



# Significance of environmental dredging on metal mobility from contaminated sediments in the Oskarshamn Harbor, Sweden



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## HIGHLIGHTS

- Concentration and speciation of metals released from highly contaminated sediments.
- Potential impacts of pseudo-dredging operations on water quality.
- Geochemical investigations of metals in mixture of water slurries.
- Sediments are as sink rather than source for the most of metals in disturbed environment.

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## ABSTRACT

Metals are often seen as immobile in bottom sediments as long as these environmental sinks remain undisturbed. The aim of this paper was to evaluate the potential metal mobility due to resuspension under pseudo-dredging conditions of contaminated sediments in the Oskarshamn Harbor that are likely to be dredged as part of a remediation program established in Sweden. To address this concern, mixtures of water slurries were sampled from pore, leaching, and surface water over a period of nearly 36 d, and the major ions and trace metal concentrations determined. The results of this study pointed out the potential mobility and toxicity of metals posed by temporary changes during dredging operations, and highlighted the potential release of Cu, Pb, Zn, Mn, and Ni to the environment. Among the toxic metals, regarding pre and post dredging, Cu and Pb significantly demonstrated to be in ionic form, apparently because of dissolution of Fe–Mn oxy/hydroxides and decomposition of organic matter.

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## 1. Introduction

The establishment and maintenance of long-term protection of human health and environment, along with secure and continuous delivery of ecosystem services, pose unique challenges for applying sustainable development criteria for management of contaminated sites, particularly in coastal regions. The first quantitative report of cumulative impacts of anthropogenic stressors on Baltic Sea, disclosed that the highest estimated impacts were in the southern and south-western part of the sea and in the Gulf of Finland, whilst hazardous substances accounted for 30% of the total cumulative impact (Korpinen et al., 2012). However, although extensive and considerable efforts through authorized international commissions established (see London Convention 1972, HELCOM 1974,

Barcelona Convention 1992, Bucharest Convention 1992 and OSPAR 1992) the levels of certain pollutants in Baltic Sea pose serious risks to environmental and human health (SEPA, 2005). The Swedish National Food Agency recommended pregnant women and children not to eat fish and shellfish species such as salmon and herring more than 2–3 times a year (SNFA, 2007; SNFA, 2008). As the world's largest brackish water body, Baltic Sea is one of the most polluted seas in the world as a consequence of about 85 million people living in the surrounding drainage basin (Sweitzer et al., 1996; HELCOM, 2010) that pose significant pressure through different anthropogenic activities, which are more likely accelerated by further trade flows and external stressors. Thereby, Swedish government established an environmental policy considering 16 environmental quality objectives covering from unpolluted air to a non-toxic environment and a balanced marine environment, flourishing coastal areas and archipelagos to promote the quality of environment and human health (SEPA,

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2012a). In spite of several steps taken by Swedish Environmental Protection Agency (SEPA), current evaluation demonstrated that 14 of the 16 environmental quality objectives will not be achieved by the target year 2020 (SEPA, 2012b). More specifically, strategies on two of the objectives; a non-toxic environment and a balanced marine environment, flourishing coastal areas and archipelagos are closely acting in accordance to the European Water Framework Directive and Environmental Quality Standard Directive, which established that at least a “Good” water status for all water bodies are achieved by the year 2015 (EC, 2000, 2008).

According to Bortone et al., European countries for different remedial goals, dredged about 100–200 million m<sup>3</sup> of contaminated sediments annually (Bortone et al., 2004). In Sweden, 80,000 contaminated sites have been identified (SEPA, 2011), and the total volume of dredged contaminated sediments is estimated to be more than 1 million m<sup>3</sup> in the coming years (Wilhelmsson, 2012). There are over 200 ports located on the Baltic Sea with about 839 million tons of cargo (Baltic port, 2012), where the Oskarshamn Harbor, in south east of Sweden, with annual leakage to the Baltic Sea of approximately 700 kg Cu, 350 kg As, 250 kg Pb, and 20 kg Cd to Baltic Sea, is characterized as one of the most severely contaminated site in Sweden (Länsstyrelsen Kalmar län, 2010). Ecological and chemical status of Oskarshamn basin is determined as poor to moderate; thereby measures are implemented to achieve a “good” water status by the year 2021 (VISS, 2013; HELCOM, 2013). During the past years, some studies confirmed a large distribution of highly polluted sediments over the studied basin; mostly inner harbor; with both inorganic and organic contaminants (Tobiasson, 2012; Andersson, 2012; SMOCS, 2012). Moreover, speciation studies of metals in sediments have shown higher mobility of Zn and Cd (Fathollahzadeh et al., 2014). Consequently, the SEPA together with other involved sectors are contributing for monitoring, assessment and remediation with a goal of long-term reduction of contaminants discharge from the Oskarshamn basin to the Baltic Sea (Länsstyrelsen Kalmar län, 2011). Due to environmental constraints with dumping at sea and landfill disposal of dredged sediments, feasibility of stabilization/solidification was carried out (Wilhelmsson, 2012; Elander and Larson, 2012; Lindmark and Wilhelmsson, 2012). Additionally, based on reduction of environmental footprints of cleanup and effects of external drivers (e.g., increased rainfall); recovery of valuable materials such as Cu and Zn from sediments, referred as sediment mining; has been suggested as a sustainable strategy (Fathollahzadeh et al., 2012).

Although, European and regional guidelines concerning marine contamination, pollution effects and sea disposal of dredged material have been developed (HELCOME, 2007; EC, 2010), there is a lack of detailed approach regarding dredging impacts and associated drawbacks (e.g., resuspension) on sustainable management of contaminated sediments, particularly in the Baltic Sea context. Therefore, the aim of this current study was to evaluate the risks associated with the resuspension of contaminants during dredging procedures. Furthermore, the impacts of dredging on water quality and dynamics of heavy metals, besides surface water (SW) samples, leaching water (actual leachate; LW) and pore water (PW) samples were also subject of investigation. Due to considerable variations in term of elutriation preparation (Novelli et al., 2006), collection of LW samples during dredging was carried out in a way that resembled real dredging operation. In addition, to the best of our knowledge, geochemical speciation studies of leaching, pore and surface waters have not been reported in the literature, so in order to simulate natural sediment resuspension and distribution of heavy metals before and after dredging, geochemical modeling (Visual MINTEQ Gustafsson, 2010) was performed to address boundaries for the contaminated system.

## 2. Materials and methods

### 2.1. Study area

The site of investigation was the Oskarshamn basin with an approximate area of 1.2 km<sup>2</sup> and located in the Southeastern part of Sweden at approximately 410 km south of Stockholm (Fig. 1). The basin has a water depth up to 17 m and contaminants have been discharged in the basin since mid-1800s and an approximate 700,000 m<sup>3</sup> of bottom sediments are contaminated. Major pollution sources of the basin, are related to the discharges of industrial and urban activities such as Ni-Fe/Ni-Cd batteries factory, copper board production, shipyards and stormwater runoff. High contamination of metals in the last years has raised serious concerns among the authorities in relation to severe threats to the Baltic Sea ecosystem.

### 2.2. Sampling and preparation

Bottom sediment samples were taken by a Van-Veen grab sampler (Carlbergs AB, Gothenburg, Sweden) on 30<sup>th</sup> of May 2012 according to (Fathollahzadeh et al., 2014). Leaching water (LW) of the first sampling point (O1) was collected instantaneously and further stored in acid washed (10% v/v HNO<sub>3</sub>) (Scharlau Chemie S.A, Barcelona, Spain) 0.5 L polyethylene containers, covered by aluminum foil paper. The collection of LW at the second sampling point (O2) was not completed due to small quantity. Sediments taken from O1 and O2 were stored in acid washed 1 L polyethylene that were completely filled and then covered to minimize oxidation. Moreover, surface water samples (SW) at O2 and at a reference site (R) (ca. 16 m deep) outside of the basin (as a control sample) (each consisted of four composite samples) were taken on 24<sup>th</sup> of May 2012 (N57°16,436'E16°29,457'). Also, in order to assess variation in heavy metal concentration after dredging of sediments as illustrated above, collection of water samples at O2 was carried out on 28<sup>th</sup> of June 2012. The speed and direction of current at O2 were measured with a flow cross and the speed ranging between 0.018 and 0.028 (m/s) with a NW (North West) direction was observed. Collected samples were placed in iceboxes at 4 °C and transported to the laboratory for further analysis.

The extraction of the aqueous phase for investigations on PW and LW was carried out by placing wet sediments and water samples in 100 mL polyethylene centrifuge tubes and for centrifugation at 10,000 rpm during 20 min (Beckman Avanti-J25). In order to preserve natural conditions, no centrifugation applied to SW and R samples. All tubes, containers, and glassware were soaked in dilute HNO<sub>3</sub> (10%, v/v) for eight hours, followed by rinsing with ultrapure water produced by a Milli-Q™ apparatus (Millipore, 18.2 MΩ cm<sup>-1</sup> resistivity). The analytical methods followed are described elsewhere (Fathollahzadeh et al., 2014).

### 2.3. Chemical analysis

All water chemical analysis were carried out using national and international standard methods, accredited by SWEDAC (Swedish Board for Accreditation and Conformity Assessment), unless otherwise stated. The description of each chemical analysis is summarized in Supplementary material. After preparing PW, LW, SW, and R samples, pH, ORP (oxidation reduction potential), chemical oxygen demand (COD) and total organic carbon (TOC) were measured. Measurements of pH and ORP were done with a Phenomenal pH lab set pH 1000 L, VWR. The redox potential (also known as ORP and Eh, unit mV) for SW and R were determined based

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