Impact of mine tailing on SGD-driven metal fluxes in Portman Bay

Treball de fi de Grau

Ciències Ambientals

Tutors:
Jordi Garcia Orellana

Aaron Alorda Kleinglass

UAB
Universitat Autònoma
de Barcelona

icta

**Institut de Ciència
i Tecnologia Ambientals-UAB**

June 2016

Bellaterra

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*"...come on you target
for faraway laughter,
come on you stranger,
you legend, you martyr,
and shine!"*

Shine on you crazy diamond

Pink Floyd

Acknowledgments

0.   <u>Justification</u>

An environmental problem is defined by a variation of the normal conditions of an environment, creating a problem that affects all the different parts that are related to it (Figure 0.1). In our case, in Portman, there was a variation on the conditions of the bay because of the mining. In the 1960's, while the principles of the environmental sciences were established in USA, on the other side of the Atlantic, in Spain, the major environmental catastrophe of the Mediterranean Sea was just starting. The magnitude of its problem didn't just affect biological and landscaping issues, it spread its roots to all the sectors that an environmental problem is defined for.

The geological structure and composition of the "Sierra Minera" was affected because of the mining activities, empting mantles materials and redistributing the tailings around the altered mountains. The geochemistry and hydrochemistry of the bay changed in a radical way, creating low pH waters and metal remobilization. Marine and terrestrial lives were affected too, with the destruction of entire ecosystems with the creation of open pit mines. Marine environments and habitats vanished with the disappearance of the bay. Even the surrounding marine environments where compromised by the increase of metals concentrations.

But, this environmental catastrophe that was evidenced in the 70's, does not just affect external human factors. The landscape of the entire Sierra Minera has modified. Maritime transportation vanished, with a lower sea level inside the bay. The economic collapse dragged all the population related into a social collapse. No jobs were offered, unemployment raised up, poverty started to be a pattern, plus a massive emigration to find new opportunities. And the health of the community did not escape neither form the effects of the tailings inside the bay. Because of the high concentration of Pb, Hg and As, people breath the dust that is spread from the sediments to village, and accumulate those inside their organisms. This same dust flies to all the crops that are in the surrounding zone, so people and animals are accumulating little amounts of these metals.

Even though, environment also means policy. Ecologists and social organizations had been fighting for a solution since the 1980's. Press covered actuations like Greenpeace and society started to pressure harder to politicians. After a decade of continuous social pressure, authorities started to act in 1991 with the stop of discharges inside the bay. Ecologists, social organizations, administration and the mining company agreed to find a solution. After more than two decades a national program, with European funding, was design to correct the environmental impact in the area in order to try to restore the bay. However, until today, no actions have been taken. Nonetheless this final project of an environmental science degree, is part of a national project called "NUevos REtos en la investigación de cañones submarinos" (NUREIEV), coordinated by the Universitat de Barcelona and the Universitat Autonoma de Barcelona. Where we will analyze the mobilization of metals from the bay into the sea by Submarine Groundwater Discharge (SGD) as an estimation of the quantity of dissolved metals that are being introduced into the sea and affecting its environment.

In the Environmental Science degree of the Universitat Autònoma de Barcelona there are many subjects related to the impact of the human on the environment and several of them are focused on them. Although several teaching examples always can help to understand the complications

of several environmental problems, the opportunity of working directly on a real unsolved environmental catastrophe may help to a future environmentalist to understand which can of work can be developed in the future carrier. Thus, the final project of an environmental science degree can be used as an integration tool of many concepts that were presented during the four years. This final project represents an ambitious work where part of the most important environmental catastrophe of the Mediterranean Basin is partially studied.
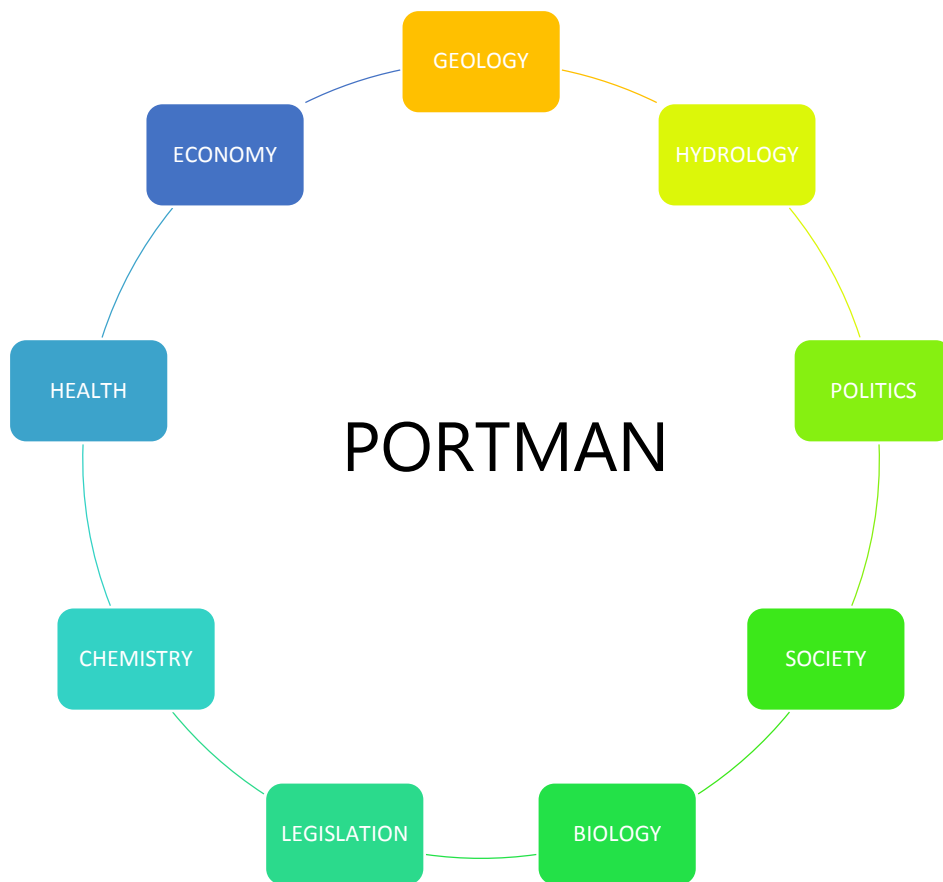
Figure 0. 1. Scheme of Portman's environmental problems

1. <u>Introduction</u>

1.1.   History of Portman Bay

Portman is situated in the south west of the Mediterranean Sea, more specifically in the region of Murcia (Spain), situated at the end of the "Sistema Bético" in "Sierra de Cartagena touching the Mediterranean Sea.
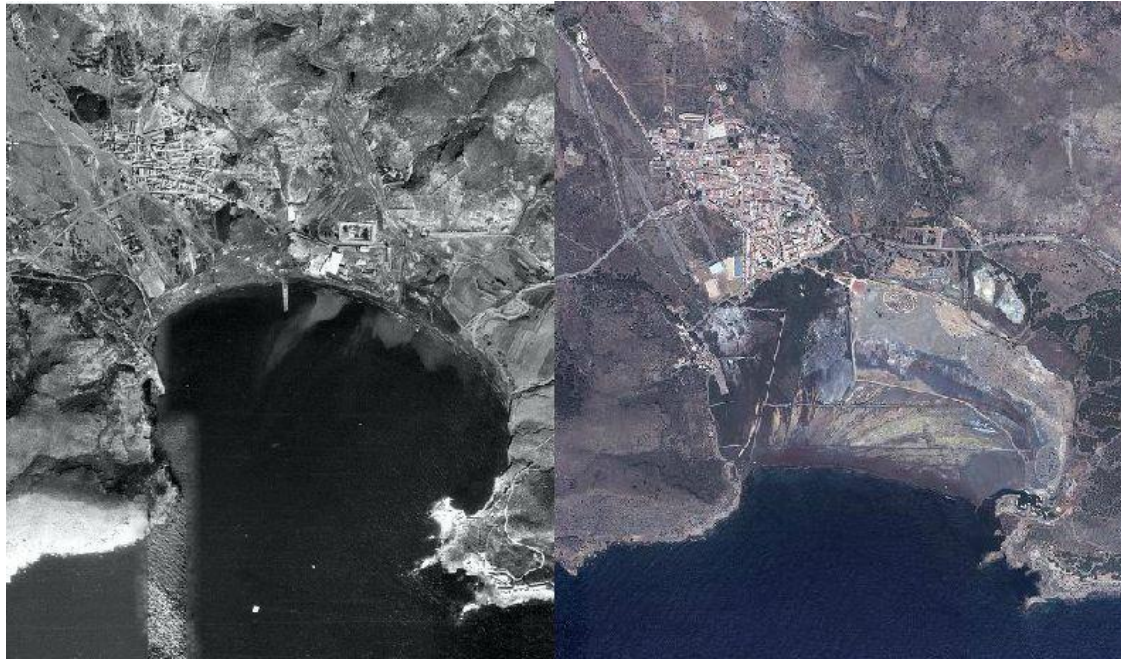
Figure 1. 1. Evolution of the bay (1957-2013) (www.worldpress.com).

Because of the high concentrations of lead and silver contained in it is mountains, this zone has been exploited since the Carthaginians in the 3rd Century B.C., followed by the romans in the 2nd Century B.C, known as Portus Magnus (Big port), which became one of the largest commercial and strategical points of the empire. In the XIX and XX century it became one of the most important and richest regions of Spain, due to its mining activity (Lorenzo Solano, 1986). At the beginning of the XX Century the decadence of this sector started. The principal factor that affected this crisis was that the technologies used to extract the minerals were dated, been to unproductive as it was slow and requiring a big workforce. Plus, the First World War finished and the financial system was in bankrupt (crisis 1929). All this factors contributed to the drop of mineral prices, minor exportations and increscent of the extraction cost (Isabel Banos-Gonzalez and Pedro Baños Páez, 2013). But it is not until 1957 that the small underground exploitation stops, and the open pit exercise introduced by "Socidad Minero Metalúrgica Peñarroya España" (SMMPE) starts (Oyarzun et al., 2013). From this moment on, the big transformation of this little mining village and, the environmental catastrophe starts.

1.1.1.   Peñarroya activity

Once the mining company Peñarroya had the control of the zone, it starts to practice of open pit mining, instead of the tunnels system that they had exercised before. They started to dynamite all the old galleries and to open different pits along the mountain system. All the minerals extracted from the pits were transported to the "Lavadero Roberto", a processing mineral installation that separated the lead (Pb) and zinc (Zn) from the rest of the material. The process was very simple, minerals like galena (PbS), sphalerite (ZnS) or pirite (FeS_2) and the other materials were introduced into two different grinding procedures so the head was as thin as

possible (Oyarzun et al., 2013). After that they introduced it into diverse baths. The mineral they were interested in (Pb and Zn) remained inside the bubbles, and the gangue was eliminated and deposited inside the bay, what is commonly called the forth flotation procedure (Kawatra, 2011).

Because of the accumulation of the tailings inside the bay, SMMPE designed a pipeline that transported the gangue from "Lavadero Roberto" to "Punta de la Galera", a strategical point where the waste was not supposed to return into the bay. Once that was done, the tailings were moved and stored by the dominant currents in the coastline. Those currents change seasonally, depending on the winds that are predominating in each season (Figure 1.2.A). Therefore, in summer, the drift currents move tailings clockwise, starting entering into the bay form the southwest and leaving from the southeast, producing the infilling of the tailings. Meanwhile, during winter, drift currents move counterclockwise from southeast to southwest. Plus, another current moves from east to west without entering into the bay (Pauc and Thibault ,1976). Referring to the amounts of waste deposited into the sea (Oyarzun et al., 2013), it is calculated that more than 57 million tons of tailings, created in 34 years (1957-1991), produced an advancement of the shoreline of 650 meters into the sea (Figure 1.2.B,C). As we can see in Figure 1.2.D, different layers were formed, alternating yellow slimes, clays and sulfates with black magnetite sands.
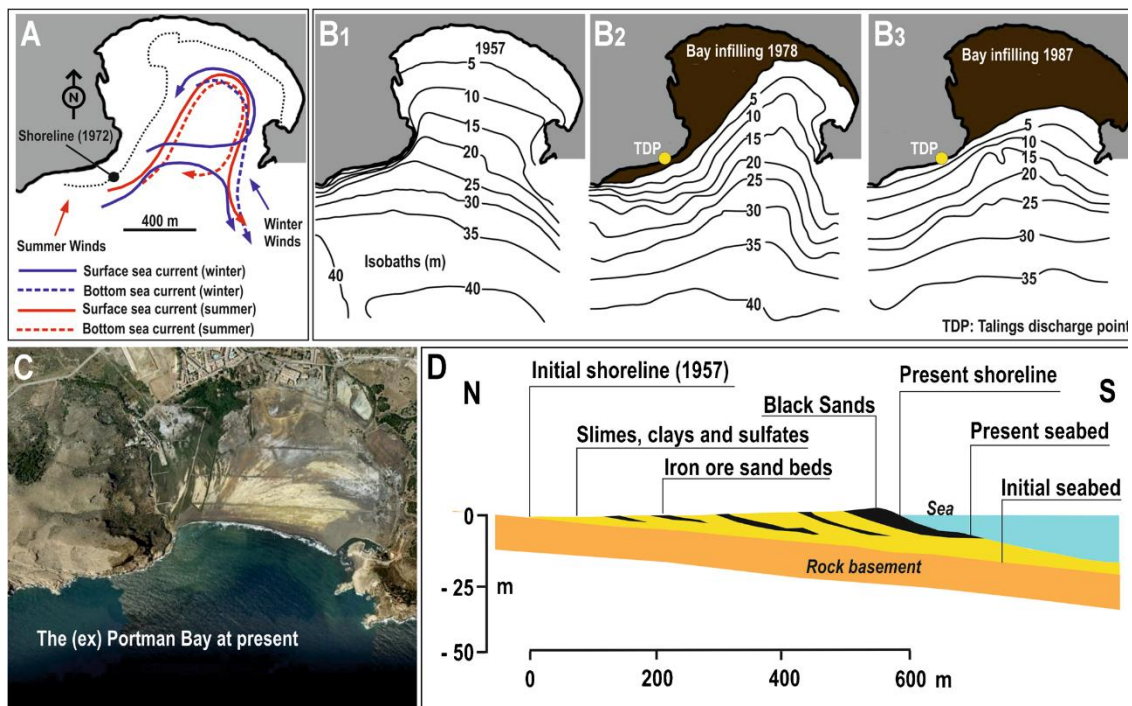
Figure 1. 2. Infilling evolution of Portman (Manteca et al., 2014)

By the time SMMPE bought the mining rights and started the open pit mining, all the villages along the "Sierra de Cartagena" were coming from a rising moment in its history, where people were creating great wealth from the mining activities, transportation and business. Work was demanded, workers where offered a house, and the local economy was in its best moment. By the moment SMMPE arrived, Portman was a small town where little mining activities and fishing were the motors of the bay. The new company was well received in Portman bay, people were given a job and house, in property of the company because the terrain where it remained was

theirs. The village lived a new expansion and new generations started their lives in the bay. Generations replaced the jobs of their ancestors in the mine. This led to a new social structure.

Fishermen activities and families started to disappear from the social tissue because of the contamination. At the same time, mining started to monopolize the economy and lives of the Portman's Bay society. In the decade of 1970, the effects of the pollution where so big that the bay already had a completely different configuration than it had twenty years ago. The problem was so big, even the central government authorized a renovation of the mining permit, allowing to SMMPE to throw form 3000 t·day^{-1} to 6000 t·day^{-1} of tailing directly to the sea. It was not until the 1980's that social pressure started against the pouring of tailings into the sea, with the consequent silting and contamination of the bay and its surroundings. In 1986 Greenpeace manifestations became important enough to stop for several moments the pipeline and normal function of "Lavadero Roberto". This mobilization increased with the bad conditions of work and salaries that miners had to suffer. In the end, in 1988, because of the instability with the workers, plus the financial bankrupt of SMMPE, the company is sold to "Portman Golf S.A" a new company that had new ideas for the bay, including remodelizacion of the entire bay structure, converting most of the lands into a touristic site. In other words, converting the mining town into a touristic complex (Isabel Banos-González and Pedro Baños Perez, 2013).

1.1.2. Portman Golf S.A

In this new paradigm, as we know from Jose Anduca and Daniel Portero, miners started to fear for their jobs. They knew that the new company had no intentions to continue with the old business, so their syndicate went to speak with the new owners to find answers. The result of the first contact between the two parts was that:

-   They would not be any layoffs.
-   All miner would continue with their job for 5 more years.
-   After the period of closing, workers would be introduced into the construction or the service sector.
-   People who had their house in Portman Golf's property would have a new home if theirs had to be destroyed for the new project.
-   They would have a new and better life.
-   The regeneration of the bay would be completed in a few years, so contamination would not be a problem anymore.
-   Hotels and chalets would attract new people into the bay.

Nevertheless, political and social pressure continued on Portman Golf S.A. Until 1991, when the deposition of tailings into the sea finally stopped. From this moment on, miners started a strike, closing themselves inside Lavadero Roberto, to make sure that the conditions of the old company were respected. Syndicate and company initiated dialog, but as they conversation advanced, the company became reluctant to offer more. The anger and frustration of the miners was so intense that they broke in the owner's chalet and did as much destruction as they could. As a consequence, after this episode, the company blackmailed the syndicate to stop the strike. If they refused, they would take the syndicate, but not the miners, to court. In the end, the syndicate accepted that miners would be fired and no money would be given, and therefore the company did not press charges.

Once tensions had calmed, Portman organized its population to be represented by "La Liga de Vecinos de Portman" which would fight for the regeneration of the bay. After years of conversations and negotiations between the neighbors of Portman, administration and Portman Golf S.A they settled an agreement.

Because of the debt that the company had contracted, and its financial bankruptcy, the central government of Spain would pay for the regeneration of the bay, financed by the European Union. Half of the terrains and the major part of the houses that were from Portman Golf S.A would be given to the citizens of Portman.

But before this agreement, several events happened (Isabel Banos-González and Pedro Baños Perez, 2013):

In 1995 the guidelines were approved for the land use plan (LUP) for Portman Bay and "Sierra minera", even though, one week later, after the elections, the program was suspended and, in 2004 it was canceled with no exercise executed. One year later, in 1996 the Ministerio de Obras Públicas, Transportes y Medio Ambiente published the public tender of the environmental impact study (BOE de 21/02/1996), in which they were committed to add that the tailings had to be deposited in San Jose's short. Incidentally due to the guidelines, and change of government, it was suspended. Afterwards, in 1997 the central government dictated a new project to drain the sediments in Escombreras port, thus the European money for the regeneration of Portman's bay was canceled. In 2001 an agreement was signed between the administration and the private sector to start working on the regeneration of the bay. Later on in 2002 Portman Golf S.A signed a concession in order to make a technical report about the situation of the bay. After two years, in 2004 the new government approves a new agreement between the administration and the private sector to started working on the regeneration of the bay. The same year, the Ministerio de Medio Ambiente releases a document with the three alternatives for the restoration of the bay:

- o 1. Sealing of the tailings.
- o 2. Restoration of the beach 250m further to the sea respect the position in 1957, plus a sport port.
- o 3. Restoration of the beach 100m further to the sea respect the position in 1957, plus a sport port.

In 2005 the Ministerio de Medio Ambiente decided that the best alternative was the idea of sealing the bay. The reaction of the village and the ecologists against that decision was to create a fourth alternative that should be considered. Also, a manifestation on the beach with a photo of a human message saying "NO AL SELLADO", no to the sealing. The new alternative proposed the full regeneration of the bay, plus the old fishing port, (incorporated in BOE nº45 2011). A year after the project IN SITU was approved. In 2007 the administration announces the beginning of the pilot works by the company TRAG-SATEC with the collaboration of the Universidad de Murcia. The company would have a budget of 118.97 million euros to complete the entire project and finalized in 2011. And finally, in 2013 the second part of the project was supposed to start, but since 2012 it is completely stopped by the administration.

Figure 1. 3. Virtual model of the 4th alternative. (Isabel Banos-González and Pedro Baños Perez, 2013)

1.1.3. Actuality

Today, in 2016, the project still has not started. The budget that new companies are talking about is, more or less, 20 million euros, fact that makes the original idea impossible. Several trimmings are done to reduce the budget and important parts of the project are never going to be done (Jose Anduca y Daniel Portero).

In this new scenario, the neighbors of Portman do not know what to do. They feel cheated by the administration and the companies. They see how their children have to breathe every day arsenic, lead, cadmium from the sand of the bay. Many people have left the town to go to a better place to leave, as they see nothing is going to be done. Daniel Portero and Jose Anduca, president and vice president of the La Liga de Vecinos de Portman, remain stick to their ideas. They keep fighting for the bay, and even though the local, regional or central administration is interested in repairing the problem, they prefer to ignore it.

1.2.   Groundwater flows

In the following part of the introduction, the importance and significance of groundwater flows will be explained.

1.2.1. SGD

Groundwater has always been a fundamental asset in human's lives. All places were fresh superficial water is not the most common or abundant thing, people had engineered to get that water "that came from the inside of mountains or from the underground". Wells, fountains and oasis had been the main providers of fresh groundwater for thousands of years, making possible human civilization in places like desserts or savannas, even for the Mediterranean culture, it has been one of the most important assets for its development. Nevertheless, it was not until this last century that the global community has realized that fresh water is not unlimited, and most rivers and lakes that had been the largest providers of fresh water, are now contaminated or dry. It is then when the focus of countries and the scientific community started to investigate the importance of fresh groundwater.

1.2.1.1.   Characteristics

Submarine Groundwater Discharge (SGD) has been a controversial term to define. Burnnet et al., (2003) defined it as "any and all flow of water in continental margins from the seabed to the coastal ocean, regardless of fluid composition or diving force", but it does not include processes as deep hydrothermal circulation, fluid expulsion at convergent margins and density-driven cold seeps on continental (Burnett et al., 2003). In our study, we do not contemplate small and short scale mechanisms of pore water flow, such as bioirrigation or shear flow, that are unusually not quantified using the commonly applied SGD techniques and models (Santos et al., 2012). So we can define SGD as Moore (2010) said, "SGD is the flow of water through continental margins form the seabed to the coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition or diving force". That includes, as Burnett et al., (2006) said:

-   Hydrothermal oceanic circulation.
-   Exit fluxes in convergent margins.
-   Cold water filtrations due to a pressure difference in continental coast.

As in figure (x), we can describe SGD when leads into the sea in to three different sources (Taniguchi et al., 2002):

a.   Meteoric fresh groundwater.
b.   Saline groundwater, recirculated seawater through the coastal aquifer.
c.   Connate groundwater, whose salinity has been raised by dissolution of salts within the aquifer.

While the most common in coastal settings is fresh groundwater and recirculated seawater (Rodellas, 2014), the mixing of salty and fresh groundwater through coastal aquifers mostly depends on (Moore, 1999):

-   Terrestrial and marine forces.
-   Nature of costal settings.
     o   May be produced by assemblages of confined, semi-confined and unconfined systems.

Furthermore, we find subterranean estuaries in the coastal aquifers, where meteoric fresh groundwater mixes with seawater that has introduced itself into it (Moore, 1999), zones that act similarly to estuaries, transferring freshwater loaded with metals, nutrients and other constituents to coastal waters (Beck et al., 2010).

SGD is affected by the multiple factors that affect coastal zones, as aquifer characteristics, coastal geomorphology, temporal variability and the major physical (five) forces that drive groundwater to the sea (Santos et al., 2012). Terrestrial hydraulic gradient, is the major factor that interferes with the SGD movement, caused by the hydraulic difference, in the saturated zone, among two different hydrologic points, thus follows Darcy's law. In other words, it is the difference between the aquifer's recharge and discharge points conditioned by the geological matrix, precipitation and evapotranspiration (Burnett et al., 2003). Large seasonal oscillations can produce the recoil of the freshwater mass, hence drive the seawater into the coastal aquifer (Michael et al., 2005). Oceanic forces, such as tidal pumping, waves, storms, or sea level fluctuation produce seawater infiltrations because of the gradient pressure produced. The movement of pore water through a permeable barrier, as a consequence of the variance level

of two water masses, is another driven flux to consider (Reich et al., 2002). Also, density-driven convection of pore waters may develop when salinity or temperature of these differ from the overlying seawater. Nevertheless, we can't avoid the fact of anthropogenic acts, as waterproofing of the ground, water pumping, infrastructures… That also influence the equilibrium of freshwater and seawater in the interface, and its consequent seawater intrusion into the coastal aquifer because of the reduction of freshwater inflow (Cantero et al., 2016).

1.2.1.2.   Importance of SGD

The study of SGD has become a strategical asset for most of the countries of the Mediterranean or zones with none-permanent superficial stream systems, where SGD can be the major, or even the only, hydrologic connection between land and sea (Knee and Paytan, 2011). The magnitude of this issue has been benefiting society in several ways, from drinking water as the only source of irrigation to sustain communities, transporting nutrients, organic matter and fresh water, to coastal zones and, creating hot spots of biomass production and fishing spots. Its magnitude in global scale reaches from 0.2 to 10% of the total surface water inputs (Burnett et al., 2003). Even in the Atlantic it is estimated that the flux of SGD represents up to an 80 to a 160% of the total amount of the inputs of freshwater (Moore et al., 2008).

Nevertheless, we can emphaticize the importance of SGD into two parts (Rodellas, 2014):

-    <u>Hydrogeological importance.</u>
     Water of proper quality has become a strategical resource for social and economic development, as its need for drinking water and also as its use for agriculture. Nowadays, it is more common to speak about drought, fresh water importation and contaminated water, than talking about crystalline and potable water. For these reason, UNESCO (2004) says that the discharge of fresh groundwater should be considered as a waste, because the fresh groundwater discharge has the potential to be used as a freshwater source. The quantification of SGD in exploited coastal aquifers is crucial for its maintenance. If it is not considered overexploitation, it can be produced and several damages can be produced, such as terrain subsidence, salinization of the aquifer or groundwater depletion. That is why a correct knowledge of the aquifer and the consideration of the SGD process are so important to maintain the survival of communities around the entire world. As UNESCO published in 2001, 50 % of the population lived in the further 200km from the coast in 2001, and where there will live 6.300 million people in 2050, the 75% of the total population.

-    <u>Biogeochemical importance.</u>
     Submarine Groundwater Discharge is recognized as an important mechanism for transferring material from land to sea (Moore, 1999). Water goes from the inland ground to its ending destination, the sea, transporting all kind of compounds in it, metals, nutrients, carbon, pollutants, etc., where its concentrations will be an average of the natural and anthropogenic compounds. The discharge of this material into the sea can have profound ecological implications (Knee and Paytan, 2011), creating phytoplankton blooms, promoting eutrophication of coastal waters (Hwang et al., 2005).
     "Trace metals (such as Ag, Cd, Co, Cu, Fe, Hg, Ni, Pb or Zn) can become naturally enriched in groundwater due to its prolonged interaction with the metal-containing aquifer substrate", Rodellas (2014). Metals are part from the common chemical structure of

matrix soils. When groundwater goes through it, several reactions might occur, modulated by pH, oxidation-reduction potential, salinity and abundance of colloids (Beck et al., 2007). Depending on the substrate where those reactions are formed, water will transport a different proportion of metals and species, producing one or other reactions to the environment where it is diffused. Several studies had been done in different soils and environments, such like mining districts in Gorguel bay by Trezzi et al., (2016) with higher Zn and Pb fluxes than Rodellas et al., (2014), in Palma de Mallorca, or Tovar-Sánchez et al., (2014), in the Western Open Mediterranean Sea. Most of metals are key points, working as micronutrients for the majority of ecosystems, as Fe, fact that makes SGD one of its major suppliers (Windom et al., 2006). But it can also be a toxic provider of Pb or Hg. In conclusion, SGD plays a major role in the transporting pathway from ground to sea ecosystems, but always dependent on its soil matrix, making an ecosystem spread or disappear.

Other compounds might be transported to, such as carbon, fuels, pharmaceuticals, insecticides, artificial compounds, etc. That might affect the ecosystem where are discharged in function of their composition.

1.2.1.3.   Quantification SGD fluxes

Numerous methods had been designed to detect and quantify SGD, because of its complexity discharge process, underground nature, and heterogeneity; it makes it a difficult asset to follow.

a. Thermal imaging has been used to detect SGD wherever there is a difference between the seawater temperature and the discharge water's temperature (Johnson et al., 2008). Using thermal infrared imaging (TIR), SGD can be viewed in any scale, from satellite imaging to ground detection with portable TIR technologies.

b. A common technique to describe underground in geology is to measure electrical resistivity. This technic, by the difference of salinities, allows to identify and map freshwater and seawater interference.

c. Seepages meters were created to quantify the loss of water trough irrigation canals by Isralesen and Reeve in 1944. But it was not until Lee (1977) adapted this technic to quantify SGD. The instruments are compound by a metal ring covered on one side and pushed into the sediment on the other. SGD moves through the sediment pushing the column of seawater inside the chamber. This one moves into the plastic bag that's situated above and accumulated. In function of the amount of water moved into the plastic bag and the time that has passed, the flux is calculated. The main problems with these methodologies are that we can't extrapolate small scale procedure to represent the entire study zone (Michael, 2003), plus, it can't be practiced in rough environments and there can't be any preferential pathways for SGD, as karstic or volcanic environments Burnett et al., 2006).

d. Water balances are calculated in function of the inputs and outputs of a system. If we can calculate precipitation and the total amount of outputs, the difference it would be the SGD, supposing that inputs and outputs are equal. The major problems of those balances are that, the system has to be described into the last detail, all directions and flows of water have to be controlled and quantified, the system can't be changed during

the calculation, which normally can't be controlled as such detail. Moreover, recirculation in coastal aquifers is not considered.

e. Tracer technics normally use chemical tracers that can be found naturally in the coastal groundwater with low reactivity (Moore, 2010). The major advantage of those is that they are present in the aquifer and introduced into the water column by all the SGD pathways, allowing small-scale spatial and temporal monitoring of SGD (Burnett et al., 2001). We use two main procedures to analyse natural geotracers. On one hand, we can measure the concentration of the analyte compared to its concentration inside the sea, and on the other hand we can make a vertical profile of the aquifer sediments, always supposing that the distribution is vertically. Yet, the second technic is not functional in homogenies environments. Although the most common procedure is the first method described before, once we have the difference of concentrations, we can calculate the SGD mass flux or by the mass balance (Charette et al., 2006).

One of the best SGD tracers is radium (Ra), and one of its facts is that it is enriched in SGD compared to seawater, which behaves conservatively in marine environments (Charette et al., 2008). Furthermore, SGD is the dominant source of Ra isotopes (Beck et al., 2007; Garcia-Solsona et al., 2008; Moore, 1996). In addition, Ra isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) have half-lives between 3.7 days and 1600 years, fact that makes them a great tracer to see SGD fluxes in different scale times, that will permit differentiate different SGD sources in function of its residence time (Charette et al., 2008).

Most of those facts made Moore (1996) describe the basis of the SGD study by Ra isotopes. He distinguished five different paths to determine the importance of ocean and coastal aquifers exchange:

i.   Identify derivatives tracers of the aquifer that are not recirculated.
ii.   Calculate the exchange velocity from the aquifer to the sea.
iii.   Calculate the tracer flux among the aquifer to the sea.
iv.   Measure the tracer concertation inside the aquifer to know the fluid flux.
v.   Calculation of others parameter of the aquifer to calculate their fluxes.

By this investigation he opened an entire new way of investigating and calculating SGD in a more precise way, which will get a huge importance by the following decades.

1.2.2.   Ra-isotopes as tracers of SGD

In the following section we will explain we Ra-isotopes is a good tracer for SGD and its characteristics and how it is used.

1.2.2.1.   *Ra characteristics*

Radium, with the 88th number in the periodic table and symbol Ra, has an atomic mass of 226.0254 uma, and forms part of the alkaline earth metals, group 2. Nevertheless, its importance has been crucial for the society that now we live in, because it is the element that gave birth to the radioactivity, by Marie Curie in 1898.

Because of its natural precedence, from three of the natural disintegration chains (^{238}U, ^{236}U and ^{235}Th), it is present in most of the soils as a consequence of an alpha (α) disintegration of its father, Thorium (Th), an insoluble element that is present in most matrix rocks and soils, mostly in metamorphic and igneous rocks. In nature we can find the four Ra isotopes, ^{223}Ra, ^{224}Ra, ^{226}Ra,

[228]Ra, with their correspondent semidesintegration periods [223]Ra ($T_{1/2}$=11.4 d), [224]Ra ($T_{1/2}$=3.66 d), [226]Ra ($T_{1/2}$=1600 y), [228]Ra ($T_{1/2}$=5.75 y).

Ra can be in an ionic mode as Ra^{2+} thanks to its high electro-positivity. Its geochemical properties make it be associated to organic matter, as Mn or Fe oxides, inside the sediment (Charette and Sholkovits, 2006). But in dissolution, depending on salinity parameters, we will find it in different ways. If we are under conditions of freshwater, Ra will be associated to colloids, suspended particles, like clays or metallic hydroxides, or in minor proportion Ra^{2+} (Krest et al., 1999). When it gets in contact with salty water, interphase among the aquifer and sea, Ra starts to be replaced by sodium cations (Na^+) (Webster et al., 1995; Moore, 1996). Finally, when Ra is in a truly salty environment, the sea, gets a highly dissolved, complexed as $ClRa^+$ (Porcelli and Swazenski, 2003).

1.2.2.2.   SGD estimation methods

The first estimation of SGD using Ra isotopes was realized by Moore (1996) and repeated in other experiments with success like Garcia-Orellana et al., (2014), Trezzi et al., (2016), Garcia-Solsona et al., (2008), Moore et al., (2008), Rodellas et al., (2012) and others. It consists in calculating what he described as Ra exces (Ra_{ex}), the difference among inputs and outputs in a steady state. What can be calculated, in function of the isotope as:

$$^xRa_{ex} = \frac{[^xRa - {}^xRa_{ocn}] \cdot V}{\tau_w} + [\lambda \cdot {}^xRa \cdot V] - [F_{sed} \cdot A_{sed}] - [^xRa_{Riv} \cdot F_{Riv}] \quad (1.1)$$

Where:

- ^xRa: The average activity of the isotope in the study zone.
- $^xRa_{ocn}$: The activity in the sea.
- V: the volume of the study zone.
- τ_w: The time residence of the water.
- λ: The decay constant of the isotope.
- F_{sed}: The diffusive Ra flux from sediments.
- A_{sed}: The bottom area of the study zone.
- $^xRa_{Riv}$: The activity in the river.
- F_{Riv}: The river flow.

Once we know the $^x Ra_{ex}$, we can divide it with the Ra isotope activity of the SGD endmember, to determine the SGD flow.

$$SGD = \frac{^xRa_{ex}}{^xRa_{gw}} \quad (1.2)$$

Where $^xRa_{gw}$ it is the Ra isotope activity of the SGD endmember.

In 2000, Moore (2000) described a second way to calculate de SGD flux, in controlled eddy diffusive mixing, where Fa short-lived isotopes distribution from the sea only are conditioned by diffusive mixing and decay. Assuming that all Ra inputs are at the shoreline, K_h (horizontal diffusion coefficient) can be determined by the corrected equations that Li and Cai (2011) determined with the advection offshore (u).

$$K_h = L_2^2 \lambda_2 + L_2 u = L_1^2 \lambda_1 + L_1 u \quad (1.3)$$

$$u = \frac{L_1^2 \lambda_1 - L_2^2 \lambda_2}{L_1 - L_2} \quad (1.4)$$

Where:

- L_1: The inverse (1/m) of the slope from the long-linear fit for ^{223}Ra.
- L_2: The inverse (1/m) of the slope from the long-linear fit for ^{224}Ra.
- λ_1: The radioactive decay coefficients of ^{223}Ra.
- λ_2: The radioactive decay coefficients of ^{224}Ra.

Once we have the K_h (m^2/s), we can calculate any offshore conservative material flux by multiplying it to the concentration/activity gradient $\left(\frac{\partial A}{\partial x}\right)$ (Rodellas, 2014).

For example, to estimate the flux offshore of the long-lived Ra isotope (F_{Ra-off}):

$$F_{Ra-off} = \left[K_h \left(\frac{\partial A}{\partial x}\right)\right] \cdot z \cdot L \quad (1.5)$$

Where:

- z: The surface layer depth.
- L: The shoreline length.

In 2003 Moore (2003) developed a new model based on the different signals of distinct Ra sources (endmembers) by the following equations:

$$f_{ocn} + f_{SGDi} + f_{SGDii} = 1 \quad (1.6)$$

$$^{226}Ra_{ocn} \cdot f_{ocn} + {}^{226}Ra_{SGDi} \cdot f_{SGDi} + {}^{226}Ra_{SGDii} \cdot f_{SGDii} = {}^{226}Ra_{std} \quad (1.7)$$

$$^{228}Ra_{ocn} \cdot f_{ocn} + {}^{228}Ra_{SGDi} \cdot f_{SGDi} + {}^{228}Ra_{SGDii} \cdot f_{SGDii} = {}^{228}Ra_{std} \quad (1.8)$$

Where:

- f: The fraction of each of the three endmembers.
- ^{x}Ra$_y$: The activity of the isotope x in each endmember y.
  - std: The study site.
  - SGDi: The first type of SGD water.
  - SGDii: The second type of SGD water.
  - Ocn: The coastal ocean water.

The same estimation can be done with short-lived isotopes, but their decay term ($e^{-\lambda \cdot \tau}$) has to be added in the equations 1.7 and 1.8 (Rodellas, 2014).

Finally, to calculate the SGD of the endmembers:

$$SGD_{SGDx} = \frac{f_{SGDx} \cdot V}{T_w} \quad (1.9)$$

Where:

- V: The volume of the study zone.
- T_w: The apparent water age.

With any of the techniques described above, once we had calculated the SGD flux we can multiply it by the concentration of our conservative analyte to determine its flux. If the analyte is not conservative we will have to assume the error implicated (Santos et al., 2008).

1.2.2.3.   SGD-driven metal fluxes

The importance of metal fluxes to the sea are crucial for the marine environment. Dissolved metals can act as micronutrients for the ecosystem functioning science they are in most of the main biomolecules (eg. Fe, in hemoglobin) or create phytoplankton blooms (Downs et al 2008). But also can act negatively as a toxic agent (eg. Pb or Hg) affecting enzymatic systems (Torres et al., 2008). Another important factor where metal fluxes can affect, is when those increase metal dissolved concentrations up to threshold levels that may induce detrimental effects (Jordi et al.,2012). The importance of SGD-driven metal fluxes increases as the SGD role gets importance, for example the Mediterranean Sea, where SGD inputs represent up to 5-30% (Rodellas et al., 2015). However, only a few sites have been investigated to calculate those metal fluxes in the Mediterranean Sea (Rodellas et al., 2014; Trezzi et al., 2016; Martinez-Soto et al., 2016), so more investigations should take place to reveal the importance and implications of those fluxes.

2.   <u>Objectives</u>

2.1.   General

The aim of this project is to explain what occurred in the bay of Portman that made it become the most contaminated mine zone in the Mediterranean. We will try to prove that there is a contamination of the seawater because of the SGD fluxes.

2.2.   Specific

- To do so, we will calculate de dissolved metal concentrations in sweater as in porewater to prove the presence of high concentrations.
- Compare the metal concentrations with other sites where have been studied so we can evaluate the importance of the metal concentrations in Portman Bay.
- Calculate the SGD flux by using Ra isotopes as tracers, so we can know the precedence of those fluxes as the magnitude they represent.
- Estimate the metal flux by using the SGD flux and compare those with other sites where those have been calculated to have an estimation of the importance of those fluxes.

3.   Site description

The southeast of the Penisnula Ibrica is characterized by its semidesert environment with the influence of the Mediterranean. Soft winters and hot summers rule the temperatures, with an annual mean temperature of 18ºC. Rainfall is sporadic and intense, with an annual average of 200-300mm. These parameters, plus the topography of the bay, produce fast-flowing streams (Conesa et al., 2008).

3.1. Geology

The Sierra of Cartagena-La Unión is the most oriental peninsular sector of the Cordillera Bética, and it is situated in the domain of Alboran (Robles-Arenas, 2007). This area is characterized by its complex lithogenic structure. It is formed by three overthrust mantles, and it constitutes one of the biggest accumulations of lead (Pb) and zinc (Zn) of the Península Ibérica.
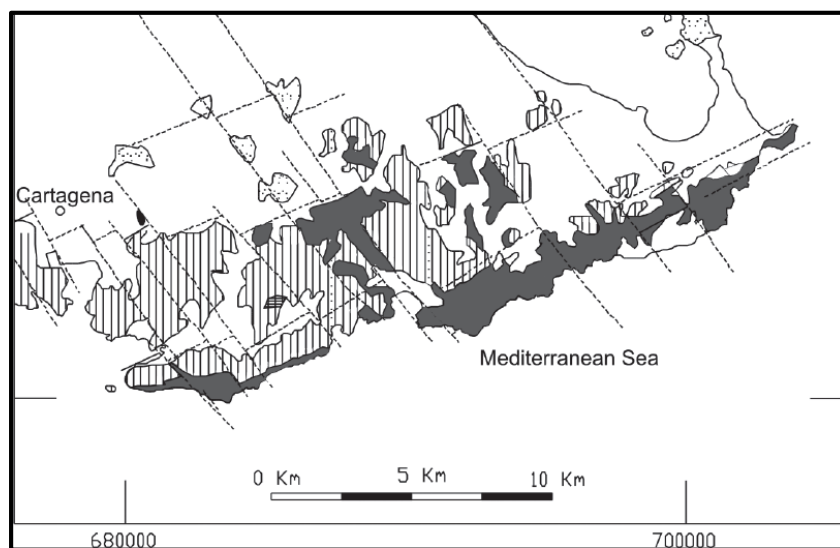
Legend:
- Neogene and Quaternary Basins
- Basalts. Plio-Quaternary volcanism
- Andesites . Pliocene volcanism
- Maláguide complex
- Alpujárride complex
- Nevado-Filábride complex
- ------ Fault

Figure 3. 1. Serra Minera geology (Robles-Arenas et al., 2010)

The formation of the Cordillera Bética started in the Paleozoic, crating formations of mostly micaschists, continuously the Triassic gave place to metamorphic and sedimentary rocks, mainly carbonate, that will emerge overthrusted because of the alpine orogeny. With the convergence of the African and European plate during the alpine orogeny, gave place to the first stage of the Cordillera Bética. Subsequently the lifting of the mantles of the mountain system, it became a strong erosive period of refilling of the basins. Later on, in the Miocene a fracturing and distension period occurred, that generated two big faults, plus volcanism that gave place to hydrothermal activity that gave place to the polymetallic mining in the southeast of the

Peninsula (Garcia-Lorenzo et al., 2014). Since then, until today, a new compression orogeny its acting by the compression of the African and European plates (Robles-Arenas, 2007).

The Alpujárride complex is composed by three different units with a variable thickness (Manteca and Ovejero 1992, Ovejero et al., 1976):

- San Girnés (250 m)
- Portman (150 m)
- Gorguel (30 m)

Nonetheless García-Tortosa et al., (2000) proved that the Gorguel's unit it is a prolongation of Portman's.

3.2.   Geochemistry

The geochemistry of the bay is defined by the composition of the tailings. The mantles of those change in function of the activities that where done in the Lavadero Roberto. As the flotation technique started, for every 100 t of materials that where processed, 95 t ended into the bay as tailings, so all the phases of the bay deposits are directly engaged to the materials processed. All those came from two different stratabound ore deposits mantles, composed by two mineral parageneses respectively (Oen et al., 1975; Manteca and Ovejero, 1992):

- Mantle 1: Chlorite, sulfides (pyrite, sphalerite, galena), carbonates and silica.
- Mantle 2: Greenalite, magnetite, sulfides (pyrite, sphalerite, galena), carbonates and silica.

The bay has a composition of an intermittent change of "black sands" and "yellow crusts". The composition of which are Fe 40.5%, Pb 0.27%, Zn 0.72%, Cu 98 ppm, As 559 ppm, Cd 63 ppm and Hg 39 ppm for the black sands, and sulfates for the yellow crusts (Manteca et al., 2014). But not all have exactly the same composition, in function of the period of activity the sediments differ from one another. From 1965 to 1973 SMMPE did not remove pyrite, for the production of sulfuric acid (H_2SO_4) to process the sulfates ores, it means that the tailings between those years will be richer in pyrite than the others. However, from 1959 to 1967 magnetite was removed by magnetic separation, and as a consequence, the tailings from these years do not have such a big amount of Fe as the others (Manteca et al., 2014).

3.3.   Hydrology

Portman's hydrology is defined by its climatology and the structure of its aquifers. Superficial runoff is defined by ten different creeks, of which, on one hand, five finish in the Mediterranean, and on the other hand, five more end in the Mar Menor. None of those are perennial, so they are conditioned by the local climatology.
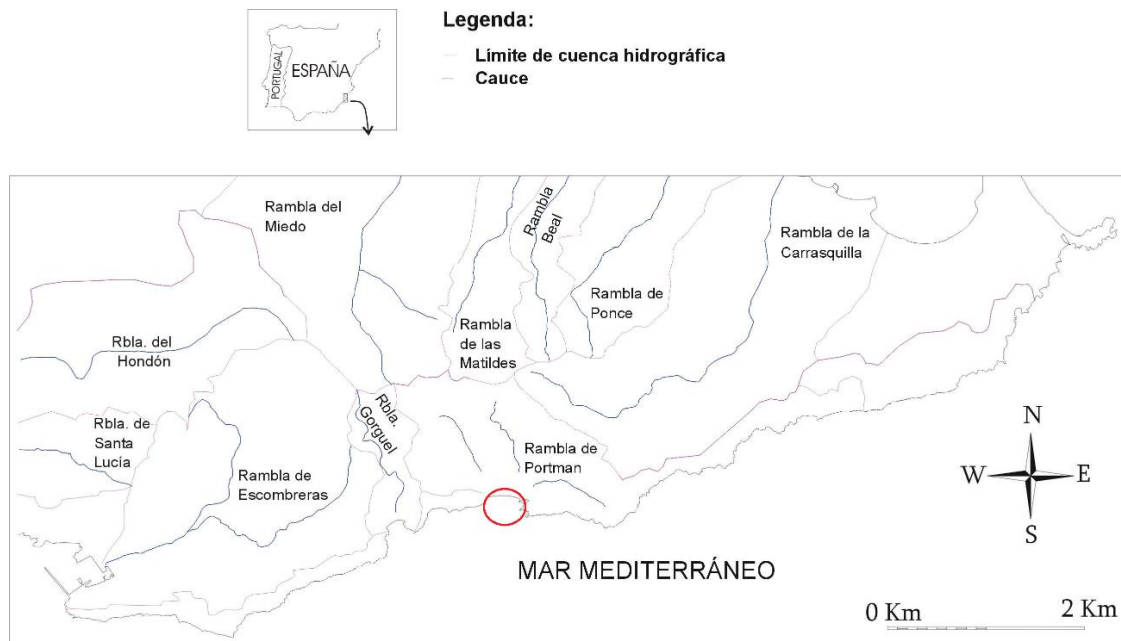
Figure 3. 2. Superficial hydrologic system (Robles-Arenas, 2007)

Surface runoff is mainly sporicidal, but it transports big amounts of sediments, due to the breve and violent storms and the erosionated terrain, affected by the mining activity and pore vegetation.

The aquifer is characterized to be composed by a hard-rock of schists, quartzites, phyllites, limestones and marbles, with an 800 to 400 m thickness (Trezzi et al., 2016). Recharge is exclusively because rainfall, that is helped by the faults, mining activity and the kastification of the zone (Robles-Arenas et al., 2006).

In addition, the lakes that have been created in the mountain system were produced because of the abandoned open-pits (Robles-Arenas and Candela, 2010), creating lakes, such as Brunita, with a 30 m depth and a 620,000 m^3 of water stored (García, 2004).

All those facts produce a flux of metals into the aquifer, creating high concentrations of Zn, Pb, Ag and Fe (Robles-Arenass and Candela, 2010). Thus, we can see evidence of fluxes of metals threw Submarine Groundwater Discharge (SGD) in Gorguel bay (Trezzi et al., 2016). Therefore, there is a continuous metal contamination of the groundwater that is favored by the intense evaporative concentration in open-pit lakes, and acidification (Robles-Arenas and Candela, 2010).

Yet, the entire zone can't use local sources for drinking water because spring water does not meet water quality standards. As a result of this issue, they are providing themselves from external sources. Meanwhile, agriculture uses groundwater and the Tajo-Segura water transfer (Robles-Arenas and Candela, 2010).

3.4.   Other investigations in the bay

Portman and its surroundings have been investigated since the day mining started in the zone. Carthaginians, Romans, Berbers, Middle age men, SMMPE's engineers and scientist of the XXI century had been investigating it until now. Also, the environmental aspects related to mining

activities in the Region de Murcia are described in the book by María Jesús Ramos Amorós in 1999.

All is social and most actual history, related to the mining impact, has been described by the book "PORTMAN. DE *EL PORTUS MAGNUS* DEL MEDITERRANEO OCCIDENTAL A *LA BAHIA ATERRADA"* by Isabel Banos-González and Pedro Baños Páez in 2013.

The mining history and its infilling has been described by Manteca (2014). Its environmental impact has been reported by several studies as Oyarzun et al., (2013) describing how the infilling of the bay was produced and its consequences or, Martinez-Sanchez et al., (2008) describing the mobility of metals inside the different sediments inside the bay. Even Martinez-Gomez has certificated that form different contaminated waters in the Mediterranean, Portman's red mullets where the ones with a major concentration of Pb and Hg. Its geological composition and formation has been described by Robles-Arenas (2007) in its thesis.

Private companies and others have been studding its possible regeneration and no further action has been taken. Fact that shows we still do not understand the parameters of the bay and its dynamism to act on it, plus there is not any political will.

3.5. Legislation

The legislation that affects the contamination of Portman relics to three different entities. Where the European parliament creates directives that have to be incorporate by the state members into their legal framework.

Table 1. Legislation			
	Waters	Mining	Environmental impact
Europe	- Directive 2000/60/EC - Directive 2006/118/EC	- Directive 2006/21/EC - IED, 2010/75/EU - Seveso II directive 96/82/EC	- EIA directive 2011/92/EU - SEA directive 2001/42/EC
Spain	- Ley 2/2013 - Ley 62/2003 - Decreto legislativo 1/2001	- Ley 22/1973 - Real decreto 105/2008 - Ley 5/2013	- Art 45. Consitución Española 1978 - Ley 21/2013
Murcia	- Ley 4/2009	- Ley 22/1973 - Ley 54/1980 - Real decreto 2857/1978	- Ley 1/1995

4. Methodology

This project has been divided in two campaigns. One onboard of the Angeles Alvariño oceanographic ship, and a second one on land. In booth campaigns metal and Ra samples have been taken in several points.
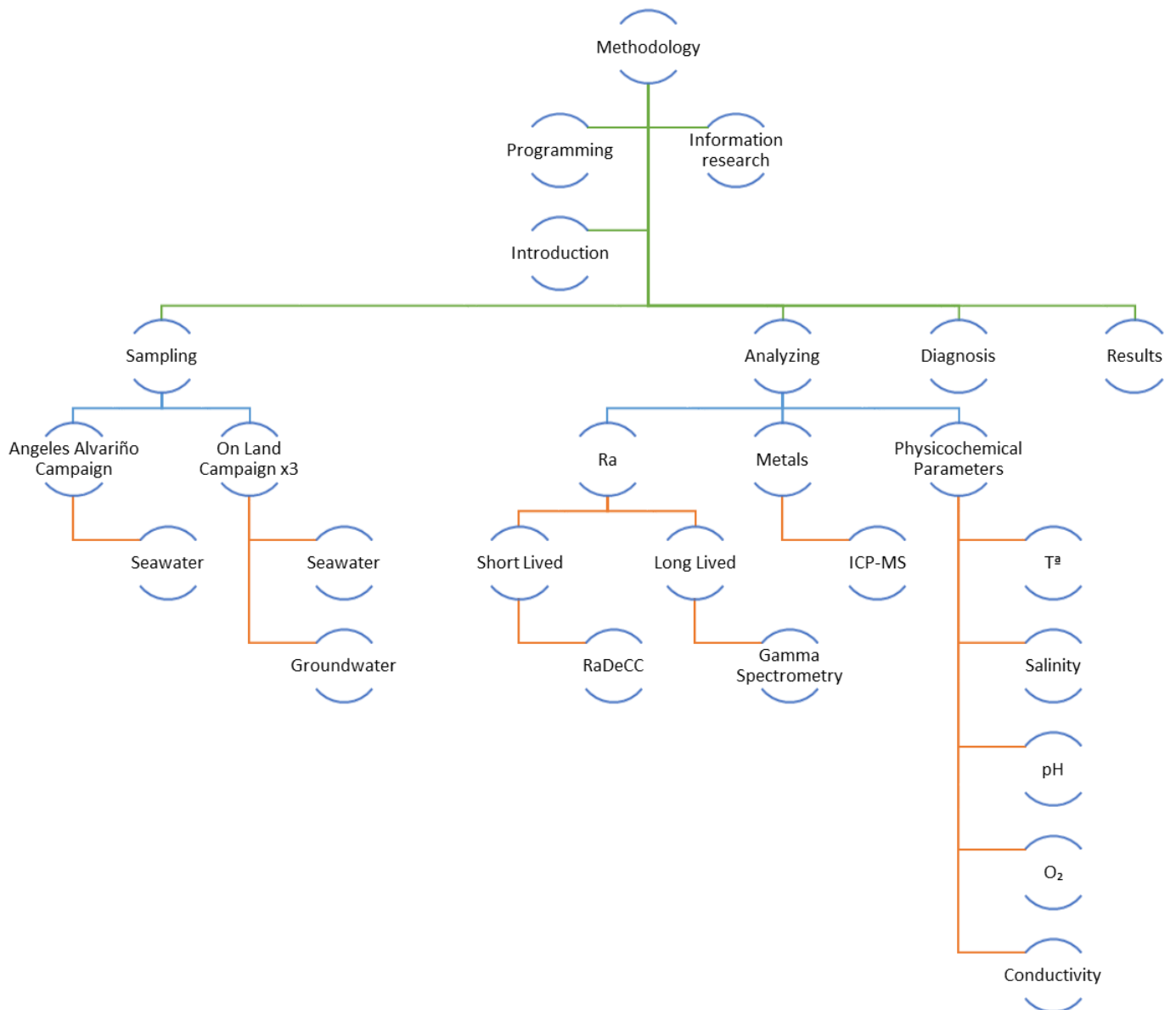
Figure 4. 1. Mothodology guidelines

4.1. Sampling

The sampling of the different elements that will be used in this study have been divided in function of the nature of the sample, with a Seawater campaign and a Porewater campaign.

4.1.1. Seawater campaign

In March 13th to 19th of 2015 the seawater campaign was performed aboard of the oceanographic vessel Angeles Alvariño, from the Spanish Oceanographic Institute. Three, perpendicular to the coast, different transects where established, where in each one where taken samples from eight different points. One sample of metals and Ra was taken in each point of the west (W) and east (E) transects, meanwhile the central (C) transect had several samples in two of its points.
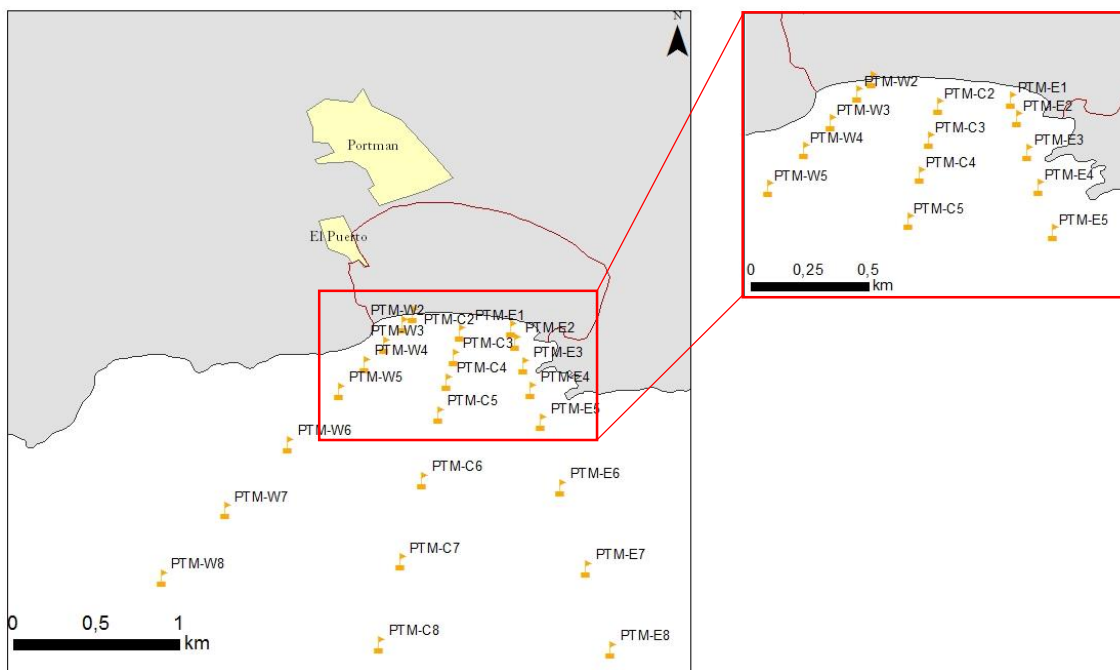
Figure 4. 2. Seawater campaign samples map

4.1.2. Porewater campaign

In January 26th to 27th of 2016 the porewater campaign was realized. Three different coastal seawater Ra and metals samples were taken, one at the east of the bay, a second one at the center, and one more at the east. Four, 2.2 meter, slotted piezometers where installed along the bay and sampled on Ra and metals. Plus, six pore water samples, at the west of the bay, of Ra and metals were taken to define one transect, and, describe the mixing layer. In all samples temperature, salinity and conductivity had been taken, plus in pore water and piezometers samples O_2 concentration and pH had been measured.
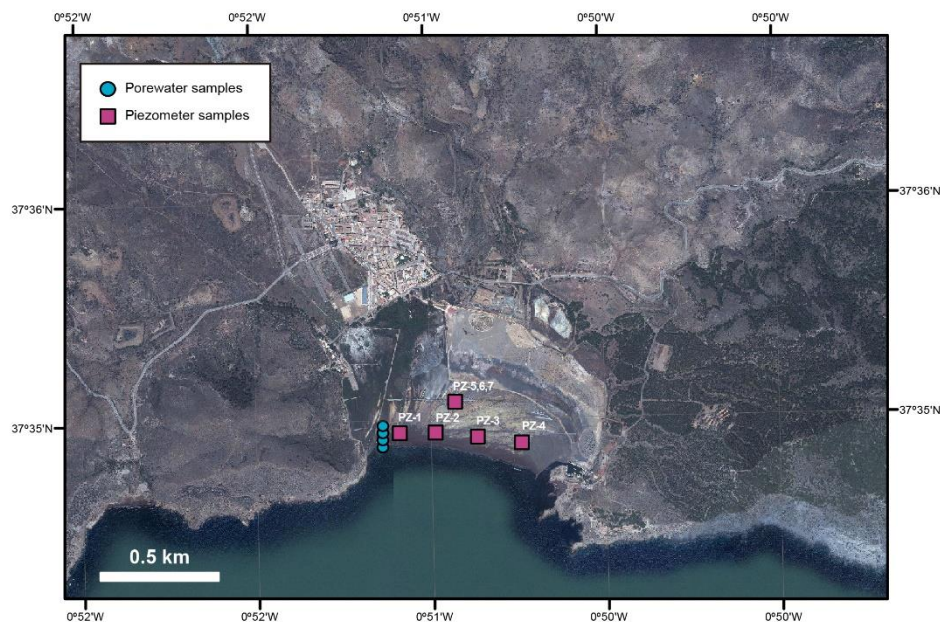
Figure 4. 3. Porewater campaign map

The volume of Ra samples had been taken differently, seawater samples had been taken in 60L containers, pore water samples in 10L barrels, and piezometers samples in 25L barrels.

4.2. Analytical methods

To quantify the concentrations of each element we had to pretreat samples and then use their correspondent analytical method.

4.2.1.   Pretreatment of samples

The pretreatment of samples is specific for each type of analyte that we want to measure, so we difference between Ra-isotopes and dissolved metals.

4.2.1.1.   Ra-isotopes

Because Ra concentrations are low in seawater and freshwater, samples have to be preconcentrated. To make that, we have used Moore's (1976) technic, by using MnO_2 fibers that absorb the Ra isotopes and remain trapped. MnO_2 fibers had been provided by Scientific Computer Instruments.

Before using the fibers those have been expanded, to increase its potential surface, and then separated in 25g amounts and into plastic bags.

On field, water samples had been taken with a portable electric pump, introducing the water from its source to the containers. Once in, a plastic tube will be connected from the tap to a plastic column. For the preparation of the column, first it has been introduced the 25g MnO_2 fiber and then a little of white fiber to filter the water that it will through it. The tub has to be connected to the head, with the white fiber, and into the tap of the container. When the tap is opened water will flow through it leaving the Ra inside the fiber. The water flow has to be slow enough (1L/min) so the maximum of Ra is absorbed (97-99%) (Moore et al., 1995; Garcia-Solsona et al., 2008). Once the filtration has finished the MnO_2 fiber is returned to its bag.

4.2.1.2.   Metals

Trace-metal samples will be stored inside a 0.5L acid-cleaned low-density polyethylene plastic bottle for metals. Then they had been washed three times with Millipore. On field, water has been extracted with a peristaltic pump, connected to an acid-cleaned rubber tube and filtered through an acid-cleaned polypropylene cartridge filter (0.22µm; MSI, Calyx®). All procedures had been done with latex gloves to prevent contamination. After sampling, trace-metal samples were acidified to very low pH (<2) with ultrapure HCl, and stored for at least a month before extraction. All trace-metal samples had been sent to the Mediterranean Institute for Advanced Studies (IMEDEA), in Esporles (Balearic Islands, Spain), to be analyzed.

4.2.2.   Ra-isotopes preparation samples

Before Ra samples are measured, they have to be conditioned. First we had washed them inside their bags with Millipore, so particles or salt does not interfere with the Rn emanation during measurement. Further on, fibers have to be dried, with absorbing paper, until they weight 50g, so the mass ratio between water and fiber is 1, fact that will increase the efficiency of the counting to its optimal (Sun and Torgersen, 1998).

4.2.2.1.   Ra analytical method (RaDeCC)

When sampling and preparation of the fibers had been done, we introduced the fiber into a new plastic column the will be placed into the Radium Delayed Coincidence Counter (RaDeCC).

Designed by Giffin (1963) and remastered for Ra by Moore and Arnold (1996), the RaDeCC system is a detector of α particles capable to distinguish among the Ra short-lived isotopes ([223]Ra ($T_{1/2}$=11.4 d) and [224]Ra ($T_{1/2}$=3.66 d). The closed system, moves He gas by a pump that introduces He into the column, pulling the Rn, as consequence of the Ra decay, and sending it to a ZnS coated 1.1L scintillation cell, connected to a photomultiplier to detect radioactive decay events, where an electronic gateway system records the different signals of the decays and classify them

in three diferent channels, [219]Rn ([223]Ra decay), [220]Rn ([224]Ra decay) and "total" (summarization off all the signals).
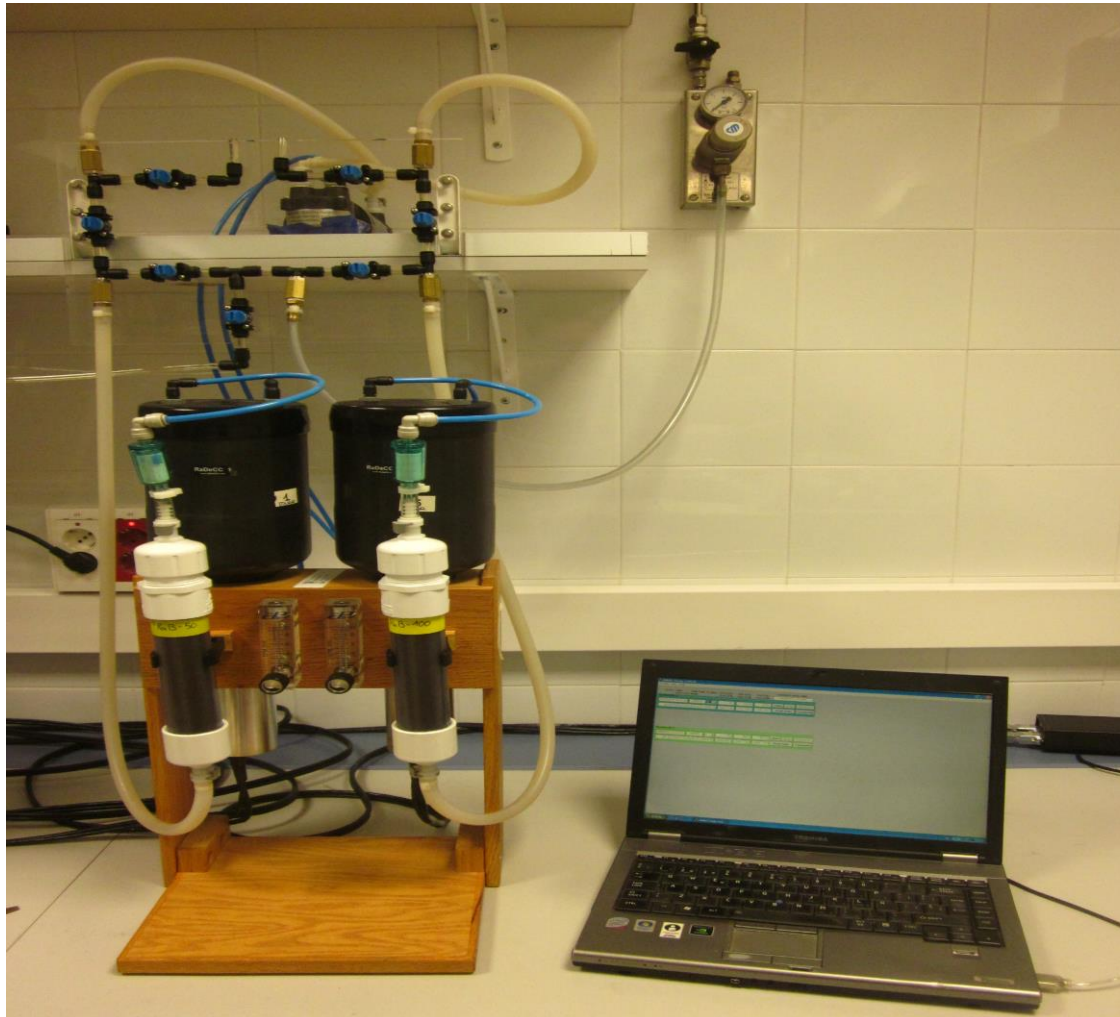
Figure 4. 4. Two RaDeCC sistems (Rodellas, 2014)

When an α decay of Rn is produced inside the scintillation cell a signal is recorded in the total channel, a signal is produced to open the gate of a delayed coincidence circuit. This gate is open for 5.6 ms for the [219]Rn channel and 600 ms for the [220]Rn channel. When a signal is produced inside the gap time when the gates are open, it will give be counted to its respective channel. Inferences are produced by error counting, [222]Rn decays produced by [226]Ra and background, which will be corrected by a mathematical procedure (Garcia-Solsona et al., 2008).

For each Ra fiber, we had measured it three times:

- 1st measure: Among the day of sampling and three days after to determine [224]Ra. (1-4h counting).
- 2nd measure: 7 to 10 days after sampling to determine [223]Ra. (8-16h counting).
- 3rd measure: 1 month after sampling to determine the [224]Ra produced by its father [228]Th. (8 hours counting).

For a correct measure and use of the RaDeCC system we followed the next five steps:

1. Background. With no column placed, and with the system opened. We run the system for approximately 20 minutes so we can determinate the environmental radiation.
2. We introduce the fiber inside the columns and close the system.
3. Configure the keys system so He can be introduced inside the system with a 7 Lpm flux for 1 to 3 minutes so the system is purged.
4. Close the keys system so the He does not scape, plus activate the pumps.
5. One 7 minutes have passed, and ^{220}Rn and ^{219}Rn are in secular equilibrium with their fathers, the counting system can be turned on.

4.2.2.2.   Gamma spectrometry

To measure the Ra long-live isotopes (^{226}Ra and ^{228}Ra), the most common procedure is to do it by gamma spectrometry, where each photon emission is related to a unique energy signature for each isotope.

Once we had measured the Ra short-live isotopes, we started the preparation for the gamma spectrometry. The preparation consists in a reduction of the MnO$_2$ fibers volume. We introduced them into porcelain containers (250ml) and burn them to ashes for 16 hours at 820ºC. Then the ash was introduced into a cylindrical counting vial and sealed with parafilm to prevent the escape ^{222}Rn. Finally, samples were stored for three weeks before analysis, time needed for the radioactive equilibrium of ^{226}Ra and ^{214}Pb.

Figure 4. 5. HPGe (Rodellas, 2014)

After the equilibrium period, samples were placed into a high-purity germanium detector (HPGe) and counted for 1-4 days depending on the counting rate of the selected radionuclides. ^{228}Ra activity was determined by the photopeak of its daughter ^{228}Ac at 911.6 keV. ^{226}Ra activity was determined by the photopeak of ^{214}Pb at 351.9 keV. ^{214}Pb was used to calculate the ^{226}Ra because it has a lower background.

4.2.3. Metals analytical method

Metal dissolved (<22 μm) concentrations were determined by preconcentrating samples by APDC/DDDC organic extraction method and analyzed by ICP-MS (PerkinElmer ELAN DRC-e) (Tovar-Sánchez, 2012; Rodellas et al., 2015).

4.3. Software

All maps have been developed with the Geographic Information System (GIS) software ArcGIS® by the database sheets of the Instituto Nacional Geografico (IGN) and the georeferenced results of concentrations obtained of the two campaigns.

Graphs have been processed with the analyzer software OriginPro 8® with the data that has been obtained from the campaigns.

5. Results

In the following chapter of this project we will expose the different results that have been obtained. Represented by maps, graphs and tables as so the manipulation of them to obtain other parameters and relations.

The first measure of the central (C) transect was not made because of the bad conditions of the sea. The measures that have a 0 value the Fe (Figure 5.3) are exposed in white because of the sample contamination that had been produced during the sampling.

5.1.   Seawater results

Seawater surface samples showed that there is a trend offshore with salinities concentrations, where depth profiles also showed the existence of a superficial fresher layer (<1.5 m) offshore. Moreover, a trend can be appreciated long the bay, much lower salinity values (35-36) where situated in the west of the bay compared to the east much salty values (39-40) describing a major fresher layer discharging in the west of the bay.

Short-lived Ra isotopes (^{223}Ra and ^{224}Ra) were enriched near the shoreline compared to concentration values of both Ra isotopes offshore (Figure 5.1). Range from 14.67 ± 0.83 to 1.64 ± 0.11 at 20 m offshore and from 0.984 ± 0.135 to 0.107 ± 0.030 dpm·100L^{-1} at 2000 m for ^{224}Ra and ^{223}Ra, respectively. This trend suggests that most of the inputs of short-lived Ra isotopes were from the shoreline. Long-lived Ra isotopes (^{226}Ra and ^{228}Ra) did not show any trend offshore. Values range from 15.0 ± 0.7 to 9.2 ± 0.8 dpm·100L^{-1} for ^{226}Ra values, and from 6.1 ± 0.3 to 2.7 ± 0.4 dpm·100L^{-1} for ^{228}Ra. This pattern suggests that there is not a clear enrichment of SGD by tailings because of their low concentrations in these two Ra isotopes that revealed the porewater samples.

If we observe Figure 5.2, different depth ^{223}Ra and ^{224}Ra concentrations are represented, where the first 2.5 m show higher concentrations of Ra which give place to the superficial fresher layer that has been described before with the salinity concentrations.

Figure 5. 1. Distribution of Ra isotopes concentrations in function of the distance to the bay
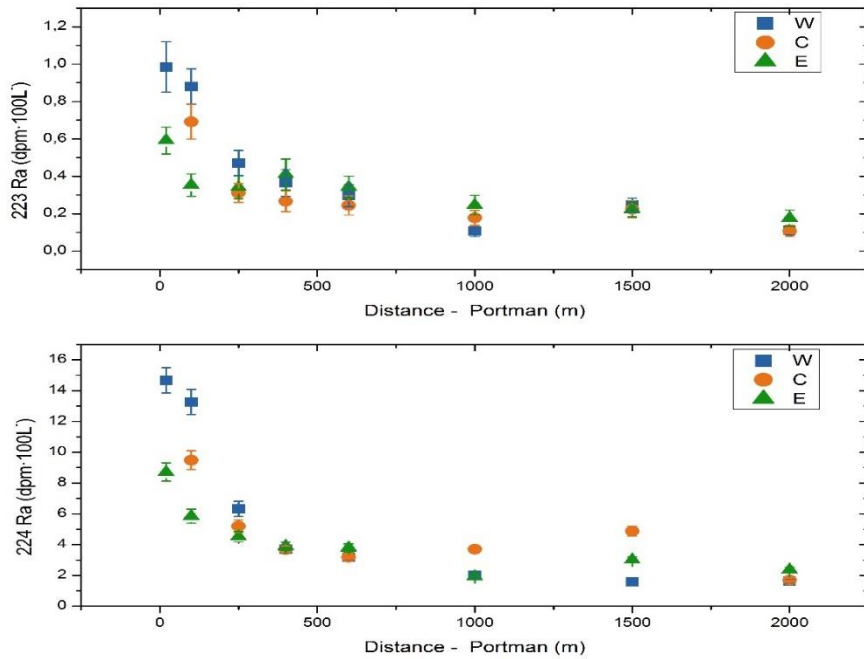
West (W) transect is represented by blue squares, Central (C) by orange cycles and East (E) by green triangles.

Figure 5. 2. Ra depth distribution
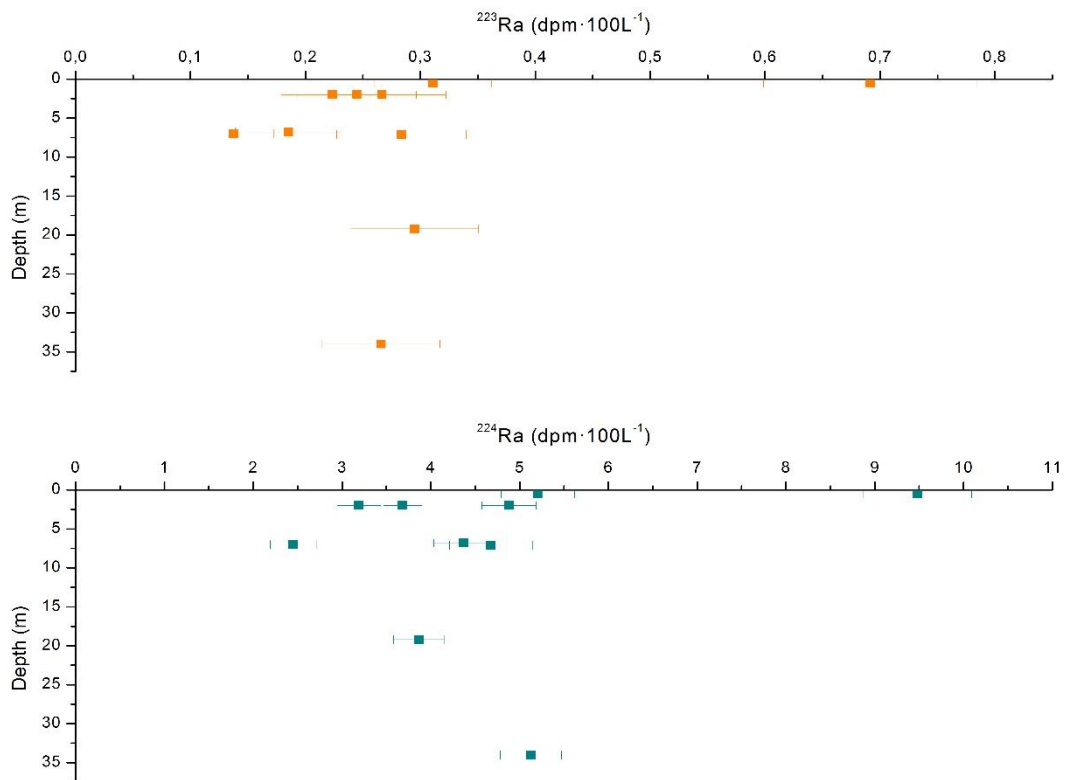
Ag, Cd, Pb and Zn concentrations followed an exponential enrichment from offshore to the bay, with values at 20 m offshore of 0.124, 2.58, 5.59 and 488 nM, respectively, down to values at 2000 m from the bay of $5.38 \cdot 10^{-3}$, 0.212, 0.915 and 3.67 nM, respectively (Figure 5.3). Hereafter, Co considered with no gradient offshore, could be seen with as it had it, if we look at its plot, that suggests a slightly negative slope, but that cannot be compared to the other gradient offshore plots. However, Co, Cu, Fe, Mo and Ni, did not seem to be enriched near shore or follow an exponential decrease (Figure 5.4).

Figure 5. 3. Distribution of metals concentrations offshore (Ag, Cd, Pb, Zn)
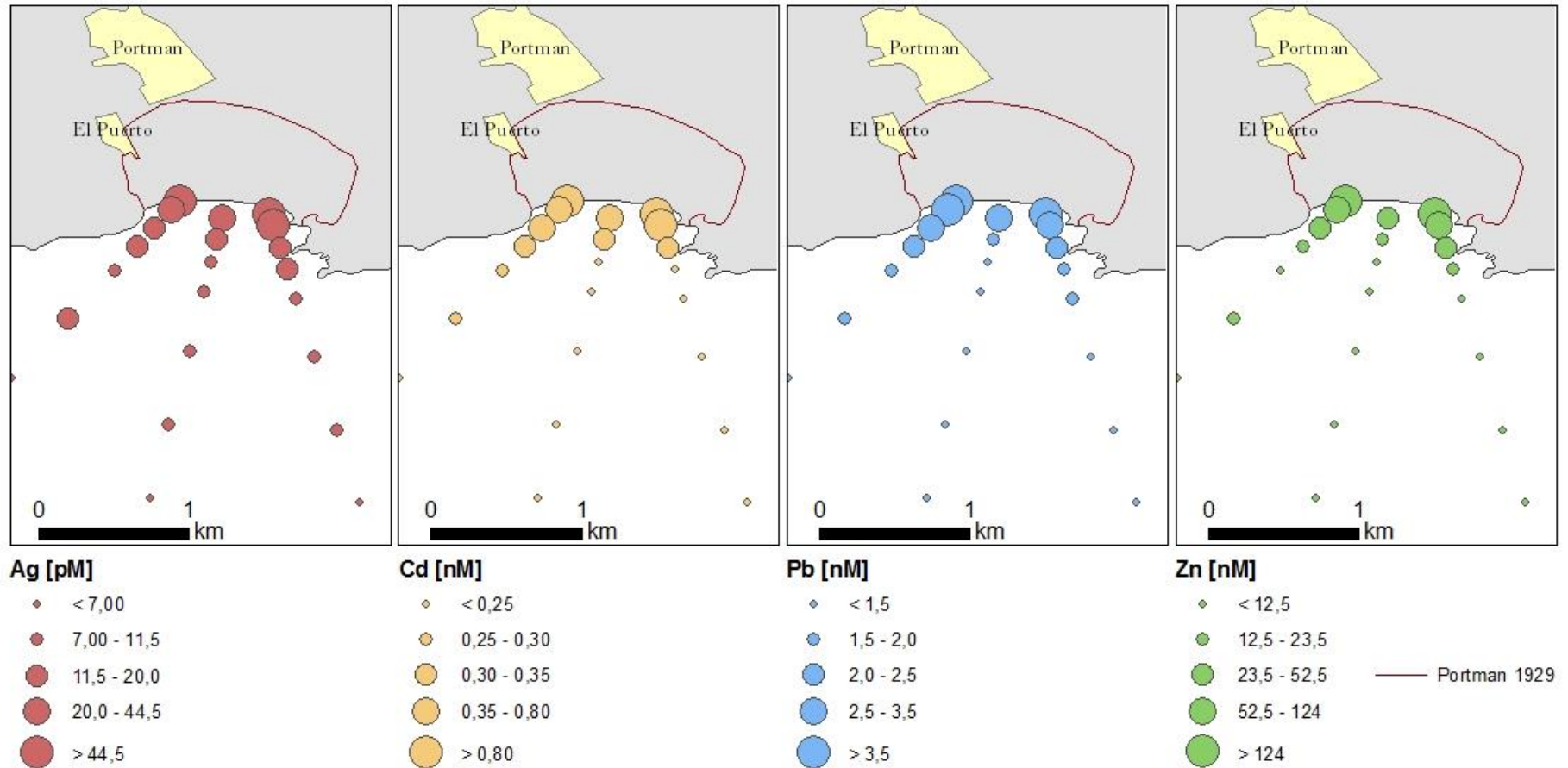
Ag [pM]
- < 7,00
- 7,00 - 11,5
- 11,5 - 20,0
- 20,0 - 44,5
- > 44,5

Cd [nM]
- < 0,25
- 0,25 - 0,30
- 0,30 - 0,35
- 0,35 - 0,80
- > 0,80

Pb [nM]
- < 1,5
- 1,5 - 2,0
- 2,0 - 2,5
- 2,5 - 3,5
- > 3,5

Zn [nM]
- < 12,5
- 12,5 - 23,5
- 23,5 - 52,5
- 52,5 - 124
- > 124

—— Portman 1929

Metal concentrations are represented in each sampled point by circles that increase in function of the metal concentration.

Figure 5. 4. Distribution of metals concentrations offshore (Co, Cu, Fe, Mo, Ni)
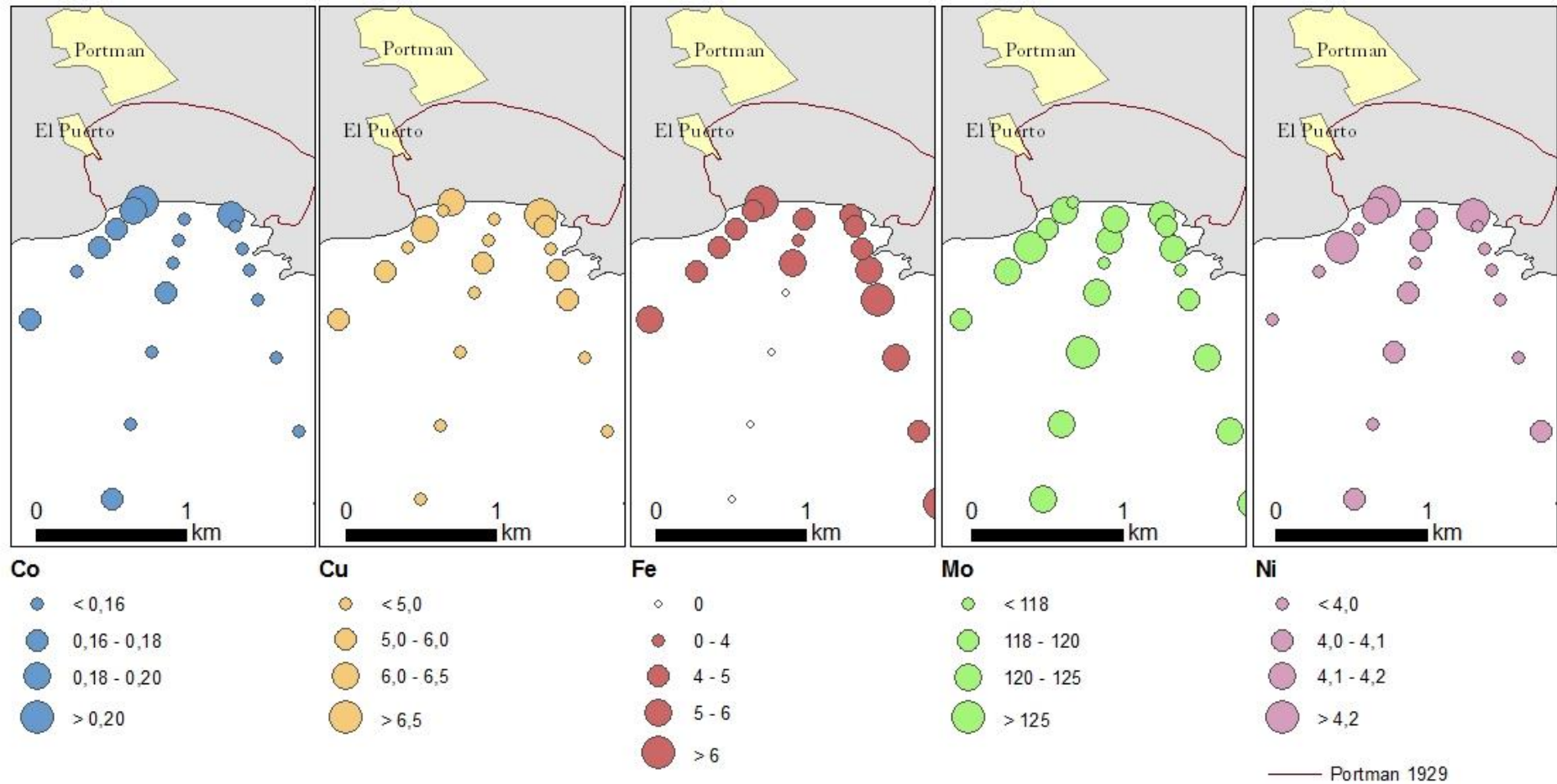
Metal concentrations are represented in each sampled point by circles that increase in function of the metal concentration. Zero concentrations values are given to represent contaminated Fe samples.

Dissolved metal concentrations in depth, shown in Figure 5.5 show more less the same patterns in function the element we analyze. Dissolved metals describe higher concentrations in surface waters, indicating a richer superior layer between 0 and 1.5 m. Demonstrating that the fresh water layer described before that was reach in Ra-isotopes, it is also in metals. Deeper samples show how all metals, except Cu, decrease gradually until they concentrations increase again at 20 m, where Cu concentrations are even smaller. Finally, the deepest samples show a decrease of the metal dissolved concentrations, except Cu that its concentrations get bigger.

Figure 5. 5. Metal depth concentrations
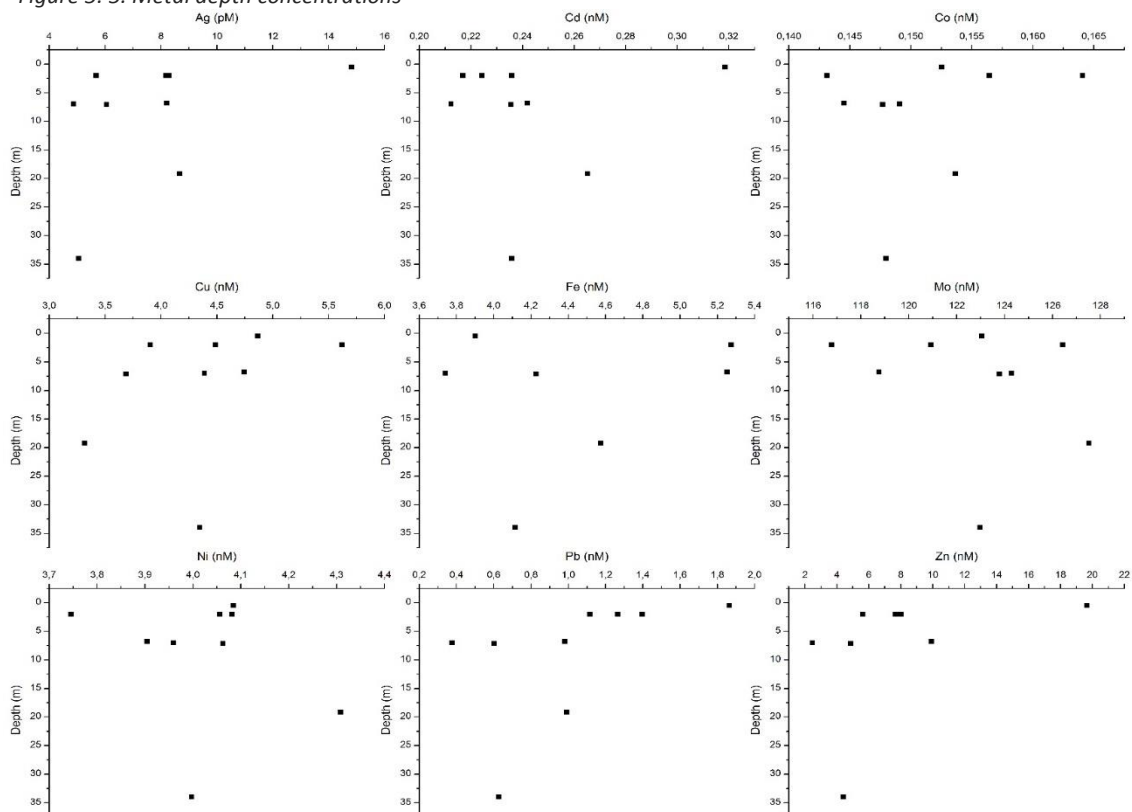
All samples have been taken in the central transect, at diferent points offshore and depth.

5.2.   Porewater results

Physicochemical parameters and Ra-isotopes concentrations of porewater samples are shown in Figure 5.6, where all of them described in Table 1.

Table 1. Porewater physicochemical parameters and Ra concentrations																
	Salinity	T	pH	O_2	Depth	^{223}Ra			^{224}Ra			^{226}Ra			^{228}Ra		
Units	-	ºC	-	$mg \cdot L^{-1}$	m	$dpm \cdot 100L^{-1}$			$dpm \cdot 100L^{-1}$			$dpm \cdot 100L^{-1}$			$dpm \cdot 100L^{-1}$		
PZ 01	14.3	15.7	7.27	1.7	2.2	63	±	3	228	±	13	51	±	2	47	±	3
PZ 02	14.3	20.0	6.46	2.1	2.2	13	±	1	58	±	3	15	±	1	17	±	2
PZ 03	14.7	19.7	5.68	3.7	2.2	0.9	±	0.2	15	±	1	0	±	0	8	±	2
PZ 04	28.4	18.9	6.23	4.2	2,2	6	±	1	79	±	4	5	±	2	30	±	2
PW1	8.6	16.4	6.99	14.4	1,6	64	±	5	237	±	11	99	±	9	50	±	16
PW2	8.2	18.4	6.55	7.1	2,0	69	±	6	327	±	17	25	±	3	24	±	5
PW4	15.0	18.6	6.31	3.0	2,0	27	±	3	105	±	8	23	±	1	18	±	2
PW5	18.5	17.2	6.47	10.2	1,8	37	±	3	147	±	11	19	±	3	22	±	4
PW6	33.3	15.6	6.60	11.6	1,8	19	±	2	74	±	6	101	±	6	33	±	4
PW3	35.4	14.2	6.94	20.6	1,8	36	±	4	123	±	10	58	±	4	32	±	3

Salinity values of the southern porewater samples ranged from 35.4, to freshwaters values, at the northern porewater samples, up to values of 8.2. Salinity around 14 was measured in piezometers except for the eastern piezometer (PZ 04) with a maximum value of 28.4. In piezometers samples a diminution of O_2 concentrations from east to west, with values from 4.2 in PZ 04 to 1.7 in PZ 01, was observed. Meanwhile, the transect samples showed how O_2 increased from the interior of the bay to the shoreline, except PW04 that had an inferior value. Temperature showed small variations in porewater, increasing from a value of 16.4 in PW 01 to a maximum of 18.6 at PW 04, from this sample decreases to 14.2ºC in PW 03. Piezometers values remained constant with values of 19.0 ºC except PZ 01 with 15.7 ºC. pH remained in all samples approximately constant with values varying from 5 to 7.

Piezometer samples showed how in the western part of the bay, PZ 01, Ra-isotopes concentrations are higher than in the rest of the bay, with maximum values of 63 ± 3, 228 ± 13, 51 ± 2, 47 ± 3, for ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra, respectively. And the central-eastern part, PZ 03, the lowest, with minimums of 0.9 ± 0.2, 15 ± 1, 0, 8 ± 2, for ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra, respectively. Samples of the porewater transect showed how, except PW4, Ra-isotopes concentrations decrease from PW1 to PW5, where then get stabilized to seawater concentration values.

Figure 5. 6. Concentrations of ^{224}Ra and ^{223}Ra inland
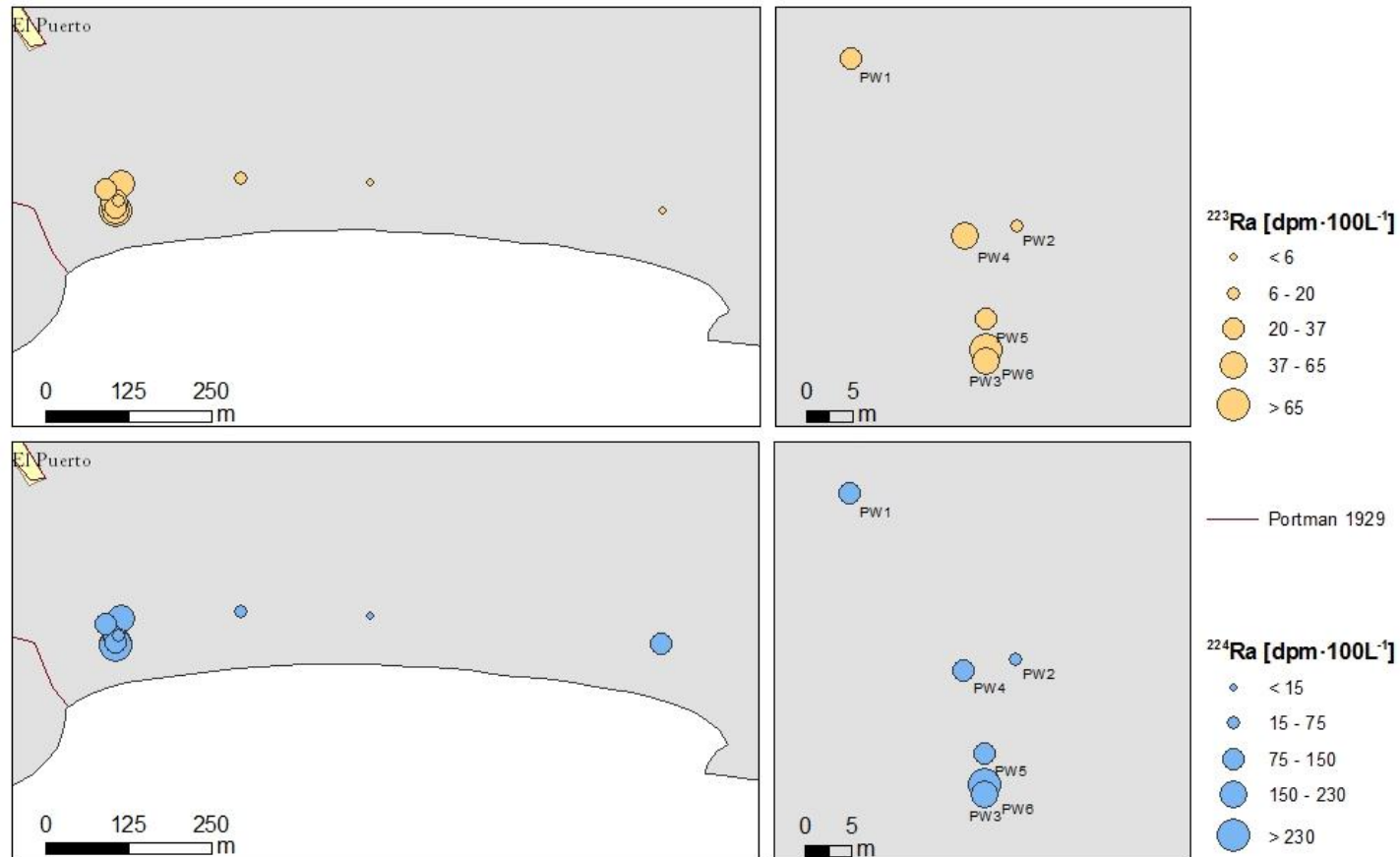
Ra concentrations are represented in each sampled point by circles that increase in function of the Ra concentration. Piezometers samples are shown from West to East and a Transcect zoom has been aded to show porewater concentration going from south to north.

Porewater dissolved metal concentrations presented much higher values than samples in seawater for Cd (2.4 – 1231), Co (16 – 533), Fe (11011 – 732922), Ni (49 – 1677), Pb (149 – 7744) and Zn (613 – 103901). Nonetheless, Ag, Cu and Mo, were under the detection limit in porewater samples, indicating that the enrichment of those metals in seawater are not produced by the bay superficial tailings. Piezometers, PZ 02 and PZ 03, as we can see in Table 2, present maximum values of all the measured metals, and those correspond to the samples with lower Ra-isotopes concentrations. The transect revealed how metals as Cd, Pb and Zn get higher values as we approach the shoreline. Instead, Co, Fe and Ni just get enriched from PW1 to PW4 where then values decrease until reach PW3.

Table 2. Metal concentrations in porewater samples							
	Salinity	Cd	Co	Fe	Ni	Pb	V	Zn
Units	-	nM						
PZ 01	14	3	49	178552	49	204	-	1830
PZ 02	14	619	533	128527	1677	590	-	103902
PZ 03	15	914	72	732922	133	7744	-	12801
PZ 04	28	3	16	165405	71	562	-	613
PW1	9	62	55	110101	91	149	-	20343
PW2	8	199	142	165734	301	360	1690	24847
PW4	15	507	100	174916	317	6477	1555	6347
PW5	19	436	51	169563	97	1112	2006	16591
PW6	33	1231	79	145863	191	1166	-	27814
PW3	35	983	70	152331	132	1556	-	24309

5.3.   Seawater metal concentrations in other environments and Portman bays.

Seawater dissolved metal concentrations in Portman Bay presented to be high values if they are compared to other sites where have been calculated, as we can see in Table 3.

The measured dissolved Ag concentrations have been high enough to be detected in seawater. Cd, considerate a toxic in high doses, and related to Pb and Zn mining activities, presented maximum values that are higher than the reported in El Gorguel (Trezzi et al., 2016). Other sites like, Algeziras, Cadiz or Ferrol, known for their anthropogenic contamination, have a similar concentrations of Cu. Nonetheless, Fe concentrations showed to be similar to a natural site as Palma de Mallorca, even though the porewater concentrations were six magnitude orders higher. Ni concentrations were much smaller than in Palma de Mallorca, but similar to other contaminated sites as El Gorguel, Port de Maó or Vigo. Lead levels in Portman Bay can be considerate one of the highest values in the Mediterranean, just one magnitude order under Algeziras concentrations. Zn dissolved concentrations have been the highest reported until now in the Mediterranean Sea, with a maximum concentration of 488 nM.

In conclusion, dissolved metal concentrations in Portman Bay, show to be one of the highest metal concentrated seawater in the Mediterranean.

Table 3. Sea metal concentrations examples								
	Ag	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
nM								
Portman	0.005 - 2	0.18 - 4	0.14 - 0.26	3 - 7	4 - 8	110 - 127	4 - 5	0.38 - 6	3 - 488
Gorguel[a]	-	-	-	2.7 - 8.2	-	-	2.3 - 4.3	0.65 - 2.4	-
Ferrol[b]	-	0.09-0.10	-	6.7 - 9.2	-	-	-	0.20 - 0.30	17-24
Vigo[c]	-	0.02-0.10	0.30-1.6	1.1 - 5.3	-	-	1.7-7.8	0.08 - 0.25	7.4-19
Palma[d]	-	-	-	5.9 - 13	3.0 - 6.0	81 - 160	2.9-56	0.28 - 0.40	3.3-10
Cadiz[e]	-	0.1 ± 0.03	-	6.7 ± 3.9	-	117 - 130	-	230 ± 150	17±9
Algeziras[f]	-	0.2 ± 0.1	-	17 ± 8	-	120 - 133	-	14 ± 2	130 ± 60
Aegean[g]	-	0.08 - 0.12	0.12 - 0.29	1.8 - 4.4	2.1 - 4.0	110 - 130	-	-	-
Black sea[g]	-	0.06 - 0.09	0.18 - 0.37	6 - 8.8	1.8 - 3.7	39 - 47	-	-	-
Maó[h]	-	0.1 - 0.4	0.1 - 0.6	2 - 54	1.2 - 35	95 - 150	2.7 - 5.9	0.2 -2 .4	2 - 59

a Trezzi et al., (2016); b Cobelo-Garcia et al., (2005); c Echenadia-Santos et al., (2009); d Rodellas et al., (2014); e Morillo et al., (2015); g Tovar-Sanchez et al., (2014); h Martinez-Soto et al., (2016)

6. Discussion

The metal concentrations that have been exposed in the last chapter can be used to explain some of the processes that are taking place in the bay groundwater and its following discharge inside the sea.

The presence of lower salt concentrations, higher O_2 and high Ra isotopes concentrations, in the west side of the bay, indicates us that we have the presence of a freshwater layer in this site of the bay. However, the rest of the bay showed the opposite pattern, as this other site had no inputs of a fresh layer.

Porewater samples showed an inverse proportional correlation between ^{224}Ra and salinity concentrations. This pattern does not match other related publications as Rodellas et al., (2014), Trezzi et al., (2016), Garcia-Solsona et al., (2012), where ^{224}Ra concentration is function of salinity. The ionic strength (salinity) of groundwater has long been recognized as a major influence on the Ra adsorption, with Ra desorption increasing significantly with salinity (Webster et al., 1995). Afterwards, as freshwater mixes with seawater, Ra concentrations decrease because of the mixing process. However, in Portman we observed a different pattern, where Ra concentrations in groundwater started to decrease from a salinity of 10, suggesting that after this salinity only the dilution process with seawater is visible, having no observed increase with salinity, and where the mixing process is the only one observed. Another variable that conditions Ra concentrations in groundwater is the fact that the large amount of dissolved iron available that may scavenge the Ra isotopes when salinity increases too. As we observed in PZ03, where after extracting brackish groundwater with low O_2 concentrations, iron precipitated in contact with environmental conditions and no Ra was detected in this sample.

Figure 6. 1. Salinity ^{224}Ra in porewater
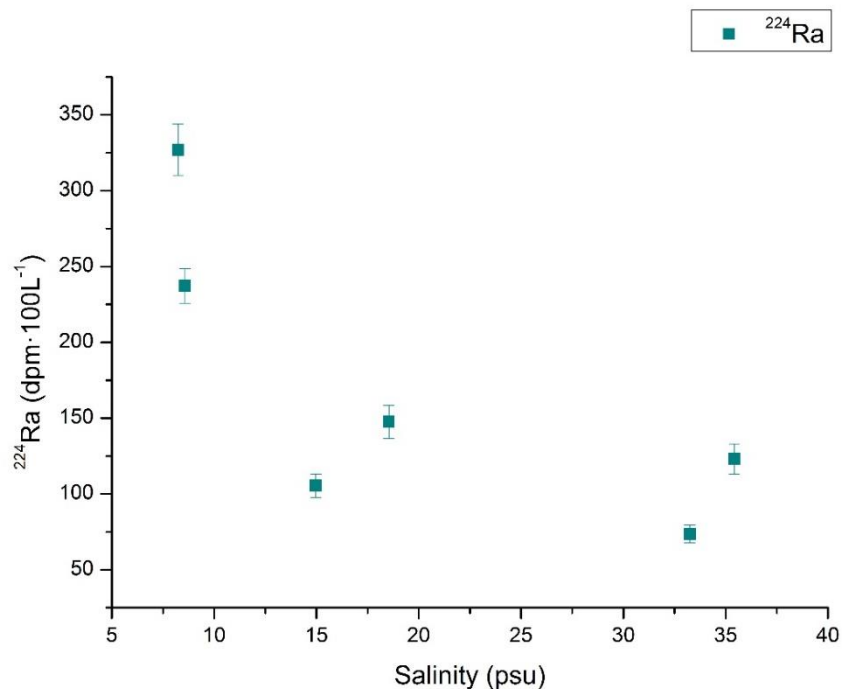
^{224}Ra porewater transect samples represented in function of their salinity.

Metal dissolved concentrations in porewater (Figure 2) reveal how the west part from the bay are having a different physicochemical from the rest. Cd, Co, Pb and Zn had higher concentrations in the western piezometers (PZ01 and PZ02), revealing that those metals are being dissolved into the fresh layer. If we observe the porewater transect samples we can see how those metals are enriched from PW01 to PW06, and then, when they contact seawater, the concentrations go down because of a dissipation process. Nonetheless Fe and Ni show an opposite pattern. The high concentrations, in the east of the bay, are produced because of the low O_2 concentrations, maintaining Fe^{2+} in a dissolved state. When we observe the western part, the enrichment of O_2 produces de oxidation of Fe^{2+} into Fe^{3+}, which is instantly complexed and precipitated. This fact could be explained by the "iron curtain", situation produced when a low O_2 enriched water contacts with a higher value, Fe^{2+} gets oxidized to Fe^{3+} and then attached to other particles, creating a precipitation line (Trezzi et al., 2016; Windom et al., 2006). In addition, we observe this process better in the porewater transect, where iron concentrations decrease as we contact oxidized waters. Ni shows the same pattern as Fe, this can be explained because of the iron curtain, where Ni dissolved particles get scavenged by the Fe precipitated particles.

Figure 6. 2. Porewater metal distribution
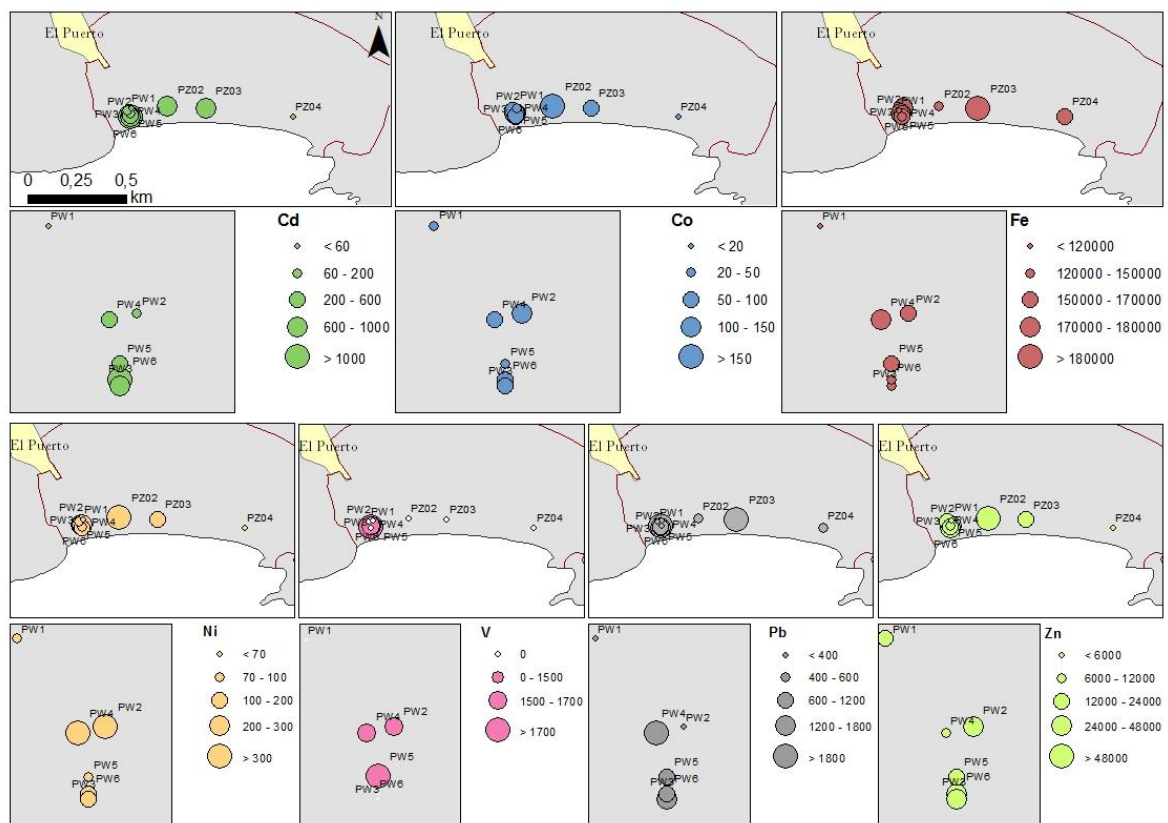
If we observe the evolution of Cd, Pb and Zn concentrations in seawater we can see that it describes an exponential decrease. This fact, shown in Figure 6.2, could be explained because of the SGD discharged from the bay is enriched mostly, by this elements, that have been the target for the old mining industry placed in the bay. Consequently, metal concentrations start to decrease exponentially because of their reactive particle nature, trough scavenging, biota

absorption, precipitation or complexed to other molecules, until the remain with their open seawater concentration values. The remaining quantified dissolved metals, Co, Cu, Fe, Mo and Ni, do not show any trend. Even though Co, Cu, Fe and Ni show their highest concentration value at 20 meters offshore.

Figure 6. 3. Distribution of Ag, Cd, Pb and Zn concentrations
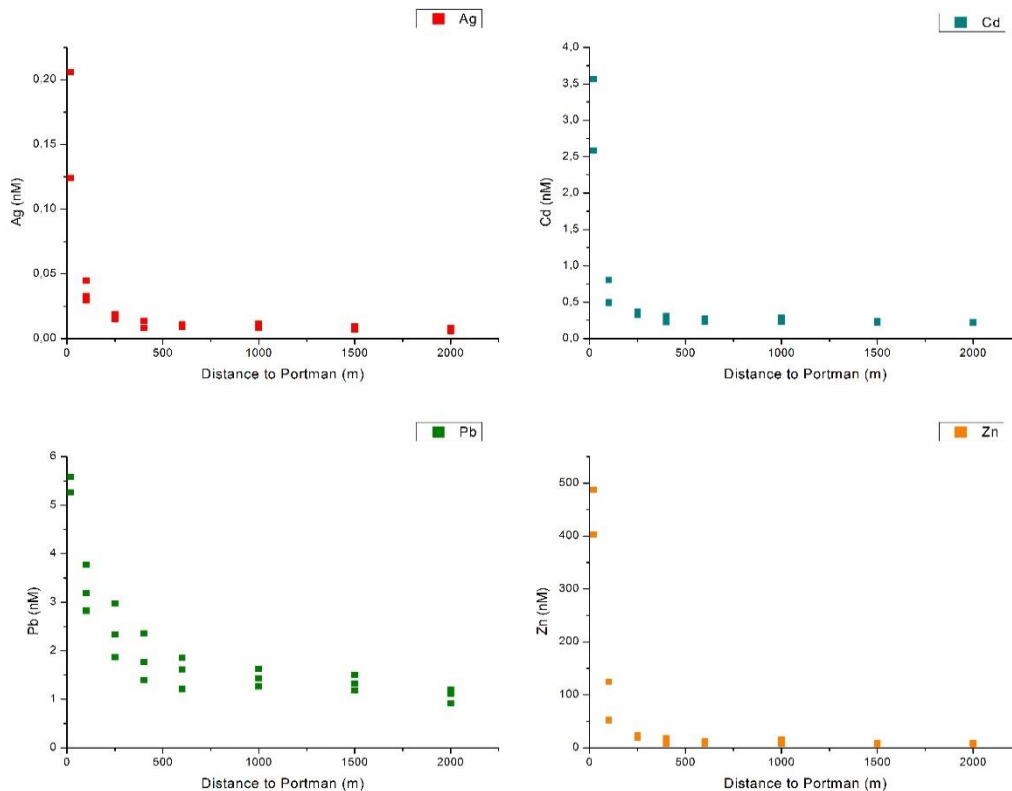
The European legislation, as the Spanish legislation have Cd, Cu, Ni, Pb, and Zn concentration limits established in the Directive 2008/105/CE and the Real Decreto 60/2011, respectively. Even though our maximum metal concentrations measured in seawater don't reach the levels established as the maximum amount permitted. Nonetheless Cd values are near the minimum limit, fact that concerns the risk that all those materials are supposing to the population that is living next to it.

Table 4. Legislation and Portman seawater metal concentrations								
	Ag	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
µg/L								
Legislation*	-	0,45-1.5	-	25	-	-	20	7,2	60
max	0,02	0,40	0,02	0,42	0,43	12	0,26	1,2	32
Natural**	0,0005	0,02	0,01	0,18	0,20	11	0,22	0,20	0,24

Real Decreto 60/2011

**We consider natural values as the constant values offshore.*

In addition, risk has been calculated in function of one of the UNESCO indicators, developed by Costa (2002) and then modified, Table 5 shows how we deference the type of problem, the contamination risk as the chemical state. To do so, we compare the value obtained, to the limit value that the legislation establishes (VL) and the natural value (VN).

Table 5. UNESCO indicator			
Operative value	Type of problem	Contamination risk	Chemical state
> 1000% VL	Very serious	Contamination	Bad
> 100% VL	Serious		
> 50% VL	Moderate	Risk	Good
< 50% VL>VN	Slight		
VN	Zero	No risk	

Applying Table 5 we can consider that the seawater bay has a slight problem with Pb and a moderate problem with Cd and Zn supposing a contamination risk but still a good chemical state. As we had discussed before, the metals that where excreted by the mining industry in Portman Bay are the ones that are affecting and contaminating the environment.

Porewater metal concentrations could not be compared to legal limits because there are not so.

6.1.   Fluxes results

To evaluate the influence of SGD metal-driven fluxes and to evaluate its impacts in to the bay, we will use three different methods based in Ra isotopes concentrations and metals to estimate the different sources of groundwater in to the bay. Surface runoff water fluxes have been neglected because of the absence of rivers or permanent superficial water fluxes in the study zone. The fact of semiarid climate guaranties that superficial streams created by spontaneous storms could not be monitored in this study, leaving us to reject Ra runoff inputs. Diffusion inputs have been considerate negligible because of the sediment composition and reports that prove (Beck et al., 2007; Garcia-Solsona et al., 2014; Rodellas et al., 2015) that this input would not represent a 10% of the inputs. That leaves us as in a stage were SGD is the main Ra input in Portman Bay.

The first method used to calculate metal fluxes has been described by Rijkemnberg et al., (2012) with the use of D, Okubo's (1971) parameterization to estimate horizontal turbulent flux. This method has been normally used in open waters by Gerringa et al., (2012) in Antarctic peninsula, for example, or by Ardelan et al., (2010) in Monterey Bay to calculate dissolved Fe.

Nonetheless, we applied the methodology by using the following equation to firstly calculate the D value, scale length defined as the distance over which concentrations of dissolved Fe decrease 1/e of the initial value (Johnson et al., 1997).

Formula 1: Exponential equation for D

$$C_{(x)} = c_0 e^{-x/D}$$

Where C_0 is the initial concentration, x the distance from the initial station to the other measured, and $C_{(x)}$ the final concentration at the other station.

Once we had calculated D for each dissolved metal, we observed that only the metals with a decreasing slope could be estimated.

We calculated the flux of each metal by using formula 2.

Formula 2: Flux equation using Okubo's (1971) D

$$Flux = -7.3 \cdot 10^{-4} D^{0.15}$$

After resolving equation 2 for each metal, no logical results were obtained. As consequence, this method was rejected.

Metal fluxes should have been calculated by the methods exposed in Chapter 1, where fresh water is calculated by the method that Moore (2000) developed and then Li and Cai (2011) improved. Because of the results of long lived Ra isotopes ([226]Ra and [228]Ra) in seawater are too low and no gradient trend was reflected in seawater concentrations, we will calculate the metal fluxes with the method that Moore (2003) developed.

6.1.1.   Moore (2000) method

To calculate fluxes by this method, we will have to calculate the parameters of Formula 3:

Formula 3: Metal flux

$$F_{m-off} = \left[K_h \left(\frac{\partial A}{\partial x} \right) \right] \cdot z \cdot L$$

Where:

Formula 4: K_h

$$K_h = L_2^2 \lambda_2 + L_2 u = L_1^2 \lambda_1 + L_1 u$$

Formula 5: u

$$u = \frac{L_1^2 \lambda_1 - L_2^2 \lambda_2}{L_1 - L_2}$$

$\left(\frac{\partial A}{\partial x} \right)$ is the metal gradient

z the depth where is the surface layer depth over which Ra is transported
L is the shoreline length.

And where:

- L_1: The inverse (1/m) of the slope from the long-linear fit for [223]Ra.

- L_2: The inverse (1/m) of the slope from the long-linear fit for [224]Ra.

- λ_1: The radioactive decay coefficients of [223]Ra.

- λ_2: The radioactive decay coefficients of [224]Ra.

In the following Table 3 we expose the results of the different parameters that were used to calculate K_h, all the samples of the three transects to have an average value.

Table 6. Kh and parameters					
L_1	L_2	λ_{223}	λ_{224}	u	K_h
m^{-1}	m^{-1}	s^{-1}	s^{-1}	$m \cdot s^{-1}$	$m^2 \cdot s^{-1}$
588 ± 147	434 ± 69	$7,03 \cdot 10^{-7}$	$2,19 \cdot 10^{-6}$	$1,1 \cdot 10^{-3}$ ± $1,7 \cdot 10^{-3}$	0,90 ± 0,62

Because there was no ^{228}Ra or ^{226}Ra gradient in seawater samples, this method couldn't be used.

6.1.2. Moore (2003) method

To evaluate the influence of SGD metal-driven fluxes and to evaluate its impacts in the bay, the first step is to evaluate the amount of SGD flow into the bay. In order to estimate the method developed by Moore (2003) based on end-member mixing model of Ra isotopes was used. Surface runoff water fluxes have been neglected because of the absence of rivers or permanent superficial water fluxes in the study zone. The fact of semiarid climate guaranties that superficial streams created by spontaneous storms could not be monitored in this study, leaving us to reject Ra runoff inputs. Diffusion inputs have been considerate negligible because of the sediment composition and reports that prove (Beck et al., 2007; Garcia-Solsona et al., 2014; Rodellas et al., 2015) that this input would not represent a 10% of the inputs.

To calculate the freshwater flux that goes into the sea, we will use Formula 4, 5, 6, and 7, formulas that have been adapted due to the lack of long lived Ra isotopes:

Formula 4: Fractions water sum.

$$f_{ocn} + f_{SGD} = 1$$

Formula 6: ^{224}Ra water fractions

$$^{224}Ra_{ocn} \cdot f_{ocn} + {}^{224}Ra_{SGD} \cdot f_{SGD} = {}^{224}Ra_{cw} \cdot e^{\lambda_{224} \cdot \tau_r}$$

Formula 7: Apparent water residence time (Knee et al., 2010)

$$\tau_r = \frac{\ln(1 - \sqrt{(\delta^{224}Ra)^2 + (\delta^{223}Ra)^2}}{\lambda_{223} - \lambda_{224}}$$

Using the method described by Moore (2003) the apparent residence time resulted to be negative, meaning that the real time it was less that one day. To calculate it we had used the equation 4 developed by Knee et al., 2010 and then modified.

Formula 8: ^{224}Ra SGD flux (Moore, 2003 and modified by Gracia-Solsona et al., 2010).

$$SGD_{^{224}Ra} = \frac{f_{SGD} \cdot V}{\tau_r}$$

The results and parameters calculated with the previous formulas are showed in Table 4:

Table 7. Results and parameters of Moore (2003) method				
Parameters	Units			
$^{224}Ra_{cw}$	$dpm \cdot 100L^{-1}$	5	±	1
$^{224}Ra_{ocn}$	$dpm \cdot 100L^{-1}$	3,5	±	0,4
$^{224}Ra_{SGD}$	$dpm \cdot 100L^{-1}$	237	±	11
τ_r	d	0.6		
$\lambda 223$	d^{-1}	0.06		
$\lambda 224$	d^{-1}	0.2		
V	m^3	795066		
f_{ocn}	-	0.998	±	0.07
f_{SGD}	-	0.012	±	0.002
SGD	$m^3 \cdot d^{-1}$	6382	±	1340

The $^{224}Ra_{SGD}$ had been calculated by the average of the piezometers ^{224}Ra concentrations. The $^{224}Ra_{ocn}$ had been calculated by the average of the offshore (2000 meters' seawater samples) ^{224}Ra concentrations. The $^{224}Ra_{cw}$ had been calculated by the normalization of ^{224}Ra concentrations in the bay seawater. We have divided the bay in three areas where activities in each are similar. Zone 1 comprises from 0 to 100 m, zone 2 from 100 to 250 m and zone 3 from 250 to 600 m from Portman Bay. We only count until 600 m because it is where ^{224}Ra concentrations started to remain constant.

Results obtained from equation 4 show how the time residence is very low. The fraction waters (f_{ocn} and f_{SGD}) show that nearly all the water enriched with ^{224}Ra comes from the sea, 98.8%, and only a 1.2% from fresh-SGD component. Indicating that has a very high recirculation component.

The SGD flux obtained of 6382 ± 1340 $m^3 \cdot day^{-1}$ can be compared with other sites by normalizing the flux with the bay length (0.988 km) and obtaining the normalized flux per year, 2.4±0.5·10^6 $m^3 \cdot km^{-1} \cdot y^{-1}$. Other investigations in the Mediterranean Sea, as in Palma de Mallorca (Balearic Islands, Spain) (Rodellas et al., 2015) with aproximatly 20·10^6 $m^3 \cdot km^{-1} \cdot y^{-1}$ or in El Gorguel (Murcia, Spain) (Trezzi et al., 2016) with a similar SGD flux, showing that our flux is much smaller, down to one magnitude order below. Nonetheless, as Rodellas (2015) described, those fluxes are small if they are compared with other SGD fluxes calculated around the Mediterranean Sea.

Table 8. Porewater dissolved metal concentrations								
	Cd	Co	Cu	Fe	Ni	Pb	V	Zn
nM	2 – 1231	16 – 533	-	11011 – 732922	49 – 1677	149 – 7744	1555 – 2006	613 – 103901

Once we have calculated the SGD flux, we can multiply it with the metal concentrations of Table 8 so we finally have an approximation of the metal fluxes (Table 9).

Table 9. Metal fluxes calculated in Portman Bay																				
Metal	Cd			Co			Fe			Ni			Pb			V			Zn		
	mol·dia^{-1}																				
Min.	0.016	±	0.003	0.10	±	0.02	70	±	15	0.31	±	0.07	1	±	0.2	10	±	2	4	±	1
Max.	8	±	2	3	±	1	4678	±	982	11	±	2	49	±	10	13	±	3	663	±	139
Av.	3	±	1	0.5	±	0.1	1057	±	222	0.9	±	0.2	5	±	1	11	±	2	118	±	25

6.2.   Portman Bay fluxes

If we compare our values to a natural anthropized site, Palma de Mallorca ([a]Rodellas et al., 2014), on one hand, we can observe as our values go up to four magnitude order with Pb and Zn. Fe and Ni are also the highest reported until now in the Mediterranean Sea. But in the other hand, we observe as Cu could not be calculated because of its low concentrations in porewater. If we compare our values with another sight that is contaminated because the industry activities as Port de Maó (Martinez-Soto et al., 2016), we observe as Portman's Zn and Pb fluxes are still two and three magnitude order above, respectively. Yet, Zn flux values are higher the flux reported in el Gorguel (Trezzi et al., 2016) as Pb. Nonetheless, there is a big difference between Zn and Pb concentrations or fluxes, this fact can be explained because the different geochemical behavior that they have, meanwhile Pb gets complexed very easily to oxides, Zn gets mobilized very easily with acid pH variations.

Table 10: Mediterranean sites fluxes						
Site		Cu	Fe	Ni	Pb	Zn
Portman, Murcia, Spain		0	70 - 4678	0.31 - 11	1 - 49	4 - 663
Palma Beach, Balearic Islands, Spain[a]	mol·day^{-1}·km^{-1}	0.07 – 0.53	0.4 - 20	0.13 – 0.65	0 – 0.011	0.1 – 1.4
Gorguel, Murcia, Spain[b]		0.8 - 2.3	4-32	0.9 - 2.8	0.20 - 0.60	47 - 180
Port de Maó, Balearic Islands, Spain[c]		0.466	4.11	0.466	0.0493	1.64

Iron had been deposited as waste inside the bay during the mining activities, being the main element (magnetite) of the tailings of Portman (Oyarzun et al., 2013). The big amount of this material inside the bay should be related to high dissolved Fe fluxes, however, the reported Fe fluxes are highest than any other site in the Mediterranean, but the resulting concentrations in

seawater do not correspond to such fluxes. This fact could be explained by the "iron curtain", situation produced when a low O_2 enriched water contacts with a higher value, Fe^{2+} gets oxidized to Fe^{3+} and then attached to other particles, creating a precipitation line (Trezzi et al., 2016; Windom et al., 2006. This fact might reduce the amount of dissolved Fe and the other metals mentioned that are not so enriched as Pb and Zn in seawater.

Silver concentrations seem to come from the remobilization of the shore materials. Porewater concentrations were under the limit detection, indicating the origin of seawater concentrations did not come from the bay. The negative exponential trend in seawater concentrations how near shore Ag is remobilized from the sediment and then suffers the same processes that Cd, Pb and Zn showed.

6.3.   Possible consequences after the Ministerio's rehabilitation project

In Chapter 1 we had introduced the history of the bay and its actual state, further on in Chapter 4 and 5 we had proved that there is a constant metal flux into the sea (6382 ± 1340 $m^3 \cdot d^{-1}$), with values that prove that the levels are much higher than in a natural sight and can be considerate as a risk. Also, it has been explained that metal concentrations increase as we go from offshore to inside of the bay, describing as the metal flux is coming through the tailings by SGD recirculation and eventual runoff into the sea. So we understand that the exterior border of the bay has been drained since 1991 and most of the dissolved metals have been extracted from the exterior tailing border. With this actual scenario, the project dictated by the Spanish government is going to begin in June of 2016. As it was exposed before, the project has had several cuts in its budget, leaving it in this moment at 32 million euros and four years to be finished. Nevertheless, the project objectives have not been modified, 2500 tons of the sea sediments and bay tailings will be extracted to San Jose crick, the old fishing port will be restored as expanded to a sport port, the beach will be restored and an aerial conveyor belt will be constructed and used to move the tailings.

If the actual project is executed, consequences for the environmental zone may be catastrophic. If we focus on the process of removing the tailings, automatically we may have to expect a remobilization off all those, with much high metal concentrations than the ones that actually are in contact with the seawater, this process may spread toxic metal concentrations that are in the bay (the highest reported until now in the Mediterranean Sea) near the closer seawaters affecting all type of marine life. In addition, once the anthropic remobilization has finished, the metal concentration fluxes would increase intensely, producing the export of metals to the sea as in 1991, so all the removal produced until now will have to be produced again until the system gets drained. In conclusion, if in the expected future, no containing barriers in booth sides of the construction works, are done and hermetically sealed the worst environmental impact could start again, as in the 1950's. It seems that because of the budged reduction, several aspects might be removed from the government's project. The situation could be critical if barriers are affected by this changes, and it seems, because of the last times decisions and the current encysted corruption, that an environment contamination, in major or minor scale, will happen.

7. <u>Conclusions</u>

In conclusion, the results of the samples taken in Portman Bay reveled how there is a heterogeneous distribution inside the bay. Physicochemical parameters indicate the is a fresher layer with higher maximum values of O_2 (14.4) in the west of the bay, and how the opposite site seems to be stagnate with brackish water (28.4) and low O_2 concentrations (4.2). Ra-isotopes, used as tracer, revealed with higher concentrations in the western part of the bay, that there is a SGD flow.

The results obtained by this study have revealed that high concentrations of metals, some of them toxic as Cd, are present in the seawaters of Portman in very high concentrations (2.58 nM). The highest dissolved Zn concentration (488nM) in seawater that has been registered until now in the Mediterranean has been obtained by this investigation. Metals as Pb have registered higher concentrations than in El Gorguel (2.4 nM) (Trezzi et al., 2016). It has been proved that SGD produces by remobilization an extraction of metals into the sea. Even though the limit concentration values are under the limits that the Spanish and European legislation determine.

The metal fluxes calculation method has revealed that the 98.8% of the fluxes are produced by recirculation, and only a 1.2% from groundwater discharge. Even dough, Portman Bay have become to be the highest metal fluxes of the Mediterranean Sea. The bay fluxes are ruled by the tailings composition and distribution leading to the fact that some metals have been affected by the "iron curtain" and fluxes have been narrowed. As in El Gorguel, metal fluxes have been significantly higher than in other locations worldwide. Specifically, for Pb (1 – 49 mol·day^{-1}), Zn (4 – 663 mol·day^{-1}) and Cd (0.016 – 8 mol·day^{-1}).

Nevertheless, the amounts of metals that have been measured in porewaters have revealed very high levels of Cd (1231 nM), Fe (732922 nM), Pb (6477nM) and Zn (103902 nM). In addition, the possible enrichment of those after the rehabilitation project may affect the marine environment. With this scenario metal cycles inside the bay should be properly studied such as the actual, or future state of the environment of Portman Bay.

8. Improvements

This last chapter describes the three main lines that should be done to improve some of the aspects observed with this investigation.

We divide our improvements in three action lines, in order of its importance:

- Health protection

    o People's health should be the first studied and evaluated aspect in any contaminated site, that's why a strict health study of all the habitants of Portman and its surroundings should be done to determine the state and effects that the mining tailings and old mining industries are creating.

- Scientific

    o The different aspects of this study that should be studied or continued for a better knowledge of the bay for a future effective and permanent solutions to the tailings should be the next step to take. This line has been divided in three different actions ordered in function of their actual viability:

        ▪ Research in the viability of a new method to calculate metal fluxes.

        ▪ Research in how metal concentrations are affecting marine life.

        ▪ Research in the metal's cycle in Portman Bay.

- Restoration

    o Once we have the knowledge of how materials interact and which are their cycles restoration can be made. To do that, two consecutive actions have been determined so the Bay's state returns to the most natural state as is possible and then that this state is conserved.

Strategic line	Health protection.
Action	Evaluation of the actual health state, metal and toxics levels of Portman Bay's population and its surroundings because of the salt efflorescence.
Description	No public reports or investigations have been done about the effect of Portman Bay's toxics and pollutants are affecting its population. Large extensions of salt efflorescence appear in the bay, which may have an impact at the local population, surrounding crops, farms… People health's cannot be forgotten or underrated, there is a need to know if people are dying because of the Bay's contamination or if they are suffering any diseases because of it.
Objectives	Evaluation of the health state of Portman's habitants and impact of the salt efflorescence.
Responsible	Gobierno de España, Ministerio de Sanidad.
Implicated actors	Medical experts in environmental intoxications and diseases, environmental experts with air pollutants and experts in soils and crops contamination.
Timing	4 years.
Budget	200.000€.
Benefits	The knowledge of if there is an intoxication of the habitants because of the toxic substances that remain from the mining industry and its aerial influence.
Indicators	DE_{50}: Effective dosses DL_{50}: Lethal dosses CE_{50}: Effective concentration CL_{50}: Lethal concentration CI_{50}: Inhibition concentration NOAEL: No observed adverse effect level LOAEL: Lowest observed adverse effect level
Observations	The influence of the contamination of Portman Bay may be transported by air to kilometers of distance, an evaluation of the distance that those pollutants can reach should be done before.

Strategic line	Scientific
Action	Research in the viability of the new method.
Description	The method developed by Moore (2003) to calculate fluxes, could be adapted to metal concentrations. Ag, Cd, Pb and Zn showed to have an exponential decrease trend offshore, where gradients could be calculated in order to replace the lack of ^{226}Ra and ^{228}Ra.
Objectives	Full understanding of the new method and its possible applications.
Responsible	The author of the present document.
Implicated actors	The author and tutor of the present document.
Timing	1 month
Budget	0€
Benefits	The knowledge of a new method to calculate metal fluxes for the scientific community.

Strategic line	Scientific	
Action	Research in how metal concentrations are affecting marine life	
Description	The metal concentrations and fluxes that have been calculated in the present document are high enough to have a concern of how those metals are affecting the marine life.	
	Stage 1	Shoreline benthos communities
	Description	Analyze the state of the communities at the shoreline of the bay, as the accumulated metals that they present, biochemical effects to the different species and communities.
	Stage 2	Benthos and pelagic state communities
	Description	Analyze the state of the communities nearshore, as the accumulated metals that they present, biochemical effects to the different species and communities.
	Stage 3	Food chain
	Description	Describe how bio cumulative metals go through the food chain and which effects could have on people's health in function of the specie consumed.
Objectives	Evaluation of the state of marine life affected by metals in Portman and its consequences.	
Responsible	Gobierno de España, Ministerio de Medio Ambiente.	
Implicated actors	Specialized investigators group. Environmental scientists, biologists, geologist, oceanographer.	
Timing	4 years.	
Budget	200.000€	
Benefits	The knowledge of actual state of the environment and its possible solutions.	
Indicators	Contamination rates, concentrations of toxic metals in organisms.	
Observations	This research can be crucial for the tuna farm situated near Portman and El Gorguel Beach	

Strategic line		Scientific
Action		Research in the metal's cycle in Portman Bay.
Description		Once we have detected all the inputs and outputs of the metals from the bay, they should be quantified and modeled so we could have an integral understanding of all the processes
	Stage 1	Characterization of the metal concentrations in the mine tailings of the bay.
	Description	Analyze the bay's metal concentrations in the mine tailings so a map could be developed indicating the proportion of metals along and inside the bay.
	Sage 2	Characterization of particle and dissolved rates in the mine tailings of the bay.
	Description	Determine how metals are interacting inside groundwater and porewater in function of its physiochemical parameters.
	Stage 3	Characterization of particle and dissolved rates in nearshore seawater of the bay as its sediments.
	Description	Determine how metals are interacting in seawater in function of its physiochemical parameters and the sediment metal concentrations.
	Stage 4	Describe the relation of storms and metal exportation to the sea.
	Description	Analyze the variability and importance of metal fluxes related to strong rain runoffs and intense wave storms from normal static conditions.
	Stage 5	Determine how the different metals get out of the water column
	Description	Analyze the different exits of the different metals and the importance of each one. (Scavenging, Biota absorption, complexation, precipitation...)
Objectives		Evaluation of the state of metals in Portman and its consequences.
Responsible		Gobierno de España, Ministerio de Medio Ambiente.
Implicated actors		Specialized investigators group.
Timing		4 years.
Budget		500.000€
Benefits		The knowledge of the metal cycle in Portman bay.
Indicators		Contamination rates, concentrations of toxic metals in organisms, dissolved/particulate ratios, transportation ratios...
Observations		No measures should be taken without understanding the real process that metals are doing in Portman Bay.

Strategic line	Restoration
Action	Monitoring of the contamination parameters
Description	Once we have solved the tailings issue, and the most natural conditions have been back to Portman Bay's waters, a strategical sensors network has to be installed to avoid any leaks.
Objectives	Monitoring of the possible water pollutants.
Responsible	Gobierno de España, Ministerio de Medio Ambiente, regional and local government.
Implicated actors	Environmental technicians.
Timing	6 months
Budget	100.000€
Benefits	The security of an environmental sensors network that advises of new contaminations.
Indicators	Metal concentrations, nitrates, virus, pathogenic bacteria, organic compounds, pesticides…
Observations	After a such a big investment in restoring the bay, a thorough control has to be done to preserve what has been achieved.

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10. Planning

Activities	March 2015	January 2016	Februray 2016	March 2016	April 2016	May 2016	June 2016	July 2016
A.1. Collection Of Information	6	6	6	6	6			
A.2. Writing		6	6	6	6	6	6	6
A.2.1. Introduction			6	6	6			
A.2.2. Results				6	6	6	6	
A.2.3. Conclutions						6	6	6
A.2.4. Final							6	6
A.3. Deliveries				6		6	6	6
A.3.1. Introduction				6				
A.3.2. Results						6	6	6
A.3.3. Conclutions							6	6
A.3.4. Final						6	6	6
A.4. Exposition				6		6	6	6
A.4.1. Introduction				6				6
A.4.2. Results						6		6
A.4.3. Final								6
A.5. Seawater Campaign	1,2,3							
A.6. Porewater Campaign		1,3		1,3		1,3		
A.7. Sample Analysing	4,6	4,5,6	4,5,6	4,5,6	4,5,6	4,5,6	4,5,6	
A.7.1. A.Alvariño Campaign	4,6	4,6	4,5,6	5,6				
A.7.2. On Land Campaign		4,6	4,5,6	4,5,6	4,5,6	5,6		
A.8. Revision	6	6	6	6	6	6	6	6

Material Legend	
Car	1
Vessel	2
Campign Ra and metals materials	3
RaDeCC	4
γ detection	5
Computer	6

11. <u>Budget</u>

	Concept	Specifications	Cost €
Direct costs			
Human Resources	Hours of work	One researcher, working 15 hours per week, during 24 weeks, with a 15 €/hour salary	5400€
Campaign costs — Transport	Weekly transport (Barcelona-UAB)	2X Train 3-month bonus (T-Jove) 2 zones, 142€	284€
	Van renting from Barcelona to Portman-Bay	7 days. With a cost of 170€/day	1705.2€
		2X 1288 km and a consumption of 0.20€/km	
	Tolls	2x Barcelona-Cartagena 42.2€	168.8€
		2x Cartagena-Barcelona 42.2€	
Accomodations	Hotel	Hotel Los Habaneros 30€/night, for 6 nights	180€
Diets	Diets during campaings	30€/day, during 7 days	210€
Sampling	Vassel Angeles Alvariño	6000€/day, for 2 days	12000€
Expendables	Printings	3x 77 pages 0.15€/page	34.65€
	CD's	6 CD's pack at 3€/pack	3€
	Markers	5 markers at 1.2€/marker	6€
	Pens	5 pens at 0.5€/pen	2.5€
	Notebook	1 notebook at 2€/notebook	2€
∑ Direct costs			19996.15€
Indirect Costs (20% Direct costs)			3999.23€
∑ Direct and indirect costs			23995.38€
Taxes (21%)			5039.03€
∑ Costs and taxes			29034.41€

12. Carbon footprint

Concept	Specifications	Emissions
Desk work	Light: Room lighting with an average total power of 90 W, during 5 hours per week, during 20 weeks and a carbon footprint of 302 g CO_2/kWh	2.718 kg CO_2
	Laptop: Working 10 hours per week, during 20 weeks, with an average power of 60 W and a carbon footprint of 302 g CO_2/kWh	3.624 kg CO_2
∑ kg emisionsCO₂		6.436 kg CO_2
Transport	Van: Two 1288 km trip with an emission rate of 149 g CO_2/km	383.824 kg CO_2
	Train: 4 trips per week during 20 weeks, along a 20 km trip with a consumption of 29.43 g CO_2/passenger·km	47.088 kg CO_2
	Vessel (diesel motors): 24 h use with a consumption of 74.4L/h of diesel with a carbon footprint of 2.6256 kg CO_2/L	4688.27 kg CO_2
∑ kg emisionsCO₂		5131.96 kg CO_2
Materials	TFG: Three copies of 77 pages with a carbon footprint of 3.88 g CO_2/page	0.896 kg CO_2
	Article: Two copies of 15 pages with a carbon footprint of 3.88 g g CO_2/page	0.116 kg CO_2
	CD's: 6 CD's with a 620 g CO_2/CD	3.7 kg CO_2
∑ kg emisionsCO₂		4.712 kg CO_2
∑ kg emisionsCO₂		5143.108 kg CO_2