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Research article

Low impact leaching agents as remediation media for organotin and metal contaminated sediments

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ABSTRACT

All over the world, elevated levels of metals and the toxic compound tributyltin (TBT) and its degradation products are found in sediments, especially close to areas associated with shipping and anthropogenic activities. Ports require regular removal of sediments. As a result, large volumes of often contaminated sediments must be managed.

The aim of this study was to investigate enhanced leaching as a treatment method for organotin (TBT) and metal (Cu and Zn) contaminated marine sediments. Thus, enabling the possibility to reuse these cleaner masses e. g. in construction. In addition to using acid and alkaline leaching agents that extract the OTs and metals but reduce the management options post treatment, innovative alternatives such as EDDS, hydroxypropyl cellulose, humic acid, iron colloids, ultra-pure Milli-Q water, saponified tall oil ("soap"), and NaCl were tested. Organotin removal ranged from 36 to 75%, where the most efficient leaching agent was Milli-Q water, which was also the leaching agent achieving the highest removal rate for TBT (46%), followed by soap (34%). The TBT reduction accomplished by Milli-Q water and soap leaching enabled a change in Swedish sediment classification from the highest class to the second highest class. The highest reduction of Zn was in HPC leached samples (39% removal) and Cu in EDDS leached samples (33% removal). Although high metal and OT leaching were achieved, none of the investigated leaching agents are sufficiently effective for the removal of both metals and OTs. The results of this study indicate that leaching with ultra-clean water, such as Milli-Q water, may be sufficient to treat TBT contaminated sediments and potentially allow mass reuse.

Author contribution

Anna Norén: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Karin Karlfeldt Fedje: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Funding acquisition, Ann-Margret Strömwall: Conceptualization, Writing – original draft, Writing – review & editing, Methodology, Funding acquisition. Sebastien Rauch: Conceptualization, Writing – original draft, Writing – review & editing, Methodology, Funding acquisition. Yvonne Andersson-Sköld: Conceptualization, Writing – original draft, Writing – review & editing, Methodology, Funding acquisition.

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1. Introduction

Sediment dredging must be carried out regularly to maintain or increase water depth in important maritime areas, such as ports. World-wide, elevated levels of organotin compounds (OTs) and metals are found in the sediment, especially close to areas with high levels of anthropogenic activities, such as cities, industries, and marine structures, including ports and marinas. Organotins, which include tributyltin (TBT) and its derivatives dibutyltin (DBT) and monobutyltin (MBT), have a negative effect on biota through hormone disruption (OSPAR Commission, 2011). Negative effects have been found at concentrations as low as 1 ng/L TBT in water (European Commission, 2005). Tributyltin is a stable compound with hydrophobic properties (European Commission, 2005) and accordingly, sorbs fairly easily to the

Abbreviations

BK	Björlanda Kile (a sampling site)
CV	Cityvarvet (a sampling site)
DBT	Dibutyltin
EDDS	(S,S)-ethylenediamine-N,N'-disuccinic acid
EDS	Energy dispersive X-ray spectrometer
ESEM	Environmental scanning electron microscopy
Fe colloids	Iron colloids
HA	Humic acid
HPC	Hydroxypropyl cellulose
ISQG	Interim sediment quality guideline
MBT	Monobutyltin
OT	Organotin
TBT	Tributyltin

organic matter in the sediment (Hoch and Schwesig, 2004). Not only is the sediment's organic content important for TBT sorption, but so are characteristics such as particle size, redox conditions, and iron oxide content (Dowson et al., 1996; Hoch and Schwesig, 2004). When caught in sediment, TBT has a long half-life of up to 90 years (Vigilino et al., 2004), before degrading into DBT, then MBT, and finally tin (Sn). The long half-life means that high TBT contents are still found in sediment today, although the use of boat paints containing TBT as an antifouling agent was banned for smaller vessels in the EU in 1989 (Directive 89/677/EEC), and for larger vessels in 2003 (EU Regulation (EC) No 782/2003).

The most common management method for OT contaminated sediment is either landfilling or deep-sea disposal (Bortone et al., 2004; Akcil et al., 2015). The choice of treatment depends on the degree of contamination, sediment properties, as well as local conditions and regulations (Norén et al., 2020). Different methods can be used to remediate TBT contaminated sediment, including thermal treatment, steam stripping, chemical/electrochemical oxidation, and biodegradation/phytoremediation (Du et al., 2014). These techniques are often expensive, involve high energy or chemical consumption, or have not been tried at full scale. Another option is soil/sediment washing, i.e. leaching, which may be less costly, but requires a large amount of leaching liquid, which depending on treatment conditions could be harmful to biota if released into the environment (Akcil et al., 2015; Peng et al., 2018). Another risk is that leaching agent residues could remain in the sediment and impact the environment during its disposal or use. Consequently, there is a need for finding environmentally sustainable methods, using leaching agents with less environmental impact than conventional techniques (Akcil et al., 2015; Hou and O'Connor, 2020).

In this study different leaching agents have been tested, including hydroxypropyl cellulose (HPC), saponified tall oil ("soap"), humic acid (HA), iron colloids (Fe colloids), (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), Milli-Q water, and NaCl, in addition to alterations in pH. Both HPC and soap are in theory water soluble organic compounds with both hydrophobic and hydrophilic properties and could potentially sorb the hydrophobic part of TBT. Hence both HPC and soap could potentially extract TBT from sediments to water. Additionally, both have the advantage of being biodegradable (Qi et al., 2014). Organotins are likely to sorb to both inorganic and organic colloids, through the formation of complexes (Dubascoux et al., 2008). Humic acid and Fe colloids dissolved in water have also been found to sorb metals through complexation (Fent and Looser, 1995; Lyvén et al., 2003; Kalmykova et al., 2008a; Wang and Mulligan, 2009; Boechat et al., 2016). This means that HA and Fe colloids could potentially extract TBT from sediment into a leachate. Additionally, TBT degradation is facilitated by the presence of Fe colloids (Yamashita et al., 2012). Complex substances, such as

ethylenediaminetetraacetic acid (EDTA), are used in laboratories to extract TBT and metals from sample matrices prior to analysis (Rauret, 1998; Ehsan et al., 2007; Rivero-Huguet and Marshall, 2011). However, EDTA is difficult to biodegrade and instead the similar aminopolycarboxylate chelating agent (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS) has the potential to complex bind the positively charged TBT and metals whilst being more easily biodegradable than EDTA (Vandevivere et al., 2001; Karlfeldt Fedje et al., 2013; Begum et al., 2016). Further, the salinity and pH of surrounding waters are major factors affecting the sorption and desorption of TBT (Fent, 1996; Hoch et al., 2003; Burton et al., 2004; Hoch, 2004; Hoch and Schwesig, 2004; Pynaert and Speleers, 2004; Nystroem et al., 2006; Yoo et al., 2013). Increasing salinity favors TBT desorption from sediments, however high salinity also prevents degradation of TBT in the water phase (Fent, 1996; Stichnothe et al., 2001; Hoch et al., 2003). Studies have shown that the most common form of TBT used in antifouling paint is bis(tributyltin) oxide (TBTO) which has a high solubility in fresh water (4 mg/L) (Müller et al., 2013). The sorption of TBT to sediment is highest around pH 6–8, with decreasing affinity at higher and lower pH (Burton et al., 2004; Hoch and Schwesig, 2004; Pynaert and Speleers, 2004). No studies on the desorption properties of OTs at extreme pH values, such as pH 0 or 13, where potentially the highest pH-induced leaching would occur, or the effects on the residues have been found.

As high TBT contents and high metal contents are often found together (Pynaert and Speleers, 2004; Scancar et al., 2007), a method for extracting both simultaneously is of high interest; and this may be achievable using the aforementioned leachate agents. The potential for metal remediation and recovery, as investigated by Norén et al. (2020) suggests that it may be of both economic and environmental interest to remediate and recover metals from contaminated sediments.

The aim of this project was to remove OTs and to simultaneously leach metals from contaminated marine sediments. Potential suitable leaching agents with "low impact" (here defined as having a lower environmental impact, including lower risk of causing chemical changes, and lower toxicity, to aquatic organisms, compared to conventional leaching agents and be of non-fossil origin) were investigated. Based on a literature review, EDDS, HPC, HA, Fe colloids, Milli-Q water, NaCl, and soap were chosen and tested in lab scale experiments. In addition, leaching was performed in highly acidic and alkaline conditions to compare achieved reduction of OTs and metal in the sediments with results given by the *low impact leaching agents*. The sediment residues after leaching were also studied.

2. Materials and method

2.1. Sample collection and preparation

Sediment was sampled from a marina and a port in Gothenburg, Sweden, Fig. 1. The marina Björlanda Kile (BK) has been operating since 1971 and, with 2400 berths, is the largest marina in Northern Europe (Björlanda Kile Segelsällskap, n.d.; Göteborgsregionens Fritidshamn, n.d.). It is known that the sediment in the marina has a high OT content (Sveriges geologiska undersökning, n.d.). Additional samples were taken from the inner port of Gothenburg, outside a former shipyard, Cityvarvet (CV), where the OT content in the sediment is also known to be high. The Port of Gothenburg has been in operation since the 1700s and is the largest port in Scandinavia (Göteborgs hamn, 2013). Several subsamples were collected from BK, at a depth of 0–10 cm, using an Ekman grab sampler. These were then combined to form a sample with a total volume of 12 L. Coarser objects, such as mussel shells, were removed before the subsamples were mixed to produce a homogenous sample. Samples were also collected at CV with a total volume of 40 L, some using an Ekman grab sampler, and some by a diver. The sediment was homogenized as described for the BK sediment. For logistical reasons, the samples from CV were stored at 7 °C, and those from BK were frozen at −22 °C. Prior to usage, the frozen sediment was thawed at 4 °C and

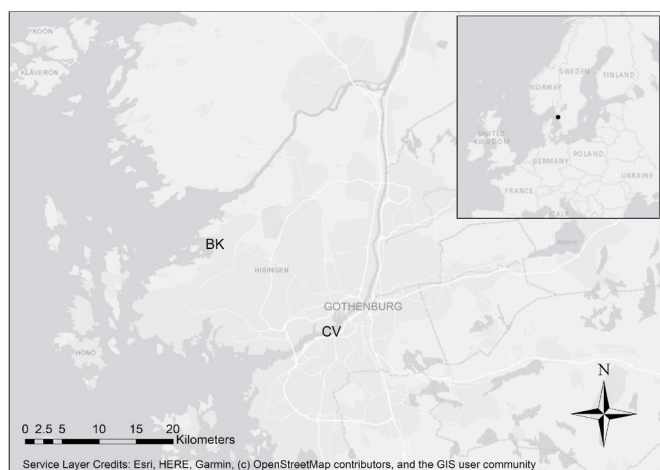


Fig. 1. Location of sediment sampling sites Björlanda Kile (BK) and Cityvarvet (CV) in Gothenburg, Sweden. In the upper right corner, the location of Gothenburg is marked with a dot.

dewatered through natural collapse of the pore structure. Environmental scanning electron microscopy (ESEM), energy dispersive X-ray spectrometer (EDS), OT and metal content analyses displayed no difference before and after freezing and thawing.

2.2. Characterization of sediments

The original sediments were characterized by ocular inspection (ISO 22412:2017). Dry weight (DW) and loss on ignition (LOI) were measured following the standard SS 028113. Evaluation of the morphology and shape of sediment particles and investigation of element distribution in the solid samples were carried out using an environmental scanning electron microscopy (ESEM, FEI Quanta200 FEG-ESEM) with an Oxford INCA energy dispersive X-ray spectrometer (EDS). The samples had a DW content of 40–60% and elemental mapping was used for EDS. The samples were prepared by applying a thin layer of wet sediment on a piece of silicon wafer and was dried at ambient conditions. Thereafter the samples were placed on a sample holder and inserted in the ESEM without any coating procedure. The ESEM analysis was performed in low vacuum pressure. The grain size distribution was investigated for the BK and CV samples using ISO 11277:2009.

The total element amounts for selected major and minor elements in the sediment samples were analyzed according to SS EN ISO 17294-1,2 (mod)/EPA-method 200.8, SS 028150-2 or ISO 11466/EN13346 (mod), as well as for OTs (TBT, DBT, MBT) (ISO 23161:2011 and DIN, 19744). Measurement uncertainties for metals range between ~18 and 25% and are ~27% for OTs. Organotin and metal contents were compared to Swedish, Canadian, and Norwegian reference values and risk classes. Canadian and Norwegian reference values are often used to complement the Swedish reference values (INSURE, 2017), as these only cover OTs, and the countries have similar geology and climate.

Sequential extraction was used to evaluate the mobility of metals in the sediment. A modified 5-step sequential extraction scheme based on (Hall et al., 1996a, 1996b; Tessier et al., 2002) was performed on sediments, using 1 M NaOAc pH 5 to extract easily adsorbed, water soluble and exchangeable metals and carbonates, followed by $\text{Na}_4\text{P}_2\text{O}_7$ to extract labile organic forms of metals, 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.1 M HCl at 60 °C was then used to extract amorphous iron and manganese oxides, after which 1.0 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% CH_3COOH at 90 °C was used to extract crystalline iron oxides, and finally KClO_3 in 12 M HCl 4M HNO_3 at 90 °C was used to extract the stable organic forms and sulfides. After each leaching step, the leachate was sampled and analyzed for selected minor and major elements according to the methods stated above. The

risk assessment code (RAC) was used to evaluate the risk to the environment by comparing the percentage of the total metal content released in the exchangeable and carbonates phase with the given criteria (Perin et al., 1985; Jain, 2004).

2.3. Leaching experiments

2.3.1. Batch leaching

Ultra-pure water (Milli-Q water), 0.06 M [S,S]-EDDS, 0.52 mM hydroxypropyl cellulose (HPC), 0.01% (v/v) saponified tall oil (“soap”), 1.59 g/L humic acid (HA) (Florence, 1982), and 0.52 mg/L Fe colloids (Florence, 1982) were individually tested as leaching agents (see Fig. 2 for the experimental setup and Supplementary material Table S1 for more information about the chemicals used). Wet BK sediment (60g, ~60% DW) was mixed with each leaching agent at an L/S of 10 (calculated on sediment dry weight). The slurry was placed on a shaking table for 1 h at a speed of 125 rpm. The samples were left to settle for a few minutes, then the leachate slurry containing fine suspended particles was decanted and collected. The settled coarse-grained sediment at the bottom of the beaker was collected separately. The obtained leachate was centrifuged for 3 min at 3000 G. The supernatant was decanted, and the fine-grained solid residues were collected and stored at 4 °C until analysis. Two samples were taken from the supernatant; the first was not filtrated, while the second sample was filtrated using a cellulose acetate membrane filter with a pore size of 0.45 μm . The filtrated supernatant was also used for analyzing zeta potential and particle size distribution curve. The metals in the liquid samples were dissolved with acid and stored at 4 °C for further analysis. The experiments were done in triplicate. The sediments were weighed before and after leaching. Coarse- and fine-grained sediments were analyzed, and the final sediment contents were calculated by summing contents multiplied with the corresponding weight percentage of the coarse- and fine-grained sediment residues.

2.3.2. Saltwater leaching with vigorous shaking

This method was inspired by the batch leaching procedure described by Stichnothe et al. (2001), with some modifications. A sample of 420 g CV sediment (~40% DW) was mixed with 0.7 L NaCl (5 M) and placed in a turn-over-end-shaker (1 rpm) (Fig. 2). After 24 h the sediment mixture was self-filtrated through a Munktell paper filter with a pore size of 4–7 μm . The filtrate and the solid residue were collected and stored at 4 °C until analysis. Prior to metal analysis, the filtrate was filtrated using a cellulose acetate membrane filter with a pore size of 0.45 μm and dissolved with acid.

2.3.3. Acidic leaching

Previous studies on leaching of ashes and soils with acid yielded a high metal recovery (Karlfeldt Fedje et al., 2013; Karlfeldt Fedje and Strömwall, 2019). An enhanced batch leaching method for metal removal from soils (Karlfeldt Fedje et al., 2013) was modified for this sediment application. A sediment sample from CV (500 g, ~40% DW) was mixed with 0.1 L waste acid (~1 M HCl) for 30 min using a magnet stirrer (Fig. 2). The waste acid is highly acidic with a pH of ~0 and is generated from the wet flue gas cleaning process employed in the incineration of municipal and industrial solid waste. The concentrations of different elements in the acidic process water vary to some extent due to incineration conditions. After leaching, the sediment-slurry was vacuum-filtrated through a Munktell paper filter with 4–7 μm pore size and the filtrate was collected. The solid residue was washed with 100 ml of Milli-Q water through vacuum-filtration and the washing filtrate was collected. Both filtrates and the solid residue were stored at 4 °C until analysis. Both filtrates were filtrated using a cellulose acetate membrane filter with a pore size of 0.45 μm and dissolved with acid prior to metal analysis.

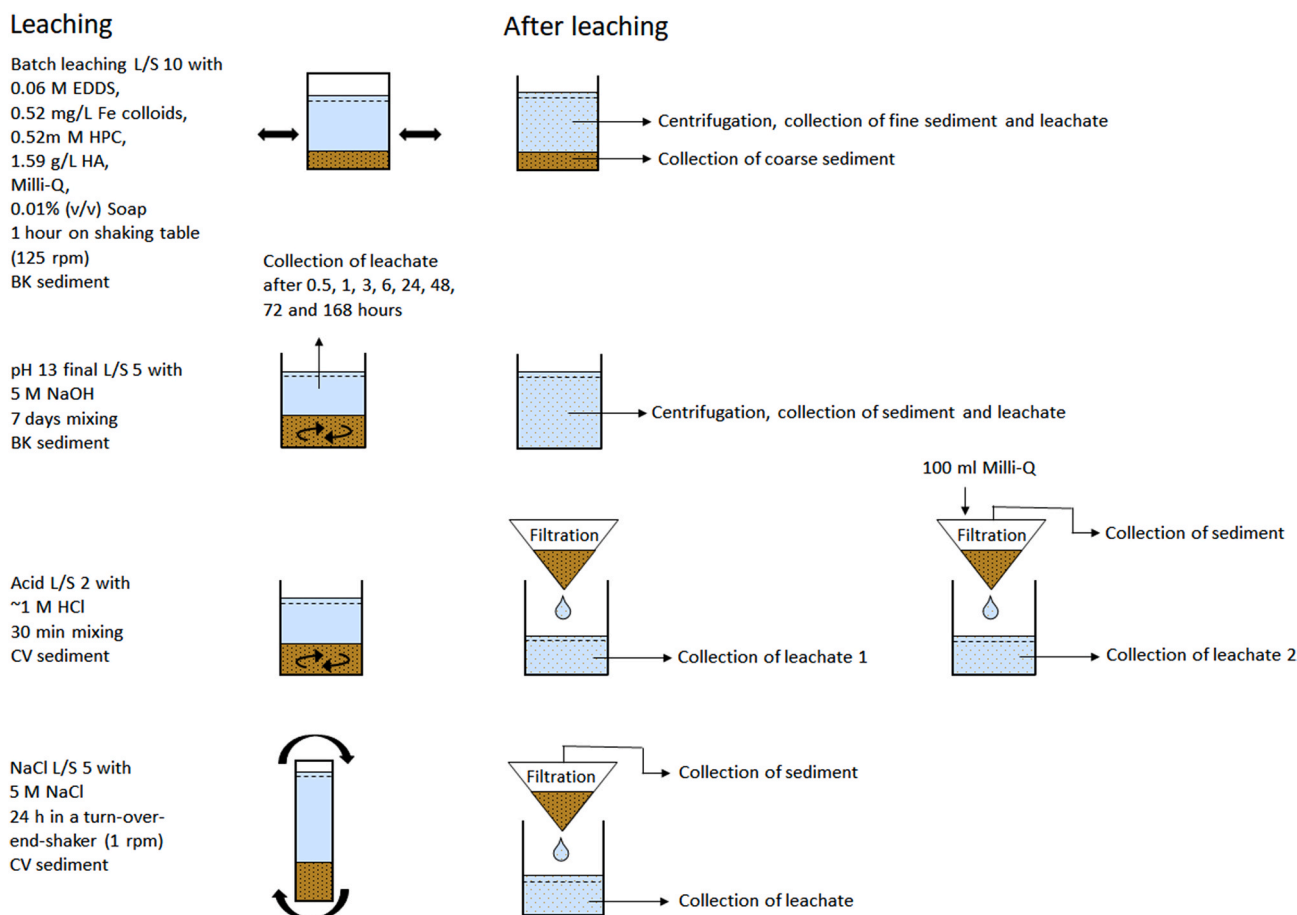


Fig. 2. Set up for the experiments performed on Björlanda Kile (BK) and Cityvarvet (CV) sediments using the leaching agents (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), iron colloids (Fe colloids), hydroxypropyl cellulose (HPC), humic acid (HA), Milli-Q (Milli-Q water), saponified tall oil (soap), NaOH (pH13), HCl (acid), and NaCl.

2.3.4. Alkaline leaching

pH-static leaching tests at pH 11 and 13 were performed using 180 g BK sediment (~40% DW) and ultra-pure water at an initial L/S ratio of 4, calculated on sediment dry matter (Fig. 2). Sodium hydroxide (NaOH), 5 M, was added using a Titroline® 7000 by SI Analytics, to reach the desired pH. Final L/S ratios were 4.1 and 4.5, calculated on sediment dry mass for pH 11 and 13, respectively. Duplicate liquid samples were taken after 0.5, 1, 3, 6, 24, 48, 72, and 168 h. One of each duplicate was filtrated using a cellulose acetate membrane filter with pore size 0.45 µm, while the other sample was not filtrated. All liquid samples were dissolved using acid and stored at 4 °C prior to metal analysis. The experiment ended after 7 days, i.e. 168 h. The slurry was left to settle for a few minutes, then decanted and centrifuged at 3000 G for 3 min. The solid residues and the liquid were collected separately and stored at 4 °C until analysis. The concentrations of OTs in the final pH 13 leachate were all significantly higher than in the pH 11 leachate, that is why the results for pH 11 have been omitted.

2.4. Analysis of leachates and sediment residues

Metal concentrations in the leachates were determined using ISO 11885:1995, SS 028150-2/ICP-MS(AES), and SS EN ISO 17294-1,2/EPA-method 200.8 with a measurement uncertainty of ~12–30%. Organotin compounds in leachates were analyzed according to ISO17353:2004 with a measurement uncertainty of ~32%. Conductivity and pH were measured using a multiline Multi 350i by WTW. An Anton Paar Litesizer 500 was used to analyze selected leachates for particle size distribution (ISO norm 22412:2017) and zeta potential

measurements (ISO 13099-2:2012). The samples were filtrated using a cellulose acetate membrane filter with pore size 0.45 µm prior to analysis. Investigation of DW, LOI, metals, and OT contents, as well as ESEM and EDS imaging, were carried out on selected solid residues using the methods described in subchapter 3.2 *Characterization of sediments*.

3. Results and discussion

3.1. Characterization of original samples

3.1.1. Physical characterization

Ocular inspection (ISO 22412:2017) characterized BK and CV sediments as silty clay/clayey silt containing pieces of shells, which confirmed an earlier study about the area (Johannesson et al., 2000). ESEM images of both sediments showed a relatively homogeneous material, mainly consisting of angular clay mineral flakes of different sizes (Fig. 3 a-b). The similarities of the sediments are also visible in the grain size distribution curves, in particular for grain sizes up to 0.03 mm (Supplementary Material Figure S1). The sediments studied here consisted of fine particles and the performed ESEM/EDS-analyses indicated that the elements were fairly evenly distributed between particles and that marginally more metals are seen in CV (Supplementary material Figures S2–S3). Spectra images from EDS analysis show great likeness between the sediment (Supplementary material Figures S4–S5). The reason for the lack of metal and grain size correlation is probably that the metal contents were below the EDS's detection limit. Although TBT is frequently found in paint flakes within sediments (Lagerström et al., 2017), Sn, and corresponding OT compounds, could not be correlated to

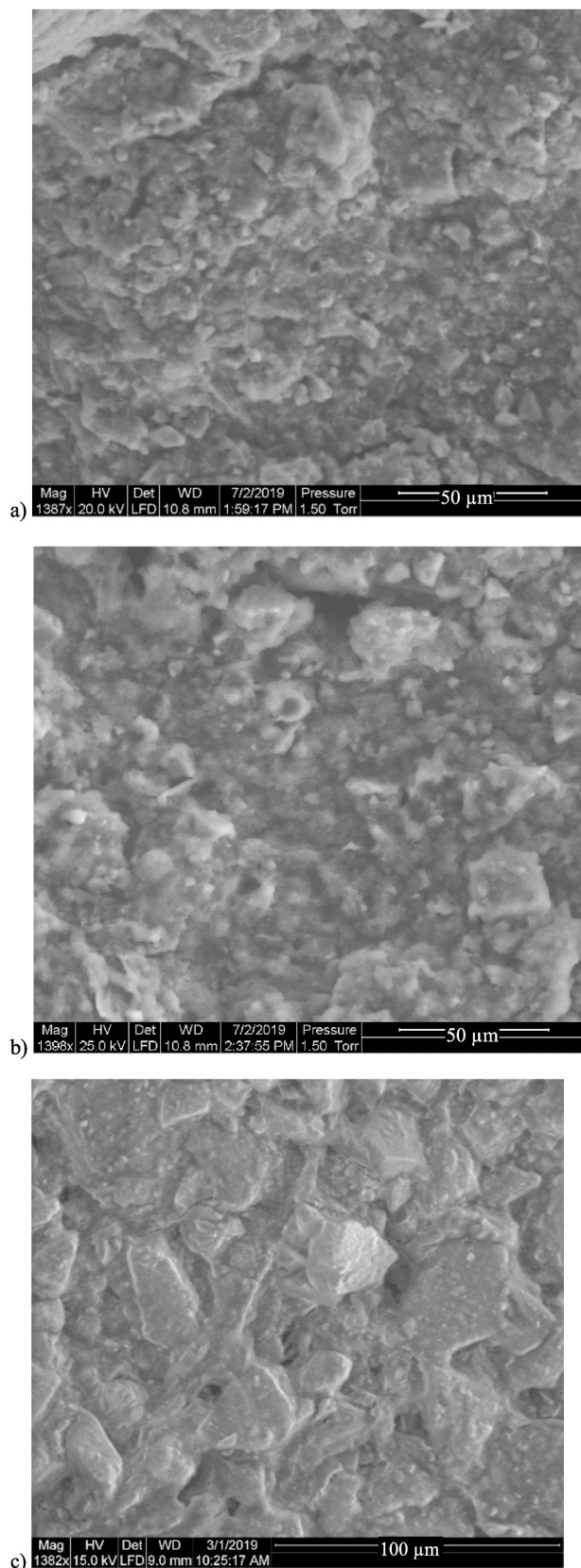


Fig. 3. ESEM images of a) Björlanda Kile (BK) sediment sample magnified 1387 times, b) Cityvarvet (CV) sediment sample magnified 1398 times, c) pH 13 leached sediment from BK magnified 1382 times.

any specific particles. This illustrates the complexity of the sediment matrix, especially as these paint flakes do not always dissolve during normal lab analysis. A result may be that the TBT content increase after treatment, due to paint degradation. The LOI was higher in the samples from BK than in those from CV; 6.7% compared to 2.3% DW (Table 1). This could be of interest as TBT is often found in the organic fractions of sediment (Hoch and Schwesig, 2004). The wet bulk density for the original sediments was 1.4 g/cm³. To conclude, the sediments have similarities, making it favorable to compare leaching results between them. The possibility to compare sites and remediation results is something inquired by Mulligan et al. (2001) in their review of treatment techniques.

3.1.2. Level of contamination

Initial contents of OTs and metals in sediment from BK and CV are presented in Table 1. The OT contents found in the sediments range from 70 to 1300 µg/kg DW. The highest TBT content was found in the CV sediment and classified as having an ‘extensive acute toxic effect’ according to the Norwegian classification (Direktoratsgruppen vanndirektivet, 2018). The original BK sediment sample was less contaminated but is still classified as ‘acute toxic’. According to the Swedish quality criteria, the contents in both sediments are classed as ‘very high’ (SGU, 2017). At BK, the contents of MBT > DBT > TBT. The opposite order of magnitude was found in the samples from CV. This indicates that the OTs at BK have come further in the degradation process than those at CV (Garg et al., 2009), which may be due to the later ban of OT-containing paints for larger vessels (>25 m), which were present at CV but not at BK.

The metal contents pose a less severe environmental risk than the OT contents. Zinc contents at both sites were large enough to potentially cause chronic effects after long term exposure, and the same was true for Cu at BK (Direktoratsgruppen vanndirektivet, 2018). Copper contents at CV are classified as having ‘extensive acute toxic effects’ (Direktoratsgruppen vanndirektivet, 2018), and also reach the Canadian ‘probable effect’ level, implying that marine organisms are affected at the site (Canadian Council of Ministers of the Environment, n.d.). The remaining metals were found in contents classified as ‘background levels’ or ‘not causing toxic effects’ according to the Norwegian classification (Direktoratsgruppen vanndirektivet, 2018), while the Canadian guidelines

Table 1

Average and standard deviation for organotin and metal contents in Björlanda Kile (BK) and Cityvarvet (CV).

Sediment	BK		CV	
	Average	Standard deviation	Average	Standard deviation
DW [%]	43	2.6	40	1.1
LOI [% DW]	6.7	1	8.8	1.5
Organotins [µg/kg DW]				
TBT	73	4.3	1300	110
DBT	430	26	440	67
MBT	470	28	85	11
Metals [mg/kg DW]				
Ag	0.13	0.029	–	–
As	16	2.6	9.0	2.2
Ba	71	5.7	110	6.7
Cd	0.13	0.014	0.29	0.024
Co	8.9	1.2	11	0.79
Cr	48	2.8	57	1.6
Cu	78	7.4	230	13
Fe	26400	–	35000	–
Hg	<0.2	–	<0.2	–
Mo	1.9	0.27	4.7	0.86
Ni	20	1	22	0.6
Pb	32	1.9	32	8.7
Sb	0.39	0.049	4.7	0.5
Sn	3.2	0.22	12	1.1
V	56	3.6	53	3.3
Zn	200	20	360	27

classify the levels as at or below the limit where effects may start to occur (Interim sediment quality guideline (ISQG)) (Canadian Council of Ministers of the Environment, n.d.).

In summary, the sediments' environmental risk is mainly due to the TBT contents and reducing TBT contents in the sediments is therefore motivated from a risk perspective; the same is true for Cu and Zn. Copper and Zn are widely used as substitutes for TBT in boat bottom paints and depending on the global increase of leisure boats these metals will be even more important to study in the future (Ytreberg et al., 2016).

To fully evaluate the environmental risk of the sediments, further investigations can be performed, such as identifying metals species, physico-chemical parameters, as well as performing toxicity tests (Khosrovyan et al., 2015; Namieśnik and Rabajczyk, 2015; Rodriguez-Romero et al., 2016).

3.1.3. Sequential extraction

Sequential extraction procedures are often used to evaluate the potential metal mobility in sediments (Hall et al., 1996a, 1996b), and the element distribution between the sequential extraction steps indicated that 100% metal removal using the leaching methods tried out in this study could not be expected (Fig. 4). The BK and CV sediments showed similar potential element mobility in all stages, from the easily soluble fraction (1) to the stable residue fraction (5) (Fig. 4). However, at CV a larger fraction was bound to crystalline iron oxides and a smaller one to labile organic forms, than at BK. This may be explained by the relatively low content of organic matter in the CV sediment, in comparison with BK (Table 1). As a result, the metals at CV, despite being present in higher contents, may pose a lower environmental risk than for BK, where a higher percentage of the metals were bio-available and relative easily soluble (Fig. 4). The toxic metals, >30% of which were found in the easily soluble fraction, were Cd, Pb, and Zn at both sites. In the BK sediment, Cu, which is classified as 'causing chronic effects to marine organisms', according to the Norwegian classification (Direktoratsgruppen vanndirektivet, 2018), was to a large extent bound to the labile organic forms, and therefore less mobile, which can be explained by the fact that Cu forms stable complexes with humic acids (Kalmykova et al., 2008a). However, in the samples from CV, where Cu is causing extensive acute toxic effects, a higher percentage was found in the most easily soluble fraction, further motivating the need to reduce the contents to limit the environmental risk.

Metals in CV were to a slightly larger extent found in step 3 and step 4, both steps associated with Fe in the sediment, than in BK sediments. This may be related to the higher Fe content in the CV sediment (Table 1). While most metals were mobile in most steps, Sn was closely associated with organic compounds at both CV and BK (Fig. 4). About 50% of the Sn in the sediment from BK was bound to stable organic compounds and sulfates, while the remaining Sn was bound to labile organic compounds. This indicates that, in theory, almost 50% of the Sn would be easily leachable, while the rest may be difficult to attain, as it is bound to stable compounds. As there is a strong affiliation of OTs to organic matter and humic acids (Fent and Looser, 1995; Berg et al., 2001), the OTs may bind to any or both of the organic steps. The contents of butyltins at CV corresponded to ~8% of the total Sn content; at BK the corresponding percentage was ~17%. Other forms of OTs, not investigated in this study, may also contribute to the OT content, including phenyltin compounds, which have also been used in anti-fouling paints (Lagerström et al., 2017).

Regarding risk classification according to RAC, the sediments are similar, apart from Cu and Cd that pose a higher risk in CV than in BK (Perin et al., 1985; Jain, 2004). In CV, Cd is classified as 'very high risk', while is classified as 'high risk' in BK. Copper is posing a 'high risk' in CV and 'medium risk' in BK. For both sites Pb and Zn are 'high risk', Ba, Co, Ni are 'medium risk', V, Mo, As and Cr are 'low risk' and Sn and Hg are 'no risk'. When weighing up the risks associated with the metal contents and the risk of metal release, it is seen that Zn at both sites and Cu at CV are 'high risk' in both categories. Cadmium in CV is likely to spread but

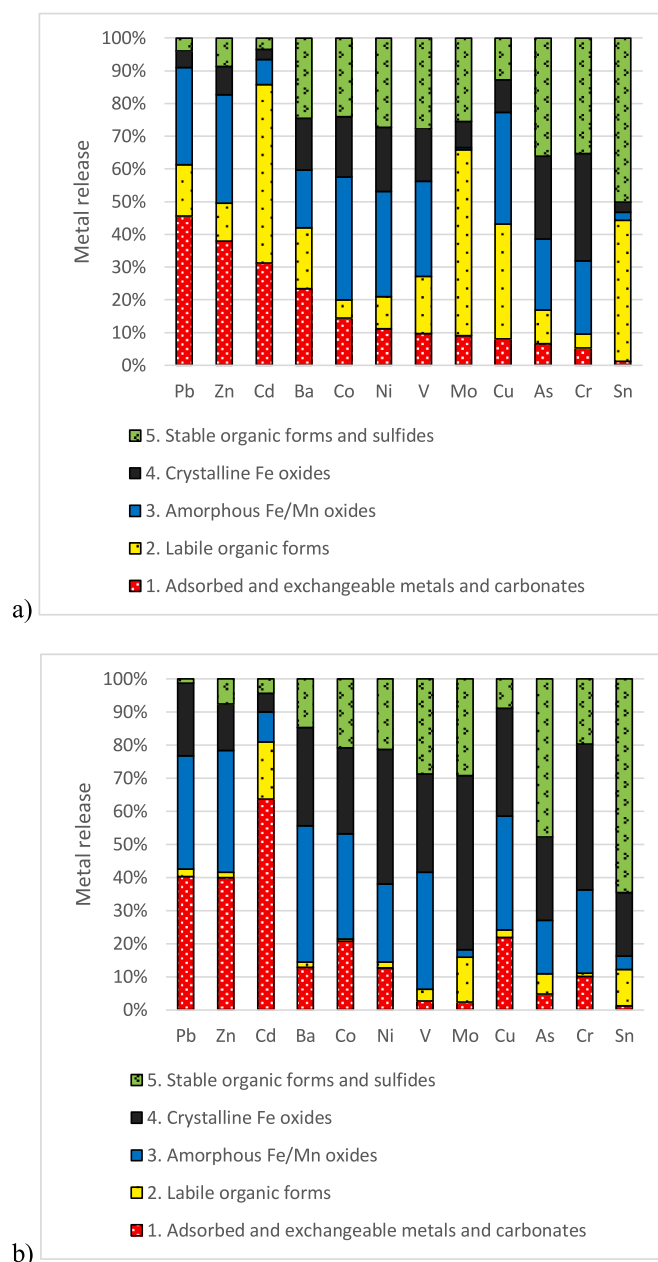


Fig. 4. Results from the five-step sequential extraction leaching for a) Björlanda Kile (BK) sediment b) Cityvarvet (CV) sediment.

is on the other hand present in low content, potentially lowering the overall risk for this metal.

3.2. Leaching experiments

3.2.1. Organotin

All leaching experiments using the low environmental impact leaching agents resulted in a decrease in the total OT content by 36–75% (Tables 1–3). The most efficient reduction of the total OT content, to 25% of the initial content, was achieved with Milli-Q water. This was also the most efficient way to remove TBT from the sediment, to 53% of the initial content. The NaCl leaching also led to reduced contents of all OTs in the sediment, as salinity favors release from sediment (Fent, 1996; Stichnothe et al., 2001; Hoch et al., 2003). In the study by Stichnothe et al. (2001) 40–75% of the initial TBT content was removed after treating two sediments at the same NaCl concentration as used in this study (5 M NaCl). In our study was 35% of the original TBT content

Table 2

Organotin and metal contents in Björlanda Kile (BK) sediments after leaching with EDDS, humic acids (HA), hydroxypropyl cellulose (HPC), Fe colloids (Fe), Milli-Q (Milli-Q water), saponified tall oil (soap), alkaline NaOH (pH 13).

Sediment	EDDS	HA	HPC	Fe	Milli-Q	Soap	pH 13
DW [%]	40	43	43	44	44	40	44
LOI [% DW]	8.8	7.1	9.2	6.9	6.9	6.9	4.2
Organotins [µg/kg DW]							
TBT	56	110	56	91	39	48	140
DBT	150	170	150	150	83	150	120
MBT	210	250	180	240	120	190	440
Metals [mg/kg DW]							
Ag	0.12	0.12	0.09	0.11	0.12	0.11	0.16
As	11	17	8.9	13	12	13	9.8
Ba	59	79	53	58	62	53	100
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Co	5.4	7.1	4.5	5.9	7.4	6.3	14
Cr	42	52	31	42	39	38	62
Cu	52	72	55	53	66	55	59
Hg	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mo	1.8	1.8	1.6	1.8	1.8	2.3	2.2
Ni	19	19	15	19	16	18	31
Pb	23	28	24	24	25	25	42
Sb	0.3	0.3	0.3	0.3	0.3	0.4	0.3
Sn	3.7	3.6	3.0	3.7	3.4	3.9	3.9
V	49	35	19	49	46	28	66
Zn	160	180	120	150	180	130	280

Table 3

Organotin and metal contents in Cityvarvet (CV) sediments after leaching with wet flue gas cleaning process acid (acid), and NaCl.

Sediment	Acid	NaCl
DW [%]	42	48
LOI [% DW]	3.3	5
Organotins [µg/kg DW]		
TBT	2300	1100
DBT	340	190
MBT	89	57
Metals [mg/kg DW]		
Ag	–	–
As	9	8.1
Ba	100	84
Cd	0.5	0.2
Co	10	8.7
Cr	45	41
Cu	250	180
Hg	1.6	0.2
Mo	9.8	5.8
Ni	19	17
Pb	39	25
Sb	5.9	1.9
Sn	15	9.9
V	48	43
Zn	280	270

removed, which is slightly less, and could be due to shorter treatment time (24 h vs 36 h), mixing conditions (turn-over-end-shaker vs mixing), a lower L/S ratio (5 vs 10), a lower initial TBT content (180 vs 380, and 97 000 µg/kg DW) and differences in sediment characteristics, which is not specified in the article. However, the TBT reduction was less for NaCl than for Milli-Q water. Shaking with Milli-Q water may facilitate the release of TBT from the sediments, in particular for TBTO, which was the most commonly used form of TBT in antifouling paints and has a high solubility in water (4 mg/L) (Müller et al., 2013; Lagerström et al., 2017). The degradation products DBT and MBT have low sediment-water distribution coefficients, making them more soluble in water (Berg et al., 2001). Another explanation could be that OTs have both hydrophobic and hydrophilic properties and when exposed to ultra-pure water, hydrophobic OT dispersion could be promoted due to low conductivity, low ion strength, and low concentrations of dissolved gas, which enhance release from the sediment (Pashley et al., 2005;

Lindahl et al., 2013). Milli-Q water contains low concentrations of dissolved gasses and if the gas concentration is further reduced, higher concentrations of OTs could potentially be released from the sediment (Pashley et al., 2005; Nithyanandan et al., 2006; Lindahl et al., 2013).

Soap was the second-best performing leaching agent for reducing both total OT and TBT, with a removal rate of 60% and 34%, respectively. This may be explained by the sorption of the OTs' lipophilic part to the fatty and resin acids in the tall oil (Andersson and Strömvall, 2001). The high OT removal achieved with soap could additionally be explained by the fact that the soap surfactant forms emulsions that allow hydrophobic TBT and small TBT-containing particles to remain in suspension. Particle size analysis did show that the soap sample had the highest number of colloids in the liquid phase after leaching. If the OTs occur as positive ions, there may also be a complexation with the carboxylic groups of the acids in the soap. Both Milli-Q water and soap treated sediment could be reclassified according to the Swedish classification system, from 'very high' to 'high' TBT content, but the decrease was not enough to alter the Norwegian sediment risk class. For all leaching agents, a reduction of DBT and MBT was observed in the sediments.

In order, the batch leaching agents that achieved the highest TBT reduction were Milli-Q water, followed by soap, HPC, and EDDS. On the contrary, the TBT contents increased in samples leached with Fe colloids and HA (Table 2). This could be explained by that mechanical mixing of sediment may release earlier encapsulated TBT from boat paint in the sediment (Lagerström et al., 2017). Analyses of the zeta potential for the particles in the leachates with TBT and HA (−12 mV) and Fe colloids (−20 mV) showed that these colloids with bounded TBT may agglomerate and precipitate back into the sediment (Kumar and Dixit, 2017). However, the zeta potentials for other leaching agents indicate that this newly released TBT could remain in the solution or degrade. A study has shown that TBT effectively binds to HA due to the hydrophobic properties of the humic acids (Fent, 1996), however, during leaching the originally dark opaque HA-liquid changed in color, becoming a clear see-through liquid, which indicates precipitation of the HA into the sediment. The TBT sorption to the organic parts of the molecules may cause formed complexes to agglomerate and precipitate in the sediment. Additionally, the low TBT reduction by Fe colloids could be due to experiments being carried out at temperatures that were too low (21 °C), as degradation is enhanced with increasing temperature (Yamashita et al., 2012). Even if none of the investigated leaching agents achieved a complete TBT degradation, some of them, e.g. Milli-Q water, and soap, may provide sufficient treatment for other sediments than those investigated here, by lower the TBT content to an acceptable level for reuse. Additionally, the methods could be further developed and improved for a full-scale usage by investigating e.g. the optimal leaching time, L/S ratio, and concentrations of leaching agents in addition to site-specific adjustments.

The results in Tables 2 and 3 indicate that OT contents in the sediment were higher after the acidic and alkaline leaching. However, leachate analysis indicates that OTs leached out in both acidic and alkaline conditions, and especially in the latter. The contents found in the alkaline leachate corresponded to 25% TBT, 10% DBT, and 75% MBT of the initial OT contents in the sediment, respectively. The pH-dependent leaching of OTs showed that TBT is mainly released at high or low pH values, whereas DBT, and MBT in particular, are less affected by pH changes (Pynaert and Speleers, 2004). At high pH values, when TBT is mainly found as the neutrally charged TBTOH, the hydrophobic effects have a greater impact than the electric charge (Burton et al., 2004). Possible explanations for the high TBT content found in the pH 13 leachate include that the hydrophobic properties of organic matter in the sediment decreased due to the higher pH (Ertli et al., 2004), or that the hydrophobic compounds were released into the aquatic phase, as the LOI was lower in the sediment after treatment (Tables 1 and 2). At lower pH values, TBT is mainly present as TBT cations, and because positively charged sediment sites are abundant and cause electrostatic repulsion of

the cations (Xiao et al., 2011), TBT is released from the sediment. The ionic strength is also high both during acidic and alkaline leaching, which facilitates leaching. On other hand, Milli-Q water has low ionic strength and achieved the highest TBT removal. This may imply that the leaching effect is not solely dependent on the leaching agents' ionic strength, but rather a combination of different physico-chemical parameters, including the ionic strength, influence the TBT removal (Burton et al., 2004; Hoch and Schwesig, 2004).

Another possible reason for the higher OT contents found in the sediments post-leaching under extreme pH is that this likely impacts the sediment matrices themselves (Kuo et al., 2006; Moutsatsou et al., 2006). This could cause parts of the sediment to dissolve; examples include seashells containing carbonates being dissolved during acidic conditions. The ESEM images for selected leaching agents all looked similar to the corresponding original sample, except for the pH 13 sediment (Fig. 3 b and c). The sediment leached at pH 13 contained more distinct and larger flakes. An explanation may be that the high alkaline pH in combination with long-term mixing makes the particles wear down into small particles (Rodella et al., 2017). Small particles remain suspended and are therefore removed with the leachates. Filtration of the sub-samples became more difficult as the leaching time progressed, indicating an increase in the number of particles present in the leachate. Such a change in the sediment matrix may affect the relative density of the sediment, in turn also affecting the relative contents. TBT and OTs are often not homogeneously distributed in samples due to being introduced into the sediment, either through sorption from water or when OT containing antifouling paint flakes are covered by fresh sediment (Singh and Turner, 2009; Lagerström et al., 2017). For the alkaline sediment, it may also be the case that the naturally occurring HA in the sediment is present in the form of curled uncharged particles at low pH dissolves as the pH increases ($\text{pH} > \text{pK}_a \sim 5$) due to the negative charges caused by the deprotonation of the acids. This would then cause them to be released from the sediment (Kalmykova et al., 2008b). Despite having a constant high pH and mixing conditions for one week it was not enough to fully remove all TBT, indicating that altering the pH alone is not sufficient to obtain sediment without TBT. Also, the residual sediment would most likely require further treatment to neutralize the pH during mass management.

3.2.2. Metals

From an environmental risk perspective, the presence of Cu and Zn are the most important metals to reduce in the original sediments. The highest reduction of Cu was obtained using low environmental impact leaching agents, EDDS (33%), Fe colloids (32%), HPC (30%), and soap (29%) (Table 2). Despite the reduced Cu contents, none of these were effective enough to lower the risk classification. None the less, HPC managed to lower Zn to the Canadian risk class <ISQG (Canadian Council of Ministers of the Environment, n.d.), by reducing the content to 39% from the initial level. For Zn, the 'no toxic effects' level was reached with both HPC and soap, the latter by achieving a 33% reduction. Leaching changes the particle fractionation and chemical composition of the sediment, affecting the metals' mobility and form (Yoo et al., 2013). This may impact the bioavailability and toxicity of the metals, and thereby the environmental impact of the sediments after leaching. Of all the leaching agents tested, HPC lowered the metals' risk classes the most. It also achieved the highest average metal removal.

Milli-Q water achieved the greatest decrease in TBT content in the sediment but was not effective for metal removal. This suggests that Milli-Q water is suitable for facilitating TBT removal from sediment, however, where metal removal is also needed, additional treatment is required. Soap achieved the second-highest TBT reduction and was able to reduce both Cu and Zn, probably by binding the metals to the soap's COO^- groups. The sediment residues after saltwater leaching showed a reduced content of all studied metals. Previous studies have managed to extract 20% Pb and 55% Cd, but <5% for Cu and Zn from sediment using NaCl (Nystroem et al., 2006). Here, the metal contents were reduced by

25% Zn, 22% Cu, 22% Pb, and 21% Cd, respectively (Table 3). A higher metal removal should be achieved by lowering the pH (now 7.4) (Yoo et al., 2013). After NaCl treatment, the sediment's risk class was reduced to ISQG for Zn.

Humic acids were not effective for the removal of neither OT nor metal. Kalmykova et al. (2008a) have otherwise shown a strong sorption capacity of metals to HA. This can be explained by the fact that HAs have high stability complexation constants with metals; these are particularly high with Cu and Pb. However, results from the HA leached sediment demonstrated increased contents of Cu, Pb, and TBT after leaching. As described for the OTs, the HA seemed to agglomerate and precipitate in the sediment. The leachate had a pH of 9.6, and at this pH humic acids are normally dissolved in water. Additionally, at such a high pH the metal sorption to humic acids is usually high. However, Co, Ni, Cu, Zn, and Pb are mainly attached to Fe colloids rather than humic acids at $\text{pH} > 8$, as the point of zero charge for Fe colloids is $\sim \text{pH} 8$ (Lyvén et al., 2003). These metals were all removed to a higher degree by Fe colloids than by HA.

The fine-grained sediments obtained after centrifugation of the leachate slurry from the *low impact agents* contained higher contents of most metals than the original samples. This increase in metal content in fine fractions after leaching is consistent with previous results (Yoo et al., 2013; Rodella et al., 2017; Ma et al., 2019). Ma et al. (2019) suggest that hydrodynamic shear force and physical friction force remove metals from larger particles. The released metals then bind to the finer particles, due to their stronger metal sorption capacity in comparison to larger particles. Several studies have shown that OTs and metals are often attached to finer particles and that targeting the fine particles for treatment is a way of reducing the need and cost of treatment (Quevauviller et al., 1991; Adiyiah et al., 2014; Rodella et al., 2017). However, such a separation may be difficult for the sediment studied here, due to fine particles making up the bulk of the sediment (Fig. 3).

For acid leaching ($\text{pH} \sim 0$) in the study by Karlfeldt Fedje et al. (2013) all metals in the soil decreased, however, an increase in Cd, Cu, Hg, Pb, Mo, and Sn was observed in the residual sediment (Table 3). This can be explained by the fact that the waste acid contains metals, which need to be removed before it is used as leaching agent (Karlfeldt Fedje and Strömval, 2019). The alkaline leaching was effective for the removal of the metalloids As and Sb, as these form anions at high pH (Johansson et al., 2010; Wilson et al., 2010). Fifty-seven percent and 88% of the original BK sediment contents were removed for As and Sb respectively (Tables 1 and 2). Other metals remained in contents similar to, or higher than, in the original BK sample. The alkaline mixing resulted in metal precipitation on particle surfaces, thereby the metals became incorporated into the sediment matrices. Further, the dissolution of compounds within the sediment at this extreme pH affected the weight of the solid residues, thereby changing the relative weight relationship between the metals and the sediments, as previously discussed for OTs.

The final alkaline leachate, i.e. after one week's leaching, contained the highest metal concentrations of all leachates. Of the metal content in the original BK sediment, $\sim 60\%$ of Co, Ni, Cu, and Zn, respectively, were found in the unfiltered samples after one week of leaching, while the corresponding percentages in filtered samples were <5% for Co, Ni and Zn, and 30% for Cu (Fig. 5). This may be explained by the fact that Cu is more truly dissolved, whereas Co, Ni, and Zn are mainly sorbed to particles. As time progressed the un-filtered metal concentrations continued to increase, while most filtered metal concentrations stopped increasing after ~ 48 h (Fig. 5). This indicates that metals are mainly sorbed to suspended particles $< 0.45 \mu\text{m}$ and that the sediment degrades into finer particles over time (Yoo et al., 2013), rather than the metals becoming increasingly dissolved. For the *low impact agents*, the differences between un-filtrated and filtrated leachate samples were less obvious. Those leachates contained <5% of most metals from the original BK sediment. A notable exception was EDDS, which managed to extract 23% of the initial content of Zn in the BK sediment, as well as

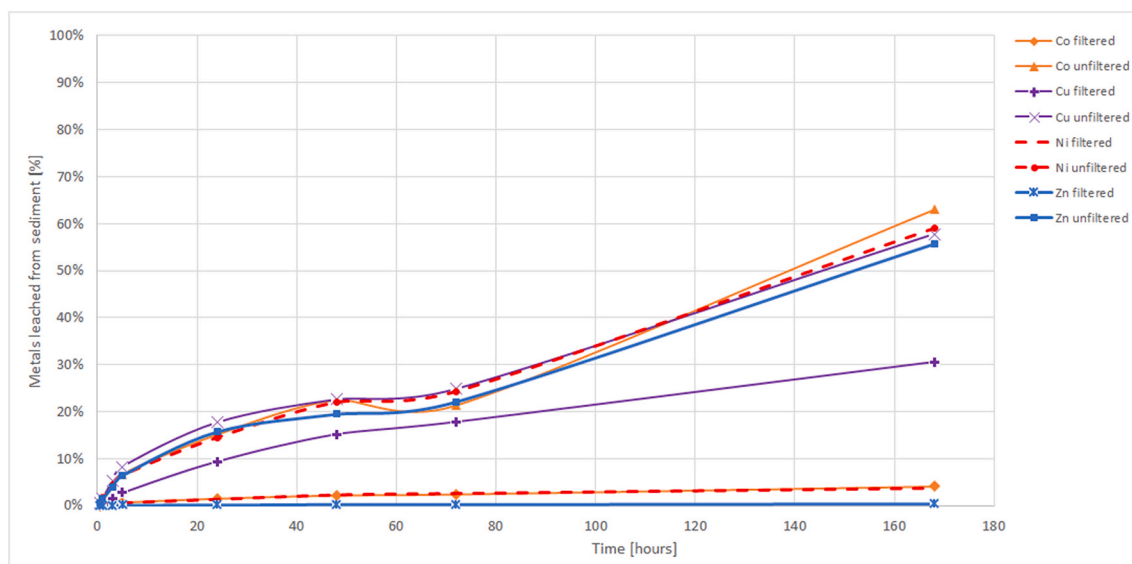


Fig. 5. Percentage of selected metal ions, in filtered and unfiltered samples, leached over time from the original Björlanda Kile (BK) sediment sample during the pH 13 alkaline leaching.

21% of the Pb and 16% of the Cu, which is within the range compiled by Begum et al. (2016).

The highest metal concentration reached in the pH 13 leachate was Zn (29 mg/L). This concentration is too low to be economically viable for metal recovery with current technology. However, if the Zn was to be concentrated further, recovery may become of interest in the future. For instance, further metal accumulation could be achieved by using e.g. conventional precipitation, or an alternative technique such as bio-electrochemical systems, which may enable recovery of metals from low concentrated solutions (Karlfeldt Fedje et al., 2015).

The contents removed by leaching were lower than expected from the results of the sequential leaching test. This may be due to the difference in the leaching methods. Firstly, the leaching times varied, and secondly, the L/S ratios from the sequential leaching test were a lot higher (40–112 times). Additionally, higher concentrations of reactants were used than in the experiments carried out in this study.

4. Conclusions

Contaminated sediments are a worldwide concern. Ports require frequent dredging and the recovered sediments need to be either land-filled or treated owing to elevated contents of OTs and metals. This study is the first investigation of low environmental impact leaching agents to remove OTs and metals from contaminated marine sediments. Leaching at low or high pH was investigated for comparison. Ultrapure water (i.e. Milli-Q water) was found to be the most effective leaching agent for both TBT and OTs with removals rates of ~50% and 75%, respectively. Leaching with either Milli-Q water or soap resulted in the reclassification of residual sediments from ‘very high content’ to ‘high content’ in the Swedish sediment classification system. For metals, the leaching agents that resulted in reduced risk classification were HPC and soap. The most effective leaching agents for Cu and Zn were EDDS (33% removal) and HPC(39% removal), respectively.

This study shows that low environmental leaching agents provide an opportunity to develop an innovative and sustainable method for full-scale remediation of contaminated sediments and thus enabling potential sediment reuse. Although the results indicate that the investigated leaching agents are not sufficiently effective on an individual basis to treat OTs and metals simultaneously, the combination of leaching agents (e.g. in batch sequence tests with Milli-Q water and HPC) should be studied. However, the first leaching step might affect the sediment and

reduce the effectiveness of the subsequent step and has to be assessed in experiments together with optimization of leaching parameters. Additionally, toxicity tests could be performed to evaluate the potential environmental risks before and after leaching.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2020.111906>.

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