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Using sediment quality guidelines for dredged material management in commercial ports from Spain

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Abstract

Dredged material contamination was assessed in different commercial ports from Spain: Port of Cádiz and Huelva, South West; Bilbao and Pasajes, North; Cartagena and Barcelona, East; Coruña, North West. Sediment from different locations of these ports was sampled and was characterized following the Spanish recommendations for dredged material management. This characterization included grain size distribution, organic matter content and concentration of the chemical compounds included in the list of pollutants and hazardous substances (As, Cd, Cu, Cr, Hg, Ni, Pb and Zn; PCB congeners IUPAC number 28, 52, 101, 118, 138, 153 and 180; PAHs were also analyzed). The results were compared to the limit values of Spanish Action Levels that define the different categories for assessment and management. A set of empirically derived sediment quality guidelines (SQG) was used to assess the possible toxicity of the dredged materials and to improve the use of the chemical approach to characterize dredged material for its management.

Keywords: Contaminated sediments; Harbor; Sediment quality guidelines

1. Introduction

Although anthropogenic emissions to the aquatic environment have been reduced considerably in the late years as control measures were implemented, harbor sediments are still a sink for many pollutants as a result of poor environmental management in the past, diffuse sources and ship accidental spills (PIANC, 1997). The most important groups of contaminants in dredged materials include metals, PCBs and dioxin-like compounds, PAHs, organochloride pesticides (OCPs), oil, radio-nuclides, rare earth metals and organotin compounds (Stronkhorst, 2003, PIANC, 1999).

In order to maintain navigation in large harbors in Spain sediments are periodically dredged (Guerra, 2004). Dredged material management is regulated since 1994 (RRGMD; CEDEX, 1994), namely, the disposal of contaminated sediments into the sea in order to minimize adverse effects in the aquatic environment. After the first physico-chemical characterization, dredged materials are classified in three categories on the basis of the predictable effects of a chemical concentration on the marine biota by comparing the measured chemical concentrations to single-species Sediment Quality Guidelines (SQGs), named Action Levels (AL). Although toxicity studies are explicitly mentioned in the Spanish recommendations to establish the biological significance of sediment-bound contaminants, these tests are not still included in the current decision-making framework for dredged management. In this context, SQGs are being used as a screening tool to assess the biological significance of sediment-bound contaminants in the absence of direct biological effects data (den Besten et al., 2003; Birch and Taylor, 2002; GIPME, 2000).

It is accepted that without defensible SQGs, it would be difficult to assess the extent of sediment contamination (Jones-Lee and Lee, 2005; McCauley et al., 2000). During the last years, several efforts have been devoted to develop environ-

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mental quality guidelines designed specifically to support contaminated sediments and dredged material management and to implement policies and regulatory strategies. Different technical approaches have been used to develop numerical SQGs. Adams et al. (1992) reviewed the three main approaches used in the United States to estimate biological effects of contaminated sediments based on chemical data alone. The equilibrium partitioning model–EqP–has been developed theoretically to account for the factors that likely influence metal and nonionic organic chemicals bioavailability in bed anaerobic sediments (Ankley et al., 1996; Hansen et al., 1996; DiToro et al., 1991). Other approach, the co-occurrence method, developed SQGs empirically using different statistical methods but always on the basis of the observed associations between large data sets of measured adverse biological effects and the concentration of potentially toxic substances present in the environment (Long et al., 1995; MacDonald, 1993). The third of the approaches, named the Consensus Approach and proposed by Swartz (1999), combined sediment guidelines from correlative and EqP approaches to develop consensus SQGs.

Although false positives and false negatives are expected, the EqP methodology is currently adopted by the U.S. Environmental Protection Agency (USEPA, 1995), even if there is a number of research needs that are being addressed, as this approach is implemented including sediment quality modeling, sediment toxicity identification evaluations (TIEs), studies that address bio-availability, studies that address the relative importance of exposure via sediment ingestion or ingestion of contaminated benthos, studies demonstrations of applicability of any SQGs, field verification, extension of the non-ionic mixture models to non-PAH compounds, and the establishment of toxicological databases (with benthic organisms) for standard toxicity endpoints (McCauley et al., 2000).

The National Oceanic and Atmospheric Administration (NOAA) developed a set of empirical SQGs (Long et al., 1995) that provides two values, effects range low (ERL) and effects range high (ERM), which delineate three concentration ranges for each particular chemical and the corresponding estimation of the potential biological effect. The concentrations below ERL represent a minimal-effects range, which is intended to estimate conditions where biological effects are rarely observed. Concentrations equal to, or greater than ERL, but less than ERM represent a range within which biological effects occur occasionally. Concentrations at or above ERM values represent a probable effect range within which adverse biological effects frequently occur. This set of SQGs has been shown to have some predictive ability although do not account for chemical bioavailability and was not based upon experiments in which causality was determined (Long et al., 1998, 2000). These co-occurrence-based SQGs have been widely applied for contaminated sediment assessment (Jones et al., 2005; Roach, 2005; Pekey et al., 2004; Birch and Taylor, 2002; Wakeman and Themelis, 2001; Bothner et al., 1998; O'Connor et al., 1998) even if the suitability has been further discussed together with the potential implications to the regulated community (Lee and Jones-Lee, 1996; Crane, 2003). Nevertheless, the studies to establish regionally action levels and to evaluate the negative effects of contaminated sediments and dredged materials on the biota are under development around the world (GIPME, 2000).

This paper reports the state of sediment contamination in different Spanish commercial ports. This has been done on the basis of evaluations of the sediment chemistry data compared to the single-species sediment quality guidelines used in Spain for dredged material management (the so called Action Levels). In addition, two sets of empirically derived SQGs have been used to study the probability of observing acute toxicity: the ERL-ERM guidelines developed by Long et al. (1995) and the SQGs developed by Riba et al. (2004) using chemical and ecotoxicological data from sediment quality assessment studies in the Atlantic coast of Spain. Finally, the differences when using these sets of SQGs on the decision-making framework for dredged material management in Spain are discussed.

2. Materials and methods

2.1. Sediment sampling

25 sediment samples were collected at 7 commercial ports along the Spanish coast in November 2001 and April 2003. The selection of the sampling sites in each port was based on the need to examine specific point sources (identified by means of available data) and to cover a broad spatial coverage of the ports and thus allowing a general assessment of sediment quality (DelValls et al., 2003). The port area was virtually divided in segments. Three stations were sampled in the ports of Pasajes (PA#), La Coruña (CO#) and Bilbao (BI#) and four in Cartagena, Barcelona, Huelva and Cádiz (C#, B#, H# and CA#, respectively) (Fig. 1). In each site, sediments were collected with a 0.025-m^2 Van Veen grab from approximately the top 20 cm of the sediment and were brought to the laboratory, homogenized and stored at 4 °C and darkness prior to analysis.

2.2. Sediment characterization

All the analyses for sediment physical and chemical characterization were made according to Spanish recommendations for dredged materials and following the recommended protocols (CEDEX, 1994). The dry weight fraction was determined by weight loss at 105 °C. For the rest of analyses, sediments were dried at 40 °C for 24 h. Grain size distribution followed UNE 103 101 and total organic carbon (TOC) content was estimated by loss of ignition (LOI) at 550 °C and gravimetric determination as recommended for small dredged volumes and applying the following expression to express the results as total organic carbon (CEDEX, 1994):

$$\mathrm{TOC}\left(\mathrm{g\ kg^{-1}}\right) = 0.35\mathrm{LOI}\left(\mathrm{g\ kg^{-1}}\right)$$

Metals were determined in microwave acid-digested samples (HNO_3 and aqua regia in a proportion 1:3) in Teflon

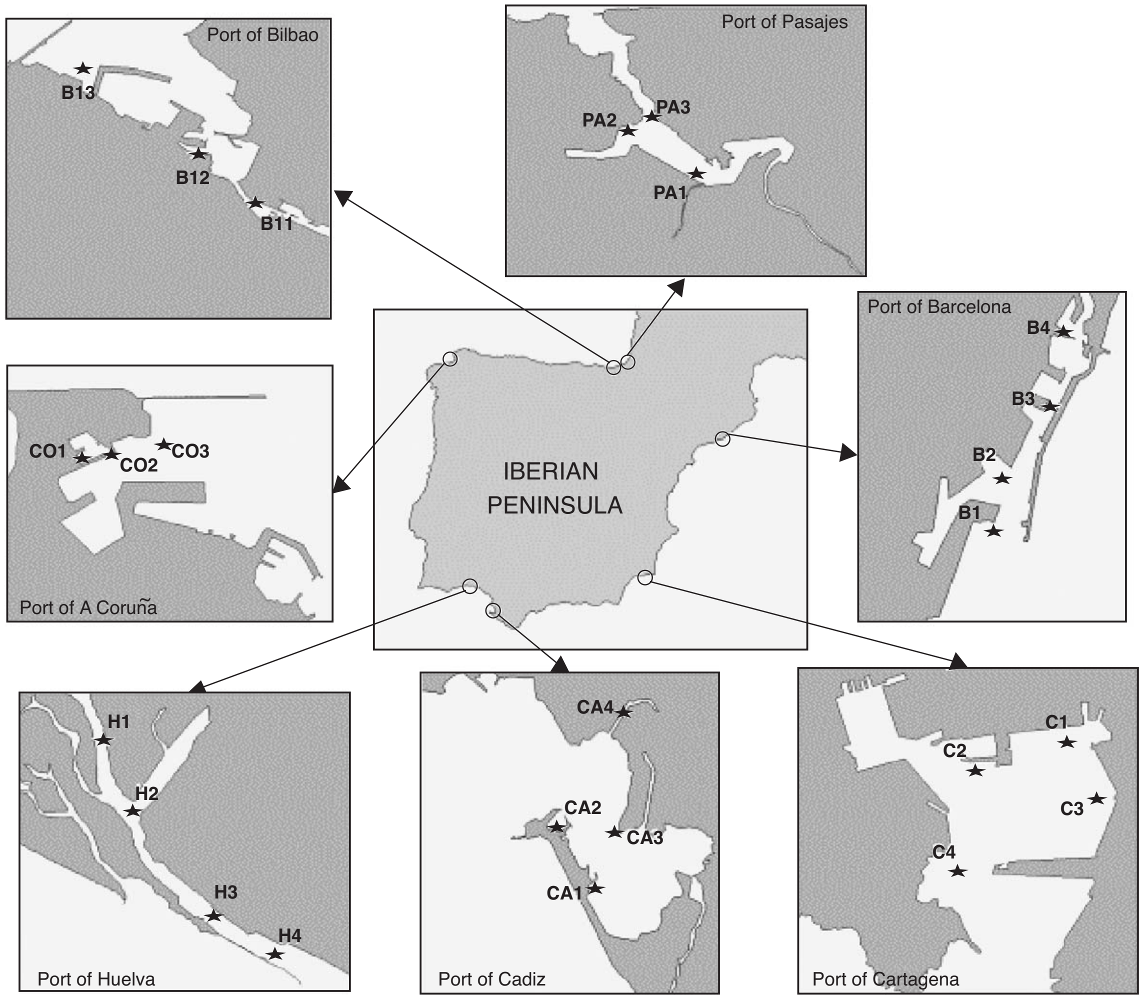

Fig. 1. Map showing the sampling sites of commercial ports. Selected ports are the port of Pasajes (PA#), La Coruña (CO#), Bilbao (BI#) the port of Cartagena (C#), Barcelona (B#), Huelva (H#) and Cádiz (CA#).

vessels and adjusted to volume with boric acid 5.6%. For Hg, the cold vapour technique was used and for As hydride generation, and both quantified using atomic absorption spectrometry. The concentrations of Cd, Pb, Cu, Zn and Cr were determined using flame or furnace atomic absorption spectrometry, depending on the metal content.

PCB congeners 28, 52, 101, 118, 138, 153 and 180 and polycyclic aromatic hydrocarbons (PAHs) were quantified after extraction with cyclohexane and dichloromethane by means of ultrasound treatment and concentration and clean-up with column chromatography. Determination of PCBs was made with gas chromatography with electron capture detection (GC-ECD) (EPA 8080) and 12 PAHs (acenaphtylene, acenaphtene, anthracene, benz(*a*)anthracene, benz(*a*)pyrene, chrysene, dibenz(*a*,*h*)anthracene, phenanthrene, fluoranthene, fluorene, naphthalene and pyrene) were determined with HPLC with fluorescence detection (EPA 8310). Detection limits were 0.8 and 10–30 μg kg^{-1} dry weight of sediment of PCBs and PAHs, respectively. Recoveries of analytes determined ranged from 60% to 120%.

All the analytical procedures were checked with reference materials (Marine Reference Sediment Material for Trace Metal-1, National Research Council (NRC), Certified Reference Material, 277 BCR, and Conseil National de Reserches Canada, 277 BCR, for heavy metals; and NRC-CNRC HS-1 for PCBs and PAHs) and allow agreement with certified values higher than 90%.

2.3. Sediment quality guidelines

To evaluate the sediment contamination and potential ecotoxicological effects associated with the observed concentrations of contaminants, different published Sediment Quality Guidelines (SQGs) have been used (Table 1). In Spain, Action Levels (named AL1 and AL2) are used to characterize dredged material (AL; CEDEX, 1994) and represent hazardous concentrations for organisms based on physicochemical criteria. We used firstly AL1 to identify stations where additional investigations are mandatory (if the AL1 is exceeded for any of the compounds) and AL2 to identify the dredged materials that are not adequate for open water disposal (if any AL2 is exceeded).

Two different sets of empirically derived guidelines were also used to compare the results of the chemical composition. One set is that proposed by Long et al. (1995) although it was derived using data from the U.S Coast: the effects-range-low

Table 1
Sediment quality guidelines for marine sediments included in this study

	CEDEX, 1994		Long et al., 1995		Riba et al., 2004	
	AL1	AL2	ERL	ERM	V1	V2
As	80	200	8.2	70	27.4	213
Cd	1.0	5.0	1.2	9.6	0.51	0.96
Cr	200	1000	81	370	–	–
Cu	100	400	34	270	209	979
Hg	0.6	3.0	0.15	0.71	0.54	1.47
Ni	100	400	20.9	51.6	–	–
Pb	120	600	46.7	218	260	270
Zn	500	3000	150	410	513	1310
Σ_7-PCB	30	100	22.7	180	54	254
Σ_{13}-PAHs	–	–	0.35	2.36	–	–

All values are expressed as mg·kg^{-1} except Σ_7-PCB expressed as μg·kg^{-1}. AL1 and AL2 are Spanish Action Levels for dredged material management; ERL and ERM are effect range low and effect range medium and V1 and V2 are sediment quality guidelines developed using data from the Atlantic coast of Spain.

(ERL) and effects-range-median (ERM) values. These values represent the concentrations below which adverse effects are expected to occur and are equal to the 10th and 50th percentile concentrations, respectively, of each contaminant represented in the data set that showed significant adverse effects (ERL is the concentration at which adverse biological effects begin to be seen, and ERM is the level associated with adverse effect). Because a small degree of variability that is likely attributable to regional differences in the geochemistry of sediments and the relative bioavailability of sediment-associated toxicants can lead to differences in the predictive abilities of sediment guidelines (Long et al., 2000), a set of SQGs developed using data from the West Atlantic coast of Spain (Riba et al., 2004) has been also used. This set is defined by the highest concentration of a contaminant non-associated with adverse biological effects (V1) and the lowest concentration associated with adverse biological effect (V2). While the ERL and ERM were developed using acute toxicity data, it should be noted that this last set of SQGs was developed using acute toxicity data but also sublethal and histopathological data from laboratory tests.

All these SQGs can be used to assess individual chemicals by comparing the chemical concentration with the limit concentrations or to estimate the probability of acute sediment toxicity and to determine the possible biological effect of combined toxicant groups by calculating mean quotients for a large range of contaminants. This mean ERM quotient (m-ERM-Q) has been calculated according to Long et al. (1998):

$$\mathrm{m-ERM-Q} = \sum (C_i/\mathrm{ERM}_i)/n$$

where C_i is the sediment concentration of compound i, ERM_i is the ERM for compound i and n is the number of compounds. Mean ERM quotients have been related to the probability of toxicity (Long and MacDonald, 1998; Long et al., 2000) based on the analyses of matching chemical and toxicity data from 1068 samples from the USA estuaries. The mean ERM quotient of <0.1 has a 9% probability of being toxic; a mean ERM quotient of 0.11–0.5 has a 21% probability of toxicity; a mean ERM quotient of 0.51–1.5 has a 49% of being toxic; and mean ERM quotient of >1.50 has a 76% of toxicity.

3. Results

3.1. Sediment characterization of conventional parameters

The results of the measured conventional parameters of the samples are included in Table 2. The general characteristics of the sediments vary considerably between ports and between stations: some areas are sandy, whereas others contain a great proportion of fine grain sizes. Most of the dredged sediments from Spanish ports used in this study could be considered fine sediments. Sample CA1 from Cádiz had 99% sand (0.63 μm<size<2 mm) and H4 80% coarse (>2 mm). The percentage of fines (silt and clay, <0.63 μm) for the rest of samples ranged from 31% registered in sample C3 from the port of Cartagena to 99.59% for sample CA4, from Cádiz. Such large variability is also observed for organic matter. Total organic carbon ranged from 1% (samples H4 and CA1) to 24% (sample CA4). The highest value for each port was found for sample CA4, H1, C1, B4, CO2, PA3 and BI3, all values higher than 10% except for CO2. In general, the lowest values were found for the port of Barcelona and Coruña.

3.2. Concentrations of contaminants

Summarized results of the chemical analyses are shown in Table 3. The chemical data indicated that most of the samples

Table 2
Conventional parameters of harbor sediment samples used in this study (Port of Cádiz, CA#; Port of Huelva, H#; Port of Barcelona, B#; Port of Cartagena, C#; Port of Bilbao, BI#; Port of Coruña, CO#; Port of Pasajes, PA#)

Sample	% Coarse	% Sand	% Fines	TOC (g·kg^{-1})
CA1	0.19	99.77	0.04	1.07
CA2	0.05	40.42	59.53	13.75
CA3	0.30	17.80	81.90	20.30
CA4	0.03	0.38	99.59	24.33
H1	0.07	9.71	90.22	20.27
H2	0.19	9.60	90.21	10.64
H3	0.03	56.02	43.95	6.30
H4	80.34	19.65	0.01	1.00
B1	1.43	64.72	33.86	3.06
B2	5.50	57.92	36.58	4.55
B3	3.89	42.13	53.98	4.81
B4	1.41	39.89	58.70	17.56
C1	3.95	38.24	57.81	10.54
C2	5.22	53.59	41.19	9.12
C3	0.93	67.20	31.87	7.19
C4	0.90	50.01	49.10	9.87
BI1	2.39	20.28	77.33	14.81
BI2	38.12	14.48	47.40	15.07
BI3	0.19	6.22	93.59	16.73
CO1	n.a.	n.a.	49.71	5.97
CO2	n.a.	n.a.	84.33	7.53
CO3	n.a.	n.a.	74.75	5.07
PA1	0.84	28.87	70.29	14.43
PA2	3.67	5.08	91.24	18.47
PA3	1.82	38.53	59.65	19.81

n.a. means not available data.

Table 3
Chemical characterization of the dredged materials (Port of Cádiz, CA#; Port of Huelva, H#; Port of Barcelona, B#; Port of Cartagena, C#; Port of Bilbao, BI#; Port of Coruña, CO#; Port of Pasajes, PA#)

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PCBs[a]	PAHs[b]
CA1	3.42	0.92	0.10	6.98	0.05	0.06	2.28	21.27	n.d.[c]	n.d.
CA2	30.77	1.32	14.94	202.80	1.98	20.14	86.90	378.25	144.90	n.d.
CA3	16.61	1.23	8.43	46.76	0.28	16.90	17.61	135.50	n.d.	n.d.
CA4	7.81	1.25	14.22	32.07	0.05	21.25	5.14	65.67	n.d.	n.d.
H1	840.00	4.35	32.89	1938.00	2.38	34.57	383.10	2458.00	2.00	n.d.
H2	531.00	2.50	24.10	1497.00	1.99	7.10	384.70	1857.00	2.29	n.d.
H3	273.00	1.32	8.13	772.00	1.20	129.00	217.60	1176.00	n.d.	n.d.
H4	4.70	n.d.	9.70	1.90	0.04	0.80	5.30	20.90	n.d.	n.d.
B1	17.39	0.93	105.20	74.88	0.94	18.87	86.66	253.80	49.20	0.28
B2	21.19	1.52	103.70	159.70	1.12	29.12	103.50	424.00	138.30	0.37
B3	18.56	0.62	59.53	102.10	1.15	22.24	91.90	219.70	85.30	0.61
B4	28.99	2.88	93.86	601.10	4.12	32.30	455.30	1165.00	272.90	1.80
C1	101.50	98.49	66.64	665.90	136.40	29.04	1397.00	8661.00	123.00	0.91
C2	64.71	17.47	45.61	313.40	32.71	15.33	748.30	1885.00	468.20	1.03
C3	88.00	31.88	57.57	453.30	115.20	19.32	1397.00	3310.00	107.60	0.66
C4	62.55	6.79	29.48	171.10	21.59	19.32	486.70	900.80	118.90	1.24
BI1	67.26	2.00	18.27	102.60	0.74	26.39	147.50	476.10	111.60	66.71
BI2	104.00	2.00	23.11	204.10	1.43	32.00	285.90	777.50	256.20	13.90
BI3	21.71	0.04	3.48	23.03	0.18	15.72	40.70	122.35	22.12	0.63
CO1	27.43	0.96	28.67	209.10	6.41	19.90	259.60	513.20	254.40	7.38
CO2	22.50	0.51	31.43	53.12	0.47	19.96	82.37	191.40	58.80	7.07
CO3	13.57	0.25	33.43	35.28	0.54	19.23	54.10	134.90	40.40	1.94
PA1	39.13	0.68	26.73	158.10	1.07	33.49	293.70	1085.00	610.00	n.d.
PA2	28.86	0.70	23.42	167.10	1.29	28.48	246.00	763.00	740.00	1.06
PA3	23.78	0.04	18.61	162.50	1.36	19.61	154.90	576.00	240.00	0.26

Results are expressed as mg kg^{-1} dry weight basis except PCBs, in μg kg^{-1} dry weight.
[a] Σ_7-PCBs.
[b] Σ_{12}-PAHs.
[c] n.d. means not detected.

contained mixtures of contaminants, including trace metals, PAHs, and chlorinated hydrocarbons. The concentration of most trace metals ranged from two to three orders of magnitude and even four for Hg with the lowest values corresponding to the sediments that reported the lowest proportion of fine sediment particles. The highest concentrations for most of the compounds were found in the port of Cartagena and in the port of Huelva: sample C1 showed the highest concentration of Cd, Hg, Pb and Zn and sample H1 of As, Cu and Ni. The concentrations of PCBs were less than the detection limit for most of the samples at the ports of Cádiz and Huelva. The highest concentration was found in the port of Pasajes but these kinds of compounds were also present in the ports of Barcelona, Bilbao and Cartagena. The concentrations of the PAHs were most often less than the detection limits. The highest concentrations were found in the port of Bilbao (samples BI1 and BI2).

3.3. Comparison with SQGs

The comparison with the different SQGs is resumed in Table 4. The two different ways of comparison have been included: the number of single-species limit values exceeded and the mean quotient calculated for the two empirically derived sets of SQGs, using the V2 value reported by Riba et al. (2004) and the ERM value reported by Long et al. (1995). Only three of the samples, 12% of the sediments, did not fail any of the AL1

Table 4
Number of exceeded Action Levels (AL1 and AL2 from CEDEX, 1994) and SQGs (V1 and V2 from Riba et al., 2004 and ERL and ERM from Long et al., 1995) and mean quotients using the ERM and the V2 values

Samples	AL1	AL2	V1	V2	ERL	ERM	m-V2-q	m-ERM-q
CA1	0	0	1	0	0	0	0.15	0.03
CA2	4	1	4	2	7	1	0.61	0.67
CA3	1	0	1	1	4	0	0.25	0.17
CA4	1	0	1	1	2	0	0.21	0.11
H1	6	2	6	6	7	5	2.20	3.15
H2	6	2	6	6	6	5	1.55	2.27
H3	7	2	5	2	7	6	0.85	1.50
H4	0	0	0	0	0	0	0.01	0.02
B1	2	0	2	0	9	1	0.35	0.39
B2	4	1	3	1	7	1	0.55	0.58
B3	3	0	3	0	9	1	0.35	0.44
B4	6	3	7	4	7	5	1.46	1.63
C1	7	6	7	4	8	6	29.83	23.53
C2	6	4	7	5	7	6	6.73	6.11
C3	7	6	7	4	7	6	17.23	18.42
C4	6	3	6	3	7	3	3.60	3.83
BI1	5	2	4	1	9	3	0.62	1.23
BI2	8	2	6	3	9	5	0.92	1.12
BI3	0	0	0	0	2	0	0.09	0.16
CO1	5	2	7	3	6	4	1.15	1.54
CO2	1	0	2	0	6	0	0.24	0.36
CO3	1	0	0	0	5	0	0.17	0.26
PA1	5	1	6	2	7	4	0.87	1.08
PA2	5	1	5	1	7	4	0.90	1.11
PA3	5	1	3	0	6	3	0.46	0.69

values: CA1 in the Port of Cádiz, H4 in the Port of Huelva and BI3 in the port of Bilbao. All the rest of the samples failed any of the AL1 values and a total of 16 samples that account for more than the 50% of the sediments failed at least one AL2 value.

It has been suggested that sediment toxicity is unlikely when bulk concentrations in sediment of all chemicals listed are below the effects-range-low (ERL) value. Conversely, toxicity is probable when any chemical concentration exceeds an effects-range-median (ERM) value (Long et al., 1995). For the set of 25 samples studied, 18 failed at least one of the ERM values, and thus, toxicity can be considered probable for more than the 70% of the dredged sediments. Only two samples, CA1 and H4, did not exceed any ERL value. There are five samples, sample BI3 in the port of Bilbao, two samples in the port of Cádiz, and two samples in the port of Coruña, that showed an intermediate level of contamination and are not included in none of these two categories with different probabilities of toxicity. If we use the SQGs reported by Riba et al. (2004), three of the samples did not exceed any of the V1 values: H4, BI3 and CO3. Those that exceed at least one V2 were in total 16. Six of the sediment samples are not classified in any of both groups.

Mean ERM quotients ranged from 0.02 to 23.53 (values reported for H4 and C1 respectively). Eleven samples showed values higher than 1. When the V2 values are used to calculate the mean quotient, the values ranged from 0.01 to 29.83 (values reported for H4 and C1 respectively). In this case, only eight of the samples reported values higher than 1.

4. Discussion

The first objective of this study is to assess the state of contamination of the selected commercial ports. The ports of Huelva and Cartagena (samples named H# and C#), located in two areas historically affected by mining activities (CEDEX, 1999), reported high concentrations of metallic compounds. The ports of Barcelona, Bilbao, Coruña and Pasajes were mainly affected by Cu, Hg, Pb and Zn and the measured organic compounds at different concentrations. The stations in the port of Cádiz showed a more variable grade of contamination. In this study, one sample showed low levels of contamination (sample CA1), but CA2, located in the inner part of the port, showed higher concentrations of PCBs and Cd, Cu and Hg. For the other two samples from this port, CA3 and CA4, located in the inner part of the bay but not in the inner harbor, intermediate concentrations were registered. This zone has been previously well characterized and has reported low levels of contamination (DelValls et al., 1998a; Campana et al., 2005), but it seems that closer to the inner harbor, unusually higher chemical contaminations are expected in the dredged sediments maybe attributable to the shipping and urban activities. This pattern has also been identified in most of the ports studied since the stations located at the inner part of each port were between the 13 stations that exceeded any of the AL2 values. While this influence is more clear in ports such as Coruña or Bilbao, it is not that clear in others such as Cartagena or Barcelona. In these ports, the contamination registered at the stations is more heterogeneous and there is not a clear contamination gradient. This can be due to particular anthropogenic inputs or as a result from the nature of the particles.

The two samples characterized by the low proportion of fine sediment particles and the lowest organic matter content (CA1 in the port of Cádiz and H4 in the port of Huelva) reported the lowest contamination levels. Nevertheless, the consideration that dredged material contamination is likely to appear together with a high organic matter content and a high proportion of fine grain size (mainly related to urban and industrial wastes) is accomplished in the ports included in this study. The sediment organic content has been shown to be strongly linked to the proportion of fines in the sediment and fine sediments are usually considered to adsorb organic and metallic pollutants more than coarse fractions (Carpentier et al., 2002). In this sense, samples H1 and H2 reported the highest concentrations in the port of Huelva, C1 reported the highest contamination in the port of Cartagena and B4 for the port of Barcelona. Even if fine sediments are highly correlated to organic matter content, correlation analysis on our results did not showed significant associations between the chemical concentrations and these two sediment parameters (data not showed) maybe due to the high variability between the ports.

The characterization process for the dredged sediments tried to mimic as much as possible the characterization process that is usually recommended for dredged material management in Spain but due to the large number of ports, the number of sampling sites for each port have been reduced. The decision-making framework is tiered and proceeds through sequential steps (named tiers) defined as different grades and depths of information. The first tier includes the review of the available information including physical, chemical and biological data that can be reported from the zones of study. While sometimes this information is sufficient to match a dredged material as suitable for open water disposal if no effects are expected, in other cases, further assessments are required, and then the process follows to the next tier. Nevertheless, all the previous information that is reported in this first tier can give clear information (historical sources of contamination, current regimes of the zone, etc.) that can point out possible sinks for pollutants and zones of special concern, such as those in the inner harbor, or can identify zones that are not needed of further chemical characterization because the materials are sandy or coarse sediments. The next tier in the management framework includes the list of contaminants that are analyzed on the sediment fraction <63 μm and is the set of compounds here reported. Undoubtedly, some samples contained chemicals that were not quantified or for which there are no SQGs and then the potential effects cannot be predicted. In this sense, the use of the SQGs make the major assumption that chemical analytes used are indeed representative of the toxicologically significant chemical mixture in the samples regardless of which chemicals were quantified in the analyses. As pointed by Fairey et al. (2001), this is a simplistic approach because of the infinite number of chemicals in field-collected sediments. The selection of the list of priority pollutants should be site-specific and made according to the particular objectives using the information provided in the first tier, although the use of chemicals that occur most commonly will improve the applicability to a wide range of environmental conditions. In this sense, the use in this study of the list of contaminants developed by the CEDEX (1994) seems justified since it is the one recommended by the Spanish related agencies on dredged material management but this limitation should be taken into account when considering the potential toxicity of the sediments according to the chemical results. Furthermore, the presence of ammonia, hydrogen sulfide or low-dissolved oxygen in dredged materials and contaminated sediments have been reported as the most common causes of sediment toxicity (Lee and Jones-Lee, 1996) but none have been included in the recommendations for dredged material management and the SQGs used in this study.

A résumé of the classification of the samples according to the decision-making framework proposed in Spain for dredged material management is included in Table 5. As mentioned before, the bay of Cádiz has reported low grades of contamination and main sources are related to urban wastes (DelValls et al., 1998b; Lara-Martín et al., 2005). The dredged materials from the inner harbor have shown in this study potential biological adverse effects, but on the other hand, there is a station suitable for beneficial uses or open water disposal that correspond to sandy sediments. The intermediate grade of contamination of the other two samples together with the high percentage of fines and high organic content point out that further assessments are required before the best management option is selected. Other ports such as Huelva or Cartagena stand particular historical sources of metallic pollution, and thus, the dredged sediments reported extremely high concentrations of some compounds that make them not suitable for open water disposal. The rest of ports are between those that stand higher maritime traffic in Spain, although no other important sources of contamination are present. The mixture of compounds and the high concentrations reported, mainly attributed to the port activities themselves, makes the dredged sediments not suitable for open water disposal or is needed of further assessments to ensure that no adverse effect is expected. The set of limit values routinely used to manage dredged sediments in Spain does not classify materials definitely; in most of the studied ports, further assessment is needed to clearly identify the potential toxicity of some sediments, but no recommendations have been established yet describing suitable tools as those available for the chemical characterization. Only the sediments clearly not toxic and those with very high concentrations of contaminants (12% and 64% of the sediment samples, respectively) are effectively classified, remaining a wide zone of uncertain effects.

When co-occurrence-based SQGs are used the number of sediments that do not exceed the lower limit values are quite similar, although some slight differences are found when using the ERL and the V1: if sample CA1 is not included in this category when using the SQGs developed by Riba et al. (2004) due to the lower V1 for the metal Cd, sample BI3 exceeds the ERL for the PAHs, for which AL and V1 have not been developed. Nevertheless, special attention should be paid on sample CA1 since the V1 and V2 values were developed using data from studies on Cadiz and Huelva. This same tendency is found when considering the higher limit values: despite the fact that a total of 64% of sediments are not suitable for open water disposal according to the Spanish Action Levels for dredged materials and this percentage increases to 72% when using the ERMs and to 64% when the V2 values are used, the ports of Cadiz and Huelva report higher number of SQGs exceeded possibly due to the regional specificity of these values.

Both the empirically derived SQGs do not elucidate the potential adverse biological effects of these stations and the number of materials matched in this category is still high (Tables 4 and 6). The m-ERM-q, used to obtain some information about the number of exceeded values and the extent to which the SQGs are exceeded, has been related to four different categories with the related biological adverse effects expected instead of the three included in the Spanish recommendations for dredged material management. Only the two samples H4 and CA1 are classified as "Low-Priority

Table 5
Classification of the different stations and its management requirements according to the Spanish recommendations for dredged material (CEDEX, 1994)

Port	Sample	Potential effects	Management requirements
Cádiz	CA1	Physical	Materials can be freely dumped, normal discharge authorization
	CA2	Biological adverse effects	Isolation and/or bioremediation
	CA3, CA4	Further assessment	Special authorization including biological studies
Huelva	H1, H2, H3	Biological adverse effects	Isolation and/or bioremediation
	H4	Physical	Materials can be freely dumped, normal discharge authorization
Barcelona	B1, B3	Further assessment	Special authorization including biological studies
	B2, B4	Biological adverse effects	Isolation and/or bioremediation
Cartagena	C1, C2, C3, C4	Biological adverse effects	Isolation and/or bioremediation
Bilbao	BI1, BI2	Biological adverse effects	Isolation and/or bioremediation
	BI3	Physical	Materials can be freely dumped, normal discharge authorization
Coruña	CO1	Biological adverse effects	Isolation and/or bioremediation
	CO2, CO3	Further assessment	Special authorization including biological studies
Pasajes	PA1, PA2, PA3	Biological adverse effects	Isolation and/or bioremediation

Table 6
Classification of probabilities of toxicity for each sample according to the calculated mean ERM quotients

Mean ERM quotient	Probability of toxicity (%)	Priority area	Samples
>1.5	76	Highest	H1, H2 B4 C1, C2, C3, C4 CO1
0.51–1.50	49	Medium–high	CA2 H3 B2 BI1, BI2 PA1, PA2, PA3
0.11–0.5	21	Medium–low	CA3, CA4 B1, B3 BI3 CO2, CO3
<0.1	9	Lowest	CA1 H4

Sites”, and BI3 would now be a “Medium–Low-Priority Site.” Eight sites that represent 36% of the samples had an ERM quotient higher than 1.5, which classifies them as “High-Priority Sites”: the four sites located in the port of Cartagena, two sites in the port of Huelva, and one in Coruña and Barcelona. The rest of the samples are classified as “Medium–High-Priority Sites” or “Medium–Low-Priority Sites.” The use of the limit values developed for the Atlantic coast of Spain makes some differences when the mean quotient is calculated using the V2. Mean quotients are lower when using the V2 in the ports of Pasajes, Coruña Bilbao or Barcelona, but this can be explained by the absence of limit values for PAHs that are of special concern in these ports. Moreover, the spatial scale at what the different sets of limit values can be used is uncertain and one of the outstanding questions related to the used of SQGs. The cost in time and materials needed to satisfy the minimum data requirements for determining no effects levels for sediment biota is high, and the cost-effectiveness for the different jurisdictions to develop separate SQGs has not been decided. Nevertheless, the confidence of transferring the limit concentrations developed in different jurisdictions is unknown.

Because of the uncertainties related to the SQGs, these are typically conservative; it means over-protective, and only for those samples that have negligible ecological risk, highest reliance and reliability are placed. The number of samples from this study that have been matched in this category is little; thus, little number of false negatives is expected as well (defined as toxic materials that have been incorrectly classified) but we have to consider that according to the Spanish recommendations for dredged material management, two of these three sediments would not need chemical characterization after a first assessment of some conventional parameters of the sediment such as the grain size distribution. One of the approaches to clarify the interpretation of the chemical data in a regulatory context is the use of background concentrations that can inform about contaminant concentrations prior to anthropogenic inputs, but as for the SQGs, the spatial scale at what these values can be used is uncertain. This approach, together with the assessment of the potential risk based on contaminant concentrations at reference areas, used as benchmarks against which to compare the exposed sites have been recommended for dredged material management. These areas, intended to represent the optimal range of minimally impaired conditions that can be achieved at sites anticipated to be ecologically similar, are not easily found, and moreover, they must be acceptable by local stakeholders, reasonable and appropriately represent reference conditions (Krantzberg et al., 2000). Some of the outstanding questions on the development and use of SQGs for sediment and dredged materials have been pointed out in the last years (Crane, 2003; DelValls et al., 2004) with the aim to improve the different decision-making frameworks and to truly evaluate the use of these limit values. Some of the questions, such as the possible weakness of the approach for a mandatory standard or the uncertainties when using the SQGs as mandatory and legally enforceable pass/fail limits, are solved using the SQGs as an early, conservative screening tool in a tiered risk assessment framework. Other questions have been addressed by the related national agencies and the research needed is been carried out, but there are still no SQGs or background levels developed for the regional characteristics that can be applied with confidence.

Although the classification of the dredged materials has been made using different approaches for the development of the used SQGs, the results do not differ that much: commercial ports are zones of concern themselves due to different anthropogenic inputs, and moreover, potential biological effects are likely to occur due to the high concentrations of a mixture of compounds that are expected. Even if the percentages of sediments can vary depending on the SQGs used, the lack of local sediment effect data makes not possible to verify the validity of using the different sets of SQGs. These guidelines are useful as a screening tool to prioritize contaminants or even areas of concern using the medium quotients. Nevertheless, since the list of contaminants in the national recommendations does not include all the chemicals of concern and with possible adverse effects, and moreover, because only in case of extreme contamination the chemical data alone compared to the SQGs are able to predict toxicity, it seems highly recommendable to include toxicity bioassays in the next tiers when managing dredged sediments in Spain as it has been done in other countries (den Besten et al., 2003).

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