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**ANALYSIS OF TRACE METALS IN SEAWATERS SAMPLES FROM
A GALICIAN ESTUARY (RIA DE AROSA), SPAIN**

**ANÁLISIS DE METALES TRAZA EN MUESTRAS DE AGUA DE MAR
DE ESTUARIOS DE GALICIA (RÍA DE AROSA), ESPAÑA**

**ANÁLISE DE METAIS TRAZA EN MOSTRAS DE AUGO DE MAR DE
ESTUARIOS DE GALICIA (RÍA DE AROUSA), ESPAÑA**

Karyna Tsupa

Name of Academic Tutor (UDC): Dra. Soledad Muniategui
Lorenzo

Name of Academic Tutor (Foreigner University): Dra. Anastasiya
Volchek



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The work “**ANALYSIS OF TRACE METALS IN SEAWATERS SAMPLES FROM A GALICIAN ESTUARY (RIA DE AROSA), SPAIN**”, wich constitutes the Master's Thesis of student Ms. **KARYNA TSUPA** (Brest State Technical University, Republic of Belarus) was carried out at the Departament of Analytical Chemistry (Universidade da Coruña). This work was tutorized and supervised by Professor Dr. Soledad Muniategui Lorenzo as principal supervisor, with the collaboration of Dr. Carmen M^a Moscoso Pérez, Researcher of the Applied Analytical Chemistry Research Group at Universidade da Coruña.

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Prof. Dr. Soledad Muniategui Lorenzo

SUMMARY

Metals are natural constituents of the environment. Copper and zinc, for example, are oligoelements whose presence in small amounts in nature is essential for living organisms. Other metals, in contrast, do not have any known biological role, as is the case for mercury and cadmium.

At high concentrations trace metals can become toxic for living organisms and behave as conservative pollutants. Therefore, human beings located at the top of the trophic chain are especially sensitive to these contaminants due to bioaccumulation. This possibility provides a further reason for compiling the available information in the heavy metal field.

Metals enter the environment and oceans by two means:

- (1) natural processes (including erosion of orebearing rocks, wind-blown dust, volcanic activity and forest fires);
- (2) processes derived from human activities by means of atmospheric deposition, rivers, direct discharges or dumping.

For some metals, natural and anthropogenic inputs are of the same order (for example Hg and Cd), whereas for others (for example Pb) inputs due to human activities dwarf natural inputs. Human activity is mainly located in the fluvial watersheds and in the rias and estuarine margins. These areas are therefore important for the fate of contaminants due to coastal industrial activity and human settlement. The Galician Rias are sensitive to anthropogenic influence due to the socioeconomic importance generated in these areas by industry, aquaculture, portactivities, fishing, tourism, and recently designated natural parks.

The aim of this study is to investigate the trace metal composition in seawater from the Galician Ría de Arosa (NW Spain) and its compliance with water quality standards.

The Master's Thesis consists of seven chapters. The first one is an introduction devoted to seawater pollution and its effects on human health. In the second chapter, the objectives are described. Chapter 3 deals with the main sources of heavy metal pollution in marine environment. Chapters 4 and 5 are focused on the description of the experimental work and the result and discussion, respectively. Finally, the main conclusions and references are included in Chapters 5 and 6.

Keywords: heavy metal, marine pollution, Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

RESUMO

Os metais son constituíntes naturais do medio ambiente. Cobre e cinc, por exemplo, son oligoelements cuxa presenza en pequenas cantidades na natureza é esencial para os organismos vivos. Outros metais, en cambio, non teñen ningún papel biolóxico coñecido, como é o caso do mercurio e cadmio.

En altas concentracións, os metais traza poden chegar a ser tóxicos para os organismos vivos e comportarse como contaminantes. Polo tanto, os seres humanos situados na parte superior da cadea trófica son especialmente sensibles a estes contaminantes debido á bioaccumulacion. Por todo isto, o estudio dos metais pesados no medio ambiente é de gran interés.

Os metais introdúcense no medio ambiente e nos océanos por dous medios:

- (1) procesos naturais (incluíndo a erosión dos minerais das rochas, polvo arrastrado polo vento, actividade volcánica e incendios forestais);
- (2) os procesos derivados das actividades humanas por medio da deposición atmosférica, ríos, vertidos directos ou vertedeiros.

Para algúns metais, as fontes naturais e antropoxénicas son da mesma orde (por exemplo Hg e Cd), mentras que para outros (por exemplo Pb) os procesos debidos as actividades humanas son maiores que os debidos as fontes naturais. A actividade humana está principalmente localizada nas concas hidrográficas fluviales e nas rías e nos marxes dos estuarios. Estas áreas son, polo tanto, importantes para o destino dos contaminantes debido a actividade industrial na costa e o asentamento humano. As Rías son sensibles a influencia antropoxénica debido á importancia socioeconómica xerada nestas zonas por parte da industria, a acuicultura, as actividades portuarias, a pesca, o turismo, e, recentemente, os parques naturais.

O obxectivo deste estudio é investigar a composición de metais traza en auga de mar da Ría de Arousa galega (NW España) e o seu cumprimento cos estándares de calidade da auga. O traballo Fin de Máster inclúe sete capítulos. O primeiro é

unha introdución relacionada coa contaminación da auga de mar e os seus efectos na saúde humana. No segundo capítulo descríbense os obxectivos. No Capítulo 3 trátanse as principais fontes de contaminación de metais pesados no medio mariño. Os capítulos 4 e 5 céntranse na descrición do traballo experimental e os resultados e discusión, respectivamente. Finalmente, as conclusións principais e as referencias inclúense nos capítulos 6 e 7.

Palabras clave: metais pesados, contaminación mariña, Espectrometría de Masas con Plasma Acoplado Inductivamente (ICP-MS).

RESUMEN

Los metales son componentes naturales del medio ambiente. El cobre y el zinc, por ejemplo, son oligoelementos, cuya presencia en pequeñas cantidades en la naturaleza es esencial para los organismos vivos. A otros metales, en cambio, no se les conoce ningún papel biológico, como es el caso del mercurio y el cadmio.

A altas concentraciones, los metales traza pueden llegar a ser tóxicos para los organismos vivos y comportarse como contaminantes. Por lo tanto, los seres humanos que se encuentra en la parte superior de la cadena trófica, son especialmente sensibles a estos contaminantes debido a la bioacumulación. Por todo ello, el estudio de los metales pesados en el medio ambiente es de gran interés.

Los metales entran en el medio ambiente y los océanos a través de dos vías:

- (1) los procesos naturales (incluyendo la erosión de los minerales de las rocas, polvo arrastrado por el viento, la actividad volcánica y los incendios forestales);
- (2) los procesos derivados de las actividades humanas por medio de la deposición atmosférica, los ríos, los vertidos directos o vertederos.

Para algunos metales, las fuentes naturales y antropogénicas son del mismo orden (por ejemplo, Hg y Cd), mientras que para otros (por ejemplo Pb) los procesos debidos a las actividades humanas son mayores que los causados por fuentes naturales. La actividad humana está principalmente localizada en las cuencas fluviales y en las rías y en los márgenes de los estuarios. Estas áreas son importantes para el destino de los contaminantes debido a la actividad industrial costera y el asentamiento humano. Las Rías Gallegas son sensibles a la influencia antropogénica debido a la importancia socioeconómica generada en estas áreas por parte de la industria, la acuicultura, la actividad portuaria, la pesca, el turismo, y los parques naturales.

El objetivo de este estudio es investigar la composición de metales traza en agua de mar de la Ría de Arosa gallega (NW España) y su cumplimiento con los estándares de calidad del agua. El trabajo Fin de Máster incluye siete capítulos. El

primero es una introducción relacionada con la contaminación del agua de mar y sus efectos en la salud humana. En el segundo capítulo se describen los objetivos del trabajo. En el capítulo 3 se tratan las principales fuentes de contaminación de metales pesados en el medio marino. Los capítulos 4 y 5 se centran en la descripción del trabajo experimental y los resultados y discusión, respectivamente. Finalmente, las conclusiones principales y las referencias se incluyen en los capítulos 6 y 7.

Palabras clave: metales pesados, contaminación marina, Espectrometría de Masas con Plasma Acoplado Inductivamente (ICP-MS).

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CHAPTER 1. INTRODUCTION

Water pollution is defined as introduction by man, directly or indirectly, of substances or energy to the aquatic environment resulting in deleterious effects such as hazards to human health, hindrance of fish activities, impairment of water quality and reduction of climate amenities. Contamination also, caused when an input from human activities causes an increase of a substance in fresh or seawater, sediments and organisms above the natural background level for that area and for those organisms.¹ Industrial development in the developing and undeveloped countries has resulted in heavy metal (HM) contamination of local water. Metal pollution may damage aquatic organisms (either fresh or marine water) at the cellular levels and possibly affect ecological balance. Exposure and ingestion of polluted aquatic marine products such as seafood can cause health problems in human and animals including neurological and reproductive problems.²

Heavy metals (elements with an atomic density greater than 6 g/cm^3) are one of the most persistent pollutants in water. Unlike other pollutants, they are difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. Their presence in water is due to discharges from residential dwellings, groundwater infiltration and industrial discharges. The discharge of wastewater containing high concentrations of heavy metals to receiving water bodies has serious adverse environmental effects. Their occurrence and accumulation in the environment is a result of direct or indirect human activities, such as rapid industrialization, urbanization and anthropogenic sources.³

Heavy metals have been used in many different areas for thousands of years. Lead has been primarily used at least 5000 years ago in building materials, pigments for glazing ceramics and pipes for transporting water. In ancient Rome, lead acetate was used to sweeten old wine and some Romans might have consumed as much as gram of lead a day. Mercury was alleged to be used by the Roman as a

salve to alleviate infants teething pain and was later (13th-18th century) employed as remedy for syphilis. Adverse health effects of heavy metals have been known for a long time, due to continuous exposure to HM and working in the gold mines in many parts of Latin America. Arsenic is still a common constituent in wood preservatives and tetraethyl lead remains a common additive to petrol, although this use has decreased dramatically in the developed countries. Since the middle of the 19th century, production of heavy metals increased steeply for more than 100 years, with concomitant emission to the environment.⁴

Heavy metal pollution is a global issue, although severity and levels of pollution differs from place to place. At least 20 metals are classified as toxic with half of them emitted into environment in concentrations that pose great risks to human health. The common heavy metals that have been identified in polluted water include arsenic, copper, cadmium, lead, chromium, nickel mercury and zinc. The release of these metals without proper treatment poses a significant threat to public health because of their persistence, biomagnification and accumulation in food chain. Severe effects include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system.⁵

The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. For example, cadmium and zinc can lead to acute gastrointestinal and respiratory damages to brain, heart and kidney damages.

Seawater is under the risk of high pollution because of domestic wastewater, industrial wastewater, sea traffic, accident potential, port services and wastewater, bilge and ballast water disposals related to port services. Marine waters are identified as having the following beneficial uses: a habitat for marine organisms generally, recreational bathing beach.

Marine pollution is a global environmental problem; human activities in the coastal area and marine water contribute to the discharge of various kinds of pollutants such as heavy metals into the marine ecosystems.⁶ The main reason for the metal contamination is considered as persistent and due to their toxic properties, could create several problems for different kinds of marine ecosystems and could be accumulating in marine organisms.⁷ Many marine organisms have the potential to bioconcentrate high levels of metals from their environment.⁸

In recent years, contamination of sea water by heavy metals is becoming major problem for aquatic life and human health. The well known long term toxic effects of heavy metals lead (Pb) and nickel (Ni) are of both scientific and environmental concerns. The presence of these heavy metals in water, create a societal health risk that, which is useful for fisheries. Fish play an important role in human nutrition and therefore need to be carefully and routinely screened to ensure that there are no high levels of heavy metals being transferred to man through their consumption.⁹

The Galician Rias, comprising 25% of the Iberian Peninsula coastline, form a unique system within the European continental Atlantic coast and provide a useful reference area for studies of metals. These rias are sensitive to anthropogenic influence due to the socioeconomic importance generated in these areas by industry, aquaculture, port activities, fishing, tourism.

The Galician Rias are partially stratified estuaries with positive residual circulation with fresh and salt water mixing inside the basins. This behaviour has

direct consequences on metal fluxes whereby the rias behave as a barrier and accumulate metals in the sediments. Metals tend to deposit close to point sources and remobilization occurs inside the ria, leading to a seaward decrease in metal concentration. With the exception of the Ulla (Arosa Ria) and Eume (Ares-Betanzos Ria) head rivers and the Lagares river (Vigo Ria) the available data suggest that riverine freshwater inputs are not the main source of contamination.

Metal studies reported in the literature mainly relate to Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, and to a lesser extent Hg and Sn.¹⁰

In connection with the above, the aim of the study is to determine the content of heavy metals in the Ría de Arousa and localities with the highest concentration.

The Water Framework Directive 2000/60/EC of the European Parliament and of the Council lays down a strategy against the pollution of water. That strategy involves the identification of priority substances amongst those that pose a significant risk to, or via, the aquatic environment at European Union level. In addition, it establishes the concentration limits for a number of substances to be controlled under the Water Framework Directive. These provisions lay down some amendments to Directives 2000/60/EC, 2008/105/EC and 2013/39/EU as regards priority substances in the field of water policy. It is hereby established that the Commission shall review the adopted list of priority substances at least every six years. Heavy metals as cadmium, lead mercury and nickel and its compounds are included in the list of priority substances in Directive 2013/39/EU setting Environmental Quality Standards (EQS) for these compounds.

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CHAPTER 2. OBJECTIVE

Chemical pollution of surface water poses a threat to the aquatic environment, with effects such as acute and chronic toxicity in aquatic organisms, accumulation of pollutants in the ecosystem and loss of habitats and biodiversity, and also poses a threat to human health.

As a matter of priority, causes of pollution should be identified and emissions of pollutants should be dealt with at source, in the most economically and environmentally effective manner.

The presence of heavy metal in seawaters is a problem of increasing importance. Considerable quantities of heavy metals in seawater can be detected and in some coastal areas these pollutants reach threatening concentrations. In addition, some of these metals can be accumulated in the body of marine organisms and finally they come through the foodchain to the human beings.

The aim of this study is to investigate the distribution of trace metal in seawater from the Galician Ría de Arosa (NW Spain) and its compliance with water quality standards. Sampling is carried out in the Ría de Arosa estuary at 38 selected stations and the trace metals are determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

The Ría de Arosa is the most extensive estuary of the Rías Baixas (Galicia, NW Spain). From the economic viewpoint, it must be stressed that the wealth of Arosa region comes mainly to the shellfish sector, fishing, agriculture, the preserve industry and tourism. Therefore, it is of paramount importance to preserve the good seawater quality.

CHAPTER 3. HEAVY METALS

3.1. Sources of heavy metals pollution

The sources of heavy metals were reported by The FAO as follows: mining effluents, industrial effluents, domestic effluents, urban storm-water, leaching of metals from garbage and solid wastes dump, metal inputs from rural areas, batteries, pigments, paints, glass, fertilizers, textiles, dental and cosmetics, atmospheric sources and petroleum industrial activities.¹¹ Moreover, heavy metal pollution can arise from many sources as smelting of copper, preparation of nuclear fuels, electroplating with chromium and cadmium.

Cadmium, lead and zinc are released into tiny particles as dust from rubber tires on road surface. These small size particles allow these toxic metals to raise on the wind to be inhaled, or transported onto top soil or edible plants. Cadmium compounds are used as stabilizers in PVC (Polyvinyl chloride) products, color pigments, several alloys and now most commonly in rechargeable nickel-cadmium batteries. Metallic cadmium mostly used as an anticorrosion agent. Cadmium is present also as a pollutant in phosphate fertilizers. The anthropogenic sources of cadmium, including industrial emission and application of fertilizers, sewage sludge to farmland, may lead to contamination of soils to increase cadmium uptake by crops and vegetables grown for human consumption. Cigarette smoking is a major source of cadmium exposure. Food is the most important source of cadmium exposure in the general non-smoking population.^{12 - 14}

General population is exposed primarily to mercury via food, fish being a major source of methyl mercury exposure and, dental amalgam. A major use of mercury is in the chlor-alkali industry, in the electrochemical process of manufacturing chlorine, where mercury is used as an electrode. Organic mercury exists as methyl mercury, which is very stable and accumulates in food chain. Methyl mercury was commonly used for control of fungi on grain seeds.^{15 - 16}

Occupational exposure to inorganic lead occurs in mines and smelters as well as welding or lead painters and in the battery plants. Low or moderate exposure may also take place in the glass industry. High levels of lead in air emission may pollute areas near lead mines and smelters. Airborne lead can be deposited on soil and water, thus reaching human via the food chain.¹⁷ Lead emissions are related mainly to road transport and thus most uniformly distributed over space.

Arsenic is a widely distributed metalloid, occurring in the rocks and in water used for drinking in several countries all over the world (e.g. Bangladesh, Chile and China), whereas organic compounds (such as arsenobetain) are primarily found in fish causing human exposure. Smelting of non-ferrous metals and the production of energy from fossil fuel are the two major industrial processes that lead to arsenic contamination of air, water and soil, smelting activities being the largest single anthropogenic source of atmospheric pollution. Other sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives.¹⁸

In the following lines a more detailed revision is presented for some of the trace metals of major environmental concern in the European Union, such as cadmium , lead and mercury.

3.2. Cadmium

Cadmium occurs naturally in geological ores and is found at background levels in the marine environment. Cadmium for industrial or commercial use is derived from mining, smelting and refining of zinc. Its main use in batteries has almost ceased in Europe. It is still used as intermediate and catalyst for electroplating, in pigment in paint, in stabilizer for plastic, in photographic processes and in dyes.

What is the problem?

Cadmium is toxic and liable to bioaccumulate and thus is a contaminant of concern both for the marine environment and for human consumption of fish and other seafood. The main sources of cadmium to the environment are emissions from combustion processes primarily in power plants and industry, but also other commercial and domestic sources. Other relevant sources are releases to water and air including from the metallurgical industry, road transport and waste streams. The main pathway of cadmium to the sea is via air by which it can be carried long distances from its source. With the closure of cadmium refineries in Europe in response to marketing and use restriction regulations, diffuse sources, especially waste streams, are gaining relative importance.

What has been done?

Specific marketing and use restrictions in the EU framework restrict the use of cadmium in batteries and in a variety of uses, applications and consumer products, including for example fertilisers, sewage sludge, metal plating, toys and packaging and packaging waste.

How does this affect the marine environment?

Concentrations of cadmium in the marine environment have generally decreased over the period 1990 to 2007 where trends can be detected, but have not been consistently upwards or downwards over the period 1998 – 2007. However, concentrations remain above background in many areas and in some areas are still at levels where there is potential for significant adverse effects to the environment, or to human health. In sediment, concentrations of cadmium are generally near or just above background. However, concentrations in some areas, such as around the industrial estuaries of the Rhine, Seine, Tyne, Tees, Thames as well as in certain industrialised estuaries in Norway (Inner Sør fjord) and Spain (Ria de Pontevedra) and the inner German Bight are at levels which may pose a significant risk of

pollution effects. Concentrations of cadmium in fish and shellfish were above EU dietary limits in some of these areas. The high concentrations are mainly found around the coasts of Denmark, and at occasional locations in the UK, France, and also in Iceland and Norway where geological factors are likely to increase concentrations locally. Concentrations in fish and shellfish are at or below background at a good proportion of sites in Northern Spain, the Bay of Biscay, the Channel coast of France and parts of Ireland and Scotland.

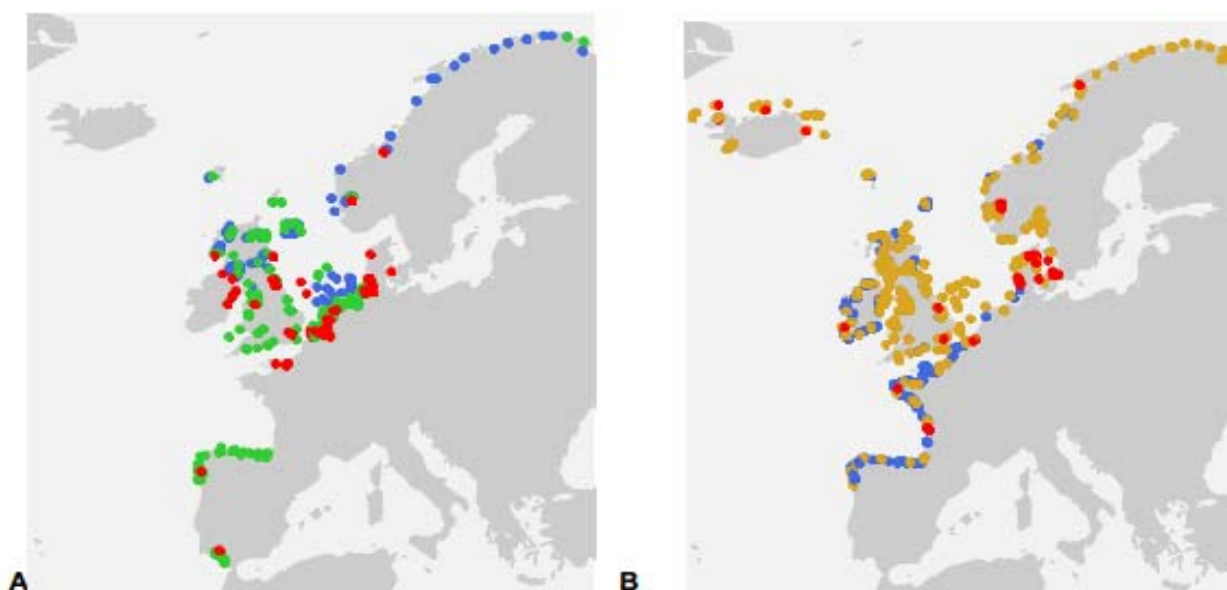


Figure 1. Status of cadmium concentrations in (A) sediments and (B) biota: background (blue), acceptable (green) or below EU dietary limits (amber), and unacceptable (red).

The following are the emissions of cadmium to water reporting of 2008 data.

Reported emissions (releases) relate to the following E-PRTR sectors: animal and vegetable products from the food and beverage sector; chemical industry; energy; mineral industry; paper and wood production and processing; production and processing of metals; waste and water management; other activities.

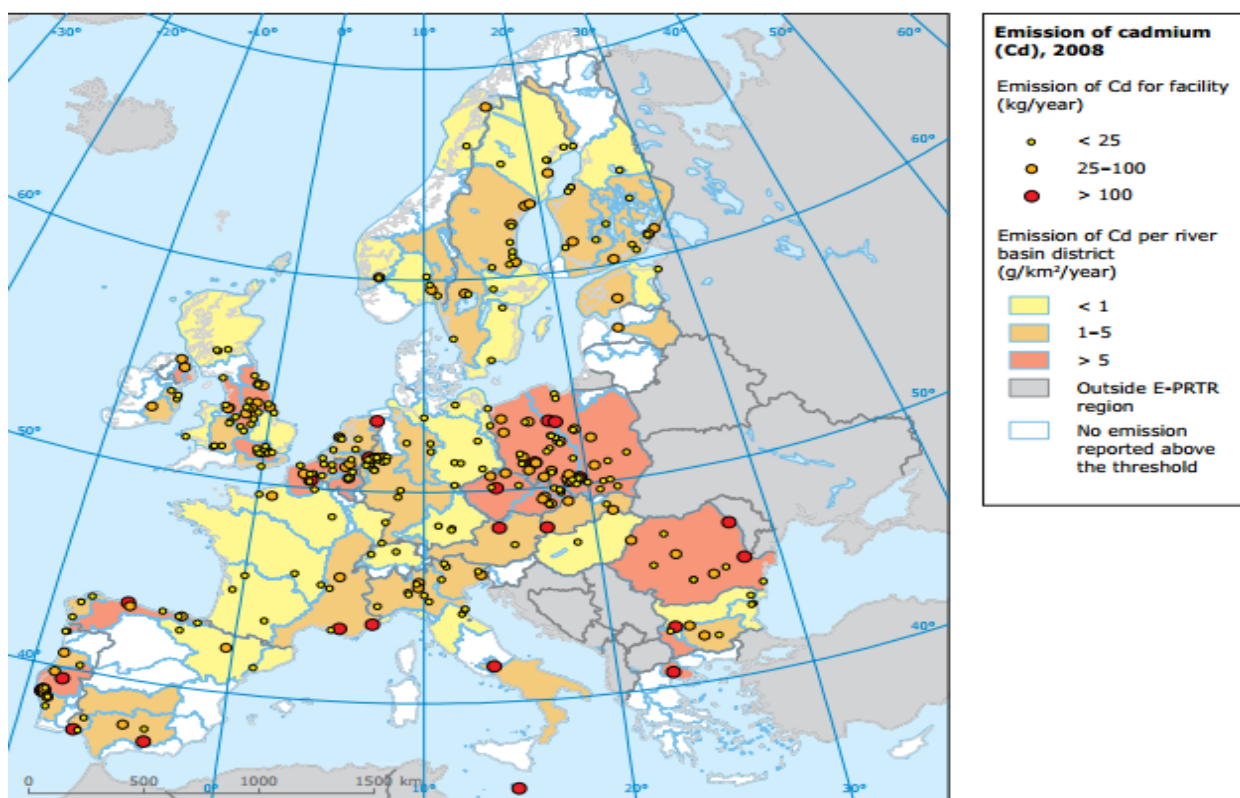


Figure 2. Emissions of cadmium to water based on E-PRTR reporting of 2008 data¹⁹.

3.3. Lead

Lead occurs naturally in the environment and it is a vital element in everyday life. Mining, smelting and industrial use of lead has led to the widespread elevation of environmental lead concentrations. Lead for industrial or commercial use is derived from mining, smelting and refining of geological ores. Its main use worldwide has been for lead-acid batteries for vehicles, emergency systems and industrial batteries. It is also used in accumulators, lead shots, boat keels, building products such as paint, leaded petrol, glass, electronic and electrical equipment, plastic, and ceramic products.

What is the problem?

Lead is persistent and an acute toxic compound for mammals and aquatic organisms and thus is a contaminant of concern both for the marine environment and for human consumption of fish and other seafood. The main sources of lead to

the environment are primary production processes such as ferrous and non-ferrous metal production and mining. Other relevant sources are transport, glass production and recycling processes, ceramics production, offshore industry, and waste incineration and disposal. The main pathway of lead to the sea is via air and it can be carried long distances from its source.

What has been done?

Specific restrictions in the EU framework promote the substitution of lead in paints, PVC products and in various other products and articles, include limit values for lead in ambient air and prohibit marketing of leaded petrol.

How does this affect the marine environment?

Where they can be detected trends in lead concentrations over the period 1990–2006 are generally downward. The picture of downward trends since 2000 is slightly more significant than for cadmium and mercury. Concentrations of lead in sediment are at levels which may pose a unacceptable risk of pollution effects over large parts of the southern North Sea, both inshore and offshore, the Channel and the Irish Sea. Scattered high concentrations are also found along the coast of Norway and in some locations near urban industrialised areas in northern Spain. However, concentrations in the northern UK, northern Norway and northern Spain are generally approaching or at background. Concentrations in biota exceeding EU dietary limits are less widespread, and the locations can generally be linked to urban and industrial activity, *e.g.* around Denmark, several UK estuaries and certain sites in southern Ireland and northern Spain. Concentrations in the offshore area around the Dogger Bank are at near coastal levels. This has been attributed to enhanced fine sediment fraction and riverine humic acids in that area which are carriers for lead. Concentrations above background at sites around Iceland may be the result of natural geological factors.

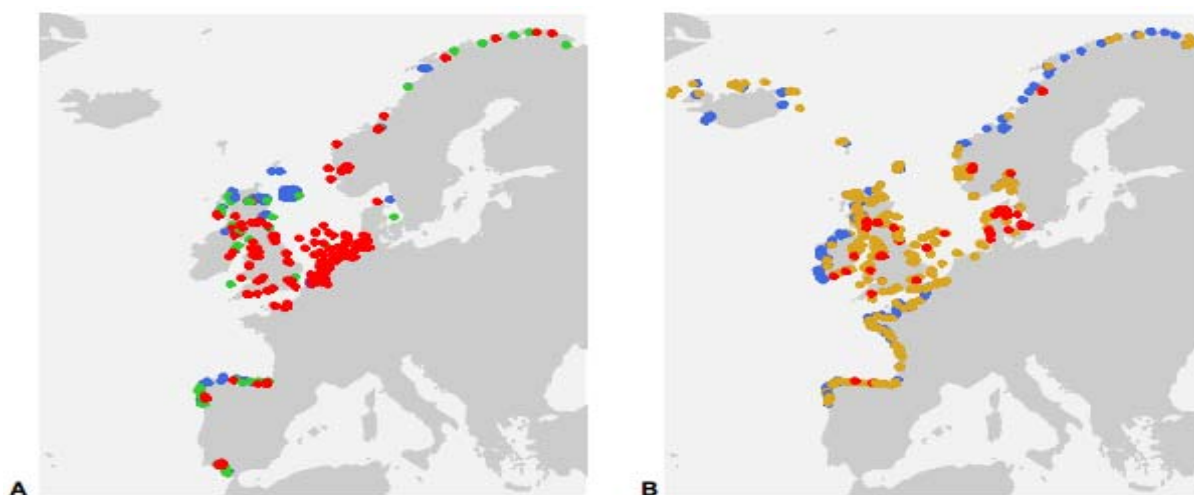


Figure 3. Status of lead concentrations in (A) sediments and (B) biota: background (blue), acceptable (green) or below EU dietary limits (amber), and unacceptable (red).

3.4. Mercury

Mercury is an extremely rare element in the earth's crust but occurs in concentrated ores in young geologically active areas *e.g.* often in hot springs or volcanic regions. It is obtained commercial from the ore cinnabar. Industrial and commercial use of mercury has led to the dispersion of mercury and the elevation of environmental mercury concentrations in certain locations. Due to its heavy liquid state, mercury has specific technical applications in a number of products including dental amalgam, batteries, industrial control instruments, laboratory and medical instruments and lighting appliances.

What is the problem?

Mercury is extremely toxic to both man and biota and can be transformed within the aquatic environment into more toxic organic compounds (*e.g.* methyl mercury). A main pathway of mercury to the sea is atmospheric and it can be carried long distances from its source. The main sources of mercury to the environment are natural atmospheric emissions from volcanoes and anthropogenic emissions from coal-fired power stations and metal production and cement production. Mercury also enters into the environment through the disposal products

containing mercury including: car parts, batteries, fluorescent bulbs, medical products, thermometers, and thermostats. Emissions from crematoria are a small but widespread source. Many of the releases of industrial mercury during the 1900s came from the mercury cell chlor-alkali process used to produce chlorine. Due to the introduction of new technology, this source has largely been phased out over the last twenty years.

How does this affect the marine environment?

Almost all temporal trends in mercury concentrations in sediments are downwards. Both upward and downward temporal trends occur in biota. A number of upward trends of mercury in biota were detected in southern Norway. Concentrations of mercury in sediments indicate a risk of pollution effects in the southern North Sea, at many of the other locations monitored on coast of the UK, west coast of Norway and some locations in near urban industrialized areas in northern and southern Spain. Concentrations around the Dogger Bank are also high, but elsewhere in offshore areas of the North Sea are lower, and at background in some locations. Background concentrations also occur in parts of northern Scotland and in northern Norway. Mercury concentrations in fish and shellfish are at background at a large proportion of stations on the Channel coast of France, and the French and Spanish coasts of the Bay of Biscay. Background concentrations are also found at some stations in Ireland, Scotland, and western Norway. Concentrations above EU dietary limits occur mainly around Denmark and in certain industrialized estuaries in Norway and the UK. Elevated concentrations close to Iceland may be a consequence of geological conditions.

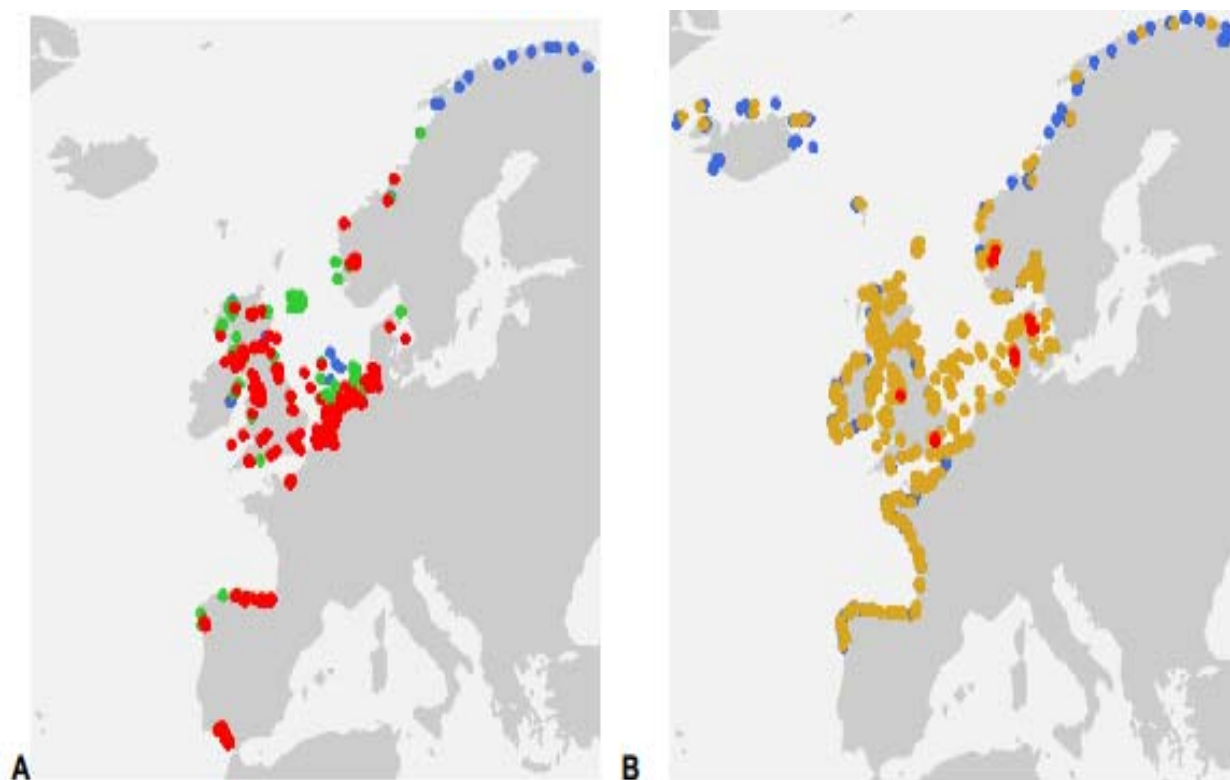


Figure 4. Status of mercury concentrations in (A) sediments and (B) biota: background (blue), acceptable (green) or below EU dietary limits (amber), and unacceptable (red).

The following are the emissions of mercury to water reporting of 2008 data (Figure 5).

Reported emissions (releases) relate to the following E-PRTR sectors: animal and vegetable products from the food and beverage sector; chemical industry; energy; mineral industry; paper and wood production and processing; production and processing of metals; waste and water management; other activities.

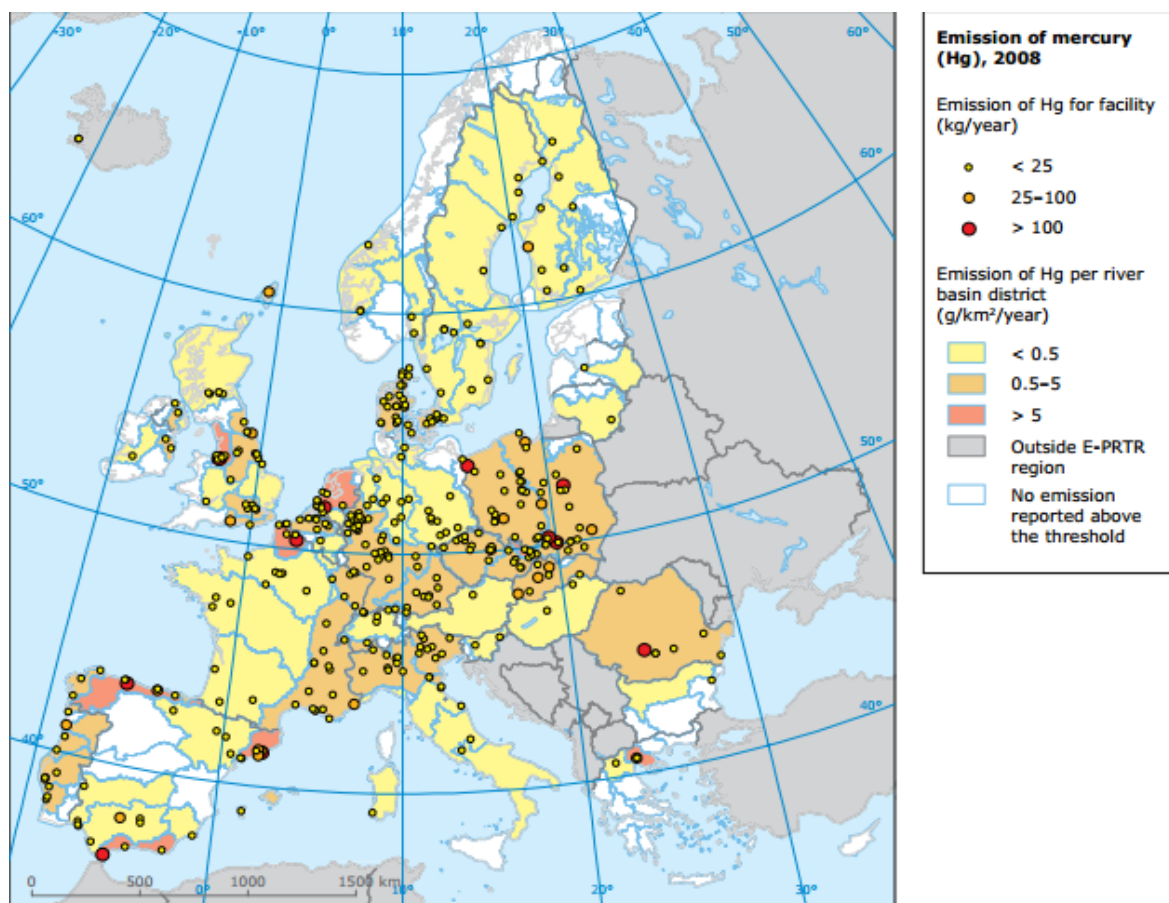


Figure 5. Emissions of mercury to water based on E-PRTR reporting of 2008 data²⁰.

3.5. Importance determination of heavy metals in natural water

The pollution increase, caused by heavy metals and organometallic compounds is one of the today's most serious problems. The common characteristic is that all are insoluble and have tendency to accumulate in vital organs.

Cadmium represents one of the most toxic metals. It is usually brought into organism through anthropogenic source.

In the organism, Cadmium accumulates and causes weakness or total loss of kidney, liver and pancreas functions. Furthermore, it destroys DNA and leads to damage of the red blood cells. The basis of psychological influence of cadmium has its similarity with zinc in so that cadmium replaces zinc as microelement in some enzymes which then leads to complete change of enzymes stereo-structure

and its characteristic features. The researches have shown that on the bioavailability of cadmium influences also other constituents in water and food; like calcium, phosphor and steel.

Zinc and copper fall into metalloids category, ie. metals of essential importance necessary for different biochemical and psychological processes in the organism and toxic only above the “exactly” determined concentration. The “concentration window” of these heavy metals is somewhere around toxic and maximum allowed limit, and it is very slight.

The toxicity level of metals significantly differs and depends on their physical-chemical form. According to the World Health Organization (WHO), about 400 million people in developing countries suffer from the diseases which are caused by use of contaminated water.²¹ In table 1. the critical concentrations of heavy metals in natural waters by EPA are given.²²

Metal	Maximum allowed concentration (µgr/l)
Mercury	0.002
Arsenic	0.5
Lead	0.5
Copper	0.6
Zinc	5
Cadmium	0.04

Table 1. Critical concentrations of heavy metals in natural water by EPA.

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CHAPTER 4. MATERIALS AND METHODS

4.1. Study area and sample collection

Study area

The Ría de Arousa is a saline estuary, that forms a firth situated on Galicia, Spain. It is one of the five Rías Baixas (Figure 6). The Ría de Arousa estuary is the largest of the estuaries of Galicia. It is part of the Rias Baixas and is located between the estuary of Muros and Noia to the north and the Pontevedra estuary to the south. The peninsulas of Barbanza, in the province of A Coruña, and O Salnés, in the province of Pontevedra, are those who define their coasts on the north and south, respectively.

It is the largest estuary, although not reaching the higher levels bathymetric, at 69 m maximum depth at the mouth. It has numerous islands and islets among which the island of Arousa, A Toxa, Sálvora in the mouth and Cortegada at the entrance. The main rivers that flow to it are the Ulla river at its headwaters and the river Umia in the cove that forms the peninsula of O Grove with the coast of Cambados.

The most important river towns are Ribeira, Pobra do Caramiñal, Rianxo and Boiro to the north, and Vilagarcía de Arousa, Vilanova de Arousa, Cambados and O Grove to the south, and Arousa in the homonymous island.

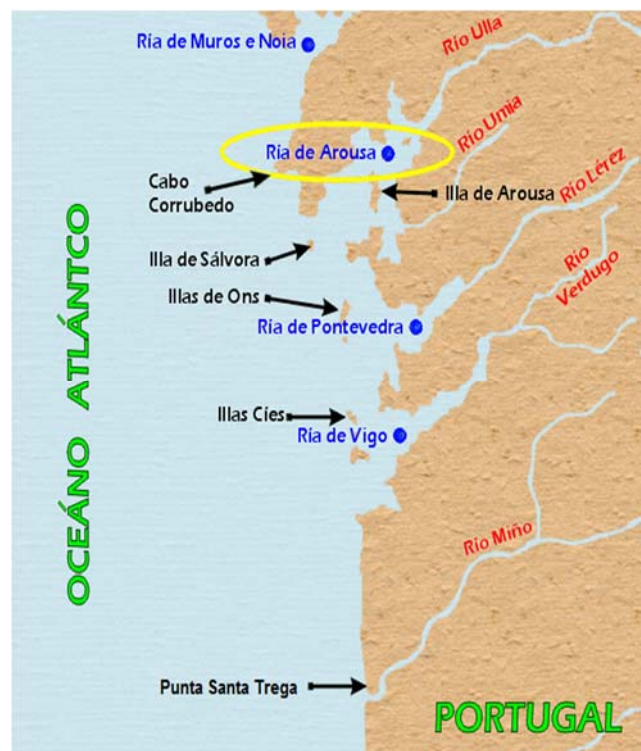
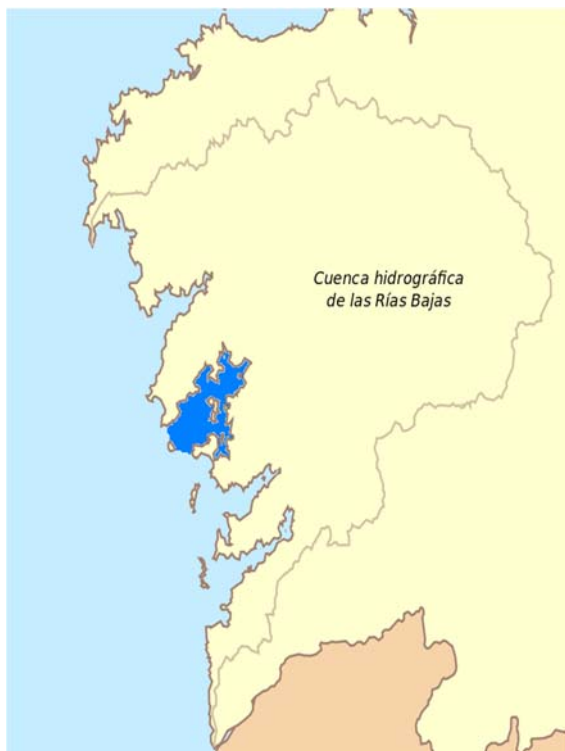


Figure 6. The Ría de Arousa

Zones

The northern zone, corresponding to the province of A Coruña, is relatively steep, with the Serra da Barbanza near the coast. The beaches take a few metres depth from the shore, forming sand banks in the interior bays.

The southern zone, corresponding to the province of Pontevedra, is a flood zone, where the river Umia ends. The characteristic of the coast is shallow, with extensive formation of sand banks, where many arenicolous bivalves are grown like cockles or clams. The most well-known banks of Sarrido belong to the delta of Umia river and Os Lombos do Ulla belonging to the homonymous river delta. This southern area is relatively flat up to the highlands of Mount Castrove, which separates it from the Ría de Pontevedra, and is characterized by small farm plots usually cultivated with vegetables (Padrón peppers, tomato, lettuce and legumes) or grapevines. The grapevines in the O Salnés area is mostly white grape Salnés (varieties Albariño wine). There are also cultivated dark grapes for the production of red wine also known Barrantes. There are also pink grape cultivated with which Catalan wine is made.

Fauna

Its physical configuration allows a high production of phytoplankton, with a characteristic ocean flow that makes this river famous for its rich marine life. It is the area of greatest mussel production in all the world. They are grown in nurseries, cultivated in floating rafts.

Sampling collection

Estuary Ria of Arosa was selected in this study in order to know the chemical status of seawater quality regarding the levels of trace metals identifying the main sources of pollution in this area. The studied area represents a transition zone between land and ocean; consequently, morphology parameters reflects historical and present-day changes in sea level, human activities within the coastal zone, river loads and sediment.

Sampling points were chosen near possible sources of contamination taking into account the greater urban pressure and economic activities from the main cities in this estuary, including samples of the main ports in the area.

In the Ría de Arousa, 38 sampling stations were selected (represented by ST-number of the station in Figure 7). The main centers of population of the estuary are: Vilagarcía de Arousa, Ribeira, Vilanova de Arousa, Illa de Arousa, Cambados, Rianxo, Boiro, Pobra do Caramiñal and O Grove.

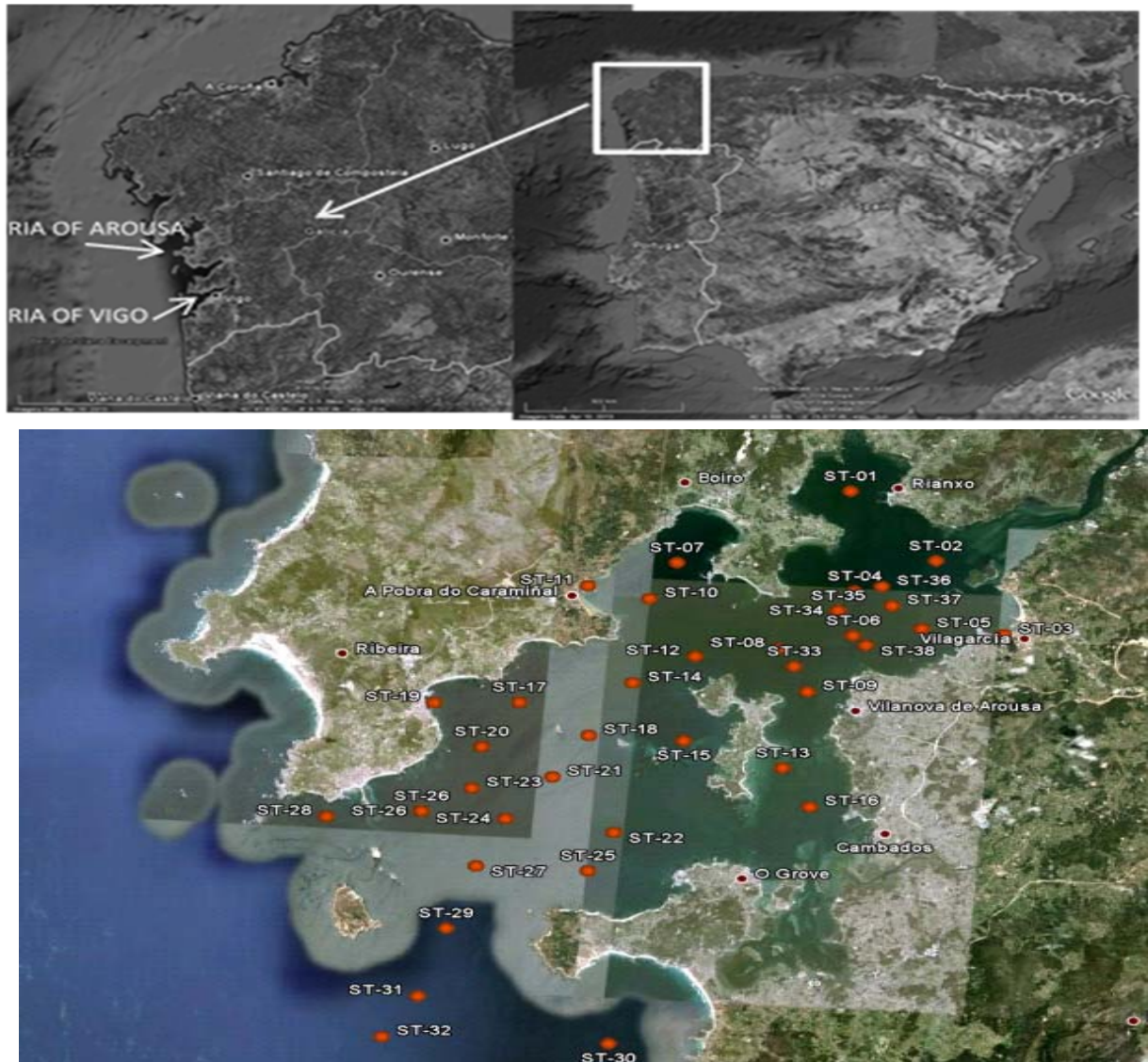


Figure 7. Sampling stations in Ría Arousa (38 stations)

4.2. Sampling and analytical methods

The samples were taken from a depth of 1 m below the surface using glass bottles (2 L) attached to the top of 3-4 m long telescopic bar (Figure 8).

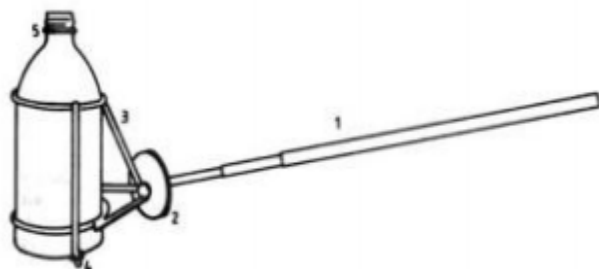


Figure 8. Equipment for sampling seawater.

After sample bottles were rinsed three times with seawater, bottles were filled fully. The temperature of seawater was determined using digital thermometer dipped below sea.

To analyze metals in seawater, it is necessary to deionize the water before its analysis by ICP-MS. Deionization is the complete removal of all ionic species from a solution.

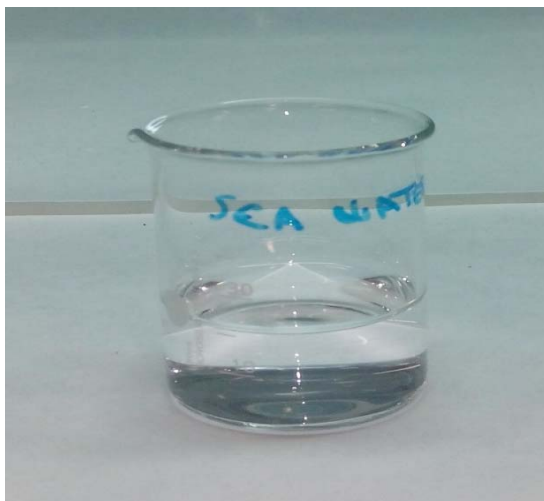


Figure 9. Seawater sampling.

For these purposes, 20 mL of seawater sample is mixed with an ion exchange resin (AG 501 - X8 and Bio - Rex MSZ 501(D)).

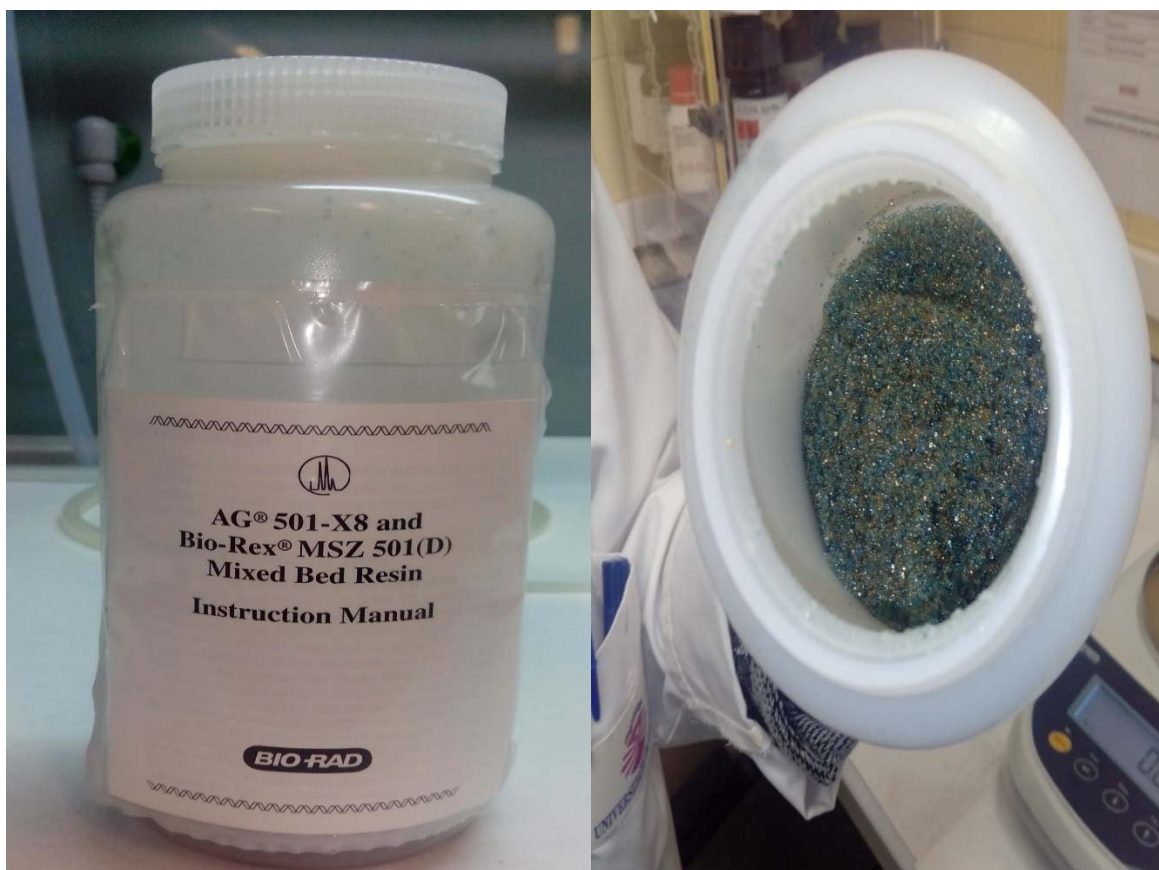


Figure 10. AG 501 – X8 and Bio – Rex MSZ 501(D). Mixed Bed Resin

We need to weigh 5 g AG 501 – X8 and Bio – Rex MSZ 501(D). For this purpose we use a weight room with certain conditions (humidity – 43%; temperature – 20⁰C).



Figure 11. Special conditions.



Figure 12. The process of obtaining 5 g of the AG 501 – X8 and Bio – Rex MSZ 501(D).

After that, the mixing with seawater (Figure 13) is mixed for 30 minutes with magnetic stirrer (Figure 14).

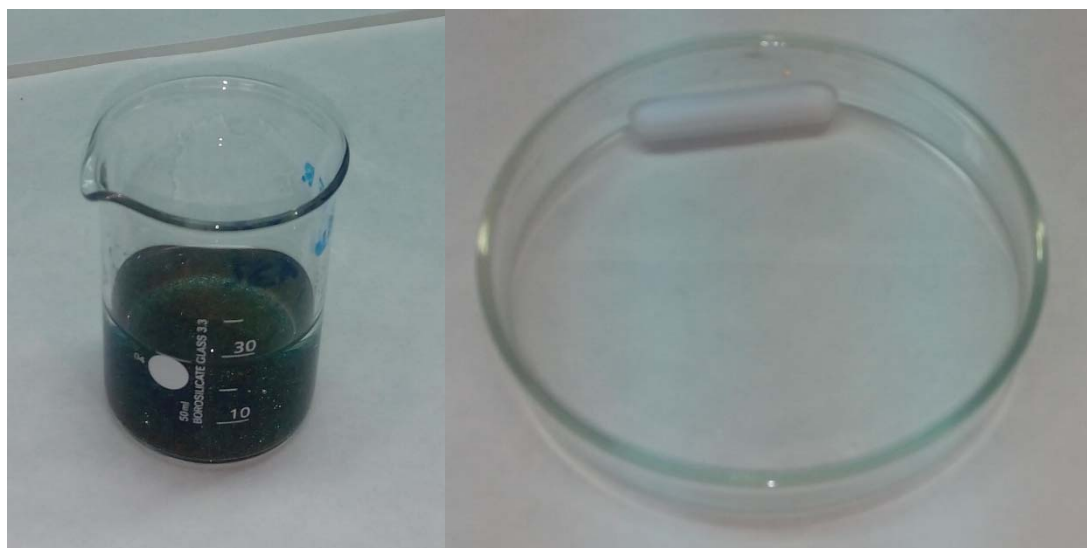


Figure 13. The water sample for mixing.



Figure 14. Magnetic stirrer.



Figure 15. The mixing process.

After 30 minutes, the water sample should be filtered (Figure 16) using filter papers Whatman® n°40 (Figure 17).

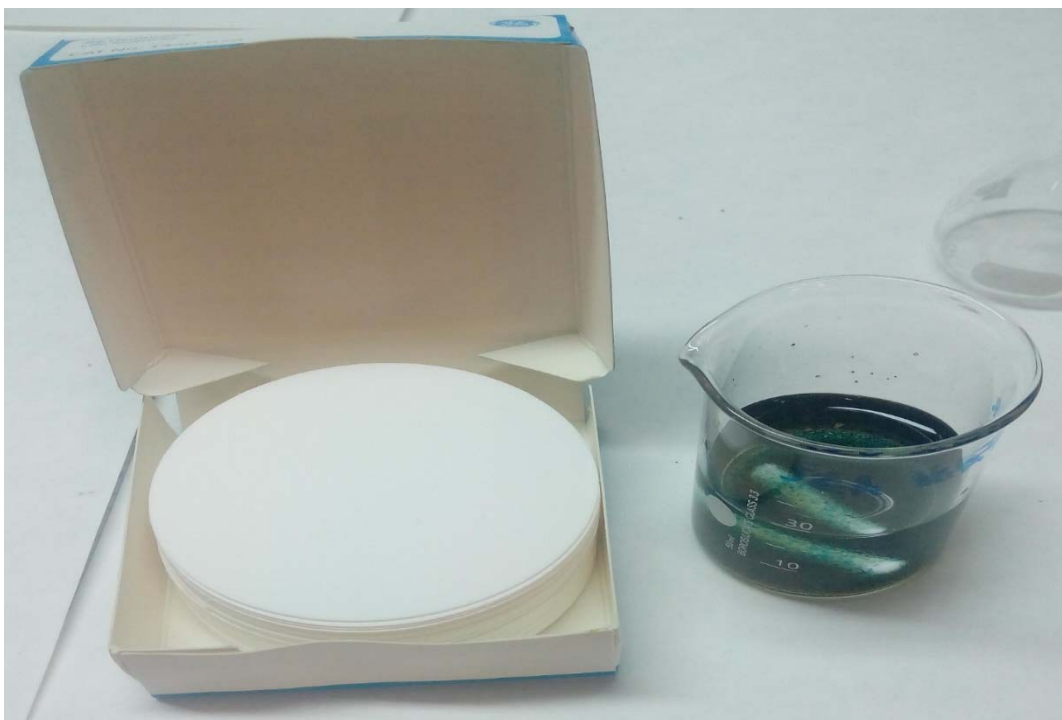


Figure 16. Filter papers (diameter 70 mm).



Figure 17. The filtering process.

After the filtering process, according to the instructions, is necessary to dilute the sample until 25 ml. For this purpose, we use distilled water (Figure 18).



Figure 18. Water sample without salt.

The determination of metals concentrations is made by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Figure 19).

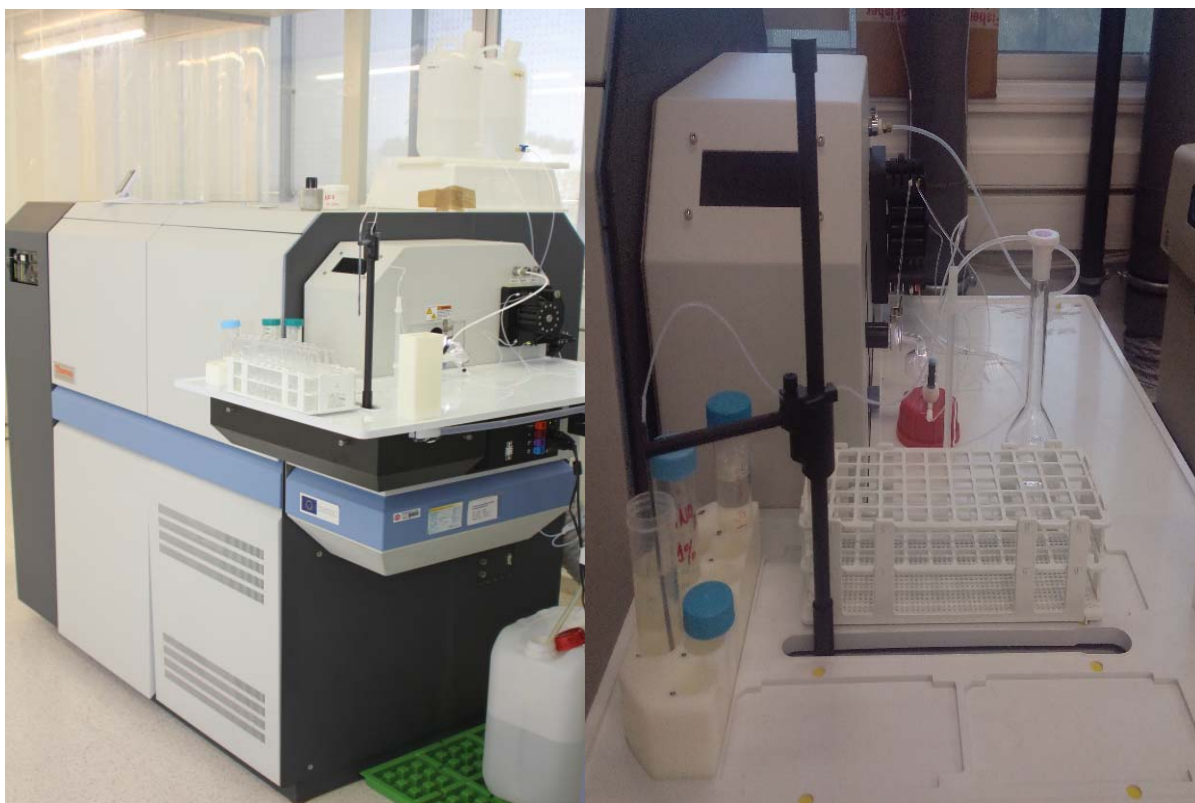


Figure 19. ICP-MS high resolution magnetic sector Element XR.

OPERATING ICP-MS CONDITIONS:

- Radiofrequency power: 1,35-1,40 kW;
- Nebulizer gas flow: 0,90-1,00 mL/min;
- Auxiliary gas flow: 0,90-1,00 mL/min;
- Cool gas flow: 15,0-16,0 mL/min;
- Pneumatic nebulizer: Cross flow;
- Nebulizer chamber: Cyclonic;
- Cones: Nickel;
- Measurement mode: Scan Sweeps: 300 Dwell time: 300 μ s channels by mass: 25;
- Detection mode: DUAL (pulse count/Analog);
- Calibration: External; Linear adjustment by least squares;
- Isotopes: ^{27}Al , ^{51}V , ^{52}Cr , ^{55}Mn , ^{56}Fe , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{75}As , ^{111}Cd , ^{208}Pb ;
- Internal standards: ^{45}Sc , ^{72}Ge , ^{115}In , ^{205}Tl , ^{209}Bi .

CHAPTER 5. RESULTS AND DISCUSSION

Throughout worldwide anthropogenic input is major source for the heavy metal pollution along the coastal environment.

The aim of water preservation within each country seeks to be achieved through the increased concern about the water, which often means controlling of the water quality.

Chemical analysis and speciation of traces of heavy metals such as lead, cadmium, zinc, copper, etc. is of great importance.

The heavy metals also includes number of physiologically important elements such as Cu, Fe, Zn; than the highly toxic Pb, Mn, Cd, hg, As, Sb and less toxic as Au, Ag and Cr, etc.

Concentrations in which heavy metals can occur depend from source of pollution and features of system in which they are found, so they can range from traces to very high concentrations.

The concentration of metals such as Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, V, Zn, Br, Hg, I and Sn in the seawater was studied in Ria de Arosa.

In order to establish the status of metal pollution, there is a need to establish background or 'natural' concentrations. It is well known that the behavior of trace metals in waters (e.g . bioavailability, toxicity, transport, adsorption/desorption, etc.) is dependent on the physico- chemical form of the element. Therefore, the knowledge of total metal concentration is, in general, not enough to predict its activity.

The following graph (Figure 20) shows the ratio of heavy metals in seawater were identified in the course of the study. Priority metals are Fe, Zn, Br, I, Al, Ba, Cu, Mn, Ni, Pb, Sr, Hg, Sn, Cd, Co, Cr.

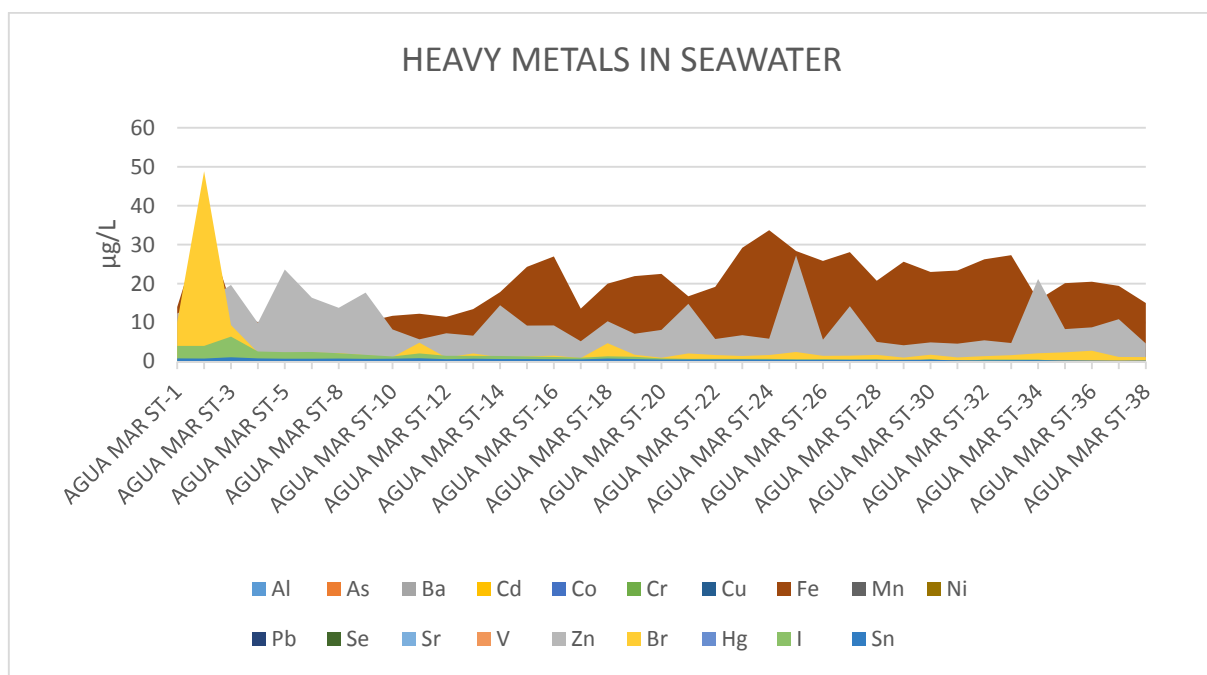


Figure 20. Heavy metals in seawater (38 sampling stations).

As and V has a value less than 0,5 µg/L in all considered points. Cd and Se are the measured values less than 1 µg/L, but at the second sampling stations Cd has a value 0,16 µg/L, and Se on the fourth station – 3,4 µg/L.

The values and ranges of element concentrations in the water samples taken from the surface – 5 m depth are presented on figures. Consider each metal on its own chart (Figures 21 – 35).

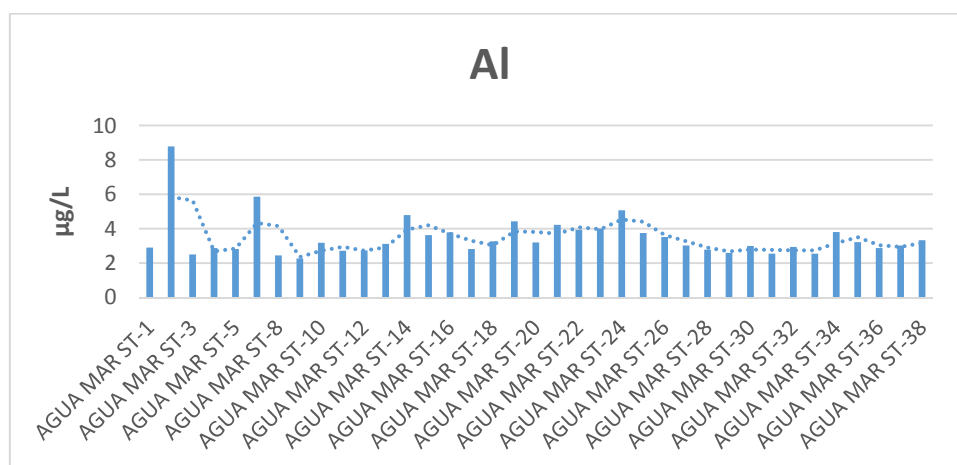


Figure 21. Changing the value of Al in water, depending on the station.

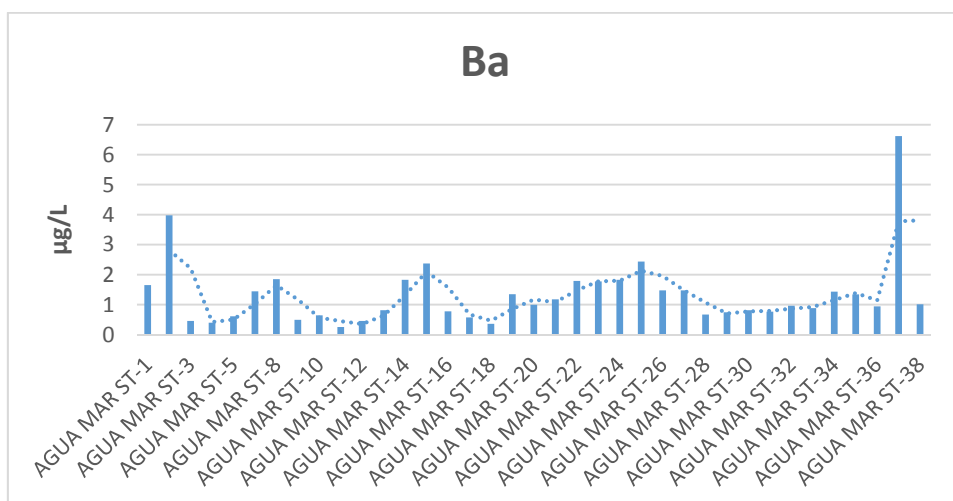


Figure 22. Changing the value of Ba in water, depending on the station.

The concentration of Al in seawater ranged between 2,26 µg/L and 8,79 µg/L (station 2), with a mean value of 3,47 µg/L; and concentration of Ba between 0,25µg/L and 6,62 µg/L (station 37), with a mean value of 1,33 µg/L.

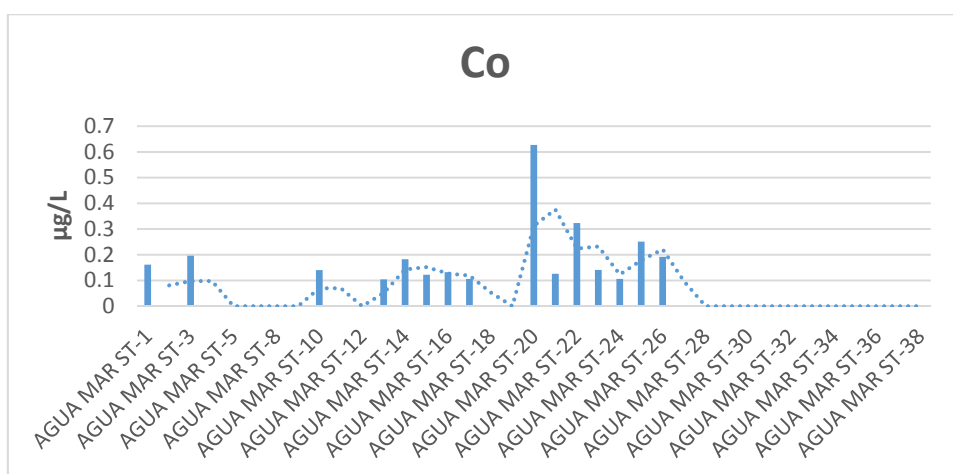


Figure 23. Changing the value of Co in water, depending on the station.

The maximum concentration of cobalt – 0,63 µg/L (station 20). With the majority of measurements showed values less than 0,1 µg/L. The concentration of chromium in seawater ranged between <0,5 and 0,802µg/L (station 11). The global median value for Cr in ocean waters is 0,3 µg/L.²³ As Cr, the concentration of cuprum is less than 0,5 µg/L, however, at the station 23 reaches the maximum – 1,81µg/L.

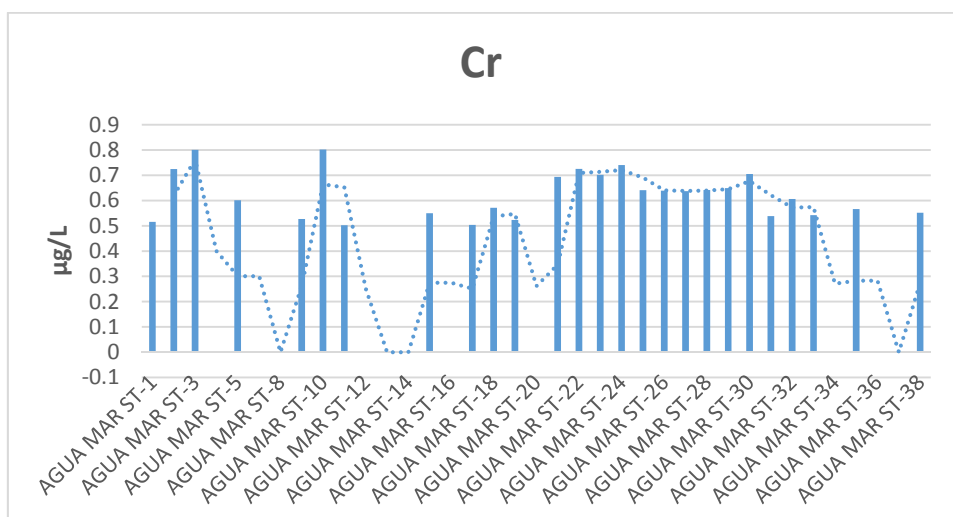


Figure 24. Changing the value of Cr in water, depending on the station.

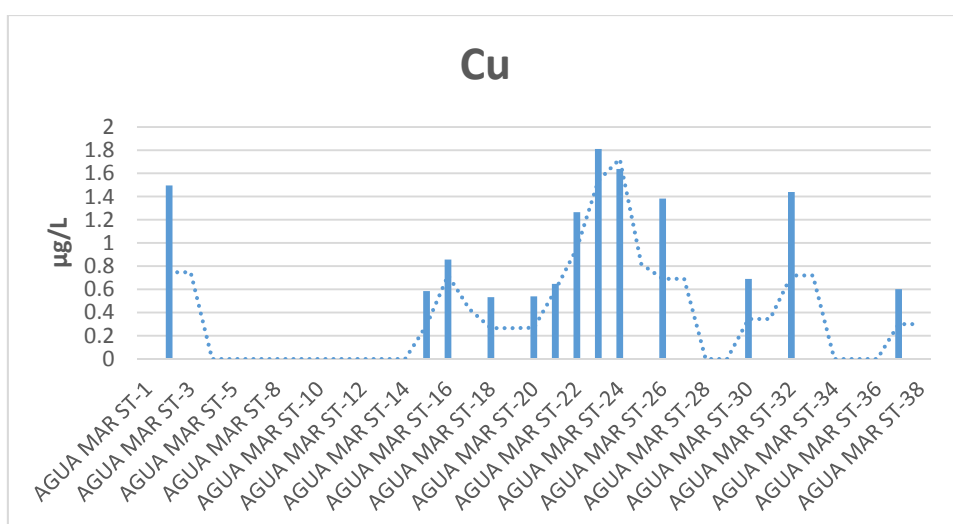


Figure 25. Changing the value of Cu in water, depending on the station.

The iron content of seawater ranged between 10,02 µg/L and 36,03 µg/L, with a mean value of 19,9 µg/L (Figure 26). The average Fe concentration observed in the present study was higher than the values recorded in the Visakhapatnam coast²⁴ (12,3 µg/L), coastal and offshore waters of western Bay of Bengal²⁵ (5,48 and 4.84 µg/L). However, in the present study the concentration was lower than the world ocean range of 25–743 µg/L²⁶.

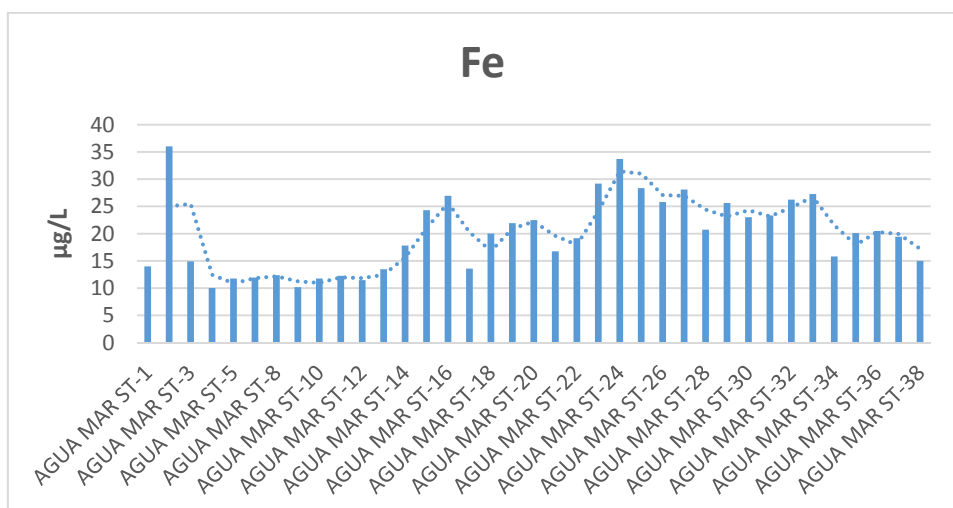


Figure 26. Changing the value of Fe in water, depending on the station.

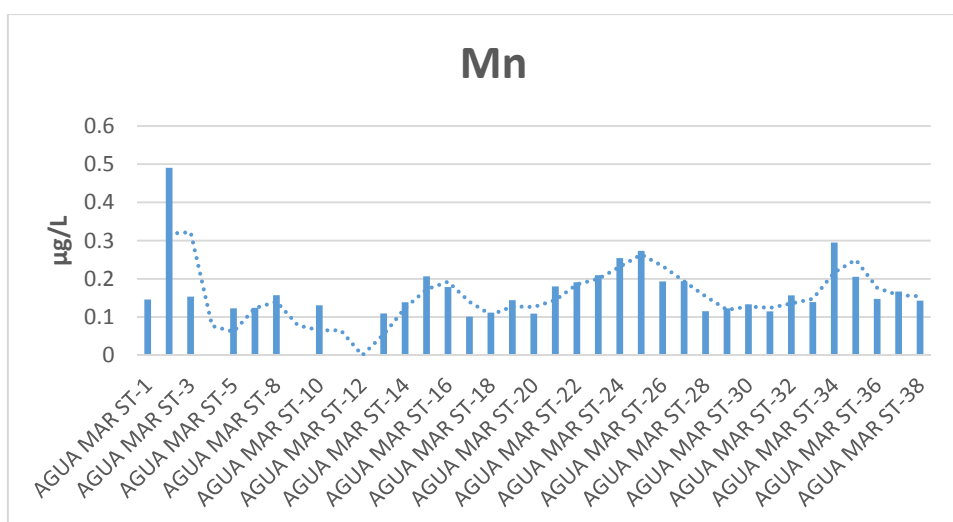


Figure 27. Changing the value of Mn in water, depending on the station.

The concentration of manganese in seawater ranged between 0,11 µg/L and 0,49 µg/L, with a mean value of 0,17 µg/L (Figure 27). The average concentration observed in the present study was lower than the values obtained for the Visakhapatnam coast²⁴ (21,16 µg/L), coastal and offshore waters of western Bay of Bengal²⁷ (4,04 and 3,97µg/L), and northern Bay of Bengal (3,5 µg/L for coastal and 3,4 µg/L for offshore waters).

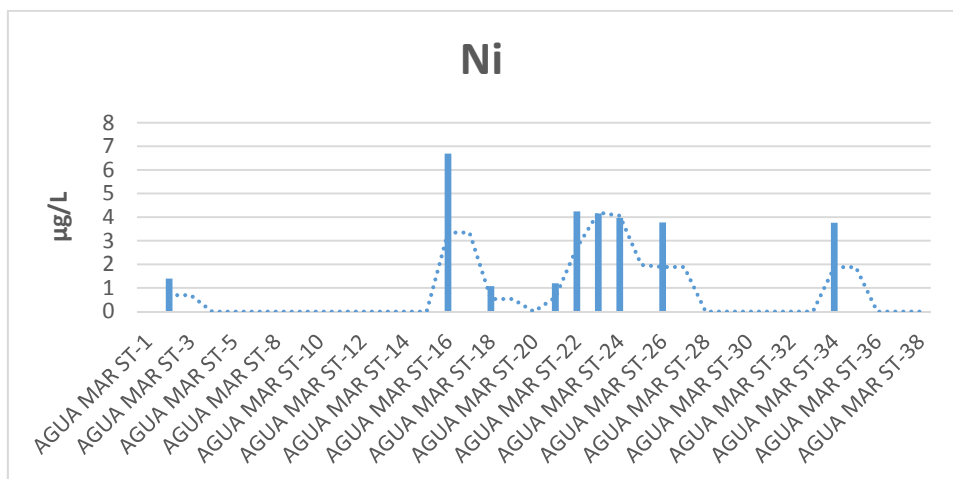


Figure 28. Changing the value of Ni in water, depending on the station.

The concentration of Ni in seawater reaches a maximum at station 16 (6,69µg/L).

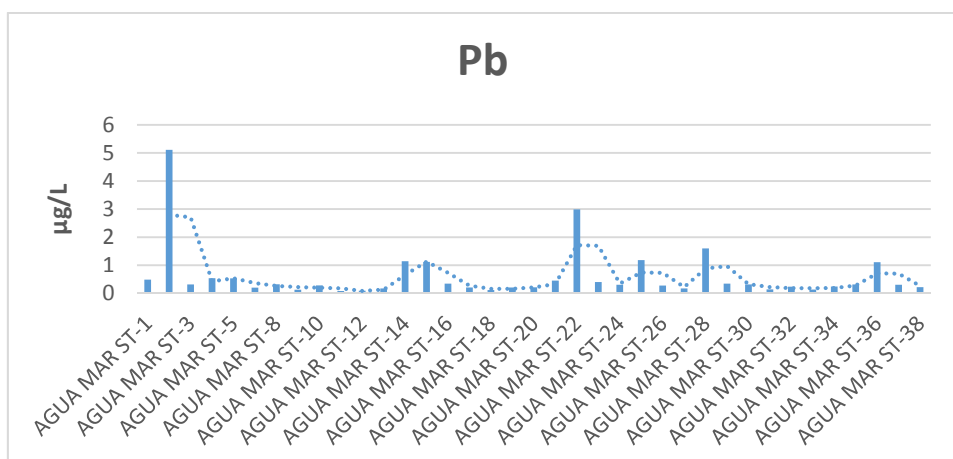


Figure 29. Changing the value of Pb in water, depending on the station.

Of the known environmental pollutants, Pb has few competitors as a persistent pollutant, which causes harmful effects on the ecosystem. It occurs in the environment mainly as Pb^{2+} and its compounds are mostly insoluble in water. The toxicity of Pb is not only due to its total concentration but also due to its forms.

The concentration of lead in seawater varied from 0,08 µg/L to 5,11 µg/L, with a mean value of 0,61 µg/L. The median Pb content in the ocean waters has been calculated to be 0,03 µg/L.²³

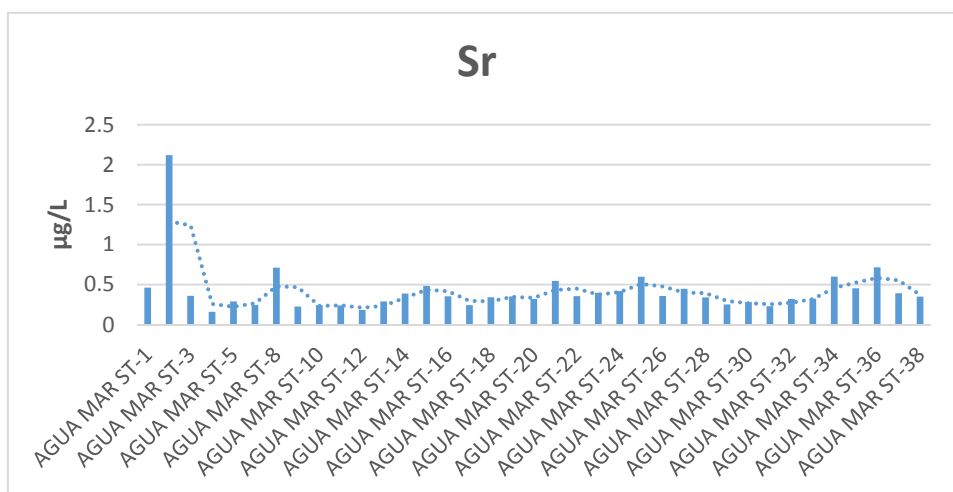


Figure 30. Changing the value of Sr in water, depending on the station.

The concentration of Sr in seawater ranged between 0,16 µg/L and 2,12 µg/L (station 2), with a mean value of 0,42 µg/L.

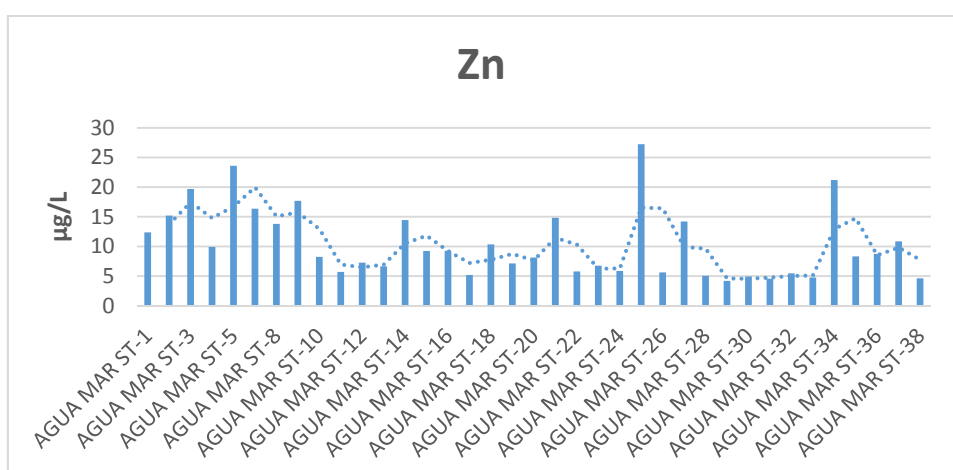


Figure 31. Changing the value of Zn in water, depending on the station.

The concentration of zinc in seawater varied from 4,18 µg/L to 27,2 µg/L, with a mean value of 10,35 µg/L. The average concentration observed in the present study was lower than that observed in the Visakhapatnam coast²⁴ (245,95 µg/L) and northern Bay of Bengal²⁷ (25,3 µg/L for coastal and 25,7 µg/L for offshore waters) and higher than the coastal and offshore waters of western Bay of Bengal²⁵ (1,82 and 1,04 µg/L). The median Zn concentration range for world ocean waters has been estimated to be 0.5–4.9 µg/L.²⁶

The concentration of bromine in seawater ranged between 0,88 $\mu\text{g/L}$ and 48,82 $\mu\text{g/L}$ (station 2), with a mean value of 3,53 $\mu\text{g/L}$ (Figure 32); mercury ranged between 0,055 $\mu\text{g/L}$ and 0,11 $\mu\text{g/L}$ (station 3), with a mean value of 0,067 $\mu\text{g/L}$ (Figure 33).

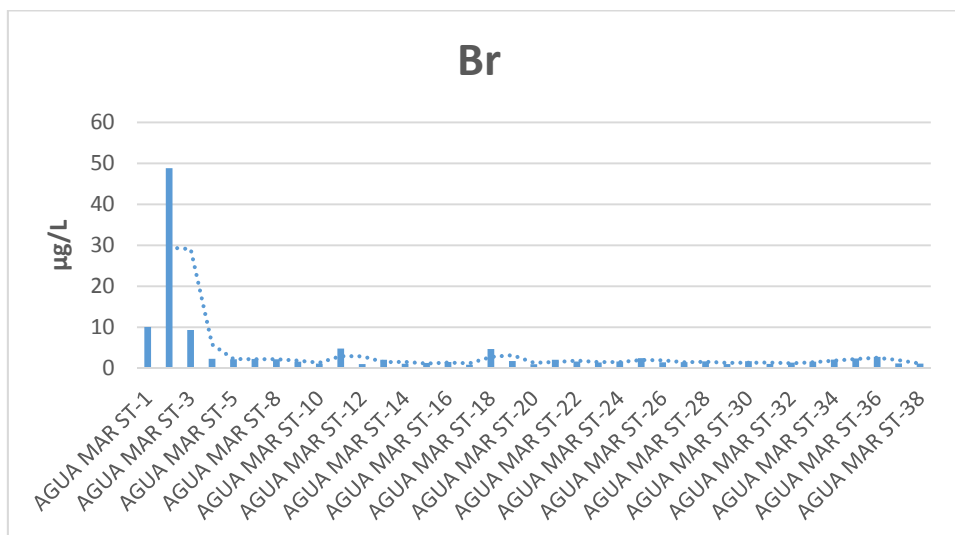


Figure 32. Changing the value of Br in water, depending on the station.

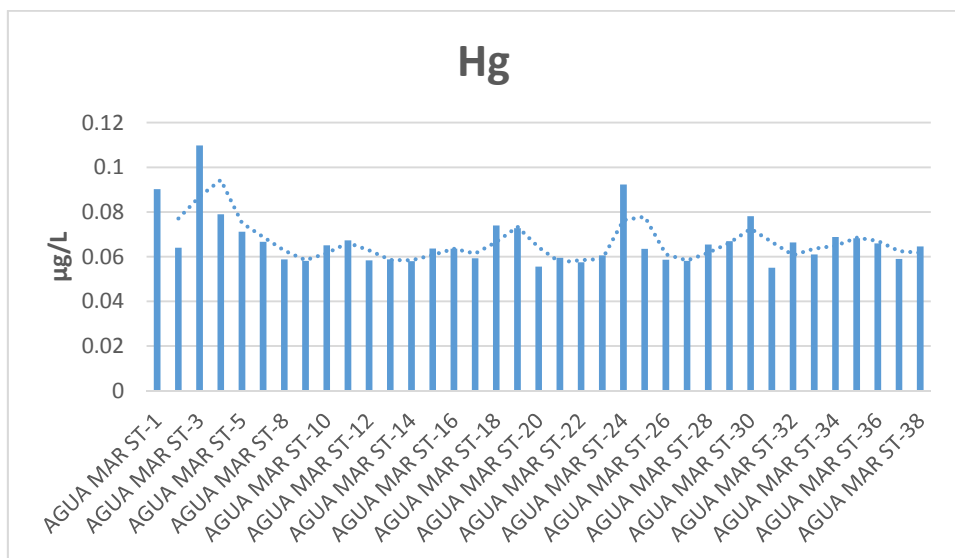


Figure 33. Changing the value of Hg in water, depending on the station.

The concentration of iodine in seawater ranged between 0,501 $\mu\text{g/L}$ and 6,38 $\mu\text{g/L}$ (station 3), with a mean value of 1,52 $\mu\text{g/L}$ (Figure 34); tin ranged between 0,25 $\mu\text{g/L}$ and 1,081 $\mu\text{g/L}$ (station 3), with a mean value of 0,56 $\mu\text{g/L}$ (Figure 35).

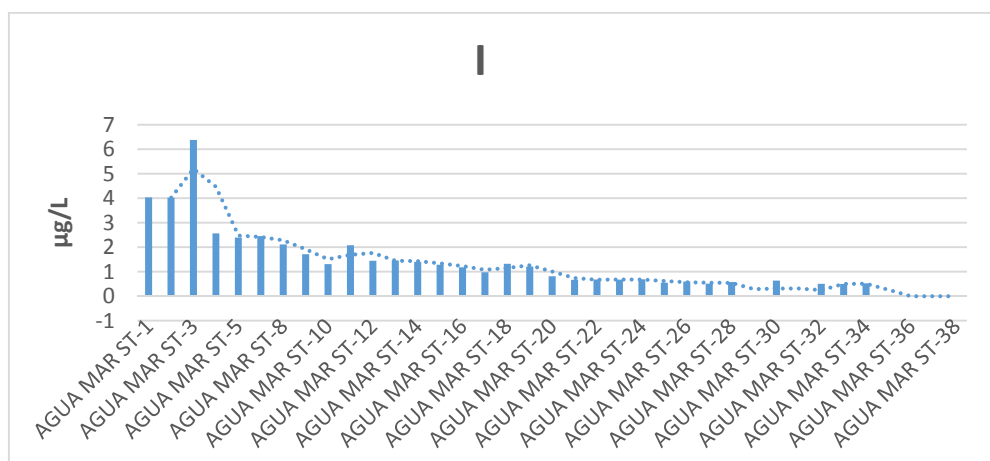


Figure 34. Changing the value of I in water, depending on the station.

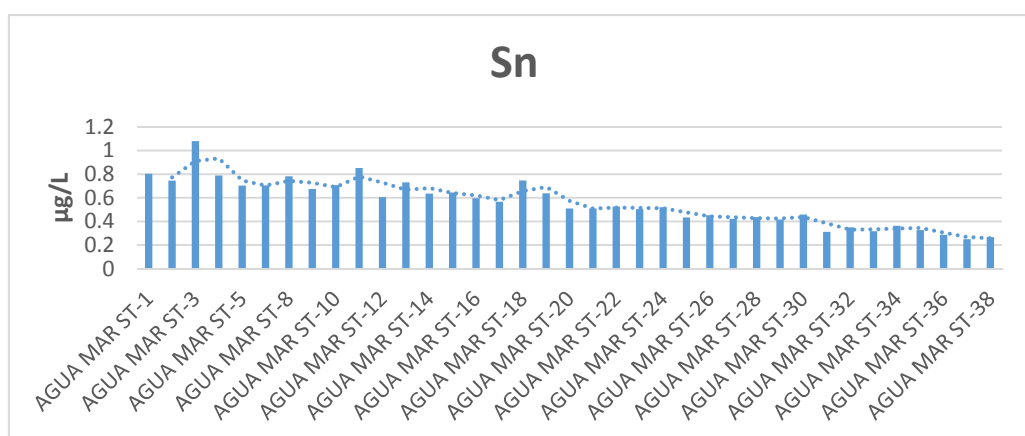


Figure 35. Changing the value of Sn in water, depending on the station.

And on the other hand consider the variation in content of heavy metals depending on the sampling stations (Figures 36 – 42).

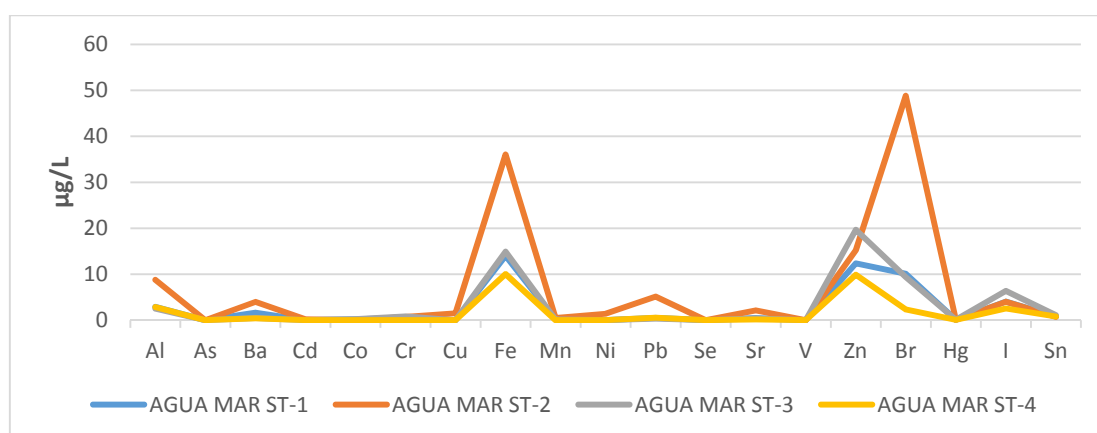


Figure 36. Changing the values of heavy metals in water, depending on the station (1 – 4).

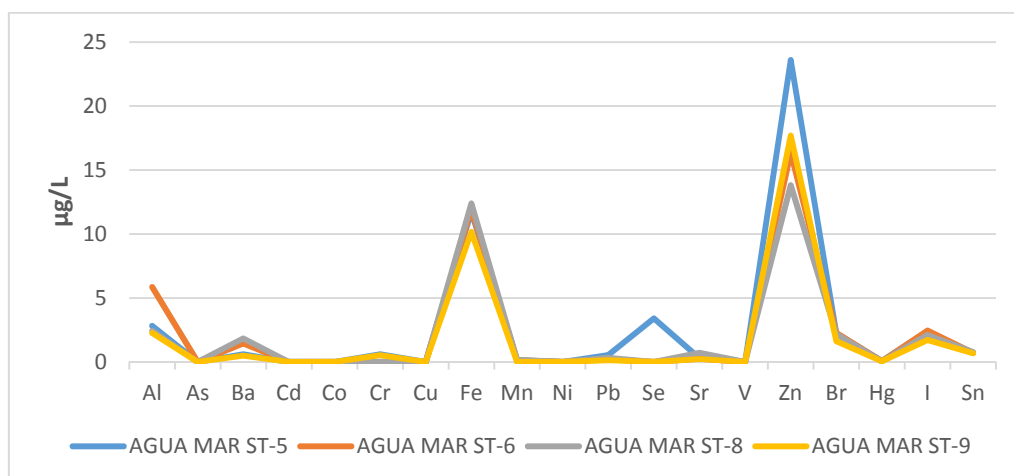


Figure 37. Changing the values of heavy metals in water, depending on the station (5 – 9).

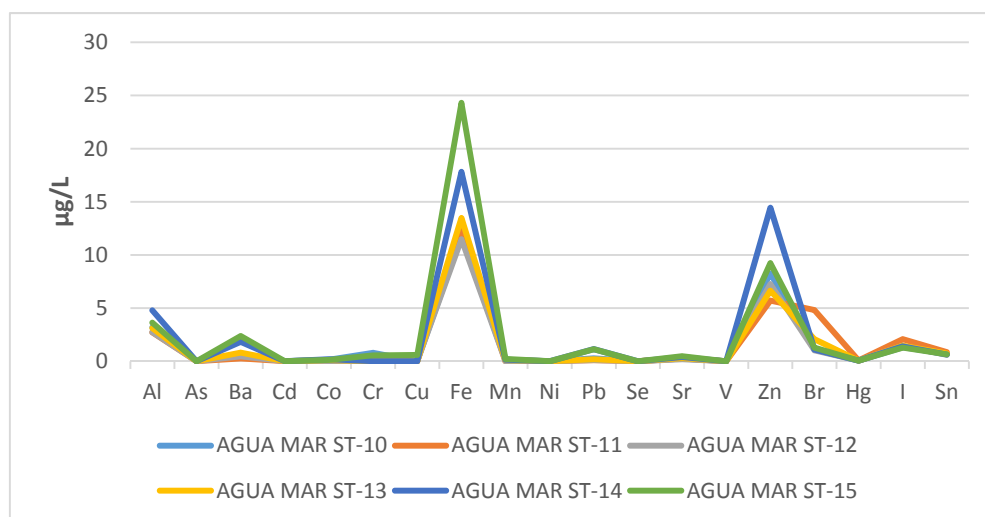


Figure 38. Changing the values of heavy metals in water, depending on the station (10 – 15).

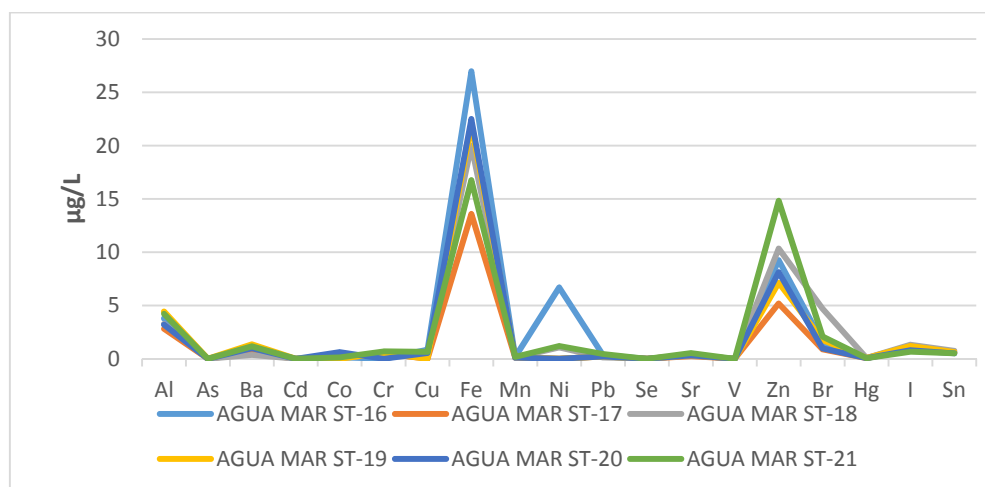


Figure 39. Changing the values of heavy metals in water, depending on the station (16 – 21).

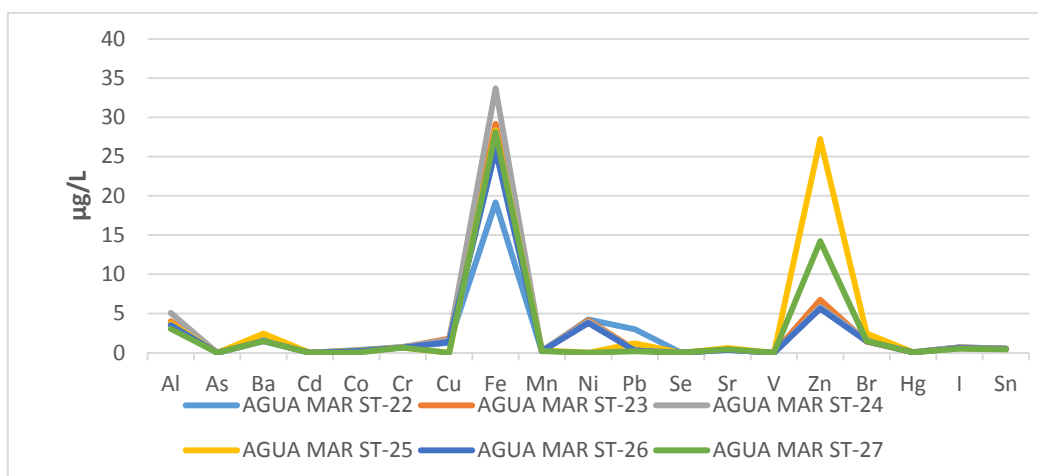


Figure 40. Changing the values of heavy metals in water, depending on the station (22 – 27).

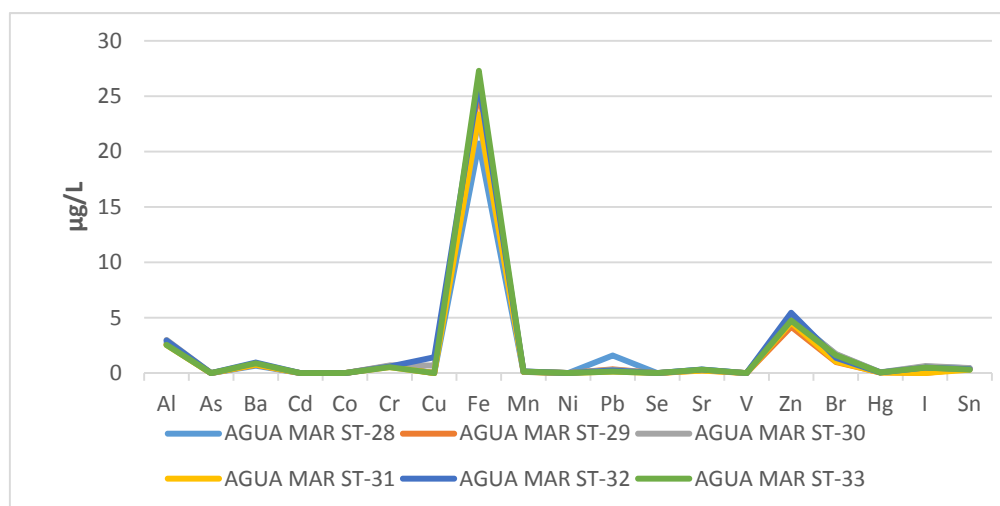


Figure 41. Changing the values of heavy metals in water, depending on the station (28 – 33).

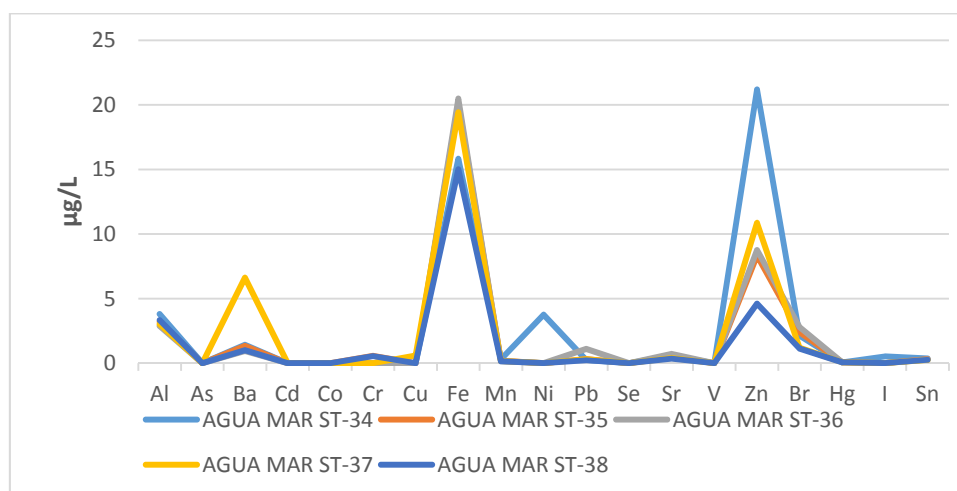


Figure 42. Changing the values of heavy metals in water, depending on the station (34 – 38).

Metals in estuarine waters may show a wide range of concentrations, depending on the anthropogenic impact above the background levels of open sea waters. The presence and impact of heavy metals in the environment, especially in marine ecosystems from anthropogenic contamination, essentially requires descriptive understanding and monitoring, research on transport fluxes and biogeochemical processes and the impact of those metals on organisms.

The concentration of Zn, found in the sampling sites, with a higher values – 27,2 µg/L and Fe – 36,0 µg/L.

Lead concentration in river estuaries and coastal areas reaches the highest concentrations at station 2 (5,12 µg/L). The maximum value at station 2 also reach values Al (8,79 µg/L), Cd (0,168 µg/L), Fe (36,03 µg/L), Mn (0,491 µg/L), Pb (5,107µg/L), Sr (2,12 µg/L), Br (48,8 µg/L); and at sampling station 3 – Hg (0,109µg/L), I (6,38 µg/L) and Sn (1,081 µg/L).

Station 2 in the Ria de Arousa, pointing out the obvious anthropogen impacts on this area.

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CHAPTER 6. CONCLUSIONS. CONCLUSIONES. CONCLUSIÓNS

In Ria Arousa, the sampling station with the highest concentration of metals, especially for Al, Ba, Cr, Cu, Fe, Mn, Pb and Sr, was ST2, located just in the mouth of the Ulla river. This fact indicates that most of metal inputs are related to river Ulla discharges. High trace element (Ba, Cr, Cu, Fe, Mn and Zn) levels have been found in sampling locations (ST3, ST10, ST16, ST20, ST23 and ST24) near to the villages and harbours of Villagarcía de Arousa and Rianxo.

The presence of some of these metals in Ria Arousa can be explained by the existence of a metallurgical industry and also a smelting industry in the surrounding area.

The continuation of coastal environmental studies requires an enlargement of the sampling locations as well as systematic and periodic analysis of known pollution sources in order to decide whether coastal regeneration action is needed.

Current awareness of the rias suggests that it is not contaminated although there is some evidence of important enrichments at the Ulla River estuary (Cu, Cr, Mn, Ni; Zn) in the Arosa Ria.

CONCLUSIONES

En la Ría de Arousa, la estación de muestreo con la más alta concentración de metales, especialmente de Al, Ba, Cr, Cu, Fe, Mn, Pb y Sr, fue ST2, que se encuentra justo en la desembocadura del río Ulla. Este hecho indica que la mayoría de la entrada de metales están relacionados con las descargas del río Ulla. Las más altas concentraciones de elementos traza (Ab, Cr, Cu, Fe, Mn y Zn) se han encontrado en las localidades de muestreo (ST3, ST10, ST16, ST20, ST23 y ST24) cerca de las aldeas y de los puertos de Villagarcía de Arousa y Rianxo.

La presencia de algunos de estos metales en la Ría de Arousa puede ser explicada por la existencia de una industria metalúrgica y también una industria de fundición en la zona de los alrededores.

La continuación de los estudios ambientales requiere una ampliación de los lugares de muestreo, así como el análisis periódico y sistemático de las fuentes de contaminación con el fin de decidir si la regeneración de costas es necesaria.

El nivel de conocimiento de las rías sugiere que no está contaminada aunque hay alguna evidencia de importantes enriquecimientos localizados en el estuario del Río Ulla (Cu, Cr, Mn, Ni, Zn) en la de Arosa.

CONCLUSIONES

Na Ría de Arousa, a estación de mostraxe con maior concentración de metais, especialmente de Al, Ba, Cr, Cu, Fe, Mn, Pb e Sr, foi ST2, situado na desembocadura do río Ulla. Este feito indica que a maioría de entradas de metais están relacionados coas descargas no río Ulla. Altas concentracións de oligoelemento (Ba, Cr, Cu, Fe, Mn e Zn), atoparonse nas localidades (ST3, ST10, ST16, ST20, ST23 e ST24) preto de aldeas e vilas de Villagarcía de Arousa e Rianxo.

A presenza de algúns destes metais na Ría de Arousa, pode ser explicado pola existencia dunha industria metalúrxica e tamén unha industria de fundición na área circundante.

A continuación dos estudos ambientais require unha ampliación das localidades de mostraxe así como a análise sistemática e periódica das fontes de contaminación, a fin de decidir se a rexeneración costeira é necesaria.

O nivel de coñecemento das rías suxire que non está contaminada aínda que hai algunha evidencia de importantes enriquecementos situados na desembocadura do Río Ulla (Cu, Cr, Mn, Ni, Zn) na Ría Arosa.