

Textural changes and heavy metal distribution in sediments after decontamination treatment by soil washing and attrition scrubber

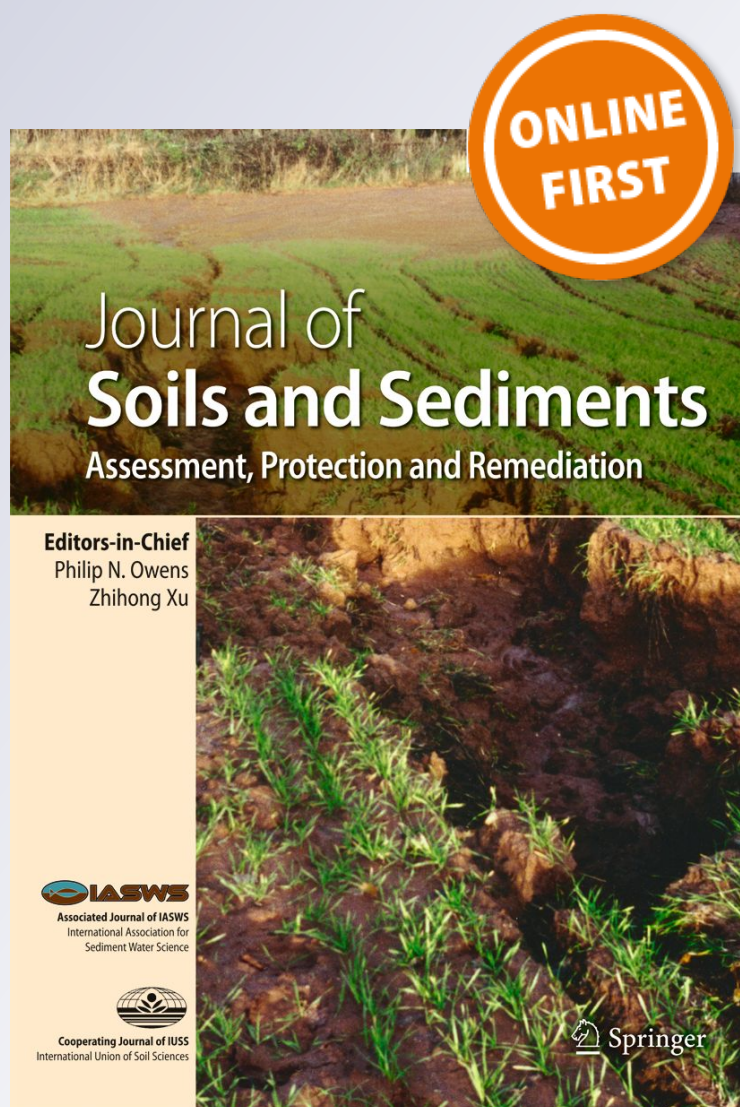
**Ilaria Rodella, Carmela Vaccaro,
Massimiliano Melchiorre, Umberto
Simeoni, Tiziana Campisi & Corinne
Corbau**

Journal of Soils and Sediments

ISSN 1439-0108

J Soils Sediments

DOI 10.1007/s11368-017-1896-9



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag GmbH Germany, part of Springer Nature. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Textural changes and heavy metal distribution in sediments after decontamination treatment by soil washing and attrition scrubber

Ilaria Rodella¹ · Carmela Vaccaro¹ · Massimiliano Melchiorre² · Umberto Simeoni¹ · Tiziana Campisi³ · Corinne Corbau¹

Received: 9 January 2017 / Accepted: 10 December 2017
© Springer-Verlag GmbH Germany, part of Springer Nature 2017

Abstract

Purpose The study was aimed to provide information on the decontamination of sediments polluted with heavy metals by soil washing and attrition scrubber techniques, assessing the efficiency of a prototype machinery for the improvement of sediment quality dredged in the Ravenna Harbor (Italy). An additional purpose was to compare the heavy metal distribution in sediment fractions collected after these treatments.

Materials and methods Textural and geochemical characteristics were determined in bulk sediments and after the treatments of soil washing and attrition scrubbing by a smaller scale prototype. Statistical analyses were carried out to verify the heavy metal correlations at each step of the treatments.

Results and discussion Textural features after treatments showed moderate separation of sand and silt/clay fractions after soil washing and an increase of the fine fractions after attrition scrubbing. Bulk sediments polluted by arsenic (As) were decontaminated after treatments. Concerning heavy metals, mercury was concentrated in the sand while aluminum, As, cadmium, chrome, iron, manganese, zinc, and vanadium were concentrated in the silt/clay fraction. Bivariate plots showed a significant correlation of heavy metals with sand percentage after soil washing and attrition scrubbing.

Conclusions The results suggest that heavy metal concentrations were significantly affected by grain size distribution. Soil washing resulted in the complete decontamination of As in the sediments. The heavy metal concentration was altered in each step of the treatments according to three different trends.

Keywords Attrition scrubber · Dredged sediment · Heavy metals · Remediation · Soil washing

1 Introduction

Marine sediments near large industrial and urban areas usually show high levels of contamination. Pollutants are usually rep-

resented by heavy metals (Romano et al. 2004; Colacicco et al. 2010; Lepland et al. 2010), polycyclic aromatic hydrocarbons (PAHs; Simpson et al. 1996; Alebic-Juretic 2011), tributyltins (TBTs; Bhosle et al. 2006; Antizar-Ladislao 2008), organochloride pesticides (OCPs), oil, radionuclides, rare earth metals, and other organic compounds that originate from anthropogenic activities (Galkus et al. 2012). The problem of managing contaminated sediments is strictly related to the activities of remediation (Agius and Porebski 2008) in addition to the need for periodical dredging in order to preserve navigability in ports and waterways (Simonini et al. 2005).

Heavy metals are very common contaminants (Gibbs 1993; Mezencevova et al. 2012; Yamagata et al. 2015). As reported by European Environmental Agency (2011) and Liao et al. (2016), heavy metal-contaminated sites have reached about 37.3% of the total contaminated European soil and 20.17% of Italian soil. Heavy metals usually transfer significant toxicity to aquatic organisms and thereby affect human health through the

Responsible editor: Gijs D. Breedveld

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11368-017-1896-9>) contains supplementary material, which is available to authorized users.

✉ Ilaria Rodella
rdllri@unife.it

¹ Department of Physics and Earth Sciences, Ferrara University, via Saragat 1, 44123 Ferrara, Italy

² Group of Dynamics of the Lithosphere, Institute of Earth Sciences Jaume Almera ICTJA – CSIC, Lluís Solé i Sabarís s/n, 08028 Barcelona, Spain

³ CRSA MED Ingegneria Ltd., via Tito Strozzi 18, 44121 Ferrara, Italy

food chain (Peng et al. 2009). In sediments, heavy metals can be occluded in amorphous materials, adsorbed on clay surfaces or precipitated with iron/manganese oxy-hydroxides, integrated with organic matter, or found in the lattice of primary minerals such as silicates (Peng et al. 2009) and secondary minerals like carbonates, sulfates, or oxides. High heavy metal levels in sediments require decontamination treatments that lower their concentrations. These interventions include physical remediation (soil replacement, thermal desorption, slurry injection, dehydration, and particle separation); chemical remediation by leaching, using fresh water, reagents, and others (fluids or gas, electrokinetics, or vitrifying techniques); and biological remediation (phytoremediation and microbiological remediation) (Yao et al. 2012; Kim et al. 2016). Among these treatments, particle separation through soil washing is considered one of the best methods for remediation of heavy metal contaminated sites; it is mostly used for polluted soils, but it is also useful for sediments (Mulligan et al. 2001; Peng et al. 2009). The soil washing process exploits a physical-chemical approach used in mining to concentrate metals in specific particle fractions, using trommels, screw classifiers, attrition mills, or hydrocyclones (Mann 1999; Dermont et al. 2008). Hydrocyclones use centrifugal force to separate solids from liquid streams (Wu et al. 2012; He et al. 2013). The system has no movable parts, operates simply, and is low-cost and space-saving (Kim et al. 2016). Soil washing separates and treats gravel and sand fractions, so that they may be re-used as clean backfill. It may also concentrate through physical separation up to 90% of contaminants in the finer fraction, that is, silts and clays with a mean diameter of 50 μm or less (Lee et al. 1997; Gomes et al. 2016), for further treatment or disposal (Mann 1999). Physical separation concentrates metal contaminants into a smaller volume of soil by exploiting differences in physical characteristics of particles, such as size, density, magnetism, and hydrophobic surface properties (Griffiths 1995; Anderson et al. 1999; Dermont et al. 2008). However, Clozel et al. (2006) showed that metal distribution within the sediments were not completely transferred from the sandy fraction to the silty-clayey fraction; thus, in some cases, sieving may be insufficient to separate a polluted fine fraction from a non-polluted coarse one. Attrition scrubbing may improve the efficiency of separation methods by hydro-classification (Williford et al. 1999) or shaking table (Marino et al. 1997; Bisone et al. 2013) and has therefore been applied in several studies to improve sediment cleaning (Stražišar and Sešelj 1999; Bayley and Biggs 2005; Pétavy et al. 2009a). The attrition scrubber has been employed as a suitable remediation process for contaminated sediments because it may remove particles and contaminants from the surface of sediments, reducing the viscosity of the slurry and allowing the sand to settle quickly in the soil washing plant (Kuhlman and Greenfield 1999). Moreover, the attrition process causes abrasion, scrubbing, scouring, and particle disintegration (Jiang et al. 2009) that affect the physical

parameters of agglomerated particles (Marino et al. 1997; Stražišar and Sešelj 1999). A direct link between the duration of attrition and the efficiency of removal (the ratio between the removed contaminant and the input quantity) was found by Stražišar and Sešelj (1999), with 90% of contaminants removed in 90 min for lead-contaminated calcite samples. The same authors also reported an increase in the removal efficiency related to an increase in the range of particle size (46% for a size range 0.1–0.4 mm and 65% for a size range 0.8–1.25 mm). Treatment times also play a role in addition to particle size: the duration of attrition is positively correlated with the production of fine particles (Pétavy et al. 2009b), from 17 to 31% of the total mass (during 30 and 180 s of attrition, respectively).

The attrition scrubbing favorably compared with other remediation technologies (for instance, ultrasonic separation and jet reactors). Attrition provides excellent mixing and surface abrasion and has been successfully used to speed up the leaching dynamics of gold ores (Feng et al. 2001). Jobin et al. (2015) reported that attrition significantly increased the efficiency of gravity separation due to a change in shape of soil particles and to higher release of the contaminants by breaking and separation of agglomerated particles. Attrition may also improve the effectiveness of particle density separation (Peters 1999) in comparison to other techniques. An added advantage is that the equipment cost and maintenance can be significantly lower to other systems (Feng et al. 2001).

Unfortunately, studies on heavy metal decontamination are limited and experimental data on the operative conditions of the attrition scrubber are still incomplete. Moreover, a comparison of heavy metal concentration before and after soil washing and before and after attrition scrubbing has never been performed.

This study examines the distribution of the heavy metals after each step of the decontamination process with the following purposes: separate the polluted fractions using a tailored treatment based on soil washing, attrition scrubbing, and sieving; determine the efficiency of a physical test for decontamination of dredged sediments by soil washing, followed by attrition scrubbing; and compare heavy metal concentrations in sediment fractions.

2 Materials and methods

2.1 Study area

Sediment samples were collected into the Candiano channel (Fig. 1), next to the harbor of Ravenna (Emilia-Romagna Region, northern Italy). Ravenna is one of the most important Italian harbors for commercial trade with the eastern Mediterranean Sea and the Black Sea, occurring by bulk cargo and general cargo (approximately 30% of the total Italian national trade excluding oil products). The traded products are mostly concrete, timber, and electrical coils, amounting to about 25,962,764 tons and 234,511 container voyages in

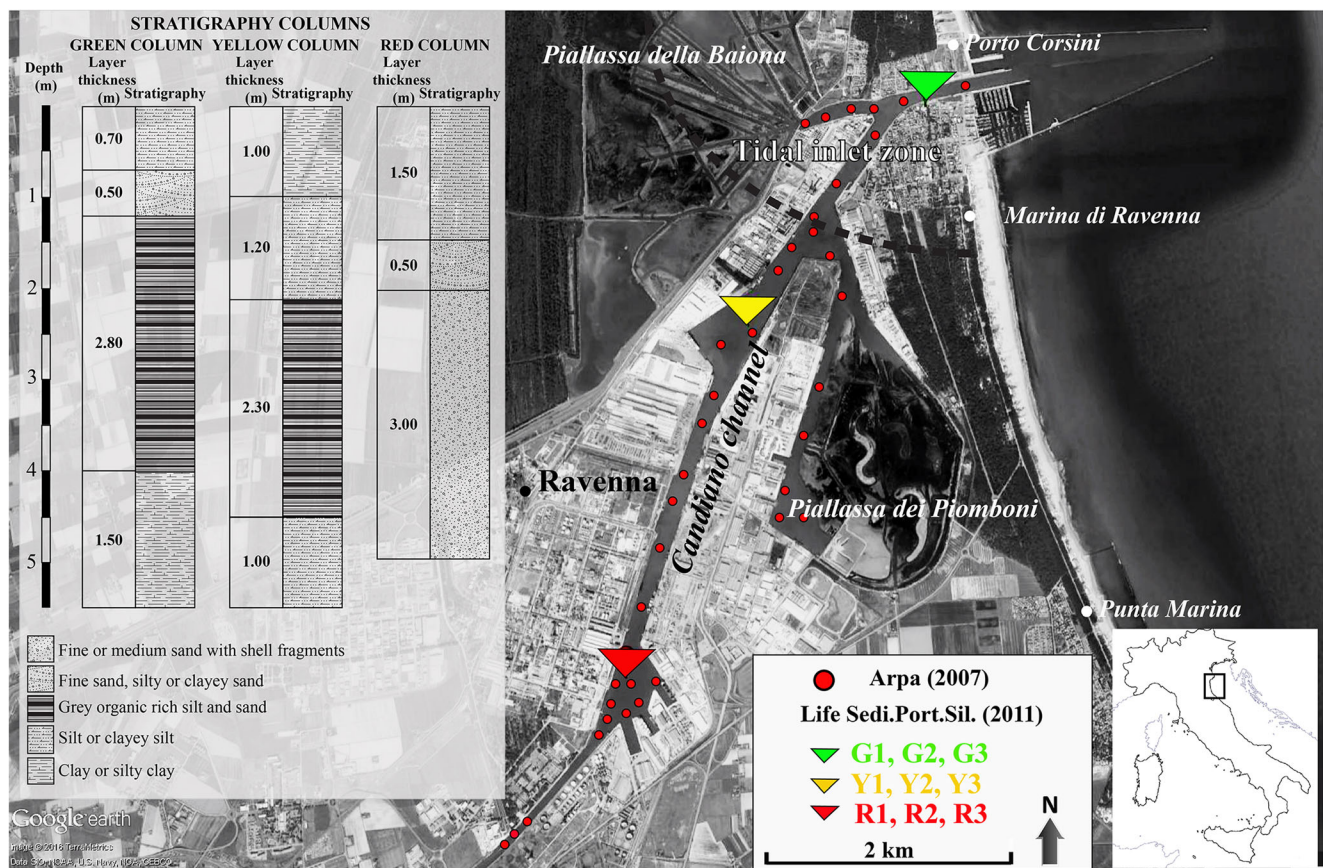


Fig. 1 Map of locations of the sediment sampling (modified after LIFE SEDI.PORT.SIL. 2011). G, Y, and R sampling sites refer to levels of contamination by Corsini et al. (2007) according to the Italian Legislative Decree 152/2006, UE directive (2000/60/CE; 91/156/CEE;

75/442/CEE, 91/689/CEE and 94/63/CE), and LIFE SEDI.PORT.SIL. (2012). Red dots indicate the sites of a previous survey carried out by the Ravenna Port Authority with the support of the Regional Agency for Prevention, Environment and Energy (ARPA) in 2007

2016 (Ravenna Port Authority 2017). In the sediments of the Candiano channel and of the adjacent lagoon “Pialassa della Baiona” (Fig. 1), high levels of hydrocarbons have been reported, as well as contamination by mercury (Misericocchi et al. 1993; Fabbri et al. 2003; Matteucci et al. 2005), related to the large amount of mercury spilled between 1957 and 1977 in the lagoon by a local acetaldehyde factory (Covelli et al. 2001).

2.1.1 Sampling

Sediments were sampled in 2011 at three different sites, labeled “green” (G), “yellow” (Y), and “red” (R) along the Candiano channel in Ravenna Harbor (Fig. 1) (LIFE SEDI.PORT.SIL. 2011). The sampling sites were identified on the basis of previous geochemical characterizations carried out in the Candiano channel from 1998 to 2008 and by an official survey by local authorities in 2007, aimed to define the spatial distribution of pollutants in the study area (LIFE SEDI.PORT.SIL. 2011).

The G site was located between the urban areas of Marina di Ravenna and Porto Corsini, the Y site was in the intermediate

area of the Candiano channel, and the R site was in the innermost part of the channel, near the industrial area of the harbor (Fig. 1). For each site, three sampling points (G1–3, Y1–3, R1–3) were randomly selected and for each point about 10 m³ of wet sediment was collected by a sealed bucket, coupled with a core sample for stratigraphic characterization, reaching a dredged depth between 5 and 5.5 m. All sediments were analyzed and characterized in situ by measuring temperature, pH, and redox status (data not shown) and later in the laboratory according to the Italian Legislative Decree 152/2006, A column for national standard levels of heavy metal contents, the Nitrates Directive (Council Directive 91/676/EEC; European Community 1991), and the Water Framework Directive (Directive 2000/60/EC; European Community 2000).

2.2 Treatments

The experimental treatments were carried out by a soil washing prototype (Diemme Soil Washing Ltd., Lugo, Ravenna, Italy) (Fig. 2) during the project “Recovery of dredged SEDiments of the PORT of Ravenna and SILicon extraction”

LIFE ENV/IT/000158 (LIFE SEDI.PORT.SIL.) to test an *ex situ* remediation process with harbor sediments. In the soil washing tests, each sediment sample was separated at the fraction cutoff thresholds reported in Fig. 2 (CF, coarse fraction; IF, intermediate fraction; FF, fine fraction). A hydrocyclone Warman C4 (Weir Minerals Ltd., Glasgow, UK) was employed, characterized by an inner cylinder section diameter of 100 mm and a cone angle of 10° . A centrifugal pump with 67 l/min capacity at 18°C was used to feed dredged sediments into the hydrocyclone; a pressure gauge and flowmeter (Diemme Soil Washing Ltd.) were also installed. Ball valves were set up in front of the flowmeter and after the centrifugal pump in order to control the flow rate. The inflow velocity of the hydrocyclone was 3 m/s, and the operative pressure was 80 kPa.

A second phase of the treatment consisted in applying an attrition test and a cutoff at $< 3.75 \phi$ to the IF of each sample. The attrition tests removed the contaminants from the surface of the particles, with special attention to residual heavy metals. The attrition apparatus consisted of a cell LIGHTNIN Attrition Scrubber (Lightnin SPX Flow, Rochester, New York, USA) with a vertical tree and three levels of stirring paddles supplied by a 3-kW electric engine at 1490 rpm. The attrition time was set at 10 min according to Jobin et al. (2015). The cell had a capacity of 15–20 l and treated dry matter at 60–70% of solid ratio, close to the best solid ratios (65 and 75%) obtained respectively by Gül et al. (2006) and Feng et al. (2001), with a density of 1.5–1.8 kg/l. The FF was pressed to reduce volume and finally discharged.

The prototype used in this study was configured for semi-industrial use with a work capacity of 1 ton per hour (24 tons

per day), calibrated for the experiments carried out within the LIFE SEDI.PORT.SIL. project. Consequently, the prototype was smaller than a common industrial treatment plant (2000–6000 tons per day) but had the same technical characteristics.

2.3 Textural and chemical analyses

Textural and chemical analyses were performed on bulk sediments, on the two sediment fractions before treatment (IF and FF), on the fractions obtained by soil washing (IF_{sw} and FF_{sw}), and during the attrition process (IF_{att}) (Fig. 2). The analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara (Ferrara, Italy) and at CRSA MED Ingegneria Ltd. (Marina di Ravenna, Ravenna, Italy).

The bulk sediments were wet sieved through a $3.75\text{-}\phi$ sieve to separate the finer fraction (silt and clay) from the intermediate one (sand fraction). The IF particle size, between -1 and 3.75ϕ , was measured by using a settling tube, while the FF ($< 3.75 \phi$) was determined with a sedigraph (Micromeritics 5100, Japan). Finally, the Wentworth scale was used to classify the sediments, and the textural parameters were obtained through the statistics package Gradistat (Blott and Pye 2001) applying the Folk and Ward (1957) classification.

Heavy metals (aluminum, Al; arsenic, As; cadmium, Cd; total chromium, Cr_{tot} ; exavalent chromium, Cr_{vi} ; iron, Fe; manganese, Mn; mercury, Hg; nickel, Ni; lead, Pb; copper, Cu; vanadium, V; zinc, Zn) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) Model X (Thermo Fisher Scientific, Waltham, Massachusetts, USA) after total dissolution with HF and HNO_3 , following the methods EPA 3051A 2007 (EPA 2007a) and EPA 6010C 2007 (EPA 2007b) for heavy metal analysis with a detection limit of 0.1 mg kg^{-1} . The EPA Reference Standard SS-1 (a type B naturally contaminated soil) and the EPA Reference Standard SS-2 (a type C naturally contaminated soil) were used to crosscheck and validate the results. These total dissolution procedures included a total digestion of sediment samples using HF and HNO_3 , accordingly to widely used for ICP-MS analysis of polluted harbor sediments, as applied by Adamo et al. (2005) in Naples (Italy), Caplat et al. (2005) in Port-en-Bessin (France), Mendoza et al. (1996) in Hidalgo State (Mexico), and Miserocchi et al. (1993) in Ravenna (Italy).

The physical-chemical parameters of sediments, including temperature, pH, and redox potential, were measured by a multi-parameter Multiline P4 (WTW, Rozzano, Milan, Italy).

2.4 Statistical analyses

Statistical analyses were performed by the Statistical Package for Social Sciences (SPSS) version 20 (Statistics Solutions) and Microsoft Excel version 2017 (Microsoft Office, Redmond, Washington, USA). All measured variables of IF

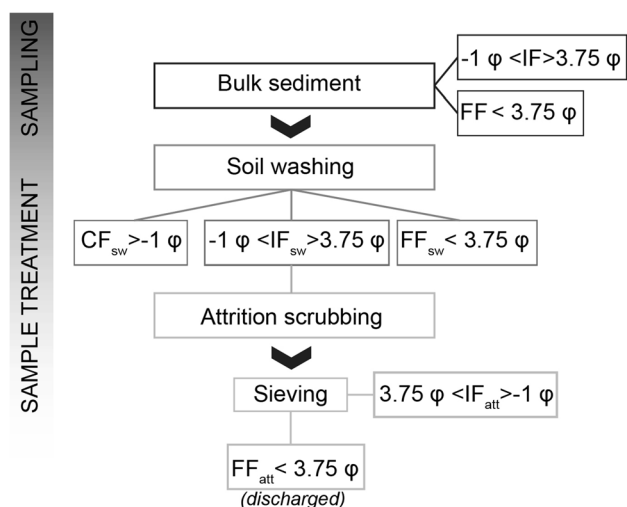


Fig. 2 Experimental protocol for treatment of dredged sediments in three phases (soil washing, attrition, and sieving). IF intermediate fraction, FF fine fraction, CF_{sw} coarse fraction after soil washing, IF_{sw} intermediate fraction after soil washing, FF_{sw} fine fraction after soil washing, IF_{att} intermediate fraction after attrition scrubbing, FF_{att} fine fraction after attrition scrubbing

and FF were elaborated using a correlation matrix before and after treatments. The matrix was generated using the Pearson correlation coefficient. Linear regressions were elaborated to identify the relationship among heavy metals under the different treatment conditions. All statistical data were presented in the Electronic Supplementary Material (S1-S4).

3 Results

3.1 Characterization of bulk sediments

Bulk sediments corresponded to coarse silt or very coarse silt in accordance with the classification system by Folk and Ward (1957). Overall, the mean diameter and the sorting index varied from 4.19 to 5.32 ϕ and from 0.98 to 1.63 ϕ , respectively (Table 1). Red samples (mean diameter between 4.19 to 4.33 ϕ and sorting index ranging from 0.98 to 1.09 ϕ) showed textural parameters very similar to the green samples (mean diameter between 4.40 and 4.61 ϕ and a sorting index between 1.21 and 1.35 ϕ) (Table 1). Yellow samples had the highest mean diameter (between 5.00 and 5.32 ϕ) and sorting index (1.45–1.63 ϕ). The sand content varied from 23.47% in the Y2 sample to 65.5% in the R3 sample (Table 1). Heavy metal concentrations in bulk sediments, also reported in Table 1, were compared with the thresholds for intervention according to the Italian standards for soils (Legislative Decree n. 152/2006). All bulk sediments showed concentrations below the legislative limits, except As in sample R2 (32.9 mg kg⁻¹), that exceeded the lower risk threshold of the Legislative Decree n. 152/2006-A Column. The values of Al, Fe, and Mn concentrations were not considered because the Italian law had not yet defined intervention thresholds for these metals (Table 1). The distribution of heavy metals in IF and FF of the bulk sediments was analyzed in order to determine their enrichment in relation to particle size. The general tendency observed was that the IF of bulk sediments (corresponding to the sand fractions >3.75 ϕ sieved in the laboratory before treatment) was depleted in heavy metals, while the FF (silt and clay <3.75 ϕ of bulk sediments) showed the highest concentrations (Table 1 and Fig. 3). This trend was clearly observed for Al, Cr_{tot}, Cu, Fe, Ni, Pb, and V. The elements As, Cd, Mn, and Zn had also a similar behavior, although in some samples, the concentration value of a given metal in bulk sediments, IF and FF, was about the same. Compared to the other heavy metals, Hg showed an inverse distribution between IF and FF, with a higher concentration in IF (Fig. 3). The Hg content in IF was even higher than in the bulk sediments, except in samples R2 and Y1. A correlation matrix of heavy metal concentrations was reported in the Electronic Supplementary Material S1 for IF and for FF before treatments. The results showed a similar correlation of Al, Cr_{tot}, Fe, Mn, and V both in IF and FF, but As, Cd, and Cr_{vi}

showed different correlations in the two fractions. The As content had a significant correlation only with Pb in IF, but was correlated with Cr_{vi}, Ni, Pb, and Cu in FF, and Cd correlated with Pb and Cu in IF, but correlated to Cr_{tot}, Cr_{vi}, Fe, Pb, Cu, V, and Zn in FF. Finally, Cr_{vi} significantly correlated with Fe and Mn in IF and with Pb and Cu in FF. The element Hg did not show any significant correlation with other heavy metals in either IF or FF.

3.2 Characterization of treated sediments

3.2.1 Textural changes induced by treatments

The soil washing process separated the bulk sediments into sandy and silt-clay fractions. However, the separation performed by our prototype did not allow a complete separation; thus, a percentage between 13 and 25.32% of silt and clay was found in the sandy fraction (Table 2). The obtained sands were classified as fine sands (or very fine sands in the case of sample R3); they were moderately well-sorted (0.55 ϕ) or poorly sorted (1.12 ϕ), with a mean diameter ranging between 2.24 and 3.00 ϕ (Table 2). After the attrition scrubbing process, the intermediate fraction treated with attrition scrubber (IF_{att}), classified as fine sand, showed a mean diameter of 2.49–3.15 ϕ and a sorting index of 0.71–1.23 ϕ (Table 2). The IF_{att} had a mean diameter slightly lower than that of sand obtained by the soil washing treatment. The abrasion process of the sandy fraction induced a slight increase of the silt and clay (2.15% in sample G1 and 3.54% in sample R1). In sample Y1, the percentage of silt and clay decreased by 5.88%. The abrasion also produced an increase of the sorting index compared to the washed samples (from +0.10 to +0.64 ϕ).

3.2.2 Heavy metal distribution after soil washing

Heavy metal concentrations in sediments after soil washing were reported in Table 3. The As distribution induced by the soil washing treatment showed a similar removal efficiency for the treatment of each fraction, and as expected, the As concentration decreased in all samples. In detail, in sample R2 which had the highest As content, As decreased from 28.0 to 8.1 mg kg⁻¹ in IF before and after soil washing and from 42.0 to 12.0 mg kg⁻¹ in FF before and after soil washing, obtaining an As removal higher than 28.6%. The physical parameters of IF and FF after soil washing were described in the Electronic Supplementary Material S2. The IF and FF showed similarities in their residual sediment moisture (ranging from 95.52 to 99.00 g kg⁻¹), while the average dry sediment percentage ranged from 66.99 to 73.63% in FF and IF, respectively. Some differences were observed in pH and redox potential between the two fractions (Electronic Supplementary Material S2). To investigate the relations between physical parameters and heavy metal concentrations in

Table 1 Textural parameters and heavy metal concentrations of bulk sediments before treatments compared with the risk threshold levels according to the Italian standard for polluted soils (Legislative Decree n. 152/2006, A Column). In bold are the values exceeding the limits of the Legislative Decree, and in italic are the values exceeding the limits of the Legislative Decree in the separated fractions

Textural parameters		Heavy metals (mg kg ⁻¹)																
Sample	Sand (%)	Silt-Clay (%)	Mean diameter (φ)	Sorting (φ)	Al	As	Cd	Cr _{tot}	Cr _{vi}	Fe	Mn	Hg	Ni	Pb	Cu	St	V	Zn
R1	53.2	46.8	4.26	0.99	6.48E+03	18.49	0.22	29.40	<0.2	1.10E+04	271.10	0.24	28.46	18.34	25.16	<0.1	12.83	39.41
R1 (IF)					3.14E+03	14.54	0.17	15.97	<0.2	5.55E+03	156.80	0.25	16.62	10.75	12.62	<0.1	6.53	22.90
R1 (FF)					1.03E+04	22.98	0.27	44.67	<0.2	1.72E+04	401.03	0.23	41.92	26.97	39.41	<0.1	19.99	58.18
R2	49.99	50.01	4.33	1.09	8.14E+03	32.88	0.26	37.30	<0.2	1.41E+04	348.30	0.41	35.24	19.35	29.58	<0.1	15.67	46.04
R2 (IF)					4.14E+03	27.98	0.18	21.00	0.1	7.25E+03	221.00	0.14	23.00	12.00	15.90	0.1	11.00	33.00
R2 (FF)					1.10E+04	<i>41.97</i>	0.21	55.00	0.1	2.09E+04	532.00	0.12	58.92	29.00	48.00	0.1	26.00	76.00
R3	65.55	34.45	4.19	0.98	4.20E+03	16.53	0.20	20.09	<0.2	7.88E+03	213.40	0.23	21.67	12.87	15.70	<0.1	8.40	25.43
R3 (IF)					2.01E+03	14.20	0.15	14.00	0.1	3.32E+03	101.00	0.25	16.00	8.00	7.50	0.1	3.89	19.00
R3 (FF)					6.87E+03	17.04	0.24	31.00	0.1	1.34E+04	289.00	0.18	28.00	18.30	25.00	0.1	12.00	41.30
Y1	26.46	73.54	5.00	1.45	9.03E+03	9.74	0.15	31.83	<0.2	1.39E+04	362.80	0.09	28.47	8.97	23.41	<0.1	15.85	51.42
Y1 (IF)					5.57E+03	9.69	0.14	22.40	<0.2	8.64E+03	238.00	<0.1	19.29	5.57	13.93	<0.1	10.80	36.00
Y1 (FF)					1.02E+04	9.75	0.15	34.92	<0.2	1.57E+04	403.74	<0.1	31.48	10.08	26.52	<0.1	17.51	56.48
Y2	23.47	76.53	5.32	1.63	3.65E+03	8.03	0.07	14.54	<0.2	5.94E+03	150.20	0.09	15.58	3.90	6.92	<0.1	7.56	18.01
Y2 (IF)					3.21E+03	5.32	0.06	11.85	0.1	2.87E+03	111.32	0.09	11.96	2.35	5.99	0.1	5.60	12.30
Y2 (FF)					5.01E+03	8.30	0.08	17.56	0.2	7.23E+03	173.66	0.09	18.66	5.10	9.34	0.1	8.74	19.19
Y3	25.47	74.53	5.03	1.45	4.10E+03	8.49	0.08	15.97	<0.2	7.16E+03	205.50	0.09	17.23	5.13	10.49	<0.1	7.97	26.28
Y3 (IF)					2.99E+03	7.11	0.07	12.36	0.2	5.50E+03	201.00	0.11	13.25	4.25	6.24	0.1	5.10	19.65
Y3 (FF)					5.70E+03	9.21	0.09	21.30	0.2	9.12E+03	209.00	0.08	25.31	6.23	11.92	0.1	9.12	32.10
G1	40.22	59.78	4.61	1.30	6.86E+03	8.62	0.14	24.04	<0.2	1.04E+04	297.20	0.36	23.31	7.41	13.56	<0.1	12.71	37.62
G1 (IF)					5.80E+03	7.91	0.11	20.85	<0.2	9.19E+03	256.54	0.40	20.52	6.40	11.60	<0.1	11.23	33.22
G1 (FF)					9.23E+03	10.18	0.20	31.15	<0.2	1.32E+04	387.70	0.26	29.51	9.64	17.92	<0.1	16.00	47.42
G2	55.40	44.60	4.40	1.21	1.01E+04	10.69	0.18	34.56	<0.2	1.67E+04	495.90	0.31	32.42	8.62	17.38	<0.1	18.32	47.60
G2 (IF)					5.21E+03	7.28	0.16	29.00	0.2	6.95E+03	369.60	0.33	23.24	5.36	15.45	0.1	17.02	41.90
G2 (FF)					1.32E+04	13.21	0.18	42.50	0.2	2.01E+04	536.00	0.28	43.92	12.26	19.32	0.1	20.97	59.60
G3	47.25	52.75	4.58	1.35	1.02E+04	9.12	0.17	34.65	<0.2	1.60E+04	469.50	0.30	31.20	8.71	17.39	<0.1	18.22	47.25
G3 (IF)					6.66E+03	7.56	0.12	34.65	0.2	1.20E+04	400.50	0.30	27.56	8.71	16.30	0.1	15.02	42.18
G3 (FF)					1.37E+04	11.35	0.21	44.20	0.2	2.17E+04	530.36	0.27	37.64	9.35	19.84	0.1	23.68	58.32
					Threshold limits	20	2	150	2	-	-	1	120	100	120	1	90	150
					for land use ^a													
					Threshold limits	50	15	800	15	-	-	5	500	1000	600	350	250	1500
					for industrial use ^a													

^a Legislative Decree n. 152/2006, A Column

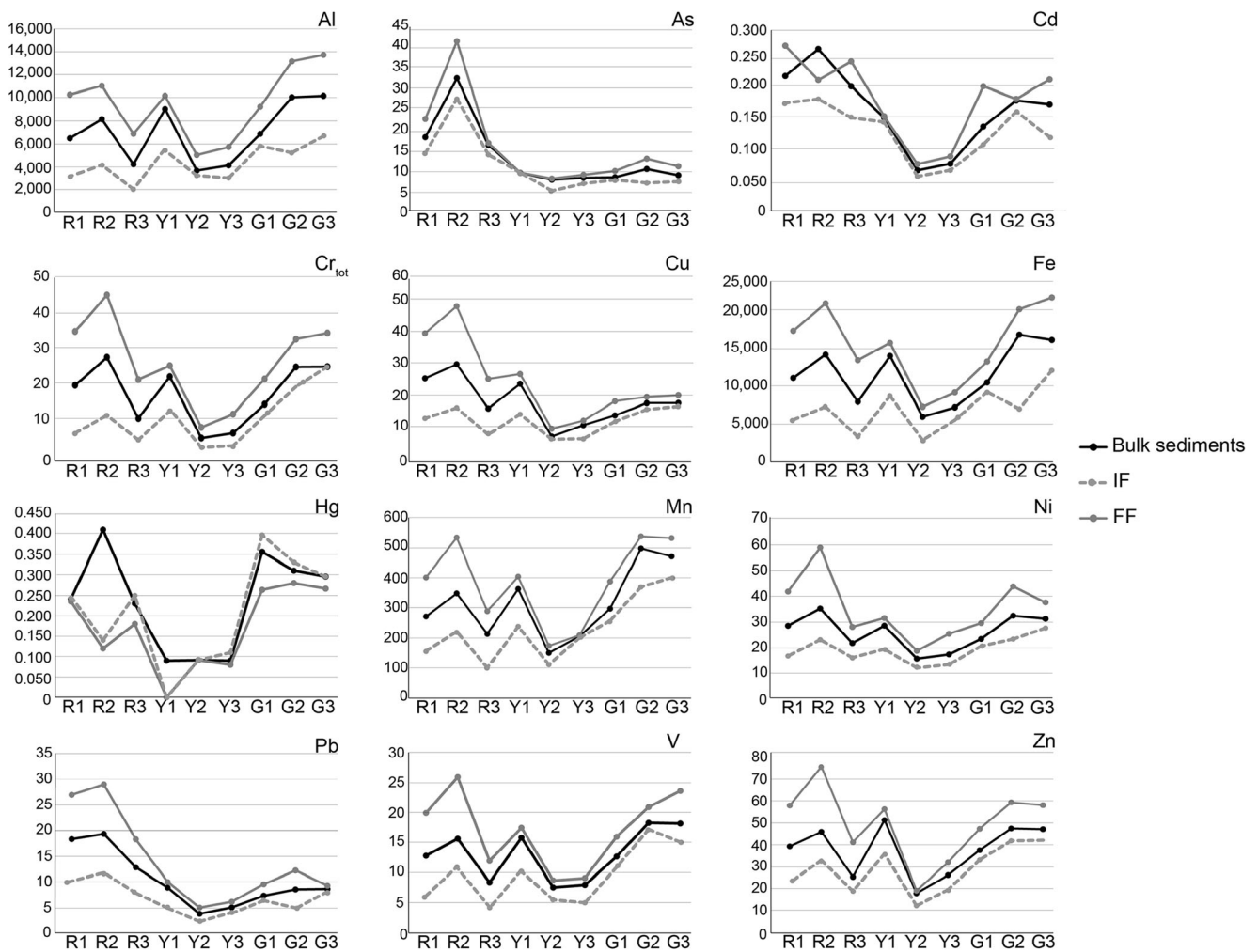


Fig. 3 Heavy metal concentrations (mg kg^{-1}) in bulk sediments, IF and FF fractions. R1–3 sampling points in R site, Y1–3 sampling points in Y site, G1–3 sampling points in G site

IF after soil washing, a correlation matrix was generated (Electronic Supplementary Material S3), which showed a significant correlation between temperature, pH, and redox potential. However, after treatment Al, Hg, V, and Zn positively correlated with temperature and negatively with redox

potential. Negative correlations were also observed between residual moisture and Cr_{tot} , Ni, and Fe, while As, Cd, and Pb did not show significant correlations with other heavy metals or physical parameters. Concerning correlations among metals, Al was positively correlated with Fe, Mn, Hg, V, and

Table 2 Textural parameters of IF fractions after soil washing and attrition scrubbing treatments

	R1	R2	R3	Y1	Y2	Y3	G1	G2	G3
IF after soil washing									
Sand (%)	85.88	85.00	82.00	74.68	82.00	87.00	81.35	85.00	80.00
Silt-clay (%)	14.12	15.00	18.00	25.32	18.00	13.00	18.65	15.00	20.00
Mean diameter (φ)	2.24	2.79	2.85	3.00	2.85	2.27	2.88	2.28	2.90
Sorting (φ)	0.55	0.56	1.00	1.12	1.00	0.60	1.02	0.56	1.04
IF after attrition scrubber									
Sand (%)	82.34	n.d.	n.d.	80.56	n.d.	n.d.	79.20	n.d.	n.d.
Silt-clay (%)	17.66	n.d.	n.d.	19.44	n.d.	n.d.	20.80	n.d.	n.d.
Mean diameter (φ)	2.56	3.10	3.00	3.10	2.90	2.65	2.99	2.49	3.15
Sorting (φ)	0.81	1.20	1.18	1.22	1.19	0.87	1.15	0.71	1.23

n.d. not determined

Table 3 Heavy metal contents in IF_{sw} and FF_{sw} after soil washing

Heavy metals (mg kg ⁻¹)												
	Al	As	Cd	Cr _{tot}	Fe	Mn	Hg	Ni	Pb	Cu	V	Zn
IF _{sw}												
R1	4.91E+03	7.35	0.01	38.16	6.57E+03	312.60	0.18	27.89	16.57	4.75	10.18	22.10
R2	4.53E+03	8.06	0.01	38.60	6.57E+03	320.80	0.41	27.75	4.13	4.62	9.75	17.81
R3	2.14E+03	7.01	0.16	9.63	4.24E+03	110.70	0.07	10.78	5.83	7.43	4.12	10.43
Y1	5.31E+03	8.05	0.01	23.45	8.34E+03	485.40	0.58	27.05	5.09	8.42	10.77	38.96
Y2	4.99E+03	6.18	0.01	26.88	6.46E+03	357.90	0.49	22.99	3.62	5.63	10.91	28.21
Y3	4.01E+03	5.83	0.01	29.34	5.69E+03	302.10	0.34	23.09	2.79	3.93	8.62	21.48
G1	5.80E+03	7.78	0.01	28.10	8.17E+03	422.40	0.54	22.93	3.98	5.74	12.80	32.28
G2	7.31E+03	11.23	0.06	30.54	1.26E+04	432.00	0.63	28.90	6.58	3.89	11.39	32.52
G3	8.41E+03	7.28	0.01	39.69	9.77E+03	520.30	0.64	31.37	6.02	6.01	15.00	43.93
Mean	5.27E+03	7.64	0.03	29.38	7.60E+03	362.69	0.43	24.75	6.07	5.60	10.39	27.52
Std. deviation	1.82E+03	1.55	0.05	9.37	2.48E+03	122.33	0.20	6.01	4.13	1.54	2.99	10.61
FF _{sw}												
R1	4.78E+03	10.64	0.18	20.78	8.02E+03	186.43	0.11	19.49	12.54	18.35	9.31	27.04
R2	6.60E+03	12.00	0.17	29.47	1.14E+04	271.47	0.29	27.10	14.08	23.40	12.47	34.82
R3	5.31E+03	7.85	0.01	44.80	7.32E+03	343.10	0.38	31.42	4.67	4.85	11.23	22.72
Mean	5.57E+03	10.16	0.12	31.68	8.91E+03	267.00	0.26	26.00	10.43	15.53	11.00	28.19
Std. deviation	9.37E+02	2.11	0.10	12.16	2.18E+03	78.43	0.14	6.04	5.05	9.59	1.60	6.13

Zn, and Cr_{tot} showed positive correlations with Ni. Highly significant correlations (<0.01) were found between Mn-Zn and Hg-Zn, and significant correlations (<0.05) were also found between Hg-Mn, Hg-V, Cu-Mn, and V-Zn (Electronic Supplementary Material S1).

3.2.3 Heavy metal distribution after attrition scrubbing

Heavy metal concentrations in IF after attrition scrubbing were reported in Table 4, and the related correlation matrix was presented in the Electronic Supplementary Material S4. After treatment, Al correlated with Fe, Pb, and V. Negative correlations were also observed between As, Mn, Cu, and Zn, but As did not show any significant correlation in IF treated by soil washing (Electronic Supplementary Material S3). The element Cd was negatively correlated with Pb, while Cr_{tot} showed a positive correlation with Ni and a negative correlation with Zn after soil washing (Electronic Supplementary Material S3). The element Fe was correlated with Mn and V and with Mn and Cu. Unlike what observed for IF after soil washing (Electronic Supplementary Material S3), Hg did not show a significant correlation with any other heavy metal, while Pb was correlated with Al and Cd. The element V positively correlated with Al, Mn, Fe, and Cu after soil washing (Electronic Supplementary Material S3). Finally, Zn was negatively correlated with As, Cr_{tot}, and Ni.

4 Discussion

4.1 Bulk sediments

Previous studies (Miserocchi et al. 1993) indicated a sand percentage from 10 to 21% in the tidal inlet zone of the Candiano channel. These values were much lower than those detected in R and G samples, whose sand contents were 56 and 47%, respectively. The high percentages of sand in the Candiano channel are probably due to the specific sediment features. Recent stratigraphic studies (LIFE SEDI.PORT.SIL. 2011) reported that the Candiano channel sediments were characterized by a 3-m-thick sand layer at 2 m depth in the R site. According to these data, the G site showed a surface layer of silty clay of thickness 0.70 m and a layer of fine sand to a depth of 1.2 m, followed by thin layers of silt and sand. Finally, the Y site was characterized by a 1-m-thick layer of silty clay, followed by alternating layers of silt, clayey silt, and sand. The results of the textural analysis confirm the prevalence of sand in the red and green samples.

The observed heavy metal contents (Table 1) are lower than those measured by Matteucci et al. (2005) for Cd, Cu, Hg, Pb, and Zn near Pialassa della Baiona. These authors indicated an average value of 1.5 mg kg⁻¹ for Cd and a range of 66–75 mg kg⁻¹ for Cu, 24–70 mg kg⁻¹ for Hg, 43–47 mg kg⁻¹ for Pb, and 148–501 mg kg⁻¹ for Zn. In our samples, the average values were 0.16 mg kg⁻¹ for Cd, 17.9 mg kg⁻¹ for Cu, 0.22 mg kg⁻¹ for Hg, 10.5 mg kg⁻¹ for Pb, and

Table 4 Heavy metal contents in IF_{att} after attrition scrubbing

Heavy metals (mg kg ⁻¹)												
Sample	Al	As	Cd	Cr _{tot}	Fe	Mn	Hg	Ni	Pb	Cu	V	Zn
IF _{att}												
R1	5.05E+03	7.16	0.19	43.81	7.00E+03	370.00	0.42	33.17	4.84	4.15	11.18	22.67
R2	4.59E+03	7.46	0.19	49.28	6.21E+03	341.60	0.42	29.24	3.00	2.84	9.80	21.71
R3	5.27E+03	7.51	0.18	51.02	7.11E+03	360.20	0.50	32.03	3.53	3.72	11.42	21.08
Y1	4.60E+03	6.57	0.19	27.44	6.43E+03	368.10	0.50	23.90	2.71	4.54	10.12	27.49
Y2	4.85E+03	6.04	0.19	31.61	6.73E+03	408.40	0.30	24.73	4.01	5.07	10.69	28.43
Y3	5.99E+03	6.00	0.18	35.21	8.15E+03	430.20	0.30	30.38	3.99	5.75	13.87	31.28
G1	5.74E+03	6.38	0.19	24.43	7.11E+03	389.00	0.49	21.00	3.58	5.26	11.99	35.51
G2	5.99E+03	6.33	0.05	33.35	6.52E+03	321.39	0.55	20.21	5.73	3.38	9.57	32.52
G3	7.31E+03	5.82	0.12	49.22	9.37E+03	452.43	0.53	27.28	5.90	5.23	16.11	30.51
Mean	5.49E+03	6.58	0.16	38.37	7.18E+03	382.37	0.45	26.88	4.14	4.44	11.64	27.91
Std. deviation	8.76E+02	0.64	0.05	10.13	9.94E+02	42.05	0.09	4.70	1.13	0.98	2.13	5.12

38.8 mg kg⁻¹ for Zn. The average concentrations in bulk sediments measured in our samples were 0.16 mg kg⁻¹ for Cd, 17.9 mg kg⁻¹ for Cu, 0.22 mg kg⁻¹ for Hg, 10.5 mg kg⁻¹ for Pb, and 38.8 mg kg⁻¹ for Zn. These results may be easily explained based on the different depths at which sediments were sampled: Matteucci et al. (2005) analyzed heavy metals of sediments near the surface sediments, while we sampled sediments at depths up to 5–5.5 m. Other studies found a decrease of heavy metal concentrations with depth, for example, in Boston, USA (Bothner et al. 1998), in Naples, Italy (Adamo et al. 2005), in Port-en-Bessin, France (Caplat et al. 2005), and in Haiphong, Vietnam (Ho et al. 2012).

According to Chen et al. (2012), Hg content in sediments should not be related to particle size ($p > 0.05$). In the Candiano channel sediments, the low correlation between textural characteristics and Hg concentration is due to the anthropogenic origin of the metal (Misericocchi et al. 1993; Covelli et al. 2001; Fabbri et al. 2003; Matteucci et al. 2005). Excluding the Hg-specific distribution, our results of IF and FF before treatments are in agreement with those of Pétavy et al. (2009a), indicating a depletion of inorganic pollutants in the coarsest fraction (> 2000 μm) of all samples and a depletion of Cd, Cr, Cu, and Zn in the fractions between 80 and 2000 μm. The highest heavy metal values were recorded in the finest fraction (< 80 μm), as previously observed by Pétavy et al. (2009a). The concentrations of Al, Cr, Fe, Mn, Ni, Cu, V, and Zn are often associated with mineral lattice structures (Hornberger et al. 1999) or with fine particulate terrigenous sediments, due to weathering processes (Ni et al. 2009).

Correlations similar to those found in Ravenna Harbor for Al-Cr-V, Al-Cu-Fe-Cr, and Cr-Cu (Electronic Supplementary Material S1) were previously reported by Hornberger et al. (1999), Chen et al. (2007), and Xu et al. (2016). The fact that

Hg did not show a significant correlation with other heavy metals in IF and FF was also reported by Liao et al. (2009) and Xu et al. (2014–2016); these authors explained the result as due to the competition with mineral particles that have larger specific surface area (e.g., Fe, Mn, or Al hydroxides).

4.2 Textural and heavy metal changes induced by the treatments

The incomplete separation of sand and silt-clay fractions after soil washing is probably due to the diameter of the hydrocyclone used for separation (100 mm). Kim et al. (2016) showed that the separation efficiency was higher with an internal diameter of 50 mm in comparison to a diameter of 100 mm, especially for particle size of silt, clay, and very fine sand (from 0.001 to 0.1 mm), when the inflow flux velocity was constant, as it was in our tests. The same authors also suggested an operative condition of 60 kPa of pressure and 150 l/min as a flow rate for a 100-mm-diameter hydrocyclone (Kim et al. 2016), while we employed a pressure of 80 kPa and a flow rate of 67 l/min. This pressure had no negative effects on the separation of sand and fine particles, although it was higher than that recommended by Kim et al. (2016). The lower flow rate probably induced the incomplete separation of silt and clay from the sandy fraction (Wang and Wang 2012).

According to Jobin et al. (2015), after attrition scrubbing, the increase in fine size particles could be due to their positive correlation with the diameter of the sand introduced in the scrubber: the authors observed an increase up to 7% of fine particles for the 0.250–1 mm sand fraction and up to 10% for the 1–2 mm fraction.

In our tests, the IF_{att} showed an increase in fine particles from + 2.15% in G samples to + 3.54% in R samples.

Another interesting result is that the soil washing induced complete As removal. As previously detected for soil (Kumpiene et al. 2008), the behavior of As during ex situ treatment was mainly controlled by adsorption/desorption processes, redox processes, and co-precipitation with the metal oxides of Fe and, to a lesser extent, of Al and Mn.

Chloride, nitrate, and sulfate ions have no relation with changes in As concentration, but the presence of waste products (electrical semiconductors, insecticides, pesticides, weed controllers, industrial, and sewage materials or paint products) may inhibit the mobility of arsenical compounds (Livesey and Huang 1981; Sisir et al. 2007; Jang et al. 2016). It should be noted that the sediments treated in this study were polluted by benzo(a)pyrene, benzo(g,h,i)perylene, chrysene, and PCBs derived from industrial pollution and the total hydrocarbons produced by harbor traffic (LIFE SEDI.PORT.SIL. 2012). The mobility of As should therefore be affected also by these pollutants and by the precipitation of the As minerals during mechanical weathering.

The pH value strongly affects the solubility of heavy metals: a high pH promotes adsorption and precipitation while a low pH weakens the strength of metal association and prevents the retention of metals by sediments (Belzile et al. 2004; Guven and Akinci 2013). In our case, the lowest pH values were associated with the most polluted fractions before treatments (FF of red samples) that were automatically discarded by the plant and processed into pressed filter panels.

Bivariate plots of heavy metal concentrations versus sand percentage of each sample were used to identify correlations between heavy metals in sediment textures at each step of the treatments (Fig. 4). Three different trends could be identified. The first trend showed that heavy metal concentrations of bulk sediments were higher than in fractions after treatments: the plots therefore displayed a negative correlation of heavy metal concentrations against sand percentage. This trend was observed for Al, As, Fe, Pb, and Cu (Fig. 4) that were accumulated in the finest particles. A similar distribution has been observed in several studies as the result of sand

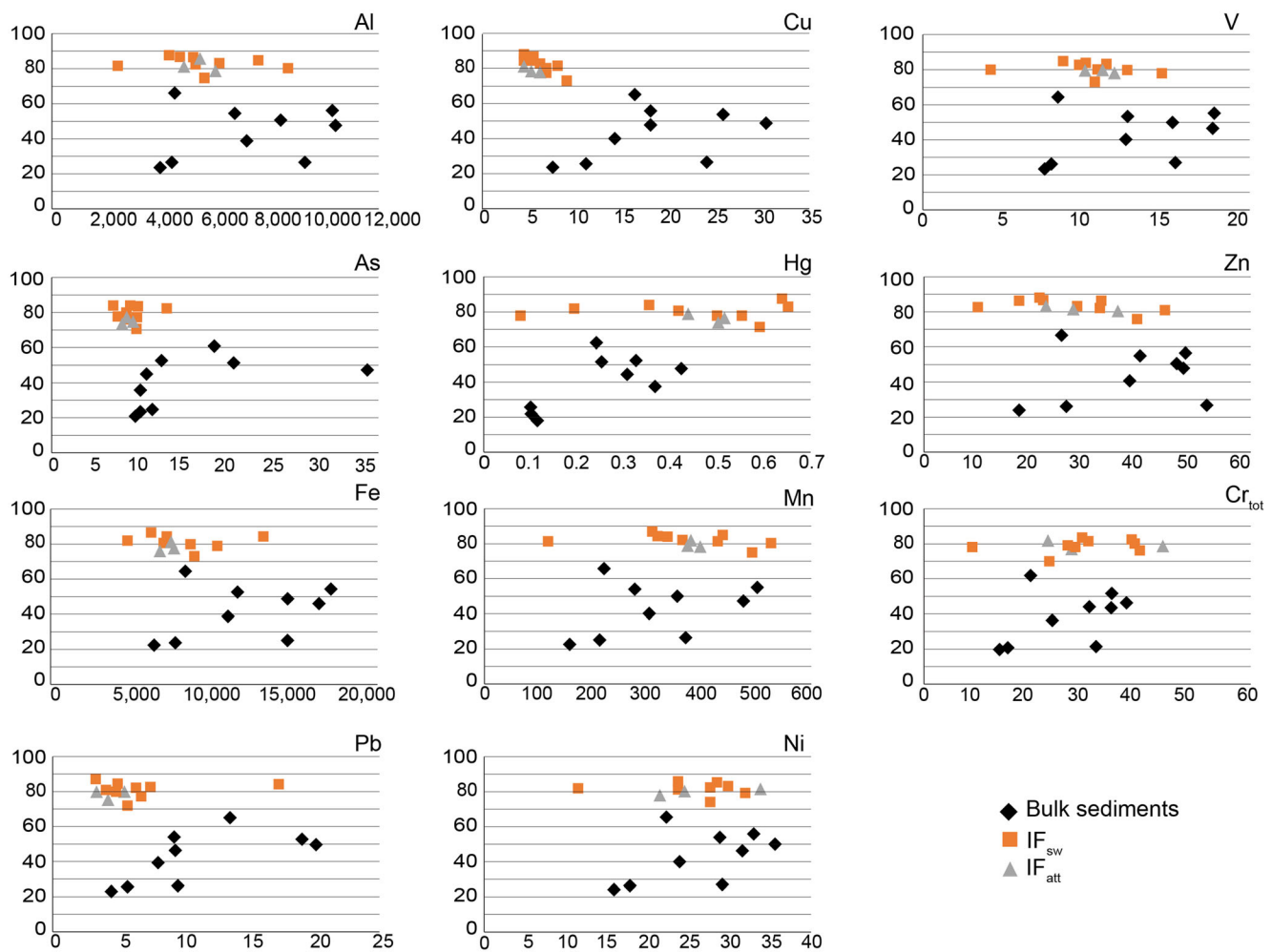


Fig. 4 Bivariate plots of heavy metal concentrations vs sand percentage for bulk sediments, IF after soil washing (IF_{sw}) and IF after attrition scrubbing (IF_{att})

decontamination during the treatment. For example, Williford et al. (1999) indicated a depletion of Pb in fine and very fine sand (fractions 2–4 ϕ) after hydro-classification treatment. They also reported a decrease of Pb between 7.1 to 1.5% in sands after the attrition scrubbing and therefore an increase of this metal in the fine particle fraction amounting to about 87% (Williford et al. 1999). Another study by U.S. Environmental Protection Agency (2002) in Winslow Township (New Jersey) reported a decontamination of bulk sediments to produce clean sands with a As concentration reduced by about 69% after soil washing. Mann (1999) performed several soil washing and attrition scrubber tests on soil, obtaining a Cu reduction and clean decontaminated sands.

The second trend showed a positive correlation between heavy metal concentrations after treatment and the sand percentage. Treated sands were enriched in Hg and Mn more than bulk sediments: this result could be explained based on the origin of sediments, because the metal contamination in industrial soils is usually distributed in the different particle size fractions (Yarlagadda et al. 1995; Dahlin et al. 2002). Furthermore, the high residence time, allowing to accumulate oxide coatings and associated metals, together with the presence of coarse fractions of dredged sediments, may be responsible for the level of metals in the coarse size fractions at the R site. In this case, separation based only on size could not accomplish a sufficient separation of metal contaminants. A separation based on density or floatability should therefore be investigated as suggested by Dermont et al. (2008).

In the third trend, the concentrations of bulk sediments and treated sands did not show any specific distribution for Ni, V, Zn, and Cr_{tot}: these heavy metals showed similar concentrations before and after treatment. Similar results were also reported by Pétavy et al. (2009b) in sediments from Cheviré Island (France), especially concerning the concentrations of Ni and Zn in fractions >2000 μm . However, our trend of Cr_{tot} was different from that reported by Williford et al. (1999), indicating Cr partitioning after attrition scrubbing.

5 Conclusions

We analyzed the distribution of heavy metals in sediments dredged near Ravenna Harbor after soil washing and attrition scrubbing. The main conclusions of our study may be summarized as follows:

1. The soil washing treatment, together with the attrition scrubbing, acts on the textural characteristics of the sediments due to the separation of sandy and clayey-silty fractions. This process represents an essential phase in decontamination protocol and reuse of the sediments, although the results of the textural analyses on the washed
2. The total metal content in the sandy and clayey-silty fractions confirmed the quality of the sediments for what concerned metal pollution. According to Italian laws, the only heavy metal pollution was that of As, which was identified in sediments from the inner part of the Candiano channel: the amount of As was completely removed by our treatments.
3. The comparisons of sandy fractions after soil washing and attrition scrubbing showed that heavy metal concentrations were altered by treatments. The results of correlation matrices supported the conclusion that the composition of heavy metals changed in each treatment step, affected by the grain size distribution. Comparing the sediments after soil washing and attrition scrubbing, an increase of the finer percentage clearly due to the abrasion of particles was detected.
4. The further separation of the finer fraction abrasion by sieving could be a suitable solution at an industrial scale. Consequently, the residual concentrations of contaminants and of clayey-silty particles may be completely eliminated.

For full-scale applications of soil washing and attrition scrubbing, further investigations are needed in order to evaluate the influence of the liquid/solid ratio and the operative conditions (hydrocyclone geometry, water recirculation and disposal, contaminated slurry separation after abrasion) and to assess the energetic and economic balance.

Acknowledgements The authors would like to thank Diemme Soil Washing Srl (Dr. D. Bettoli, Dr. D. Collini, and Dr. M. Contarini) and the Department of Physics and Earth Science of the University of Ferrara (Dr. U. Tessari for the particle size analyses of soil and Dr. F. Droghetti for the surveys and samplings). The study was co-funded by LIFE SEDI.PORT.SIL. Project (LIFE 09 ENV/IT/000158). The authors also thank the project managers Dr. E. Ulazzi and Dr. L. Magagnini and the Ravenna Port Authority. Thanks are also due to Dr. M. Chicca for the help in the final revision of the manuscript. English editing by G. G. Buffett.

References

- Adamo P, Arienzo M, Imperato M, Naimo D, Nardi G, Stanzione D (2005) Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. *Chemosphere* 61(6): 800–809. <https://doi.org/10.1016/j.chemosphere.2005.04.001>
- Agius SJ, Porebski L (2008) Towards the assessment and management of contaminated dredged materials. *Integr Environ Assess Manag* 4(2): 255–260. https://doi.org/10.1897/IEAM_2007-058.1
- Alebic-Juretic A (2011) Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006. *Mar Pollut Bull* 62(4):863–869. <https://doi.org/10.1016/j.marpolbul.2011.01.035>
- Anderson R, Rasor E, Van Ryn F (1999) Particle size separation via soil washing to obtain volume reduction. *J Hazard Mater* 66(1-2):89–98. [https://doi.org/10.1016/S0304-3894\(98\)00210-6](https://doi.org/10.1016/S0304-3894(98)00210-6)

- Antizar-Ladislao B (2008) Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. A review. *Environ Int* 34(2):292–308. <https://doi.org/10.1016/j.envint.2007.09.005>
- Bayley RW, Biggs CA (2005) Characterisation of an attrition scrubber for the removal of high molecular weight contaminants in sand. *Chem Eng J* 111(1):71–79. <https://doi.org/10.1016/j.cej.2005.05.009>
- Belzile N, Chen Y-W, Gunn JM, Dixit SS (2004) Sediment trace metal profiles in lakes of Killarney Park, Canada: from regional to continental influence. *Environ Pollut* 130(2):239–248. <https://doi.org/10.1016/j.envpol.2003.12.003>
- Bhosle NB, Garg A, Harji R, Jadhav S, Sawant SS, Krishnamurthy V, Anil C (2006) Butyltins in the sediments of Kochi and Mumbai harbours, west coast of India. *Environ Int* 32(2):252–258. <https://doi.org/10.1016/j.envint.2005.08.020>
- Bisone S, Mercier G, Blais JF (2013) Decontamination of metals and polycyclic aromatic hydrocarbons from slag-polluted soil. *Environ Technol* 34:2633–2648
- Blott SJ, Pye K (2001) Technical communication Gradistat: a grain size distribution and statistics package for the analysis of unconsolidated sediments. *Earth Surf Process Landsf* 26(11):1237–1248. <https://doi.org/10.1002/esp.261>
- Bothner MH, Buchholtz ten Brink M, Manheim FT (1998) Metal concentrations in surface sediments of Boston Harbor—changes with time. *Mar Environ Res* 45(2):127–155. [https://doi.org/10.1016/S0141-1136\(97\)00027-5](https://doi.org/10.1016/S0141-1136(97)00027-5)
- Caplat C, Texier H, Barillier D, Lelievre C (2005) Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. *Mar Pollut Bull* 50(5):504–511. <https://doi.org/10.1016/j.marpolbul.2004.08.004>
- Chen C-W, Chen C-F, Dong C-D (2012) Distribution and accumulation of mercury in sediments of Kaohsiung River Mouth, Taiwan. *APCBE Proc* 1:153–158. <https://doi.org/10.1016/j.apcbee.2012.03.025>
- Chen C-W, Kao C-M, Chen C-F, Dong C-D (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere* 66(8):1431–1440. <https://doi.org/10.1016/j.chemosphere.2006.09.030>
- Clozel B, Ruban V, Durand C, Conil P (2006) Origin and mobility of heavy metals in contaminated sediments from retention and infiltration ponds. *Appl Geochem* 21(10):1781–1798. <https://doi.org/10.1016/j.apgeochem.2006.06.017>
- Colacicco A, De Gioannis G, Muntoni A, Pettinao E, Poletti A, Pomi R (2010) Enhanced electrokinetic treatment of marine sediments contaminated by heavy metals and PAHs. *Chemosphere* 81(1):46–56. <https://doi.org/10.1016/j.chemosphere.2010.07.004>
- Corsini S, Onorati F, Pellegrini D (2007) Manuale per la movimentazione di sedimenti marini. ICRAM APAT. <http://www.isprambiente.gov.it/contentfiles/00006700/6770-manuale-apat-icram-2007.pdf>. Accessed 20 September 2016
- Covelli S, Faganeli J, Horvat M, Brambati A (2001) Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). *Appl Geochem* 16(5):541–558. [https://doi.org/10.1016/S0883-2927\(00\)00042-1](https://doi.org/10.1016/S0883-2927(00)00042-1)
- Dahlin CL, Williamson CA, Keith Collins W, Dahlin DC (2002) Sequential extraction versus comprehensive characterization of heavy metal species in brownfield soils. *Environ Forensic* 3(2):191–201. <https://doi.org/10.1006/enfo.2002.0090>
- Dermont G, Bergeron M, Mercier G, Richer-Lafleche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. *J Hazard Mater* 152(1):1–31. <https://doi.org/10.1016/j.jhazmat.2007.10.043>
- European Community (1991) Council Directive 91/676/EEC of 31 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. <http://eur-lex.europa.eu/eli/dir/1991/676/oj>. Accessed 10 August 2017
- European Community (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. <https://www.ecolex.org/details/legislation/directive-200060ec-of-the-european-parliament-and-of-the-council-establishing-a-framework-for-community-action-in-the-field-of-water-policy-lex-faoc023005/>. Accessed 20 October 2016
- European Environmental Agency (2011) Overview of contaminants affecting soil and groundwater in Europe. <https://www.eea.europa.eu/data-and-maps/figures/overview-of-contaminants-affecting-soil-and-groundwater-in-europe>. Accessed 14 August 2017
- Environmental Protection Agency (2007a) EPA 3051A microwave assisted acid digestion of sediments, sludges, soils, and oils. <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf>. Accessed 25 July 2017
- Environmental Protection Agency (2007b) Method 6010C (SW-846): inductively coupled plasma-atomic emission spectrometry, revision 3. <https://www.epa.gov/sites/production/files/2015-07/documents/epa-6010c.pdf>. Accessed 25 July 2017
- Fabbri D, Vassura I, Sun C-G, Snape CE, McRae C, Fallick AE (2003) Source apportionment of polycyclic aromatic hydrocarbons in a coastal lagoon by molecular and isotopic characterisation. *Mar Chem* 84(1–2):123–135. [https://doi.org/10.1016/S0304-4203\(03\)00135-X](https://doi.org/10.1016/S0304-4203(03)00135-X)
- Feng D, Lorenzen L, Aldrich C, Maré PW (2001) Ex situ diesel contaminated soil washing with mechanical methods. *Miner Eng* 14(9):1093–1100. [https://doi.org/10.1016/S0892-6875\(01\)00114-5](https://doi.org/10.1016/S0892-6875(01)00114-5)
- Folk RL, Ward WC (1957) Brazos River bar: a study in the significance of grain size parameters. *J Sediment Res* 27(1):3–26. <https://doi.org/10.1306/74D70646-2B21-11D7-8648000102C1865D>
- Galkus A, Joksas K, Stakeniene R, Lagunaviciene L (2012) Heavy metal contamination of harbor bottom sediments. *Pol J Environ Stud* 21:1583–1594
- Gibbs RJ (1993) Metals of the bottom muds in Townsville Harbor, Australia. *Environ Pollut* 81(3):297–300. [https://doi.org/10.1016/0269-7491\(93\)90212-7](https://doi.org/10.1016/0269-7491(93)90212-7)
- Gomes P, Valente T, Braga MAS, Grande JA, de la Torre ML (2016) Enrichment of trace elements in the clay size fraction of mining soils. *Environ Sci Pollut Res* 23(7):6039–6045. <https://doi.org/10.1007/s11356-015-4236-x>
- Griffiths RA (1995) Soil-washing technology and practice. *J Hazard Mater* 40(2):175–189. [https://doi.org/10.1016/0304-3894\(94\)00064-N](https://doi.org/10.1016/0304-3894(94)00064-N)
- Gül A, Kaytaz Y, Önal G (2006) Beneficiation of colemanite tailings by attrition and flotation. *Miner Eng* 19(4):368–369. <https://doi.org/10.1016/j.mineng.2005.09.046>
- Güven DE, Akinci G (2013) Effect of sediment size on bioleaching of heavy metals from contaminated sediments of Izmir Inner Bay. *J Environ Sci* 25(9):1784–1794. [https://doi.org/10.1016/S1001-0742\(12\)60198-3](https://doi.org/10.1016/S1001-0742(12)60198-3)
- He F, Zhang Y, Wang J, Yang Q, Wang H, Tan Y (2013) Flow patterns in mini-hydrocyclones with different vortex finder depths. *Chem Eng Technol* 36(11):1935–1942. <https://doi.org/10.1002/ceat.201300204>
- Ho HH, Swennen R, Cappuyns V, Vassilieva E, Van Tran T (2012) Necessity of normalization to aluminum to assess the contamination by heavy metals and arsenic in sediments near Haiphong Harbor, Vietnam. *J Asian Earth Sci* 56:229–239. <https://doi.org/10.1016/j.jseaes.2012.05.015>
- Hornberger MI, Luoma SN, van Geen A, Fuller C, Anima R (1999) Historical trends of metals in the sediments of San Francisco Bay, California. *Mar Chem* 64(1–2):39–55. [https://doi.org/10.1016/S0304-4203\(98\)80083-2](https://doi.org/10.1016/S0304-4203(98)80083-2)
- Jang YC, Somanna Y, Kim (2016) Source, distribution, toxicity and remediation of arsenic in the environment—a review. *Int J Appl Environ Sci* 11:559–581

- Jiang XM, Zhou LS, Liu JG, Han XX (2009) A model on attrition of quartzite particles as a bed material in fluidized beds. *Powder Technol* 195(1):44–49. <https://doi.org/10.1016/j.powtec.2009.05.009>
- Jobin P, Mercier G, Blais J-F, Taillard V (2015) Understanding the effect of attrition scrubbing on the efficiency of gravity separation of six inorganic contaminants. *Water Air Soil Pollut* 226(5):162. <https://doi.org/10.1007/s11270-015-2422-6>
- Kim J-O, Choi J, Lee S, Chung J (2016) Evaluation of hydrocyclone and post-treatment technologies for remediation of contaminated dredged sediments. *J Environ Manag* 166:94–102. <https://doi.org/10.1016/j.jenvman.2015.10.009>
- Kuhlman MI, Greenfield TM (1999) Simplified soil washing processes for a variety of soils. *J Hazard Mater* 66(1-2):31–45. [https://doi.org/10.1016/S0304-3894\(98\)00212-X](https://doi.org/10.1016/S0304-3894(98)00212-X)
- Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. *Waste Manag* 28(1):215–225. <https://doi.org/10.1016/j.wasman.2006.12.012>
- Lee P-K, Touray J-C, Baillif P, Ildefonse J-P (1997) Heavy metal contamination of settling particles in a retention pond along the A-71 motorway in Sologne, France. *Sci Total Environ* 201(1):1–15. [https://doi.org/10.1016/S0048-9697\(97\)84048-X](https://doi.org/10.1016/S0048-9697(97)84048-X)
- Legislative Decree n.152/2006 (2006) Legislative decree approving the code on the environment. Supplemento Ordinario alla Gazzetta Ufficiale della Repubblica Italiana, n.88, 14 April 2006
- Lepland A, Andersen TJ, Lepland A, Arp HPH, Alve E, Breedveld GD, Rindby A (2010) Sedimentation and chronology of heavy metal pollution in Oslo harbor, Norway. *Mar Pollut Bull* 60(9):1512–1522. <https://doi.org/10.1016/j.marpolbul.2010.04.017>
- Liao X, Li Y, Yan X (2016) Removal of heavy metals and arsenic from a co-contaminated soil by sieving combined with washing process. *J Environ Sci* 41:202–210. <https://doi.org/10.1016/j.jes.2015.06.017>
- Liao L, Selim HM, DeLaune RD (2009) Mercury adsorption–desorption and transport in soils. *J Environ Qual* 38(4):1608–1616. <https://doi.org/10.2134/jeq2008.0343>
- LIFE SEDI.PORT.SIL. (2011) Bibliographic review of Port of Ravenna sediments. Technical report of SediPortSil project—action 2—subaction2a, http://www.lifesediportsil.eu/it/publicazioni/i-report-del-progetto-sedi-port-sil_168c1.html. Accessed 26 July 2017
- LIFE SEDI.PORT.SIL. (2012) Sediment characterisation analysis report before the treatment. Technical report of SediPortSil project—action 3—subaction3b. http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=SEDI.PORT.SIL_proceedings_v01.pdf. Accessed 24 July 2017
- Livesey NT, Huang PM (1981) Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *J Soil Sci* 131(2):88–94. <https://doi.org/10.1097/00010694-198102000-00004>
- Mann MJ (1999) Full-scale and pilot-scale soil washing. *J Hazard Mater* 66(1-2):119–136. [https://doi.org/10.1016/S0304-3894\(98\)00207-6](https://doi.org/10.1016/S0304-3894(98)00207-6)
- Marino MA, Brica RM, Neale CN (1997) Heavy metal soil remediation: the effects of attrition scrubbing on a wet gravity concentration process. *Environ Prog* 16(3):208–214. <https://doi.org/10.1002/ep.3300160318>
- Matteucci G, Rossini P, Guerzoni S, Arcangeli A, Fonti P, Langone L, Miserocchi S (2005) Recent evolution of sedimentary heavy metals in a coastal lagoon contaminated by industrial wastewaters (Pialassa Baiona, Ravenna, Italy). *Hydrobiologia* 550(1):167–173. <https://doi.org/10.1007/s10750-005-4374-0>
- Mendoza CA, Cortes G, Munoz D (1996) Heavy metal pollution in soils and sediments of rural developing district 063, Mexico. *Environ Toxicol Water Qual* 11(4):327–333. [https://doi.org/10.1002/\(SICI\)1098-2256\(1996\)11:4<327::AID-TOX7>3.0.CO;2-B](https://doi.org/10.1002/(SICI)1098-2256(1996)11:4<327::AID-TOX7>3.0.CO;2-B)
- Mezencevova A, Yeboah NN, Burns SE, Kahn LF, Kurtis KE (2012) Utilization of Savannah Harbor river sediment as the primary raw material in production of fired brick. *J Environ Manag* 113:128–136. <https://doi.org/10.1016/j.jenvman.2012.08.030>
- Miserocchi S, Langone L, Guerzoni S (1993) The fate of Hg contaminated sediments of the Ravenna Lagoon (Italy): final burial or potential remobilization. *Water Sci Technol* 28:349–358
- Mulligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng Geol* 60(1-4):193–207. [https://doi.org/10.1016/S0013-7952\(00\)00101-0](https://doi.org/10.1016/S0013-7952(00)00101-0)
- Ni S, Ju Y, Hou Q, Wang S, Liu Q, Wu Y, Xiao L (2009) Enrichment of heavy metal elements and their adsorption on iron oxides during carbonate rock weathering process. *Prog Nat Sci* 19(9):1133–1139. <https://doi.org/10.1016/j.pnsc.2009.01.008>
- Peng J-F, Song Y-H, Yuan P, Cui X-Y, Qiu G-L (2009) The remediation of heavy metals contaminated sediment. *J Hazard Mater* 161(2-3):633–640. <https://doi.org/10.1016/j.jhazmat.2008.04.061>
- Pétavy F, Ruban V, Conil P (2009a) Treatment of stormwater sediments: efficiency of an attrition scrubber—laboratory and pilot-scale studies. *Chem Eng J* 145(3):475–482. <https://doi.org/10.1016/j.cej.2008.04.039>
- Pétavy F, Ruban V, Conil P, Viau JY (2009b) Attrition efficiency in the decontamination of stormwater sediments. *Appl Geochem* 24(1):153–161. <https://doi.org/10.1016/j.apgeochem.2008.09.014>
- Peters RW (1999) Chelant extraction of heavy metals from contaminated soils. *J Hazard Mater* 66(1-2):151–210. [https://doi.org/10.1016/S0304-3894\(99\)00010-2](https://doi.org/10.1016/S0304-3894(99)00010-2)
- Ravenna Port Authority (2017) <http://www.port.ravenna.it/wp-content/uploads/2017/02/Ravenna-IT-2016-Trim-4.pdf>. Accessed 13 August 2017
- Romano E, Ausili A, Zharova N, Celia Magno M, Pavoni B, Gabellini M (2004) Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. *Mar Pollut Bull* 49(5-6):487–495. <https://doi.org/10.1016/j.marpolbul.2004.03.014>
- Simonini R, Ansaloni I, Cavallini F, Graziosi F, Iotti M, Massamba N'Siala G, Mauri M, Montanari G, Preti M, Prevedelli D (2005) Effects of long-term dumping of harbor-dredged material on macrozoobenthos at four disposal sites along the Emilia-Romagna coast (northern Adriatic Sea, Italy). *Mar Pollut Bull* 50(12):1595–1605. <https://doi.org/10.1016/j.marpolbul.2005.06.031>
- Simpson CD, Mosi AA, Cullen WR, Reimer KJ (1996) Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. *Sci Total Environ* 181(3):265–278. [https://doi.org/10.1016/0048-9697\(95\)05026-4](https://doi.org/10.1016/0048-9697(95)05026-4)
- Sisr L, Mihaljević M, Ettlér V, Strnad L, Šebek O (2007) Effect of application of phosphate and organic manure-based fertilizers on arsenic transformation in soil columns. *Environ Monit Assess* 135(1-3):465–473. <https://doi.org/10.1007/s10661-007-9666-6>
- Stražičar J, Sešelj A (1999) Attrition as a process of comminution and separation. *Powder Technol* 105(1-3):205–209. [https://doi.org/10.1016/S0032-5910\(99\)00139-4](https://doi.org/10.1016/S0032-5910(99)00139-4)
- U.S. Environmental Protection Agency (2002) Arsenic treatment technologies for solid, waste, and water. https://clu-in.org/download/remed/542r02004/arsenic_report.pdf. Accessed 13 June 2017
- Wang LZ, Wang JM (2012) Experimental study of the drag reduction and separation efficiency for a new hydrocyclone with a reducing pressure drop stick. *Sep Purif Technol* 98:7–15. <https://doi.org/10.1016/j.seppur.2012.07.008>
- Williford CW Jr, Li Z, Wang Z, Bricka RM (1999) Vertical column hydroclassification of metal-contaminated soils. *J Hazard Mater* 66(1-2):15–30. [https://doi.org/10.1016/S0304-3894\(98\)00213-1](https://doi.org/10.1016/S0304-3894(98)00213-1)
- Wu L, Long T, Lu X (2012) Improvement of separation efficiency and production capacity of a hydrocyclone. *Water Sci Technol Water Supply* 12(3):281–299. <https://doi.org/10.2166/ws.2011.083>
- Xu X, Cao Z, Zhang Z, Li R, Hu B (2016) Spatial distribution and pollution assessment of heavy metals in the surface sediments of the Bohai and Yellow Seas. *Mar Pollut Bull* 110(1):596–602. <https://doi.org/10.1016/j.marpolbul.2016.05.079>

- Xu J, Kleja DB, Biester H, Lagerkvist A, Kumpiene J (2014) Influence of particle size distribution, organic carbon, pH and chlorides on washing of mercury contaminated soil. *Chemosphere* 109:99–105. <https://doi.org/10.1016/j.chemosphere.2014.02.058>
- Yamagata T, Shozugawa K, Okumura R, Takamiya K, Matsuo M (2015) A study on redox sensitive elements in the sediments at dredged trenches in Tokyo Bay by instrumental neutron activation analysis. *J Radioanal Nucl Chem* 303(2):1179–1183. <https://doi.org/10.1007/s10967-014-3503-5>
- Yao Z, Li J, Xie H, Yu C (2012) Review on remediation technologies of soil contaminated by heavy metals. *Procedia Environ Sci* 16:722–729. <https://doi.org/10.1016/j.proenv.2012.10.099>
- Yarlagadda PS, Matsumoto MR, VanBenschoten JE, Kathuria A (1995) Characteristics of heavy metals in contaminated soils. *J Environ Eng* 121(4):276–286. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1995\)121:4\(276\)](https://doi.org/10.1061/(ASCE)0733-9372(1995)121:4(276))