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Speciation of metals in contaminated sediments in the Kalmar County, Sweden:

An initial approach toward sediment mining

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Credits: 30 hp
Level: Advanced E
Course title: Independent project in Environmental Science – Master's thesis
Course code: EX0431
Programme/education: Soil and Water Management

Place of publication: Uppsala
Year of publication: 2012
Picture Cover: Oskarshamn harbor basin – Destination Gotland - © Homayoun Fathollahzadeh
Online publication: http://stud.epsilon.slu.se

Key Words: Sediment mining, harbor, semi-enclosed bay, speciation, metals, sequential extraction procedure, recovery, sustainable, environmental footprint, environmental assessment

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Abstract

In response to the growing numbers of contaminated sites, concerns about proper management with reduced environmental footprints have been raised. In the present study, mining of highly contaminated sediments to recover valuable elements such as metals and nutrients is proposed as sustainable approach, both through enhancing resilience of ecosystems and remediation, beside probable turnovers. Thereby, in order to evaluate feasibility of metal recovery, fractionation of thirteen heavy and trace metals (Fe, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn) in Oskarshamn harbor and Malmfjärden semi-enclosed bay surface sediments taken from five polluted locations in Kalmar County in southeast of Sweden was studied. The dissolution experiment by a modified BCR (Community Bureau of Reference, now SM&T) sequential extraction procedure (BCR-SEP) was used to determine the partitioning of elements. Oskarshamn and Malmfjärden sediments showed highest mobility for Zn and Cd, which can be leached out easily by small changes in environment conditions, whereas Al, Ba, and Hg in both sites, beside Cr and Fe in Malmfjärden exhibited high percentage in residual fraction. Moreover, total digestion results turn out that Oskarshamn in comparing to Malmfjärden sediments tended to result in larger contents of total extractable heavy metals (except Al), which is strongly attributed to factories, wastewater treatment plants, and ships traffic in Oskarshamn basin and diffusive sources in Malmfjärden. Despite the smaller magnitude of pollution in Malmfjärden relative to Oskarshamn, besides dredging and removal of sediments, in situ remediation techniques such as capping, using amendments and phytoremediation could be suggested. The results indicated that among different metals in the sediments, particularly in Oskarshamn, Cu and Pb followed by As, Cr and Ni can be considered for future sediment mining.

Keywords: Sediment mining, harbor, semi-enclosed bay, speciation, metals, sequential extraction procedure, recovery, sustainable, environmental footprint, environmental assessment

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1 – Introduction

Over decades, bay and harbor areas have been experienced a relatively rapid urbanization and industrialization where anthropogenic activities are leaking significant sources of waste to the environment and sediment. As consequence of hydrological, biogeochemical and erosion cycles, sediments are mostly final and major sinks of contaminants which after settlement likely can be distributed to water phase due to biogeochemical reactions or within mechanical operations by human. The magnitude of the pollution mainly could be influenced by shifting between "points" such as municipal-industrial wastewater effluents) and "non-points" such as run off, storm waters and atmospheric deposition sources, beside factors that are controlling amount of discharges separately. The excess concentrations of contaminants in sediments, due to anthropogenic activities deteriorate aquatic flora and fauna, which in sequence, may affect human health in large scale. Primarily, in industrialized and relatively high density urban areas, metals pollution dominated and due to their potential adverse effects and bioaccumulation along the food chain requiring a great deal of action. In this context, according to Järup et al. (1995), found that resident living near a closed nickel-cadmium factory had higher urinary cadmium concentration than those inhabiting farther away which may cause kidney damage.

Although evaluation of total metal concentrations have been applied widely, on the other side single (Pérez et al., 2002; Arian et al., 2008), combined (Cappuyns et al., 2007; Maes et al., 2003) and modified (Nemati et al., 2011; Horváth et al., 2012; Guillén et al., 2012) extraction methods to present different fraction of metals have been vastly improved. Even though total metal concentrations are still used as indicator for environmental assessment, they have not been developed to specify risk of exposure and bioavailability by their specific fractions to environment. Hence, to determine and quantify different forms inside a complex matrix such as sediments, employing appropriate methods with fewer artifacts during extraction procedure are more essential than before. To the best of our knowledge, despite of numerous sequential extraction procedures (SEPs) that have been made, the 5-step SEP by Tessier (Tessier et al., 1979), short SEP by Maize(Maize et al., 1997), the 6-step Kersten-Förstner procedure(Kersten and Förstner., 1986) are the three most standard methods for speciation of metals in a range environmental materials. Although these procedures are well designed to study origin, fate and bioavailability of metals, evaluation of the data, due to operational variation during extraction such as quantity and quality of reagents, temperature, and time, do not show significant outputs of comparison at the end. For that reason, the European Standards, Measurements and Testing Program(SM&T); formerly the European Community Bureau of Reference (BCR) started to unify tested procedures for speciation of extractable trace metals (Ure et al., 1993; Rauret et al., 1999), which has been revised through a new three-step SEP and validated by certified reference material (BCR-701) for Zn, Ni, Cd, Cr, Cu and Pb (Rauret et al., 2001).

Development of Sweden as one of highly industrialized country in the world, has left about 80,000 contaminated sites which around 60,000 of these have been risk-assessed according to the industrial activity and 18700 according to the ‘‘MIFO’’ (i.e., the Method for Inventory of

Contaminated Sites) (Swedish EPA, 2011). There are approximately 925 sites in very high risk (risk class 1) and almost 4800 in the second highest class (risk class 2) (Swedish EPA, 2011). Since 1990, Swedish EPA as central national environmental authority is launching most of monitoring, assessment and remedial actions while in 2011 allocated SEK 635 million (around £ 63 million) for remediation of 30 contaminated sites. Additionally, 16 projects were in queue to receive contributions for a total of approximately SEK 700 million (Swedish EPA, 2011). These proceedings are related to the objective of a non-toxic environment to fulfill national environmental objectives (Swedish EPA, 2007). The Oskarshamn harbor (referred to simply as ”Oskarshamn” hereafter) in the Kalmar County, Sweden is the largest port along the coast of Småland and industrial activities has developed about one and half centuries ago. Since it is located in a forest area, the port is an important site in the region for exporting cut wooden goods, timber and pulpwood, beside has one of two available ferry stations to the largest island of Sweden, Gotland. The harbor basin area is about 1.5 Km^2 where sediments contaminated by activities carried out since the mid 1850’s. The contaminants found in the sediments in both types of heavy metals such as Cd, Cu, As, Zn and Pb, and organic pollutants such as dioxin, PCB and organotin compounds (Länsstyrelsen Kalmar län, 2010). The annual leakage from basin to Baltic Sea approximated to about 700 Kg Cu, 350 Kg As, 250 Kg Pb, and 20 Kg Cd (Länsstyrelsen Kalmar län, 2010). Tobassion (2012) concluded that overall ecological status of the basin is generally moderate to poor maybe due to highly polluted sediments and status of ship trafics that contributing to low level of oxygen. In addition, Andersson (2012) measured heavy metals and toxins in blue mussels (Mytilus edulis) between 2010 and 2011, and results showed elevated levels of Cd, Pb, Cu, PCBs, TBT and dioxins. Since the mid-1990s preliminary investigation started, Oskarshamn as highest priority (risk class 1) site in Kalmar County have been recognized for remedial actions (Länsstyrelsen Kalmar län, 2010). Investment decision is under progress and clean-up is expected to take about 3 years and is planned to be finished in 2015 (Länsstyrelsen Kalmar län, 2010). The second site, Malmfjärden as a semi-enclosed bay located in central part of Kalmar city, and with a relatively high population density provides services to the ecosystem and people in the region. Also traffic is dense, thus it is expected that level of pollution become higher than other area as well as storm waters discharges. Formerly, the bay had longer coastlines with Kalmar strait but later along city development and construction of Öland Bridge, ecosystem was subjected to changes in geomorphology and current regime. There is limited data about chemical and biological analysis of sediments and water in Malmfjärden. Moreover, in the priority list of contaminated sites in Kalmar County, Malmfjärden is not included, so comparing to Oskarshamn, at Malmfjärden less number of surveys are available (Länsstyrelsen Kalmar län, 2011).

A large number of studies have been developed for depollution objectives since contaminated sediment has become global problem. Generally, it categorized to in situ and ex situ remediation techniques where first aims at increasing the stabilization (i.e., by amendments, capping, phytoremediation, etc.); whereas the ex situ directed toward sediment removal from its origin medium (i.e., washing, electrochemical remediation, flotation, etc.) (Peng et al., 2009). With respect to Swedish environmental quality objectives, Sweden's environment should be free of toxic materials that cause damages to human health or biological diversity. Furthermore, Baltic Sea must have a sustainable product activity while industry, recreation and other utilization of the seas and coasts are appropriate with the advancement of sustainable development. Thereby to enhance ecosystem resilience, with respect to further development and planning strategies at both sites (i.e., shipping requirement in Oskarshamn and highly standard-safe swimming area in Malmfjärden), the term ‘‘sediment mining’’ is proposed through a closed loop system (Fig. 1). Sediment mining can be defined as the process of excavation, treatment and extraction of valuable materials in bottom sediments. It is well established that soon industries will face with challenges such as limited material resources, market, and environmental pressures; hence within closing the disrupted flows and return deposited metals in sediments by extraction and recovery methods, valuable resources can be created. As well, these in turn entail less risk of metal leaching and final treated sediments can be used as filling material for further construction on the site or beach nourishment. Together, these processes optimize functions of sediment, aquatic and terrestrial ecosystems within the system, besides providing services for a variety of organisms.

2. Aim

Based on the fact that, sediments in Oskarshamn will be subjected to dredging, capping, and further solidification/stabilization (Växjö land and environment court, 2012), the main aim of current study was focused on a detailed characterization of metal speciation by a modified sequential extraction procedure (SEP). Thus, data analysis of speciation results, prepare primary information for decision makers and involved parties on which metals could be appropriate to recover considering both environmental and economical points of view.

In addition, other specific of this study are:

- Assessment of sediments contamination by contamination factor (C_f) and degree (C_d)
- Calculation and compare pollution load indexe (PLI) and risk assessment code (RAC)
- Calculation of potential ecological risk factor (E_i) and potential risk index (E_{RI})
- Classification of sediment samples according to Swedish EPA values (coasts and seas)
- Classification of sediment samples according to Venice protocol (dredged materials)
- Statistical analysis

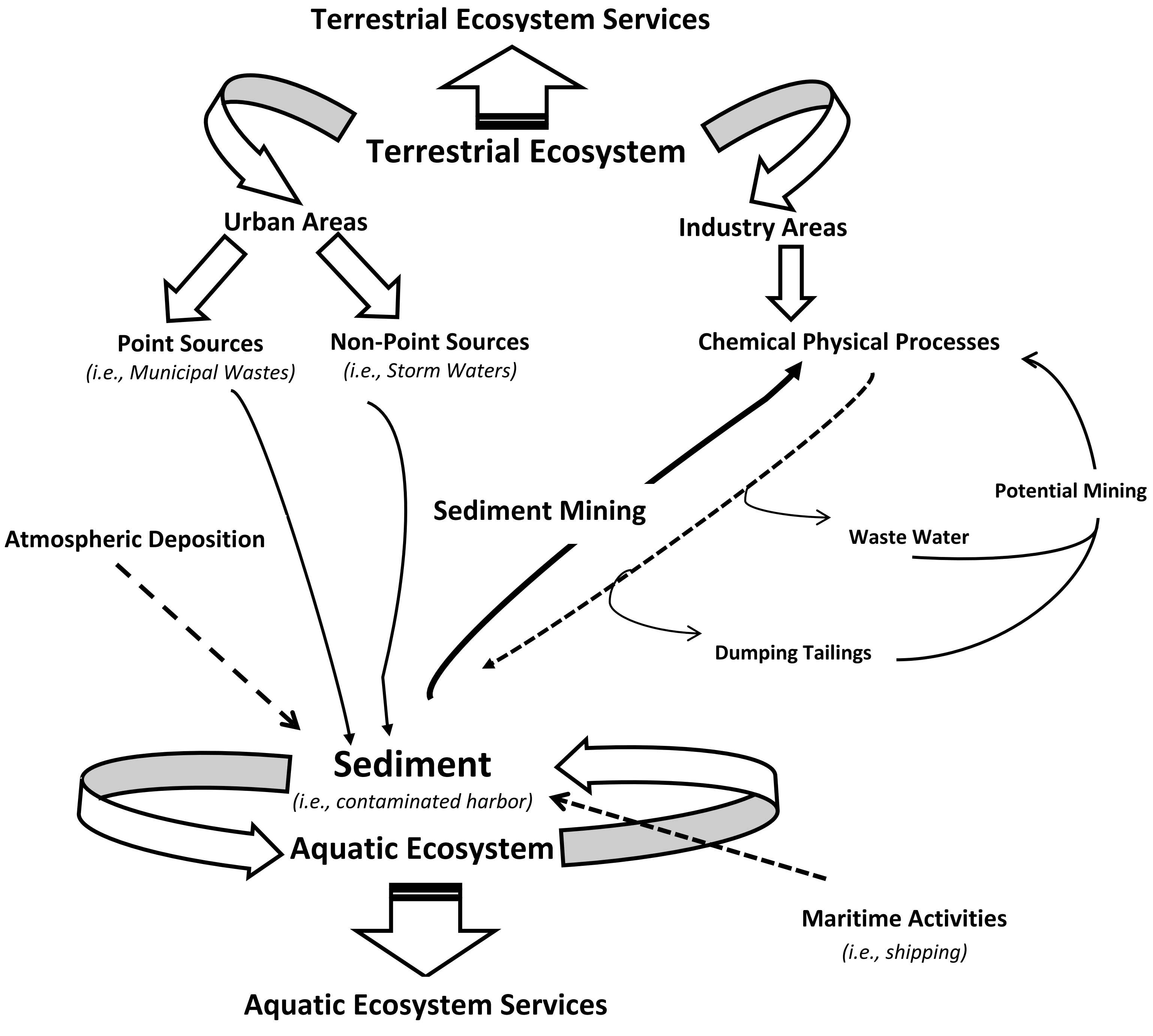


Fig. 1. Conceptual diagram of link between different closed loops (sediment, urban and industry areas, atmospheric deposition, maritime activities) and ways (sediment mining) to return them to the closed loop system

3. Experiment

3.1. Study areas

Oskarshamn is one of the fastest growing industrial cities in the Kalmar County. It is located about 65 km north of Kalmar which is the capital city in the County. Also it is about 30-Km south of one of active nuclear power plants (OKG) in Sweden. The area of Oskarshamn basin is approximately 1.2 km^2 and the estimated volume of contaminated sediments is about 700,000 m^3. Major industrial units in Oskarshamn include Ni-Fe/Ni-Cd batteries factory, copper board, heavy machines factory, shipyard, candle manufacture, press-steel industry, hardwood/timber factory, etc. In addition, one significant feature of Oskarshamn industry is planning for storage of spent nuclear fuel by OKG and SKB (Swedish Nuclear Fuel and Waste Management Company). The second study area located in Kalmar, with area about 1km^2, and on west side of Öland Bridge that connect Kalmar and Öland; second largest island in Sweden. With respect to southward currency in Kalmar strait and water levels the basin has three main connections from and to Baltic Sea. The bay has some small islands scattered around and are mainly occupied by protected bird's species such as gulls, coot, warblers, and dabbling ducks which nesting in reed belts and shallow muddy bottoms (Persson, 2011). In north of the bay, there is a small boat workshop that people before winter season repairing boats and using antifouling paint that normally made of zinc and copper oxides. Also, around one century ago, on the west side of the bay, a sport stadium and training fields was constructed on a landfill derived from sediments and might be have leakage of pollutant to the environment as well as discharged storm waters (Mistafa et al., 2006).

3.2. Sampling

To characterize different fraction of metals and their bioavailability in surface sediments, five sampling stations in Kalmar County were spotted and taken in May 2012. Two stations (O1, O2) were selected from Oskarshamn, one close to Copper factory and another in mouth of basin, and three stations (M1, M2, M3) were taken collected from Malmfjärden, a natural habitat for protected birds. (Table 1, Fig. 2). The sediment samples were taken by a Van-Veer grabber on 30th (Oskarshamn) and 31st (Malmfjärden) of May 2012, and every sample collected from each site, consisted of three composite samples. After homogenization and separating large object as gravel and residue of plants, the samples were stored in acid washed PE (Polyethylene) containers, covered by aluminum foil paper, labeled and kept cool by putting them in ice boxes. In the laboratory, after re-checking of large objects, samples air dried by a fume cupboard at room temperature. After that, dried samples powdered in mortar and pestle, then passed through a 1mm stainless mesh. The main physical difference between Oskarshamn and Malmfjärden samples was their color which surface of harbor's sediment there was about 1 cm orange - brown oxidized layer with black mud in bottom while at Malmfjärden sediments dominated with green and olive gray. (Fig. 3) Both sites mainly dominated by fine silt clay with moderate to high organic content. Estimation of organic matter contents based on loss on ignition (LOI, % dry weight) with different weight, temperature and time of ignition was applied to sediments (Luczak et al., 1997). The average LOI ranges increased from Oskarshamn to Malmfjärden (O1=9.7% O2=11%, M1=11.8%, M2=14.8%, M3=15.8%)

3.3. Reagents

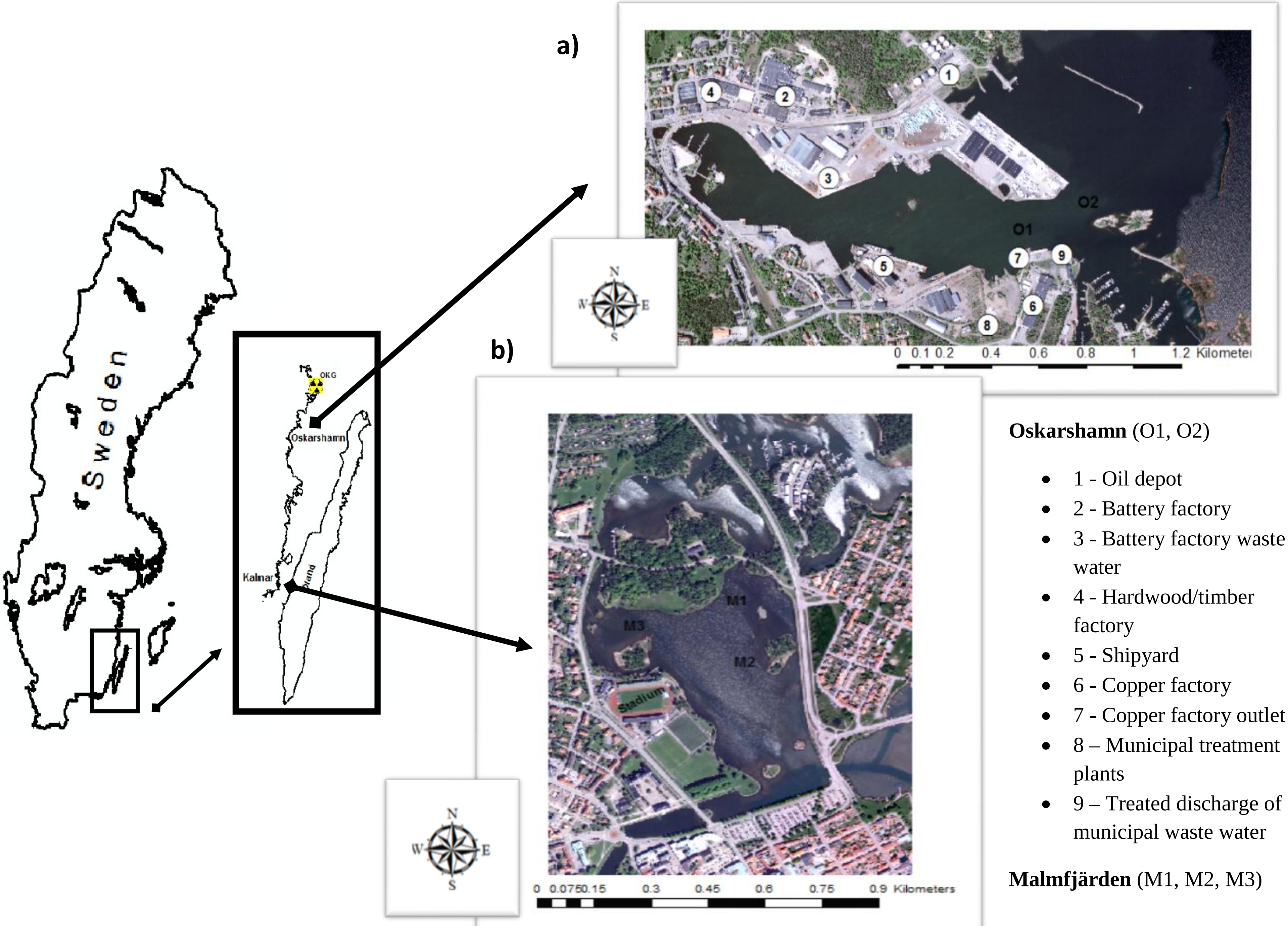
All dilution series were prepared with ultrapure water (Milli-Q Millipore 18.2 MΩ/cm resistivity). All reagents to perform extraction were analytical grade as described by following order: Acetic acid glacial, 0.11 M (100%, Scharlau Chemie S.A, Barcelona, Spain), hydroxyl ammonium chloride, 0.5 M (Scharlau Chemie S.A, Barcelona, Spain), hydrogen peroxide, 8.8M (30%, Scharlau Chemie S.A, Barcelona, Spain),ammonium acetate(Fisher Scientific, Loughborough, Leicestershire, UK) , nitric acid (65%, Scharlau Chemie S.A, Barcelona, Spain), hydrochloric acid (36%, Fisher Scientific, Loughborough, Leicestershire, UK) and hydrofluoric acid (40%, Scharlau Chemie S.A, Barcelona, Spain). Blank samples analysis showed small quantity of elements, which corrected for observed samples (Table 1SD). All tubes and glassware were cleaned by soaking in dilute HNO_3 (10%, v/v) over a night and were washed with Milli-Q and deionized water. Preparation of four solutions for extraction carried out according to the BCR three step SEP (Nemati et al., 2011; Rauret et al., 1999).

3.4. Apparatus

Metal content determinations were achieved by ICP-AES (Perkin Elmer, Optima) and ICP-SFMS (Thermo, Element) in certain types of samples. Calibration has been made by standard metal solutions in the laboratory. A centrifuge system (Beckman Avanti-J25) during extraction for separating of solid and liquid phases was applied. Acid washed polypropylene (PP) tubes used to store the supernatant extracts at each step.

Table 1 – Geographical locations and depth of sampling stations

Sampling stations	Latitude	Longitude	Depth(m)
O1	N 57° 15,757'	E 16° 28,551'	8.5-10
O2	N 57° 15,831'	E 16° 28,901'	13.5-15
M1	N 56° 40,324'	E 16° 28,841'	1
M2	N 56° 40,206'	E 16° 21,839'	1.1
M3	N 56° 40,276'	E 16° 21,606'	1.2



Oskarshamn (O1, O2)

- 1 - Oil depot
- 2 - Battery factory
- 3 - Battery factory waste water
- 4 - Hardwood/timber factory
- 5 - Shipyard
- 6 - Copper factory
- 7 - Copper factory outlet
- 8 – Municipal treatment plants
- 9 – Treated discharge of municipal waste water

Malmfjärden (M1, M2, M3)

Fig 2. Stations of sediment sampling in Oskarshamn (a) and Malmfjärden (b) with industries in Oskarshamn and stadium and training fields made on landfill in Malmfjärden
Data are derived from Lantmäteriet (Swedish mapping, cadastral and land registration authority)

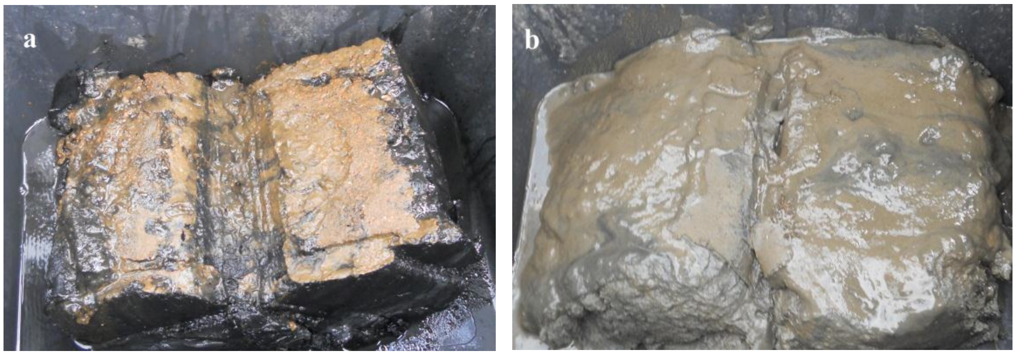


Fig 3. Sediment texture and color for Oskarshamn (a) and Malmfjärden (b)

3.5. Sediment total metal digestion

In order to evaluate accuracy and consistency of the method, total metal content of both areas along with fractionation of heavy metal by SEP was carried out. For each sample, 50 mL PP tubes filled with two portion of 0.5 g sediments and 10 mL mixture of aqua regia and HF (15 mL HNO_3+ 5 mL HCL + 2 mL HF) , and then heated in a sand bath heater (Nemati et al., 2011; Rauret et al., 1999). After digestion completed, supernatant from two tubes (totally 1g sediment with 20 mL solution) were filtered through Whatman filter paper (Ø110 mm, Munktell) into 50 mL PP tubes.

3.6. Sequential extraction procedure (SEP)

Extraction was performed by a three step improved procedure, approved by BCR with digestion the residue of third step (Nemati et al., 2011; Rauret et al., 1999). The productions of extracts were completed for 16 h (overnight) at ambient temperature, using a mechanical shaker. For detachment of liquid and solid phase, tubes were centrifuged at 3000 rpm for 20 min, and supernatant depleted into acid washed PP tubes. Remains of each step was rinsed by 20 mL of distilled water, shaken for 15 min on the end-over-end shaker, and centrifuged at 3000 rpm form min and the supernatant decanted very carefully to eliminate any of sediment particle. Prior to analysis, all tubes were stored in a refrigerator at 4 °C. Moreover, to evaluate stability and consistency of procedure during extraction and with samples, the SRM- CRM 701(Sediment Reference Material - Certified Reference Material) was purchased from The Institute for Reference Materials and Measurements (IRMM) and exposed to the same procedure.

3. 6. 1. Step 1 (acid extractable/exchange fraction - bound to carbonates)

As experiment carried out in duplicate, thus for each sample two portion 0.5 g dry sediment(total 1 g) were filled in a centrifuge tube while 20 mL of 0.11M acetic acid added which shaken for 16 h at room temperature. Then the leachate was separated by centrifugation, rinsed, shaken and stored in acid washed tubes as explained before.

3. 6. 2. Step 2 (reducible fraction - bound to Fe/Mn oxides)

Twenty milliliter of fresh hydroxyl ammonium chloride (pH adjusted to around 1.5 by adding of 2 mol/L HNO_3), was added to the residue of first step and shaken for 16 h at room temperature. After the time, the separation, storing and washing of residue were the same as outlined before.

3. 6. 3. Step 3 (oxidizable fraction – bound to organic matters and sulfides)

At this step, adding hydrogen peroxide to the residue of previous step carried out in two times. First acid stabilized to pH about 2-3, then 5 mL of solution, in small volume, carefully was added to the residue of step 2 in centrifuge tube. The loosely covered tube digested at room temperature for 1 h, subsequently digested for another 1 h at 85±2 °C in a water bath. After the time, tips of tubes removed and while heating was continued, initial volume decreased to about 2-3 mL. Then, another 5 mL pH adjusted hydrogen peroxide was added to the tube, covered and heated same as previous one until the volume reached to 2-3 mL. When tubes cooled, 25 mL of 1.0 M ammonium acetate was added and shaken for 16 h at room temperature. After the time, the separation, storing and washing of residue were the same as described before.

3. 6. 4. Step 4 (residual fraction – strongly associated to the crystalline structures of the minerals)

The residue from last step was digested with mixture of aqua regia and HF.

4. Results and discussion

4.1. Metal speciation in Oskarshamn

To study metal distribution in different fractions in Oskarshamn, sediments from two sites were collected in duplicate (O1-O2). The results of metal analysis in sediments of both sites at Oskarshamn are shown in Table 2. The variation of elements in different fractions is presented in Fig 4. The percentage of each fraction for each metal was calculated from the ratio between the concentration and the sum of concentrations in all fractions.

Table 2 – Metals concentration at each site in Oskarshamn

O1

Element (%)	F1	RSD (%)	F2	RSD (%)	F3	RSD (%)	R	RSD (%)	Three step + R	Total	RSD (%)	Recovery
Fe	3300	8%	66399	1%	413	13%	20912	3%	91023	117983	6%	77%
Al	169	9%	3280	0%	15.55	39%	9303	1%	12767	9154	30%	139%
As	2.29	12%	75.60	3%	0.01	33%	69.45	1%	147	202	5%	73%
Ba	5.67	8%	38.59	3%	5.14	9%	119	2%	169	117	15%	144%
Cd	2.59	6%	2.75	3%	0.25	7%	0.42	51%	6	7.34	1%	82%
Co	7.20	7%	12.42	1%	3.62	1%	12.42	1%	36	45.59	3%	78%
Cr	0.63	8%	29.59	0%	5.72	1%	16.17	6%	52	60.46	1%	86%
Cu	85.16	7%	756	1%	133	2%	37.35	1%	1011	1217	7%	83%
Hg	0.10	16%	0.39	5%	0.05	8%	1.08	1%	1.62	3.22	11%	50%
Mn	24.42	7%	33.56	1%	25.08	2%	128	3%	211	275	2%	77%
Ni	4.3	7%	10.70	1%	5.15	2%	9.38	3%	30	34.78	4%	85%
Pb	47.78	7%	872	0%	0.59	21%	32.28	16%	953	1173	6%	81%
Zn	758	6%	840	0%	42.35	8%	154	2%	1794	2314	3%	78%

O2

Element (%)	F1	RSD (%)	F2	RSD (%)	F3	RSD (%)	R	RSD (%)	Three step + R	Total	RSD (%)	Recovery
Fe	5242	27%	74999	1%	640	9%	18362	0%	99243	115083	3%	86%
Al	185	19%	3900	1%	42.88	44%	12048	0%	16176	11774	1%	137%

As	1.61	53%	116	3%	0.07	50%	57.98	3%	176	201	2%	87%
Ba	5.63	18%	46.45	4%	7.55	14%	118	9%	177	151	12%	117%
Cd	3.82	17%	3.92	1%	0.34	5%	0.21	6%	8.29	9.04	4%	92%
Co	9.60	15%	13.24	1%	3.69	4%	6.90	2%	33	38.49	4%	87%
Cr	0.98	26%	35.15	2%	7.10	6%	18.87	3%	62	69.66	1%	89%
Cu	129	16%	1640	1%	236	4%	38.03	0%	2043	2230	2%	92%
Hg	0.11	40%	0.35	7%	0.04	40%	1.66±	1%	2.17	3.27	0%	66%
Mn	23.94	14%	51.18	0%	33.80	4%	172	3%	281	368	3%	76%
Ni	9.02	16%	20.50	1%	5.55	4%	8.18	3%	43	47.78	4%	91%
Pb	35.38	15%	786	1%	2.18	12%	20.13	0%	844	918	3%	92%
Zn	1304	14%	812	1%	46.66	3%	94.44	4%	2257	2744	3%	82%

Mean and relative standard deviation (RSD %) of two samples for each station are shown.
F1: acid extractable/exchange fraction; F2: reducible fraction; F3: oxidizable fraction; R: residual fraction
The data are presented in µg/g dry weight.
Recovery (%) = [Σ (F1+F2+F3+R)/ (Total content)] ×100

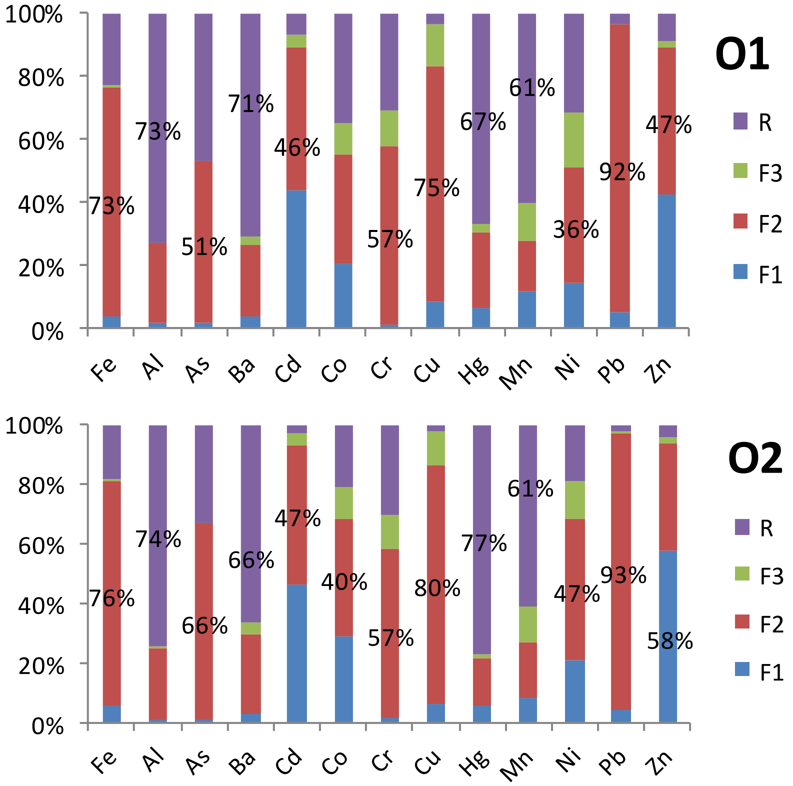


Fig 4. The average percentage of element fractionation in Oskarshamn using modified BCR SEP method (Highest percentage among fractions for each individual element is shown)

4.1.1. Extractable/exchange fraction (F1)

The first fraction of BCR method reflects metals which are weakly associated and bounded to carbonates and exchangeable fractions, so they indicate the pollution potential of metals that sediment stored from anthropogenic era. The result showed that Zn, among all metals in second station of Oskarshamn had the highest percentage (around 60% of the total content), and then Cd in both stations was the metal with more percentage in first fraction (more than 43% of the total content). It can be connected to copper complex and battery factory which release waste to the basin. These values are consistent with earlier studies where Cd and Zn showed high proportion of total content (Delgado et al., 2011; Guevara-Riba et al., 2004) where high proportion of easily soluble fraction could induce higher toxicity by these elements. Vasile et al., (2008) investigated Zn partition in the spring, summer and autumn at 11 sites and concluded most important part of total zinc accumulated in first fraction with few variation between different season, varied from 23-73% (average value for all samples, 45.4%). On the contrary, the percentage of mobile fraction for Ni and Co varied from 15 to 30% and the rest of the studied elements (Al, Cr< As< Ba< Fe< Pb<Hg<Cu<Mn) exhibited less than 12% of the total content.

4.1.2. Reducible fraction (F2)

In second step of SEP, association of metals with oxides and hydroxides of Fe and Mn was characterized. In both sites Pb was the largest proportion in reducible fraction (more than 90% of the total content), followed by Cu and Fe (75% to 80% and 73% to 76% of the total content respectively), which can be explained by large adsorption surface areas of Fe-Mn oxides/hydroxides (Passos et al., 2010). Moreover, significance amounts in reducible fraction for following elements in decreasing order have been found: Co<Zn<Ni<Cr<As. (35% to 66% of the total content). Overall, both sites except for major elements such as Al, Ba, Mn and Hg as trace metal (metalloid), indicated highest proportion in step 2 which based on Salomons (1995) overall mobility could be stirred through unstable oxygen status between sediment and overlaying water phase (e.g. Hypoxia) (Table 3). Additionally, in both sites, more than half of total As content (around 100 µg/g dry weight) exhibited in reducible fraction which can be desorbed by dissolution of Fe-Mn oxi/hydroxides in highly acidic and highly reducing potential conditions (Reczynski et al., 2004). Despite the dominant chemical reactions, studies by Beauchemin and Kwong (2006) also found that arsenic transformation and speciation can be microbially mediated.

4.1.3. Oxidizable fraction (F3)

Metals that bounded to organic matter and sulfides were presented as third fraction. Comparing to other fractions, oxidizable fraction showed smallest proportion, whereas the highest values belonged to Ni at first station, which had 17% of the total content. The obtained partitioning of metal in third fraction was probably due to relatively low organic matter in sediments, which analyzed through LOI estimation (O1=9.7%, O2=11%) as well as earlier decomposition of organic matter during sampling and treatment which was preserved by anoxic conditions in bottom of basin , thus this fraction redistributed and presented in second fraction.

4.1.4. Residual fraction (R)

Residual fraction values representing metals that are bounded to aluminosilicate minerals which have low mobility; hence impose less adverse effects on aquatic system. Amongst all fractions, the highest amount for Hg, Ba, Al and Mn indicated in their residual fractions (61% to 77% of total content), therefore, except Hg for Ba, Al and Mn can be relevant to natural origin in earth crust which released by weathering or erosion. Although recent Hg speciation analysis have been focusing on methods to determine Hg based on inorganic mercury (Hg^{2+}) and/or methyl mercury ($MeHg^{+}$) (Maggi et al., 2009), non-sulfide-bound Hg fraction (non-Hgs) and sulfide-bound fraction (Fernández-Martínez and Rucandio, 2003), and five different fractions (Bloom et al., 2003), on the other side applicability of modified BCR SEP was not studied well. In the present study, results showed that it can be applied at least to get overall estimate of residual and non-residual fraction of Hg in the total content which for mercury at both sites residual fractions was higher than sum of three fractions (non-residual).

Table 3 – Qualitative mobility and biological availability of trace metals (Revised from Salomons. 1995)

Metal species and association		Relative mobility
Exchangeable cations	**(F1)**	High - Changes in major cationic composition (e.g. estuarine environment, mono-divalent cations) may cause a release due to ion exchange
Metals associated with Fe-Mn hydroxides	**(F2)**	Medium - Changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present
Metals associated with OM phase	**(F3)**	Medium - Decomposition of organic matter by favorable conditions
Metals associated with sulphide phase		Strongly dependent on environmental conditions. Under oxygen-rich conditions, oxidation of sulfide minerals leads to release of metals
Metals fixed in mineral particles	**(R)**	Low. available after weathering or decomposition

4.2. Metal speciation in Malmfjärden

To study metal distribution in different fractions in Malmfjärden, sediments from three sites were collected in duplicate (M1-M2-M3). Additionally, comparison of data between Oskarshamn as harbor and Malmfjärden as a semi-enclosed bay distinguished geographical, natural and anthropogenic impacts on both sites. The results of metal analysis in sediments of selected sites at Malmfjärden are shown in Table 4. The variation of elements in different fractions is presented in Fig 5. The percentage of each fraction for each metal was calculated from the ratio between the concentration and the sum of concentrations in all fractions.

4.2.1. Extractable/exchange fraction (F1)

Metal retention by carbonate/exchangeable phase in Malmfjärden samples ranged between 27% and 48% and 29% - 39% of the total content for Cd and Zn respectively; whereas value for Cr was almost zero (all stations). Hence, mobility of the metal from this fraction in Malmfjärden was in order Cd>Zn>Co>As>Mn>Ni>Pb, Hg>Cu, Ba>Al, Fe. Interestingly, even though Oskarhamn sediments showed higher arsenic total concentration (about 20 times) rather than Malmfjärden but Comparing to Oskarshamn, As in F1 indicated higher percentage about 10 times which this implies that arsenic probably be more mobile in the semi-enclosed area than open basin.

Table 4 – Metals concentration at each site in Malmfjärden

							M1						
Element	**F1**	**RSD (%)**	**F2**	**RSD (%)**	**F3**	**RSD (%)**	**R**	**RSD (%)**	**Three step + R**	**Total**	**RSD (%)**	**Recovery (%)**	
Fe	176	10%	2798	2%	7101	3%	11130	0%	21205	27400	4%	77%	
Al	115	7%	2580±6	0%	697	5%	13300	1%	16692	18214	4%	92%	
As	1.78	4%	2.08	2%	1.50	8%	2.72	1%	8	10.17	2%	79%	
Ba	1.84	7%	12.41	3%	4.14	4%	105	8%	124	147	1%	84%	
Cd	0.54	7%	1.32	1%	0.05	72%	0.12	68%	2.03	2.11	3%	96%	
Co	1.87	5%	1.77	1%	2.31	0%	2.32	0%	8.27	9.62	4%	86%	
Cr	0.05	24%	3.33	9%	9.55	1%	18.27	7%	31	38.16	6%	82%	
Cu	0.56	7%	27.99	2%	14.06	0%	4.52	1%	47	48.40	1%	97%	
Hg	0.03	8%	0.26	5%	0.21	13%	0.39	11%	0.89	1.27	7%	70%	
Mn	25.60	4%	28.20	2%	53.78	2%	100	2%	208	259	3%	80%	
Ni	2.50	4%	5.06±	4%	8.31	0%	6.88	9%	23	24.28	4%	94%	
Pb	2.27	4%	52.88	0%	1.20	10%	7.07	20%	63	70.84	5%	90%	
Zn	62.60	5%	112	2%	14.56	7%	27.24	37%	216	236	8%	91%	
							M2						
Element	**F1**	**RSD (%)**	**F2**	**RSD (%)**	**F3**	**RSD (%)**	**R**	**RSD (%)**	**Three step + R**	**Total**	**RSD (%)**	**Recovery (%)**	
Fe	164	2%	4040	2%	7420	5%	13185	7%	24809	31700	1%	78%	
Al	132	1%	2990	0%	849	8%	14028	6%	17999	22864	4%	79%	
As	1.32	2%	2.85	2%	1.12	5%	2.58	5%	7.86	9.03	0%	87%	

Table 4 (continued)

Ba	2.18	2%	13.93	3%	4.73	0%	112	7%	133	117	3%	113%
Cd	0.75	4%	0.89	1%	0.005	26%	0.05	37%	1.69	1.62	1%	104%
Co	1.91	5%	2.00	1%	2.16	2%	2.74	5%	9	10.20	4%	86%
Cr	0.07	10%	3.99	9%	11.44	0%	21.42	9%	37	45.06	0%	82%
Cu	1.35	4%	35.95	2%	11.12	3%	5.11	3%	54	54.50	5%	98%
Hg	0.03	8%	0.19	5%	0.16	4%	0.28	6%	0.66	1.09	3%	60%
Mn	39	3%	37.42	2%	79.65	1%	109	7%	264	321	0%	82%
Ni	3.03	4%	5.98	4%	9.64	2%	8.33	7%	27	28.1	1%	96%
Pb	2.68	0%	61.28	0%	1.17	7%	5.68	0%	71	79.4	0%	89%
Zn	78±	5%	91.11	2%	15.54	4%	26.94	7%	212	218	2%	97%

M3

Element	F1	RSD (%)	F2	RSD (%)	F3	RSD (%)	R	RSD (%)	Three step + R	Total	RSD (%)	Recovery (%)
Fe	164	10%	4114	4%	6898	0%	11737	2%	22914	27900	1%	82%
Al	111	9%	2848	2%	762	2%	12948	1%	16668	16254	17%	103%
As	0.93	8%	3.03	9%	0.63	23%	2.01	4%	6.6	7.28	2%	91%
Ba	1.90	6%	10.27	2%	4.47	1%	111	4%	127	118	34%	108%
Cd	0.70	12%	0.69	4%	0.004	3%	0.07	51%	1.47	1.44	1%	101%
Co	1.32	8%	1.77	3%	2.32	1%	2.38	3%	7.8	8.37	2%	93%
Cr	0.04	15%	3.97	3%	10.74	1%	18.49	0%	33	38.86	0%	86%

Table 4 (continued)

Cu	1.80	9%	42.53	11%	11.71	2%	4.78	3%	61	56.70	4%	107%
Hg	0.03	8%	0.15	6%	0.13	13%	0.21	1%	0.5	0.86	6%	61%
Mn	26.94	8%	34.38	1%	111	0%	99	4%	272	319	1%	85%
Ni	2.43	11%	5.42	0%	9.29	2%	6.72	0%	24	24.88	2%	96%
Pb	2.51	10%	60.48	5%	1.24	3%	5.75	12%	70	73.64	2%	95%
Zn	77	10%	80.31	5%	15.23	2%	24.47	16%	197	214	2%	92%

Mean and relative standard deviation (RSD %) of two samples for each station are shown.
F1: acid extractable/exchange fraction; F2: reducible fraction; F3: oxidizable fraction; R: residual fraction
The data are presented in µg/g dry weight.
Recovery (%) = [Σ (F1+F2+F3+R)/ (Total content)] ×100

4.2.2. Reducible fraction (F2)

Among all fractions, Pb like Oskarshamn sediments showed by far the highest proportion of total content in second fraction; where between 83% and 87% in M1 and M2 respectively were bound to Fe-Mn hydrous oxides, which maybe release to environment under anoxic conditions (low Eh). Also Cu showed strong affinity with second fraction, so mobility and solubility of this element controlled by formation of Fe/Mn hydroxide and oxides. Contrary to Oskarshamn sediments, Ba and Cr showed lowest percentage in reducible fraction.

4.2.3. Oxidizable fraction (F3)

The highest percentage of elements in the oxidizable fraction was found for Mn and Ni at M3 (41% and 39%, respectively). On the other side, Cd, Pb, Ba, and Zn had less complexation with organic matters and sulfide phases. Increased content of Iron, arsenic and aluminum (about 33, 18, 5 times) in F3 relative to Oskarshamn samples coincide with increased organic content suggesting that the behavior of these elements are linked to organic matter and sulfide cycle. Under oxidizing conditions, decomposition of organic matter may lead to release of soluble trace metals (Tessier et al., 1979), thus high percentage of oxidizable fraction along with prior phases, may pose a major threat to ecosystem.

4.2.4. Residual fraction (R)

Ba in all stations showed highest percentage in the residual fraction (M1=85%, M2=84%, M3=87%), followed by Al and Cr indicating that they are strongly bound to primary and secondary minerals in sediments. With regard to residual fraction in three stations, most of elements showed similar distribution pattern that illustrated in Fig 5.

4.3. Total metal digestion

Along with partial digestion, total digestion of samples was carried out to evaluate accuracy of the experiment by comparing total metal concentration with the sum of the four individual fractions, and was calculated as percentage of the recovery as follows:

$$Recovery\ (\%) = \left[\frac{Sum\ of\ the\ four\ fractions}{Total\ content}\right] \times 100 \qquad (1)$$

The results (referred as total in Table 2 and 4) indicated satisfactory accuracy for most of elements, between 80% to 144% in Oskarshamn, and 80% to 113% in Malmfjärden, hence the method used is reliable and reproducible. As discussed before (3.1.4), Hg produced less significant recovery by the procedure but overall it is useful tools in polluted area like studied area where concentration is higher than detection limit. Thereby low reproducibility of Hg can be explained by reagents selectivity (Gómez Ariza et al., 2000) and volatility during several heating and oxidation, particularly in third steps. In case of Al, it can be correlated to pH during treatment and mineral surfaces that can affect aluminum affinity.

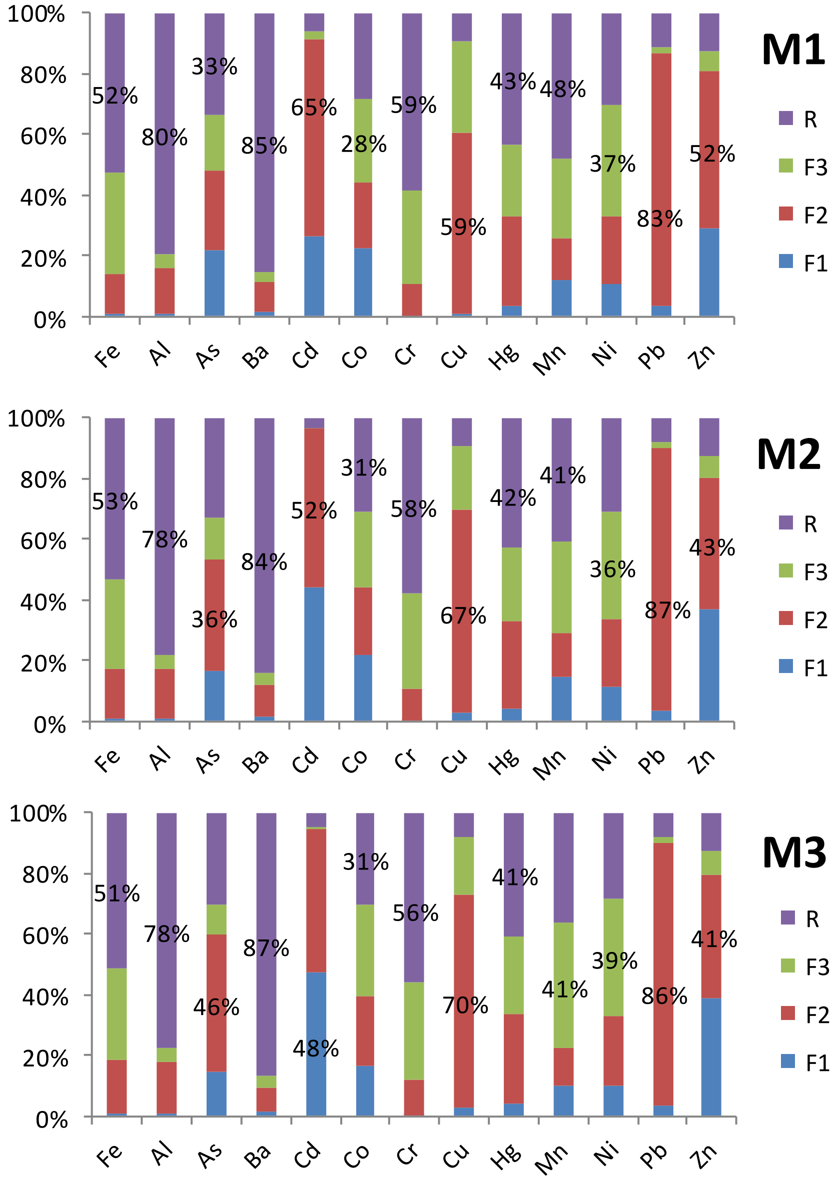


Fig 5. The average percentage of element fractionation in Malmfjärden using modified BCR-SEP method (Highest percentage among fractions for each individual element is shown)

In addition, classification of total element concentration with regard to stations presented in Table 5. Highest total concentration of elements, totally exhibited at two sites in Oskarshamn, except Al, which had different trend, probably formed during mineral weathering and diffused from car traffic, road runoff and storm waters. Also Wæren (2011) measured metal concentration in ground water on landfill where stadium was constructed and concentration of Al and Mn was much higher than reference value and might be dissolved aluminum and manganese leached out to the basin over time. Surprisingly, although in Oskarshamn the first site (O1) sampled close to the copper factory, showed less total content of Cu compared to second site (O2) which located in mouth of basin. In accordance with results of speciation and mobility analysis, it can be demonstrated by increased mobility of Cu via shipping traffics that accelerate resuspension of metals between sediment-water interfaces.

Table 5 – Evaluation of total element concentration in different stations using total digestion

Elements	Concentration in total digestion
Fe	O1>O2>M2>M3>M1
Al	M2>M1>M3>O2>O1
As	O1>O2>M1>M2>M3
Ba	O2>M1>M3>M2≥O1
Cd	O2>O1>M1>M2>M3
Co	O1>O2>M2>M1>M3
Cr	O2>O1>M2>M3>M1
Cu	O2>O1>M3>M2>M1
Hg	O2>O1>M1>M2>M3
Mn	O2>M2>M3>O1>M1
Ni	O2>O1>M2>M3>M1
Pb	O1>O2>M2>M3>M1
Zn	O2>O1>M1>M2>M3

In order to understand impact of metals loading (total concentration) on dynamic phase (non-residual and acid/exchangeable fraction) which are appropriate indication of mobility and bioavailability in sediments, the total concentration of elements by total digestion in this study was used to compare with non-residual (F1+F2+F3) and first fraction (F1) derived by SEPs. The concentrations of total non-residual fractions and exchangeable/extractable fractions for Zn, Ni, Cu, Cr, and Fe linearly increased with the increasing of their total concentration while arsenic linearly declined, which indicates that dynamics and behavior of As containing sediment is complicated (Fig 6). The figures of Zn, Ni, Cu, Cr, and Fe with data on non-residual, first fraction and fractionation of elements are given as supporting document (Table 2SD, Fig 1SD).

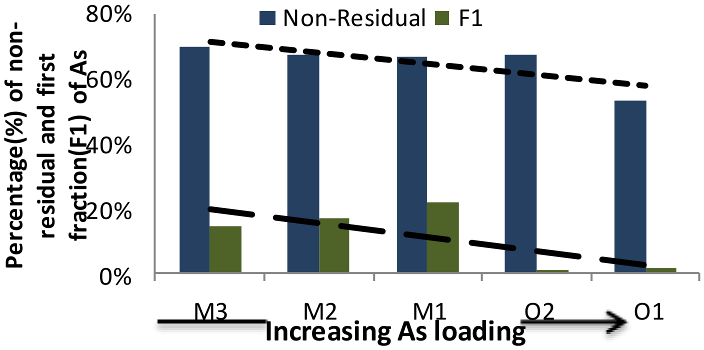


Fig 6. Variation of F1 and non-residual fractions of As with increasing concentration of total As

4.4. Metal speciation in sediment reference material (SRM)

To assess the accuracy of the sequential extraction method, as well as analyzing of total digestion, a standard sediment reference material (SRM- CRM 701) was used as control in duplicate. The comparison of results which presented in Table 6, for six element including Cd, Cr, Cu, Ni, Pb, Zn showed good agreement with certified values (91% to 109%). Also, the extractable contents of each element in each extraction step are presented in Fig 7. Cd and Zn showed highest mobility (63% and 43%, respectively) while Hg, Al, and Fe submitted higher proportion in residual forms. Overall, the distribution pattern of SRM and Oskarshamn samples showed similar trend rather than Malmfjärden

Table 6 - Summary of metal SEP analysis of standard reference materials (SRM- CRM 701) compared with certified analyzed values

	Cd	Cr	Cu	Ni	Pb	Zn
Step 1 (F1)						
Certified	7.34±0.35	2.26±0.16	49.3±1.7	15.4±0.9	3.18±0.21	205±6
Analyzed	6.54	1.88	45	14.1	1.19	187
Step 2 (F2)						
Certified	3.77±0.28	45.7±2.0	124±3	26.6±1.3	126±3	114±5
Analyzed	3.58	117	175	35.6	130	136
Step 3 (F3)						
Certified	0.27±0.06	143±7	55.2±4.0	15.3±0.9	9.3±2.0	45.7±4.0
Analyzed	0.16	100	27.6	16.2	ND	36.1
Residue (R)						
Certified	0.13±0.08	62.5±7.4	38.5±11.2	41.4±4.0	11.0±5.2	95±13
Analyzed	0.17	58	20.9	28.	15.4	80
Recovery (%)	91%	109%	100%	95%	-	95%

Average of two replicate for each SRM are shown. The data were presented in µg/g dry weight.

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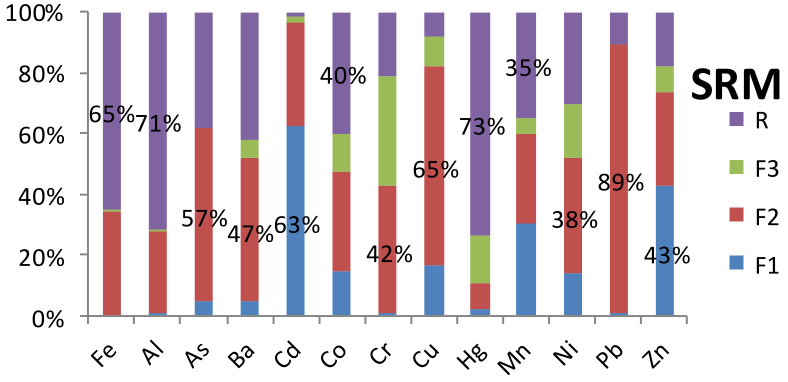

Fig 7. The average percentage of element fractionation in sediment reference material (SRM) using modified BCR-SEP method (Highest percentage among fractions for each individual element is shown)

4.5. Redistribution of elements during SEP

Results for the recovery of individual element during sequential extraction procedure in each station and for sediment reference material were shown before in Table 2, 4 and 6. As discussed, regardless of different types of sediment, practically different metals presented good recoveries. Nevertheless, reproducibility for Al, Ba, and Hg in sediment samples at Oskarshamn and Malmfjärden sites, beside Cr and Pb in sediment reference materials (SRMs) presented variable recoveries. Generally, the cause for that might be related to loss and selectivity of reagents during the process of extraction and digestion. Hg, particularly in O1, showed 50% recovery that can be explained by loss during heating; mainly through vaporing especially in third step. Moreover, recoveries for Al and Ba suggested that, released metal at each step can redistributed or diffused again in next steps, which might be due to the different numbers of binding sites that are not activated (Li et al., 2001).

4.6. Assessment of sediment contamination

To evaluate sediment contamination, geochemical and ecological assessment tools applied to sediments. In Geochemical survey of samples, individual contamination factors (C_f) indicate retention of elements in sediment and sum of C_f values give degree of contamination (C_d) in the area. Quantifying pollution load indexes (PLI) provide information for understanding of the quality of estuarine and coastal sediments. Moreover, calculated risk assessment code (RAC) highlight which elements are more likely to pose environmental effects and enter the food chain. In addition, the potential ecological risk based on toxic-response factor for a given contaminant was conducted. Finally deviations of values from reference values were carried out.

4.6.1 Contamination factor (C_f), Contamination degree and Pollution load Index

The contamination factor (concentration factor) of elements in both sites was estimated as suggested by Fernandes (1997). It is calculated by sum of the element concentration in the mobile phase (non-residue phase) of the sediment divided by the residual phase which derived by SEP (Sequential Extraction Procedure) as follows:

$$Contamination\ factor = \left[\frac{F1 + F2 + F3}{Residual}\right] \qquad (2)$$

Also the pollution load index (PLI), suggested by Tomlinson et al. (1980) was used in this study to examine the quality of estuarine and coastal sediments (Equation 3), whilst an index value of zero represents perfection, a value of one suggesting that quality reflects baseline levels of contaminants, and values above one indicate quality of site deteriorated (Tomlinson et al., 1980). The PLI value shows an increasing trend from Malmfjärden to Oskarshamn (Table 7). In addition, the calculation of contamination factor and PLI regarding to worldwide shale (Turekian and Wedepohl, 1961) and Baltic proper pre-industrial (Borg and Jonsson, 1996) values is given as supporting document (Table 2SD).

$$PLI = \sqrt[n]{C_{f1} \times C_{f2} \times C_{f3} \times \ldots \times C_{fn}} \qquad (3)$$

Table 7 - Mean of contamination factor (C_f), contamination degree (C_d), and pollution load index (PLI) for sediments from Oskarshamn and Malmfjärden based on modified BCR SEP method.

	C_f													C_d	PLI
	Fe	Al	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn		
O1	3.35	0.37	1.12	0.41	13	1.87	2.22	26	0.50	0.65	2.15	29	11	91	2.53
O2	4.40	0.34	2.04	0.51	38	3.84	2.29	53	0.30	0.63	4.29	41	23	173	3.66
M1	0.91	0.26	1.97	0.17	16	2.56	0.71	9.42	1.29	1.07	2.31	7.97	6.93	51	1.88
M2	0.88	0.28	2.05	0.19	31	2.21	0.72	9.47	1.35	1.43	2.24	11	6.85	71	2.10
M3	0.95	0.29	2.29	0.15	19	2.27	0.80	12	1.48	1.74	2.55	11	7.05	62	2.14

Contamination factor values as indicators provide comparative data on the overall metal retention, for which higher C_f values demonstrate lower retention time and higher risk to the environment. The highest contamination factor value with respect to ‘’modified BCR SEP’’ in all stations was for Cu at O2 which indicate anthropogenic activities increased its concentration about 50 times more than background level, following by Pb and Cd which were 35 times more than residual content , whereas the lowest values was found for Al and Ba in sediments. Even though for As, station M3 exhibited highest value but overall, Oskarshamn (O1-O2) due to ship traffics and factories showed higher contamination. These results are in consistent with calculated Cf and PLI values with respect to worldwide and Baltic proper values, except Hg and As for which obtained non-residual fraction were not much higher than residual, hence calculated contamination factors were relatively low. On the other side, calculated values based on worldwide shale and Baltic proper indicated striking increase, in particular for Hg compared to Baltic proper that was 82, the highest calculated values. Therefore, the combined effect of Cu, Zn, Pb, and Cd in high concentration and mobility add more possible risk of these metals to the Oskarshamn basin. Contamination degree of all sites, indicated that second site at Oskarshamn (O2) is the most polluted, while M1 had lowest contamination amongst both environment. In sum, with respect to classification suggested by Hakanson (1980) for contamination factor and degree of contamination, beside pollution load index values (Tomlinson et al., 1980), which were arranged together in Table 8, moderate to severe pollution was observed for studied sediments.

Table 8 – Classification of contamination factor, contamination degree and pollution load index values

Contamination Factor			**Contamination Degree** **(n= number of metals)**			**Pollution load Index**		
C_f	$C_f<1$	Low	**C_d**	$C_d<n$	Low	**PLI**	PLI = 0	Perfection
	$1\le C_f<3$	Moderate		$n\le C_d<2n$	Moderate		PLI = 1	Baseline level
	$3\le C_f<6$	Considerable		$2n \le C_d< 4n$	Considerable		PLI > 1	Deteriorated
	$C_f\ge 6$	Very High		$C_d\ge 4n$	Very High			

4.6.2 Risk assessment code (RAC)

The mobility and stability of elements which relatively define their toxicity strongly depend on binding forms in different phase. The risk assessment code (RAC) as suggested by Perin et al. (1985), considered partition of metal which can leach in exchangeable and/or carbonate phase (%F1 at BCR SEP), and can be remobilized easily to the aquatic environment through biochemical reactions between sediment-water interface, and subsequently can uptake by biota. It was determined by dividing first fraction (F1) to sum of three and residual steps (F1+F2+F3+R) and presented in Fig. 8. According to RAC, less than 1% of total metal in exchangeable/carbonate phase has no adverse impact on aquatic environment. Low risk defined in range between 1% and 10%, while medium risk is 11-30%, and 31-50% indicates high risk. Higher percentage than 50% of the total metal has very high risk and can poses dangerous impact by entering into food chain. (Perin et al., 1985; Jain, 2004; Sharmin et al., 2011)

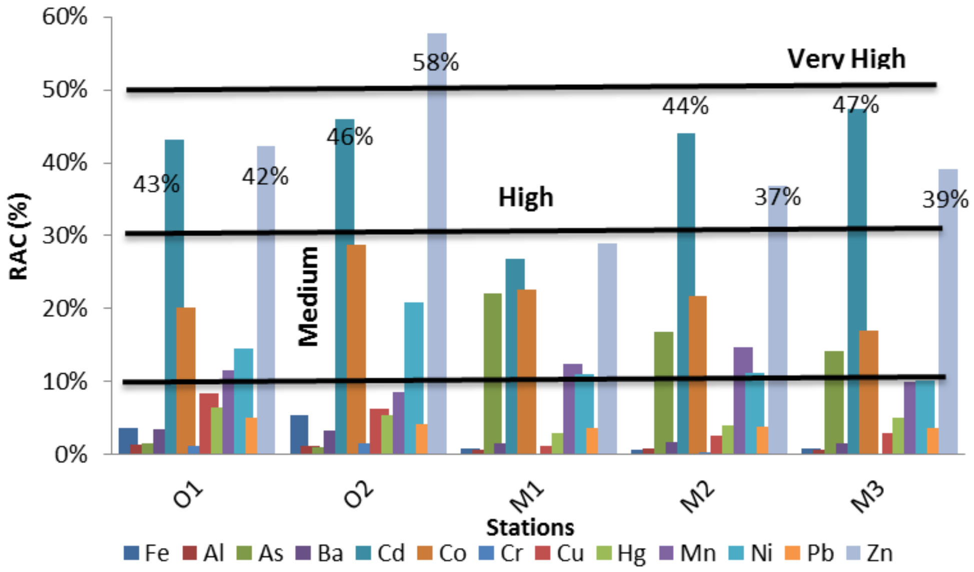

Fig 8. Risk assessment codes (RAC) for all elements and stations

Table 9 presents the results of RAC classification for all stations and elements. In general, the sediments exhibited no risk for Cr in Malmfjärden, low risk for Fe, Al, Ba, Cu, Hg, Pb in all sites, and As, Cr at Oskarshamn, and Mn at O2 and M3, and Ni at M3; so, the results of this evaluation indicated that most of elements (*i.e.*, 39 of 65 probable risk by elements) had no significant mobility. On the contrary, sediments for As (except at Oskarshamn), Co, Mn (except at O2 and M3), Zn at M1, and Ni (except at M3) indicated medium risk. Cd at Oskarshamn and Malmfjärden (except at M1), and Zn (except at O2 and M1) showed high risk, while that Zn at O2 submitted very high risk value which indicate its high sensitivity to be released easily, so it should be considered at high priority for further remediation actions.

Table 9 – Risk assessment codes for sediments from Oskarshamn and Malmfjärden

	Fe	Al	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
O1	L	L	L	L	H	M	L	L	L	M	M	L	H
O2	L	L	L	L	H	M	L	L	L	L	M	L	VH
M1	L	L	M	L	M	M	N	L	L	M	M	L	M
M2	L	L	M	L	H	M	N	L	L	M	M	L	H
M3	L	L	M	L	H	M	N	L	L	L	L	L	H

4.6.3 Ecological risk assessment

In order to obtain a broader evaluation of both sites, in terms of ecological risk, the quantitative approach to estimate potential ecological risk factor and potential risk index proposed by Håkanson (1980) was calculated as:

$$E_i = T_i \frac{C_i}{C_0} \qquad (4)$$

$$E_{RI} = \sum_{i-1}^{8} E_i \qquad (5)$$

Where E_i is the potential ecological risk factor for a given element, T_i is the toxic-response factor for a given element (As=10, Cd=30, Cr=2, Cu=5, Hg=40, Ni=5, Pb=5, Zn=1), C_i and C_0 represent concentration of selected element in sediment and its background (baseline) value, respectively. In current study, values derived for sediment of coasts and seas published by Swedish EPA were used as background values and results presented in Table 10 (As=10, Cd=0.2, Co=14, Cr=80, Cu=15, Hg=0.04, Ni=33, Pb=31, Zn=85 mg/kg DW) (Swedish EPA, 2000). Moreover, the calculation of E_i and E_{RI} regarding to worldwide shale (Turekian and

Wedepohl, 1961) and Baltic proper pre-industrial (Borg and Jonsson, 1996) values is given as supporting document (Table 3SD).

Table 10 – Ecological risk factor (E_i) and potential risk index (E_{RI}) of sediments from Oskarshamn and Malmfjärden for eight elements with Swedish background values (C_0)

	E_i								E_{RI}
Stations/ Metals	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
O1	202	1102	2	406	3219	5	189	27	5152
O2	201	1357	2	743	3269	7	148	32	5760
M1	10	317	1	16	1267	4	11	3	1629
M2	9	244	1	18	1089	4	13	3	1381
M3	7	217	1	19	855	4	12	3	1117

The following categories, according to Håkanson (1980) classification, were used to rank estimated values of ecological risk factor and potential risk index:

$E_i < 40$, $E_{RI} < 150$ Low ecological risk

$40 \leq E_i < 80$, $150 \leq E_{RI} < 300$ Moderate ecological risk

$80 \leq E_i < 160$, $300 \leq E_{RI} < 600$ Considerable ecological risk

$160 \leq E_i < 320$, $E_{RI} \geq 600$ Very high ecological risk

$Ei \geq 320$ Dangerous

The ecological risk factors in the sediments of Oskarshamn reveal that the values of all metals (except Cr, Ni, Zn) were higher than 80, indicating that these metals posed considerable, very high, and dangerous ecological risk for the basin. On the contrary, E_i values in Malmfjärden sediments (except Cd and Hg) suggesting that they posed low ecological risk. Among the eight elements in both environments, Hg submitted highest ecological risk, mainly because of its high toxicity factor (T_i=40) and relatively high content of Hg in sediments comparing to background value. In general, levels are higher in sediments from Oskarshamn than in Malmfjärden. An explanation for this is that in Oskarsham sediments affected with factories discharges. The results of the experiment, in terms of toxicity for Cd and Cr were in concurrence with the RAC values which previously tested. Furthermore, according to RAC categories, in particular Hg even showed low mobility in all stations, but due to high toxic-response factor had high ecological risk to deteriorate marine ecosystem. On the other side, ecological risk factors acquired concerning to Baltic proper and worldwide shale showed different level of risk for Cu and Pb, while former declined by three times and latter increased a bit. The results of this comparative evaluation for copper is overshadowed by reference concentration, however, Baltic proper values seem closer to regional data.

To evaluate magnitude of pollution by eight elements, the potential ecological risk indices (E_{RI}) were calculated in both sites. The values for all stations were more than 600 indicating that they had very high potential risk from heavy metals. The results demonstrated that both environments, significantly influenced by human activities, which exceeded heavy metals concentration relative to background values.

4.6.4 Deviation from Swedish EPA values

Even though the universal accepted indices for assessment of sediment were applied, national classification by Swedish EPA (2000) to estimate extent of human impact by calculating deviations from reference values carried out. The boundary between two first classes is equal to the reference value while between classes 4 and 5 is correspond to the 99th percentile of data gathered from unpolluted sediments (Swedish EPA, 2000). Deviation obtained by dividing measured values of total metal content to reference values based on dry weight (mg/kg) (As=10, Cd=0.2, Co=14, Cr=80, Cu=15, Hg=0.04, Ni=33, Pb=31, Zn=85). Calculated values compared to classification of deviation in Table 11, and summarized in Table 12. According to Swedish EPA the magnitude of deviation is usually classified into five different classes, while class 1 indicates little or insignificant deviation, which means has no or little impact of human. Following classes with increased levels of deviation implies larger effects of human during anthropogenic period. These results are in consistence with those derived by ecological risk factor studies that explained previously, specifically for As, Cd, and Hg.

Table 11 – Classification of deviation from reference values for metals in surface sediments according to the Swedish Environmental Protection Agency (2000)

Deviation Metal	Class 1 None	Class 2 Slight	Class 3 Significant	Class 4 Large	Class 5 Very large
As	< 1.0	1.0 - 1.6	1.6 - 2.6	2.6 - 4.0	> 4.0
Cd	< 1.0	1.0 - 2.5	2.5 - 6.0	6.0 - 15	> 15
Co	< 1.0	1.0 - 1.4	1.4 - 2.0	2.0 - 2.8	> 2.8
Cr	< 1.0	1.0 - 1.4	1.4 - 2.0	2.0 - 2.8	> 2.8
Cu	< 1.0	1.0 - 2.0	2.0 - 4.0	4.0 - 8.0	> 8.0
Hg	< 1.0	1.0 - 2.6	2.6 - 6.8	6.8 - 18	> 18
Ni	< 1.0	1.0 - 1.3	1.3 - 1.7	1.7 - 2.4	> 2.4
Pb	< 1.0	1.0 - 1.5	1.5 – 2.2	2.2 - 3.3	> 3.3
Zn	< 1.0	1.0 - 1.5	1.5 – 2.3	2.3 - 3.5	> 3.5

Table 12 – Classification of sediments for 9 elements in Oskarshamn and Malmfjärden according to the Swedish Environmental Protection Agency

	As	Class	Cd	Class	Co	Class	Cr	Class	Cu	Class	Hg	Class	Ni	Class	Pb	Class	Zn	Class
O1	20	5	37	5	3.3	5	0.8	1	81	5	80	5	1.1	2	38	5	27	5
O2	20	5	45	5	2.7	4	0.9	1	149	5	82	5	1.4	3	30	5	32	5
M1	1.02	2	11	4	0.7	1	0.5	1	3.2	3	32	5	0.7	1	2.3	4	2.8	4
M2	0.9	1	8	4	0.7	1	0.6	1	3.6	3	27	5	0.9	1	2.6	4	2.6	4
M3	0.7	1	7	4	0.6	1	0.5	1	3.8	3	21	5	0.8	1	2.4	4	2.5	4

4.7 Venice protocol for dredged sediments

Oskarshamn and Malmfjärden sediments (as shown in Table 13) were classified according to quality criteria for dredged sediments in the Venice Lagoon (Italian Ministry of the Environment, 1993). Based on chemical characterization of dredged sediments, Venice Protocol determines four different disposal options (A, B, C and >C). Class A sediments (not polluted) are dredged materials that can be re-used in the lagoon for 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 new islands but must be controlled to reduce their contact with the environment; and finally sediments with higher concentration than limit for type C must be dumped outside with permanent control. Oskarshamn 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 to minimize toxicological effects of contaminated sediments. In this context, Roberts (2012) has reported that re-suspension of contaminated sediments is a frequent cause of ceaseless ecological risks to marine habitats, which might be hard to control.

Table 13 – Classification of sediment samples according to Venice protocol for dredged sediments (Italian Ministry of the Environment, 1993).

Element (µg/g)	**Oskarshamn**		**Malmfjärden**			**Venice Protocol 1993**			**Classification**				
	O1	O2	M1	M2	M3	Class A	Class B	Class C	O1	O2	M1	M2	M3
As	202	201	10	9.03	7.28	15	25	50	>C	>C	A	A	A
Cd	7.34	9.04	2.11	1.62	1.44	1	5	20	C	C	B	B	B
Cr	60	70	38	45	39	20	100	500	B	B	B	B	B
Cu	1217	2230	48	55	57	40	50	400	>C	>C	B	B	B
Hg	3.22	3.27	1.27	1.09	0.86	0.5	2	10	C	C	B	B	B
Ni	35	48	24	28	25	45	50	150	A	B	A	A	A
Pb	1173	918	71	79	74	45	100	500	>C	>C	B	B	B
Zn	2314	2744	236	218	214	200	400	3000	C	C	B	B	B

Even though, Elander & Larson (2012) suggested that stabilized sediments can be used as low cost materials in the harbor, the criteria become becomes even more critical when organic pollutants are added to the list, which in case of Oskarshamn the presence of dioxine, PCB, and TBT has been reported (Länsstyrelsen Kalmar län, 2010; Andersson, 2012; Elander and Larson 2012). Moreover, despite of internal parameters of contaminated sites, variability of external drivers and stressor, need to be accounted. For instance, climate variability play significant role on mercury methylation and de-methylation rates (Stern et al., 2012; AMAP, 2011). Furthermore, Kirchner et al., (2012) indicated that remediation efficiency at abandoned mercury mining site have decreased by about 7% only in response to changes in weather conditions.

4.8 Statistical analysis

In order to measure the strength of correlation between variables, the Pearson correlation (PC) for both sites and between average total concentrations of different elements were performed with Graph Pad Prism (version 5.04 for Windows, San Diego, USA) and the obtained correlation matrices presented in Table 14.

In Oskarshamn sediments, a strong correlation was found between Cd, Cr, Cu, Mn, Ni, and Zn (except between Zn and Mn), which can be related to discharges of copper, Ni-Cd battery factories (anthropogenic sources), and redox sensitive fraction (F2), which showed significant concentration of metals. For instance, Cr showed highest affinity to Mn/Fe fraction in Oskarshamn sediments (Fig 4). Furthermore, strong correlation was observed between Fe and As, and between Co and Pb, which are in consistence with results derived from a river affected by wastewater from copper mine plant (Varol and Şen, 2012). Fe is a relatively abundant element in the Earth's crust, and contamination factors showed relative moderate to considerable contamination in Oskarshamn sediments (Table 7, Table 4SD), therefore it can be derived from both natural and anthropogenic sources. Meanwhile, weathering of crustal rocks such as sulphides (Arsenopyrite: FeAsS, As bearing pyrite: FeS_2) is evident mechanism by which sediments receive the arsenic load(Bhattacharya et al., 2002; Smedley & Kininburgh, 2002; Raymahashay & Khare, 2003; Reczynski et al., 2004). Even though strong correlation between most of metals distinguished, Al, Ba, and Hg do not show any correlation with other metals. Similarly, Hallberg (1991) reported that Hg did not show correlation and it can be related to extensive mobilization processes of Hg and environmental conditions (i.e., redox conditions, pH, atmospheric input and distribution of organic matter).

On the other side, Malmfjärden sediments showed different trend where significant correlation found between Hg, As and Cd. Mistafa et al. (2006) reported that Malmfjärden showed high level of mercury, cadmium and lead, hence storm waters and atmospheric deposition can be major sources for mentioned metals and other elements. Moreover, the positive correlation between Pb, Fe, Cr, and Ni can be explained by weathering of minerals that contained deposited metals and their similar association to sediment particles. Strong negative correlations were observed for Cd with Cu and Mn, suggesting that these metals are not associated with each other; beside these metals have diverse anthropogenic and natural sources.

Table 14 - Correlation matrices for average concentration of metals (µg/g) in sediment samples (A = Oskarshamn, B = Malmfjärden)

A	**Fe**	**Al**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
Fe	1.00												
Al	-0.89	1.00											
As	**0.98**	-0.79	1.00										
Ba	0.48	-0.05	0.64	1.00									
Cd	-0.09	0.49	0.12	0.83	1.00								
Co	0.54	-0.71	0.37	-0.39	-0.79	1.00							
Cr	-0.09	0.43	0.12	0.80	**0.97**	-0.86	1.00						
Cu	-0.12	0.45	0.08	0.78	**0.97**	-0.88	**1.00**	1.00					
Hg	0.85	-0.77	0.88	0.56	0.12	0.12	0.23	0.21	1.00				
Mn	-0.26	0.61	-0.06	0.72	**0.98**	-0.90	**0.98**	**0.98**	0.02	1.00			
Ni	-0.06	0.43	0.15	0.83	**0.99**	-0.83	**1.00**	**0.99**	0.23	**0.98**	1.00		
Pb	0.59	-0.80	0.41	-0.39	-0.83	**0.98**	-0.86	-0.87	0.24	-0.92	-0.83	1.00	
Zn	0.09	0.31	0.29	0.91	**0.98**	-0.74	**0.98**	**0.97**	0.33	0.94	**0.99**	-0.74	1.00

B	**Fe**	**Al**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Ni**	**Pb**	**Zn**
Fe	1.00												
Al	**0.84**	1.00											
As	0.04	0.32	1.00										
Ba	-0.20	0.33	0.35	1.00									
Cd	-0.31	0.03	**0.93**	0.46	1.00								
Co	0.63	0.63	0.73	-0.04	0.44	1.00							
Cr	**0.98**	0.76	0.08	-0.27	-0.27	0.69	1.00						
Cu	0.29	-0.13	-0.79	-0.67	**-0.84**	-0.42	0.25	1.00					
Hg	-0.13	0.15	**0.90**	0.21	**0.84**	0.59	-0.13	-0.72	1.00				
Mn	0.63	0.27	-0.74	-0.44	**-0.91**	-0.13	0.61	0.79	-0.81	1.00			
Ni	**0.98**	0.71	0.02	-0.39	-0.33	0.64	**0.99**	0.37	-0.14	0.64	1.00		
Pb	**0.92**	0.57	-0.11	-0.47	-0.42	0.54	**0.96**	0.45	-0.30	0.73	**0.97**	1.00	
Zn	-0.07	0.01	0.68	0.24	0.75	0.40	0.03	-0.49	0.37	-0.51	-0.03	0.00	1.00

Bold values are significant at $p<0.05$.

5. Conclusion

In the present study, chemical analysis and speciation of Fe, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in forms of carbonate/exchangeable, reducibale, oxidizable and residual fractions, following by total metal digestion in contaminated sediments (Oskarshamn harbor and Malmfjärden semi-enclosed bay) has investigated. The results indicated that Malmfjärden sediments, which is mainly associated with metals containing minerals and influenced by storm waters and possible leachate from artificial landfill (non-point sources), comparing to Oskarshamn contain smaller amounts of total extractable metals (except Al). Sediments of Oskarshamn basin are strongly affected by factories discharges and ship traffics which, eventuate moderate to very high in contamination factors (Hg, Cu, Pb, Cd, Zn, As) and deteriorated quality of sediments. Therefore, the combined effect of high concentration and mobility with respect to non-residual fraction (F1+F2+F3) for Cu, Zn, Pb, Cd, As, Ni, Cr, Co contribute to more potential risk of these metals to the studied area.

Effectiveness of dredged contaminated sediments as filler even after stabilization under external drivers is still unclear when considering effects of climate change such as increased rainfall and rising water level can stimulate leaching of substances into the environment (In particular, for countries such as Sweden which is located in Artic region). Thus, regarding to worst sediment status derived by tools of this study (C_f, RAC, PLI, E_i, deviation from Swedish EPA values, Venice Protocol) the present study proposes excavation, extraction and recovery of valuable constituents (sediment mining) as sustainable strategy. Sediment mining can turn widespread challenge; contaminated sediments to valuable opportunity which, consequently enhance productivity and sustainability of connected ecosystems. The results of study provided preliminary knowledge which metals can be potential candidate for extraction, recovery, and mining. With regard to results Cu and Pb followed by As, Cr and Ni in Oskarshamn were recognized for mining. Cu and Pb were detected in relatively high concentration emphasizing even more the preference of these two metals for further operation in mining feasibility. Although both Cu and Pb had less than 10% of the total concentration in the first fraction (F1), about 90% were available in the second and third fractions (F2+F3) which, can be controlled for recovering by mediated microbial and chemical mining. On the contrary, Malmfjärden sediments might not be as economical for sediment mining due to less content of metal, thus beside dredging, application of in-situ remediation techniques such as capping, using amendments (i.e., activated carbon, minerals, etc), phytoremediation, in particular macrophyte could be more appropriate and cost effective remedial actions. Moreover, dredged sediments based on Venice Protocol can be used under controlled conditions. Further studies should focus on application of novel technologies to recovery highlighted metals from contaminated sediments.

6. Acknowledgment

This work was supported by NOVA FoU (Center for University Studies, Research and Development). Author acknowledges his main supervisor Prof. William Hogland at Linnaeus University (LNU), his co-supervisor Dr. Brian Huser at Swedish University of Agricultural Sciences (SLU), Dr. Amit Bhatnagar, Dr. Fabio Kaczala at Linnaeus University (LNU), The Environmental Science and Engineering Group, and Dr. Mark Dopson at Linnaeus University (LNU), The Systems Biology of Microorganisms Research Group. I also give special thanks to Dr. Roland Engkvist for guiding me through the project and taking samples from Oskarshamn and Malmfjärden. I would like to thank Sara Gunnarsson and my friend Jean-Christophe De Bortoli for their assistance in laboratory. Last but not least, author is highly thankful to his lovely parents and sister for all of the supports and believing in me during studies.

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Speciation of metals in contaminated sediments in the Kalmar County, Sweden: Oskarshamn harbor and Malmfjärden semi-enclosed bay. An initial approach toward sediment mining

8. Supporting documents

Table 1SD – Summary of blank analysis for each individual metal during sequential extraction procedure (SEP)

ELEMENT	S1 blank	S2 blank	S3 blank	S4 blank	Unit
Fe	<0.004	0.0297	0.0083	0.875	mg/l
Al	26	48.9	15.9	1820	µg/l
As	<0.5	<3	<0.5	4.77	µg/l
Ba	1.37	3.84	4.47	21.5	µg/l
Cd	<0.02	<0.02	0.15	0.313	µg/l
Co	<0.05	0.582	0.308	0.683	µg/l
Cr	0.361	3.33	1.56	32.1	µg/l
Cu	<1	3.76	3.18	9.86	µg/l
Hg	<0.1	0.298	<0.1	5.04	µg/l
Mn	<0.3	0.555	2.17	11.3	µg/l
Ni	<0.5	1.89	0.842	15.9	µg/l
Pb	0.594	2.95	2.45	3.12	µg/l
Zn	<2	2.35	58	294	µg/l

S1 = Step 1, S2= Step 2, S3= Step 3, S4 = Step 4 (Based on modified BCR sequential extraction procedure)

Table 2SD – The average percentage of elements of non-residual, first fraction and fractionation in Oskarshamn and Malmfjärden using modified BCR-SEP

	M3	M2	M1	O1	O2
Cd (Non-Residual %)	95%	97%	97%	93%	97%
(F1%)	48%	44%	27%	43%	46%
	M3	**M2**	**M1**	**O1**	**O2**
Zn (Non-Residual %)	88%	87%	87%	91%	96%
(F1%)	**39%**	**37%**	**29%**	**42%**	**58%**
	M1	M3	M2	O2	O1
Pb (Non-Residual %)	**89%**	**92%**	**92%**	**98%**	**97%**
(F1%)	4%	4%	4%	4%	5%
	M3	**M2**	**M1**	**O2**	**O1**
As (Non-Residual %)	70%	67%	67%	67%	53%
(F1%)	14%	17%	22%	1%	2%
	M1	**M2**	**M3**	**O1**	**O2**
Cu (Non-Residual %)	90%	90%	92%	96%	98%
(F1%)	1%	3%	3%	8%	6%
	M1	**M3**	**M2**	**O1**	**O2**
Cr (Non-Residual %)	41%	44%	42%	69%	70%
(F1%)	0%	0%	0%	1%	2%
	M3	**M2**	**M1**	**O1**	**O2**
Hg (Non-Residual %)	59%	58%	57%	33%	23%
(F1%)	4%	4%	4%	6%	5%
	M1	**O1**	**M3**	**M2**	**O2**
Mn (Non-Residual %)	52%	39%	64%	59%	39%
(F1%)	12%	12%	10%	15%	9%
	M1	**M3**	**M2**	**O1**	**O2**
Ni (Non-Residual %)	70%	69%	69%	68%	81%
(F1%)	11%	10%	11%	15%	21%
	M3	**M1**	**M2**	**O2**	**O1**
Co (Non-Residual %)	69%	72%	69%	79%	65%
(F1%)	17%	23%	22%	29%	20%
	M1	**M3**	**M2**	**O2**	**O1**
Fe (Non-Residual %)	48%	49%	47%	81%	77%
(F1%)	1%	1%	1%	5%	4%
	O1	**O2**	**M3**	**M1**	**M2**
Al (Non-Residual %)	27%	26%	22%	20%	22%
(F1%)	1%	1%	1%	1%	1%
	O1	**M2**	**M3**	**M1**	**O2**
Ba (Non-Residual %)	29%	16%	13%	15%	34%
(F1%)	3%	2%	1%	1%	3%

Table 2SD (continued)

	O1				O2				M1				M2				M3			
Ratio%	F1	F2	F3	R	F1	F2	F3	R	F1	F2	F3	R	F1	F2	F3	R	F1	F2	F3	R
Fe	4%	73%	0%	23%	5%	76%	1%	19%	1%	13%	33%	52%	1%	16%	30%	53%	1%	18%	30%	51%
Al	1%	26%	0%	73%	1%	24%	0%	74%	1%	15%	4%	80%	1%	17%	5%	78%	1%	17%	5%	78%
As	2%	51%	0%	47%	1%	66%	0%	33%	22%	26%	18%	33%	17%	36%	14%	33%	14%	46%	10%	30%
Ba	3%	23%	3%	71%	3%	26%	4%	66%	1%	10%	3%	85%	2%	11%	4%	84%	1%	8%	4%	87%
Cd	43%	46%	4%	7%	46%	47%	4%	3%	27%	65%	2%	6%	44%	52%	0%	3%	48%	47%	0%	5%
Co	20%	35%	10%	35%	29%	40%	11%	21%	23%	21%	28%	28%	22%	23%	24%	31%	17%	23%	30%	31%
Cr	1%	57%	11%	31%	2%	57%	11%	30%	0%	11%	31%	59%	0%	11%	31%	58%	0%	12%	32%	56%
Cu	8%	75%	13%	4%	6%	80%	12%	2%	1%	59%	30%	10%	3%	67%	21%	10%	3%	70%	19%	8%
Hg	6%	24%	3%	67%	5%	16%	1%	77%	4%	29%	24%	43%	4%	29%	25%	42%	4%	30%	26%	41%
Mn	12%	16%	12%	61%	9%	18%	12%	61%	12%	14%	26%	48%	15%	14%	30%	41%	10%	13%	41%	36%
Ni	15%	36%	17%	32%	21%	47%	13%	19%	11%	22%	37%	30%	11%	22%	36%	31%	10%	23%	39%	28%
Pb	5%	92%	0%	3%	4%	93%	0%	2%	4%	83%	2%	11%	4%	87%	2%	8%	4%	86%	2%	8%
Zn	42%	47%	2%	9%	58%	36%	2%	4%	29%	52%	7%	13%	37%	43%	7%	13%	39%	41%	8%	12%

F1: acid extractable/exchange fraction; F2: reducible fraction; F3: oxidizable fraction; R: residual fraction
Non – residual = F1+F2+F3

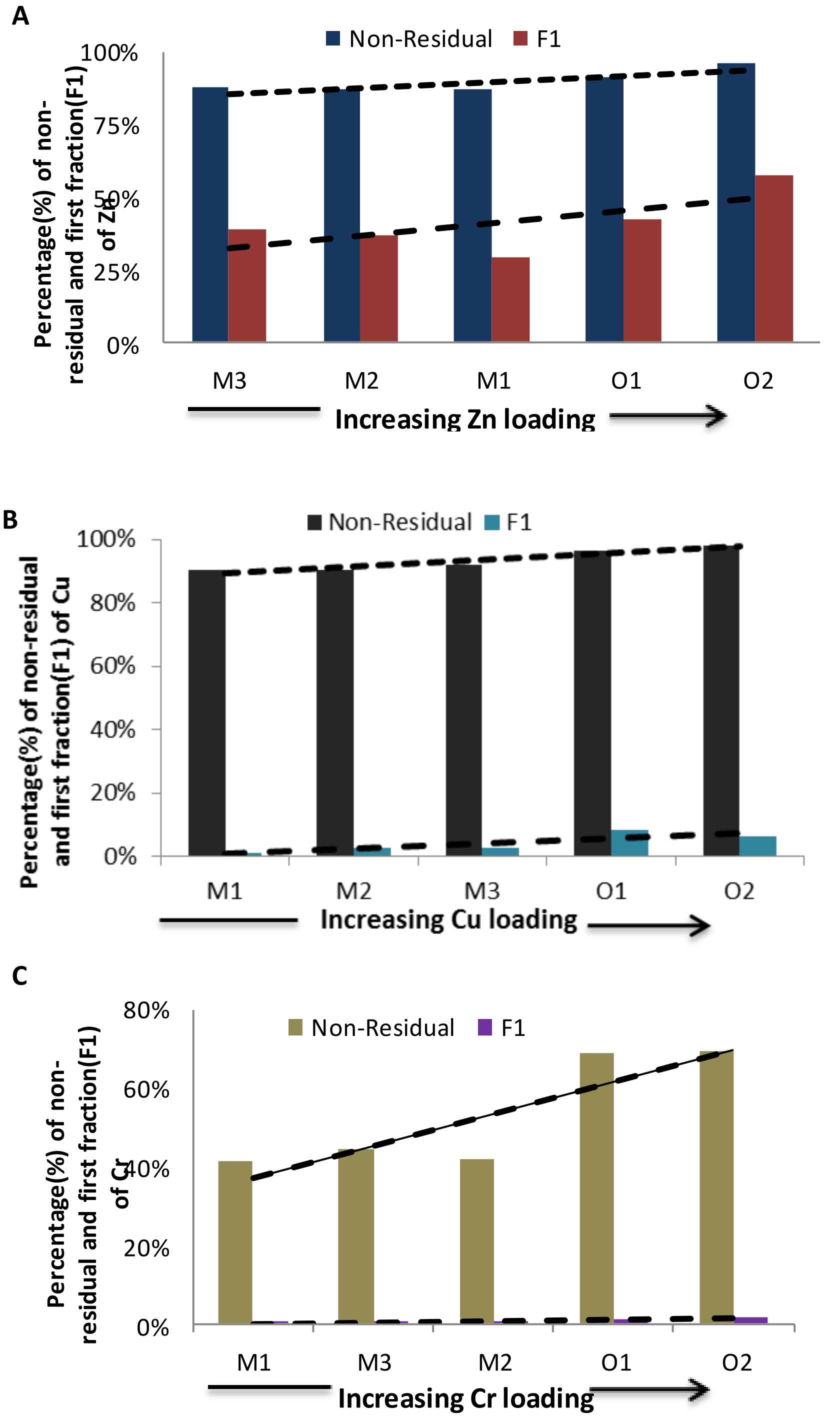

Fig 1SD – (A) Variation of F1 and non-residual fractions of Zn with increasing concentration of total Zn, (B) Variation of F1 and non-residual fractions of Cu with increasing concentration of total Cu, (C) Variation of F1 and non-residual fractions of Cr with increasing concentration of total Cr, (D) Variation of F1 and non-residual fractions of Ni with increasing concentration of total Ni, (E) Variation of F1 and non-residual fractions of Fe with increasing concentration of total Fe

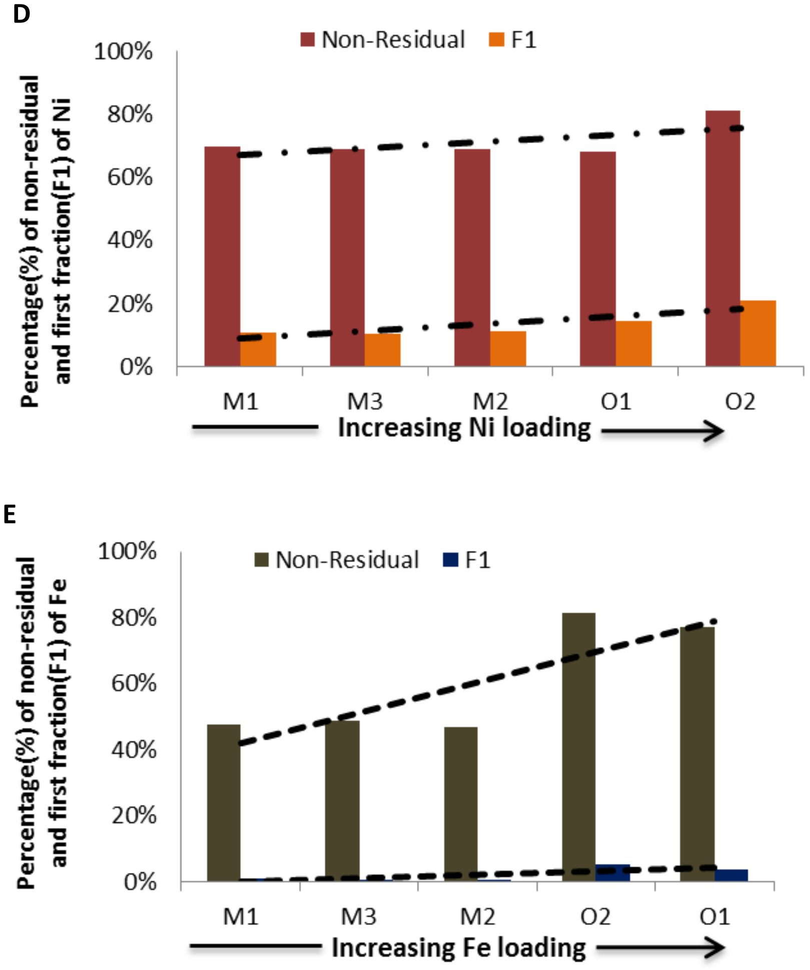

Fig 1SD (Continued)

Table 3SD - Ecological risk factor (E_i) and potential risk index (E_{RI}) of sediments from Oskarshamn and Malmfjärden for eight elements with Baltic proper and worldwide shale values (C_0)

		E_i			**Based on Baltic proper(Pre-ind.) values**				**E_{RI}**				**E_i**		**Based on Worldwide shale**				**E_{RI}**
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn			As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
O1	225	711	2	135	3219	4	235	19	4550	O1	156	734	1	135	322	3	293	24	1669
O2	224	875	3	248	3269	6	184	23	4831	O2	155	904	2	248	327	4	229	29	1897
M1	11	205	1	5	1267	3	14	2	1509	M1	8	211	1	5	127	2	18	2	374
M2	10	157	2	6	1089	4	16	2	1285	M2	7	162	1	6	109	2	20	2	310
M3	8	140	1	6	855	3	15	2	1031	M3	6	144	1	6	86	2	18	2	265

$$E_i = T_i \frac{C_i}{C_0}$$

T_i = Toxic-response factor for a given element (As=10, Cd=30, Cr=2, Cu=5, Hg=40, Ni=5, Pb=5, Zn=1), C_i = Concentration of metal in the sediment, C_0 = Background or reference value of that metal (References are Worldwide shale and Baltic proper values)

$$E_{RI} = \sum_{i-1}^{\infty} E_i$$

Table 4SD – The calculated contamination factors (C_f) and pollution load index (PLI) for Oskarshamn and Malmfjärden sediments with respect to worldwide shale and Baltic proper (Pre-industrial) values

			C_f							C_f			
	O1	O2	M1	M2	M3	Worldwide shale		O1	O2	M1	M2	M3	Baltic proper(Pre-ind.)
Fe	2.5	2.4	0.6	0.7	0.6	47200	Fe	2.5	2.4	0.6	0.7	0.6	47000
Al	0.01	0.01	0.02	0.03	0.02	800000	Al	-	-	-	-	-	-
As	16	15	0.8	0.7	0.6	13	As	22	22	1.1	1.0	0.8	9
Ba	0.2	0.3	0.3	0.2	0.2	580	Ba	-	-	-	-	-	-
Cd	24	30	7.0	5.4	4.8	0.3	Cd	24	29	6.8	5.2	4.7	0.31
Co	2.4	2.0	0.5	0.5	0.4	19	Co	2.8	2.4	0.6	0.6	0.5	16
Cr	0.7	0.8	0.4	0.5	0.4	90	Cr	1.2	1.3	0.7	0.9	0.7	52
Cu	27	50	1.1	1.2	1.3	45	Cu	27	50	1.1	1.2	1.3	45
Hg	8.0	8.2	3.2	2.7	2.1	0.4	Hg	80	82	32	27	21	0.04
Mn	0.3	0.4	0.3	0.4	0.4	850	Mn	0.5	0.6	0.4	0.5	0.5	600
Ni	0.5	0.7	0.4	0.4	0.4	68	Ni	0.9	1.2	0.6	0.7	0.6	39
Pb	59	46	3.5	4.0	3.7	20	Pb	47	37	2.8	3.2	2.9	25
Zn	24	29	2.5	2.3	2.3	95	Zn	19	23	2.0	1.8	1.8	120
PLI	2.54	2.91	0.71	0.73	0.65		PLI	7.38	8.32	1.52	1.57	1.40	

$$Contamination\ factor = \left[\frac{C\ metal}{C\ background}\right]$$

C_{metal} = Concentration of metal in the sediment, $C_{background}$ = Background or reference value of that metal (References are Worldwide shale and Baltic proper values)

$$PLI\ = \sqrt[n]{C_{f1} \times C_{f2} \times C_{f3} \times \ldots} \times C_{fn}$$

n = number of metals

Malmfjärden - September 2012

Oskarshamn Basin –May 2012