

SEDIMENT MINING: A SUSTAINABLE STRATEGY FOR CONTAMINATED SEDIMENTS

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ABSTRACT

The main dilemma of contaminated sediments has been the proper management with reduced environmental footprints. Furthermore, by considering the fact that global warming and climate change may complicate the choice of management options, finding appropriate solutions become extremely critical. In the present work, mining of contaminated sediments to recover valuable constituents such as metals and nutrients is proposed as sustainable strategy, both through enhancing resilience of ecosystem and remediation. Contaminated sediments in the Oskarshamn harbor, southeast of Sweden were collected and analyzed through a modified sequential extraction in order to evaluate the feasibility of metals recovery. The results have shown that among different metals present in the sediments, Cu and Pb can be initially considered as economically feasible to recover. The shifting in the concept of dredging and further remediation of contaminated sediments towards sediment mining and recover of valuable metals can be considered in the near future as a sustainable strategy to tackle contaminated harbor/ports areas. However, it must be highlighted that short and long-term environmental impacts related to such activities should be addressed.

KEYWORDS

Sediments mining, sustainable, valuable metals, recovery, speciation, environmental footprint, harbor

1 INTRODUCTION

The former and ongoing urbanization and industrialization in estuarine and coastal areas coincide with increased frequency of emerging environmental pollution. Although novel technologies have been developed, handling of contaminated sediments even after operation of remedial actions can be more challenging since a number of factors and environmental stressors are

involved during and after remediation processes. Moreover, despite of biogeochemical and physical parameters of contaminated sites, variability of external drivers, such as climate changes, needs to be accounted. As an example, climate changes play significant role on mercury methylation and de-methylation rates [1, 2]. Additionally, changes in weather conditions have decreased the remediation efficiency by about 7% at abandoned mercury mining sites according to Kirchner et al., [3]. Based on alleviation of environmental footprints of the cleanup and reduction of environmental impacts, the term ‘sediment mining’ is proposed as follows (Fig 1). The process of excavation, treatment, extraction and recovery of valuable materials that have been accumulated in the bottom sediments can be defined as sediment mining.

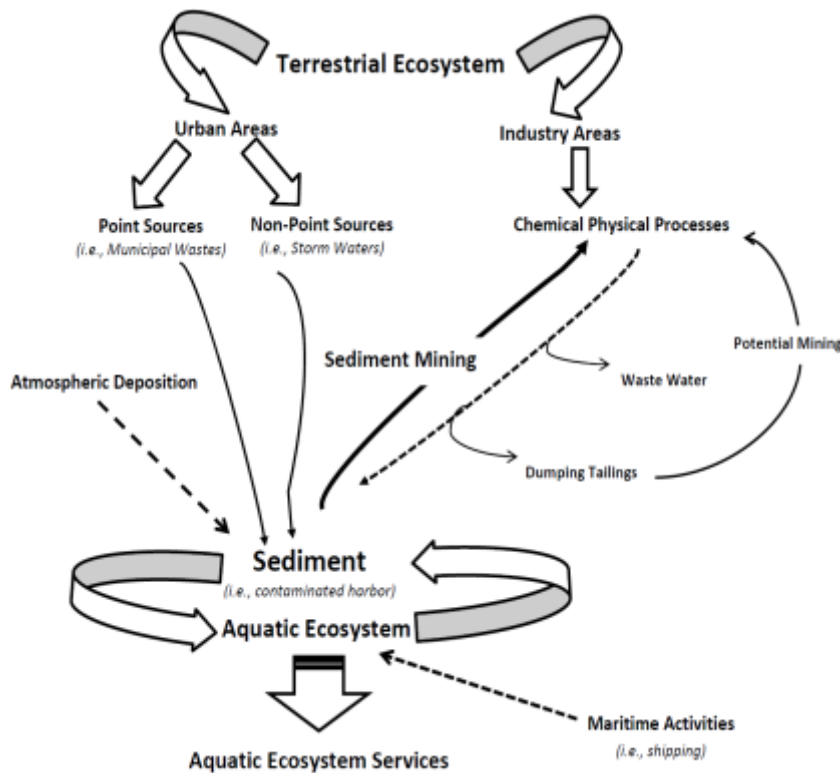


Figure. 1. Conceptual diagram of link between different closed loops (sediment, urban and industry areas, atmospheric deposition, maritime activities) and ways to return them to the closed loop system

Extraction and recovery of contaminants in bottom sediments, (Fig 1) can turn challenges into opportunities and cleaned sediments can be used as filling material for further construction on the site. Furthermore, sediment mining can be considered an environmentally feasible solution that could be applied for the removal of pollutants (i.e., valuable metals) and production of raw materials for metallurgy industries, simultaneously. There are around 80,000 contaminated sites in Sweden, and about 1000 are listed as priority to be remediated by the year of 2050 [4]. Oskarshamn harbor, the largest port along the coast of Småland, in Southeast of Sweden, is characterized as the highest priority site in the Kalmar County [5]. The bottom sediments at

Oskarshamn harbor are contaminated with both types of heavy metals such as Cu, Cd, As, Zn and Pb, and organic contaminants such as dioxin, PCB and organotin compounds [5]. Based on the fact that, sediments will be subjected to dredging [6], and further solidification/stabilization, this current study was focused on applying a modified sequential extraction procedure in order to have a better understanding on the metal speciation to provide preliminary information for decision makers on which metals could be appropriate to recover considering both environmental and economical points of view.

2 MATERIAL AND METHODS

The sediment samples were taken by a Van-Veer grabber sampler on 30th of May 2012, and every sample collected from each site, consisted of three composite samples. After homogenization and removal of large objects, air dried samples were powdered and passed through a 1mm stainless mesh sieve. Characterization of different fraction of metals from two sampling sites within Oskarshamn harbor area (O1 and O2) was carried by a three-step improved procedure, approved by BCR (Community Bureau of Reference, now SM&T) with digestion of the final residue of third step [7, 8]. The first fraction (F1) reflects metals in carbonates and exchangeable forms, F2 metals in oxides of Fe/Mn, F3 metals bounded to organic matter and sulphides, and residual (R) is remaining fraction (aluminosilicate minerals). The accuracy and consistency of the extraction procedure was evaluated through a pseudo-total digestion of the total content in the sediments [7, 8]. Metal content determination were measured by ICP-AES (Perkin Elmer, Optima), ICP-SFMS (Thermo, Element). Additionally a handheld XRF analyzer (Delta TM series/Olympus-USA) was used.

3 RESULTS AND DISCUSSION

The results obtained from the modified sequential extraction from the different samples taken in O1 and O2 are given in Table 1. It was found that sediments had significant quantities of highly enriched Cu, Pb, As, Cd and Zn. Furthermore, Cu concentration in O2 was found approximately 50 times more than Baltic pre-industrial values (Table 1) [9]. As a comparison, the Cu content in the ore mined at Aitik, Sweden is about 2500 mg.kg⁻¹ [10]. XRF values of metal analysis (except Cr, Cd, and Ni) showed strong correlation with total digestion and BCR-SEP methods, which means XRF handheld analyzer could be a reliable instrument for further operations and screening of sediments during dredging on-site. Also distributions of metal speciation (F1, F2, F3, and R) in Oskarshamn sediments are shown in Fig 2. Fractionation results indicated high proportion of Zn and Cd in exchangeable fraction (F1) which means due to relative higher mobility suggesting that these metals can be possibly release to the environment and result in environmental impacts and toxicity to aquatic organisms [11]. Furthermore, Pb and, Cu exhibited high affinity with Fe/Mn oxides and hydroxides (F2 = reducible fraction), which can raise some environmental concerns since depending on redox conditions; this fraction can be released from sediments. Among all investigated metals, As was considerably detected in the residual fraction (47% and 33% of the total content at O1 and O2 respectively), even though As highest contents were detected in F2 (66% and 51% of the total content at O1 and O2 respectively), which can be desorbed in highly acidic and reducing potential conditions [12]. The actual percentage of metals observed in F3 (oxidizable fraction) in comparison to the other fractions (F1, F2, and residual) was small probably due to relatively low organic matter, which analyzed by loss on ignition (LOI=10%) [13].

Element	ΣBCR-SEP		Total digestion		XRF		Elander Larson	& Baltic proper
	O1	O2	O1	O2	O1	O2		
As	147	176	202	201	197	216	35-363	9
Cd	6	8.29	7.34	9.04	<LOD	<LOD	13-18	0.31
Cr	52	62	60	70	111	111	ND	52
Cu	1011	2043	1217	2230	972	1843	418-1950	45
Ni	30	43	35	48	<LOD	<LOD	ND	39
Pb	953	844	1173	918	1023	838	235-1360	25
Zn	1794	2257	2314	2744	1744	2281	1240-4880	120

- Σ BCR-SEP = Σ (F1+F2+F3+R)
- Elander & Larson (2012)
- Baltic proper pre-industrial values (Borg and Jonsson, 1996)
- LOD = Limit of Detection
- ND = Not Detected

Table 1 - Metals concentration at each of the sampling sites in Oskarshamn (O1 and O2) based on sum of BCR-sequential extraction procedure (BCR-SEP), total digestion, XRF and compared to values by Elander and Larson (2012). (Values given in $\mu\text{g/g}$ dry weight).

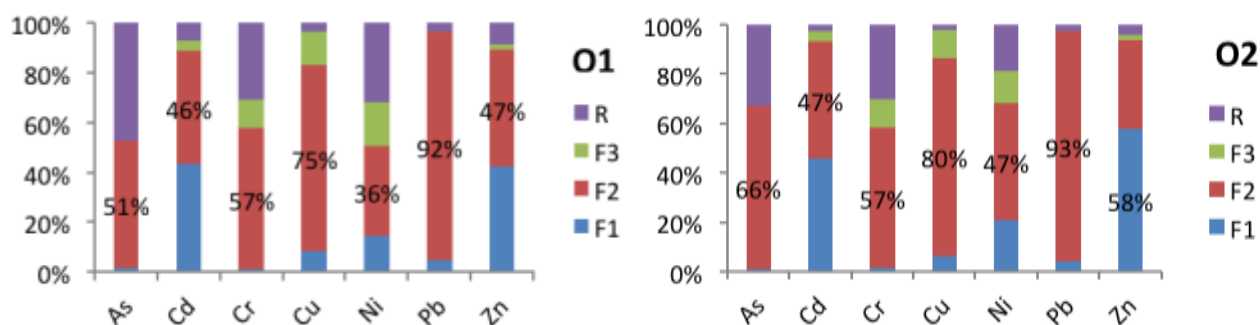


Figure 2 . The average percentage of element fractionation in Oskarshamn using modified BCR SEP method.

Oskarshamn sediments (as shown in Table 2) were classified according to quality criteria for dredged sediments in the Venice Lagoon [14]. Regarding to chemical characterization of dredged materials, Venice Protocol determines their disposal options to four different classes of quality (A, B, C and >C). Type A sediments (not polluted) are dredged materials that can be re-used in the lagoon for morphology restoration; class B sediments (slightly polluted) can be used to restore islands inside lagoon but should be controlled to avoid the release of contaminants; type C sediments (polluted) can be used for raising of new islands but must be controlled to minimize their contact with the environment; and finally sediments with higher concentration than limit for type C must be dumped outside and permanently controlled. In the present work, the collected sediments were in most cases classified as C and >C suggesting that according to the Venice

Protocol, treatment/remediation after dredging should be carried out in Oskarshamn in order to avoid toxicological effects of re-suspended contaminated sediments. Roberts [15] has reported that re-suspension of contaminated sediments is a frequent cause of incessant ecological risks to marine habitats. Even though, Elander & Larson [6] demonstrated that stabilized sediments can be used as low cost materials in the harbor, the criteria becomes even more critical when persistent organic pollutants are added to the list of potential stressors in which is the case of Oskarshamn that is known to have besides toxic metals, the presence of dioxin, PCB, and TBT [5, 16].

Element($\mu\text{g/g}$)	Oskarshamn Stations		Venice Protocol 1993			Classification	
	O1	O2	Class A	Class B	Class C	O1	O2
As	202	201	15	25	50	>C	>C
Cd	7.34	9.04	1	5	20	C	C
Cr	60	70	20	100	500	B	B
Cu	1217	2230	40	50	400	>C	>C
Ni	35	48	45	50	150	A	B
Pb	1173	918	45	100	500	>C	>C
Zn	2314	2744	200	400	3000	C	C

Table 2 – Classification of sediment samples according to Venice protocol for dredged sediments (Italian Ministry of the Environment, 1993).

4 CONCLUSIONS

Chemical analysis and speciation of As, Cd, Cr, Cu, Ni, Pb, and Zn in contaminated sediments, followed by a modified BCR sequential extraction procedure, total digestion and XRF handheld analyzer was studied. The results have shown that bottom sediments in the Oskarshamn harbor, southeast of Sweden had considerable levels of contamination in Oskarshamn raising environmental concerns and the clear necessity of designing and implementing sustainable management strategies are required. The use of dredged contaminated sediments as filler after stabilization has been proposed as a cost-effective method, however, it is important to highlight that it is still unclear the effectiveness of such methods when considering climate change outcomes such as increased amount of rainfall and rising water levels that can accelerate the risks of substances leaching into the environment (in particular, for countries such as Sweden which is located in Arctic region). Thus, the current work proposes excavation, extraction and recovery of valuable substances (sediment mining) from contaminated sediments before carrying out any final disposal action as a sustainable strategy. The first step of contaminated sediments mining should be a better understanding on which species metals are present and according to the current results Cu and Pb followed by As, Cr and Ni would be those metals to be focused in Oskarshamn for future mining. Cu and Pb were detected in relatively high concentrations emphasizing even more the selection of these two metals for further studies in mining feasibility. Whereas both metals had less than 10% of total concentration in the first fraction (mobile fraction), which can be easily released during dredging and re-suspension, more than 90% were available in the second and third fractions which can be subjected for recovering purposes through mediated

microbial and chemical mining. Distribution map of different contaminants in the Oskarshamn basin represent hotspots, thereby with respect to degree and type of contamination, selective mining for highlighted contaminants could be performed faster and efficient. Further investigation should focus on application of novel technologies to extract selected metals from contaminated sediments.

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