Chemistry and Ecology

Integrated physical–chemical and ecotoxicological approach in the management of dredging sediments from Palermo Harbour

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With regard to the impact of dredging activities in harbour environments on aquatic ecosystems, the aim of this study was to integrate results obtained from a research project carried out in Palermo Harbour in 1999. In particular, an ecotoxicological approach, together with physical–chemical analysis, was introduced to assess the quality of the dredging sediment. This study provides important data and information for the realisation of a handbook on handling of marine sediments in Italy.

Keywords: marine sediments; ecotoxicology; dredging; harbour; management

1.   Introduction

Harbour management often requires dredging operations in order to maintain safe internal navigation. However, these activities can have a serious environmental impact on aquatic ecosystems, due to frequent sediment contamination [1]. At present, both industrial and domestic effluents directly or indirectly reach marine sediments, which certainly form the most important part of aquatic ecosystems, being the primary site of biogeochemical cycles and the base of food webs [2].

High concentrations of chemicals in dredged material can be toxic to biota in the areas in which the material is deposited [3–5]. Therefore, adequate sediment quality assessment is crucial to establish the best environmental management options for dredged material [6].

The assessment of chemicals in sediments has developed over the past 30 years [7]; for monitoring purposes, it is usually carried out by measuring the concentrations of selected contaminants and comparison of the obtained values with numerical sediment quality guidelines [8]. However, chemical characterisation alone does not provide specific biological information about the potential hazard to organisms [9] and is not sufficient to predict environmental risk [3].

A more accurate assessment of sediment contamination and its relationship to environmental risk should be based on a multidisciplinary approach, which integrates different lines-of-evidence (LOE), such as physical and chemical analysis and bioassays to assess toxic effects [9,10].

Ecotoxicity tests, in addition to chemical analysis, have been recommended at the international level for the assessment of dredged material quality [11–14], and many studies have proved the success of bioassay batteries with different target organisms and exposure routes [15–19].

The ISPRA (formerly APAT and ICRAM) Handbook [20], which defines sampling and analytical methods for dredging sediments and the criteria for their qualitative classification, represents the only available Italian tool for the quality and management assessment of dredged material.

In this regard, the study of sediment quality at Palermo Harbour, carried out by ISPRA in 1999 after a specific request by the Palermo Port Authority, is fundamental. At the time, a relative lack of knowledge about sediment quality assessment and the sources of contamination at Palermo Harbour, together with the large area and amount of sedimentary material to be removed, made environmental investigations necessary. The main purpose of the investigations was to provide qualitative and quantitative information for sediment management that was more accurate than that required by the legislation in force at the time.

The aim of this study was to discuss the results obtained from this project using an integrated approach to assess sediment quality, providing knowledge to support the realisation of the ISPRA Handbook [20].

2. Materials and methods

2.1. *Sampling activities*

In order to restore internal navigation for tourism and commercial purposes in Palermo Harbour, dredging was necessary. In particular, the bottom had to be dredged from an average depth of -11 m to -15 m.

According to a Ministerial Decree of 24 January 1996, 101 sampling stations were chosen in harbour areas where 8 of a total of 18 industrial and domestic official sewage outlets were located (Figure 1).

A total of 179 sediment samples were collected from April to May 1999 by means of a vibro-corer and a Van Veen grab (for superficial sediment, ∼20 cm). According to the above-mentioned Ministerial Decree, two sediment sections of 20 cm were sampled from cores up to 1.5-m long (at the upper and lower levels), three sections of 20 cm were collected from cores up to 2-m long (at the upper, intermediate and lower levels) and further sections representative of lower layers were collected from cores >2 m, in addition to the three above. Each collected core layer was labelled with the letters 'a', 'b', 'c', 'd' and 'e' in the order of depth.

In certain cases, when the retrieved sediment was scarce, composite samples were obtained by pooling and mixing the corresponding layers of cores.

2.2. *Physical–chemical analyses*

Granulometric analysis was used to determinate the main fractions (gravel, sand and silt). Each sample was treated (24/48 h, room temperature) with hydrogen peroxide solution (30%) and distilled water and then washed. Samples were wet-separated into two fractions using a sieve with a <63 μm mesh. The coarse and fine fractions were oven-dried at 40 °C and weighed. The coarse fraction was sieved by mechanical movement on ASTM sieves with meshes of 2 and 1 mm, and the sediment from each sieve was weighed. Finally, the proportion among the three fractions (gravel, sand, silt) was calculated.

Samples for chemical determinations were stored at −20 °C until analyses.

The concentrations of some trace metals (As, Cd, Cr, Cu, Hg, Pb, Zn), the 16 US-EPA priority polycyclic aromatic hydrocarbon (PAH) congeners [21], selected polychlorinated biphenyl
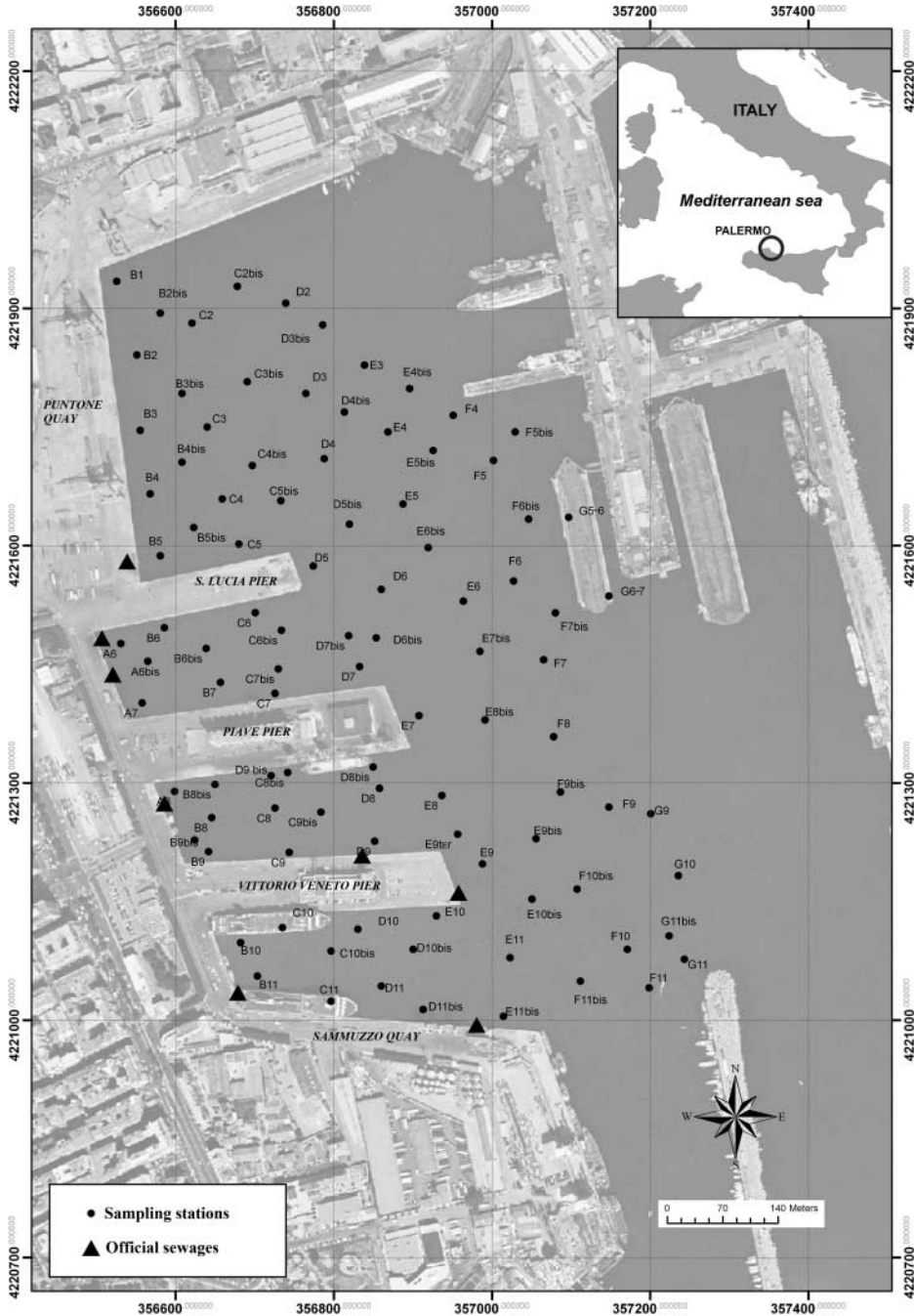
Figure 1. Study area and sampling stations.

(PCB) congeners (28, 52, 101, 118, 138, 153, 180, 209) and organochlorine pesticides (hex-achlorobenzene (HCB); hexachlorocyclohexane (HCH) isomers: α-HCH; β-HCH and γ-HCH; heptachlor epoxide; chlordane; dichlorodiphenyltrichloroethane (DDT) and their metabolites) were measured.

Trace metals were determined, after total acid microwave-assisted digestion, using atomic absorption spectrometry (AAS) techniques [22], whereas PCBs, organochlorine pesticides and PAHs were determined by chromatographic methods [23,24].

The quality assurance and quality control (QA/QC) procedures included the verification of accuracy using certified reference materials by the National Research Council of Canada. All metals showed $>90\%$ recovery, except chromium (82%). The quantification limits were: $0.03 \, \text{mg} \cdot \text{kg}^{-1}$ for trace metals, $0.001 \, \text{mg} \cdot \text{kg}^{-1}$ for PAHs and $0.01 \, \mu\text{g} \cdot \text{kg}^{-1}$ for organochlorine pesticides.

All reagents used were analytically graded.

2.3. *Toxicity testing*

Two types of ecotoxicological tests were carried out on some superficial sediment samples: a mortality test with *Corophium orientale* and a bioluminescence test using the marine bacterium *Vibrio fischeri* (Microtox®). The first bioassay, carried out following the OSPAR protocol [25], assesses mortality in sub-adults after 28 days of exposure to whole sediment in comparison with control (Δm). The results were classified on the basis of toxicity scales given in Table 1 [20].

Microtox® is a bioassay of acute toxicity based on natural bioluminescence modulation in the presence of pollutants. Measurement of bioluminescence inhibition or, sometimes, biostimulation (hormesis) allows us to assess sediment toxicity. Microtox® was carried out using standardised protocols and was applied to centrifuged sediment (large-sample procedure of solid-phase test, after 30 min exposure) and elutriate (comparison test, two readings after 5 and 15 min exposure, respectively) [26]. The solid-phase test gives information about contaminants bound to the sediment particles, with regard to their chemical characteristics (hydrophyilicity, adsorption and complexing degree with organic matter), whereas elutriate gives information about hydrosoluble contaminants that may be reintroduced by mechanical agitation [27]; this environmental matrix is the most representative in the case of dredging [28].

The elutriate was obtained by agitation of a whole sediment aliquot [dry sediment diluted in artificial sea water (ASW), 1:4 w/v) for 1 h at room temperature; the sample was centrifuged to 3500 rpm for 20 min at 15 °C and the obtained supernatant was tested, after filtration (0.45 μm) to avoid spectrophotometric interference due to suspended particles.

The results of Microtox® on the solid-phase were expressed as the Sediment Toxicity Index (STI), which represents the real acute toxicity of the analysed sample considering granulometric characteristics [29], and classified according to Table 2 [27]. Elutriate testing was expressed as percentage variation of bioluminescence (ΔB) with respect to the control (ASW) (Table 2).

Population sensitivities were checked before testing using AAS standard solutions of Cu^{2+} and Cd^{2+} as reference toxicants (positive controls) for *V. fischeri* and *C. orientale*, respectively. The obtained half maximal effective concentration (EC_{50}) values fell within the ranges of 0.42–$1.16 \, \text{mg} \cdot \text{L}^{-1}$ and 1.21–$7.23 \, \text{mg} \cdot \text{L}^{-1}$ reported by Onorati et al. [30] and Lera et al. [31], for *V. fischeri* and *C. orientale*, respectively.

Table 1. Toxicity scale for *Corophium orientale* bioassay [20]. Toxicity is expressed as the percentage difference (Δm) in mortality between samples to be tested and the control, according to the significance level of that difference.

Δm	Toxicity
Δm < 15 ($P = 0.05$)	Absent
Δm $= 15$ ($P < 0.05$)	Low
$15 < \Delta$m $= 30$ ($P < 0.05$)	Medium
$30 < \Delta$m < 60 ($P < 0.05$)	High
Δm < 60 ($P < 0.05$)	Very high

Table 2. Toxicity scale for Microtox® on elutriate and on solid phase: the former is expressed as percentage difference between observed bioluminescence in the sample and the control (ΔB); the latter is expressed as Sediment Toxicity Index (STI) [29].

Elutriate	Solid phase	
ΔB	STI	Toxicity
$\Delta B < -5$		Hormesis
$-5 < \Delta B < 5$	$0 < STI < 1.00$	Absent
$5 < \Delta B < 20$	$1.01 < STI < 3.00$	Low
$20 < \Delta B < 40$	$3.01 < STI < 6.00$	Medium
$40 < \Delta B < 80$	$6.01 < STI < 12.00$	High
$\Delta B > 80$	$STI > 12.00$	Very high

2.4. *Statistical analysis*

In order to evaluate the multivariate relationship between chemicals and ecotoxicological responses in the study area, multifactorial analysis (focused principal component analysis) was performed [32]. This technique is similar to principal component analysis (PCA), which conveys the structure of a correlation matrix into a low-dimensional diagram but, unlike PCA, it makes it possible to represent accurately the correlations between a given dependent variable and the other variables. The relationships between non-dependent variables are interpreted like in a PCA: correlated variables are closed or diametrically opposite (for negative correlations) with respect the dependent variable, whereas independent variables form a right angle with the origin. The focus on the dependent variable leads to a formal partialisation of the correlations between the non-dependent variables and the dependent variable. In this case, the dependent variables are the ecotoxicological data.

3. Results and discussion

The physical and chemical data are summarised in Table 3 and the ecotoxicological results are reported in Tables 4 and 5, which referr to *V. fischeri* (elutriate and solid-phase) and *C. orientale*, respectively.

Grain size data showed relatively homogeneity in both superficial sediments and deeper layers. All samples are mainly sandy (62–92% sand), except for some deposits of silt–clay material close to official sewage outlets. Geologically, Palermo Harbour is part of Palermo Basin; it is bounded by Meso-Cenozoic carbonate promontories (like Monte Pellegrino) and is filled by Quaternary marine and continental deposits, mostly calcarenitic formations; this may explain the observed physical homogeneity [33].

The characterised harbour sediments showed high level of organic contaminants, with a negative vertical gradient regarding all investigated compounds. In particular, the areas close to piers and quays had the highest contamination, mostly located in the first 2 m of sediments. The observed decrease from superficial to deeper layers is probably due to the sedimentation rate and the higher vertical diffusion of chemicals in the calcarenitic sediments.

The concentrations of analysed trace metals were generally lower than mean levels in superficial sediments of Italian coasts detected before 1999 [34–40].

The sediment hazard was assessed using the ISPRA Handbook, following the criterion based on limit chemical level (LCL) [20]; this reference level was derived from the probable effect level (PEL) [41] adapted for Italian coastal sediments. PEL represents the lowest concentration of a substance beyond which there is a high probability of adverse effects to aquatic communities [41].

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Table 3.   Basic statistics of the investigated physical–chemical parameters.

Parameter		Unit	Layer "a"	Layer "b"	Layer "c"	Layer "d"	Layer "e"
Gravel	# samples	Tot. 179	78	55	30	14	2
	Min.		0.00	0.00	0.00	0.00	0.00
	Max		50.73	56.34	51.11	44.55	0.00
	Average	%	8.12	11.53	9.69	13.57	0.00
	Std. dev.		13.48	16.10	15.24	18.90	0.00
	Medion		0.02	0.30	0.00	0.00	0.00
Sand	# samples	Tot. 179	78	55	30	14	2
	Min.		21.46	18.39	12.25	30.90	89.54
	Max		98.86	98.93	99.10	99.08	96.35
	Average	%	65.25	62.82	62.43	71.66	92.95
	Std. dev.		20.77	25.24	27.17	24.89	4.82
	Median		66.24	59.84	55.81	86 .52	92.95
Silt	# samples	Tot. 179	78	55	30	14	2
	Min.		4.14	1.07	0.90	0.92	3.65
	Max		76.18	80.24	87.75	34.04	10.46
	Average	%	26.34	25.52	28.47	14.77	7.06
	Std. dev.		18.25	61.61	24.00	8.51	4.82
	Median		21.54	18.24	17.51	13.48	7.06
PAHs	# samples	Tot. 173	77	52	28	14	2
	Min.		0.001	0.001	0.001	0.001	0.001
	Max		0.348	0.359	0.204	0.046	0.001
	Average	$mg\,kg^{-1}$	0.040	0.033	0.010	0.001	0.001
	Std. dev.		0.068	0.068	0.040	0.012	0.001
	Median		0.012	0.001	0.001	0.001	0.001
PCBs	# samples	Tot. 175	78	53	28	14	2
	Min.		1.04	0.01	0.01	0.26	5.90
	Max		488.72	377.61	181.09	159.00	47.70
	Average	$\mu g\,kg^{-1}$	115.60	48.47	30.78	30.53	26.80
	Std. dev.		95.47	81.57	51.43	45.43	29.56
	Median		91.20	14.90	4.l0	10.20	26.80
HCB	# samples	Tot. 147	63	45	27	10	2
	Min.		0.01	0.01	0.01	0.01	0.05
	Max		8.51	13.16	1.40	0.90	0.5
	Average	$\mu g\,kg^{-1}$	0.79	0.63	0.24	0.22	0.28
	Std. dev.		1.33	2.02	0.37	0.33	0.32
	Median		0.46	0.03	0.05	0.05	0.28
α-HCH	# samples	Tot. 146	62	45	27	10	2
	Min.		0.01	0.01	0.01	0.01	0.20
	Max		55.60	47.10	20.40	12.90	0.30
	Average	$\mu g\,kg^{-1}$	10 10	11.16	3.92	4.06	0.25
	Std. dev.		14.67	15.62	5.70	5.52	0.07
	Median		1.78	2.18	0.41	0.40	0.25
β-HCH	# samples	Tot. 147	63	45	27	10	2
	Min.		0.01	0.01	0.01	0.01	9.20
	Max		744.10	184.90	307.50	250.10	80.7
	Average	$\mu g\,kg^{-1}$	89.86	29.43	43.72	64.65	44.95
	Std. dev.		163.78	44.80	88.13	80.92	50.56
	Median		1.09	3.32	0.01	38.60	44.95
γ-HCH	# samples	Tot. 87	42	26	16	3	0
	Min.		0.01	0.01	0.01	<0.01	–
	Max		61.01	7.84	0.72	<0.01	–
	Average	$\mu g\,kg^{-1}$	2.56	0.91	0.08	<0.01	–
	Std. dev.		9.32	1.98	0.19	<0.01	–
	Median		0.74	0.01	0.01	<0.01	
Hep. epox	# samples	Tot. 86	41	26	16	3	0
	Min.		0.04	0.01	0.01	0.01	–
	Max	$\mu g\,kg^{-1}$	16.12	42.65	0.37	0.05	–

(*Continued*)

Table 3. Continued

Parameter		Unit	Layer "a"	Layer "b"	Layer "c"	Layer "d"	Layer "e"
	Average		4.33	3.90	0.09	0.02	–
	Std. dev.		3.96	9.47	0.09	0.02	–
	Median		4.05	0.15	0.07	0.01	–
Chlordane	# samples	Tot. 88	43	26	16	3	0
	Min.		0.16	0.01	0.01	0.01	–
	Max		175.84	53.4	0.68	0.08	–
	Average	$\mu g\,kg^{-1}$	15.63	7.99	0.19	0.03	–
	Std. dev.		27.97	16.06	0.20	0.04	–
	Median		10.15	0.44	0.15	0.01	–
DDT	# samples	Tot. 88	43	26	16	3	0
	Min.		0.01	0.01	0.01	0.01	–
	Max		366.15	332.95	6.91	0.47	–
	Average	$\mu g\,kg^{-1}$	62.77	47.33	1.44	0.16	–
	Std. dev.		80.14	94.10	2.05	0.26	–
	Median		39.06	4.60	0.44	0.01	–
DDE	# samples	Tot. 88	43	26	16	3	0
	Min.		0.11	0.01	0.01	0.01	–
	Max		172.56	208.82	2.00	0.08	–
	Average	$\mu g\,kg^{-1}$	21.67	22.48	0.46	0.05	–
	Std. dev.		31.03	55.24	0.60	0.04	–
	Median		13.72	0.75	0.30	0.06	–
DDD	# samples	Tot. 88	43	26	16	3	0
	Min.		0.13	0.01	0.10	0.08	–
	Max		705.33	236.82	11.85	0.81	–
	Average	$\mu g\,kg^{-1}$	74.23	31.22	2.34	0.41	–
	Std. dev.		112.61	59.96	3.67	0.37	–
	Median		55.07	3.44	0.91	0.36	–
Al	# samples	Tot. 178	77	55	30	14	2
	Min.		2.10	1.60	1.10	1.00	1.40
	Max		5.60	31.00	4.00	1.90	1.50
	Average	%	3.17	2.96	2.06	1.43	1.45
	Std. dev.		0.58	3.89	0.69	0.30	0.07
	Median		3.10	2.50	1.90	1.40	1.45
As	# samples	Tot. 178	77	55	30	14	2
	Min.		7.80	3.90	3.10	3.20	3.70
	Max		21.50	19.20	13.10	10.60	4.20
	Average	$mg\,kg^{-1}$	12.64	9.06	6.75	6.46	3.95
	Std. dev.		3.33	2.73	2.63	2.03	0.35
	Median		11.80	8.90	6.50	6.60	3.95
Cd	# samples	Tot. 176	77	55	30	14	0
	Min.		0.04	0.07	0.05	0.06	–
	Max		0.44	0.31	0.20	0.15	–
	Average	$mg\,kg^{-1}$	0.21	0.16	0.12	0.09	–
	Std. dev.		0.08	0.05	0.04	0.03	–
	Median		0.21	0.15	0.11	0.09	
Cr	# samples	Tot. 178	77	55	30	14	2
	Min.		27.0	21.5	25.2	20.8	28.0
	Max		112.0	89.3	68.3	40.1	30.0
	Average	$mg\,kg^{-1}$	64.3	53.0	44.4	31.7	29.0
	Std. dev.		17.8	16.7	11.0	6.2	1.41
	Median		61.5	51.5	41.8	30	29.0
Cu	# samples	Tot. 178	77	55	30	14	2
	Min.		1.3	14.8	9.5	7.5	11.5
	Max		65.7	55.1	48.0	28.5	12.3
	Average	$mg\,kg^{-1}$	34.8	26.8	18.5	14.6	11.9
	Std. dev.		11.0	9.1	8.5	6.4	0.6
	Median		33.3	25.2	16.1	11.7	11.9

(*Continued*)

Table 3.   Continued

Parameter		Unit	Layer "a"	Layer "b"	Layer "c"	Layer "d"	Layer "e"
Hg	# samples	Tot. 174	77	55	28	13	0
	Min.		0.15	0.05	0.05	0.03	–
	Max		0.52	0.38	0.16	0.09	–
	Average	mg kg^{-1}	0.26	0.15	0.10	0.06	–
	Std. dev.		0.08	0.06	0.02	0.02	–
	Median		0.25	0.15	0.10	0.06	–
Ni	# samples	Tot. 178	77	55	30	14	2
	Min.		18.8	12.6	10.9	10.7	10.7
	Max		39.1	30.6	22.5	21.2	18.6
	Average	mg kg^{-1}	28.9	21.4	17.2	15.1	14.7
	Std. dev.		4.5	4.0	3.3	3.0	5.6
	Median		29.6	20.5	16.8	15.0	14.7
Pb	# samples	Tot. 178	77	55	30	14	2
	Min.		21.5	15.7	10.1	10.9	10.9
	Max		81.2	75.6	48.5	40.9	31.5
	Average	mg kg^{-1}	39.1	31.3	22.1	20.8	21.2
	Std. dev.		15.2	14.7	11.1	5.8	14.6
	Median		33.2	25.4	18.5	18.2	21.2
Zn	# samples	Tot. 178	77	55	30	14	2
	Min.		38.9	30.2	21.2	21.1	10.2
	Max		151.2	131.5	83.2	49.2	29.1
	Average	mg kg^{-1}	71.42	58.6	45.5	38.4	19.6
	Std. dev.		15.1	18.9	13.4	8.0	13.4
	Median		69.1	53.8	41.3	40.1	19.6

Table 4.   Main statistics of the Microtox® bioassay results applied to elutriate (30 sediment samples) and solid-phase (21 sediment samples).

	Elutriate				Solid phase		
Exposure	5 min ΔB (%)	15 min ΔB (%)	Average ΔB(%)	Significance level (%)	Measured toxicity (TU)	R^2 (%)	STI
Min	−8.9	−8.9	−8.9	60.0	108	74.14	0.68
Max	28.8	33.8	31.3	99.9	105,532	100	92.19
Average	7.5	9.2	7.8	91.3	1950	94.69	15.82
SD	10.9	13.9	12.3	16.4	2893	7.94	23.75
Median	1.7	1.5	1.3	99.9	902	98.04	6.71

Note: ΔB, percentage variation of bioluminescence; STI, Sediment Toxicity Index [29].

Table 5.   Main statistics of *Corophium orientale* bioassay results applied to whole sediment (30 sediment samples).

	Δm (%)
Min	2.0
Max	32.0
Average	15.8
SD	8.7
Median	15.0

Note: Δm, difference in mortality between sample and control.

Table 6. Chemical hazard quotients (HQ) calculated as the ratio of mean concentration for each layer ($\pm$SD) and the corresponding LCL.

| Parameter	LCL	Units	HQ $\pm$ SD				
			Layer 'a'	Layer 'b'	Layer 'c'	Layer 'd'	Layer 'e'
As	32	mg·kg^{-1}	0.40 ± 0.10	0.60 ± 0.09	0.21 ± 0.08	0.15 ± 0.06	0.12 ± 0.01
Cd	0.8	mg·kg^{-1}	0.26 ± 0.10	0.20 ± 0.06	0.15 ± 0.05	0.11 ± 0.04	–
Cr	360	mg·kg^{-1}	0.18 ± 0.05	0.15 ± 0.05	0.12 ± 0.03	0.09 ± 0.02	0.08 ± 0.01
Cu	52	mg·kg^{-1}	0.67 ± 0.21	0.52 ± 0.18	0.36 ± 0.16	0.28 ± 0.12	0.23 ± 0.01
Hg	0.8	mg·kg^{-1}	0.33 ± 0.10	0.19 ± 0.08	0.13 ± 0.03	0.08 ± 0.03	–
Ni	75	mg·kg^{-1}	0.39 ± 0.06	0.29 ± 0.05	0.23 ± 0.04	0.20 ± 0.04	0.20 ± 0.07
Pb	70	mg·kg^{-1}	0.56 ± 0.22	0.45 ± 0.21	0.32 ± 0.16	0.30 ± 0.08	0.30 ± 0.21
Zn	170	mg·kg^{-1}	0.42 ± 0.09	0.34 ± 0.11	0.27 ± 0.08	0.23 ± 0.05	0.12 ± 0.08
PCBs	189	µg·kg^{-1}	0.61 ± 0.52	0.26 ± 0.43	0.16 ± 0.27	0.16 ± 0.24	0.14 ± 0.16
DDDs	7.8	µg·kg^{-1}	**9.52 ± 14.44**	**4.00 ± 7.69**	0.30 ± 0.47	0.05 ± 0.05	–
DDEs	3.7	µg·kg^{-1}	**5.86 ± 8.39**	**6.08 ± 14.93**	0.12 ± 0.16	0.01 ± 0.01	–
DDTs	4.8	µg·kg^{-1}	**13.08 ± 16.70**	**9.86 ± 19.60**	0.3 ± 0.43	0.03 ± 0.05	–
Chlordane	4.8	µg·kg^{-1}	**3.26 ± 5.83**	**1.66 ± 3.35**	0.04 ± 0.04	0.01 ± 0.01	–
HCHs	1.0	µg·kg^{-1}	**101.5 ± 174.7**	**41.50 ± 62.40**	**47.72 ± 94.01**	**68.72 ± 86.47**	**45.2 ± 90.4**
Hept epox	2.7	µg·kg^{-1}	**1.60 ± 1.47**	**1.44 ± 3.51**	0.03 ± 0.03	0.01 ± 0.01	
PAHs	4000	µg·kg^{-1}	0.04 ± 0.07	0.03 ± 0.07	0.01 ± 0.04	0.01 ± 0.01	0.01 ± 0.01

Note: HQs > 1 are marked in bold.
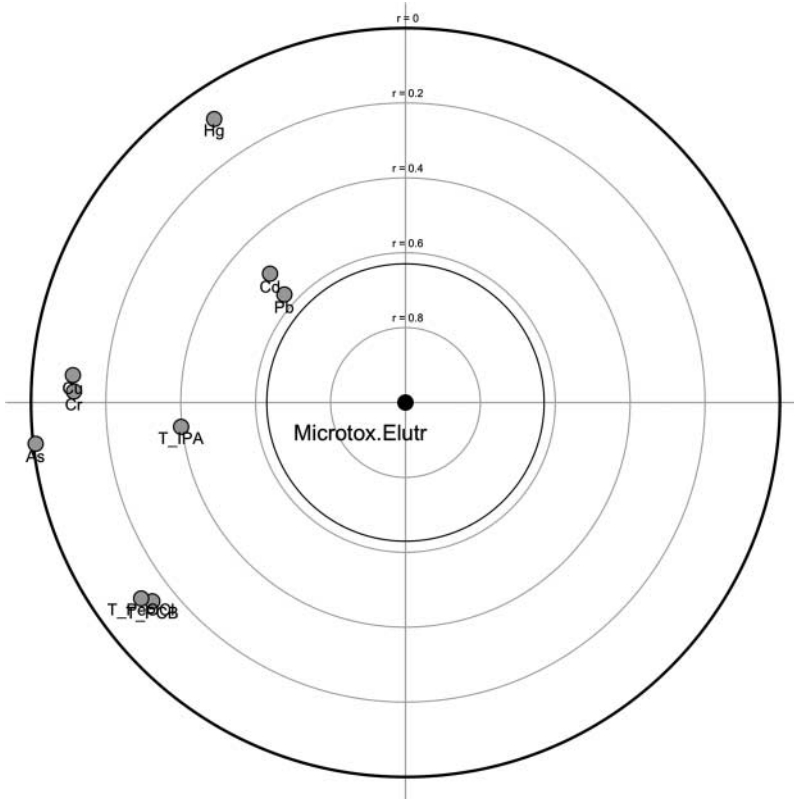
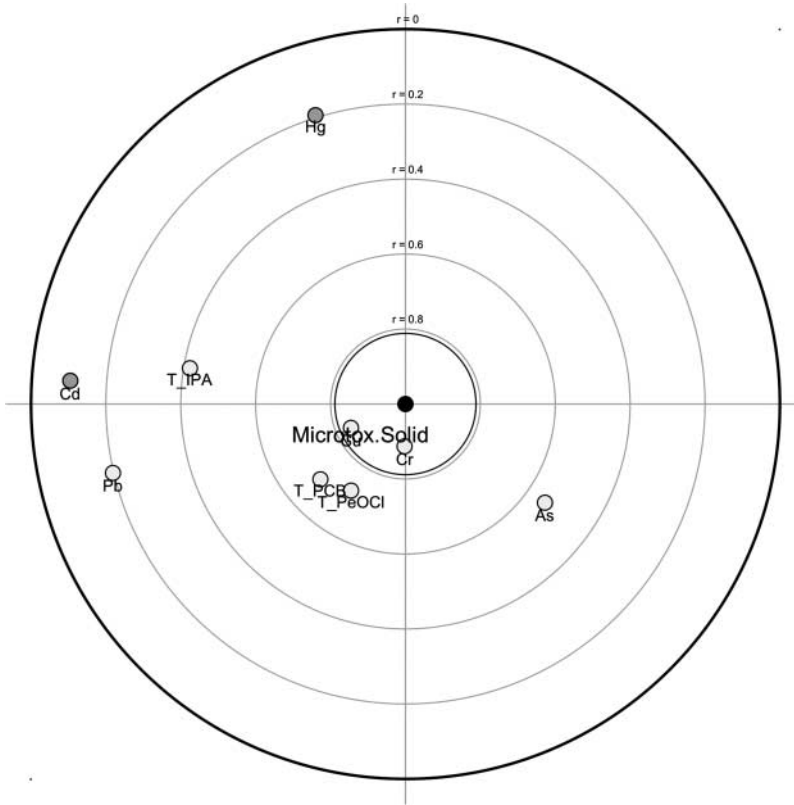Figure 2. Focused PCA between Microtox® on elutriate and measured chemicals.

Figure 3.   Focused PCA between Microtox® on solid phase and measured chemicals.

In Table 6 hazard quotients calculated in comparison with LCL [20] are summarised for those substances for which a reference value is available.

The decreasing trend with depth was confirmed for all parameters. However, high sediment hazard is posed mainly by organochlorine pesticides such as DDT (and its metabolites), chlordane and heptachlor epoxide for layers 'a' and 'b' (up to the first 2 m of sediment) and HCH for all the analysed layers.

Regarding superficial sediments, this high chemical hazard is in good agreement with eco-toxicological responses. In particular, bioassays applied to the solid-phase showed general high toxicity, probably due to a mixture of hydrophobic bioavailable compounds.

The focused PCA plots are showed in Figures 2–4, using Microtox® on elutriate, Microtox® on solid-phase and *C. orientale* on whole sediment as dependent variables. The bold inner circle in each plot corresponds to the level of significance ($P < 0.05$). Grey variables in the plots have a tendency to be positively correlated with the dependent variable, whereas white variables have a tendency to be negatively correlated. In the plot with Microtox® on elutriate (Figure 2), none of the independent variables fall inside the significance circle, so no direct correlation between ecotoxicological responses and single contaminants was found. Cr and Cu are negatively correlated with Microtox® on the solid-phase (Figure 3), as well as Cd in the plot with *C. orientale* (Figure 4). Nevertheless, this latter result might be a statistical artefact without any environmental meaning, because in general the toxicity could not increase due to a decrease in the concentration of trace metals.
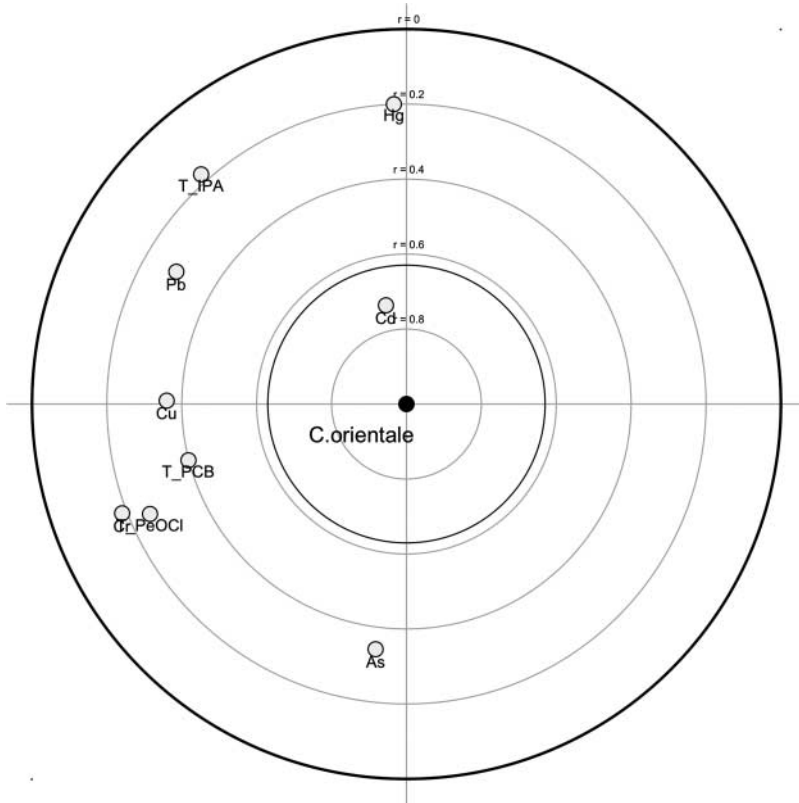
Figure 4.   Focused PCA between bioassay with *Corophium orientale* and measured chemicals.

The results show that none of the considered substances alone was responsible for the measured toxic responses. However, all chemicals (mostly organic compounds) may act simultaneously and in synergy causing the observed adverse biological effects.

4.   Conclusions

The use of two LOEs (physical–chemical and ecotoxicological approaches) allowed us to assess sediment quality in Palermo Harbour.

Hazard quotients calculated in comparison with LCL and ecotoxicity tests revealed contamination located: (1) within S. Lucia and Piave piers and Sammuzzo quay for a sediment layer between −0.5 m and −2.0 m and (2) between S. Lucia pier and Puntone quay for a sediment layer of −0.5 m.

The sediment hazard seemed to be mainly due to a mixture of organic compounds such as DDTs and HCHs, which are probably present in a bioavailable form, and may be responsible for the measured toxicity in solid-phase bioassays.

In summary, through the integration of these criteria, different management options were proposed: the above-mentioned hazardous sediments may be dredged and disposed in of specific confined disposal facilities, whereas the deeper sandy sediments may be used for beach nourishment or dumped at sites authorised by Ministry of Environment and located >3 nautical miles from the coastline. In these two latter cases, a specific environmental monitoring plan, according to Ministerial Decree January 24, 1996, should be carried out.

These issues have provided insights into the criteria for sediment quality evaluation and classification with the individuation of proper environmentally sustainable management options, further developed in the *Manual for the Handling of Marine Sediments* [20].

Acknowledgements

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