IMplementing MEasuRes for Sustainable Estuaries (IMMERSE)

Environmental Assessment and Treatment of Organotin and Metal Contaminated Dredged Sediment

WP 4. Measures: Assessments, tests, and pilots

Report for WP 4.3: Assess existing pilot on stabilisation/solidification of dredged masses and develop methods for recovery of metals and polluted sediments in the Göta Älv

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1. Introduction

Today, everyday life and the global economy are dependent on shipping as more than 80% of the global trade volume is transported by sea and that number is annually increasing [1]. However, for cargo vessels to access ports and other important marine structures, both the vessels and the traffic routes need to be maintained. Removal of sediment (dredging) is vital for maintaining water depths and allow ships to enter ports. In major ports, large amounts of masses are often handled. As an example, the largest port in Scandinavia, the Port of Gothenburg (Sweden), needs to remove around 200 000 m^3 dredged materials every three to five years, of which 75% is contaminated with tributyltin (TBT) and metals.

One of the most challenging contaminants in sediment is TBT, which is a man-made chemical with a toxicity similar to dioxins. Tributyltin was introduced in boat paint during the 1960s to inhibit the growth of marine organisms (such as barnacles) on ship hulls and marine structures [2]. However, it was discovered that the release of the compound lay behind the destruction of seabed ecosystems. In 1989, its usage in boat paint for vessels <25 m was banned in Europe (Directive 89/677/EEC), and later in 2003 larger vessels were also included in the prohibition (EU Regulation (EC) No 782/2003). TBT is now known to be a persistent compound and the half-life could reach up to 90 years under unfavorable conditions such as dark, anoxic conditions which could be the case deep down in sediment [3]. Today, 30 years after the ban, high levels of TBT and its toxic degradation products dibutyltin (DBT) and monobutyltin (MBT) are still found in the environment.

Metals are found in sediment and the content varies due to natural differences in geology [4]. Some metals are vital for the survival of many organisms but have toxic effects at high concentrations (e.g., copper (Cu) and zinc (Zn)), while others, such as cadmium (Cd) and mercury (Hg), only have negative effects [5]. Over the years different anthropogenic actives, e.g., traffic, and industries, have resulted in elevated metal contents in sediment at many sites, especially in sediment around cities, industrial and maritime areas [4]. Metals such as e.g., Cu and Zn are commonly used in antifouling paint and are often found in elevated content in the sediment together with TBT [6, 7]. This motivates the need for techniques that remove both TBT and metals.

Apart from the problem with contaminants, sediment in Sweden often consist of fine grains such as silt and clay, which is not optimal for use in construction [8]. This limits the management alternatives and in Sweden in 2018, 86% of the dredged masses were disposed of at sea or were landfilled [9]. Internationally, these are the most common management options for dredged masses as well [10]. However, neither of these disposal methods are favored by European or Swedish waste management policies, which instead encourage reuse, recycling, and recovery. This motivates the need to find alternative management strategies [11]. A third management option is stabilization and solidification (S/S) in which the sediment is mixed with binders, such as cement, to create a concrete-like solid, which enables use in e.g., port constructions. This could be an economic and environmental alternative to conventional disposal by lowering the need for available land, and landfill monitoring, thus lowering the landfill costs. In addition, virgin resources could be saved by substituting otherwise excavated material used in construction. Although sediment stabilization, in theory, traps the contaminants in the construction, the risk of contaminants leaching to the surrounding environment still remains. To reduce the risk of contaminants spreading, regardless of which management alternative is used, the sediment could be pretreated by removing TBT and selected metal. Less contaminated sediment is associated with lower management costs and could be handled in more ways, compared to highly contaminated sediment. Additionally, metals could be recovered and reused in society [12]. The extracted metals could partially cover the treatment and management cost, especially as both the use of metals and metal prices are increasing, and as metal recovery techniques are improving and developed due to the increased demand. To evaluate the environmental impact of different management alternatives, an integrated assessment through multicriteria assessment (MCA) and life cycle assessment (LCA) could be done, to provide clarity and compare strengths and weaknesses over time [13, 14].

Regular dredging must be done to maintain waterborne transport, and ultimately international trading and economy. This results in a need to handle large quantities of contaminated sediment which often have limited usage and are associated with high costs. Finding alternatives to deep-sea disposal and landfilling is more important than ever, as environmental legislation is becoming stricter, and as society wants to move towards a circular economy. This highlights the need to investigate and evaluate sustainable sediment treatment methods and sediment management alternatives.

The aim of this project was to develop innovative, sustainable, and effective treatment techniques for organotin (TBT, DBT, and MBT) and metal contaminated sediment which also enables metal recovery. Additionally, the aim was to investigate how sediment could be managed, and if treated sediment could serve as a construction material. Overall, it can be summarized with the question: Is it possible to degrade or remove toxic organotin compounds and regain metals to achieve cleaner sediment and enable the use of sediment residues in e.g., constructions?

To reach the overall aims, the following research questions were addressed:

1) What is the value in metal contaminated sediments and could integrated assessment be used to identify the best approach to deal with contaminated sediments in ports, marinas, and waterways? (presented in Paper I)

2) How effective are low impact leaching agents as remediation media for organotin and metal contaminated sediments? (presented in Paper II)

3) Is it possible to degrade the highly persistent organotin compounds in sediments by Fenton's reagent and electrochemical oxidation methods and how applicable are the methods? (presented in Paper III)

4) Could sediment treated with electrolysis be stabilized with an acceptable compression strength and low leachability of the residual organotin compounds and metals? (presented in Paper IV)

5) Could LCA be used to investigate sediment management options' climate impact and identify the need for potential method development? (presented in Paper V)

List of papers (for links to papers see Appendix 1 page 69):

Paper I: Norén, A., Karlfeldt Fedje, K., Strömvall, A-M., Rauch, S., and Andersson-Sköld, Y. (2020). Integrated assessment of management strategies for metal-contaminated dredged sediments – What are the best approaches for ports, marinas and waterways?. Science of the Total Environment **716**, 135510. doi:10.1016/j.scitotenv.2019.135510

Paper II: Norén, A., Karlfeldt Fedje, K., Strömvall, A-M., Rauch, S., and Andersson-Sköld, Y. (2021). Low impact leaching agents as remediation media for organotin and metal contaminated sediments. Journal of Environmental Management **282**, 111906. doi:10.1016/j.jenvman.2020.111906

Paper III: Norén, A., Lointier, C., Modin, O., Strömvall, A-M., Rauch, S., Andersson-Sköld, Y., and Karlfeldt Fedje, K. (2022). Removal of organotin compounds and metals from Swedish marine sediment using Fenton’s reagent and electrochemical treatment. Environmental Science and Pollution Reserach 29, 27988-28004

Paper IV: Norén, A., Strömvall, A-M., Rauch, S., Andersson-Sköld, Y., Modin, O., and Karlfeldt Fedje, K. Stabilization and solidification of organotin contaminated sediment: Electrolysis pretreatment, leaching, and compression strength (Under review)

Paper V: Svensson, N., Norén, A., Modin, O., Karlfeldt Fedje, K., Rauch, S., Strömvall, A-M., Andersson-Sköld, Y. (2022). Integrated cost and environmental impact assessment of management options for dredged sediment. Waste Management 138, pp 30 – 40.

2. Background

2.1 Sediment and selected contaminants

2.1.1 What is sediment

Sediment is defined as a solid material that has been deposited in a liquid or material deposited by wind, water, or glaciers [15]. The sediment's composition is often similar to the geologic composition at the site, but the sediment could also have an origin far away from the site, as weathered and eroded material can be transported far distances by wind and water. Depending on the geology and water movements in the area the sediment could consist of different particles of different shapes and sizes, such as gravel, sand, silt, and sand. Sediment does often contain organic material, originating from organisms in the water but also from terrestrial organisms. Altogether, many different factors affect sediment composition, which can vary greatly between different locations.

The sediment composition is also affected by anthropogenic activities, as contaminants are transported with stormwater or are directly introduced to the water at the site through different point sources (e.g., wastewater treatment plants) and diffuse sources (e.g., boat traffic). Examples of contaminants are, in addition to metals, and organotin compounds (e.g., tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT)), persistent organic pollutants (e.g., polycyclic aromatic hydrocarbons (PAHs)), pharmaceuticals, and nutrients. Depending on the content of these contaminants, the sediment ecological status and suitable management options could be assessed.

2.1.2 Tributyltin

Tributyltin (TBT) is the name commonly used for compounds including the cation (C4H9)3Sn+ and belongs to the organotin compounds, or stannanes. These are organo-metallic compounds and are commonly denoted as R4SnX, R3SnX2, R2SnX3, and RSnX3, consisting of tin (Sn4+) and one or more organic groups (R) and an anion (X), such as chloride, fluoride, hydroxide, and oxide, or a hydride. Nowadays more than 800 organotin compounds are known, with methyltin being the only naturally occurring organotin, which can be produced by bacteria [2]. In contrast to inorganic tin, which is considered a low toxicity metal, many organotin compounds are persistent and have highly toxic effects. The toxicity of different organotin compounds varies greatly and is related to the number and the type of attached organic groups [16]. Apart from tetra-organotin compounds, which generally are stable and low toxic compounds, the higher number of organic groups are generally more toxic.

Tributyltin is a persistent compound and is degraded through debutylalization. Degradation is caused by biological, chemical, photochemical, and physical processes. The degradation process is enhanced by light and aerobic conditions and is prolonged in dark and anoxic settings [17]. The half-life in nature has been reported to range between one to three years, up to 10 to 90 years in sediment [3, 17] but is quicker when TBT is in the water column [18, 19]. Tributyltin degrades into dibutyltin (DBT), then monobutyltin (MBT), and as a final step inorganic Sn (Equation 1).

$$\begin{array}{ccccccc} (C_4H_9)_3Sn^+ & \rightarrow & (C_4H_9)_2Sn^{2+} & \rightarrow & (C_4H_9)Sn^+ & \rightarrow & Sn^{4+} \\ \text{TBT} & & \text{DBT} & & \text{MBT} & & \text{Tin} \end{array} \qquad \text{Equation 1}$$

Tributyltin is hydrophobic and sorbs to both inorganic and organic colloids through the formation of complexes [20]. In sediment TBT mainly sorbs to organic matter and fine particle fractions, such as silt and clay particles [21, 22]. Other factors controlling the sediment sorption are pH, salinity, redox conditions, and iron oxide content [17, 21]. The aging of TBT may be important for the TBT sorption, as an older contamination sorb more to sediment than freshly deposited TBT, especially in sediment with an organic content above 2.6% [23]. Initially, TBT remains accessible in the sediment's surficial structures but migrates with time into less accessible inner areas. The sediment sorption is reversible, and in marine waters, TBT can be found in the form of e.g., chloride (TBTCl), hydroxide (TBTOH), and carbonate (TBTHCO3) [24]. The most commonly used form in antifouling paint was tributyltin (di-)oxide (TBTO) [24-27].

Due to its toxic properties, TBT has mainly been used as a biocide, first introduced for controlling schistosomiasis, and later found use as an antifouling agent in paint, for wood preservation and treatment, but also as an antifungal agent in textiles [28]. Sources of TBT in the aquatic environment include leaching from boat paint on ship hulls and paint flakes, waste treatment and runoff from waste sorting sites, leachate from landfills and sewage treatment plants (Figure 1) [29]. The main source for TBT in the North East Atlantic and the Baltic Sea is antifouling paint, while point sources such as wastewater treatment plants are considered less significant [29, 30]. In seawater, it has been reported to be toxic in as low concentrations as 1 ng/L TBT [31]. Tributyltin is a hormone disruptor and can cause imposex in gastropods and mollusks, leading to a decrease in fertility and premature death. It has also been reported as an obesogenic and is thought to have a negative impact on the immune system [32]. Tributyltin bioaccumulates and impacts higher order species such as fish, mammals, and humans. In humans TBT and its degradation products DBT and MBT have been found in blood and inside the liver, most likely originating from seafood consumption [33]. No experiments on the effect of TBT on humans have been done, but data from cases where humans have been exposed to TBT (e.g., factory workers, and boat owners exposed to TBT in paint) reports respiratory problems after inhalation and dermal irritation after skin contact [25]. Based on animal experiments, it is also believed to be neurotoxic, cancerogenic, obesogenic, causing a suppressed immune system, endocrine disruption, decreased reproduction and inhibited development in humans [33]. Dibutyltin is estimated to be three times less toxic than TBT and is believed to also impact the metabolism and immune system. However, some species are more sensitive to DBT than TBT [32]. Dibutyltin is degraded into less toxic MBT (Equation 1), which in turn degrades into the inorganic tin, which during overexposure could cause metabolic disruption [2].

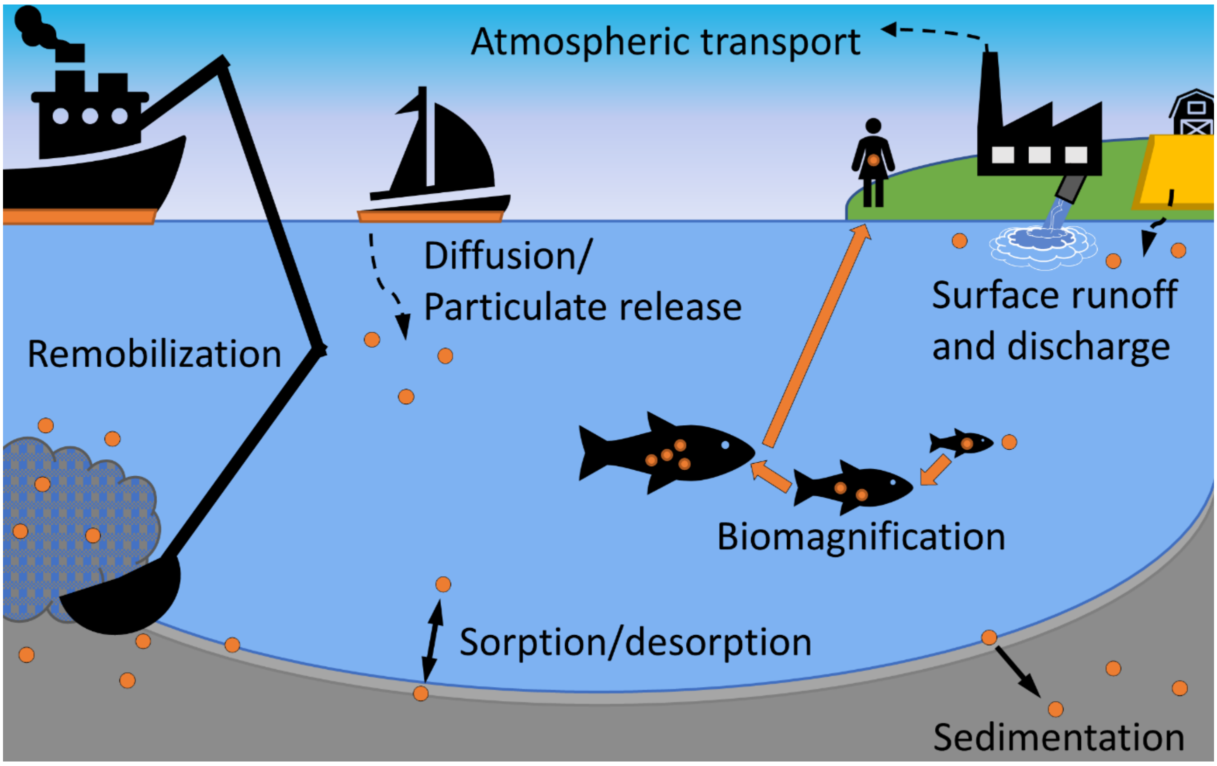


Figure 1. Overview of some TBT sources and transport pathways.

During 1975-1982 it was discovered in France that oysters had severe problems with both reproduction and shell calcification and TBT was identified as the cause of these issues [34]. Similar cases were soon observed elsewhere, and the use of TBT in antifouling paint was banned as a consequence. In 1989 the use of TBT was prohibited on leisure boats and boats <25 m in Europe (Directive 89/677/EEC), and in 2003 the ban was extended to larger vessels (EU Regulation (EC) No 782/2003). Despite its ban, TBT is still found in the environment, and in Europe, it is one of the prioritized compounds in the Water Framework Directive [31].

2.1.3 Metals

Sediment naturally contain metals, but elevated levels of metal are commonly originating from the urban environment [4, 35]. Metals such as Cu and Zn have many applications in society and are used on large scale, e.g., copper roofs, galvanized surfaces, in cars, etc. Other metals, such as Co, are used in smaller quantities but are vital for society and used in e.g., modern electronics like smartphones.

Metals are spread in the environment with the wind, through particulate and gas emissions but also with water as dissolved ions and attached to particles, often ending up in stormwater, and finally, in sediment. Dependent on environmental factors, e.g., pH and redox conditions, metals could form different complexes with varying toxicity and risk being spread in the environment through bioaccumulation [36]. Although many metals are vital for survival (e.g., Cu and Zn) they could also cause acute toxic effects when present in elevated concentrations [37, 38]. Both Cu and Zn have been used in antifouling paint, like TBT, and are commonly found together with TBT in sediment [39].

The production of metals is associated with high impacts on the environment and is sensitive to socioeconomic changes as it is done in a few places in the world [40]. The demand for metals is expected to increase 2-6 folds until 2100 [41], and metal prices are not declining [42], thus metal recovery has been identified as a must to guarantee future metal needs. Metal recovery from sediment could be a possibility in the future if the recovery rate is high. However, the metal content in sediment is often low in comparison to ore, but metals could be obtained whilst the sediment may have more management options due to decreased metal content.

2.2 Management of dredged sediment

Marine transport is important for the world economy as around 80% of the volume and more than 70% of the weight of the global trade is transported by sea [1]. To enable transportation dredging is regularly done in waterways and ports to increase or remain water depth for ships and boats. However, dredging can also be done to remove highly polluted sediment which poses a risk to the surrounding water environment. Depending on the type of sediment (characteristics such as grain size, organic content, salinity) and the level of contamination, local restriction, costs, and treatment methods determine which management options are applicable [43]. Internationally, landfilling and deep-sea disposal are the most common management alternatives when masses cannot be used [10]. In Sweden in 2018, 59% of dredged sediment was disposed of at sea and 27% was landfilled, and the remaining part was used as a filling material in construction [9]. The low usage of Swedish sediment is due to the amount of fine-grained particles [8]. It also commonly contains elevated levels of TBT, but also secondarily metals.

Landfilling impacts the land use and local ecosystem during the time the landfill is active but also after it has closed. Leaching of contaminants to the surrounding environment must be prevented during the landfill's active years but also long after the mass disposition has stopped. Disposal of marine sediment is often associated with high costs due to high water content and salinity, which need to be considered to prevent salt leaching to the environment. Not all landfills accept dredged sediment masses since certain permits are required to handle these. Thus, the landfill transport distances are often long, especially if the sediment is classified as hazardous waste, as only a minority of the landfills have such permits. A high organic content could additionally lead to a release of greenhouse gases as they decompose, if not properly managed. The benefits with landfills are that the landfilled material is kept in a designated area and the impact on the surrounding environment can be controlled and measures could be taken when needed. Additionally, this provides the opportunity to perform urban mining to reclaim valuable resources from landfills in the future. The introduction of the Landfill directive in Europe in 1999 resulted in the closing of landfills, tougher requirements on existing ones, and made it more difficult to open new landfills [44]. This resulted in less available landfill space and an increase in landfilling prices. This in turn resulted in an increased willingness to look for other alternatives in mass management [11].

Deep-sea disposal should preferably be done on a carefully selected accumulation bottom and should fulfill demand on the sediment's content (see chapter 2.3). During the disposal, there are risks for particle dispersion and contaminants spreading far away from the disposal site, as well as covering benthic organisms [45]. If low volumes are disposed of after long time intervals the bottom may recover. However, frequent, and large disposal operations could permanently damage the site and prevent recovery. A benefit of deep-sea disposal is that the energy consumption and greenhouse gas emissions are less when transported with a barge to the disposal site, in comparison to transport on land to a landfill [46]. Changes in the European legislation have resulted in a reduced amount of polluted sediment being disposed of at sea, aiming at encouraging resource recovery and use the dredged masses in e.g., construction.

One alternative to disposal which enables the use of fine-grained sediment is the stabilization and solidification (S/S) technique (further described in chapter 2.4.2.4). In this method, dredged sediment is mixed with binders, e.g., cement, which result in a concrete-like product that can be used in e.g., port constructions. This reduces the need for excavation of e.g., crushed stone for construction use while reducing the disposal need. This is an option that may receive increasing interest in the future, due to increasing landfill costs [44]. Additionally, if the S/S is done close to the dredging site, transport emissions are low in comparison to landfilling.

2.3 Sediment classification and management criteria

To classify sediment, different environmental guidelines values and management criteria are applied (Table 1). The environmental guidelines give an indication of the sediment quality and environmental effect, while the management criteria determine what management options are possible for the sediment: e.g., deep-sea disposal, inert landfill, non-hazardous waste landfill, hazardous waste landfill, and use in construction.

The Swedish sediment classification contains comparative values for TBT, DBT, and MBT and is used to estimate how contaminated the sediment is in comparison to other Swedish sediments [47]. There are four classes, from class 1 Very low content up to class 4 Very high content. The classification does not indicate how toxic the sediment is nor cover metals. In Sweden, the sediment content is often also compared to the Canadian and Norwegian guidelines [48]. The Norwegian guidelines consist of five classes describing the deviations from the natural conditions. The two lowest describe good chemical and ecologic conditions (background levels and no toxic effects) [49, 50]. The three upper levels denote bad chemical conditions and the ecologic status as causing chronic effects at long time exposure, acute toxic effects at short-time exposure, and extensive acute toxic effects. The guidelines are for metals, TBT, DBT, and MBT. The Canadian sediment

Table 1 Canadian, Norwegian, and Swedish guidelines, classification, and limit values for sediment together with Swedish soil, Swedish hazardous waste, and Vinga disposal criteria **[47, 49-56]**.

	Canadian sediment[a]		Norwegian sediment[b]					Swedish sediment[c]				Sweden soil[d]		Swedish masses[e]	Disposal
	ISQG	**PEL**	**N1**	**N2**	**N3**	**N4**	**N5**	**S1**	**S2**	**S3**	**S4**	**SLU**	**LSLU**	**HW**	**Vinga[f]**
Organotin compounds [µg/kg DW]															
TBT	-	-	-	0	0.02	0.032	> 0.032	<1	1-10	10-26	≥20	150	300	-	50
DBT	-	-	-	-	-	-	-	<1	1-10	10-26	≥26	1500	5000	-	-
MBT	-	-	-	-	-	-	-	<1	1-19	19-55	≥55	250	800	-	-
Metals [mg/kg DW]															
Ag	-	-	-	-	-	-	-	-	-	-	-	-	-		-
As	7.24	42	15	18	71	580	> 580	-	-	-	-	10	25	1000	45
Ba	-	-	-	-	-	-	-	-	-	-	-	200	300	50,000	-
Cd	0.7	4.2	0.2	2.5	16	157	> 157	-	-	-	-	0.8	12	1000	3
Co	-	-	-	-	-	-	-	-	-	-	-	15	35	1000	60
Cr	52.3	160	60	660	6000	15,500	15,500-25,000	-	-	-	-	80	150	10,000	70
Cr (VI)	-	-	-	-	-	-	-	-	-	-	-	2	10	1000	0.7
Cu	18.7	108	20	84	84	147	> 147	-	-	-	-	80	200	2500	80
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-		-
Hg	0.13	0.7	0.05	0.52	0.75	1.45	> 1.45	-	-	-	-	0.25	2.5	50	0.7
Mn	-	-	-	-	-	-	-	-	-	-	-	-	-		-
Mo	-	-	-	-	-	-	-	-	-	-	-	40	100		-
Ni	-	-	30	42	271	533	> 533	-	-	-	-	40	120	1000	100
Pb	30.2	112	25	150	1480	2000	2000-2500	-	-	-	-	50	400	2500	110
Se	-	-	-	-	-	-	-	-	-	-	-	-	-		-
Sb	-	-	-	-	-	-	-	-	-	-	-	12	30	10,000	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-		-
V	-	-	-	-	-	-	-	-	-	-	-	100	200	10,000	-
Zn	124	271	90	139	750	6690	> 6690	-	-	-	-	250	500	2500	360

a

[a] *ISQG = interim sediment quality guidelines, PEL = probable effect level.* [b] *N1 = Background, N2 = No toxic effect, N3 = Chronic toxic effect at long time exposure, N4 = Acute toxic effects at short-time exposure, N5 Extensive acute toxic effects.*[c] *S1 Low content, S2 Medium content, S3 High content, S4 Very high content* [d] *SLU sensitive land use, LSLU = less sensitive land use.* [e] *HW = hazardous waste.* [f] *Vinga = SSV Vinga disposal site.*

guidelines cover metals and TBT and classify the limit where effects may start to occur (Interim sediment quality guideline (ISQG)) and the probable effect level (PEL) [51]. Both Canadian, Norwegian, and Swedish guidelines and comparative values are all based on the total content and do not include contaminant mobility.

The deep-sea disposal site SSV Vinga (Vinga) in the Gothenburg archipelago has a limit on the allowed maximum content of TBT and certain metals in the sediment [52]. It is based on earlier measured content at the site. For mass disposal at Swedish landfills, there are hazardous waste content limit values for material that is handled, but for the other types of waste i.e., inert and non-hazardous waste there is no content limit. Instead, leaching tests, such as the SS-EN 12457-4 test, are commonly used for waste materials prior to landfilling [53, 54]. For disposal of sediment, there are no general guidelines, however, guidelines for soil contamination are often applied to indicate the disposal options, even though leaching tests are required before the disposal. The soil guidelines give an indication of the degree of contamination and indicate if the masses are suitable for sensitive land use (SLU) for use in e.g., housing areas and less sensitive land use (LSLU) for use in e.g., industrial areas [55, 56].

A new terminal in the area Arendal in Gothenburg, Sweden, will be built by the Port of Gothenburg between 2018 and 2025 by stabilizing and solidifying sediment from the river waterway. There is no limiting value regarding the content of the sediment being used. However, the final product must reach a sheer strength of 70 kPa [57], which corresponds to compression strength of 140 kPa according to the Tresca criterion and 121 kPa according to the Mises criterion.

2.4 Sediment remediation

As sediment often contains TBT and metal at a level that causes problems for both sediment managers and the environment, methods with the capacity to remove both contaminants simultaneously are preferred. TBT was estimated to pose a bigger threat to the environment than metals in the sediment studied in this project, therefore focus has primarily been given to TBT reducing techniques in this review [58, 59]. In this chapter first, a general overview of available is presented, thereafter the treatment methods developed in this project are introduced.

2.4.1 Reviewed treatment methods

In situ remediation could be feasible alternatives where the sediment does not need to be dredged or be used as a method to reduce TBT levels prior to dredging, but this requires planning as most of these types of methods take a long time. In situ treatments could be done in different ways. Natural recovery is when sediment is left without treatment allowing natural processes to degrade the contaminants, or allowing natural deposition of sediment, covering older more contaminated layers which makes the contaminants less available for biota. However, with this method, there is a risk that increased water movements, caused by e.g., storms, sediment slides, and boat traffic, could re-expose the contaminated sediment to water and risk spreading contaminants either in a dissolved phase or on particulate matter [60, 61]. Also, as for TBT, the dark and anoxic settings could prevent the wanted degradation to occur [17]. As for metals, they will remain there. The sediment recovery could also be enhanced by e.g., injection of substances aiming to lower its mobility or increase the degradation rate to provide a better environment for microorganisms that could degrade the TBT compound.

In sites, e.g., ports, where the sediment must be removed to have a sufficient water depth or to lower the contaminant level ex situ methods could be applied. This could be done using biological, physical, chemical, or combined treatment methods. For example, <98% TBT degradation has been reported to be degraded by using thermal treatment and steam stripping [22]. These techniques are often expensive due to high energy consumption to heat the sediment. Thermal treatment could be efficient for the treatment of some metals, such as As, Cd, and Hg which become vaporized and could be caught and managed [62]. Other metals may become immobilized while the leachability of other metals increases.

Phytoremediation using barley removed ~40% TBT from marine sediment [63]. The uptake of TBT into plants is low, instead, degradation is probably occurring as the plants may make the environment more suitable for microbial degradation, by drying and aerating the sediment and promoting microbial activity. Phytoremediation requires a long time, in another study TBT decreased by 30% over 9 months [22]. Another con is that it cannot be done on too contaminated or saline sediment, as this might kill the plant and microbial organisms [22, 62]. Thus, this is not suitable for highly contaminated marine sediment. Phytoremediation may be beneficial if metals are sorbed in the plants as they could be harvested, incinerated and the metal could be extracted from the ash [62].

Other alternatives are chemical washing and oxidation. Chemical leaching/washing has been proven efficient. However, leaching might require the need a lot of chemicals added, and traditional leaching media often have a high environmental impact and could be harmful to biota, whereas this type of treatment would limit the potential use of the sediment [10, 62]. Therefore, the development of environmentally sustainable leaching methods is requested [10, 64]. Using oxidative methods, such as Fenton's reagent (a combination of hydrogen peroxide (H2O2) and ferrous iron (Fe2+)) [65], and electrolysis [24, 66, 67], organic material can be oxidized by reacting with the formed hydroxyl (HO•)and hydroperoxyl (HO2•) radicals and degrade TBT (Equation 2).

$$C_{12}H_{28}Sn + 80\ HO\bullet + 4H^{+} \rightarrow 12CO_2 + Sn^{4+} + 56H_2O \qquad \text{Equation 2}$$

During the oxidation potentially unwanted reactive species are created, e.g., adsorbable organic halides which could form toxic non-degradable metal complexes. These could be managed through the addition of e.g., granulated activated carbon, which sorbs chlorinated organics and reduces the oxidants [24].

2.4.2 Studied treatment methods

Sediment leaching

Chemical washing could be done with several different active ingredients. The TBT sorption to sediment is most strong around pH 6-8, while at higher and lower pH the release is increased [21, 58, 68]. Additionally, at a low pH most metals become mobile, unlike at a high pH. Leaching at extremely high pH (~13) and low pH (~0) has not been investigated before and could potentially release TBT. However, such treatment could greatly affect the sediment residue, requiring further treatment before disposal or use. Instead, if the impact on the sediment is lowered, and the leaching agent is not harmful to the environment, leaching could potentially be done more sustainable in comparison to traditional leaching agents such as ethylenediaminetetraacetic acid (EDTA). EDTA is a complex binding substance that efficiently binds to TBT but is difficult to biodegrade, and is used to extract TBT and metals from sample matrices prior to laboratory analysis [69-71]. Another complex binding substance is aminopolycarboxylate chelating agent (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS) which has a higher biodegradability and could complex bind the positively charged TBT and metals [72-74]. Both humic acid (HA) and iron colloids (Fe colloids) are water-soluble colloids and could potentially sorb TBT and metals as well [75-79]. A high concentration of Fe could facilitate TBT degradation, and as TBT sorb to inorganic colloids through the formation of complexes, leaching with Fe colloids could be possible [20, 80]. As TBT tends to sorb to organic matter and organic colloids, leaching with humic acid (HA) could be another alternative [20]. Other innovative leaching agent alternatives could be hydroxypropyl cellulose (HPC) and saponified tall tree oil (soap). As TBT is hydrophilic, substances that have both hydrophobic and hydrophilic properties, such as biodegradable compounds hydroxypropyl cellulose (HPC) and soap [81], could potentially bind to TBT whilst being water-soluble. Thus, they could potentially be used for extracting TBT from sediment.

Tributyltinoxide (TBTO), which was the most commonly used form of TBT in antifouling paint, has a high solubility in freshwater (4 mg/L) [25]. Thus, leaching in ultra-pure water may be effective for TBT removal. On the contrary, a high salinity has been reported to release TBT from sediment to water but also preventing it from degradation [82-84]. This means that highly saline water potentially could remove TBT from the sediment, even if the degradation effect is limited.

Fenton’s reaction

Fenton’s reagent is chemical oxidation caused by the addition of hydrogen peroxide (H2O2) and ferrous iron (Fe2+) which results in the formation of hydroxyl radicals which could degrade TBT [85]. The amount of radicals created is dependent on the ratio of H2O2 and Fe2+ [86-88]. The optimal ratio of H2O2:Fe2+ depends on many factors, including sediment composition (e.g., natural TOC and Fe content) and the wanted compound to be oxidized. Fenton’s reagent has mainly been studied for use in wastewater treatment, but the usage in sediment is limited. In a study comparing photo-Fenton, photocatalysis, and classic Fenton, the three methods showed similar removal efficiencies [65]. The complete reactions occurring in sediment are not fully known and most likely, the reactions are more complex in sediment than in water. The classic Fenton reactions are seen in Equations 3-9 and the degradation for TBT is seen in Equation 2 [85].

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO\bullet$ Equation 3
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+$ Equation 4
$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$ Equation 5
$HO\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ Equation 6
$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2H^+$ Equation 7
$Fe^{2+} + HO_2\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$ Equation 8
$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$ Equation 9

Electrochemical treatment

Electrochemical remediation was identified to have the potential to treat both sediment and water contaminated with TBT [22]. Electrolysis has been reported to be effective for metal removal from aquatic solutions but experience with metal removal directly from sediment without pH adjustment is limited [89-91]. In the method electrodes are submerged in the sample and current is applied. At the anode water and chlorine ions are oxidized (Equations 10 and 11), while hydrogen ions are reduced at the cathode (Equation 12). Organic contaminants are degraded by direct oxidation at the anode or by the generated oxidants, such as hydroxyl radicals (HO•) (Equation 2). Chlorinated species, e.g., hypochlorite (ClO-) could be formed depending on the pH (Equation 13) and may also contribute to degradation (Equations 14 and 15) [24, 92, 93]. However, as discussed for Fenton's reaction in chapter 2.4.2.2, the full reactions that occur when electrolyzing sediment is not fully known. In electrochemical oxidation processes, contaminants are degraded by the oxidants generated by the anode, or by direct oxidation at the anode as seen in the example in Equation 16. Different types of electrodes could be used, e.g., boron-doped diamond (BDD) anodes and titanium cathodes. The combination of electrodes could impact the removal, and BDD anodes have been reviewed to have the highest oxidation potential [94]. Titanium (Ti) is a relatively inert metal that has previously been used for the cathodic recovery of metals in aqueous solutions [95], and could potentially be efficient for metal recovery in sediments. The production of electrodes is associated with high climate impact, but if an environmentally friendly electricity source is used, the environmental impact can be lowered.

$H_2O \rightarrow HO\bullet + e^- + H^+$ Equation 10
$2Cl^- \rightarrow Cl_2 + 2e^-$ Equation 11
$2H^+ + 2e^- \rightarrow H_2$ Equation 12
$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$ Equation 13
$(C_4H_9)_3Sn^+ + 4Cl^- + 5/2H_2 \rightarrow SnCl_2 + 3C_4H_{10} + 2HCl$ Equation 14
$2(C_4H_9)_3Sn^+ + 3ClO^- + 2O_2 + 3H_2O \rightarrow 2SnO_2 + 6(C_4H_9)OH + 3Cl^-$ Equation 15
$BDD + H_2O \rightarrow BDD(HO\bullet)_{absorbed} + H^+ + e^-$ Equation 16

Stabilization and solidification

The method stabilization and solidification (S/S) have two major functions; stabilization which refers to contaminants being immobilized; and solidification which refers to the increased solidity and decreased permeability. Stabilization and solidification of sediment creates a material with higher structural integrity and less leachability of contaminants in comparison to untreated sediment (Figure 2). The method involves sediment being mixed with binders such as e.g., cement, and ground granulated blast-furnace slag (GGBS).

Cement is a limestone and clay mixture that is heated up to ~1450 ℃ and its production is associated with large emissions of CO2 [96]. The cement industry is accountable for 10% of the world's CO2 emissions of which 40% is from the heating during production and 60% from chemical reactions during the limestone calcination. Hydraulic cement, e.g., Portland cement, is used for S/S as it could be used in an underwater environment, unlike non-hydraulic cement. When the cement is in contact with water hydration chemical reaction starts causing a solidification and hardening of minerals. Calcium silicate hydrate (3 CaO·2SiO2·4H2O), which is commonly denoted C-S-H, is important for the strength development is formed together with portlandite (Ca(OH)2) under the hydration of the cement (Equations 17 and 18). Another group of hydrates is calcium aluminate hydrates (C-A-H) which consists of CaO and Al2O3. One form of C-A-H is tricalcium aluminate (3CaO·Al2O3) that together with gypsum (CaSO4·2H2O) forms ettringite (3CaO·Al2O3·3CaSO4·32H2O) (Equations 19 and 20). Together C-A-H and C-S-H are the two major components that increase the stabilized sediment's strength by interlocking the sediment and physically encapsulate contaminants [97].

$$Ca_3SiO_5 + 7H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + 3Ca(OH)_2 \qquad \text{Equation 17}$$

$$2Ca_2SiO_4 + 5H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + Ca(OH)_2 \qquad \text{Equation 18}$$

$$3CaO{\cdot}Al_2O_3 + 3CaSO_4{\cdot}2H_2O + 26H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O \qquad \text{Equation 19}$$

$$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + 2(3CaO{\cdot}Al_2O_3) + 4H_2O \rightarrow 3(3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O) \qquad \text{Equation 20}$$

Ground granulated blast furnace slag (GGBS) is a residue product from the production of steel and is formed as a by-product when water is added during the cooldown of molten blast furnace slag. The gravel-sized product is then grounded down to finer grain size, similar to the one used for cement. It is commonly used as a supplement to cement, to lower the environmental impact in comparison to if only cement would have been used [98]. Additionally, the strength and the immobilization of contaminants could increase by using a suitable cement-GGBS ratio in comparison to if only cement would have been used [98, 99].

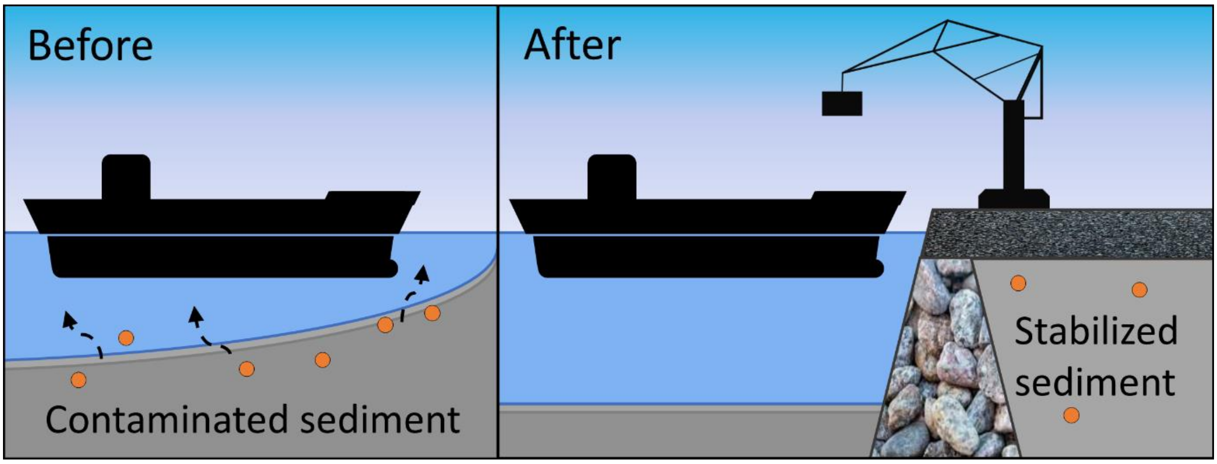


Figure 2 Simplified conceptual idea of the S/S-method. Sediment is dredged and mixed with binders, e.g., cement, and used in construction.

2.5 Environmental impact assessments

Traditionally sediment management is often determined only based on cost, regulations, and contamination levels in the sediment. However, with climate change and increasingly affected environment, investigation of the environmental impacts caused by different sediment management strategies must be done to get sustainable sediment management [100].

A method that could be used to assess the environmental aspects associated with different alternatives is life cycle assessment (LCA). An LCA follows a product during a specified time interval, e.g., from cradle to grave, and different environmental effects are estimated and calculated in functional units (e.g., kg oil produced, kg carbon dioxide (CO2) emitted, m3 water used) [101, 102]. To estimate the climate impact, it is common to calculate the emission of different greenhouse gases (e.g., CO2, methane (CH4). As different greenhouse gases' impact on global warming differs, the release is often converted to the unit CO2 equivalents (CO2 eq). Life cycle assessments have mainly been developed and done for soil projects, but the use of LCA in sediment projects is limited [100].

However, as not all environmental impacts could be quantified, e.g., the effect on biota and health [101], and different functional units could be difficult to compare, as an example, the effect of eutrophication is difficult to compare with the effect of climate change. Here, multicriteria analysis (MCA) could be used to facilitate comparison. Different alternatives' effects on identified criteria, such as biota, land use, are given a score based on estimated impacts retrieved from the literature review [103]. The score could then be compared to estimated different alternatives impacts. The results from LCA and MCA could be useful for decision-makers when comparing alternatives [100].

3. Method and Materials

3.1 Site descriptions

Organotin and metal contaminated sediments from different sites in Sweden were used in the studies presented in this project. Papers II, III, and IV involved sampling at selected sites and the sediment was used in experimental work, while in Papers I and V data from previously performed sampling occasions were obtained and processed for environmental sustainability assessments.

3.1.1 Sampling sites used in experimental work

For the experimental work in Papers II – IV, sediment was sampled at three different sites in Gothenburg, Sweden: the marina Björlanda Kile småbåtshamn (BK), the former shipyard Cityvarvet (CV), and the river Göta Älv's waterway (GBG). Sediment from BK and CV was used in Paper II and was collected using a grab sampler, while sediment from the GBG waterway was collected during a dredging operation performed by the port authorities and used in Papers III and IV. The location of the sites is seen in Figure 3.

3.1.2 Sites used in the environmental sustainability assessments

For the environmental sustainability assessments in Papers I and V data from the previous sampling operations were collected and compiled, see Table 2. In Paper I data were used from the waterway Lövstaviken and the leisure boat marinas Björlanda Kile småbåtshamn in Gothenburg, and Havdens båtklubb and Stenungsunds båtklubb in Stenungsund. Data from the port of Gothenburg and port of Oskarshamn were used in Papers I and V. Most of the sites are located on the Swedish west coast, characterized by saline conditions, while the port of Oskarshamn is located in the Baltic Sea on the east coast, characterized by brackish conditions, see Figure 4.

The waterway Lövstaviken is located in Falkenberg (Figure 4) and is the passage leading from a marina out to sea. It is delimited by the mainland and a jetty, which was built using landfill material as a construction material. Potential leaching from the jetty could together with antifouling paint from boats in the marina contribute with contaminants to the sediment. In the marinas, antifouling paint is identified as the major contributor to contaminants in the sediment. The number of berths at the sites differs greatly, representing both small and large marinas (Table 2). Björlanda Kile småbåtshamn is the largest marina in northern Europe and is located in Gothenburg, while the two smaller marinas Havdens båtklubb and Stenungsunds båtklubb are both located in Stenungsund (Figure 4).

The port of Gothenburg is the largest port in Scandinavia and dates back before 1620. Located in the river Göta Älv's estuary (Figure 4), it receives contaminants from shipping activities, road traffic, wastewater treatment plant, and other activities upstream. The most problematic compound here is tributyltin (TBT) but the sediment also contains elevated content of metals (Table 2).

Table 2. Information about the studied sites, including the type of activity, when the site was established, number of berths of the marinas, the size of the site, number of sample locations, the total number of samples, and average content and standard deviation (in italics) for selected contaminants at each site. n.d. denotes no data.

Site[a]	**P1**	**P2**	**M1**	**M2**	**M3**	**W**
Activity	Port	Port	Marina	Marina	Marina	Waterway
Start	1620s	1860s	1971	~1988	1957	~1964
Area [1000 m^2]	11 274	874.5	195.3	7.5	6	37.9
No of berths	n.d.	n.d.	2400	80	130	260
No. of sampling locations	26	40	3	2	2	6
No. of samples	52	103	5	3	4	11
TBT [µg/kg DW]	150 *±230*	n.d.	310 *±240*	50 *±50*	210 *±230*	70 *±60*
Cd [mg/kg DW]	0.4 *±0.5*	0.5 *±0.6*	0.2 *±0.1*	0.4 *±0.1*	0.2 *±0*	0.8 *±0.4*
Cr [mg/kg DW]	40 *±10*	40 *±10*	60 *±10*	30 *±0*	30 *±10*	50 *±20*
Cu [mg/kg DW]	50 *±30*	50 *±30*	190 *±80*	40 *±20*	40 *±20*	40 *±20*
Ni [mg/kg DW]	20 *±10*	20 *±10*	30 *±10*	20 *±0*	20 *±0*	20 *±10*
Pb [mg/kg DW]	40 *±50*	50 *±60*	40 *±10*	20 *±10*	20 *±0*	30 *±10*
Zn [mg/kg DW]	200 *±100*	200 *±100*	400 *±200*	100 *±100*	100 *±0*	200 *±100*

[a] *The the sources of sampling data are the following: port of Gothenburg (P1) [104], port of Oskarshamn (P2) [105], Björlanda Kile småbåtshamn (M1) [106, 107], Havden båtklubb(M2) [108], and Stenungsunds båtklubb (M3) [108], and Lövstaviken (W) [109].*

The port of Oskarshamn is located in Oskarshamn (Figure 4) and it was previously the most contaminated site in Sweden and was identified as one of the biggest emitters of dioxins to the Baltic Sea [110]. It also had a high content of metals such as As, Cd, Cu, Hg, Pb, and Zn originating from shipping activities and industries in the area (Table 2). In 2016-2018 dredging was done to lower the contaminate release from the sediment, but all analysis in this project was done on data obtained before the dredging.

Other sites brought up in the environmental sustainability assessment are the deep-sea disposal site Vinga (Papers I and V) and Arendal (Paper V), see Figure 3. Arendal is the area in Gothenburg where a new port terminal is built in 2018-2025 using sediment dredged from the waterway [57]. The sediment is stabilized with cement and GGBS and used in the construction. Vinga is a deep-sea disposal site located in the Gothenburg archipelago. The site is ~1.7 km2 and has been used since the 1980s [111]. Sediment content criteria which were specified by the Swedish Land and Environment Court of Appeal must be met to allow mass disposal [52]. The criteria were set based on the measurements of contaminant content in the sediment at the site, so that disposed masses will not contain contaminants in higher content than observed at the site.

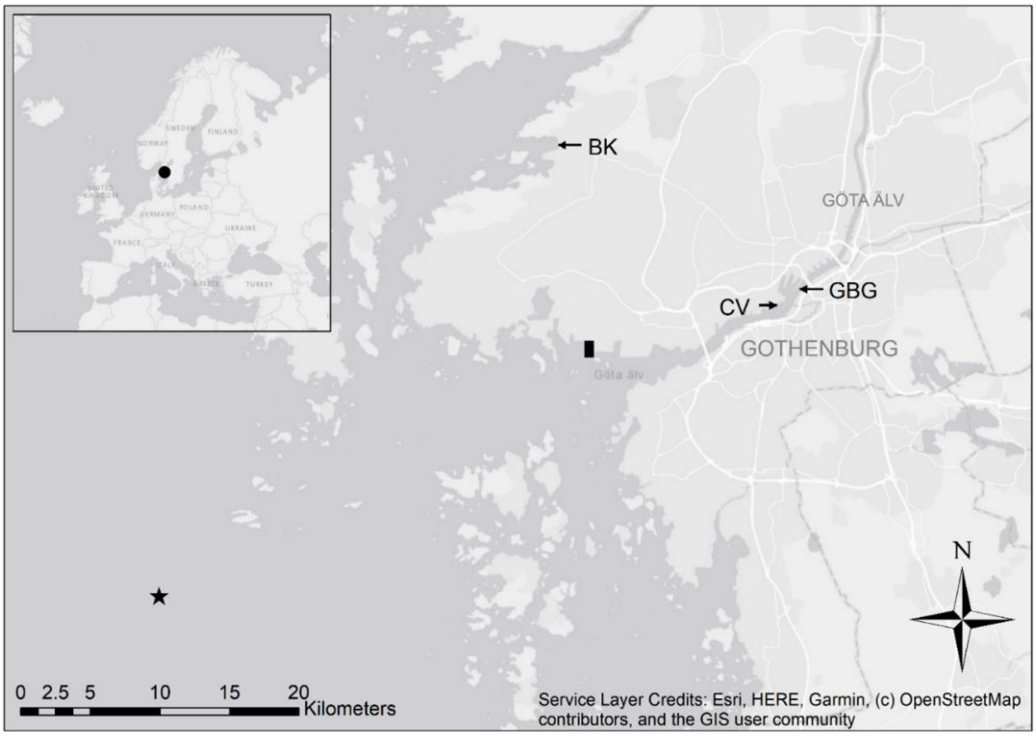


Figure 3. Location of the sites in Gothenburg, Sweden: marina Björlanda Kile småbåtshamn (BK), former shipyard Cityvarvet (CV), the waterway in Göta Älv (GBG), the construction site in Arendal (rectangle), and the Vinga deep-sea disposal site (star).

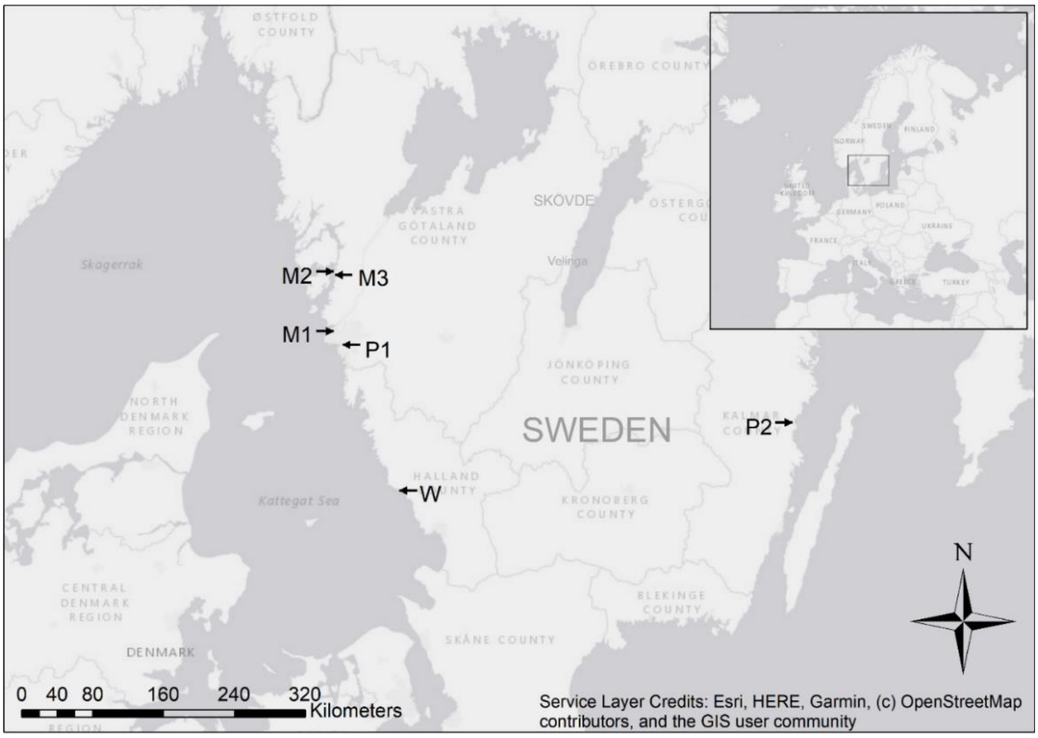


Figure 4. Locations of the studied sites in the environmental sustainability assessments: port of Gothenburg (P1), port of Oskarshamn (P2), marina Björlanda Kile småbåtshamn (M1), marina Havdens båtklubb (M2) and marina Stenungsunds båtklubb (M3).

3.2 Experimental work

This chapter describes the methods used for sampling, experimental setups, and analysis in this project. For a more extensive description of the methods applied, see the paper referred to in the text.

3.2.1 Sampling and sediment pretreatment

To collect sediment samples in BK and CV (Paper II) an Ekman grab sampler was used, which collects sediment at a depth of 0-10 cm. At CV additional samples were collected by a diver. The sediment from the river Göta Älv's waterway (GBG) (Paper III and IV) was collected during a dredging operation performed by the local port authorities. The sediment was dredged using a grab dredger and was transported to land where it was sampled. After sampling larger objects, such as mussels, etc., were removed from all sediments. The sediments were homogenized by mixing and stored at 7℃ or -22℃ due to logistic reasons. Prior to usage, the frozen samples were thawed at 4℃.

Some of the sediment from GBG was spiked with TBT (Paper III). Tributyltin chloride (TBTCl) was dissolved in methanol and ultra-pure water and was added to GBG sediment. Water was also spiked by dissolving TBTCl in methanol and adding it to saline (35 g/L sea salts) and slightly salinity (2.4 g/L sea salts) water (Paper III).

3.2.2 Treatment methods

Oxidation (Paper III)

In Paper III the TBT, DBT, MBT, and metal removal from spiked and GBG sediment was investigated by using chemical oxidation (Fenton's reagent) and electrochemical oxidation (electrolysis).

Fenton's reagent

Ferrous sulfate heptahydrate in ultra-pure water was added to the sediments and the pH was adjusted to pH 3 using sulfuric acid to increase the Fenton's reaction rate (Figure 5) [85, 112]. Hydrogen peroxide was added as 6 equal aliquots at 20-minute intervals to increase the concentrations of hydroxyl and hydroperoxyl radicals to increase degradation [113]. The sediment slurry was continuously mixed for 23 h and was then allowed to settle for 1 h. The supernatant was centrifuged. Sediment was obtained from the initial setting, but also after centrifugation, and both these sediments were collected and mixed before analysis. The supernatant after centrifugation was collected for further analysis.

Electrochemical degradation

Sediment and ultra-pure water were added to a beaker and electrodes were submerged (Figure 6). For the spiked samples a 5x10 cm2 niobium anode mesh, coated with boron-doped diamond (Nb/BDD) (~120 cm2 surface area) and a 5x10 cm2 titanium plate cathode were used, while for

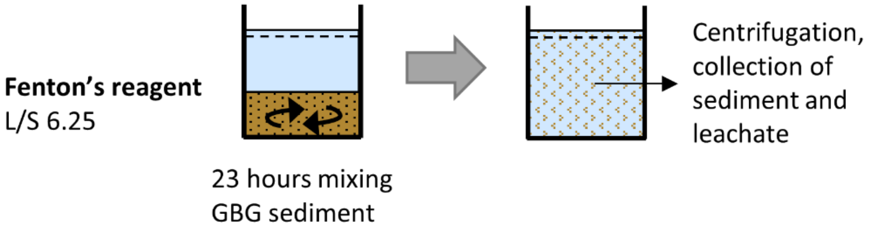


Figure 5. Set up for the Fenton's reagent experiment.

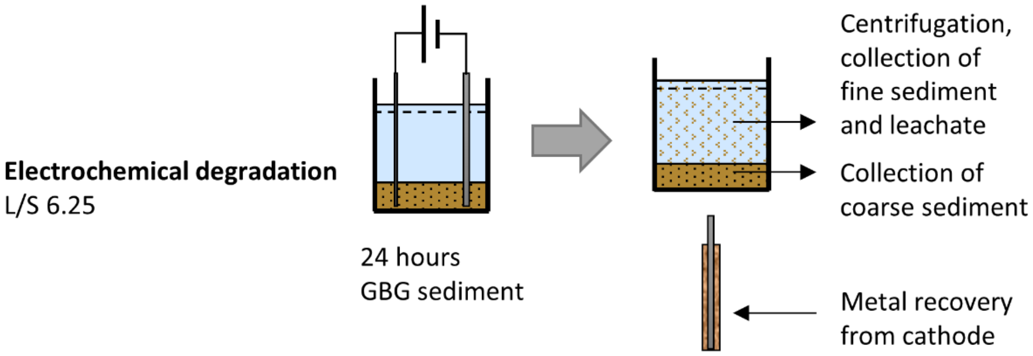


Figure 6. Set up for the electrochemical degradation experiment.

the GBG sediment 10x10 cm2 Nb/BDD anode and 10x10 cm2 titanium cathode were used. A 30 DC power source was used to control the applied voltage and a digital multimeter was used to measure the current. After each experimental run, the sediment slurry was centrifuged, and sediments and leachates were collected and analyzed separately.

The same equipment and experimental setup used for treating the GBG sediment were also used for treating the TBT spiked saline and slightly saline water samples. For each water sample treated, a TBT spiked blank sample was kept to investigate how much degradation would occur without an applied current.

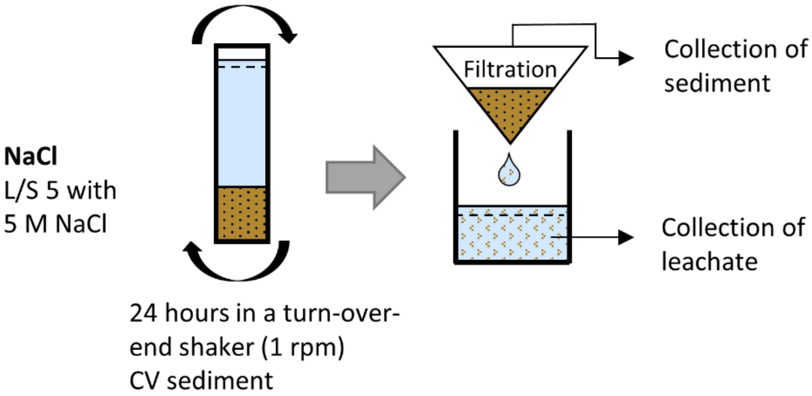


Figure 7. Set up for the NaCl leaching experiment.

Enhanced leaching (Paper II)

In Paper II the TBT, DBT, MBT, and metal removal by leaching were investigated. The methods were tested on either BK or CV sediment. The NaCl and batch leaching was chosen as they were identified to potentially be gentle leaching agents to remove primarily TBT and secondarily metals. The acid and alkaline leaching were done to see if extreme pH enables a full TBT release from the sediment.

NaCl leaching

Sediment from CV was mixed with NaCl (5 M) in a turn-over-end-shaker (1 rpm) for 24 hours (Figure 7). The sediment slurry was then filtrated. The filtrate and the solid residue were collected and analyzed.

Acid leaching

Sediment from CV was mixed with waste acid (~1 M HCl, pH ~0) for 30 minutes using a magnet stirrer (Figure 8). The acid originated from the Renova municipal and industrial waste incineration plant in Gothenburg, Sweden and its concentration of different elements vary due to the waste incinerated [114]. After the leaching, the sediment slurry was filtrated, and the filtrate was collected. The solid residue was washed with ultra-pure water and after that, the washing filtrate and solid residue were collected. Both filtrates and the solid residue were analyzed.

pH 13 leaching

A Titroline® 7000 titrator was used to reach and keep a constant pH of 13 by adding 5 M pH NaOH (Merck) to a BK sediment and ultra-pure water slurry under mixing conditions (Figure 9). The leachate slurry was sampled after 0.5, 1, 3, 6, 24, 48, 72, and 168 hours. The experiment ended after one week (i.e., 168 hours) and the sediment was left to settle for a few minutes, and thereafter decanted and centrifuged. The solid residues and the liquids were collected separately and analyzed.

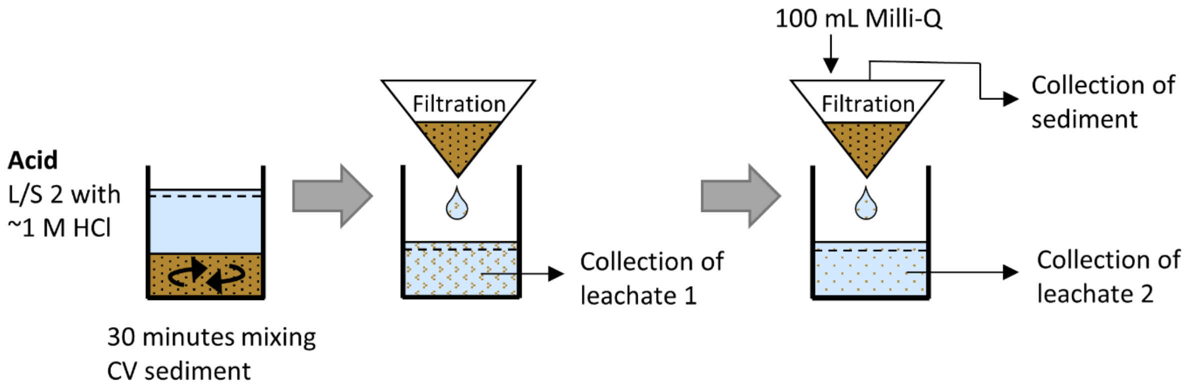


Figure 8. Set up for the acid leaching experiment.

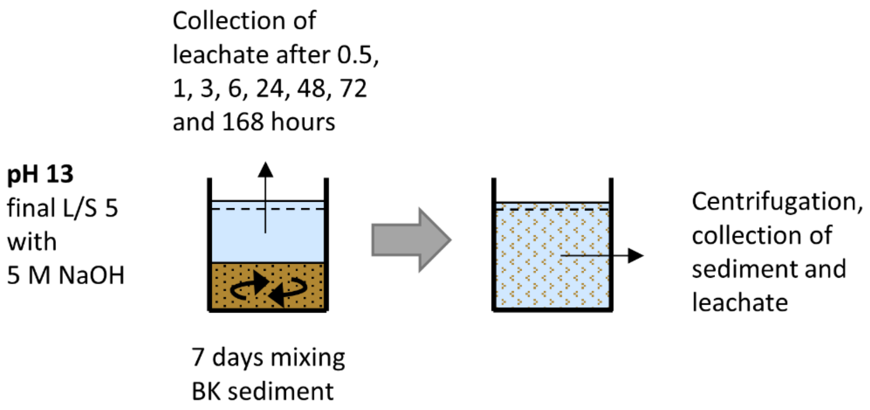


Figure 9. Set up for the alkaline leaching experiment.

Batch leaching

Enhanced leaching was done using different leaching agents with a low environmental impact which was individually tested on BK sediment. The tested leaching agents were [S,S]-Ethylenediamine-N,N'-disuccinic acid trisodium salt solution (EDDS), hydroxypropyl cellulose (HPC), saponified tall oil ("soap"), humic acid (HA), and iron(III)nitrate nonahydrate, extra pure, (Fe colloids) (the latter two prepared according to [115]), and ultra-pure water (U-P). All leaching agents were mixed with ultra-pure water to reach the desired concentration (except U-P which only consisted of ultra-pure water) (Figure 10). The slurry was put on a shaking table for one hour. 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, decanted, and the fine-grained solid residues were collected. Coarse- and fine-grained sediments were analyzed, and the final sediment

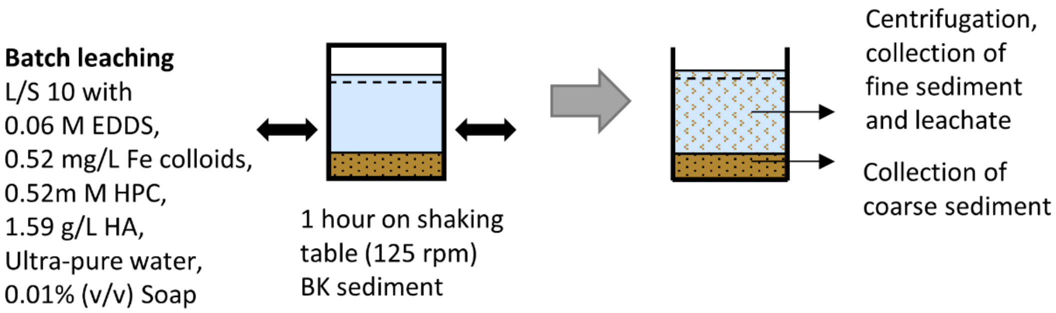


Figure 10. Set up for the batch leaching experiment, including the use of the following leaching agents: [S,S]-Ethylenediamine-N,N'-disuccinic acid trisodium salt solution (EDDS), iron(III)nitrate nonahydrate (Fe colloids), hydroxypropyl cellulose (HPC), humic acid (HA), ultra-pure water, and saponified tall oil ("soap").

contents were calculated by summing contents multiplied with the corresponding weight percentage of the coarse- and fine-grained sediment residues.

Stabilization and solidification (Paper IV)

In this experiment, untreated sediment from GBG and electrochemically treated GBG sediment were stabilized and solidified (Figure 11). This was done to investigate the pretreatment impact on TBT degradation and strength development and leaching of TBT, DBT, MBT, and metals. Electrolysis was done according to the method described in chapter 3.2.2.1.

Sediment was mixed with CEM II/A-LL 42.5R cement, and GGBS (Ecocem) to get a final binder content of 150 kg/m3 (50% cement and 50% GGBS) (Figure 11), using the recipe developed for this sediment to be used in the S/S project in Arendal, Gothenburg [57]. The stabilized sediment was cast in molds covered with plastic foil to prevent evaporation and after 24 hours the samples were demolded. Some of the samples were submerged in ultra-pure or saline (35 g/L NaCl) water to cure for 28, 56, or 90 days, and other samples were used directly in the surface diffusion test standard EA NEN7375:2004.

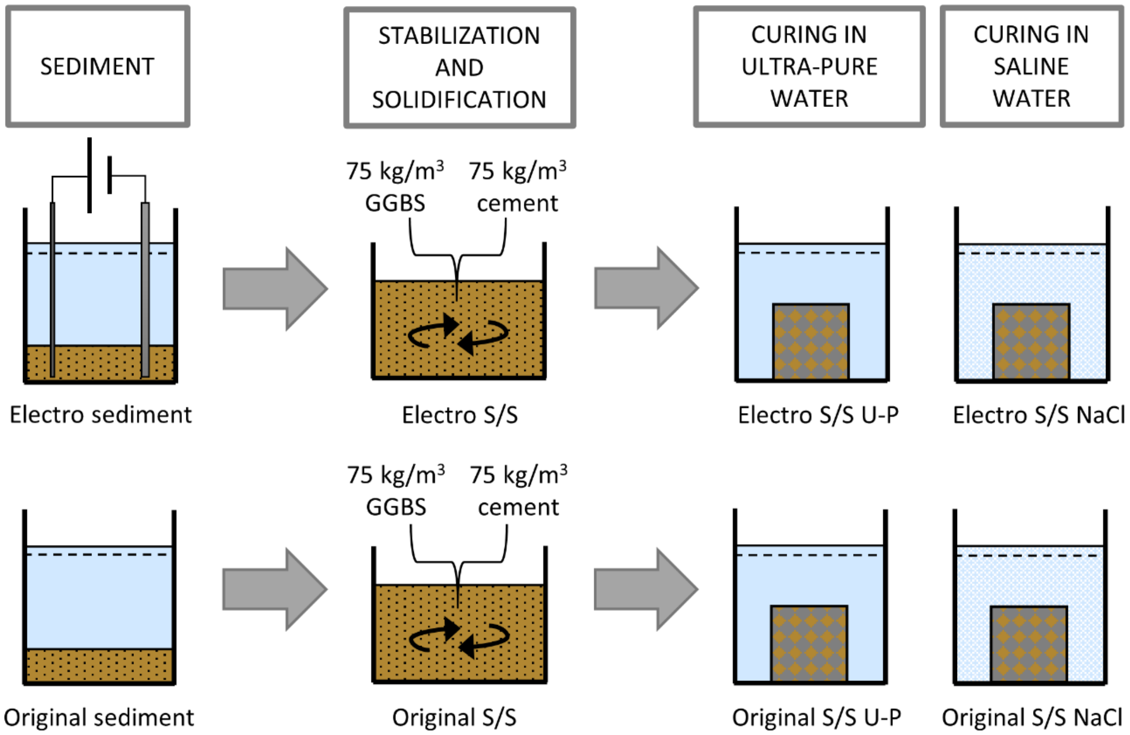


Figure 11 Simplified procedure for the stabilization and solidification of original sediment (i.e., untreated Göta Älv waterway (GBG) sediment), and electro sediment (i.e., electrolyzed GBG sediment). In the second step, the sediments are mixed with ground granulated blast furnace slag (GGBS) and cement to create test pieces. In the final step, the test pieces are cured in either ultra-pure water (U-P) or saline water (NaCl).

The surface diffusion test is done to estimate the leaching mechanisms for inorganic elements from waste and building materials over time, but here the leaching of TBT, DBT, and MBT was also investigated. The samples were submerged either in ultra-pure, brackish (15 g/L NaCl), saline (35 g/L NaCl) water, ultra-pure water with added dissolved organic carbon (DOC) (6 mg/L humic acid), or saline water with added DOC (6 mg/L humic acid) to investigate how the surrounding water impact the leaching. The liquids sampled were replenished after given time intervals and the solid was weighed during each replenishment. By plotting the cumulative and derived leaching curves over time leaching mechanisms such as surface wash-off, diffusion, and depletion could be identified by studying the slope of the leaching curves.

Compression tests were done on curing days 28, 56, and 90 on stabilized sediments using an MTS 880 servohydraulic testing machine to investigate the strength development over time. After the compression tests were done, crushed samples were used in the compliance test for leaching of granular waste material, standard SS-EN 12457-4. That leaching test is a one-stage batch test in which a liquid to solid ratio of 10 is used to indicate the maximum leaching of a solid material. Here, the samples were leached in ultra-pure or saline water to investigate if differences in salinity impact the leaching.

3.2.3 Analytical methods

After sampling ocular inspection of all sediments was done according to ISO 22412:2017. The particle size distribution was determined according to ISO 11277:2009 through sieving and sedimentation at an external accredited laboratory (Papers II, III, and IV). The element distribution and shape of particles was investigated in sediment in Papers II, III, and IV, and in Paper IV stabilized sediment (days 3, 29, 57, and 90), cement and GGBS was also analyzed using an environmental scanning electron microscopy (ESEM, FEI Quanta200 FEG-ESEM) with an Oxford INCA energy dispersive X-ray spectrometer (EDS) under low vacuum pressure. The samples were mounted on carbon tape and dried at ambient conditions without any coating procedure. In the ESEM samples are being scanned with an electrode beam. The electrodes returning from the samples are processed and an image is produced indicating sample topography and content. The EDS method includes scanning a sample using X-ray beams, and a sensor registering the number and energy of X-rays returning, and an electromagnetic spectrum is created. By studying the spectrum peaks, it indicates which elements are present in the sample as different elements give unique peaks.

All sediment and stabilized sediments' loss on ignition (LOI) and dry weight (DW) were measured using method SS-EN 028113 by measuring the samples' weight loss after incineration at 105℃ and 550℃ respectively (Papers II, III, and IV). Total organic carbon (TOC) was measured at an external accredited laboratory according to CSN ISO 10694, CSN EN 13137:2002, and CSN EN 15936DW by incinerating the samples and analyze the presence of carbon in the emitted fumes (Papers II, III, and IV). The contents of TBT, DBT, and MBT in sediment and stabilized sediment were analyzed at an external accredited laboratory using ISO 23161:2011 while the concentrations in leachates were analyzed according to ISO17353:2004 (Papers II, III, and IV). In both methods the cations of TBT, DBT, and MBT are determined. For the solids, the samples are pretreated by extraction using acetic acid, methanol, and ultra-pure water in an ultra-sonic bath. After this step, the analytical procedure is the same for solid and liquid samples: The pH is set to 4-5, sodium tetraethylborate is used for derivatization simultaneously as hexane is used for extraction, followed by analysis in a gas chromatograph (GC) coupled with inductively coupled plasma mass spectrometry (ICP-MS).

Total amount analyses of major and minor elements in both sediment (Papers II, III, and IV), and leachates (Papers II and III) were analyzed at an external laboratory according to standards SS EN ISO 17294-2:2016 and EPA-method 200.8:1994. For liquid samples, filtering using an 0.45 µm filter is done to investigate dissolved metals while for investigation of the total content no filtration is done. For the digestion, the sample is put in an autoclave with nitric acid, except when analyzing Ag when hydrochloric acid is used instead of nitric acid. For solid samples pretreatment include drying and leaching in nitric acid (except for when analyzing Ag, Mo, Sb, and Sn, when aqua regia is used) in a block heater. Both liquid and solid samples may, depending on the amount of ions in the sample, be diluted to reach the requirement of the machine used for the analysis. The samples were then analyzed using inductively coupled plasma sector field mass spectrometry (ICP-SFMS), except for Hg in water samples which were determined by atomic fluorescence spectrometry (AFS).

Major and minor elements in leachates in Paper IV were analyzed by ICP-MS at the Chalmers Water and Environmental Laboratory using a Thermo Scientific ICAP Q instrument with an SC-FAST sample introduction system. Each leachate sample was divided, where one part was filtered with a 0.45 µm filter and one part was not filtered to investigate if the elements were attached to suspended particles or dissolved. The samples were then diluted to levels in the instrument's analytical range while reducing the potential impact of salt on instrument performance, and were acidified with nitric acid.

3.3 Environmental sustainability assessment

In Paper I an integrated monetary and environmental assessment method was developed based on the methodology developed by Andersson-Sköld, et al. [116] and [117] and it was tested by investigating environmental and economic effects of different combinations of sediment management approaches. The approaches included conventional ones such as sending masses for deep-sea disposal, landfill, and as well as natural remediation but also the more innovative option of metal recovery. The option of metal extraction is introduced to reduce the toxicity of the sediment and thereby lower sediment classification, whilst also obtaining precious metals. The alternatives were applied to six case studies in Sweden of different sizes, including two ports, three marinas, and one waterway (presented in chapter 3.1.2). All approaches were compared with sending all masses to landfill as this was identified as the most common approach, but also as this approach should preferably be avoided in the future [9-11].

The method developed for investigating and comparing different management options is seen in Figure 12. In the first step, site-specific characteristics, such as the content of pollutants, and local restrictions are investigated. Depending on the sediment quality, different management strategies are possible. In step two, identification of which suitable management alternatives are done. Here, other jurisdictions and limiting values might be needed to be fulfilled, apart from the strictly environmental. The sediment volume could also influence which options are possible, as an example, there might be restrictions on how much masses are allowed to be disposed of at e.g., a deep-sea disposal site during a given time interval. Thus, many managements alternatives might be applicable for a site. In step three, costs associated with the investigated management alternatives are estimated. In the fourth step, different costs associated with different management options are compared. Here, the potential income from the option of metal extraction, if applicable, is investigated by comparing the metal content and current metal prices. As an example, by performing metal extraction the sediment classification could potentially be altered, which might result in a management cost reduction. Additionally, precious metals could be retained and sold to refining industries yielding an income [12], which potentially could lower the overall management cost. In step five, environmental impacts are investigated on short- and long-term associated with different management alternatives. In the final step information from previous steps is weighted

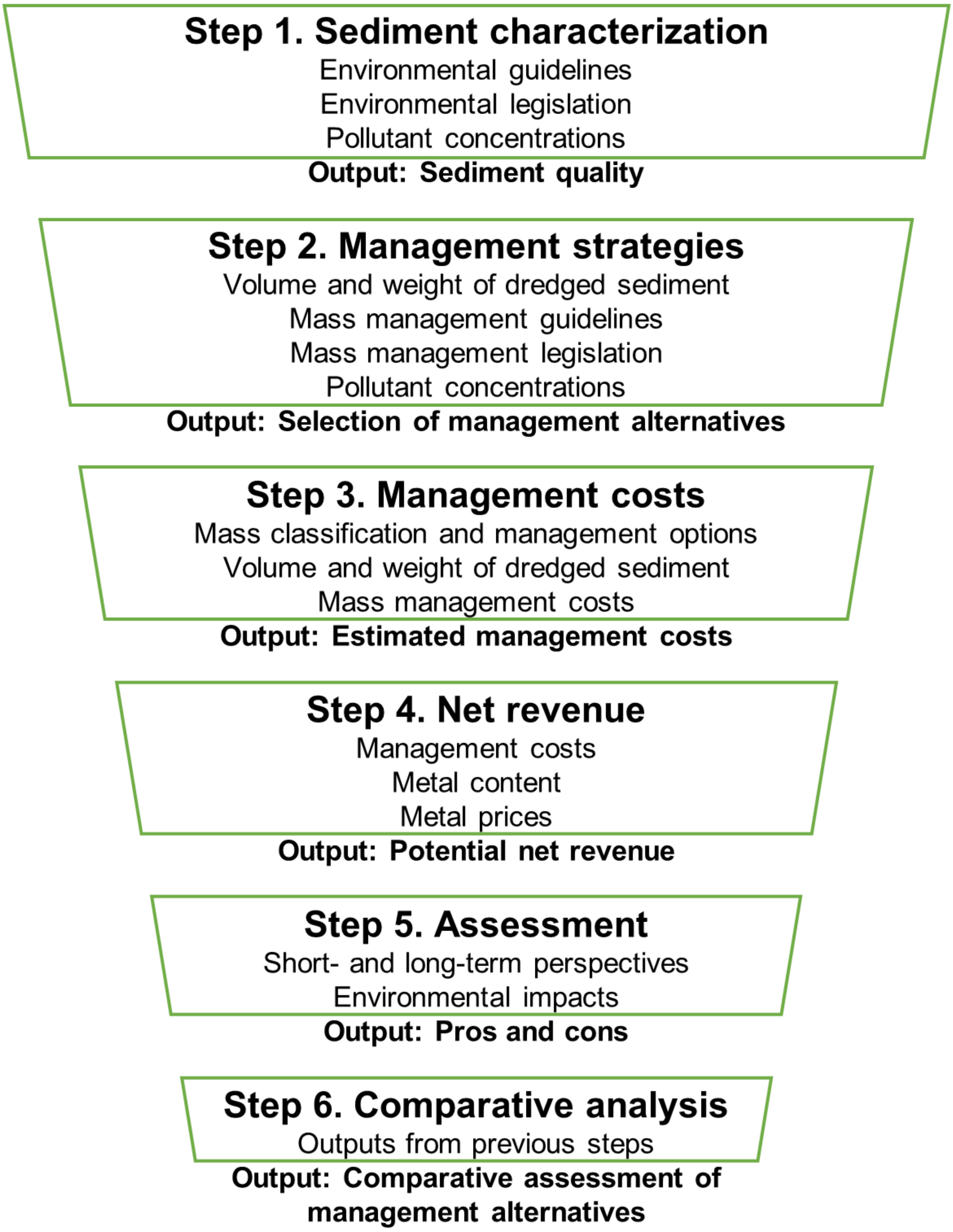


Figure 12 Developed method for investigating and comparing sediment management options [118].

together and could be used as a basis for decision analysis. Depending on the stage of the project, this structured way of working can be developed further to provide a useful tool for sediment management. In this way, different options could be compared and assessed. Additionally, conflicts of interest between economic and environmental aspect can be identified.

The integrated assessment method was further developed in Paper V by including LCA. The LCA software SimaPro® EPD (2018) and the database Ecoinvent, v. 3 were used together with real site data to estimate global warming potential (in CO2 eq.) associated with different management scenarios during a given time interval. The alternatives investigated here were all applied for the port of Gothenburg case study settings, although sediment with two different levels of contamination was investigated to see how the metal content impacts the results of the model. To represent low contaminated sediment the data from the port of Gothenburg was used and to represent a high contaminated sediment data from the port of Oskarshamn were used in the model (Table 2). Additionally, S/S were added as a management alternative and different management scenarios were coupled with metal recovery through electrolysis. For the LCA assessment, a functional unit and a time frame must be set for all calculations [101, 102]. Here, the functional unit was set to 100 m3 sediment, and the time frame was limited to management after dredging, as dredging will be done in all approaches.

4. Results and discussion

4.1 Treatment of contaminated sediment

4.1.1 Characterization of sediment

Sediment was sampled at the marina Björlanda Kile småbåtshamn (BK) (Paper II), the former shipyard Cityvarvet (CV) (Paper II), and the river Göta Älv's waterway (GBG) (Paper III), all situated in Gothenburg, Sweden. The content of organotin compounds (TBT, DBT, and MBT) and metals are presented in Table 3 and compared to the Swedish, Norwegian, and Canadian guidelines, which are compiled in Table 1. According to the Swedish sediment classification the TBT and DBT contents at all sites, and MBT content at BK and CV, are very high, while MBT at GBG is high [47]. The Norwegian environmental classification for marine sediment indicates that TBT contents at all sites have extensive acute toxic effects [49]. In the BK sediment, the content of TBT is less than the content of DBT and MBT, which indicates that TBT degradation occurs. However, at CV and GBG the TBT content is higher than the content of DBT and MBT, which indicates that the degradation processes are slower in these sediments. Both CV and GBG could also have had more recent contamination of TBT as larger vessels are common at those sites, unlike in the marina BK, and TBT containing boat paint for larger vessels was more recently banned (in 2003 and 1989 respectively) (Directive 89/677/EEC, EU Regulation (EC) No 782/2003).

Zinc contents in the sediment at BK and CV, and Cu content at BK, were high enough to potentially cause chronic effects after long-term exposure according to the Norwegian environmental sediment status classification, while Cu at CV could cause extensive acute toxic effects [49]. Copper contents at CV also reach the Canadian probable effect level, implying that marine organisms are affected at the site [51]. In GBG the metal pollution of sediment was less severe as Cu and Hg contents were above the levels where effects may start to occur in aquatic organisms (Interim sediment quality guideline (ISQG)) but were below the probable effect level [51]. The Hg content was not causing toxic effects according to the Norwegian environmental sediment status classification [49]. The other analyzed metals did not have guidelines or were classified as present in background levels or not causing toxic effects according to the Norwegian classification [49, 50] and were below the limit where effects may start to occur (ISQG) according to Canadian guidelines [51]. To conclude, TBT and Cu are the contaminants of major concern in all three sediments, as well as Zn in BK and CV.

The sediments' metal contents are within the same range as presented by Qian, et al. [35], in which data from 52 sites worldwide have been compiled. However, the Cu content at CV is in the upper range of the mean values presented. In the same study, it was also seen that metals were mainly found on finer particle sizes. A higher affinity to finer particles has also been reported to be the case for TBT [20, 22]. The different sediments' grain size composition for the sediments studied here, according to ISO 14688-1:2002, is given in Table 4 and it is seen that all sediments consist

Table 3. Average and standard deviation (STD) of initial dry weight (DW), and total organic content (TOC), tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), and metal content in sediments used in experiments originating from the sites Björlanda Kile småbåtshamn (BK), Cityvarvet (CV), and the Göta Älv waterway (GBG).

Sediment	**BK**		**CV**		**GBG**	
	Average	**STD**	**Average**	**STD**	**Average**	**STD**
DW [%]	43	2.6	40	1.1	52	4.2
TOC [% DW]	2.4	-	2.1	-	2.2	0.18
Organotin compounds [µg/kg DW]						
TBT	73	4.3	1300	110	160	53
DBT	430	26	440	67	39	11
MBT	470	28	85	11	19	9.1
Metals [mg/kg DW]						
Ag	0.13	0.029	-	-	0.21	0.089
As	16	2.6	9.0	2.2	4.6	0.10
Ba	71	5.7	110	6.7	61	8.1
Cd	0.13	0.014	0.29	0.024	0.27	0.038
Co	8.9	1.2	11	0.79	7.3	0.41
Cr	48	2.8	57	1.6	28	4.0
Cu	78	7.4	230	13	31	4.9
Fe	26,000	-	35,000	-	18,000	2,800
Hg	<0.20	-	<0.20	-	0.25	0.039
Mo	1.9	0.27	4.7	0.86	1.8	0.11
Ni	20	1.0	22	0.60	14	0.94
Pb	32	1.9	32	8.7	23	2.1
Sb	0.39	0.050	4.7	0.50	0.60	0.10
Sn	3.2	0.20	12	1.1	3.2	0.57
V	56	3.6	53	3.3	38	2.5
Zn	200	20	360	27	120	9.3

Table 4. Sediment grain size distribution from sites Björlanda Kile småbåtshamn (BK), Cityvarvet (CV), and the Göta Älv waterway (GBG) according to ISO 14688-1:2002.

Fraction [%]	**Size [mm]**	**BK**	**CV**	**GBG**
Clay	≤0.002	13.8	14.4	21.0
Silt	0.002–0.06	47.9	53.3	40.5
Sand	0.06-2	31.2	18.5	38.5
>Sand	>2	7.10	13.8	-

mainly of silt. For sediment which has a grain size distribution differs greatly, size separation could be a method to separate clean coarser sediment and more contaminated fine-grained sediment to focus treatment on the latter. However, in sediment such as those investigated in this study that consists of mainly fine particles, size separation to focus on a specific fraction could provide difficulty if applied to a full-scale process.

4.1.2 Organotin removal

Natural sediment

The results from the different methods used to remove TBT from the sediments in this project are summarized in Table 5. The highest removal was seen for the oxidative methods Fenton's reagent (64%), and electrolysis (58%), followed by stabilization and solidification (46%) and leaching in ultra-pure water (46%).

Oxidation (Paper III)

The highest TBT removal percentages were seen for the two investigated oxidative methods, Fenton's reagent and electrolysis (Table 5). During both processes' hydroxyl radicals (HO•) are formed which break the covalent bonds that are between the Sn atom and butyl groups and degrade TBT to DBT, MBT, and finally Sn. A higher reduction in the Fenton experiment might be that the low pH (~2) is facilitating the release of TBT from the sediment and making it more exposed for radicals in the aquatic phase, in comparison to the electrolysis, which was done with a relatively neutral pH, ~7.5. The addition of H2O2 seems to be important for the TBT removal, while an increased amount of Fe2+ did not result in a higher TBT removal. This may be due to the sediment

Table 5. Reduction of TBT, DBT, and MBT in sediment percentage after treatment. The origin of the sediment (site origin), treatment method applied (method), removal in percentage from the corresponding original sediment, and the reference to the paper where the treatment was investigated (Paper no.). A negative removal indicates an increase in relation to the original content in the sediment while a positive removal indicates that the content has been reduced.

Method[a]	**Acid**	**pH 13**	**NaCl**	**EDDS**	**HA**	**HPC**	**Fe colloids**	**U-P**	**Soap**	**Electro**	**Fenton**	**S/S**
Site[b]	CV	BK	CV	BK	BK	BK	BK	BK	BK	GBG	GBG	GBG
Paper	II	II	II	II	II	II	II	II	II	III	III	IV
Removal [%]												
TBT	-76	-97	16	23	-46	23	-25	46	34	58	64	46
DBT	22	71	56	64	59	66	64	81	64	43	22	61
MBT	-4	5	33	55	47	62	48	74	59	51	63	-13

[a] *The methods used are (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), iron colloids (Fe colloids), humic acid (HA), hydroxypropyl cellulose (HPC), ultra-pure water (U-P), saponified tall oil (soap), NaOH (pH13), HCl (acid), NaCl, Fenton's reagent (Fenton) and electrochemical treatment (Electro) as well as stabilization and solidification (S/S).*

[b] *The sites are CV= Cityvarvet, BK= Björlanda Kile småbåtshamn, GBG = Göta Älv waterway.*

naturally containing Fe2+. In another study [65], Fenton's reagent removed 81% of the TBT content, however, the liquid to solid (L/S) ratio in those experiments was not specified, making a comparison between the results difficult. After the Fenton treatment, a change in sediment grain size with an increase of finer particles was observed in comparison to the original GBG sediment.

In the electrolysis experiments, it was seen that the TBT removal was positively correlated to the applied current. Two previous studies on electrochemical TBT oxidation with different experimental setups have observed higher removal efficiencies than in this study (83–94%) and at lower current density [67, 92]. However, in these studies, sandy sediment was treated, and different type of electrodes was used (Ti/IrO2 anode and steel cathode instead of Nb/BDD anode and Ti cathode), although Arevalo and Calmano (2007) did not observe any significant differences for the treatment of TBT contaminated saline water when comparing Ti/IrO2 or BDD anodes in another study. IrO2 produces less hydroxyl and hydroperoxyl radicals in comparison to BDD but could potentially produce more reactive chlorine species [92, 94, 119]. The reactive chlorine species could also contribute to the oxidation of TBT [24]. Other compounds in the sediment could also compete for the reactions, resulting in a lower TBT degradation [93].

Leaching (Paper II)

The results show that the best leaching agent with low environmental impacts for TBT removal was ultra-pure water with a 46% removal. This was also the leaching agent that removed the highest content of all the studied organotin compounds (TBT, DBT, and MBT). The high release could be due to that a low ion strength and low conductivity facilitate a hydrophobic dispersion of TBT [120, 121]. Soap performed second-best of the low environmental leaching agents and removed 34% of the TBT from the sediment. The soap, and TBT, both possess hydrophilic and hydrophobic properties. Here, it is likely that TBT and soap together form an emulsion that also allows the suspension of fine particles in the leachate. The hydrophobic and hydrophilic HPC removed 23% of the TBT, which was also the efficiency for EDDS. EDDS is similar to EDTA, which could be used to extract TBT from sediments before chemical analysis. Both the investigated colloids, humic acid and iron colloids, seemed to sorb to the sediment, resulting in TBT binding more strongly to the colloids and becoming more attached to the sediment. In theory, a high release of TBT should be seen at high or low pH [58]. However, the leaching at both high and low pH demonstrated an increase of TBT in the sediment, while high TBT concentrations were also found in the leachates. This is partly due to the sediment itself dissolving by the extreme pH and partly due to the degradation of TBT-containing antifouling flakes. As the TBT content remained similar to the content before the treatment and the weight of sediment has decreased after the treatment, the relative TBT to sediment ratio has increased. Thus, the remaining TBT in the sediment might be seen as higher. A high salinity of the leaching agents was positive for the removal of TBT, DBT, and MBT as previously reported [82, 83].

Paper II shows the complexity of the sorption and release mechanisms of TBT. The comparable low difference in TBT removals between tougher and less environmental impact leaching agents display the difficulties in removing the substance but also highlights that it might be sufficient to use more gentle remediation methods, and a combination of such could potentially be put in a process line.

Stabilization and solidification (Paper IV)

Fenton reached the highest TBT reduction but due to the low pH (~2) in the residue, it was not deemed suitable for direct use in S/S [99]. Instead, electrochemically treated sediment was used, as the method had less impact on the sediment residue, in regard to pH and particle size changes.

Stabilization and solidification was done on sediment from GBG and the TBT content in untreated and electrochemically pretreated stabilized sediment was compared. By performing S/S on the sediment TBT is stabilized, which means that the ability to leach out is reduced. However, analysis of TBT content in stabilized sediment after curing 1 day in the molds (no water contact) indicates that 46% of the TBT degraded during the stabilization process, and this result is when taking dilution due to the addition of cement and GGBS into account (Table 5). For untreated sediment with an initial TBT content of 169 µg/kg DW would with dilution be lowered to 153 µg/kg DW (Figure 13). However, the analysis showed a final content of 82 µg/kg DW TBT. The same was seen for electrolyzed pretreated samples during stabilization, with a starting content of 132 µg/kg DW TBT, the theoretical content after dilution would be 119 µg/kg DW TBT but a final content of 75 µg/kg DW TBT was measured. In Paper IV, the TBT degradation caused by the electrolysis was lower than the one reached in Paper III. This was since the sediment was treated in larger batches, 0.5 kg instead of 0.2 kg, to produce all sediment required for the stabilization (~40 kg). After a curation time of 90 days for the stabilized sediments, it was seen that the TBT content in the electrolyzed and untreated stabilized sediment had been further reduced, except for the original samples cured in a saline liquid, where the TBT content seems to be unaffected (Figure 13). This can be explained by the results found in Paper II, showing that saline conditions leached out less TBT than in ultra-pure solutions, which is also seen in Table 5 [82, 83]. As saline conditions are most similar to the condition in the field this indicates the importance to investigate if a higher risk of TBT leaching is associated with untreated S/S. A higher TBT content in the stabilized sample does not necessarily alone determine if the leachate poses a higher risk, but the surrounding environmental impact the risk. Additionally, long-term effects must be investigated.

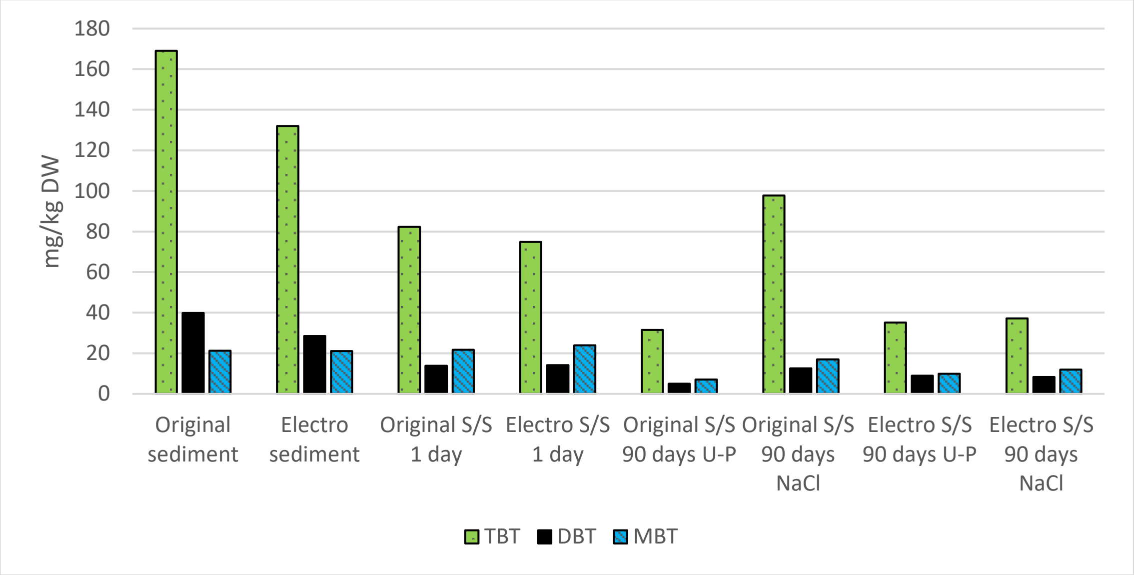


Figure 13. Content of tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) in sediment and stabilized sediment samples (S/S) originating from the Göta Älv waterway. For stabilized samples, the age of the samples (1 or 90 days) is presented together with the curing liquid for 90 days old samples (U-P= ultra-pure water and NaCl=saline water).

Spiked sediment

In Paper III, sediment was spiked with TBTCl aiming to see clearer trends in TBT degradation. The TBT content in the spiked sediment was 25,000 µg/kg DW, while in the original GBG sample the content was much lower, 160 µg/kg DW. This means that ~99.6% of the TBT in the spiked samples was the introduced TBTCl. Both Fenton's reagent and electrochemical treatment were used as treatment methods and both methods were sufficient to reach an almost complete removal, 98% reduction for the former and ~100% for the latter. However, such high TBT reduction was not reached in the original (non-spiked) sediment even if a higher addition of H2O2 or increased voltage was used on the samples. This can be explained by the introduction of TBT to the sediment in form for TBTCl in the spiked samples, while in the original samples TBT is more likely to be in the form of TBTO. In other studies, it was seen that old TBT was more difficult to treat than recently deposited TBT [23]. With time, the TBT seems to migrate into the inner structure of the sediment where it may be less available for reactions. Also, in the original sediment, TBT is most likely partly incorporated in paint flakes, which could protect the molecule from degradation [122]. Consequently, a good TBT reduction in spiked samples does not mean that the same results could be expected when using the same experimental setup on a non-spiked TBT contaminated sediment. Other studies also found that spiking the samples overestimate the efficiency of a method [17, 66], highlighting the need to test the real (non-spiked) samples to find an optimized technique. Although, spiking could still be used as an indicator of suitable techniques. The distribution of different forms of TBT (TBTO, TBTCl, TBTF) in the sediment could be investigated to get a similar composition in the spiked samples, and as well be allowed to age before treatment, to better mimic the conditions for natural TBT-containing samples. Therefore, spiking could be a good indicator of a method's potential, however, it is important to experiment with non-spiked samples as well, as it is proven to be more difficult.

Water phase

In Paper III, degradation experiments were done on slightly saline water (2.4 g/L NaCl) and saline water (35 g/L NaCl) spiked with TBTCl to see if electrolysis was efficient for treating TBT contaminated water. The results showed that all organotin contents were lowered to below the detection limit (<20 ng/L for TBT and <100 ng/L for DBT and MBT), while for the blank sample where no current was applied, the TBT content remained at the initial concentration of ~600 ng/L. These results were similar to the results in another study where TBT was reduced from 13,000 ng/L to 8 ng/L when treating water from a shipyard [24]. These results show the potential of treating TBT contaminated water with electrolysis and could be an interesting method to combine with sediment remediation to further treat leachates or other waters with elevated TBT concentrations. As seen in Papers II and III, the removal of TBT from the sediment is not only due to degradation. After treatment, a fraction of the reduced TBT was found in the leachates. In a natural environment, TBT degrades faster in the water phase compared to when sorbed to sediments [18, 19]. However, after the investigated treatment techniques TBT was sometimes found in leachates in levels exceeding the European quality standard of 0.2 ng/L [31]. This highlights the need to further treat the leachates and treatment with electrolysis may be a suitable and effective option.

4.1.3 Metal removal

According to Norwegian and Canadian sediment guidelines, the metals that were found in elevated contents in the investigated sediment were Cu and Zn, as discussed in chapter 4.1.1. Therefore, the focus will be on the removal of these two metals. The metal removal from the three sediments was researched with different methods and the removal in percent in comparison to the corresponding original site is seen in Table 6. As seen in the table, the methods that were most efficient for the removal of Cu from sediments were Fenton (45%), EDDS (33%), iron colloids (32%), and the complex binding leaching agents HPC and soap (30% each). Zinc removal was the highest with Fenton and HPC (40% each), followed by soap (35%) and iron colloids (26%). Despite the high removal of many metals reductions in risk classification was not seen always seen, but Fenton reduced the Cu content, and HPC and soap reduced Zn, below both the Norwegian background level [49] and the Canadian interim sediment quality guidelines [51] for GBG and BK sediment respectively. Zinc was also reduced down to below the Canadian probable effect level but above the interim sediment quality guidelines [51] for both acid and NaCl which was done on the CV sediment.

Table 6. Reduction of metals in sediment in percentage after treatment. The origin of the sediment (site origin), treatment method applied (method), removal in percentage from the corresponding original sediment, and the reference to the paper where the treatment was investigated (Paper no.). A negative removal indicates an increase in relation to the original content in the sediment while a positive removal indicates that the content has been reduced. Results for the critical metals Cu and Zn are marked in bold.

Method[a]	**Acid**	**pH 13**	**NaCl**	**EDDS**	**HA**	**HPC**	**Fe colloids**	**U-P**	**Soap**	**Electro**	**Fenton**	**S/S**
Site[b]	CV	BK	CV	BK	BK	BK	BK	BK	BK	GBG	GBG	GBG
Paper	II	II	II	II	II	II	II	II	II	III	III	IV
Removal [%]												
As	0	39	10	34	-7	44	21	27	21	-6	15	-5
Ba	9	-45	24	18	-10	26	18	13	25	12	22	-74
Co	9	-54	21	39	20	49	34	16	29	-4	21	-9
Cr	21	-29	28	14	-8	36	13	19	22	12	28	13
Cu	**-9**	**25**	**22**	**33**	**8**	**30**	**32**	**15**	**29**	**13**	**45**	**-31**
Mo	-111	-16	-25	9	4	15	4	7	-18	27	19	14
Ni	14	-56	23	5	2	22	6	17	11	6	27	-11
Pb	-22	-31	22	28	10	26	25	21	21	14	15	9
Sb	-27	17	59	14	19	27	15	11	2	26	35	-11
Sn	-25	-20	18	-15	-12	7	-14	-4	-21	9	26	28
V	9	-17	19	12	38	67	12	19	49	3	26	3
Zn	**22**	**-40**	**25**	**19**	**9**	**39**	**24**	**12**	**33**	**13**	**40**	**5**

[a] *The methods used are (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), iron colloids (Fe colloids), humic acid (HA), hydroxypropyl cellulose (HPC), ultra-pure water (U-P), saponified tall oil (soap), NaOH (pH13), HCl (acid), NaCl, Fenton's reagent (Fenton) and electrochemical treatment (Electro) as well as stabilization and solidification (S/S).*

[b] *The sites are CV= Cityvarvet, BK= Björlanda Kile småbåtshamn, GBG = Göta Älv waterway.*

Oxidation (Paper III)

Fenton was done at low pH (~2), which is favorable for the release of most metals from sediments, as can be seen in Table 6. Electrolysis did also enable the release of some metals, but to a lesser extent in comparison to Fenton (Table 6). The electrolysis method removed more metals from sediment than in a previous study which reported no metal removal [66]. The difference in metal removal may be due to differences in how the metals bind in the different sediments (Paper II). The metal removal could potentially be further increased by lowering the pH under the electrolysis treatment [91]. However, during the treatment process deposition on the cathode emerged over time. Analysis of the build-up showed that it contained major elements as; 60% Ca, 28% Fe, 4.9% Mg, and 3.4% Al, while Cu and Zn only accounted for 0.5% and 0.2% respectively. For treatment with electrolysis, it is important to investigate the lifetime of the electrodes, as delamination of the anode occurred during the treatment of sediment. In total, ~40 kg sediment was treated to be used in the stabilization tests and it is highly likely that the reduction of metals and organotin compounds was not consistent over time.

Leaching (Paper II)

EDDS was the best to remove Cu of the investigated leaching agents (33%), due to its ability to complex bond to metals. Soap was beneficial for metal removal, probably due to the binding of metals to the soap's COO- groups. The other hydrophobic and hydrophilic compound, HPC, removed an even higher percentage of every metal in comparison to soap (Table 6). Leaching with HPC was the best method to remove As, Ba, Co, Cr, V of all investigated methods, but had a slightly lower removal of Cu (30%) and Zn (39%) in comparison to Fenton that got the highest reduction of these critical metals (Cu 45% and Zn 40%). Thus, HPC could be an alternative for metal reduction if pH should remain unchanged. Leaching in ultra-pure water and NaCl was also efficient for metal removal, but all metals apart from As were leached to a larger extent in NaCl. For the colloids, i.e., HA and Fe colloids, the best metal removal was seen for the Fe colloids. This could be due to that metals sorb to Fe colloids rather than HA colloids at pH >8, which was the condition in the sediment slurry (pH ~8). The HA seemed to be sorbed to the sediment during treatment, preventing metals from leaching, as discussed for TBT in chapter 4.1.2.1. Leaching in acid and pH13 were the only leaching agents that resulted in an increase of Cu (acid) and Zn (pH13) in the sediment. The alkaline leaching resulted in an increase of most metals as alkaline conditions do not promote metals to release. As discussed in chapter 4.1.2.1 dissolution of the sediment was seen, so the relative metal to sediment ratio might have been altered due to changes in sediment. In addition to this, the increase of Cu and other metals in the acid leached residue are originating from the acid used. The acid was a by-product from a local waste incineration plant and contained metals originating from the waste [114]. Pretreatment of the acid could have been done to lower its metal concentrations, prior to the use of it as a leaching agent. However, despite the low pH in which metals normally are solved, it was seen that the metals sorbed to the sediment, which indicates that pH alternations alone are not sufficient to reach a full metal removal. This could be due to how the metal bind to the sediment (Paper II) and a complete release should not be expected.

Stabilization and solidification (Paper IV)

Changes in the metal content after S/S with cement and GGBS were investigated (Table 6). The content of most metals was seen to increase in relation to the sediment's original content. This is because the added cement and GGBS contain metals such as e.g., Ba (Paper IV). This addition of binders also causes a dilution of other metals found in the sediment.

4.1.4 Comparative discussion

When comparing which method was the best for the removal of TBT and metals (Table 7), it was seen that oxidation, which breaks the covalent bond between the butyl groups and Sn in TBT, got higher removal in comparison to methods where TBT was leached out. Fenton was most efficient both for TBT removal (64%) and removal of most metals but in particular Cu (45%) and Zn (40%). However, the following methods that were almost as efficient for TBT removal were electrolysis (58%), S/S (46%), and leaching in ultra-pure water (46%), but these methods were not the best to remove Cu and Zn. Of those four methods, the Cu and Zn removal trend followed the same as seen for TBT removal: Fenton's reagent had the highest Cu and Zn removal, followed by electrolysis, S/S, and ultra-pure water. As TBT is the major issue at the investigated sites, it is also the most important compound to be removed. If further metal reduction would be needed, alternatives such as HPC, soap, and iron colloids could be coupled with one of the mentioned TBT reducing methods.

The best TBT reducing methods (Fenton, electrolysis, S/S, and ultra-pure water leaching) are different and have different advantages and disadvantages, of which some are presented in Table 7. Fenton was the most effective method for TBT and metal removal; however, the residual sediment would need further treatment to be safely managed due to the low pH (~2). It also requires chemicals that put certain demands on a treatment facility, such as acid-safe containers and chemical storage. Both Fenton and electrolysis also need proper ventilation and equipment that would not oxidize during the treatment. A disadvantage with electrochemical treatments is the high environmental impact caused by the production of electrodes, but also the choice of the origin of the electricity used for treatment affects the environmental load and cost [123]. Stabilization and solidification lowered the TBT content and attain properties desirable when used in construction. However, it is also associated with a large environmental impact due to the addition of cement [99]. The suitability of the S/S technique is also affected by the need to have an S/S construction. High TBT removal (46%) was reached, but the impact on the sediment residue could potentially limit the use in other applications. The methods with less impact on the sediment residue, in regard to pH and particle size changes, were electrochemical treatment and the low impact leaching agents. These techniques are potentially more suitable for direct mass use. Leaching in ultra-pure water reduced the TBT by 46% and had a low impact on the sediment properties. However, this treatment technique would require large amounts of ultra-pure water to be used. This is method also uses electricity to purify the water, and as for the electrolysis, the origin of the electricity is important for the overall environmental impact. Also, it would require equipment which could be associated with high costs. Additionally, all of these four methods need to include some form of treatment of the residual leachate.

Table 7. Advantages and disadvantages associated with the methods studied in this project (i.e. electrochemical oxidation, Fenton's reagent oxidation, stabilization and solidification, ultra-pure water) with the highest TBT removal.

	Electrochemical oxidation	**Fenton reagent oxidation**	**Stabilization and solidification**	**Ultra-pure water**
Removal [%]				
TBT	58	64	46[a], 51[b]	46
Cu	13	45	61[a], 61[b]	15
Zn	13	40	-13[a], -24[b]	12
Advantages	Relatively unchanged sediment residue, which enables potential use in construction.	The highest reduction of TBT and high reduction of metals.	Enables use in constructions.	Unchanged sediment residue, which enables potential use in construction. Low working environment risks.
Disadvantages	High environmental impact by the pro-duction of electrodes. Working environment risks (gas production during electrolysis). Management of leachate.	Low pH, changed sediment residue (smaller particles). Working environ-ment risks (handling of chemicals, gas production during treatment). Management of leachate.	The addition of cement contributes to a high release of CO_2. Working environment risks (handling of cement). Management of leachate.	Expensive equipment for the production of the leaching agent. Management of leachate.

[a] *Reduction with S/S alone from initial original content (dilution effect excluded).*

[b] *Reduction with electrolysis pretreatment followed by S/S from initial original content (dilution effect excluded).*

To make sure that the applied methods do not result in an even more toxic byproduct, ecotoxicological tests are advised to be done to not underestimate risks associated with treatment [124]. Further, such tests in combination with sequential extraction tests could show if the TBT and metal reduction resulted in less availability for spreading and affecting the biota [125]. The leachability of the remaining TBT and metals in the sediment after treatment could be further researched to see how and if changes in the contaminant-sediment bond have occurred. This as leaching can change the metal mobility and form [126]. Potentially, the applied methods targeted specific TBT and metal mobility fractions, and the remaining contaminants could be more strongly bond to the sediment (i.e., stable organic forms and sulfides), thus posing a lower risk than contaminants bond to carbonates in the sediment. Difficulties to remove metals from sediment highlight the importance of site-specific assessment and not only consider the total content analysis. By performing sequential leaching and toxicity tests, as well as content analysis, the results could together be used to assess if additional treatment is required to lower the toxicity or to identify other risks associated with the investigated treatments.

4.2 Use of sediment in construction

In Paper IV electrolyzed and original sediment from GBG was stabilized and solidified in laboratory tests and the compression strength and leachability were investigated to see differences in performance caused by the electrolysis pretreatment.

4.2.1 Compressive strength

Compression tests were done after 28, 56, and 90 days and the results (Figure 14) show that all samples fulfilled the Arendal strength requirement [57]. The strength requirement for the field condition is 70 kPa in sheer strength, which corresponds to a compression strength of 140 kPa according to the Tresca criteria. It is also seen that at day 90, the best solidification effect (highest compression strength) was reached by stabilized untreated (original) sediment sample, but it is also for this sediment the recipe was developed. Hence, other mixing combinations of GGBS and cement could potentially result in a better strength for the electrolyzed sediment. In the figure, it is also seen that initially, the strength for the electrolyzed sediment was higher than for the original sediments, cured in both ultra-pure water and saline (NaCl) water. However, the strength development for electrolyzed sediment shows no significant increase. For the electrolyzed samples cured in NaCl a low increase in strength is seen, but for samples cured in ultra-pure water, the strength is even decreasing. It would be interesting to study the strength development over an even longer time than the 90 days studied here, to see if the same would occur for the other electrolyzed samples and if the strength at day 90 is kept.

The reason for the inferior performance of the treated sediment is most likely due to changes within the sediment that have occurred during the electrolysis. Analysis of the build-up on the cathode showed that the build-up consisted of 60% Ca. In the surface diffusion leaching test for electrolyzed stabilized samples, it was seen that Ca did not leach, and the same was true for Mg in ultra-pure water (Figure 16). This indicates that in the electrolyzed stabilized samples Ca may have been substituted with Mg in important reactions, which is negative for the strength development [97].

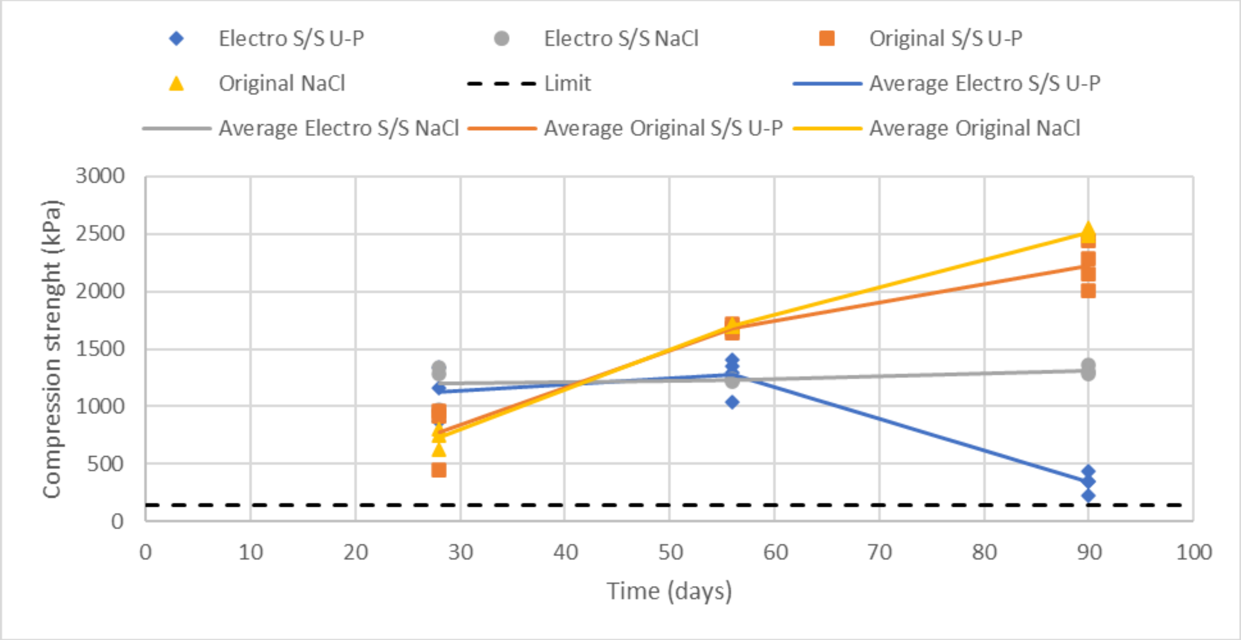


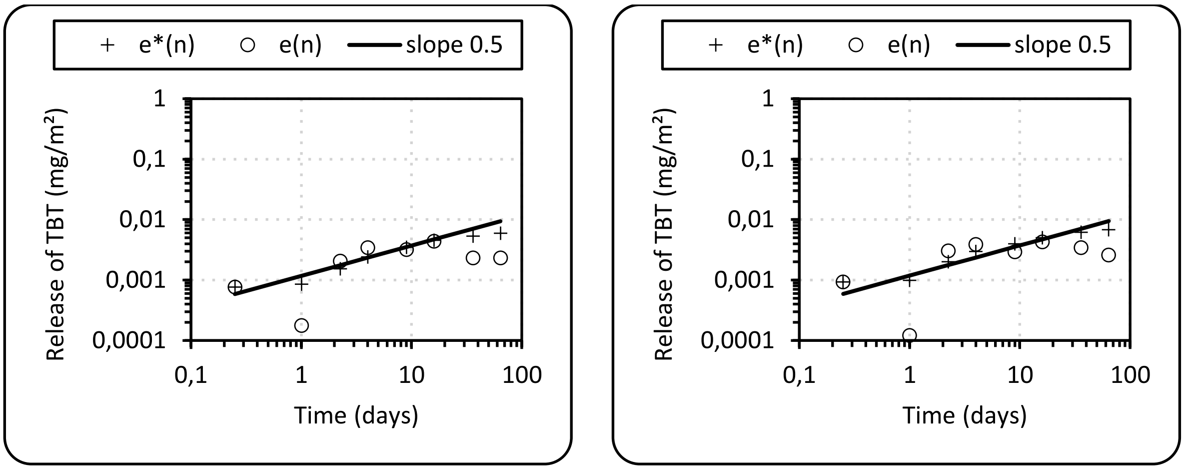
Figure 14. Compressive strength for electrochemically pretreated (Electro) and untreated (Original) stabilized samples cured in ultra-pure (U-P) and saline (NaCl) water. Each dot represents a sample and the line show the average value. The dashed line denotes the strength requirements for construction in Arendal, Gothenburg.

Another reason could be due to the decomposition of organic material in the stabilized sediment [127]. However, no drop in TOC was seen for the electrolyzed sediment (Paper IV), but other studies have shown that during the electrolysis the humic matter is transformed to fulvic matter [128], which potentially could affect the strength development without significantly decrease the TOC. Other reasons include that the presence of ions or compounds formed during the electrolysis might negatively impact the strength development or caused a shift in time for different hydrolysis reactions, which could cause expansion/shrinkage of the samples. Thus, electrochemical treatment might not be optimal prior to S/S. Instead, batch leaching with ultra-pure and soap might be a more suitable pretreatment as both TBT and metals could potentially be lowered before S/S. The created leachate could be treated with electrolysis as earlier discussed in chapter 4.1.2.3.

Another interesting finding from Paper IV is the impact of curing liquid on strength development. Samples cured in ultra-pure water reached an equally high strength as samples cured in saline water for days 28 and 56, but for day 90 all samples cured in ultra-pure water performed worse than samples cured in saline water. This could be due to a low ionic strength in the liquid, which could cause important ions to leach out to reach an ionic equilibrium in the curing liquid. However, S/S will not be done in water with such low ionic strength in the field, but similar trends could potentially be seen if S/S would be done in freshwater with low ionic strength. The difference in performance based on the curing liquid should be considered when testing and developing recipes for S/S for field conditions to get more reliable results.

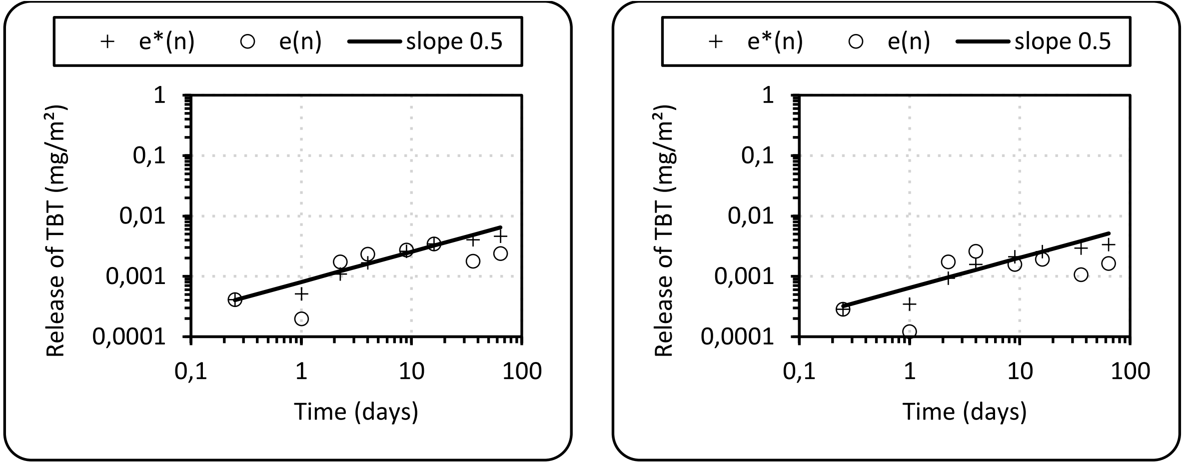
4.2.2 Leaching

The leaching of TBT and metals from the stabilized sediments was investigated in the surface diffusion leaching test (EA NEN7375:2004). It showed that TBT leached out during the entire 64-day test period (Figure 15). The leached amount was far less than the content reduction seen in Figure 13. This indicates that TBT also has been degraded. For the stabilized samples leached in ultra-pure water the start of depletion is indicated by downgoing leaching curves (Figure 15). However, a longer testing period is required to see how the leaching develops. As the test is designed for inorganic components, TBT concentrations measured at the last points in time might be less reliable, as TBT is degrading faster in water than in sediment [18, 19]. The leaching curves for DBT indicate that dissolution is starting to occur in the latter stages of the experiments, which may be due to the degradation of TBT rather than that more DBT is leached out with time. Electrolyzed stabilized samples leached marginally less TBT than original stabilized samples. Instead, the ionic concentration of the surrounding leaching agent seemed to be more important for the TBT leaching than if pretreatment had been done or not. The highest TBT concentrations were found in the ultra-pure water leachates and the lowest in saline water leachate with DOC. This indicates that a high ionic strength of surrounding water may prevent TBT to be leached out in comparison to water with low ionic strength, as seen for the NaCl and ultra-pure water leaching in Paper II.



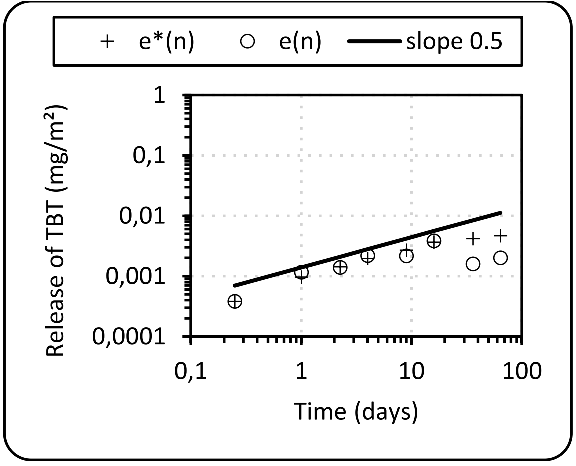
Electro stabilized sample in ultra-pure water

Original stabilized sample in ultra-pure water



Electro stabilized sample in saline water

Original stabilized sample in saline water

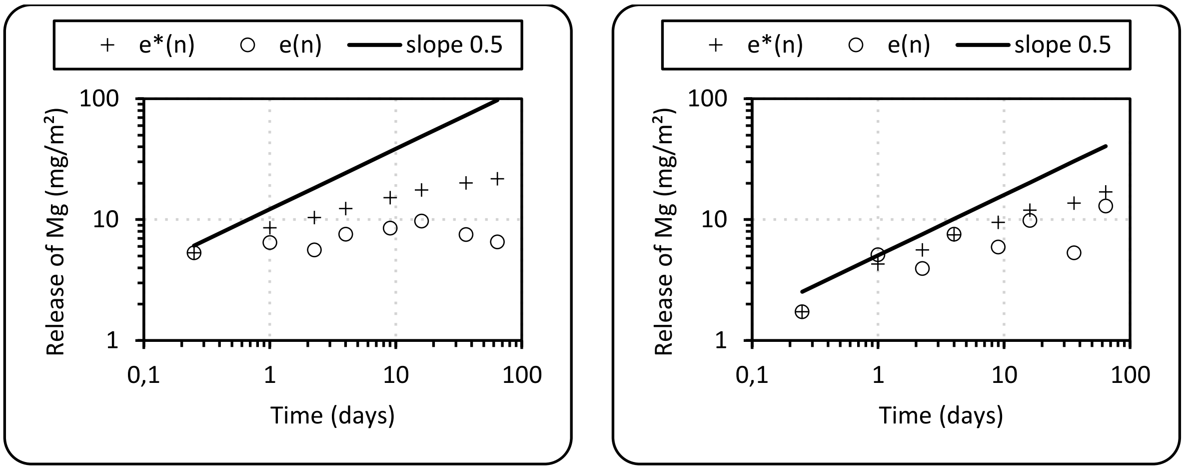


Electro stabilized sample in saline water with DOC

Figure 15 TBT leaching from electrochemically pretreated (electro) and untreated (original) stabilized samples cured in ultra-pure water, saline water, as well as saline water with dissolved organic carbon (DOC). The vertical axis displays the release in mg/m2 and the horizontal axis the time in days. e*(n) displays the measured cumulative leaching and e(n) displays the derived cumulative leaching.

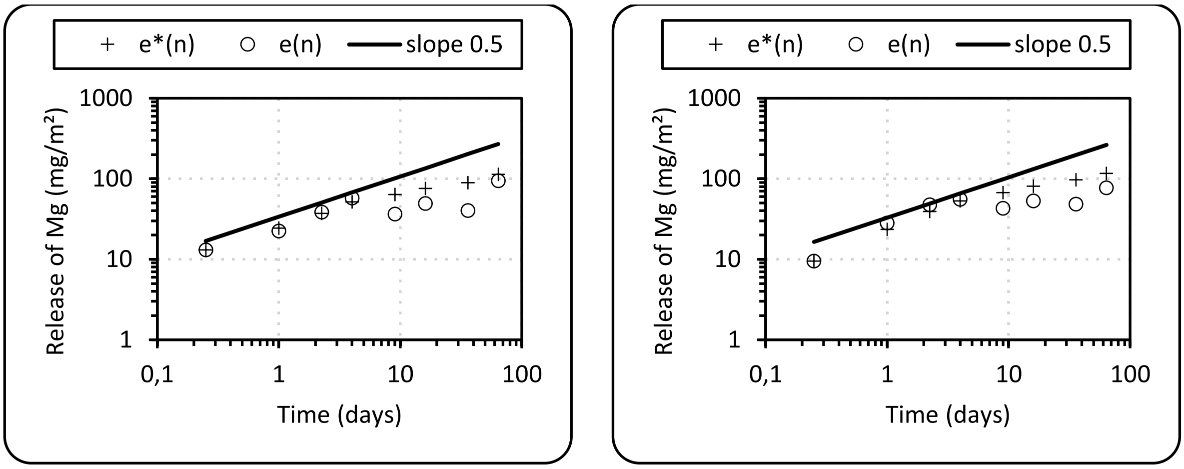
For metals, high salinity was instead correlated to higher leaching (Figures 16, 17, and 18), as also seen in Paper II. An example is for Mg, where depletion is seen by the downgoing leaching curves in the sample for electrochemically treated stabilized sediment in ultra-pure water (Figure 16). This could be due to that Mg has substituted Ca in important S/S reactions, which resulted in a decrease in compression strength (Figure 14), as discussed in chapter 4.2.1. A similar trend to what is seen for Mg is also seen for Cu, where the electrolyzed stabilized sample in ultra-pure water is depleting (Figure 17), but this is not observed for Zn (Figure 18). Depletion was observed to a larger extent in electrolyzed stabilized samples (23% of all samples and leaching agents) in comparison to original stabilized samples (16% of all samples and leaching agents), which indicates that the electrochemical treatment lowers the risk for metals to leach after stabilization. The electrolysis may have changed how the metals bind to the sediment, e.g., by changing the form of organic matter [128]. Thus, it is recommended to do sequential leaching tests before and after electrolysis, or other treatments, to observe differences in metal mobility.

In the SS-EN 12457-4 leaching test, it was seen that recently stabilized samples (day 1 and no curing) had the lowest metal release, but no reduction in leaching was seen over time at the investigated days 28, 56, and 90. This could indicate that the stabilization effect (reduced risk of leaching) is early reached and could be due to that most hydrolysis reactions occur directly after the cement is cast. The leaching did not differ much between electrolyzed and original stabilized samples and this could be due to similar pH values. Instead, the curing environment had a higher impact on the leaching, regardless of which leaching agent had been used. Samples cured in saline conditions leached more than samples cured in ultra-pure water. In ultra-pure water more metals need to be released from the stabilized sediment during the curing to reach an ionic equilibrium, while in a saline environment more of the metals could remain in the stabilized sediment, but risk being released during leaching.



Electro stabilized sample in ultra-pure water

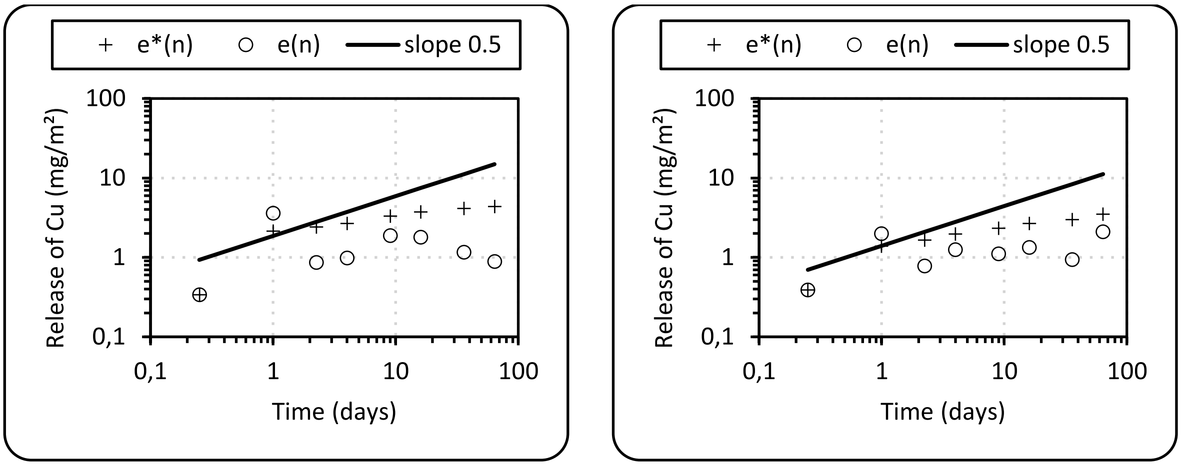
Original stabilized sample in ultra-pure water



Electro stabilized samples in saline water

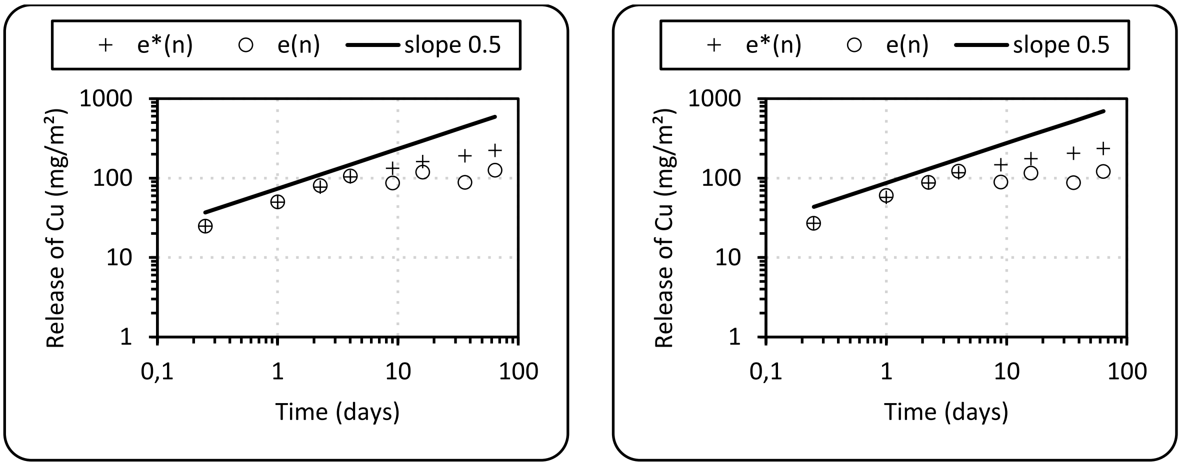
Original stabilized sample in saline water

Figure 16 Mg leaching from electrochemically pretreated (electro) and untreated (original) stabilized samples cured in ultra-pure water and saline water. The vertical axis displays the release in mg/m2 and the horizontal axis the time in days. e*(n) displays the measured cumulative leaching and e(n) displays the derived cumulative leaching.



Electro stabilized sample in ultra-pure water

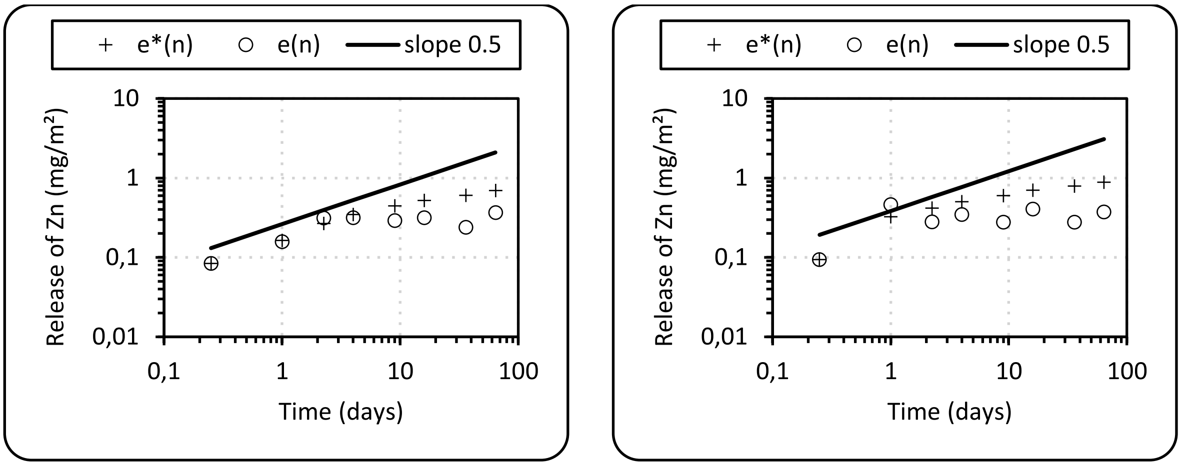
Original stabilized sample in ultra-pure water



Electro stabilized sample in saline water

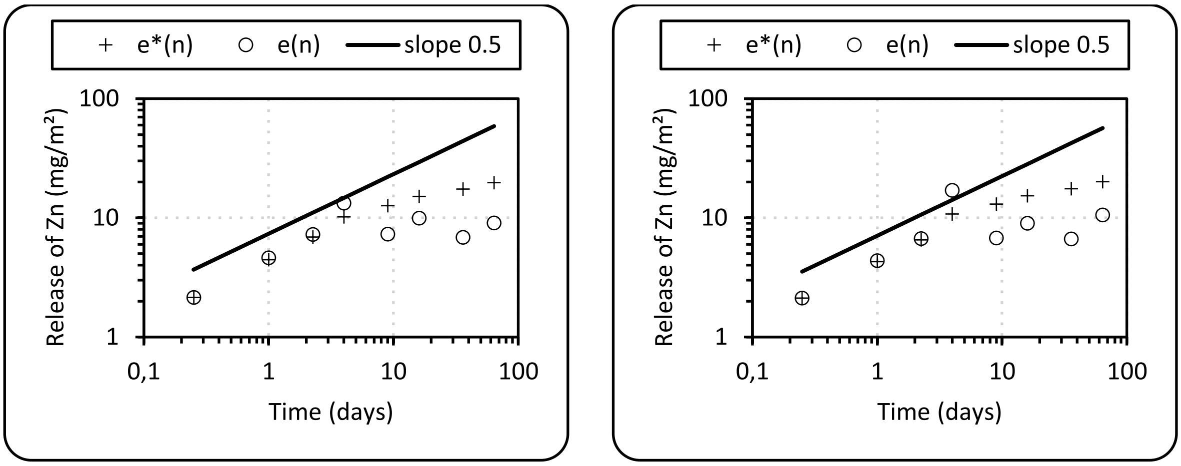
Original stabilized sample in saline water

Figure 17. Cu leaching from electrochemically pretreated (electro) and untreated (original) stabilized samples cured in ultra-pure water and saline water. The vertical axis displays the release in mg/m2 and the horizontal axis the time in days. e*(n) displays the measured cumulative leaching and e(n) displays the derived cumulative leaching.



Electro stabilized sample in ultra-pure water

Original stabilized sample in ultra-pure water



Electro stabilized sample in saline water

Original stabilized sample in saline water

Figure 18. Zn leaching from electrochemically pretreated (electro) and untreated (original) stabilized samples cured in ultra-pure water and saline water. The vertical axis displays the release in mg/m2 and the horizontal axis the time in days. e*(n) displays the measured cumulative leaching and e(n) displays the derived cumulative leaching.

4.3 Environmental sustainability assessments

4.3.1 Economic and environmental impacts

In Paper I different management options' environmental short- and long-term effects were investigated in comparison to the most common management alternative, landfilling. Each alternative's potential net revenue from saved landfill cost and potential metal recovery gain, as well as the environmental impact in short- and long-term perspective was investigated for the two ports (the port of Gothenburg and the port of Oskarshamn), the waterway Lövstaviken, and the three marinas (Björlanda Kile småbåtshamn (BK), Havdens båtklubb, and Stenungsunds båtklubb) (presented in chapter 3.1.2). A finding was that each case study site has to be individually assessed. The results show that from an environmental view it would be best to let the sediment remain untouched and allow polluted sediment to be covered by clean masses. This was also seen in another study comparing the environmental impacts from natural recovery with or without an active cover layer as treatment methods [100]. However, this option requires that the pollutant situation is not too severe and does not pose a significant environmental risk [60, 61]. The natural recovery alternative was the most beneficial one from the short-term perspective and since no dredging or management was required, little to no cost is associated with this alternative. However, this alternative may not be suitable if dredging is required, as for the ports and waterway.

In dredging scenarios, as for ports and waterways, it might be economic and environmentally motivated to treat the sediment by reducing the TBT content and recovering metals. Additionally, the recovered metals have a market value, thus, making it possible to cover some of the management costs. In both Papers I and V it was seen that, naturally, metal recovery is particularly interesting for heavily metal-polluted sediment, as more metals can be recovered. Also, the treated sediment enables other management options, and landfilling costs could be lowered as a more contaminated sediment is associated with higher landfill costs. As deposition criteria are getting tougher, and the landfill cost and metal prices are increasing, metal recovery is likely to be more economically interesting in the future [40, 44]. Landfilling all masses was found to be the most costly and least environmentally beneficial option, compared to all other investigated management approaches that include dredging (combinations of landfilling, deep-sea disposal, and metal recovery). Options with landfills include transports, as landfills are not closely located in the dredging area. In general, the more contaminated sediment, the longer distance it is to a landfill approved for such waste. This causes more CO2 to be released in comparison to if sediment could be deposited at a local landfill, see Figure 19. If deep-sea disposal is used, less CO2 is emitted as barges could transport larger quantities of sediment mass in comparison to trucks, which results in a lower CO2/km for transport by sea [46].

In Paper I, the approach that included dredging and was identified as the most economic and best for the environment, on both short and long-time perspectives, was a combination of deep-sea disposal and metal recovery. However, in Paper V where the option of S/S was introduced, S/S was identified to be the best alternative from an environmental point of view apart from the emissions of CO2. The origin of the CO2 is mainly due to the emissions of greenhouse gases from cement production (Figure 19). This could be improved by incorporating carbon capture and storage techniques during the cement production. For the alternatives containing electrolysis, it is seen that the origin of the electricity used under treatment is important. By choosing renewable energy for metal recovery, the environmental impacts are far less in comparison to options such as oil combustion. However, the choice of electrodes used does also contributes to how much CO2 is released (Figure 19).

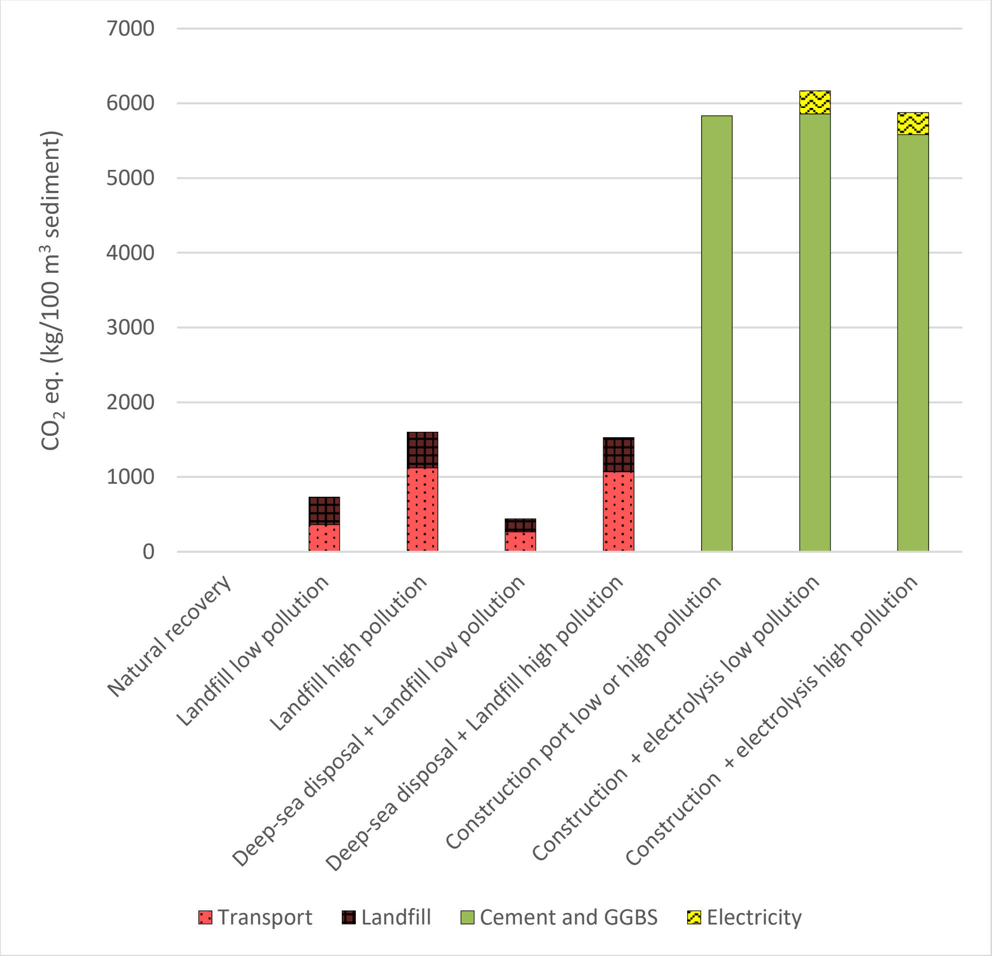


Figure 19. Proportion of CO2 equivalents (CO2 eq.) released for 100 m3 sediment with low metal pollution (low pollution) from the case study Port of Gothenburg and high metal pollution (high pollution) from the Port of Oskarshamn, during different scenarios with combinations of landfilling, deep-sea disposal, construction in port using stabilization and solidification, and electrolysis.

A combined LCA and MCA approach could prove useful during decision-making by covering all aspects of importance [100]. This type of methodology points out possible conflicting aspects and is useful to identify where new, innovative solutions are needed e.g., to lower CO2 emissions. The results also show the importance to consider how the environment is affected in the short and long term. This model could be further developed by including social aspects to fill the full sustainability spectra (social, economic, and environmental) to make informed decisions.

4.3.2 The potential of metal recovery

Results in Paper I showed that there is a potential value in the metals found in the sediment and by removing metals the management costs and environmental impacts could be reduced. However, the costs for metal extraction were not included in the calculations. Instead, the maximum allowable metal extraction cost was calculated, so that the overall sediment management cost (including potential metal extraction), would not exceed the management cost to landfill all masses. This resulted in an average maximum metal extraction cost of ~200 USD/tonne sediment. Large-scale metal extraction on sediment has not yet been performed, but smaller operations have had costs of 100-250 USD/tonne [129]. However, these remediation projects have mainly been done on sediment with coarse grain size, such as sand, and not on finer grain size, such as silt or clay that is common for many sediments in Sweden and other countries around the North Sea, as well as in the case study sites in this project.

The choice of technique for metal recovery is greatly going to affect the overall environmental impact for the management scenario, and each technique's environmental impact must be assessed. With further technique development, the metal recovery cost might decrease. Additionally, increasing management costs and metal prices together with tougher environmental criteria could make metal recovery a more attractive option in the future. In the LCA assessment (Paper V), 90% of the metals were estimated to be extracted through electrolysis. However, the electrolysis setup (Paper III) removed up to 45% of the metals. The removal efficiency has the potential to increase, as the experimental setup was done to optimize TBT reduction rather than remove metals. Studies with electrolysis on wastewater achieved a higher metal reduction, of up to 90% metal removal [89, 90]. This implies that electrolysis could be done more effectively if the procedure would be altered or coupled with other methods. The choice of electrolysis to extract the metals might not be the most efficient as a one-step method, instead, other methods could be used to extract metals to a liquid, which then could be electrochemically treated to obtain the metals or oxidate remaining TBT (Paper III). This is also more gentle for the electrodes compared to using them directly in sediment, possibly giving them a longer service life [119]. The electrodes' climate impact depends on the choice of electrode material, but carbon captioning techniques could additionally lower this impact. Further, different types of electrodes could be tested to investigate different electrodes removal efficiencies. The methods to extract the metals and TBT to water phase should preferably have a low environmental impact as the electrodes cause high CO2 eq emissions during their production (Paper V). Soap or HPC could be feasible alternatives to reduce the metal content, and also did not affect the residue sediment to a large extent.

4.3.3 Solidification and stabilization of sediment

It was seen in Paper IV that all stabilized sediment samples reached the compression strength limit of 140 kPa but the untreated (i.e., original) stabilized sediment performed better than the electrolyzed stabilized sediment. If additional or different pretreatment would have been done the results may have been better. Since the value of and demand for metals are high (Paper I) it would be beneficial to recover important and rare metals, such as Co, before the sediment is stabilized. Potential treatment methods that do not decrease the suitability for stabilization could be further investigated, e.g., different low environmental impact leaching agents like soap or ultra-pure water (Paper II).

As discussed in chapter 4.3.1, the S/S is associated with large CO2 emissions compared to other investigated options (Figure 19). However, S/S resulted in a TBT content reduction and enable the use of sediment in society. However, this means that suitability to perform S/S greatly depends on the need for stabilized sediment. Currently, the use of marine fine-grained sediment is limited due to its saline content and poor geotechnical properties. To present knowledge, stabilized sediment has only been used in construction projects in ports in Sweden. By stabilizing the sediment, the geotechnical properties are improved but the risk of chlorides and contaminants being emitted from the construction may lower the possibility to use the stabilized sediment in other applications. Further research should be done on methods that enable the use of S/S in other projects than port constructions. Additionally, other innovative uses of dredged sediment apart from S/S should be researched, to reduce the need for sediment disposal.

5. Conclusions

The aim of this project was to develop innovative, sustainable, and effective treatment techniques for the removal of organotin and metals from contaminated marine sediment and to investigate the environmental sustainability of different sediment management strategies. The most important conclusions answering the research questions are as follows.

To remediate the sediment different techniques were tested: Leaching agents with low environmental impact as well as tougher leaching agents (Paper II), and oxidative methods (Paper III). The TBT reduction by the S/S method was also analyzed (Paper IV). The highest TBT reduction was reached with Fenton's reagent (64%), followed by electrolysis (58%), S/S (46%), and ultra-pure water leaching (46%). Experiments showed that spiked sediment was easier to treat, with removal rates >98% for TBT, in comparison to non-spiked samples, highlighting the need to also work with real site sediment to not overestimate the efficiency when designing TBT remediation methods. Organotin compounds in water were easier to degrade as TBT, DBT, and MBT in spiked water were reduced to under the detection limit. The primary contaminant in the studied sediment was TBT, but elevated levels of the metals Cu and Zn were found as well. The methods removing most Cu were Fenton's reagent (45%) followed by the low impact leaching agents EDDS (33%), iron colloids (32%), and HPC and soap (30% each). While, for Zn, the best methods were Fenton and HPC (40% each), followed by soap (35%) and iron colloids (26%). Thus, using Fenton's reagent was the method that was most effective for removing TBT, Cu, and Zn, however, the treatment results in a low pH fine-grained slurry, that would require further treatment regardless of how it will be managed further. This points out the importance of finding gentle remediation methods that do not create a residue with other or even more hazardous properties than what the sediment initially had.

In Paper IV electrochemically treated sediment was used for stabilization and solidification (S/S), as well as non-treated sediment to investigate differences in leachability and strength caused by the pretreatment. Both pretreated and untreated stabilized sediment reached the set goal of 140 kPa in compression strength which indicates that treated sediment could be used as construction material. The best stabilization effect (immobilization of contaminants) was reached by stabilized pretreated sediment, while the best solidification effect (higher compression strength) was reached by stabilized untreated sediment. Regardless of the sediment was pretreated or not, a high salinity of the surrounding water both during curing and leaching was correlated to increased strength. High salinity also reduced the TBT release but increased the leaching of metals such as Cu and Zn. The same correlation of salinity in surrounding water and leaching trends for TBT and metals was also seen for sediment (non-stabilized) in Paper II. This highlights the need to perform S/S tests in water similar to the one surrounding the construction in the field.

Regularly, large quantities of organotin and metal contaminated sediment must be handled. To identify which management options are the most suitable, a method was developed combining integrated assessment, to identify possible management options, with MCA, to investigate the environmental impacts caused by different alternatives (Paper I). In Paper V the method included more management alternatives and supplemented with an LCA. Stabilization and solidification was the management alternative identified to have the largest negative climate impact with a high release of CO2 but other environmental factors, e.g., impact on land use, had a more positive impact in comparison to other investigated management alternatives. It was seen that it could be both economic and environmentally beneficial to recover metals from sediment and that metal recovery could partly cover management costs, especially as metal prices are increasing and as a lower sediment contamination level results in lower management costs in comparison to a higher sediment contamination level. However, the metal recovery from sediment must be further developed to increase the recovery potential but also to have it done sustainably. Performing electrolysis on highly contaminated sediment to recover metals was seen to be positive but the method was estimated to be less beneficial for low contaminated sediment. Further, the production of electrodes was associated with a high climate impact through emissions of CO2. It was seen that different alternatives' environmental impacts differ in short- and long-term perspectives. Overall, it is seen that what is considered to be the most effective and sustainable solution differs from site to site. This stresses the need to individually assess each site's precondition when investigating and deciding management alternatives. The results highlight the complexity to assess environmental impacts and the benefits of combining methods, e.g., integrated assessment, LCA, and MCA, to clarify possibilities, advantages, and disadvantages associated with different management alternatives. The developed methods could be useful in the decision-making process for stakeholders working with sediment.

6. Summary

Modern society is dependent on international trade and most traded goods are transported by sea. To enable this, regular dredging must be done to maintain water depth in ports and waterways, resulting in large quantities of often contaminated sediment that must be handled. Management options are limited due to regulations and depend on the content of contaminants such as tributyltin (TBT) and metals (e.g., zinc and copper) in the sediment. Consequently, there is a need to investigate new treatment techniques and evaluate the sustainability of management alternatives.

In this project, several techniques to remove TBT and metal from sediment were developed and tested in laboratory studies, including chemical oxidation by electrolysis and Fenton's reagent (Fenton) (Paper III), leaching with ultra-pure water, EDDS, saponified tall oil, iron colloids, humic acid, hydroxypropyl cellulose, and acid and alkaline solutions (Paper II). The highest TBT removal from natural sediment was reached using Fenton (64%) followed by electrolysis (58%). On TBT spiked sediment, Fenton and electrolysis reduced the TBT content by 98% by 100% respectively. In spiked water, TBT was degraded 100% by electrolysis. The most effective method for simultaneous TBT and metal removal was Fenton. However, due to the low pH of Fenton residue, electrolyzed sediment was instead chosen for stabilization and solidification, a method that forms a concrete-like product that could be used in construction (Paper IV). The impacts of electrolysis pre-treatment on compression strength and leaching patterns were investigated. The results show that stabilized pre-treated sediment leached less but had lower compression strength than stabilized untreated samples. The surrounding environment during curing was important, as a saline solution increased the compression strength and decreased TBT leaching, but increased metal leaching compared to a less saline solution.

Environmental impacts and costs associated with different sediment management strategies were studied using life cycle assessment (Paper V) and integrated monetary and environmental multicriteria analysis (Paper I). Metal recovery from sediment was identified as a potential future alternative, with increasing metal prices and economic incentives as highly contaminated sediments cost more to handle. However, effective and sustainable metal recovery techniques need to be further developed. The results highlight the importance of individually assessing each site when evaluating risk, determining management strategies, and assessing short- and long-term environmental impacts. The developed methods are useful for identifying economic and environmental conflicts and synergetic effects and could be useful tools in decision-making processes. The results of this project could contribute further to the development of full-scale treatment methods to remediate and enable the use of contaminated dredged sediment.

7. Further studies

The results from this project have brought up some recommendations and suggestions for future works.

- Further research can be done on gentle and sustainable methods that reduce the TBT, DBT, and MBT content in contaminated sediments. For instance, simple measures such as long-time mixing of the sediment to mechanically grind down the potential presence of paint flakes. Also, during the mixing oxygen could be introduced into the sediment and aid the degradation further.
- In the experiments conducted in this study, up to 45% of metals were removed from the sediment. However, the possibility to extract more of the metals in a sustainable manner can be studied, e.g., by developing the electrolysis method. Treatment of sediment could enable more uses in construction, give a safer residue to handle as less hazardous waste if disposed of at land or sea, or other potential usages.
- Stabilization and solidification is a good method to enable the use of sediment. However, there is a limited need for new port terminals and other usages of this method could be explored. Here regulation and construction requirements are important to find other potential usages. Also, finding other alternative uses than only S/S for saline fine-grained sediment is important. Additionally, during the S/S it was seen that the TBT content was reduced and not only through the dilution through the addition of binders. Further research to investigate what mechanisms are causing the reduction during the S/S is of high interest.
- It was seen that even though the electrochemically pretreated stabilized sediment fulfilled the strength criteria it performed worse in compression tests than stabilized untreated sediments. This could be due to that the recipe was originally developed for untreated sediment. Hence, alterations in the recipe might be needed to increase the strength development of treated sediments. Also, alterations or additional treatment steps could be done on the electrochemical pretreatment to increase the strength of stabilized sediment and further reduce leachability. Alternatively, electrochemical pretreatment could be changed to another type of pretreatment before stabilization, such as e.g., leaching in ultra-pure water.
- When performing S/S at sites similar to the Göta Älv estuary, with a temperature and salinity changing over the year, the impact of freezing and thawing cycles, as well as varying surrounding salinity on strength and leachability, should be further studied.
- In order for the treatment methods to come to use it is important to scale up the treatment and investigate if changes in the method are needed to guarantee a good quality of the treated sediment.
- Currently, only sediment content analysis (e.g., of organotin compounds and metals) is used to investigate risks associated with contaminated sediment in many countries. However, this simplified approach might misjudge the sediment’s risk. In future projects, it is of importance not only to study the total contents of the pollutants but also to investigate the

processes of how metals bind to the sediment and what changes in environmental conditions may increase the metals' leachability. For instance, in the leaching tests (Paper II) only a part of the contaminants was released, and potentially, those are the only fraction that needs to be considered when estimating the risk that they pose in the sediment. Further, no toxicity test is done on sediments to investigate if the combination of TBT and metals, and other pollutants have synergistic effects on the toxicity (i.e., the cocktail effect). If toxicity tests are introduced, it will give a truer risk assessment of the polluted sediments than just the analysis of the content of different pollutants. Additionally, sequential leaching could be investigated how available metals and TBT in the sediments are after being treated, potentially, they are not currently available for biota, but changes in the environment, e.g., pH, could potentially make it available. This could be used to motivate if further treatment is needed to further reduce the content of organotin compounds and extract metals, as well as investigate if the residue needs to be further treated for safe management. For instance, the Fenton, acid, and pH13 treated sediment residues would need to be pH adjusted in an additional treatment step.

- The sustainability assessment methods could be further developed not only to include costs and the environmental impact but also to include social aspects to cover the full sustainability perspective of different management alternatives. This could be done through a comprehensive multi-criteria decision analysis that includes all the dimensions of the concept of sustainable development.

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Appendix 1. Link to the scientific papers.

Paper 1: Norén, A., Karlfeldt Fedje, K., Strömvall, A-M., Rauch, S., and Andersson-Sköld, Y. (2020). Integrated assessment of management strategies for metal-contaminated dredged sediments – What are the best approaches for ports, marinas and waterways?. Science of the Total Environment 716, 135510. doi:10.1016/j.scitotenv.2019.135510

https://www.sciencedirect.com/science/article/pii/S0048969719355044

Paper II: Norén, A., Karlfeldt Fedje, K., Strömvall, A-M., Rauch, S., and Andersson-Sköld, Y. (2021). Low impact leaching agents as remediation media for organotin and metal contaminated sediments. Journal of Environmental Management 282, 111906. doi:10.1016/j.jenvman.2020.111906

https://www.sciencedirect.com/science/article/pii/S0301479720318314

Paper III: Norén, A., Lointier, C., Modin, O., Strömvall, A-M., Rauch, S., Andersson-Sköld, Y., and Karlfeldt Fedje, K. (2022). Removal of organotin compounds and metals from Swedish marine sediment using Fenton's reagent and electrochemical treatment. Environmental Science and Pollution Reserach 29, 27988-28004

https://link.springer.com/article/10.1007/s11356-021-17554-8

Paper IV: Norén, A., Strömvall, A-M., Rauch, S., Andersson-Sköld, Y., Modin, O., and Karlfeldt Fedje, K. Stabilization and solidification of organotin contaminated sediment: Electrolysis pretreatment, leaching, and compression strength (Under review)

Paper V: Svensson, N., Norén, A., Modin, O., Karlfeldt Fedje, K., Rauch, S., Strömvall, A-M., Andersson-Sköld, Y. (2022). Integrated cost and environmental impact assessment of management options for dredged sediment. Waste Management 138, pp 30 – 40.

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