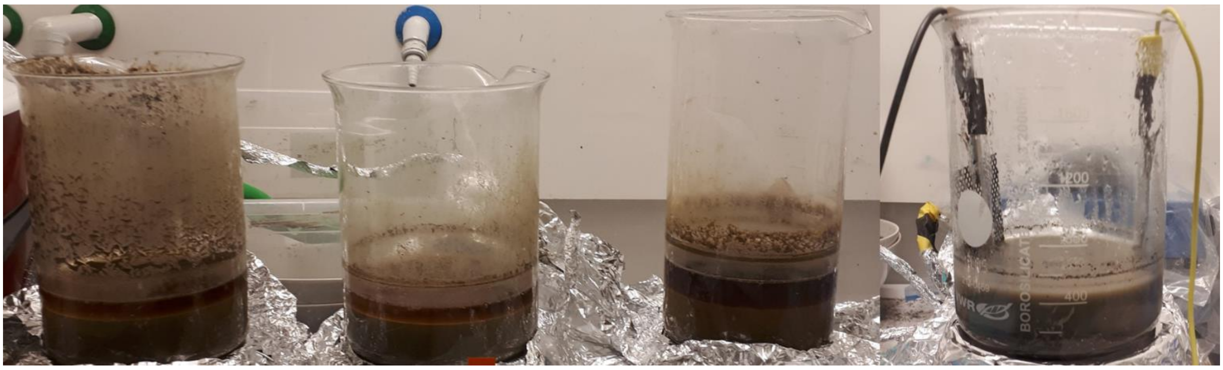

Degradation of Organotin Compounds in Marine Sediment

Master's thesis in Civil Engineering and Water Management

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

Tributyltin (TBT) was the main active compound in anti-fouling paints for 40 years and was spread throughout the environment. TBT is toxic for a wide range of aquatic species at low concentrations in water and sediment. With a long half-life time in anoxic conditions, TBT and its metabolites (i.e. dibutyltin, monobutyltin) remain the main contaminants in sediments from many ports and shipyards. Every three to five years, the Port of Gothenburg dredges sediment which is often contaminated by organotin compounds (OTC). As the regulations become stricter for TBT, there is a need for upgrading the management of the dredged material, which is currently mainly deep-sea disposal and landfilling. The degradation of TBT and its metabolites using classic Fenton's reagent and electrochemical remediation was investigated in this study. Classic Fenton's reagent and electrochemical degradation were performed on a slurry containing dry sediment mixed in Milli-Q water (L/S≈ 6). The experiments were performed on spiked sediments containing 6800-11200 µg/kg OTC and 1700 µg/kg OTC, and on unspiked polluted sediments from Gothenburg port containing 80 µg/kg OTC.

The results using classic Fenton's reagent show a degradation up to 96% of the total OTC on the spiked sediments using [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 15 over 24h for a price of 79 SEK/kg. Tested ratios [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 5 achieved 94% OTC degradation on the spiked sediments containing 1700 µg/kg OTC; 70% OTC degradation on unspiked sediments; but only 14% degradation on the spiked sediments containing 6800-11200 µg/kg OTC. Classic Fenton's reagent would thus be a good method for old sediments but demonstrates its inefficiency on sediments recently polluted with extremely high concentrations. Electrochemical remediation achieved an OTC removal of ~100% on the spiked sediments containing 6800-11200 µg/kg OTC over 24h using Nb/BDD electrode at the anode and titanium at the cathode with a current density was 7 mA/cm². The electricity consumption was 0.092 kWh/kg corresponding to a cost of 4.8 SEK/kg. . On the other hand, the concentrations in the liquid phase was extremely high and the method needs to be further developed to also include a step for degradation OTC in the liquid followed by metal extraction. The spiked sediments post electrochemical remediation could be dumped at a deep-sea storage site without restrictions in 7 out of 8 countries, whereas it may not be possible to dump them after Fenton's degradation. Electrochemical remediation seems to be a possible solution for managing sediment from the port of Gothenburg if the method can be further developed to more effectively degrade the OTC in the liquid phase after the electrolysis

Keywords: remediation, marine sediments, port, organotin, tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), classic Fenton's reagent, electrochemical degradation

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Interreg
North Sea Region
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List of abbreviations

OTC: Organotin compounds
TBT: Tributyltin
TBTO: Tributyltin oxide
TBTCL: Tributyltin chloride
DBT: Dibutyltin
MBT: Monobutyltin
TPT: Triphenyltin
UV: Ultraviolet light
PAHs: Polyaromatic hydrocarbons
TOC: Total organic carbon
LD_{50}: Lethal dose for 50% of the population
PCB: Polychlorinated biphenyl
ICP-MS: Inductively coupled plasma mass spectrometry
BDD: Boron Dopped Diamond
H_2O_2: Hydrogen peroxide

1 Introduction

Tin is a metal widely used in the anti-fouling paint industry: the main active biocide in the anti-fouling paint is tributyltin (TBT), an organic molecule constituted with an atom of tin and three butyl chains (PubChem) and is an extremely toxic molecule (Danish Ministry of the Environment, 2013; EFSA, 2004, Ayanda et al, 2012). Anti-fouling paints aim for avoiding the growth of biofilm and algae on the boat hull (Du et al, 2014). Because of its democratized application on all types of boats, TBT concentration in the seawater and sediments caused death of marine species with high commercial value (Alzieu, 1991), therefore TBT has been banned in Europe in the 80's on the small ships but remained still applied on the large vessels until the European ban in 2003 (EFSA, 2004).

TBT and organotin compounds (OTC) in general are organic molecules with high affinity for organic materials such as sediments (Ayanda et al, 2012). They have a long lifetime in the environment: the degradation under aerobic and UV condition occurs in few days/weeks but its degradation in anaerobic without UV is much longer (Dowson et al, 1996). TBT has been spread throughout the environment by being applied on boats and is remaining highly concentrated in sediments of harbors and shipyard (Ayanda et al, 2012). The main solution nowadays for the contaminated sediments is disposal in deep sea or landfilling but could lead to the pollution of the groundwater (Kotrikla, 2009). The regulations for dumping OTC contaminated sediments become stricter. In order to upgrade the waste management of the sediments, it is necessary to develop cost effective ways to degrade TBT and its degradation products (Du et al, 2014). Nowadays, remediation methods for polluted sediments are developed, e.g. electrochemical remediation, chemical degradation, thermal degradation, UV, photocatalysis. Most of these methods showed to be efficient in laboratory scale but there are barriers for their application: costs of remediation, persistence of TBT added to the extreme specificity of the sediments, time, by-products (Ayanda et al, 2012).

The port of Gothenburg is in the south west of Sweden at the estuarine of the Göta älv river (Figure 1).

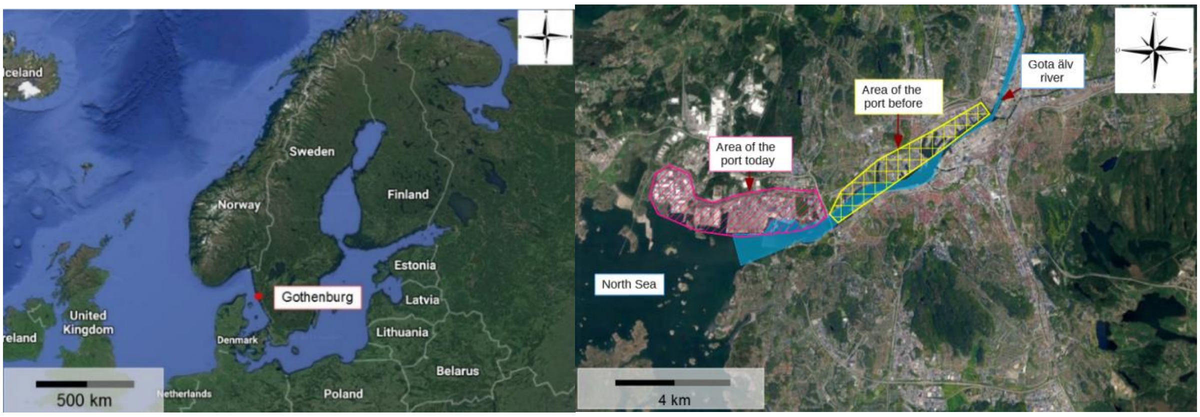


Figure 1. Location of Gothenburg (Source: Google Maps, 2019), to the left and port of Gothenburg (Source: Google Earth, 2018), to the right.

Its history began in 1620. Until the 19th century, the port was relatively small. Throughout the 19th century, it became a major port for the transport of merchandise but also for the emigration. During the 20th century, Gothenburg was a very important port for the import of oil and coal. In 1915, a major shipyard was founded with the development of the company Eriksberg. The shipyard was closed in 1979 (Port of Gothenburg, 2019). In the port, contaminated sediments are dredged during maintenance of the port every three to five years, and one of the main contaminants found in the sediments is TBT.

1.1 Aim & Objectives

The OTC are spread all around the world and mostly concentrated in the sediments from ports and shipyards. Those sediments remain problematic and are a limitation factor for the reusability of the sediments. This work aims to develop a method for the degradation of the organotin present in the marine sediments from the port of Gothenburg. The specific goals are as follows :

- Develop a method for the remediation of OTC in the marine sediments using Fenton’s reagent.
- Develop a method for the remediation of OTC in the marine sediments using electrochemistry.
- Compare the developed treatment techniques for their effectivity to degrade OTC in the sediments.
- Compare the developed treatment techniques for their cost.
- Determine if the remediation reached by the technique is meeting the regulation in Europe for dumping the sediments.

1.2 Research questions

In order to fulfill the objectives of the present work, research questions are formulated.

1. Is it possible to oxidize organotin compounds in the sediments using Fenton’s reagent and electrochemistry?
2. What is the best method to use for the degradation of organotin: Fenton’s reagent or electrochemistry ?
3. How does the degradation vary depending on the concentration of target contaminants ?
4. Are the OTC concentrations after degradation under the limitations for dumping the sediments?

1.3 Limitations

The report will focus on the degradation of TBT from marine sediments with Fenton’s reagent and electrochemical remediation methods.

These methods will only be developed for marine sediments from the port of Gothenburg, and thus not necessarily applicable to other sediments.

2 Theoretical background

This part presents all the theory necessary for understanding the experimental part. At first some generalities about sediments and tin are presented before focusing on what the OTC are, their usage together with the regulations the sediments need to meet, their toxicity and mode of action. Finally, the literature review is separated in two parts: the chemical degradation and the electrochemical degradation.

The shipping became very intense during the 19th century in the port of Gothenburg and has not stopped increasing since then (Port of Gothenburg, 2019). Moreover, its location (Figure 1) between the sea and a major river in Sweden: the Göta älv favors the deposition of sediments in the port leading to the need of dredging operations every three to five years in the port to remain the water depth. The sediments are mainly composed by clay and silt and from the dredged sediments a large part is contaminated, as a result of the current and past activities. The main contaminants of the sediments in this specific port are TBT (tributyltin), PCB (polychlorinated biphenyls) , PAH (polycyclic aromatic hydrocarbons) (Port of Gothenburg, 2019).

Sediment is a solid material that is moved and deposited in a new location. It can consist of rocks, minerals, remains of plants or animals. The marine sediments are represented by the deposit of material on the seafloor. According to Masi (2016) the marine sediments have very specific properties such a low hydraulic permeability, high salinity and a strong acid-neutralizing capacity due to high presence of organic matters and carbonates (Mulligan et al, 2009). But also, marine sediments are very complex with different chemical compositions, different size, resulting in very different matrix depending on the location (Ferrarese & Andreottola, 2008).

2.1 Tin and organotins

Tin is a chemical element with the symbol Sn and atomic number 50. At standard conditions of temperature and pressure, the metallic tin is under solid form. This atom has 8 different oxidation states (Royal Society of Chemistry). Tin is a soft, pliable, silvery-white metal. In the environment, tin is insoluble and thus its level in soil and water is low. The global production of tin exceeds 140 000 tons per year, but its mining is mainly destinated to produce tin organic compounds.

The diagram presented in Figure 2 helps identifying the natural form of metallic tin in the water depending on the pH and the potential. In the field of the water, as the work will be done in this master's thesis, the tin can be under the form of Sn^{2+} at acidic pH. At neutral pH, the metallic tin is mainly under the precipitated form SnO_2. At higher pH, the tin is under the form of $HSnO_2^-$ at low potential or SnO_3^{2-} at higher potential. In the field of the water the metallic tin is never under its metallic form Sn but under precipitated form SnO_2.

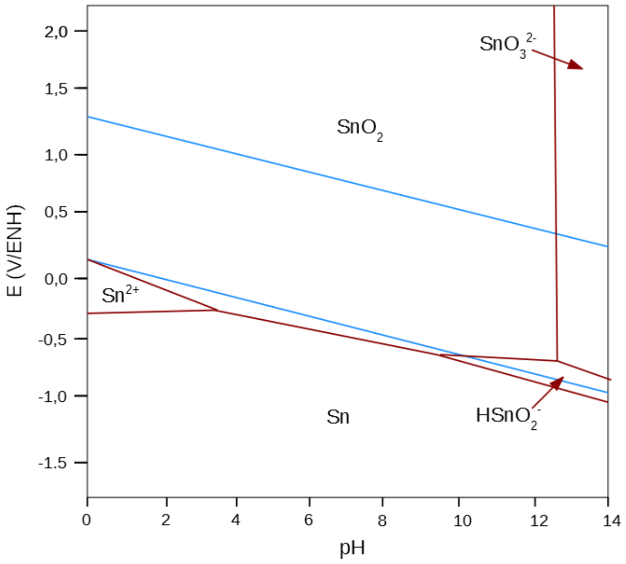
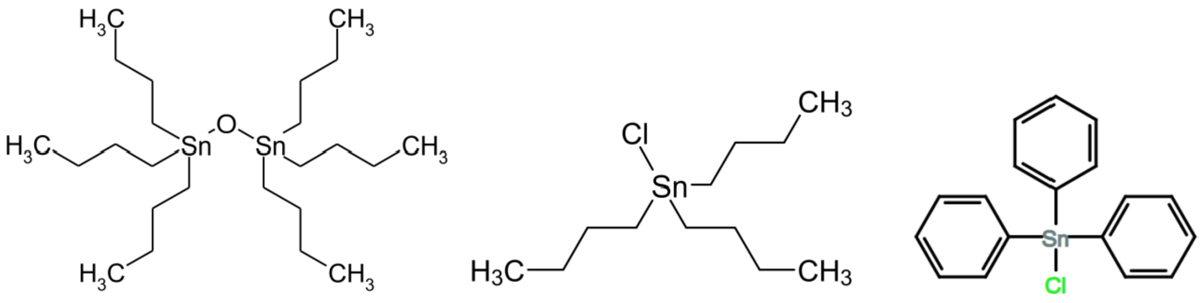


Figure 2. Pourbaix diagram of tin in water

2.1.1 Organotins

Organotins are organic molecules formed with a central tin atom usually strongly bonded to hydrocarbon substituents. There are four groups of organotin compounds, they can contain up to four organic chains and it may be represented by an alkyl chain such as butyl or octyl; or by an aromatic ring such as phenyl. The OTC can contain other chemical groups: inorganics (chloride, oxide) or organics (carboxylate) (KEMI, Swedish Chemical Agency).

The general formula of OTC is $R_xSnL_{(4-x)}$, where R is an organic alkyl or aryl group and L represent one or more organic. Some organotin are presented in Figure 3.



Tributyltin oxide

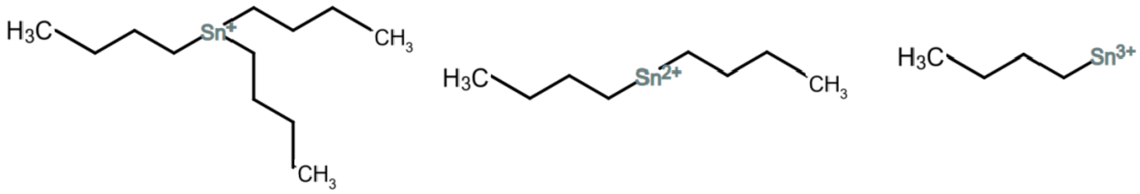
Tributyltin chloride

Triphenyltin chloride

Figure 3. Organotins molecules

TBT is formed by three butyl chain bonded to a tetravalent atom of tin. The general formula is (n-C4H9)3Sn-X where X is an anion e.g. Cl, F, OH, CO3 or a group linked covalently through a heteroatom (Danish Ministry of the Environment, 2013). The most customary representatives of the TBT group are tributyltin oxide (Walmsley, 2006), tributyltin benzoate, tributyltin naphtanate, and tributyltin acetate. In seawater and under normal conditions, TBT exists as three species: hydroxide, chloride, and carbonate remaining in equilibrium (Arevalo & Calmano, 2007). TBT shows biocidal properties towards a wide range of species, and is especially efficient against bacteria, fungi, algae and mollusks (Danish Ministry of the Environment, 2013).

The organotins studied and analysed in this report are the butyl group; tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT). Their structure is presented in Figure 4 below. Note that at the positive charge often there is another atom generally halogenated group such as chloride (Du et al, 2014).



Tributyltin

Dibutylbutyltin

Monobutyltin

Figure 4. Organotin compounds studied

Few physico chemicals properties of TBT, DBT and MBT compounds are presented in the following Table 1.

Table 1. Selected properties of TBT, DBT, MBT

Name	**Tributyltin**	**Dibutyltin**	**Monobutyltin**
Molecular formula	$C_{12}H_{27}Sn$	$C_8H_{18}Sn$	C_4H_9Sn
Molar mass (g/mol)	290.058	232.942	175.826
Log K_{ow}	4.76 - 3.84*	0.97-5.33**	0.41***
Vapor pressure (mm Hg)	<0.01mmHg*	<0.01mmHg**	<0.01mmHg***
Solubility in the water (mg/L	75.8*	320**	high

** Found for tributyltin chloride- tributyltin oxide*

*** Found for dibutyltin dichloride-dibutyltin oxide*

**** Found for monobutyltin trichloride*

The vapor pressure of the OTC is very low for all the compounds studied; it should not easily evaporate into air. The log K_{ow} is the coefficient of partition octanol-water (PubChem). Its value corresponds to the ratio of the concentration of a solute found between octanol and water at a specified temperature. This is an indicator of the hydrophobicity of a compound. For environmental application, it indicates the tendency to be found preferably in the soil, fatty tissue, sediments than in the water. The log K_{ow} is usually inversely related to the water solubility (ChemSafetyPro, Ecetoc). The log Kow is highly related to a high factor of bioconcentration reflecting the accumulation of a chemical compound in fat (Bertelsen et al, 1998).

From Table 1, TBT chloride and oxide have a high log Kow; it is thus likely to find TBT compounds adsorbed onto sediments, or in fatty tissues. Regarding DBT and MBT compounds, log Kow is lower and thus preferably found in the water phase when the substituent is chloride. On the other hand, for DBT oxide, the log Kow is considered as very high and this compound is then found adsorbed to fatty tissue and soils.

According to their chemical properties, OTC preferably adsorb quickly onto the sediments. This process has been studied by Berg et al (2001) and proved to be reversible; the sorption of OTC onto sediments is a fast and reversible process involving primarily particulate organic matter as sorbents. An example of the desorption ability of OTC is during dredging operation of the port, there is disturbance and some fraction of OTC are released in the water column. This process increases the bioavailability of OTC and its ability to enter the food chain.

2.1.2 Usage and regulations of OTC

The OTC were used in many different industries, but the most common was in antifouling paint manufacturing for boats (Ayanda et al, 2012). Antifouling paints have been introduced in the late 1950's and are used to prevent the growth of marine species on the structures. The growth on boat hulls may increase the friction with the water and the weight of the boat resulting by slowing the ship, using more fuel and increasing the maintenance of the ship (Du et al, 2014). In the mid 1990's organotin compounds, such as n-tributyltin (TBT) were the most toxic substances produced in a large scale with annual production of 50 000 ton per year. OTC may be used in textile industry, as pesticides or as plastic stabilizer in food wrapping (Danish Ministry of the Environment, 2013). Due to these usages, the OTC can easily enter the food chain. OTC are mostly lipophilic compounds and the molecules go through the aquatic environment attached to particulate matters. When the particulate settle, the OTC follow and are then accumulated in sediments until benthic animals, such as clams, absorb it. Thereafter, the OTC is part of the food chain and is found in fish and other aquatic species (EFSA, 2004).The usage of TBT was first prohibited on small ships (<25m length) in France in 1982, followed by United Kingdom in 1987. Then most of European and Canada, United States, Australia banned the usage of TBT in smaller ships between 1987 and 1990 (Walmsley, 2006). The European

Union (Regulation 782/2003/EC) requires that the application on ships of organotin compounds which act as biocides in antifouling systems are prohibited as from July 2003 (EFSA, 2004). Furthermore, according to the regulation as well as to a convention developed in IMO (International Maritime Organization, United Nations), from January 2008 ships that bear TBT are not allowed. The TBT should either be removed or enclosed (Danish Ministry of the Environment, 2013).

Different guidelines about the limitation of OTC compounds from different countries are presented in Table 2. The concentrations are presented as µgSn/kg DM. The classification for most of the countries is divided into two to three categories at the exception of Norway who has 5 categories. Norway has the 5 following categories :

- <1 corresponding to the background level,
- 1-5 corresponding to good quality,
- 5-20 corresponding to a moderate level,
- 20-100 corresponding to a bad quality,
- >100 corresponding to a very bad quality.

The 5 categories do not correspond with the categories (Table 2) made for the need of this master's thesis because the dumping is allowed up to 35µg/kg DM, require further studies between 35 and 100µg/kg and the dumping may not be performed above 100µg/kg DM. The classification has thus been rearranged this way (Naturvårdverket, 2009).

Table 2. Limitation of TBT in the dredged material in different countries (Source: Naturvårdverket, 2009)

Country	**Level 1 Safe dumping with no restriction of further studies**	**Level 2 Further ecotoxicological studies required**	**Level 3 Dumping may not be possible**
Belgium	<3	3-7	>7
Denmark	<7	7-200	>200
Finland (TBT+TPhT)	<3	3-200	>200
Holland	<0.007	0.007-250	>250
Ireland (TBT+DBT+MBT)	<100	100-500	>500
Norway	<35	35 - 100	>100
United Kingdom (TBT+DBT+MBT)	<100	100-500	>500
Germany	<20	20-60	>60

Table 2 has been made by Swedish authorities in order to engage a discussion about the appropriate regulations about OTC to apply in the country. For now, no general guidelines for Sweden are established at the exception of the following one presented in Table 3.

Table 3. Swedish guidelines for reuse of OTC *contaminated ground/dredged material (source:* Naturvårdsverket, 2016)

Element (µg Sn/kg DM)	**Sensitive land usage**	**Less sensitive land usage**
OTC	<250	250-500
TBT	<150	150-300

These guidelines are not restrictions and will probably be abandoned in the few upcoming years. Concerning the guidelines on the water, guidelines were found in Canada and Australia/New Zealand. The guidelines are presented in Table 4 below. The guidelines in Australia and New Zealand are expressed in tin. The guideline of TBT in marine water offer according to them a high reliability trigger value considered sufficiently protective to moderately disturbed ecosystems (Australian Government Initiative, 2019).

Table 4. Guidelines for concentrations of *TBT in the marine and freshwater (source: CCME Canadian Council of Ministers, of the Environment and Australian Government Initiative)*

Country	TBT in marine water (ng/L)	TBT in freshwater (ng/L)
Canada	1	8
Australia & New Zealand	6 expressed as [Sn]	2 expressed as [Sn]

2.1.3 Toxicity of OTC

In the environment, the biotoxicity of the OTC was first showed in France leading to the ban of TBT in anti-fouling paint for smaller vessels. It occurred in the Arcachon Basin, France between 1975 and 1982. In this area, located in Gironde, the commerce of oyster is source of tourism and commerce activities and thus a crucial economic resource for the inhabitants since the 18th century (Alzieu, 1991). In the years 1970's, the boat traffic became very important with the tourism increase and about 15 000 boats were counted between July and August. In the meantime, the oyster's population was severely damaged because of calcification shell problems and no reproduction (Alzieu, 1991). Similar consequences on oysters were identified in UK (Walmsley, 2006). Consequently, researchers started to measure concentrations of TBT in water and sediments of the bay. OTC and especially TBT from anti-fouling paint was deposited in high concentration in the sediments and water column and caused damage on the oyster population (Alzieu et al, 1981). Indeed, a concentration of tributyltin fluoride of 0.5µg/L results to 100% mortality of the oyster after 35 days (Alzieu et al, 1981), and show inhibition of the fecundation at a concentration of 100µg/L for Crassostrea gigas oyster larvae, but also at 10µg/L the cleavage of 20% of the eggs is affected and the larval development is inhibited at 1µg/L and already affected at 0.1µg/L (His et al, 1980). There are as well cases of deformities and sexual organs deformities caused by the masculinization, also called imposex on marine snails and whelks (Arevalo & Calmano, 2007; Evans et al, 2000). TBT and Triphenyltin (TPT) cause masculinization in female snails and fish at low concentration (1ng/L). This phenomenon suggest TBT is an endocrine disruptor (EFSA, 2004). This level of toxicity varies from an OTC to another, and for bis-tributyltin oxide the toxicity level on fish and mussel is 1µg/L or less (U'Ren, 1983).

Afterwards toxicity researches have been done on the TBT and other OTC. For a single dose, the oral LD_{50} for TBTO (tributyltin oxide, $(C_4H_9)_6 2Sn\text{-}O$) adsorbed by rat was found to be 94–234mg/kg. With other cation the same order of magnitude was found. For mice, LD_{50} was 44–230mg/kg for TBTO. LD_{50} for DBT was 100mg/kg and DBTO 520mg/kg for the male rat. In the mice LD_{50} was 25 and 24mg/kg. Different intakes of TBTO to rats showed on a 4 weeks lifetime a reduction in the body weight and lower food consumption, weakness, emaciation, roughened fur, but no mortality after one week in the group fed by 16mg/kg/day. Decrease in white blood cell (lymphocytes), serum glucose, liver glycogen, hemoglobin, weight of brain, heart, liver, spleen were reported. Another study on 6 weeks oral intake on the same species of rat showed a decrease of thyroid activity, and serum insulin. TBTO caused no significant genotoxicity; the carcinogenicity could not be determined, neither neurotoxicity but it showed immunotoxicity; TBT has an influence on reproduction. TBT and with less evidence DBT and TPT may disrupt sex steroid metabolism by affecting both androgen activation and synthesis of estrogens. In the rat, it is stored in the liver and kidney. A rat mother at day 18 of pregnancy had a single oral dose of TBT and the concentration in the fetal tissues is like the concentration in the mother tissue leading to the conclusion that TBT can cross the placenta. In the rabbit, the transfer of TBT in the brain had occurred.

Intakes of DBT showed nonspecific effects: reduced body weight, changes in various biochemical and hematological parameters. Affect the liver and bile. For DBT, the carcinogenicity could not be determined; but the test was positive on the Chinese hamster ovary cell. DBT caused mutation in the ovary, revealing to be genotoxic. DBT is also immunotoxic, present teratogenicity and embryotoxicity and induce a maternal toxicity.

It has been established that the toxicity of OTC is the highest for TBT. Therefore, eco-toxicity increases dramatically in the order MBT < DBT < TBT (Ayanda et al, 2012).

Concerning the bioaccumulation, TBTO as a high coefficient octanol-water partition (log k_{ow}=3.84, Table 1). The bioaccumulation occurs then in the aquatic organism prior to water. The bioconcentration factor vary depending on the species. It can be up to 7000 in mollusks and fish from laboratory experiments whereas values up to 30 000 were reported in field investigations. There is on the contrary no indication of biomagnification of TBT throughout the marine environment (Danish Ministry of the Environment, 2013).

The adverse effects showed previously and the capacity of OTC to accumulate in the sediments and fatty tissues cause concern for the human, animal and environmental health. The toxicity of OTC has been assessed in many studies, and synthesis of all relevant studies have been realized in reports made by EFSA in 2004 and the Danish Ministry of the Environment in 2013. It has been found that the main contaminations sources for humans come from the food consumption, the ingestion of contaminated sediments, the dermal absorption and the inhalation. . The calculated concentration of OTC in seafood were generally higher than in fish. Samples of seafood purchased from markets in different countries showed concentration from 4.6 to 40 µg/kg. In mussels from Denmark the concentration ranges from 0.5 to 60 µg Sn/kg (1.2-146 µgTBT/kg). In fish in general the concentration is low. From these findings, the human food may contain TBT residues and especially seafood. The TBT uptake from food ranged from 0.8 to 2.6 µg/day/person. Intake of TBT via inhalation is possible.

The human liver microsome may metabolize the TBT because DBT is the form detected while TBT is not. The results have shown a total butyltin concentration in the liver of 10.7µg/kg from Danes, 59-96µg/kg from Japanese, and 2.4–-11 µg/kg from Polish. Moreover, the total butyltin concentration was measured in the human blood between 0.17 µg/L and 0.67 µg/L in Germans and ranging from not detected to 101 µg/l for total butyltin in Americans. The storage of butyltin had been found to be in the liver and in the blood.

2.1.4 Mode of action

As a biocide, TBT is efficient against a wide range of species because it is an inhibitor of the oxidative phosphorylation (Alzieu et al 1981). The Danish Ministry of the Environment (2013) and EFSA (2004) described the mode of action shared by OTC.Various OTC seem to share the mechanism of interruption of chemical energy supply for neurons. Trimethyltin, triethyltin and triphenyltin were shown to decouple oxidative phosphorylation and inhibit mitochondrial ATPase. High concentration of OTC induces necrosis via inhibition of important mitochondrial functions: ATP synthesis and collapse of ion gradients at the plasma membrane. The breakdown of ion gradients is responsible for the irreversible swelling of the cytoplasm and its organelles. The cell then disintegrates and release its constituent inducing an inflammation of the surrounding tissue. OTC is responsible for the generation of an increase in intracellular Ca^{2+} concentration cause mitochondrial dysfunction and binding of TBT to extrinsic “death receptor” and induced apoptotic cell death but the results in vivo do not reflect the effect obtained in vitro with TBT and TPT (The Danish Ministry of the Environment, 2013; EFSA, 2004).Calcium concentration is very low in resting cells, but with a TBT contact the concentration of Ca^{2+} increase. It may be the result of the opening of various calcium channel in the plasma membrane or the release of the storage. Mitochondria are sensitive to exposure to organotin because TBT inhibits substrate uptake by the mitochondria and inhibits the ATP synthesis, alter ions transport across membranes. The mitochondria signal the presence of TBT by releasing small apoptotic proteins (cytochrome c). The two intrinsic apoptic signaling (increase in calcium and release of cytochrome c) induce the formation of reactive oxygen able to fragmentate the DNA. TBT induce as well apoptic signal pathway in human T and B-lymphocytes involving activation of so-called death receptors.

2.1.5 Summary

In order to summarize the information collected on fate in the environment of TBT, the following conceptual scheme is presented in Figure 5. This scheme is not extensive and should only be considered as a tool for the understanding of the distribution of metabolites of TBT in the environment.

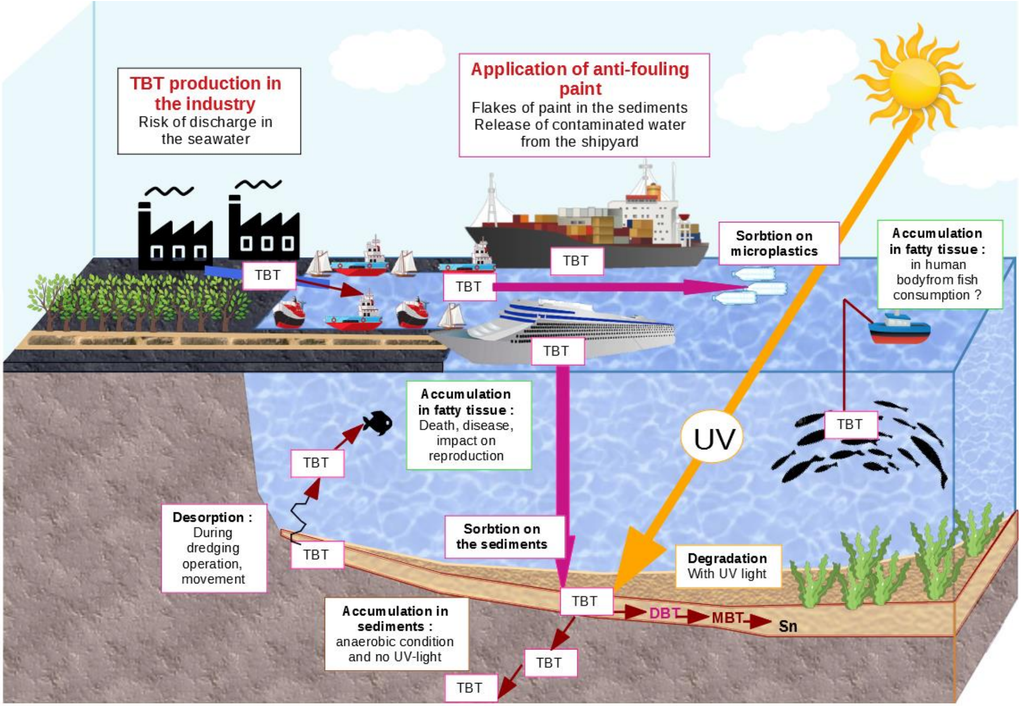


Figure 5. Conceptual scheme of TBT behavior in the environment

2.2 Treatment techniques for OTC

The degradation of OTC in polluted ecosystems is a function of different processes:

- Physical process by sorption in sediments.
- Chemical and photochemical degradation are the fastest process.
- Biological mechanisms occur more efficiently in the water column.

The degradation mechanisms are possible by biotic and abiotic processes and was showed by Gadd (2000) following the reaction below.

$$R_4SnX \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$$

Hoch et al (2003) showed marine bivalves can accumulate much more OTC because of an efficient enzymatic degradation mechanism. Dowson et al (1996) found that in aerobic conditions TBT half-life ranges from one to three years. Under anaerobic conditions, the half-life of TBT could not be determined by the authors and appeared to be in the order of ten years.

Different processes of remediation of OTC were investigated in the past few years such as chemical degradation, thermal degradation, electrochemical degradation, biological degradation. In this report, the focus is about chemical degradation and electrochemical remediation of the organotin in the marine sediments since the thermal remediation might be too costly for a full-scale process, and the biological degradation too slow (Ayanda et al, 2012).

At the exception of Brosillon et al (2016) and according to the present knowledges no article reports the degradation of OTC using Fenton's reagent. In addition, Brosillon et al (2016) do not report a precise degradation method for the OTC contaminated sediments. In order to have further knowledges about this process and its experimental conditions, articles about the degradation using classical Fenton's reagent on other refractory organic compounds (PAHs, pharmaceuticals, synthetic dyes) are used.

2.2.1 Chemical degradation

The oxidation with permanganate potassium of the OTC could be possible and is due to the high oxidation potential of the manganese ion (Yan & Schwartz, 1999). Beuselinck et al (2008) oxidized TBT in water with potassium permanganate in pilot-scale. The results showed the removal rates were superior to 96%. The most cost-effective results for butyl-tins were obtained using a 15% potassium permanganate solution, with a removal rate of TBT and DBT around 90%. With this method, the degradation of TBT is more favorable than for another OTC. This method seemed to not be adapted to the degradation of TBT adsorbed onto the sediments, therefore the research where more focused-on Fenton's reagent.

Fenton's reagent is an oxidative mixture created by the contact between hydrogen peroxide and ferric iron (Fe^{2+}), leading to the generation of one of the most powerful oxidants known (E =2.73 V) (Pignatello et al, 2006). Iron is a catalyst of the decomposition of hydrogen peroxide. While decomposing, hydrogen peroxide generates hydroxyl radicals: a powerful compound able to react with stable reactive compounds. Fenton's reagent is an "advanced oxidation processes" (AOP). These processes are based on the generation of reactive species such as hydroxyl radicals $OH^{\cdot}$, able to react with a large panel of organic compounds. Other processes classified as AOP are for example ozonation, ultrasounds and UV (Benatti et al, 2006). Fenton's reagent was discovered in 1894 by Fenton when a low concentration of iron and hydrogen peroxide was in contact with tartaric acid resulting to the formation of dihydroxy maleic acid (Fenton, 1894).

The Fenton's reagent has been commonly used since the 1960's for the degradation of the organic compounds in wastewater and industrial water. Therefore, it was used for thickening the sludge, more recently for the degradation of PAHs, pharmaceutical effluents or other refractory organic compounds present in industrial effluent in large concentrations (Neyens et al, 2003; Kuo, 1992, Solozhenko et al, 1995, Tekin et al, 2006; Martins et al, 2010). In the ideal case the Fenton's reagent achieve a complete destruction of contaminants to harmless compounds: CO_2, water and inorganic salts (Neyens et al, 2003). Fenton's reagent is often described as safe, inexpensive and environmentally friendly but of course it depends on the concentration and quantity of reactant used. One disadvantage of Fenton is the production of sludge (Pignatello et al, 2006). Iron precipitation occurs at pH higher than 4.0 and leads to obstruction of the activation processes (Usman et al, 2016). The Fenton's reagent results from the catalytic decomposition of the hydrogen peroxide by ferrous iron. The mechanism was first described first by Haber and Weiss in 1934 as follow.

(1) $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$
(2) $RH + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$
(3) $R^{\cdot} + Fe^{3+} \rightarrow R^+ + Fe^{2+}$
(4) $Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^-$

The first reaction (1) shows the catalytic decomposition of hydrogen peroxide with iron, and the generation of hydroxyl ions, hydroxyl radical and ferric iron. The second reaction (2) shows the reaction between the organic matter and the hydroxyl radical producing an organic radical. This last compound can further react with ferric iron and reduce it in ferrous iron (3). The ferrous iron is thus reused for the catalytic decomposition of hydrogen peroxide or interfere with the hydroxyl radical produced by reacting with it resulting in the termination of the chain reaction. (4) Occurs when the concentration of Fe^{2+} is too high compare to the hydrogen peroxide, the production of hydroxyl radical is minimized, and the chain reaction ends faster (Neyens et al, 2003).

Nevertheless, the mechanism described by Haber-Weiss is not complete, and other mechanism was proposed including the generation of hydroxyl radicals but also other reactions. They described the reaction occurring in what is called today the classical Fenton's reagent. The complete mechanism of Fenton's reaction is presented in the equations below (Pignatello et al, 2006).

(1) $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH^{\cdot}$
(2) $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+}$
(3) $OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$
(4) $OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$
(5) $Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2H^{+}$
(6) $Fe^{2+} + HO_2^{\cdot} + H^{+} \rightarrow Fe^{3+} + H_2O_2$
(7) $HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$

Certain compounds can interfere with one or more of the reactions leading to a lower rate of degradation or stop completing the reaction. Those compounds are for instance phosphate, sulfate, organo-sulfonate, fluoride, bromide, and chloride ions. The interference generated depends on the concentration of each species in the solution. Sulfate are present in seawater in high concentration, thus in the marine sediments and could interfere with the Fenton reaction (Pignatello et al, 2006).

2.2.1.1 *Fenton's reagent for the degradation of pollutants in soils*

For remediation of polluted areas, Fenton oxidation is mostly used for treatment of polluted groundwater i.e. in-situ chemical oxidation (Chen et al, 2001; Neyens et al, 2003; Asghar et al, 2015). Concerning soils or sediments few articles are available on the degradation of organic compounds by application of Fenton's reagent. Brosillon et al (2016) investigated for the first time according to the current knowledge, the photo-oxidation of TBT, DBT and MBT in marine sediments. The investigations focused on the photocatalytic and photo-Fenton degradation of OTC in the sediments. They also compared the efficiency of these new technologies to the efficiency of a classic Fenton's degradation. The experiments were carried out on certified marine sediments and their concentration is presented in Table 5.

Table 5. Concentration of OTC in the the certified marine sediments (source: Brosillon et al, 2016)

Compound	**TBT**	**DBT**	**MBT**	**Total OTC**
Concentration (µg(Sn)/kg)	832	1100	700	2632
%degradation using Fenton's reagent	81	68	30	60

The experiments of photo-Fenton and Fenton were carried at a pH of 3. Important to highlight is TOC (total organic carbon) concentrations in the sediments: the hydroxyl radicals will react with all organic matters present in the sample depending on their availability (Neyens et al, 2003). The TOC in these sediments was 3.3%. The results for classic Fenton's oxidation process show a degradation after 1h of reaction for MBT, DBT and TBT of respectively 30, 68 and 81%. For the total butyltin, the photocatalysis is less efficient than photo-Fenton but still more efficient than classic Fenton (Brosillon et al, 2016).

Brosillon et al (2016), is the only available article on Fenton's oxidation of OTC. The following articles target the degradation of polycyclic aromatic hydrocarbons (PAHs) in soils. PAHs, as well as OTC, are organic compounds very stable and persistent in the environment. PAHs are composed with 2 or more fused benzene rings and are mainly produced by the combustion of fossil fuel (Kawahara et al, 1995).

A pioneer in the Fenton's degradation of PAHs in soil was Kawahara et al in 1995. They investigated the treatment of soil from a wood-treating site in Ohio polluted with creosote. The aim of the experiment was to study the PAHs release from the soil. For the degradation experiment a slurry was formed with 10g of dry soil and 30mL of water. The slurry was treated with Fenton's reagent with a ratio between iron and hydrogen peroxide of $1.5x10^5$. The experiments were carried in the dark at 25°C. The addition of the Fenton's reagent was done adding 20 mL of both hydrogen peroxide and iron sulfate via a peristaltic pump during 30 min. The reaction was carried without pH adjustment on a soil with a pH of 7. The results showed the decrease of the concentration of PAHs contained in the soil and the increase of the 12PAHs extractability by 13 to 56% after 1hour of reaction. The study made by Kawahara et al (1995), show it is possible to improve the extractability of PAHs from soils by applying Fenton.

The research aim in the framework of this master's thesis is much more corresponding to the aim of Watts et al (2002) and Flotron et al (2005) : the mineralization of sorbed PAHs. Watts et al (2002) studied the mineralization of Benzo[a]pyrene (BaP), a hydrophobic and toxic PAH. Two soils were used in order to compare the effect of the matrix on the efficiency of the reaction. The oxidation experiments were carried with 5 g of silica sand or Palouse loess spiked with 0.1 mmol/kg C-BaP. The pH of the slurry was adjusted to 3 and the reaction time was 24h. At the optimum condition, there was 59% mineralization of C-BaP. Finally, Flotron et al, 2005 compared the removal of sorbed PAHs from three different types of samples: soil, sludge and sediment for three PAHs: fluoranthene, benzo[b]fluoranthene and benzo[a]pyrene. All have a low solubility in the water and a high log of K_{ow}; like the OTC investigated in this master's thesis. The experiments were carried at the natural pH of the soils, at room temperature for 24h in the dark to avoid photolytic reaction. The suspension was prepared with 2g of the sample and 10mL of water. The chemical characteristics of the samples are presented in Table 6.

Table 6. Concentration of different chemical compounds in the samples (Flotron et al, 2005)

Parameters	**Sludge**	**Soil**	**Sediment**
pH	8.8	7.1	4.4
Fluoranthene (mg/kg)	1.20	0.107	0.017
Benzo[b]fluoranthene (mg/kg)	0.43	0.064	0.123
Benzo[a]pyrene (mg/kg)	0.31	0.051	0.003
TOC (%)	36.1	3.0	10.4
Iron (g/kg)	94	n.d	30

The degradation of native sorbed PAHs is efficient on the sludge sample but the native PAHs removal on the 2 other matrix is inefficient. In the sediment sample only one of the PAHs could be removed , in the soil sample any was oxidized. The results of the degradation are presented in Table 7.

Table 7. Removal rate of the PAHs (Flotron et al, 2005)

Sample	**Sludge (native-spiked)**	**Soil (native-spiked)**	**Sediment (native-spiked)**
Fluoranthene removal (%)	46.2-38.0	9.7-97.8	0.0-85.7
Benzo[b]fluoranthene removal (%)	36.2-42.0	85.0-97.6	8.0-87.4
Benzo[a]pyrene removal (%)	48.1-67.0	16.9-99.1	0.0-88.6

The partial degradation of the natural PAHs in the sludge sample is explained by insufficient concentration of hydroxyl radical or by the inhibition of PAH oxidation caused by the presence of organic matters. Moreover, the non-degradation of the PAHs contained in the soil sample can be explained by an interesting finding. When the organic content of a soil is inferior to 5% the contaminants are mainly adsorbed into the micropores, and less available than when they are adsorbed onto the organic matter (Bogan and Trbovic, 2003). It is clear in that case that the removal of the spiked sediments is much easier when the samples are spiked because of the availability of the contaminants. Nam et al (2001) reported as well this phenomenon.

2.2.1.2 *Fenton's reagent for the degradation of pollutants in the water*

In the present study, the degradation of OTC using Fenton's reagent does not target the removal on the water media but onto the sediments. Since several studies have been done using Fenton's reagent in water, it is still important to investigate the results obtained from those studies.

Many investigations have been conducted on the degradation and decolorization of dyes. Kuo, in 1992 published his work on the decolorization of wastewater containing 0.3 g/L of dye using Fenton's reagent. Different pH were tested and the best value for decolorization was reached for a pH below 3.5. Also, the removal rate of the chemical oxygen demand (COD) was about 90%. The ratio H_2O_2:Fe^{2+} studied varied from 4 to 11. Solozhenko et al (1995) studied as well, the decolorization of Azodye using Fenton's reagent. They reached a decolorization rate of 95-97% with a ratio H_2O_2:Fe^{2+} was 5. They found during the experiments that the decolorization rate is intensified by the exposition to solar radiation or by increasing the temperature. Later, Meriç et al in 2004 investigated the color and COD removal of the Black 5 dye from the wastewater. The best results for 84% COD removal were obtained with 200 mg/L of Black 5 in the wastewater and a ratio H_2O_2:Fe^{2+} equal to 20. The optimum pH found was 3.0 and the optimum temperature: 40°C. The degradation of dye was investigated by Rodrigues et al (2009). This experiment is different from the other because the authors are combining the chemical degradation in order to enhance the biodegradability of the effluent for finally submitting it to a biological degradation. They worked at a pH of 3.5, with an initial DOC of 140–161 mg C/L and a BOD5 of 239–247mg O_2/L. They reached a DOC reduction of 58.3% removal after 120 min at 73.6°C and the ratio H_2O_2:Fe^{2+} giving the best removal of DOC was 33.

Improvement of wastewater biodegradability is also one of the main applications of Fenton's reagent. Tekin et al (2006) improved the biodegradability of pharmaceutical wastewater. This type of effluent contains high proportion of refractory organic compounds and led to the removal rate of DOC of 45 - 65%. A first test was conducted for the adjustment of the ratio between H_2O_2 and the concentration of organic compounds to degrade, with a concentration of Fe^{2+} kept constant. Then the concentration of H_2O_2 was kept constant and the ratio of Fe^{2+} was adjusted. The best efficiency was achieved with an optimum ratio between H_2O_2 and iron of 150 and 250. A higher efficiency was reached, with a COD removal of 98% when Fenton's oxidation was coupled with aerobic degradation in sequencing batch reactor. Still on the same topic, Martins et al (2010) studied the oxidation of phenolic wastewater for a biodegradability enhancement with a ratio H_2O_2:Fe^{2+} of 30. Hydrogen peroxide was injected in small aliquots each 30min during 6h because it leads to a quick conversion in hydroxyl radicals. Finally, Gotvajn et al (2011) investigated the treatment of municipal landfill leachate with Fenton's reaction. The concentrations which gave the bests degradation results were 4 M for H_2O_2 and 0.3 M for Fe^{2+}, with a temperature of 40°C. 60 to 80% of DOC was removed thanks to Fenton's oxidation process and the treated effluent was more bio treatable, probably because the persistent organics compounds were degraded in smaller biodegradable compounds available then for microorganisms.

Tang & Huang in 1997 investigated the stoichiometry of Fenton's reagent for the oxidation of chlorinated aliphatic organic pollutants. They found optimum ratio between iron and hydrogen peroxide varying between 5 and 11. They based their experiments on the calculation of a theorical ratio for the degradation of organic compounds of 11. However, the studies indicate a ratio very different depending on the molecule to oxidized. The experiments were conducted at room temperature and the addition of hydrogen peroxide was done in aliquots. Finally, the optimal ratio H_2O_2:$Fe^{2+}$for the degradation was 5 and optimal pH 3.5. They concluded the quantity of H_2O_2 to introduce depend on the concentration of the molecule of interest to oxidize. Finally, Benatti et al (2006) were optimizing the Fenton's oxidation on the wastewater from chemical laboratory in order to destroy toxic organic compounds by the help of the response surface methodology. The maximum COD removal was 92.3% on wastewater at pH equal to 4 with ratios [COD]:[H_2O_2]=1:9 and [H_2O_2]:[Fe^{2+}]=4.5:1.

2.2.1.3 *Comparison of the methods used for Fenton's reagent*

All Fenton's degradations are carried at pH between 3.0 and 3.5. In fact, the reaction (1), is independent of the pH below pH 3.

(1) $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\cdot$

On the contrary, at a pH value above 3 the reaction become dependent because of the formation of $Fe(OH)_2$ much faster than the formation of Fe^{2+} (Pignatello et al, 2006).

Some experiments using Fenton's reagent on solid samples are done using natural pH, sometimes the buffering capacity is too high resulting in a high consumption of concentrated acid to reach the range of pH 3.0 to 3.5. Flotron et al (2005) achieved the degradation rate of 38.0 to 99.1% for PAHs spiked solid samples at pH of 8.8, 7.1 and 4.4. This experiment might require more iron than necessary because of the formation of $Fe(OH)_2$. At natural pH, another option taken by Tian et al (2011) is the protection of iron from precipitation by trapping it into a solid by using the heterogenous catalysis of decomposition of hydrogen peroxide. Iron molybdate was used for the degradation of a dye at a pH of 6.7, the degradation rate of the dye was 94.1% after 1h reaction. This experiment was led on an aqueous media, meaning that the pollutants were much more accessible than when they are sorbed onto sediments.

Most of the studies agree on the positive effect of the temperature for Fenton's oxidation process: higher the temperature is, the better is the degradation. On the other hand, heating is not industrially sustainable in the framework of this project since the polluted sediments are located in Sweden, it will by consequence consume too much energy. In order to get reproductible results, all the authors agreed the experiments should be carried out in the dark; meaning that all agree that UV light greatly affect the Fenton's reaction. According to Ayanda et al (2012), Haug et al used the hydrogen peroxide as a photocatalyst of TBT in wastewater. Enough strong UV source coupled with the adding of 300 ppm of H_2O_2 resulted in the degradation below 100 ng/L within 2 min of treatment. Brosillon et al (2016) studied the degradation of TBT, DBT, and MBT with photo-Fenton reaction. They used Fenton's reagent coupled with a UV lamp (Lambda max = 365nm). They demonstrated the energy provided by the UV lamp (339 kJ/mol) is enough to break the bond between the tin and the butyl chain. The dissociation energy of the bond Sn-C is around 190-220 kJ/mol. The TBT degradation with photo-Fenton about 99.8% was achieved after 7 min of reaction, 30 min for photocatalysis with TiO_2.

Some parameters are condensed in the Table 8 in order to give an overview on the previous work done with the Fenton reagent. Moreover, Table 8 is used for the elaboration of the degradation protocol in the Methodology part (3.2.1).

Table 8. Summary of the experiment parameters for Fenton's degradation found in the literature

Compound of interest	**Concentration (mol/L)**	**$[H_2O_2]$ (mol/L)**	**$[Fe^{2+}]$ (mol/L)**	**Ratio H_2O_2:Fe^{2+}**	**Ratio H_2O_2:C**	**T° (°C)**	**Name**
Soil							
PAHs	TOC: 3, 10.4 and 30%.	4.90	0.01	490	/	Room	*Flotron et al, 2005*
PAHs	n.m	8.84	5.9x10-5	$1.5x10^{5}$	/	25	*Kawahara et al, 1995*
PAHs	3722 mg/kg	3.00	0.18	17	/	20 – 45	*Watts et al, 2002*
OTC ***TOC***	1.375 µg/kg 2.5mol/kg	0.01	$7.27x10^{-4}$	14	/	Room	*Brosillon et al, 2016*
Water							
Leachate (TOC)	0.028	4.00	0.30	13	142	40	*Gotvajn et al, 2011*
Azodye	40mg/L	$5x10^{-4}$	$9.2x10^{-5}$	5	/	25	*Solozhenko 1995*
Dye: Back 5	2x10-4	0.03	$1.5x10^{-3}$	20	150	40	*Meriç et al, 2004*
Phenolic acid (TOC)	0.031	0.488	$16x10^{-3}$	30	16	Room	*Martins et al, 2010*
Dye (DOC)	0.013	0.206	$6.30x10^{-3}$	33	16	73.6	*Rodrigues et al, 2009*
Pharmaceutical Compounds (COD)	900-7000 mg O_2/L	2.5-5	0.01	150-250	/	50	*Tekin et al, 2006*
Organics	n.m	n.m	n.m	4.5	9	Room	*Benatti et al, 2006*
Chlorinated aliphatics	n.m	n.m	n.m	11	/	Room	*Tang et al, 1997*
Dye	0.3g/L	8.6x10-3 – 0.026	$2.2x10^{-3}$- $4.41x10^{-3}$	4-11	/	50	*Kuo et al, 1992*

Other parameters similar in each experiment is the duration of the reaction mainly carried for 24h in the case of the degradation of pollutants sorbed onto solid matrix (Table 8). Moreover, the research on the degradation of pollutants in wastewater permit to predict that the hydrogen peroxide concentration needs to be much higher than the concentration of organic pollutants in the water, including TOC. A similar observation is made for the ratio between hydrogen peroxide and iron: hydrogen peroxide concentration needs to be higher than iron (Table 8).

Nevertheless, the ratios used in the different articles are all very different (Table 8). Regarding the H_2O_2:organics ratio, it could not be determined on the soil investigations because of the lack of information but could be determined in the literature research on aqueous media. The ratios vary from 9 (Benatti etal., 2006) to 150 (Meriç et al, 2004). For H_2O_2:Fe^{2+} the ratio is varying from 4 (Kuo et al, 1992; Benatti et al, 2006) to 490 (Kawahara et al, 1995). These different studies demonstrate the ratio of H_2O_2:organics and H_2O_2:Fe^{2+} depend on the compound to degrade and the aim of the study. Since the ratios are varying depending on the compounds to degrade it is necessary to proceed as Tekin et al (2006) did in their study. Moreover, even if the OTC are not completely degraded at the end of the experiments it is still possible to use this method for improving the biodegradability of OTC in the sediments such as Martins et al (2010), Gotvajn et al (2011) and Tekin et al (2006) described.

Other important information was available for the interpretation of the results. Flotron et al (2005) highlighted in their research work that it seems more likely to degrade highly contaminated samples with the help of Fenton's reagent compared to low concentration matrix. This finding is particularly interesting for the degradation of OTC in the sediments. The remediation technique is investigated for spiked sediments. The contaminant concentration is major compared to organic matters present in the sample. In this specific case, the contaminant is available to hydroxyl radicals; whereas the degradation on the original sediments may be trickier because of the low concentration of pollutants. Although, because of the low concentration of organic matter in the sediments studied during the master's thesis (TOC=3%) the contaminants may then be adsorbed into the micropores of the sediments.

2.2.2 Electrochemical degradation

The theory behind electrochemistry had been developed since 19th century by famous scientists: Quike (1861), Helmholtz (1879), Nernst (1888), Planck (1890) and Warburg (1899) (Ferrarese & Andreottola, 2008). Electrochemistry finds a lot of applications in many fields, with for instance energy storage and conversion, water treatment, metallurgy. This method has shown its special capacity to desorb and degrade the chemical pollutants from low porosity geological material such as marine sediments (Ferrarese & Andreottola, 2008).

2.2.2.1 *General*

Different transports are implied in electrochemistry. At the anode because of the oxidation reaction, H^+ is created and at the cathode, OH^- is generated. The difference in pH between the two electrodes generate a gradient, leading to a displacement (Ferrarese & Andreottola, 2008). There are three mechanisms governing the reactions in electrochemical remediation: electroosmosis, electro-mitigation and electrophoresis. The second, electro-mitigation is the transport of ions to the electrode of the opposite charge (Benamard & Barraud, 2011). The electrophoresis is the transport of charged particles or colloids under the influence of the electric field governed by Lorentz force: the cations, mostly represented by metals, move towards the cathode while the anions move towards the anode. The electroosmosis correspond to the bulk transport of the water or soil moisture, it is how the water flow though the soil because of the applied electric current from the anode to the cathode and the water arise in the cathode compartment (Benamard & Barraud, 2011; Ferrarese & Andreottola, 2008).

The electrolysis principle is based on the electric current circulation in a material by application of electricity at the anode, conduction and circulation to the cathode. The circulation of the current induces redox reactions because of the potential difference between the two electrodes. In aqueous liquid it provokes the dissociation or oxidation of the water at the anode while reduction of the water occurs at the cathode creating hydrogen ions at the anode and hydroxyl ions at the cathode presented in Equation 1 and 2 (Reddy & Cameselle, 2009; Stichnothe et al, 2005).

(1) At the anode: $2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ E0= -1.229 V (oxidation)
(2) At the cathode: $4H2O + 4e- \rightarrow 2H2(g) + 4OH-(aq)$ E0= -0.828 V (reduction)

In the case of BDD electrode, the decomposition of the water at the anode is orientated to form hydroxyl radical species instead of oxygen according to the Equation 3 (Muruganathan et al, 2008).

(3) At the anode : $BDD + H_2O \rightarrow BDD(°OH) + H^+ + e^-$ (oxidation)

Marine sediments contain high concentrations of chloride. When the electrochemistry principle is applied to marine sediments, the chloride ions are oxidized at the anode and forms hypochlorite and chlorine (Equation 4 and 5) (Muruganathan et al, 2008).

(4) At the anode : $2 Cl^- \rightarrow Cl_2 + 2e^-$ (oxidation)
(5) At the anode : $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$ (oxidation)

Chlorine and hypochlorite are formed by the oxidation of chloride, whereas oxygen is formed during the water decomposition at the anode (Equations 1,3,4,5). At the cathode, hydrogen is created (Equation 2). All these species may react with the OTC present in the solution according to the Equation 6 and 7. (Stichnothe et al, 2005)

(6) At the anode : $2(C_4H_9)_3Sn^+ + 3OCl^- + 2O_2 + 3H_2O \rightarrow 2SnO_2 + 6C_4H_9OH + 3Cl^-$ (oxidation)
(7) At the cathode : $(C_4H_9)_3Sn^+ + 4Cl^- + H_2 \rightarrow SnCl_2 + 3C_4H_{10} + 2HCl$ (reduction)

The compounds formed can interact with organic matters and degrade it. Taking the example of organotin, the reactive species attack the bonds between the tin and the hydrocarbon chains, also called debutylation (Stichnothe et al, 2005). In addition to the formation of the previous species, hydrogen peroxide and ozone can be formed at the anode (Stichnothe et al, 2005). Especially in the soil pores, hydrogen peroxide is very likely to be produced because the soil pore water system can be considered as a small-scale electrochemical cell where oxidative and reductive reactions occurs. Hydrogen peroxide is produced following the Equation 8 presented below (Ferrarese & Andreottola, 2008).

(8) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

The presence of conductor, and semi-conductor at microscale in the sediments can enhance the electrochemical degradation : iron, manganese, titanium, calcium carbonate and humic substances. They are already present in the soil and mainly come from the weathering but can also have their source from anthropogenic activities. The electric field polarize those micro-conductors and they may act as electrodes in the soil inducing more degradation. Moreover, hydrogen peroxide can be formed in the soil pore, and when there is presence of iron, the hydrogen peroxide decomposes into highly oxidative species increasing the organic degradation rate. This is called Fenton's reagent (Ferrarese & Andreottola, 2008).
The low conductivity of the soil is also an advantage for the electrochemical remediation. It has been demonstrated by Acar et al (1996) the efficiency of the electrochemical remediation occurs inversely proportionally to the grain size.

2.2.2.2 *Literature review: degradation of organics by electrochemistry*

Electrochemical treatment can convert organic material into simple, and relatively harmless inorganic material. This technique has been applied to environmental remediation since the 90's and a significant number of scientific articles were published since and during this decade. A short presentation of the research done on contaminated soil, sediments and wastewater is given in this part. Ferrarese & Andreottola (2008) studied the PAHs removal in marine sediments and found 90% of PAHs removal within one month using steel electrodes to promote a cost-effective remediation. The best efficiency and cost efficient was achieved for 1 V/cm. They found when the voltage is increased, the degradation time is lowered but higher voltage results in more risk for the workers and a more complex setup for a real scale application. The removal was equally efficient throughout all the sediments independently to the distance with the electrodes confirming micro-conductors and pores may act as electrodes itself. The removal of PAHs by volatilization was measured at the electrode and the results confirmed a non-significant volatilization (Ferrarese & Andreottola, 2008).

Concerning the remediation of TBT some important studies were carried out on electrokinetic removal. Pedersen et al (2017) studied the electrodialytic removal of various pollutants, heavy metals and TBT on sediments in Greenland (Sisimiut) and Norway (Hammerfest). The sediments were sampled from the 10 cm top layer of the seabed adjacent to the shipyard in Sisimiut and adjacent the previous sewage discharge and outlet of the freshwater lake, Storvatn in Hammerfest. They found a removal efficiency for TBT and heavy metals and PCB superior to 40% and a low removal efficiency for PAH contrary to Stichnothe et al (2002) who found a removal efficiency for TBT and PAHs higher than PCB. They used Pt/TiO_2 electrodes and investigated the removal efficiency at a temperature of 4°C. Muff & Søgaard (2010) studied the electrochemical oxidation of PAH in water from harbor sediments purification with Ti/PtIr anode and steel cathode. They remove the PAHs under the Danish discharged limit with energy consumption of 13.2 kWh/m^3. The best electrolyte was 0.1 M NaCl for the enhancement of the degradation. Their conclusion was electrochemical remediation is possible but could be responsible for the formation of by-products.

Arevalo & Calmano (2007) studied the electrochemical remediation of wastewater from a shipyard containing high concentration of TBT and of other OTC compounds. The degradation was performed on synthetic and real shipyard wastewater containing 25000 ng/L of TBT (as Sn) and 5000 ng/L of DBT (as Sn) and 1.6 g/L Cl-. The degradation was achieved down to 100 ng/L (as Sn) using Boron Dopped Diamond (BDD) electrodes and Ti/IrO2 as a comparison. The BDD electrode has not shown any better efficiency because the oxidation is not only due to the reaction with the hydroxyl radicals but also with the reactive chlorine compounds formed due to the high concentration of chloride in the wastewater. The range of current densities tested was between 6 and 70 mA/cm² and the results showed the removal is possible with consumption of electricity comprised between 7 and 10 kWh/m^3. Concerning the technical parameters of the experiments the electrode content in boron was 2000mg/kg and the area of the Nb/BDD electrode was 170m². The distance between the two electrodes was 10 mm. This study shows very promising results for the treatment of the shipyard wastewater containing mobile OTC.

Stichnothe et al (2000) investigated the degradation of the OTC in sediments from the Port of Hamburg in order to develop a full-scale treatment process on site for the contaminated sediments. The sediments used are real samples collected next to Hamburg port containing TBT with a concentration of 100 000 µg/kg for the first sample and 400 µg/kg for the second sample. The remediation of sediments was achieved in 24 hours for 200 g of sediments suspended in sodium chloride solution. A partial degradation of TBT and DBT was achieved while the process seemed to not affect so much MBT concentration. The concentration of TBT was on a sample significantly removed from the highly concentrated sediments with 96600 µg/kg to 110 µg/kg. DBT was reduced from 4250 µg/kg to 2400 µg/kg and MBT was increased from 890 µg/kg to 14000 µg/kg. This increase results from the partial degradation of TBT and DBT in MBT.

In 2002, Stichnothe et al, studied the reduction of TBT in the sediments from the Port of Hamburg at larger scale: reactor of 30 L. The electrode used were IrO_2 for the anode and steel for the cathode with a surface ration of 1:2. In addition, they investigated the reduction of PAHs and PCB. The process showed high degradation efficiency for OTC and PAHs but the degradation of PCB set a limit at this process. No electrolyte was used for the marine sediments since they contain enough already. The experiments were carried with a current density at the anode of 80 mA/cm². The results show a degradation down to 100 µg/kg of TBT. The next article written by Stichnothe et al came in 2005 for the setup of a pilot scale experiment. The results confirm the results obtained in 2002: the degradation of TBT and PAHs was achieved but the degradation of PCB was very low. This series of publication is very encouraging for the degradation of OTC in the marine sediments from the Port of Gothenburg.

Removal efficiency depend highly on the sediments properties which vary even between marine sediments from different harbors. Difficulties in electrochemical remediation is also to find material resistant to corrosion and cheap because electrodes need to be changed frequently. For Muff & Søgaard (2010) the methods would not be applicable to the treatment of water containing PAHs but for Stichnothe & al. (2005) the methods would be cost effective for the removal of PAHs, and TBT from the marine sediments.

2.2.2.3 *Summary*

The oxidation of organic pollutants in marine sediments will be achieved by different electrochemical processes. The main one is due to the formation of reactive species explained by dissociation of water occurring at the anode. Then the high concentration of chloride in the suspension will lead to the formation of reactive chloride species able to oxidize organic compounds. Moreover, the sediments are composed of fine silts and clay containing small pores; in the pores there is the generation of hydrogen peroxide. In addition, the marine sediments are originated from a port and may contain many micro-conductor species, enhancing the catalytic decomposition of hydrogen peroxide but also acting as micro-electrodes. These processes should be responsible of a homogeneous remediation independently of the distance to the electrodes.

The literature research put in evidence that some parameters are important for achieving a good remediation such as the type of the electrodes, their size, the distance between them and the nature of the electrolyte. The applied current and the time of reaction seems to have a major role. The parameters by the authors in the previous degradation experiment using electrochemical remediation are summarized in Table 9 below.

Table 9. Summary of the experiment parameters for electrochemical degradation found in the literature

Compound	**Concentration**	**Applied current (mA.cm^2)**	**Electrodes**	**Time (h)**	**Removal rate (%)**	**Name**
5 PAHs	0.15 – 1.5 µg/L	/	Ti/Pt$_{90}$-Ir$_{10}$ Steel	/	40	Muff & Søgaard (2010)
TBT	25000 ng/L	6-70	Nb/BDD - Ti		99.6	Arevalo & Calmano (2007)
TBT	100000µg/kg 400µg/kg	80	IrO$_2$-steel	24	99.9	Stichnothe et al (2000)

The advantage of these electrochemical methods is the absence of use of chemical species to achieve a convenient degradation. These methods should be safe as long as the applied current density is not too high, at the exception of the production of by-products when the mineralization is not complete.

3 Methodology

In this part, the chemical composition of the original sediments is presented together with the method for the preparation of the spiked sediments and the detailed protocols used for the degradation of OTC with Fenton's reagent, electrochemical remediation and the analysis of the samples.

3.1 Material

The samples were collected from the River Göta Älv in Gothenburg, Sweden the 11/04/2019. The samples were collected during a dredging operation in the Port of Gothenburg, performed to remain the water depth, but also to be used for building the new terminal of the port. The sampling location is presented in Figure 6. The sediments studied in the context of this master's thesis were originated from the location presented in Figure 6.

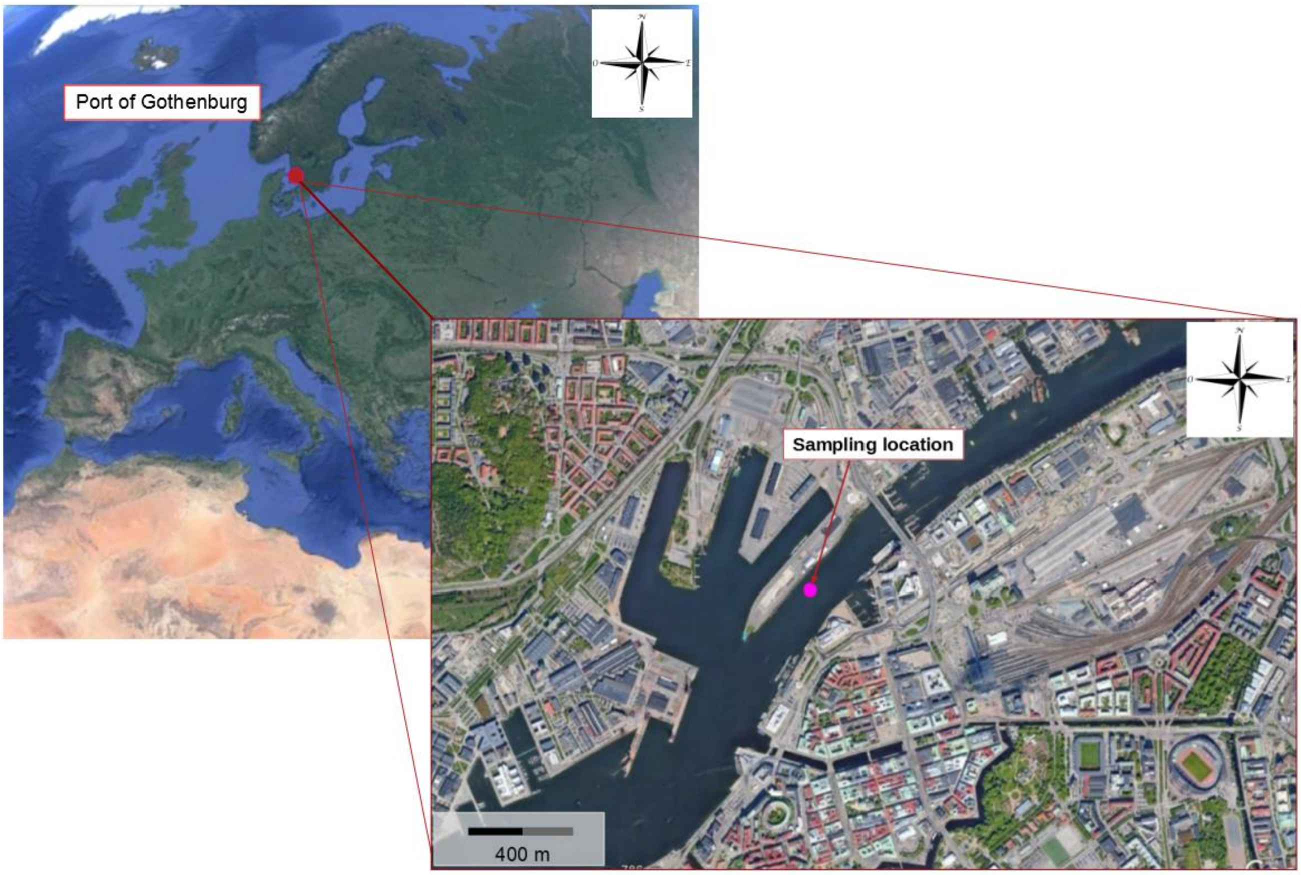


Figure 6. Location for the sampling of OTC polluted sediment (Source: GoogleEarth, 2015-2018)

The original unspiked sediments presented in Figure 7 were stored in plastic boxes in the dark at a temperature of 4°C and sent for analysis of grain size, metals, TOC, and organotin.

Figure 7. Dry original sediments

The Original sediments may contain a low concentration of OTC; therefore the sediments were spiked in order to notice a decrease superior to the standard deviation on the OTC concentration after using a degradation method.

The sediments were spiked the 3rd of April 2019. A droplet of tributyltin chloride (TBTCl) 96% Sigma Aldrich was mixed with methanol and Milli-Q water and introduced in the sediments; corresponding to a concentration of TBTCl about 30 mg/kg. The water and methanol were then evaporated under mixing from the sediments first at 40°C for 5 days and thereafter 17 days at room temperature . The dried samples were therefore homogenized and stored in a closed opaque container (Figure 8) in order to avoid photolytic degradation. Analysis were performed on triplicate of the sediments Spiked1 for metals, PAHs, OTC and TOC 22 days after the spiking. One sample of the sediments was analyzed again after 72 days from the spiking (50 days after the analysis of Spiked1) for OTC, TOC and Sn; and were sent for analysis in the wet form after 24 h stirring and protected from UV-light; called Spiked2.

Figure 8. Opaque container for the storage of dry spiked sediments

Regarding the high concentration of OTC in the spiked sediments, spiked sediments with a lower concentration were used. They were made by mixing about 100 g (99 % DM) of spiked sediments with 400 g (99 % DM) of original sediments in order to reach a concentration of 5 mg/kg TBT. One sample was sent for analysis of OTC and tin and called Medium1.

3.2 Method

The methods used for the degradation of OTC in the sediments with Fenton's reagent and electrochemistry are presented in this section.

3.2.1 Method: Fenton's reagent

The following protocol was mainly inspired from Tekin et al (2006) ; Flotron et al (2005) ; Kawahara et al (1995) ; Watts et al (2002).

80 g of dry sediments (99% DM) were placed in a 2 L beaker, wrapped in aluminum foil. Then carefully Milli-Q water, and ferrous sulfate heptahydrate >99,0% Sigma Aldrich were added to the sediments. The quantity of each reactant for each experiment are described precisely in Table 10. For all experiment, before starting the addition of hydrogen peroxide, all samples were containing 410 – 420 mL of aqueous solution. Aqueous solution was the result of mixing water, hydrogen peroxide and ferrous sulfate heptahydrate solution.

Then the slurry was mixed with a magnetic stirrer until the reaction was stopped, and the preparation of samples for analysis starts. The pH was adjusted with few droplets of sulfuric acid until the solution reach a pH of 3. The control was done with pH papers for the spiked sediments because of the high toxicity it was not a possibility to use any other accurate tool without contaminating it.

After adjusting the pH to 3, a first aliquot of hydrogen peroxide was added. From this time the solution was let reacting for 24 h. The first aliquot is added at t = 0 min, then five other aliquots were added every 15 min. The total volume of liquid at the end of the addition was 500 mL.

After 23 h of reaction the stirring was stopped, and the sediments were let settling down for an hour. The supernatant was centrifuged for 5 min at a speed of 4339 tour/min and relative centrifuge force (RCF) of 3999: the aqueous solution was stored and the sediments from the centrifugation were mixed with the sediments left in the beaker. Both water and sediments samples were stored at 4°C in the dark before being sent for analysis.

Figure 9. Fenton's degradation experiment with OTC polluted sediments

All experiments carried out for Fenton's are presented in Table 10.

Table 10. Design of all experiments carried out with Fenton's reagent

Ratio H_2O_2:TOC	Ratio H_2O_2:Fe^{2+}	[H_2O_2] (mol/L)	[Fe^{2+}] (mol/L)	Sediments
0	0	0.00	0	Spiked
0.01	5	0.003	0.0007	Spiked
0.2	5	0.07	0.01	Spiked
1	5	0.33	0.07	Spiked
5	5	1.67	0.33	Spiked
7	5	2.33	0.47	Spiked
9	5	3.00	0.60	Spiked
0	0	0.00	0.00	Spiked
5	40	1.67	0.04	Spiked
5	20	1.67	0.08	Spiked
5	15	1.67	0.11	Spiked
5	10	1.67	0.17	Spiked
5	2	1.67	0.84	Spiked
5	5	1.67	0.33	Spiked
5	5	1.67	0.33	Medium
5	5	1.67	0.33	Natural
1	2	0.33	0.17	Spiked
1	2	0.33	0.17	Medium
1	2	0.33	0.17	Natural

The first step of the experiments of degradation of OTC concerned the establishment of the optimum parameters with Fenton's reagent. These parameters are established for the spiked sediments and then the same parameters were applied for the degradation of OTC in the sediments Medium1 and Original1.

The establishment of the optimum parameters for the application of Fenton's reagent concerned:

- The determination of the ratio H_2O_2:TOC (Table 11)
- The determination of the ratio H_2O_2:Fe^{2+} (Table 12)

In order to reach a good OTC degradation in the sediments, the ratio between hydrogen peroxide and TOC was first investigated (Table 11). For this experiment one reference and six degradation experiments were performed with a fixed ratio between H_2O_2:Fe^{2+} equal to 5. The tests were carried on spiked sediments.

Table 11. Experimental design and analysis program for Exp1 with Fenton's reagent

Ratio H_2O_2:TOC	**Reference**	**0.01**	**0.2**	**1**	**5**	**7**	**9**
TOC %	2	2	2	2	2	2	2
Total volume (L)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
[H_2O_2] (mol/L)	/	0.003	0.07	0.33	1.67	2.33	3.00
Concentration of Fe^{2+}	/	0.0007	0.01	0.07	0.33	0.47	0.60
[H_2O_2]mother solution (mol/L)	/	0.02	0.40	2.00	8.84	8.84	8.84
V[H_2O_2] mL	/	94	83	83	83	132	170
*Number of aliquots**	/	6	6	6	6	12	12
*Analysis made on water***	Sn_{filt}, Sn	Sn_{filt}, Sn	Sn_{filt}, Sn, OTC	Sn_{filt}, Sn	Sn_{filt}, Sn, OTC	$Metals_{filt}$ and metals, OTC	$Metals_{filt}$ and metals OTC
Analysis made on sediments	TOC, Sn	TOC, Sn	TOC, Sn, OTC	TOC, Sn	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC

Note: The ratio 7 and 9 were added after interpreting the results of the ratio from 0.01 to 5. .

*For the ratio H_2O_2:TOC 7 and 9, the quantity of hydrogen peroxide to add for each of the six aliquots was about 22 mL and 28 mL. When adding this quantity, vapour and bubbles were formed and could be a safety issue for the laboratory worker. The aliquots were thus divided by 2 and added every 7 min instead of 6 every 15 mins.

** $Metals_{filt}$ or Sn_{filt} correspond to an analysis of various metals after a filtration on a 0.45µm filter cellulose acetate filter

The second step of the Fenton's degradation was the adjustment of the ratio between hydrogen peroxide and iron (Table 12). This time the ratio between hydrogen peroxide and TOC was fixed to 5, as it was the optimum parameter observed for a higher degradation of OTC. Thus, the concentration of hydrogen peroxide to add was 1.67 mol/L. Using the hydrogen peroxide 30% it gave a volume to add equal to 94 mL. The experiments were carried on spiked sediments.

Table 12. Experimental design and analysis program for Exp2 with Fenton's reagent

Ratio H_2O_2:Fe^{2+}	**Ratio H_2O_2:Fe^{2+}**	**Reference**	**40**	**20**	**15**	**10**	**2**
TOC %	TOC %	2	2	2	2	2	2
Total volume (L)	Total volume (L)	0.5	0.5	0.5	0.5	0.5	0.5
[H_2O_2] (mol/L)	[H_2O_2] (mol/L)	/	1.67	1.67	1.67	1.67	1.67
Concentration of Fe^{2+}	Concentration of Fe^{2+}	/	0.04	0.08	0.11	0.17	0.84
[Fe^{2+}]mother solution (mol/L)	[Fe^{2+}]mother solution (mol/L)	/	0.5	0.5	0.5	0.5	2.5
Analysis made on water	Analysis made on water	Sn	Sn	Sn	Sn	Sn	Sn
Analysis made on sediments	Analysis made on sediments	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC

When the optimum parameters on the spiked sediments were determined, the same parameters were applied to the sediments Medium1 and to the Original1 sediments. In Table 13, the ending Expx.S means Spiked, Expx.M means Medium1 and Expx.O means Original1.

Table 13. Experimental design for the reproduction on Spiked sediments, Medium1 and Original1 with Fenton's reagent and analysis program

Sediments	**Spiked Exp3.S**	**Spiked Exp4.S**	**Medium Exp3.M**	**Medium Exp4.M**	**Original Exp3.O**	**Original Exp4.O**
H_2O_2:TOC	5	1	5	1	5	1
H_2O_2:Fe^{2+}	5	2	5	2	5	2
TOC %	2	2	2	2	2	2
Total volume (L)	0.5	0.5	0.5	0.5	0.5	0.5
[H_2O_2] (mol/L)	1.67	0.33	1.67	0.33	1.67	0.33
Concentration of Fe^{2+}	0.33	0.17	0.33	0.17	0.33	0.17
[Fe^{2+}]mother solution (mol/L)	0.5	0.5	0.5	0.5	0.5	0.5
Analysis made on water	Sn, OTC	Sn, OTC	Sn, OTC	Sn, OTC	Sn, OTC	Sn, OTC
Analysis made on sediments	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC	TOC, Sn, OTC

3.2.2 Method: Electrochemical remediation

The following method has been mainly inspired by Arevalo and Calmano (2007) ; Stichnothe et al (2000, 2002, 2005). 80 g of dry sediments were added in a 2 L beaker with 500mL of Milli-Q water because the marine sediments contained enough electrolyte for allowing electric conduction. The electrodes were composed by a 5 x 10 cm^2 plate as an anode made of Niobium/Boron Diamond Dopped (Nb/BDD) (Neocoat, Switzerland) (Figure 10) and a 5 x 10 cm^2 cathode plate of the same size made of titanium were placed in the beaker in contact with the slurry and 10cm away from each other. About 6 cm of the electrodes were submerged in the water when the slurry was mixed by magnetic stirring.

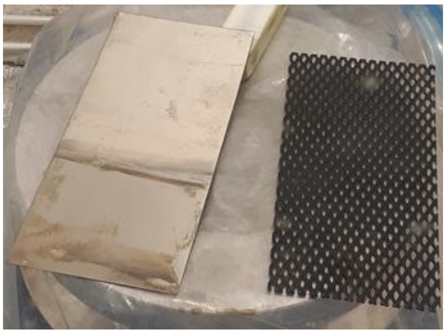


Figure 10. Electrodes used for degradation. On the left: cathode made of titanium. On the right: Nb/BDD anode electrode

The current was measured across a 10 ohm resistor using a digital multimeter. The beaker was covered with aluminum foil in order to avoid photolytic degradation of TBT. Then the water was centrifuged for 10min at a speed of 4339 tour/min and RCF of 3999 G and sent for analysis, the aspect of the sediments before and after centrifugation are presented in Figure 11 and Figure 12. The sediments were collected for analysis as well. The montage used for the experiments is presented in Figure 13, 14 and 15 below.

Figure 11. Slurry before centrifugation

Figure 12. Slurry after centrifugation

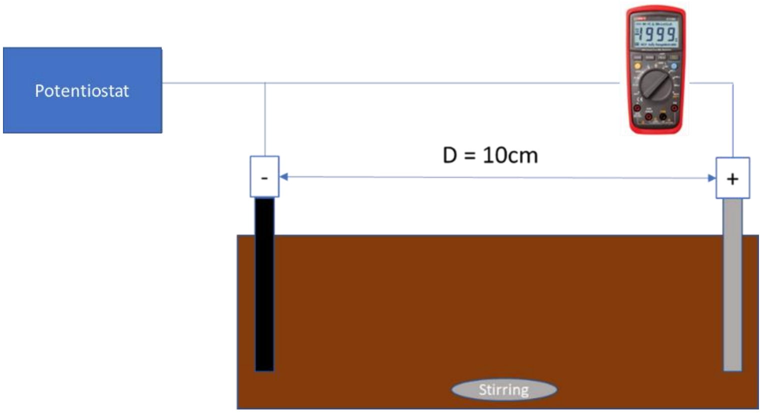


Figure 13. Scheme of the equipment for the electrochemical remediation test

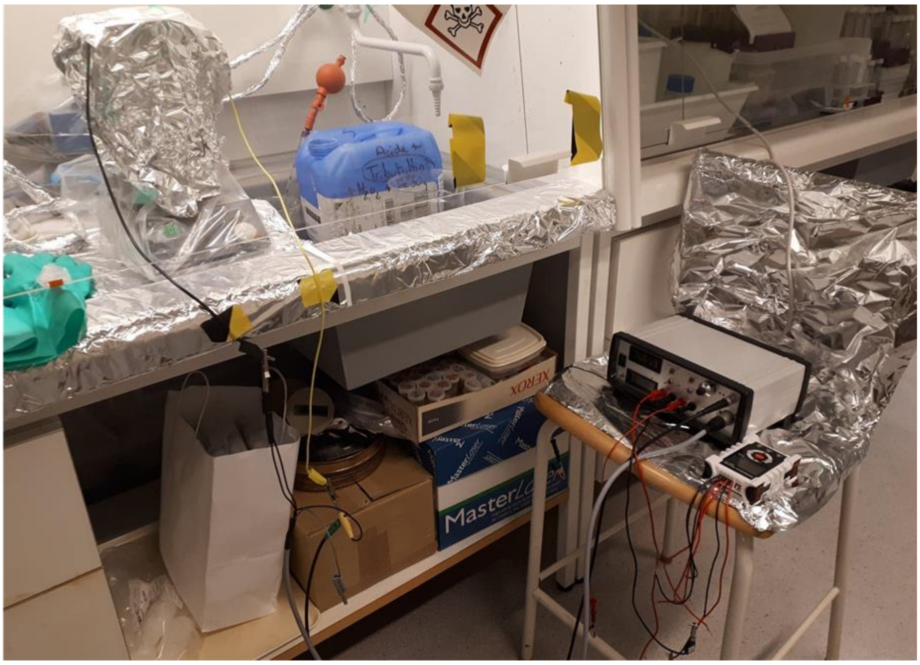


Figure 14. Equipment used for the electrochemical remediation of the OTC contaminated sediments

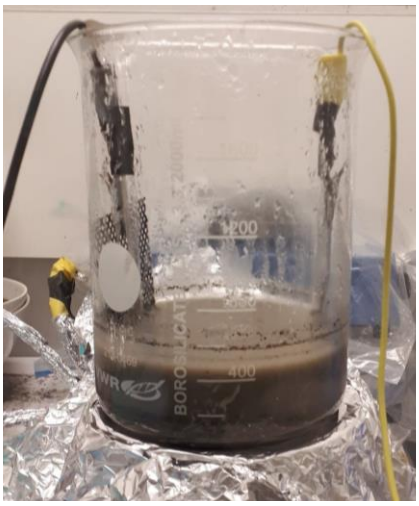


Figure 15. Equipment used for the electrochemical remediation of the OTC contaminated sediments

A first experiment was done on the natural sediments in order to set up the experiment before working with contaminated sediments. The results are presented in Appendix 1.

The experiments conditions for the electrolysis experiments carried through are presented in Table 14. In Table 14, the ending Expx.S means Spiked, Expx.M means Medium1 and Expx.O means Original1.

Table 14. Design of electrochemistry experiments

Sample	**Time (h)**	**Voltage (V)**	**Intensity (mA)**	**Current density (mA/cm²)**
Electro1.S	24	5	30	0.6
Electro2.S	72	5	30	0.6
Electro3.S	24	8	100	2
Electro4.S	24	23	350	7
Electro4.S2	24	21	350	7
Electro4.M	24	21	350	7
Electro4.O	24	21	350	7

3.3 Safety

The laboratory work in this master's thesis was mainly performed on spiked sediments. These sediments had a concentration of TBT of ~24500µg/kg. As explained in chapter 2.1.3, TBT and in general OTC can be very dangerous for the health of living species. TBT is recognized to be toxic for humans and aquatic life and may lead to death (PubChem). Inhalation cause bleeding, irritation, headache, sore throat, wheezing and coughing, loss of appetite, nausea, vomiting, watery eyes, adenopathy. Dermal contact of paint containing TBT cause itchiness, skin burning, swelling, blisters and dermatisis. The symptoms appear 5 to 10 hours after the exposure. It is thus important to follow all security rules for the experiments with these extremely toxic sediments.

In the laboratory the spiked sediments were handled under the fume with a pair of laboratory gloves covered by a pair of dishes gloves in order to guarantee a maximal protection. The sediments are composed of fine particles, thus when moved they dust. By consequence, the use of a mask is highly recommended in case sediments would escape from the fume. Regarding the material used, everything needs to be protected when staying under the fume.

3.4 Analyses

Table 15 below present a summary of the analysis performed on the initial sediments used for the different degradation experiments.

Table 15. Analysis performed on initial sediments

Sediments	**Spiked 1**	**Spiked 2**	**Medium1**	**Original**
TOC	x	x	x	x
Sn	x	x	x	x
Metals	x	-	x	x
OTC	x	x	x	x
PAHs	x	-	-	-
Grain size	-	-	-	x

Table 16 below present a summary of the analysis performed on the aqueous phase and the sediments after degradation. In Table 16, the ending Expx.S means Spiked, Expx.M means Medium1 and Expx.O means Original1.

Table 16. Analysis performed on the samples

Experiment	**Fenton Exp1**	**Fenton Exp2**	**Fenton Exp3/4 S/M/O**	**Electro 1&2**	**Electro 3, 4**	**Electro4. S/M/O**
Aqueous phase						
Sn	x	-	x	x	-	-
Sn (0.45µm)	x	x	-	x	x	x
Metals	x	x	x	x	x	-
OTC	x	-	x	x	x	x
Note	Exp1.6 and Exp1.7 only Sn analysis was performed					
Sediments						
TOC	x	x	x	x	x	x
Sn	x	x	x	x	x	x
Metals	-	-	x	-	-	x
TBT	x	x	x	x	x	x

3.4.1 pH analysis

To perform the analysis of pH in the samples the determination with pH paper was most appropriated regarding the toxicity of the sediments. This analysis was performed using Fisherbrand pH-Fix 0-14 pH paper (Figure 16). The solution was stirred, the pH paper was then introduced for 30 sec in the slurry. The pH was determined according to the color taken by the paper.

Figure 16. Fisherbrand pH paper used for pH measurement

3.4.2 Metal analysis with ICP-MS

This part concern only the analysis done in the Environmental laboratory of Chalmers University of Technology (Figure 17). All the samples were prepared with 18.2MΩ.cm water at 25°C and acidified with 1% HNO_3 (65%) for the trace analysis. The samples were analyzed with inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS is an analysis technology able to detect most of the period table elements at a concentration on the order of the milligram or nanogram per liter. (ThermoFisher Scientific)

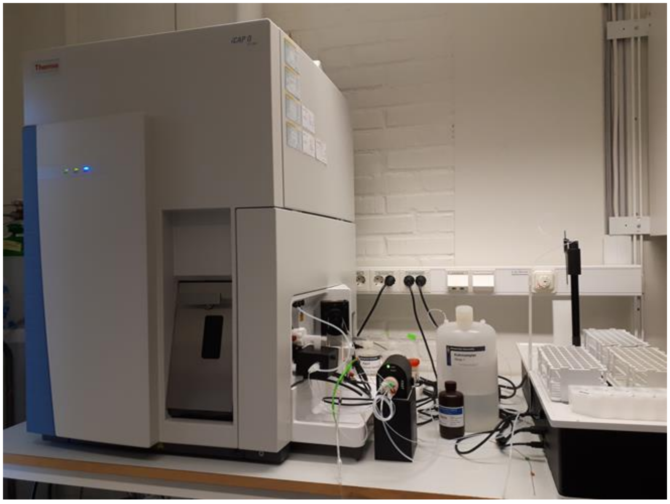


Figure 17. ICP-MS used for the metal analysis

The ICP part is an ionization source, like Electron ionization or Electrospray Ionization are ionization sources placed beforehand the mass-spectrometer (Labcompare). The sample was placed and pumped into the spray chamber and nebulizer. In this part, fine droplets of samples were generated to be carried out with argon gas into the plasma where the chemical compounds are fully decomposed and reduced to atomic constituents. In the plasma the atoms are also ionized. Therefore, the ions are transported into the mass part depending on vacuum and are separated in a quadrupole by the application of an electromagnetic field. With the MS part, the atomic ions are sorted depending on their atomic mass on charge (m/z) (ThermoFisher Scientific).

The samples for the metal analysis were prepared as described in Table 17. The difference between the dilutions factors is explained by the different concentration of iron present in the sediments. The concentration of iron was high in some samples and could thus spoil the ICP-MS, by creating iron deposit. Or also iron could cause interference for the detection of other compounds.

Table 17. Preparation of samples for metals analysis with ICP-MS

Type	**H_2O_2:TOC**	**H_2O_2:Fe^{2+}**	**Dilution**
Electrochemistry 1,2,3,4,5	/	/	100
Fenton References	/	/	100
Fenton 1	5	5	1000
Fenton 1	1	5	500
Fenton 1	0.2	5	100
Fenton 1	0.01	5	100
Fenton 1	7	5	1000
Fenton 1	9	5	1000
Fenton 2	5	40	100
Fenton 2	5	20	1000
Fenton 2	5	15	1000
Fenton 2	5	10	1000
Fenton 2	5	2	1000

3.4.3 Size distribution analysis

The size distribution was measured on all samples for which a measurement of OTC concentration was carried in the liquid. First, the samples were shaken in a shaking machine during 10min at 125 tour/min. The samples were once again shook before taking out liquid with a 2.5mL pipette. The sample was introduced in a cuve rinced two times with Milli-Q water before. The samples were analyzed for filtrated and non-filtrated sample. When the sample was filtrated, it was done using 0.45µm syringe-filters. The size distribution was then measured with a particle Analyzer Anton Paar Litesizer500 presented in Figure 18.

Figure 18. Particle Analyzer Anton Paar Litesizer500

3.4.4 External analyses

The following analyses were carried out by the external laboratory ALS and are presented in Table 18 below.

Table 18. Analysis carried out by ALS on the liquid and solid phase

Analysis	**Matrix**	**Material**	**Method**	**Limit detection**
Filtration for metals analysis	Liquid	0,45µm cellulose acetate filter	/	/
Dry matter	Sediments	Oven	SS 02 81 13-1	/
TOC	Sediments		DIN EN 15936:2012	0.01%
OTCs	Liquid	GC-ICP-SFMS	ISO 17353:2004	0.001 µg/L
OTCs	Sediments	GC-ICP-SFMS	Acid extraction SS 028113. ISO 23161: 2011	0.001 mg/kg
Metals	Liquid	ICP-SFMS ICP-AES	SS EN ISO 17294-2: 2016 EPA-method 200.8: 1994	/
Metals	Sediments		SS EN ISO 17294-1, 2 EPA-metod 200.8	/
PAHs	Sediments	GC-MS	Microwave extraction EPA 8270C/D	0.01 mg/kg

4 Results & Discussion

In this part, the results obtained for the initial sediments, and after their degradation using Fenton's reagent or electrochemistry are presented and discussed.

4.1 Initial sediments

All sediments used as a start for the degradation experiments are presented in this part. The report of analysis provided by ALS for original sediments are presented in the Appendix 5 and in the Appendix 6, 7, 8 for respectively Spiked 1, Spiked 2, Medium1.

4.1.1 Original sediments

The original sediments were collected, and the wet sediments were sent for analysis of OTC, TOC, Sn, metals, particle size distribution. Some of the results are presented in Table 19 below.

Table 19. Maximum, minimum and average concentrations of OTC, Sn, Fe and TOC in the original sediments

Compound	**Maximum**	**Minimum**	**Average**
TOC (%)	2.2	2.0	2.1
TBT (µg/kg)	255	73	129
DBT (µg/kg)	45	20	35
MBT (µg/kg)	26	11	17
OTC (µg Sn/kg)	145	48	82
Sn (µg/kg)	3120	2700	2928
Fe (g/kg)	-	-	22

The average TOC is equal to 2.1%. Bogan & Trbovic (2003) and Nam et al (2001) reported a lower degradation when the TOC is less than 5% because the pollutants are not anymore adsorbed onto the organic matter but located in the micropores being less available for degradation.
The percentual composition of the tin species in the original sediments is presented in Figure 19.

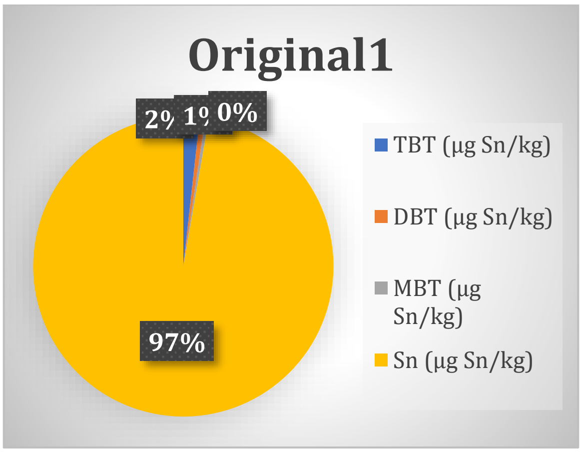


Figure 19. Percentual composition of the tin species in the Original1 sediments

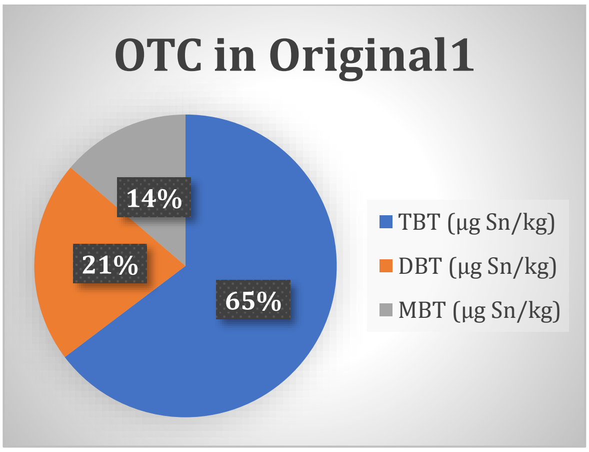


Figure 20. Percentual composition of the OTC species in the Original1 sediments

In the Original1 sediments, presented in Figure 19, the major tin species is tin in inorganic metallic form (97%) > TBT (2%) > DBT (1%) > MBT (<1%). Due to the high concentration of tin compared to OTC, Figure 20 present only the relative percentual composition of OTC in the sediments. TBT is the major compound with 65% >DBT (21%) > MBT (14%).

Other metals and elements were analyzed in the original sediment, and the results are presented in the Appendix 2 and Appendix 3. A high concentration of major elements aluminum and iron were found. This high concentration of iron (22 g/kg DM) is particularly interesting for Fenton's reaction, because it acts as a catalyst if dissolved in the form Fe^{2+}. No information on the form of Fe is not given by the ICP-MS analysis, it is thus impossible to determine its role in the Fenton´s reaction. Moreover, the sediments contain micro-conductor species (titanium, iron) enhancing the catalytic decomposition of hydrogen peroxide but also acting as micro-electrodes for the electrochemistry. The sediments contain as well toxic trace metals such as arsenic with an average of 4.5 mg/kg; 30.6 mg/kg chromium; 32.4 mg/kg copper; 125 mg/kg zinc; 23.9 mg/kg lead.

Grain size distribution of the original sediment samples taken at different depths are presented in Appendix 4. The fraction of fine sand 0.06 < x < 0.2mm is higher in the top 5 centimeters; 48% compared to 26% at the depth 20–30cm. The clay fraction x < 0.002 mm is equal to 21% in both samples.

4.1.2 Spiked sediments

The results from the analysis of the spiked sediments Spiked1, Spiked2 and Medium1 are presented in Table 20 below.

Table 20. Concentrations of TOC, TBT, DBT, MBT, Sn and Fe in the spiked sediments Spiked1 and Spiked2, and the spiked sample mixed with the original sample Medium1

Sample	**Spiked1 after 22 days***	**Spiked2 after 72 days + mixing in water**	**Medium1**
TOC (%)	2.2	2.6	2.4
TBT (µg/kg)	24500	11600	2710
DBT (µg/kg)	2427	1700	594
MBT (µg/kg)	726	794	379
OTC (µg Sn/kg)	11767	6157	1669
Sn (mg/kg)	14.7	16.0	4.4
Fe (g/kg)	14.3 – 19.0	-	-

*mean value of triplicates

The TOC is ~ 2.4% in the spiked sediments and corresponds to the TOC found in the natural sediments. The concentration of tin in the Spiked1 samples is ~15 mg/kg. Compared to the natural sediments the concentrations of tin was increased by about 12–13mg/kg in Spiked1 and Spiked2.

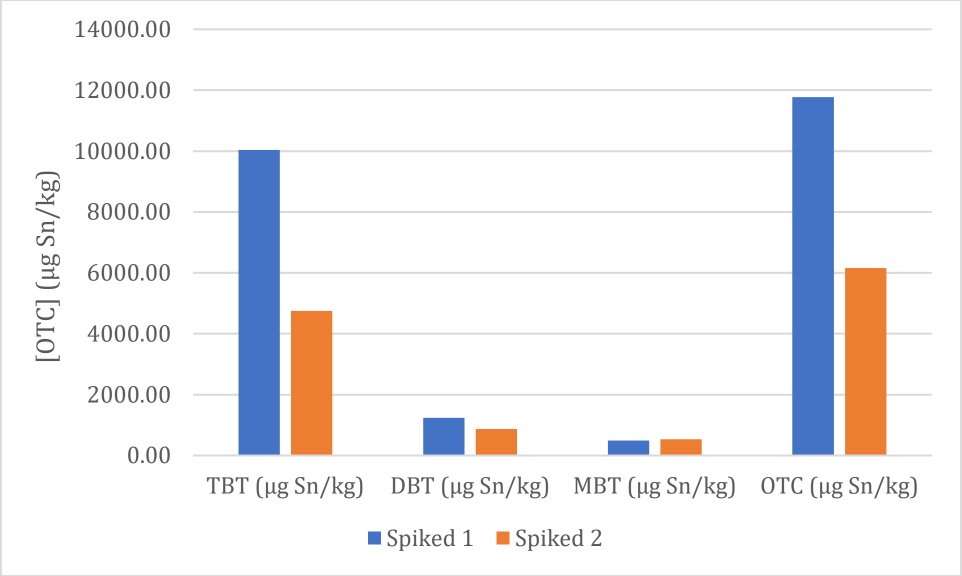


Figure 21. Difference in OTC concentrations in the sediments Spiked1 and Spiked2, were the latter was analyzed 50 days later

The total concentration of OTC and TBT in Spiked2 has been reduced by a factor 2 and DBT has been diminished by a factor of 1.4. Very low concentration of inorganic tin Sn was found in the aqueous phase after mixing of the Spiked2 sample excluding the possibility that the OTC was emitted to the water phase. The reduction of the concentration of OTC is not either due to photolytic degradation of the spiked sediments because they were stored in a UV-proof container. The following explanations are possible: adsorption of OTC onto the plastic of the container, and/or bacterial growth contributing to the degradation in the sediments, and/or oxygen in the air and mixing water may be responsible for the oxidation of easily degradable and accessible compounds. Otherwise, the concentrations may also be different because of the heterogeneity of the sediments. The hypothesis of the degradation is supported by the fact that Medium1 has OTC, TBT and Sn concentration corresponding to one fifth of Spiked2 (Table 20).

The percentual composition of the OTC in Spiked2 is presented in Figure 22 and when compared to the composition in Figure 23 made for Spiked1 it shows similarities but also differences.

In Spiked1, the proportion of tin is very low compared to the proportion of OTC: 4% only is in Sn inorganic metallic form when 96% of Sn is in organic form with TBT as a major constituent (82%) > DBT (10%) > MBT (4%).

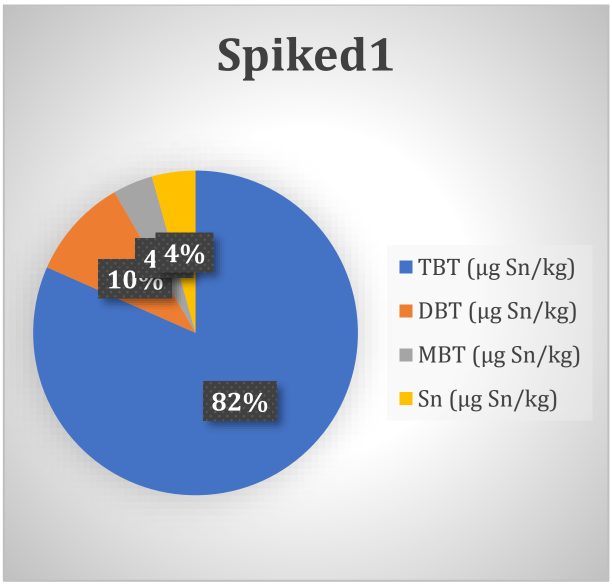


Figure 22. Percentual composition of the tin species in the sediments Spiked1

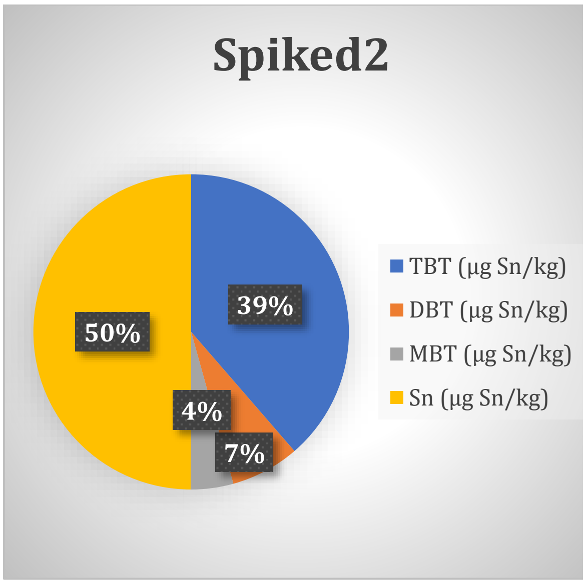


Figure 23. Percentual composition of the tin species in the sediments Spiked2

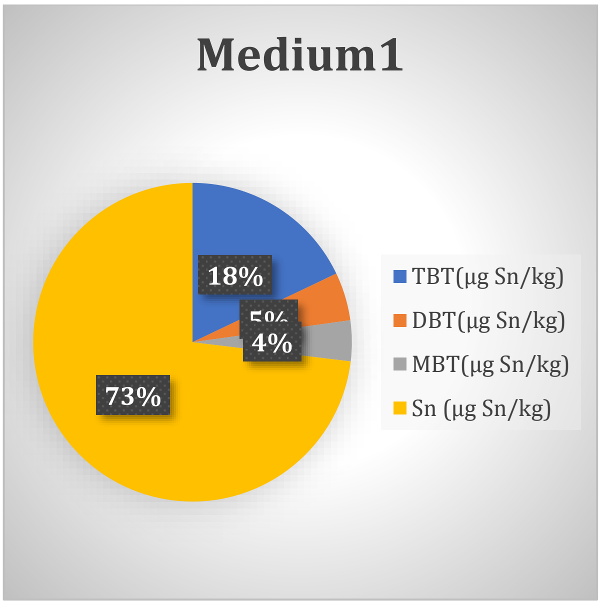


Figure 24. Percentual composition of the tin species in the sediments Medium1

In the sample Spiked 2, the major constituent is metallic tin (50%) > TBT (39%) > DBT (7%) > MBT (4%). When considering only the OTC, TBT is still the major compound. The increase in the proportion of tin coupled with the data from Figure 21, presenting in Spiked 2 a reduction of the OTC, TBT and DBT compared to Spiked 1 support the hypothesis of the degradation of OTC in Spiked2. On the other hand, triplicate analysis of OTC were done on Spiked 1 but only one was done on Spiked2 depending on shortage of the spiked sediments. For these reasons, it is not possible to prove that a degradation occurred. Therefore, the experimental degradation results in this study is given in a range based on a high estimation using results from Spiked 2 and on a low estimation using results from Spiked 1.
Metallic tin is the major species of the total tin in the sediments Medium1 with 73% > TBT (18%) > DBT (5%) > MBT (4%) (Figure 24).
Other metals and elements were analyzed, and the results are presented in the Appendix 9. The concentration of metals in the spiked sediments (Appendix 9) have the same order of magnitude as the natural sediments (Appendix 5) with the exception of tin.

Sixteen Polycyclic Aromatic Hydrocarbons (PAHs) were analyzed in the spiked sediments and presented in Appendix 10. The results show the sum of the sixteen PAHs is equal to 1.2 mg/kg PAHs:

- PAH L: 0.063 mg/kg,
- PAH M: 0.58 mg/kg,
- PAH H: 0.69 mg/kg.

The PAHs are present in low concentration and the trace of PAHs may come from the fuel usage in the port, and by ships.

4.1.3 Comparison of sediments used for degradation

A summary of the important parameters in the original sediments, the spiked and the mixed samples is presented in Table 21. The concentration of tin is the mean value of the result of all analysis made on each sediment: initial sediments but also after degradation experiment using Fenton's reagent to give a more precise result due to the heterogeneity of the sediments. Using Fenton's reagent there is no risk of tin removal except its dissolution in the aqueous phase measured in µg/L. The results after electrochemistry are not considered in the average of the tin's concentration because of the possible electrodeposition on the electrodes.

Table 21. Concentrations of different compounds in the sediments used for the degradation tests

Analysis	**Average in original sediments**	**Average in spiked sediments (Spiked2-Spiked1)**	**Medium sediments**
TOC %	2.1	2.4	2.4
Iron (mg/kg)	22 000	1800	/
Sn (mg/kg)	2.8*	12.0 +/- 3.2**	6.2 +/- 2.3***
TBT (µg/kg)	130	12000-25000	2700
DBT (µg/kg)	345	1700-2400	590
MBT (µg/kg)	17	790-730	380
OTC (µg Sn/kg)	82	6200-12000	1700
OTC/Sn (%)	3	50-96	38

*Mean value of * = 6 samples with a standard deviation of 0.4 mg/kg, ** = 20 samples with a standard deviation of 3.2 mg/kg and *** = 3 samples with a standard deviation of 2.3 mg/kg.*

Table 21 show that similar concentration of TOC, and iron are found in the sediments with slight variations due to the heterogeneity of the sediments. Compared to the concentration of OTC in the natural sediments, the concentration of TBT in spiked sediments had been increased ~200 times, the concentration of DBT by 70 times and MBT by 44 in the spiked samples. The total OTC concentration has increased with a factor of 144. Although, between the spiked and the natural sediments, the proportion of organotin compared to tin is different. The percentage of OTC of all the tin in the sediments is equal to 2.8% for the natural sediments and is much higher (50–96%) for the spiked sediments. When the spiked sediments were analyzed again further in time, the concentrations of OTC decreased by a factor 2 and the percentage of organotin of total tin of the sediments decreased by 2 as well. In the mixed medium sediments, the organotin content is equal to 38%. The concentration of OTC has been reduced by 10 compared to the initial spiked sediments and by 4.5 times compared to the Spiked 2.

4.2 Degradation of OTC in the marine sediments using Fenton

In total, eleven experiments were carried out in order to determine the ratios between hydrogen peroxide, TOC and iron, 2 references samples were used as well.

In addition, six experiments were performed in order to test the reproducibility with different concentrations. Pictures of the slurry after the degradation experiment is presented in Figure 25 and 26. The ratio used influence the production of sludge as seen in Exp1.3 and Exp4.S/M/O.

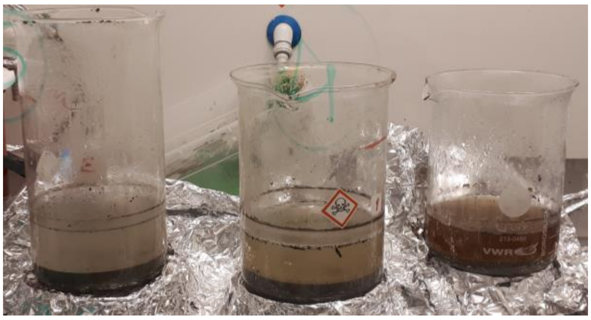


Figure 25. Slurry after degradation experiment using Fenton's reagent (Exp1.5; 1.4; 1.3)

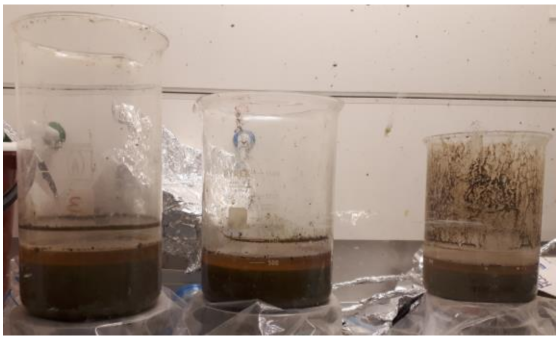


Figure 26. Slurry after degradation using Fenton's reagent (Exp4.S/M/O)

4.2.1 Degradation in spiked sediments

The experiments described in this part focus on the adjustment of the ratios between hydrogen peroxide, TOC and iron in the spiked sediments. Analysis were performed on the aqueous phase and the sediments. The results from the different phase are treated separately to make the interpretation easier.

The reports delivered by ALS for the analysis of the sediments and liquid after degradation Experiment 1 are presented in Appendix 11, for Experiment 2 are presented in Appendix 12.

4.2.1.1 *Sediments*

The results of the OTC's degradation in the sediments using Fenton's reagent are presented in the Appendix 13.

The analysis of TOC shows a concentration of 2% in the original reference sample, see Appendix 13. The TOC content in the other samples varies between 1.5 and 6.5%. In the sample Exp1.4, the TOC concentration is higher (6.5%) compare to all other experiments, it could correspond to the presence of paint flakes in the sample.

Tin in the initial spiked sediments Spiked1 was 15mg/kg DM. The concentration of tin in the Spiked2 was 16mg/kg DM. Tin analyzed after each degradation experiment using Fenton's reagent varied from 5.9 to 16 mg/L. Apart from the dissolution of a small fraction of tin into the water, the degradation process cannot remove the tin from the sediments, except for sample 2.4 and 2.5 where the tin concentration was reduced by a factor ~2. The differences observed demonstrates the heterogeneity throughout the sediments, the differences could be explained by the standard deviation attributed to each analysis. The minimum standard deviation was 1.9mg/kg, the maximum 5.3mg/kg, and the average was 3.3mg/kg.

The results of the concentrations of organotin in each sediment sample after degradation are presented in Figure 27 below.

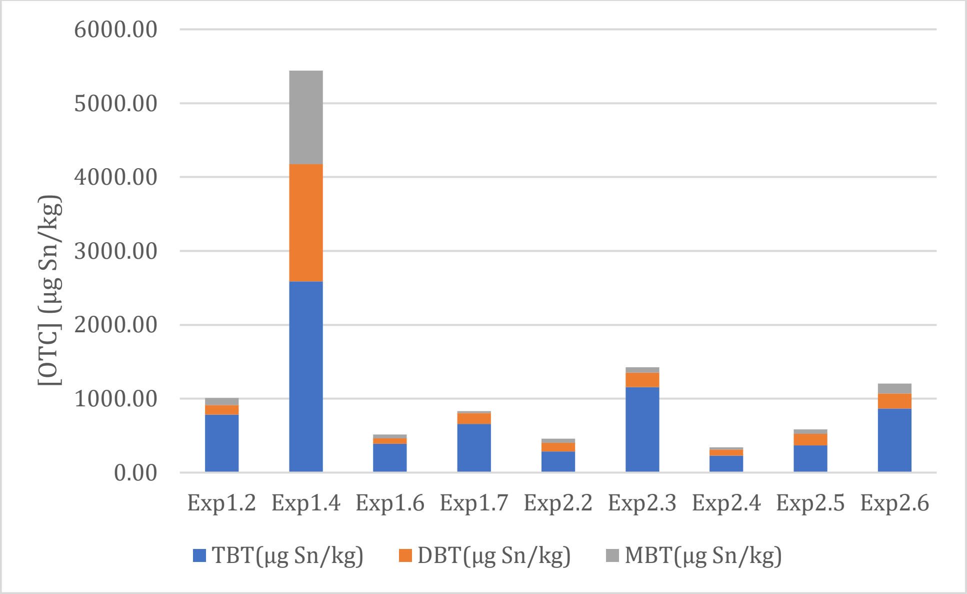


Figure 27. Concentrations of OTC in the sediments after the degradation using Fenton's reagent

The degradation of the total OTC, TBT, DBT and MBT are presented in the Appendix 14. The degradation is calculated relatively Spiked1 and Spiked 2 to establish a range of possible degradation. The average of the range is presented and the column "+/-" indicates the minimum and maximum value. Figure 28 is made in order to give an overview of the degradation ranges for each OTC presented in the Appendix 14.

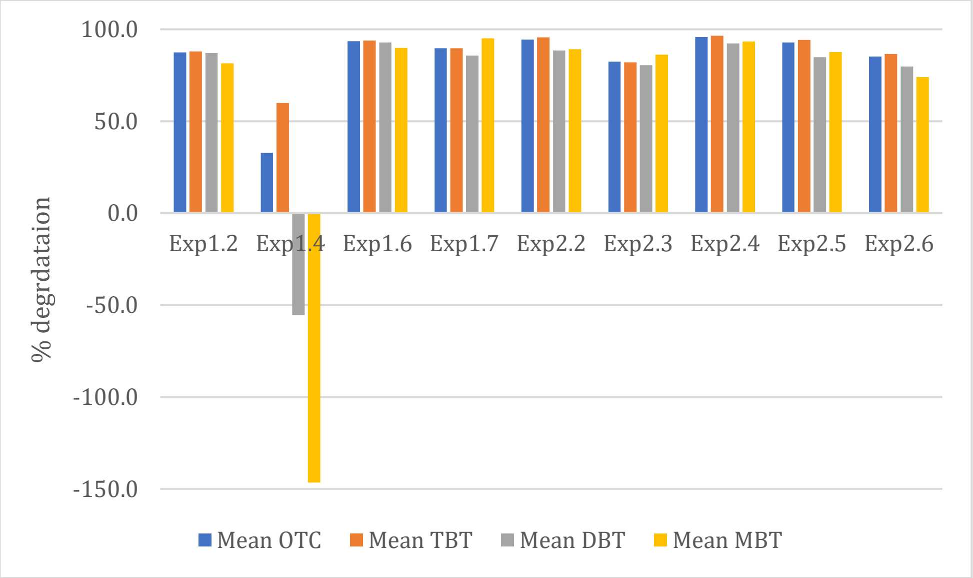


Figure 28. Degradation percentage of OTC, TBT, DBT and MBT in the sediments calculated with the lower and higher concentrations of OTC found in Spiked1 and Spiked2

The analysis shown in the Appendix 14 and Figure 27 reveals for OTC very different concentrations in the treated sediments depending on the ratios of H_2O_2 and Fe used. The concentrations of OTC and their relative percentage in the residual sediment after treatment are presented in Figure 28.

The sample presenting highest concentrations of OTC after degradation in the sediments is Exp1.4 using [H_2O_2:TOC]= 0.2 and [H_2O_2:Fe^{2+}]=5 (Appendix 14, Figure 27). This experiment still showed degradation of 33% +/- 21%. of total OTC, and the degradation of 60% +/- 14% of TBT, -56% +/- 27% of DBT and -150% +/- 11% of MBT. The results obtained for Exp1.4 prove the conditions of the experiment are not adapted to the OTC degradation in the sediments from the port of Gothenburg: the ratio H_2O_2:TOC must be equal or higher than 1 to lead to an acceptable degradation.

The sample with the lowest concentration of total OTC after degradation is Exp2.4. Then come: Exp1.6 >Exp2.2>Exp2.5. The differences in OTC concentrations can also be due to the standard deviation of each analysis performed on the sediments. All these samples showed low concentrations of OTC compared to the untreated samples Spiked 1 and Spiked 2 (Appendix 14, Figure 27). Figure 27 illustrates the main form of OTC remaining after degradation experiments is TBT > DBT > MBT. Best degradations were obtained for Exp1.6 and 2.4, but all degradations were satisfying except for Exp1.4. All other degradations were investigated with a ratio H_2O_2:TOC superior or equal to 1.

The best degradation was reached in Exp2.4 and for total OTC and TBT both with a degradation of 96% =/- 1.3 (Figure 28) using [H_2O_2:TOC]= 5 and [H_2O_2:Fe^{2+}]=15.The best degradation for DBT was in Exp1.6 with 93% +/- 1.3%, showing also very good degradation of total OTC, TBT, DBT and MBT. The best degradation found for MBT was in Exp1.7 corresponding to 95% +/- 0.2% degradation. All the conditions of the experiments 1.6; 1.7; 2.2; 2.4 and 2.6 can be considered as good for the degradation of OTC in the spiked sediments from the port of Gothenburg. Even the lower degradation reached with the experimental conditions used for experiments 1.2; 2.3 and 2.6 are acceptable .

4.2.1.2 *Aqueous phase*

The different parameters analyzed in the aqueous phase after each degradation experiment are presented in Table 22 . 1.Ref and 2.Ref correspond to the stirring for 24h of the initial sediments with Mili-Q water. The sample called 1.Ref is the reference of the experiment 1 (marked 1.x). The sample called 2.Ref is the reference of the experiment 2 (marked 2.x). The sample 2.Ref correspond to the same sample called Spiked 2, is only called 2.Ref when used for the aqueous phase. The percentage of colloidal or dissolved tin was calculated using the difference between the tin concentration in filtrated and non-filtrated sample divided by the concentration of tin in the non-filtrated sample.

Table 22. Spiked sediments: Results of analysis in the aqueous phase at the end of the degradation Fenton 1

Sample	**1.Ref**	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**	**1.7**
H_2O_2:TOC	/	5	1	0.2	0.01	7	9
H_2O_2:Fe	/	5	5	5	5	5	5
Time of reaction (h)	24	24	24	24	24	24	24
Sn non filtered (µg/L)	2.11	186.50	31.90	7.81	11.00	287.00	422.00
Sn filtered 0.45µm (µg/L)	1.23	209.50	24.50	6.53	8.36	-	-
% Sn on colloids	42	0	23	16	24	-	-
TBT (ng/L)	n.a	5100	n.a	28300	n.a	879	915
DBT (ng/L)	n.a	11600	n.a	5710	n.a	2950	4270
MBT (ng/L)	n.a	810	n.a	1730	n.a	1410	1480
OTC (ng/L)	n.a	8554	n.a	15676	n.a	2818	3553
% of initial OTC in the water	n.a	0.5	n.a	0.8	n.a	0.15	0.19
% Degradation OTC	-	87.5	-	32.7	-	93.6	89.7

Table 23. Spiked sediments: Results of analysis in the aqueous phase at the end of the degradation Fenton 2

Sample	**2.Ref**	**2.2**	**2.3**	**2.4**	**2.5**	**2.6**
H_2O_2:TOC	-	5	5	5	5	5
H_2O_2:Fe	-	40	20	15	10	2
Time of reaction (h)	24	24	24	24	24	24
Sn filtered (µg/L)	1.07	27.40	37.10	92.90	117	370
% Degradation OTC	-	94.3	82.4	95.8	92.8	85.1

In 1.Ref, the tin concentration was 1.2µg/L for filtered solution and 2.1µg/L for the non-filtered. In 2.Ref, the concentration of tin in the aqueous phase was 1.1µg/L (Table 22). In both references, the aqueous phase had a concentration of about 1µg/L confirming that tin is not desorbed from the sediments due to the stirring.

The analysis of tin in the experiment 1 shows concentration in the aqueous phase varying from 7.8 to 190µg/L on the unfiltered water and from 6.5 to 210µg/L on the filtered water. Generally higher concentration of tin is observed in the non-filtrated samples with up to 42% of the tin in the dissolved phase where it may be in ionic and/or colloidal forms of tin (Table 22). One sample (Exp1.2) present a higher concentration of tin in the filtered sample than in the non-filtered explained by a high standard deviation for the filtered of 39µg/L, and for the non-filtered of 35µg/L. In experiment 2 and 1.5 and 1.6, the samples were also analyzed for tin in the aqueous phase. The concentrations of tin in the filtered samples vary from 27 to 370 µg/L.

All samples contain more tin in the aqueous phase than the two references. The presence of Fenton's reagent has an influence on its release. The influence of the concentration of the ratio H_2O_2:TOC and H_2O_2:Fe^{2+} is studied in Appendix 15. Appendix 15 shows that the release of tin into the aqueous phase is linearly influenced by the ratio H_2O_2:TOC. Appendix 16 illustrates the ratio H_2O_2:Fe^{2+} with the concentration of tin. Appendix 16 shows a decrease of the concentration of tin in the aqueous phase when the concentration of iron introduced is lower. Since higher tin concentration in the aqueous phase could be a good indicator of the degradation of OTC in the sediments, the existence of a relation between the concentration of tin in the aqueous phase and the degradation of OTC in the sediments is investigated but no relation between the OTC degradation and the tin concentration in the liquid was found. On the other hand, below 27 µg/L tin measured in the aqueous phase, the degradation of OTC in the sediments was very limited (Table 22, 23). An assumption was made after the first experiment: more tin measured in the water phase caused higher degradation of OTC in the sediments. This allowed to save time because the results of the analysis of OTC in the aqueous phase and sediments take minimum 4 weeks to be delivered.

During the first experiment, the analysis of OTC in the water were done only on two samples for the ratio H_2O_2:TOC equal to 5 (Exp1.2) and 0.2 (Exp1.4) corresponding to the higher and lower respectively concentrations of tin in the water and potential attributed to higher and lower degradation. Experiments (Exp1.6 and Exp1.7) were added to the investigation the optimum ratio of H_2O_2:TOC. The concentrations of OTC measured in the aqueous samples are presented in ng/L of tin in Figure 29.

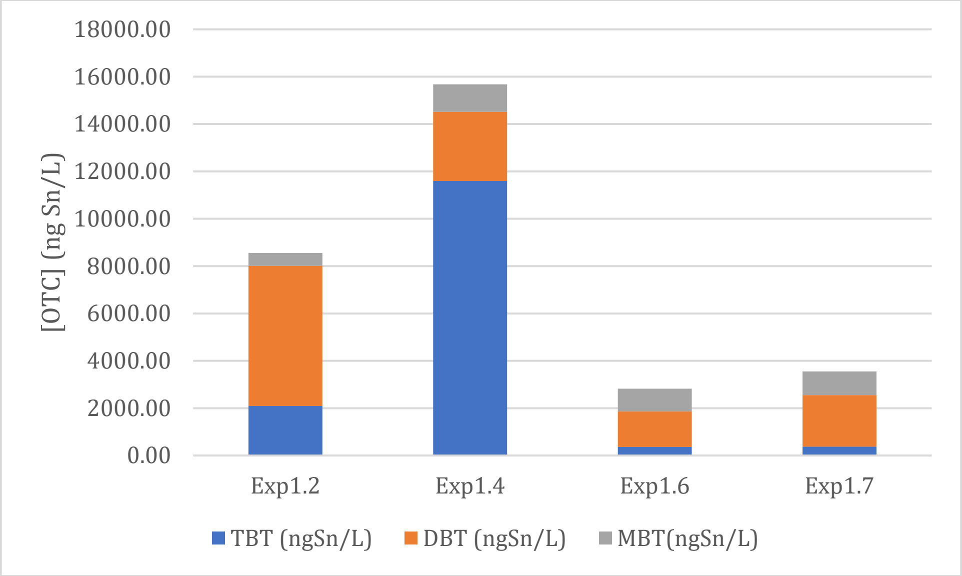


Figure 29. Concentration of OTC, TBT, DBT and MBT in the aqueous samples after 24 h of Fenton reaction in a slurry with polluted sediments

According to Figure 29, the concentration of total OTC is twice as high in the aqueous phase of 1.4 than in 1.2. In the experiment 1.2, the total of dissolved OTC was 8600 ng Sn/L and equal to 0.45% of the initial load of OTC in the spiked sediments before degradation. The concentration of dissolved OTC in 1.4 was equal to 16 000 ng Sn/L and correspond to 0.83% of the initial load of OTC. The concentration of OTC in the aqueous phase after the experiments 1.6 and 1.7 were lower than in Exp1.2 and Exp1.4. The major compound in these two experiments is DBT, similarly as in the Exp1.2. Then MBT > TBT. These results show better degradation of OTC in the sediments and less OTC are present in the aqueous phase.

The concentration of OTC compared to the concentration of tin measured in the aqueous phase are compared in the Appendix 17. The concentrations of OTC in 1.2, 1.6 and 1.7 were very low compared to the concentration of tin, it corresponds to 5%, 1% and 0.8% of the total tin dissolved in the aqueous phase, see Appendix 17. On the contrary, in 1.4 the concentration of OTC is like the concentration of tin meaning 100% of the tin is under organic form. The samples are not filtrated for the measurement of OTC, simply the presence of OTC could be due to its adsorption onto colloids. In order get a better idea of the repartition of OTC in the liquid, the particle size distribution was analyzed in each filtrated and non-filtrated sample. The results are not discussed but are presented in the Appendix 18.

4.2.2 Degradation in the sediments with different concentrations

The optimum ratios were determined in the previous part, thereafter the aim was to reproduce the same experiments under the same conditions but with different concentrations. In order to save time, the conditions that cause the highest concentrations of tin measured in the water were assumed to cause the best degradation of OTC in the sediments.

The ratio tested on spiked sediments, Medium sediments, and Original sediments were the following. One experiment was called Exp3 and used the same ratios as Exp1.2:

- H_2O_2:TOC = 5
- H_2O_2:Fe^{2+} = 5

Another experiment was called Exp4 :

- H_2O_2:TOC = 1
- H_2O_2:Fe^{2+} = 2

All the reports delivered by ALS for the analysis of the spiked, medium and original sediments after Fenton's degradation Experiment 3 are presented in Appendix 19. All the reports delivered by ALS for the analysis of the spiked, medium and original sediments after Fenton's degradation Experiment 4 are presented in Appendix 20.

4.2.2.1 *Reproduction of the experiment with spiked sediments*

In this part, the experiments were carried out on spiked sediments. The samples called Spiked 1 and Spiked 2 represent the initial spiked sediments, at different time. Sample Exp1.2 gave the best degradation (88%) in experiment 1 for the determination of the ratio H_2O_2:TOC. Sample Exp2.6 gave the highest concentration of tin measured in the aqueous phase (370 µg/L) supposed to cause the best degradation of OTC but gave 85% degradation. The Exp3.S correspond to the reproduction of Exp1.2. Exp4.S had the same ratio H_2O_2:Fe^{2+} = 2 but the ratio between H_2O_2:TOC was initially 5 in Exp2.6 and was changed to 1 in Exp4.S. The results of the degradations of Exp3.S and Exp4.S are presented and compared to Spiked1,Spiked2, Exp1.2 and Exp2.6 in Appendix 21, Figures 30 and 31.

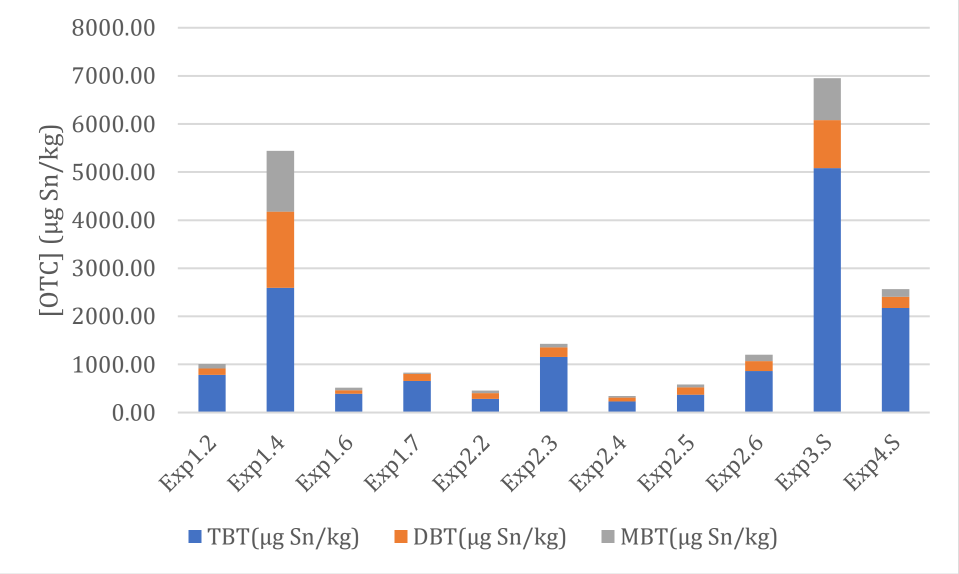


Figure 30. Concentration of OTC in all the degradation experiment carried with Fenton on the spiked sediments. Exp3.S and Exp1.2 : H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=5; Exp4.S: H_2O_2:TOC =1 H_2O_2:Fe^{2+}=2 and Exp2.6: H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=2.

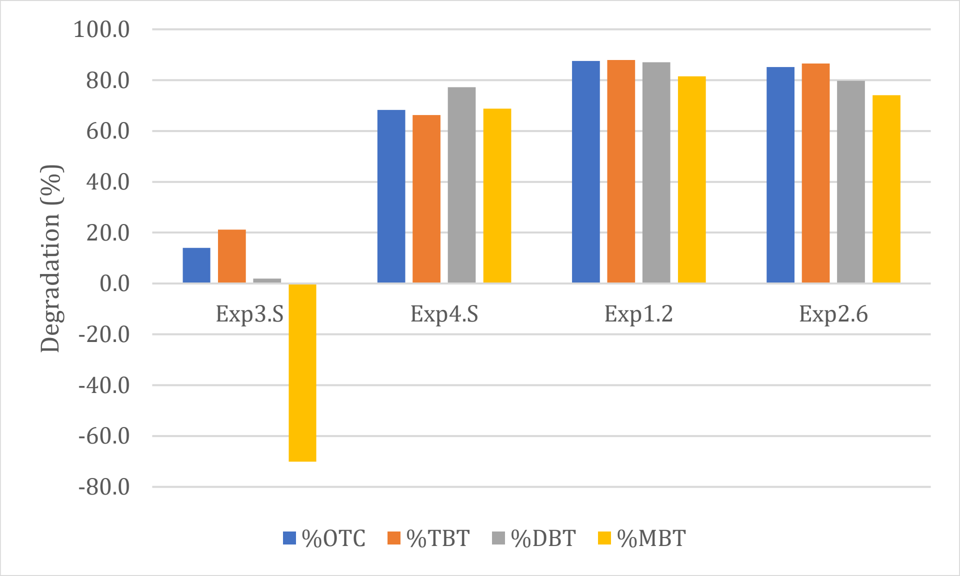


Figure 31. Degradation of OTC in the spiked sediments: Exp3.S and Exp1.2 : H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=5; Exp4.S: H_2O_2:TOC =1 H_2O_2:Fe^{2+}=2 and Exp2.6: H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=2.

For the Exp3.S, the reproduction of the experiment 1.2, the concentration of OTC is equal to the concentrations found in initial sediments Spiked 2. The concentration of TBT after the degradation was 5 times higher in Exp3.S, the DBT and MBT were 10 times higher and the total concentration of OTC 7 times higher than when the experiment was carried out the first time (Figure 30). Moreover, the degradation (Figure 31) is showing very low effect for OTC, TBT, DBT, and negative effect for MBT, compared to the previous experiment 1.2 showing 87.5% degradation of total OTC and similar degradation for TBT, DBT and 80% degradation of MBT. Another unexpected results is shown in the Figure 30, where the concentrations of OTC after the degradation with Exp1.2 show very low concentration, whereas the Exp3.S show the highest concentration of remaining OTC after the degradation, even higher than the worst degradation ever achieved (Exp1.4). Although, the percentage of OTC contained in the tin of the sediments is equal to 8.7% for the experiment 1.2 and for the experiment Exp3.S equal to 60%.
The two experiments using the parameters H_2O_2:TOC =5 H_2O_2:Fe^{2+}= 5 (Exp1.2 and Exp3.S) were performed about a month and a half later based on the same spiked sediments. It is possible that a degradation had occurred in the initial sediments, and the movement induced by sampling the spiked sediments for the experiments, are making the remaining OTC more difficult to degrade because more sorbed and trapped in the inner pores of the sediments (Flotron et al, 2005). Although, when the organic content of a soil is inferior to 5% the contaminants are mainly adsorbed into the micropores, and less available than when they are adsorbed onto the organic matter (Bogan and Trbovic, 2003).

Exp4.S was compared to Exp2.6 as a reference because the sediments are degraded with the same ratio H_2O_2:Fe^{2+}=2. The concentration of total OTC was two times higher than in Exp2.6, but there is less OTC than in Spiked1 and Spiked2. The concentration of TBT after degradation in Exp4.S was 2.5 times higher, DBT and MBT were present in the same concentration as Exp2.6 (Figure 30). Concerning the degradation, for Exp2.6, the degradation of total OTC was 85%, with a degradation of 87% of TBT, 80% of DBT and 74% of MBT. With Exp4.S, the degradation of OTC has diminished to 68% with degradation of 66% TBT, 77% of DBT and 69% of MBT. So, in conclusion, the degradation in Exp4.S has lowered OTC and TBT concentrations by 20% for while DBT and MBT remained unchanged (Figure 31). When compared with post-degradation OTC concentration on spiked sediments from other experiments, Exp4.S had the highest concentration (with the exceptions of Exp3.S and Exp1.4) (Figure 30). The experiment Exp4.S was performed 23 days after Exp2.6 and a change of the ratio H_2O_2:TOC was made explaining the differences between the results.

Lastly, the release of OTC in the aqueous phase is presented in Appendix 22, and the proportion of OTC compared to the concentration of tin in Appendix 23. A low concentration of OTC in the water is seen for both Exp3.S and Exp4 compared to all the other experiments performed on spiked sediments. The tin contained in the water is mainly composed by metallic tin and not organotin (Appendix 23).

In conclusion, both reproduced experiments Exp3.S and Exp4.S show a decrease in the effect of the OTC degradation. Nonetheless, the Exp4.S shows higher effect for the degradation of the OTC, with a ratio of H_2O_2:TOC = 1 and H_2O_2: Fe^{2+} = 2. These results highlight that the sediment specificity has high influence on the degradation of OTC. It also caused the necessity to reproduce more experiment to determine the potential of Fenton's reagent as an efficient way to degrade OTC. Moreover, if the experiment Exp2.4 was carried out again on older spiked sediments, would it still achieve an efficient degradation ?

4.2.2.2 *Reproduction on medium and original sediments*

The degradation experiments were reproduced on less polluted sediments: Medium1 ([OTC] = 1700 µg/kg) and Original1 ([OTC] = 81 µg/kg). These experiments help defining if the Fenton's reagent may provide enough degradation to get OTC under the thresholds.

Medium1 was the sample used for the degradation experiment Exp3.M and Exp4.M. The concentrations of OTC before and after degradation are presented in Appendix 24. The concentrations of OTC in both Exp3.M and Exp4.M were reduced compared to Medium1. In Exp3.M the degradation of OTC is equal to 94%, and the degradation of TBT is 95%, of DBT is 92% and of MBT is 94%. In Exp4.M the degradation of OTC was lower (86%) comprising the degradation of TBT (87%), DBT of 80 % and MBT of 85%. Even if the degradation of OTC was higher in Exp3.M, the results are similar, and both achieve a satisfying degradation of OTC. During the degradation some OTC were released in the aqueous phase and their concentration after degradation is presented in the Appendix 25. In Exp3.M, less OTC were released in the aqueous phase ([OTC] = 38 ng Sn/L) compare to Exp4.M ([OTC] = 1200 ng Sn/L). The main compound in the aqueous phase of Exp3.M was DBT and then MBT whereas TBT was present in very low concentration. This could be explained by a difference in the solubility of these compounds (2.1.1, Table 1).

Original 1 was used as initial sediments for the degradation of OTC using Fenton's reagent with two different ratios: Exp3.O and Exp4.O. The results of the concentrations of OTC before and after degradation experiments are presented in Appendix 26. After degradation in Exp3.O, the concentration of OTC was reduced to 25 µg Sn/Kg and in Exp4.O to 40 µg Sn/kg. The degradation of OTC, TBT, DBT and MBT for Exp3.O is equal to 70%, 93%, 36% and 15% respectively and in Exp4.O is equal to 50%, 91%, -0.9% and -58% respectively. Regarding the degradation percentage of each OTC it is evident that the experiment Exp3.O achieved the best reduction of OTC. The degradation of TBT in both cases was very high and reached 93% and 91%. On the other hand, the degradation of DBT and MBT was lower in Exp3.O and negative in Exp4.O. This is explained by a high degradation of TBT, producing DBT and MBT. Then there is high concentration of DBT and MBT and it is possible with these ratios that the reaction between iron Fe^{2+} and the hydroxyl radicals, especially when high concentration of iron is added such as in Exp4 where the ratios were H_2O_2:TOC=1 and H_2O_2:Fe^{2+}=2 (Neyens et al, 2003). It would be interesting in this case to investigate the degradation of OTC with the optimum ratio found for the degradation of OTC in the spiked sediments known as H_2O_2:TOC =5 and H_2O_2:Fe^{2+} = 15. In the aqueous phase the concentrations of tin were under the detection limit in both samples. The concentration of OTC measured in the aqueous phase is presented in Appendix 27. The concentration of OTC released from the sediments into the aqueous phase was higher in the case of Exp3.N, showing the best degradation of OTC in the sediments. The concentration of total OTC was equal to 8 ng/L whereas Exp4.N show 1.8ng/L exclusively composed by DBT released from the sediments.

Using [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 5; the OTC degradation was at first for the spiked sediments 88%, the second time 14%; then 94% for the medium sediments and 70% for the original sediments. The reproduction experiment exhibit different OTC removals for the same spiked sediments showing the non-reproducibility. The OTC removal is also different with the OTC concentration in the sediments. Using [H_2O_2:TOC] = 1; [H_2O_2:Fe^{2+}] = 2; the OTC degradation for the spiked sediments was 85%; then 86% for the medium sediments and 50% for the original sediments.

A lower concentration of OTC may imply a higher difficulty to degrade because more sorbed and trapped in the inner pores of the sediments (Flotron et al, 2005). Although, when the organic content of a soil is inferior to 5% the contaminants are mainly adsorbed into the micropores, and less available than when they are adsorbed onto the organic matter (Bogan and Trbovic, 2003).

4.3 Degradation of OTC in the marine sediments using electrochemistry

In total, 4 experiments have been carried out in order to determine good parameters to degrade the OTC in the sediments.

In addition, 3 experiments were carried in order to test the reproducibility with different concentrations.

Figure 32 and Figure 33 present the appearance of the slurry after electrochemical degradation (Electro4). The slurry is very foamy, and the particles do not settle down.

Figure 32. Appearance of the slurry after electrochemical degradation (Electro4)

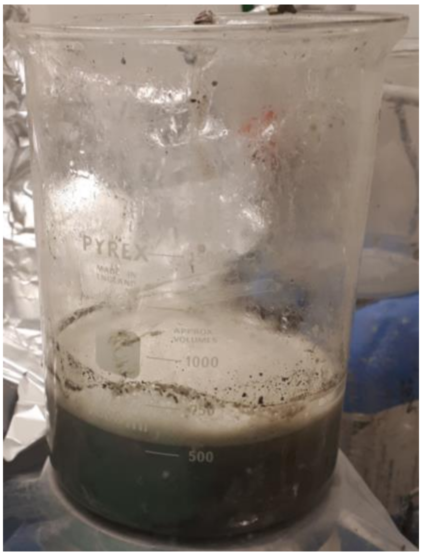


Figure 33. Appearance of the slurry after electrochemical degradation (Electro4)

All the reports delivered by ALS for the analysis of the spiked sediments after electrochemical degradation 1 are presented in Appendix 28; after electrochemical degradation 2 are presented in Appendix 29; after electrochemical degradation 3 are presented in Appendix 30; after electrochemical degradation 4 are presented in Appendix 31.

4.3.1 Degradation in spiked sediments

The results from the aqueous phase and the sediments phase are treated separately to simplify the interpretation of the results.

4.3.1.1 *Sediments phase*

The results from the experiments with electrochemistry are presented in Table 24 below.

Table 24. Results for the degradation experiments with electrochemistry

Sample name	**Initial**	**Electro 1**	**Electro 2**	**Electro 3**	**Electro 4**
Voltage (V)	/	5.0	5.0	15.0	21.0
Initial current (mA)	/	29	27	100	350
Final intensity (mA)	/	25	25	80	310
Current density (mA/cm²)	/	0.6	0.5	2.0	7.0
Time (h)	/	24	72	24	24
TOC %	2.0	2.2	5.2	2.4	2.1
Sn (mg/kg)	14.7	12.8	12.0	14.6	17.3
TBT(µg/kg)	24500	25000	22300	97	1
DBT(µg/kg)	2427	2410	2250	132	0.00
MBT(µg/kg)	726	2920	4560	19	0.00
Total OTC(µg Sn/kg)	117667	13445	133656	120	0.5
% Degradation OTC	0	0	0	99.0	99.999

According to the results presented in Table 24, the degradation of organotin reached 99.99% after 24h experiment with a current density of 7 mA/cm² used in experiment 4. Only 1.21µg/kg of TBT is detected in the sediments. This experiment is reproduced for spiked sediments, medium sediments and original sediments.

Experiment 3 shows 99% degradation with application of 2mA/cm² over 24h. These conditions show very high degradation of OTC as well and it would be interesting to reproduce it as well. This experiment compared to the experiment 4, would be more cost effective.

The experiment 1 and 2 led to no degradation with a current density of 0.6mA/cm², even after 72h.

Figure 34 present the repartition of OTC and their concentration, in the sediments after the degradation experiments.

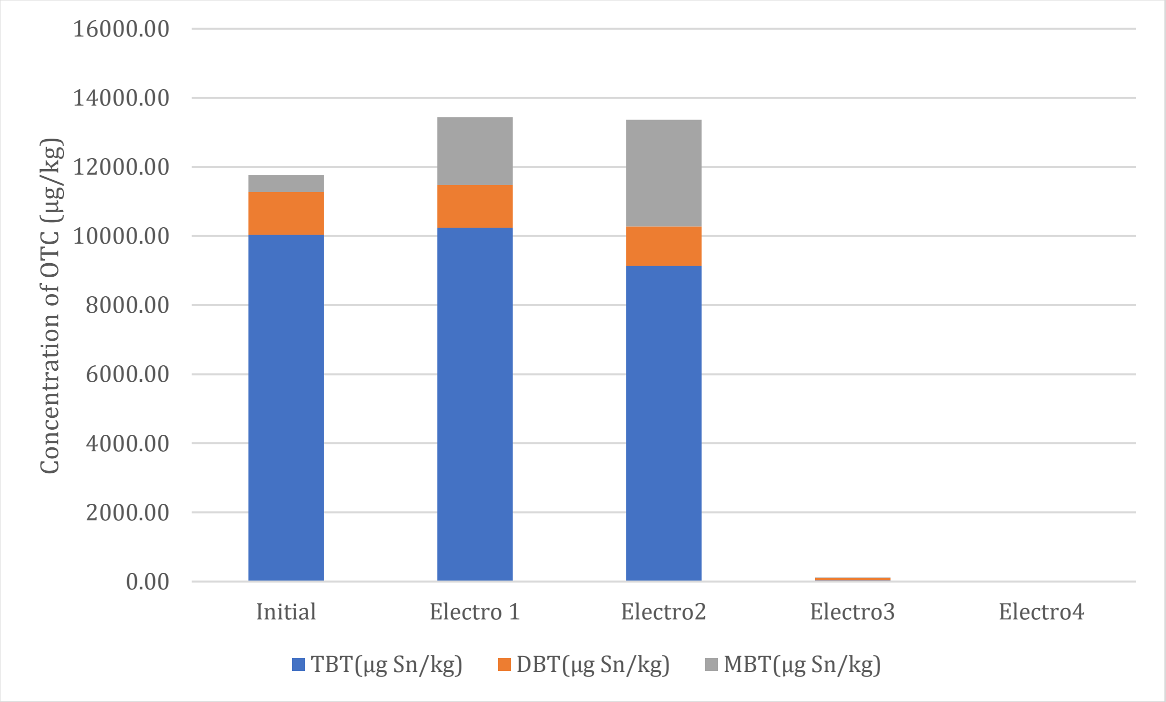


Figure 34. Repartition of OTC after degradation experiments with electrochemistry

Figure 34 shows in samples 1 and 2, a little degradation might have occurred because there is a higher concentration of MBT compare to the initial spiked sediments. In sample 3, there is higher concentration of DBT and MBT compared to the initial sediments revealing that a degradation has occurred and giving the confirmation that the degradation of TBT happens by debutylation. In sample 4, there is only a low concentration of TBT left. This TBT might be in extremely inaccessible pores of the sediments.

4.3.1.2 *Aqueous phase*

In Table 25, the results of the experiments with electrochemical degradation on the aqueous phase are presented.

Table 25. Concentration of tin and organotin in the aqueous phase after electrochemical degradation

Sample names	**Electro1**	**Electro2**	**Electro3**	**Electro4**
Voltage (V)	5.00	5.00	15.00	21.00
Initial Intensity (mA)	29.00	26.00	100.00	350.00
Current density (mA/cm²)	0.58	0.52	2.00	7.00
Filtration for Sn	No	No	Yes	Yes
Sn (µg/L)	3.03-4.82*	3.38 - 8.65*	79.3	17.4
TBT (ng/L)	2530	4850	42100	23100
DBT (ng/l)	692	1300	51900	25300
MBT (ng/L)	3250	4860	36200	23500
Total OTC (ng Sn/L)	3585	5933	68180	38247
% OTC	0.2	0.3	3.6	2.0

**For the tin analysis in the sample 1 and 2, the tin has been analyzed on filtrated media and on non-filtrated media. Blue color represents the results of the non-filtrated samples.*

In sample 1 and 2, the concentration of tin dissolved in the water is lower when the sample has been filtrated meaning that many particles stays in suspension even after centrifugation and could carry adsorbed OTC.

The TBT was analyzed on non-filtrated samples in order to have a better understanding of what would be the conditions in the case of an industrial process.

Something interesting here to highlight is that the concentration of OTC is much higher in sample 3 and 4 than in 1 and 2. Indeed the concentration of OTC dissolved in the water represent 3.6 to 6.9% and 2.0 to 3.9 % of the initial OTC in the initial spiked sediments for sample 3 and 4 respectively. These results are presented in the Figure 35.

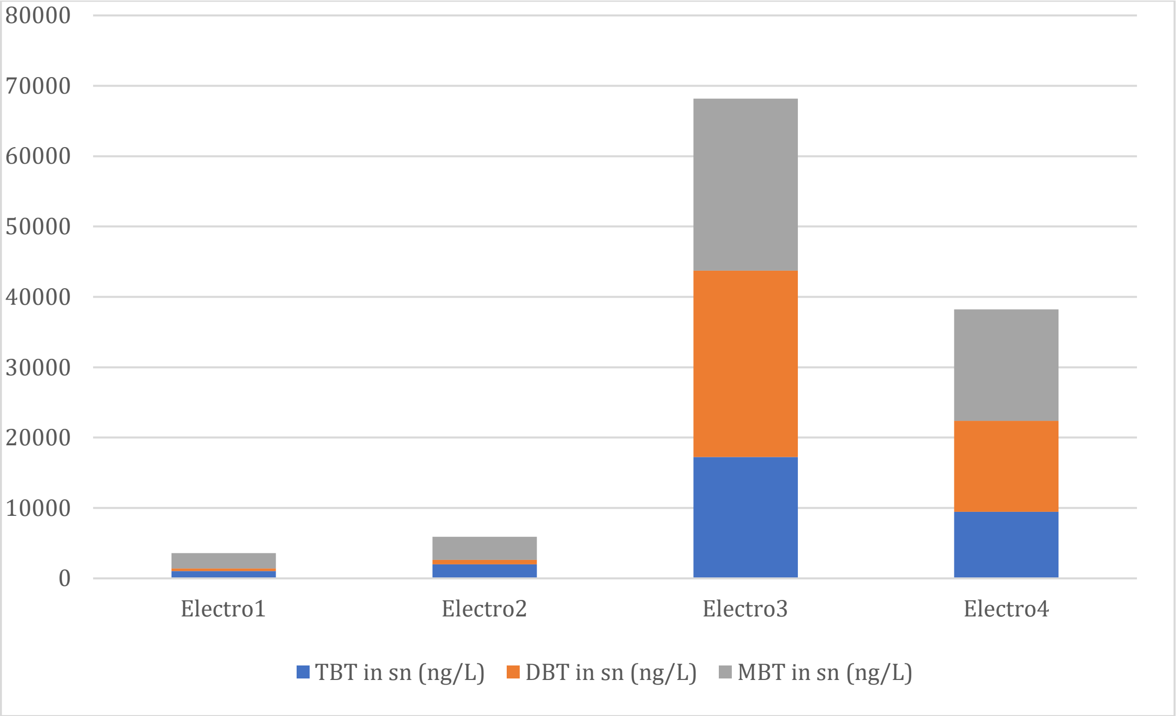


Figure 35. Repartition of OTC in the aqueous phase

According to Figure 35 and Table 25, it is evident that the concentration of OTC dissolved in the aqueous phase is much higher for sample 3 and 4 than for sample 1 and 2: there is more OTC dissolved in the aqueous phase when the degradation is very high in the sediments. A non-linear relationship between the concentration of OTC in the water and the degradation of OTC might be possible to establish with more experiments using different current densities.

In all samples, TBT is not the major component. It is either DBT or MBT. The degradation causes a desorption of OTC in the aqueous phase, or the DBT and MBT are more soluble in water than TBT that is why there is higher concentration of them dissolved. (2.1.1, Table 1) It is also possible the OTC are adsorbed onto colloids since the liquid phase was not filtrated before their analysis. In order to understand better, the forms of the OTC present in the liquid phase, the particle size distribution measurement is presented in Appendix 32 but is not discussed.

4.3.2 Degradation in the sediments with different concentrations

Reproduction of the experimental conditions of Electro4 have been carried on spiked, medium and original sediments. Some results are arrived but do not permit to assess the degradation of OTC. These results are thus not treated but presented in Appendix 33.

4.4 Metal analysis

The results of the metals analysis on the sediments are presented in the Appendix 34, the results of the metal analysis on the liquid phase are presented in the Appendix 35 after electrochemical degradation and in the Appendix 36 after Fenton's degradation.

On the sediments, the results show the concentrations of different metals in the sediments before and after degradation. All the concentrations of all metals are in the same range for all the samples at the exception of Ex4.N revealing high concentration of cobalt, copper and nickel. This samples reveal either a heterogeneity of the sediments or a problem in the measurement.

On the contrary (Appendix 35), in the liquid the comparison between Electro1, Electro2 with Electro3 and Electro4 shows a higher concentration of titanium, chromium, manganese, iron, cobalt, copper, zinc, cadmium, tin and lead. Using Fenton's reagent (Appendix 36), the same metals are leaching out from the sediments to the liquid phase.

5 Discussion

In this part the outcome and discussion are discussed separately for Fenton and Electrochemistry. In each part, the general outcome is presented, followed by the comparison of the best results obtained with the regulation in different countries. The safety and environmental issues are then discussed. Finally, the methods are compared and discussed together.

5.1 Fenton

The regulation applied on TBT and OTC in the dredged material or in the aqueous solution is compared with the concentration reached after the degradation using Fenton's reagent in Table 26 and Table 27. The different levels for the sediments are attributed according to the guidelines summarized in the document of Naturvårdsverket published in 2009. This document has already been presented in the 2.1.2, Table 2. The different levels for the aqueous phase are attributed according to the guidelines summarized in the 2.1.2, Table 4. In Table 26, the levels correspond to:

- Level 1: dumping of the sediments allowed without any restriction,
- Level 2: necessitate further ecotoxicological investigations to determine whether the sediments can be dumped or not.
- Level 3: the dumping of the sediments may not be possible.

The experiments used for the comparison with the guidelines in Table 26 and 27 are:

- Exp2.4: the best degradation of OTC and TBT achieved for the spiked sediments using Fenton's reagent. (H_2O_2:TOC=5 and H_2O_2:Fe^{2+}=15)
- Exp3.M and Exp4.M are the degradation carried on medium spiked sediments Medium1. (Exp3.M: H_2O_2:TOC=5 and H_2O_2:Fe^{2+}=5 and Exp4.M: H_2O_2:TOC=1 and H_2O_2:Fe^{2+}=2)
- Exp3.O and Exp4.O are the degradation carried on original sediments. (Exp3.O: H_2O_2:TOC=5 and H_2O_2:Fe^{2+}=5 and Exp4.O: H_2O_2:TOC=1 and H_2O_2:Fe^{2+}=2)

Table 26. Comparison of the results of OTC concentration in the sediments after degradation using Fenton's reagent with regulations in different countries

Country	Ex2.4	Exp3.M	Exp4.M	Exp3.O	Exp4.O
Belgium	Level 3	Level 3	Level 3	Level 2	Level 2
Denmark	Level 3	Level 2	Level 2	Level 1	Level 1
Finland (TBT+TPhT)	Level 3	Level 2	Level 2	Level 2	Level 2
Holland	Level 3	Level 2	Level 2	Level 2	Level 2
Ireland (TBT+DBT+MBT)	Level 2	Level 2	Level 2	Level 1	Level 1
Norway	Level 3	Level 2	Level 3	Level 1	Level 1
United Kingdom (TBT+DBT+MBT)	Level 2	Level 2	Level 2	Level 1	Level 1
Germany	Level 3	Level 3	Level 3	Level 1	Level 1
Sweden	Non sensitive use	Sensitive use	Non sensitive use	Sensitive use	Sensitive use

According to Table 26 and the guidelines for concentration of OTC or TBT in the sediments presented in 2.1.2, Table 2:

- Exp2.4: the best degradation achieved using Fenton's reagent on the spiked sediments would not be accepted for dumping in 6 out of 9 countries. These sediments would require another management. In United Kingdom and Ireland, these sediments would require further ecotoxicological investigations to determine whether they can be dumped or not. In Sweden, these sediments could be reused for non-sensitive usage.
- Exp3.M and Exp4.M: the medium spiked sediments after degradation in experiment 3 would require further ecotoxicological investigations in 6 countries out of 9, the dumping would not be accepted in Belgium and Germany. On the contrary, in Sweden these sediments could be reuse for a sensitive usage. In experiment Exp4.M, in 5 countries out of 9 the sediments require further ecotoxicological investigations. In Belgium, Norway and Germany the dumping may not be possible. In Sweden, the sediments could be reuse for non-sensitive usage.
- Exp3.N and Exp4.N: the original sediments in both case after degradation using Fenton's reagent, the dumping would be allowed without any restriction or further experiments in 5 countries out of 9. In Belgium, Finland and Netherland, the sediments would require further ecotoxicological investigations. In Sweden both could be reuse in the case of sensitive usage.

According to the legislation, the spiked sediments and medium sediments would need either further ecotoxicological investigations or it would not be possible to dump them. These sediments require therefore a more powerful degradation.

In the case of the real-life sediments, the concentrations achieved after degradation are acceptable in a legislative point of view. In 3 countries, there is a need for further ecotoxicological investigations, but in other countries the remediation of TBT and OTC is enough to dump them without any restrictions.

Table 27. Comparison of the results of OTC concentration in the aqueous phase after degradation using Fenton's reagent with regulations in different countries

Country	Exp1.6	Exp3.M	Exp4.M	Exp3.O	Exp4.O
Canada	Higher	Higher	Higher	Lower	Lower
Australia & NZ	Higher	Lower	Higher	Lower	Lower

According to Table 27 and the guidelines for concentration of OTC or TBT in the water presented in 2.1.2, Table 4:

- the OTC or TBT concentration released in the aqueous phase using Fenton's reagent shows in the Exp1.6 and using medium spiked sediments, the concentration of OTC and TBT are too high and would cause major disturbance of the aquatic environment. The release of this aqueous phase would not be allowed and would need further treatments.
- The OTC or TBT concentration released in the aqueous phase using Fenton's reagent shows using original sediments as a base for the degradation is acceptable because the concentration measured are below the guidelines. These concentrations should thus not disturb too much the aquatic ecosystem.

In conclusion, Fenton's reagent cannot achieve good enough degradation in sediments and in aqueous phase for spiked sediments. On the contrary, Fenton's reagent can be adapted to the degradation of low concentrated sediments: the original sediments.

The required amount of reactant for treating OTC contaminated sediments with different ratios and linked to the degradation of OTC reached is presented in Table 28 below.

According to Sigma Aldrich, the cost of hydrogen peroxide 30% is 56 SEK/L. In one liter of 30% hydrogen peroxide there is 8.84M corresponding to 300.56g. The cost of ferrous sulfate heptahydrate is 66 SEK/kg, it contains 3.06M Fe^{2+}, leading to the content of 198g Fe^{2+} per kilogram. In green are highlighted the experiments leading to the best degradation. In yellow are highlighted the conditions reproduced onto spiked and original sediments.

Table 28. Quantity of reactants for treating OTC contaminated sediments using Fenton's reagent

Corresponding experiment	**Ratio H_2O_2:TOC**	**Ratio H_2O_2:Fe^{2+}**	**H_2O_2 (g/kg)**	**Fe^{2+} (g/kg)**	**OTC (%)**	**"+/-"**	**Cost (SEK/kg)**
Exp1.4	0.2	5	14.2	4.6	32.7	21.1	0
Exp1.2	5	5	354.9	114.5	87.5	3.9	4
Exp1.6	7	5	495.1	161.6	93.6	2.0	21
Exp1.7	9	5	637.5	206.3	89.7	3.2	104
Exp2.2	5	40	354.9	14.3	94.3	1.8	146
Exp2.3	5	20	354.9	28.6	82.4	5.5	188
Exp2.4	5	15	354.9	38.2	95.8	1.3	71
Exp2.5	5	10	354.9	57.4	92.8	2.3	76
Exp2.6	5	2	354.9	287.0	85.1	4.7	79

The two ratios tested for Exp1.2 and Exp2.6 were for the first experiments achieving an acceptable degradation of OTC. When it was reproduced on spiked, medium and natural sediments, the degradation achieved was not very efficient on the spiked sediments and natural sediments but acceptable for the medium sediments.

The cost of the degradation is important to take into consideration. The choice of the optimum ratio would be orientated towards the experiment Exp2.2 or 2.4 (in green in Table 28) allowing a higher degradation of the OTC in the spiked sediments for a lower price: 146 SEK/kg and 71 SEK/kg. This price is high for an industrial scale application. But this price may be lowered by ordering large quantities of reactants.

5.2 Electrochemistry

The regulation of TBT or OTC in the dredged material or in the aqueous solution is compared with the concentration reached after the degradation using electrochemistry in Table 29 and Table 31. The different levels for the sediments are attributed according to the guidelines summarized in the document of Naturvårdsverket published in 2009. This document has already been presented in the 2.1.2, Table 2. The different levels for the aqueous phase are attributed according to the guidelines summarized in the 2.1.2, Table 4. In Table 29, the levels correspond to:

- Level 1: dumping of the sediments allowed without any restriction,
- Level 2: necessitate further ecotoxicological investigations to determine whether the sediments can be dumped or not.
- Level 3: the dumping of the sediments may not be possible.

The experiments used for the comparison with the guidelines in Table 29 and 30 are:

- Electro3: 24h experiment using 100 mA, 15 V achieving a degradation of 99.0% of OTC.
- Electro4: 24h experiment using 350 mA, 21 V achieving a degradation of 99.99% of OTC.

Table 29. Comparison of the results of OTC concentration in the sediments after degradation using Electrochemistry with regulations in different countries

Country	Electro 3	Electro 4
Belgium	Level 3	Level 1
Denmark	Level 2	Level 1
Finland (TBT+TPhT)	Level 2	Level 1
Holland	Level 2	Level 2
Ireland (TBT+DBT+MBT)	Level 2	Level 1
Norway	Level 2	Level 1
United Kingdom (TBT+DBT+MBT)	Level 2	Level 1
Germany	Level 2	Level 1
Sweden	Sensitive use	Sensitive use

According to Table 29 and the guidelines for concentration of OTC or TBT in the sediments presented in 2.1.2, Table 2:

- The spiked sediments after Electro 3 would need in 7 countries out of 9 further ecotoxicological investigations to determine if the dumping is possible. In Belgium, the dumping may not be allowed and in Sweden these sediments could be reuse for sensitive usage.
- The spiked sediments after Electro4 would be allowed to be dumped without any restriction in 8 countries out of 9. In Netherland, these sediments would require further ecotoxicological investigations. In Sweden these sediments could be reuse for sensitive usage.

Table 30. Comparison of the results of OTC concentration in the aqueous phase after degradation using Electrochemistry with regulations in different countries

Country	Electro 3	Electro 4
Canada	Higher	Higher
Australia & NZ	Higher	Higher

According to Table 30 and the guidelines for concentration of OTC or TBT in the water presented in 2.1.2, Table 4:

- The aqueous phase from Electro3 and Electro4 present too high concentrations of TBT for being released without further treatment. It would cause otherwise severe damage of the aquatic ecosystem.

In conclusion, the sediments of Electro3 need further ecotoxicological experiments to determine whether they could be dumped or not. In some countries these sediments would not be allowed to be dumped and would thus need further degradation experiment in order to ensure a great management. All the other sediments can be dumped without any restrictions or in the case of the Netherlands requiring additional ecotoxicological experiments. On the other hand, the OTC are released in the aqueous phase in too high concentration after degradation with all parameters tested at the exception of Electro4.O.

In the case of Electro3, both sediments and aqueous phase do not meet the guidelines.

In the case of Electro4, the sediments do meet the guidelines and could be dumped without any restrictions except in the Netherland. On the contrary, the TBT contained in the aqueous phase need to be degraded to ensure limited damages on the aquatic ecosystem.

According to the website Costtotravel.com, the price for 1kWh in Gothenburg is equal to 2.168 SEK. In the calculation of the cost, only the electricity consumption is considered. The cost calculation is based on the electricity consumption for the degradation of OTC for 80g of sediments. Then the cost is calculated with the electricity consumption for the remediation of 1kg of sediments.

Table 31. Electricity consumption and cost per kilogram of contaminated sediments

Sample name	**Voltage (V)**	**Initial intensity (mA)**	**Current density (mA/cm²)**	**Electric consumption (kWh/kg)**	**Degradation of OTC after 24h**	**Cost 24h (SEK/kg)**	**Cost 72h (SEK/kg)**
Electro3	15.00	100.00	2.00	1.9×10^{-2}	99.0	0.1	2.9
Electro4	21.00	350.00	7.00	9.2×10^{-2}	99.999	4.8	14.3

According to Table 31, the electric consumption for the remediation of one kilogram of sediments with Electro 3 is 5 times lower than using the parameters of Electro4 although the degradation of OTC is higher with Electro4. Using Electro3 parameters over 72hours would remain cheaper than using Electro 4 for 24hours.

The parameters used with Electro3 could achieve 99.0% degradation of OTC in the spiked sediments in 24hours (Table 31), maybe applying these parameters for longer time would permit to reach similar degradation of OTC than Electro4 and permit to considerably reduce the costs.

In the cost calculations, the cost of the electrodes has not been calculated. The cost of maintenance, changing conductors' pieces has not been calculated. One drawback of the industrial application of electrochemistry is the need to change the electrodes often, or install a sacrificial anode (Reddy & Cameselle, 2009). The electrodes, especially the anode in Nb/BDD could not be used at industrial scale because of high prices. According to Reddy & Cameselle (2009), the electrokinetic treatment of organic contaminated soil is roughly equal in cost to some thermal technologies but with innovations and further studies the price should drop.

5.3 Choice of the best method

Fenton's reagent achieves good degradation but present inconvenients such as requiring qualified technicians, being non-reproducible with different concentrations of OTC in the sediments. It is thus difficult to ensure the admissions of the sediments in deposit sites after the degradation using Fenton's. In addition, Fenton's reagent present safety issues especially because of the creation of oxidant solution. When hydrogen peroxide is added the creation of fume is also an aspect to manage with at industrial scale. Classic Fenton's reagent occurs preferably in an acidic media. The reaction requires the usage of sulfuric acid nonetheless the buffering capacity of the sediments can be high (Masi, 2016) requiring high concentration to introduce. Using acid add safety issues increases risks for the workers. Moreover, using non recoverable reactant is costly. Using Fenton's reagent requires iron, having a negative environmental impact, such as high CO_2 emissions due to mining, and transport (Dudka & Adriano, 1997) in addition to be a pollutant as well when it is introduced in large concentration. There are examples of severe damage on the ecosystems caused by the release of bauxite, a by-product of the mining of iron such as in Ajka, Hungary (Winkler, 2013). Fenton's reagent increases the production of sludge and thus would result to have additional sediment management costs (Pignatello et al, 2006). If this technique is chosen for the remediation of contaminated sediments with OTC, it would be more interesting to carry it at the sediment's natural pH using iron contained in a solid catalyst (Tian et al, 2011). In this way, the iron is trapped and reduces the potential toxicity of the sediments after treatment because of iron. Another option is the photo-assisted decomposition of hydrogen peroxide, as done in Brosillon et al in 2016, for achieving higher degradation of TBT. Lastly, sulfates ions are present in seawater in high concentration and could interfere with the Fenton reaction (Pignatello et al, 2006).

Electrochemistry achieves a very good remediation of OTC in the sediments, with numerous advantages. No reactant is needed reducing considerably the cost of the experiment and no toxicity can be induced by using electrochemical remediation at the exception of the creation of by-products of degradation. The only safety issue is the usage of electricity which can be dangerous if not well managed. Another aspect to consider is the corrosion of the electrodes reported, inducing a need to change them often. The use of cheaper electrodes for the remediation should be investigated. Something important to mention once again, is the presence of OTC in the aqueous phase. Further experiments necessitate to be done to evaluate if the degradation require longer time, or if another method should be used on the OTC in the aqueous phase. Maybe instead of applying electricity in a slurry, it could work better applying it in the wet sediments directly. Electrochemistry offers as the well the possibility of recovering metals and to do the treatment of hot-spots of pollution in-situ when there is no dredging need. Thus, the cost for the dredging of the sediments and transport is avoided.

In conclusion, electrochemistry offers more advantages, is more cost effective, safe for workers and environment and is more efficient for the degradation of OTC compared to Fenton's reagent. Electrochemistry seems promising for the industrial application of OTC remediation in marine sediments.

6 Conclusion

The degradation of TBT and its metabolites (i.e. DBT and MBT) was investigated using classic Fenton's reagent and electrochemical remediation.

The results achieved with Fenton's reagent showedthe best OTC degradation of 96% using [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 15 over 24h on the most concentrated spiked sediments(6800 – 11200 µg/kg OTC. The remediation cost associated to these conditions is 79 SEK/kg. Experiments were reproduced on the three types of sediments using [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 5 and [H_2O_2:TOC] = 1; [H_2O_2:Fe^{2+}] = 2. These parameters were determined according to a relation found after the first step; the determination of the ratio [H_2O_2:TOC]. With a higher concentration of tin leached out in the liquid, the resulting degradation of OTC was higher. The only correlation found was when dissolved tin was <30 µg/L and then the degradation of OTC was limited. Using [H_2O_2:TOC] = 5; [H_2O_2:Fe^{2+}] = 5; the OTC degradation was at first for the most concentrated spiked sediments 88%, the second time 14%; and 94% for the less concentrated spiked sediments (1700 µg/kg OTC) and 70% for the original sediments (80 µg/kg OTC). The reproduced experiments exhibit different OTC removal for the same spiked sediments showing the non-reproducibility. The OTC removal was also different with varying OTC concentration in the sediments. All spiked sediments still contained high concentrations of OTC and would still not be allowed to be dumped at all or need further ecotoxicological investigations. The resulting OTC concentration in the original sediments after degradation would permit to dump the sediments at a deep-sea storage site without any restriction in 5 out of 8 countries. The liquid from the spiked sediments could not be released without additional treatment whereas it could be released without for the original sediments.

Electrochemical remediation achieved an OTC degradation of 99.999% on spiked sediments containing 6800–11200 µg/kg OTC over 24h at room temperature protected from UV-light using Nb/BDD electrode at the anode and titanium at the cathode with a current density was 7 mA/cm². The electricity consumption was 0.092 kWh/kg corresponding to a cost of 4.8 SEK/kg. The resulting sediments could be dumped at a deep-sea storage site without restrictions in 7 out of 8 countries whereas the resulting liquid could not be discharged without further treatment. Another electrochemical experiment reached an OTC removal of 99% on spiked sediments containing 6800–11200 µg/kg OTC over 24h with a current density of 2mA/cm². The electricity consumption was 0.019 kWh/kg corresponding to a cost of 0.1 SEK/kg. The resulting sediments need further ecotoxicological investigation to determine if the dumping is allowed whereas the resulting liquid could not be discharged without further treatment. In both cases, 24hours reaction was not enough to degrade all OTC. With elongation of the degradation time, the concentration of OTC may be reduced to reach the quality guidelines in both water and sediments.

With safety issues, high concentration of iron added, higher remediation cost, additional sludge production, non-reproducibility of the experiment with a need for qualified worker for achieving lower OTC degradation, classic Fenton's reagent offers many disadvantages compared to the efficiency and cost effectivity of the electrochemical remediation. In conclusion, electrochemistry seems promising for industrial application of OTC remediation in marine sediments.

Nevertheless, even if classic Fenton's demonstrated weaknesses, it could still be interesting to investigate modified Fenton's reagent. Using heterogenous catalysis as an example could be promising because the experiment could be carried out at natural pH with iron is trapped into a solid catalyst, thus recoverable. This solution would decrease the price of the remediation and limit iron to be found in the sediments . Photo-assisted Fenton's would also decrease the need of iron and improve the OTC degradation.

In order to confirm the applicability of the electrochemical remediation to sediments from the port of Gothenburg, experimentation on different concentration in the sediments needs to be done and the reproducibility of the experiments needs to be investigated. Experiments over a longer period should be carried out to determine if the liquid would pass the water quality guideline. If not, Fenton's reagent as an example could be applied. For a future industrial scale application another issue is to be solved, the high price of the electrodes used for the degradation and other cheaper electrodes should be tested. Other electrodes then the one used in this study could also potentially accomplish metal removal meanwhile the OTC degradation is achieved in the sediments.

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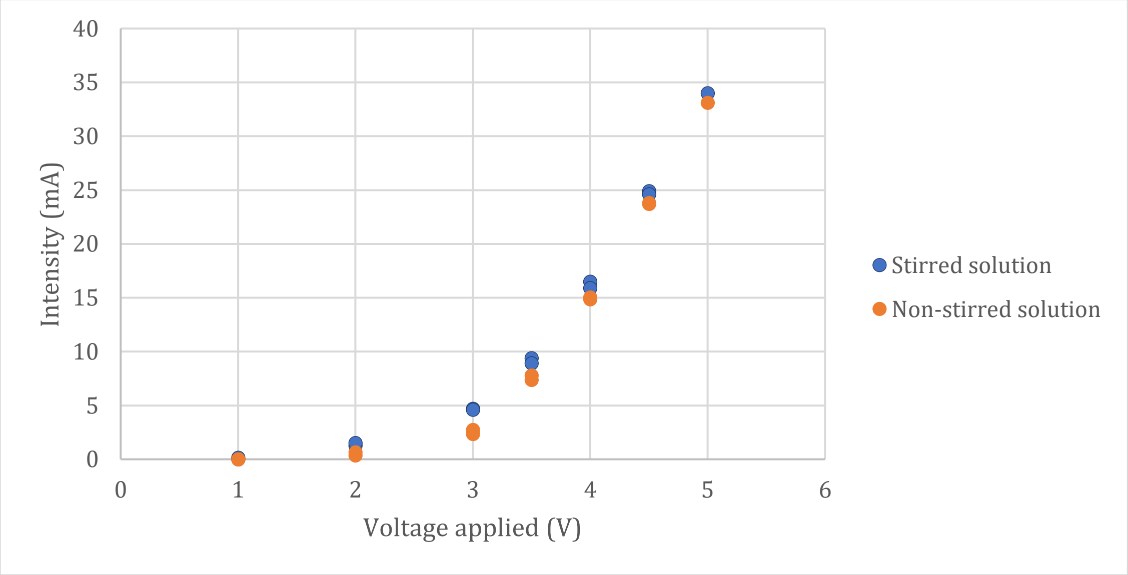
8 Appendix

Appendix 1. Setup of the electrochemical remediation experiment

The two electrodes of Nb/BDD and Ti were the same size and placed 10 cm from each other in a 2 L beaker, with 500 mL of Milli-Q water and 80 g of dry natural sediments. Then current was applied at the cathode with a potentiostat. The current applied varied between 0 and 5 V. The resulting intensity was measured between the two electrodes.

Applied current (V)	**Intensity measured (stirred) (mA)**	**Intensity measured (non-stirred) (mA)**
1	0	0
2	1.28	0.66
3	4.7	2.73
3.5	9.4	7.77
4	16.5	15.02
4.5	24.9	23.8
5	34	33.1
4.5	24.6	23.7
4	15.9	14.84
3.5	8.9	7.37
3	4.6	2.34
2	1.5	0.34
1	0	0



Appendix 2. Metal analysis - Original sediments

ELEMENT	SAMPLE	A01	A10	A40	Average
TS	%	54.2	51.1	50.6	52.0
As	mg/kg TS	4.56	4.71	4.37	4.5
Ba	mg/kg TS	57.3	72.7	65.1	65.0
Cd	mg/kg TS	0.316	0.253	0.257	0.3
Co	mg/kg TS	7.51	7.55	7.53	7.5
Cr	mg/kg TS	29.9	31.8	30.1	30.6
Cu	mg/kg TS	38.5	29.5	29.2	32.4
Hg	mg/kg TS	0.222	<0.2	<0.2	0.2
Ni	mg/kg TS	14.6	14.3	14.1	14.3
Pb	mg/kg TS	25.3	23	23.5	23.9
V	mg/kg TS	37.1	41.1	39.4	39.2
Zn	mg/kg TS	137	118	120	125.0
Ag	mg/kg TS	0.171	0.159	0.17	0.2
Mo	mg/kg TS	1.93	1.75	1.64	1.8
Sb	mg/kg TS	0.563	0.49	0.525	0.5
Sn	mg/kg TS	3.55	2.99	3.26	3.3

Appendix 3. Metal analysis - Original sediments

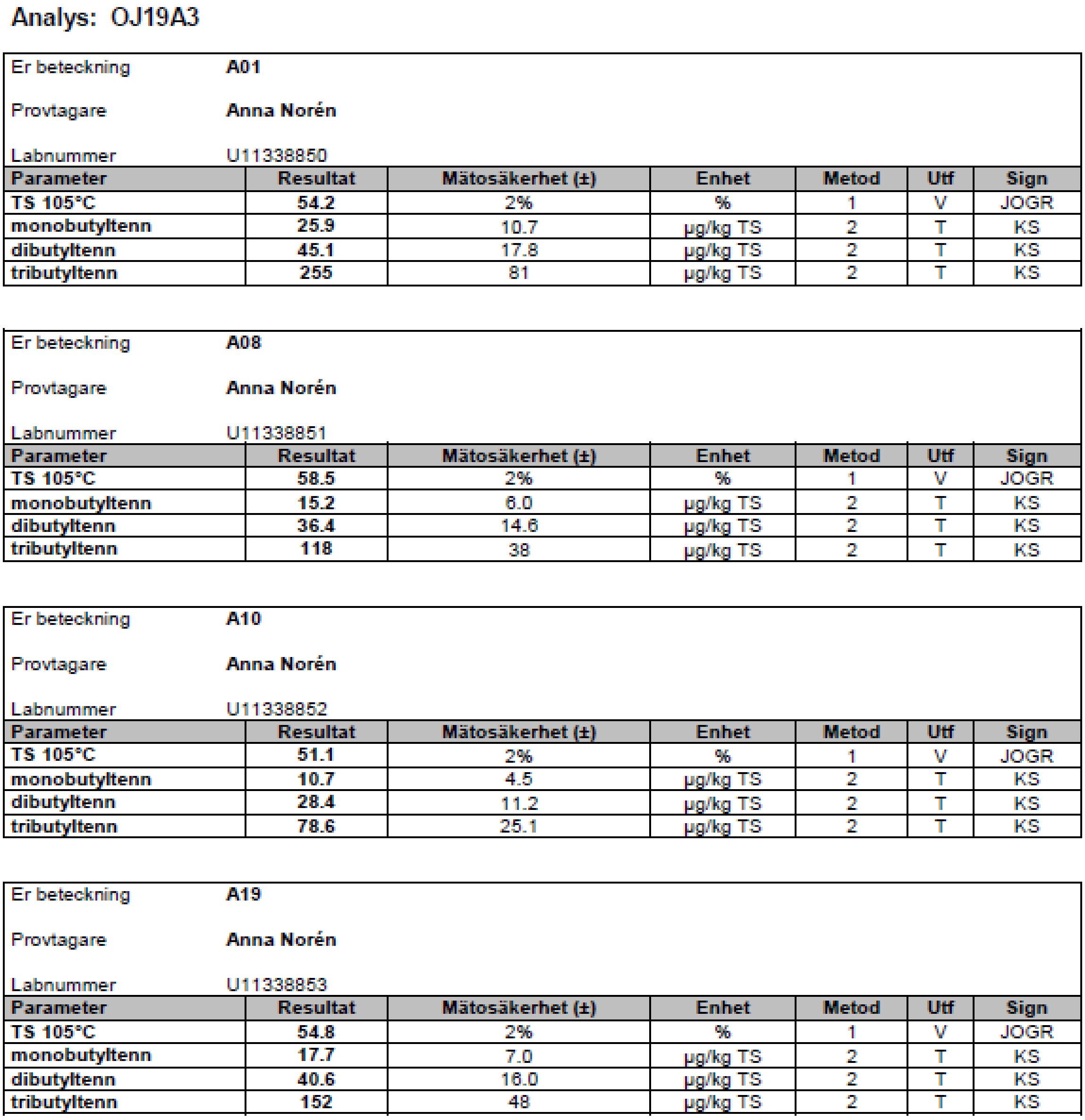
Metal	**Concentration (mg/kg TS)**	***Metal***	**Concentration (mg/kg TS)**
Ag	0,152	*Mg*	6340
Al	15400	*Mn*	303
As	5,69	*Mo*	2,15
B	25,6	*Na*	8390
Ba	58	*Ni*	15,7
Be	0,899	*P*	671
Ca	4910	*Pb*	25,4
Cd	0,278	*S*	6340
Co	7,58	*Sb*	0,523
Cr	30,4	*Se*	<5
Cu	32,2	*Sn*	3,17
Fe	22000	*Sr*	40,8
Hg	0,277	*V*	45,7
K	5240	*Zn*	129
Li	20,4	*Mg*	6340

Appendix 4. Grain size distribution – Original sediments

Table 32 Grain size fraction (%) for sediments sampled at depth 0-5 and 20-30 cm

Sample depth	**0-5cm**	**20-30 cm**
Grain size fraction	(%)	(%)
6.0 < x < 20.0 mm	<1	<1
2.0 < x < 6.0 mm	<1	<1
0.6 < x < 2.0 mm	<1	<1
0.2 < x < 0.6 mm	1	2
0.06 < x < 0.2 mm	48	26
0.02 < x < 0.06 mm	12	30
0.006 < x < 0.02 mm	10	13
0.002 < x < 0.006 mm	8	8
< 0.002 mm	21	21
< 0.06 mm	51	72

Appendix 5. Reports delivered by ALS for the analysis - Original sediments



Analys: OJ19A3

Er beteckning **A01**

Provtagare **Anna Norén**

Labnummer U11338850

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**54.2**	2%	%	1	V	JOGR
monobutyltenn	**25.9**	10.7	µg/kg TS	2	T	KS
dibutyltenn	**45.1**	17.8	µg/kg TS	2	T	KS
tributyltenn	**255**	81	µg/kg TS	2	T	KS

Er beteckning **A08**

Provtagare **Anna Norén**

Labnummer U11338851

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**58.5**	2%	%	1	V	JOGR
monobutyltenn	**15.2**	6.0	µg/kg TS	2	T	KS
dibutyltenn	**36.4**	14.6	µg/kg TS	2	T	KS
tributyltenn	**118**	38	µg/kg TS	2	T	KS

Er beteckning **A10**

Provtagare **Anna Norén**

Labnummer U11338852

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**51.1**	2%	%	1	V	JOGR
monobutyltenn	**10.7**	4.5	µg/kg TS	2	T	KS
dibutyltenn	**28.4**	11.2	µg/kg TS	2	T	KS
tributyltenn	**78.6**	25.1	µg/kg TS	2	T	KS

Er beteckning **A19**

Provtagare **Anna Norén**

Labnummer U11338853

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**54.8**	2%	%	1	V	JOGR
monobutyltenn	**17.7**	7.0	µg/kg TS	2	T	KS
dibutyltenn	**40.6**	16.0	µg/kg TS	2	T	KS
tributyltenn	**152**	48	µg/kg TS	2	T	KS

Er beteckning **A26**

Provtagare **Anna Norén**

Labnummer U11338854

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**54.1**	2%	%	1	V	JOGR
monobutyltenn	**14.2**	5.6	µg/kg TS	2	T	KS
dibutyltenn	**43.1**	17.1	µg/kg TS	2	T	KS
tributyltenn	**136**	43	µg/kg TS	2	T	KS

Er beteckning **A33**

Provtagare **Anna Norén**

Labnummer U11338855

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**59.5**	2%	%	1	V	JOGR
monobutyltenn	**10.9**	4.3	µg/kg TS	2	T	KS
dibutyltenn	**19.9**	8.0	µg/kg TS	2	T	KS
tributyltenn	**73.3**	23.5	µg/kg TS	2	T	KS

Er beteckning **A40**

Provtagare **Anna Norén**

Labnummer U11338856

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**50.6**	2%	%	1	V	JOGR
monobutyltenn	**21.9**	8.9	µg/kg TS	2	T	KS
dibutyltenn	**28.7**	11.4	µg/kg TS	2	T	KS
tributyltenn	**92.2**	29.7	µg/kg TS	2	T	KS

Analys: MAR-S

Er beteckning	**A08**
Provtagare	**Anna Norén**
Labnummer	U11338846

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	PECA
TS	58.5	2%	%	2	V	JOGR
Sn	3.12	0.97	mg/kg TS	3	H	NATO
TOC	2.21		% TS	4	1	SH

Er beteckning	**A19**
Provtagare	**Anna Norén**
Labnummer	U11338847

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	PECA
TS	54.8	2%	%	2	V	JOGR
Sn	3.05	0.95	mg/kg TS	3	H	NATO

Er beteckning	**A26**
Provtagare	**Anna Norén**
Labnummer	U11338848

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	PECA
TS	54.1	2%	%	2	V	JOGR
Sn	2.84	0.89	mg/kg TS	3	H	NATO

Er beteckning	**A33**
Provtagare	**Anna Norén**
Labnummer	U11338849

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	PECA
TS	59.5	2%	%	2	V	JOGR
Sn	2.70	0.84	mg/kg TS	3	H	NATO
TOC	2.02		% TS	4	1	SH

Analys: M-KM1-S

Er beteckning	**A01**
Provtagare	**Anna Norén**
Labnummer	U11338843

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	PECA
TS	54.2	2%	%	2	V	JOGR
As	4.56	0.95	mg/kg TS	3	H	NATO
Ba	57.3	14.6	mg/kg TS	3	H	NATO
Cd	0.316	0.065	mg/kg TS	3	H	NATO
Co	7.51	1.54	mg/kg TS	3	H	NATO
Cr	29.9	6.1	mg/kg TS	3	H	NATO
Cu	38.5	8.2	mg/kg TS	3	H	NATO
Hg	0.222	0.074	mg/kg TS	3	H	NATO
Ni	14.6	2.9	mg/kg TS	3	H	NATO
Pb	25.3	6.0	mg/kg TS	3	H	NATO
V	37.1	7.6	mg/kg TS	3	H	NATO
Zn	137	29	mg/kg TS	3	H	NATO
Ag	0.171	0.049	mg/kg TS	4	H	NATO
Mo	1.93	0.39	mg/kg TS	4	H	NATO
Sb	0.563	0.157	mg/kg TS	4	H	NATO
Sn	3.55	0.67	mg/kg TS	4	H	NATO

Er beteckning **A10**

Provtagare **Anna Norén**

Labnummer U11338844

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**51.1**	2%	%	2	V	JOGR
As	**4.71**	0.97	mg/kg TS	3	H	NATO
Ba	**72.7**	18.5	mg/kg TS	3	H	NATO
Cd	**0.253**	0.049	mg/kg TS	3	H	NATO
Co	**7.55**	1.56	mg/kg TS	3	H	NATO
Cr	**31.8**	6.5	mg/kg TS	3	H	NATO
Cu	**29.5**	6.3	mg/kg TS	3	H	NATO
Hg	**<0.2**		mg/kg TS	3	H	NATO
Ni	**14.3**	3.0	mg/kg TS	3	H	NATO
Pb	**23.0**	5.4	mg/kg TS	3	H	NATO
V	**41.1**	8.4	mg/kg TS	3	H	NATO
Zn	**118**	25	mg/kg TS	3	H	NATO
Ag	**0.159**	0.045	mg/kg TS	4	H	NATO
Mo	**1.75**	0.33	mg/kg TS	4	H	NATO
Sb	**0.490**	0.118	mg/kg TS	4	H	NATO
Sn	**2.99**	0.57	mg/kg TS	4	H	NATO
TOC	**2.50**		% TS	5	1	SH

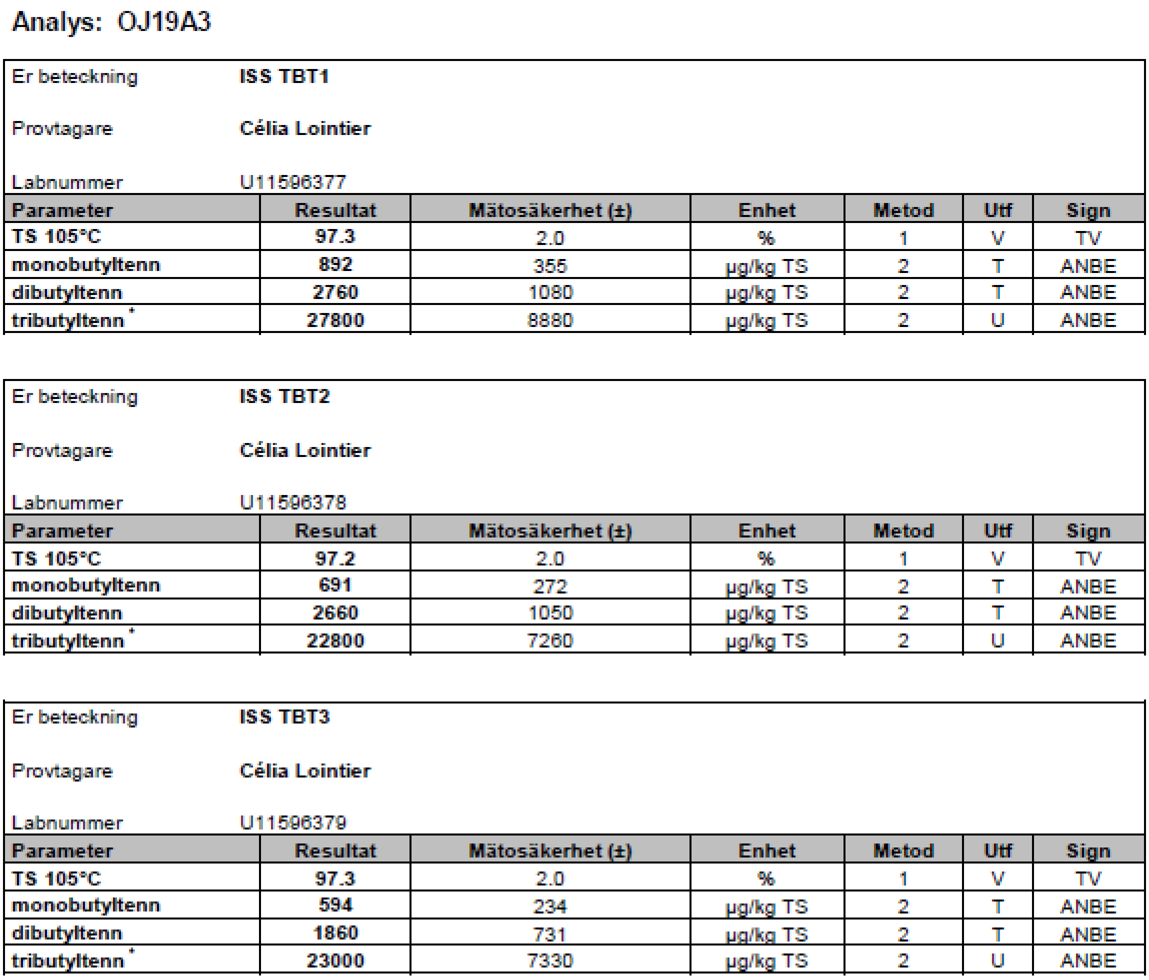
Er beteckning **A40**

Provtagare **Anna Norén**

Labnummer U11338845

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**50.6**	2%	%	2	V	JOGR
As	**4.37**	0.90	mg/kg TS	3	H	NATO
Ba	**65.1**	16.5	mg/kg TS	3	H	NATO
Cd	**0.257**	0.050	mg/kg TS	3	H	NATO
Co	**7.53**	1.53	mg/kg TS	3	H	NATO
Cr	**30.1**	6.1	mg/kg TS	3	H	NATO
Cu	**29.2**	6.2	mg/kg TS	3	H	NATO
Hg	**<0.2**		mg/kg TS	3	H	NATO
Ni	**14.1**	2.8	mg/kg TS	3	H	NATO
Pb	**23.5**	5.5	mg/kg TS	3	H	NATO
V	**39.4**	8.0	mg/kg TS	3	H	NATO
Zn	**120**	26	mg/kg TS	3	H	NATO
Ag	**0.170**	0.048	mg/kg TS	4	H	NATO
Mo	**1.64**	0.33	mg/kg TS	4	H	NATO
Sb	**0.525**	0.126	mg/kg TS	4	H	NATO
Sn	**3.26**	0.61	mg/kg TS	4	H	NATO

Appendix 6. Analytic reports delivered by ALS – Spiked1 sediments



Analys: OJ19A3

Er beteckning	**ISS TBT1**
Provtagare	**Célia Lointier**
Labnummer	U11596377

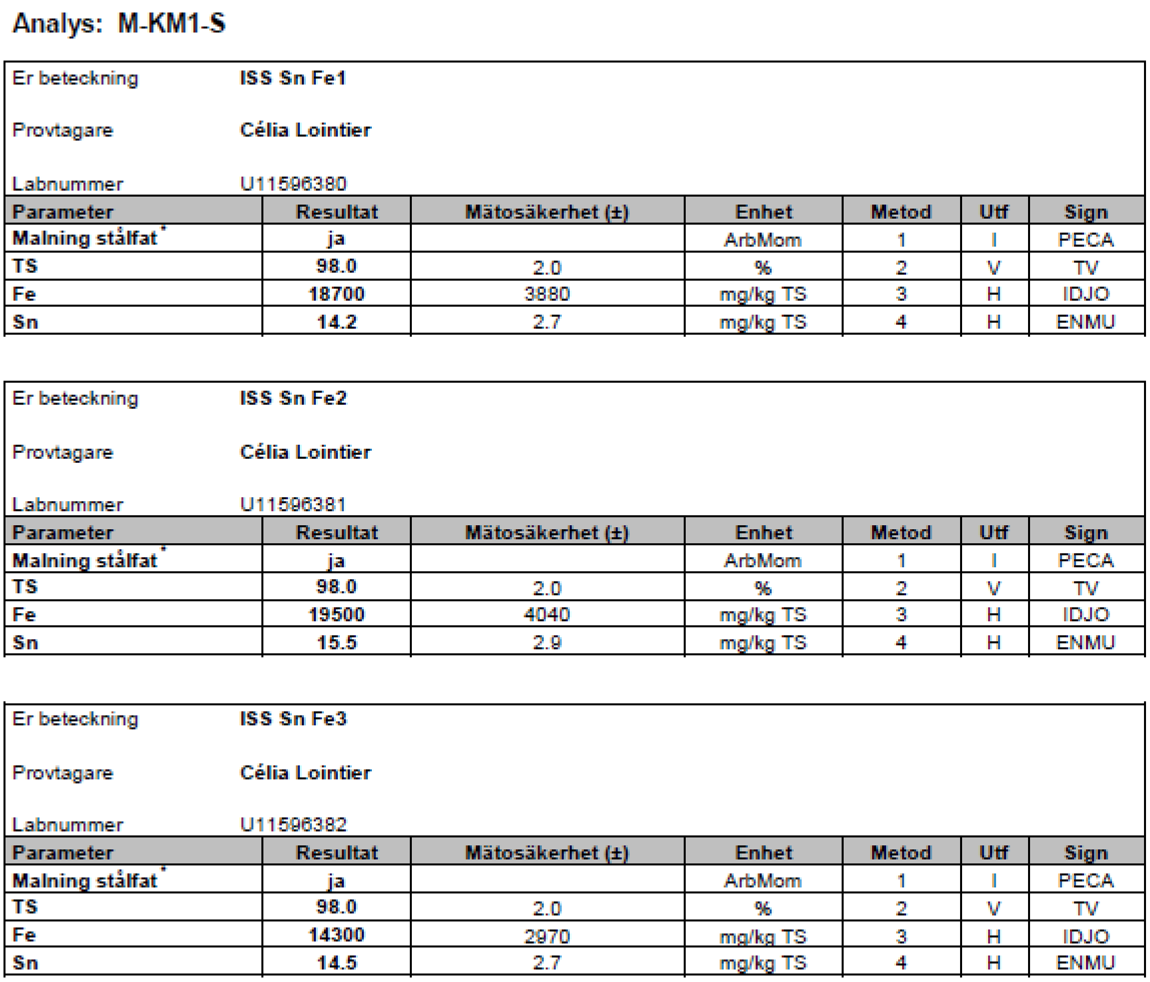
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**97.3**	2.0	%	1	V	TV
monobutyltenn	**892**	355	µg/kg TS	2	T	ANBE
dibutyltenn	**2760**	1080	µg/kg TS	2	T	ANBE
tributyltenn *	**27800**	8880	µg/kg TS	2	U	ANBE

Er beteckning	**ISS TBT2**
Provtagare	**Célia Lointier**
Labnummer	U11596378

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**97.2**	2.0	%	1	V	TV
monobutyltenn	**691**	272	µg/kg TS	2	T	ANBE
dibutyltenn	**2660**	1050	µg/kg TS	2	T	ANBE
tributyltenn *	**22800**	7260	µg/kg TS	2	U	ANBE

Er beteckning	**ISS TBT3**
Provtagare	**Célia Lointier**
Labnummer	U11596379

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**97.3**	2.0	%	1	V	TV
monobutyltenn	**594**	234	µg/kg TS	2	T	ANBE
dibutyltenn	**1860**	731	µg/kg TS	2	T	ANBE
tributyltenn *	**23000**	7330	µg/kg TS	2	U	ANBE



Analys: M-KM1-S

Er beteckning	**ISS Sn Fe1**
Provtagare	**Célia Lointier**
Labnummer	U11596380

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**98.0**	2.0	%	2	V	TV
Fe	**18700**	3880	mg/kg TS	3	H	IDJO
Sn	**14.2**	2.7	mg/kg TS	4	H	ENMU

Er beteckning	**ISS Sn Fe2**
Provtagare	**Célia Lointier**
Labnummer	U11596381

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**98.0**	2.0	%	2	V	TV
Fe	**19500**	4040	mg/kg TS	3	H	IDJO
Sn	**15.5**	2.9	mg/kg TS	4	H	ENMU

Er beteckning	**ISS Sn Fe3**
Provtagare	**Célia Lointier**
Labnummer	U11596382

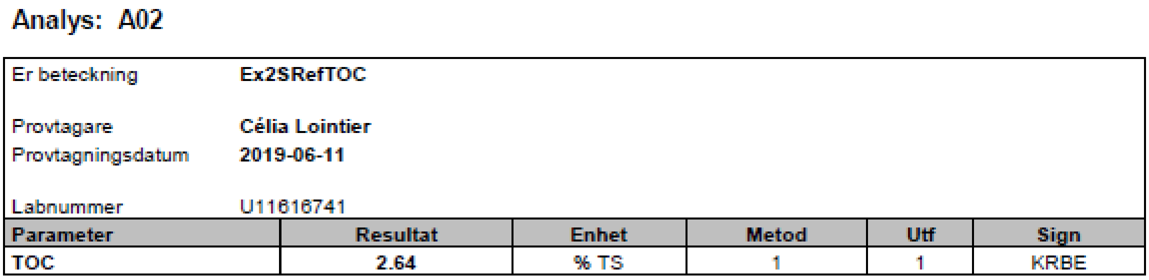
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**98.0**	2.0	%	2	V	TV
Fe	**14300**	2970	mg/kg TS	3	H	IDJO
Sn	**14.5**	2.7	mg/kg TS	4	H	ENMU

Analys av fast prov

Er beteckning	**ISS PAH TOC**
Provtagare	**Célia Lointier**
Labnummer	O11135767

Parameter	Resultat	Osäkerhet (±)	Enhet	Metod	Utf	Sign
TS (frystorkning) *	----------		%	1	1	ULKA
naftalen	**0.035**	0.0067	mg/kg TS	1	1	ULKA
acenaftylen	**0.014**	0.0027	mg/kg TS	1	1	ULKA
acenaften	**0.014**	0.0027	mg/kg TS	1	1	ULKA
fluoren	**0.025**	0.0048	mg/kg TS	1	1	ULKA
fenantren	**0.098**	0.019	mg/kg TS	1	1	ULKA
antracen	**0.056**	0.011	mg/kg TS	1	1	ULKA
fluoranten	**0.22**	0.042	mg/kg TS	1	1	ULKA
pyren	**0.18**	0.035	mg/kg TS	1	1	ULKA
bens(a)antracen	**0.11**	0.021	mg/kg TS	1	1	ULKA
krysen	**0.099**	0.019	mg/kg TS	1	1	ULKA
bens(b)fluoranten	**0.10**	0.020	mg/kg TS	1	1	ULKA
bens(k)fluoranten	**0.058**	0.011	mg/kg TS	1	1	ULKA
bens(a)pyren	**0.11**	0.021	mg/kg TS	1	1	ULKA
dibens(ah)antracen	**0.024**	0.0046	mg/kg TS	1	1	ULKA
benso(ghi)perylen	**0.090**	0.017	mg/kg TS	1	1	ULKA
indeno(123cd)pyren	**0.098**	0.019	mg/kg TS	1	1	ULKA
PAH, summa 16 *	**1.3**		mg/kg TS	1	1	ULKA
PAH, summa cancerogena *	**0.60**		mg/kg TS	1	1	ULKA
PAH, summa övriga *	**0.73**		mg/kg TS	1	1	ULKA
PAH, summa L *	**0.063**		mg/kg TS	1	1	ULKA
PAH, summa M *	**0.58**		mg/kg TS	1	1	ULKA
PAH, summa H *	**0.69**		mg/kg TS	1	1	ULKA
PAH, summa 11 *	**1.2**		mg/kg TS	1	1	ULKA
TS_105°C	**97.4**	1.9	%	2	1	ULKA
TOC	**2.2**	0.21	% av TS	2	1	ULKA

Appendix 7: Analytic reports delivered by ALS – Spiked2 sediments



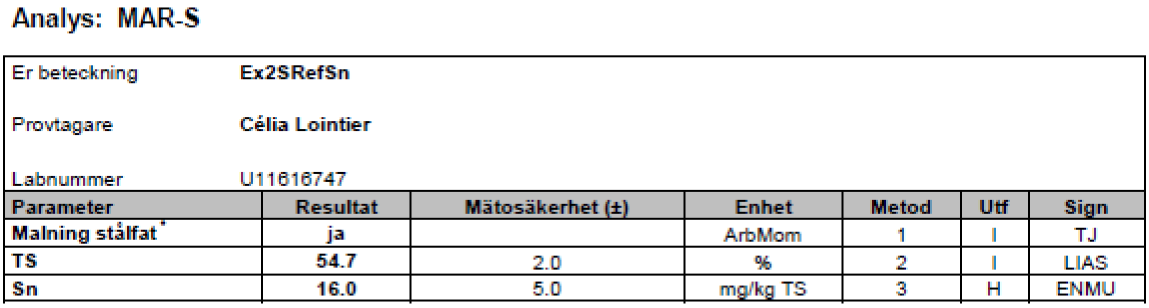
Analys: A02

Er beteckning **Ex2SRefTOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616741

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.64**	% TS	1	1	KRBE



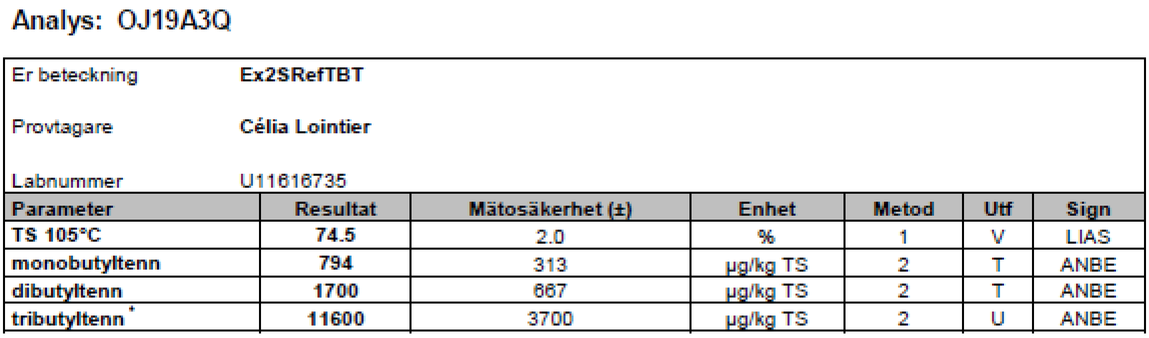
Analys: MAR-S

Er beteckning **Ex2SRefSn**

Provtagare **Célia Lointier**

Labnummer U11616747

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat *	**ja**		ArbMom	1	I	TJ
TS	**54.7**	2.0	%	2	I	LIAS
Sn	**16.0**	5.0	mg/kg TS	3	H	ENMU



Analys: OJ19A3Q

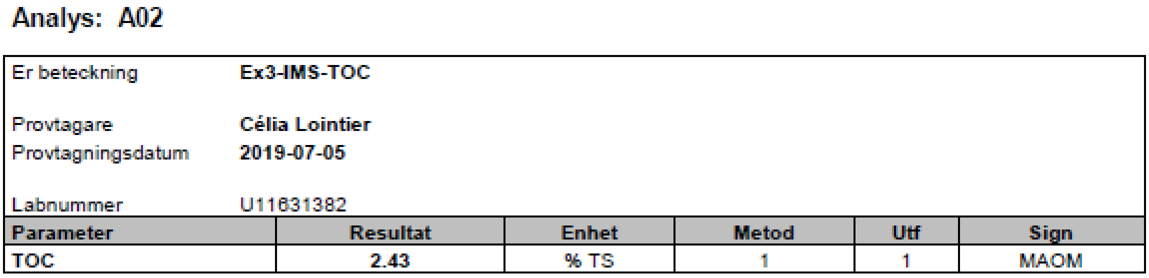
Er beteckning **Ex2SRefTBT**

Provtagare **Célia Lointier**

Labnummer U11616735

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**74.5**	2.0	%	1	V	LIAS
monobutyltenn	**794**	313	µg/kg TS	2	T	ANBE
dibutyltenn	**1700**	667	µg/kg TS	2	T	ANBE
tributyltenn *	**11600**	3700	µg/kg TS	2	U	ANBE

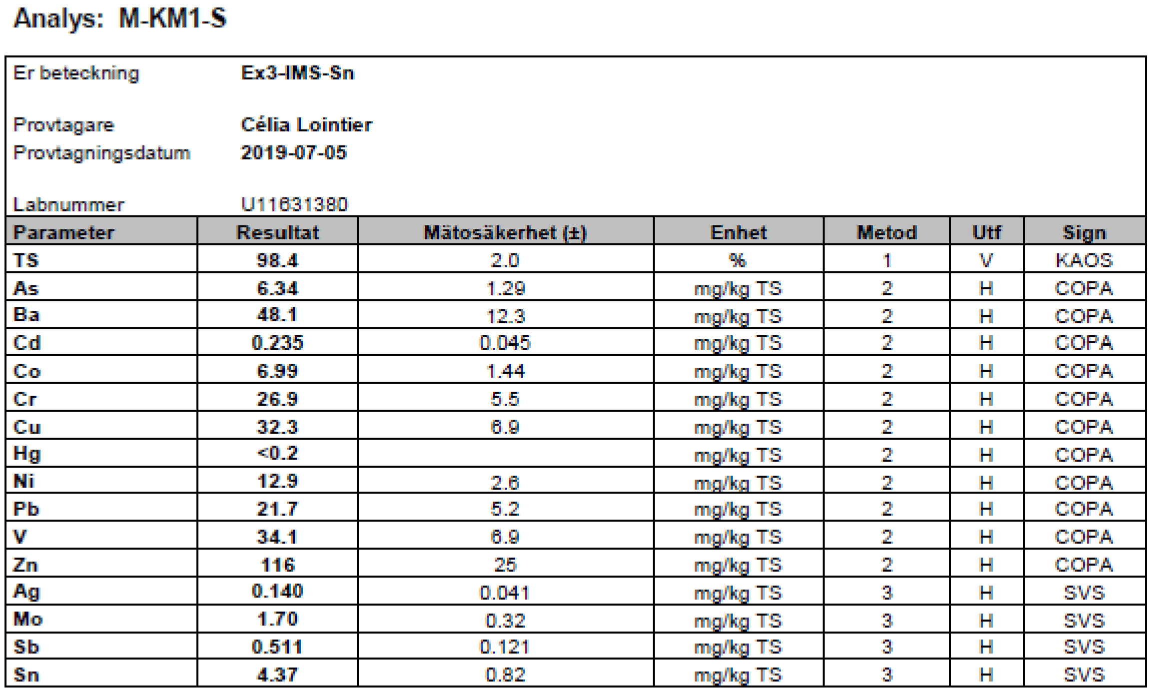
Appendix 8: Analytic reports delivered by ALS – Medium1 sediments



Analys: A02

Er beteckning	**Ex3-IMS-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11631382

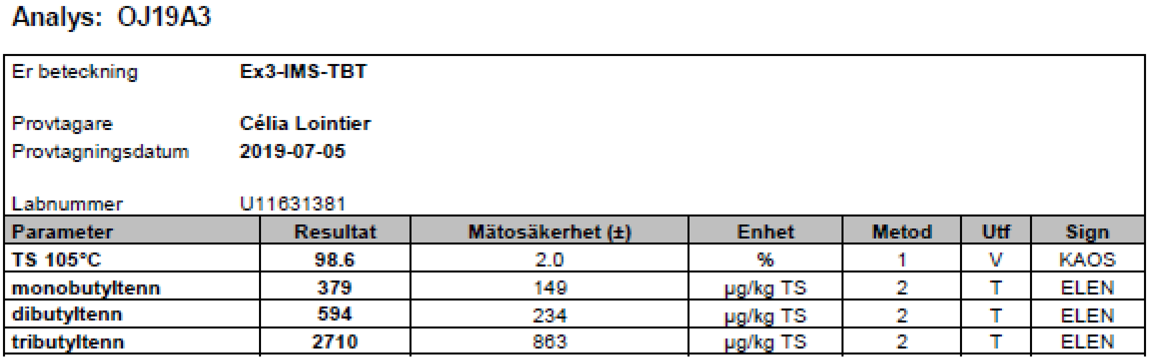
Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.43**	% TS	1	1	MAOM



Analys: M-KM1-S

Er beteckning	**Ex3-IMS-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11631380

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS	**98.4**	2.0	%	1	V	KAOS
As	**6.34**	1.29	mg/kg TS	2	H	COPA
Ba	**48.1**	12.3	mg/kg TS	2	H	COPA
Cd	**0.235**	0.045	mg/kg TS	2	H	COPA
Co	**6.99**	1.44	mg/kg TS	2	H	COPA
Cr	**26.9**	5.5	mg/kg TS	2	H	COPA
Cu	**32.3**	6.9	mg/kg TS	2	H	COPA
Hg	**<0.2**		mg/kg TS	2	H	COPA
Ni	**12.9**	2.6	mg/kg TS	2	H	COPA
Pb	**21.7**	5.2	mg/kg TS	2	H	COPA
V	**34.1**	6.9	mg/kg TS	2	H	COPA
Zn	**116**	25	mg/kg TS	2	H	COPA
Ag	**0.140**	0.041	mg/kg TS	3	H	SVS
Mo	**1.70**	0.32	mg/kg TS	3	H	SVS
Sb	**0.511**	0.121	mg/kg TS	3	H	SVS
Sn	**4.37**	0.82	mg/kg TS	3	H	SVS



Analys: OJ19A3

Er beteckning	**Ex3-IMS-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11631381

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**98.6**	2.0	%	1	V	KAOS
monobutyltenn	**379**	149	µg/kg TS	2	T	ELEN
dibutyltenn	**594**	234	µg/kg TS	2	T	ELEN
tributyltenn	**2710**	863	µg/kg TS	2	T	ELEN

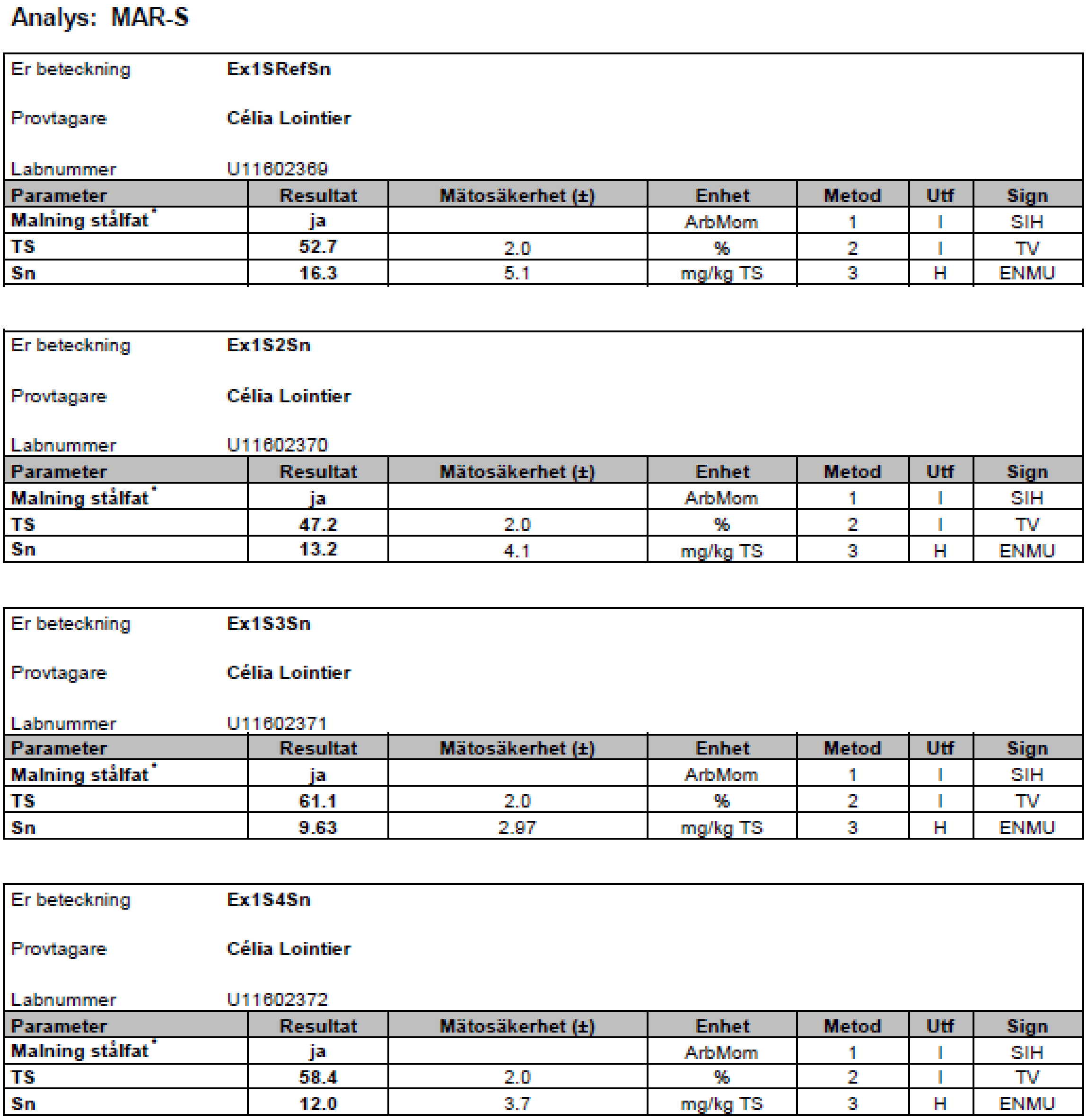
Appendix 9. Results of analysis on metals - Spiked sediments

ELEMENT	**SAMPLE**	**Spiked**
TS	%	97.9
As	mg/kg TS	5.26
Ba	mg/kg TS	49.5
Cd	mg/kg TS	0.225
Co	mg/kg TS	7.62
Cr	mg/kg TS	26.7
Cu	mg/kg TS	25.8
Hg	mg/kg TS	0.237
Ni	mg/kg TS	14.4
Pb	mg/kg TS	25.4
V	mg/kg TS	36.6
Zn	mg/kg TS	114
Ag	mg/kg TS	0.151
Mo	mg/kg TS	1.75
Sb	mg/kg TS	0.514
Sn	mg/kg TS	14.2

Appendix 10. Results of analysis on PAHs - Spiked sediments

ELEMENT	SAMPLE	ISS PAH TOC	ELEMENT	SAMPLE	ISS PAH TOC
naftalen	mg/kg TS	0.035	bens(a)pyren	mg/kg TS	0.11
acenaftylen	mg/kg TS	0.014	dibens(ah)antracen	mg/kg TS	0.024
acenaften	mg/kg TS	0.014	benso(ghi)perylen	mg/kg TS	0.09
fluoren	mg/kg TS	0.025	indeno(123cd)pyren	mg/kg TS	0.098
fenantren	mg/kg TS	0.098	PAH, summa 16	mg/kg TS	1.3
antracen	mg/kg TS	0.056	PAH, summa cancerogena	mg/kg TS	0.6
fluoranten	mg/kg TS	0.22	PAH, summa övriga	mg/kg TS	0.73
pyren	mg/kg TS	0.18	PAH, summa L	mg/kg TS	0.063
bens(a)antracen	mg/kg TS	0.11	PAH, summa M	mg/kg TS	0.58
krysen	mg/kg TS	0.099	PAH, summa H	mg/kg TS	0.69
bens(b)fluoranten	mg/kg TS	0.1	PAH, summa 11	mg/kg TS	1.2

Appendix 11: Analytic reports delivered by ALS – Fenton's degradation, Experiment 1



Analys: MAR-S

Er beteckning **Ex1SRefSn**
Provtagare **Célia Lointier**
Labnummer U11602369

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	SIH
TS	**52.7**	2.0	%	2	I	TV
Sn	**16.3**	5.1	mg/kg TS	3	H	ENMU

Er beteckning **Ex1S2Sn**
Provtagare **Célia Lointier**
Labnummer U11602370

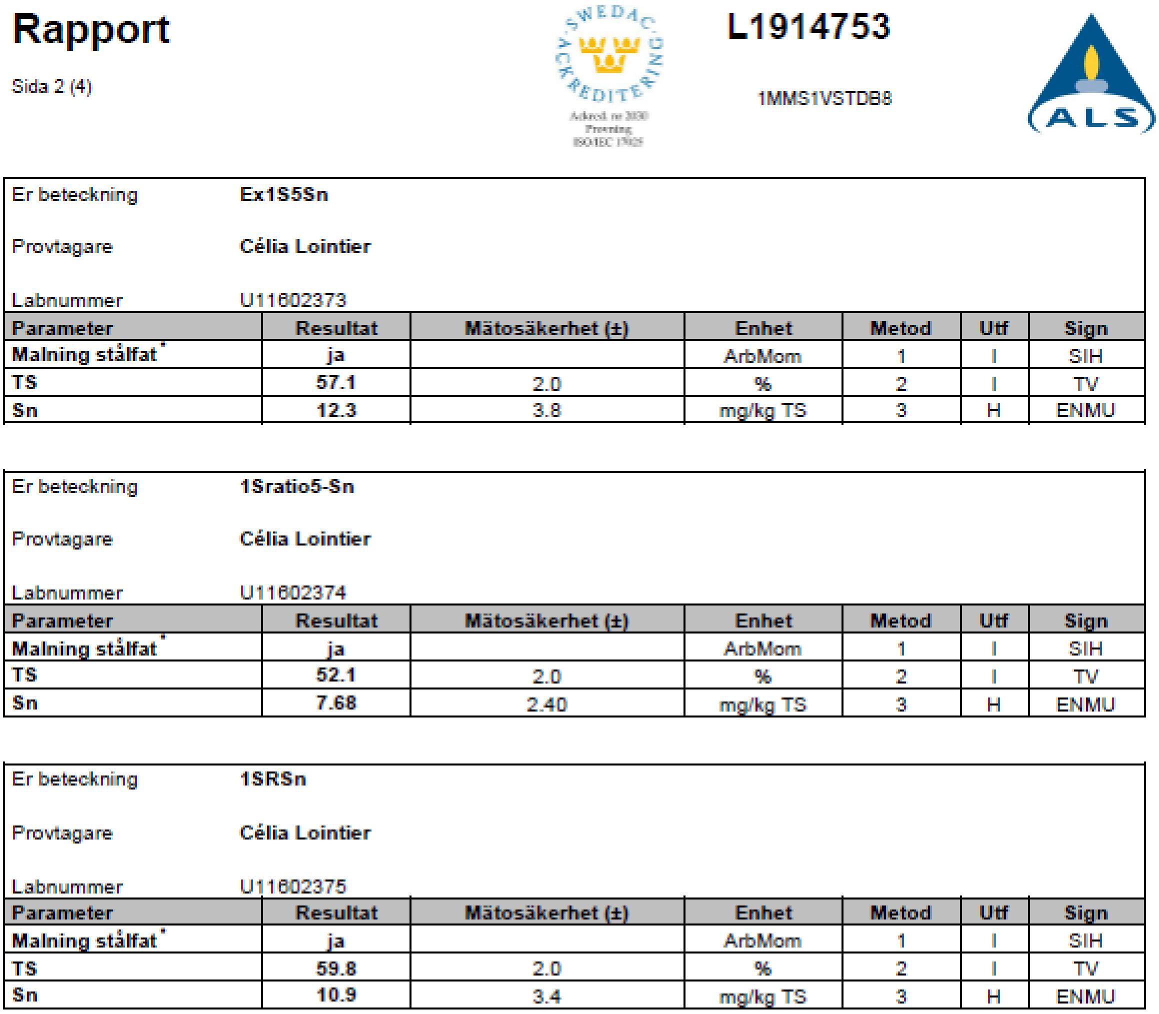
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	SIH
TS	**47.2**	2.0	%	2	I	TV
Sn	**13.2**	4.1	mg/kg TS	3	H	ENMU

Er beteckning **Ex1S3Sn**
Provtagare **Célia Lointier**
Labnummer U11602371

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	SIH
TS	**61.1**	2.0	%	2	I	TV
Sn	**9.63**	2.97	mg/kg TS	3	H	ENMU

Er beteckning **Ex1S4Sn**
Provtagare **Célia Lointier**
Labnummer U11602372

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	SIH
TS	**58.4**	2.0	%	2	I	TV
Sn	**12.0**	3.7	mg/kg TS	3	H	ENMU



Rapport

Sida 2 (4)

Ackred. nr 2030 Provning ISO/IEC 17025

L1914753

1MMS1VSTDB8

Er beteckning **Ex1S5Sn**

Provtagare **Célia Lointier**

Labnummer U11602373

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat *	ja		ArbMom	1	I	SIH
TS	**57.1**	2.0	%	2	I	TV
Sn	**12.3**	3.8	mg/kg TS	3	H	ENMU

Er beteckning **1Sratio5-Sn**

Provtagare **Célia Lointier**

Labnummer U11602374

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat *	ja		ArbMom	1	I	SIH
TS	**52.1**	2.0	%	2	I	TV
Sn	**7.68**	2.40	mg/kg TS	3	H	ENMU

Er beteckning **1SRSn**

Provtagare **Célia Lointier**

Labnummer U11602375

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat *	ja		ArbMom	1	I	SIH
TS	**59.8**	2.0	%	2	I	TV
Sn	**10.9**	3.4	mg/kg TS	3	H	ENMU

Analys: A02

Er beteckning	**Ex1SRefTOC**
Provtagare	**Célia Lointier**
Labnummer	U11602362

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.04	% TS	1	1	MAOM

Er beteckning	**Ex1S2TOC**
Provtagare	**Célia Lointier**
Labnummer	U11602363

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	1.85	% TS	1	1	MAOM

Er beteckning	**Ex1S3TOC**
Provtagare	**Célia Lointier**
Labnummer	U11602364

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	1.62	% TS	1	1	MAOM

Er beteckning	**Ex1S4TOC**
Provtagare	**Célia Lointier**
Labnummer	U11602365

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	6.49	% TS	1	1	MAOM

Er beteckning	**Ex1S5TOC**
Provtagare	**Célia Lointier**
Labnummer	U11602366

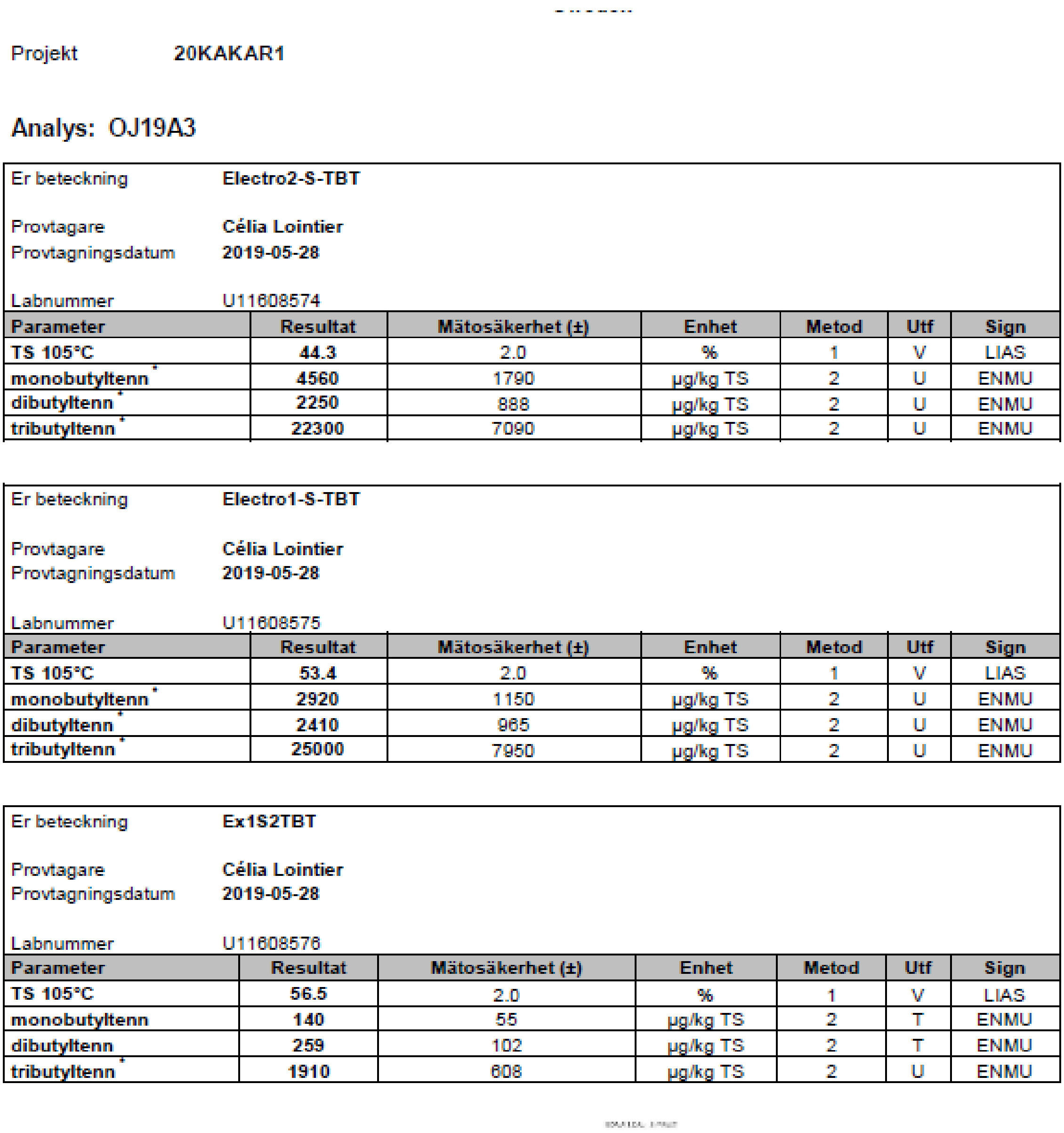
Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.15	% TS	1	1	MAOM

Er beteckning	**ExASRefTOC**
Provtagare	**Célia Lointier**
Labnummer	U11602367

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.27	% TS	1	1	MAOM

Er beteckning	**ExAS2TOC**
Provtagare	**Célia Lointier**
Labnummer	U11602368

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	1.76	% TS	1	1	MAOM



Projekt 20KAKAR1

Analys: OJ19A3

Er beteckning	**Electro2-S-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-05-28**
Labnummer	U11608574

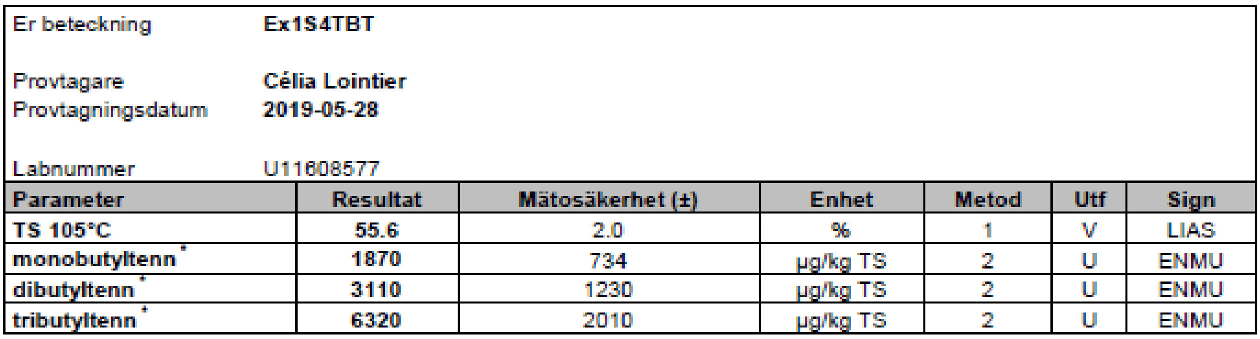
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**44.3**	2.0	%	1	V	LIAS
monobutyltenn *	**4560**	1790	µg/kg TS	2	U	ENMU
dibutyltenn *	**2250**	888	µg/kg TS	2	U	ENMU
tributyltenn *	**22300**	7090	µg/kg TS	2	U	ENMU

Er beteckning	**Electro1-S-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-05-28**
Labnummer	U11608575

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**53.4**	2.0	%	1	V	LIAS
monobutyltenn *	**2920**	1150	µg/kg TS	2	U	ENMU
dibutyltenn *	**2410**	965	µg/kg TS	2	U	ENMU
tributyltenn *	**25000**	7950	µg/kg TS	2	U	ENMU

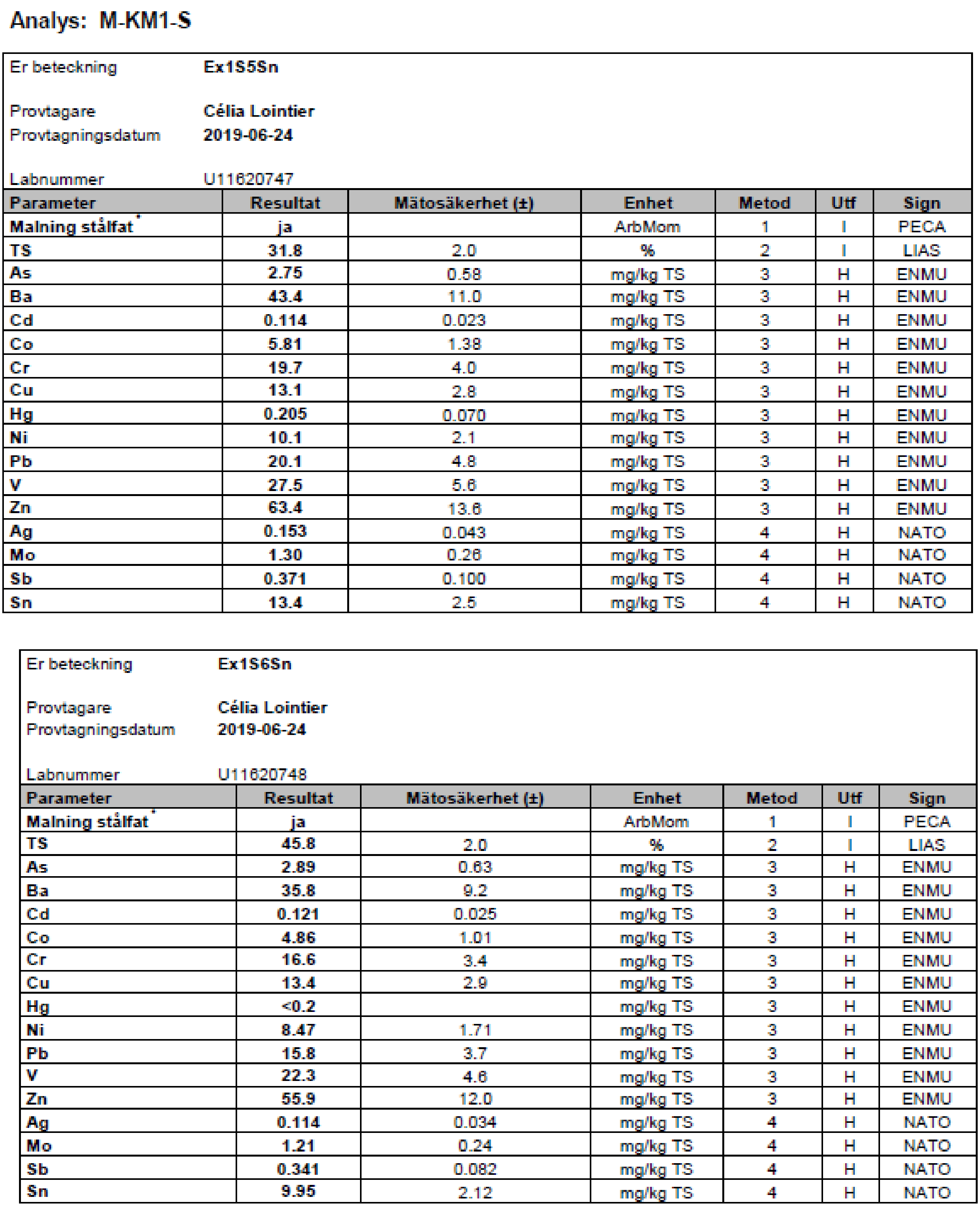
Er beteckning	**Ex1S2TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-05-28**
Labnummer	U11608576

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**56.5**	2.0	%	1	V	LIAS
monobutyltenn	**140**	55	µg/kg TS	2	T	ENMU
dibutyltenn	**259**	102	µg/kg TS	2	T	ENMU
tributyltenn *	**1910**	608	µg/kg TS	2	U	ENMU



Er beteckning	**Ex1S4TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-05-28**
Labnummer	U11608577

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**55.6**	2.0	%	1	V	LIAS
monobutyltenn *	**1870**	734	µg/kg TS	2	U	ENMU
dibutyltenn *	**3110**	1230	µg/kg TS	2	U	ENMU
tributyltenn *	**6320**	2010	µg/kg TS	2	U	ENMU



Analys: M-KM1-S

Er beteckning	**Ex1S5Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-06-24**
Labnummer	U11620747

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**31.8**	2.0	%	2	I	LIAS
As	**2.75**	0.58	mg/kg TS	3	H	ENMU
Ba	**43.4**	11.0	mg/kg TS	3	H	ENMU
Cd	**0.114**	0.023	mg/kg TS	3	H	ENMU
Co	**5.81**	1.38	mg/kg TS	3	H	ENMU
Cr	**19.7**	4.0	mg/kg TS	3	H	ENMU
Cu	**13.1**	2.8	mg/kg TS	3	H	ENMU
Hg	**0.205**	0.070	mg/kg TS	3	H	ENMU
Ni	**10.1**	2.1	mg/kg TS	3	H	ENMU
Pb	**20.1**	4.8	mg/kg TS	3	H	ENMU
V	**27.5**	5.6	mg/kg TS	3	H	ENMU
Zn	**63.4**	13.6	mg/kg TS	3	H	ENMU
Ag	**0.153**	0.043	mg/kg TS	4	H	NATO
Mo	**1.30**	0.26	mg/kg TS	4	H	NATO
Sb	**0.371**	0.100	mg/kg TS	4	H	NATO
Sn	**13.4**	2.5	mg/kg TS	4	H	NATO

Er beteckning	**Ex1S6Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-06-24**
Labnummer	U11620748

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	PECA
TS	**45.8**	2.0	%	2	I	LIAS
As	**2.89**	0.63	mg/kg TS	3	H	ENMU
Ba	**35.8**	9.2	mg/kg TS	3	H	ENMU
Cd	**0.121**	0.025	mg/kg TS	3	H	ENMU
Co	**4.86**	1.01	mg/kg TS	3	H	ENMU
Cr	**16.6**	3.4	mg/kg TS	3	H	ENMU
Cu	**13.4**	2.9	mg/kg TS	3	H	ENMU
Hg	**<0.2**		mg/kg TS	3	H	ENMU
Ni	**8.47**	1.71	mg/kg TS	3	H	ENMU
Pb	**15.8**	3.7	mg/kg TS	3	H	ENMU
V	**22.3**	4.6	mg/kg TS	3	H	ENMU
Zn	**55.9**	12.0	mg/kg TS	3	H	ENMU
Ag	**0.114**	0.034	mg/kg TS	4	H	NATO
Mo	**1.21**	0.24	mg/kg TS	4	H	NATO
Sb	**0.341**	0.082	mg/kg TS	4	H	NATO
Sn	**9.95**	2.12	mg/kg TS	4	H	NATO

Analys: A02

Er beteckning **Ex1S5TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-24**

Labnummer U11620745

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.53**	% TS	1	1	HUCH

Er beteckning **Ex1S6TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-24**

Labnummer U11620746

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**1.49**	% TS	1	1	HUCH

Analys: OJ19A3

Er beteckning **Ex1S5TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-24**

Labnummer U11620743

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**51.5**	2.0	%	1	V	LIAS
monobutyltenn	**76.4**	30.1	µg/kg TS	2	T	ANBE
dibutyltenn	**143**	56	µg/kg TS	2	T	ANBE
tributyltenn	**956**	304	µg/kg TS	2	T	ANBE

Er beteckning **Ex1S6TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-24**

Labnummer U11620744

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**37.3**	2.0	%	1	V	LIAS
monobutyltenn	**156**	61	µg/kg TS	2	T	ANBE
dibutyltenn	**287**	114	µg/kg TS	2	T	ANBE
tributyltenn *	**1610**	514	µg/kg TS	2	U	ANBE

Analys: V3BBAS

Er beteckning	**Ex1W1Snf**
Provtagare	**Célia Lointier**
Labnummer	U11602203

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	1.23	0.34	µg/l	1	H	HEAN

Er beteckning	**Ex1W2SnF**
Provtagare	**Célia Lointier**
Labnummer	U11602204

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	200	39	µg/l	1	H	HEAN

Er beteckning	**Ex1W3SnF**
Provtagare	**Célia Lointier**
Labnummer	U11602205

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	24.5	4.8	µg/l	1	H	HEAN

Er beteckning	**Ex1W4SnF**
Provtagare	**Célia Lointier**
Labnummer	U11602206

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	6.53	1.34	µg/l	1	H	HEAN

Er beteckning ExAW5SnF

Provtagare Célia Lointier

Labnummer U11602207

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	8.36	1.57	µg/l	1	H	HEAN

Er beteckning ExAWRefSnF

Provtagare Célia Lointier

Labnummer U11602208

Parameter	Resultat	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja		1	I	CAJO
Sn	<0.5	µg/l	1	H	HEAN

Er beteckning ExAW2SnF

Provtagare Célia Lointier

Labnummer U11602209

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	Ja			1	I	CAJO
Sn	219	45	µg/l	1	H	HEAN

Er beteckning Ex1WRefSn

Provtagare Célia Lointier

Labnummer U11602210

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	2.11	0.45	µg/l	1	H	HEAN

Er beteckning Ex1W2Sn

Provtagare Célia Lointier

Labnummer U11602211

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	191	35	µg/l	1	H	HEAN

Er beteckning Ex1W3Sn

Provtagare Célia Lointier

Labnummer U11602212

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	31.9	6.0	µg/l	1	H	HEAN

Er beteckning **Ex1W4Sn**

Provtagare **Célia Lointier**

Labnummer U11602213

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**7.81**	1.47	µg/l	1	H	HEAN

Er beteckning **Ex1W5Sn**

Provtagare **Célia Lointier**

Labnummer U11602214

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**11.0**	2.1	µg/l	1	H	HEAN

Er beteckning **ExAWRefSn**

Provtagare **Célia Lointier**

Labnummer U11602215

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**0.525**	0.149	µg/l	1	H	HEAN

Er beteckning **ExAW2Sn**

Provtagare **Célia Lointier**

Labnummer U11602216

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**182**	36	µg/l	1	H	HEAN

Analys: V3BBAS

Er beteckning	**Ex1W5Sn**
Provtagare	**Célia Lointier**
Labnummer	U11619454

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**287**	57	µg/l	1	H	NIPA

Er beteckning	**Ex1W5SnF**
Provtagare	**Célia Lointier**
Labnummer	U11619455

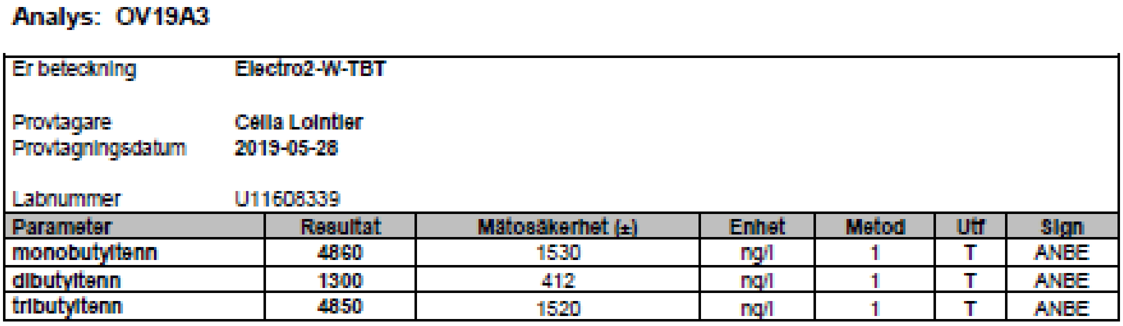
Parameter	Resultat	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys *	Ja		1	I	HUCH
Sn *	----------	µg/l	1	I	SH

Er beteckning	**Ex1W6Sn**
Provtagare	**Célia Lointier**
Labnummer	U11619456

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**422**	85	µg/l	1	H	NIPA

Er beteckning	**Ex1W6SnF**
Provtagare	**Célia Lointier**
Labnummer	U11619457

Parameter	Resultat	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys *	Ja		1	I	HUCH
Sn *	----------	µg/l	1	I	SH



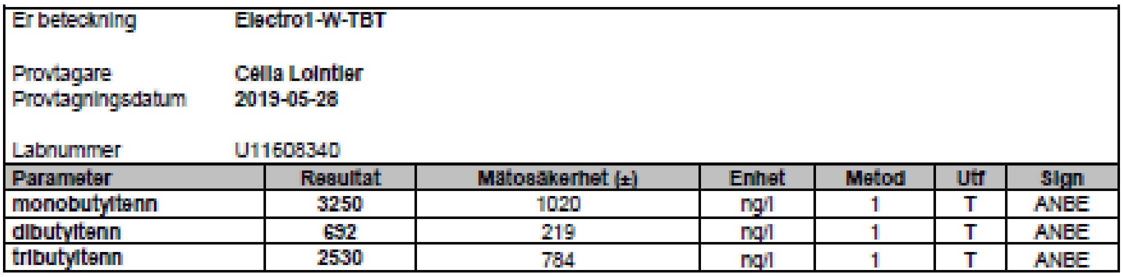
Analys: OV19A3

Er beteckning **Electro2-W-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608339

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
monobutyltenn	**4860**	1530	ng/l	1	T	ANBE
dibutyltenn	**1300**	412	ng/l	1	T	ANBE
tributyltenn	**4850**	1520	ng/l	1	T	ANBE

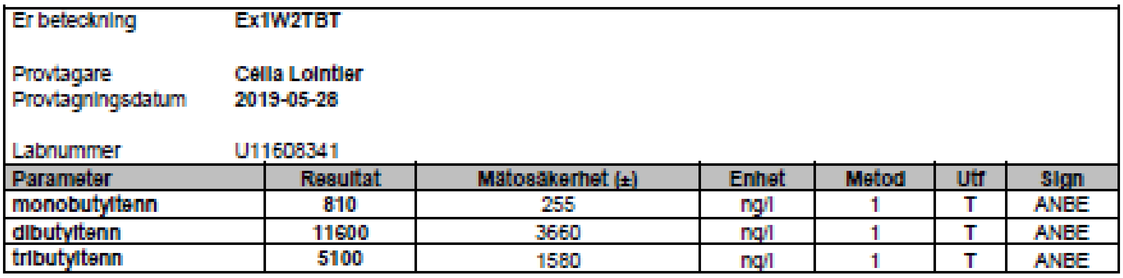


Er beteckning **Electro1-W-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608340

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
monobutyltenn	**3250**	1020	ng/l	1	T	ANBE
dibutyltenn	**692**	219	ng/l	1	T	ANBE
tributyltenn	**2530**	784	ng/l	1	T	ANBE

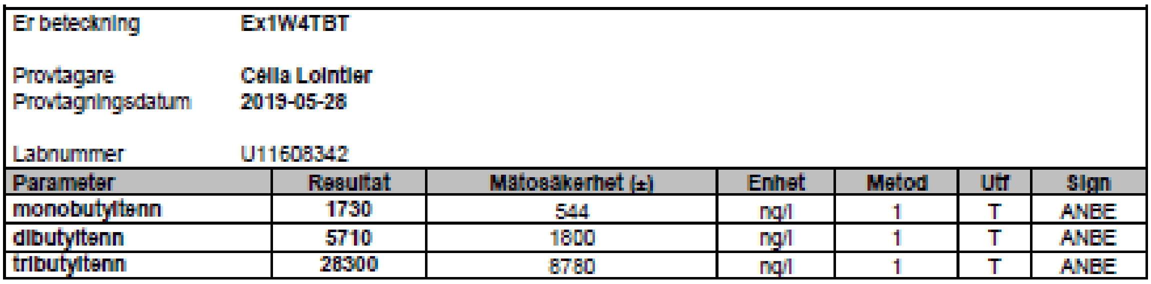


Er beteckning **Ex1W2TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608341

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
monobutyltenn	**810**	255	ng/l	1	T	ANBE
dibutyltenn	**11600**	3660	ng/l	1	T	ANBE
tributyltenn	**5100**	1580	ng/l	1	T	ANBE



Er beteckning **Ex1W4TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608342

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
monobutyltenn	**1730**	544	ng/l	1	T	ANBE
dibutyltenn	**5710**	1800	ng/l	1	T	ANBE
tributyltenn	**28300**	8780	ng/l	1	T	ANBE

Analys: OV19A3

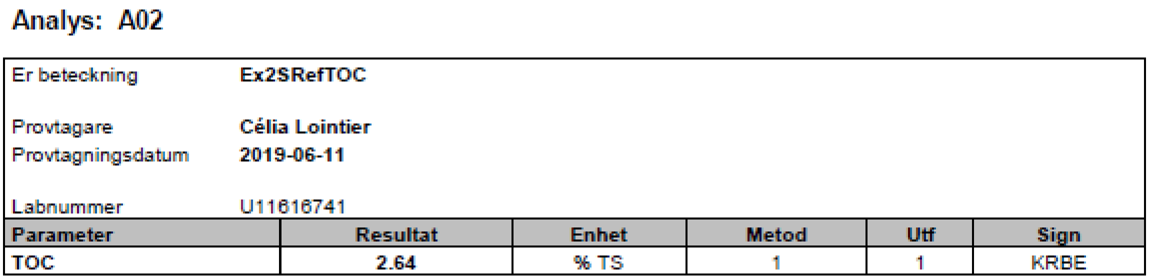
Er beteckning	**Ex1W5TBT**
Provtagare	**Célia Lointier**
Labnummer	U11619452

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**1410**	445	ng/l	1	T	ANBE
dibutyltenn	**2950**	931	ng/l	1	T	ANBE
tributyltenn	**879**	273	ng/l	1	T	ANBE

Er beteckning	**Ex1W6TBT**
Provtagare	**Célia Lointier**
Labnummer	U11619453

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**1480**	465	ng/l	1	T	ANBE
dibutyltenn	**4270**	1360	ng/l	1	T	ANBE
tributyltenn	**915**	283	ng/l	1	T	ANBE

Appendix 12: Analytic reports delivered by ALS – Fenton's degradation, Experiment 2



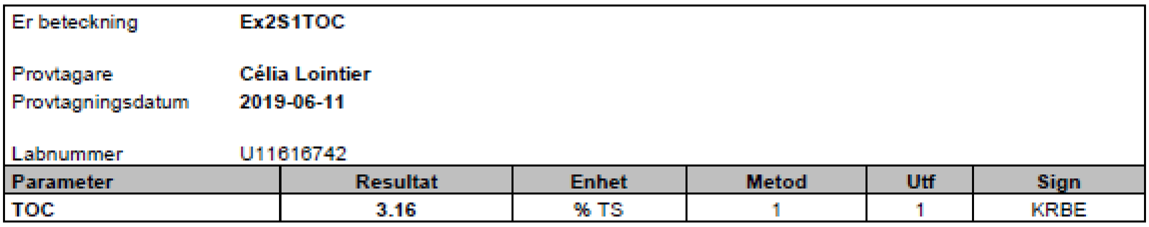
Analys: A02

Er beteckning **Ex2SRefTOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616741

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.64	% TS	1	1	KRBE

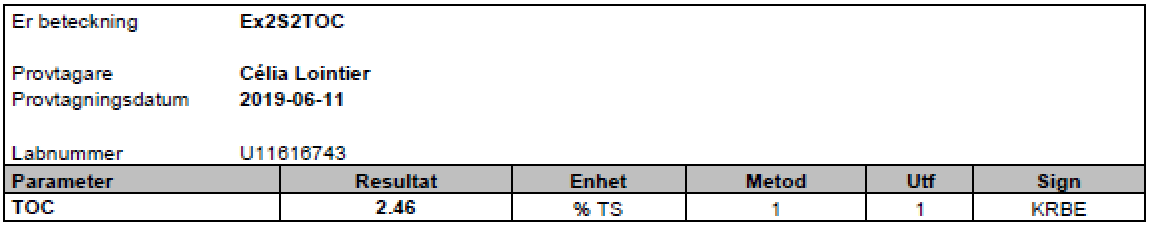


Er beteckning **Ex2S1TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616742

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	3.16	% TS	1	1	KRBE

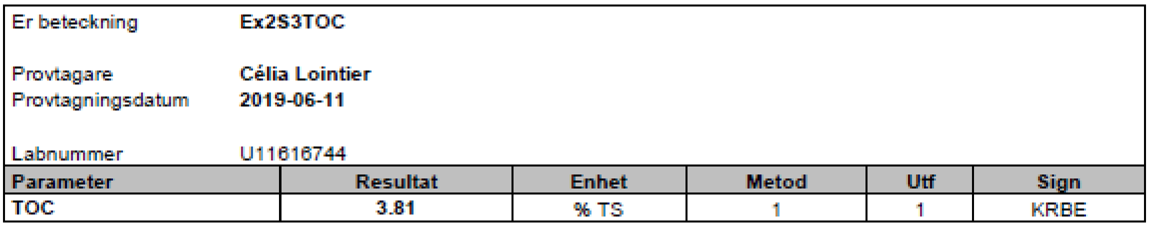


Er beteckning **Ex2S2TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616743

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.46	% TS	1	1	KRBE

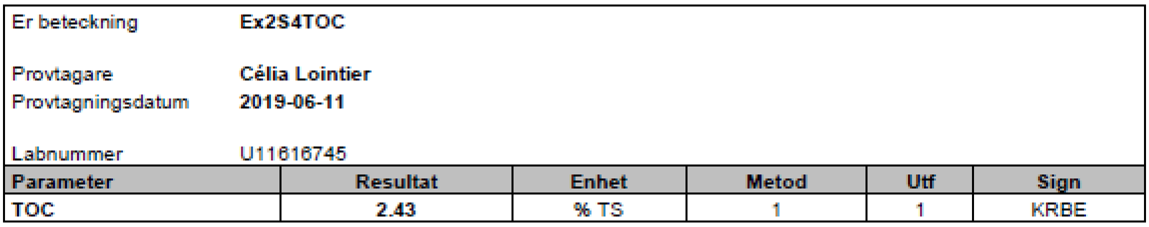


Er beteckning **Ex2S3TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616744

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	3.81	% TS	1	1	KRBE

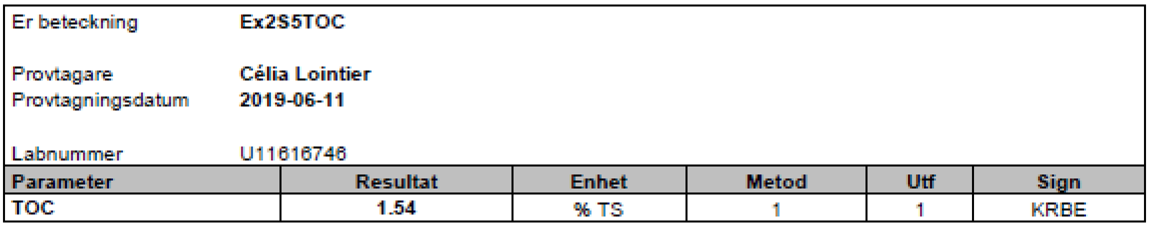


Er beteckning **Ex2S4TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616745

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	2.43	% TS	1	1	KRBE



Er beteckning **Ex2S5TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11616746

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	1.54	% TS	1	1	KRBE

Analys: MAR-S

Er beteckning **Ex2SRefSn**

Provtagare **Célia Lointier**

Labnummer U11616747

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**54.7**	2.0	%	2	I	LIAS
Sn	**16.0**	5.0	mg/kg TS	3	H	ENMU

Er beteckning **Ex2S1Sn**

Provtagare **Célia Lointier**

Labnummer U11616748

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**70.8**	2.0	%	2	I	LIAS
Sn	**9.96**	3.08	mg/kg TS	3	H	ENMU

Er beteckning **Ex2S2Sn**

Provtagare **Célia Lointier**

Labnummer U11616749

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**54.7**	2.0	%	2	I	LIAS
Sn	**16.1**	5.3	mg/kg TS	3	H	ENMU

Er beteckning **Ex2S3Sn**

Provtagare **Célia Lointier**

Labnummer U11616750

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**64.8**	2.0	%	2	I	LIAS
Sn	**5.90**	1.85	mg/kg TS	3	H	ENMU

Er beteckning **Ex2S4Sn**

Provtagare **Célia Lointier**

Labnummer U11616751

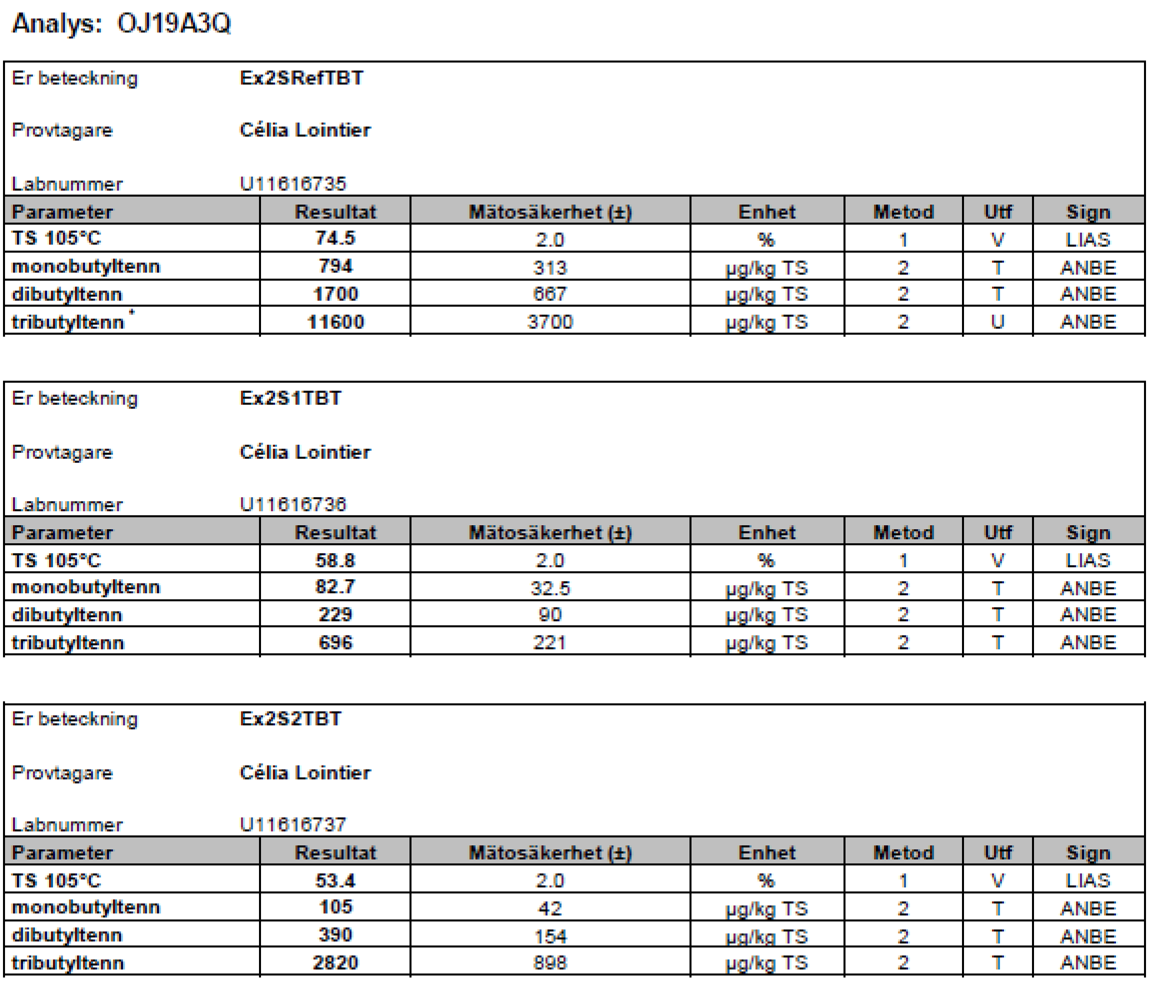
Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**52.5**	2.0	%	2	I	LIAS
Sn	**6.55**	2.12	mg/kg TS	3	H	ENMU

Er beteckning **Ex2S5Sn**

Provtagare **Célia Lointier**

Labnummer U11616761

Parameter	**Resultat**	**Mätosäkerhet (±)**	**Enhet**	**Metod**	**Utf**	**Sign**
Malning stålfat*	ja		ArbMom	1	I	TJ
TS	**56.1**	2.0	%	2	I	LIAS
Sn	**9.33**	3.11	mg/kg TS	3	H	ENMU



Analys: OJ19A3Q

Er beteckning	**Ex2SRefTBT**
Provtagare	**Célia Lointier**
Labnummer	U11616735

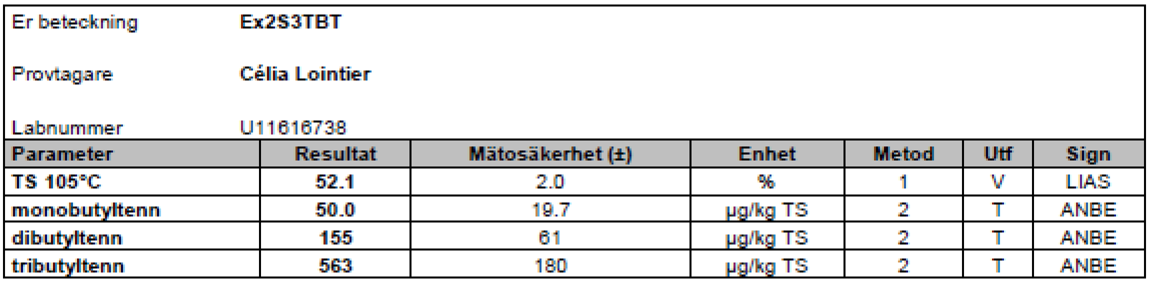
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**74.5**	2.0	%	1	V	LIAS
monobutyltenn	**794**	313	µg/kg TS	2	T	ANBE
dibutyltenn	**1700**	667	µg/kg TS	2	T	ANBE
tributyltenn *	**11600**	3700	µg/kg TS	2	U	ANBE

Er beteckning	**Ex2S1TBT**
Provtagare	**Célia Lointier**
Labnummer	U11616736

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**58.8**	2.0	%	1	V	LIAS
monobutyltenn	**82.7**	32.5	µg/kg TS	2	T	ANBE
dibutyltenn	**229**	90	µg/kg TS	2	T	ANBE
tributyltenn	**696**	221	µg/kg TS	2	T	ANBE

Er beteckning	**Ex2S2TBT**
Provtagare	**Célia Lointier**
Labnummer	U11616737

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**53.4**	2.0	%	1	V	LIAS
monobutyltenn	**105**	42	µg/kg TS	2	T	ANBE
dibutyltenn	**390**	154	µg/kg TS	2	T	ANBE
tributyltenn	**2820**	898	µg/kg TS	2	T	ANBE

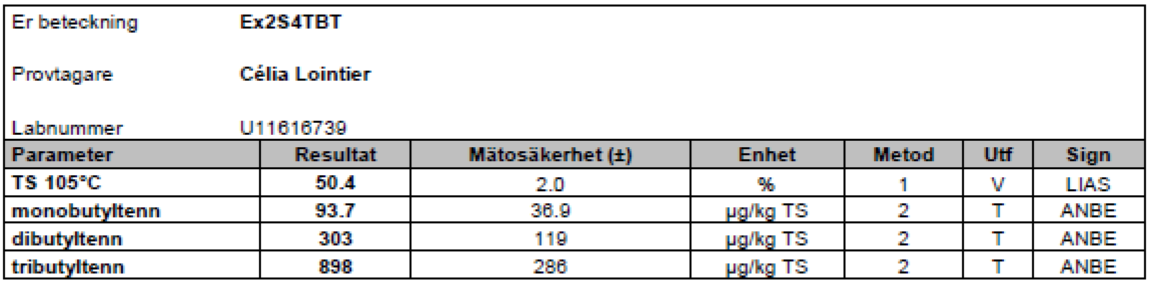


Er beteckning **Ex2S3TBT**

Provtagare **Célia Lointier**

Labnummer U11616738

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**52.1**	2.0	%	1	V	LIAS
monobutyltenn	**50.0**	19.7	µg/kg TS	2	T	ANBE
dibutyltenn	**155**	61	µg/kg TS	2	T	ANBE
tributyltenn	**563**	180	µg/kg TS	2	T	ANBE

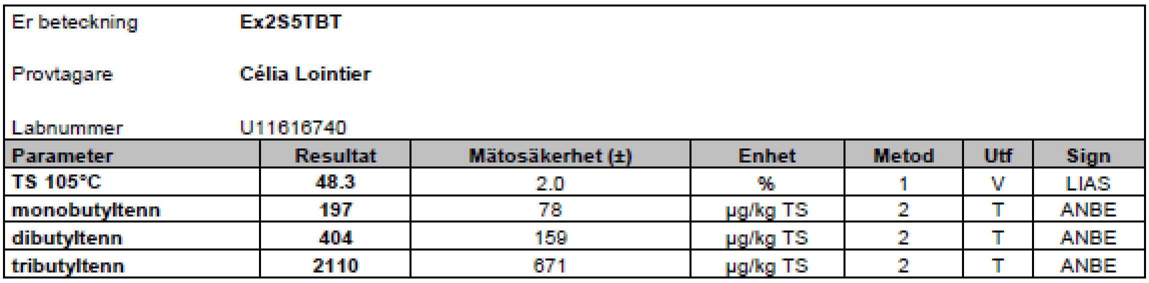


Er beteckning **Ex2S4TBT**

Provtagare **Célia Lointier**

Labnummer U11616739

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**50.4**	2.0	%	1	V	LIAS
monobutyltenn	**93.7**	36.9	µg/kg TS	2	T	ANBE
dibutyltenn	**303**	119	µg/kg TS	2	T	ANBE
tributyltenn	**898**	286	µg/kg TS	2	T	ANBE



Er beteckning **Ex2S5TBT**

Provtagare **Célia Lointier**

Labnummer U11616740

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**48.3**	2.0	%	1	V	LIAS
monobutyltenn	**197**	78	µg/kg TS	2	T	ANBE
dibutyltenn	**404**	159	µg/kg TS	2	T	ANBE
tributyltenn	**2110**	671	µg/kg TS	2	T	ANBE

Analys: V3BBAS

Er beteckning **Ex2WRefSn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614941

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**1.07**	0.24	µg/l	1	H	HEAN

Er beteckning **Ex2W1Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614942

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**27.4**	5.6	µg/l	1	H	HEAN

Er beteckning **Ex2W2Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614943

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**37.1**	8.0	µg/l	1	H	HEAN

Er beteckning **Ex2W3Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614944

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**92.9**	19.9	µg/l	1	H	HEAN

Er beteckning **Ex2W4Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614945

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**117**	24	µg/l	1	H	HEAN

Er beteckning **Ex2W5Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-11**

Labnummer U11614946

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	EMLI
Sn	**370**	72	µg/l	1	H	HEAN

Appendix 13. Fenton's reagent - OTC degradation in the sediments

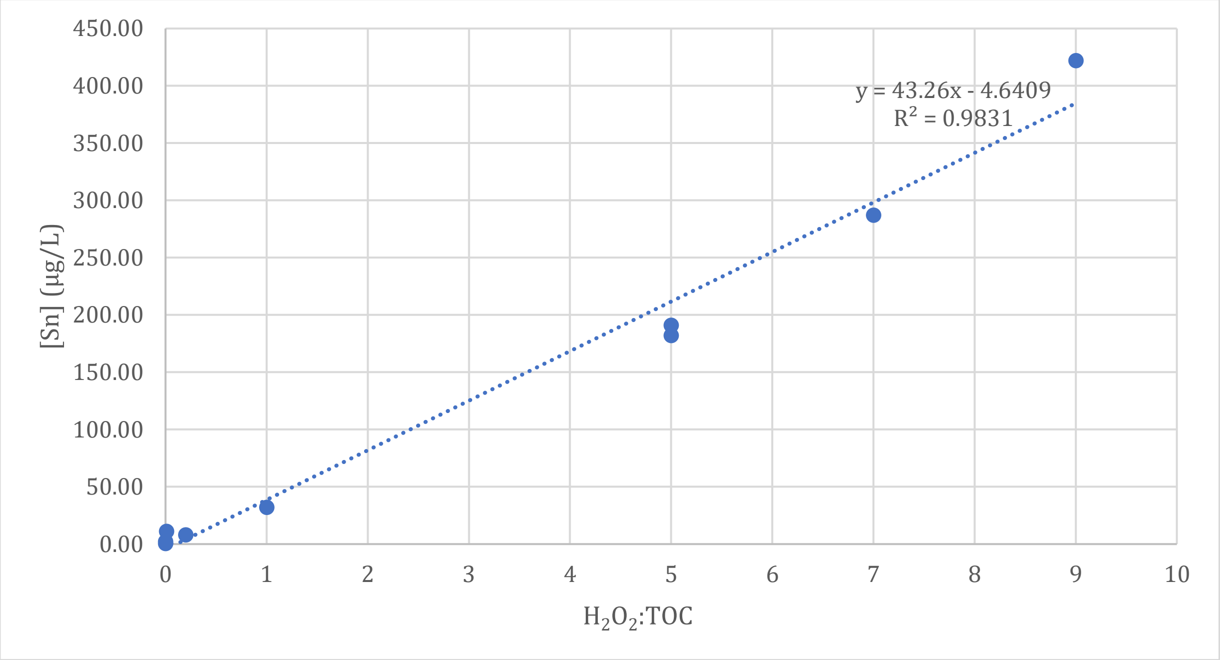
Sample	**1.Ref**	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**	**1.7**	**2.2**	**2.3**	**2.4**	**2.5**	**2.6**
H_2O_2:TOC	/	5	1	0.2	0.01	7	9	5	5	5	5	5
H_2O_2:Fe	/	5	5	5	5	5	5	40	20	15	10	2
Time of reaction (h)	24	24	24	24	24	24	24	24	24	24	24	24
TOC (%)	2.0	1.8	1.6	6.5	2.2	2.5	1.5	3.2	2.5	3.8	2.4	1.5
Sn (mg/kg)	13.60	10.40	9.63	12.00	12.30	13.40	9.95	9.96	16.10	5.90	6.55	9.33
TBT (µg/kg)	n.a	1910	n.a	6320	n.a	956	1610	696	2820	563	898	2110
DBT (µg/kg)	n.a	259	n.a	3110	n.a	143	287	229	390	155	303	404
MBT (µg/kg)	n.a	140	n.a	1870	n.a	76	37	83	105	50	94	197
OTC (µg/kg)	n.a	1009	n.a	5439	n.a	516	831	458	1425	344	586	1204
Degradation OTC (%)	n.a	87.5	n.a	32.7	n.a	93.6	89.7	94.3	82.4	95.8	92.8	85.1
+/-(%)*	n.a	3.9	n.a	21.1	n.a	2.0	3.2	1.8	5.5	1.3	2.3	4.7

Appendix 14. Fenton's reagent -Degradation percentage of OTC, TBT, DBT and MBT

Sample	**Mean OTC**	**"+/-"**	**Mean TBT**	**"+/-"**	**Mean DBT**	**"+/-"**	**Mean MBT**	**"+/-"**
Exp1.2	88	4	88	4	87	2	82	1
Exp1.4	33	21	60	14	-56	27	-147	11
Exp1.6	94	2	94	2	93	1	90	0
Exp1.7	90	3	90	4	86	3	95	0
Exp2.2	94	2	96	2	89	2	89	0
Exp2.3	82	6	82	6	80	3	86	1
Exp2.4	96	1	96	1	92	1	93	0
Exp2.5	93	2	94	2	85	3	88	1
Exp2.6	85	5	87	5	80	4	74	1

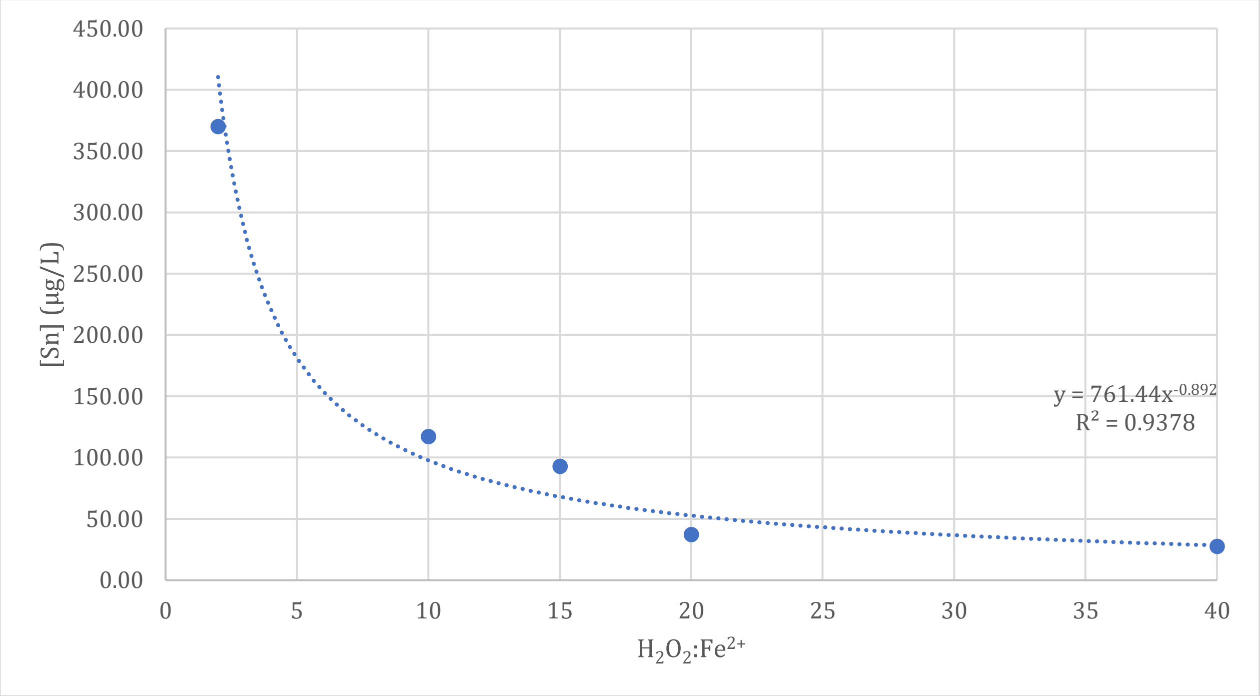
Appendix 15. Fenton's reagent - Concentration of tin in the water depending on the ratio H_2O_2:TOC.

The ratio $H_2O_2:Fe^{2+}$ is 5.

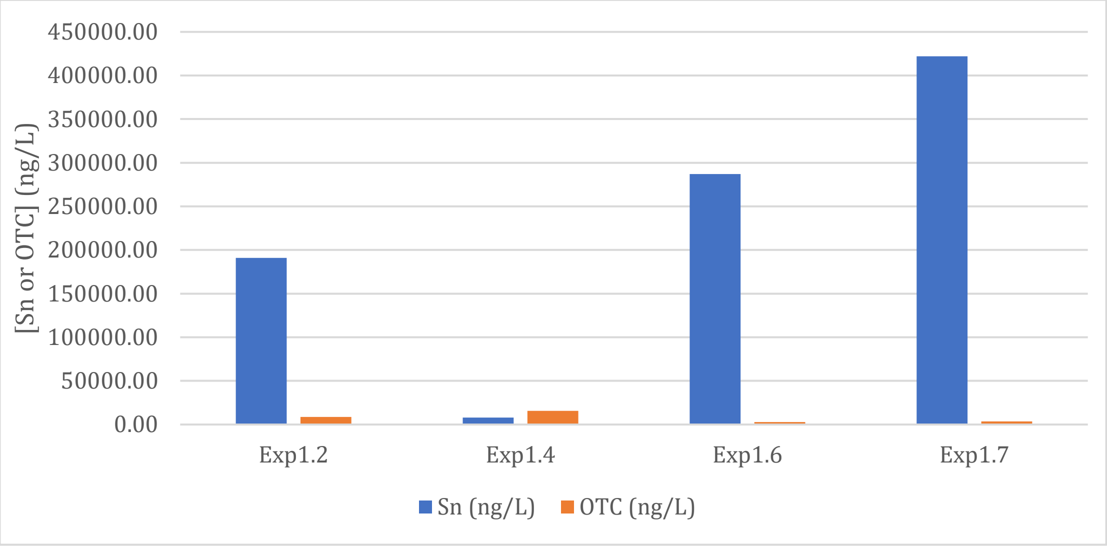


Appendix 16. Fenton's reagent - Concentration of tin in the water depending on the ratio $H_2O_2:Fe^{2+}$.

The ratio H_2O_2:TOC is 5 and the concentration of H_2O_2 introduced is the same for all experiments, only the concentration of iron is diminished.



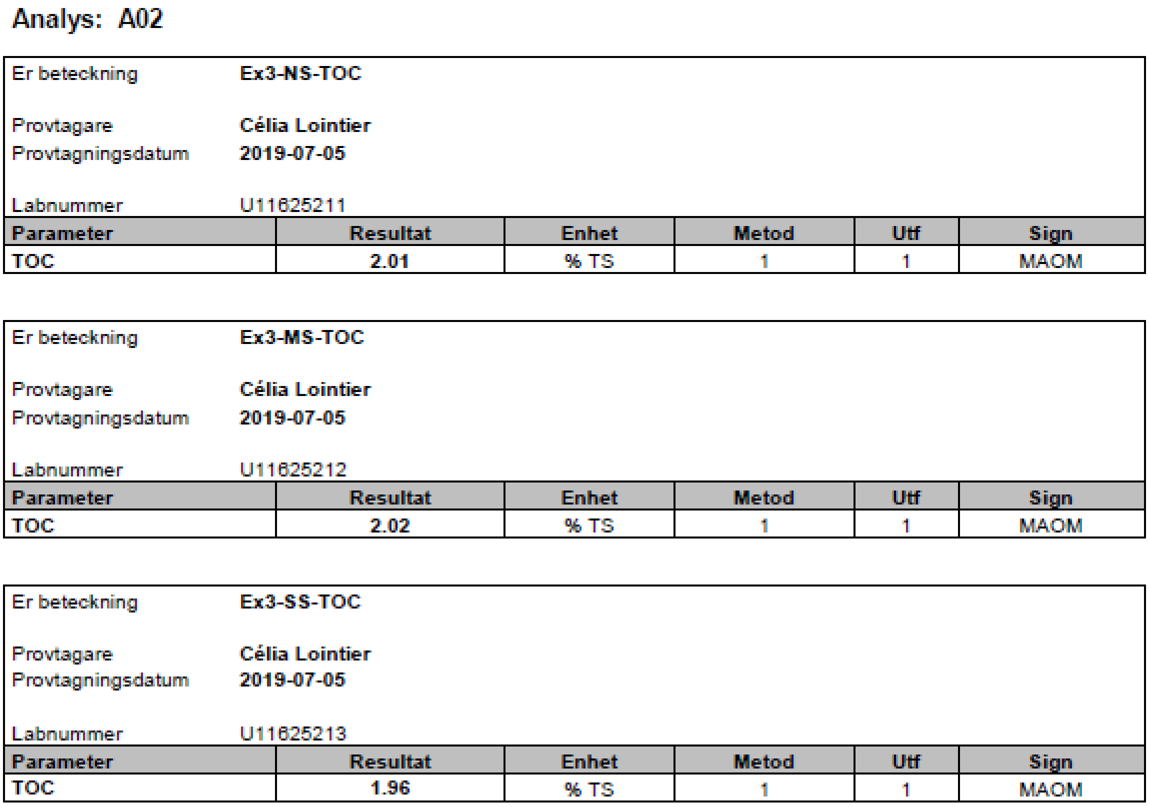
Appendix 17. Fenton's reagent – Experiment 1 -Tin and OTC in the liquid phase



Appendix 18. Fenton's reagent - Particle size distribution in the liquid

Name	Filtration	Hydrodynamic diam (µm)	Peak 1 (µm)	Peak 2 (µm)
Exp1.2	No	88.89	2.66	
Exp1.2	Yes	0.00	6.74	0.39
Exp1.4	No	63.70	3.50	
Exp1.4	Yes	0.00		
Exp1.6	No	23.82	0.30	
Exp1.6	Yes	297.52		
Exp1.7	No	10.33	8.85	0.28
Exp1.7	Yes	115.52	0.88	0.57
Exp3.S	No	57.54		
Exp3.M	No	189.44		
Exp3.O	No	535.41		
Exp4.S	No	172.34		
Exp4.M	No	203.68		
Exp4.O	No	650.27	0.00	

Appendix 19 : Reports delivered by ALS for the analysis – Fenton's reagent - Experiment 3



Analys: A02

Er beteckning	**Ex3-NS-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625211

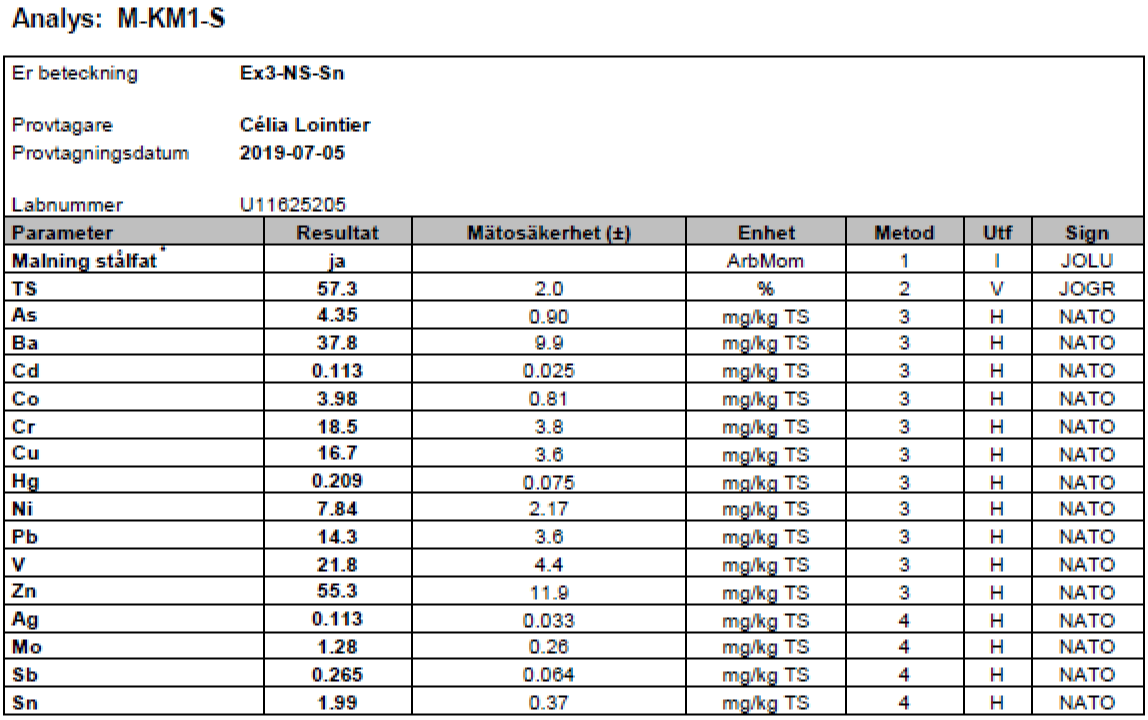
Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.01**	% TS	1	1	MAOM

Er beteckning	**Ex3-MS-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625212

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.02**	% TS	1	1	MAOM

Er beteckning	**Ex3-SS-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625213

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**1.96**	% TS	1	1	MAOM



Analys: M-KM1-S

Er beteckning	**Ex3-NS-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625205

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	JOLU
TS	**57.3**	2.0	%	2	V	JOGR
As	**4.35**	0.90	mg/kg TS	3	H	NATO
Ba	**37.8**	9.9	mg/kg TS	3	H	NATO
Cd	**0.113**	0.025	mg/kg TS	3	H	NATO
Co	**3.98**	0.81	mg/kg TS	3	H	NATO
Cr	**18.5**	3.8	mg/kg TS	3	H	NATO
Cu	**16.7**	3.6	mg/kg TS	3	H	NATO
Hg	**0.209**	0.075	mg/kg TS	3	H	NATO
Ni	**7.84**	2.17	mg/kg TS	3	H	NATO
Pb	**14.3**	3.6	mg/kg TS	3	H	NATO
V	**21.8**	4.4	mg/kg TS	3	H	NATO
Zn	**55.3**	11.9	mg/kg TS	3	H	NATO
Ag	**0.113**	0.033	mg/kg TS	4	H	NATO
Mo	**1.28**	0.26	mg/kg TS	4	H	NATO
Sb	**0.265**	0.064	mg/kg TS	4	H	NATO
Sn	**1.99**	0.37	mg/kg TS	4	H	NATO

Er beteckning **Ex3-MS-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

Labnummer U11625206

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	JOLU
TS	**56.6**	2.0	%	2	V	JOGR
As	**3.44**	0.77	mg/kg TS	3	H	NATO
Ba	**45.3**	11.6	mg/kg TS	3	H	NATO
Cd	**0.124**	0.025	mg/kg TS	3	H	NATO
Co	**5.13**	1.05	mg/kg TS	3	H	NATO
Cr	**18.8**	3.8	mg/kg TS	3	H	NATO
Cu	**15.7**	3.4	mg/kg TS	3	H	NATO
Hg	**0.253**	0.085	mg/kg TS	3	H	NATO
Ni	**9.59**	2.28	mg/kg TS	3	H	NATO
Pb	**16.0**	3.8	mg/kg TS	3	H	NATO
V	**25.3**	5.2	mg/kg TS	3	H	NATO
Zn	**67.8**	14.5	mg/kg TS	3	H	NATO
Ag	**0.132**	0.038	mg/kg TS	4	H	NATO
Mo	**1.39**	0.27	mg/kg TS	4	H	NATO
Sb	**0.348**	0.086	mg/kg TS	4	H	NATO
Sn	**8.80**	1.69	mg/kg TS	4	H	NATO

Er beteckning **Ex3-SS-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

Labnummer U11625207

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	JOLU
TS	**37.1**	2.0	%	2	V	JOGR
As	**3.99**	0.82	mg/kg TS	3	H	NATO
Ba	**48.8**	12.5	mg/kg TS	3	H	NATO
Cd	**<0.1**		mg/kg TS	3	H	NATO
Co	**5.21**	1.09	mg/kg TS	3	H	NATO
Cr	**19.7**	4.0	mg/kg TS	3	H	NATO
Cu	**15.0**	3.3	mg/kg TS	3	H	NATO
Hg	**0.260**	0.089	mg/kg TS	3	H	NATO
Ni	**10.3**	2.1	mg/kg TS	3	H	NATO
Pb	**21.2**	5.0	mg/kg TS	3	H	NATO
V	**27.3**	5.7	mg/kg TS	3	H	NATO
Zn	**70.7**	15.1	mg/kg TS	3	H	NATO
Ag	**0.159**	0.045	mg/kg TS	4	H	NATO
Mo	**1.40**	0.34	mg/kg TS	4	H	NATO
Sb	**0.391**	0.094	mg/kg TS	4	H	NATO
Sn	**3.74**	0.73	mg/kg TS	4	H	NATO

Analys: OJ19A3

Er beteckning	**Ex3-NS-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-05**
Labnummer	U11625208

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**49.8**	2.0	%	1	V	LIAS
monobutyltenn	**14.1**	5.5	µg/kg TS	2	T	ENMU
dibutyltenn	**22.1**	8.7	µg/kg TS	2	T	ENMU
tributyltenn	**9.72**	3.10	µg/kg TS	2	T	ENMU

Er beteckning	**Ex3-MS-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-05**
Labnummer	U11625209

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**50.3**	2.0	%	1	V	LIAS
monobutyltenn	**1290**	507	µg/kg TS	2	T	ENMU
dibutyltenn	**1960**	770	µg/kg TS	2	T	ENMU
tributyltenn *	**12400**	3940	µg/kg TS	2	U	ENMU

Er beteckning	**Ex3-SS-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-05**
Labnummer	U11625210

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**55.4**	2.0	%	1	V	LIAS
monobutyltenn	**22.8**	9.0	µg/kg TS	2	T	ENMU
dibutyltenn	**50.4**	19.9	µg/kg TS	2	T	ENMU
tributyltenn	**149**	48	µg/kg TS	2	T	ENMU

Analys: V3BBAS

Er beteckning	**Exp3-WN-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-06-27**
Labnummer	U11625811

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Nej**			1	I	HUCH
As	**346**	77	µg/l	1	H	IDJO
Ba	**<100**		µg/l	1	H	IDJO
Cd	**34.1**	6.6	µg/l	1	H	IDJO
Co	**451**	85	µg/l	1	H	IDJO
Cr	**937**	180	µg/l	1	H	IDJO
Cu	**6010**	1150	µg/l	1	H	IDJO
Mo	**<50**		µg/l	1	H	IDJO
Ni	**738**	199	µg/l	1	H	IDJO
Pb	**<50**		µg/l	1	H	IDJO
Sn	**<50**		µg/l	1	H	IDJO
V	**680**	145	µg/l	1	H	IDJO
Zn	**14600**	3120	µg/l	1	H	IDJO

Er beteckning	**Exp3-WM-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-06-27**
Labnummer	U11625812

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Nej**			1	I	HUCH
As	**360**	66	µg/l	1	H	IDJO
Ba	**<100**		µg/l	1	H	IDJO
Cd	**40.1**	6.9	µg/l	1	H	IDJO
Co	**477**	103	µg/l	1	H	IDJO
Cr	**889**	174	µg/l	1	H	IDJO
Cu	**4570**	855	µg/l	1	H	IDJO
Mo	**<50**		µg/l	1	H	IDJO
Ni	**609**	138	µg/l	1	H	IDJO
Pb	**86.5**	16.7	µg/l	1	H	IDJO
Sn	**<50**		µg/l	1	H	IDJO
V	**701**	149	µg/l	1	H	IDJO
Zn	**11600**	2460	µg/l	1	H	IDJO

Er beteckning	**Exp3-WS-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-06-27**
Labnummer	U11625813

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Nej**			1	I	HUCH
As	**205**	58	µg/l	1	H	IDJO
Ba	**<100**		µg/l	1	H	IDJO
Cd	**37.7**	7.2	µg/l	1	H	IDJO
Co	**405**	82	µg/l	1	H	IDJO
Cr	**398**	81	µg/l	1	H	IDJO
Cu	**3040**	556	µg/l	1	H	IDJO
Mo	**<50**		µg/l	1	H	IDJO
Ni	**607**	281	µg/l	1	H	IDJO
Pb	**249**	47	µg/l	1	H	IDJO
Sn	**598**	113	µg/l	1	H	IDJO
V	**669**	127	µg/l	1	H	IDJO
Zn	**9250**	1930	µg/l	1	H	IDJO

Analys: OV19A3Q

Er beteckning **Exp3-WN-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625817

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**6.81**	2.15	ng/l	1	T	ENMU
dibutyltenn	**6.84**	2.16	ng/l	1	T	ENMU
tributyltenn	**<0.2**		ng/l	1	T	ENMU

Er beteckning **Exp3-WM-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625818

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**14.6**	4.6	ng/l	1	T	ENMU
dibutyltenn	**52.7**	16.6	ng/l	1	T	ENMU
tributyltenn	**2.38**	0.74	ng/l	1	T	ENMU

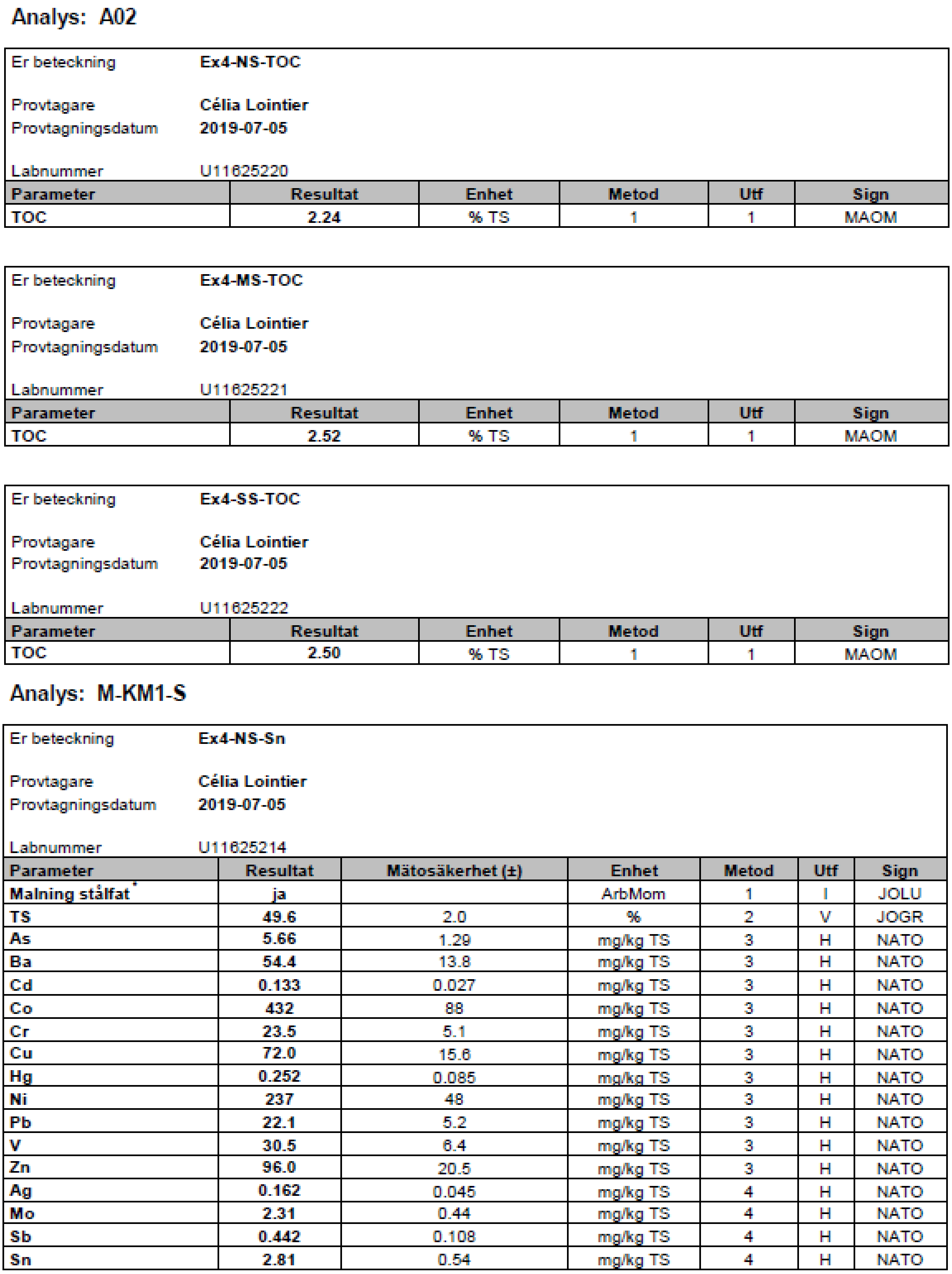
Er beteckning **Exp3-WS-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625819

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**71.4**	22.5	ng/l	1	T	ENMU
dibutyltenn	**333**	105	ng/l	1	T	ENMU
tributyltenn	**54.9**	17.0	ng/l	1	T	ENMU

Appendix 20: Reports delivered by ALS for the analysis – Fenton’s reagent - Experiment 4



Analys: A02

Er beteckning **Ex4-NS-TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

Labnummer U11625220

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.24**	% TS	1	1	MAOM

Er beteckning **Ex4-MS-TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

Labnummer U11625221

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.52**	% TS	1	1	MAOM

Er beteckning **Ex4-SS-TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

Labnummer U11625222

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.50**	% TS	1	1	MAOM

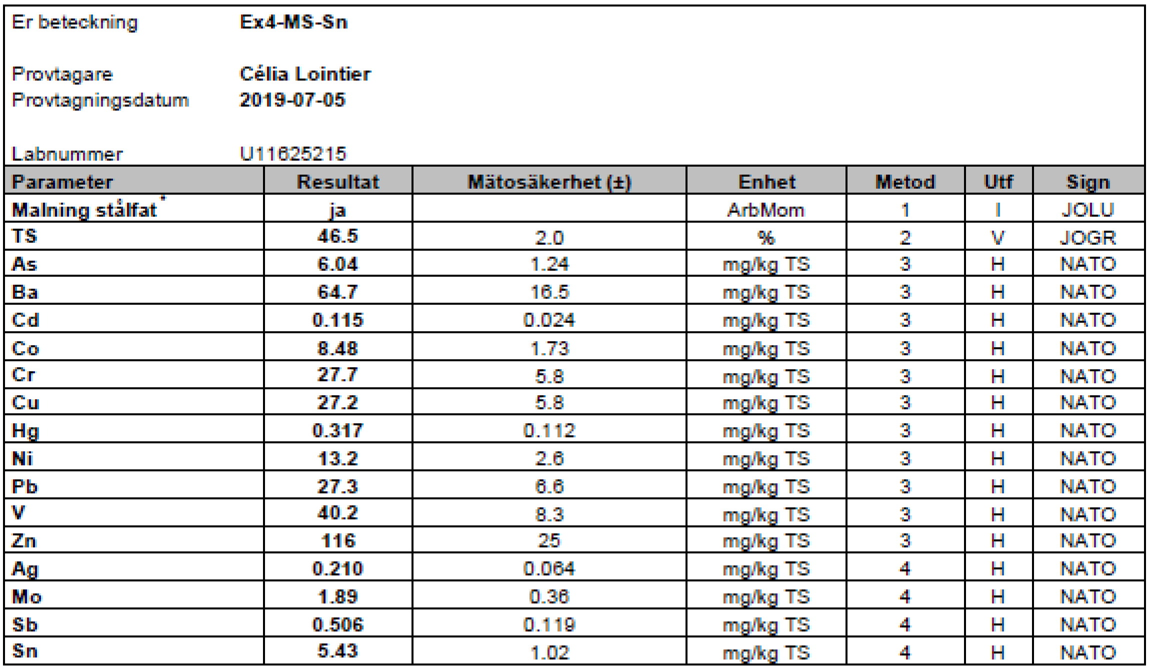
Analys: M-KM1-S

Er beteckning **Ex4-NS-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-07-05**

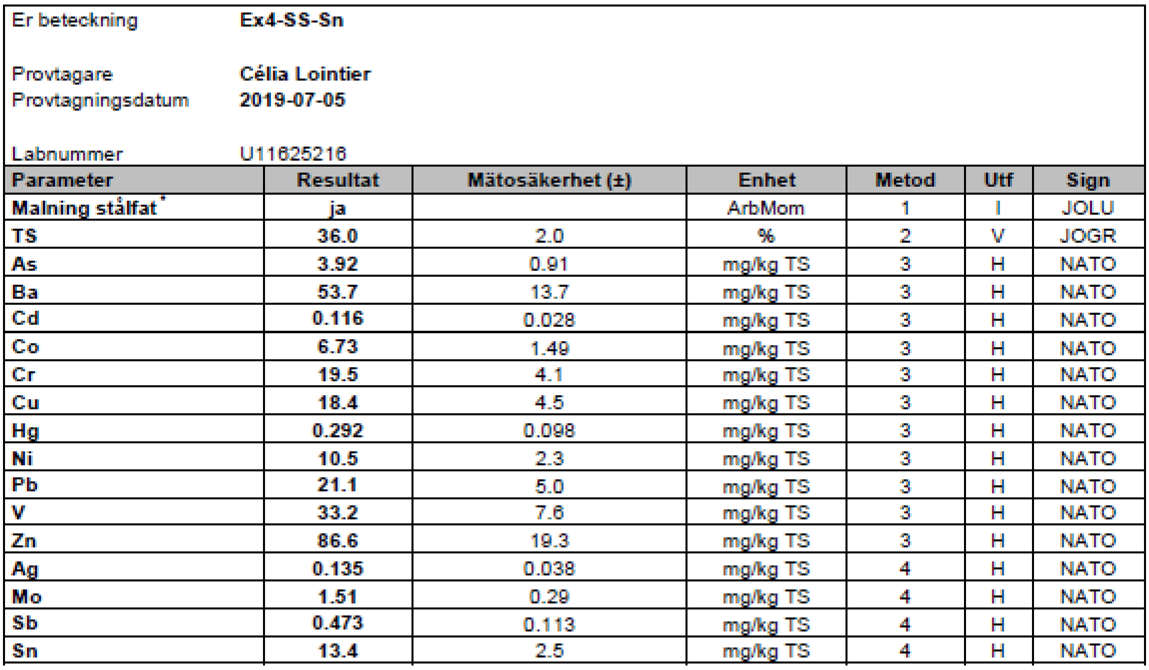
Labnummer U11625214

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	JOLU
TS	**49.6**	2.0	%	2	V	JOGR
As	**5.66**	1.29	mg/kg TS	3	H	NATO
Ba	**54.4**	13.8	mg/kg TS	3	H	NATO
Cd	**0.133**	0.027	mg/kg TS	3	H	NATO
Co	**432**	88	mg/kg TS	3	H	NATO
Cr	**23.5**	5.1	mg/kg TS	3	H	NATO
Cu	**72.0**	15.6	mg/kg TS	3	H	NATO
Hg	**0.252**	0.085	mg/kg TS	3	H	NATO
Ni	**237**	48	mg/kg TS	3	H	NATO
Pb	**22.1**	5.2	mg/kg TS	3	H	NATO
V	**30.5**	6.4	mg/kg TS	3	H	NATO
Zn	**96.0**	20.5	mg/kg TS	3	H	NATO
Ag	**0.162**	0.045	mg/kg TS	4	H	NATO
Mo	**2.31**	0.44	mg/kg TS	4	H	NATO
Sb	**0.442**	0.108	mg/kg TS	4	H	NATO
Sn	**2.81**	0.54	mg/kg TS	4	H	NATO



Er beteckning	**Ex4-MS-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625215

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	JOLU
TS	**46.5**	2.0	%	2	V	JOGR
As	**6.04**	1.24	mg/kg TS	3	H	NATO
Ba	**64.7**	16.5	mg/kg TS	3	H	NATO
Cd	**0.115**	0.024	mg/kg TS	3	H	NATO
Co	**8.48**	1.73	mg/kg TS	3	H	NATO
Cr	**27.7**	5.8	mg/kg TS	3	H	NATO
Cu	**27.2**	5.8	mg/kg TS	3	H	NATO
Hg	**0.317**	0.112	mg/kg TS	3	H	NATO
Ni	**13.2**	2.6	mg/kg TS	3	H	NATO
Pb	**27.3**	6.6	mg/kg TS	3	H	NATO
V	**40.2**	8.3	mg/kg TS	3	H	NATO
Zn	**116**	25	mg/kg TS	3	H	NATO
Ag	**0.210**	0.064	mg/kg TS	4	H	NATO
Mo	**1.89**	0.36	mg/kg TS	4	H	NATO
Sb	**0.506**	0.119	mg/kg TS	4	H	NATO
Sn	**5.43**	1.02	mg/kg TS	4	H	NATO



Er beteckning	**Ex4-SS-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-07-05**
Labnummer	U11625216

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	JOLU
TS	**36.0**	2.0	%	2	V	JOGR
As	**3.92**	0.91	mg/kg TS	3	H	NATO
Ba	**53.7**	13.7	mg/kg TS	3	H	NATO
Cd	**0.116**	0.028	mg/kg TS	3	H	NATO
Co	**6.73**	1.49	mg/kg TS	3	H	NATO
Cr	**19.5**	4.1	mg/kg TS	3	H	NATO
Cu	**18.4**	4.5	mg/kg TS	3	H	NATO
Hg	**0.292**	0.098	mg/kg TS	3	H	NATO
Ni	**10.5**	2.3	mg/kg TS	3	H	NATO
Pb	**21.1**	5.0	mg/kg TS	3	H	NATO
V	**33.2**	7.6	mg/kg TS	3	H	NATO
Zn	**86.6**	19.3	mg/kg TS	3	H	NATO
Ag	**0.135**	0.038	mg/kg TS	4	H	NATO
Mo	**1.51**	0.29	mg/kg TS	4	H	NATO
Sb	**0.473**	0.113	mg/kg TS	4	H	NATO
Sn	**13.4**	2.5	mg/kg TS	4	H	NATO

Analys: OJ19A3

Er beteckning **Ex4-NS-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-05**

Labnummer U11625217

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**35.4**	2.0	%	1	V	LIAS
monobutyltenn	**26.3**	10.3	µg/kg TS	2	T	ENMU
dibutyltenn	**34.9**	13.7	µg/kg TS	2	T	ENMU
tributyltenn	**12.3**	3.9	µg/kg TS	2	T	ENMU

Er beteckning **Ex4-MS-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-05**

Labnummer U11625218

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**46.6**	2.0	%	1	V	LIAS
monobutyltenn	**58.9**	23.2	µg/kg TS	2	T	ENMU
dibutyltenn	**119**	47	µg/kg TS	2	T	ENMU
tributyltenn	**347**	111	µg/kg TS	2	T	ENMU

Er beteckning **Ex4-SS-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-05**

Labnummer U11625219

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**58.9**	2.0	%	1	V	LIAS
monobutyltenn	**237**	93	µg/kg TS	2	T	ENMU
dibutyltenn	**456**	179	µg/kg TS	2	T	ENMU
tributyltenn	**5310**	1690	µg/kg TS	2	T	ENMU

Er beteckning **Exp4-WN-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625814

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys *	**Nej**			1	I	HUCH
As	**80.3**	21.9	µg/l	1	H	IDJO
Ba	**<50**		µg/l	1	H	IDJO
Cd	**38.7**	6.4	µg/l	1	H	IDJO
Co	**178000**	32400	µg/l	1	H	IDJO
Cr	**524**	102	µg/l	1	H	IDJO
Cu	**21300**	3910	µg/l	1	H	IDJO
Mo	**<30**		µg/l	1	H	IDJO
Ni	**100000**	19100	µg/l	1	H	IDJO
Pb	**195**	37	µg/l	1	H	IDJO
Sn	**<30**		µg/l	1	H	IDJO
V	**700**	135	µg/l	1	H	IDJO
Zn	**12200**	2540	µg/l	1	H	IDJO

Er beteckning **Exp4-WM-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625815

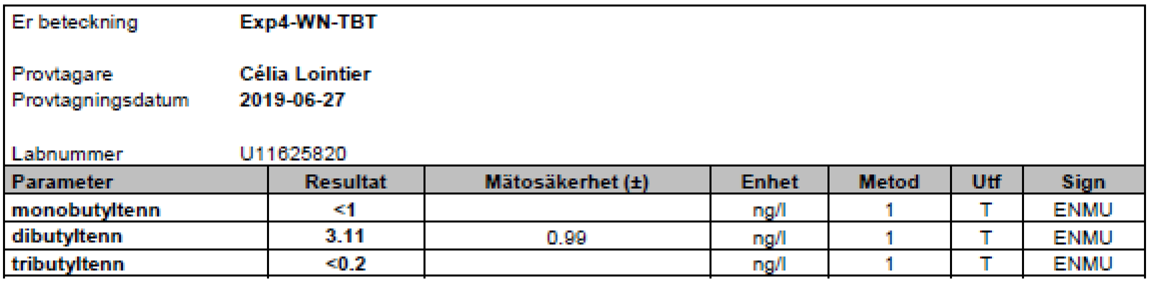
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys[*]	**Nej**			1	I	HUCH
As	**183**	46	µg/l	1	H	IDJO
Ba	**<50**		µg/l	1	H	IDJO
Cd	**41.2**	6.8	µg/l	1	H	IDJO
Co	**355**	67	µg/l	1	H	IDJO
Cr	**385**	74	µg/l	1	H	IDJO
Cu	**3460**	643	µg/l	1	H	IDJO
Mo	**<30**		µg/l	1	H	IDJO
Ni	**582**	118	µg/l	1	H	IDJO
Pb	**157**	31	µg/l	1	H	IDJO
Sn	**<30**		µg/l	1	H	IDJO
V	**624**	121	µg/l	1	H	IDJO
Zn	**9650**	2010	µg/l	1	H	IDJO

Er beteckning **Exp4-WS-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625816

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys[*]	**Nej**			1	I	HUCH
As	**199**	65	µg/l	1	H	IDJO
Ba	**<50**		µg/l	1	H	IDJO
Cd	**39.8**	6.6	µg/l	1	H	IDJO
Co	**381**	78	µg/l	1	H	IDJO
Cr	**410**	88	µg/l	1	H	IDJO
Cu	**3250**	590	µg/l	1	H	IDJO
Mo	**<30**		µg/l	1	H	IDJO
Ni	**538**	176	µg/l	1	H	IDJO
Pb	**163**	31	µg/l	1	H	IDJO
Sn	**143**	27	µg/l	1	H	IDJO
V	**698**	134	µg/l	1	H	IDJO
Zn	**10600**	2200	µg/l	1	H	IDJO

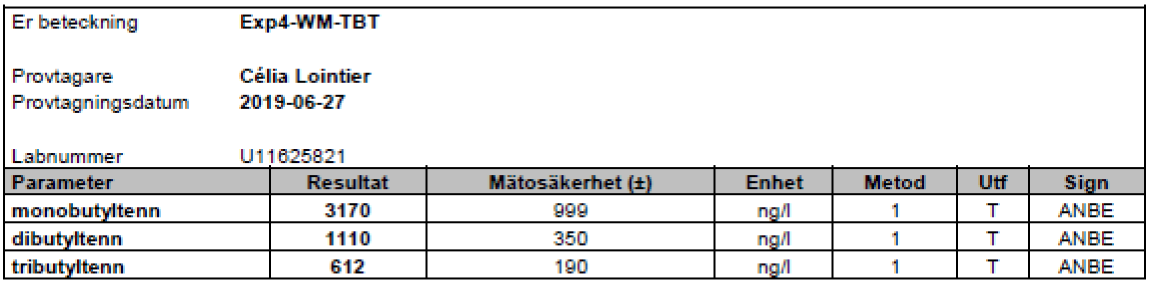


Er beteckning **Exp4-WN-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625820

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**<1**		ng/l	1	T	ENMU
dibutyltenn	**3.11**	0.99	ng/l	1	T	ENMU
tributyltenn	**<0.2**		ng/l	1	T	ENMU

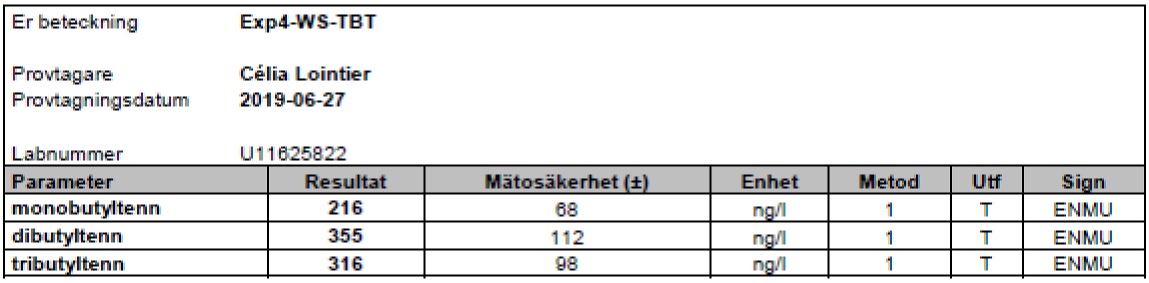


Er beteckning **Exp4-WM-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625821

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**3170**	999	ng/l	1	T	ANBE
dibutyltenn	**1110**	350	ng/l	1	T	ANBE
tributyltenn	**612**	190	ng/l	1	T	ANBE



Er beteckning **Exp4-WS-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11625822

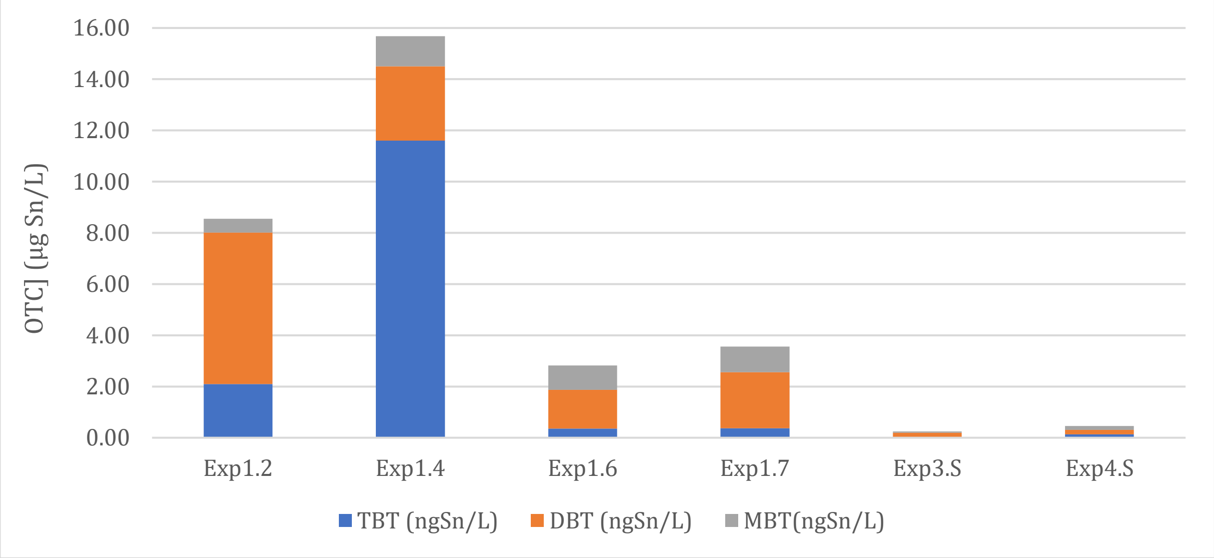
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**216**	68	ng/l	1	T	ENMU
dibutyltenn	**355**	112	ng/l	1	T	ENMU
tributyltenn	**316**	98	ng/l	1	T	ENMU

Appendix 21. Fenton's reagent - Concentrations measured in the Spiked sediments before and after the degradation experiments

Sample	**H2O2:TOC**	**H2O2:Fe**	**Sn sediments(mg/kg)**	**TOC**	**TBT(µg/kg)**	**DBT(µg/kg)**	**MBT(µg/kg)**	**OTC (µg Sn/kg)**
Spiked 1	0	0	14.7	2.1	24500	2427	726	11767
Spiked 2	0	0	16.00	2.64	11600	1700	794	6156
Exp3.S	5	5	14.70	1.96	12400	1960	1290	6952
Exp4.S	1	2	13.40	2.50	5310	456	237	2568

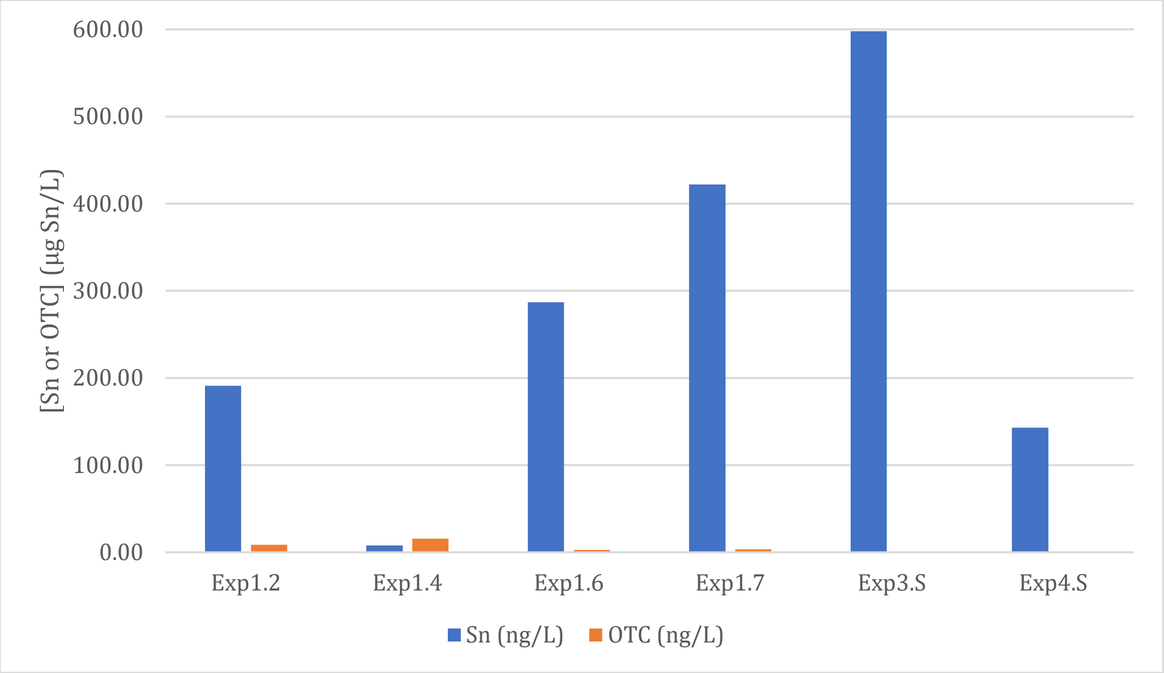
Appendix 22. Fenton's reagent - Concentrations measured in the liquid of Spiked sediments before and after the degradation experiments

Sample	**H2O2:TOC**	**H2O2:Fe**	**Filtration**	**Sn (µg/L)**	**TBT (ng/L)**	**DBT (ng/L)**	**MBT (ng/L)**	**OTC (ng/L)**
Exp3.S	5	5	No	598.00	54.9	333	71.4	240.59
Exp4.S	5	2	No	143	316	355	216	456.49



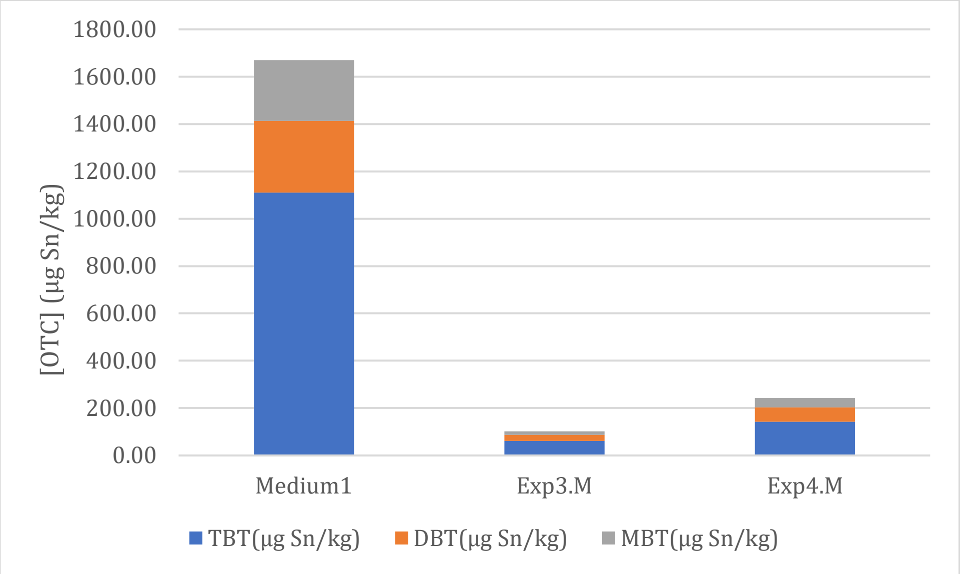
Appendix 23. Fenton’s reagent - Concentration of OTC compared to the concentration of tin measured in the aqueous phase.

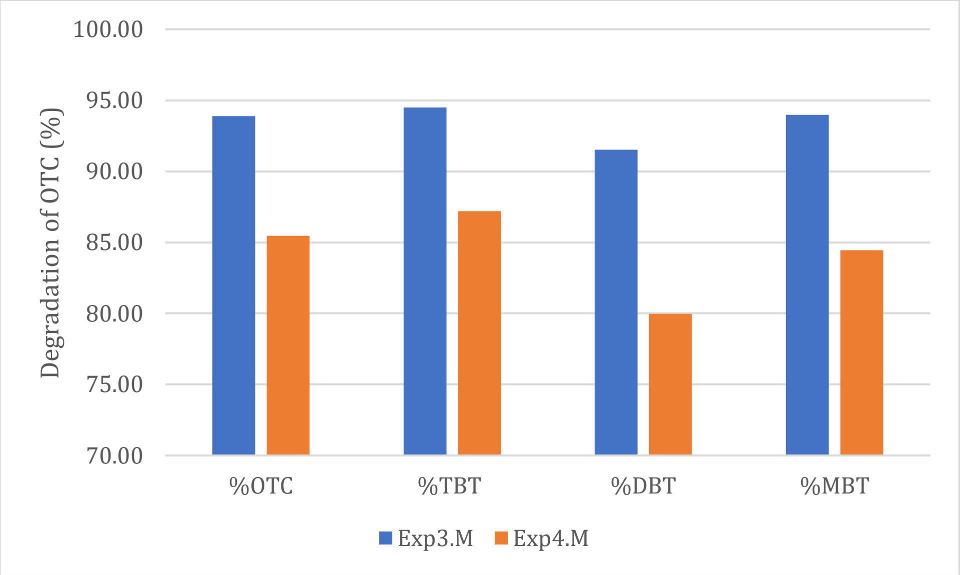
Exp3.S and Exp1.2 : H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=5; Exp4.S: H_2O_2:TOC =1 H_2O_2:Fe^{2+}=2 and Exp2.6: H_2O_2:TOC = 5 H_2O_2:Fe^{2+}=2.



Appendix 24. Fenton's reagent - Concentrations measured in the medium1 sediments before and after the degradation experiments

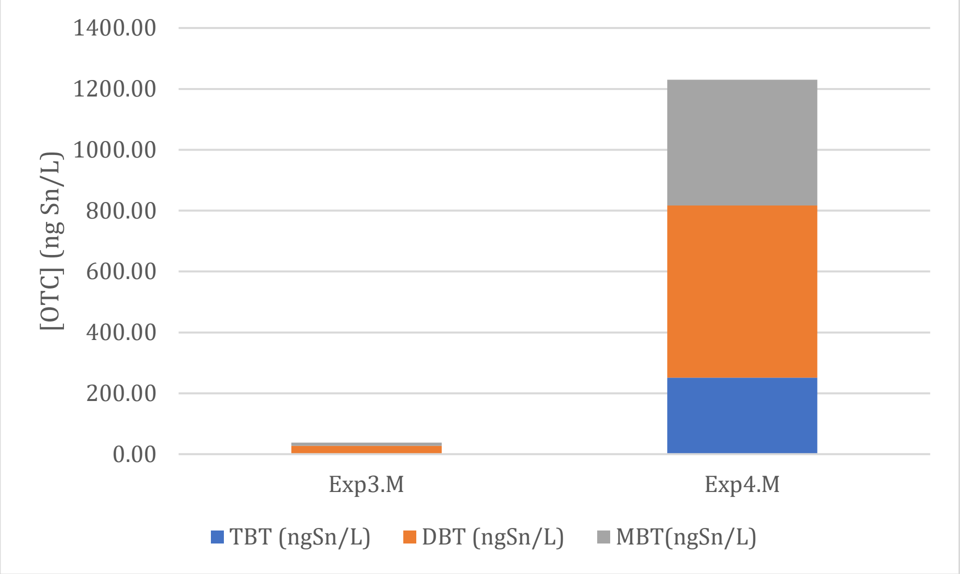
Sample	**H_2O_2:TOC**	**H_2O_2:Fe^{2+}**	**Sn (mg/kg)**	**TOC**	**TBT(µg/kg)**	**DBT(µg/kg)**	**MBT(µg/kg)**	**OTC (µg Sn/kg)**
Medium1	/	/	4.4	2.4	2710	594	379	1669
Exp3.M	5	5	8.8	2.0	149	50	23	102
Exp4.M	1	2	5.4	2.5	347	119	59	242





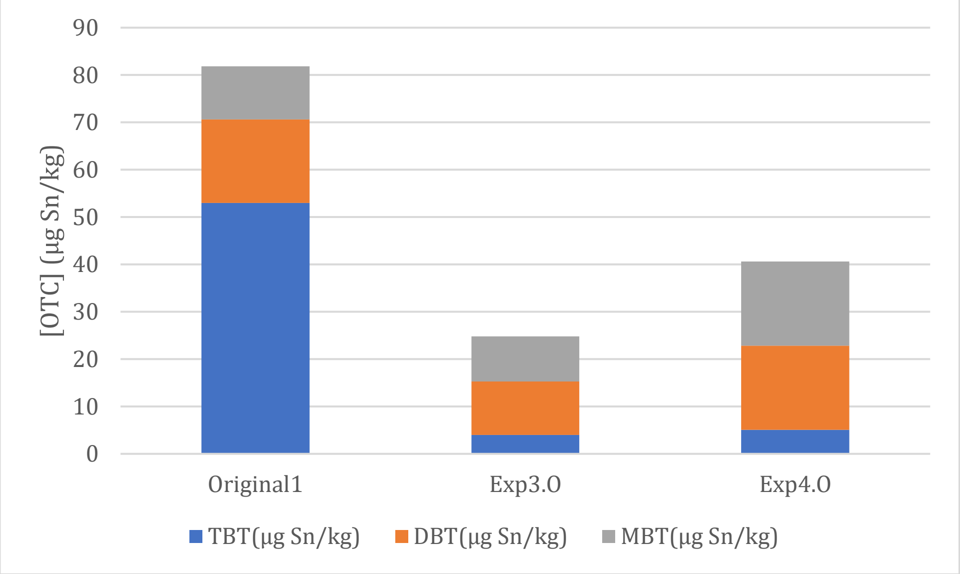
Appendix 25. Fenton's reagent - Concentrations measured in the liquid of medium1 sediments before and after the degradation experiments

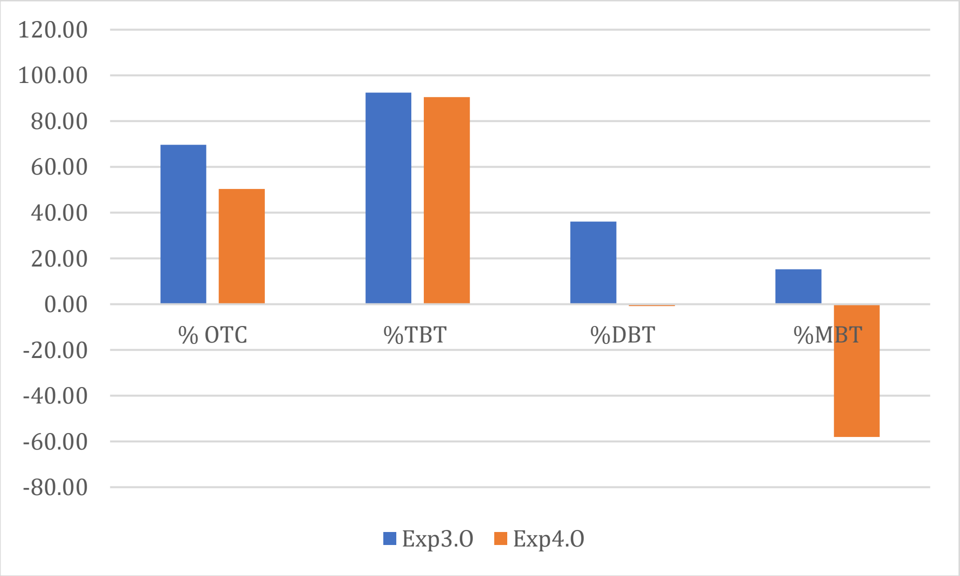
Sample	**H2O2:TOC**	**H2O2:Fe**	**Filtration**	**Sn (µg/L)**	**TBT (ng/L)**	**DBT (ng/L)**	**MBT (ng/L)**	**OTC (ng/L)**
Exp3.M	5	5	No	<50	2.38	52.7	14.6	37.72
Exp4.M	5	2	No	<30	612	1110	612	1230.42



Appendix 26. Fenton's reagent - Concentrations measured in the original sediments before and after the degradation experiments

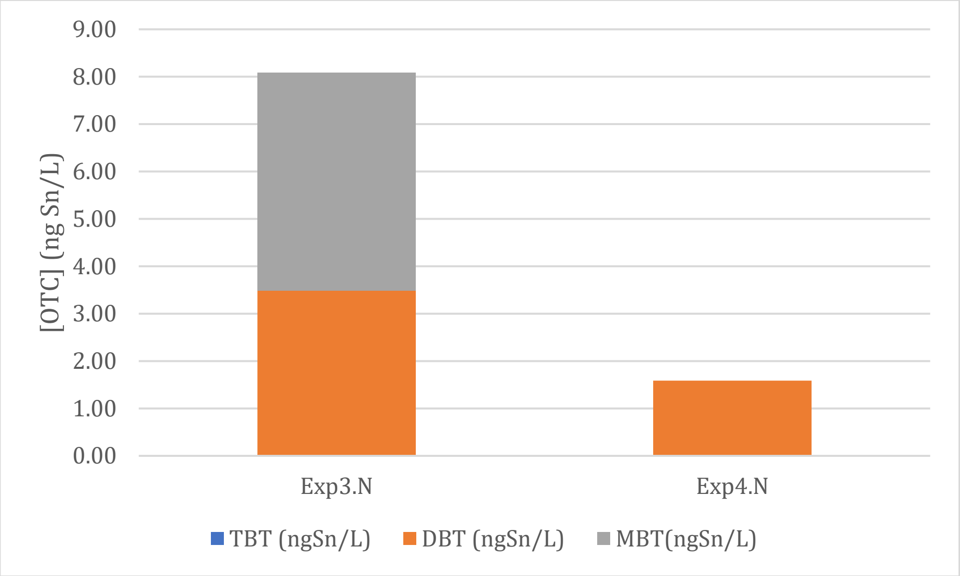
Sample	H_2O_2:TOC	H_2O_2:Fe^{2+}	Sn (mg/kg)	TOC	TBT(μg/kg)	DBT(μg/kg)	MBT(μg/kg)	OTC (μg Sn/kg)
Original1			2.9	2.1	129	35	17	82
Exp3.O	5	5	2.0	2.0	10	22	14	25
Exp4.O	1	2	2.8	2.2	12	35	26	41





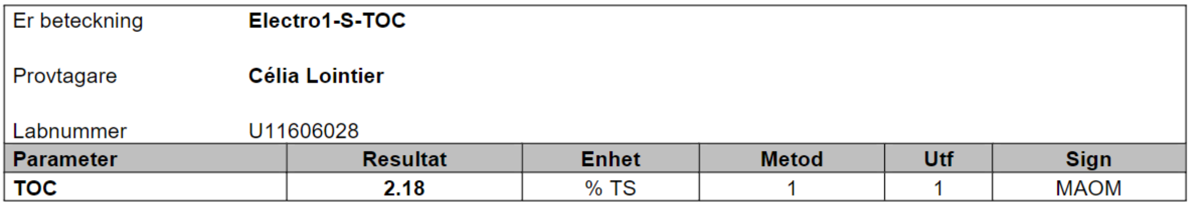
Appendix 27. Fenton's reagent - Concentrations measured in the liquid of original sediments before and after the degradation experiments

Sample	**H2O2:TOC**	**H2O2:Fe**	**Filtration**	**Sn (µg/L)**	**TBT (ng/L)**	**DBT (ng/L)**	**MBT (ng/L)**	**OTC (ng/L)**
Exp3.N	5	5	No	<50	<0.2	6.84	6.81	8.09
Exp4.N	5	2	No	<30	<0.2	3.11	<1	1.59



Appendix 28: Reports delivered by ALS for the analysis – Electrochemistry - Experiment 1

analysis on electrochemistry 1

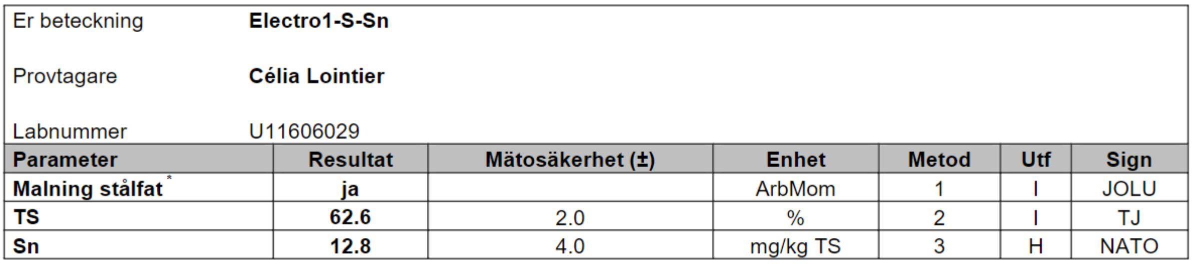


Er beteckning **Electro1-S-TOC**

Provtagare **Célia Lointier**

Labnummer U11606028

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.18**	% TS	1	1	MAOM

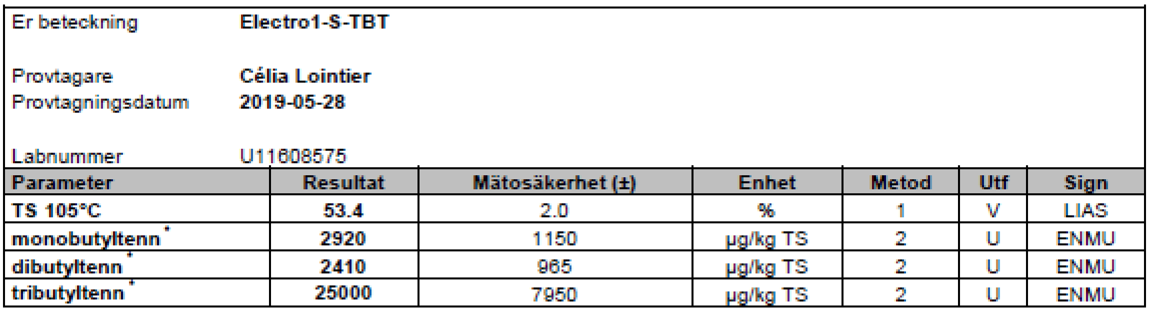


Er beteckning **Electro1-S-Sn**

Provtagare **Célia Lointier**

Labnummer U11606029

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	JOLU
TS	**62.6**	2.0	%	2	I	TJ
Sn	**12.8**	4.0	mg/kg TS	3	H	NATO

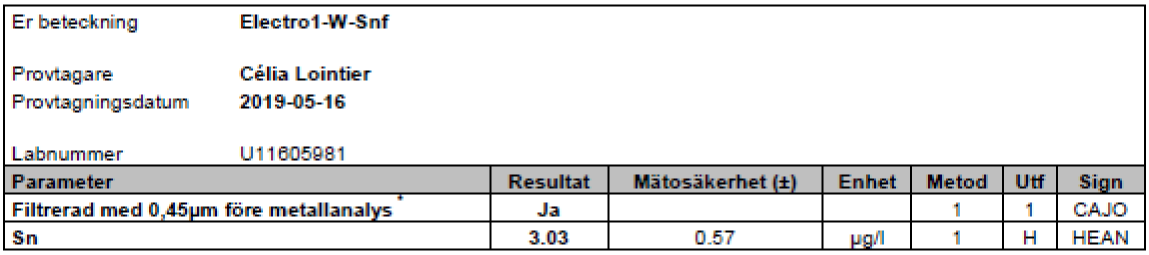


Er beteckning **Electro1-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608575

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**53.4**	2.0	%	1	V	LIAS
monobutyltenn*	**2920**	1150	µg/kg TS	2	U	ENMU
dibutyltenn*	**2410**	965	µg/kg TS	2	U	ENMU
tributyltenn*	**25000**	7950	µg/kg TS	2	U	ENMU

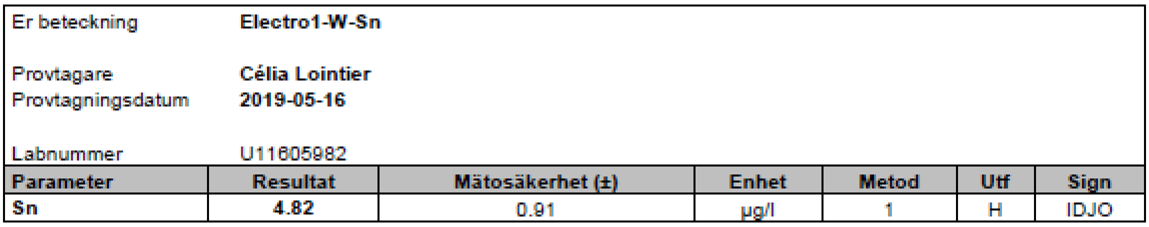


Er beteckning **Electro1-W-Snf**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-16**

Labnummer U11605981

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	1	CAJO
Sn	**3.03**	0.57	µg/l	1	H	HEAN



Er beteckning **Electro1-W-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-16**

Labnummer U11605982

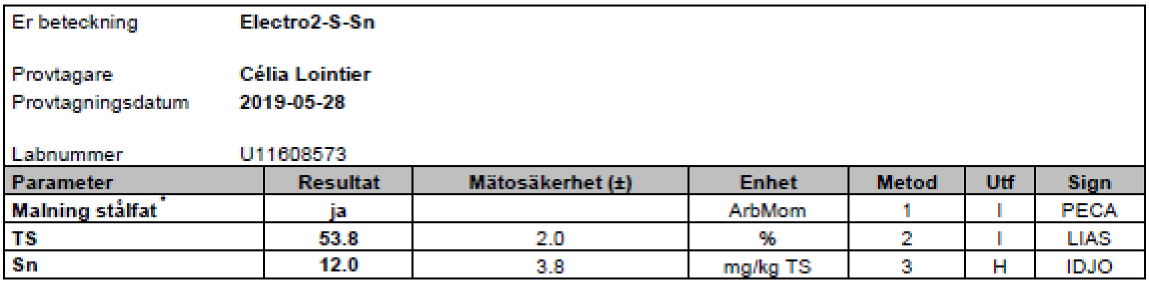
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**4.82**	0.91	µg/l	1	H	IDJO

Er beteckning	**Electro1-W-TBT**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-05-28**
Labnummer	U11608340

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**3250**	1020	ng/l	1	T	ANBE
dibutyltenn	**692**	219	ng/l	1	T	ANBE
tributyltenn	**2530**	784	ng/l	1	T	ANBE

Appendix 29 : Reports delivered by ALS for the analysis – Electrochemistry - Experiment 2

analysis on electrochemistry 2

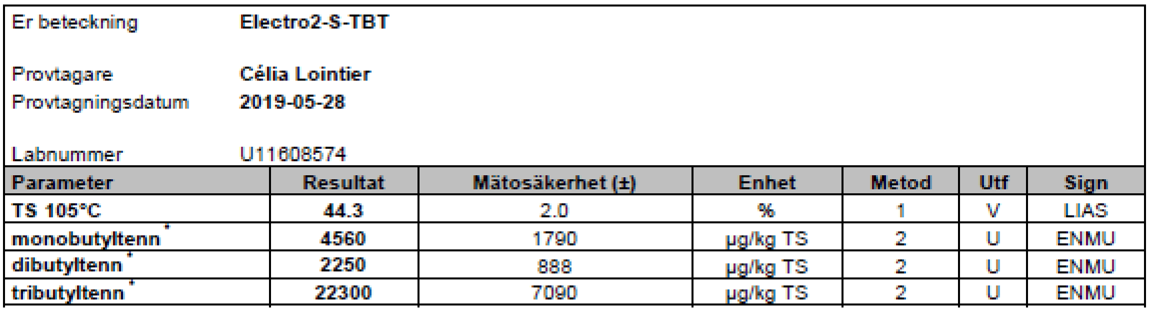


Er beteckning **Electro2-S-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608573

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat *	ja		ArbMom	1	I	PECA
TS	53.8	2.0	%	2	I	LIAS
Sn	**12.0**	3.8	mg/kg TS	3	H	IDJO

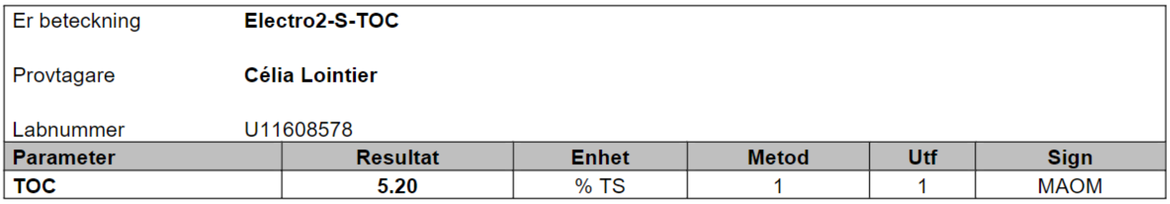


Er beteckning **Electro2-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608574

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**44.3**	2.0	%	1	V	LIAS
monobutyltenn *	**4560**	1790	µg/kg TS	2	U	ENMU
dibutyltenn *	**2250**	888	µg/kg TS	2	U	ENMU
tributyltenn *	**22300**	7090	µg/kg TS	2	U	ENMU

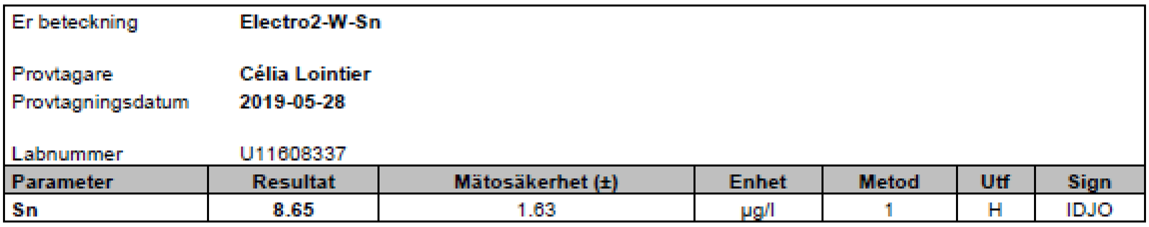


Er beteckning **Electro2-S-TOC**

Provtagare **Célia Lointier**

Labnummer U11608578

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**5.20**	% TS	1	1	MAOM

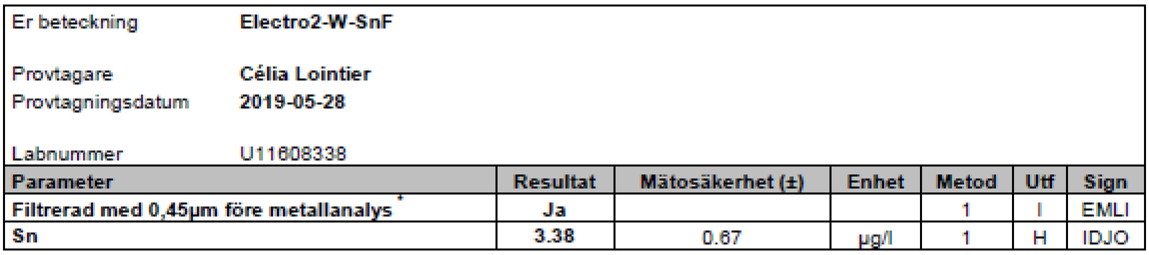


Er beteckning **Electro2-W-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608337

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**8.65**	1.63	µg/l	1	H	IDJO

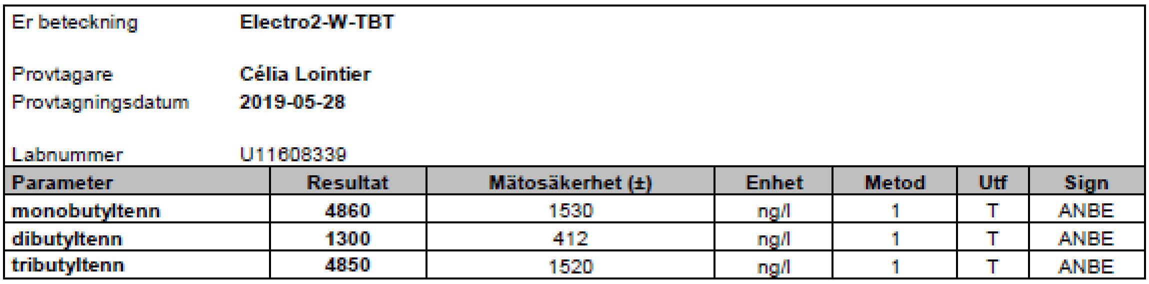


Er beteckning **Electro2-W-SnF**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608338

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys *	**Ja**			1	I	EMLI
Sn	**3.38**	0.67	µg/l	1	H	IDJO



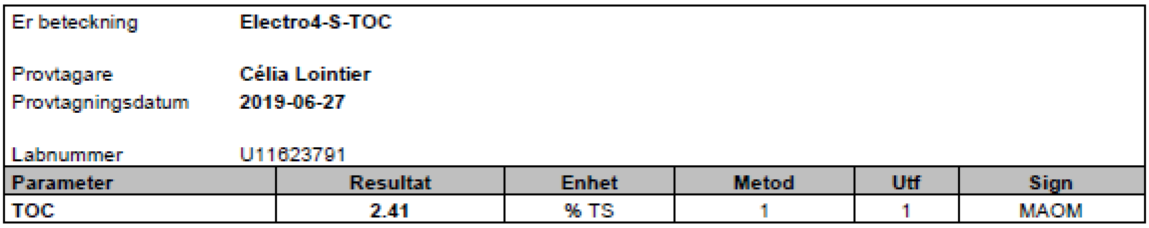
Er beteckning **Electro2-W-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-05-28**

Labnummer U11608339

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**4860**	1530	ng/l	1	T	ANBE
dibutyltenn	**1300**	412	ng/l	1	T	ANBE
tributyltenn	**4850**	1520	ng/l	1	T	ANBE

Appendix 30 : Reports delivered by ALS for the analysis – Electrochemistry - Experiment 3

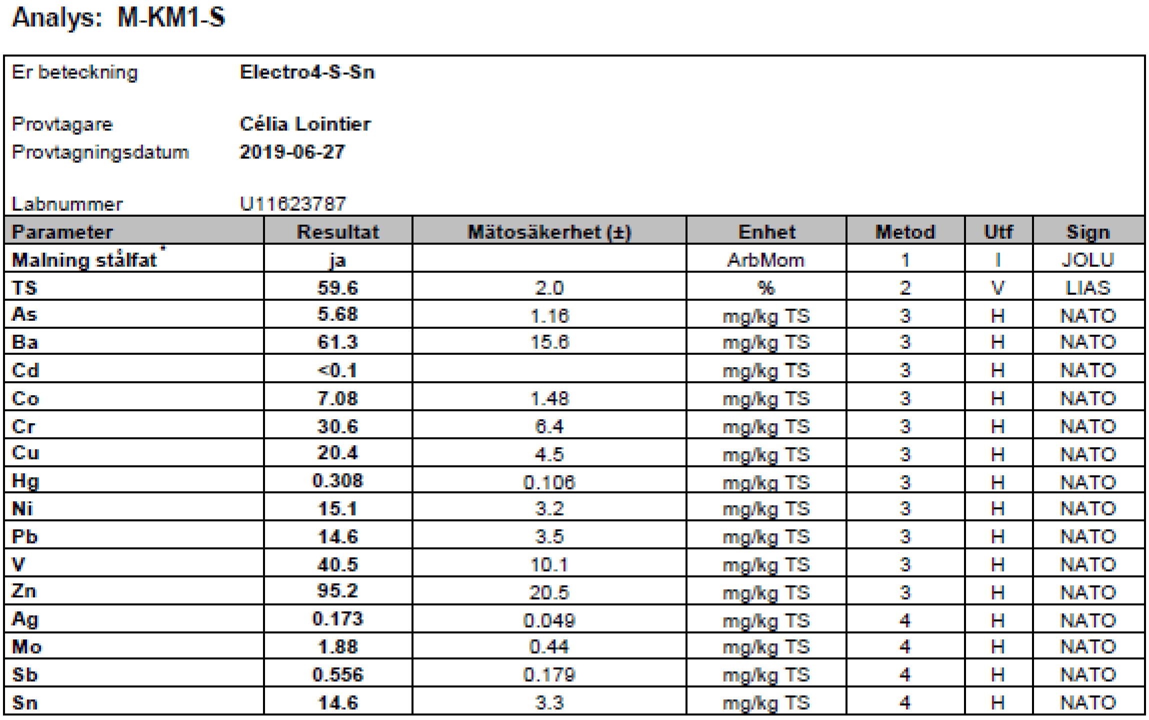


Er beteckning **Electro4-S-TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623791

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.41**	% TS	1	1	MAOM



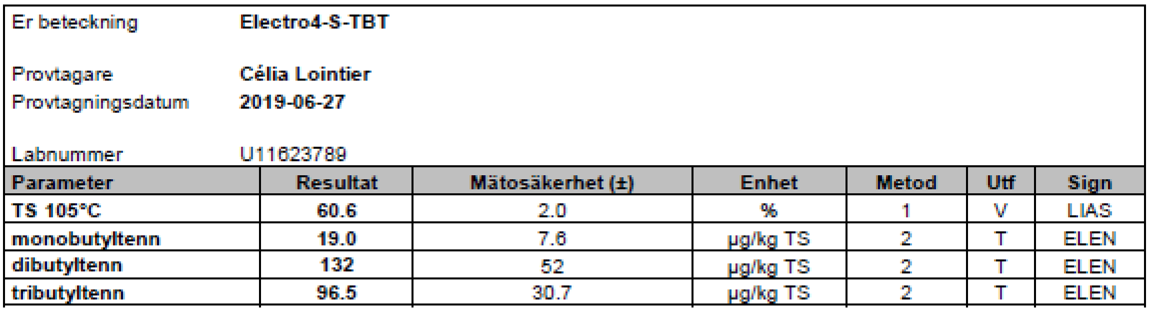
Analys: M-KM1-S

Er beteckning **Electro4-S-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623787

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	ja		ArbMom	1	I	JOLU
TS	**59.6**	2.0	%	2	V	LIAS
As	**5.68**	1.16	mg/kg TS	3	H	NATO
Ba	**61.3**	15.6	mg/kg TS	3	H	NATO
Cd	**<0.1**		mg/kg TS	3	H	NATO
Co	**7.08**	1.48	mg/kg TS	3	H	NATO
Cr	**30.6**	6.4	mg/kg TS	3	H	NATO
Cu	**20.4**	4.5	mg/kg TS	3	H	NATO
Hg	**0.308**	0.106	mg/kg TS	3	H	NATO
Ni	**15.1**	3.2	mg/kg TS	3	H	NATO
Pb	**14.6**	3.5	mg/kg TS	3	H	NATO
V	**40.5**	10.1	mg/kg TS	3	H	NATO
Zn	**95.2**	20.5	mg/kg TS	3	H	NATO
Ag	**0.173**	0.049	mg/kg TS	4	H	NATO
Mo	**1.88**	0.44	mg/kg TS	4	H	NATO
Sb	**0.556**	0.179	mg/kg TS	4	H	NATO
Sn	**14.6**	3.3	mg/kg TS	4	H	NATO

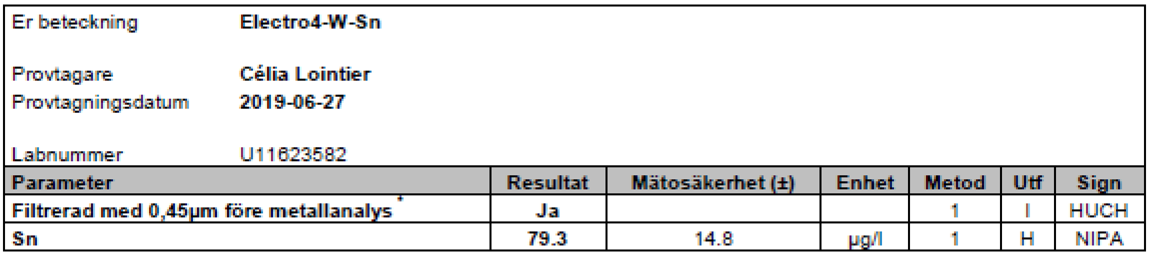


Er beteckning **Electro4-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623789

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**60.6**	2.0	%	1	V	LIAS
monobutyltenn	**19.0**	7.6	µg/kg TS	2	T	ELEN
dibutyltenn	**132**	52	µg/kg TS	2	T	ELEN
tributyltenn	**96.5**	30.7	µg/kg TS	2	T	ELEN

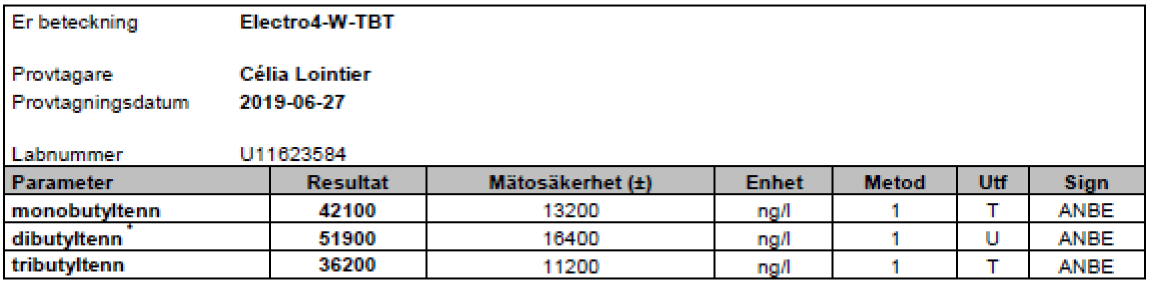


Er beteckning **Electro4-W-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623582

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	HUCH
Sn	**79.3**	14.8	µg/l	1	H	NIPA



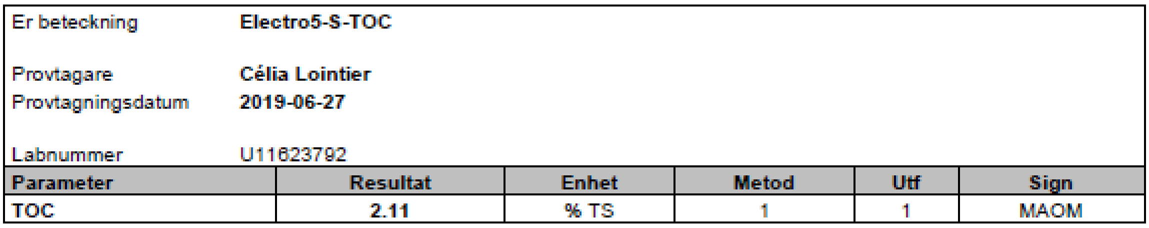
Er beteckning **Electro4-W-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623584

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**42100**	13200	ng/l	1	T	ANBE
dibutyltenn*	**51900**	16400	ng/l	1	U	ANBE
tributyltenn	**36200**	11200	ng/l	1	T	ANBE

Appendix 31 : Reports delivered by ALS for the analysis – Electrochemistry - Experiment 4

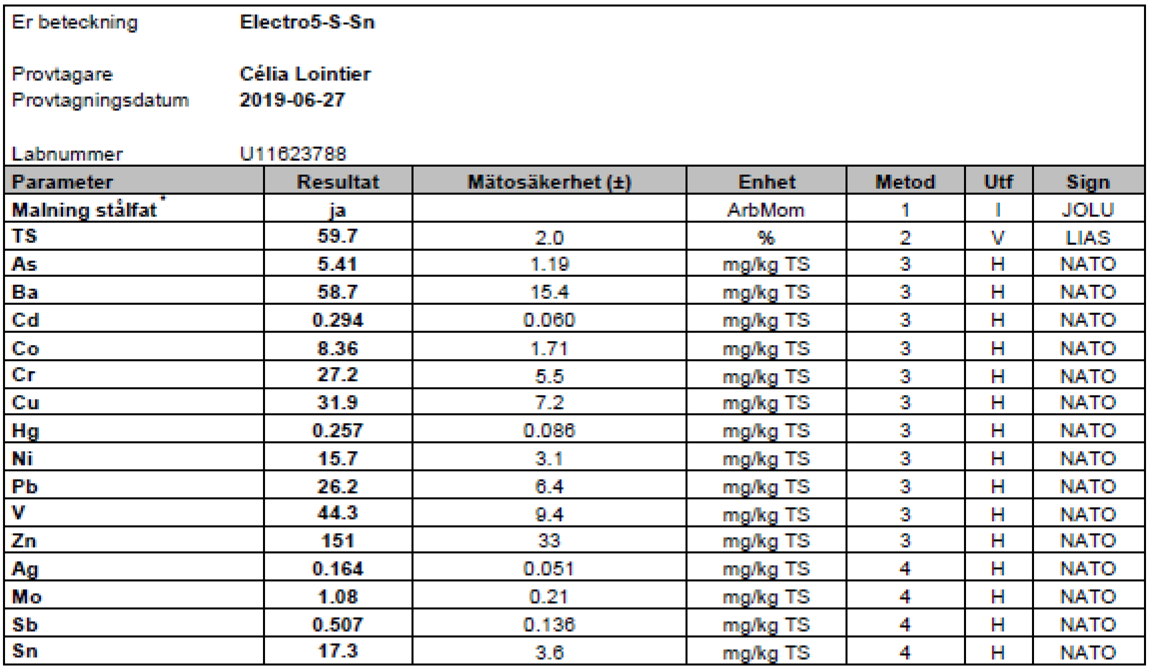


Er beteckning **Electro5-S-TOC**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623792

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.11**	% TS	1	1	MAOM

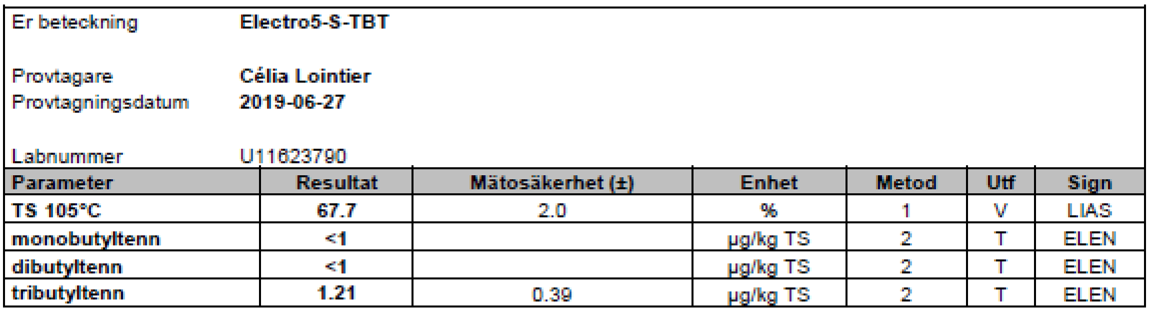


Er beteckning **Electro5-S-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623788

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Malning stålfat*	**ja**		ArbMom	1	I	JOLU
TS	**59.7**	2.0	%	2	V	LIAS
As	**5.41**	1.19	mg/kg TS	3	H	NATO
Ba	**58.7**	15.4	mg/kg TS	3	H	NATO
Cd	**0.294**	0.060	mg/kg TS	3	H	NATO
Co	**8.36**	1.71	mg/kg TS	3	H	NATO
Cr	**27.2**	5.5	mg/kg TS	3	H	NATO
Cu	**31.9**	7.2	mg/kg TS	3	H	NATO
Hg	**0.257**	0.086	mg/kg TS	3	H	NATO
Ni	**15.7**	3.1	mg/kg TS	3	H	NATO
Pb	**26.2**	6.4	mg/kg TS	3	H	NATO
V	**44.3**	9.4	mg/kg TS	3	H	NATO
Zn	**151**	33	mg/kg TS	3	H	NATO
Ag	**0.164**	0.051	mg/kg TS	4	H	NATO
Mo	**1.08**	0.21	mg/kg TS	4	H	NATO
Sb	**0.507**	0.136	mg/kg TS	4	H	NATO
Sn	**17.3**	3.6	mg/kg TS	4	H	NATO

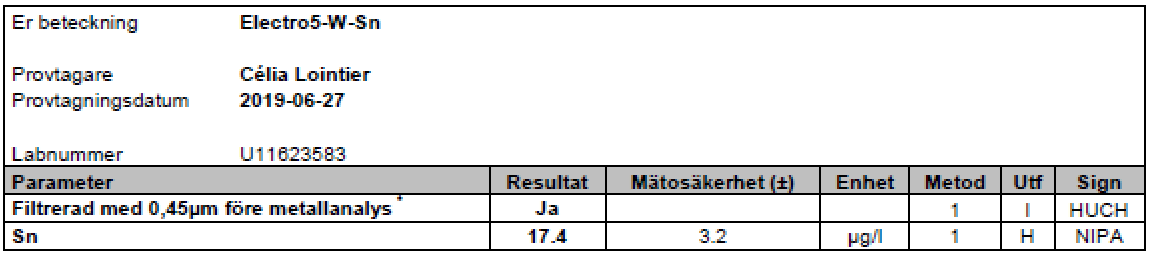


Er beteckning **Electro5-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623790

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**67.7**	2.0	%	1	V	LIAS
monobutyltenn	**<1**		µg/kg TS	2	T	ELEN
dibutyltenn	**<1**		µg/kg TS	2	T	ELEN
tributyltenn	**1.21**	0.39	µg/kg TS	2	T	ELEN

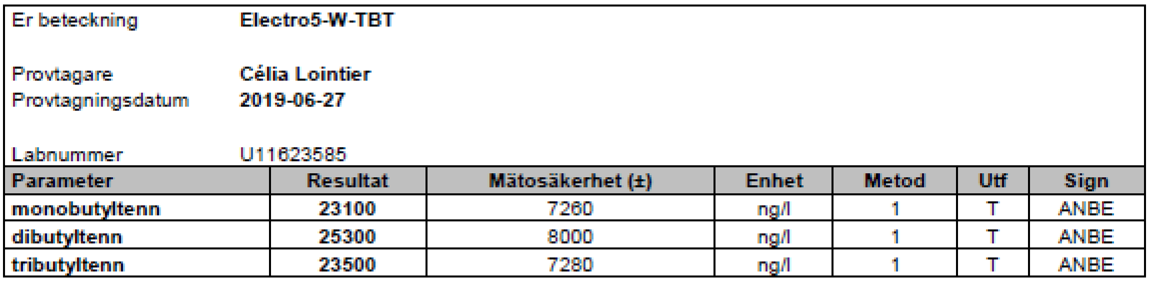


Er beteckning **Electro5-W-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

Labnummer U11623583

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Filtrerad med 0,45µm före metallanalys*	**Ja**			1	I	HUCH
Sn	**17.4**	3.2	µg/l	1	H	NIPA



Er beteckning **Electro5-W-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-06-27**

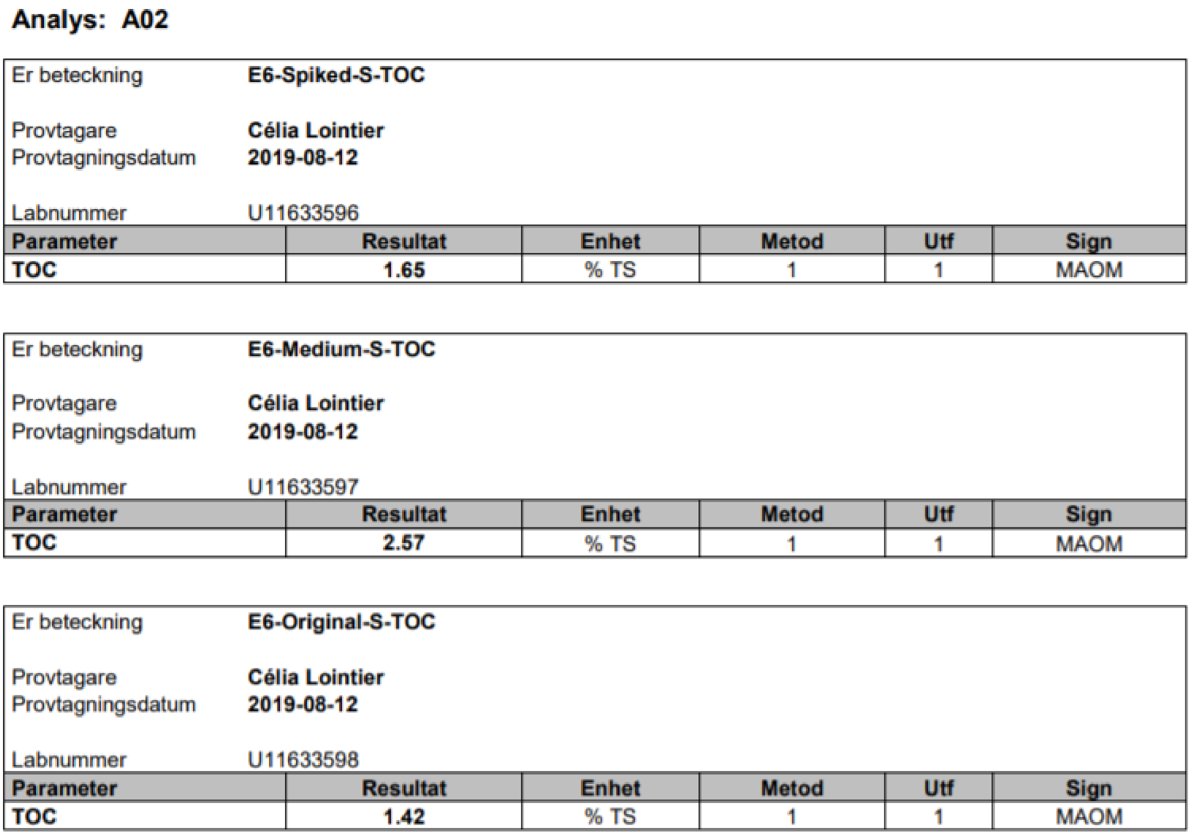
Labnummer U11623585

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**23100**	7260	ng/l	1	T	ANBE
dibutyltenn	**25300**	8000	ng/l	1	T	ANBE
tributyltenn	**23500**	7280	ng/l	1	T	ANBE

Appendix 32. Electrochemistry - Particle size distribution in the liquid

Name	Filtration	Hydrodynamic diam (µm)	Peak 1 (µm)	Peak 2 (µm)
Electro1	No	371.61		
Electro1	Yes	7.35	1.76	0.16
Electro2	No	769.57		
Electro2	Yes	0.00		
Electro4	No	118.18		
Electro4	Yes	0.01		
Electro5	No	495.76		
Electro5	Yes	55.93		
Electro4.S	No	22.15	0.84	2.32
Electro4.M	No	43.88	5.56	0.85
Electro4.O	No	307.58		

Appendix 33 : Reports delivered by ALS for the analysis – Electrochemistry - Experiment 4 on original, medium and spiked sediments



Analys: A02

Er beteckning	**E6-Spiked-S-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-12**
Labnummer	U11633596

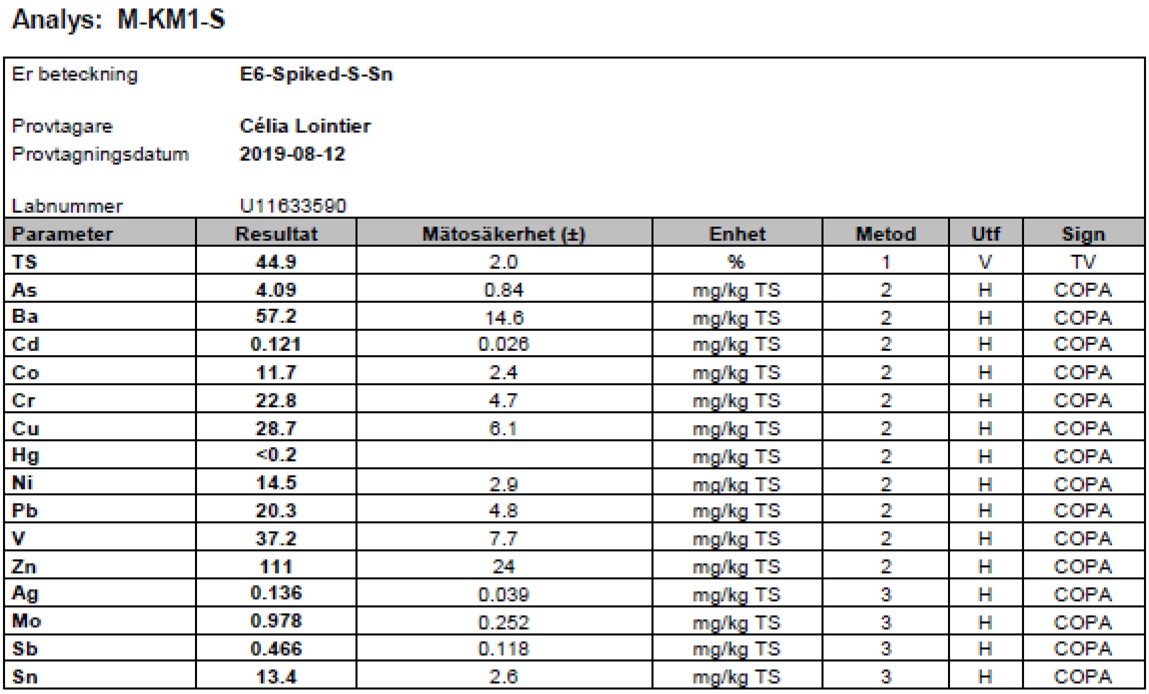
Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**1.65**	% TS	1	1	MAOM

Er beteckning	**E6-Medium-S-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-12**
Labnummer	U11633597

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**2.57**	% TS	1	1	MAOM

Er beteckning	**E6-Original-S-TOC**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-12**
Labnummer	U11633598

Parameter	Resultat	Enhet	Metod	Utf	Sign
TOC	**1.42**	% TS	1	1	MAOM



Analys: M-KM1-S

Er beteckning	**E6-Spiked-S-Sn**
Provtagare	**Célia Lointier**
Provtagningsdatum	**2019-08-12**
Labnummer	U11633590

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS	**44.9**	2.0	%	1	V	TV
As	**4.09**	0.84	mg/kg TS	2	H	COPA
Ba	**57.2**	14.6	mg/kg TS	2	H	COPA
Cd	**0.121**	0.026	mg/kg TS	2	H	COPA
Co	**11.7**	2.4	mg/kg TS	2	H	COPA
Cr	**22.8**	4.7	mg/kg TS	2	H	COPA
Cu	**28.7**	6.1	mg/kg TS	2	H	COPA
Hg	**<0.2**		mg/kg TS	2	H	COPA
Ni	**14.5**	2.9	mg/kg TS	2	H	COPA
Pb	**20.3**	4.8	mg/kg TS	2	H	COPA
V	**37.2**	7.7	mg/kg TS	2	H	COPA
Zn	**111**	24	mg/kg TS	2	H	COPA
Ag	**0.136**	0.039	mg/kg TS	3	H	COPA
Mo	**0.978**	0.252	mg/kg TS	3	H	COPA
Sb	**0.466**	0.118	mg/kg TS	3	H	COPA
Sn	**13.4**	2.6	mg/kg TS	3	H	COPA

Er beteckning **E6-Medium-S-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-12**

Labnummer U11633591

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS	**29.2**	2.0	%	1	V	TV
As	**3.74**	0.81	mg/kg TS	2	H	COPA
Ba	**39.3**	10.0	mg/kg TS	2	H	COPA
Cd	**<0.1**		mg/kg TS	2	H	COPA
Co	**5.12**	1.07	mg/kg TS	2	H	COPA
Cr	**17.6**	3.7	mg/kg TS	2	H	COPA
Cu	**21.5**	4.6	mg/kg TS	2	H	COPA
Hg	**<0.2**		mg/kg TS	2	H	COPA
Ni	**8.00**	1.84	mg/kg TS	2	H	COPA
Pb	**16.1**	3.9	mg/kg TS	2	H	COPA
V	**27.9**	5.7	mg/kg TS	2	H	COPA
Zn	**81.0**	17.9	mg/kg TS	2	H	COPA
Ag	**0.118**	0.035	mg/kg TS	3	H	COPA
Mo	**0.959**	0.199	mg/kg TS	3	H	COPA
Sb	**0.312**	0.085	mg/kg TS	3	H	COPA
Sn	**3.86**	0.74	mg/kg TS	3	H	COPA

Er beteckning **E6-Original-S-Sn**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-12**

Labnummer U11633592

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS	**36.1**	2.0	%	1	V	TV
As	**5.84**	1.21	mg/kg TS	2	H	COPA
Ba	**51.8**	13.2	mg/kg TS	2	H	COPA
Cd	**<0.1**		mg/kg TS	2	H	COPA
Co	**7.07**	1.45	mg/kg TS	2	H	COPA
Cr	**25.5**	5.4	mg/kg TS	2	H	COPA
Cu	**35.3**	7.5	mg/kg TS	2	H	COPA
Hg	**<0.2**		mg/kg TS	2	H	COPA
Ni	**11.7**	2.4	mg/kg TS	2	H	COPA
Pb	**21.6**	5.1	mg/kg TS	2	H	COPA
V	**37.9**	7.7	mg/kg TS	2	H	COPA
Zn	**118**	26	mg/kg TS	2	H	COPA
Ag	**0.128**	0.036	mg/kg TS	3	H	COPA
Mo	**1.13**	0.23	mg/kg TS	3	H	COPA
Sb	**0.356**	0.088	mg/kg TS	3	H	COPA
Sn	**2.93**	0.55	mg/kg TS	3	H	COPA

Er beteckning **E6-Spiked-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-12**

Labnummer U11633593

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**43.9**	2.0	%	1	I	TV
monobutyltenn	**1900**	746	µg/kg TS	2	T	ANBE
dibutyltenn	**2310**	911	µg/kg TS	2	T	ANBE
tributyltenn	**4210**	1340	µg/kg TS	2	T	ANBE

Er beteckning **E6-Medium-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-12**

Labnummer U11633594

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**54.0**	2.0	%	1	I	TV
monobutyltenn	**671**	264	µg/kg TS	2	T	ANBE
dibutyltenn	**840**	331	µg/kg TS	2	T	ANBE
tributyltenn	**735**	234	µg/kg TS	2	T	ANBE

Er beteckning **E6-Original-S-TBT**

Provtagare **Célia Lointier**
Provtagningsdatum **2019-08-12**

Labnummer U11633595

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
TS 105°C	**44.5**	2.0	%	1	I	TV
monobutyltenn	**115**	45	µg/kg TS	2	T	ANBE
dibutyltenn	**72.3**	28.5	µg/kg TS	2	T	ANBE
tributyltenn	**16.4**	5.2	µg/kg TS	2	T	ANBE

Analys: V3BBAS

Er beteckning **E6-Spiked-W-Sn**

Provtagare **Célia Lointier**

Labnummer U11633574

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**75.5**	14.1	µg/l	1	H	SVS

Analys av Sn

Er beteckning **E6-Medium-W-Sn**

Provtagare **Célia Lointier**

Labnummer U11633575

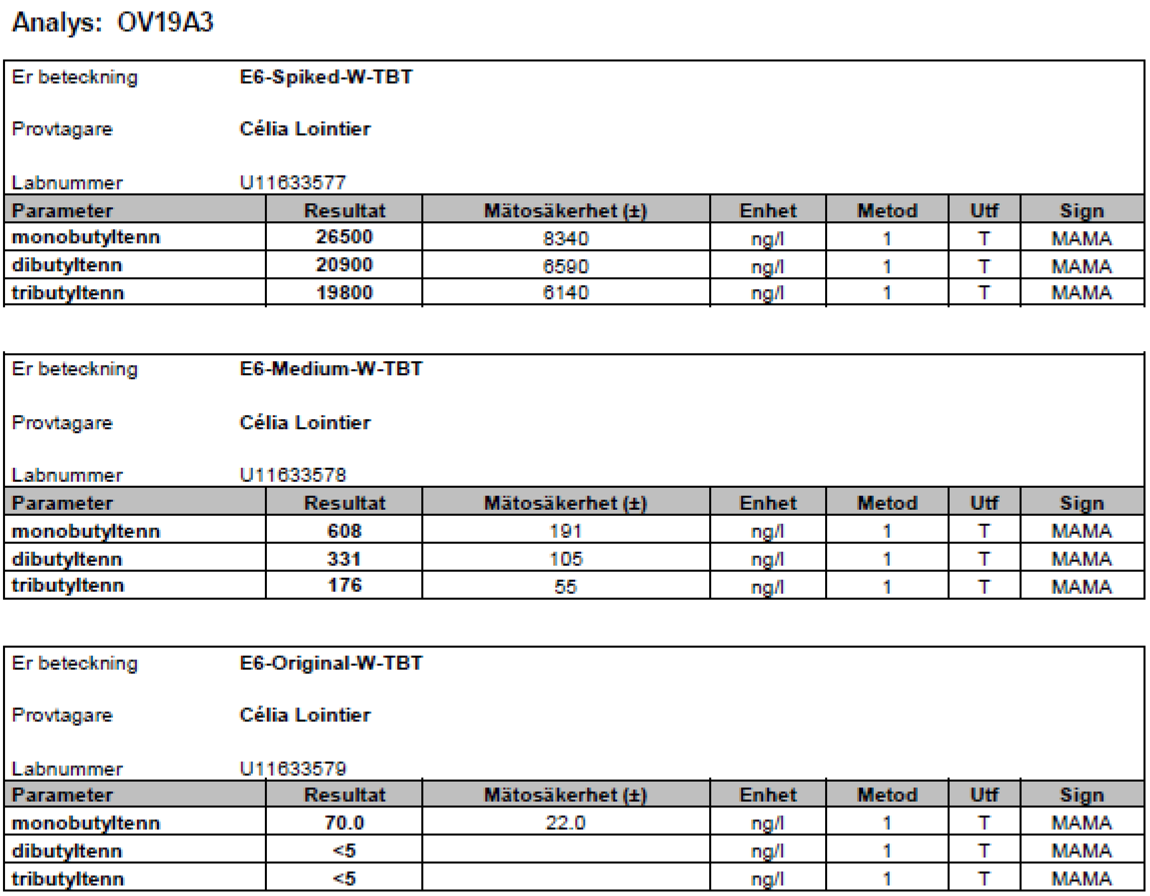
Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**4.99**	0.92	µg/l	1	H	SVS

Er beteckning **E6-Original-W-Sn**

Provtagare **Célia Lointier**

Labnummer U11633576

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
Sn	**0.661**	0.152	µg/l	1	H	SVS



Analys: OV19A3

Er beteckning	**E6-Spiked-W-TBT**
Provtagare	**Célia Lointier**
Labnummer	U11633577

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**26500**	8340	ng/l	1	T	MAMA
dibutyltenn	**20900**	6590	ng/l	1	T	MAMA
tributyltenn	**19800**	6140	ng/l	1	T	MAMA

Er beteckning	**E6-Medium-W-TBT**
Provtagare	**Célia Lointier**
Labnummer	U11633578

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**608**	191	ng/l	1	T	MAMA
dibutyltenn	**331**	105	ng/l	1	T	MAMA
tributyltenn	**176**	55	ng/l	1	T	MAMA

Er beteckning	**E6-Original-W-TBT**
Provtagare	**Célia Lointier**
Labnummer	U11633579

Parameter	Resultat	Mätosäkerhet (±)	Enhet	Metod	Utf	Sign
monobutyltenn	**70.0**	22.0	ng/l	1	T	MAMA
dibutyltenn	**<5**		ng/l	1	T	MAMA
tributyltenn	**<5**		ng/l	1	T	MAMA

Appendix 34. Metals concentration in the sediments

ELEMENT	Original 1	Medium 1	Spiked 1	Ex3.N	Ex4.N	Ex3.M	Ex4.M	Ex3.S	Ex4.S	Electro3	Electro4
As	4.6	6.3	5.3	4.4	5.7	3.4	6.0	4.0	3.9	5.7	5.4
Ba	65.0	48.1	49.5	37.8	54.4	45.3	64.7	48.8	53.7	61.3	58.7
Cd	0.3	0.2	0.2	0.1	0.1	0.1	0.1	<0.1	0.1	<0.1	0.3
Co	7.5	7.0	7.6	4.0	432.0	5.1	8.5	5.2	6.7	7.1	8.4
Cr	30.6	26.9	26.7	18.5	23.5	18.8	27.7	19.7	19.5	30.6	27.2
Cu	32.4	32.3	25.8	16.7	72.0	15.7	27.2	15.0	18.4	20.4	31.9
Hg	0.2	<0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Ni	14.3	12.9	14.4	7.8	237.0	9.6	13.2	10.3	10.5	15.1	15.7
Pb	23.9	21.7	25.4	14.3	22.1	16.0	27.3	21.2	21.1	14.6	26.2
V	39.2	34.1	36.6	21.8	30.5	25.3	40.2	27.3	33.2	40.5	44.3
Zn	125.0	116.0	114.0	55.3	96.0	67.8	116.0	70.7	86.6	95.2	151.0
Ag	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.2	0.1	0.2	0.2
Mo	1.8	1.7	1.8	1.3	2.3	1.4	1.9	1.4	1.5	1.9	1.1
Sb	0.5	0.5	0.5	0.3	0.4	0.3	0.5	0.4	0.5	0.6	0.5
Sn	3.3	4.4	14.2	2.0	2.8	8.8	5.4	3.7	13.4	14.6	17.3

Appendix 35. Metal concentration in the liquid phase after Electrochemical degradation

Element	**Concentration**	**Electro1**	**Electro2**	**Electro3**	**Electro4**
Ti	ng/L	441.82	421.65	3859.69	3685.99
V	ng/L	0.07	0.12	1.94	0.32
Cr	ng/L	13.63	11.95	527.52	228.80
Mn	ng/L	131.34	58.93	6838.90	1293.99
Fe	ng/L	2175.02	1185.78	175997.54	60869.55
Co	ng/L	3.20	2.78	441.45	45.70
Ni	ng/L	0.01	0.01	0.56	0.08
Cu	ng/L	63.59	88.08	2969.69	370.68
Zn	ng/L	497.94	751.56	9618.05	2925.57
Cd	ng/L	0.00	0.53	32.19	2.69
Sn	ng/L	0.00	0.00	122415.87	33460.11
Sb	ng/L	4.21	13.77	0.00	13.59
Pb	ng/L	0.01	0.00	0.62	0.16

Appendix 36. Metal concentration in the liquid phase after Fenton's degradation

Sample	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Cd**	**Sn**	**Sb**	**Pb**
	ng/L	**ng/L**	**ng/L**	**ng/L**	**mg/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Exp1.Ref	2536	0	14	3557	0	246	0	105	6033	23	3648	0	0
Exp1.2	27883	1	935	47265	2	3079	3	15031	85955	299	128300	0	3
Exp1.3	3918	1	415	15261	2	376	0	3001	10907	28	3773	0	1
Exp1.4	605	0	137	3262	1	65	0	517	1652	4	8427	0	0
Exp1.5	532	0	85	3065	1	47	0	347	1575	3	15220	0	0
Exp1.6	13846	2	1903	64447	23	858	1	5182	16249	42	242770	0	0
Exp1.7	9735	1	2054	75825	27	913	1	5182	12840	39	298118	0	0
Exp2.Ref	1732	0	3	2989	0	109	0	69	2857	10	0	0	0
Exp2.2	827	0	155	5627	2	75	0	522	2372	5	14843	0	0
Exp2.3	4915	1	1332	35834	7	654	1	5733	16902	41	3774	0	1
Exp2.4	4847	1	1281	27030	5	597	1	5396	47682	49	0	0	1
Exp2.5	44189	8	11624	107343	22	4944	5	45568	101052	397	943540	0	20
Exp2.6	4253	1	1085	22279	4	500	1	4633	21875	40	0	0	1

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