Environmental quality in sediments of Cadiz and Algeciras Bays based on a weight of evidence approach (southern Spanish coast)

José Antonio Usero[a], Daniel Rosado*[a,b] , José Usero[a], José Morillo[a]

[a] Department of Chemical and Environmental Engineering, Universidad de Sevilla, 41092 Sevilla, Spain

[b] Department of Chemistry, Universidad Técnica Particular de Loja, 11 01 608 Loja, Ecuador

HIGHLIGHTS:

- A WOE approach has been applied to sediments of Cadiz and Algeciras Bays.
- In Cadiz Bay, the Inner Bay showed highest degradation.
- In Algeciras Bay, industrialised areas were the most degraded.
- Some areas exceed guidelines for aqua regia extractable metals and toxicity.

CORRESPONDING AUTHOR:

* Department of Chemical and Environmental Engineering, Universidad de Sevilla, Camino de los Descubrimientos, s/n, 41092 Sevilla, Spain. Tel.: 0034 954 487 274; E-mail address: danrosalc@alum.us.es, djrosado@utpl.edu.ec (Daniel Jesús Rosado Alcarria).

Abstract

This research applies an integrated sediment quality assessment method using a weight of evidence approach to Cadiz and Algeciras Bays (southern Spain). The method is composed of several analysis (particle size profile, aqua regia extractable metals, acid labile metals, total organic carbon, toxicity bioassay with *Photobacterium phosphoreum* and macrobenthic community alteration).

The proposed method provides a single result, the environmental degradation index (EDI). EDI defined samples as low degraded (outer areas of both bays) and moderately degraded (Inner Bay of Cadiz Bay, surroundings of Algeciras port and the north of Algeciras Bay). These samples showed the highest concentration of aqua regia extractable metals, which exceeded effects range-low (ERL) for Zn (51-176 mg/l), Cu (11-54 mg/l), As (4.3-9.5 mg/l), Hg (0.17-0.28 mg/l), Ni (23-82 mg/l), and. Cr (37-134 mg/l). They also exceeded some quality criteria for total organic carbon (4.0-6.5%) and toxicity (120-240 TU/g) and showed poor results for macrobenthic community.

Keywords

Sediment quality; ecological risk assessment; trace metals; sediment toxicity; benthic macroinvertebrates; Cadiz Algeciras Bays.

1 Introduction

Waste has been dumped into the aquatic ecosystems for decades (Ahuja, 2013; Earnhart, 2013), and pollution is reaching worrying levels in some areas (Baldassin et al., 2016; Vandermeersch et al., 2015; Zhou et al., 2016). In the aquatic environment, many pollutants bind onto sediments and can reach concentrations higher than those in the water column. Changes in environmental conditions, such as pH or redox potential, can release a fraction of the contaminants retained in the sediments and re-solubilize them in water (Wang et al., 2015) . Thus, sediments may act as a sink or a source of contamination and, in the latter case, may affect aquatic life, or even humans, through the food chain (Mackay et al., 2016). This was the case of Minamata Bay and the Jinzu River basin (Horiguchi, 2014; Mason et al., 2006; Tomiyasu et al., 2006). The population of Minamata Bay was exposed to methylmercury through the consumption of seafood during the 50s and 60s of the last century. Methylmercury was discharged into the sea by a nearby factory and caused mental disorders to between 700 and 4,000 people and death to a percentage of them (Harrison, 2001). Regarding the Jinzu River, mining companies released cadmium into the river during the last century. The river was used mainly for irrigation of rice fields. This led to high cadmium levels in the people fed with this rice and itai itai desease (Horiguchi, 2014). As of July 2009, 195 persons were officially designated as Itai-Itai disease patients in the region (Nogawa and Suwazono, 2011).

Because of this, contaminants in the sediments of aquatic ecosystems have become one of the most important environmental problem at present (Chapman and Wang, 2001; Ruiz et al., 2008; Sainz and Ruiz, 2006) and many researches are carried out in this topic (Chapman and Smith, 2012; Chapman et al., 2013; Foster et al., 2015; Nowell et al., 2016; Rosado et al., 2016, 2015a; Testa et al., 2013; Yunker et al., 2015).

Trace elements are bioavailable and persistent in the environment causing bioaccumulation and toxicity effects in the biota. Typically, benthic invertebrates start bioaccumulation by both the absorption from interstitial water and ingested sediment and transfer them to higher trophic levels, extending the hazard (Conti et al., 2016). The uptake of trace metals by benthic organisms depends largely on their chemical forms (Morillo et al., 2008).

Integrated sediment quality assessment methods using a weight of evidence (WOE) approach measure and integrate metrics from different lines of evidence, e.g., chemical characterization, toxicity testing, and biological surveys (Anderson et al., 2003; Chapman, 2002, 1992, 1990; Chapman et al., 1997; Cherry, 2001; Crane, 2003; Ghirardini et al., 1999; Khosrovyan et al., 2015; Long and Chapman, 1985; Qi et al., 2015). This allows to conduct a comprehensive assessment of the quality of sediment, as they provide more reliable information than the use of single techniques (Buruaem et al., 2013; Chapman and Hollert, 2006; Chapman, 2007; Riba et al., 2004).

This research has two main objectives. First, to test a modified version of an integrated sediment quality assessment method previously proposed by Rosado et al. (2015b) using a WOE approach which is simple, low-cost and provides an easily understandable and comparable result. Second, to implement the modified version of the integrated sediment quality assessment method in the Algeciras and Cadiz Bays, where anthropogenic sources of pollutants and areas of high ecological and economic value coexist in a relatively small zone.

2 Study area

The areas studied are the bays of Cadiz and Algeciras, located in southern Spain (Figure 1), whose sediments are affected by discharges from major urban centers, large and small industries, intense port activity and, to a lesser extent, farming.

2.1 Cadiz Bay

Cadiz Bay is located in the southwest of the Spanish Atlantic coast, between the town of Rota and the city of Cadiz, and covers an area of 110 km^2. It can be divided into two main maritime regions. The Inner Bay, located south of the bridge José Leon de Carranza, is characterized by a maximum depth of five meters and a low rate of water renewal, which favors accumulation of pollutants discharged. The Outer Bay, that is extended northward from the bridge up to Rota, is deeper, open to the Atlantic Ocean and thus, the renewal of its waters is faster (Araújo et al., 2009; Ligero et al., 2002, 2004).

The prevailing currents in the coasts of the Gulf of Cadiz come from west-northwest generating an anticlockwise circular current in the Outer Bay. The Inner Bay is protected from the surge and, partially, the wind, so water dynamics are tidally controlled causing a less defined current with several gyres (Ligero et al., 2002; Periáñez, 2009; Periáñez et al., 2013). In the Outer Bay empties the Guadalete River, the main river in the area.

Cadiz Bay hosts several towns (Rota, El Puerto de Santa María, Puerto Real, San Fernando, Chiclana de la Frontera and Cadiz) whose population exceeds 400,000 inhabitants (Carrasco et al., 2003). In this bay also takes place a remarkable industrial activity, including shipyards and car and aircraft components manufacturers. Furthermore, there is a high maritime traffic due to merchant ships and, increasingly, to cruises and ferries between the Iberian Peninsula and the north of Africa and the Canary Islands.

Cadiz Bay includes some areas cataloged as Special Protection Area under European Union's Birds Directive: the Cadiz Bay Natural Park and the Trocadero Island and Sancti Petri Marshes nature reserves.

2.2 Algeciras Bay

Algeciras Bay is located on the southern end of the Iberian Peninsula, next to the Strait of Gibraltar, between two important water bodies, the Atlantic Ocean and the Mediterranean Sea, and two continents, Europe and Africa. This bay is a semi-enclosed water body in a horseshoe shape, with a maximum width of 9 km and a north-south length of about 10 km. The endpoints that define the mouth of the bay are Punta Carnero in the west and Punta Europa in the east, defining a water surface of about 75 km^2 with a depth of up to 400 m (Sammartino et al., 2014). The main rivers which drain into the bay are the Guadarranque and Palmones rivers.

Westerly winds are predominant in the area and they lead to a clockwise water circulation, i.e., runs along the coast starting at the west end (Punta Carnero) to the east end (Punta Europa). This current can be switched to anticlockwise in the case of easterly winds (Periáñez, 2012; Sánchez-Garrido et al., 2014). The maximum tidal stands at 0.8 m along the entire shore (Periáñez, 2012).

Five important cities located around the bay (Algeciras, Los Barrios, San Roque, La Línea de la Concepción and Gibraltar) are home to more than 250,000 inhabitants (Kosore et al., 2015). The major industries in the area are mainly located in the northern part of the bay and include petrochemical and petroleum refineries, a stainless steel manufacturing plant, four power plants and a biofuel production plant (Tarazona et al., 1991). Two ports are also located in this bay: Gibraltar and Algeciras. The first is one of the Europe's top port for refueling. The latter is ranked among the most important ports of the world (Kosore et al., 2015). Thus, bay waters are subject to one of the most intense maritime traffic all over the Mediterranean Sea (Díaz-de Alba et al., 2011) and large amounts of pollutants are discharged into the bay (Carballo and Naranjo, 2002; Morillo et al., 2007; Tarazona et al., 1991).

Within the Algeciras Bay is located the Palmones River Marshes Nature Reserve, cataloged as a Special Protection Area under European Union's Birds Directive, where birds stop for their migrations. Next to the southwestern end of the Algeciras Bay there is another protected area, the Strait of Gibraltar Natural Park.

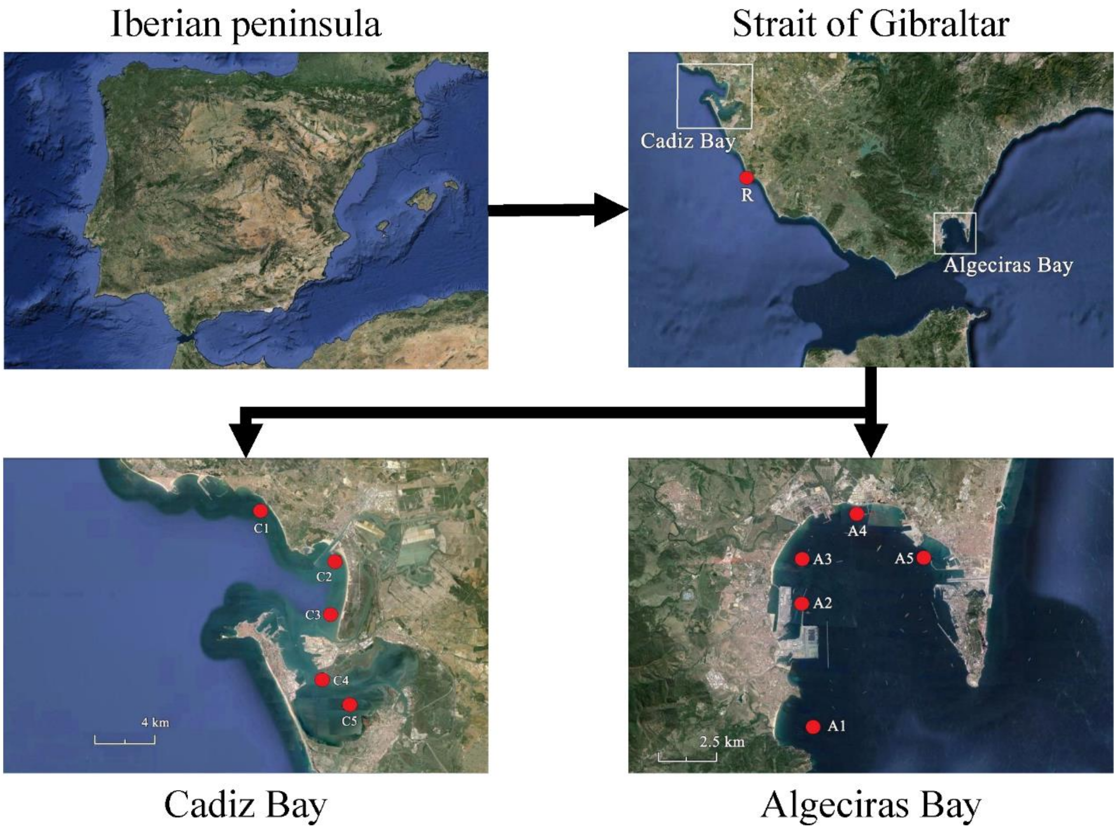

Figure 1. Location of the sampling points in Cadiz and Algeciras Bays.

3 Materials and methods

3.1 Sampling and sample pre-treatment

5 sampling points were located in Algeciras Bay (A1-A5), 5 in Cadiz Bay (C1-C5) and 1 in a pollution free zone (R) of Cadiz Littoral to serve as a reference (see Table 1 and Figure 1).

Table 1. Coordinates of the sampling points.

Station	**North**	**West**
R	36º17'34"	6º09'09"
A1	36º05'42"	5º25'27"
A2	36º08'31"	5º25'53"
A3	36º09'35"	5º25'46"
A4	36º10'42"	5º24'06"
A5	36º09'39"	5º22'22"
C1	36º36'14"	6º17'04"
C2	36º34'32"	6º13'52"
C3	36º32'33"	6º14'24"
C4	36º30'16"	6º14'42"
C5	36º29'26"	6º13'20"

Sediment samples were taken in February 2015 with a Van Veen grab and in duplicate at each station. Only grabs that achieved adequate penetration (2/3 of total volume) to collect the first 5 cm of the sediment and that showed no evidence of leakage or surface disturbance were retained, transferred and stored in a dark cooler at 4 °C.

In the laboratory, samples were divided into two fractions as shown in Table 2: fraction 1, without any further treatment, to determine particle size profiles, and fraction 2, dried (60 ºC) and sieved (<63 µm), to perform metal analysis (aqua regia extractable and acid labile fractions), total organic carbon and the toxicity bioassay. All conventional sediment parameters were expressed as percentages of total dry sample weight (105 ºC).

Organism samples were taken in duplicate in the same sampling points and dates as the sediment samples. Every sample was composed of five subsamples collected with a 0.05 m^2 surface Van Veen grab. Subsamples were sieved in situ through a 0.5-mm mesh and were preserved in a solution made of ethanol and bengal rose stain (0.4 g of bengal rose in 1 L of ethanol) for one week.

Table 2. Sample pre-treatment and related analysis.

	Drying temperature	Grain size	Analysis
Sediment sample (Fraction 1)	-	-	Particle size profile
Sediment sample (Fraction 2)	60 ^{o}C	<63 µm	Aqua regia extractable metals Acid labile metals Total organic carbon Toxicity bioassay
Organism sample	-	>500 µm	Macrobenthic community

3.2 Sediment analysis

3.2.1 Particle size profiles

Particle size profiles were determined by wet sieving the sediments through a column of sieves with different mesh sizes according to the Wentworth classification (Wentworth, 1922): <4 µm clay; 4-63 µm silt; 63–125 µm very fine sand; 125–250 µm fine sand; 250–500 µm medium sand; 500–1,000 µm coarse sand; 1,000–2,000 µm very coarse sand; 2,000–4,000 µm granulate gravel; 4,000-64,000 µm pebble gravel.

3.2.2 Aqua regia extractable metals

To determine aqua regia extractable metals content, sediment underwent the method proposed by the Community Bureau of Reference (BCR) (Pueyo et al., 2001), in which 3 g of every sample are digested with 28 ml of aqua regia (commercial nitric and hydrochloric acids, 1:3 by volume) in a reaction flask with a reflux condenser and a sand bath. Then, the extract was centrifuged 20 min at 4,200 rpm (3,000 g) to separate the solid and liquid phases.

The analysis of Zn, Cu, Cd, Mn, Pb, Ni, Fe, and Cr in the solutions obtained following sample digestion were carried out by atomic absorption spectrophotometry (AAS) using a double-beam Perkin–Elmer 2380 AAS with deuterium background correction and, in the case of low concentrations, by graphite furnace atomic absorption spectrometry (GFAAS) using a Varian spectra 220 with Zeeman-effect background correction. The hydride-generation technique was used to determine As, and the cold vapor technique was utilized for Hg, both employing a Perkin–Elmer MSH-10 connected to the Perkin–Elmer 2380 spectrophotometer.

Aqua regia extractable metals determination was tested using the reference material, BCR-701. The concentrations obtained for each of the elements analyzed demonstrated recoveries greater than 90%, which can be considered satisfactory for this type of analysis (Pueyo et al., 2001).

3.2.3 Acid labile metals

The bioavailable fraction was estimated as the acid soluble fraction extracted following the procedure proposed by the BCR (Pueyo et al., 2001). To this end, 1 g of every sample were digested with 40 ml of acetic acid solution (0.11 M) for 16 h at room temperature with magnetic stirring (250 rpm). Then, the suspensions were centrifuged for 20 min at 4,200 rpm (3,000 g). The supernatant was used to determine Zn, Cu, Cd, Mn, Pb, Ni, Fe and Cr as described for the aqua regia extractable metals.

As in the case of the aqua regia extractable metals, acid labile metals results were validated using the reference material, BCR-701, and recovery rates exceeded 90% in all the analyzed elements, which can be considered satisfactory (Pueyo et al., 2001).

3.2.4 Total organic carbon

The total organic carbon was determined in sediment samples using a Shimadzu TOC–VCSH analyzer connected to a solid sample module (Shimadzu, Model SSM-5000 A). For this purpose, 40 mg samples were pretreated with HCl 4M and heated on a hot plate to remove inorganic carbon that otherwise would have interfered with the measurement.

3.2.5 Toxicity bioassay with *Photobacterium phosphoreum*

The toxicity on the sediment samples was determined using a marine luminescent bacterium *(P. phosphoreum)* according to the procedure described by Svenson et al. (1996), in which a preassay allows to estimate the toxicity prior to the main assessment. A suspension of 3 g of sediment sample was prepared in 30 ml of a 2% NaCl solution and was magnetically stirred for 10 min; then a series of dilutions were made and bacteria were exposed to these dilutions and to a blank (2% NaCl solution). Bioluminescence at 15 ^{o}C was measured with a Microtox luminescence meter (Microbics Corp., Carlsbad, CA) after 30 min of incubation. Inhibition was expressed as toxicity units per g of dry soil (TU_{50}), calculated as the inverse of EC_{50} multiplied by 100, instead of common half maximal effective concentration (EC_{50}). TU_{50} provides a more intuitive scale since the higher the toxicity the higher the value of TU_{50}, contrary to EC_{50} (Van den Brink and Kater, 2006).

3.3 Organism sample analysis

Macrobenthic organisms were sorted, numbered and identified to the lowest possible taxon, usually to family level as suggested by many authors (Estacio et al., 1997; Mucha et al., 2003; Sánchez-Montoya et al., 2010). Data on families were used to calculate the M-AMBI index (multivariate - AZTI' Marine Biotic Index) with the software developed by the authors (Muxika et al., 2007).

3.4 Integrated sediment quality assessment method

3.4.1 Pollution indices

The indices are based on those proposed by Usero et al. (2008) and Rosado et al. (2015b) and, as shown in Table 3, consist in 5 pollution indices related to one analysis each: inorganic contamination index (ICI, aqua regia extractable metals), bioavailability index (BI, acid labile metals), organic contamination index (OCI, total organic carbon), toxicity index (TI, bioassay with *P. phosphoreum*) and macrobenthic alteration index (MAI, 1/M-AMBI index). Pollution indices are higher the higher the levels of contamination. Thus, the inverse of M-AMBI has been used to calculate MAI, as M-AMBI is inversely proportional to the alteration degree of the macrobenthos.

Table 3. Calculation of the environmental degradation index in every sampling point.

Analysis	Analysis output	Normalized Values (NV)	Pollution indices	
Aqua regia extractable metals	$Metal_1$ (mg/kg) … $Metal_{10}$ (mg/kg)	$NV_{ICI,1}$ … $NV_{ICI,11}$	Inorganic contamination index (ICI)	Environmental degradation index (EDI)
Acid labile metals	$Metal_1$ (mg/kg) … $Metal_8$ (mg/kg)	$NV_{BI,1}$ … $NV_{BI,8}$	Bioavailability index (BI)	
Total organic carbon	%	NV_{OCI}	Organic contamination index (OCI)	
Toxicity bioassay	TU/g	NV_{TI}	Toxicity index (TI)	
Macrobenthic community	1/M-AMBI	NV_{MAI}	Macrobenthic alteration index (MAI)	

To determine pollution indices at each of the sampling points, first, normalized values (NVs) related to the reference station (R) are calculated with the following equation:

$$NV_i = \frac{P_{iE}}{P_{iR}}$$

NV_i, P_{iE} and P_{iR} respectively refer to the normalized value of the parameter i, the parameter i in the sampling station E and the parameter i in the reference station R. Next, the indices mentioned above are calculated as the NV's geometric mean in the corresponding analysis according to the expression:

$$\mathrm{X} = \sqrt[\mathrm{n}]{\mathrm{NV}_1 \times \mathrm{NV}_2 \times \ldots \times \mathrm{NV}_\mathrm{n}}$$

X refers to the ICI, BI, OCI, TI, and MAI indices.

In cases when the index is composed of a single analytical result (OCI, TI and MAI), there is only one NV and it matches the index value. However, in the case of ICI and BI, there are several NVs (one for each metal) and the index and the NV's differ.

3.4.2 Environmental degradation index

The environmental degradation index (EDI) at each station is calculated as the geometric mean of the indices calculated in the previous section. It could therefore be called an index of indices, which summarizes the main characteristics of the environmental situation of each sampling point.

$$\mathrm{EDI} = \sqrt[5]{\mathrm{ICI} \times \mathrm{BI} \times \mathrm{OCI} \times \mathrm{TI} \times \mathrm{MAI}}$$

The EDI has a special interest because it summarizes in a single number the main environmental quality features of the sediment and allows for an unequivocal comparison of two samples, unlike a simple set of analytical results, in which not all of a stations results are greater than the other.

3.4.3 Five-axis plots

To provide an overall view of the environmental quality of the analyzed sediments, a five-axis plot was represented for each station. A module vector equal to the value obtained for each of the pollution indices studied was plotted on each axis (ICI, BI, OCI, TI, and MAI). Connecting the values for each axis, a pentagon is obtained. Two pentagons were represented in each plot, one for the station in question (green for Cadiz Bay and orange for Algeciras Bay) and another corresponding to the reference station (R, blue) for comparison. This type of graph allows to determine the stations with the highest degradation at a single glance by the sizes of the obtained polygons. In addition, the deformation of the polygons shows the main type of degradation in the samples.

4 Results and discussion

4.1 Sediment analysis

4.1.1 Particle size profiles

As shown in Table 4, fine sands represent 5 of the 11 sampling points, being the most abundant particle size profile in the study area. In Cadiz Bay, the texture is slightly thinner, with grain sizes of fine sand and smaller, except for station C3. The sampling point C5 (silt) has the finest texture of all studied because the water moves more slowly in the Inner Bay and allows smaller particles to settle. In Algeciras Bay, the texture is slightly thicker, with grain sizes of fine sand and bigger. The station A5 (very coarse sand) has the thickest texture due to the large number of biodetritic remains, such as shells and calcareous algae.

Table 4. Results of the tests conducted in the laboratory (mean ± SD).

	R	C1	C2	C3	C4	C5	A1	A2	A3	A4	A5
Particle size profiles											
Sediment type [1]	FS	FS	VFS	MS	VFS	S	FS	FS	MS	FS	VCS
Aqua regia extractable metals (mg/kg)											
Zn	38 ±0.63%	46 ±1.04%	85 ±2.38%	78 ±3.34%	124 ±0.23%	176 ±0.46%	39 ±2.93%	154 ±1.64%	43 ±0.45%	51 ±4.43%	46 ±4.79%
Cu	5.6 ±5.68%	6.2 ±5.98%	13 ±0.32%	12 ±5.24%	35 ±7.55%	41 ±3.63%	8.5 ±2.43%	54 ±0.65%	8.9 ±8.65%	11 ±3.21%	9.4 ±8.41%
Cd	0.3 ±1.79%	0.3 ±8.23%	0.4 ±10.61%	0.3 ±7.25%	0.3 ±14.59%	0.4 ±13.48%	0.4 ±13.37%	0.5 ±9.70%	0.4 ±12.44%	0.7 ±8.04%	0.4 ±14.81%
Pb	6.1 ±8.70%	7.5 ±4.07%	11 ±6.43%	10 ±4.68%	28 ±0.16%	30 ±8.29%	7.2 ±2.15%	23 ±9.67%	7.8 ±8.64%	16 ±6.87%	7.9 ±2.20%
Fe [2]	22 ±0.43%	22.5 ±0.76%	23.4 ±0.82%	24.1 ±3.75%	29 ±4.06%	28.5 ±3.20%	21.4 ±4.52%	24.2 ±3.51%	21.7 ±2.54%	26.2 ±0.04%	22.5 ±1.40%
As	3.7 ±8.74%	3.9 ±4.98%	7.3 ±6.61%	4.2 ±9.62%	7.9 ±0.23%	9.5 ±6.13%	3.9 ±9.59%	7.8 ±4.62%	4.2 ±6.29%	4.3 ±4.08%	4.2 ±7.07%
Hg	0.10 ±7.23%	0.11 ±5.78%	0.14 ±7.24%	0.12 ±9.91%	0.28 ±4.34%	0.24 ±10.51%	0.12 ±11.00%	0.17 ±1.69%	0.13 ±5.97%	0.27 ±14.44%	0.14 ±8.40%
Mn	410 ±0.65%	404 ±4.22%	430 ±0.72%	420 ±2.59%	416 ±3.43%	395 ±1.91%	410 ±1.59%	460 ±4.81%	324 ±0.48%	368 ±3.11%	350 ±2.11%
Ni	4.0 ±7.41%	4.0 ±2.35%	12 ±6.81%	15 ±1.85%	23 ±5.85%	25 ±9.19%	19 ±6.44%	50 ±1.68%	20 ±7.64%	82 ±6.32%	50 ±8.50%
Cr	14 ±4.53%	16 ±1.65%	18 ±0.26%	25 ±0.36%	37 ±1.69%	52 ±1.70%	25 ±0.83%	95 ±4.31%	28 ±3.68%	134 ±4.50%	80 ±2.31%
Acid labile metals (mg/kg)											
Zn	1.7 ±6.14%	2.9 ±0.71%	7.3 ±5.08%	3.6 ±6.32%	6.9 ±8.29%	13 ±1.40%	2.5 ±2.00%	13 ±6.49%	3.1 ±3.97%	6.1 ±7.05%	3.6 ±9.94%
Cu	0.6 ±2.85%	0.7 ±6.37%	1.3 ±8.39%	1.4 ±5.19%	4.6 ±9.17%	6.6 ±9.61%	1.2 ±10.73%	6.5 ±9.20%	1.2 ±8.73%	2.0 ±2.00%	1.4 ±9.55%
Cd	0.03 ±3.82%	0.03 ±0.24%	0.06 ±9.54%	0.03 ±11.24%	0.04 ±10.05%	0.06 ±11.28%	0.04 ±1.07%	0.06 ±1.24%	0.04 ±5.59%	0.11 ±9.99%	0.06 ±12.21%
Pb	1.0 ±6.26%	1.1 ±11.28%	2.1 ±6.94%	1.9 ±9.98%	3.9 ±4.98%	5.7 ±6.04%	1.4 ±13.73%	6.9 ±3.38%	0.7 ±2.24%	2.7 ±11.59%	1.0 ±3.30%
Fe	264 ±3.49%	360 ±4.32%	234 ±1.05%	193 ±0.38%	232 ±4.23%	399 ±2.44%	257 ±2.47%	436 ±4.51%	412 ±1.00%	550 ±0.52%	360 ±2.40%
Mn	119 ±2.73%	117 ±2.65%	155 ± 3.20%	139 ±1.15%	125 ±4.25%	134 ±2.07%	119 ±1.85%	161 ±2.84%	94 ±0.66%	121 ±0.71%	109 ±0.52%
Ni	0.44 ±2.39%	0.48 ±4.66%	1.3 ±7.68%	1.5 ±8.72%	1.8 ±0.96%	3.5 ±9.15%	2.7 ± 7.73%	9.0 ±1.09%	3.6 ±1.31%	17 ±3.60%	6.5 ±9.07%
Cr	1.1 ±7.85%	2.1 ±5.81%	2.5 ±1.97%	2.0 ±9.84%	4.4 ±13.18%	7.8 ±3.33%	2.5 ±6.73%	15 ±13.62%	2.7 ±0.04%	27 ±14.37%	10 ±10.53%
Total organic carbon (%)											
	1.2 ±4.70%	1.3 ±5.21%	3.9 ±9.48%	1.8 ±1.45%	5.3 ±8.95%	6.5 ±5.39%	1.5 ±8.48%	5.0 ±2.78%	1.8 ±5.87%	4.0 ±8.67%	2.4 ±0.86%
Toxicity bioassay (TU/g)											
	39 ±6.95%	42 ±13.17%	90 ±8.36%	48 ±5.06%	120 ±6.97%	240 ±3.43%	43 ±1.44%	210 ±4.57%	62 ±11.31%	170 ±4.66%	51 ±0.21%
Macrobenthic community											
Number of families	48 ±8.20%	43 ±6.20%	33 ±1.37%	40 ±1.21%	30 ±7.54%	24 ±6.02%	43 ±3.83%	28 ±9.05%	50 ±3.34%	31 ±6.75%	56 ±4.91%
M-AMBI index	0.89 ±5.29%	0.86 ±5.16%	0.76 ±0.31%	0.76 ±0.44%	0.65 ±5.18%	0.62 ±4.38%	0.81 ±0.56%	0.70 ±1.92%	0.93 ±2.36%	0.75 ±4.77%	0.99 ±2.99%

[1] VCS: very coarse sand; CS: coarse sand; MS: medium sand; FS: fine sand; VFS: very fine sand; S: silt; [2] Fe total content is expressed in g/kg.

4.1.2 Aqua regia extractable metals

In Cadiz Bay, the highest concentrations of most metals are found in the Inner Bay (C4 and C5), as shown in Table 4. Pb, As, Ni and Hg differences are significant ($p<0.05$) between the Inner Bay and the concentrations in other sampling points of Cadiz Bay. The Inner Bay is an area of shallow draft (with depths below 5 meters), fine sediment grain size (fine sand or silt) and low water renewal, which favors the accumulation of pollutants from sewage, factories, maritime traffic, etc.

Maximum concentrations of most metals (Zn, Cu, Pb, As, Ni, and Cr) in Cadiz Bay are located at the station C5 since it is more isolated from the open sea than the sampling point C4. Differences between stations C5 and C4 are significant ($p<0.05$) for Zn, Cu and Cr. However, highest concentrations of Hg and Fe are found in the station C4.

Aqua regia extractable metals in the Outer Bay (C1 to C3) are similar or slightly higher than those in the reference station (R), far from sources of pollution. These results are explained by higher depth, coarser particle size and short flushing time (Periáñez et al., 2013), which favors the dispersion of the pollutants discharged. The lowest concentrations of most metals in the Outer Bay are found in station C1. However, only Zn shows a significant difference ($p<0.05$) between C1 and both C2 and C3. By contrast, in station C2 occur the highest concentrations of Zn, Cu, Pb, Cd, As and Mn by the influence of the Guadalete river. Nevertheless, only As shows a significant difference between C2 and both C1 and C3. Mn in station C2 reach the highest concentration in Cadiz Bay, including the Inner Bay.

In Algeciras Bay, the highest concentrations of metals ($p<0.05$) are located at sampling points A2 (Cu, Zn, Pb, As and Mn), in the vicinity of Algeciras municipality and its port, and A4 (Ni, Cr, Cd and Hg), which concentrates the largest industrial activity in the bay.

Highest concentration of Fe is also found at sampling point A4. However, difference is not significant between A4 and A2 ($p>0.05$). Lowest concentrations of metals occur in stations A1 (Zn, Cu, Pb, As, Fe, Cr, Ni and Hg) and A3. Nonetheless, only Mn shows significant difference between A1 and A3 ($p<0.05$).

Reference station (R) shows the lowest concentrations of Zn, Cu, Pb, As, Cr, Hg and Ni in all areas studied. The reference point is also most likely to be the lowest value for Cd given the lower standard deviation. The reference point is above the minimum value recorded in some metals (Fe and Mn) whose natural concentrations are higher and the influence of pollution is less relevant.

Table 5 shows the quality criteria for sediments proposed by both Long et al. (1995) and the Centro de Estudios y Experimentación de Obras Públicas (CEDEX) (DelValls et al., 2004). Long et al. (1995) criteria are based on the potential to induce toxic effects on marine organisms. The criteria are divided into two values: effects range-low (ERL) and range-mediated effects (ERM). The ERL refers to the concentration at which toxic effects were identified in the lower 10th percentile for each chemical. The ERM denotes the same concept but applied to the median, or 50th percentile. CEDEX’s criteria are widely used by Spanish scientists to decide the proper management for dredged material in Spanish ports (DelValls et al., 2004). When concentrations of all metals are below AL1, sediments are considered not contaminated and can be discharged freely into the sea. If the concentration of any metal is between AL1 and AL2, the sediment is defined as moderately contaminated. In this case, it is required to select a disposal area justifying its suitability. It is also necessary to study the possible transport of the fine fraction, estimate the impact on the ecosystem and design an environmental monitoring program. If the concentration of any metal exceeds AL2, the sediment is classified as highly contaminated. Thus, justification about treatment prior to disposal and confinement is necessary.

Table 5. Quality criteria for total metal concentrations in sediments (mg/kg, dry weight).

Metal	Long et al. (1995)		DelValls et al. (2004)	
	ERL[1]	ERM[2]	AL1[3]	AL2[4]
Zn	150	410	500	3000
Cu	34	270	100	400
Cd	1.2	9.6	1.0	5.0
Pb	46.7	218	120	600
Fe	-	-	-	-
As	8.2	70	80	200
Hg	0.15	0.71	0.6	3.0
Mn	-	-	-	-
Ni	20.9	51.6	100	400
Cr	81	370	200	1000

[1] ERL: effects range-low.
[2] ERM: effects range-median.
[3] AL1: action level 1.
[4] AL2: action level 2.

In Cadiz Bay, aqua regia extractable metals in the sediments of the Outer Bay are below the quality criteria proposed by Long et al. (1995), whereas both stations in the Inner Bay (C4 and C5) exceed the ERL's for Ni, Cu and Hg. Furthermore, C5 station exceeds ERL for Zn and As. In Algeciras Bay, station A2 exceeds ERLs for Zn, Ni, Cr, Cu and Hg and station A4 exceeds ERL for Cr and ERM for Ni. In the reference station (R) none of the quality criteria proposed by Long et al. (1995) are exceeded.

None of the analyzed samples exceed CEDEX recommended action level 1, indicating that these sediments could be dumped into the sea without taking special precautions.

4.1.3 Acid labile metals

Around 30% of Mn is part of the acid soluble fraction, being the metal with the highest percentage (Table 4). Thus, Mn is bound more weakly to sediments, has the greatest mobility and is, probably, the most bioavailable. These high percentages of Mn in acid soluble fraction are probably related to a large amount of manganese carbonates in sediments (Dassenakis et al., 2003). Other studies of marine sediments also found high percentages of Mn in the acid soluble fraction (Kiratli and Ergin, 1996; Marin and Giresse, 2001; Morillo et al., 2002).

Fe is the metal with the lowest percentage in the acid soluble fraction (slightly above 1%) and thus, the strongest attached to sediment and the least mobile. It is probably due to its fundamentally natural origin and its abundance in the Earth's crust. These results agree with those published by Morillo et al. (2007) who found that most of Fe in sediments forms crystalline oxides (goethite, limonite, magnetite, etc.) strongly attached to the sediment.

Zn shows the second lower percentage in the acid soluble fraction (less than 9%). These results agree with those obtained in other studies (Dawson and Macklin, 1998; Hudson-Edwards et al., 1996; Moalla et al., 1997) in which most of the Zn was in the reducible fraction (second step of the BCR protocol).

In the reference station (R), the lowest percentages of extraction is obtained for most elements. This fact is related to the natural origin of metals in this station, which tend to be more firmly attached to the sediment than those from an anthropogenic source (Rosado et al., 2015b). By contrast, in Algeciras Bay are located higher percentages in the acid soluble fraction for Ni, Cr, Cu and Zn.

4.1.4 Total organic carbon

The total organic carbon shows no significant difference between the Cadiz and Algeciras Bays ($p>0.05$), although large differences within each area are appreciated. The highest concentrations ($p<0.05$) of total organic carbon in the Cadiz Bay (Table 4) are located in the Inner Bay (C4, 5.3%; C5, 6.5%), followed by the surroundings of the Guadalete river mouth (C2, 3.9%). The Inner Bay accumulates pollutants present in sewage from urban areas near the Bay (San Fernando, Puerto Real, Puerto de Santa Maria and Cadiz) by low water renewal and shallow draft. The Guadalete River is affected by sewage from large populations, such as Jerez and Arcos, discharges from winemaking and sugar industries, effluents from agricultural activities, etc.

In Algeciras Bay, the largest average concentrations of total organic carbon found in the vicinity of Algeciras municipality and its port (A2, 5.0%), followed by the surroundings of the oil refinery (A4, 4.0%), which concentrates the largest industrial activity in the bay. The values reached in these sampling points are significantly higher ($p<0.05$) than the rest of the stations in the area and the median total organic carbon content in the sediments of coastlines around the world, set at 1.5% (Seiter et al., 2004).

Lowest levels of total organic carbon in the sediments are located at the reference station (R, 1.2%), in the outer areas of the bays (C1, 1.3%; A1, 1.5%) and the outermost stations of discharges (C3, 1.8%; A3, 1.8%). The total organic carbon values of these stations show no significant difference with the reference point ($p>0.05$) and are similar to the median of total organic carbon content in sediment coastlines around the world, set at 1.5% (Seiter et al., 2004).

4.1.5 Toxicity bioassay with *P. phosphoreum*

The results of the toxicity bioassay (Table 4) are similar to those of total organic carbon and metals in terms of areas and sampling points with highest and lowest values. Thus, major toxicities of Cadiz Bay ($p<0.05$) occur in the Inner Bay (C5, 240 TU/g; C4, 120 TU/g). These are followed by the surroundings of the Guadalete river mouth (C2, 90 TU/g). In Algeciras Bay, the area with greater toxicity ($p<0.05$) corresponds to the surroundings of Algeciras municipality and its port (A2, 210 TU/g) and the vicinity of the oil refinery (A4, 170 TU/g). These values are similar to those found by Martínez-Lladó et al. (2007) in the sediments of the Port of Barcelona (average 240 TU/g).

The lowest toxicity is located in the reference station (R, 39 TU/g) and in the outer areas of both bays (C1, 42 TU/g; A1, 43 TU/g). These values are similar to those obtained in a nearby coast, the Huelva Littoral, with an average of 35 TU/g (Usero et al., 2008).

Considering the sediment toxicity quality criteria established in 100 TU/g (Environment Canada, 2002) and 133 TU/g (Casado-Martínez et al., 2006; DelValls et al., 2004; Morales-Caselles et al., 2008), C5, A2 and A4 samples are considered toxic by both thresholds, while C4 is only considered toxic according to the threshold set by Environment Canada (2002). None of the other stations are considered toxic.

4.2 Organism sample analysis

The analyses of the macrobenthic community in sediments have identified a total of 11 taxonomic groups, three of which are well represented: annelids (25 families), crustaceans (32 families) and molluscs (28 families). To a lesser extent are also present echinoderms (3 families) and cnidarians (2 families) and 6 other groups with only one family each (nemertea, phoronida, cephalochordate, sipuncula, tunicate and turbellaria).

The predominant group corresponds to the annelids, which has the largest number of families in all sampling points, except for the L2, O1 and T1. The group of annelids is only represented by polychaete class, mainly organisms of families Spionidae, Capitellidae and Syllidae. These families are composed of opportunistic species or primary colonizers who take advantage of any alteration of the environment to occupy a large ecological niche.

Crustaceans are the next largest group, accounting for 20-45% of families in all sampling points. Among them, amphipods class is the most widely represented (15 families) including families Apseudidae, Corophiidae and Haustoridae. Molluscs are the third largest group, ranging from 8-35% of families in all sampling points. They represent 35% of all families in station A1, becoming the most abundant taxonomic group. The other groups, composed of 8 taxa, only represent between 5-17% of families in all sampling points.

Regarding the number of families and the M-AMBI index, results show a wider diversity in macrobenthic community where pollution is lower. As shown in Table 4, number of families and M-AMBI index are lower in stations A2 and A4 in Algeciras Bay and C4 and C5, the Inner Bay of Cadiz Bay. The latter (C5) reaches the lowest value of the entire study area. This fact is undoubtedly related to two peculiarities. First, C5 hosts the highest levels of Zn, Pb, As and toxicity of the study area. Second, the particle size is very fine (silt), which complicate organisms to inhabit the sediment due to the small gaps between particles. Overall, in similar sediments the number and diversity of macrobenthic community is higher in coarser particle size (Rosado et al., 2015b).

4.3 Integrated sediment quality assessment method

4.3.1 Pollution indices

As shown in the Figure 2, the results of four indices (ICI, IB, ICO and IT) follow a common pattern. In Cadiz Bay, the maximum values of these indices are located in the Inner Bay (C4 and C5), followed by the surroundings of the Guadalete river mouth (C2). In Algeciras Bay, these indices reach their highest in the vicinity of Algeciras municipality and its port (A2). The lowest values of these indices are located in the outer areas of the bays (C1 and A1) and the reference station (R). The latter (R) shows the lowest values for the four indices, indicating that fulfills its function correctly as a reference sample. The macrobenthic alteration index (MAI) shows a slightly different pattern, since the lower values are located in the stations A5 (0.84) and A3 (0.93) instead of the reference station (R, 1.00). It can be explained because both stations presents larger grain size (A5: very coarse sand; A3: medium sand) than the average. As mentioned above, a coarse grain size favors a diverse macrobenthic community compared to a fine-grained sediment.

Furthermore, the degree of pollution is intermediate compared to others in the study area.

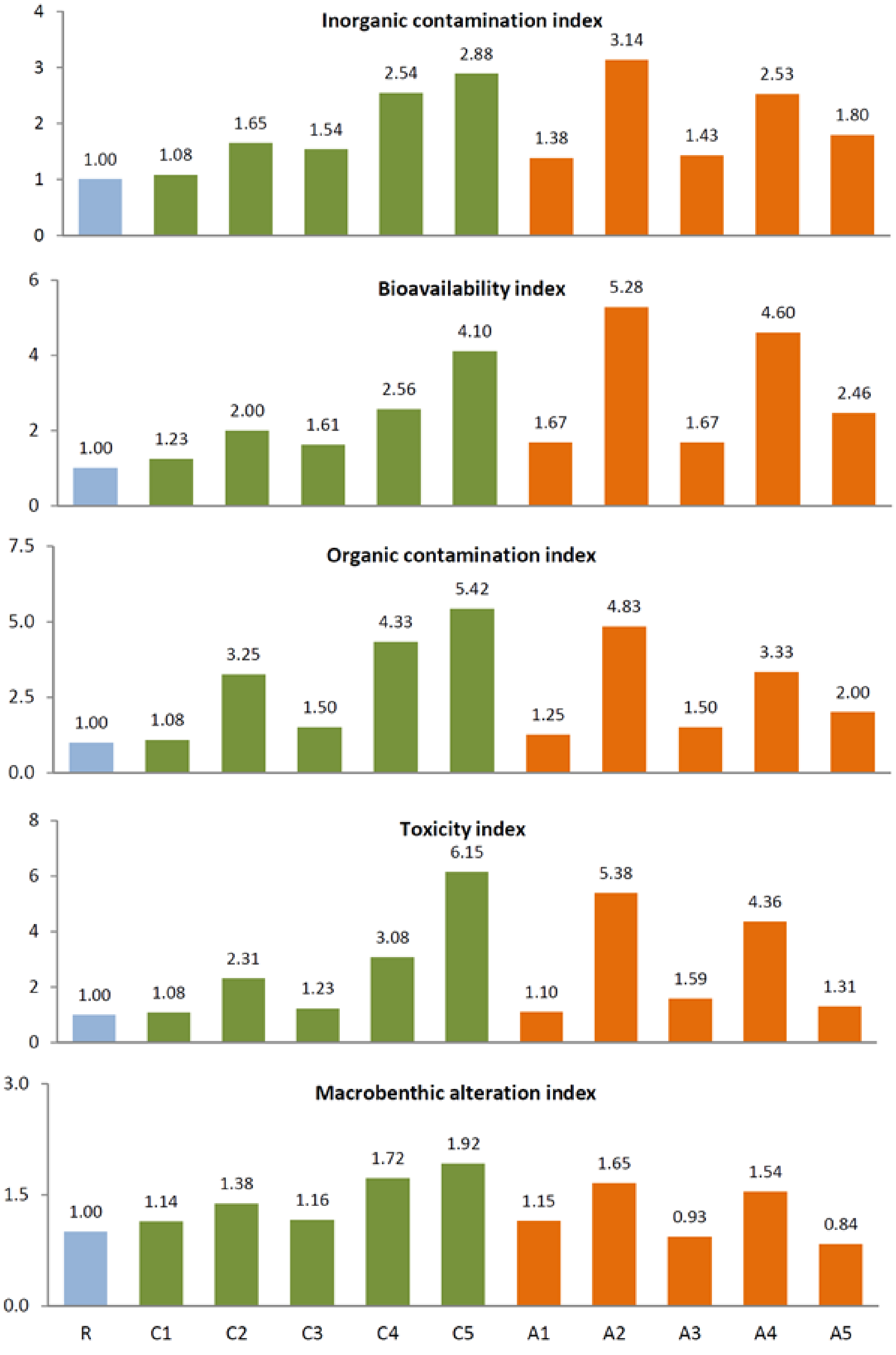

Figure 2. Values of pollution indices in the reference station (R) and Cadiz (Cx) and Algeciras (Ax) Bays.

4.3.2 Environmental degradation index

The environmental degradation index (EDI) represented in Figure 3, ranks the stations by its environmental degradation as follows:

R<C1<A1<A3=C3<A5<C2<C4<A4<A2<C5

Following the guidelines of Rosado et al. (2015b), samples were classified according to specific thresholds of EDI into two groups. First, low degradation (EDI<2): this group comprises the stations in the outer areas of both bays (C1, C2, C3, R, A1, A3 and A5). Station C2 has been included in this group despite exceeding the criterion. This is because it is closer to the stations with a low degradation than those with a moderate. Second, Moderate degradation (EDI≥2): this group includes the stations in the Inner Bay of Cadiz Bay (C4 and C5), the station located in the vicinity of Algeciras municipality and its port (A2) and the station situated in the area with the largest industrial activity in Algeciras Bay (A4).

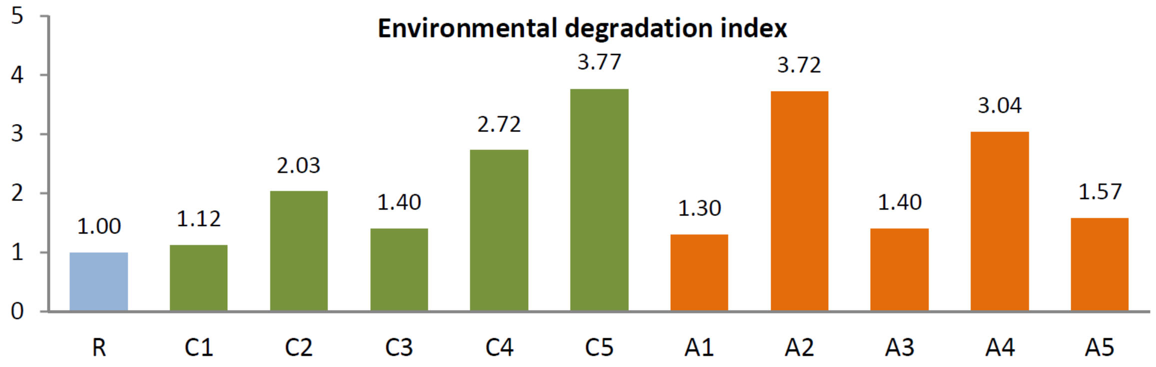

Figure 3. Values of the environmental degradation index in the reference station (R) and Cadiz (Cx) and Algeciras (Ax) Bays.

4.3.3 Five-axis plots

Pentagons in the plots of Figure 4 represent the five pollution indices at each station (green, Cadiz Bay; orange, Algeciras Bay) compared to the reference station (R, blue). This representation allows a quick view of sediment degradation by the sizes of the pentagons.

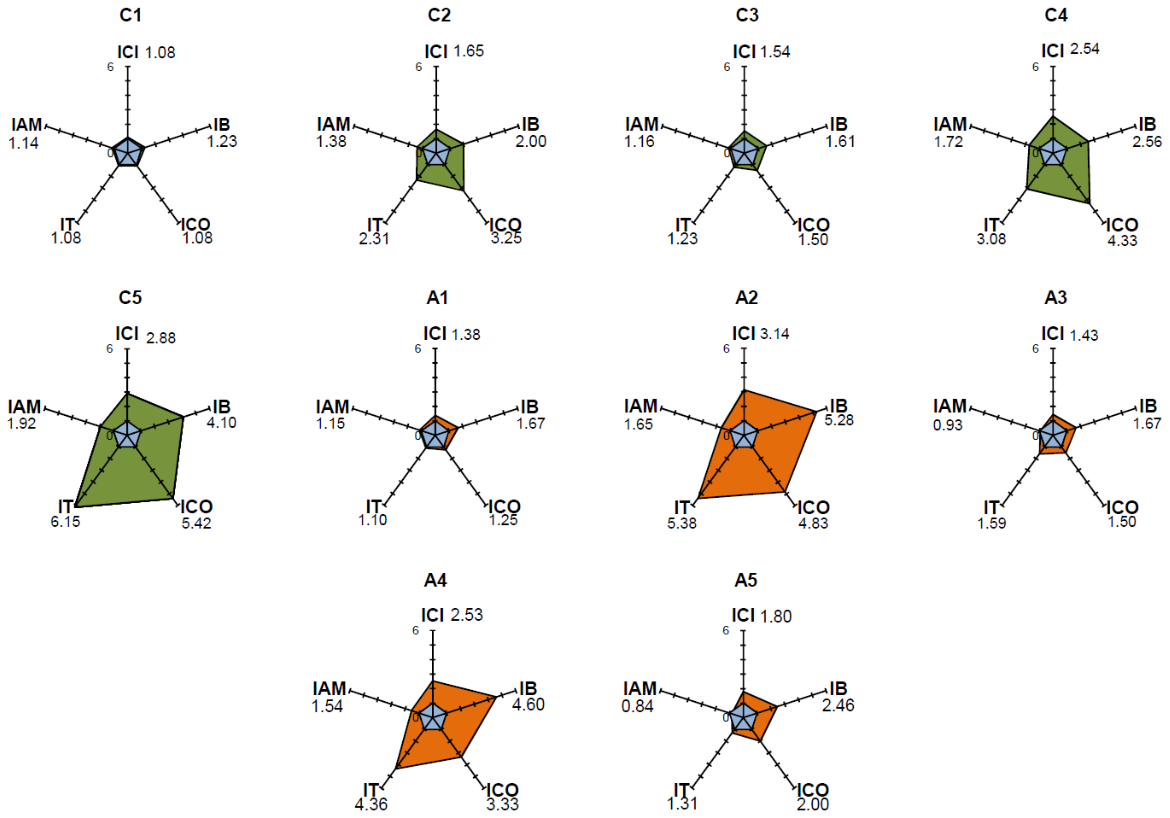

Figure 4. Five-axis plot representation of pollution indices in the reference station (R, blue) and Cadiz (Cx, green) and Algeciras (Ax, organge) Bays.

Stations C1 and A1 have the lowest values for all pollution indices and, therefore, their pentagons are only slightly bigger than that for the reference station. These results occur because they are located in the outer areas of the bays and away from the main sources of pollution.

Stations C3 and A3 show a slightly higher degradation than those cited above, which resulted in greater pentagons. Both stations are characterized by relatively low pollution indices, especially macrobenthic alteration index (MAI) due to their particle size profile (medium sand) above the average. The station A5 resembles the C3 and A3 stations in their low MAI and its larger grain size (very coarse sand). However, degradation is greater in A5.

The highest pollution indices are located in the stations C4 and C5 (Inner Bay of Cadiz Bay), A2 (vicinity of Algeciras municipality and its port) and A4 (area with the largest Industrial activity in Algeciras Bay). Thus, the aforementioned stations have the highest pentagons of Figure 4. Plots show that toxicity index (TI), organic contamination index (OCI) and bioavailability index (BI) are the main sources of degradation between stations.

5 Conclusions

A modified version of the integrated sediment quality assessment method proposed by Rosado et al. (2015b) using a weight of evidence approach and composed of several tests (particle size profile, aqua regia extractable metals, acid labile metals, total organic carbon, toxicity bioassay with *P. phosphoreum* and macrobenthic community alteration) has been applied to sediment samples from the Cadiz and Algeciras Bays.

The proposed method has satisfactorily complied with its main goals: providing an easily understandable and comparable result being applicable to all kinds of sediments, simple and low cost.

The sediment samples were classified on the basis of their environmental degradation index in two groups. First, low degradation: the samples in the outer areas of both bays (C1, C2, C3, R, A1, A3 and A5). Second, moderate degradation: the stations in the Inner Bay of Cadiz Bay (C4 and C5), the station located in the vicinity of Algeciras municipality and its port (A2) and the station situated in the area with the largest industrial activity in Algeciras Bay (A4). Stations C5 (located in the Inner Bay of Cadiz Bay) and A2 (surroundings of Algeciras municipality and its port) have the highest environmental degradation index values of all stations studied: 3.77 (C5) and 3.72 (A2).

References

Ahuja, S., 2013. Monitoring Water Quality: Pollution Assessment, Analysis, and Remediation, Monitoring Water Quality: Pollution Assessment, Analysis, and Remediation.

Anderson, B.S., Hunt, J.W., Phillips, B.M., Nicely, P.A., Vlaming, V. d., Connor, V., Richard, N., Tjeerdema, R.S., 2003. Integrated assessment of the impacts of agricultural drainwater in the Salinas River (California, USA). Environ. Pollut. 124, 523–532. doi:10.1016/S0269-7491(03)00012-5

Araújo, C.V.M., Diz, F.R., Laiz, I., Lubián, L.M., Blasco, J., Moreno-Garrido, I., 2009. Sediment integrative assessment of the Bay of Cádiz (Spain): an ecotoxicological and chemical approach. Environ. Int. 35, 831–41. doi:10.1016/j.envint.2009.02.003

Baldassin, P., Taniguchi, S., Gallo, H., Maranho, A., Kolesnikovas, C., Amorim, D.B., Mansilla, M., Navarro, R.M., Tabeira, L.C., Bicego, M.C., Montone, R.C., 2016. Persistent organic pollutants in juvenile Magellanic Penguins (Spheniscus magellanicus) in South America. Chemosphere 149, 391–9. doi:10.1016/j.chemosphere.2016.01.016

Buruaem, L.M., de Castro, Í.B., Hortellani, M.A., Taniguchi, S., Fillmann, G., Sasaki, S.T., Varella Petti, M.A., Sarkis, J.E. de S., Bícego, M.C., Maranho, L.A., Davanso, M.B., Nonato, E.F., Cesar, A., Costa-Lotufo, L.V., Abessa, D.M. de S., 2013. Integrated quality assessment of sediments from harbour areas in Santos-São Vicente Estuarine System, Southern Brazil. Estuar. Coast. Shelf Sci. 130, 179–189. doi:10.1016/j.ecss.2013.06.006

Canada, E., 2002. Biological Test Method: Reference Method for Determining the Toxicity of Sediment Using Luminescent Bacteria in a Solid-Phase Test - Science and Technology - Environment Canada.

Carballo, J.L., Naranjo, S., 2002. Environmental assessment of a large industrial marine complex based on a community of benthic filter-feeders. Mar. Pollut. Bull. 44, 605–610. doi:10.1016/S0025-326X(01)00295-8

Carrasco, M., López-Ramírez, J.A., Benavente, J., López-Aguayo, F., Sales, D., 2003. Assessment of urban and industrial contamination levels in the bay of Cádiz, SW Spain. Mar. Pollut. Bull. 46, 335–45. doi:10.1016/S0025-326X(02)00420-4

Casado-Martínez, M.C., Campisi, T., Díaz, A., Obispo, R., Postma, J.F., Riba, I., Sneekes, A.C., Buceta, J.L., Del Valls, T.A., 2006. Interlaboratory assessment of marine bioassays to evaluate the environmental quality of coastal sediments in Spain. II. Bioluminescence inhibition test for rapid sediment toxicity assessment.

Chapman, P.M., 2007. Determining when contamination is pollution - weight of evidence determinations for sediments and effluents. Environ. Int. 33, 492–501. doi:10.1016/j.envint.2006.09.001

Chapman, P.M., 2002. Integrating toxicology and ecology: putting the “eco” into ecotoxicology. Mar. Pollut. Bull. 44, 7–15. doi:10.1016/S0025-326X(01)00253-3

Chapman, P.M., 1992. Pollution status of North Sea sediments - an international integrative study. Mar. Ecol. Prog. Ser. 91, 313–322. doi:10.3354/meps091313

Chapman, P.M., 1990. The sediment quality triad approach to determining pollutioninduced degradation. Sci. Total Environ. 97-98, 815–825. doi:10.1016/0048-9697(90)90277-2

Chapman, P.M., Anderson, B., Carr, S., Engle, V., Green, R., Hameedi, J., Harmon, M., Haverland, P., Hyland, J., Ingersoll, C., Long, E., Rodgers, J., Salazar, M., Sibley, P.K., Smith, P.J., Swartz, R.C., Thompson, B., Windom, H., 1997. General guidelines for using the sediment quality triad. Mar. Pollut. Bull. 34, 368–372. doi:10.1016/S0025-326X(96)00138-5

Chapman, P.M., Hollert, H., 2006. Should the Sediment Quality Triad Become a Tetrad, a Pentad, or Possibly even a Hexad? J. Soils Sediments 6, 4–8. doi:10.1065/jss2006.01.152

Chapman, P.M., Smith, M., 2012. Assessing, managing and monitoring contaminated aquatic sediments. Mar. Pollut. Bull. 64, 2000–4. doi:10.1016/j.marpolbul.2012.07.023

Chapman, P.M., Wang, F., 2001. Assessing sediment contamination in estuaries. Environ. Toxicol. Chem. 20, 3–22. doi:10.1002/etc.5620200102

Chapman, P.M., Wang, F., Caeiro, S.S., 2013. Assessing and managing sediment contamination in transitional waters. Environ. Int. 55, 71–91. doi:10.1016/j.envint.2013.02.009

Cherry, D., 2001. An integrative assessment of a watershed impacted by abandoned mined land discharges. Environ. Pollut. 111, 377–388. doi:10.1016/S0269-7491(00)00093-2

Conti, E., Dattilo, S., Costa, G., Puglisi, C., 2016. Bioaccumulation of trace elements in the sandhopper Talitrus saltator (Montagu) from the Ionian sandy coasts of Sicily. Ecotoxicol. Environ. Saf. 129, 57–65. doi:10.1016/j.ecoenv.2016.03.008

Crane, M., 2003. Proposed development of Sediment Quality Guidelines under the European Water Framework Directive: a critique. Toxicol. Lett. 142, 195–206. doi:10.1016/S0378-4274(03)00069-9

Dassenakis, M., Andrianos, H., Depiazi, G., Konstantas, A., Karabela, M., Sakellari, A., Scoullos, M., 2003. The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece. Appl. Geochemistry 18, 781–794. doi:10.1016/S0883-2927(02)00186-5

Dawson, E.J., Macklin, M.G., 1998. Speciation of Heavy Metals in Floodplain and Flood Sediments: a Reconnaissance Survey of the Aire Valley, West Yorkshire, Great Britain. Environ. Geochem. Health 20, 67–76. doi:10.1023/A:1006541724394

DelValls, T.A., Andres, A., Belzunce, M.J., Buceta, J.L., Casado-Martinez, M.C., Castro, R., Riba, I., Viguri, J.R., Blasco, J., 2004. Chemical and ecotoxicological guidelines for managing disposal of dredged material. TrAC Trends Anal. Chem. 23, 819–828. doi:10.1016/j.trac.2004.07.014

Díaz-de Alba, M., Galindo-Riaño, M.D., Casanueva-Marenco, M.J., García-Vargas, M., Kosore, C.M., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. J. Hazard. Mater. 190, 177–187. doi:10.1016/j.jhazmat.2011.03.020

Earnhart, D., 2013. Water Pollution from Industrial Sources, in: Encyclopedia of Energy, Natural Resource, and Environmental Economics. pp. 114–120. doi:http://dx.doi.org/10.1016/B978-0-12-375067-9.00091-7

Estacio, F.J., García-adiego, E.M., Fa, D.A., García-Gómez, J.C., Daza, J.L., Hortas, F., Gómez-Ariza, J.L., 1997. Ecological analysis in a polluted area of Algeciras Bay (southern Spain): External “versus” internal outfalls and environmental implications. Mar. Pollut. Bull. 34, 780–793. doi:10.1016/S0025-326X(97)00046-5

Foster, K.L., Stern, G.A., Carrie, J., Bailey, J.N.-L., Outridge, P.M., Sanei, H., Macdonald, R.W., 2015. Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay, Eastern Canadian Arctic. Sci. Total Environ. 506-507, 430–43. doi:10.1016/j.scitotenv.2014.11.002

Ghirardini, A.V., Birkemeyer, T., Novelli, A.A., Delaney, E., Pavoni, B., Ghetti, P.F., 1999. An integrated approach to sediment quality assessment: the Venetian lagoon as a case study. Aquat. Ecosyst. Health Manag. 2, 435–447. doi:10.1080/14634989908656981

Harrison, R.M., 2001. Pollution: Causes, Effects and Control.

Horiguchi, H., 2014. Encyclopedia of Toxicology, Encyclopedia of Toxicology. Elsevier. doi:10.1016/B978-0-12-386454-3.00033-6

Hudson-Edwards, K.A., Macklin, M.G., Curtis, C.D., Vaughan, D.J., 1996. Processes of Formation and Distribution of Pb-, Zn-, Cd-, and Cu-Bearing Minerals in the Tyne Basin, Northeast England: Implications for Metal-Contaminated River Systems. Environ. Sci. Technol. 30, 72–80. doi:10.1021/es9500724

Khosrovyan, A., Rodríguez-Romero, A., Antequera Ramos, M., DelValls, T.A., Riba, I., 2015. Comparative analysis of two weight-of-evidence methodologies for integrated sediment quality assessment. Chemosphere 120, 138–44. doi:10.1016/j.chemosphere.2014.06.043

Kiratli, N., Ergin, M., 1996. Partitioning of heavy metals in surface Black Sea sediments. Appl. Geochemistry 11, 775–788. doi:10.1016/S0883-2927(96)00037-6

Kosore, C.M., Galindo-Riaño, M.D., Díaz-de-Alba, M., 2015. Assessing trace-element mobility in Algeciras Bay (Spain) sediments by acid and complexing screening. Arab. J. Chem. doi:10.1016/j.arabjc.2015.06.041

Ligero, R.., Barrera, M., Casas-Ruiz, M., Sales, D., López-Aguayo, F., 2002. Dating of marine sediments and time evolution of heavy metal concentrations in the Bay of Cádiz, Spain. Environ. Pollut. 118, 97–108. doi:10.1016/S0269-7491(01)00209-3

Ligero, R.A., Casas-Ruiz, M., Barrera, M., López-Aguayo, F., Sales, D., García, D., 2004. Environmental impact of unleaded gasolines in the bay of Cádiz (Spain). Environ. Int. 30, 99–104. doi:10.1016/S0160-4120(03)00152-1

Long, E.R., Chapman, P.M., 1985. A Sediment Quality Triad: Measures of sediment contamination, toxicity and infaunal community composition in Puget Sound. Mar. Pollut. Bull. 16, 405–415. doi:10.1016/0025-326X(85)90290-5

Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage.

Mackay, D., Celsie, A.K.D., Arnot, J.A., Powell, D.E., 2016. Processes influencing chemical biomagnification and trophic magnification factors in aquatic ecosystems: Implications for chemical hazard and risk assessment. Chemosphere 154, 99–108. doi:10.1016/j.chemosphere.2016.03.048

Marin, B., Giresse, P., 2001. Particulate manganese and iron in recent sediments of the Gulf of Lions continental margin (north-western Mediterranean Sea): deposition and diagenetic process. Mar. Geol. 172, 147–165. doi:10.1016/S0025-3227(00)00124-9

Martínez-Lladó, X., Gibert, O., Martí, V., Díez, S., Romo, J., Bayona, J.M., de Pablo, J., 2007. Distribution of polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT) in Barcelona harbour sediments and their impact on benthic communities. Environ. Pollut. 149, 104–13. doi:10.1016/j.envpol.2006.11.020

Mason, R.P., Kim, E.-H., Cornwell, J., Heyes, D., 2006. An examination of the factors influencing the flux of mercury, methylmercury and other constituents from estuarine sediment. Mar. Chem. 102, 96–110. doi:10.1016/j.marchem.2005.09.021

Moalla, S.M.N., Awadallah, R.M., Rashed, M.N., Soltan, M.E., 1997. Distribution and chemical fractionation of some heavy metals in bottom sediments of Lake Nasser. Hydrobiologia 364, 31–40. doi:10.1023/A:1003112008122

Morales-Caselles, C., Kalman, J., Micaelo, C., Ferreira, A.M., Vale, C., Riba, I., Delvalls, T.A., 2008. Sediment contamination, bioavailability and toxicity of sediments affected by an acute oil spill: Four years after the sinking of the tanker Prestige (2002). Chemosphere 71, 1207–13. doi:10.1016/j.chemosphere.2007.12.013

Morillo, J., Usero, J., Gracia, I., 2007. Potential Mobility of Metals in Polluted Coastal Sediments in Two Bays of Southern Spain. J. Coast. Res. 232, 352–361. doi:10.2112/04-0246.1

Morillo, J., Usero, J., Gracia, I., 2002. Partitioning of metals in sediments from the Odiel River (Spain). Environ. Int. 28, 263–271. doi:10.1016/S0160-4120(02)00033-8

Morillo, J., Usero, J., Rojas, R., 2008. Fractionation of metals and As in sediments from a biosphere reserve (Odiel salt marshes) affected by acidic mine drainage. Environ. Monit. Assess. 139, 329–37. doi:10.1007/s10661-007-9839-3

Mucha, A.P., Vasconcelos, M.T.S.., Bordalo, A.A., 2003. Macrobenthic community in the Douro estuary: relations with trace metals and natural sediment characteristics. Environ. Pollut. 121, 169–180. doi:10.1016/S0269-7491(02)00229-4

Muxika, I., Borja, A., Bald, J., 2007. Using historical data, expert judgement and multivariate analysis in assessing reference conditions and benthic ecological status, according to the European Water Framework Directive. Mar. Pollut. Bull. 55, 16–29. doi:10.1016/j.marpolbul.2006.05.025

Nogawa, K., Suwazono, Y., 2011. Encyclopedia of Environmental Health, Encyclopedia of Environmental Health. Elsevier. doi:10.1016/B978-0-444-52272-6.00312-3

Nowell, L.H., Norman, J.E., Ingersoll, C.G., Moran, P.W., 2016. Development and application of freshwater sediment-toxicity benchmarks for currently used pesticides. Sci. Total Environ. 550, 835–850. doi:10.1016/j.scitotenv.2016.01.081

Periáñez, R., 2012. Modelling the environmental behaviour of pollutants in Algeciras Bay (south Spain). Mar. Pollut. Bull. 64, 221–232. doi:10.1016/j.marpolbul.2011.11.030

Periáñez, R., 2009. Environmental modelling in the Gulf of Cadiz: heavy metal distributions in water and sediments. Sci. Total Environ. 407, 3392–406. doi:10.1016/j.scitotenv.2009.01.023

Periáñez, R., Casas-Ruíz, M., Bolívar, J.P., 2013. Tidal circulation, sediment and pollutant transport in Cádiz Bay (SW Spain): A modelling study. Ocean Eng. 69, 60–69.

doi:10.1016/j.oceaneng.2013.05.016

Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, P., López-Sánchez, J.F., 2001. Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. J. Environ. Monit. 3, 243–250. doi:10.1039/b010235k

Qi, H.-X., Li, H.-Z., Ma, P., You, J., 2015. Integrated sediment quality assessment through biomarker responses and bioavailability measurements: Application in Tai Lake, China. Ecotoxicol. Environ. Saf. 119, 148–54. doi:10.1016/j.ecoenv.2015.05.007

Riba, I., Forja, J.M., Gómez-Parra, A., DelValls, T.A., 2004. Sediment quality in littoral regions of the Gulf of Cádiz: a triad approach to address the influence of mining activities. Environ. Pollut. 132, 341–53. doi:10.1016/j.envpol.2004.03.021

Rosado, D., Usero, J., Morillo, J., 2016. Assessment of heavy metals bioavailability and toxicity toward Vibrio fischeri in sediment of the Huelva estuary. Chemosphere 153, 10–17. doi:10.1016/j.chemosphere.2016.03.040

Rosado, D., Usero, J., Morillo, J., 2015a. Ability of 3 extraction methods (BCR, Tessier and protease K) to estimate bioavailable metals in sediments from Huelva estuary (Southwestern Spain). Mar. Pollut. Bull. 102, 65–71. doi:10.1016/j.marpolbul.2015.11.057

Rosado, D., Usero, J., Morillo, J., 2015b. Application of a new integrated sediment quality assessment method to Huelva estuary and its littoral of influence (Southwestern Spain). Mar. Pollut. Bull. 98, 106–14. doi:10.1016/j.marpolbul.2015.07.008

Ruiz, F., Borrego, J., González-Regalado, M.L., López González, N., Carro, B., Abad, M., 2008. Impact of millennial mining activities on sediments and microfauna of the Tinto River estuary (SW Spain). Mar. Pollut. Bull. 56, 1258–64. doi:10.1016/j.marpolbul.2008.04.036

Sainz, A., Ruiz, F., 2006. Influence of the very polluted inputs of the Tinto-Odiel system on the adjacent littoral sediments of southwestern Spain: a statistical approach. Chemosphere 62, 1612–22. doi:10.1016/j.chemosphere.2005.06.045

Sammartino, S., García Lafuente, J., Sánchez Garrido, J.C., De los Santos, F.J., Álvarez Fanjul, E., Naranjo, C., Bruno, M., Calero, C., 2014. A numerical model analysis of the tidal flows in the Bay of Algeciras, Strait of Gibraltar. Cont. Shelf Res. 72, 34–46. doi:10.1016/j.csr.2013.11.002

Sánchez-Garrido, J.C., Lafuente, J.G., Sammartino, S., Naranjo, C., de los Santos, F.J., Álvarez Fanjul, E., 2014. Meteorologically-driven circulation and flushing times of the Bay of Algeciras, Strait of Gibraltar. Mar. Pollut. Bull. 80, 97–106. doi:10.1016/j.marpolbul.2014.01.036

Sánchez-Montoya, M.M., Vidal-Abarca, M.R., Suárez, M.L., 2010. Comparing the sensitivity of diverse macroinvertebrate metrics to a multiple stressor gradient in Mediterranean streams and its influence on the assessment of ecological status. Ecol. Indic. 10, 896–904. doi:10.1016/j.ecolind.2010.01.008

Seiter, K., Hensen, C., Schröter, J., Zabel, M., 2004. Organic carbon content in surface sediments—defining regional provinces. Deep Sea Res. Part I Oceanogr. Res. Pap. 51, 2001–2026. doi:10.1016/j.dsr.2004.06.014

Svenson, A., Cardoso, G.A., Thuren, A., Kaj, L., Dave, G., 1996. Microtox toxicity in soils. Evaluation of the direct contact test with luminescent bacteria. Environ. Toxicol. Water Qual. 11, 293–300.

Tarazona, J. V., Muñoz, M.J., Carbonell, G., Carballo, M., Ortiz, J.A., Castaño, A., 1991. A toxicological assessment of water pollution and its relationship to aquaculture development in Algeciras Bay, Cadiz, Spain. Arch. Environ. Contam. Toxicol. 20, 480–487. doi:10.1007/BF01065836

Testa, J.M., Brady, D.C., Di Toro, D.M., Boynton, W.R., Cornwell, J.C., Kemp, W.M., 2013. Sediment flux modeling: Simulating nitrogen, phosphorus, and silica cycles. Estuar. Coast. Shelf Sci. 131, 245–263. doi:10.1016/j.ecss.2013.06.014

Tomiyasu, T., Matsuyama, A., Eguchi, T., Fuchigami, Y., Oki, K., Horvat, M., Rajar, R., Akagi, H., 2006. Spatial variations of mercury in sediment of Minamata Bay, Japan. Sci. Total Environ. 368, 283–90. doi:10.1016/j.scitotenv.2005.09.090

Usero, J., Morillo, J., El Bakouri, H., 2008. A general integrated ecotoxicological method for marine sediment quality assessment: application to sediments from littoral ecosystems on Southern Spain’s Atlantic coast. Mar. Pollut. Bull. 56, 2027–36. doi:10.1016/j.marpolbul.2008.08.009

Van den Brink, P.J., Kater, B.J., 2006. Chemical and biological evaluation of sediments from the Wadden Sea, The Netherlands. Ecotoxicology 15, 451–60. doi:10.1007/s10646-006-0080-6

Vandermeersch, G., Lourenço, H.M., Alvarez-Muñoz, D., Cunha, S., Diogène, J., Cano-Sancho, G., Sloth, J.J., Kwadijk, C., Barcelo, D., Allegaert, W., Bekaert, K., Fernandes, J.O., Marques, A., Robbens, J., 2015. Environmental contaminants of emerging concern in seafood – European database on contaminant levels. Environ. Res. 143, 29–45. doi:10.1016/j.envres.2015.06.011

Wang, Z., Wang, Y., Zhao, P., Chen, L., Yan, C., Yan, Y., Chi, Q., 2015. Metal release from contaminated coastal sediments under changing pH conditions: Implications for metal mobilization in acidified oceans. Mar. Pollut. Bull. 101, 707–15. doi:10.1016/j.marpolbul.2015.10.026

Wentworth, C.K., 1922. A Scale of Grade and Class Terms for Clastic Sediments. J. Geol. 30, 377–392.

Yunker, M.B., Macdonald, R.W., Ross, P.S., Johannessen, S.C., Dangerfield, N., 2015. Alkane and PAH provenance and potential bioavailability in coastal marine sediments subject to a gradient of anthropogenic sources in British Columbia, Canada. Org. Geochem. 89-90, 80–116. doi:10.1016/j.orggeochem.2015.10.002

Zhou, P., Huang, J., Pontius, R.G., Hong, H., 2016. New insight into the correlations between land use and water quality in a coastal watershed of China: Does point source pollution weaken it? Sci. Total Environ. 543, 591–600. doi:10.1016/j.scitotenv.2015.11.063