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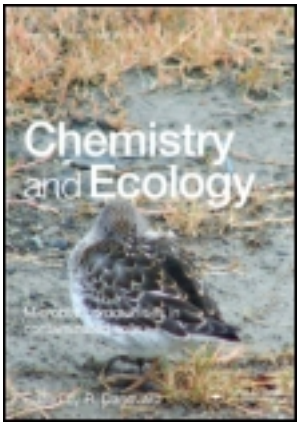

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Sequential extraction analysis provides decision-making tools for the use of contaminated sediments

Elisabetta Petrucci [a], Daniele Montanaro [a] & Carlo Merli [a]
[a] Department of Chemical Engineering Materials & Environment, Sapienza University of Rome, Rome, Italy

Available online: 18 Feb 2011

To cite this article: Elisabetta Petrucci, Daniele Montanaro & Carlo Merli (2011): Sequential extraction analysis provides decision-making tools for the use of contaminated sediments, Chemistry and Ecology, 27:S1, 107-118

To link to this article: http://dx.doi.org/10.1080/02757540.2010.536155

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Chemistry and Ecology
Vol. 27, Supplement, February 2011, 107–118

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Sequential extraction analysis provides decision-making tools for the use of contaminated sediments

Elisabetta Petrucci*, Daniele Montanaro and Carlo Merli

Department of Chemical Engineering Materials & Environment, Sapienza University of Rome, Rome, Italy

(*Received 12 January 2010; final version received 27 October 2010*)

To construct a new tourist harbour in Marina di Ragusa (Sicily), the dredging of 300,000 m^3 of marine sediment is required. To evaluate potential disposal options, a detailed physico-chemical characterisation of this material is needed. A very cost-effective solution is represented by the re-use of the dredged material for beach nourishment. To this aim, compliance with environmental standards and a strong homogeneity between the receiving beach and the source sediments must be proved. Analytical determinations for the main parameters show an arsenic content exceeding the Italian quality standard (12 $mg \cdot kg^{-1}$). In order to evaluate arsenic mobility and availability, and therefore the actual release into the environment, a three-step sequential extraction procedure was applied to a limited number of samples. The results obtained seem to exclude the risk, showing that arsenic is almost totally bound to the resistant fraction and thus does not represent an impediment to the beneficial re-use of sediment.

Keywords: arsenic; sediments; sequential extraction; metals' mobility; nourishment

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1. Introduction

New harbour construction and the maintenance of existing structures require the dredging and disposal of considerable amounts of sediments. These materials contain several compounds [1] of environmental concern that, once discharged into the sea, can deposit and accumulate in the bottom sediments, commonly associated with the finest material fractions [2–4] However, in recent studies on heavy metals distribution conducted in specific areas, a significant contamination of coarser fractions has also been evidenced [5,6].

During their mobilisation, sediments can induce the resuspension of the pollutants, thus behaving as a source of pollution and therefore extensive characterisation of these materials should precede any dredging operations. Particular attention has to be given to metals' content since the variation of oxic–anoxic conditions, favoured by dredging operations, make them likely to be released [7]. For this reason, when their concentrations exceed legal limits, the risk associated with material displacement and re-use has to be carefully assessed, evaluating not only their total concentration, but also their fractionation [8]. In fact, the distribution of the metal content into

*Corresponding author. Email: elisabetta.petrucci@uniroma1.it

ISSN 0275-7540 print/ISSN 1029-0370 online
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DOI: 10.1080/02757540.2010.536155
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different fractions strongly affects their mobility and therefore their availability [9,10]. It is known that metals are released more easily into the environment when bound to carbonates, to hydrous oxides of Fe and Mn and to organic matter, whereas no risk is associated with metals strongly linked to the mineral structure, mainly aluminosilicates [11].

A valid method to verify the metals fractionation is represented by the sequential extraction procedure which, using extractants of increasing strength, induces the metals' selective release [12]. Many sequential extraction schemes differing in extractant agents and number of steps, have already been described in the literature and widely applied in both soils and sediments [13–16]. The European Community Bureau of Reference (BCR) has recently approved and standardised a three-step sequential extraction procedure that verifies the metal content associated with acid-soluble, reducible, oxidisable and residual phases. This procedure has already been applied in the study of polluted and non-polluted soils and sediments [16–20].

Quality assessment of the dredged material is an indispensable precondition for decision making on sediments relocation [21]. When no contaminants are found, a possible destination for the dredged material can be open-water disposal [21,22], although an accurate evaluation of the effects on the receiving site (i.e. covering of the seabed, local increases in suspended solids levels and turbidity, smothering of benthic organisms) is needed before considering this management option as a suitable choice [23,24]. By contrast, when contamination does not permit relocation of the material, sediments are normally placed in confined disposal facilities or in landfill or they can be treated to remove the pollutants [25]. A correct environmental policy suggests that dredged material, as well as any other waste, should be considered as a valuable resource for beneficial use [26–28].

The re-use of uncontaminated marine sediments for beach nourishment actually represents a very cost-effective solution to fight beach erosion. Such a phenomenon, due to both natural and human activities, severely affects many coastal areas [29,30]. To evaluate the feasibility of such an operation, characterisation of both the source sediments and the receiving beach is necessary in order to verify the homogeneity of grain size distribution and physico-chemical properties [31].

This article presents a case study of the beneficial re-use of sediments resulting from dredging activities in Marina di Ragusa, a seaside resort located on the southeastern coast of Sicily (Italy). Because of the increasing tourist development of this area, the construction of a new tourist harbour has been planned with the displacement of 300,000 m^3 of material whose most advantageous destination would be represented by the nourishment of an adjacent beach.

As reported previously [32,33], the area investigated is known to suffer from significant natural erosive processes that have recently been enhanced by anthropogenic activities so that a plan for the coastal protection has been adopted by local authorities to pursue the objective of an environmental re-qualification [34].

In Italy, in the absence of a specific law devoted to sediment characterisation and disposal, nourishment activity is approved by competent authorities when the dredged material is in compliance with the quality standard indicated, for a restricted numbers of parameters, in Table 2 of the national Decree-Law No. 367/2003 [35]. APAT-ICRAM, a government agency of the Italian Environmental Ministry, indicates two concentration limits, LCB and LCL, for metals and a few classes of organic compounds [22]. The basis chemical level (LCB) represents concentrations in sediments that are close to the background value, corresponding to absent or unlikely ecotoxicological risk. The limit chemical level (LCL) corresponds to a concentration above which ecotoxicological risk is probable. Another international quality guideline is given by the effect range low (ERL) [36], defined as the concentration below which effects are rarely observed. A comparison of these values is reported in Table 1.

The aim of this study is to investigate the quality of sediments obtained by dredging the Marina di Ragusa harbour, and based on a risk-based approach, to predict the potential environmental impact of re-using the material for nourishment. To assess the quality of marine sediments, a

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Table 1. Comparison between national and international guidelines for sediments.

		Italian Decree Law 367/2003	ICRAM-APAT Environmental Ministry		
			LCB	LCL	ERL
As		12	17	32	8.2
Cd		0.3	0.2	0.8	1.2
Cr		50	50	360	81
Cu	($mg \cdot kg^{-1}$)	–	15	52	34
Hg		0.3	0.2	0.8	0.15
Ni		30	40	75	20.9
Pb		30	25	70	46.7
Zn		–	50	170	150
Total PCB	($\mu g \cdot kg^{-1}$)	4	5	189	22.7
Total PAH		200	900	4000	4022

Notes: LCB, basis chemical level; LCL, limit chemical level; PCB, polychlorinated biphenyl; PAH, polycyclic aromatc hydrocarbon.

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detailed characterisation of the area of concern was performed by means of an accurate sampling campaign followed by physical and chemical analysis. For those contaminants found to be at a concentration level exceeding quality standards, the risk associated with material displacement and re-use was assessed with the application of the BCR sequential extraction procedure.

2. Materials and methods

2.1. *Sampling design*

The sampling campaign was carried out in June 2007. The estimated volume of material to be dredged was 300,000 m^3.

A gravity core sampler was used to sample 19 stations located in the area of concern, as illustrated in Figure 1. From each core, a top sample (consisting of the first 20 cm of material) and a bottom sample (the last 20 cm) were collected. An intermediate sample was further collected from cores longer than 150 cm (sampling stations 1, 9, 15, 16, 17, 18). In total, 43 marine sediment samples were collected, grouped according to their depth and indicated in the text as D1 (0–20 cm), D2 (60–90 cm) and D3 (120–150 cm). Six additional surface samples (0–20 cm) were also collected from the beach to be nourished as reported in Figure 1, and labelled B1 to B6. All the samples were homogenised, immediately refrigerated and analysed in three days.

2.2. *Analyses*

Samples for grain size analysis were pre-treated with a H_2O_2 solution and fractionated by wet sieving using ASTM series sieves from 2 to 0.063 mm.

Total organic carbon (TOC) was determined according to DM 13/09/99 GU248 21/10/99 Met. VII using a Hewlett Packard elemental analyser. All the samples were preliminarily treated with 1 M HCl in silver capsules for carbonate removal.

Total hydrocarbons (THC) were determined according to method ISO/TR 11046 which consists of an extraction with 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) followed by purification on a Florisil column and determination by Fourier transform infrared spectrometry (FTIR). The detection limit of the method was estimated as 1 $mg \cdot kg^{-1}$. All the results are reported as concentration on dry weight (DW) basis.

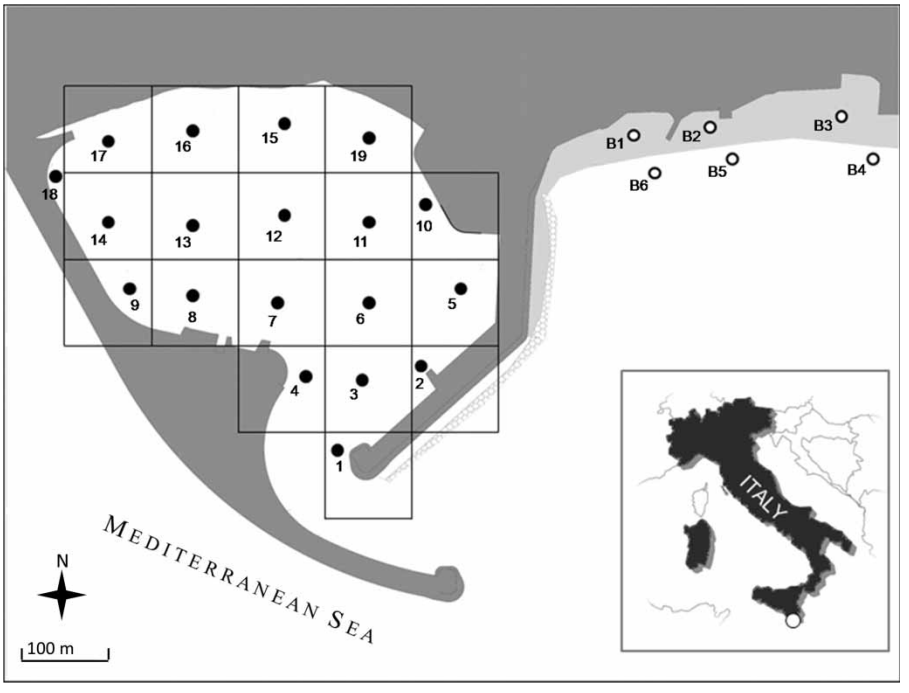

Figure 1. Study area and sampling stations.

For polycyclic aromatic hydrocarbon (PAHs) determination, sediment samples were air dried and homogenised, then extracted using a preliminary ultrasound extraction using methylene chloride. The extract was then concentrated, purified on silica gel and determined by capillary column gas chromatography with mass spectrometric detection (EPA methods 3550C and 8270D). The detection limit of the method was estimated as $10\,\mu g{\cdot}kg^{-1}$. All the results were calculated with respect to dry weight and expressed as the sum of the 16 total priority PAHs detected: (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benz[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, dibenzo[a,e]pyrene).

For polychlorinated biphenyl (PCBs) determination, sediment samples, air-dried and homogenised, underwent ultrasound extraction with methylene chloride. The extract was then concentrated, desulforated and purified using Florisil and analysed by capillary column gas chromatography with electron capture detection (ECD) (EPA methods 3550C and 8082A). The detection limit of the method was estimated as $100\,ng{\cdot}kg^{-1}$. All the results were calculated as concentration on a dry weight basis and expressed as the sum of the seven congeners detected (52, 77, 81, 128, 138, 153, 169).

For organochlorine pesticide (OCPs) determination, sediment samples, air-dried and homogenised, underwent ultrasound extraction with a mixture of methylene chloride acetone. The extract was then concentrated and purified using Florisil and analysed by capillary column gas chromatography with ECD (EPA methods 3550 C and 8270D). The detection limit of the method was estimated as $1\,\mu g{\cdot}kg^{-1}$. Concentrations are reported on a dry weight basis.

Heavy metals concentrations were measured by microwave-assisted acid digestion of samples previously air-dried and sieved through a 2 mm sieve according to EPA method 3051A. Analyses were performed by inductively coupled plasma mass spectrometry (ICP-MS; EPA method 6010C) except for mercury for which analysis was performed by cold vapour AAS (EPA method 7471A).

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The detection limit of the method was estimated as $1\,mg{\cdot}kg^{-1}$ for all the metals, apart from mercury and cadmium, for which the detection limit was 0.08 and $0.02\,mg{\cdot}kg^{-1}$, respectively. All the metal concentrations are reported on a dry weight basis.

For all the analyses, reproducibility estimated on triplicate samples was >90%.

To assess the method performance a standard reference material (SRM 1944) was used. This reference material is a mixture of marine sediment from New York and New Jersey which is certified by National Institute of Standard & Technology (NIST) for the determination of PAH, PCB, OCP and several other trace elements. Recovery rates were generally >90%.

2.3. *BCR sequential extraction*

To evaluate the mobility and availability of arsenic, the BCR sequential extraction procedure was adopted. This method, consisting of three steps and a residual extraction of 1-g sediment sample, provides measurement of extractable metal using different media with increasing strength. In particular, in the first extraction step, to determine the arsenic exchangeable and weak-acid soluble fraction, acetic acid (CH_3COOH $0.11\,mol{\cdot}L^{-1}$ at pH 2.85) was used.

On the washed residue from the first step the determination of the reducible fraction was carried out using hydroxylammonium chloride ($NH_2OH{\bullet}HCl$ $0.1\,mol{\cdot}L^{-1}$ at pH 2 by addition of HNO_3).

On the washed residue from the second step, extraction of the oxidisable fraction occurred using ammonium acetate (CH_3COONH_4 $1.0\,mol{\cdot}L^{-1}$ at pH 2 by addition of concentrated HNO_3) after the addition of two aliquots of hydrogen peroxide.

To determine the residual arsenic non-silicate bound content an aqua regia ($3\,HCl{+}HNO_3$) digestion of the residue from the third step was performed.

Finally, an aqua regia digestion of a further 1-g sediment sample was carried out and the result was compared with the sum of the four fractions determined previously.

All the tests were carried out in triplicate.

2.4. *Bioassays*

Microtox acute toxicity tests were carried out according to standard procedures reported in the Azur Environmental Microtox© Manual. The tests were performed on sediment pore water obtained by centrifugation (6000 rpm, 60 min) of a sample aliquot diluted with synthetic seawater in a ratio of 1 : 4 (dry weigth on water volume). In these bioassays, the decrease in *Vibrio fisherii* luminescence is calculated after an exposure time of 5, 15 and 30 min to the diluted extracts.

3. Results and discussion

The physico-chemical characterisation of all the samples is reported in Table 2. For each class of samples, the results are expressed as mean and median value. Standard deviation and coefficient of variation are also calculated.

Grain size fractions are classified as silt-clay (<0.063 mm), sand (0.063–2 mm) and gravel (>2 mm). As can be observed, the prevalent fraction in all the samples is represented by sand, whereas the percentage of gravel was almost always negligible.

In particular, all the samples from the receiving beach as well as the D2 samples presented an almost identical distribution, with an average sand content of 95%, the remainder being constituted by the fine fraction. Data referring to top samples (D1), although similar in gravel and sand content, showed a high variability in the fine fraction, from 1 to 36%, as stressed by a standard deviation of 7%. A different distribution was shown by the deepest samples (D3) where an average gravel

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Table 2. Basic statistics for grain size, organic compounds and heavy metals.

		Gravel >2 mm (%)	Sand 0.063–2 mm (%)	Silt-clay <0.063 mm (%)	TOC (%)	THC ($mg \cdot kg^{-1}$)	PCB ($mg \cdot kg^{-1}$)	PAH ($mg \cdot kg^{-1}$)	OCP ($mg \cdot kg^{-1}$)	Al ($mg \cdot kg^{-1}$)
Beach	No. samples: 6									
	Mean	0.00	95.01	4.99	0.235	n.d.	0.00020	n.d.	n.d.	1111
	Median	0.00	95.30	4.70	0.231	–	0.00015	–	–	1140
	SD	0.00	1.33	1.33	0.044	–	0.00023	–	–	153.6
	CV	0.00	0.01	0.27	0.188	–	1.14	–	–	0.14
D1 samples	No. samples: 19									
	Mean	0.03	92.95	7.02	0.300	1.89	0.00027	0.025	n.d.	1684
	Median	0.00	95.37	4.63	0.233	0.00	0.00	0.00	–	1533
	SD	0.11	7.66	7.64	0.272	6.14	0.00056	0.077	–	841.86
	CV	4.36	0.08	1.09	0.907	3.24	2.05	3.06	–	0.50
D2 samples	No. samples: 18									
	Mean	0.19	95.43	4.55	0.185	n.d.	0.00005	n.d.	n.d.	1342
	Median	0.00	95.67	4.30	0.177	–	0.00	–	–	1282
	SD	0.01	1.98	1.97	0.036	–	0.00015	–	–	332.66
	CV	0.08	0.02	0.43	0.194	–	2.93	–	–	0.25
D3 samples	No. samples: 6									
	Mean	10.01	83.72	6.27	0.248	n.d.	0.00007	n.d.	n.d.	1304
	Median	6.26	84.25	3.76	0.215	–	0.00	–	–	1151.5
	SD	12.3	9.95	6.92	0.121	–	0.00016	–	–	400.31
	CV	1.23	0.12	1.10	0.486	–	2.45	–	–	0.31

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		As ($mg \cdot kg^{-1}$)	Cd ($mg \cdot kg^{-1}$)	Cr ($mg \cdot kg^{-1}$)	Cu ($mg \cdot kg^{-1}$)	Hg ($mg \cdot kg^{-1}$)	Ni ($mg \cdot kg^{-1}$)	Pb ($mg \cdot kg^{-1}$)	Zn ($mg \cdot kg^{-1}$)
Beach	No. samples: 6								
	Mean	17.47	0.18	2.95	0.91	n.d.	2.93	3.50	9.90
	Median	17.25	0.19	2.95	0.93	–	2.95	3.50	10.10
	SD	1.41	0.01	0.29	0.15	–	0.27	0.20	1.12
	CV	0.08	0.07	0.10	0.17	–	0.09	0.06	0.11
D1 samples	No. samples: 19								
	Mean	17.41	0.20	4.59	1.86	n.d.	4.35	6.57	12.76
	Median	17.10	0.20	4.40	1.30	–	4.00	5.50	11.50
	SD	1.23	0.03	1.57	1.39	–	1.24	2.34	3.78
	CV	0.07	0.13	0.34	0.75	–	0.29	0.36	0.30
D2 samples	No. samples: 18								
	Mean	16.86	0.19	4.74	1.24	n.d.	4.17	5.51	11.18
	Median	16.80	0.19	4.75	1.20	–	4.15	4.75	10.85
	SD	1.12	0.01	1.51	0.25	–	0.79	1.84	1.74
	CV	0.07	0.08	0.32	0.20	–	0.19	0.33	0.16
D3 samples	No. samples: 6								
	Mean	15.15	0.18	4.50	1.52	n.d.	4.68	4.15	10.48
	Median	15.70	0.18	3.90	1.15	–	4.45	4.05	9.70
	SD	1.99	0.03	1.58	0.91	–	1.39	0.57	2.40
	CV	0.13	0.15	0.35	0.60	–	0.30	0.14	0.23

Notes: n.d., not detected; SD, standard deviation, CV, coefficient of variation.

content of 10% was found. However, this data is not fully representative due to the limited number of samples analysed. Actually, a significant gravel fraction (∼20%) was detected in only three of six samples, all from close areas in the inner zone of harbour basin (stations 16, 17, 18). On the whole, the comparison between surface samples taken from the beach to be nourished and marine sediments showed high homogeneity.

TOC content in marine sediments is commonly highly variable. Although standard limits are not available, data from the literature report average values of 0.5% in deep ocean sediments [37] and a range of 0.10–1.5% [38] and 0.10–0.75% [39] for unpolluted coastal samples. Considering that the TOC content does not exceed 0.3% in all the samples analysed, the literature data support the conclusion that the study area is reasonably unaffected by organic pollution. High homogeneity for this parameter between beach and marine sediment is also evidenced.

Characterisation of the organic compounds indicated that OCP values were always below the analytical detection limit. Similar results were found for THC and PAH, except for two samples representing the uppermost part of the cores from stations 9 and 15. In particular, the top sample of station 9, with a total PAH content of 0.29 $mg \cdot kg^{-1}$, exceeded the quality standard of 0.2 $mg \cdot kg^{-1}$. However, it is worth noticing that all the congeners were always found to be in compliance with the law. PCB content (expressed as the sum of the concentrations of the seven indicator congeners 52, 77, 81, 128, 138, 153 and 169) was found to be above the detection limit in 11 of the 49 samples, although values were negligible, being about two orders of magnitude lower than the quality standard of 4 $\mu g \cdot kg^{-1}$. Speciation analysis indicates that in seven samples, PCBs 138 and 153 accounted for ∼100% of the total PCB content, whereas in four, all from the core top layer, a small percentage can be attributed also to PCBs 77 and 81. Good general agreement can be found between the organic characteristics of the marine sediment and samples from the beach to be nourished.

Data on the metals content shows that the mercury concentration was always below the detection limit of 0.08 $mg \cdot kg^{-1}$. For aluminium, although a limit concentration is not available, the values found in all the samples can reasonably be attributed to the mineralogical composition of the sediments. This statement is supported by literature data indicating some background values for different areas of the Mediterranean Sea. In particular, Buccolieri et al. [40] report an aluminium background concentration of 36.866 $mg \cdot kg^{-1}$ in Taranto Gulf (Italy) and 70.000 $mg \cdot kg^{-1}$ in Milos Bay (Greece). The chromium, nickel and lead contents are well below the quality standards (50, 30 and 30 $mg \cdot kg^{-1}$ respectively), with concentrations slightly lower in the sand of the receiving beach. Cadmium, with a content ranging from 0.18 to 0.20 $mg \cdot kg^{-1}$, showed concentrations in compliance with the limit of 0.3 $mg \cdot kg^{-1}$ in both beach and source sediment. Copper and zinc concentrations were significantly lower than the national and international values reported in Table 1.

Arsenic concentration exceeded the quality standard in almost all the samples. A slightly higher content in beach samples and a quite weak dependence on sediment depth was also noted.

Arsenic is widely known as a major threat to environmental ecosystems because inorganic arsenic compounds, As(III) and As(V), exhibit high toxicity to humans, even though the dominant species in sediments are low-toxicity organoarsenic forms [41,42]. Contamination can occur from both natural and anthropogenic processes and As accumulation in sediments is due to chemical and physical binding or adsorption onto organic and inorganic particles [43]. For food and water intake, the US EPA indicates an arsenic oral reference dose (RfD) of 0.3 $\mu g \cdot kg^{-1} \cdot day^{-1}$ [44]. This concentration represents the daily exposure to the human population that is likely to have no appreciable risk of deleterious effects over a lifetime. However, the toxicity effects on humans of arsenic-contaminated soils and sediments have not been sufficiently investigated.

Arsenic concentrations in all the samples are reported in Figure 2, where the quality standard (12 $mg \cdot kg^{-1}$) and the LCB value (17 $mg \cdot kg^{-1}$) recommended by Italian Environmental Ministry are highlighted. Our results show that 43% of samples exceeded the limit of 17 $mg \cdot kg^{-1}$. However, all exhibited an arsenic concentration <20 $mg \cdot kg^{-1}$.

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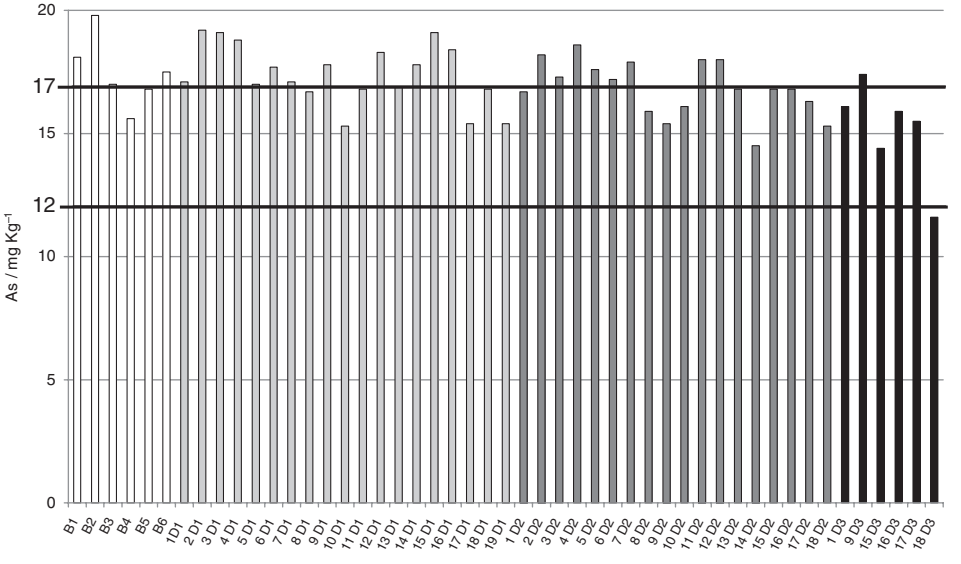

Figure 2. Arsenic concentration in beach sand sample (white), D1 samples (light grey), D2 samples (dark grey) and D3 samples (black).

Previous studies conducted on sediments from two different nature reserves in Sicily [45,46], one very close to Marina di Ragusa, reported similar higher arsenic content, thus suggesting a geochemical origin for this element and therefore the need for a site-specific background limit for this area.

To corroborate the hypothesis of a high background level of arsenic in the area of concern, a more in-depth study of this element availability was needed. In particular, to accurately assess arsenic mobility and therefore predict the risk associated with its release into the environment, a sequential extraction test was carried out, adopting a three-step procedure. The procedure was applied to a limited, but representative, number of samples. Three of them came from the receiving beach, and eight samples were collected from the marine sediment cores.

The arsenic fractionation is presented in Table 3. the data indicate significant differences in the arsenic percentage detectable in each phase after extraction. Similar behaviours for both marine

Table 3. Arsenic content, expressed as $mg \cdot kg^{-1}$ and %, obtained in the three steps of the BCR sequential extraction and in the acid attack.

	Arsenic sequential extraction							
	Exchangeable		Reducible		Oxidisable		Residual	
Sample	$mg \cdot kg^{-1}$	%	$mg \cdot kg^{-1}$	%	$mg \cdot kg^{-1}$	%	$mg \cdot kg^{-1}$	%
B2	n.d.	<1	1.30	6.57	0.66	3.33	17.54	88.59
B4	0.39	2.50	1.32	8.46	0.63	4.04	13.26	85.00
2 D1	0.60	3.12	1.12	5.83	1.05	5.47	16.43	85.57
2 D2	0.33	1.81	1.37	7.53	0.79	4.34	15.71	86.32
4 D1	0.39	2.07	1.21	6.44	0.58	3.08	16.62	88.40
9 D1	1.41	7.92	1.30	7.30	1.17	6.57	13.92	78.20
12 D1	n.d.	<1	1.15	6.28	0.88	4.81	15.97	87.27
15 D1	n.d.	<1	1.49	6.80	0.93	4.25	19.18	87.58
15 D3	0.75	5.21	1.14	7.92	0.84	5.83	11.67	81.04
16 D1	n.d.	<1	1.23	6.68	n.d.	<1	16.57	90.05

Note: n.d., not detected.

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sediments and receiving beach samples are also highlighted. In particular, results show that the exchangeable and weak acid soluble fraction accounted, on average, for only 2.2% of total arsenic with values ranging from 0 to 7.8%. This implies that arsenic does not undergo prompt release into the environment.

In accordance with previous studies [47,48], the reducible fraction exhibits the higher available arsenic content ($6.98 \pm 0.80\%$). However, dissolution of iron and manganese, leading to the release of arsenic bound to their oxides, occurs only in highly acidic and highly reducing potential conditions [49]. Further studies have also proven the important role played by the microbial activity of metal-reducing bacteria [50].

The arsenic bound to the organic fraction and therefore released under oxidising conditions, accounted on average for $4.42 \pm 1.28\%$. In a previous study [51] in which *in vivo* tests on pigs were carried out, a strong correlation was found between the arsenic dissolved in the animals' stomach and the arsenic present in both the exchangeable and reducible fraction, calculated in sequential extraction tests. This suggests that the As in the oxidisable fraction, although potentially available, represents a toxicological risk of minor concern.

The residual fraction in eight samples ranged between 85and 90%, while in the remaining two samples, 9 D1 and 15 D3, a lower arsenic residual fraction ($\sim$80%) was found. Considering that in the samples studied, the total arsenic content ranges from 14.8 to 19.8 $mg \cdot kg^{-1}$ and that the residual fraction accounts for 80–90%, the data clearly indicate that the concentration released immediately and that potentially available is never >3.8 mg kg^{-1} with an average value of 2.5 $mg \cdot kg^{-1}$.

Preliminary toxicological tests performed on sediments' pore water by Microtox bioassays showed no acute toxicity. The concentration corresponding to a bioluminescent inhibition of 20% (EC_{20}) was always $>90\%$ also after 30 min of incubation. Chronic effects, although unlikely, cannot be excluded.

4. Conclusions

The analytical investigation of sediments collected in the basin of Marina di Ragusa (Sicily, Italy) shows that all the samples exhibit substantial compliance with the quality standards, with many parameters below the detection limit. Moreover, a high homogeneity between marine sediments and the sand of an adjacent beach has been proved, thus suggesting the possible re-use of the dredged material for the beach nourishment.

Arsenic levels exceeded the quality standard slightly. However, the results obtained from a three-step sequential extraction procedure indicate that $>80\%$ of the total arsenic content is associated with the residual phase. Preliminary tests have also excluded an acute toxicity effect. In the absence of anthropogenic contributions and considering the consistency of concentrations in all the samples, arsenic content can reasonably be attributed to the mineralogical composition of the site, thus indicating the advisability of introducing a site specific background limit supported by further toxicity studies.

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