

August 2009

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Recommended Citation

Gente, Vincenzo; Geraldini, Serena; La Marca, Floriana; Gabellini, Massimo; and Palombo, Francesco (2009) "Chemical-Physical Treatments Of Marine Contaminated Sediments – A Comparison," *International Journal of Soil, Sediment and Water*: Vol. 2 : Iss. 2 , Article 5.

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CHEMICAL-PHYSICAL TREATMENTS OF MARINE CONTAMINATED SEDIMENTS – A COMPARISON

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ABSTRACT

Managing of sediments coming from dredging operations in ports, harbor areas and navigation waterways has to deal with huge quantities of highly contaminated material. As a matter of fact, due to routine operations, to the need of deepening fairways and ports, and, eventually, to remediation activities, every year more than $200 \cdot 10^6 \text{ m}^3$ of dredged materials are produced throughout Europe.

Chemical-physical treatments are generally used in order to separate the contaminated fraction from the clean one in order to reduce the quantity of sediments to be disposed of.

Within this research work, carried out by the Department of Chemical Material Environment Engineering of Sapienza University of Rome and ISPRA (High Institute for Environmental Protection and Research), former ICRAM, sediments coming from a harbor area characterized by metal contamination have been treated adopting three different technologies: sieving, flotation, and hydro-cycloning.

Results show that sieving, flotation, and hydro-cycloning are able to separate products in which metal contaminants generally present lower concentrations compared to that of untreated dredged sediments.

Nevertheless, in order to further reduce metal content in the cleaned fraction, the examined treatment cannot stand alone as single step, but a multi steps or a combination of treatments have to be considered.

Keywords: sediment, remediation, sieving, flotation, hydro-cyclone

1. INTRODUCTION

In harbor areas, due to the scarce water flowing and to the strong presence of anthropic activities, contaminants can rapidly accumulate in sediments.

The Italian Ministry of Environment has classified 26 marine and brackish areas (Law 426/98, Law 388/2000, Law 179/02, D.M. 471/99, D.M. 468/01 and Budget Law 266/05) as “contaminated sites of national interest” (Figure 1) and has charged ISPRA (High Institute for Environmental Protection and Research), former ICRAM, of the definition of their characterization strategy.

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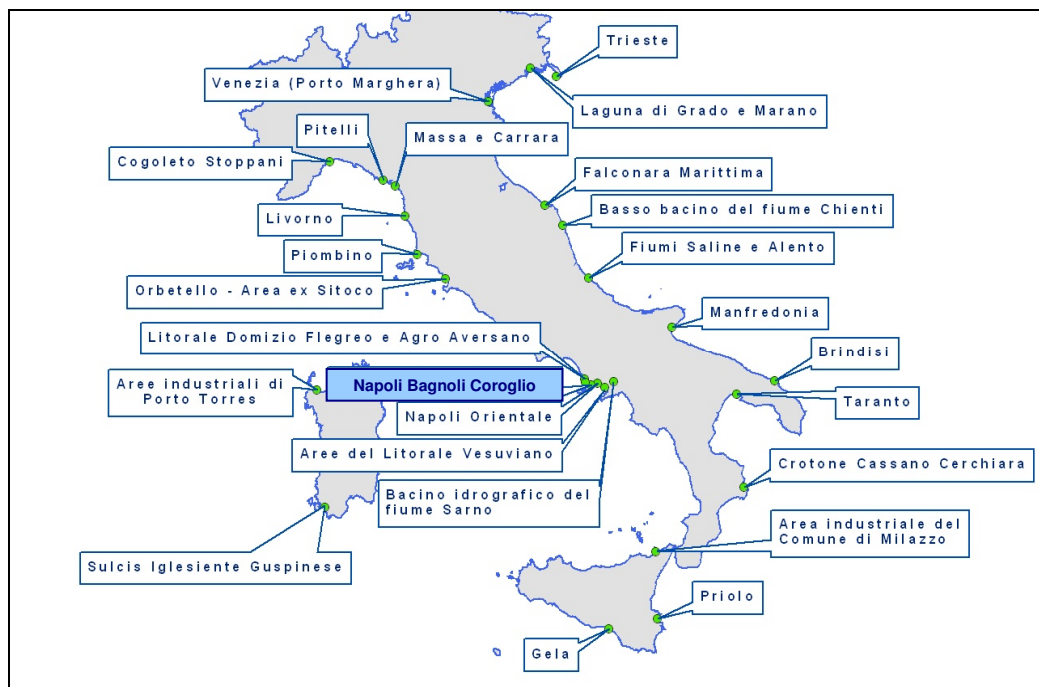


Figure 1. Contaminated Sites of National Relevance concerning sea areas.

These sites, distributed all along the Italian coast, are extremely heterogeneous for extension, geo-morphological characteristics, hydrodynamics, contamination history, and uses.

In compliance with the institutional assignment, due to the lack of a specific pertinent legislation, such as the Law 152/06 for soil, subsoil and groundwater, ISPRA has defined a systematic approach for defining a large scale characterization strategy for marine coastal and lagoon areas; the aim is to investigate the spatial distribution of contaminants in order to identify the hazard situations with respect to the different uses, and to define emergency actions and proper interventions for remediation and environmental restoration.

For the evaluation of sediment contamination and of the correspondent potential danger for the aquatic environment, ISPRA has defined different “action levels” for several coastal and marine water bodies highly modified due to past or present human activities (port areas, industrial areas, etc.). The action levels have been determined on the basis of a combined chemical and ecotoxicological criteria, and taking into account local geochemical and mineralogical characteristics. Therefore, they represent a very useful tool for the identification of the areas where intervention actions are urgently needed and for the selection of the most proper management options for the contaminated sediments of a specific area.

The characterization activities, carried out on the above described sites, have highlighted that coastal areas are the receptors of mineral or organic solid particles, coming from natural chemical and physical processes, and of contaminants, discharged by industrial effluents into water bodies, either sea, river or lake, that eventually build up in sediments.

In particular, in harbor areas, in order to preserve navigability, to protect coastlines from erosion and to reclaim contaminated sites, dredging operations take periodically place. Managing of sediments coming from dredging operations has to deal with huge quantities of highly contaminated material. As a matter of fact, due to routine operations, to the need of deepening

fairways and ports and, eventually, to remediation activities, every year more than $200 \cdot 10^6 \text{ m}^3$ of dredged materials are produced throughout Europe (source: www.sednet.org).

Generally, dredged contaminated sediments, even in consideration of given standards or regulations, are not allowed to be free disposed in the aquatic system. Therefore, open water disposal and disposal into confined facilities (CDFs), that have been historically the principal managing options for dredged sediments (Olin-Estes and Palermo, 2001), as well as landfill disposal, cannot be taken into consideration without the precautionary adoption of treatments with the aims of separating a contaminated and a clean fraction. In this way it is possible to reduce the contaminated fraction of sediments for final disposal and to obtain a clean fraction that can be addressed for a beneficial re-use (e.g. civil works, coastal restoration).

As a matter of fact, dredged sediments can be submitted to chemical-physical processes for the separation of particles on the basis of size, density or surface chemistry differences (Olin-Estes and Palermo, 2001, Jones et al., 1998, Mulligan et al., 2001).

Within this research work, carried out by the Department of Chemical Material Environment Engineering of Sapienza University of Rome and ISPRA, former ICRAM, sediments coming from a harbor area characterized by inorganic contamination have been submitted to chemical-physical treatments. In particular, three different technologies have been tested: sieving, flotation, and hydro-cycloning. The tests have been conducted in lab-scale under different operation conditions.

Dredged sediments and the fractions obtained by laboratory treatments have been analyzed by Inductively Coupled Plasma-mass Spectrometry (ICP-AES) for determining the metal content. Moreover, size-distributions have been determined in order to correlate the efficacy of the chemical-physical treatments with grain-sizes and contamination.

2. MATERIALS AND METHODS

Sediments were collected during dredging operations in the Bagnoli area, that is located near the city of Naples, in the center of Italy, and is included in the 26 marine and brackish sites classified as contaminated sites of national interest.

After dredging, sediments have been preserved in plastic drums. In order to obtain the proper amount of sediments, samples of dredged material have been collected from the drums, after homogenizing.

2.1 Analysis and characterization

Physical and chemical analyses have been carried out in order to characterize the dredged sediments before laboratory tests.

2.1.1 Size-distribution analyses

Collected dredged sediments and products coming from the different treatment tests have been analyzed by manual sieving and, for particles with dimension $< 63 \mu\text{m}$, by laser granulometer SYMPATEC HELOS/KA.

The results of the size-distribution analyses for the dredged sediment before treatment tests are shown in Figure 2, both in terms of size distribution and soil classification.

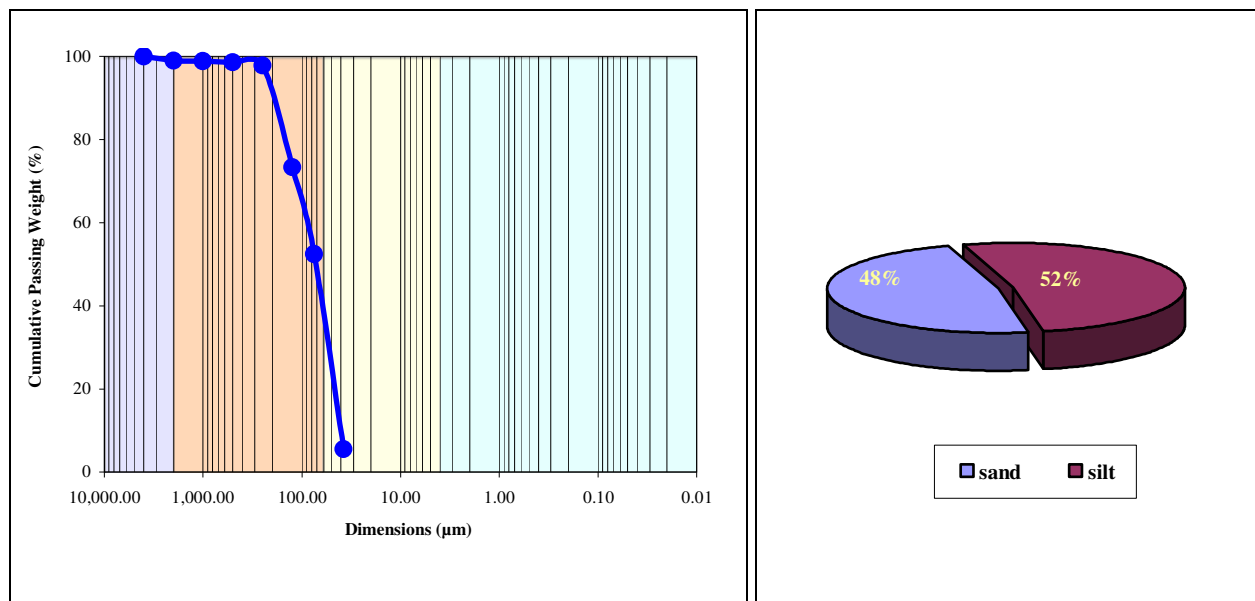


Figure 2. Size distribution and classification of dredged sediments.

2.1.2 Water content determination

The water content of the dredged sediments has been determined by mass loss, heating the sediments at 105 °C. The results have shown a water content of about 29,79% in weight.

2.1.3 Chemical analyses

In order to determine the metal content, single mineralization has been carried out on sediments' samples. The following metal species have been investigated: As, Ba, Cd, Cr, Fe, Mn, Hg, Ni, Pb, Cu and Zn.

The metal contents have been determined by Inductively Coupled Plasma-mass Spectrometry (ICP-OES), following the methodology EPA 3051A modified.

The mineralization procedure, adopted to determine the total metal concentrations on solids, has foreseen the microwave-assisted digestion of sediment using a Milestone mod. MLS1200 MEGA system. Half gram of sediments, after drying at 35 °C for 48 h, has been mill-ground and digested with 6 ml of HNO₃ and 9 ml of HCl in an advanced composite vessel. After cooling, the digested sediments have been put in a 50 ml volumetric flask and diluted to with distilled water.

As for Hg content determination, analyses have been carried out adopting thermal decomposition technique by DMA-80 (Direct Mercury Analyzer).

The average contents of metals, resulting from chemical analyses carried out on samples of dredged sediment, shown in Table 1, are compared with the ISPRA action levels, determined for the specific area.

Table 1. Average metal content in dredged sediment (the values above the action levels are highlighted).

Metals	Concentration (ppm)	ISPRA action levels
As	42.640	50
Ba	172.360	-
Cd	0.262	1
Cr	25.560	160
Fe	271700	-
Mn	2,023.663	-
Hg	0.174	0,7
Ni	11.560	60
Pb	215.226	160
Cu	25.797	65
Zn	523.870	300

2.2 Chemical-physical treatments

In order to assess the effectiveness of chemical-physical treatments in the separation of a contaminated and clean fraction of dredged sediments, three different technologies have been adopted for laboratory tests. In particular the collected sediments have been submitted to sieving, flotation tests, and hydro-cycling. These treatments have been selected since they can be carried out on wet sediments and, therefore, they can be realized as on-site treatments nearby costal areas or on mobile-platforms.

2.2.1 Sieving tests

Sieving tests have been adopted in order to separate sediments on the basis of grain-size. As a matter of fact, generally metal contaminants concentrate in fine fractions. Samples of dredged sediments have been classified adopting 2.00 mm, 125 μm and 63 μm sieves. The adopted sieves consist of stainless still woven wires. Sieving tests have been realized staking the sieves in a sieve shaker.

2.2.2 Flotation tests

Flotation processes allow to separate particulate materials on the basis of their superficial properties and can be also influenced by grain-size and grain density. In order to enhance the recovery of selected materials, reagents can be introduced to modify superficial properties of particulate materials (Vanthuyne and Maes, 2002; Vanthuyne et al., 2003, Cauwemberg et al., 1998). Flotation tests have been conducted adopting two flotation cells: a Minimet P1 flotation cell and a Denver 7320A flotation cell. In Table 2, operating conditions adopted for flotation tests are reported.

2.2.3 Hydro-cyclone tests

Hydro-cyclone has been adopted in order to separate sediments on the basis of density and grain size. A 50 mm hydro-cyclone Mozley C700 MK II has been adopted. A vortex finder of 14 mm and a spigot cap of 6.4 mm have been fixed; a pressure of 0.4 bar has been foreseen as operating condition. The adopted solid-liquid weight ratio has been equal to 1:15.

Table 2. Operating condition of flotation tests.

	Minimet cell		Denver cell	
	Cell volume	1 l	3 l	3 l
Solid-liquid weight ratio	1:1	1:3	1:3	1:3
Rotor velocity	1,200 rpm	1,200 rpm	1,500 rpm	1,500 rpm
Chemical reagents	-	-	pine oil	pine oil+amyl xanthate

3. RESULTS AND DISCUSSION

The products of the treatment tests have been analyzed in order to determine the metals' concentration and recovery. In this way it has been possible to compare the effectiveness of each adopted technology in concentrating metal contaminants and in separating as much as possible clean sediments, suitable for beneficial re-use (Jones et al., 1998).

From the sieving tests, four size classes have been obtained, but, also in consideration of Italian regulation on contaminated soil, the +2.00 mm size class has not been submitted to chemical analysis. Results of sieving tests are shown in Table 3.

Results highlight that most of the metals (Cd, Fe, Mn, Ni, Pb, Cu, and Zn) concentrate in the -63 μm fraction, and that it is possible to recover from 66% (Cd) up to 95% (Fe and Mn) of metals separating together the two size classes -125 μm +63 μm and -63 μm .

Also Cr concentrates in the -63 μm fraction, but results show that its content in the -2 mm +125 μm and -125 μm +63 μm fractions are comparable.

The remaining elements (As, Ba, and Hg) show an inverse behavior, because contaminants concentrate in the -2 mm +125 μm fraction.

Flotation tests carried out by means of Minimet cell have not given significant results in terms of separation contaminated and clean fractions.

Table 3. Results of sieving tests.

Metals	-2.00 mm +125 μm		-125 μm +63 μm		-63 μm	
	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
Weight	13.3 (%)		48.5 (%)		38.2 (%)	
As	56.666	21.436	37.318	51.503	24.943	27.061
Ba	223.955	17.089	170.410	47.442	162.067	35.469
Cd	0.431	33.860	0.149	42.707	0.104	23.433
Cr	84.769	12.621	82.956	45.062	99.097	42.317
Fe	64,062.500	4.270	161,923.000	39.379	294,754.000	56.351
Mn	950.647	5.613	2,070.468	44.599	2,940.252	49.788
Hg	0.960	26.802	0.640	65.190	0.100	8.007
Ni	10.928	10.420	13.032	45.337	16.177	44.242
Pb	218.272	12.723	222.604	47.340	238.882	39.936
Cu	13.959	8.156	19.034	40.571	30.599	51.273
Zn	373.370	8.243	606.803	48.875	677.263	42.883

Results of flotation test carried out by mean of Denver cell are shown in Table 4 and Table 5. In Table 4 results are reported for the test in which only pine oil has been used as reagent (*flotation test A*); Table 5 shows results for the test in which pine oil and amyl xanthate have been used (*flotation test B*).

In both flotation tests, metals, with the exception of Ba, Fe and Mn, concentrate in float products. As shows comparable concentration values in float and sink products in both tests. The metal recoveries in float products are in the range of 6.6-9.4% for flotation test A and 6.9-31.5% flotation test B, for those metals that concentrate in float products.

Hydro-cyclone process gives as results two products: an underflow, collected at the bottom of the device, and an overflow, collected at the top of the device. In order to recover all the materials, at the end of the test, it has been collected also the fraction that remains in the device as a tailing. In the underflow and tailings the coarse fraction collects, whilst the overflow contains a higher percentage of fine fraction. Results of Hydro-cyclone test are shown in Table 6.

Table 4. Results of flotation test A (Denver cell, reagent: pine oil).

	Float		Sink	
Weight	5.4 (%)		94.6 (%)	
Metals	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
As	42.616	5.139	45.282	94.861
Ba	97.377	3.336	162.399	96.664
Cd	2.001	8.731	1.204	91.269
Cr	49.380	8.702	29.822	91.298
Fe	18.643	3.283	31.618	96.717
Mn	1,671.035	4.181	2,204.680	95.819
Hg	1.555	6.677	1.251	93.323
Ni	29.154	8.342	18.438	91.658
Pb	274.616	7.502	194.900	92.498
Cu	37.558	9.373	20.903	90.627
Zn	683.213	6.585	557.930	93.415

Table 5. Results of flotation test B (Denver cell, reagent: pine oil+ amyl xanthate).

	Float		Sink	
Weight	5.1 (%)		94.9 (%)	
Metals	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
As	39.680	6.192	32.360	93.808
Ba	104.370	3.050	178.598	96.950
Cd	0.878	31.454	0.103	68.546
Cr	178.069	8.582	102.105	91.418
Fe	128,049.000	3.395	196,137.000	96.605
Mn	1,676.700	3.786	2,293.692	96.214
Hg	2.060	28.369	0.280	71.631
Ni	32.741	8.584	18.769	91.416
Pb	403.148	10.234	190.347	89.766
Cu	44.880	10.095	21.517	89.905
Zn	789.024	6.884	574.542	93.116

Table 6. Results of hydro-cyclone test.

	Overflow		Underflow		Tailings	
Weight	2.0 (%)		80.3 (%)		17.7 (%)	
Metals	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
As	33.077	0.812	96.276	92.936	29.398	6.252
Ba	161.902	1.632	209.089	82.846	177.839	15.523
Cd	5.711	0.561	25.609	98.930	0.598	0.509
Cr	55.549	0.416	316.916	93.277	97.272	6.307
Fe	149,325.000	1.227	296,464.000	95.747	42,533.067	3.026
Mn	2,151.108	1.277	3,704.724	86.490	2,378.580	12.233
Hg	1.320	1.058	2.500	78.804	2.900	20.138
Ni	14.712	1.428	21.989	83.926	17.419	14.646
Pb	191.959	0.512	907.551	95.125	188.945	4.363
Cu	21.519	0.791	63.130	91.232	25.058	7.977
Zn	602.832	0.805	1,743.870	91.585	657.779	7.610

Results highlight higher concentrations of metals for the underflow product and that recovery of materials in the overflow product is equal to about 2.0%. Hydro-cyclone test, in this case, allows to recover the contaminants in the coarse fraction, differently from sieving and flotation tests, and from generally experienced behavior.

In a previous work (Bambara et al., 2005), results of sieving and flotation tests conducted on marine contaminated sediments sampled in the harbor of Piombino, located in central Italy, included in the list of sites of national interest, confirm the results obtained in the present research.

In Tables 7 and 8, results of chemical analysis carried out on the collected sediments and on the products of separation tests are reported.

Table 7. Results of sieving test for sediments collected in a different area.

	Collected sediments	+53 μm		-53 μm	
Weight		36.3 (%)		63.7 (%)	
Metals	Conc. (ppm)	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
As	145.514	112.358	27.77	167.198	72.23
Cd	5.650	2.276	13.76	8.162	86.24
Cr	118.629	66.045	18.97	161.449	81.03
Hg	2.920	4.830	38.54	4.409	61.46
Ni	42.580	25.374	21.46	53.139	78.54
Pb	1,120.340	530.706	15.54	1,650.060	84.46
Cu	280.525	258.776	35.08	273.994	64.92
Zn	2,512.064	850.107	10.88	3,983.238	89.12

Table 8. Results of flotation test for sediments collected in a different area.

	Collected sediments	Float		Sink	
Weight		30.0 (%)		70.0 (%)	
Metals	Conc. (ppm)	Conc. (ppm)	Recovery (%)	Conc. (ppm)	Recovery (%)
As	145.514	151.827	33.60	128.590	66.40
Cd	5.650	8.370	47.64	3.942	52.36
Cr	118.629	136.042	31.57	126.390	68.43
Hg	2.920	6.594	50.46	2.774	49.54
Ni	42.580	46.246	28.16	50.560	71.84
Pb	1,120.340	1,471.645	36.93	1,077.000	63.07
Cu	280.525	253.994	28.65	271.060	71.35
Zn	2,512.064	3,967.825	41.30	2,416.903	58.70

4. CONCLUSIONS

The considered treatment tests have shown the possibility of separating products in which metal contaminants generally present lower concentration compared to that of untreated dredged sediments.

In particular:

- in the sieving test, the -2 mm +125 μm size class has resulted the cleanest fraction for Fe, Mn, Ni, Pb, Cu and Zn, that have been concentrated in the -63 μm size class;
- in the flotation tests, for both test A and B, the sink products have similarly resulted the cleanest fractions for the following metal contaminants: Cd, Cr, Hg, Ni, Pb, Cu and Zn;
- in the hydro-cyclone test, the overflow product always presents lower concentration for all the considered metal contaminants.

From results' evaluation it is possible to highlight that treatment processes, if singularly adopted, are able to reduce efficiently the metal contents, even if the ISPRA action levels are not reached. In Figure 3 the concentrations of selected metals (Ni, Pb, Cu and Zn) are shown and compared for the different treatment processes.

The considered treatment methods allow to separate, in each case, the contaminated fractions from clean ones, with different recovery percentage. In particular, with sieving and flotation processes it has been possible to reduce the quantity of the contaminated fraction to dispose of.

Nevertheless, in order to further reduce metal content in the clean fraction and enhance the quantity of the material for possible future uses, the examined treatments cannot stand alone as a single step, but a multi steps or a combination of treatments have to be considered. In particular, taking into account the low quantity of material selected in the clean fraction of hydro-cyclone test, it is possible to suppose a sequential process in which only sieving and flotation could be adopted.

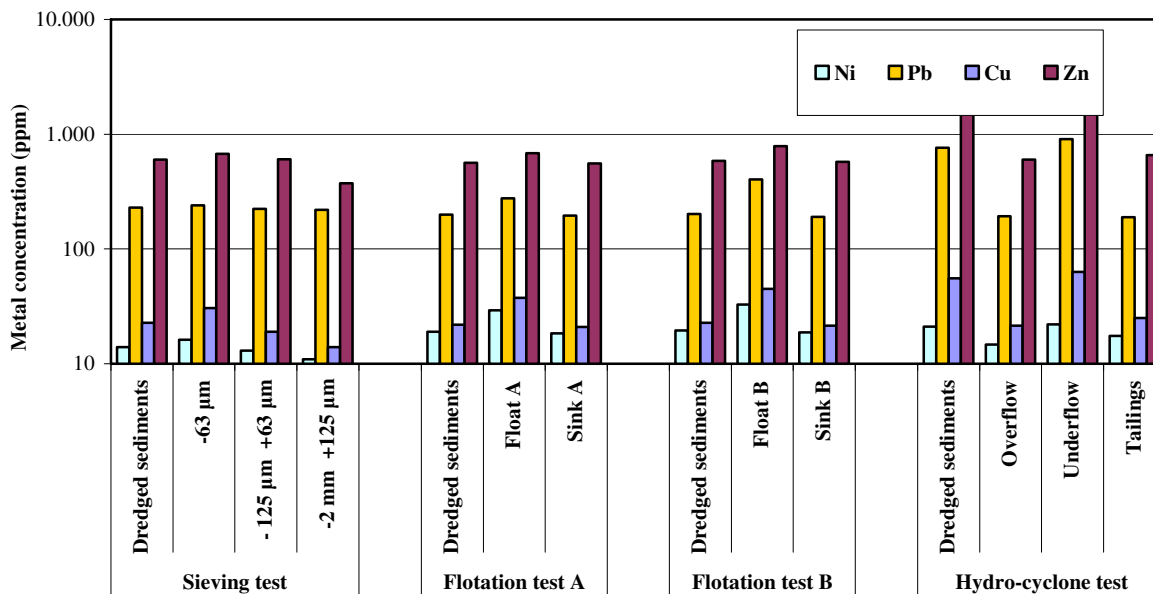


Figure 3. Comparison of results for considered treatment processes for selected metals (Ni, Pb, Cu and Zn).

On the basis of the results obtained in the lab tests, the dredged sediments could be firstly treated with a 63 µm sieve in order to separate the contaminated fine fraction and successively submit the coarse fraction to a flotation process. It would be therefore possible, considering the material percentage recovery obtained in the considered laboratory tests, to assume to attain a clean sediment fraction of about 60% in weight of the initial dredged sediments and a remaining fraction of 40% of contaminated sediments for final disposal.

The efficiency of the supposed process can be enhanced considering each metal contaminant separately and adopting specific operating conditions as for example different cut sizes, solid-liquid ratios and flotation reagents.

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