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**Longitudinal chemical gradients in estuarine
systems**

**Gradientes químicos longitudinais em sistemas
lagunares**



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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Ciências do Mar e da Atmosfera, realizada sob a orientação científica do Doutor Bruno Henriques, Investigador do Departamento de Química da Universidade de Aveiro e da Professora Eduarda Pereira, Professora Associada do Departamento de Química da Universidade de Aveiro.

Dedico este trabalho à minha família. Agradeço todo o apoio que a minha mãe, o meu pai, a minha irmã e o meu irmão me deram, pois sem eles isto não teria sido possível.

o júri

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Ecossistemas marinhos, sistemas estuarinos, elementos maioritários, elementos potencialmente tóxicos, variação longitudinal, influência da maré

resumo

Os ecossistemas costeiros estão sujeitos a mudanças periódicas nas suas características físico-químicas que influenciam o comportamento de elementos maioritários, minoritários e potencialmente tóxicos. A Ria de Aveiro é um sistema estuarino pouco profundo e verticalmente homogêneo, localizado na parte noroeste da costa atlântica de Portugal (40 ° 38'N, 8 ° 45'W). É composta por vários canais estreitos que convergem para uma única abertura para o oceano, resultando numa área com grandes planícies de lama e sapais. Este sistema está sujeito a uma intensa pressão antropológica, que é a principal fonte dos níveis elevados de contaminantes presentes dentro deste. O objetivo deste trabalho foi estudar a variabilidade longitudinal, das marés e da distribuição dos elementos maioritários, minoritários e potencialmente tóxicos num sistema estuarino bem conhecido, com propriedades físico-químicas variáveis. As áreas de estudo foram dois canais da Ria de Aveiro. Amostras de colunas de água foram recolhidas de vários pontos situados ao longo do comprimento de ambos os canais, Mira e Ílhavo, onde foram efetuadas medições de salinidade, condutividade, temperatura, pH, material particulado em suspensão e oxigênio dissolvido. A separação em frações dissolvidas e particuladas, assim como a dispersão ao longo de ambos os canais, foram avaliadas para o Li, B, Mg, Al, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba, Hg e U. Observou-se que o comportamento dos elementos determinados num canal variou substancialmente no outro canal, com variações a depender dos parâmetros físico-químicos, fluxo de água doce e proximidade a pressões antropológicas.

keywords

Marine ecosystem, estuarine systems, major elements, potential toxic elements, longitudinal and tidal variation

abstract

Coastal ecosystems are subject to periodical changes on physico-chemical characteristics that influence the behavior of major, minor and potential toxic elements. Ria de Aveiro lagoon is a shallow and vertically homogenous estuarine system, located on the northwestern part of Portugal's Atlantic coast (40° 38'N, 8° 45'W). It is composed of various narrow channels which converge onto a single opening to the ocean, resulting in an area with large mud flats and salt marshes. This system is subject to intensive anthropological pressure, which is the main source of the elevated levels of contaminants present within it. The objective of this work was to study the longitudinal and tidal variability of the distribution of major, minor and potential toxic elements in this well-known estuarine system with varying physico-chemical properties. The areas of study were two channels of the Ria de Aveiro estuary. Water column samples were collected from various points along the length of both channels, Mira and Ílhavo, as well as various measurements for water salinity, conductivity, temperature, pH, suspended particulate matter and dissolved oxygen. The partitioning in dissolved and particulate fractions as well, as the dispersion along both channels, were determined for Li, B, Mg, Al, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba, Hg and U. It was observed that the behavior of elements determined in one channel varied substantially in the other channel, with variations dependent on the physico-chemical parameters, as well as fresh water flow rate and proximity to anthropological pressures.

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1 Introduction

1.1 Estuarine systems: characteristics and contamination

1.1.1 Main physico-chemical processes in estuarine areas

An estuary or estuarine system can be defined as “a body of water partially encircled by land, directly connected with the ocean, where the seawater is substantially diluted by fresh water originating from rivers” (Morris, 1985). However, this definition relies heavily on the physical and biogeochemical properties being studied. In a less generalized manner, estuaries can be categorized according to their topography, circulation, stratification and water mixing processes, with all these features essentially being influenced by the tidal range of the sea and water flow rate of the fresh water tributaries inputting into these systems (Millward and Turner, 1995).

Chemically, an estuarine zone can be defined as a region where salty seawater (high ionic strength and buffer capacity) is diluted by the fresh riverine water (low ionic strength and buffer capacity), resulting in longitudinal, transversal and temporal gradients of several physico-chemical parameters, such as salinity (ionic strength), temperature, dissolved oxygen concentration, pH, redox potential, and suspended particulate matter characteristics and concentration, resulting in a complexity of behaviors demonstrated in chemical constituents, such as, nutrients, organic matter and metals (Millward, 1995). In estuarine systems, the interaction between fresh water and salty water induces water circulation and mixing processes, due to the differences in the density of both types of water (Morris, 1985), while also controlling the distribution, speciation and reactivity of the major chemical constituents mentioned before (Morris, 1985); these systems are, therefore, highly dynamic regions in regards to chemistry and physics (Millward and Turner, 1995). However, these systems are widely different from one another, presenting a great degree of differentiation, depending on the type and extent of the naturally occurring chemical processes and the way these processes are regulated and altered in each one of these coastal environments (Morris, 1985); even in a well-defined system, the probability for a synoptic distribution of a specific contaminant to repeat itself is quite low (Morris, 1985).

Located in coastal environments, estuaries are subject to tidal influence. The water volume exchanged during each tidal cycle (tidal prism) and the strength of the tidal currents vary according to the tidal range in the estuary opening to the Ocean, this results in spring and neap tides with largely contrasting conditions, which vary cyclically along the year. The impact such tides have on estuaries can be expressed in terms of salty water penetration, which corresponds to the distance the seawater travels inland, along the estuary, during the low to high tide transition (Morris, 1985). The tidal range and stream velocity decrease inward, as a consequence of the energy dissipation resulting from various types of friction along the way. As the most uphill part of the estuary gets closer, the velocity and duration of the ebb tide increases progressively in contrast to the flood tide, as a consequence of the discharge of riverine fresh water, inducing changes to the expected time intervals of the low and high tides, which may result in significant delays in the field (Morris, 1985).

In estuarine systems the suspended matter content is generally quite high and highly variable, this is for the most part due to the discharge of riverine water, which is usually subject to a high variability in particulate matter content, and also due to the interaction between the tides and the residual currents that develop in these aquatic systems, which, in most estuaries, are capable of remobilizing the recently bottom deposited matter (Turner et al., 1994). Generally, the increase in water velocity is directly tied to an increase in the suspended particulate matter content in estuaries, as such, this parameter is characterized as having a semi-diurnal variation and variability depending on the tidal classification on the system (Morris, 1985).

Another characteristic that most estuaries exhibit is the existence of a maximum turbidity zone; these areas are generally located in the estuarine region with the lowest salinity levels, where the suspended particulate matter concentration reaches to levels greater than those of the tributary rivers or seawater (Jiang et al., 2013)). In estuaries where tidal influence is low, these areas develop due the density of gravitational circulation, which keeps the particulate content in suspension (Burchard et al., 2010); in estuaries where the tidal influence is high, these areas are may result from periodic resuspension of local superficial sediment, induced by strong tidal currents (Burchard et al., 2010). These turbidity maximums travel along the estuary, mainly influenced by the amount of fresh water discharged by the tributary rivers. These maximum turbidity zones constitute an important

aspect in the speciation of several elements for a large number of estuaries, as these zones display a greater association of particulate content with them due to a greater amount of suspended matter and a larger specific surface area (Millward et al., 1990).

1.1.2 Contaminants in estuarine systems

The presence of contaminants, like metals, in estuarine areas poses a multitude of problems as most of them are non-biodegradable, may be toxic or sometimes convert into species with higher toxicity levels, be transported over large distances (due to their high stability) and can also have long residence times in living cells and organisms (Pereira et al., 1997). The long-term effects resulting from contaminants, especially in aquatic organisms, vary greatly, as such this subject has led to an ever-increasing amount of biochemical studies. Although some contaminants, when present in small concentrations, can be essential to enzymatic activity, when present in higher than normal concentrations, can become harmful to the normal functioning of living beings. While this is true for every contaminant, metals such as cadmium, copper, mercury and lead can be particularly toxic and can easily bioaccumulate along the trophic chain, resulting in chronic as acute health issues (Agah et al., 2007).

While present in estuarine systems, contaminants can interact with these systems various constituents, resulting in several possible associations (Le Roux et al., 2001). A fraction of such contaminants associates with organic and inorganic ligands present in solution, while another fraction associates with particulate matter, either by adsorption reactions, precipitation or by incorporation into living organisms (Turner et al., 2004a). As a result of the physical, chemical and biological processes that take place in these systems, a significant part of these contaminants tends to associate with the sediment layer (Monterroso et al., 2006). The processes inherent to the interaction between contaminants and the other aquatic system constituents are influenced by ions concentration, size and valency, and also by the solution's redox potential, ionic strength and pH.

In aquatic systems, contaminants can appear in solution as free ions (hydrated), or complexed with inorganic anions (such as Cl^-) and organic ligands (such as humic and fulvic acids), and also in solid form in a diverse range of associations (Pankow, 1991). In regards to the operational distinction between the dissolved or soluble fraction and the particulate

fraction, this distinction is generally determined by the particle size ($>0.45\mu\text{m}$), with this separation being achievable through filtration. Even after separated, not only are the elemental ions included in the dissolved fraction, but also part of the colloidal sized particles (Millward and Turner, 1995). These colloidal particles can have a significant role in estuarine systems, considering that such particles are in part composed of iron oxides and clay particles coated with humic matter, which contains a high capacity to adsorb metallic ions, regulating, in a way, the concentration of these ions in the water. Although its contribution to the total mass of suspended particulate matter is almost negligible, the colloidal fraction (ranging from $0.003\ \mu\text{m}$ to $1\ \mu\text{m}$) is comprised of a large quantity of very small particles and, as such, corresponds to a significant fraction of the total particulate superficial area. Therefore, the predominant form that many contaminants in solution assume is, usually, adsorbed onto colloidal particles.

1.1.3 Characterization of dissolved species

For most estuaries, the concentrations of dissolved contaminants are quickly removed from the solution, associating with the suspended particles; this process is particularly important in high turbidity zones, which tend to occur in lower salinity regions, where metals exhibit in-solution residence times of a few hours (Millward and Turner, 1995). In the dissolved fraction, the variation of contaminants concentrations is, frequently, a function of the salinity, the systems redox conditions and the existence of flocculation processes, complexation, precipitation and solubilization or adsorption and desorption (Turner et al., 2004a). For systems where the process of the mixing of fresh water with salty water is predominant, the dissolved constituents and the smaller colloidal matter are transported similarly to the total salt content, varying its concentration with a linearly inverted tendency, displaying a conservative behavior (Millward and Turner, 1995). However, for most estuaries, as the behavior of their constituents is non-conservative, it can be observed that a positive deviation of this linearity can occur with the solubilization of the particulate contaminant content, contaminant diffusion from interstitial waters, industrial discharges rich in contaminants or varying contaminant levels in the water originating from the estuary's tributaries; these linearity deviations are due to adsorption, precipitation and/or flocculation of colloidal particles (Millward and Turner, 1995), primarily iron precipitation

and dissolved organic matter precipitation. Generally, the constituents which present a non-conservative behavior, are often designated as reactive or interactive constituents.

Variability in the concentration of contaminants in the dissolved fraction, observed sporadically, can occur due to diffusion processes of elements in interstitial waters, where the concentrations are usually higher. Moreover, it has been observed that in some estuaries, the desorption of contaminants can happen in the regions with the highest salinity (Monterroso, 2004).

When collecting water samples for dissolved contaminant analysis, the collection should be performed in such a way as to prevent any kind of sample contamination; this precaution is particularly important with this kind of sample due to the generally low concentrations of dissolved contaminants found in natural systems. Such precautions include the washing of all sampling material in acid before sample collection and treatment of the samples with acid after collection, as well as isolating the samples from any metallic component and equipment, including the ones used during sampling.

In most studies involving the determination of contaminants in the dissolved fraction, the samples are filtered right after being collected on the field. After filtering the samples, the filtrate should be immediately acidified, up to a pH of 1 to 2, and stored at low temperature until analysis, in order to stabilize the metallic ions and minimize microbial action (Millward and Turner, 1995).

Immediate analysis of the dissolved contaminants right after filtration is the most appropriate way to accurately determine their concentrations, this is due to the lowered risks of contamination of minimal sample manipulation. Nowadays, inductively coupled plasma mass spectroscopy (ICP-MS) is a technique that can be used to very accurately determine the concentration of a wide range of elements, including most metals currently found in dissolved form in estuaries. Other more specialized techniques can also be used to accurately detect and determine metals, such as the case of determination of dissolved mercury content in samples, where flameless cold vapor atomic absorption spectrophotometry with gold amalgam pre-concentration has been used for quite some time. More recently, cold vapor atomic fluorescence spectroscopy (CV-AFS) technique has also been used in the

determination of dissolved mercury, since it provides low detection limits while also consuming very small sample volumes.

1.1.4 Suspended particulate fraction and associated contaminants characterization

Particulate matter present in estuarine systems is essentially constituted by a mixture of complex organic and inorganic matter; the main constituents of this particulate matter are clay, quartz, feldspar and carbonates, sometimes associated with iron and manganese hydroxides and organic matter from marine and land sources. Much of the solid matter present in estuaries is of anthropogenic origin, mainly originating from industrial discharges and domestic sewage; however, some solid matter may also originate from natural erosion processes or be produced in situ by chemical (flocculation) and biological (primary production) processes (Millward and Turner, 1995), with such solids presenting similar compositions to that of the ones commonly found in suspended particulate matter.

The interaction of contaminants with the various solid fractions that make up the particulate matter and their fixation onto these fractions depends on several physical and chemical processes, such as:

- the precipitation of carbonates, sulphides and metal hydroxides due to their respective solubility products having been reached;
- physical (electrostatic attraction forcing) and chemical adsorption (exchange of H^+ in layers of $SiOH$, $AlOH$ and $Al(OH)_2$) of metals contained in argillaceous minerals;
- physical and chemical adsorption and complexation of metals with humic substances and organic residue;
- physical adsorption, chemical adsorption and coprecipitation of contaminants onto iron and manganese oxides.

Particle size and composition has, generally, an effect on the concentration of contaminants that associate therewith. For the most part, a smaller particle size corresponds with a higher concentration of contaminants, primarily due to the fact that smaller particles possess a larger superficial area.

Humic substances are the main component in organic matter present in recently collected estuarine sediments (Monterroso, 2004); on average, humic substances contribute 40% to the organic matter content in sediments, however in some cases this contribution can reach up to 70%. Humic substances have an important role in estuarine systems due to the fact that their structural characteristics contribute to their interaction with various other substances, including metals, which alters their speciation, geochemical mobility and accessibility to living organisms. Humic substances have a high tendency to complexate with metallic cations, owing to the fact that these substances contain a wide range of functional groups. The contaminants quickly associate with these substances, thus, the behavior of contaminants in estuarine systems can, in part, be controlled by presence of humic substances (Förstner and Wittmann, 1981).

Iron and manganese oxides present in estuarine systems, are characterized by a high specific surface area, with such values having been determined in the order of $300 \text{ m}^2 \text{ g}^{-1}$. Even in small quantities, the influence that these oxides have in the distribution of contaminants in estuarine systems is quite relevant (Turner et al., 2004b). The adsorption of ions by these oxides, can be interpreted as being due to the formation of complexes on the surface or due to ionic exchange; hydrogen ions or other cations get desorbed as the metallic ions are adsorbed into the oxides. These facts contribute to the support of the hypothesis that establishes that iron and manganese can influence the distribution and transport of contaminants in aquatic systems.

1.1.5 Transport and deposition of particulate matter

Tidally induced water displacement in estuarine systems mobilizes a relevant quantity of suspended particles, as such it is characteristic of estuarine regions to have a high concentration and variability of suspended matter, with variations in time, space, composition and concentration of suspended particles. The particles, and simultaneously the contaminants associated with them, can be subject to a large number of depositional and resuspension cycles in an estuary, resulting in relatively long residence times while also facilitating a larger accumulation of pollutants (Millward and Turner, 1995).

The processes of transportation and deposition are dependent on various physical and chemicals characteristics acting together simultaneously, as such, it is a complex matter to

explain; among others, factors such as particle size, sediment consistency (degree of compaction), water velocity, tidal magnitude, water column stratification and type of circulation in an estuary, influence the aforementioned processes, since these processes are dependent on the horizontal and vertical transportation of particles as well as their deposition on the bottom. Therefore, a part of the suspended matter can, continually, exchange between the deposited and the suspended fraction. In general, an individual particle can be transported forward or backward while influenced by the tides or residual currents and be deposited and remobilized several times before depositing for long periods of time or even permanently. The long residence times of some particles in the water column increases the probability of occurrence of processes such as adsorption and desorption reactions and precipitation, coagulation and bioassimilation phenomena.

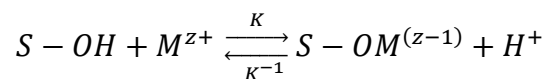
1.1.6 Equilibrium between particulate and dissolved fraction

The speed and manner at which the contaminants are transported in estuarine systems is dependent on its distribution between the dissolved and particulate fractions. In estuarine areas, the cyclic variations of temperature, pH, salinity and dissolved oxygen, originate alterations in the processes of interaction between the dissolved and particulate fractions, influencing the aggregation and transport of suspended particles and the particulate matter superficial reactivity, which alters the dissolution and precipitation phenomena. In several estuarine systems the behavior of contaminants is regulated by the transport, dispersion and sedimentation of the existing solid matter, as a direct consequence of the strong interaction that exists in these systems between the particulate matter and the contaminants and it can therefore be said that the particulate fraction has a complex role, which is nonetheless important, in controlling the chemical behavior and transport of contaminants in estuaries (Millward and Turner, 1995).

1.1.7 Retention and remobilization of elements from particulate fraction

Smaller dimension particulate matter with high surface area is capable of accumulating elements in the solid-liquid interface as a result of intermolecular forces – this process is called adsorption. Adsorption and desorption processes are relatively important in the geochemical cycles of several elements in estuarine systems, since the superficial characteristics of the particulate fraction determine the behavior and transport of such elements in these systems.

In estuarine systems most suspended particles possess an electrical charge in its surface which is predominantly negative, to the pH levels generally existent in such systems; therefore, the electrostatic interaction is favorable to the adsorption of cations and unfavorable to the anions. The existence of a charge on the surface of the particles may be due to: chemical reactions with the particle's surface, unfulfilled chemical bonds, ionization, specific adsorption, web structural imperfections, web ionic isomorphic substitutions of minerals by other ions with different valency and also adsorption of ions by Van der Waals forcing or by hydrogen bonds (Stumm and Morgan, 1981). This way, the surfaces of particulate matter have ionizable functional groups and the retention of an ion (M^{z+}) can be described in terms of a competition with protons for a place on the surface (S-OH) in the following manner (Millward and Turner, 1995):



where S can represent an iron, aluminum or manganese oxide or organic matter carbon functional groups, K and K^{-1} are direct and inverse reaction constants. An equilibrium can be established between the quantity of cations accumulated by adsorption in a substance and its respective concentration, which causes desorption to occur when its concentration decreases in the environment.

In order to comprehend the processes of retention, resuspension and remobilization, there has to be a characterization of the interaction between a solute and a surface, in relation to its physical and chemical properties. Taking into consideration the complexity and variety of natural surfaces, it would be expected that a large number of different mechanisms

contribute to the total energy involved in processes of sorption, as such, it may be difficult to distinguish between these processes (Millward and Turner, 1995).

1.2 Objective of the study

The objective of this work is to study the longitudinal gradient of major, minor and potential toxic elements in a well-known estuarine system with varying physico-chemical properties in regards to different tidal conditions, in two channels of the Ria de Aveiro estuary.

2 Materials and methods

2.1 Sampling methodology

2.1.1 Study area

The area selected for this study was the Ria de Aveiro, a shallow coastal lagoon located in Aveiro, on the northwestern part of Portugal's Atlantic coast (40° 38'N, 8° 45'W). This estuary is separated from the Atlantic Ocean by a sand bar and connected to it by a narrow artificially maintained channel, the Barra channel, which serves as the only opening through which most of the water is exchanged with the sea and through which tidal inputs are allowed to govern most of the hydrological processes therein. Ria de Aveiro lagoon is comprised of a collection of other narrower and longer channels, fed by fresh water tributaries, which connect with one another before finally reaching the sea through the Barra channel and aforementioned opening. It is situated parallel to the coast, stretching for over 45 km lengthwise and 10 km widthwise and covering an area of 83 km² in high tide and 66 km² in low tide, during spring tide. The average depth is usually about 1 m, varying slightly between the inner channels and in between dredging operations which are periodically carried out in various locations to maintain navigable conditions (Dias, Lopes, & Dekeyser, 2000). Figure 1 shows a broad view of the main regions of Ria de Aveiro for this study.



Figure 1: Ria de Aveiro and channels with significance for the study. The Mira, Barra and Ílhavo channels as represented over the map

Due to its long history of mercury contamination, the Ria de Aveiro has been the subject of many studies and considered as a prime location for this work. Due to their

characteristics and for the purpose of simplifying sample collection, the following two channels, chosen from the myriad of channels in Ria de Aveiro, were selected:

- Mira Channel, with first sampling station located behind the Praia do Areão, continuing downstream, with the final station located just before contacting the Barra channel;
- Ílhavo Channel, with sampling stations starting from Vagos, and the remaining stations stretching downstream, along the Boco river.

Several sampling stations were selected for each channel, with each station being located in slight equidistant manner, averaging at 1.4 km between stations. The entire study area, with the various sampling stations distributed along the channels, is represented in Figure 2.

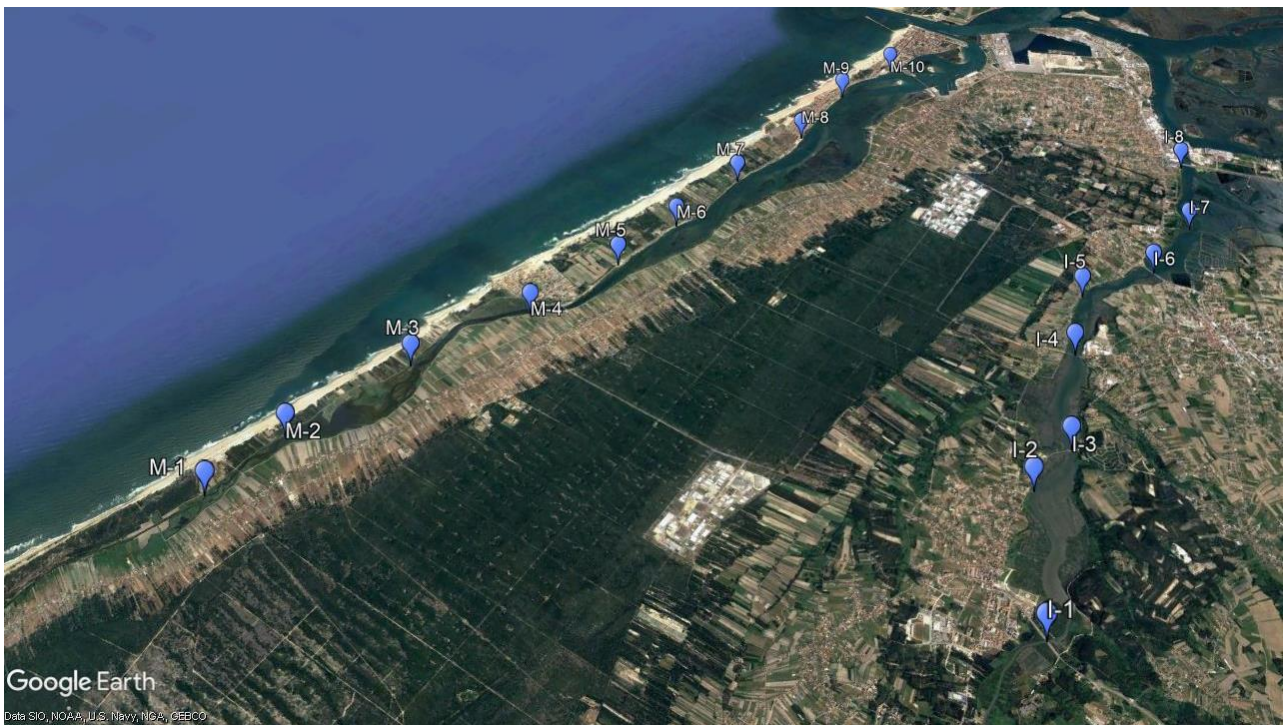


Figure 2: Close up of the two Ria de Aveiro's channels being studied, Mira and Ílhavo, with selected sampling stations

The Mira channel sampling stations will be referred to as stations M-1 through M-10, while the stations in the Ílhavo channel will be referred to as I-1 through I-8.

Available information about the area of study allows for an in-depth pre-characterization of both channels. Previous studies demonstrated that the Mira channel's water varies greatly along its length, with salinity ranging from 0 to 35.1 along its length, increasing in direction to the Barra channel (Moreira et al, 1993). The southern part of Mira channel's consists of various small rivers and ponds (Dias & Lopes, 2006) and its average flow rate has been measured as 1.68 m³/s (Silva, 1994). In the case of the Ílhavo channel, while the Boco river makes up a large part of this channel's length, it has a very negligible flow (Dias & Lopes, 2006), measured at 0.235 m³/s (Silva, 1994), as such, its water characteristics are highly susceptible to tidal influence displaying similar characteristics to seawater. In addition, both channels are surrounded by housing and industrial and agricultural activity which are, generally, a significant source of various organic and inorganic contaminants and metals.

2.1.2 Sampling strategy and methodology

After establishing the goal for this study, defining the study area taking into consideration the previously known aspects, such as its nature and dimensions, it was necessary to define the sampling strategy and methodology which includes aspects such as number of samples to be collected and necessary equipment, among others. In this phase, the interpretation of available information and field observations regarding the lagoon were important for achieving the goals of this study.

The sampling strategy was established also taking into consideration the current knowledge base on the general behavior of estuaries:

- variability, which is an intrinsic property of estuarine systems, or in other terms, the distribution of characteristics and the occurrence of processes in the field present short-term, long-term and seasonal fluctuations, even though most of these fluctuations are cyclical in nature.
- the hydrodynamic characteristics of estuarine systems, which influence the behavior of elements and, as such, knowledge about the physical dimensions, tidal ranges and water inputs are necessary for an adequate field work planning.
- the chemical characterization of estuaries, which requires previous knowledge over the various entrance routes that a constituent can be inputted, as well as its variability over time. As such, throughout the field work part of this study, several readings were made for various physico-chemical variables on the field.
- knowledge over aspects like distribution, dispersion and chemical constituent flow in estuaries, which constitutes important information for the evaluation of a possible occurrence of contamination of areas next to the ones currently polluted.

The produced results correspond to the particular conditions of the Ria de Aveiro in both channels, which allows for an approximated estimation of the transport of some metals, both in the dissolved and particulate fraction, from the areas where the study was carried out onto the rest of the lagoon.

Deposited particulate matter can have an important influence on the transport and distribution of chemical constituents in estuarine systems, due to these particles being in contact with the aqueous phase during long periods of time; processes responsible for the resuspension of these particles should then be taken into consideration. In this study, the variability of the concentration of particulate matter was assessed for different tidal conditions, as well as other aspects like the variation of the volume of fresh water discharged into the study area in comparison with the seawater and wind intensity, since these aspects can influence the resuspension of surface sediments.

Methodology for sampling and analysis, number and location of sampling stations and the frequency of sample collection, were also aspects taken into consideration during field work planning. In general, sampling campaigns suited for estuarine systems can be carried out by collecting water samples over the central region of a stream's flow, for a specific depth, while selecting locations where the salinity variations are less significant. However, due to logistical and economic reasons, the study's samples were either collected on the channel's central regions, by making use of several bridges passing over the selected water streams, or on the stream margins, in which case a special care was taken to ensure that the water and decrease in depth at the margins would not influence the collected samples. Also, in order to assess the distribution of a chemical component and its variability over time, in an estuary, a significant number of samples had to be collected in quick succession along the sections which were to be studied, this was done by making use of previously established sampling locations and a means with which to quickly travel to such locations. This rapid and successive sample collection allowed for the collection and production of comparable data on different sampling stations, enabling interpolations in space and time.

The field work was comprised of two sampling campaign which consisted in two sets of water samples collection and the sampling of various physico-chemical parameters, with each campaign being carried out in a channel during low tide and high tide. The campaign took two full days to complete, requiring one full day per channel, in order to cover the transitions between low and high tide for both. This methodology enables an evaluation of temporal and spatial variations, by characterizing the *in situ* physico-chemical properties of the water, taking into consideration factors such as, the transition between fresh water

coming from tributaries and salt water coming from the ocean and the differences in pH, salinity and particulate matter, to name a few.

The number of sampling stations and choices of parameters to determine *in situ* were established while considering the requirements for the obtention of accurate analytical results, such as, availability of laboratory material, manpower, and the capacity for immediate sample analysis or preservation of said samples until analysis is made possible.

2.1.3 Sampling stations

The criteria for selection of sampling stations is dependent on previous the knowledge of the system and its accessibility. At the time of sample collection, since the action of collecting smaller volumes from larger volumes of water brings with it representativity problems, special attention was given in order to assure sample representativity of the conditions present on the field.

The water samples were collected in several stations on the Mira and Ílhavo channels, over an extension of 13 km and 10 km, respectively. Figure 3 represents the extent of the study area with the distance between the different sampling stations, starting from the most upstream stations.



Figure 3: Close up of the study area, with the sampling stations distances represented.

The sampling stations were located approximately 1.4 km apart from their adjacent station along both channels, which resulted in the selection of 10 sampling stations for the

Mira channel and 8 sampling stations for the Ílhavo channel. The coordinates for the stations in each channel are listed in Table 1

Table 1: Coordinates for each sampling station in Mira and Ílhavo channels

Station nº Channel	1	2	3	4	5	6	7	8	9	10
Mira	40°30'59"N 8°46'35"W	40°31'36"N 8°46'30"W	40°32'33"N 8°46'10"W	40°33'25"N 8°45'40"W	40°34'13"N 8°45'23"W	40°34'51"N 8°45'13"W	40°35'36"N 8°45'5"W	40°36'25"N 8°44'53"W	40°37'9"N 8°44'53"W	40°37'47"N 8°44'39"W
Ílhavo	40°33'1"N 8°40'19"W	40°33'59"N 8°40'54"W	40°34'26"N 8°40'48"W	40°35'17"N 8°41'10"W	40°35'52"N 8°41'22"W	40°36'26"N 8°40'54"W	40°37'5"N 8°40'48"W	40°37'51"N 8°41'11"W		

2.1.4 Sampling moments

Due to the variability inherent to a complex hydrological system such as the estuarine system in study, one of the main concerns in selecting viable time frames for sample collection was the compatibility of these time frames with the tidal phases, which may have an impact on the distribution of fluvial and marine water constituents as well as other possible industrial or domestic discharges. Another significant concern was the meteorological conditions at the moments of sampling and the conditions observed in previous days, so as to assure that close to no impact could be observed from closely related raining or drought events. Every sample collection was carried out close to 15 minutes apart from each other, in both channels and both sampling campaigns, with these collections occurring on both tidal extremes, low tide and high tide.

The two campaigns for physico-chemical parameters readings and water sample collections were performed on 24th and 25th of October of 2018, for the Mira and Ílhavo channel respectively. Sample collections were carried out on all sampling stations during low tide, as well as during high tide.

2.1.5 Atmospheric and tidal conditions during sampling moments.

Atmospheric conditions relative to the amount of precipitation and wind intensity, observed three days prior to and during each sampling moment, can be found listed in Table 2.

Table 2: Precipitation and wind intensity during the sampling campaigns (and three days prior).

Sampling dates	3 days prior to sampling	Sampling day	
	Precipitation	Precipitation	Wind intensity
24/10/18	None	None	5-15 km/h
25/10/18	None	None	5-15 km/h

According to Table 2 both sampling moments had no precipitation in the days prior to and during sample collection and close to negligible wind intensity.

A springtide occurs every 28 days or so. Due to an increase in tidal range during the springtide phase of the lunar cycle, which results in a bigger contrast between low and high tides, sampling was planned in order to be performed during, or close, to a springtide. As such, the first sampling campaign was carried out during the springtide of 24th of October, 2018, and the second campaign, the following day, 25th of October, 2018, the closest possible moment to the previous springtide. Sample collection was carried out during low and high tide for each day, with each starting close to the time of expected tidal minimum and maximums

2.2 Laboratory and field work

2.2.1 Equipment

A list of the equipment used throughout the study can be found in Table 3, along with their respective manufacturer and model information:

Table 3: Equipment used during field and laboratory work with brand and model information

Type	Item	Brand	Model
Reagents	Nitric Acid 65% (HNO ₃)	EMSURE	100456 EMD Millipore Nitric acid 65% for analysis
	Hydrochloric acid fuming 37% (HCl)	EMSURE	100317 Hydrochloric acid fuming 37% for analysis
	Tin(II) chloride dehydrate (SnCl ₂)	EMSURE	107815 Tin (II) chloride dihydrate for analysis
Instruments	Analytical scale	Gibertini	E425-B
	CV-AFS system	PS Analytical	Millennium Merlin 10.036
	ICP-MS system	Thermo Scientific	X Series ICP-MS
	ICP-OES system	Jobin Yvon	Activa M ICP-OES
	Water parameter meter	WTW	Multi parameter portable meter – ProfiLine Multi 3320
	Water purification system	Merck	Milli-Q Integral ultrapure water (Type-1)
	Water distiller system	GFL	Water Still for single distillation 2004
Filters	Analytical filtration membrane	Merck	HHAWG047S6 S-Pak Filters 0.45µm 47mm white gridded
Gasses	CV-AFS carrier gas	Air Liquide	Argon (Ar)
	CV-AFS purge gas	Air Liquide	Air K (20% O ₂ , 80% N ₂)
Sample storage plastic and glassware	Conic test tubes	Deltalab	12ml Conical Polystyrene Tube
	50 mL Falcon tubes	Orange Scientific	4440100N 50ml Centrifugal Tube
	100 mL Schott bottles	Schott	CLS-1172-100, 100mL

2.2.2 Cleaning procedures

Metals and other elements in water samples can adhere or adsorb onto the container's, which can result in significant analysis errors, especially with low concentration samples, or samples with elements such as mercury which are highly susceptible to ionic exchange. These containers even when thoroughly washed may still contain small amounts of matter, from previous experiments or daily use, adhered to the walls which, in conjunction with possible imperfections of the container's walls, may act as ionic exchange surfaces.

To prevent any kind of sample contamination throughout the field and laboratorial component of this study all the sampling, preservation, storage and analysis equipment was carefully and thoroughly washed. This cleaning procedure starts by washing the equipment in running tap water, followed by distilled water and immersion in Decon detergent at 5% for at least 24 hours. Afterwards, it is again washed in running tap water, followed by distilled water and immersed in HNO_3 at 25% for at least another 24 hours. The equipment cleaning procedure then finalizes with one last pass through tap water, another thorough wash with distilled water and finally, the equipment is left to air dry for another 24 hours, while turned upside down in the case of containers so as to prevent contamination after washing. After washing and drying, the equipment was stored in clean and dry environments until needed.

2.2.3 Reagent quality

Every reagent used in this study was of “pro analysis” quality, to avoid sample contamination or interference with analysis procedures. This is especially important in the case of low concentration samples or solutions.

Most of the water used in the study was distilled water, which is acceptable for the washing of material destined for analytical usage. However, for the analysis and treatment of samples or whenever a solution needed to be prepared, they were performed with Milli-Q grade water, instead of distilled water.

2.2.4 Sampling

2.2.4.1 Sample collection

As vertical homogeneity has been observed in the Ria de Aveiro and the estuary is considered to be rather shallow, salinity doesn't vary significantly with the differences in depth, as such, the behavior of chemical constituents in estuarine systems can be adequately characterized through sampling at a single depth level. Since superficial water samples are simpler, faster and easier to collect, every water sample, and every physico chemical measurement in this study was therefore made at a surface level.

Water sampling and physico-chemical measurements were undertaken at the margin of both channels, Sampling in this case was performed by throwing the large container into the water, letting it fill with water while sinking to the same depth as the bottles, and removing the said container from the water, after which physico-chemical measurements were quickly performed on the container and its content used to fill the 1.5 L polyethylene bottles.

Sampling is often regarded as a simple and straightforward part of any study, this however is not ideal, since most analytical methods and equipment nowadays are so precise that small discrepancies produced during sampling can have a significant impact during analysis and in the final results. For this reason, the sampling portion of this research was carefully performed in such a way as to minimize errors during sample collection. Nitrile gloves were worn during sample collection to reduce contamination of the samples, and sample containers were washed with the water *in situ* before sample collection, to approximate the containers conditions to the sample's original environment. Samples were collected with care so as to prevent the resuspension of additional particulate matter or the collection of unintended sediment particles, especially in the case of sample collection on the margins of the channels. The labeling of the sample containers happened before leaving for the field, to prevent mistakes in sample labelling and collection and every sample was therefore labelled with the date and collection conditions, as well as with the tidal phase and station number from where it was collected.

2.2.4.2 Physico-chemical measurements of water conditions *in situ*

Acknowledging the need for an *in situ* characterization of the spatial and temporal variability of physico-chemical properties of the waters that flow over contaminated estuarine sediments, several parameters needed to be determined on the water *in situ*, so as to ascertain their influence in chemical reactivity and distribution; these parameters were water temperature, salinity and conductivity, pH, oxygen saturation % and suspended particulate matter (SPM) content.

Water sampling campaigns, both in Mira and Ílhavo channels and during low and high tidal conditions, were therefore undertaken in conjunction with the surface measurement of water conditions *in situ*, with a portable multi-parameter probe kit (WTW-ProfiLine 3320) capable of measuring temperature, salinity, conductivity, dissolved oxygen and pH in water. This multi-parameter kit was pre-calibrated for several parameters before every campaign. The salinity and conductivity modules were calibrated using synthetically produced seawater with well-defined salinity and conductivity values. The pH module was calibrated several times before and during the campaigns, *in situ*, using commercially available pH standards.

2.2.5 Sample pre-treatment and preservation

During the manipulation of samples, there was a constant care to reduce all possible sources of contamination, however, due to an inability to acquire a “clean room” in which to work, the analysis of the data resulting from the samples should be performed while taking into consideration not only field work conditions but also laboratory manipulation conditions. The pre-treatment of the samples was carried right after the finalization of each sampling campaign, however, due to manpower constraints, the processing of all the samples took three days to complete. During this time, the samples were maintained in dry, fresh and lightless conditions until their processing was possible.

2.2.5.1 Dissolved fraction

After collection, all water samples were filtered in the laboratory, through the use of Millipore filters with a porosity of 0.45 μm and a polyethylene filtering unit connected to a suction pump. From every sample, portions of filtered and un-filtered water were collected into 10 mL test tubes; another portion of 100 mL of filtered water was also collected into a Schott glass bottle. The filtered and un-filtered portions of water were then acidified to $\text{pH} < 2$ with a adding a concentrated solution of HNO_3 at 65% and the test tubes were enclosed with a layer of parafilm and then stored at 4°C until needed for analysis. The portions of water in Schott glass bottles were also acidified to $\text{pH} < 2$ with the same solution of HNO_3 and also stored in a refrigerator at 4°C; this method of preservation of samples for analysis of metals in dissolved fraction has been shown to be adequate in stabilizing the metals ions and minimizing microbiological activity (Millward and Turner, 1995). The acidification of samples is also intended to minimize microbiological activity which contributes to the volatilization of mercury by transforming nonvolatile inorganic mercury into more volatile forms, which contributes to losses, affecting the analysis. The refrigeration of the samples is another method for the preservation of samples destined for metal analysis, as the decrease in temperature slows down bacterial activity.

The filtered and un-filtered 10 mL portions of water contained in test tubes were destined for the analysis of total and dissolved metal content in the water samples, while the 100 mL portions of water contained in Schott glass bottles were destined for the determination of mercury content in dissolved fraction.

2.2.5.2 Suspended particulate fraction

Through the filtering of water samples, the determination of the suspended particulate fraction in the samples was also made possible. The concentration of suspended particulate matter can be defined as the measured amount of particulate matter that stays retained on a filter with a defined porosity, after filtering. The filters used for the filtering of water samples in this study, typically named membrane filters, were composed of a mixture of acetate and cellulose nitrate, measured 47 mm in diameter and had a defined porosity of 0.45 μm . This method has been used in several other studies for the determination of suspended particulate content (Santos-Echeandia, 2009). The filters don't adsorb metals and

are compatible with the acid solution used in the extraction of the mercury from the particulate fraction.

The filters were previously weighted before filtration. During filtration, the samples were manually filtered by adding 250 mL portions of sample, one at a time, until it was possible to observe a substantial deposit of solid matter on the filter, the filters were then dried in oven for over 24 hours under a constant temperature of 60°C, after which, another weight measurement was immediately performed for each filter, so as to minimize the amount of time they are exposed to air, which may induce weight differences due to humidity acquired from the air. Since filtered volumes varied from sample to sample, these volumes were registered, as well as the weight measurements before and after the procedure, in order to determine the particulate matter on each filter in relation to the filtered volume of water sample. The concentration of suspended particulate matter was determined from the total weight of the dried content retained on the filter with the corresponding volume of filtered water.

The extraction of mercury content from the suspended particulate matter retained on the filters, was performed through their digestion with 4 mol/L HNO₃, and exterior heating with heated sand bath. The resulting solution, containing the particulate mercury now in dissolved form, was filtered once again to remove the particles (mostly sediment and previous filter residues) that remained from the digestion, and stored in 50 mL Falcon tubes for later analysis. No further acidification for sample preservation was needed, due to the pH of the solution resulting from this digestion process already being pH<2.

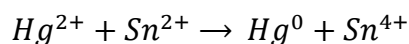
2.2.7 Methods of element analysis

All samples collected during the sampling campaigns were analyzed in order to determine the presence and concentration of mercury and other elements in the dissolved fraction and particulate fractions

2.2.7.1 Mercury analysis

The concentration of mercury in the dissolved and particulate fractions was determined by cold vapor atomic fluorescence spectroscopy (CV-AFS), with a PSA Millennium Merlin 10.036 analytical instrument.

Atomic fluorescence spectroscopy is a technique in which specific wavelengths of radiation are absorbed by an atomic vapor. This atomic vapor, produced from the atomization of the sample which is currently being analyzed, re-emits the absorbed radiation orthogonally to the original radiation source, which allows for the detection of the absorbed radiation wavelengths and its intensity with a radiation sensor, in the form of a digital signal; these measured wavelengths and intensities in digital form are then used to identify the elements and their concentration in the sample. CV-AFS is a variant of atomic fluorescence spectroscopy which uses argon (Ar) as the carrier gas, a mixture of both oxygen (O₂) and nitrogen (N₂) as the purging gas and a solution of stannous-chloride (at 2% (w/v), prepared in HCl 10% (v/v)) as the reductant. In this method, the sample is injected into the analyzer and the mercury is reduced by the stannous chloride solution, from Hg (II) to Hg (0), as represented in the following equation:



The reduced Hg (0) is then carried by a stream of water-saturated argon (Ar) gas directly onto a quartz cell, where its fluorescence is finally measured. This method was used in the determination of the mercury content in the samples due to the high sensitivity to mercury that this variant of AFS provides, which allows for the detection of mercury at the ng/L level.

The determination of the concentration of dissolved mercury in waters, through the addition of stannous chloride in acidic medium, enables the determination of reactive forms of mercury. These forms include mercury inorganic dissolved complexes, such as chloro complexes and hydro complexes, labile organic complexes and labile species of colloidal particulate mercury.

For the analysis of mercury in the dissolved fraction, the analytical instrument was calibrated for readings in the scale of ng/L, with standards ranging from 5 ng/L to 60 ng/L of mercury. For the analysis of the particulate fraction of the mercury content, the instrument was calibrated for readings in the scale of µg/L, with standards ranging from 0.05 µg/L to 0.5 µg/L. The standards were prepared using standard solutions of Hg(II) nitrate in HNO₃ 2%, prepared from a commercial stock solution. When analysis was carried out during the entirety of a day, standards were remade and reread several times, with a full day of analysis requiring at least 3 full sets of standard readings. The standards used in the determination of the dissolved and particulate fractions of mercury are listed in the following Table 4.

Table 4: Conditions for the preparation of the standards used in the calibration of the CV-AFS instrument

	Dissolved fraction standards	Particulate fraction standards
Intermediate Hg standard solutions	1 µg/L	100 µg/L
Hg standards concentrations	0, 5, 10, 20, 40, 60 ng/L	0, 0.05, 0.1, 0.2, 0.30 and 0.50 µg/L

For the determination of samples, each sample underwent at least 2 readings. During each sample reading session at least one blank of HNO₃ 2% dilution solution was also analyzed. The concentration of Hg in the samples was determined with the use of calibration curves, which were obtained from the readings of sets of five or six of the aforementioned standards. An example of a set of readings of Hg standards and the calibration curve which originated from them, can be observed in Figure 4.

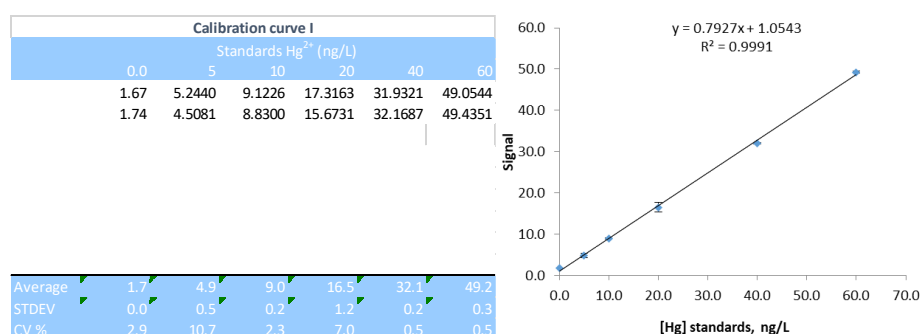


Figure 4: Representation of a table of readings of standards (on the left) and the calibration curve that originated from this table (on the right).

2.2.7.2 Major and trace elements analysis

The presence and concentration of major and trace metals was determined by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Both methods rely on the use of an inductively coupled plasma source to ionize (ICP-MS) the atoms or excite the atoms electrons (ICP-OES) of the elements found in the samples. However, they differ in the method of detection. The ICP-MS relies on a mass spectrometer in conjunction with the ICP source. In this method, the sample is first injected into the ICP source as an aerosol, which is produced by a nebulizer, in the case of liquid samples, or by a laser, in the case of solid samples. This aerosol is converted into a gaseous form and then ionized by the ICP source. The ions are then separated and detected with a mass spectrometer (Wolf, 2005). The ICP-OES on the other end relies on the detection of photons released from spontaneous emissions of the atoms and ions that have been previously excited. This method is designed for the analysis of liquid or gaseous samples and in order to analyze a sample, it must be injected directly into the ICP source as an aerosol and vaporized as free atoms in the gaseous state. The atoms are then excited through collisional excitation, forcing them to emit photons. Since every element emits energy as photons in wavelengths characteristic to themselves, by detecting the different wavelengths of these photons, it is possible to identify the elements from which they originated. The total number of photons detected by the sensor can then be used to determine the concentration of the element in the sample (Hou and Jones, 2006)

Both methods of analysis were performed in an offsite accredited laboratory, the University of Aveiro's Central Analysis Laboratory. Differentiation between the dissolved and particulate fractions was calculated by subtracting the elemental contents of the filtered samples from the contents of the un-filtered samples, where the content of an un-filtered sample represents the total concentration of a certain element, and the content of a filtered sample represents the concentration of the same element, only in the dissolved fraction.

2.2.8 Quality control of the results

Quality control for the results of mercury in the dissolved fraction and in the suspended particulate fraction was attained through the evaluation of the variability resulting from diverse experimental conditions. One aspect worth mentioning about the CV-AFS instrument readings is that the accuracy of the absorbance signals of the Hg standards decay over time during the analysis of the samples; this is why the Hg standards were reread at least 3 times over the course of one full day of analysis, in order to adapt a new calibration curve to the loss of sensitivity.

The detection limit (DL) indicates the lowest level a signal can be distinguished from noise. The quantification limit (QL) indicates the lowest level of an analyte that can be determined with precision and accuracy. The DL and QL can be calculated from the following two equations:

$$DL = M_B + 3 \times S_D$$

$$QL = M_B + 10 \times S_D$$

where M_B represents the arithmetic mean of a series of blanks and S_D the standard deviation associated. The DL's and QL's for the CV-AFS instrument, which was used for the analysis of Hg in the dissolved fraction and the particulate fraction were calculated with the blanks that were analysed during both procedures. The resulting detection and quantification limits for the CV-AFS method are described in Table 5.

Table 5: Table describing the detection limit (DL) and quantification limit (QL) in the analysis of dissolved fraction Hg and particulate fraction Hg

Analysis	Method	DL	QL
Dissolved fraction Hg	CV-AFS calibrated for ng/L	3,16 ng/L	7,17 ng/L
Particulate fraction Hg	CV-AFS calibrated for µg/L	0,019 µg/L	0,045 µg/L

Due to the ICP-MS and ICP-OES analysis being performed in analytical instruments over at the Central Analysis Laboratory of the University of Aveiro, the QL values for the various elements that were determined in the ICP-MS and ICP-OES instruments were

already provided, with no need to calculate those. These elements and their QL's values are listed in Table 6.

Table 6: Table of quantification limits of the elements detectable in ICP-MS and ICP-OES.

Method	ICP-OES			ICP-MS					
Element	Ca	K	Cu	Li	B	Mg	Al	Ti	Mn
QL (µg/L)	500	100	2.0	2.0	2.0	100	5.0	2.0	0.50
Method	ICP-MS								
Element	Fe	Co	Ni	Zn	As	Sr	Ba	U	Be
QL (µg/L)	10.0	0.10	1.0	2.0	2.0	0.20	0.10	0.02	0.10
Method	ICP-MS								
Element	Cr	Ga	Mo	Ag	Cd	Sn	Sb	Cs	La
QL (µg/L)	0.50	0.10	2.0	0.10	0.10	2.0	0.50	0.10	0.02
Method	ICP-MS								
Element	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
QL (µg/L)	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01
Method	ICP-MS								
Element	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb
QL (µg/L)	0.01	0.01	0.01	0.01	0.01	0.50	2.0	0.02	0.10

3 Results

3.1 Quality control of results

The quality control of the mercury results was done by comparing coefficients of variation (%CV) from the mercury readings. Table 8 shows a set of results obtained from mercury readings of a set of samples in the CV-AFS instrument, which were carried out during laboratorial work.

Table 7.: Table demonstrating the results produced by reading from the CV-AFS instrument, while reading samples from Ílhavo channel during high tide.

Sample index	Reading (n°)	Dissolved Fraction				Suspended Particulate Fraction			
		[Hg]	Mean	Stdev	%CV	[Hg]	Mean	Stdev	%CV
---	---	(ng/L)	(ng/L)	(ng/L)	(%)	(µg/L)	(µg/L)	(µg/L)	(%)
HT_I-1	I	28.0	27.0	1.49	5.52	0.055	0.056	0.001	1.23
	II	25.9				0.056			
HT_I-2	I	41.1	40.7	0.576	1.41	0.385	0.384	0.001	0.346
	II	40.3				0.383			
HT_I-3	I	37.7	38.0	0.525	1.38	0.222	0.213	0.014	6.49
	II	38.4				0.203			
HT_I-4	I	41.7	43.2	2.14	4.95	0.127	0.133	0.008	6.20
	II	44.7				0.139			
HT_I-5	I	24.1	23.2	1.37	5.91	0.182	0.172	0.014	8.26
	II	22.2				0.162			
HT_I-6	I	16.7	17.0	0.431	2.54	0.104	0.101	0.004	3.72
	II	17.3				0.099			
HT_I-7	I	18.7	17.8	1.26	7.09	0.173	0.172	0.001	0.778
	II	16.9				0.171			
HT_I-8	I	52.1	55.5	4.71	8.50	0.135	0.127	0.011	8.96
	II	58.8				0.119			

These results relate to the concentration values of samples collected in Ílhavo channel during high tide. The percentage values for the coefficients of variation corresponds to the quotient of the standard deviation and the mean of each set of readings. If a set of readings produced a %CV<10%, this set of readings was considered as having sufficient quality to be accepted. The %CV results from this table reflect the coefficients of variation that can be observed from similar mercury readings in remaining sets of samples.

3.2 Physico-chemical parameters

During field work, physico-chemical parameters were measured in the water. The measured parameters were salinity, conductivity, temperature, dissolved oxygen (O₂) and pH; the suspended particulate matter (SPM) content of the samples was also measured afterwards, in lab conditions. The data was organized for measurements carried out during low and high tide, along the sampling stations of both channels, with the distance increasing from the most upstream stations, farther from the Ria de Aveiro's central region, until the most downstream stations, closer to the central region. Values collected from these measurements are listed in Annex I, for the Mira channel and the Ílhavo channel.

3.2.1 Salinity and conductivity

Figures 5 and 6 represent the salinity and conductivity, both measured *in situ* along the Mira and Ílhavo channels, respectively, during the two tidal phases.

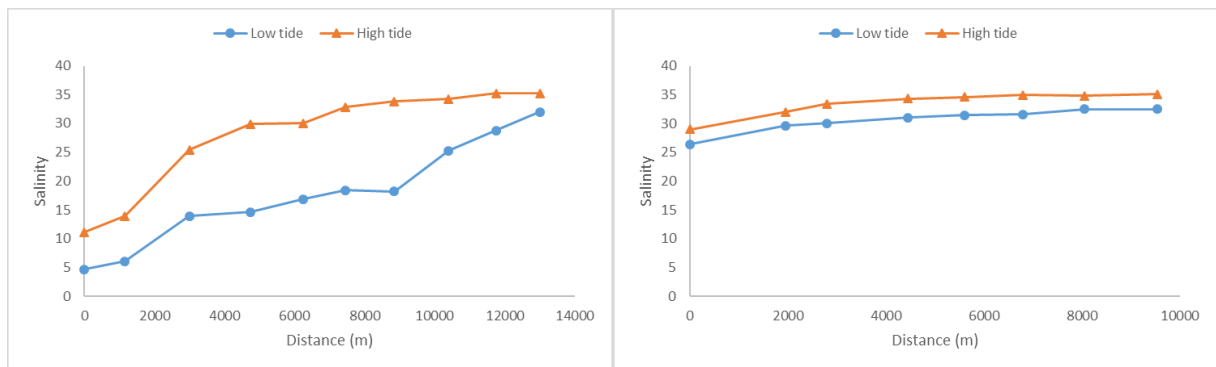


Figure 5: Salinity during low and high tide for Mira (left) and Ílhavo (right) channels.

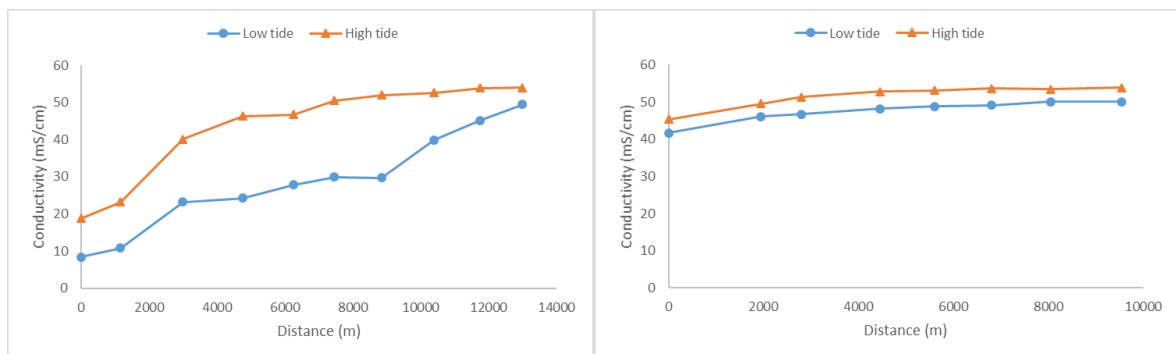


Figure 6: Conductivity during low and high tide for Mira (left) and Ílhavo (right) channels.

An increase in the values of parameters can be observed in both channels moving downstream from the initial sampling stations (M-1 and I-1) until reaching the final stations (M-10 and I-8). These parameters display similar behavior; as such, they both present higher values during high tides, with Mira channel having larger a difference between tides, which is noticeable between station M-3 and station M-10.

Salinity levels during observations in Mira channel ranged from 4.7 to 32.0 with an average of 17.9 during low tide and ranged from 11.1 to 35.2 with an average of 28.2 during high tide; salinity levels in Ílhavo channel ranged from 26.4 to 32.5 with an average of 30.6 during low tide and ranged from 29.0 to 35.1 with an average of 33.5 during high tide. Conductivity levels during observations in Mira channel ranged from 8.4 to 49.4 mS/cm and averaged at 28.8 mS/cm during low tide and 18.8 to 54.0 mS/cm with an average of 43.8 mS/cm during high tide; in Ílhavo these values ranged from 41.7 to 50.1 mS/cm, averaging at 47.6 mS/cm during low tide and 45.3 to 53.9 mS/cm with an average of 51.6 during high tide

3.2.2 Temperature

Temperature measured *in situ* for both channels are found in Figure 7.

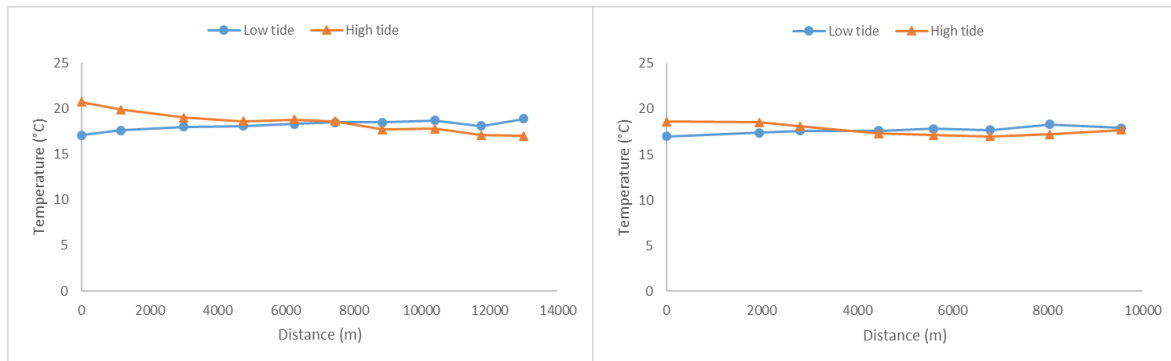


Figure 7: Temperature during low and high tide for Mira (left) and Ílhavo (right) channels.

A steady rise in temperatures is observable in both channels, during low tide, while the opposite occurs during high tide. Temperatures measured along the Mira channel ranged from 17.1 to 18.9 °C with an average of 18.2 °C, during low tide, and 17.0 to 20.7 °C with an average of 18.5 °C, during high tide; in Ílhavo channel, measured temperatures ranged from 17.0 to 18.3 °C, averaging at 17.7 °C, during low tide, and ranged from 17.0 to 18.6 °C, averaging at 17.7 °C, during high tide.

3.2.3 Dissolved oxygen

Oxygen content (O_2) of the water at the moment of sample collection along both channels is represented graphically in Figure 8.

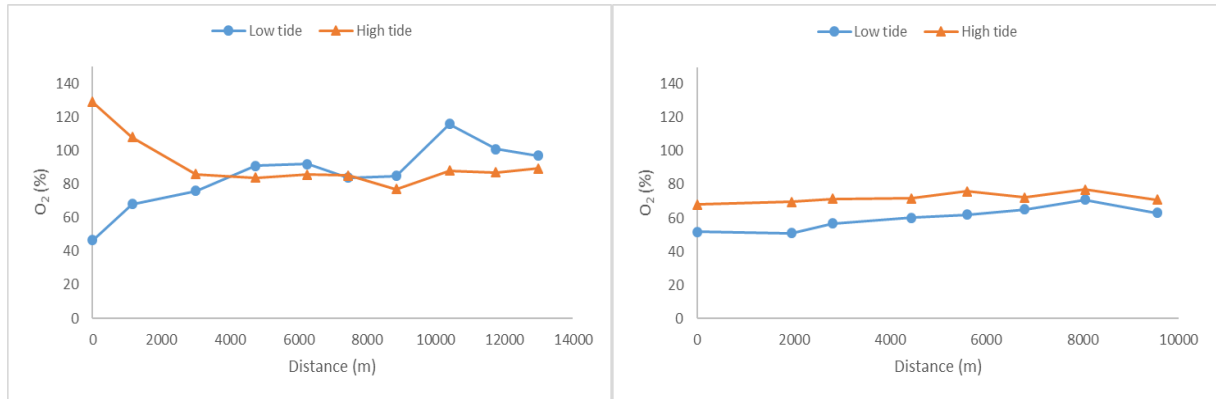


Figure 8: Dissolved oxygen percentage during low and high tide for Mira (left) and Ílhavo (right) channels.

Levels observed along the Mira channel ranged from 46.7 to 116.0 % and averaging at 85.7% during low tide and ranging from 77.0 to 129.0 % while averaging 91.9% during high tide; for Ílhavo channel, oxygen levels ranged from 51.0 to 71.0 % and averaged 60.1% during low tide while ranging from 68.0 to 77.0% and averaging at 72.1% during high tide.

In Mira, during low tide, a significant increase in the water's oxygen content appears to develop initially, however, after station M-7 and until M-10, values appear to hover around the 100% region; during high tide the oxygen content levels noticeably decrease during the initial stations (M-1, M-2 and M-3), after which the levels appear to stabilize until M-10

Oxygen levels along Ílhavo appear to behave similarly between low and high tide, demonstrating a slight increase in content between I-1 and I-8.

3.2.4 pH

Measured pH levels in Mira and Ílhavo channels can be observed in Figure 9 for both tidal phases.

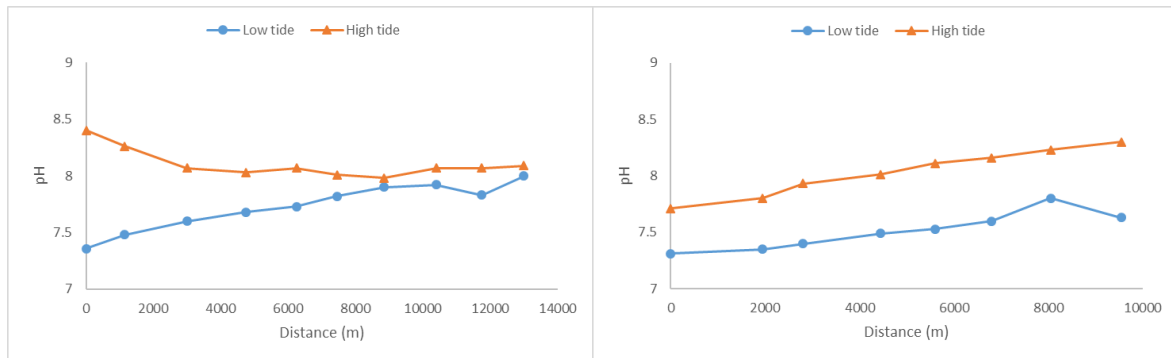


Figure 9: pH levels during low and high tide for Mira (left) and Ílhavo (right) channels.

During low tide along the Mira channel, pH levels appear to steadily rise, stabilizing around the 8.0 pH mark in the final stations, while in high tide the pH levels initially declined, appearing to also stabilize around 8.0 pH after station M-3. In Ílhavo channel, the pH levels for the two tidal phases demonstrated similar behavior to one another, with both displaying an increase between stations I-1 and I-8 (except I-7 during low tide), however, the pH levels found during low tide were lower than the levels during high tide

pH levels in Mira during low tide ranged between 7.4 and 8.0 and averaged around 7.7; during high tide pH levels ranged between 8.0 and 8.4 and averaged at 8.1. pH levels in Ílhavo ranged from 7.3 to 7.8, averaging at 7.5, during low tide, and ranged from 7.7 to 8.3 while averaging at 8.0, during high tide.

3.2.5 Suspended particulate matter

Figure 10 relates to suspended particulate matter (SPM) content in the water samples from the Mira channel and Ílhavo channel.

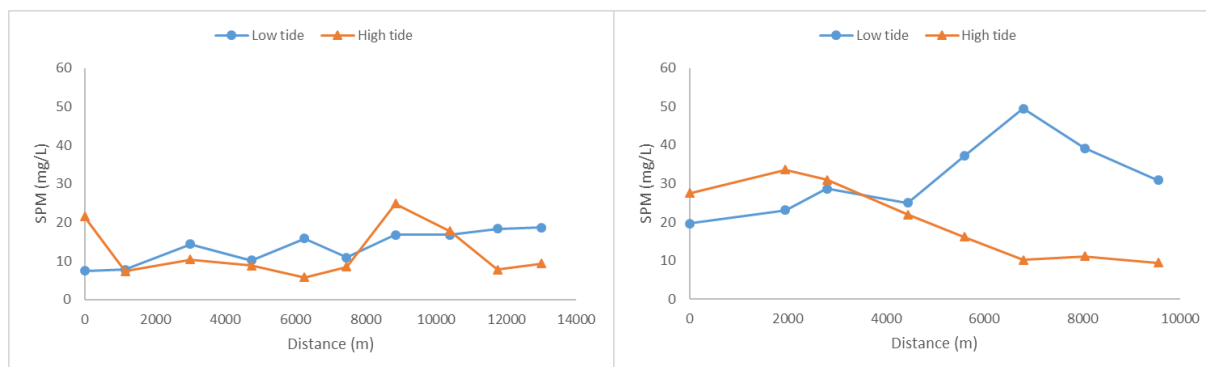


Figure 10: Suspended particulate matter concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

SPM content was determined in the laboratory, from samples collected in the Mira channel and Ílhavo channels. The results of samples from Mira channel demonstrate that, during low tide, concentrations steadily increase from M-1 to M-10, however, during high tide the SPM concentration levels were mostly constant, close to 10 mg/L, with the exception of stations M-1, M-7 and M-8, where a peak in concentrations was observed. Results from samples collected along Ílhavo channel, show that during low tide conditions, demonstrate that SPM concentrations steadily increased downstream from station I-1, however, from I-6 on, SPM concentrations started to decline, up until the last station, I-8. During high tide conditions, SPM levels increased between I-1 and I-2, after which there was a decrease in SPM concentrations up to I-6 where concentration values stabilized until I-8.

Regarding the concentration values, in Mira channel, SPM concentrations ranged from 7.4 mg/L to 18.7 mg/L, with an average of 13.7 mg/L, during low tide, and 5.8 to 24.9 mg/L with an average of 12.2 mg/L, high tide. In Ílhavo channel, SPM levels ranged from 19.6 to 49.5 mg/L and averaged at 31.6 mg/L, during low tide, while ranging from 9.5 to 33.6 mg/L, with an average of 20.1, during high tide.

3.3 Mercury

Analysis results related to dissolved and particulate mercury (Hg) fractions and total mercury are listed in Annex II, for Mira and Ílhavo channels. In the following sub-chapters, results for these fractions will be demonstrated. The sample analysis data was organized by tides, along the sampling stations of both channels, with the distance increasing from the most upstream stations, farther from the Barra channel, until the most downstream stations, closer to the central region.

3.3.1 Mercury in dissolved fraction

In Figure 11 the variation of the concentration of Hg in dissolved fraction is represented, with levels varying along both channels.

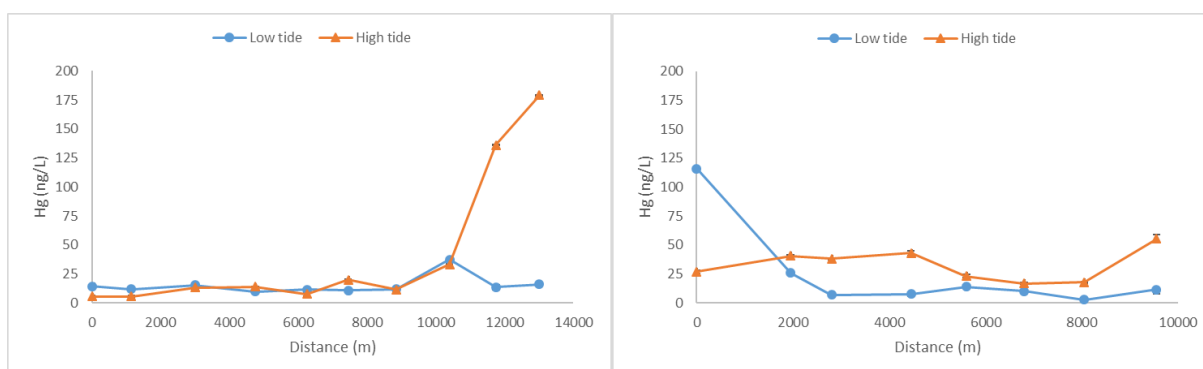


Figure 11: Dissolved Hg concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Results from the analysis of Hg in dissolved fraction were obtained directly from the content of dissolved Hg in filtered water samples, as such, concentration values are measured in terms of mass of mercury per unity of volume (ng/L).

In Mira channel, results show that during both tidal phases, samples from sampling stations M-1 to M-7 all contained dissolved Hg levels below the 20 ng/L mark, ranging from 9.91 to 15.3 ng/L during low tide and 5.42 to 19.9 during high tide. In station M-8, during low and high tide, dissolved Hg concentrations rose to 37.5 ng/L and 33.1 ng/L, respectively. However, from station M-8 forward, which refers to M-9 and M-10, a disparity in behavior developed between tidal phases, with Hg concentrations lowering once again to levels below

20 ng/L during low tide, while Hg concentrations during high tide continued to increase, reaching concentrations of 179 ng/L in station M-10.

For Ílhavo channel, results show that during low tide, dissolved Hg levels initially decreased, going from 116 ng/L in I-1 to 6.87 ng/L in I-3, with the samples from the following stations remaining all with Hg concentrations lower than 15 ng/L for the remaining stations; during high tide, results were shown to oscillate between 17.0 ng/L and 55.4 ng/L, with lower levels occurring in M-1, M-5, M-6 and M-7.

Dissolved Hg concentrations in Mira channel ranged from 9.91 ng/L to 37.5 ng/L, averaging at 15.3 ng/L during low tide; during high tide, concentrations ranged from 5.42 to 179 ng/L and averaged at 42.5 ng/L. Dissolved Hg concentrations in Ílhavo channel ranged from 2.89 ng/L to 116 ng/L and averaged at 24.3 ng/L; during high tide, concentrations ranged from 17.0 to 55.4 ng/L, averaging at 32.8.

3.3.2 Mercury in particulate fraction

Figure 12 displays the concentration of Hg in particulate matter present in water samples from Mira and Ílhavo channels, during both tidal conditions.

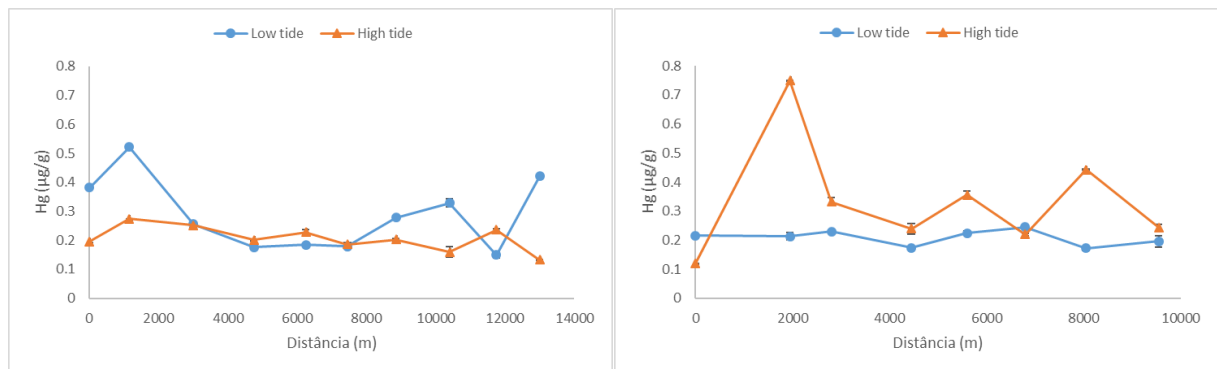


Figure 12: Particulate Hg concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Results from the analysis of Hg in the suspended particulate fraction were obtained from the content of Hg found on the particulate matter that was filtered from the water samples, as such, concentration values are measured in terms of mass of mercury per mass of particulate matter (µg/g).

Results from samples collected in the Mira channel during low tide show that the concentration of particulate Hg was greater in the first two stations, M-1 (0.38 µg/g) and M-2 (0.52 µg/g), and station M-8 (0.33 µg/g) and M-10 (0.42 µg/g). The remaining stations presented concentrations lower than 0.30 µg/g; During high tide, concentrations were more constant, all stations demonstrated concentrations lower than 0.30. A slight decreasing tendency can be observed from station M-1 to station M-10.

Observing the results of particulate Hg from samples collected in Ílhavo it appears that during low tide the concentration of Hg stayed mostly stable around the 0.2 µg/g mark; During high tide, the concentration of Hg varied greatly in the initial stations, where M-1 demonstrated a concentration of 0.12 µg/g and M-2 a concentration of 0.75 µg/g. The following stations varied less, however, oscillating from station to station.

Particulate Hg concentrations in samples from Mira channel ranged from 0.18 to 0.52 µg/g and averaged 0.29 µg/g during low tide, while ranging from 0.13 to 0.27 µg/g and averaging 0.21 µg/g during high tide. Concentrations in samples from Ílhavo channel ranged from 0.17 to 0.24 µg/g, averaging at 0.21, during low tide, and ranged from 0.12 to 0.75 µg/g and averaged at 0.34 µg/g during high tide.

3.4 Major elements

The presence and concentration of some major elements in the water samples was determined and found to be above quantification limits. These major elements were Magnesium (Mg), Potassium (K), Calcium (Ca), Aluminium (Al), Titanium (Ti), Manganese (Mn) and Iron (Fe); the totality of the resulting data for these elements is listed in Annex III-A through Annex III-G. Dissolved and particulate fractions of these elements were determined for both channels, as well as both tidal phases.

3.4.1 Magnesium, Potassium and Calcium

Figures 13, 14 and 15 represent the concentrations of magnesium, potassium and calcium in the Mira and Ílhavo channels, during the high and low tide.

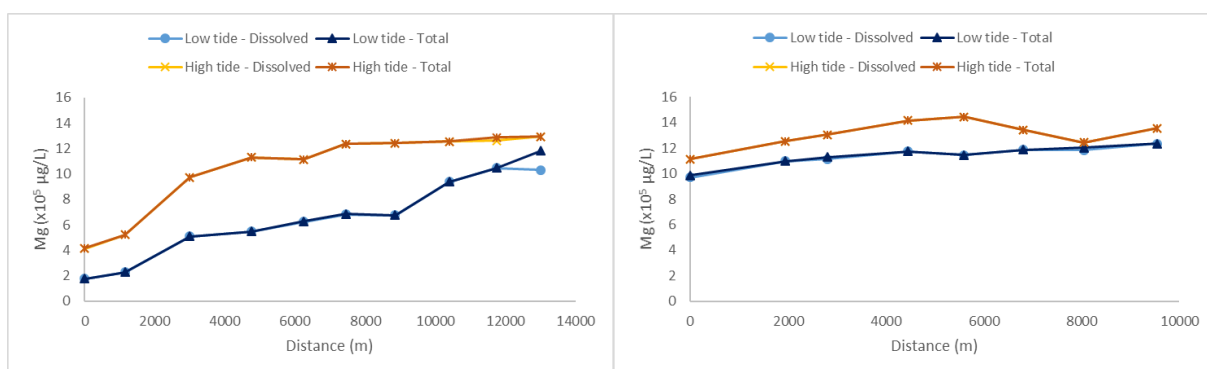


Figure 13: Magnesium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

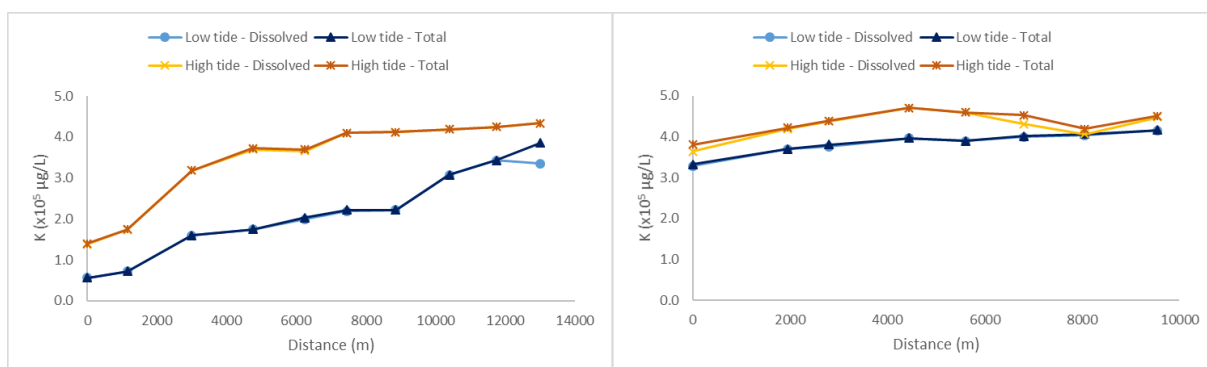


Figure 14: Potassium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

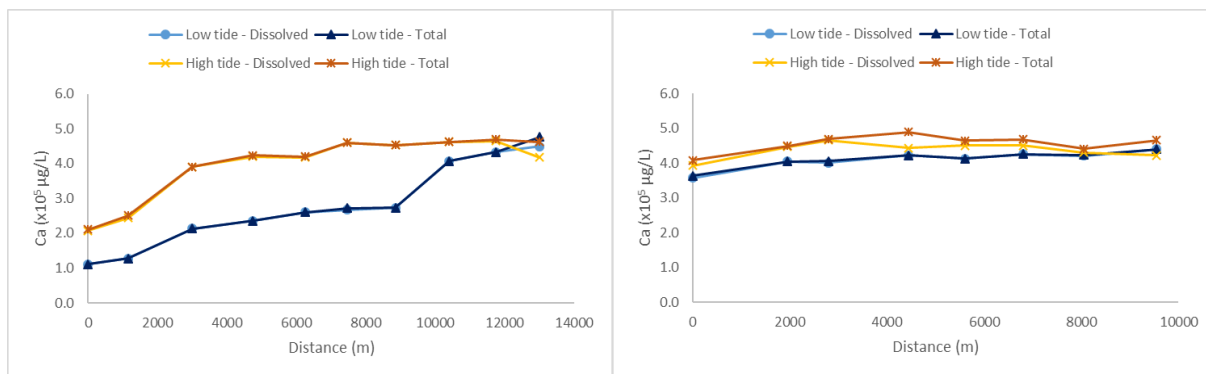


Figure 15: Calcium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Magnesium, potassium and calcium present a similar behavior, with concentrations steadily increasing along the length of Mira channel, during both tidal phases; in Ílhavo channel, with results again showing a similar behavior between elements, a steady increase of concentration can initially be observed during low tide and high tide, however, after station I-5, during high tide, concentration levels decrease, before increasing once again in station I-8.

Total magnesium levels ranged from during 0.175 to 1.182 g/L during low tide and 0.417 to 1.292 g/L during high tide in Mira, while averaging at 0.662 g/L and 1.047 g/L during low and high tide, respectively. For Ílhavo channel, levels ranged from 0.986 to 1.235 g/L during low tide and 1.114 to 1.446 g/L during high tide and averaged at 1.145 g/L and 1.310 g/L during low and high tide, respectively.

Total potassium levels ranged from 55.83 to 385.4 mg/L during low tide and 140.5 to 433.8 mg/L during high tide in Mira. The averages for low tide and high tide were 214.5 mg/L and 347.6 mg/L. For Ílhavo channel, levels ranged from 332.0 to 416.0 mg/L, averaging at 386.4 mg/L, during low tide and 380.4 to 470.0 mg/L, with an average of 436.3 mg/L during high tide.

Total calcium levels ranged from 111 to 476 mg/L and averaged 281 mg/L during low tide, and ranged from 211 to 469 mg/L, averaging 401 mg/L, during high tide, in Mira. For Ílhavo channel, levels ranged from 364 to 440 mg/L, with an average of 412 mg/L during low tide and 407 to 490 mg/L and an average of 457 mg/L during high tide.

There appears to be almost no distinction between dissolved and particulate fractions, with total concentrations mirroring dissolved concentrations on most stations. Magnesium and potassium results show that the stations with the lowest dissolved fraction to particulate fraction ratios for the two elements were stations: M-10, during low tide, where 87% of the content was in dissolved fraction; and I-6, during high tide, with 96% and 95% in dissolved fraction. Calcium had the lowest dissolved fraction ratios in stations: M-10, during high tide, with 90% of total concentration in dissolved fraction; I-4, during high tide, with 91% in dissolved fraction.

3.4.2 Aluminium

Aluminium concentration levels for the Mira and Ílhavo channels, during the high and low tide are displayed in Figure 16.

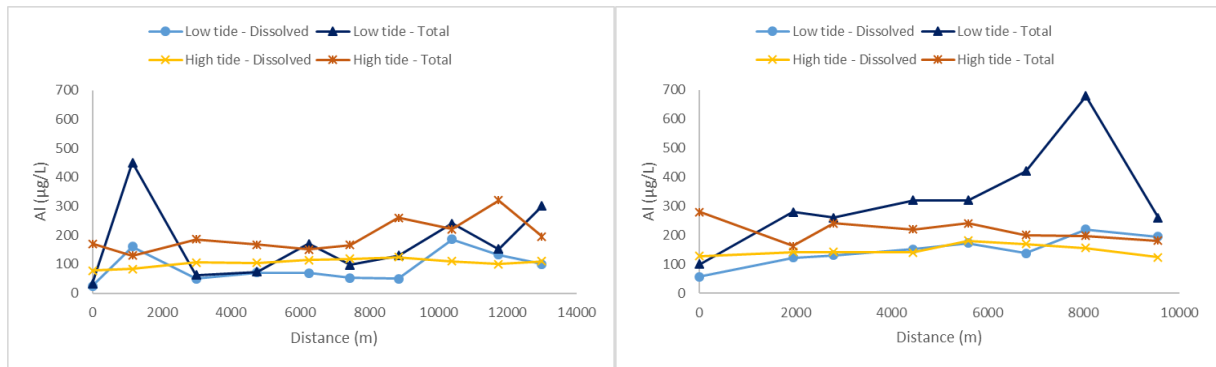


Figure 16: Aluminium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Aluminium levels appear mostly constant along the Mira channel during high tide, with only a slight difference observable on the total aluminium content, between M-7 and M-10; during low tide concentrations appear to be steadily increasing as they get closer to the end of the channel, with, however, stations M-2, M-5, M-8 and M-10 demonstrating peaks of concentration. Differences between dissolved and total aluminium content can be observed during high tide, where aluminium in dissolved fraction appears to constitute roughly half of the total aluminium content; during low tide this separation is less apparent, but still observable in stations M-2 and M-5 through M-10. Total concentrations during low tide ranged from 32 to 450 $\mu\text{g/L}$, averaging at 171 $\mu\text{g/L}$, and ranged from 130 to 320 $\mu\text{g/L}$, while averaging at 197 $\mu\text{g/L}$, during high tide; dissolved concentrations ranged from 24 to

186 $\mu\text{g/L}$ and averaged at 90 $\mu\text{g/L}$ during low tide, and ranged from 78 to 124 $\mu\text{g/L}$, averaging at 105 $\mu\text{g/L}$, during high tide.

Results from Ílhavo demonstrate almost constant concentration levels in both tides and fractions, differing only in select stations, decreasing in I-1 and increasing in I-7 during low tide and decreasing in I-2 during high tide. Separation between dissolved fraction and total content can also be observed on this channel during both tides, with dissolved fraction levels reaching levels as low as 32% of total content, in station I-7. Total concentrations in Ílhavo channel during low tide ranged from 100 to 680 $\mu\text{g/L}$ and 162 to 280 $\mu\text{g/L}$ during high tide, averaging at 330 $\mu\text{g/L}$ and 215 $\mu\text{g/L}$, while dissolved concentrations ranged from 57 to 220 $\mu\text{g/L}$ during low tide and 124 to 180 $\mu\text{g/L}$ during high tide and averaged at 148 $\mu\text{g/L}$ during both tides.

3.4.3 Titanium

Results of titanium concentrations in samples from Mira and Ílhavo channels, during the high and low tide can be found in Figure 17.

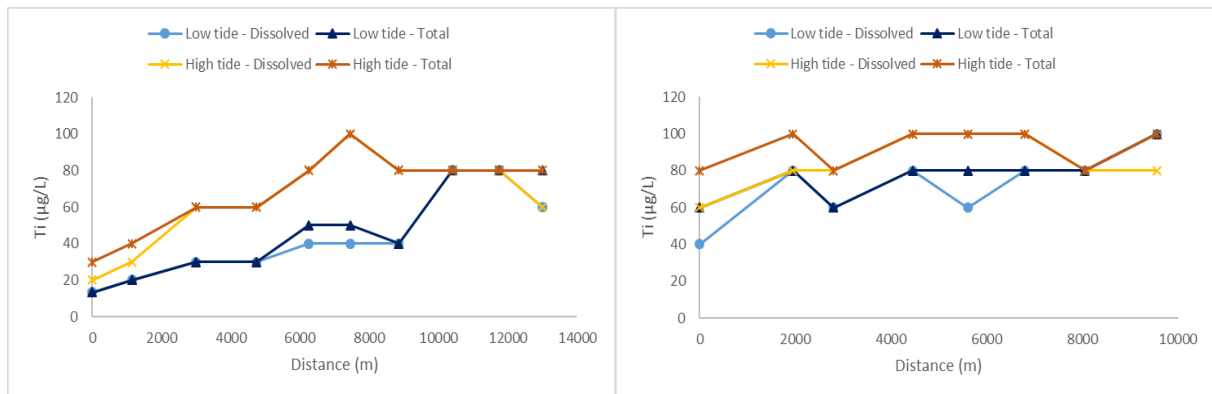


Figure 17: Titanium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

A similarity in behavior between low and high tides can be observed to occur in both channels, mostly differing only in the mean concentrations. These differences occur from stations M-7 to M-10 during low tide in Mira and from stations M-6 to M-8 also during low tide in Ílhavo.

Separation between dissolved and total titanium content is observable only in select stations, with dissolved fractions achieving a minimum of 67% in M-1 during high tide in Mira and 67% in I-1 during low tide in Ílhavo.

Total titanium levels in Mira ranged from 13 to 80 $\mu\text{g/L}$ during low tide and 30 to 100 $\mu\text{g/L}$ during high tide, averaging 47 $\mu\text{g/L}$ and 69 $\mu\text{g/L}$ during low and high tide. Total titanium levels in Ílhavo ranged from 60 to 100 $\mu\text{g/L}$, averaging at 78 $\mu\text{g/L}$, during low tide, while ranging from 80 to 100 $\mu\text{g/L}$ and averaging at 93 $\mu\text{g/L}$ during high tide.

3.4.4 Manganese and Iron

Manganese and Iron concentration levels for the Mira and Ílhavo channels, during the high and low tide are displayed in Figures 18 and 19, respectively.

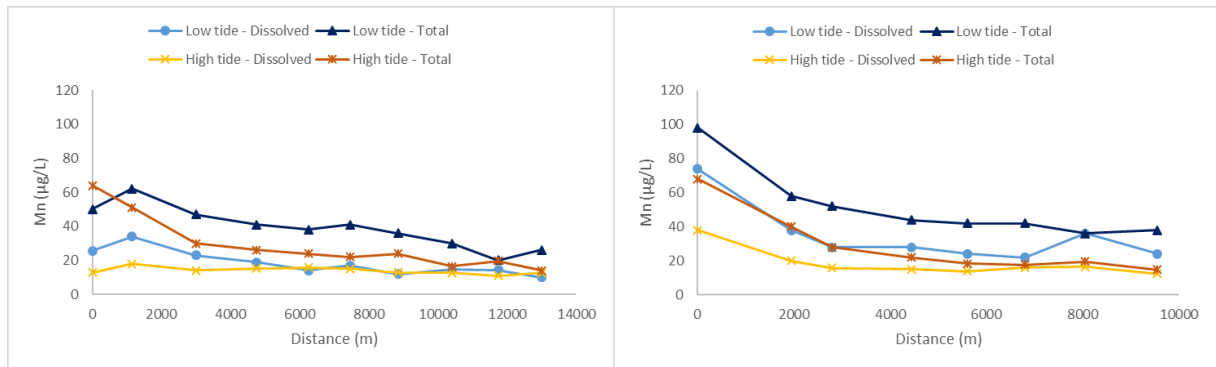


Figure 18: Manganese total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

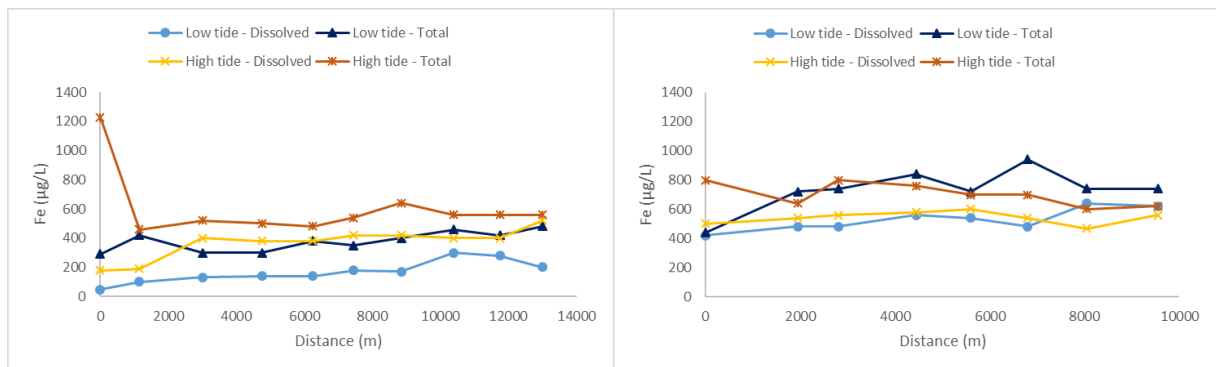


Figure 19: Iron total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

For manganese and iron, both channels display similar behavior, with concentration levels remaining almost constant during the whole length of Mira and Ílhavo channels,

differing only in the stations M-2 and I-1 for manganese, and station M-1 for iron. A distinct separation between dissolved fraction and total manganese and iron content can also be observed in both channels, with dissolved levels appearing to constitute close to half of the total content on most stations, during both tidal phases of both channels.

For manganese, total concentration levels in Mira channel ranged from 20 to 62 $\mu\text{g/L}$ and averaged at 39 $\mu\text{g/L}$ in low tide; during high tide, concentrations ranged from 14 to 64 $\mu\text{g/L}$ and averaged at 29 $\mu\text{g/L}$. Dissolved fraction concentrations of manganese in Mira ranged from 10 to 34 $\mu\text{g/L}$ during low tide and 11 to 18 $\mu\text{g/L}$ during high tide, averaging at 18 $\mu\text{g/L}$ and 14 $\mu\text{g/L}$, respectively. In Ílhavo, total concentration ranged from 36 to 98 $\mu\text{g/L}$ and averaged at 51 $\mu\text{g/L}$ during low tide and ranged from 15 to 68 $\mu\text{g/L}$ during high tide, averaging at 29 $\mu\text{g/L}$; dissolved fraction levels ranged from 22 to 74 $\mu\text{g/L}$ in low tide and 12 to 38 $\mu\text{g/L}$ in high tide, averaging at 34 $\mu\text{g/L}$ and 18 $\mu\text{g/L}$ during low and high tide.

For iron, total concentration levels in Mira channel ranged from 290 to 480 $\mu\text{g/L}$ in low tide and 460 to 1230 $\mu\text{g/L}$ in high tide, averaging at 380 $\mu\text{g/L}$ and 605 $\mu\text{g/L}$; dissolved fraction concentrations ranged from 47 to 300 $\mu\text{g/L}$, averaging at 169 $\mu\text{g/L}$, during low tide, while ranging from 47 to 520 $\mu\text{g/L}$ and averaging at 369 $\mu\text{g/L}$ during high tide. In Ílhavo, total concentration levels ranged from 440 to 940 $\mu\text{g/L}$ during low tide and 600 to 800 $\mu\text{g/L}$ during high tide and dissolved fraction levels ranged from 420 to 640 $\mu\text{g/L}$ in low tide and 468 to 600 $\mu\text{g/L}$ in high tide. Total concentration levels in Ílhavo averaged at 735 $\mu\text{g/L}$ and 703 $\mu\text{g/L}$ during low and high tide, respectively, while dissolved concentration levels averaged at 528 $\mu\text{g/L}$ and 544 $\mu\text{g/L}$ during low and high tide.

3.5 Other elements

The presence and concentrations of several other elements in the samples were also determined above quantification limits. These elements were Lithium (Li), Boron (B), Cobalt (Co), Nickel (Ni), Copper (Cu) Zinc (Zn), Arsenic (As), Strontium (Sr), Barium (Ba) and Uranium (U). The resulting data for these elements is listed in Annex IV-A through Annex IV-J.

Several other elements were detected but their concentrations were not quantifiable. Results from these elements will not be shown. These elements are Be, Cr, Ga, Mo, Ag, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl and Pb.

3.5.1 Lithium and Boron

Figures 20 and 21 represent the concentration of Lithium and Boron in the Mira and Ílhavo channels, during the high and low tide.

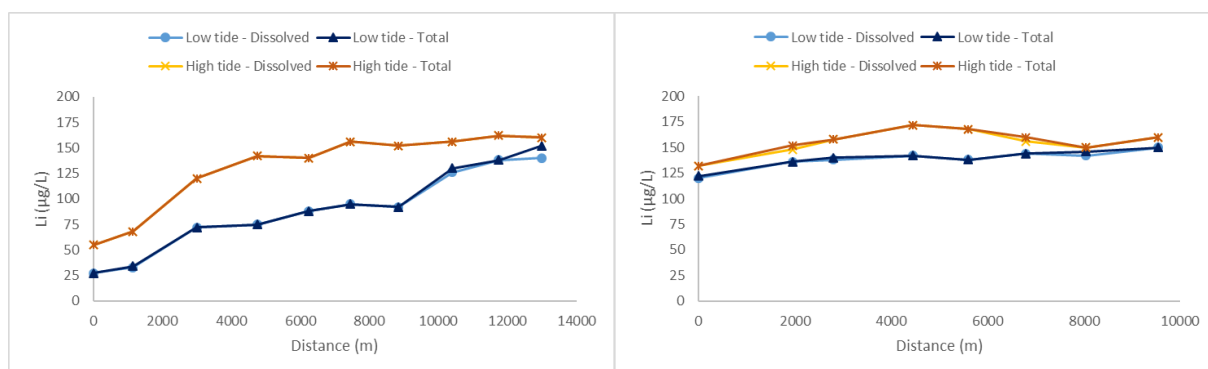


Figure 20: Lithium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

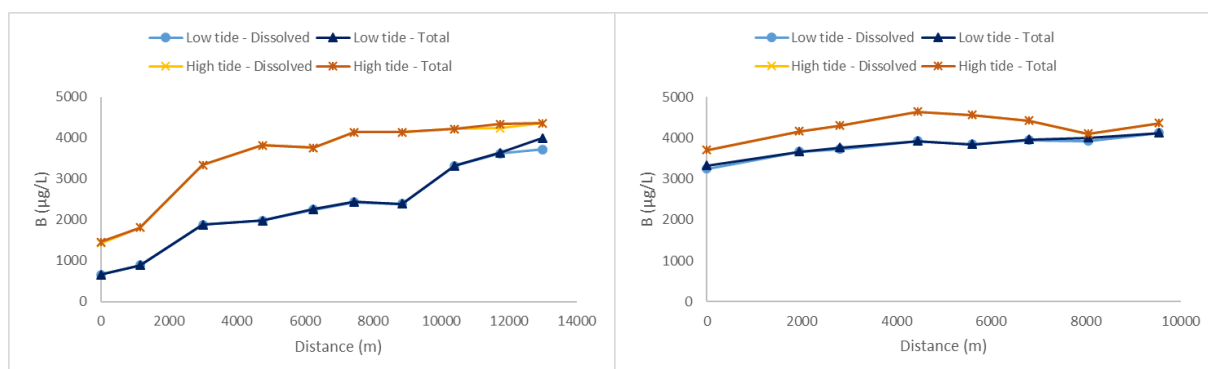


Figure 21: Boron total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Lithium and Boron display similar behavior. Concentrations steadily increase from station to station in Mira channel, during both tidal phases; Ílhavo channel results also display similarity between the elements, with a steady increase of concentrations initially observed during low tide and high tide, however, after station I-5, during high tide, concentration levels decrease, before increasing once again in station I-8.

Total Lithium levels ranged from 27 to 152 $\mu\text{g/L}$ and averaged at 90 $\mu\text{g/L}$ during low tide and 55 to 162 $\mu\text{g/L}$, while averaging at 131 $\mu\text{g/L}$ during high tide in Mira. For Ílhavo channel, levels ranged from 122 to 150 $\mu\text{g/L}$ during low tide and 132 to 172 $\mu\text{g/L}$ during high tide, while averaging 140 $\mu\text{g/L}$ and 157 $\mu\text{g/L}$ during low and high tide. Total boron levels ranged from 0.66 to 4.00 mg/L during low tide and 1.46 to 4.36 mg/L during high tide in Mira, and averaged at 2.35 mg/L and 3.54 mg/L during low and high tide. For Ílhavo channel, boron levels ranged from 3.32 to 4.12 mg/L and averaged 3.82 mg/L during low tide and 3.70 to 4.64 mg/L , while averaging at 4.28 mg/L during high tide.

There is no apparent distinction between dissolved and particulate fractions for most stations, except in M-10 during low tide, where a small decrease in dissolved content may be observed for the two elements.

3.5.2 Cobalt

Figure 22 represents the concentration of cobalt in Mira and Ílhavo channel during the high and low tides.

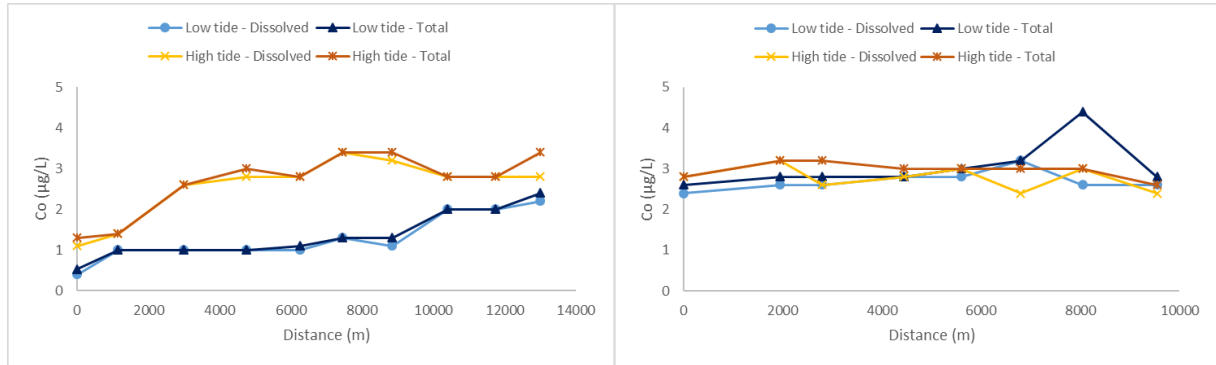


Figure 22: Cobalt total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Cobalt concentrations steadily increase from station M-1 to station M-10 in Mira channel, during both tidal phases, however, concentrations between low and high tide differ greatly; Ílhavo channel results display constant concentrations during low tide and high tide, with a peak in concentration, however, in station I-7, during low tide.

In Mira channel, total cobalt concentrations ranged from 0.53 to 2.40 $\mu\text{g/L}$ and 1.30 to 3.40 $\mu\text{g/L}$, while averaging at 1.36 $\mu\text{g/L}$ and 2.69 $\mu\text{g/L}$, during low and high tide, respectively; dissolved fraction concentrations ranged from 0.40 to 2.20 $\mu\text{g/L}$ and 1.10 to 3.40 $\mu\text{g/L}$, while averaging at 1.30 $\mu\text{g/L}$ and 2.57 $\mu\text{g/L}$, during low tide and high tide. In Ílhavo, total concentration levels ranged from 2.60 to 4.40 $\mu\text{g/L}$, averaging at 3.05 $\mu\text{g/L}$, during low tide, and ranged from 2.60 to 3.20 $\mu\text{g/L}$, while averaging at 2.98 $\mu\text{g/L}$, during high tide; dissolved fraction levels ranged from 2.40 to 3.20 $\mu\text{g/L}$ in low tide and 2.40 to 3.20 $\mu\text{g/L}$ in high tide, averaging at 2.70 $\mu\text{g/L}$ and 2.78 $\mu\text{g/L}$ during low and high tide, respectively.

3.5.3 Nickel

Figure 23 represents the concentration of nickel in Mira and Ílhavo channel during the high and low tides.

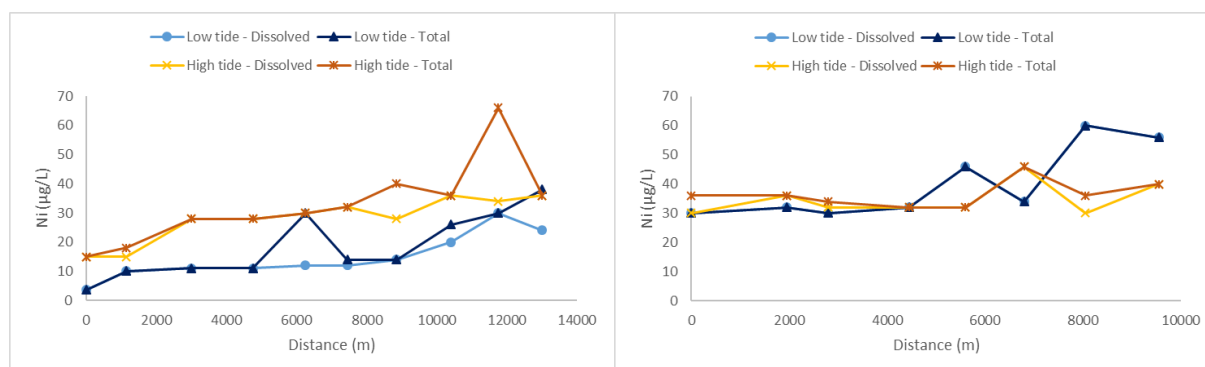


Figure 23: Nickel total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Nickel levels appear mostly constant between stations M-3 through M-7 in the Mira channel during both tides, with peaks of concentration observable on the total aluminium content in station M-9 during high tide and station M-5 during low tide. Concentrations appear to be steadily increasing between stations M-1 to M-2 and M-8 to M-10 in both tidal phases. Differences between dissolved and total nickel content can be observed in the stations with the peaks in concentration, stations M-5 and stations M-9. Results from Ílhavo channel show constant concentrations in the total nickel content in both tides, from stations I-1 through I-4. From stations I-5 to I-8, concentration levels increase irregularly.

Total concentrations during low tide ranged from 32 to 450 $\mu\text{g/L}$ and 130 to 320 $\mu\text{g/L}$ during high tide, while dissolved concentrations ranged from 24 to 186 $\mu\text{g/L}$ during low tide and 78 to 124 $\mu\text{g/L}$ during high tide. Total concentrations in Ílhavo channel during low tide ranged from 100 to 680 $\mu\text{g/L}$ and 162 to 280 $\mu\text{g/L}$ during high tide, while dissolved concentrations ranged from 57 to 220 $\mu\text{g/L}$ during low tide and 124 to 180 $\mu\text{g/L}$ during high tide. Total concentration levels averaged at 19 $\mu\text{g/L}$ and 33 $\mu\text{g/L}$ during low and high tide in Mira, while averaging at 40 $\mu\text{g/L}$ and 37 $\mu\text{g/L}$, during low and high tide in Ílhavo. Dissolved fraction concentration levels averaged at 15 $\mu\text{g/L}$ and 28 $\mu\text{g/L}$ during low and high tide in Mira and 40 $\mu\text{g/L}$ and 35 $\mu\text{g/L}$, during low and high tide, in Ílhavo.

3.5.4 Copper

Figure 24 represents the concentration of Cu in Mira and Ílhavo channel during the high and low tide.

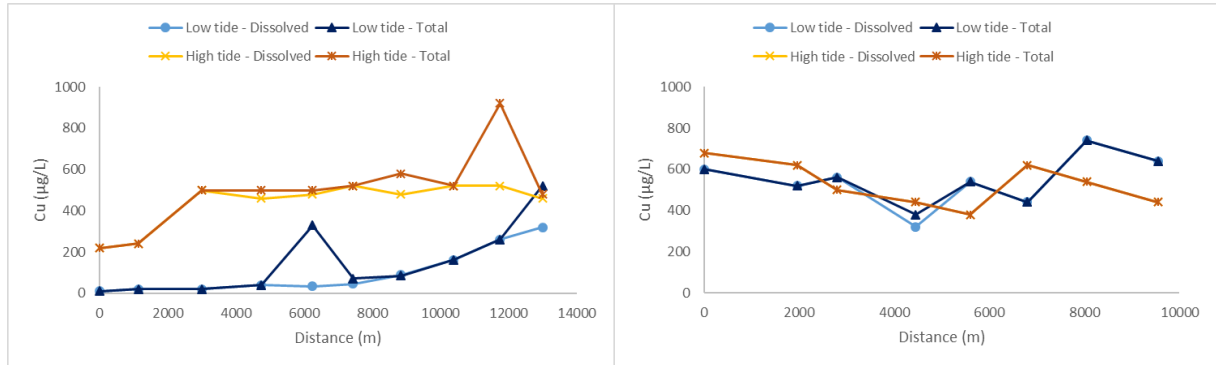


Figure 24: Copper total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

Results show that for Mira channel, concentration levels increased along the channel during low tide, having been observed two peaks of concentration in M-5 and M-10; during high tide, Cu levels initially rise in the first two stations, M-1 and M-2, however after M-3, concentration levels appear to stabilize, apart from another peak in concentration being observable in station M-9. For Ílhavo, Cu levels appear to decrease from I-1 to I-4 during both tides, oscillating around the same levels afterwards.

Total copper levels ranged from during 11 to 520 $\mu\text{g/L}$, averaging at 152 $\mu\text{g/L}$ during low tide and 220 to 920 $\mu\text{g/L}$, averaging 498 $\mu\text{g/L}$ during high tide in Mira. For Ílhavo channel, levels ranged from 380 to 740 $\mu\text{g/L}$ and averaged at 553 $\mu\text{g/L}$ during low tide and 380 to 680 $\mu\text{g/L}$, while averaging at 528, during high tide.

The lowest dissolved to particulate fraction ratios were in stations: M-5, during low tide, with 10% of the content in dissolved fraction; and I-4, during low tide, with 84% in dissolved fraction.

3.5.5 Zinc

Figure 25 represents the concentration of zinc in Mira and Ílhavo channel during the high and low tides.

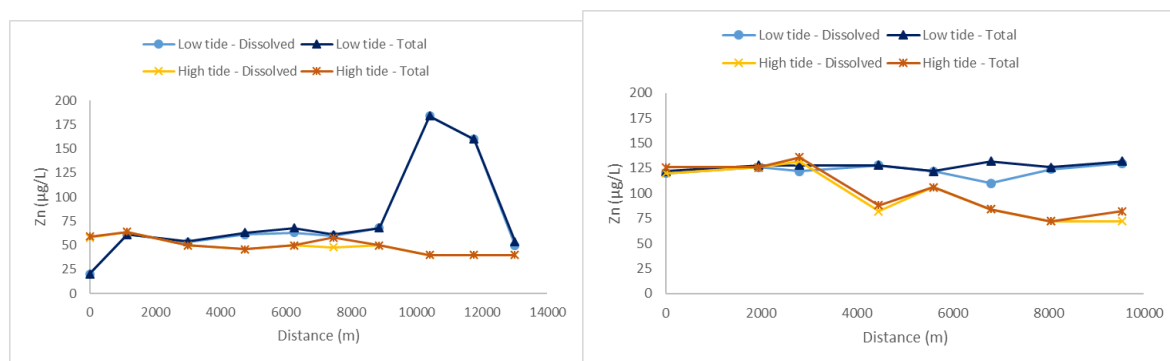


Figure 25: Zinc total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Samples obtained from Mira channel show that, from stations M-1 to M-7, zinc levels stayed mostly constant during both tidal phases, remaining constant in the following stations during high tide, however, during low tide, in stations M-8 and M-9, concentrations increased to higher levels before returning to previous concentrations levels in station M-10. In Ílhavo channel, zinc was present in higher levels during both tidal phases. During low tide, zinc levels remained constant. During high tide after station I-3, zinc levels started to decrease, continuing until station I-8.

In both channels, zinc content was mostly present in the dissolved fraction, with the lowest dissolved fraction levels reaching 93% and 83% of the total zinc content, in Mira and Ílhavo channels.

Total concentration levels for Mira channel ranged from 20 to 184 µg/L, averaging at 79 µg/L, during low tide, while ranging from 40 to 64 µg/L and averaging at 50 µg/L during high tide; total concentration levels for Ílhavo channel ranged from 122 to 132 µg/L, averaging at 127 µg/L, during low tide, and ranging from 72 to 136 µg/L, while averaging at 103 µg/L during high tide. Dissolved fraction concentration levels in Mira ranged from 20 to 184 µg/L and 40 to 64 µg/L, during low and high tide, respectively, while averaging at 78 µg/L and 49 µg/L, during low and high tide; in Ílhavo, dissolved fraction concentration

levels ranged from 120 to 130 $\mu\text{g/L}$ and 72 to 132 $\mu\text{g/L}$ during low and high tide, while averaging at 123 $\mu\text{g/L}$ during low tide and 99 $\mu\text{g/L}$ during high tide.

3.5.6 Arsenic

Figure 26 represents the concentration of arsenic in Mira and Ílhavo channel during the high and low tides.

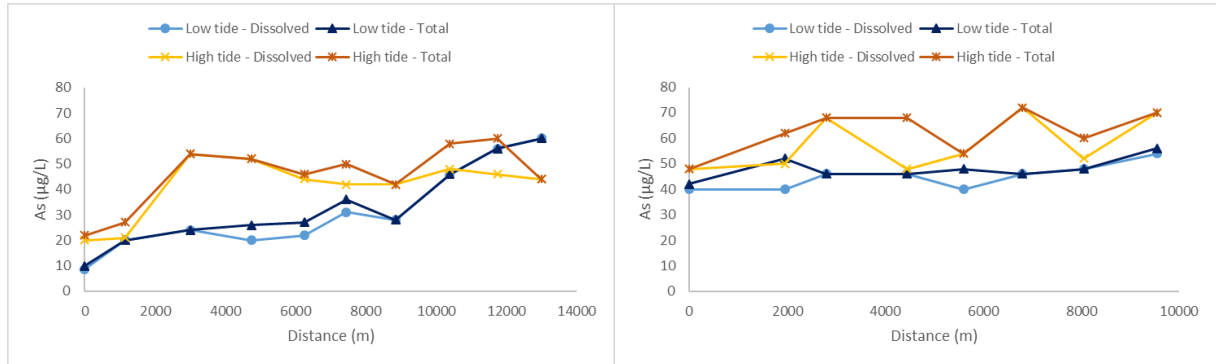


Figure 26: Arsenic total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Arsenic levels increased along the Mira channel during low tide. During high tide arsenic levels initially increased, however, after M-3, these levels remained mostly constant. In Ílhavo channel Arsenic levels appeared to oscillate slightly during high tide, but otherwise also remained constant throughout the channel, especially during low tide. Separation between dissolved and total arsenic content is observable, more in Ílhavo channel, where differences are more apparent.

In Mira channel, total concentration levels ranged from 10 to 60 $\mu\text{g/L}$, averaging at 33 $\mu\text{g/L}$, during low tide and 22 to 60 $\mu\text{g/L}$, averaging at 46 $\mu\text{g/L}$, during high tide. Dissolved fraction concentrations ranged from 9 to 60 $\mu\text{g/L}$, averaging at 32 $\mu\text{g/L}$, during low tide and 20 to 54 $\mu\text{g/L}$, averaging at 41 $\mu\text{g/L}$, during high tide.

In Ílhavo, total concentration levels ranged from 42 to 56 $\mu\text{g/L}$ and averaged at 48 $\mu\text{g/L}$ during low tide and ranged from 48 to 72 $\mu\text{g/L}$, while averaging at 63 $\mu\text{g/L}$, during high tide; dissolved fraction concentrations ranged from 40 to 54 $\mu\text{g/L}$ during low tide and 48 to 72 $\mu\text{g/L}$ during high tide, averaging at 45 $\mu\text{g/L}$ and 58 $\mu\text{g/L}$ during low and high tide.

3.5.7 Strontium

Figure 27 represents the concentration of strontium in Mira and Ílhavo channel during the high and low tides.

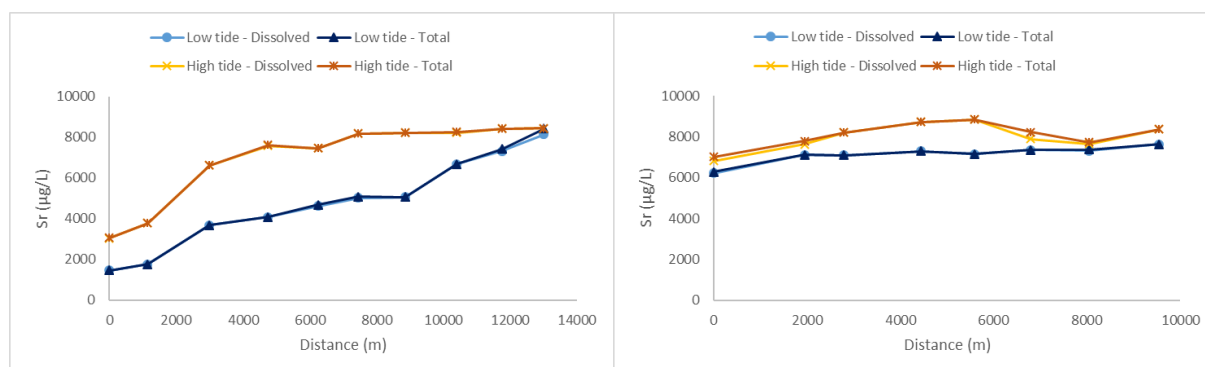


Figure 27: Strontium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Strontium concentrations steadily increase from station M-1 through station M-10 in Mira channel, during both tidal phases, with concentration levels in low tide lower than high tide until station M-10; Ílhavo channel results display constant concentrations during low tide and high tide, with a slight increase in concentration between station I-1 and I-2, during both tidal phases. There are no apparent differences between dissolved fraction strontium and total strontium content.

Total strontium concentrations in Mira ranged from 1.46 to 8.42 mg/L in low tide and 3.07 to 8.44 mg/L in high tide, averaging at 4.84 mg/L and 7.01 mg/L during low and high tide ;dissolved fraction concentrations in Mira ranged from 1.46 to 8.14 mg/L during low tide and 3.05 to 8.44 mg/L during high tide, averaging at 4.79 mg/L and 6.99 mg/L, respectively . In Ílhavo, total concentration levels ranged from 6.28 to 7.64 mg/L and averaged at 7.17 mg/L during low tide, while ranging from 7.02 to 8.86 mg/L and averaging at 8.13 mg/L during high tide; dissolved fraction levels ranged from 6.22 to 7.64 mg/L in low tide and 6.82 to 8.86 mg/L in high tide, averaging at 7.15 mg/L and 8.03 mg/L during low and high tide.

3.5.8 Barium

Figure 28 represents the concentration of barium in Mira and Ílhavo channel during the high and low tides.

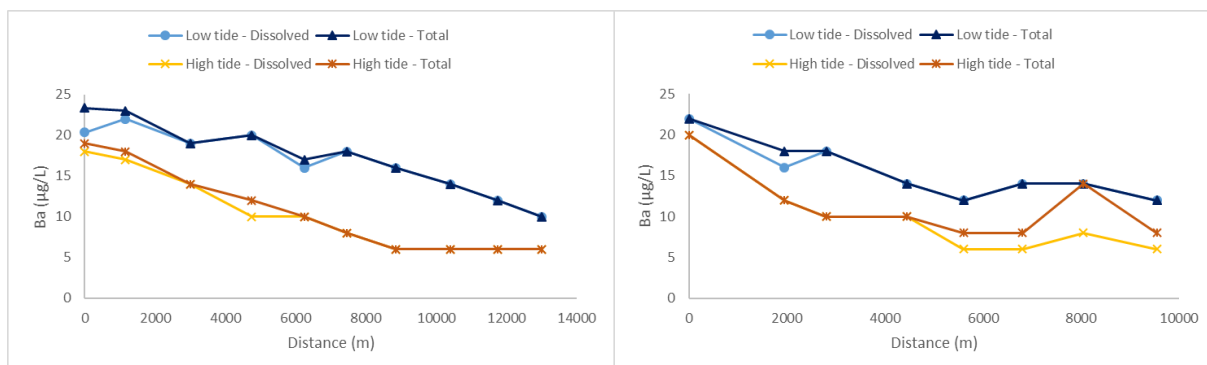


Figure 28: Barium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

Barium concentrations steadily decrease from station M-1 to station M-10 in Mira channel, during both tidal phases; Ílhavo channel also displays a decrease of barium concentrations during low tide and high tide. Some separation between dissolved and total content can be observed in both channels, with differences being low in Mira channel, while slightly more apparent in Ílhavo channel, after station I-4 and until station I-8, during high tide. Concentrations were higher during low tide in both channels.

In Mira channel, total barium concentrations ranged from 10 to 23 $\mu\text{g/L}$, averaging at 17 $\mu\text{g/L}$, in low tide, while ranging from 6 to 19 $\mu\text{g/L}$ and averaging at 11 $\mu\text{g/L}$, in high tide; dissolved fraction concentrations ranged from 10 to 22 $\mu\text{g/L}$ and averaged at 17 $\mu\text{g/L}$ during low tide, while ranging from 6 to 18 $\mu\text{g/L}$ and averaging at 10 $\mu\text{g/L}$ during high tide. In Ílhavo, total concentration levels ranged from 12 to 22 $\mu\text{g/L}$ during low tide and 8 to 20 $\mu\text{g/L}$ during high tide, averaging at 16 $\mu\text{g/L}$ and 11 $\mu\text{g/L}$ during low and high tide; dissolved fraction levels ranged from 12 to 22 $\mu\text{g/L}$ in low tide and 6 to 20 $\mu\text{g/L}$ in high tide and averaged at 15 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$ during low and high tide.

3.5.9 Uranium

Figure 29 represents the concentration of uranium in Mira and Ílhavo channel during the high and low tides.

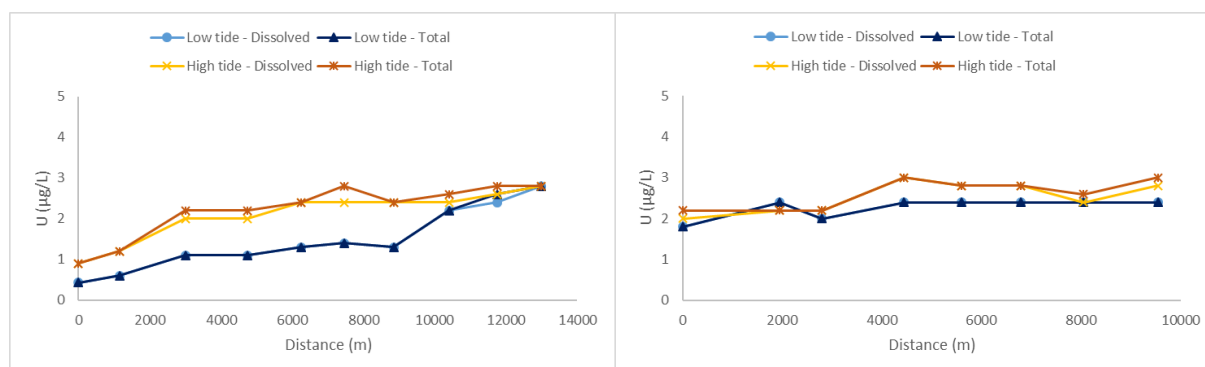


Figure 29: Uranium total and dissolved concentrations during low and high tide for Mira (left) and Ílhavo (right) channels

In Mira channel, uranium levels increase slightly from station M-1 to station M-10 in Mira channel, during both tidal phases; Ílhavo channel results display constant concentrations during low tide and high tide, with only a slight oscillation during both tidal phases. There are differences between dissolved fraction strontium and total strontium content in both channels, this difference is however relatively low, with dissolved fraction values never reaching lower than 85% of the total uranium content.

Total uranium concentrations in Mira ranged from 0.43 to 2.80 µg/L in low tide and 0.90 to 2.80 µg/L in high tide, averaging at 1.48 µg/L and 2.23 µg/L, during low and high tide; dissolved fraction concentrations ranged from 0.43 to 2.80 µg/L during low tide and 0.90 to 2.80 µg/L during high tide, averaging at 1.46 µg/L and 2.11 µg/L, during low and high tide, respectively. In Ílhavo, total concentration levels ranged from 1.80 to 2.40 µg/L, averaging at 2.28 µg/L, during low tide, and ranged from 2.20 to 3.00 µg/L, averaging at 2.60 µg/L during high tide; dissolved fraction levels ranged from 1.80 to 2.40 mg/L and averaged at 2.28 µg/L in low tide, while ranging from 2.00 to 3.00 µg/L and averaging at 2.53 µg/L in high tide.

4 Discussion

4.1 Longitudinal patterns of physico-chemistry in Mira and Ílhavo channels

4.1.1 Salinity and conductivity

As it is expected, salinity was shown to be highly dependent on the distance of the sampling station to the source of seawater, the Barra channel. This was more evident in the Mira channel, wherein the farthest a sampling station was from the initial sampling location, the closer it was to seawater, showing an almost linear relation between distance and salinity. This was observable either during low tide or high tide. While this is also observable in Ílhavo channel, the differences in salinity between the initial station and the last station, which are close to 9 km apart, are rather small in comparison with the Mira channel, where the distance between the initial and last station is close to 13 km; this is probably due to the previously mentioned lower flow of fresh water originating from the Ílhavo tributaries, and possibly due to the larger distance between the initial and final sampling stations in the case of the Mira channel.

One other interesting point to note is that during low tide in Mira, salinity increases more linearly than during high tide, which may be due to the influence of the fresh water from its tributaries and the salty water coming in from the sea, closer to the last sampling station. As a greater impact can be observed during high tide, this is probably due to a much higher volume of salty water clashing with a much smaller volume of fresh water originating from the tributaries, as higher salinities travel more upstream during high tide. The same cannot be said about the Ílhavo channel.

Salinity and conductivity are directly related. Since salinity results are reflected in the conductivity results, which is to be expected, anything mentioned about salinity was therefore also observed for conductivity.

4.1.2 Temperature

Over the length of both channels, the temperature varied almost linearly. An increase in temperatures was observed during low tide and a decrease during high tide, this however did not seem to relate to distances between both channel's sampling stations and the Barra channel. The temperature variations observed in both channels appear to reflect the time of day that sampling was undertaken. During low tide, sampling was initiated early in the morning (9h40m and 10h20m for Mira and Ílhavo), as such, the water that was previously flowing through the channels during the night was now being heated by exposure to the increasingly more incident morning sun; as sampling was underway during this time and due to the differences in the sampling time from station to station, the observed increase in water temperature varies in a way consistent with time. During high tide, the opposite can be observed in both channels, with sun exposure decreasing during high tide (sampling started at 16h15m and 16h55m for Mira and Ílhavo, respectively) leading to a reduction of temperatures along the channels. However, during high tide, the last few sampling stations (I-6 to I-8) in Ílhavo display a slight upwards curve, which may be due to an increase in proximity to larger volumes of water in the central region of the Ria de Aveiro, a region which may take longer periods of time to demonstrate losses in temperature.

4.1.3 Dissolved oxygen content

Dissolved oxygen content percentage and pattern differed greatly between channels. Dissolved oxygen content in Ílhavo reflected almost no changes between tides and stations, except a small increase in percentage throughout the whole channel during high tide, reflecting the low influence from its low tributary flow and increase in oxygen production with sun exposure. In Mira channel, however, oxygen levels appear to be much less consistent. During low tide in Mira, the initial rapid increase in O₂ percentage slows down after the first stations, contrasting with the rapid decrease in percentage in the same stations during high tide. This rapid loss and increase in oxygen content can be attributed to sun exposure, smaller water volume and proximity to agricultural activity and housing (Gabinete de Qualidade de Vida, 1993), as the initial stations are located in a narrower, more upstream part of the channel; the initial low sun exposure results in low oxygen production from phytoplankton activity in the first sampled stations. Also, the lower volume of water in these stations intensifies the impact of effluents, which can originate steep differences in oxygen

content in such small volumes of water in the early morning. However, during high tide, the now oxygen saturated water originated from the most upstream regions, clashes with the salty, now more homogenized, water from the downstream regions closer to the Barra channel.

4.1.4 pH

The pH levels in Ílhavo during low tide reflect the behavior of pH levels in high tide, albeit, at a lower level throughout the channel. In Mira, pH levels differ greatly between low tide and high tide. However, while pH levels increase during low tide and decrease during high tide, both tides tend display the same pH levels, the closer a station is to the Barra channel, as observed from stations M-7 to M-10. The decrease in pH during high tide in Mira may have occurred due to high photosynthetic activity upstream from station M-1 increasing the pH levels, which when mixing with higher salinity water would decrease as observed.

4.1.5 Suspended particulate matter

Suspended particulate matter concentrations were generally higher in Ílhavo than in Mira that demonstrated a lower variation of SPM concentrations, oscillating irregularly between stations. In Ílhavo channel, during high tide, SPM concentrations mostly decreased downstream from the initial stations, which may be due to an increase in the water column height, with the proximity to Barra channel; during low tide, SPM concentrations increased in the stations closer to the end of the Ílhavo channel, once again due to water height, which in this case was lower, promoting the resuspension of particulate matter due to the flowing water surface water being closer to bottom of the channel.

The characteristic maximum turbidity zone that most estuaries exhibit was not observable in none of the sampled channels.

4.2 Mercury partitioning and influence of water physico-chemistry

In this study, Hg was analysed in the dissolved and suspended particulate fraction during both tidal phases, and the relationship between the two fractions and the various water physicochemical parameters was tested. The coefficients of determination r^2 of the linear regression between each Hg fraction and each one of the water parameters studied, namely salinity, conductivity, temperature, pH, dissolved oxygen content and SPM are listed in Table 8, for the Mira and Ílhavo channels during both tidal phases.

Table 8: Table of values for the coefficients of determination (R^2) of dissolved Hg and particulate Hg with the measured physico-chemical parameters for both channels and tidal phases. Green coloured cells are R^2 's higher than 0.7

r^2	Tidal phase	Dissolved Fraction Hg						Particulate Fraction Hg					
		Salin	Cond	pH	SPM	T (°C)	O ₂	Salin	Cond	pH	SPM	T (°C)	O ₂
Mira	Low	0.122	0.118	0.103	0.111	0.108	0.265	0.077	0.091	0.081	0.086	0.059	0.136
	High	0.241	0.237	0.025	0.066	0.507	0.032	0.226	0.220	0.039	0.093	0.205	0.017
Ílhavo	Low	0.796	0.799	0.357	0.298	0.609	0.366	0.086	0.076	0.177	0.078	0.167	0.107
	High	0.001	0.001	0.000	0.060	0.146	0.244	0.002	0.001	0.021	0.137	0.048	0.023

Globally, both dissolved and particulate Hg concentrations showed weak relations with the physicochemical parameters measured in the water, although salinity and conductivity explained 79.6 and 79.9% of the variance observed in Hg for low tide in Ílhavo.

In Mira channel, for the dissolved fraction, mercury concentrations were low, through most of the channel during low and high tides. However, after station M-8, concentrations during high tide rose significantly with Hg levels in M-9 and M-10, being several times higher than those recorded in the previous stations. This rapid increase during high tide may be related to punctual discharges, since these stations were directly located next to high traffic wharfs, which may be a source of this contaminant. In Ílhavo, dissolved mercury levels were similar and low during low tide, with only the first station, I-1, displaying a high level of mercury. During high tide, concentration levels were all-around higher than during low tide. This difference in concentrations in Ílhavo may possibly be due to interstitial water present in previously non-submerged areas of the channel (during low tide), which are submerged while in high tide, due to a higher water column height and larger width of the channel during this tidal phase; this possibility has been observed in other studies (Pereira et al., 1998, Kim et al., 2004).

In regards to particulate matter, Hg concentration levels in Mira during low tide and high tide were similar despite the peak observed during low tide in station M-1, and the slightly variations in M-2, M-7, M-8 and M-10 that demonstrates that particulate mercury during low tide is much more variable. In Ílhavo, during low tide, concentrations were linear in every station, in contrast, during high tide, particulate mercury in the water column was much more variable. The higher concentrations observed in Ílhavo during high tide, for stations I-2, I-5 may be explained by possible discharges due to proximity to residential areas, while concentrations in I-7 may be explained by a discharge from an inland pond that was observed to be discharging during sampling.

Partitioning during mixing in estuarine systems is more complex than the chemical parameters of the water found therein (Turner, 2001). For the purpose of this part of the study, total mercury content was defined as the concentration of mercury present in dissolved form in conjunction with the mercury in the particulate form, which contained mercury associated to metal precipitates, adsorbed to suspended sediment captured during sampling or adsorbed to and absorbed into particulate organic matter and dissolved metals. The percentage of mercury present in dissolved fraction in the water column, along both channels and tidal phases was calculated from this total mercury. Figure 30 displays the percentage of Hg in the dissolved fraction of the water samples from Mira and Ílhavo channels, during both tidal conditions.

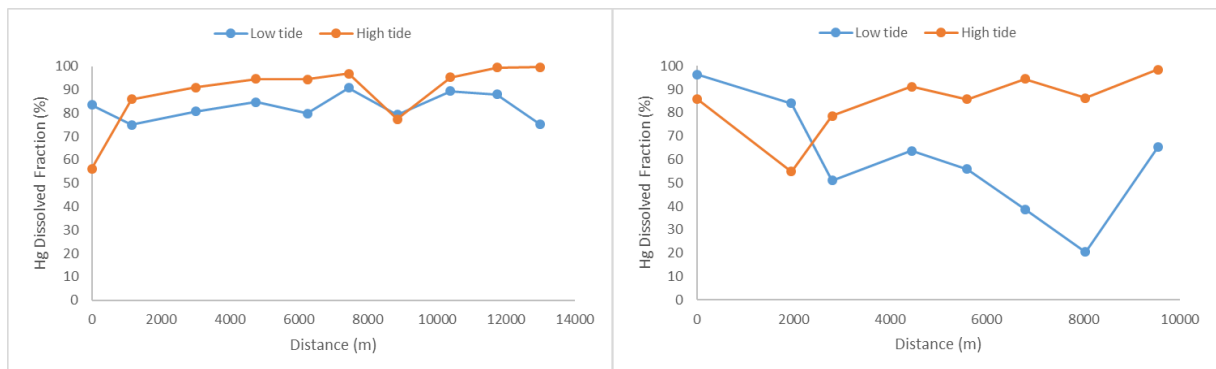


Figure 30: Dissolved Hg percentage in the total Hg concentrations during low and high tide for Mira (left) and Ílhavo (right) channels.

It is possible to observe that in the Mira channel, most of the mercury content is present in the dissolved fraction in both tidal phases, with dissolved fraction Hg percentages ranging from 75% to 91 % and an average of 83% of the total Hg during low tide and ranging

from 56% to close to 100%, with an average of 89% during high tide. In Ílhavo channel, the mercury content is more separated, with the dissolved fraction of Hg reaching values below 50% during low tide, while maintaining high percentages during high tide. Dissolved fraction Hg percentages in Ílhavo ranged from 21 to 96%, averaging at 59%, during low tide, while ranging from 55 to 99% and an average of 84% during high tide. The higher percentages of dissolved mercury in high tide may be due to chloro complexes formation.

The higher percentage of dissolved mercury in Mira may be attributed to the lower levels of SPM found in this channel, which were close to half of the SPM values found in Ílhavo. During high tide most of the mercury content in Ílhavo was in the dissolved form, decreasing during low tide, where higher levels of SPM were recorded.

4.3 Influence of water physico-chemistry on the partitioning of studied elements

For the purpose of this study, for all elements other than mercury, total content refers to the total concentration of an element present in the water sample. Therefore, by subtracting the dissolved fraction from the total content, it is possible to obtain the element particulate fraction. All elements were tested in order to ascertain their proportion of variance with the various physico-chemical parameters. These proportions of variance can be defined as a coefficients of determination R^2 . A value of $R^2 > 0.900$ will be considered as an indicator of a relation between an element and a physico-chemical parameter.

4.3.1 Magnesium, Potassium, Calcium, Lithium, Boron, Strontium

Magnesium, potassium, calcium, lithium, boron and strontium visibly followed the same trend as salinity in both channels, demonstrating to be closely related to this parameter, which can be observed in their respective R^2 for salinity (Table 9).

Table 9: Table of values for the coefficients of determination (R^2) of Mg, K, Ca, Li, B and Sr with measured physico-chemical parameters for both channels and tidal phases. Colour gradients relate to R^2 's higher than 0.7, 0.8 and 0.9

R^2	Tidal	Mg						K					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	1.000	0.999	0.843	0.774	0.700	0.717	0.999	0.998	0.844	0.773	0.695	0.717
	High	0.997	0.998	0.830	0.021	0.840	0.801	0.998	0.999	0.816	0.019	0.847	0.786
Ílhavo	Low	0.958	0.955	0.666	0.380	0.748	0.631	0.970	0.968	0.677	0.404	0.763	0.647
	High	0.631	0.633	0.325	0.148	0.500	0.220	0.681	0.685	0.342	0.147	0.489	0.148
R^2	Tidal	Ca						Li					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	0.990	0.985	0.797	0.751	0.644	0.724	0.996	0.997	0.854	0.782	0.719	0.752
	High	0.989	0.991	0.856	0.028	0.815	0.828	0.996	0.996	0.819	0.028	0.833	0.787
Ílhavo	Low	0.927	0.925	0.556	0.340	0.644	0.508	0.917	0.907	0.603	0.333	0.718	0.550
	High	0.588	0.588	0.222	0.045	0.327	0.074	0.638	0.639	0.278	0.092	0.458	0.187
R^2	Tidal	B						Sr					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	0.998	0.999	0.848	0.782	0.710	0.744	0.997	0.998	0.861	0.774	0.718	0.716
	High	0.996	0.997	0.827	0.024	0.842	0.800	0.994	0.995	0.848	0.022	0.826	0.819
Ílhavo	Low	0.958	0.956	0.670	0.388	0.740	0.638	0.916	0.910	0.512	0.300	0.648	0.449
	High	0.639	0.641	0.284	0.110	0.488	0.175	0.613	0.612	0.298	0.113	0.451	0.204

The six elements displayed values of $R^2 > 0.900$ for salinity, during low tide in Ílhavo and during both tidal phases in Mira. This affinity to salinity is an indicator that the increase in concentration from these elements is due to close proximity to a source of seawater as concentrations were shown to also be highly dependent on the distance of the sampling station to the Barra channel. Seawater is also reportedly high on concentration levels for these elements, so an increase in the concentrations of these elements during high tide is also

related, as during this tidal phase, the volume of seawater flowing through the channels is several times higher; during high tide in Ílhavo, the dependence on salinity was less observed, with $R^2 < 0.900$.

A slightly lower affinity can also be observed in the variation of pH in the water, with R^2 values being higher than 0.800 for the six elements in Mira channel, during both tidal phases, which once again may be indicative of following the trend of increasing proportions of seawater over fresh water, as seawater is also reported to usually have higher pH levels than fresh water. The same is not observed in Ílhavo, with concentrations remaining constant and similar between tides, which is probably due to the higher proportions of seawater in the channel, observable by the constantly higher salinity.

4.3.2 Copper, Iron, Zinc, Nickel and Aluminium,

Copper, iron, zinc, nickel and aluminium did not display a strong relation with any of the physico-chemical parameters, observed in Table 10.

Table 10: Table of values for the coefficients of determination (R^2) of Cu, Fe, Zn, Ni and Al with measured physico-chemical parameters for both channels and tidal phases. Colour gradients relate to R^2 's higher than 0.7, 0.8 and 0.9

R^2	Tidal phase	Cu						Fe					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	0.602	0.591	0.421	0.527	0.376	0.303	0.466	0.452	0.457	0.382	0.382	0.397
	High	0.622	0.620	0.465	0.033	0.631	0.470	0.300	0.308	0.499	0.406	0.256	0.574
Ílhavo	Low	0.010	0.005	0.170	0.000	0.167	0.092	0.575	0.596	0.240	0.454	0.292	0.290
	High	0.459	0.455	0.316	0.111	0.284	0.282	0.253	0.259	0.384	0.285	0.094	0.208
R^2	Tidal phase	Zn						Ni					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	0.358	0.360	0.263	0.304	0.164	0.614	0.766	0.760	0.569	0.690	0.504	0.576
	High	0.601	0.599	0.283	0.001	0.702	0.310	0.556	0.551	0.318	0.013	0.686	0.328
Ílhavo	Low	0.277	0.097	0.121	0.086	0.069	0.273	0.487	0.465	0.718	0.158	0.691	0.569
	High	0.495	0.514	0.708	0.794	0.612	0.303	0.037	0.040	0.120	0.239	0.033	0.023
R^2	Tidal phase	Al											
		Salin	Cond	pH	SPM	T°C	O ₂						
Mira	Low	0.018	0.014	0.020	0.004	0.031	0.041						
	High	0.314	0.309	0.138	0.085	0.478	0.140						
Ílhavo	Low	0.507	0.501	0.732	0.448	0.734	0.707						
	High	0.261	0.268	0.190	0.057	0.027	0.018						

All R^2 values were lower than 0.900 or 0.800. These elements appeared in mostly linear concentrations during high tide along both channels; during low tide, the same linearity can be observed, interrupted by punctual peaks in concentration in specific elements, which may be consistent with effluent discharges or increases in suspended particulate matter.

Aluminium and iron concentration results are listed in Annex III-D and Annex III-G. For these elements, a linearity was observed mainly during high tide in both channels. However, punctual peaks in total concentration can be observed, especially for aluminium during low tide in both channels, which is due to an increase in the particulate concentration of these elements. Concentrations in Mira were mostly higher for these two elements during high tide, however, in Ílhavo, aluminium and iron concentrations were higher during low tide, this is due to the lower pH levels that occurred during this tidal phase in Ílhavo. During high tide in Ílhavo, the mean percentage of aluminium in dissolved fraction was 56% for Mira and 70% for Ílhavo, and the mean percentage of iron in dissolved fraction was 67% for Mira and 78% for Ílhavo. During low tide, the mean percentage of aluminium and iron in dissolved fractions for Mira was 62% and 47%; for Ílhavo the percentages of dissolved fraction for aluminium and iron were 43% and 74%. As such, a clear separation between total and dissolved concentrations occurred during high and low tides, which translates into a significant amount of these elements being present in the suspended particulate fraction on the water column, albeit with different variations between channels, for each element, which means that these variations may either be related to pH variations or rather due to anthropological contamination.

Nickel and copper concentration results are listed in Annex IV-D and Annex IV-E. Regarding partitioning, these elements were mostly present in the dissolved fraction in both channels. In Mira, total concentration levels of copper and nickel rose while moving downstream during low tide, due to proximity to seawater, with higher levels of dissolved copper and nickel; during high tide, concentrations are initially low due to the higher pH levels, which may have facilitated precipitation; however, levels quickly stabilize after station M-3. The remaining peaks in concentration of copper and nickel in this channel may be due to particulate matter discharges at the location of M-7 and M-9 during high tide, since dissolved copper content in these stations was 83% and 57% of the total content and dissolved nickel content was 70% and 52%; while in M-5 and M-10 during low tide it may have been due to resuspended sediment during sample collection, with dissolved copper content representing only 10% and 62% of the total content and dissolved nickel 40% and 63%. In Ílhavo, both elements presented similar behavior, although copper appeared to decrease initially in both tidal phases which may indicate a higher copper content originating

upstream from station I-1. The similarity in behavior for both elements in I-5 and I-7 during low tide and I-6 during high tide may indicate once again anthropogenic contamination.

Zinc concentration levels were determined to be almost completely in dissolved form, and concentrations were mostly linear through most of the Mira channel, with baseline concentrations remaining in similar amounts during both tidal phases. Only stations M-1, M-8 and M-9, during low tide, demonstrated concentrations which differed considerably from the remaining stations. Stations M-8 and M-9 were situated on wharfs; the paint coating of the boats located in such places may be zinc based, which may explain the increase in occurrence of this element in these stations, since the total content of this element at these locations was determined to be completely in dissolved form.

In a previous study carried out in several locations of Ria de Aveiro (Monterroso, 2004), the variability of copper, iron and zinc was measured in various locations of the estuary. Dissolved copper, iron and zinc concentrations ranges observed in that study were mostly lower than the ranges obtained in this current study. This difference between studies may represent an increase anthropogenic contamination of the estuarine system. Studies have shown that the concentrations of copper, nickel and zinc in dissolved form in water tend to decrease as salinity increases (Kraepiel et al., 1997). This is designated as a conservative behavior, which can happen due to an increase in pH when fresh water mixes with seawater, facilitating the precipitation of humic and hydroxide compounds, which in turn removes the contaminants from the particulate fraction (Romankevick and Ljutsarev, 1990). However, previous studies in Ria de Aveiro have shown that this decrease in the concentration of dissolved metals with an increase in salinity does not always happen in this estuarine system (Monterroso, 2004). This same contradiction has been observed in the current study, in some cases, which may be indicative of anthropogenic sources.

4.3.3 Titanium, Cobalt and Arsenic

Titanium, cobalt and arsenic demonstrated higher concentration levels during high tide in both channels. In Mira channel, these elements demonstrated a strong relation with salinity, with R^2 values close to 0.900 in both tides (Table 11), except for arsenic during high tide.

Table 11: Table of values for the coefficients of determination (R^2) of Ti, Co and As with measured physico-chemical parameters for both channels and tidal phases. Colour gradients relate to R^2 's higher than 0.7, 0.8 and 0.9

R^2	Tidal phase	Ti						Co					
		Salin	Cond	pH	SPM	T ^o C	O ₂	Salin	Cond	pH	SPM	T ^o C	O ₂
Mira	Low	0.925	0.920	0.733	0.698	0.596	0.749	0.905	0.891	0.728	0.637	0.598	0.637
	High	0.827	0.828	0.712	0.036	0.591	0.649	0.882	0.883	0.850	0.007	0.672	0.792
Ílhavo	Low	0.562	0.553	0.354	0.104	0.323	0.232	0.299	0.290	0.677	0.331	0.622	0.633
	High	0.194	0.207	0.088	0.068	0.130	0.000	0.000	0.001	0.145	0.321	0.004	0.025
R^2	Tidal phase	As											
		Salin	Cond	pH	SPM	T ^o C	O ₂						
Mira	Low	0.941	0.931	0.704	0.612	0.558	0.630						
	High	0.686	0.690	0.642	0.087	0.524	0.637						
Ílhavo	Low	0.338	0.317	0.108	0.003	0.196	0.028						
	High	0.450	0.452	0.255	0.079	0.133	0.000						

The results demonstrate that these elements are in higher concentrations in the seawater originating from the Barra channel in comparison to levels present in the Mira channel. Separation between total and dissolved fraction was more significant for arsenic, however, differences were low between them. In Ílhavo, titanium and cobalt concentrations appeared very much linear, with punctual peaks or decreases and fraction separation was minimal. Titanium had slightly higher concentration during high tide, most probably due to increased intrusions of seawater amounts during this tide, while cobalt concentration levels remained unchanged between tides, with only a peak of concentration in I-7 during low tide, probably due to particulate matter captured during sample collection, as dissolved concentration remained close to the remaining stations. Arsenic in Ílhavo differed slightly from the other two elements, where it remained constant during low tide, but during high tide, concentrations almost doubled.

4.3.4 Manganese, Barium, Uranium

Manganese and barium both appeared to be originating in higher concentrations upstream from the starting stations in both channels, M-1 and I-1, as concentrations continuously decrease downstream until reaching the farthest stations, closer to the Barra channel. Also, concentrations were higher in all stations during low tide in both channels and for both elements, which can also confirm the source of these elements, since during high tide a higher amount of seawater will dilute the concentrations of these elements. Both elements also displayed a relation of variation to salinity. In relation to salinity, manganese displayed values of $R^2 > 0.900$ for both tidal phases in Ílhavo and for high tide in Mira while displaying $R^2 > 0.800$ for low tide in Mira. Barium displayed $R^2 > 0.900$ for both tides in Mira and $R^2 > 0.800$ for Ílhavo during low tide (Table 12).

Table 12: Table of values for the coefficients of determination (R^2) of Mn, Ba and U with measured physico-chemical parameters for both channels and tidal phases. Colour gradients relate to R^2 's higher than 0.7, 0.8 and 0.9

R^2	Tidal phase	Mn						Ba					
		Salin	Cond	pH	SPM	T°C	O ₂	Salin	Cond	pH	SPM	T°C	O ₂
Mira	Low	0.866	0.868	0.674	0.740	0.461	0.598	0.974	0.972	0.819	0.868	0.661	0.643
	High	0.958	0.961	0.803	0.062	0.831	0.805	0.934	0.931	0.636	0.000	0.885	0.609
Ílhavo	Low	0.958	0.962	0.571	0.414	0.767	0.567	0.867	0.881	0.568	0.397	0.629	0.576
	High	0.995	0.993	0.775	0.435	0.669	0.464	0.716	0.713	0.407	0.162	0.374	0.140
R^2	Tidal phase	U											
		Salin	Cond	pH	SPM	T°C	O ₂						
Mira	Low	0.974	0.965	0.718	0.722	0.562	0.657						
	High	0.954	0.955	0.770	0.068	0.800	0.740						
Ílhavo	Low	0.701	0.708	0.385	0.264	0.452	0.316						
	High	0.565	0.586	0.608	0.616	0.629	0.163						

Separation in dissolved and particulate fractions was observed in every station of both channels during both tides, while in the case of barium, separation was observed only punctually. Uranium was also found, however, with concentrations increasing downstream from the first station, I-1, until the last station in Mira, with higher concentrations measured during high tide. Uranium concentrations in Ílhavo were mostly constant, with no significant differences between tides. Almost no separation between fractions was observed, with most content present in the dissolved fraction. The presence of uranium in these channels may be mostly due to seawater, since concentrations increase with higher levels of salinity in both channels, however, less observable in Ílhavo due to lower salinity variation between tidal cycles.

5 Conclusion

The present study produced a collection of results for measurements of physico-chemical parameters, mercury content and content of several other major, minor and trace elements, from the water column of two different but closely related channels, located in the Ria de Aveiro estuary. With these results it was possible to determine the longitudinal variation of the physico-chemical parameters in the water along the two channels, as well as the determination of the content and partitioning of mercury and the other elements, during two distinct tidal conditions.

Both channels demonstrated different characteristics, differing in the behavior of various parameters, response to tidal variations and element distributions. Ílhavo demonstrated to vary much less between tidal phases and distance to the Barra channel. Apart from the amount of suspended particulate matter, which oscillated due to conditions found at the time of sampling, the longitudinal variation of physico-chemical parameters in the Ílhavo channel was observed to be lesser than the Mira channel, with most parameters close to flatlining from beginning to end of the channel in both tidal conditions, demonstrating a resemblance to conditions found in bodies of water closer to seawater sources, such as the Barra channel. Mira channel demonstrated a stronger tendency for the physico-chemical parameters to vary with distance to the Barra channel, as well as demonstrating a stronger variation of the parameters in response to tidal changes.

Regarding mercury content, it did not display affinity to any of the measured physico-chemical parameter. Most of the mercury was found to be present on the dissolved fraction, averaging at 83% and 89% in Mira, during low tide and high tide, respectively, while averaging at 59% and 89% in Ílhavo, during low and high tide, respectively. Dissolved mercury concentrations along the Mira channel were always measured below 20 ng/L, with the exception of the closest locations to the Barra channel, where concentrations were found to reach concentrations up to 9 times higher than the remaining channel locations. In Ílhavo, the first station, farther away from the Barra channel displayed higher dissolved mercury concentrations during low tide, however, for the remaining stations and tidal phase, concentrations remained comparably similar to Mira, however less constant along the channel, while still displaying concentrations comparable with the Mira channel, with a

mean of 24.3 during low tide and 32.8 during high tide. Regarding particulate mercury content, concentrations were found to be higher during low tide in Mira, while the opposite was observed in Ílhavo, with higher concentrations observed during high tide. Higher concentrations in the particulate fraction were observed to be punctual, possibly due to anthropogenic contamination; further studies are needed to determine the source. Mercury concentrations exceeded maximum allowed concentration levels established for inland surface waters ($0.07 \mu\text{g/L}$) (2008/105/EC) in the two last stations of Mira channel, closer to the Barra channel.

It was determined that salinity was the most influential water parameter in the tidal and longitudinal variation of magnesium, calcium, potassium, lithium, boron, strontium and barium. An increase in salinity resulted in an increase of the aforementioned elements, except barium, which concentrations decreased in response to an increase in salinity. The variation of these elements was due to seawater intrusion in the channels, with the effects intensifying with proximity to the seawater, especially during high tide.

Aluminium, iron, nickel, copper and zinc did not display a significant relation to any of the measured parameters between channels and tidal phases. Aluminium and iron occurred with significant separation between dissolved and particulate fraction, with total concentrations measured to be almost linear throughout both channels, with a slightly higher concentration present in Mira during high tide, and Ílhavo during low tide. Nickel, copper and zinc were present mostly in the dissolved fraction, with nickel and copper increasing downstream from the initial stations in both channels and zinc displaying linear concentrations along Mira.

Titanium, cobalt, arsenic, manganese and Uranium also showed affinity to salinity variations in the Mira channel, however, only manganese displayed this affinity both in Mira and Ílhavo. Titanium, cobalt and arsenic increased with proximity to the Barra channel in Mira, while concentrations remained more or less constant during both tides in Ílhavo, due to less salinity variability between stations in this channel. Manganese displayed a decrease in both tides, with proximity to the Barra channel, while also displaying a clear separation between dissolved and particulate fraction along both channels and tidal phases. Uranium increased in Mira, with proximity to the Barra channel in both tides, indicating an input of

this contaminant, probably from seawater, higher during high tide; in Ílhavo, tidal variations were less observed and concentrations were mostly linear.

A recommendation for future studies would be the study of organic matter content and the determination of elements aggregated to it, so as to better study the partitioning of different elements, especially mercury.

6 References

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-Annex I-

Tables of values for physico-chemical measurements in Mira and Ílhavo
channels

Annex I-A: Physico-chemical parameters measured from the water in situ, during the low and high tides at the Mira channel

Mira	Distance	Salinity		Conductivity		Temperature		Dissolved O ₂		pH		SPM	
		Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide
Stn (nº)	(m)	(PSU)	(PSU)	mS/cm	mS/cm	(°C)	(°C)	(%)	(%)	-	-	(mg/L)	(mg/L)
M-1	0	4.7	11.1	8.4	18.8	17.1	20.7	46.7	129.0	7.4	8.4	7.4	21.5
M-2	1150	6.1	13.9	10.8	23.2	17.6	19.9	68.0	108.0	7.5	8.3	7.7	7.3
M-3	3000	13.9	25.4	23.2	40.1	18.0	19.0	76.0	86.0	7.6	8.1	14.4	10.4
M-4	4750	14.6	29.9	24.2	46.3	18.1	18.6	90.9	83.8	7.7	8.0	10.2	8.8
M-5	6250	16.9	30.0	27.8	46.7	18.3	18.8	92.0	85.7	7.7	8.1	15.8	5.8
M-6	7450	18.4	32.8	29.9	50.5	18.5	18.6	84.0	85.2	7.8	8.0	10.9	8.4
M-7	8850	18.2	33.8	29.7	52.0	18.5	17.7	85.0	77.0	7.9	8.0	16.7	24.9
M-8	10400	25.3	34.2	39.9	52.6	18.7	17.8	116.0	88.0	7.9	8.1	16.8	17.7
M-9	11750	28.8	35.2	45.1	53.9	18.1	17.1	101.0	87.0	7.8	8.1	18.3	7.8
M-10	13000	32.0	35.2	49.4	54.0	18.9	17.0	97.1	89.3	8.0	8.1	18.7	9.3
Mean	---	17.9	28.2	28.8	43.8	18.2	18.5	85.7	91.9	7.7	8.1	13.7	12.2

Annex I-B: Physico-chemical parameters measured from the water in situ, during the low and high tides at the Ílhavo channel

Ílhavo	Distance	Salinity		Conductivity		Temperature		Dissolved O ₂		pH		SPM	
		Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide	Low Tide	High Tide
Stn (nº)	(m)	(PSU)	(PSU)	mS/cm	mS/cm	(°C)	(°C)	(%)	(%)	-	-	(mg/L)	(mg/L)
I-1	0	26.4	29.0	41.7	45.3	17.0	18.6	51.8	68.0	7.3	7.7	19.6	27.5
I-2	1950	29.6	32.0	46.1	49.5	17.4	18.5	51.0	69.7	7.4	7.8	23.1	33.6
I-3	2800	30.0	33.4	46.7	51.3	17.6	18.1	56.7	71.5	7.4	7.9	28.7	31.0
I-4	4450	31.0	34.3	48.2	52.8	17.6	17.3	60.0	71.6	7.5	8.0	25.0	21.9
I-5	5600	31.4	34.6	48.8	53.1	17.8	17.1	62.0	76.0	7.5	8.1	37.2	16.1
I-6	6800	31.6	34.9	49.1	53.6	17.7	17.0	65.0	72.3	7.6	8.2	49.5	10.2
I-7	8050	32.5	34.8	50.1	53.4	18.3	17.2	71.0	77.0	7.8	8.2	39.2	11.1
I-8	9550	32.5	35.1	50.1	53.9	17.9	17.7	63.0	71.0	7.6	8.3	30.9	9.5
Mean	---	30.6	33.5	47.6	51.6	17.7	17.7	60.1	72.1	7.5	8.0	31.6	20.1

-Annex II-

Tables of values for dissolved fraction Hg, particulate fraction Hg and total Hg in samples from Mira and Ílhavo channels

Annex II-A: Dissolved mercury and particulate mercury fractions concentrations during low and high tide determined from samples collected in the Mira channel

Mira	Distance	Dissolved Hg		Particulate Hg		Total Hg			
						Dissolved %		Particulate %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(ng/L)	(ng/L)	(µg/g)	(µg/g)	(%)	(%)	(%)	(%)
M-1	0	14.2	5.42	0.38	0.20	83	56	17	44
M-2	1150	12.0	5.47	0.52	0.27	75	86	25	14
M-3	3000	15.3	13.2	0.26	0.25	81	91	19	9.0
M-4	4750	9.91	13.8	0.18	0.20	85	95	15	5.4
M-5	6250	11.5	7.48	0.18	0.23	80	94	20	5.6
M-6	7450	11.0	19.9	0.18	0.19	91	97	9.2	3.1
M-7	8850	11.9	11.5	0.28	0.20	79	77	21	23
M-8	10400	37.5	33.1	0.33	0.16	89	95	11	4.7
M-9	11750	13.6	136	0.15	0.24	88	99	12	0.53
M-10	13000	15.9	179	0.42	0.13	75	100	25	0.28
Mean	---	15.3	42.5	0.29	0.21	83	89	17	11

Annex II-B: Dissolved mercury and particulate mercury fractions concentrations during low and high tide determined from samples collected in the Ílhavo channel

Ílhavo	Distance	Dissolved Hg		Particulate Hg		Total Hg			
						Dissolved %		Particulate %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(ng/L)	(ng/L)	(µg/g)	(µg/g)	(%)	(%)	(%)	(%)
I-1	0	116	27.0	0.22	0.12	96	86	3.5	14
I-2	1950	25.9	40.7	0.21	0.75	84	55	16	45
I-3	2800	6.87	38.0	0.23	0.33	51	79	49	21
I-4	4450	7.64	43.2	0.17	0.24	64	91	36	8.9
I-5	5600	14.1	23.2	0.22	0.36	56	86	44	14
I-6	6800	10.2	17.0	0.24	0.22	39	94	61	5.6
I-7	8050	2.89	17.8	0.17	0.44	21	86	79	14
I-8	9550	11.4	55.4	0.20	0.24	65	99	35	1.5
Mean	---	24.3	32.8	0.21	0.34	59	84	41	16

-Annex III-

Tables of values for the total content and dissolved fraction concentrations of major elements: Mg, K, Ca, Al, Ti, Mn, Fe,

Annex III-A: Total Mg concentrations, dissolved fraction Mg concentrations and percentages of dissolved Mg in total Mg content, for Mira and Ílhavo channels.

Mg	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	175666	413500	175666	417200	100	99
M-2	1150	228300	523000	228300	523000	100	100
M-3	3000	508700	975400	508700	975400	100	100
M-4	4750	547900	1132200	547900	1132200	100	100
M-5	6250	626200	1115600	629400	1115600	99	100
M-6	7450	682200	1236800	685100	1236800	100	100
M-7	8850	677200	1242200	677200	1242200	100	100
M-8	10400	939200	1256400	939200	1256400	100	100
M-9	11750	1047400	1262200	1047400	1286400	100	98
M-10	13000	1031800	1292600	1182400	1292600	87	100
Mean	---	646457	1044990	662127	1047780	99	100

Mg	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	970800	1078000	986000	1114200	98	97
I-2	1950	1097600	1244400	1097600	1254800	100	99
I-3	2800	1113200	1306000	1130000	1306000	99	100
I-4	4450	1175800	1417600	1175800	1417600	100	100
I-5	5600	1146600	1446000	1146600	1446000	100	100
I-6	6800	1187000	1282800	1187000	1342000	100	96
I-7	8050	1182800	1205200	1203400	1244800	98	97
I-8	9550	1235600	1355800	1235600	1355800	100	100
Mean	---	1138675	1291975	1145250	1310150	99	99

Annex III-B: Total K concentrations, dissolved fraction K concentrations and percentages of dissolved K in total K content, for Mira and Ílhavo and Ílhavo channels.

K	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	55833	138500	55833	140500	100	99
M-2	1150	72380	173900	72380	174300	100	100
M-3	3000	159500	318800	159500	318800	100	100
M-4	4750	174900	369400	174900	372800	100	99
M-5	6250	199600	365400	202900	369400	98	99
M-6	7450	219200	410400	221500	410400	99	100
M-7	8850	221800	411800	221800	411800	100	100
M-8	10400	308000	419400	308000	419400	100	100
M-9	11750	343200	424400	343200	425000	100	100
M-10	13000	335200	433800	385400	433800	87	100
Mean	---	208961	346580	214541	347620	98	100

K	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	328400	364000	332000	380400	99	96
I-2	1950	370000	419200	370000	422000	100	99
I-3	2800	375000	438000	380800	438800	98	100
I-4	4450	396000	470000	396000	470000	100	100
I-5	5600	389000	458800	389000	458800	100	100
I-6	6800	399600	430400	401000	452000	100	95
I-7	8050	403400	406200	406400	418400	99	97
I-8	9550	415000	447200	416000	450600	100	99
Mean	---	384550	429225	386400	436375	100	98

Annex III-C: Total Ca concentrations, dissolved fraction Ca concentrations and percentages of dissolved Ca in total Ca content, for Mira and Ílhavo channels.

Ca	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	111100	207000	111100	211200	100	98
M-2	1150	127000	243600	127000	251300	100	97
M-3	3000	213300	390400	213300	390400	100	100
M-4	4750	235300	420800	235300	424200	100	99
M-5	6250	260200	418000	260200	420800	100	99
M-6	7450	267900	460200	272400	460200	98	100
M-7	8850	273800	453000	273800	453000	100	100
M-8	10400	408000	462800	408000	462800	100	100
M-9	11750	433600	465000	433600	469400	100	99
M-10	13000	449600	417500	476400	462600	94	90
Mean	---	277980	393830	281110	400590	99	98

Ca	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	356800	392800	363800	407400	98	96
I-2	1950	404600	446400	404600	449600	100	99
I-3	2800	400400	465800	405800	468800	99	99
I-4	4450	422000	443400	422000	489600	100	91
I-5	5600	412200	450100	412200	464000	100	97
I-6	6800	425400	450200	426000	467800	100	96
I-7	8050	421200	429800	423800	441200	99	97
I-8	9550	440000	422400	440000	465200	100	91
Mean	---	410325	437613	412275	456700	99	96

Annex III-D: Total Al concentrations, dissolved fraction Al concentrations and percentages of dissolved Al in total Al content, for Mira and Ílhavo channels.

Al	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	24	78	32	170	75	46
M-2	1150	160	84	450	130	36	65
M-3	3000	50	106	62	186	81	57
M-4	4750	71	104	74	168	96	62
M-5	6250	70	114	170	150	41	76
M-6	7450	52	118	97	166	54	71
M-7	8850	50	124	130	260	38	48
M-8	10400	186	110	240	220	78	50
M-9	11750	132	100	152	320	87	31
M-10	13000	100	110	300	196	33	56
Mean	---	90	105	171	197	62	56

Al	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	57	128	100	280	43	46
I-2	1950	122	142	280	162	44	88
I-3	2800	130	142	260	240	50	59
I-4	4450	152	140	320	220	48	64
I-5	5600	172	180	320	240	54	75
I-6	6800	138	170	420	200	33	85
I-7	8050	220	156	680	198	32	79
I-8	9550	194	124	260	180	75	69
Mean	---	148	148	330	215	47	70

Annex III-E: Total Ti concentrations, dissolved fraction Ti concentrations and percentages of dissolved Ti in total Ti content, for Mira and Ílhavo channels.

Ti	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	13	20	13	30	100	67
M-2	1150	20	30	20	40	100	75
M-3	3000	30	60	30	60	100	100
M-4	4750	30	60	30	60	100	100
M-5	6250	40	80	50	80	80	100
M-6	7450	40	100	50	100	80	100
M-7	8850	40	80	40	80	100	100
M-8	10400	80	80	80	80	100	100
M-9	11750	80	80	80	80	100	100
M-10	13000	60	60	80	80	75	75
Mean	---	43	65	47	69	94	92

Ti	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	40	60	60	80	67	75
I-2	1950	80	80	80	100	100	80
I-3	2800	60	80	60	80	100	100
I-4	4450	80	100	80	100	100	100
I-5	5600	60	100	80	100	75	100
I-6	6800	80	100	80	100	100	100
I-7	8050	80	80	80	80	100	100
I-8	9550	100	80	100	100	100	80
Mean	---	73	85	78	93	93	92

Annex III-F: Total Mn concentrations, dissolved fraction Mn concentrations and percentages of dissolved Mn in total Mn content, for Mira and Ílhavo channels.

Mn	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	26	13	50	64	51	20
M-2	1150	34	18	62	51	55	35
M-3	3000	23	14	47	30	49	47
M-4	4750	19	15	41	26	46	59
M-5	6250	14	16	38	24	37	66
M-6	7450	17	15	41	22	41	68
M-7	8850	12	13	36	24	33	54
M-8	10400	15	13	30	17	49	76
M-9	11750	14	11	20	20	72	56
M-10	13000	10	13	26	14	38	89
Mean	---	18	14	39	29	47	57

Mn	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	74	38	98	68	76	56
I-2	1950	38	20	58	40	66	50
I-3	2800	28	16	52	28	54	56
I-4	4450	28	15	44	22	64	68
I-5	5600	24	14	42	18	57	75
I-6	6800	22	16	42	18	52	91
I-7	8050	36	16	36	20	100	84
I-8	9550	24	12	38	15	63	84
Mean	---	34	18	51	29	66	70

Annex III-G: Total Fe concentrations, dissolved fraction Fe concentrations and percentages of dissolved Fe in total Fe content, for Mira and Ílhavo channels.

Fe	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	47	180	290	1230	16	15
M-2	1150	100	190	420	460	24	41
M-3	3000	130	400	300	520	43	77
M-4	4750	140	380	300	500	47	76
M-5	6250	140	380	380	480	37	79
M-6	7450	180	420	350	540	51	78
M-7	8850	170	420	400	640	43	66
M-8	10400	300	400	460	560	65	71
M-9	11750	280	400	420	560	67	71
M-10	13000	200	520	480	560	42	93
Mean	---	169	369	380	605	43	67

Fe	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	420	500	440	800	95	63
I-2	1950	480	540	720	640	67	84
I-3	2800	480	560	740	800	65	70
I-4	4450	560	580	840	760	67	76
I-5	5600	540	600	720	700	75	86
I-6	6800	480	540	940	700	51	77
I-7	8050	640	468	740	600	86	78
I-8	9550	620	560	740	620	84	90
Mean	---	528	544	735	703	74	78

-Annex IV-

Tables of values for the total content and dissolved fraction concentrations of Li, B, Co, Ni, Cu, Zn, As, Sr, Ba and U

Annex IV-A: Total Li concentrations, dissolved fraction Li concentrations and percentages of dissolved Li in total Li content, for Mira and Ílhavo channels.

Li	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	27	55	27	55	100	100
M-2	1150	33	68	34	68	97	100
M-3	3000	72	120	72	120	100	100
M-4	4750	75	142	75	142	100	100
M-5	6250	88	140	88	140	100	100
M-6	7450	95	156	95	156	100	100
M-7	8850	92	152	92	152	100	100
M-8	10400	126	156	130	156	97	100
M-9	11750	138	162	138	162	100	100
M-10	13000	140	160	152	160	92	100
Mean	---	89	131	90	131	99	100

Li	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	120	132	122	132	98	100
I-2	1950	136	148	136	152	100	97
I-3	2800	138	158	140	158	99	100
I-4	4450	142	172	142	172	100	100
I-5	5600	138	168	138	168	100	100
I-6	6800	144	156	144	160	100	98
I-7	8050	142	150	146	150	97	100
I-8	9550	150	160	150	160	100	100
Mean	---	139	156	140	157	99	99

Annex IV-B: Total B concentrations, dissolved fraction B concentrations and percentages of dissolved B in total B content, for Mira and Ílhavo channels.

B	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	660	1430	660	1460	100	98
M-2	1150	890	1810	890	1810	100	100
M-3	3000	1880	3340	1880	3340	100	100
M-4	4750	1980	3820	1980	3820	100	100
M-5	6250	2250	3760	2260	3760	100	100
M-6	7450	2430	4140	2440	4140	100	100
M-7	8850	2390	4140	2390	4140	100	100
M-8	10400	3320	4220	3320	4220	100	100
M-9	11750	3620	4240	3640	4340	99	98
M-10	13000	3720	4360	4000	4360	93	100
Mean	---	2314	3526	2346	3539	99	100

B	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	3240	3560	3320	3700	98	96
I-2	1950	3660	4140	3660	4160	100	100
I-3	2800	3720	4300	3760	4300	99	100
I-4	4450	3920	4640	3920	4640	100	100
I-5	5600	3840	4560	3840	4560	100	100
I-6	6800	3940	4220	3960	4420	99	95
I-7	8050	3920	4020	4000	4100	98	98
I-8	9550	4120	4360	4120	4360	100	100
Mean	---	3795	4225	3823	4280	99	99

Annex IV-C: Total Co concentrations, dissolved fraction Co concentrations and percentages of dissolved Co in total Co content, for Mira and Ílhavo channels.

Co	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	0.40	1.10	0.53	1.30	75	85
M-2	1150	1.00	1.40	1.00	1.40	100	100
M-3	3000	1.00	2.60	1.00	2.60	100	100
M-4	4750	1.00	2.80	1.00	3.00	100	93
M-5	6250	1.00	2.80	1.10	2.80	91	100
M-6	7450	1.30	3.40	1.30	3.40	100	100
M-7	8850	1.10	3.20	1.30	3.40	85	94
M-8	10400	2.00	2.80	2.00	2.80	100	100
M-9	11750	2.00	2.80	2.00	2.80	100	100
M-10	13000	2.20	2.80	2.40	3.40	92	82
Mean	---	1.30	2.57	1.36	2.69	94	95

Co	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	2.40	2.80	2.60	2.80	92	100
I-2	1950	2.60	3.20	2.80	3.20	93	100
I-3	2800	2.60	2.60	2.80	3.20	93	81
I-4	4450	2.80	2.80	2.80	3.00	100	93
I-5	5600	2.80	3.00	3.00	3.00	93	100
I-6	6800	3.20	2.40	3.20	3.00	100	80
I-7	8050	2.60	3.00	4.40	3.00	59	100
I-8	9550	2.60	2.40	2.80	2.60	93	92
Mean	---	2.70	2.78	3.05	2.98	90	93

Annex IV-D: Total Ni concentrations, dissolved fraction Ni concentrations and percentages of dissolved Ni in total Ni content, for Mira and Ílhavo channels.

Ni	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	4	15	4	15	100	100
M-2	1150	10	15	10	18	100	83
M-3	3000	11	28	11	28	100	100
M-4	4750	11	28	11	28	100	100
M-5	6250	12	30	30	30	40	100
M-6	7450	12	32	14	32	86	100
M-7	8850	14	28	14	40	100	70
M-8	10400	20	36	26	36	77	100
M-9	11750	30	34	30	66	100	52
M-10	13000	24	36	38	36	63	100
Mean	---	15	28	19	33	87	90

Ni	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	30	30	30	36	100	83
I-2	1950	32	36	32	36	100	100
I-3	2800	30	32	30	34	100	94
I-4	4450	32	32	32	32	100	100
I-5	5600	46	32	46	32	100	100
I-6	6800	34	46	34	46	100	100
I-7	8050	60	30	60	36	100	83
I-8	9550	56	40	56	40	100	100
Mean	---	40	35	40	37	100	95

Annex IV-E: Total Cu concentrations, dissolved fraction Cu concentrations and percentages of dissolved Cu in total Cu content, for Mira and Ílhavo channels.

Cu	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	11	220	11	220	100	100
M-2	1150	20	240	20	240	100	100
M-3	3000	20	500	20	500	100	100
M-4	4750	39	460	39	500	100	92
M-5	6250	34	480	330	500	10	96
M-6	7450	46	520	71	520	65	100
M-7	8850	89	480	85	580	105	83
M-8	10400	162	520	162	520	100	100
M-9	11750	260	520	260	920	100	57
M-10	13000	320	460	520	480	62	96
Mean	---	100	440	152	498	84	92

Cu	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	600	680	600	680	100	100
I-2	1950	520	620	520	620	100	100
I-3	2800	560	500	560	500	100	100
I-4	4450	320	440	380	440	84	100
I-5	5600	540	380	540	380	100	100
I-6	6800	440	620	440	620	100	100
I-7	8050	740	540	740	540	100	100
I-8	9550	640	440	640	440	100	100
Mean	---	545	528	553	528	98	100

Annex IV-F: Total Zn concentrations, dissolved fraction Zn concentrations and percentages of dissolved Zn in total Zn content, for Mira and Ílhavo channels.

Zn	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	20	58	20	59	100	98
M-2	1150	61	64	61	64	100	100
M-3	3000	53	50	54	50	98	100
M-4	4750	61	46	63	46	97	100
M-5	6250	63	50	68	50	93	100
M-6	7450	60	48	61	58	98	83
M-7	8850	68	50	68	50	100	100
M-8	10400	184	40	184	40	100	100
M-9	11750	160	40	160	40	100	100
M-10	13000	50	40	54	40	93	100
Mean	---	78	49	79	50	98	98

Zn	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	120	120	122	126	98	95
I-2	1950	126	126	128	126	98	100
I-3	2800	122	132	128	136	95	97
I-4	4450	128	82	128	88	100	93
I-5	5600	122	106	122	106	100	100
I-6	6800	110	84	132	84	83	100
I-7	8050	124	72	126	72	98	100
I-8	9550	130	72	132	82	98	88
Mean	---	123	99	127	103	97	97

Annex IV-G: Total As concentrations, dissolved fraction As concentrations and percentages of dissolved As in total As content, for Mira and Ílhavo channels.

As	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	9	20	10	22	87	91
M-2	1150	20	21	20	27	100	78
M-3	3000	24	54	24	54	100	100
M-4	4750	20	52	26	52	77	100
M-5	6250	22	44	27	46	81	96
M-6	7450	31	42	36	50	86	84
M-7	8850	28	42	28	42	100	100
M-8	10400	46	48	46	58	100	83
M-9	11750	56	46	56	60	100	77
M-10	13000	60	44	60	44	100	100
Mean	---	32	41	33	46	93	91

As	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	40	48	42	48	95	100
I-2	1950	40	50	52	62	77	81
I-3	2800	46	68	46	68	100	100
I-4	4450	46	48	46	68	100	71
I-5	5600	40	54	48	54	83	100
I-6	6800	46	72	46	72	100	100
I-7	8050	48	52	48	60	100	87
I-8	9550	54	70	56	70	96	100
Mean	---	45	58	48	63	94	92

Annex IV-H: Total Sr concentrations, dissolved fraction Sr concentrations and percentages of dissolved Sr in total Sr content, for Mira and Ílhavo channels.

Sr	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	1460	3050	1460	3070	100	99
M-2	1150	1760	3780	1760	3780	100	100
M-3	3000	3690	6620	3690	6620	100	100
M-4	4750	4090	7580	4090	7620	100	99
M-5	6250	4620	7460	4680	7460	99	100
M-6	7450	5030	8180	5090	8180	99	100
M-7	8850	5070	8220	5070	8220	100	100
M-8	10400	6680	8220	6680	8260	100	100
M-9	11750	7320	8420	7420	8420	99	100
M-10	13000	8140	8440	8420	8440	97	100
Mean	---	4786	6997	4836	7007	99	100

Sr	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	6220	6820	6280	7020	99	97
I-2	1950	7120	7640	7120	7800	100	98
I-3	2800	7100	8220	7100	8220	100	100
I-4	4450	7300	8740	7300	8740	100	100
I-5	5600	7160	8860	7160	8860	100	100
I-6	6800	7360	7900	7360	8240	100	96
I-7	8050	7320	7660	7380	7740	99	99
I-8	9550	7640	8380	7640	8380	100	100
Mean	---	7153	8028	7168	8125	100	99

Annex IV-I: Total Ba concentrations, dissolved fraction Ba concentrations and percentages of dissolved Ba in total Ba content, for Mira and Ílhavo channels.

Ba	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	20	18	23	19	87	95
M-2	1150	22	17	23	18	96	94
M-3	3000	19	14	19	14	100	100
M-4	4750	20	10	20	12	100	83
M-5	6250	16	10	17	10	94	100
M-6	7450	18	8	18	8	100	100
M-7	8850	16	6	16	6	100	100
M-8	10400	14	6	14	6	100	100
M-9	11750	12	6	12	6	100	100
M-10	13000	10	6	10	6	100	100
Mean	---	17	10	17	11	98	97

Ba	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	22	20	22	20	100	100
I-2	1950	16	12	18	12	89	100
I-3	2800	18	10	18	10	100	100
I-4	4450	14	10	14	10	100	100
I-5	5600	12	6	12	8	100	75
I-6	6800	14	6	14	8	100	75
I-7	8050	14	8	14	14	100	57
I-8	9550	12	6	12	8	100	75
Mean	---	15	10	16	11	99	85

Annex IV-J: Total U concentrations, dissolved fraction U concentrations and percentages of dissolved U in total U content, for Mira and Ílhavo channels.

U	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
M-1	0	0.43	0.90	0.43	0.90	100	100
M-2	1150	0.60	1.20	0.60	1.20	100	100
M-3	3000	1.10	2.00	1.10	2.20	100	91
M-4	4750	1.10	2.00	1.10	2.20	100	91
M-5	6250	1.30	2.40	1.30	2.40	100	100
M-6	7450	1.40	2.40	1.40	2.80	100	86
M-7	8850	1.30	2.40	1.30	2.40	100	100
M-8	10400	2.20	2.40	2.20	2.60	100	92
M-9	11750	2.40	2.60	2.60	2.80	92	93
M-10	13000	2.80	2.80	2.80	2.80	100	100
Mean	---	1.46	2.11	1.48	2.23	99	95

U	Distance	Dissolved		Total		Dissolved %	
		Low tide	High tide	Low tide	High tide	Low tide	High tide
Stn (nº)	(m)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(%)	(%)
I-1	0	1.80	2.00	1.80	2.20	100	91
I-2	1950	2.40	2.20	2.40	2.20	100	100
I-3	2800	2.00	2.20	2.00	2.20	100	100
I-4	4450	2.40	3.00	2.40	3.00	100	100
I-5	5600	2.40	2.80	2.40	2.80	100	100
I-6	6800	2.40	2.80	2.40	2.80	100	100
I-7	8050	2.40	2.40	2.40	2.60	100	92
I-8	9550	2.40	2.80	2.40	3.00	100	93
Mean	---	2.28	2.53	2.28	2.60	100	97