

# The significance of a tailing on SGD-driven metal fluxes in Portman Bay

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ARTICLE INFO	ABSTRACT
Article history: 1 <sup>st</sup> revision 29 March 2016 2 <sup>nd</sup> revision 10 May 2016 3 <sup>rd</sup> revision 7 June 2016	Portman Bay is located in Cartagena-La Unión Pb and Zn mining district, Murcia, Spain. This site is considered the biggest environmental impact of the Mediterranean Sea basin, where 57 million tons had been deposited between 1957 and 1991. The aim of this study is to study the role of submarine groundwater discharge (SGD) of metal in this contaminated environment. Ra isotopes and metal concentrations have been determined in sea and porewater samples. Cd, Pb and Zn concentrations were higher or similar to the highest concentrations reported until now in the Mediterranean Sea, reaching up to values of 488 nM for Zn, 5.59 nM for Pb, 2.58 nM for Cd and 0.124 nM for Ag. Short live Ra isotopes ( <sup>223</sup> Ra and <sup>224</sup> Ra) allowed the calculation of a SGD flow of 6382 m <sup>3</sup> ·d <sup>-1</sup> . Metal average fluxes have resulted to be, 3 ± 1 mol·day <sup>-1</sup> for Cd, 0.5 ± 0.1 mol·day <sup>-1</sup> for Co, 1057 ± 222 mol·day <sup>-1</sup> for Fe, 0.9 ± 0.2 mol·day <sup>-1</sup> for Ni, 5 ± 1 mol·day <sup>-1</sup> for Pb, 11 ± 2 mol·day <sup>-1</sup> for V and 118 ± 25 mol·day <sup>-1</sup> for Zn, most of them the highest values calculated be now in the Mediterranean. Those results showed the significance of SGD in the transport of metals to the sea in Portman Bay after 25 years of the last deposited tailing.
Key Words:	
Submarine Groundwater Discharge (SGD)	
Mine Tailings	
Ra isotopes	
Metals	
Metal Fluxes	
Zinc	
Lead	

## Introduction

Submarine Groundwater Discharge (SGD) has been a controversial term to define. Burnett and coauthors (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 driving 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 from the seabed to the

coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition or diving force”.

The study of SGD has become a strategically 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 (Trezzi et al., submitted). Non the less it can also be the pathway to introduce contamination or high metal concentrations into the sea (Trezzi et al., 2016).

The aim of this study is to study the role of submarine groundwater discharge (SGD) of metal in this contaminated environment.

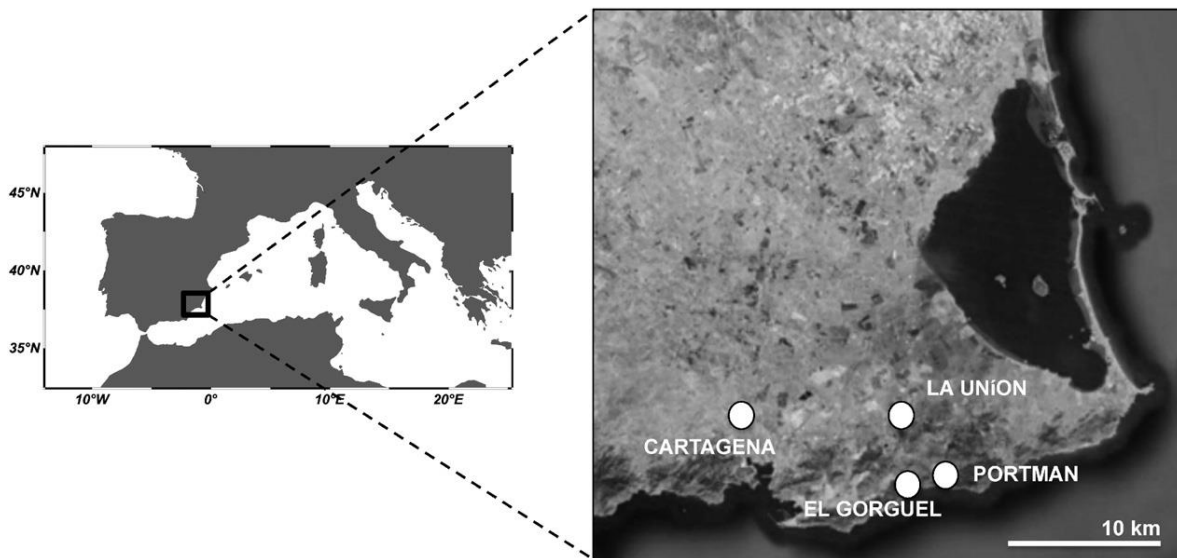


Figure 1: The study area is situated in the southwestern Mediterranean Sea (Trezzi et al., 2016).

## 2. Methods

### 2.1 Study area

Portman Bay is situated in the southeast of the Iberian Peninsula that is characterized by its semidesert environment with the influence of the Mediterranean Sea. Soft winters and hot summers rule the temperatures, with an annual mean temperature of 18°C. Rainfall is sporadic and intense, with an annual average of 200 – 300 mm. These parameters, plus the topography

of the bay, produce fast-flowing streams (Conesa et al., 2008).

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 Sea (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 Iberian Peninsula (Robles-Arenas, 2007).

The geochemistry of the bay is defined by the composition of the mine tailings. The mantles of those changes were in function of the activities that were done by “Sociedad Minero Metalúrgica Peñarroya España” (SMMPE) in the Lavadero Roberto. Between 1957 and 1991 it was processed more than 57 million tons of tailings (Oyarzun et al., 2013). The used flotation technique produced 95 t of tailings that ended into the bay for every 100 t of mineral ore. 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).

All those facts produce a flux of metals into the aquifer, creating high concentrations of Zn, Pb, Ag and Fe (Robles-Arenas and Candela, 2010). Thus, we can see evidence of fluxes of metals threw Submarine Groundwater Discharge (SGD) in Gorguel bay (Trezzi et al., 2015).

Our study is focused in the contact between sea and the mine tailings of Portman Bay. After 25 years the mine tailings have been exposed to all kind of environmental changes that have been extracting the metals from the bay. Even though the presence of all this tones makes us thing that recirculation may have an important role in the extraction of metals into the sea.

## *2.2 Sampling*

In March 13<sup>th</sup> to 19<sup>th</sup> of 2015 sea campaign was performed on board of the oceanographic vessel Angeles Alvariño (IEO). Three different transects perpendicular to the bay where established. In each station of the transects located at 20, 100, 250, 400, 600, 1000, 1500 and 2000 m offshore, seawater was collected to analyze metals and Ra. Salinity depth profiles where taken in each

station using an YSI 650. For the estimation of Ra concentrations, a 120 L barrel of superficial seawater were collected in each station with an electrical pump. Metal samples were taken in 500 ml acid-cleaned low-density polyethylene plastic bottle. Water was 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.

Groundwater samples were taken from January 26<sup>th</sup> to 27<sup>th</sup> of 2016. Four, 2.2 meter, slotted piezometers where installed along the bay and sampled for Ra and metals dissolved in porewater. Additionally, six porewater samples, at the west of the bay, were collected for Ra and metals to define one transect, and, describe the mixing layer. In all samples temperature, salinity, O<sub>2</sub> concentration and pH were also measured. For the sampling of Ra isotopes, for piezometers, 25 L and 10 L tanks were collected for piezometers and porewater transect samples, respectively. For metal samples 500 mL of porewater was collected in an acid-cleaned low-density polyethylene plastic bottle.

## *2.3 Analyses*

Water samples for Ra were filtered in the field with MnO<sub>2</sub> fibers at a flux of <1L·min<sup>-1</sup> to extract Ra isotopes (Moore and Reid, 1973). In the laboratory, fibers were rinsed with free Ra deionized water and partially dried (Sun and Torgensen, 1998). Then, fibers were introduced into a Radium Delayed Coincidence Counter (RaDeCC) to quantify short lived Ra isotopes (<sup>223</sup>Ra and <sup>224</sup>Ra) (Moore and Arnold, 1996). Uncertainties of

$^{223}\text{Ra}$  and  $^{224}\text{Ra}$  were determined following Garcia-Solsona et al., (2008). Long lived Ra isotopes ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) were determined by ashing the fibers at 820°C during 16 hours and then transferred to counting vials, stored and aged for a minimum of three weeks, and then

introduced into a well-type high-purity Ge detector and quantified by gamma spectrophotometry.  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were determined using the  $^{214}\text{Pb}$  and  $^{228}\text{Ac}$  photopeaks at 352 and 911 keV, respectively.

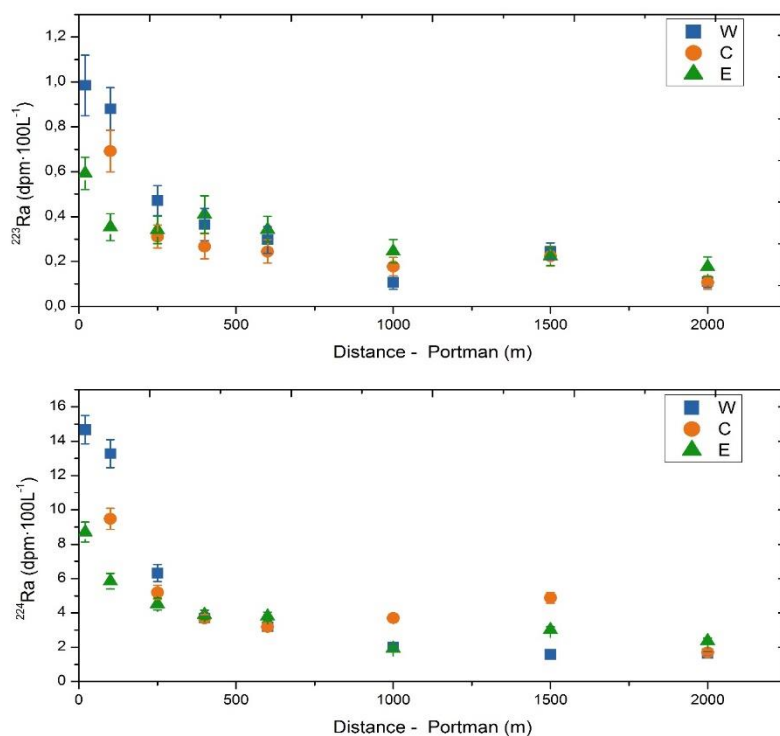


Figure 2:  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  concentrations in Portman Bay Metal concentrations are represented respect the distance offshore to Portman. Three transects are represented, W (west), C (central), and E (east).

Metal dissolved ( $<22 \mu\text{m}$ ) 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).

### 3. Results

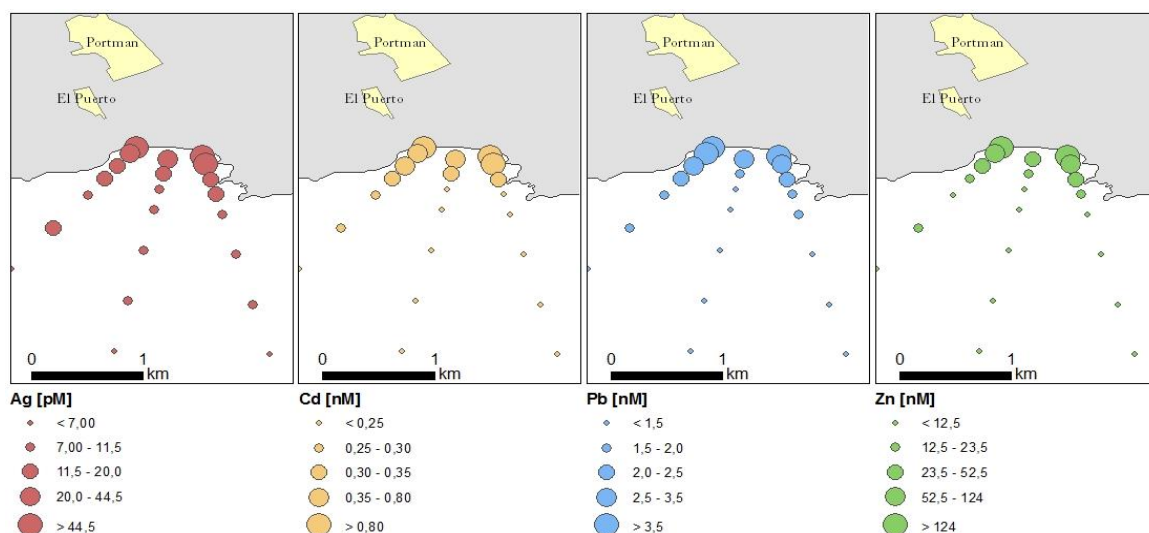


Figure 3: Ag, Cd, Pb and Zn concentrations in Portman Bay. Metal concentrations are function of the diameter of the spheres.

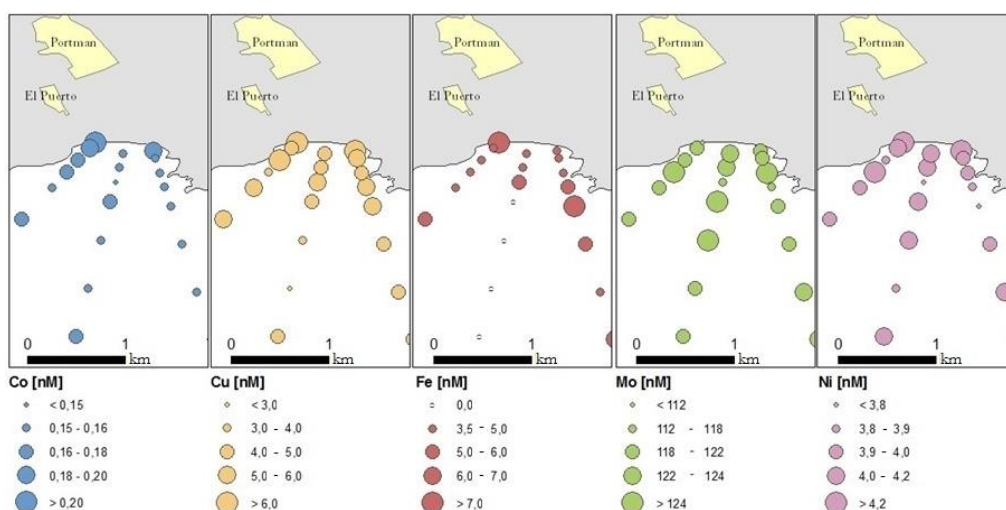


Figure 4: Co, Cu, Fe, Mo and Ni concentrations in Portman Bay. Metal concentrations are function of the diameter of the spheres.

#### 3.1 Portman seawater characterization

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. Salinity profiles are shown in appendix A.

Short lived Ra isotopes ( $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ ) were enriched near the shoreline compared to concentration values of both Ra isotopes offshore (Figure 2). Range from  $14.67 \pm 0.83$  to  $1.64 \pm 0.11$  at 20 m offshore and from  $0.984 \pm 0.135$  to  $0.107 \pm 0.030$  dpm $\cdot 100\text{L}^{-1}$  at 2000 m for  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ , respectively. This trend

suggests that most of the inputs of short lived Ra isotopes were from the shoreline.

Long lived Ra isotopes ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) did not show any trend offshore. Values range from  $15.0 \pm 0.7$  to  $9.2 \pm 0.8$  dpm $\cdot 100\text{L}^{-1}$  for  $^{226}\text{Ra}$  values, and from  $6.1 \pm 0.3$  to  $2.7 \pm 0.4$  dpm $\cdot 100\text{L}^{-1}$  for  $^{228}\text{Ra}$ . This pattern suggests that there is not a clear enrichment of SGD by the mine tailings because of their low concentrations in these two Ra isotopes.

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 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 4).

The evolution of Ag, Cd, Pb and Zn offshore concentrations describe an exponential decrease. This effect could be explained because of the groundwater discharged from the bay is enriched mostly, by this elements, that have been the target for the old mining industry placed in the bay. 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.

### *3.1 Portman porewater characterization*

Salinity values of the southern porewater samples ranged from 35.4, to freshwaters values, at the northern porewater samples, up to values of 8.24 (Table 1). 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  $\text{O}_2$  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  $\text{O}_2$  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 14.2°C in PW 03. Piezometers values remained constant with values of 19.0 °C except PZ 01 with 15.7 °C. pH remained in all samples approximately constant with values varying from 5 to 7.

Short-lived Ra isotopes ( $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ ) were the most enriched concentrations in porewater compared to long-lived Ra isotopes ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ).  $^{224}\text{Ra}$  ranged from  $74 \pm 6$  to  $327 \pm 17$  dpm $\cdot 100\text{L}^{-1}$ , and  $^{223}\text{Ra}$  ranged from  $19 \pm 2$  to  $69 \pm 6$  dpm $\cdot 100\text{L}^{-1}$ . Porewater samples showed an inverse proportional correlation between  $^{224}\text{Ra}$  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  $^{224}\text{Ra}$  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<sub>2</sub> concentrations, iron precipitated in contact with environmental conditions and

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

Table 1: Porewater physicochemical parameters

	Salinity	T	pH	O <sub>2</sub>	Depth
Units	-	°C	-	mg·L <sup>-1</sup>	m
PZ 01	14.3	15.7	7.27	1.7	2.2
PZ 02	14.3	20.0	6.46	2.1	2.2
PZ 03	14.7	19.7	5.68	3.7	2.2
PZ 04	28.4	18.9	6.23	4.2	2,2
PW1	8.6	16.4	6.99	14.4	1,6
PW2	8.2	18.4	6.55	7.1	2,0
PW4	15.0	18.6	6.31	3.0	2,0
PW5	18.5	17.2	6.47	10.2	1,8
PW6	33.3	15.6	6.60	11.6	1,8
PW3	35.4	14.2	6.94	20.6	1,8

no Ra was detected in this sample.

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

where then values decrease until reach PW3.

Metal dissolved concentrations in porewater 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

Table 2: Porewater dissolved metal concentrations in Portman Bay

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

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.

#### 4. Discussion

##### 4.1 SGD flux

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 use this method, we first calculated the SGD flux for  $^{224}Ra$  by equation 1 (Moore (2003) modified by Garcia-Solsona et al., (2010)), and then divided into the porewater  $^{224}Ra$  concentration to obtain the SGD flux.

$$SGD_{^{224}Ra} = \frac{f_{SGD} \cdot V}{\tau_r} \quad (1)$$

The SGD fraction ( $f_{SGD}$ ) had been calculated by the equations 2 and 3 modified from Moore (2003).

$$^{224}Ra_{ocn} \cdot f_{ocn} + \frac{^{224}Ra_{SGDi} \cdot f_{SGDi}}{^{224}Ra_{cw} \cdot e^{\lambda_{224} \cdot \tau_r}} = \quad (2)$$

$$f_{ocn} + f_{SGDi} = 1 \quad (3)$$

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 goes from 0 to 100 m, zone 2 from 100 to 250m and zone 3 from 250 to 600 m from Portman Bay. We only count until 600 m because it is where  $^{224}Ra$  concentrations start to remain constant.  $^{224}Ra_{SGD}$  had been calculated by using the mean concentration of the porewater values.

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

$$\tau_r = \frac{\ln(1 - \sqrt{(\delta^{224}Ra)^2 + (\delta^{223}Ra)^2})}{\lambda_{223} - \lambda_{224}} \quad (4)$$

Parameters used and calculated in equations 1, 2, 3 and 4 can be observed in Table 3.



Table 3: Results and parameters of Moore (2003) method				
Parameters	Units			
$^{224}\text{Ra}_{\text{cw}}$	dpm·100L <sup>-1</sup>	5	±	1
$^{224}\text{Ra}_{\text{ocn}}$	dpm·100L <sup>-1</sup>	3,5	±	0,4
$^{224}\text{Ra}_{\text{SGD}}$	dpm·100L <sup>-1</sup>	237	±	11
$\tau_r$	d	0.6		
$\lambda_{223}$	d <sup>-1</sup>	0.06		
$\lambda_{224}$	d <sup>-1</sup>	0.2		
V	m <sup>3</sup>	795066		
$f_{\text{ocn}}$	-	0.998	±	0.07
$f_{\text{SGD}}$	-	0.012	±	0.002
SGD	m <sup>3</sup> ·d <sup>-1</sup>	6382	±	1340

Results obtained from equation 4 shows how the time residence is very low. The fraction waters ( $f_{\text{ocn}}$  and  $f_{\text{SGDi}}$ ) show that nearly all the water enriched with  $^{224}\text{Ra}$  comes from the sea, 98.8%, and only a 1.2% from fresh-SGD component, indicating that the flux of metals will come from the remobilization that the sea produces at the shoreline.

The SGD flux obtained of  $6382 \pm 1340 \text{ m}^3 \cdot \text{day}^{-1}$  can be compared with other sites by normalizing the flux with the bay length (0.988 km) and obtaining the normalized flux per year,  $2.4 \pm 0.5 \cdot 10^6 \text{ m}^3 \cdot \text{km}^{-1} \cdot \text{y}^{-1}$ . Other investigations in the Mediterranean Sea, as in Palma de Mallorca (Balearic Islands, Spain)

(Rodellas et al., 2015) with aproximatly  $20 \cdot 10^6 \text{ m}^3 \cdot \text{km}^{-1} \cdot \text{y}^{-1}$  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.

#### 4.2 Dissolved metal fluxes

Metal fluxes have been calculated (Table 4) by multiplying the SGD flux with the dissolved metal concentration in porewater (Santos et al., 2011).

Table 4 :Metal fluxes calculated in Portman Bay																					
Metal	Cd			Co			Fe			Ni			Pb		V		Zn				
mol·dia <sup>-1</sup>																					
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

If we compare our values (Table 5) to a natural anthropized site, Palma de Mallorca

(<sup>a</sup>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.

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

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<sub>2</sub> enriched water contacts with a higher value, Fe<sup>2+</sup> gets oxidized to Fe<sup>3+</sup> 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.

Table 5: Mediterranean sites fluxes						
Site		Cu	Fe	Ni	Pb	Zn
Portman, Murcia, Spain	mol·day <sup>-1</sup> ·km <sup>-1</sup>	0	70 - 4678	0.31 - 11	1 - 49	4 - 663
Palma Beach, Balearic Islands, Spain <sup>a</sup>		0.07 – 0.53	0.4 - 20	0.13 – 0.65	0 – 0.011	0.1 – 1.4
Gorguel, Murcia, Spain <sup>b</sup>		0.8 - 2.3	4-32	0.9 - 2.8	0.20 - 0.60	47 - 180
Port de Maó, Balearic Islands, Spain <sup>c</sup>		0.466	4.11	0.466	0.0493	1.64

be related to high dissolved Fe fluxes,

Table 6: Legislation and Portman concentrations									
	Ag	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
µg/L									
Legislation*	-	0,45-1.5	-	25	-	-	20	7,2	60
Maximum	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

#### 4.3 Contamination of seawater and consequences of metal fluxes in Portman Bay

Metal concentrations in seawater caused by the metal fluxes from the bay have shown to be one of the highest polluted areas in the Mediterranean Sea, high enough to register the maximum dissolved Zn concentration reported until now with 488 nM. Even though, the metal levels found in Portman Bay seawaters are under the limits established by the European Union in the Directive 2008/105/CE or the Spanish legislation (Real Decreto 60/2011), Table 6. Even so, those fluxes have an impact inside the sea that could be affecting the entire environment as the food chain or human health.

The fact that after 25 years the bay is still exporting such a big amount of dissolved chemical compounds explains the possible risk of high contamination that could happen with the new restoration project of the bay promoted by the Spanish Government. The project consists on taking the most external tailings of the bay (2500 tones). We understand that the effect of SGD recirculation has been the main exporter of dissolved metals, creating in 25 years, a lower concentrated metal barrier, that is acting as a natural protection that contains the higher metal concentrations of the bay to be exposed to this process. If the restoration works are made with no previous impermeable contention layers, and this “natural barrier” is removed, consequences in

seawater quality could change drastically. Not just the remobilization of the sediments could increase largely the level of metals in sea water, but the amount of metals exported by the SGD-driven fluxes could make even higher the metal concentrations during decades, creating a possible contaminated scenario for the surrounding marine environments.

#### 5. Conclusions

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. 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 the Gorguel Beach (Trezzi et al., 2016). It has been proved that SGD produces by remobilization an extraction of metals into the sea.

The metal fluxes in Portman Bay have become to be the highest metal concentration in seawater of the Mediterranean Sea. Nonetheless, 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 Gorguel Beach, metal fluxes have been significantly higher than in other locations worldwide. Specifically, for Pb, Zn and Cd.

In conclusion, the metal concentrations and fluxes obtained give us an idea of the amount

of materials that is been released into the sea. The results show us the potential of environmental contamination that those tailings have, and the importance of SGD remobilization in coastal mining contamination. Even though the limit concentration values are under the limits that the Spanish and European legislation determine. Nevertheless, the amounts of metals that have been measured, and the possible enrichment of those after the rehabilitation project could affect or be affecting the 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.

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