the ends of the channels [57].

In the Mira channel the two areas that stand out coincide with the same two identified in the case of As, where the Cd maximums vary between 0.16 and 0.23 mg/kg. This observation should be associated with marinas and coastal fishing ports. This link can again be observed in the north of the Ílhavo channel, with some higher Cd concentrations near port areas as can be seen in Figure 6.4. An increase in concentrations is again detected from the area closer to the Vista Alegre factory, which may again be associated with the use of Cd in paint pigments [29]. Regarding the Espinheiro channel, appears to be an association of increased concentrations of Cd with the inflow of the Vouga River, perhaps associated with effluents from metallurgical factories that exist near the river, or due to the bridge over reconstruction and the nautical activities near the site [2]. Concerning the sediment characteristics, it is visible that several areas with higher levels of organic matter are coincident with an increase of Cd concentrations, for example, at the downstream beginning and end of the Ovar channel, or in terms of sediment type in the Mira channel, which is very sandy and is the poorest channel in Cd content in sediments.

Since a relationship between the distribution of As and Cd was noted at most sites, the correlation between them was studied (Figure 6.5)

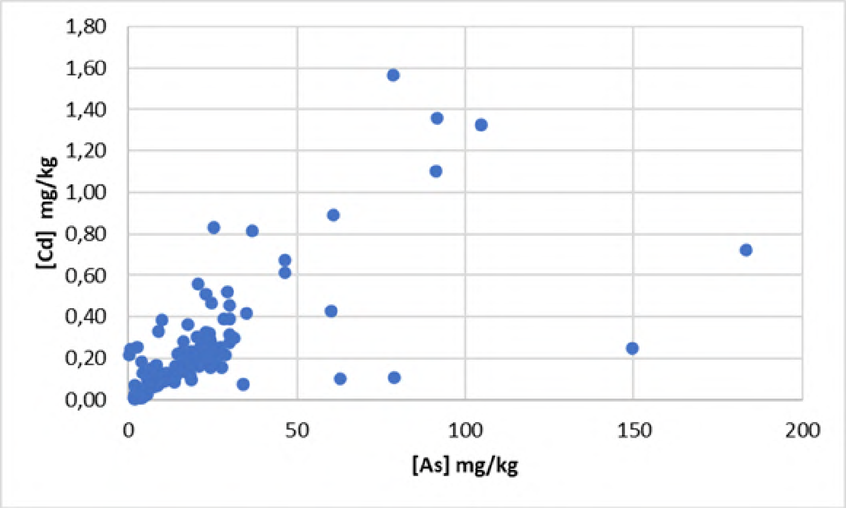


Figure 6.5: Relationship between As and Cd concentrations (mg/kg) in Ria de Aveiro sediments.

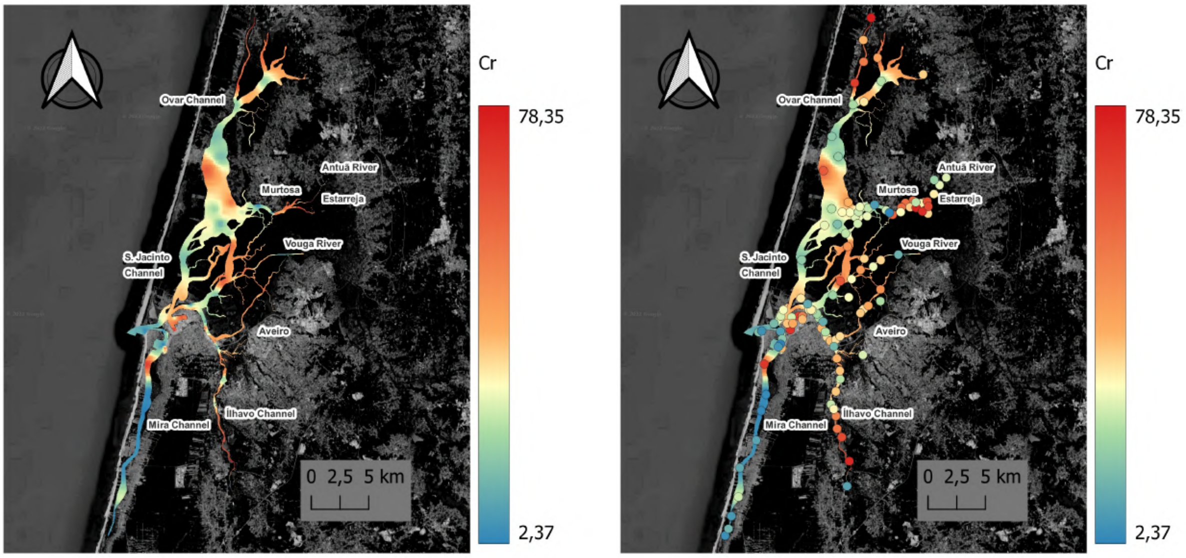
The respective Pearson correlation coefficient (r=0.79, $p<1\text{x}10^{-26}$, n=119) indicated that As and Cd concentrations were strong correlated, according to Table 6.2, which explains the tendency, in many cases, to coincide their spatial distribution and even the maximum values of As and Cd in the same sample. This correlation may be associated with the sources of As and Cd, which are often the same.

By comparing this study with the study conducted by Cachada et al. (2019) [53], it was found that in 5 of the 6 main channels of the Ria, the Cd concentrations obtained in the present study were lower, surpassing only in the Mira channel, where 0.23 mg/kg was recorded. Regarding the most contaminated channel, Murtosa, the maximum reported by Cachada et al. (2019) was 2.6 mg/kg of Cd, while in the present study does not exceed 1.85 mg/kg of Cd. Considering the data from the study conducted by Gomes and Delgado (1993) [52] it was possible to compare Cd concentrations in two sediment samples from the Ovar channel, which were the only two superficial samples with detectable Cd concentrations. A maximum of 2 mg/kg was recorded in the previous study, being a higher Cd concentration than the one recorded in this study in the Ovar channel (0.83 mg/kg) and higher than the maximum currently obtained in the entire Ria. Therefore, through these two studies, it was concluded that Cd concentrations in the Ria have reduced over the years.

Comparative to the Tagus estuary [71], Cd concentrations varied mostly between 0.01 and 0.78 mg/kg, which corresponds to a lower range than that presented in the Ria de Aveiro. However, there was a peak Cd concentration that reached 11 mg/kg near Barreiro and North Channel industrial areas, which largely exceeds the level of pollution by this contaminant in the Ria. A comparison was also made with other studies at international sites, such as the Loire estuary in France [73], which is one of the largest marine environment inputs in Europe and which is impacted from industrial and urban interferences until the river flows into the Atlantic Ocean. In this study a range of Cd concentrations between 0.40 mg/kg and 1.53 mg/kg was reported, similar to the Cd concentrations recorded in the Ria de Aveiro, in the present study. Although the Ria has an even higher range in terms of minimum and maximum concentrations obtained. Both sites share plenty of similar anthropogenic sources such as port areas, fertilizer and chemical plants, and refineries, which may favor similar ranges. Another case is the Seine estuary [74], further north in France, where the Seine River flows through Paris and its most industrialized areas. In this study a concentration range between 0.6 and 0.9 mg/kg was recorded, being much smaller compared to that recorded in the Ria de Aveiro. However, as the Ria, the Seine estuary has shown over the years a tendency to reduce its Cd concentrations. This way it is possible to admit that over the years the industrial processes and activities that contribute to the concentrations of this metal have been improving.

6.2.3 Chromium

Figure 6.6 presents the spatial distribution of Chromium (Cr) concentration (mg/kg) along the Ria de Aveiro.



(a) (b)

Figure 6.6: (a) Spatial distribution of Cr concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

In this work, Cr content ranged from 1.89 mg/Kg to 79.5 mg/kg, hence presenting a moderate range of concentrations. The average concentration was 34.8 mg/kg indicating that there is a uniform distribution of concentrations. In Figure 6.6, is possible to observe that the channel that present the highest concentration of Cr is the Ovar channel where the range of concentrations varied between 8.41 mg/kg and the maximum value recorded in the Ria, 79.5 mg/kg. The channel with the second highest Cr concentration was the Murtosa channel, with a maximum of 77.3 mg/kg, but interestingly at the same time recorded the lowest concentration in the entire Ria (1.89 mg/kg). In the case of the Ílhavo channel, the maximum Cr concentration was almost identical to that recorded in Murtosa, 77.1 and 77.3 mg/kg, respectively, and a minimum Cr concentration of 4.59 mg/kg. The commercial port area showed high levels, with a maximum Cr concentration of 69.06 mg/kg and showed a lower variation in Cr concentrations, with a minimum of 28.7 mg/kg. Finally, it was in the Mira channel where, in general, samples with lower Cr levels were found. Although, an area was identified in the north of the channel that stands out by registering 67.8 mg/kg of Cr. In summary, the Cr concentrations determined for the main channels are shown in Table 6.4.

Table 6.4: Chromium concentration ranges and averages (mg/kg) in the main channels of Ria de Aveiro.

Main Channels	[Cr] ranges (mg/kg)	[Cr] averages (mg/kg)
Ovar	8.41 -79.5	38.8
Murtosa	1.89 - 77.3	40.02
S. Jacinto	12.6 - 39.6	28.1
Espinheiro	5.63 – 60.2	31.5
Mira	2.03 – 67.8	14.5
Ílhavo	4.59 – 77.1	37.7

Concerning the possible relationships between Cr concentrations and sediment characteristics, correlations were studied using Pearson's correlation coefficient. According to Table 6.2, it is noticeable that the obtained correlation coefficients for Cr vs OM and Cr vs Si/Al (r=0.55, p$<$6.85x10^{-11}, n=119; r=-0.74, p$<$4.63x10^{-22}, n=119, respectively) indicated moderate and strong correlations, respectively. These results suggest that Cr is found in higher concentrations in fine sediments, such as muds. However, even though there is a trend regarding organic matter content and Cr, it is not so linear, as anthropogenic sources and their locations seem to influence this relationship. Nevertheless, these factors are important to consider in justifying the Cr distribution.

An analysis of the possible anthropogenic sources was done for Cr and despite having a different concentration distribution than the previous trace elements, the sources appear to be quite similar due to the various industrial applications in common. In the Ovar channel, the sample with the highest concentration of Cr in the entire Ria (79.5 mg/kg) was collected at the northern end of the channel, near a small marina. This boating activity in a section of the channel with low currents and consequently, a high residence time of particles enrriched the sediment in this metal [57, 75]. Equivalently to As and Cd, at the downstream beginning of the Ovar channel, there is a concentration of Cr (maximums around 60 mg/kg), most likely due to the hydrodynamic and sediment characteristics that exist there and was previously explained, that favor sedimentation in this area [57]. In addition, there are docks on both sides of the channel suggesting a higher ship activity at the site, contributing to the increase in Cr content. Although it is a suggested source, it is known that there is a fish canning factory near the Ovar channel that may contribute to the Cr concentrations, as the cans have this metal in their composition [76].

Regarding the Ílhavo channel, in the north area, Cr concentration increases were found near harbors, while in the south the concentrations gradually increase along the channel from the Vista Alegre factory, being this a potential source due to the Cr being used in pigments [33]. The increased residence time of the particles and the considerable organic matter present in these sediments should contribute to the samples gradually registering higher Cr values as approach the end of the channel [57]. Another area of easy correlation between the Cr concentrations and the source is the commercial port, where the Cr contents stand out and will be related to the high shipping activity in the area.

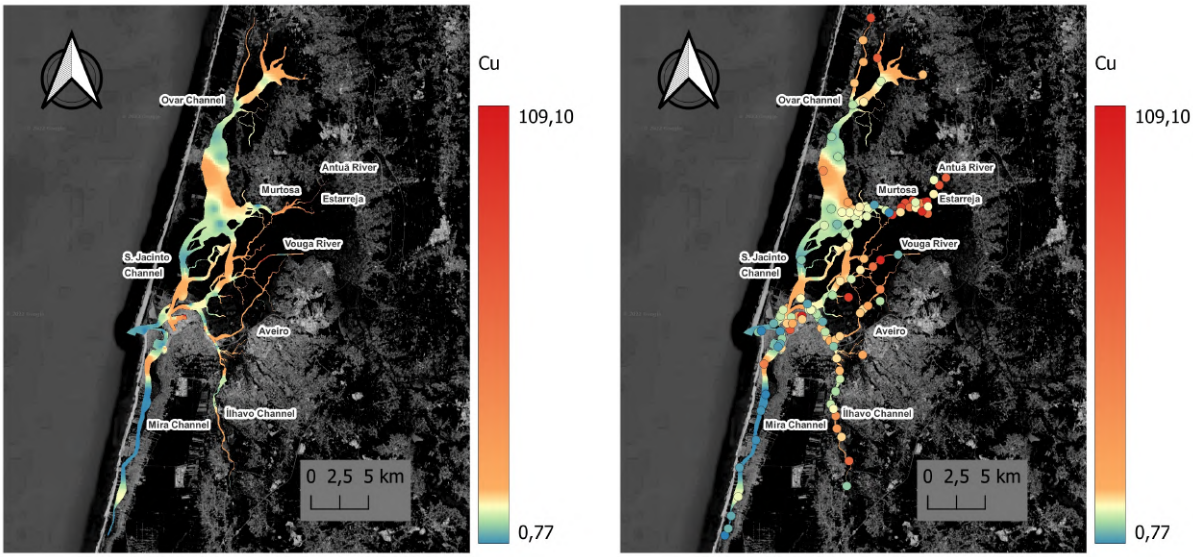
The Murtosa Channel showed higher Cr concentrations closer to the Laranjo and Estarreja areas, which is probably related to the Estarreja Industrial Park where fertilizers and chemicals are produced [5]. This element is applied in fertilizers like the other trace elements discussed, so the Murtosa channel is constantly impacted by these contaminants as has been observed in their maps of spatial distribution [33]. In the Mira channel, the increases of Cr concentrations may be related to the existence of marinas and the coastal fishing port that exist on the banks of the channel. Finally, the Espinheiro channel appears to be influenced by the Vouga River in terms of Cr concentrations, probably due to the metallurgical factories near the Vouga River that can contribute with possible discharges, the reconstruction of the bridge, the ship activity and perhaps the pulp mill along the riverbank [5, 26]. It can be concluded that in general, many of the hotspots in the Ria are associated with shipyard activities and their locations, which was expected due to the use of Cr in metallic alloys in boats to help protect the material from natural corrosion [75].

A comparison was made between the levels obtained for Cr in the Ria and previous published studies from the same site and other international study areas. In the study conducted by Gomes and Delgado (1993) [52], only four superficial sediment samples were used were used, three in the Ovar channel and the other one in the Ílhavo channel. The Cr concentrations recorded in the Ovar channel ranged from 43 to 50 mg/kg, which are in agreement with the concentrations determined in the same channel in the present work. The lowest value, 43 mg/kg of Cr, was obtained from a sample that was collected in the narrowing of the channel, identical situation identical to the one reported in the present work, which would be expected due to the hydrodynamic factors that influence the area. In the Ílhavo channel, it was only possible to compare one Cr concentration, 51 mg/kg which is in the northern part of the channel. This value is very similar to the concentrations recorded in the present work and at the same site, currently ranging from 50 to 53 mg/kg. In the study conducted by Cachada et al. (2019) [53], it was possible to have a better comparison, and it can be concluded that all the ranges reported in the previous study had maximum values below those determined in the present work. Thus, although the present work presents a higher sample representativeness than the previous study [53], which may influence both the maximums and minimums previously recorded, it is possible to conclude that Cr concentrations appear to have increased in the Ria de Aveiro, with higher maximum Cr concentrations recorded now than in the past (79.5 and 49.9 mg/kg, respectively). However, the increase does not seem to have been the same in all channels, as there have been cases where concentrations are quite similar. This increase may have occurred due to increased shipping activity in the Ria over time.

When comparing the results obtained in the Tagus estuary [71] and the Ria de Aveiro, it can be concluded that the concentrations of Cr in the Tagus are much higher (5.3 to 592 mg/kg) than in the Ria de Aveiro (1.89 to 79.5 mg/kg), demonstrating relatively lower contamination by this trace element in the Ria. At the international level, two studies were used for comparisons of Cr concentrations. The first study conducted by Bloom and Ayling (1977) [77] that studied trace elements in the Derwent estuary in Tasmania. This aquatic system belonging to one of the Australian states was found to be one of the most polluted rivers in Australia, being affected by various metallurgical wastes, partially treated or untreated sewage, and effluents from food processing plants. Eighteen samples were collected throughout the Australian study area, which showed a range of concentrations between 34 and 286 mg/kg of Cr. The Ria de Aveiro showed to be less Cr impacted than the Derwent estuary and yet did not indicate Cr as a major contamination concern in the study's conclusions. The other study conducted by Vermeulen and Wepener (1999) [78], investigated the spatial and temporal variation of metals in Richards Bay Harbour, in South Africa. This study area is impacted from various industrial inputs, mostly metal-related. The Cr concentrations obtained ranged from 10 to 295 mg/kg, showing a range very similar to that found in the previous study [77] and again higher than that recorded in the Ria de Aveiro.

6.2.4 Copper

Figure 6.7 presents the spatial distribution of Copper (Cu) concentration (mg/kg) along the Ria de Aveiro.



(a)

(b)

Figure 6.7: (a) Spatial distribution of Cu concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

Copper (Cu) content ranged from 0.72 mg/kg to 110 mg/kg, therefore presenting a high range of concentrations. The average concentration was 16.2 mg/kg, showing that more than half of the concentrations are below this level. After the analysis of Figure 6.7, it was concluded that the channel where the highest concentrations of Cu were reported was the Murtosa channel, presenting a range between 0.97 mg/kg and the highest value reported in the entire Ria (110 mg/kg). The second-highest Cu concentration determined was observed in the commercial port that presents a range of concentrations higher (7.30 to 109 mg/kg). Similarly, to all trace elements previously analyzed, the Mira channel is the channel with the lowest concentrations in general, between the lowest value obtained in the entire Ria (0.72 mg/kg) and 23.6 mg/kg. The Ílhavo channel showed a similar Cu concentration variation to the Mira channel, but its distribution along the channel is again heterogeneous, contrarily to the Mira channel. However, the third-highest Cu concentration was reported in an area that has not previously been shown to be highly enriched by other trace elements. This sample was collected in the Vouga River, flowing into the Espinheiro channel, and Cu concentration of 93.6 mg/kg. The Cu concentrations recorded for the main channels are presented in Table 6.5.

Table 6.5: Copper concentration ranges and averages (mg/kg) in the main channels of Ria de Aveiro.

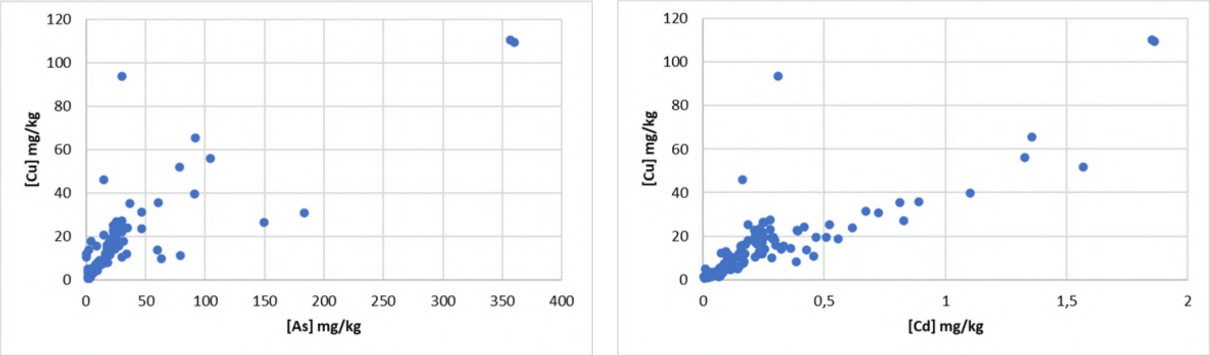
Main Channels	[Cu] ranges (mg/kg)	[Cu] averages (mg/kg)
Ovar	2.84 – 35.4	14.5
Murtosa	0.97 – 110	25.7
S. Jacinto	3.04 – 12.8	9.27
Espinheiro	1.60 – 15.1	8.49
Mira	0.72 – 23.6	4.92
Ílhavo	1.82 – 26.5	12.3

Concerning the possible relationships between Cu and sediment characteristics, correlations were studied using Pearson's correlation coefficient. It is possible to observe that the correlations between Cu, organic matter content and sediment type are both moderate (OM(%):r=0.52, $p<1.46x10^{-9}$, n=119; Si/Al:r=-0.45, $p<3.94x10^{-7}$, n=119), according to Table 6.2. This suggests that, as observed with Cd, there is no well-defined cause-effect, despite of a tendency of Cu concentrations increased with the organic matter content, in opposite to a observed decrease of Cu contents with the increase of the size of the particles. Nevertheless, these factors are important to interpret in justifying the Cu distribution.

An analysis of the anthropogenic sources for Cu was done and several similarities were found with the previously analyzed elements. In the the Ovar channel, the increases of Cu concentrations are observed in areas with higher organic matter content and longer residence time, i.e., at various upstream ends of channels (Figures 6.1 (b) and 6.7 (a)). In the downstream beginning of the channel, the same increase that has been identified occurred due to hydrodynamic factors that favor the accumulation of contaminated particles and possible anthropogenic sources such as shipping activities [33, 57]. In this same area, there is an increase in organic matter that may also justify these results. In the Murtosa channel, the possible source can be related to the same fertilizer and chemical producing factory that discharges effluents in the Estarreja area [5]. This area corresponds to the main area of Cu increments, and reported the highest Cu concentration (110 mg/kg). The commercial port is an area of an immense shipping activity, which contributes to the increase in Cu concentrations (due to the fuel, electrical devices and metallic structures used in these activities), and in addition, this same area and the downstream beginnings of the S. Jacinto and Espinheiro channels may be influenced from the Fuel Farm Tanks that complement the port [33].

In the Ílhavo channel, the increments of Cu concentrations in the north should be due to the presence of port areas and higher shipping activity. In the southern area, the gradual increase in Cu content seems to be highly related to the Vista Alegre factory probably due to the use of pigments for decoration of crockery, among other industrial processes in which Cu may be present [26, 33]. At the same time, the Cu increases in the channel correspond mostly to areas with higher organic matter content. In the Mira Channel, the hotspots observed in the north part appear to be related once again to the existing ports and marinas on the banks, since the Cu increments corresponded to the exact locations. Finally, for the high Cu concentration reported in the Vouga River (93.6 mg/kg), is not clear with the identification of a source, but it is known that several metallurgical factories exist near the river and perhaps can discharge effluents into the river and thus justify higher values in the Vouga River and Espinheiro channel. Beyond this possible hypothesis, there is the reconstruction of the bridge and the existing nautical activity near this area that most likely contribute to these increments. At the same site, there is also a peak of organic matter (13.9%) compared to the values of the Vouga River, which may favor this local increase of Cu concentrations.

After analyzing the recorded concentrations and anthropogenic sources, several similarities were identified between the distribution of Cu and two other elements, As and Cd. To this end, the Pearson correlations analysis between these elements were applied and results are presented in Figure 6.8.



(a)

(b)

Figure 6.8: Relationships between (a) Cu and As and (b) Cu and Cd concentrations (mg/kg), respectively.

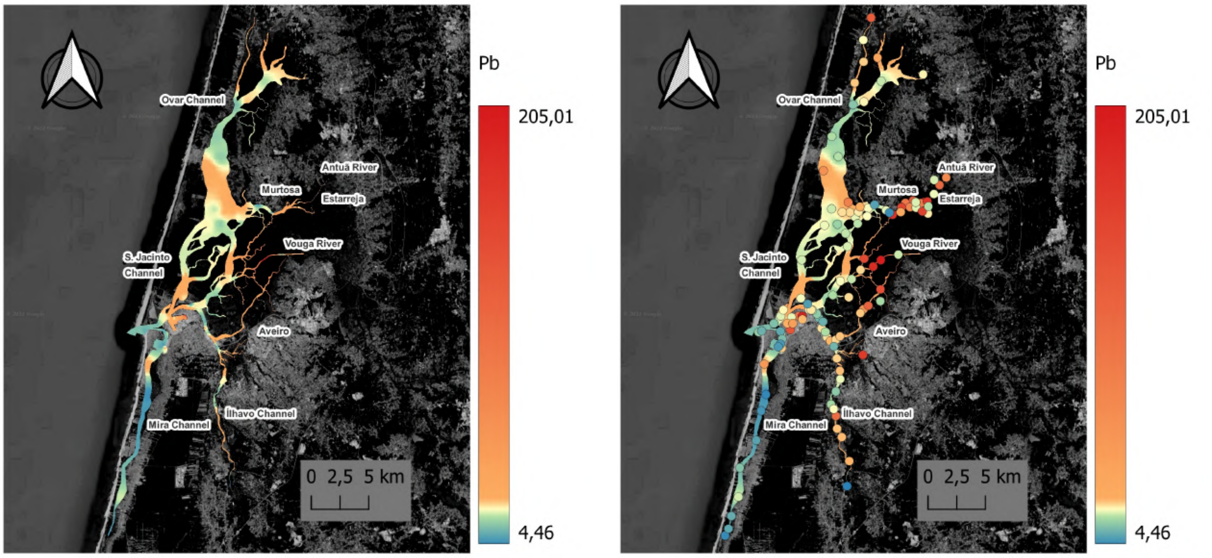
Trough the observation of the Figure 6.8 and the values obtained for the correlation coefficients, (r=0.80, p<2.73x10^{-27}, n=119 for Cu vs As and (r=0.84, p<2.31x10^{-33}, n=119) for Cu vs Cd, it can be concluded that Cu is strong correlated with As and Cd, according to Table 6.2. This justifies the frequent similarity in the distributions of these elements, most likely because the industrial applications of these elements are usually the same, thus contributing to this correlation of distributions.

A comparison of the Cu contents obtained in this present study with previous ones conducted in the Ria de Aveiro was performed. Through the study conducted by Gomes and Delgado (1993) [52], the Cu concentrations in the Ovar channel were compared, ranging from 41 to 59 mg/kg among the only 3 sediment samples collected at the surface. All levels were higher than those reported in the present work, where a maximum of 35.4 mg/kg Cu was obtained. For the Ílhavo channel where the last surface sample was collected, 33 mg/kg of Cu was reported, a concentration higher than the maximum reported in the present work (26.5 mg/kg). Compared to the study conducted by Cachada et al. (2019) [53] that presents a greater diversity of samples among all the channels, there were several differences between the results obtained by the study [53] and those obtained in this present work. For the Ovar and the Espinheiro channels, higher maximums of Cu were reported in the past, 96.1 and 18.8 mg/kg respectively, compared to the 35.4 and 15.1 mg/kg of Cu that were currently reported in the respective channels. For the Murtosa channel, the maximum obtained in the previous study, 88.9 mg/kg of Cu, was lower than the currently reported (110 mg/kg). The same was observed for the Mira channel, where the maximum obtained in the past (8.42 mg/kg) is lower than the reported in this work (23.61 mg/kg). In the Ílhavo channel the maximums of Cu concentrations were similar between studies, with Cu content of 26.5 mg/kg reported in the previous study [53] and 26.48 mg/kg of Cu obtained in the present study. Through these comparisons, it was possible to observe that there was no clear behavior of this metal over time in general in the Ria de Aveiro. Copper concentrations increased in Murtosa and Mira channels, while in Ovar and Espinheiro channels there was a decrease. Thus, it is concluded 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. Although there is no obvious conclusion, a new maximum has been recorded (110 mg/kg), and it should not be forgotten that Cu is an important micronutrient and is abundant in the earth's crust.

Regarding the Tagus estuary [71], once again, the concentrations obtained were much higher than those recorded in the Ria de Aveiro. The Cu concentrations reached 592 mg/kg in the Tagus, while in the Ria, the maximum obtained was 110.3 mg/kg of Cu. Thus, it can be concluded that the Ria is less contaminated by Cu than the Tagus estuary. A similar study was performed in the Golden Horn estuary and the Izmit bay, both in the northeast of the Marmara Sea in Turkey [79]. Both areas belong to densely urbanized and industrialized regions, but the estuary ultimately receives more effluent discharges from anthropogenic sources than the bay. The results showed that the Golden Horn estuary determined a range of Cu concentrations between 337 and 1534 mg/kg, while in Izmit bay it determined between 18 and 51 mg/kg. Compared to this study [79], the Ria de Aveiro lies between these two sites, although it is much closer to the situation described in Izmit bay. The authors concluded that the Cu concentrations are much higher and increased over time in the Golden Horn estuary, while in Izmit bay Cu contents remained generally constant. So, it was assumed that in the bay the Cu are mostly of natural origin, whereas in the estuary the Cu are mostly from anthropogenic sources. A mixture of these two cases can be considered for the situation in the Ria, leading to the belief that there are spot areas with major anthropogenic sources favoring increased Cu concentrations, and other areas are mostly subject to natural sources related to lithogenic influences.

6.2.5 Lead

Figure 6.9 presents the spatial distribution of Lead (Pb) concentration (mg/kg) along the Ria de Aveiro.



(a) (b)

Figure 6.9: (a) Spatial distribution of Pb concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

The Pb content in the analysed samples ranged from 4.46 mg/kg to 207 mg/kg, therefore presenting a large variability of concentrations. The average concentration was 27.5 mg/kg showing that more than half of the determined Pb concentrations are below this level. Analyzing the maps of Figure 6.9, it was possible to conclude that the Ovar, Espinheiro, Mira and Ílhavo channels presented Pb concentration ranges in the same order of magnitude (4.46 – 36.9 mg/kg), with similar minimum and maximum Pb concentrations. S. Jacinto was the channel with a lower range of Pb concentrations (14.9 – 26.9 mg/kg). On the other hand, Murtosa channel determined the highest Pb contents across channels, registering a range between 5.83 and 156 mg/kg. Curiously, it was not in any of the main channels that the highest concentration of Pb in the Ria was registered, but in the Vouga River (207 mg/kg). Then, the site where the second-highest concentration of Pb was registered was in the commercial port, with a maximum of 158 mg/kg. It was also at the same place that the highest minimum concentration was reported, 21.5 mg/kg. The Pb concentrations reported for the main channels are shown in Table 6.6.

Table 6.6: Lead concentration ranges and averages (mg/kg) in the main channel of Ria de Aveiro.

Main Channels	[Pb] ranges (mg/kg)	[Pb] averages (mg/kg)
Ovar	7.63 – 36.9	22.9
Murtosa	5.83 – 156	33.8
S. Jacinto	14.9 – 26.9	22.6
Espinheiro	8.22 – 26.3	18.7
Mira	6.04 – 30.8	12.6
Ílhavo	4.46 – 35.5	21.4

Concerning the possible relationships between Pb and sediment characteristics, Pearson correlations were applied, considering the organic matter content (OM) and the Si/Al ratio. The correlations of Pb vs OM and Pb vs Si/Al indicated that Pb concentrations are positive correlated with OM (r=0.51, p<3.81x10^{-9}, n=119) with a moderate Pearson correlation coefficient, and in relation to the Si/Al, Pb had an opposite behavior, presenting a moderate negative correlation(r=-0.40, p<6.44x10^{-6}, n=119), according to Table 6.2. This suggests that, as with Cu, there is no well-defined cause-effect, despite a tendency for a direct proportionality between Pb and organic matter content, and an inverse proportionality with respect to sediment type and Pb, which probably will affect the lead spatial distribution along the Ria de Aveiro.

After an evaluation of the Pb concentration distribution map (Figure 6.9), a high similarity with the Cu distribution was identified, and for this reason, the correlation between these two metals was also studied using Pearson's correlation coefficient (Figure 6.10).

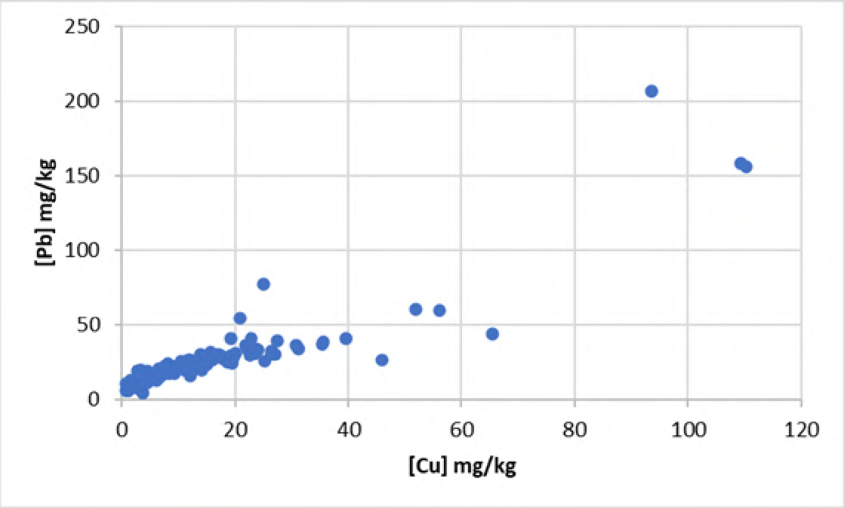


Figure 6.10: Relationship between Pb and Cu concentrations (mg/kg) along the Ria de Aveiro.

Through the analysis of the Figure 6.10 and the Pearson correlation coefficient obtained,(r=0.90, p<5.11x10^{-45}, n=119), it was concluded that there is a very strong correlation between these two elements, according to Table 6.2. This could explain the strong similarity of the Pb and Cu spatial distributions (Figures 6.9 and 6.7, respectively) and may result from a strong association of these elements to the same industrial applications and, consequently, the same sources.

Consequently, when analyzing the possible anthropogenic sources and the factors that favor Pb distribution, the hypotheses are based on the same presented to describe the distribution of Cu. Shipping activities, ports, docks, and marinas contribute to the hotspots in the channels of Ovar, Mira, Ílhavo (northern zone), and in the commercial port near the Barra entrance. In this last area, Pb may, most likely, have been used in the port structure and Fuel Farm Tank that complements the site, also contributing to the slight increase of Pb in the area and at the downstream beginning of S. Jacinto and Espinheiro channels [1, 26, 33]. Regarding the Ovar channel, there may be an extra anthropogenic source, which is the plastics factory that discharges its effluents into the channel, similarly to Cd [5]. 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, with effluents being responsible for the increases in the area between Laranjo and Estarreja.

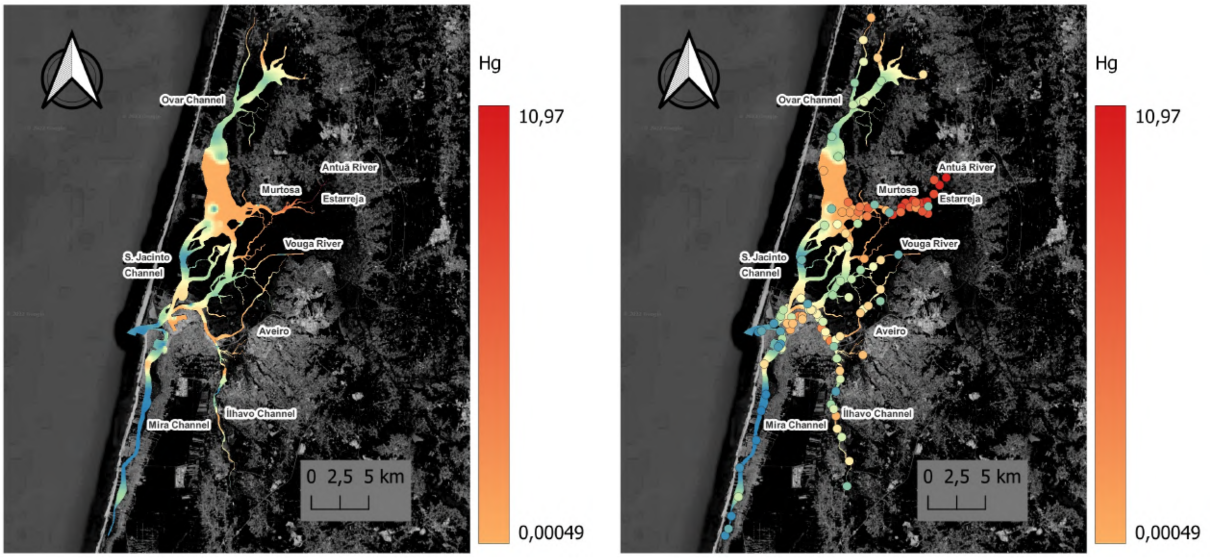
Regarding the southern part of the Ílhavo channel, the Vista Alegre factory appears to be again linked to the Pb increases due to the synchronism between the site and the new zone of increase along the channel. This could be possibly due to pigments used in the decoration of the crockery and molds, or parts of the process that use this metal in their constitution [33]. As for the maximum concentration of Pb found in the Vouga River, this may be related to the fallen bridge, which has involved construction on the site 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 [1, 33]. Regarding hydrodynamic factors and sediment characteristics, again links were found. In the Ovar channel, where the hydrodynamics, already previously explained, in the area favors the accumulation of contaminated particles at the beginning of the channel and the organic matter content appears to benefit Pb accumulation due to often coinciding with hotspot areas [57].

For a better understanding of these results, comparisons were made with Pb concentrations recorded in the Ria in the past, with the Tagus estuary and with an estuary at the international level. In the study conducted by Gomes and Delgado (1993) [52], the authors reported higher Pb concentrations in Ovar and Ílhavo channels (59 and 58 mg/kg respectively) compared to those currently recorded (36.9 and 35.5 mg/kg, respectively). Regarding the study conducted by Cachada et al. (2019) [53], that has been used to compare trace elements concentrations in the Ria, both the Murtosa and Mira channels showed lower Pb maximums (76.9 and 11.6 mg/kg, respectively) than those recorded in the present work (156 and 30.8 mg/kg, respectively). Considering the Espinheiro channel, the only sample analyzed showed a Pb concentration of 41.8 mg/kg, higher than the maximum presently obtained. The Ovar and Ílhavo channels recorded maximum values similar to those currently recorded, 31.7 and 37 mg/kg respectively [53]. All the minimum concentrations reported by Cachada et al. (2019) showed to be higher than those recorded in the present work, although this may be related to the low number of samples collected in the channels. The same situation may influence lower maximums as in Murtosa and Mira, although in the case of Murtosa, this was the channel with the highest number of samples collected. Thus, it was possible to conclude that there was no clear behavior of Pb 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 inputs over time since Pb is a metal that exists in small amounts.

Comparative to the Tagus estuary, the study conducted by Vale et al. (2008) [71] analyzed the Pb concentrations and reported a maximum of 2858 mg/kg, approximately 14 times higher than the maximum determined in the present work (207 mg/kg). Although the Ria shows relevant Pb concentration levels, the Tagus estuary definitely has a higher Pb contamination. Regarding the international study, it was decided to use the same case study as mentioned in the Cu analysis, to make a double comparison, at the trace element level and the correlation between the two metals in a different estuary. In the study conducted by Ergin et al. (1991) [79] that analyzed the concentration of trace metals in the Golden Horn estuary and Izmit Bay in Turkey, a range of Pb concentrations was recorded between 141 and 797 mg/kg in the estuary and from 24 to 83 mg/kg in the bay. As in the case of Cu, in terms of maximum Pb concentrations, the Ria de Aveiro is between these two cases. For a better understanding of the correlation between Pb and Cu, Pearson's correlation coefficient was determined for the Pb and Cu concentrations of the study conducted by Ergin et al. (1991) [79], and for the estuary, an ($r=0.72$, $p<3.62\text{x}10^{-5}$, $n=26$) was obtained, showing a strong correlation between the two elements, in opposite to the bay where ($r=0.071$, $p<0.71$, $n=31$) was obtained, suggesting the lack of correlation between Pb and Cu (according to Table 6.2). Thus, it was concluded that the affinity of these elements in the case of Ria de Aveiro is probably due to anthropogenic sources in common and not some similar chemical behavior among them.

6.2.6 Mercury

Figure 6.11 presents the spatial distribution of Mercury (Hg) concentration (mg/kg) along the Ria de Aveiro.



(a) (b)

Figure 6.11: (a) Spatial distribution of Hg concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

Mercury (Hg) in the sediments ranged from 0.00045 mg/kg (0.45 µg/kg) to 22.06 mg/kg, hence presenting a considerable variability of concentrations. The average concentration was 0.84 mg/kg showing that almost all the determined concentrations are below. By analysis of Figure 6.11, it can be observed that the area of the Ria with the highest Hg concentrations is the Murtosa channel, where the concentrations ranged between 0.015 and 22.1 mg/kg, two orders of magnitude higher than the Hg concentrations found in the other channels, and being the highest Hg levels in the entire Ria. Ovar and Ílhavo channels, showed similar ranges of concentrations, between 0.0064 and 0.40 mg/kg, and from 0.0051 to 0.30 mg/kg, respectively. In both channels the minimum concentrations reported are low and were observed in the narrowing zone of the channels. As has been observable so far for the other trace elements under analysis, the Mira channel was the one that reported the lowest Hg concentrations, in a range between the lowest Hg concentration reported in the entire Ria (0.45 µg/kg) and 0.11 mg/kg. The commercial port near the Barra entrance, did not showed high concentrations as with other trace elements, presenting concentrations quite consistent with those of the other channels, between 0.050 and 0.27 mg/kg. The Hg concentrations determined for the main channels are shown in Table 6.7.

Table 6.7: Mercury concentration ranges and averages (mg/kg) in the main channel of Ria de Aveiro.

Main Channels	[Hg] ranges (mg/kg)	[Hg] averages (mg/kg)
Ovar	0.0064 – 0.40	0.10
Murtosa	0.015 – 22.1	3.64
S. Jacinto	0.014 – 0.38	0.16
Espinheiro	0.0055 – 0.12	0.06
Mira	0.00045 – 0.11	0.02
Ílhavo	0.0051 – 0.30	0.10

Concerning the possible relationships between Hg and sediment characteristics, again, correlations were studied using Pearson's correlation coefficient. Contrarily to what might be expected, Hg concentrations were not correlated with organic matter content ($r=0.15$, $p<0.11$, $n=119$) and even with Si/Al ($r=-0.14$, $p<0.14$, $n=119$). This could indicate that, in this specific situation in the Ria de Aveiro, none of these parameters have any influence on the distribution of this metal (according to Table 6.2). Thus it appears that the anthropogenic sources and hydrodynamic factors contribute to the observed distribution.

Due to all the focus that Hg has had over the years in several studies on the Ria de Aveiro, there were already several expectations of how the trace element distribution would be currently, and the obtained results corroborated the previous studies (e.g. Pereira et al. (1998)) since the Hg hotspots observed in the previous study [7] are present at this work. The highest Hg concentrations were found in the Murtosa channel, where 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 [7]. 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 recorded. 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. This area appears to favor the transport of Hg contaminated particles from the Murtosa channel to the beginning of the Ovar channel, supporting the influence of hydrodynamic factors suggested and already explained previously for other metals [57].

However, the map through quantile ranking does not show so explicitly the reduction of concentrations in the turbid zone and a slight increase again at the beginning of the Ovar channel, also benefiting the previously suggested hydrodynamic effects as drivers of the obtained Hg distribution. 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 residence time of sediments in those areas and therefore greater sedimentation of particles [57]. The nautical activity (combustion of fossil fuels) in this area and the existence of a marina, although they do not appear to be a relevant source of Hg contamination in the area, may contribute to slightly increase the Hg contents, due to small associations to the same activities and port areas identified on the map (Figure 6.11) in other locations [80]. An example is the commercial port that presents concentrations quite similar to the situation in Ovar channel but has a much higher nautical 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, compared to places without this type of activity, it is not something that is contributing in the end to contamination by this element.

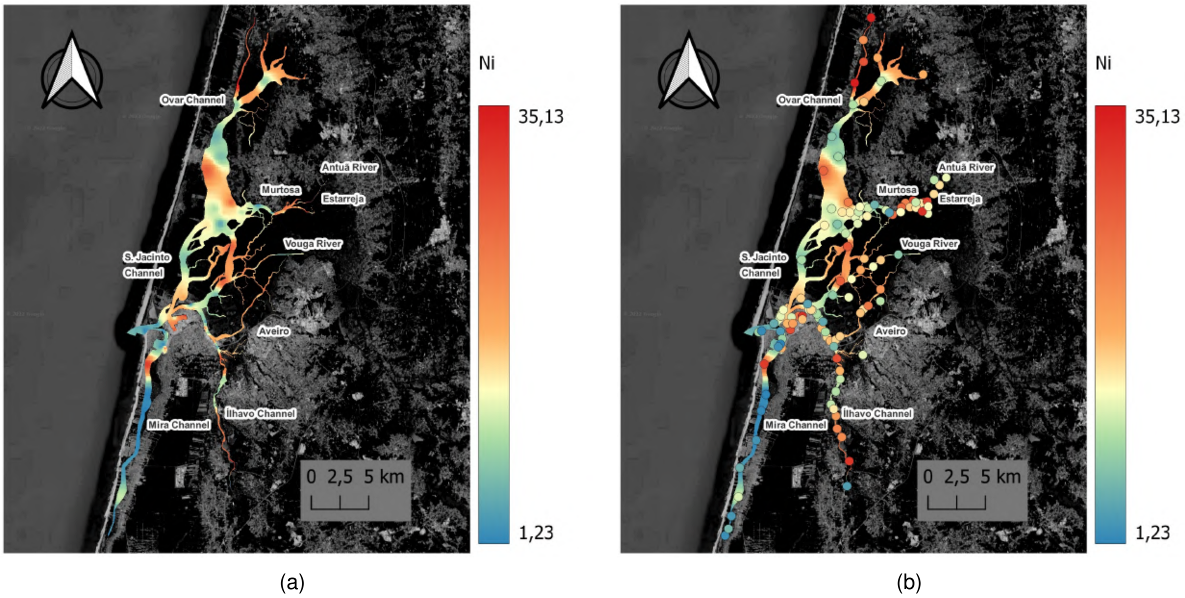
The same occurs in the north of the Mira and Ílhavo channels, where an increase in Hg concentrations can be seen in the areas of ports and marinas along the banks of the channels. In the south of the Ílhavo channel, a further increase in Hg concentration can be seen from the Vista Alegre factory. Mercury in the past was already used in paintings and therefore the increase in concentration may be due to evidence of the time when the painted decorations of the pieces still involved Hg [1].Finally, in the same order of magnitude, an increase in Hg concentrations is visible along the Vouga River, which is possibly be associated with the pulp mill residing on the river bank [5].

In the case of Hg, the discussion is based on the work conducted by Pereira et al. (1998) [7] that studied the contamination of this element in the Ria, mainly in the Murtosa channel. The authors reported Hg concentrations varying between 0.32 and 343 mg/kg along this channel. For the rest of the Ria, an average value of 0.7 mg/kg of Hg was determined. At Murtosa, the sample with the lowest Hg concentration was collected at the downstream beginning of the channel (0.015 mg/kg) while the highest Hg concentration was collected near the Estarreja area (22.1 mg/kg), close to the industrial discharges. The range of concentrations reported in the past had a much larger amplitude than that reported in the present work, in addition to much higher Hg concentrations (maximum concentration approximately 16 times higher than the current one. The same can be concluded for the average of 0.7 mg/kg Hg that was in the past considered for the rest of the Ria de Aveiro, as it is higher than any maximum concentration reported in the other channels in the present study. However, the way Hg appears to be distributed along the Murtosa channel is similar to the distribution indicated in the present. In this work, the highest Hg concentrations were also reported closer to the Estarreja area and decreased towards the beginning of the channel, although not in a gradual way or without minor exceptions. Therefore, it is concluded 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.

In the Tagus estuary, the study conducted by Canário et al. (2005) [81] analyzed Hg concentrations along the study area, and determined that the concentrations varied between 0.008 and 49.35 mg/kg. These values represent a higher range of Hg concentrations than the results reported by the present work. The maximum Hg concentration was 22.1 mg/kg, which is already a sign of contamination. For this reason, the Ria de Aveiro, compared to the Tagus, presents a lower contamination by Hg, at least when comparing surface sediments. Regarding other works that reported Hg distribution in sediments, the study conducted by Cukrov et al. (2020) [82], that evaluated Hg concentrations in the Krka River estuary was used, as it is an area that has been considered unpolluted. Surface sediment samples were collected throughout the estuary, and Hg concentrations ranging from 0.058 to 12.4 mg/kg were recorded, with an average of 1.14 mg/kg. These values are comparable to the situation in Ria de Aveiro, where it is possible to observe quite low concentrations that do not represent a contamination hazard and at the same time a maximum concentration that according to (Portaria nº 1450/2007) corresponds to the maximum pollution class [6]. Furthermore, through the average of the values, it is possible to understand that in general, the Hg concentrations are low, as also happens in Ria de Aveiro. In this study [82], it was concluded that the southern area of the Krka estuary is much more affected by this element than the northern one, mainly by association with shipyard activities, ship repair, and marinas, something that was also identified in the Ria de Aveiro. Zones within the scope of naval activities almost always showed slight increases in Hg concentrations, something that is also supported by the study conducted by Cukrov et al. (2020).

6.2.7 Nickel

Figure 6.12 presents the spatial distribution of Nickel (Ni) concentration (mg/kg) along the Ria de Aveiro.



(a) (b)

Figure 6.12: (a) Spatial distribution of Ni concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

Nickel (Ni) concentrations obtained in this study ranged from 1.13 mg/Kg to 35.5 mg/kg, hence presenting a moderate range of concentrations. The average concentration was 14.9 mg/kg indicating that there is a uniform distribution of concentrations. After an analysis of the map (Figure 6.12), it was possible to conclude that the channel with the highest nickel concentrations is the Ovar channel, with values ranging between 3.64 mg/kg and the highest value recorded in the Ria (35.5 mg/kg). Next, the channel with the highest concentrations was the Murtosa channel, with a range between 2.09 and 33.9 mg/kg. At the same time, the commercial port showed a maximum very similar to the one at Murtosa, a concentration of 33.9 mg/kg. The minimum concentration obtained was 11.8 mg/kg, the highest minimum compared to the other channels. Regarding the southern channels, both the Mira and Ílhavo channels showed very similar minimum and maximum concentrations. In the Ílhavo channel, concentrations vary between 1.93 and 31.6 mg/kg, and in the Mira channel, the values obtained are between the lowest value recorded (1.13 mg/kg) and 31.1 mg/kg. However, despite presenting similar ranges, the Ílhavo channel shows higher nickel concentrations along the channel, compared to the Mira channel, which appears to be the poorest in Ni of all channels. The Espinheiro channel also showed a maximum Ni concentration comparable to the other channels already mentioned, with a maximum value of 27.4 mg/kg. The Ni concentrations recorded for the main channels are shown in Table 6.8.

Table 6.8: Nickel concentration ranges and averages (mg/kg) in the main channel of Ria de Aveiro.

Main Channels	[Ni] ranges (mg/kg)	[Ni] averages (mg/kg)
Ovar	3.64 – 35.5	17.9
Murtosa	2.09 – 33.9	16.8
S. Jacinto	4.43 – 18.3	12.2
Espinheiro	2.35 – 27.4	13.4
Mira	1.13 – 31.1	6.39
Ílhavo	1.93 – 31.6	15.1

Concerning the possible relationships between Ni and sediment characteristics, correlations were studied using Pearson's correlation. The results obtained through the Pearson's correlations of Ni vs organic matter content and Ni vs Si/Al provided coefficient correlations of r=0.59, p<1.44x10^{-12}, n=119 and r=-0.74, p<6.81x10^{-22}, n=119, suggesting moderate positive and strong negative correlations, respectively (according to Table 6.2). These results suggested that Ni will normally be found in higher concentrations in fine sediments, such as mud, compared to coarser sediments, such as sands. However, even though there is a trend regarding organic matter content, it is not so linear, as anthropogenic sources and their locations seem to influence this relationship, like the observed with Cr. Nevertheless, these factors are relevant to consider in justifying the nickel distribution.

Through the metal distribution analysis and the correlations with the sediment characteristics, the comparison between Ni and Cr was immediate, suggesting a high correlation between them. For this reason, the correlation between these two elements was studied using Pearson's correlation (Figure 6.13).

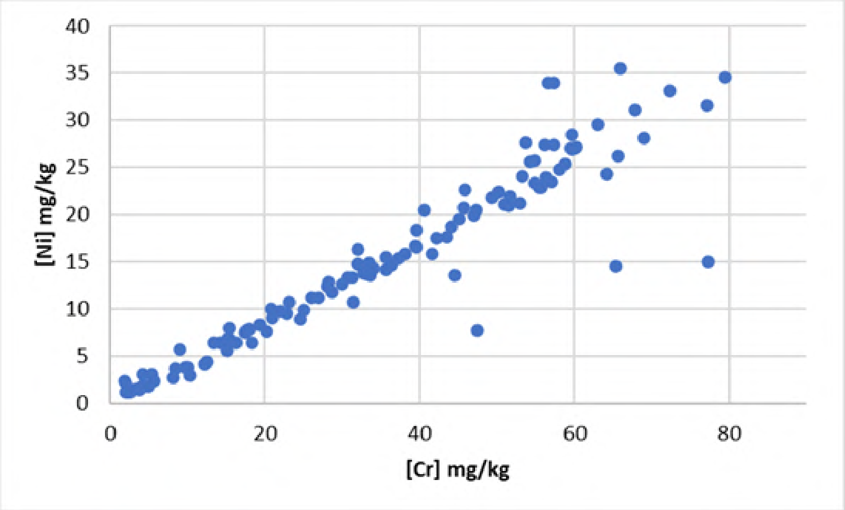


Figure 6.13: Relationship between concentrations of chromium and nickel (mg/kg).

The obtained correlation between Ni and Cr ($r=0.94$, $p<1.67\times10^{-58}$, $n=119$) indicated that these two elements are very strong correlated, according to the Table 6.2. For this reason, the distribution of both along the Ria is so similar, suggesting that this correlation may be related to common anthropogenic sources and/or similar chemical behaviors.

In this sense, the possible anthropogenic sources will be based on the same already referred for Cr, because almost all the hotspots occurred in the same channels and the same locations. Similar to Cr, the vast majority of increases in Ni concentrations occurred in areas with ports, marinas, and high shipping activity, due to the use of Ni in the boats metal alloys to prevent corrosion by an acidic environment and the combustion of fossil fuels [33, 75]. It is possible to identify these cases at the beginning and ends of the Ovar channel, where there are several areas for mooring boats. In the commercial port where the shipyard activity is enormous. In the north of the Mira channel where there are marinas and ports in the exact locations of the increased Ni concentrations, and in the north of the Ílhavo channel for the same reasons as in Mira. In the case of the Murtosa channel, the major anthropogenic influence seems to be once again the Estarreja Industrial Park and its production of fertilizers and chemicals [5].

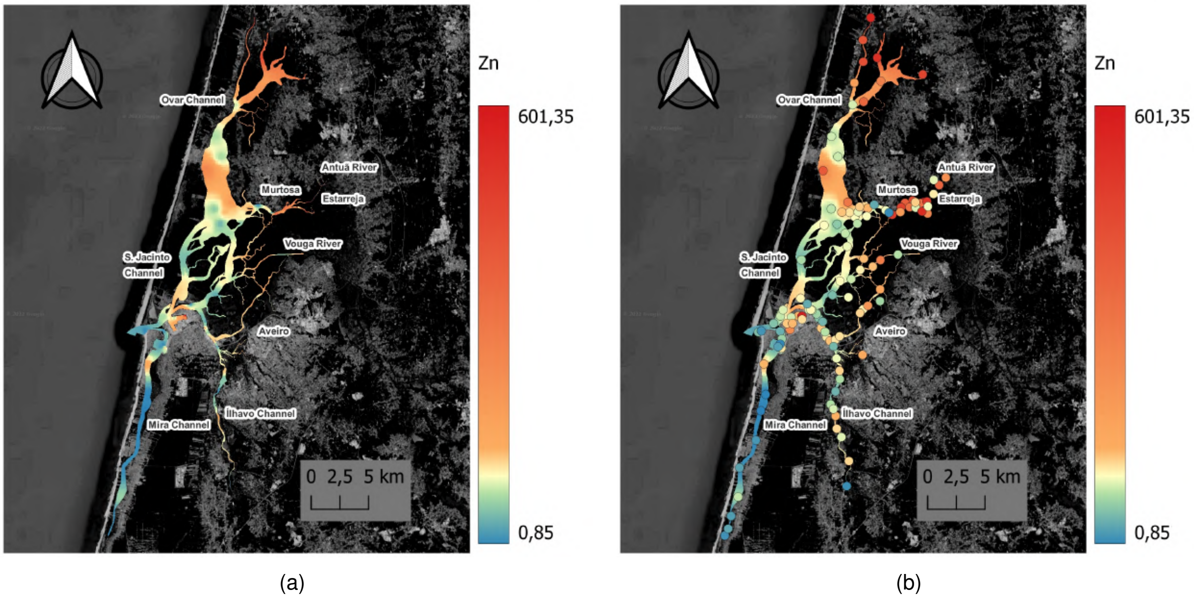
In the south of the Ílhavo channel, there is also an increase in Ni concentrations that appears to be again related to the Vista Alegre Factory, due to the use of this metal in pigments [33]. Finally, further north in the Espinheiro channel, an increase in Ni concentrations is visible (27.4 mg/kg) and appears to have the Vouga River as its source. This is most likely related to the multiple metallurgical factories that reside near the river banks and may release produced effluents into the river. The fallen bridge that was under construction at the time of the sampling could also contribute to the Ni concentrations found in this area, due to this element being used in the production of alloys, especially if it is to be in contact with water, as already explained for the boat's case [33, 75]. Additionally, nautical activity in the area contributes to the Ni content found. In terms of the hydrodynamic factors and sediment characteristics, the same reasons previously mentioned for other trace elements apply to this distribution. The currents in the Ovar channel favor sedimentation at the beginning of the channel and the high residence time of particles at the end of the channel favors sedimentation and metal accumulation [57]. The residence time also favors other places like at the end of the Ílhavo channel, where was recorded 31.61 mg/kg of Ni. In addition, there is the organic matter content and sediment type that combined with the previous factors favor the increase in concentrations. It is noticeable from Figure 6.12, that there are several locations with increased concentrations that correspond to an area with more organic matter or finer sediment, as is the case of the increase in Ni in the Espinheiro channel and the increase in concentrations in the initial zone of the Ovar channel, respectively.

For a better understanding of the results obtained, a comparison was made with Ni concentrations recorded in the Ria in the past, with the Tagus estuary and with the same international case used for Cr, in order to also compare the correlation between Ni and Cr in another estuary. Regarding the study conducted by Gomes and Delgado (1993) [52], the collected surface sample, from the channels of Ovar and Ílhavo, recorded higher Ni concentrations (49 and 63 mg/kg respectively) when compared to the ones obtained in the present study (35.5 and 31.6 mg/kg respectively. Additionally, the study conducted by Cachada et al. (2019) [53] indicated that all channels, except Murtosa, showed maximum Ni concentrations below those currently recorded (in the previous study [53]: Ovar-30.1 mg/kg, Espinheiro- 16.4 mg/kg, Ílhavo- 20.1 mg/kg and Mira-6.90 mg/kg). In the Murtosa channel, a maximum of 126 mg/kg was recorded [53], almost 4 times higher than the maximum recorded in the present work. However, it was the channel with the highest sampling grid compared to the other channels, which may justify lower maximums. Despite the uncertainties, it is possible to understand that with the exception of Murtosa where Ni contents have been reduced over time, today, the other channels do not seem to vary that much from the past. In fact, the ones that vary the most were the Espinheiro and Mira channels, but they are also the ones where fewer samples were collected, i.e., greater uncertainty.

Regarding the Tagus estuary [71], the concentrations obtained were much higher than those recorded in the Ria de Aveiro. In the Tagus estuary, the Ni levels ranged between 1 and 489 mg/kg, while in the Ria de Aveiro, the Ni concentrations ranged between 1.13 and 35.5 mg/kg. Therefore, it can be concluded that the Tagus has a higher Ni contamination, when compared with the Ria de Aveiro. The international study, the study developed by Bloom and Ayling (1977) [77], addressed the case in the Derwent estuary in Tasmania, one of the most polluted rivers in Australia. In the 18 samples analyzed, Ni concentrations ranged from 31 to 127 mg/kg. This range of Ni concentrations is much higher than that recorded in the Ria de Aveiro. However, in the final conclusions of the study, Ni was not one of the most worrying metals among all, emphasizing that the Ria de Aveiro, with its smaller variation, is not a critical situation of contamination by Ni. Additionally, was studied the correlation of Cr and Ni values obtained in the study conducted by Bloom and Ayling, to better understand the correlation of trace elements obtained in the Ria. The Pearson´s correlation coefficient obtained for these data was ($r= 0.097$, $p=0.73$, $n=15$), i.e., a lack of correlation between the two elements (according to Table 6.2). This result suggests that probably what provides such a strong correlation between Cr and Ni in the Ria de Aveiro are the anthropogenic sources in common and not a similar chemical behavior between them.

6.2.8 Zinc

Figure 6.14 presents the spatial distribution of Zinc (Zn) concentration (mg/kg) along the Ria de Aveiro.



(a)

(b)

Figure 6.14: (a) Spatial distribution of Zn concentrations (mg/kg) in the Ria de Aveiro and (b) the sample points with the respective classification. A quantile classification was used for the creation of the map.

Zinc (Zn) concentrations ranged from 0.79 mg/Kg to 603 mg/kg, showing a widest range of concentrations. The average concentration was 127 mg/kg, indicating that more than half of the observed concentrations are below this value. Through the analysis of the concentration distribution map (Figure 6.14), it can be observed that the highest concentration of zinc throughout the Ria was recorded in the commercial port and not in one of the channels. The sample with the highest Zn concentration was the same where other concentration maximums of trace elements were determined (for example, As). In the port, the lowest concentration determined was 72.7 mg/kg, presenting the highest minimum in all the Ria. Next, the channel that showed the highest Zn concentrations including the second-highest concentration, was the Murtosa channel which recorded a range from 3.56 to 602 mg/kg of Zn. The Ovar channel also recorded high concentrations throughout its area and the highest minimum concentration among all channels, showing a range of concentrations between 39.5 and 495 mg/kg. In the case of the southern channels, both the Mira and Ílhavo channels showed similar concentration ranges, especially concerning the recorded maximums. However, similarly to previous cases, despite presenting similar ranges, the Ílhavo channel recorded along its area higher zinc concentrations, between 4.81 and 152 mg/kg. The Mira channel is again the poorest one, recording concentrations between the lowest in the entire Ria and 151 mg/kg. The Zn concentrations determined for the main channels are shown in Table 6.9.

Evaluating the possible relationships between Zn and sediment characteristics, correlations were studied using Pearson's correlation. According to the obtained correlation coefficients, Zn concentrations are positively correlated with organic matter content, showing a moderate correlation (r=0.51,

Table 6.9: Zinc concentration ranges and averages (mg/kg) in the the main channels of Ria de Aveiro.

Main Channels	[Zn] ranges (mg/kg)	[Zn] averages (mg/kg)
Ovar	39.5 – 495	202
Murtosa	3.56 – 602	201
S. Jacinto	38.5 – 132	94.7
Espinheiro	11.00 – 108	67.9
Mira	0.79 – 1501	31.2
Ílhavo	4.81 – 152	78.7

$p<2.48\text{x}10^{-9}$, n=119). In opposite, Zn and Si/Al were negative correlated, also showing a moderate correlation (r=-0.53, $p<3.77\text{x}10^{-10}$, p=119). This interpretation of the results is according to Table 6.2. This suggests that there is no well-defined cause-effect, despite there is a tendency for a direct proportionality between Zn and organic matter content and an inverse proportionality with respect to sediment type and Zn. Therefore, these factors are important to consider in justifying the Zn distribution.

When evaluating the distribution of Zn (Figure 6.14), a great similarity with other distributions of other studied elements is visible, but the most similar distribution is the one of Cd. For this reason, the correlation between these two elements was analyzed using Pearson's correlation.

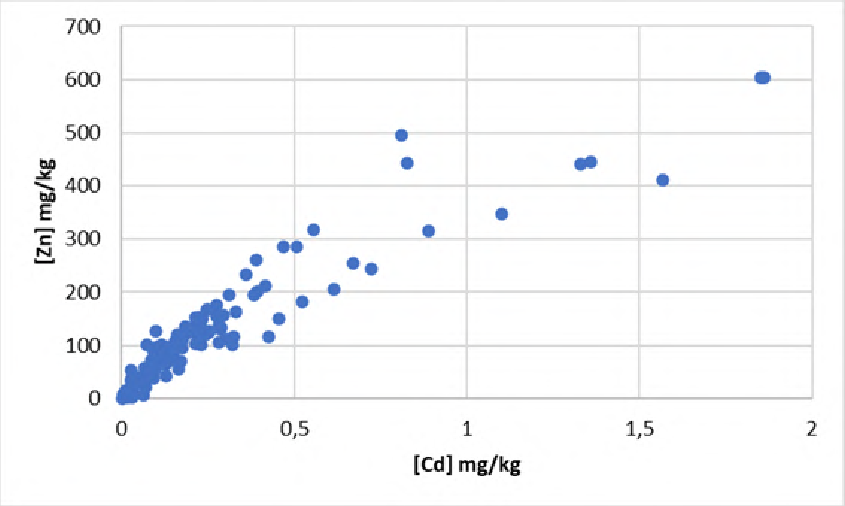


Figure 6.15: Relation between concentrations of cadmium and zinc (mg/kg)

Based on Figure 6.15 and the value for the correlation coefficient, between Zn and Cd (r=0.94, $p<3.59\text{x}10^{-55}$, n=119), it was possible to observed that there is a strong correlation between these two elements (according to Table 6.2). For this reason, the distribution of both along the Ria is similar. As with other metals with high correlations, anthropogenic sources in common are expected at the origin of the higher Zn concentrations and there is the possibility of similar chemical behaviors.

Thus, anthropogenic sources will heavily rely on those described for Cd, which are often the same as those described for other trace elements already studied. In the case of the commercial port, where the highest Zn concentration was recorded (603 mg/kg) the major source lies in the high shipyard activity and probably in the Fuel Farm Tank that completes the port, where the high presence of this element can be understood (combustion of fossil fuels and Zn is used in alloys/batteries)[33]. Therefore, it is easy to understand that several hotspots identified along the Ria appear to be associated with port 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 indicated areas, there is the presence of ports, marinas, bays, and a higher frequency of boats and ships, consequently. In the case of the Murtosa channel, where the second-highest concentration was recorded (602.37 mg/kg), the major focus is once again on the Estarreja industrial park, due to its production of fertilizers, and where Zn is commonly used [5].

Regarding the south of the Ílhavo channel, the concentration increases coincide, again, with the Vista Alegre factory, which is expected since Zn is used in the production of pigments and glass [33]. Finally, there appears to be a slight increase in Zn concentrations in the Vouga River (195 mg/kg), which, again, probably comes from the bridge under reconstruction and the existing nautical activity in the area, due to the sighting of a small bay. In addition, there is a strong possibility of influences from metallurgical plants in the Vouga River. In terms of hydrodynamic factors such as currents and particle residence time, the same conclusions are identified in this distribution, similar to what has been seen before. It is possible to detect increases in Zn favored due to the residence time of particles in some channel ends, as is the case of Ovar (maximum of 495 mg/kg) and Murtosa (maximum of 602 mg/kg). Regarding the currents, it is observed in Figure 6.14, an increase in Zn concentrations at the downstream beginning of the Ovar channel (200 mg/kg), starting from the right side (Murtosa channel side), which favors the hypothesis of contaminated suspended particles being transported from Murtosa to Ovar, due to the previously explained turbid areas. Along with the beginning of the Ovar channel, the current velocity decreases, leading to greater sedimentation of particles and favoring the increase in Zn concentrations which increases to 260 mg/kg [57]. Regarding organic matter and sediment type, there appears to be a link between most Zn hotspots and higher organic matter content, and lower grain size sediments, which was corroborated by the obtained coefficient correlations between Zn and the sediment characteristics previously discussed.

For a good interpretation of the acquired data, a comparison was made between the results obtained in this work and Zn concentrations recorded in the Ria in the past. Based on the study of Gomes and Delgado (1993) [52], through sediment surface samples in the channels of Ovar and Ílhavo, higher Zn concentrations were recorded, 1917 and 277 mg/kg, respectively, when compared with those currently identified in the same channels (maximums of 495 and 152 mg/kg, respectively). It was also reported the study developed by Cachada et al. (2019) [53], which presented a mixture of results compared to those obtained in this work. For the Ovar, Murtosa, and Espinheiro channels, maximum Zn values higher than those currently obtained were recorded, 1270 mg/kg, 704 mg/kg, and 120 mg/kg respectively. As can be seen, in the past the channel with the highest Zn concentration was the Ovar channel while now it is the Murtosa channel. Regarding the Mira and Ílhavo channels, the maximums recorded were lower than those obtained in this work (42.3 and 134 mg/kg vs 151 and 152 mg/kg, respectively), which may be from the low representativeness of samples for analysis or from a real increase of Zn concentrations in the channels over time. However, it is possible to conclude that in general, Zn concentrations have been decreasing over time.

Once again, the Ria de Aveiro presented Zn concentrations lower than those reported in the Tagus estuary [71]. The Ria presented a maximum Zn concentration (603 mg/kg), approximately five times lower than the maximum recorded in the Tagus (2854 mg/kg). An international study was also used to make a comparison of the Zn concentrations. In the study conducted by Marcovecchio et al. [83], the Bahía Blanca estuary in Argentina was studied, as it is constantly influenced by urban and industrial pressures. Surface samples were collected along the estuary, which after analysis recorded a range of Zn concentrations between 15.7 and 90.2 mg/kg. These Zn concentrations presented a much lower range than that recorded in the Ria. It was concluded in Bahía Blanca that the identified peaks were associated with anthropogenic sources such as industrial and urban effluents. Several examples given by this study in order to justify these causes were oil refineries, food factories, fishing boats, port-related operations, among others. Thus, it can be observed that several sources responsible for the increase of Zn in the Argentine estuary are common to those identified in the Ria de Aveiro. However, it was concluded that the contamination in Aveiro is much higher. Should not be forgotten that Zn is an important element for biological, metabolic and immunity functions, and is exists in natural concentrations in the environment.

6.3 Stocks

Having calculated the concentrations for the several trace elements in each sample, it was possible, based on these results, to interpolate concentrations for the studied area of the Ria de Aveiro, through what Qgis allowed using satellite maps. From 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 6.10.

Table 6.10: Stocks of trace elements (tons) determined in the sampling area of the Ria de Aveiro in the present study.

Trace Elements	Stocks (Tons)
As	60.9
Cd	0.84
Cr	124
Cu	45.8
Pb	91.9
Hg	0.60
Ni	54.7
Zn	444

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, in percentage, taking into account the real area of the Ria de Aveiro. As mentioned earlier in this work, the total area can vary between 66 and 83 km^2, depending on the tide. For this reason, an average between these two areas (74.5 km^2) was used to calculate the correspondence of the study area to the real area, represented in Table 6.11.

Table 6.11: Representativeness of the study area in relation to the real area of the Ria de Aveiro.

Total Study Area (Km^2)	**Total Real Area (km^2)**
48.4	74.5
Corresponding Area (%)	
65	

Based on this calculation, it can be 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. This implies that the stocks of the 8 studied elements correspond exclusively to 65% of the total existing mass of those metals in the Ria. 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 another aquatic environment, also suffering from a high anthropogenic influence, was made. For this, the example of the Tagus estuary was used, through the studies conducted by Canário et al. (2005) [81] and Vale et al. (2008) [71], which studied the Hg stocks and the remaining trace elements, respectively.

Table 6.12 presents the comparison of trace element stocks (tons) obtained in Ria de Aveiro and Tagus estuary.

Table 6.12: Comparison of trace element stocks (tons) obtained in Ria de Aveiro and Tagus estuary.

Trace Elements	**Stocks (tons)**	
	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

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, which was indicated, in general, in Table 6.12. 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 using the values obtained in this study, the stocks would never reach the values obtained for the Tagus estuary.

6.4 Trace elements correlations

Through the discussion of the distribution of the trace elements along the Ria, it was possible to identify several similarities between some of them, which can be a good predictor of their sources. For this reason, correlations between these trace elements were determined and analyzed using Pearson's correlation coefficient, as shown in Table 6.13.

Table 6.13: Pearson's correlation coefficient obtained by the analysis of the correlations between the trace elements studied.

Trace Elements	**As**	**Cd**	**Cr**	**Cu**	**Pb**	**Hg**	**Ni**	**Zn**
As	1.00	0.79	0.34	0.80	0.68	0.74	0.46	0.72
Cd		1.00	0.54	0.84	0.64	0.60	0.65	0.94
Cr			1.00	0.58	0.43	0.18	0.94	0.67
Cu				1.00	0.90	0.54	0.68	0.84
Pb					1.00	0.41	0.52	0.65
Hg						1.00	0.27	0.52
Ni							1.00	0.77
Zn								1.00

By analyzing the data presented in Table 6.13 it was possible to conclude that there are 3 very strong correlations between the trace elements analyzed, which were eventually mentioned throughout the discussion on their spatial distribution along the Ria de Aveiro. These correlations are between Pb and Cu, Ni and Cr and Zn and Cd. All have been shown to have anthropogenic sources in common between them, contributing to the similar distributions and these correlations. However, there are other strong relationships between several trace elements, which help explain the identification of the same anthropogenic sources for almost all. Examples of such strong correlations are the case of As and Cd with Cu or Zn with Cu. Copper, Zn, and As had the best correlations with the other trace elements, with a total of 4 strong correlations each.

On the other hand, the trace elements with the worst correlations were mercury, lead, and chromium, which only showed 1 strong correlation with another trace element. Even so, Hg and Cr managed to be the trace elements with the worst correlations overall, showing a very weak correlation between them. However, at the distribution level, Hg was the element with the most distinct distribution, most likely because most of the anthropogenic sources responsible for the significant increases in Hg are not the same as those responsible for the simultaneous concentration peaks of other metals.

6.5 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 [6], 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. Table 6.14 presents an adaptation of the classification according to Portaria nº 1450/2007 [6].

Table 6.14: Contamination degree (in classes) based on concentrations of trace elements in dredge material (adapted from Portaria nº 1450/2007 [6].

Trace Elements	Class 1	Class 2	Class 3	Class 4	Class 5
As	<20	20 - 50	50 -100	100 - 500	>500
Cd	<1	1 - 3	3 - 5	5 - 10	>10
Cr	<50	50 - 100	100 - 400	400 - 1000	>1000
Cu	<35	35 - 150	150 - 300	300 - 500	>500
Pb	<50	50 - 150	150 - 500	500 - 1000	>1000
Hg	<0.5	0.5 - 1.5	1.5 - 3	3 - 10	>10
Ni	<30	30 -75	75 - 125	125 - 250	>250
Zn	<100	100 - 600	600 - 1500	1500 - 5000	>5000

The determination of the contamination class of a sediment consists of the maximum class registered among the 8 trace elements. In this way, even if 7 out of the 8 elements present class 1 and the remaining element presents class 5, the sediment will be classified with class 5 contamination. The results obtained for the classification are presented in Table 6.15.

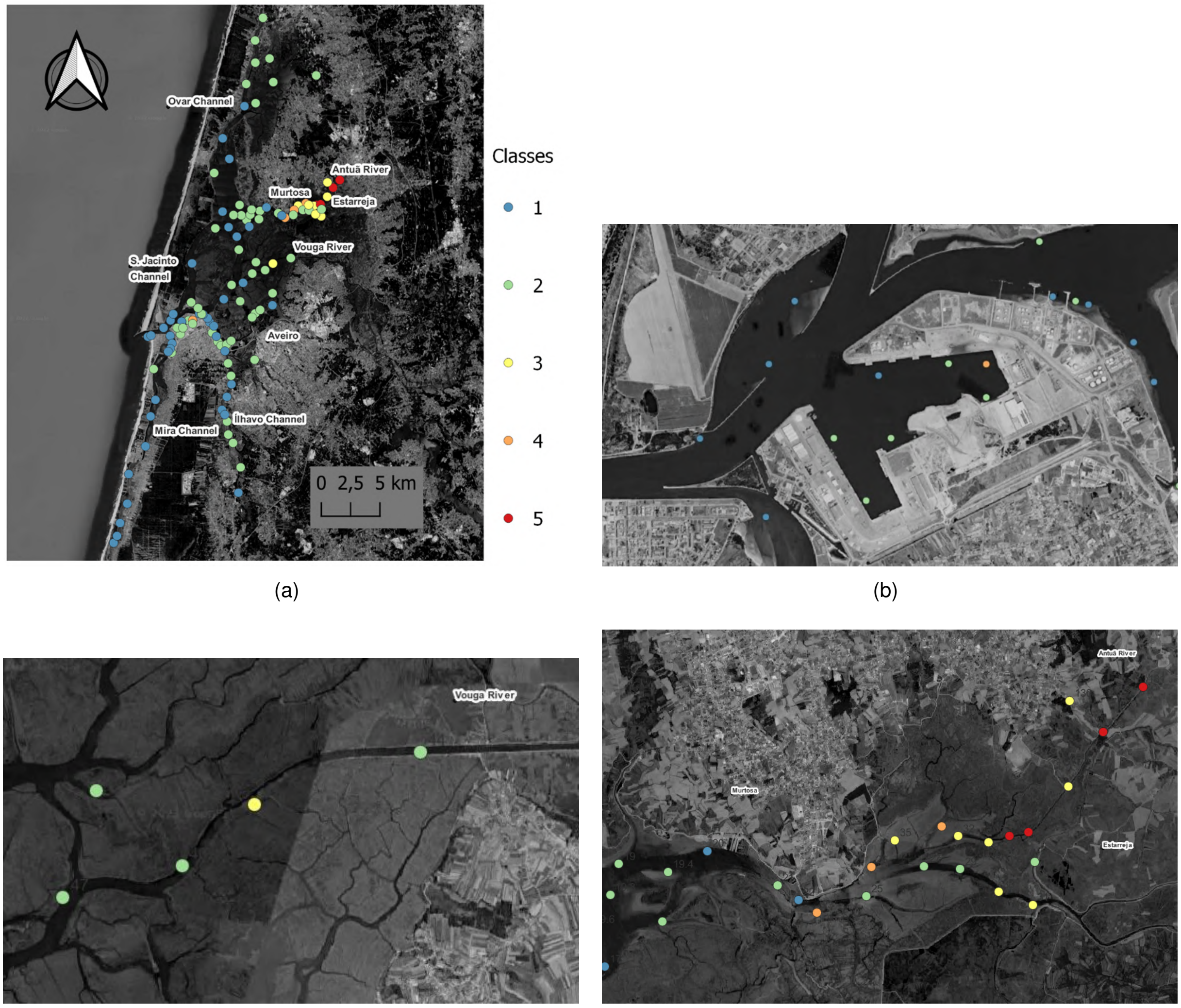
Table 6.15: Assessment of the degree of contamination of the sediments from the Ria de Aveiro sampling area.

Classes	Number of Samples	Sample Representativeness (%)
1	47	39.5
2	56	47.1
3	8	6.7
4	4	3.4
5	4	3.4
Total	119	100

In this evaluation, only the samples collected were used and no interpolations were made for the remaining are of the Ria in order to preserve the rigorousness and certainty of the evaluation made. 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. In this case and 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 [6].

In much smaller amounts, almost 7% of the samples are considered class 3, slightly contaminated sediment. From this class on, other types of care must be taken if dredging is desired. For class 3, 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 to serve for example as 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 [6].

Figure 6.16 presents the sediment classes distribution, according to the degree of contamination along the Ria de Aveiro.



(a) (b)

(c) (d)

Figure 6.16: (a) Map of sediment distribution by classes, according to the degree of contamination, (b) commercial port with the respective classification by contamination of the samples, (c) Vouga River with the respective classification by contamination of the samples, and (d) Murtosa channel with the respective classification by contamination of the samples.

Therefore, through the results obtained and by analysis of Figure 6.16, 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. The cleanest channel in the entire Ria was the Mira channel, where only two samples were presented with class 2. It was expected when this channel, throughout the analysis of the results, presented almost always the lowest concentrations of trace elements. The S. Jacinto and Espinheiro channels presented six and four samples of class 2, respectively. It is understandable that there are no classes higher than 2, due to the strong marine currents in these channels that do not favor the particles' sedimentation process. The Ovar and Ílhavo channels had a very similar number of sediments with class 2, ten and nine, respectively, which confirms a higher impact by anthropogenic sources, as already mentioned along with the analysis of the possible sources. However, there were three areas in the Ria de Aveiro that 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.

Chapter 7

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. Through this analysis, possible anthropogenic sources, natural factors, and the degree of contamination of the sampled sediments were recognized, thus making an environmental risk assessment.

The results obtained made it possible to conclude through the various distributions reached, that the two main areas of the Ria where the highest concentrations of trace elements were recorded the Murtosa channel and the commercial port near the Barra entrance. Half of the elements analyzed (As, Cd, Cu, and Zn) showed their maximums in both locations and for the remaining trace elements (Cr, Pb, Hg and Ni), at least one of these two locations recorded maximums. More occasionally, the Ovar channel registered maximum concentrations for Cr and Ni (79.5 and 35.5 mg/kg, respectively) and the Vouga river presented the maximum concentration of Pb (207 mg/kg). However, when considered the poorest area in the entire Ria regarding these contaminants, the Mira channel was a unanimous conclusion for all trace elements. For many, it was the channel where the lowest concentration was recorded (Cd, Cu, Hg, Ni, Zn) and even for the trace elements where this did not happen, the concentrations along the Mira channel were always low and quite homogeneous for all trace elements. More punctually, for As and Cr, the Murtosa channel recorded its minimum concentrations and, for Pb, the channel that recorded its minimum was the Ílhavo channel.

Regarding the possible anthropogenic sources and the natural factors influencing these distributions, the results obtained were quite similar among the various metals. Regarding anthropogenic sources, the most identified reason in almost the entire Ria is shipping activity. Several concentration increases were identified near ports, pears, and marinas, all related to ships and shipyards and their maintenance. In addition, other less general sources were identified. In the Murtosa channel the major source suggested is the Industrial Park of Estarreja. However, in the Ílhavo channel, in the south zone, the Vista Alegre Factory is suggested as the major source of trace elements concentrations. In the commercial port, besides the shipping activity, there is a contribution from the Fuel Farm Tank that completes the port and all its structure, and finally, in the Vouga River the contribution from the Paper Mill that exists on its bank, the fallen bridge that was under reconstruction at the time of sampling and possible effluents that may come from several metallurgical factories that exist near the river were suggested as major anthropogenic sources of the trace elements studied.

Considering natural factors, the hydrodynamics of the Ria and the characteristics of the sediments were taken into consideration, and several factors were determined for the distributions obtained. Regarding hydrodynamics, there are several indications, one of them being turbid areas before the beginning of the Ovar channel, in the narrowing of the Ovar channel, and in the narrowing of the Murtosa channel. These areas where there are currents with higher velocities contribute to a greater suspension of particles, leading to lower concentrations. In the case of the beginning of the Ovar channel, the hydrodynamic of the Ria favors the passage of particles from the Murtosa channel to the Ovar channel, overlapping the marine currents to the residuals currents of the rivers. Another factor is the residence time of the particles that were identified in several areas, especially in the end zones of the channels where there is less circulation of currents and with lower velocities. Regarding the sediment characteristics, through the study of the correlations between trace elements and Si/Al ratio (as a proxy of the sediment granulometry) and organic matter content, it was concluded that for most elements there is a tendency to have higher concentrations in areas with higher organic matter content and fine particles, such as mud. However, it was also concluded that this is not a general pattern, but a very particular behavior among elements.

After the correlation analysis, it was found that for the organic matter content, except for As and Hg, the other trace elements showed a moderate positive correlation, which demonstrates the tendency mentioned previously. In the case of As and Hg, which showed a weak and very weak correlation respectively, the distribution of these metals seems not to be influenced by this factor. Regarding particle size (sediment type), the correlations varied, and it was concluded that Cr and Ni have a strong positive correlation, Cd, Cu, Pb, and Zn have a moderate positive correlation, As a weak positive correlation, and Hg a very weak positive correlation. Except for As and Hg, the others appear to tend to have higher concentrations of these metals in sediments with fine particles (mud) and lower concentrations in coarse particles (sand). In the case of As and Hg, again, there appears to be no influence on distribution.

The correlation between the trace elements was also assessed, due to the various similarities identified during the distribution analysis. Three very strong positive correlations ($r \geq 0.90$) were determined between Cr and Ni, Cd and Zn, and also Cu and Pb. These elements showed very similar distribution maps, where it was concluded that these correlations stem from being used in several common industrial applications and therefore having the same sources. In contrast, two weak and one very weak correlation were identified between As and Cr, Hg and Ni, and Cr and Hg, respectively. These elements showed quite different distributions, and it was concluded that besides having fewer applications in common, the similar sources do not contribute to peak concentrations of both elements, leading to different concentration increases geographically, as seen.

Concerning the stocks obtained, it was concluded that they represent the total mass of each trace element in the first 5 cm of sediment for 65% of the Ria area. Having compared these values with the stocks obtained in the Tagus estuary, which is more than 4 times larger than the Ria, it was found that even though 100% of the Ria de Aveiro was not evaluated, all the stocks, with the exception of Zn, were much smaller than expected, being in the case of Hg 35 times smaller in comparison with the Tagus. In contrast, Zn in the Ria showed a similar stock to the Tagus, being a much smaller area, and for that reason, it was concluded that the Ria suffers from greater sources of Zn. However, from the low stocks in general, it is possible to affirm that the Ria de Aveiro is less polluted than the Tagus estuary.

Finally, by carrying out the classification and evaluation of the sediments sampled through Portaria nº 1450/2007 [6], it was possible to see that the Ria de Aveiro suffers from contamination by As, Pb, Hg, and Zn. However, 39.5% of the sediments showed to be clean (class 1), and 47.1% show trace contamination (class 2), which shows that approximately 87% of the samples do not represent a hazard and suggests that the Ria is less contaminated than was expected. The remaining 13.5% of the samples range between class 3 (slightly contaminated) and class 5 (highly contaminated) and are concentrated in three specific areas: the Vouga River, the commercial port, and the Murtosa channel. Hence, it was found that the Vouga River and the commercial port presented one sample with class 3 (slightly contaminated) and 4 (contaminated), respectively, and the remaining samples, which varied between class 3 and 5, were collected in the Murtosa channel. Therefore, it is possible to conclude that the most contaminated area of the Ria de Aveiro is the Murtosa channel. Nevertheless, from this evaluation and the stocks obtained, the Ria showed less contamination by the trace elements studied than was expected.

Chapter 8

Future Work

Through this research, it was possible to understand the importance of this type of study regarding trace elements pollution in typical aquatic ecosystem, known to be subjected to various industrial and urban inputs over time. It is crucial to continue and deepen this type of study to prevent serious consequences, both at the environmental risk and public health levels. A future study should focus on:

- Cover more complete area of the Ria de Aveiro, relatively to the sampling carried out. The Ria is composed of complex and very varied channels, and it is important to explore further to have an even more significant representation of the Ria;
- Study the speciation of Hg and As, as there are different chemical forms in which these elements may be present. This will influence their level of toxicity in the ecosystem, and consequently, alter the level of contamination;
- Study the chemical and biological availability of trace elements in contaminated sediments because, for a complete pollution analysis, it is necessary to understand which fraction of the element is available since this is the fraction that will contribute to the contamination into the organisms;
- Analyze, in addition to trace elements, persistent organic pollutants (POP's) and again assess the degree of contamination through Portaria nº 1450/2007 [6].

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