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Analysis of pollution by heavy metals in sediments and species of commercial interest of the Galician coast.

Final degree project

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Degree in Biology

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Objectives

The main goal of this project was to compare the levels of heavy metals in sediment and different species of bivalves of commercial interest in Galicia, in a paper styled format. For this several tasks were outlined:

- To organize the initial database by checking the correspondence between sites analysed for sediments and for organisms, eliminating those that did not match (in order to compare both matrices).
- To establish the total metal concentrations for each sample, normalizing the concentration in sediments by the background levels of the areas.
- To analyse the spatial pattern of metal pollution in both sediments and organisms.
- To analyse the correlation between the heavy metal levels on sediments and organisms.
- To look for guidelines of maximum allowed levels of metals in sediments and organisms and compare with the measured concentrations.

Analysis of pollution by heavy metals in sediments and species of commercial interest of the Galician coast.

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Abstract

Concentration of different heavy metals was quantified for sediments and bivalves of commercial interest from four different areas of the Galician coast (NW-Spain). Analysed species were, *Cerastoderma edule, Mytilus galloprovincialis, Ensis siliqua, Venerupis pullastra* and *Ruditapes decussatus.* Higher metal contamination in organisms than in sediments show the bioaccumulation ability of these bivalves, specially in mussels (*Mytilus galloprovincialis*) and razor shells (*Ensis siliqua*). Although two sampled areas are nowadays included in Natura 2000 network (Corrubedo and Mandeo), in 2003, when sampled, they were highly polluted, specially Mandeo and organisms from Corrubedo, these may be and indicator of different wastes and heavy metal inputs in Mandeo and time recovering differences after an oil spill. All areas showed metal concentration above the sediment quality guidelines proposed values by the NOAA, numbers established by OSPAR, and concentrations established by the UE about seafood.

Keywords: Heavy metals, Galicia, bivalves, sediment, contamination.

1. Introduction

Galicia is located in the North-West of the Iberian Peninsula and its coast cannot be described as a whole, there are many variables and characteristics that define the different sampling regions. These variables are the climate, the local oceanography and the lithological characteristics (Santiago Rivas, 2007). Among these, the most important characteristic for this study is the lithology of the region as it will determine the sediment enrichment by different metals. As a summary of the lithological information, there can be described three different coastal zones: the Cantabric part, which is mainly composed by schists, gneiss, and also sedimentary and ultrabasic rocks; approaching the west coast, there is a wide part formed by the Golfo Ártabro, composed of granite and schists and the west coast which is largely granitic (Carballeira et. al 1997). In general terms, Galician coastline covers 1.195 Km from the Eo river in the border with Asturias to the Miño in Pontevedra, besides, Galicia has 278 sandy areas as well as 70 million m^2 of intertidal zone (Mahou Lago, 2008).

Therefore, shellfishing is a very important economic activity. The following species were sampled, *Mytilus galloprovincialis*, *Cerastoderma edule*, *Ruditapes decussatus*, *Venerupis pullastra*, *Ensis siliqua* which Galician names are as follows: mexillón, berberecho, ameixa fina, ameixa babosa and longueirón. According to the data published by the Galician technological fishery platform (http//:www.pescadegalicia.com) the sum of the catches of these species (except *Mytilus galloprovincialis*) accounted for the 53,12% of the total fresh catches in 2013, being *Ruditapes decussatus* the most abundant with the 25,45% of the total captures. Also in 2013, the 70,09% of the captured *Ruditapes decussatus* and the 47,85% of *Venerupis pullastra* came from Arousa an area that encloses several of the sampled stations in Riveira.. These species are very important for this economic activity as *Ruditapes decussatus*, *Venerupis pullastra* and *Cerastoderma edule* were in 2013 the 5th, 7th and 15th most important species for Galician fisheries.

Both species of clams, *Ruditapes decussatus* and *Venerupis pullastra* live buried in the sand and mud in the Rías, *Venerupis pullastra* can be found from the low tide limit to 40 m depth , while *Ruditapes decussatu*s, prefers to live between 15 and 20 cm depth of the intertidal zone. *Cerastoderma edule* lives just under the bottom surface on sand, mud and gravel bottoms and it can be found from the intertidal zone to only a few meters depth (FAO), razor shells (*Ensis siliqua*) also live buried in sandy or muddy bottoms, on the contrary, mussels (*Mytilus galloprovincialis*) live fixed to the rocks, in dense aggregations, in the intertidal zone or exposed, this characteristic together with both high filtration rate and bioaccumulation abilities makes mussels good organisms for monitoring the quality of the water column.

Despite of shellfishing being and activity with such economic importance, there is a high risk of contamination as 40% of the population live in or near the Rías, and the main industrialized areas are also located nearby (Rubio et. al 2000). The industrial waste reaching the sea through atmospheric precipitation and dumping of urban and rural waste is mostly responsible for the input of trace metals into the marine environment, besides all the sedimentary changes produced by the construction of hotels, and urban and recreational areas.

Water analyses are the obvious methods for determining the degree of pollution, but these tests aren't easy to perform, metal concentrations are very low and samples can be contaminated during the sampling process, consequently these analyses are not very efficient. However, metals are easily fixed to suspended solid materials, and thus it will lead to their incorporation to the sediments (Rubio et. al 2000). For this reason, sediments accumulate contaminants and might act as long-term stores for metals in the environment (Spencer et. al 2002). Metal ions can be incorporated into food chains and concentrated in aquatic organisms to a level that affects their physiological state. Heavy metals have a drastic environmental impact on all organisms. Although trace metals such as Zn, Cu and Fe play a biochemical role in the life processes of all aquatic plants and animals; therefore, they are essential in the aquatic environment in trace amounts (Saeed et. al 2008).

In this study the metals that were studied are Vanadium, Arsenic, Copper, Chromium, Zinc, Manganese, Cobalt, Barium, Lead, Boron and Mercury. **Arsenic** is one of the most dangerous elements because of its toxicity. The intake over long periods can lead to chronic arsenic poisoning and it is one of the few substances that have been shown to cause cancer in humans (WHO, 2010). **Copper** is relatively abundant on the lithosphere, it is an essential element for living organisms, both in animal and plants, as it is very important for the photosynthesis and for the formation of the erythrocytes and the immunological system of vertebrates, though, in high concentrations, can be lethal. **Chromium** is also relatively abundant in the Earth's crust and it is essential for animals. **Mercury** is the only element that can occur in a liquid and vapour phase at ambient temperature. It is characterized by its high toxicity in virtually all pathways; inhalation, ingestion, contact dermal... besides the damage it does, particularly in the nervous system, with the emergence of epilepsy, but also for causing dementia, and death caused by severe poisoning. In addition, it is one of the trace elements with lower representation in the Earth's crust. **Vanadium** is an ubiquitous element in the lithosphere, presenting a significant dispersion, due to that, it might appear in more than 60 different minerals. This element isn't considered very toxic, but can produce harmful effects on several species. **Zinc** is also widely distributed and it is an essential micronutrient, yet in high amounts it might be phytotoxic. **Manganese** is a metallic transition element, very abundant in the lithosphere, with the exception of iron, its concentrations are usually higher than other micronutrients. Its importance lies in the fact that it is a part of enzymes such as oxidoreductases, transferases or hydrolases. **Cobalt**, also a metallic transition element, is quite abundant, it is essential for animals as it is a part of the vitamin B12. It is important as well for blue-green algae and nitrogen fixing organisms, but not for plants. **Barium** is relatively abundant as a constituent of different minerals. **Lead** has a low bioavaiability, however, in industrial or urban areas, concentrations in air and soil are frequently enough high to produce toxic effects on humans and organisms. **Boron** is a trace element essential for plants (Vázquez et. al 2008).

Table 1

Sampled areas in this study and analysed species for each of them, with the correspondent sampling dates and coordinates for each station.

Area	Station	Code	Location	Sampling date	Species[1]				
O Burgo	Areal grande	B1	43° 20' 22" N 8° 22' 51" W	21 April 2003	Rd	Ce	Mg		
	Areal pequeno	B2	43° 20' 18" N 8° 23' 10" W	29 April 2003	Rd	Ce		Vp	
	Carniceiro	B3	43° 20' 18" N 8° 23' 11" W	21 April 2003		Ce	Mg	Vp	
	As Maruxas	B4	43° 19' 36" N 8° 24' 30" W	21 April2003	Rd	Ce		Vp	
Mandeo	Souto	M	43° 19' 32" N 8° 12' 11" W	16 May 2003	Rd	Ce	Mg		
Ribeira	Insua	R1	42°33´17´´N 08°59´17´W	16 July 2003				Vp	
	Eguas	R2	42°32´57´´N 08°58´57´W	16 July 2003				Vp	
	Area secada	R3	42°32´32´´N 08°59´02´W	16 July 2003				Vp	
	Arribó	R4	42°32´18´´N 08°59´04´W	16 July 2003				Vp	
Corrubedo	Ladeira 1	C1	42°34´35´´N 09°03´35´W	24 July 2003					Es
	Ladeira 2	C2	42°34´16´´N 09°02´53´W	24 July 2003					Es
	Ladeira 3	C3	42°34´02´´N 09°02´40´W	24 July 2003					Es

[1] Rd: *Ruditapes decussatus*, Ce: *Cerastoderma edule*, Mg: *Mytilus galloprovincialis*, Vp: *Venerupis pullastra*, Es: *Ensis siliqua*.

2. Materials and methods

2.1. Sampling and processing

Sediment samples and organisms were collected from April to July 2003 in four Galician shellfishing areas with high social and economic relevance, O Burgo, Mandeo, Riveira and Corrubedo. Several locations were selected within each area (Fig.1, Table 1) according to their environmental characteristics and degree of human impact.

The area of **Mandeo** (site M) is located within the Ría de Betanzos, currently one of the largest marshlands in Galicia, still has a small port and boats, at the confluence of the rivers Mendo and Mandeo embrace the urban area (www.turgalicia.es) This area is included in Natura 2000 network (DOG nº62 21/03/2014). **O Burgo**, located in Ría de O Burgo (B1 to B4) formed at the mouth of the river Mero is a sheltered zone with typical estuarine characteristics and a large population, it has historically been impacted by industrial contamination and urban waste. Nowadays, shellfishing in this area has been banned due to the presence of toxic muds, high microbiological contamination, spills and also lipophilic toxins like ASP produced by red tides (www.intecmar.org). **Riveira** (R1 to R4) is a very exposed area with a considerable population, and high density as this municipality is not very large. It has a very important artisinal fishing harbour and is the site of a large number of canned fish industries. **Corrubedo** (C1 to C3) is an area with typical oceanic characteristics and a small population, but frequented by tourists. Due to its ecological and environmental attributes its is included in Natura 2000 network (DOG nº62 21/03/2014). However, in November 2002, several months before the sampling, the area was heavily impacted by the Prestige oil spill. Various cleaning operations with different gears were carried out in the area, which altered coastal sediments. Organisms where collected when available. The main ones were mussels (*Mytilus galloprovincialis*),

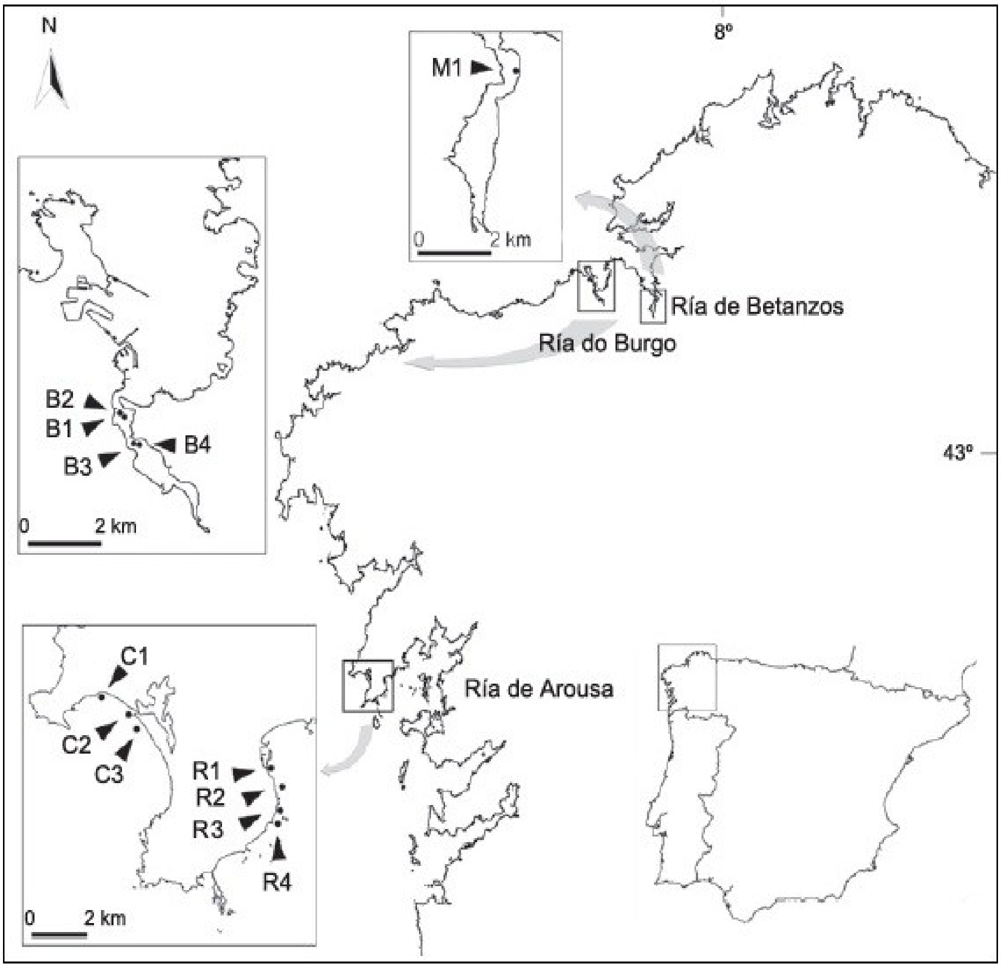

Fig.1. Map of the Galician coast (NW Spain) showing the main sampling locations and areas. Mandeo (M), O Burgo (B1 to B4), Ribeira (R1 to R4) and Corrubedo (C1 to C3). Obtained from Fernández et. al 2013.

clams (*Venerupis pullastra* and *Ruditapes decussatus*), cockles (*Cerastoderma edule*), and razor shells (*Ensis siliqua*). These species were collected by hand then cleaned eliminating the stomach contents by being kept in 15-20 μm filtered seawater for 48 hour (24 h for mussels). The individual maximum shell length was individually recorded, and then, pools (3-10 individuals) of shell-free organisms were frozen at -30ºC in amber glass vessels previously rinsed with 5% nitric acid for 48 hours.

Sediments were sampled at low tide using a

PVC core tube (Ø 4.5 cm), transported to the laboratory on ice and stored at 4ºC in the dark until use no more than 48 h after sampling. The sample cores were then transferred to glass jars and dried at room temperature for chemical analysis. As the sampling sites are areas where the sediments are often turned over for shellfishing, a randomly selected 15 cm layer was used for the analyses instead of the 2–3 cm of surface sediment usually collected for contamination studies.

The concentration of those metals whose concentration was under the detection limit of the device used to measure them, was assumed to be half of the limit of quantification (LOQ), the limit of quantification. The concentration from the sediments was normalized vy its background levels, based on the pedological, geological and chemical characteristics of the soil (Vázquez et. al 2008).

2.2. Physicochemical analysis

The dried sediment was sieved to obtain fractions >1000; 1000– 500 and <500 µm. The size distribution <500 µm was determined using a light-scattering particle size analyser Coulter LS 200 by laser Beckman coulter (Coultronics France), through 500–250, 250– 125, 125–62, 62–31, 31–16, 16–8 and 8–0 µm. The organic matter content (% OM) was estimated by dry sediment combustion at 500ºC for 4 h.

2.3. Chemical analyses

A total of 22 metals were analysed per sample. All analyses were carried out by the independent laboratory of the Servizos de Apoio á Investigación (SAI) of the University of A Coruña.

2.4. Statistical analysis

With the aim of determinating if the pollution produced by the different metals was caused by the same source, several correlations were carried, creating a correlation matrix and then the Pearson's product-moment correlation, all this after checking data normality with the Shapiro-Wilk normality test. Correlations were made between each metal concentration in organisms, sediments, grain size and percentage of organic matter.

R 3.0.1 was used for all the analysis.

3. Results

3.1. Grain size

Fig.2 Shows the grain size composition and organic matter percentage for the different areas. 71% of the sediments from O Burgo have a grain size between 250 and 125 µm, and thus could be classified as fine sand (0.25 – 0.1 mm) according to the USDA classifications. Corrubedo is also mainly composed of fine sand as the 61% of the sediments are between the same sizes. In Riveira particles are larger, as the 49% is between 250 and 125 µm and 39% is between 500 and 250 µm, being classified as fine and medium sand. Mandeo has the most homogeneous grain sizes but it has an important part of very fine sand (0.10 – 0.05 mm).

3.2. Organic matter

The highest organic matter content was found in Mandeo (7.53%). In the other areas the content of organic matter ranged from 1.09% to 2.79% (Fig. 3).

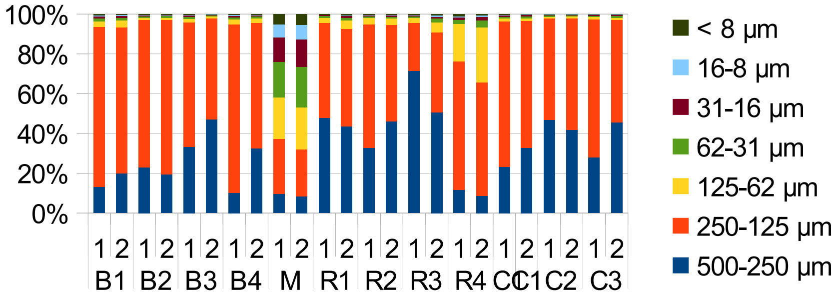

Fig.2. Grain size distribution.
((1)Surface strata 0-15 cm, (2) Deep strata 16-30 cm) from the areas of O Burgo (B1-B4), Mandeo (M), Riveira (R1-R4) and Corrubedo (C1-C3).

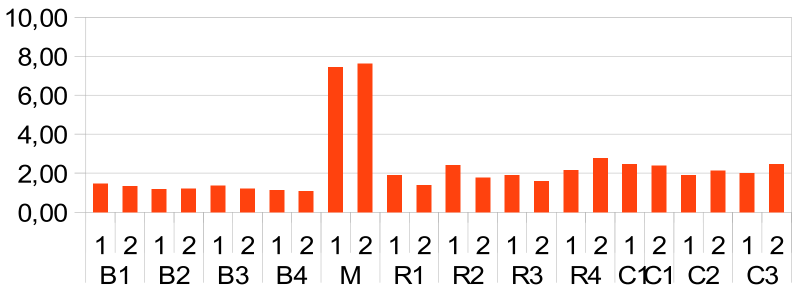

Fig. 3. *Organic matter percentage.*
((1)Surface strata 0-15 cm, (2) Deep strata 16-30 cm) from the areas of O Burgo (B1-B4), Mandeo (M), Riveira (R1-R4) and Corrubedo (C1-C3).

3.3. Pollutant concentrations3.3.1. Biota

Organisms from O Burgo have the lowest concentration of pollutants (never reaching 1ppm in total). However in Mandeo, Riveira and Corrubedo the total average concentration of the different heavy metals is close to 107.000 ppm (Fig.4 and 5). *Mytilus galloprovincialis*, is the most polluted organism, probably due to its ability to concentrate, and under certain conditions, accumulate contaminants in their tissues with respect to the ambient level (Casas et. al 2006). In O Burgo and Mandeo (the area where this mussel was collected) its total pollutant concentration is almost 3 times higher than the other organism*s.* However the pollutant concentration of V*enerupis pullastra* from Riveira and *Ensis siliqua* from Corrubedo is not very high, it is respectively 2.35 and 35.1 times higher than their surrounding sediments, showing the possibility of having similar bioaccumulation abilities, in lower extent than mussels, when their environment is polluted.

3.3.2. Sediments

The station of Souto (M) from the area of Mandeo is the most polluted, with a total average concentration (different depths) of heavy metals on the sediments of 221.350,32 ppm, 1,4, 4,9, and 71,7 times higher than the total average concentration in the other areas, O Burgo, Riveira and Corrubedo respectively. This also shows that, in comparison, the pollution in Corrubedo is very low.

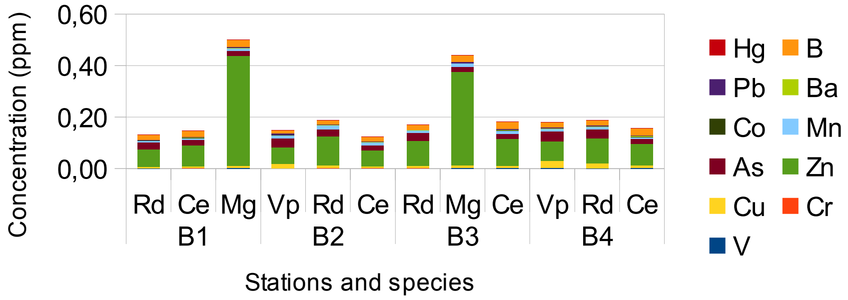

Fig .4. Heavy metals on Galician shellfish commercial species from O Burgo (stations B1 to B4).
Rd: *Ruditapes decussatus*, Ce: *Cerastoderma edule*, Mg: *Mytilus galloprovincialis*, Vp: *Venerupis pullastra*, Es: *Ensis siliqua*.

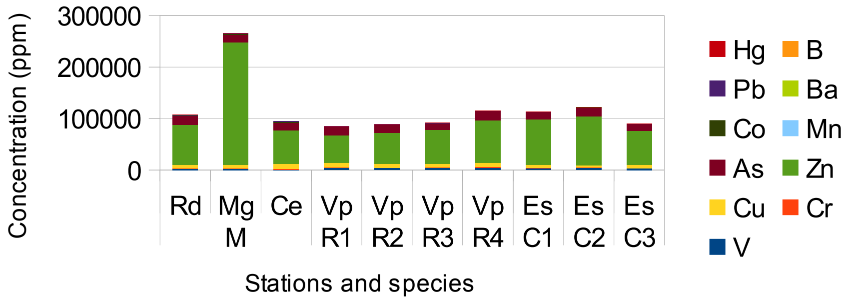

Fig.5. Heavy metals on Galician shellfish commercial species from Mandeo (M), Riveira (R1-R4) and Corrubedo (C1-C3)**.**
Rd: *Ruditapes decussatus*, Ce: *Cerastoderma edule*, Mg: *Mytilus galloprovincialis*, Vp: *Venerupis pullastra*, Es: *Ensis siliqua*.

Looking at the concentration on the sediments of each station, it shows up, that the site B4 from O Burgo, is equally or more polluted than Mandeo, in Riveira the total average concentration, increases from R1 to R4 (from the inside to the outside of the ría) being R4 2,5 times more contaminated than the previous stations. Corrubedo has the lowest total average concentration of metals. On the other hand, if we look at the different strata were the sediment samples were collected (Fig. 6), from 0 to 15 cm and from 16 to 30 cm, comes out that in O Burgo, the surface sediments are more polluted than the deep ones, the metal concentration of the upper strata is 1,5 higher than the lower strata. In Riveira is the opposite, the deep strata is 1,45 times more polluted than the surface strata, this difference is higher at the station R4 were the concentration of the deep strata is 2,2 times higher. For the stations M, C1 and C3 of Mandeo and Corrubedo, the difference of the concentration between the sediments of different depths is minimum, nevertheless, in C2 the metal concentration of the surface sediments is again higher than the deep sediments, specifically, 1,8 times higher.

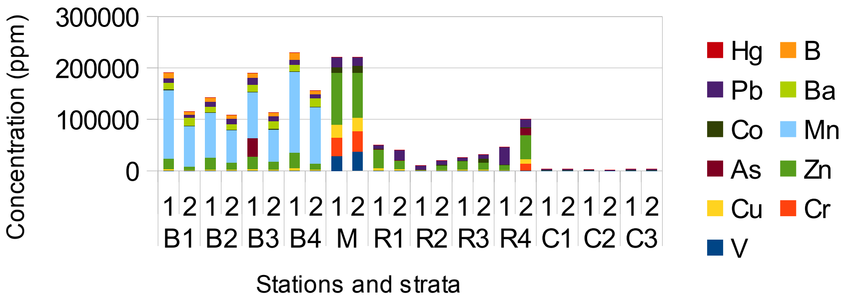

Fig.6. Heavy metal concentrations of both stratafrom the areas of O Burgo (B1-B4), Mandeo (M), Riveira (R1-R4) and Corrubedo (C1-C3). *(1)Surface strata 0-15 cm, (2) Deep strata 16-30 cm*

3.3.3. Metals

3.3.3.1. Vanadium

There were 22 sediment samples (Table 2) which were below the LOQ, only 2 samples had a significant concentration, an average of 32.852 ppm, being the second highest total concentration.

The average concentration on the different organisms was 1.449 ppm, being 3.187 ppm for Mandeo, Riveira, and Corrubedo and $1,7.10^{-3}$ ppm for O Burgo, it was the fourth highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Zn and Co. On the other hand its concentration on different bivalves was highly correlated (p-value<0,01) with Cr, Cu, Zn, Hg and B.

It is also very correlated to the organic matter percentage and the grain size.

3.3.3.2. Chromium

There were 21 sediment samples which were below the LOQ, only 2 samples had a significant concentration, an average of 29.762 ppm, being the third highest total concentration.

The average concentration on the different organisms was 368 ppm, being 810 ppm for Mandeo, Riveira, and Corrubedo and $9,5.10^{-4}$ ppm for O Burgo, it was the fifth highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Cu, Co Zn and V. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with As, Cu, Co, Hg, Zn, Pb and V.

It is also very correlated to the organic matter percentage and the grain size.

3.3.3.3. Copper

One sediment sample was below the LOQ, 23 samples had a significant concentration, an average of 4.449 ppm, being the tenth highest total concentration.

The average concentration on the different organisms was 3.266 ppm being 7.186 ppm for Mandeo, Riveira, and Corrubedo and $1{,}1.10^{-2}$ ppm for O Burgo, it was the third highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Cr. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with Zn, Pb, Co, Hg and V.

It is also very correlated to the organic matter percentage and the grain size.

3.3.3.4. Zinc

There were 7 sediment samples which were below the LOQ, 17 samples had a significant concentration, an average of 28.417 ppm, being the fourth highest total concentration.

The average concentration on the different organisms was 40.627 ppm, being 89.379 ppm for Mandeo, Riveira, and Corrubedo and $1{,}4.10^{-1}$ ppm for O Burgo, it was the highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Cr, Co, Hg, B and V. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with As, Cr, Cu, Co, Pb, Hg and V.

It is also very correlated to the organic matter percentage and the grain size.

3.3.3.5. Arsenic

There were 22 sediment samples which were below the LOQ, only 2 samples had a significant concentration, an average of 6.791 ppm, being the ninth highest total concentration.

The average concentration on the different organisms was 6.795 ppm being 15.346 ppm for Mandeo, Riveira, and Corrubedo and $2{,}6.10^{-2}$ ppm for O Burgo, it was the second highest total concentration.

Its concentration in then different bivalves was highly correlated (p-value<0,01) with the concentration of Cr, Co, Cu, Zn and Hg.

3.3.3.6. Manganese

Only in the stations from O Burgo sediments were sampled and analysed, 8 in total counting both strata, they had an average concentration of 97.912 ppm, being the highest total concentration.

The average concentration on the different organisms in O Burgo, the only area that were analysed was $9{,}6.10^{-3}$ for , the tenth highest total average concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Zn.

3.3.3.7. Cobalt

All samples had a significant concentration with an average 7.152 of ppm, being the tenth highest total concentration.

The average concentration on the different organisms was 261 ppm being 574 ppm for Mandeo, Riveira, and Corrubedo and $6{,}6.10^{-4}$ ppm for O Burgo, it was the second highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Cr, Zn and V. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with As, Cr, Cu, Zn, Ba, and Pb.

It is also very correlated to the organic matter percentage and the grain size.

3.3.3.8. Barium

Stations from O Burgo were the only sites were sediments and organisms were sampled and then analysed for this element, they had an average concentration of 13.441 ppm, being the fifth highest total concentration.

The average concentration on the different organisms in O Burgo was $1{,}7.10^{-3}$, the lowest total concentration.

Its concentration in the different bivalves was highly correlated (p-value<0,01) with the concentration of Co.

3.3.3.9. Lead

All samples had a significant concentration with an average 9.423 of ppm, being the sixth total concentration.

The average concentration on the different organisms was 318 ppm being 700 ppm for Mandeo, Riveira, and Corrubedo and $6{,}6.10^{-3}$ ppm for O Burgo, it was also the sixth highest total concentration.

Its concentration in the different bivalves was highly correlated (p-value<0,01) with the concentration of Cu, Cr, Co, Zn and Hg.

3.3.3.10. Boron

There were only 8, they had an average concentration of 8.778 ppm, being the seventh highest total concentration.

The average concentration on the different organisms in O Burgo, the only area that were sampled was $2{,}2.10^{-2}$ for , the ninth highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Zn and Mn. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with V.

3.3.3.11. Mercury

There were 20 sediment samples which were below the LOQ, only 4 samples had a significant concentration, an average of 121 ppm, being the lowest total concentration.

The average concentration on the different organisms was 33 ppm, being 73 ppm for Mandeo, Riveira, and Corrubedo and $1{,}6.10^{-4}$ ppm for O Burgo, it was the eight highest total concentration.

Its concentration in the sediments was highly correlated (p-value<0,01)with the concentration of Zn. On the other hand its concentration in different bivalves was highly correlated (p-value<0,01) with As, Cr, Cu, Zn, Hg, and V.

3.4. Statistical analysis

The Shapiro-Wilk normality test showed that all the variables (the analysed metals) had a normal distribution (p-value<0,01). Pearson's correlation test applied to the metal concentrations for both sediments and biota did not show any significant correlation, however the resulting p-value for the correlation between Zinc from both sediments and organisms was 0,08, thus, not significant. The same analysis for both correlations between metals and organic matter and metals and the grain size (the percentage with a size between 125 and 250 µm) was significant for the same metals, Chromium, Copper, Cobalt, Vanadium and Zinc, all the p-values were lower than 0,01, with the exception of Zinc for the correlation with the grain size, that was between 0,01 and 0,05. The analysis carried between all the different metals from sediments and biota showed many correlations, 35 out of the total 55 different combinations had a significant correlation (p-value<0,01) and 4 had a weak correlation (0,01<p-value<0,05). The other two correlations carried between the metals and the sediment concentrations and between metals and their concentration in the different organisms showed similar results. In the first case, 10 combinations were significantly correlated (p-value<0,01) and 4 had a weak correlation (0,01<p-value<0,05). In the case of the concentration on the organisms, tests showed that 25 out of the 55 possible metal combinations were strongly correlated (p-value<0,01) , and again 4 had a weak correlation (0,01<p-value<0,05).

4. Discussion

The most polluted area was Mandeo (M) for both sediments and bivalves. Stations from O Burgo also had high metal concentrations in sediments, but there were low for the organisms. Riveira and Corrubedo had the lowest concentrations in their sediments, specially Corrubedo. Referring the differences found in the metal concentration of the different strata, the upper stratum from B2 (O Burgo) and the deep stratum from R4 (Riveira) had concentrations that stand out above the rest.

Organisms from O Burgo had the lowest concentration of metals in their tissues, 550.000 times lower than the rest of the organisms sampled , the average concentration was 0,21ppm. This, together with the fact that it is the second most polluted area (average metal concentration of 155.000 ppm) could reveal an error during the sampling of the organisms, since bivalves have high bioaccumulation capacities and thus are used for monitoring, and the data of the organisms of this area does not reflect it.

Metal concentration on the rest of the organisms from the other sampled areas, does show their bioaccumulation ability, since the metal concentration in their tissues is higher than the concentration measured on the sediments.

Studies of monitoring are mainly focused on coastal areas, like those ones that were sampled for this study, because the response of the ecosystem to pollution control measures can be best assessed there, close to discharge and emission sources. Bivalve molluscs, in particular mussels (in our case the species *Mytilus galloprovincialis*), constitute one of the best biological indicators of coastal pollution because they exhibit several unsurpassed advantageous characteristics like their sedentary nature, wide geographical distribution, in general there are enough individuals at the sampling sites , they can be sampled easily and of course because they accumulate pollutants as contaminant levels in their tissue respond to changes in the environmental levels and pollutants accumulate with little metabolic transformation (Besada et. al 2011). Mussels from this study came to have the highest metal concentration among all the bivalves.

Correlation tests (See supplementary material) showed that in both sediments and organisms many metals' concentration was correlated, but looking at the metal correlations in sediments and organisms separately, it comes up the number of correlations in sediments is much smaller, this could mean that metals found in organisms, and their concentration, are assimilated in a similar way, and thus many of them are correlated. However, in the sediments, there are not so many correlated metals because of they may have came from different discharges, with different concentrations of metals and thus not being related to each other.

The same metals are correlated to the percentage of organic matter and with the grain size between 125 and 250 µm, Co, Cr, Cu, V and Zn. The accumulation of heavy metals in sediment is controlled by the granular composition of sediment. Grain size affects the surface area, settling velocity and depositiong rate of suspended solids in the water column, as well as the degree of chemical partitioning onto the sediment. Metals are generally found to be associated largely with the fine grain fraction of sediment that has been traditionally used to study the pollution of heavy metals in sediments. However, heavy metals sometimes accumulate in the coarse grain fraction sediment (Lin et. al 2003). In these case the linear correlation coefficient was negative, showing that contaminants accumulate in the finer sediment fraction. Regarding to the organic matter, the most polluted area is also the one with the highest content of organic matter, which agrees with the fact that metals are easily fixed to suspended solid materials, and thus incorporated to the sediments.

The National Oceanic and Atmospheric Administration (NOAA, 1999) have created sediment quality guidelines (SQGs) intended to be used, among other things, for compare the degree of contamination among sub-regions and to identify chemicals elevated in concentration above the guidelines that were also associated with measures of adverse effects (See supplementary material). They established two factors to compare our data, the ERL and the ERM. The ERL or “Effects Range-Low” are the 10th percentile values and indicate concentrations below which adverse effects rarely occur, the ERM are the “Effects Median-Range” and they are the 50th percentile which represent concentrations above which effects frequently occur. Al the data that were above the LOQ were, in general, much higher than the ERMs. However, these guidelines just gives us illustrative values as, they are American and thus have reference values from the local sediments.

OSPAR convention has also created an Agreement on Background Concentrations for Contaminants in Seawater, Biota and Sediment (OSPAR, 2005-6), were they define the term “Background concentrations” or BCs, which are assessment tools intended to represent the concentrations of certain hazardous substances that would be expected in the North-East Atlantic if certain industrial developments had not happened. Mussels from O Burgo have concentrations below the range background concentration but no those ones from Mandeo.

The European Union has also created a list with the Heavy Metal Maximum Contents in food products (UE, 2014), it includes the legislation for the EU countries but also the limit concentrations for other countries outside the European Union. According to this list, the allowed content for lead is exceeded by the clams and mussels from Mandeo. The concentration of Mercury is exceeded by all the species from Riveira and the mussels and clams from Mandeo, but not the cockles. The contents of As, Cu, Cr are also exceeded by all the species from Mandeo, Riveira and Corrubedo.

Different reports, of the same topic show lower metal concentrations in the Rías of Betanzos, Coruña and Arousa, areas were our stations were located. Saavedra et. al (2004), in their study, they explain that Redondela, in the inner part of Ría de Vigo, appears to be a major point of contamination as it has the highest industrial and urban activity in Galicia, for this, they used mussels to measure the concentration of different metals, in our case, mussels from Mandeo, exceed measured values in Redondela in a great extent (See supplementary material). Prego et. al (2003), measured metal concentrations in sediments and organisms from different parts of Galicia, data from the Rías that both reports have analysed compared with the analysed samples in this study shows again that our measured concentrations for both sediments and organisms are much higher.

After the comparison of the data with these guidelines and values, it shows up the worrisome fact that almost all the samples had metal concentrations that exceeded, by far, the acceptable concentrations, consequently, these ecosystems and their equilibria might be endangered as well as the people from these areas.

5. Conclusions

The data and results provided by this study, about heavy metals on sediments and bivalves from the Galician coast, agrees with the conclusions of other reports about metal contamination, reinforcing the fact that these areas are polluted by giving new information about the situation of the studied areas.

Despite of the scarcity and unbalanced data some certain statements can be performed: bivalves' bioaccumulation abilities result in the correlation of the accumulated metals. The lack of metal correlation on sediments could be a proof of different metal inputs. Mandeo is the most polluted area for both organisms and sediments. Sediments from Corrubedo have the lowest metal concentrations although razor shells show similar values than those measured in other species in Mandeo; O Burgo, it is the opposite case, sediments have really high concentrations and organisms have the lowest. These disparities in O Burgo may reflect either a lack of metal bioavailability due to physic-chemical local conditions or an error during the sampling or processing of the samples

In the contrary Riveira and Mandeo showed a high consistency in correlations among metals in both organisms and biota and also organic matter and grain size, showing that for an adequate assessment, this factors should be taken into account;

This study also supports the use of bivalves for environmental monitoring, specially mussels (and razor shells must be explored), and contributes with new data on the situation of this areas and how this species of high commercial interest are affected by inputs from different sources.

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References

Besada, V., Andrade, J.M., Schultze, F., González, J.J., 2011. Monitoring of heavy metals in wild mussels (Mytilus galloprovincialis) from the Spanish North-Atlantic coast. Constinental Shelf Research, 31, p.457-465.

Carballeira, A., Carral, E., Puente, X.M., Villares, R., 1997. Estado de la conservación de la costa de Galicia. Nutrientes y metales pesados en sedimentos y organismos intermareales. Universidade de Santiago de Compostela, Xunta de Galicia, Consellería de Pesca, Marisqueo e Acuicultura.

Casas, S., Bacher, C., 2006. Modelling trace metal (Hg and Pb) bioaccumulation in the Mediterranean mussel, Mytilus galloprovincialis, applied to environmental monitoring. Journal of Sea Research, 56 (2), p.168-181.

Cobelo-García, A., Labandeira, A., Prego, R., 2005. Dos casos opuestos en la acumulación de metales en el sedimento de una ría: Ferrol y Corme-Laxe (Galicia, NO Península Ibérica). Ciencias Marinas 31 (4), p.653–659.

Food and Agriculture Organization of the United Nations <http//: http://www.fao.org>.

Instituto tecnolófico para para o control do Medio Mariño en Galicia <http//:www.intecmar.org>.

Lin, J.G., Chen, S.Y., Su, C.R., 2003. Assessment of sediment toxicity by metal speciation in different particle-size fractions of river sediment. Water Science and Technology, 47(7), p.233-241.

Mahou Lago, J.M., 2008. Implementación y Gobernanza: La política del Marisqueo en Galicia. Escola galega de administración pública (EGAP). Santiago de Compostela, p.310.

NOAA, 1999. Sediment quality guideline developed for the National Status and Trend Programs. <http//:http://ccma.nos.noaa.gov/publications/sqg.pdf>.

OSPAR, 2005-6. Agreement on background concentrations for contaminants in seawater, biota and sediment.

Plataforma Tecnolóxica da pesca. Consellería do medio rural e do mar. Xunta de Galicia. <http://www.Pescadegalicia.com>.

Prego, R., Cobelo-García, A., 2003. Twentieth century overview of heavy metals in the Galician

Rías (NW Iberian Peninsula). Environmental pollution, 121, p.425-452.

R Core Team, 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. < http://www.R-project.org>.

Rivas, S.S., 2007. Contribución a la determinación de la fracción de metales traza ligados a las proteínas similares a las metalotioneínas en muestras de mejilló. Santiago de Compostela: Universidade. Servizo de Publicacións e Intercambio Científico. ISBN: 978-84-9750-858-2

Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in sediments of the ría de Vigo (NW Spain): an assessment of metal pollution. Marine Pollution Bulletin, 40, p.968–980.

Rubio, B., Nombela, M.A., Vilas, F., 2000. Heavy metal pollution in the Galician Rías Baixas: new background values for Ría de Vigo (NW Spain). Journal of Iberian Geology, 26, p.121-141.

Saavedra, Y., González, A., Fernández. P., Blanco, J., 2004. Interspecific variation of metal concentrations in three bivalve mollusks from Galicia. Archives of Environmental Contamination and Toxicology, 47, p.341-351.

Saeed, S.M., Shaker, I.M., 2008. Assessment of heavy metals pollution in water and sediments and their effect on oreochromis niloticus in the northern delta lakes. 8th International Symposium of Tilapia in Aquaculture

Xunta de Galicia, 2014. Decreto 37/2014, de 27 de Marzo, por el que se declaran zonas especials de conservación los lugares de importancia comunitaria de Galicia y se aprueba el Plan director de la Red Natura 2000 de Galicia. Diario Oficial de Galicia, 62, p. 13472.

Spencer, K.L., MacLeod, C.l., 2002. Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards. Hydrology and Earth System Sciences, 6(06), p.989-998.

UE, 2014. Contenidos máximos en metales pesados en productos alimenticios. <http//:http://plaguicidas.comercio.es/MetalPesa.pd >.

Vázquez, F.M., De Anta, R.C., 2008. Niveles genéricos de referencia de metales pesados y otros elementos traza de suelos de Galicia. Xunta de Galicia, Consellería de Medio Ambiente e Desenvolvemento Sostible.

WHO, 2010 Preventing disease through healthy environments. Exposure to arsenic: A major public health concern. <http//: http://www.who.int/ipcs/features/arsenic.pdf>.

Xunta de Galicia (2014, March 31). *Betanzos-Mandeo.* Retrieved from: <http//:http://www.turgalicia.es/ficha-recurso?langId=es_ES&cod_rec=16869&ctre=9>.

Appendix. Supplementary material

Fig. 1. Heavy metals from surface sediments (0 to 15 cm depth) from the areas of O Burgo (B1 to B4), Mandeo (M), Riveira (R1-R4), Corrubedo (C1-C3), contribution of each metal to the total metal content.

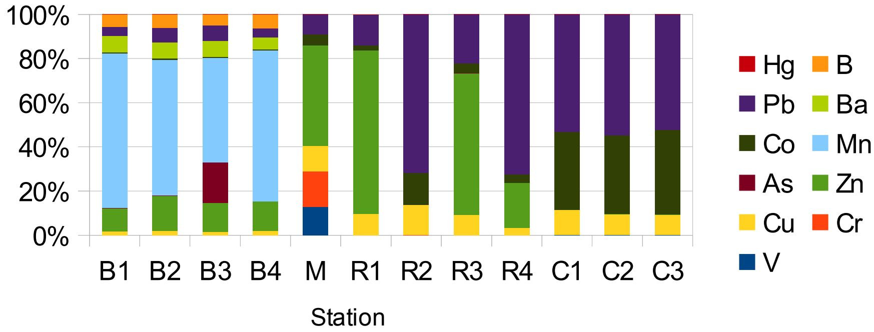

Fig. 2. Heavy metals from deep sediments (16 to30 cm depth) from the areas of O Burgo (B1 to B4), Mandeo (M), Riveira (R1-R4), Corrubedo (C1-C3), contribution of each metal to the total metal content.

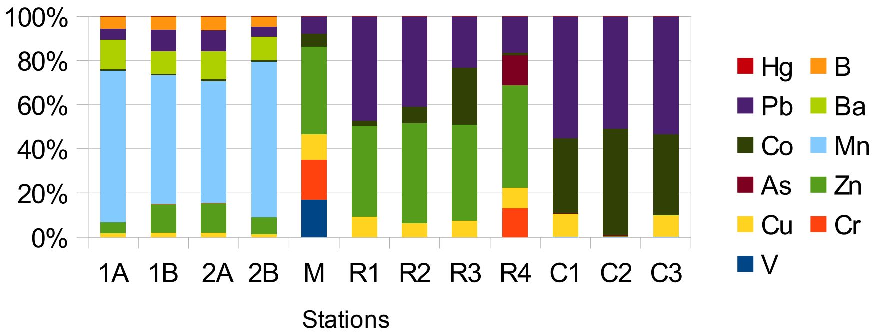

Fig. 3. Heavy metals on Galician shellfish commercial species from the areas of O Burgo (B1 to B4), Mandeo (M), Riveira (R1-R4), Corrubedo (C1-C3), contribution of each metal to the total metal content. Rd: *Ruditapes decussatus*, Ce: *Cerastoderma edule*, Mg: *Mytilus galloprovincialis*, Vp: *Venerupis pullastra*, Es: *Ensis siliqua*.

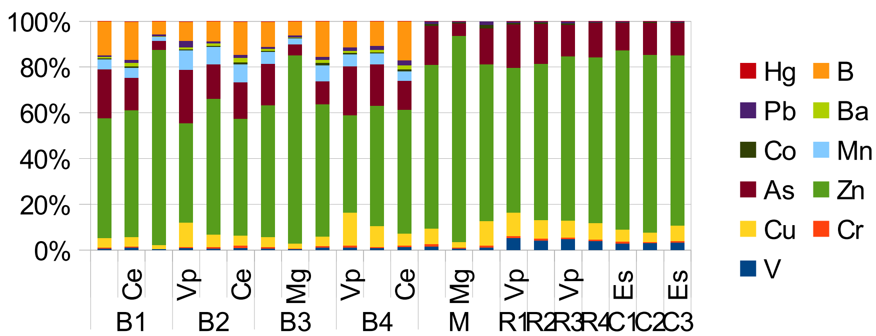

Table 1. ERL and ERM values of the Sediment Quality Guidelines from NOAA.

Sediment Quality Guidelines, NOAA		
Metals	**ERL**	**ERM**
As	8,2	70
Cr	81	370
Cu	34	270
Pb	46,7	218
Hg	0,15	0,71
Zn	150	410

Values of ERL and ERM in ppm.

ERL: Effects Range-Low

ERM: Effects Median-Range

Data from NOAA (1999)

Table 2. Heavy metal range concentration on mussels (*Mytilus galloprovincialis*) from three Galician Rías (Arousa, O Burgo and Ares-Betanzos) and Redondela, inner Ría de Vigo

Ría/Metal	As	Co	Cr	Cu	Hg	Mn	Pb	Zn
Arousa		5,4-7,2	4,1-5,9	32.7–138		2.3–5.5	1.9–11.9	195–717
Burgo		3.5–8.7	5.8–10.7	31.6–83.0		4.3–9.9	11.8–26.5	346–718
Ares-Betanzos		3.7	7.2	45.3		5.4	23.4	777
Redondela	2,2		0,20	22	0,04		0,4	1,6

Data from Arousa, O Burgo and Ares-Betanzos from Prego et. al (2003). Data about Redondela from Saavedra et. al (2004).

Table 3. Heavy metal range concentration on sediments from three Galician Rías (Arousa, O Burgo and Ares-Betanzos).

Ría/Metal	As	Co	Cr	Cu	Hg	Mn	Pb	Zn
Arousa		9-16	2-1700	4-365	0,3	120-3590	25-325	20-400
Coruña	0-15	12-16	0-115	0-315	0-0,1	170-500	0-460	0-1300
Ares-Betanzos	5-20	12-16	0-28	0-65	0-0,44	170-1320	2-95	0-250

Data from Prego et. al (2003)

Table 3. and 4. Correlations between metals and percentage of organic matter and metals with the percentage of grain size between 250-125µm respectively.

Correlation metals of sediments %OM			Correlation metals of sediments grain size %[250-125µm]		
Metal	**p-value**	**LCC[1]**	**Metal**	**p-value**	**LCC[1]**
Co	8.11e-08	0.8583705	Co	0.0008692	-0.6344459
Cr	2.94e-13	0.9565437	Cr	0.003611	-0.5703735
Cu	6.864e-10	0.9102846	Cu	0.005331	-0.5503137
V	1.739e-12	0.948752	V	0.003205	-0.5762802
Zn	2.187e-06	0.8042133	Zn	0.01285	-0.4999885

[1]: Linear correlation coefficient

Table 5. Correlated metals in sediment samples from the different areas (O Burgo, Mandeo, Riveira and Corrubedo).

Correlated metals for sediments					
Pairs of metals	**p-value**	**LCC[1]**	**Pairs of metals**	**p-value**	**LCC[1]**
Cr-Cu	< 2.2e-16	0.9794501	Cr-Co	3.359e-08	0.8699451
Cr-Zn	8.483e-10	0.9084683	Cr-V	3.042e-14	0.964775
Co-Zn	9.57e-06	0.7728571	Co-V	1.864e-09	0.9013743
Zn-Hg	0.00171	0.6056749	Zn-B	0.005023	0.8695358
Zn-V	1.082e-07	0.8543487	Mn-B	0.0034	0.8859317
Weak correlations*					
Cr-Hg	0.02306	0.4619245	Cr-Pb	0.04605	0.4109607
Co-Ba	0.04563	0.7163005	Zn-Pb	0.01051	0.5121814

[1]: Linear correlation coefficient

**: 0,01<p-value<0,05*

Table 6. Correlated metals in organisms samples from the different areas (O Burgo, Mandeo, Riveira and Corrubedo) and species (mussels, clams, cockles and razor shells).

Correlated metals for organisms					
Pairs of metals	**p-value**	**LCC[1]**	**Pairs of metals**	**p-value**	**LCC[1]**
As-Cr	8.982e-10	0.9235253	As-Cu	1.545e-12	0.9601533
As-Co	5.399e-05	0.7522045	As-Zn	1.834e-05	0.7803926
As-Hg	4.225e-08	0.8857785	Cr-Cu	1.082e-07	0.8738638
Cr-Co	1.174e-06	0.8373359	Cr-Zn	1.232e-07	0.8721269
Cr-Hg	2.681e-07	0.861125	Cr-Pb	1.147e-07	0.8730848
Cr-V	0.000707	0.6664695	Cu-Co	3.59e-06	0.8164189

Cu-Zn	0.0001603	0.719535	Cu-Hg	8.788e-05	0.7381582
Cu-Pb	7.645e-07	0.8446717	Cu-V	1.181e-06	0.837243
Co-Zn	0.0009766	0.6533637	Co-Pb	2.986e-12	0.95739
Co-Ba	6.058e-05	0.9018963	Zn-Hg	5.946e-06	0.8060258
Zn-Pb	3.244e-05	0.7659861	Zn-V	0.003257	0.5984592
Hg-Pb	0.006929	0.5582741	Hg-V	3.386e-06	0.8175839
B-V	0.003689	0.7657782			
Weak correlations*					
As-B	0.01201	-0.6956001	Cr-Ba	0.03166	0.6195756
Co-Hg	0.01962	0.4934024	Pb-V	0.01964	0.4933573

[1]: Linear correlation coefficient

**: 0,01<p-value<0,0*

Table 7. Correlated metals for both organisms and sediment samples from the different areas (O Burgo, Mandeo, Riveira and Corrubedo) and species (mussels, clams, cockles and razor shells).

Correlated metals for sediments and biota					
Pairs of metals	**p-value**	**LCC[1]**	**Pairs of metals**	**p-value**	**LCC[1]**
As-Hg	0.0008736	0.4740923	Zn-Mn	5.903e-09	0.9242609
Cr-Cu	8.882e-16	0.8788884	Zn-Hg	1.944e-07	0.6806564
Cr-Co	1.621e-14	0.8611839	Zn-Ba	8.578e-06	0.8224338
Cr-Mn	6.359e-09	0.9236127	Zn-B	1.716e-12	0.9699207
Cr-Pb	0.001986	0.444185	Zn-V	0.003441	0.4225384
Cr-Ba	1.599e-14	0.9822003	Cu-Co	7e-10	0.7631588
Cr-B	9.041e-10	0.9388827	Cu-Zn	3.106e-06	3.106e-06
Cr-V	< 2.2e-16	0.9468565	Cu-Mn	2.709e-13	0.9755546
Mn-Pb	1.051e-06	0.8617178	Cu-Hg	8.097e-05	0.5479241
Mn-Ba	2.376e-08	0.9111044	Cu-Pb	0.007245	0.3908095
Mn-B	5.995e-15	0.9840675	Cu-Ba	4.537e-08	0.904205
Mn-V	6.359e-09	0.9236126	Cu-B	< 2.2e-16	0.997806
Pb-Ba	1.978e-08	0.9129654	Cu-V	< 2.2e-16	0.8968562
Ba-B	3.56e-08	0.9068537	Co-Mn	1.169e-10	0.95156
Ba-V	1.599e-14	0.9822003	Co-Pb	0.0004384	0.4972768
B-V	9.041e-10	0.9388827	Co-Ba	4.019e-12	0.9668984
B-Pb	1.169e-08	0.9180766	Co-B	1.588e-12	0.9701831
			Co-V	1.004e-13	0.8482131
Weak correlations*					
Cr-Zn	0.01688	0.3506711	Hg-V	0.03892	0.3055538
Cr-Hg	0.02555	0.3290687	Pb-V	0.02348	0.3335751

[1]: *Linear correlation coefficient*

**: 0,01<p-value<0,05*

Table 8. Metal average concentrations on sediments (from all the areas, O Burgo, Mandeo, Riveira and Corrubedo) below the limit of detection, samples below the LOQ, and ordered respecting to their abundance.

	V	Cr	Cu	Zn	As	Mn	Co	Ba	Pb	B	Hg
<LOQ	2	3	23	17	2	8	24	8	24	8	4
[Sed]	32852	29672	4449	28417	6791	97912	7152	13441	9423	8778	121
Rank	2nd	3rd	10th	4th	9th	1st	8th	5th	6th	7th	11th

<LOQ Number of sediment samples with metal concentration below the limit of quantification (LOQ)

[Sed]: Average metal concentration on sediments, without the samples with concentrations below the LOQ.

Rank: Ordered metal concentrations, related to each other.

Table 9. Metal average concentrations on organisms (mussels, cockles, clams and razor shells) from O Burgo, Mandeo, Riveira and Corrubedo. Ordered respecting to their abundance.

	V	Cr	Cu	Zn	As	Mn	Co	Ba	Pb	B	Hg
[B]	1,74E-3	9,46E-4	1,06E-2	1,37E-1	2,62E-2	9,63E-3	9,56E-4	1,76E-3	2,63E-3	2,16E-2	1,56E-4
[MRC]	3187	810	7186	89379	15346	0	574	0	700	0	73
[T]	1449	368	3266	40627	6975	5,25E-3	261	9,58E-4	318	1,18E-2	33
Rank	4th	5th	3rd	1st	2nd	10th	7th	11th	6th	9th	8th

[B]: Average metal concentration on organisms from O Burgo.

[MRC]: Average metal concentration on organisms from Mandeo, Riveira and Corrubedo.

[T]: Total average metal concentration, from all areas (O Burgo, Mandeo, Riveira and Corrubedo).

Rank: Ordered metal concentrations, related to each other.

TRABAllO FIN DE GRAO

Nuria Fernández Rodríguez e Ramon Muíño Boedo autorizan a presentación do Traballo de Fin de Grao “Analysis of pollution by heavy metals in sediments and species of commercial interest of the Galician coast” presentado por Marta Gil Molinero para a súa defensa ante o tribunal calificador.

En A Coruña, a 22 de xullo de 2014

Asdo.: Nuria Ferández Asdo. Ramon Muíño