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Anthropogenic Chemicals in North Jutland Coastline Sediments and Remediation Technology – Final Report

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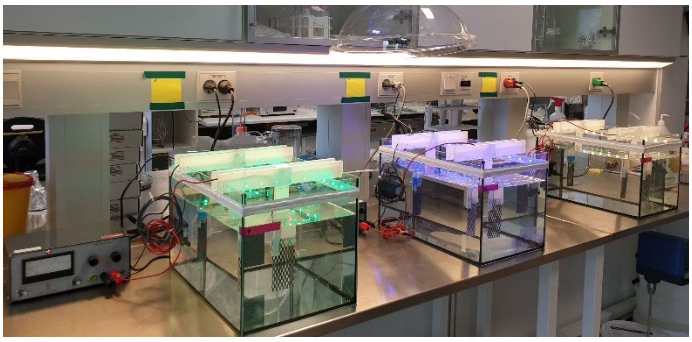
Anthropogenic Chemicals in North Jutland Coastline Sediments and Remediation Technology – Final Report



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Preface

This report has been prepared by Lucia Margheritini mluc@build.aau.dk as final report for the Velux project Anthropogenic Chemicals in North Jutland Coastline Sediments.

Here the results from the analysis of sediment samples taken in 21 location along the North Jutland Coast are presented. The analysis includes grain size distributions, heavy metals, PHAs, TBTs and flame retardants. For the last three, an external laboratory was engaged to conduct the analysis. The sampling and analysis have been affected by the covid 19 related lockdowns and therefore this projected, approved in July 2018 and initially ending in January 2021, was then extended to August 2021. It has been challenging to conduct work as planned, especially as the time schedule being shifted prevented us to monitor seasonal variations as initially planned. Nevertheless at least two different samples for each of the location were collected and analysed.

Additionally, we have tested in the laboratory an innovative remediation technology. The results rom the laboratory experiments are also presented here. The projected, approved in July 2018 and initially ending in January 2021, was then extended, due to covid19 to August 2021.

Version	date	Comments
0.0	31/08/2021	
0.1	22/09/2021	Added report number – unit measures in tables checked and corrected – added short summary

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Introduction

In 1998, the National Programme NOVA monitored heavy metals and other hazardous substances in coastal waters under the responsibility of the regional councils and in open waters under the responsibility of the National Environmental Research Institute (Fig. 1). The regional stations were chosen to represent gradients from point sources such as towns and harbours. The open-water stations were chosen to represent diffuse contamination or background levels. In 2009, the National Environmental Research Institute released a status report that included a new monitoring programme (NOVANA): one NOVA station from each region had been retained in order to maintain the time series, whereas the regions can chose to place the remaining stations in different locations each year in order to determine spatial variation. The Coast of North Jutland does not have any monitoring station, not in NOVA nor in NOVANA; therefore, data is missing in regards to assessment of possible heavy metals and other anthropogenic chemicals in the Limfjord and coast-near sediments. Only fragmented and indirect knowledge is available for the North Jutland region of Denmark. A possibly already outdated study from 2006 (Strand et al. 2006. “Tributyltin (TBT) Forekomst og effekter i Skagerrak”. Uddevalla, Sweden: Forum Skagerrak II. 39 s.) showed TBT contamination in the Skagerrak and Kattegat where an extensive set of Nordic data on TBT concentrations in seawater, mussels and sediment were combined into an index of the environmental conditions. A recent study by DTU-Aqua on seaweed quality in the Limfjord showed concentrations of some heavy metals exceeding present criteria for foods. Generally, neither chemical levels nor chemical sources are identified/quantified for the three groups of anthropogenic chemicals considered here. On the other hand, hotspots of sediment contamination are relevant as part of coastal and fjord planning. Besides national interests, the project creates awareness and new knowledge on marine pollution relevant also to the EU Marine Strategy Framework Directive, Helsinki Convention and OSPAR. A better administration and use of the coastal and fjord areas requires knowledge of the location of pristine coastal sediments as well as contaminated sediment hotspots. With this project we add valuable reference data for heavy metals, PHAs and TBTs along the North Jutland Coast and East part of the Limfjord.

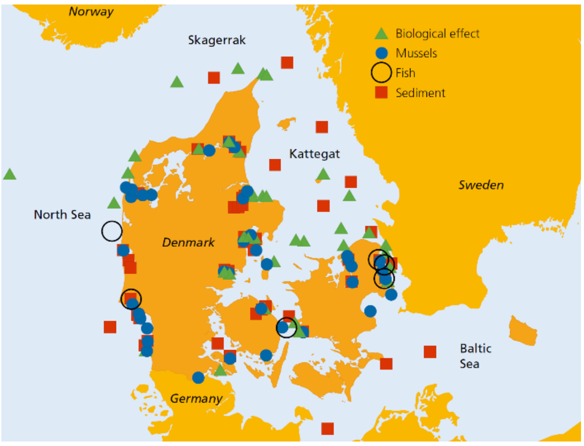


Figure 1. Figure 1. Map of monitoring stations for hazardous substances during NOVA (source: Hazardous and Radioactive Substances in Danish Marine Waters, Status and Temporal Trends, National Environmental Research Institute, Arhus University, 2009).

Additionally, we thinking that indicating the degree of pollution of the collected sediments is not sufficient, when also remediation and mitigation technologies should be discussed. We therefore want to propose the use of local seawater electrolysis as an effective way to both reduce sediment heavy metal contamination. We have tested this innovative technology in the laboratory and we have very promising results that indicate that further development and optimization are needed to create a product that will contribute effectively to clean up polluted waters and sediments.

Objectives

The project investigated the presence of three groups of anthropogenic chemicals – heavy metals (Hg, Cd, Cu and Pb, Zn, Ni), poly-aromatic hydrocarbons (PHAs), and Tributyltin (TBT) – in sediments at the coast/in the fjord between the five major harbours of North Jutland: Hanstholm, Hirtshals, Frederikshavn and Aalborg. Further, an innovative method for remediation of contaminated seawater was tested in a controlled environment at Aalborg University (AAU).

The project is structured in two main activities: the Monitoring Campaign and relative analysis of samples and the Feasibility of new Remediation Technology.

1. Monitoring Campaign
   - Sampling: We selected monitoring locations that follow the possible contaminant plume from the harbours in the longshore current. The monitoring around Aalborg Harbour includes locations from Nibe to Hals (East Limfjord).
   - Laboratory analysis: heavy metals (Hg, Cd, Cu and Pb, Zn, Ni), PHAs and TBT were measured at AAU, Dept. of the Built Environment and Erurofinns laboratories. The laboratory is equipped with state-of-the-art analytical instruments, including ICP-OES and GC- and HPLC-MS systems. Additionally, under request of Velux and additional analysis on flame retardants was added. Background levels and threshold values for the different metals will be discussed and a comparison between fjord and coast concentrations will be part of the analysis.
   - Applicability map: mapping of possible locations along the north Jutland coast and fjord for the application of the technology will be produced with concept designs that include basic in situ setup and technical requirements for the installation. The location will be selected based on assessed need and most suitable conditions.

2. Feasibility of new Remediation Technology
   - Tests in controlled environment: experiments took place in the Environmental Laboratories at AAU. The objective was to assess the effectiveness of the process of seawater electrolysis and consequent mineral deposition to trap metallic contaminants in seawater thanks in the calcareous deposit.

Procedures

The monitoring campaign starts with the selection of location following the possible contaminant plume from the harbours and other sources in the longshore and fjord current.

A total of 21 location have been selected (Fig. 2): 5 harbours, 7 on the beach, 3 estuaries, 6 on the Limfjord.

The classification of the locations in one category or an other reflects primarily the type of sediment that was sampled. For examples Blokhus sample was taken into a freshwater input (possible water pollution source) ending at the entrance of the Blokhus beach and is therefore classified as estuary. Aalborg has 2 harbour locations because in both places the sediment was a dark, anoxic, contaminated sludge/mud that is usually present in harbours.

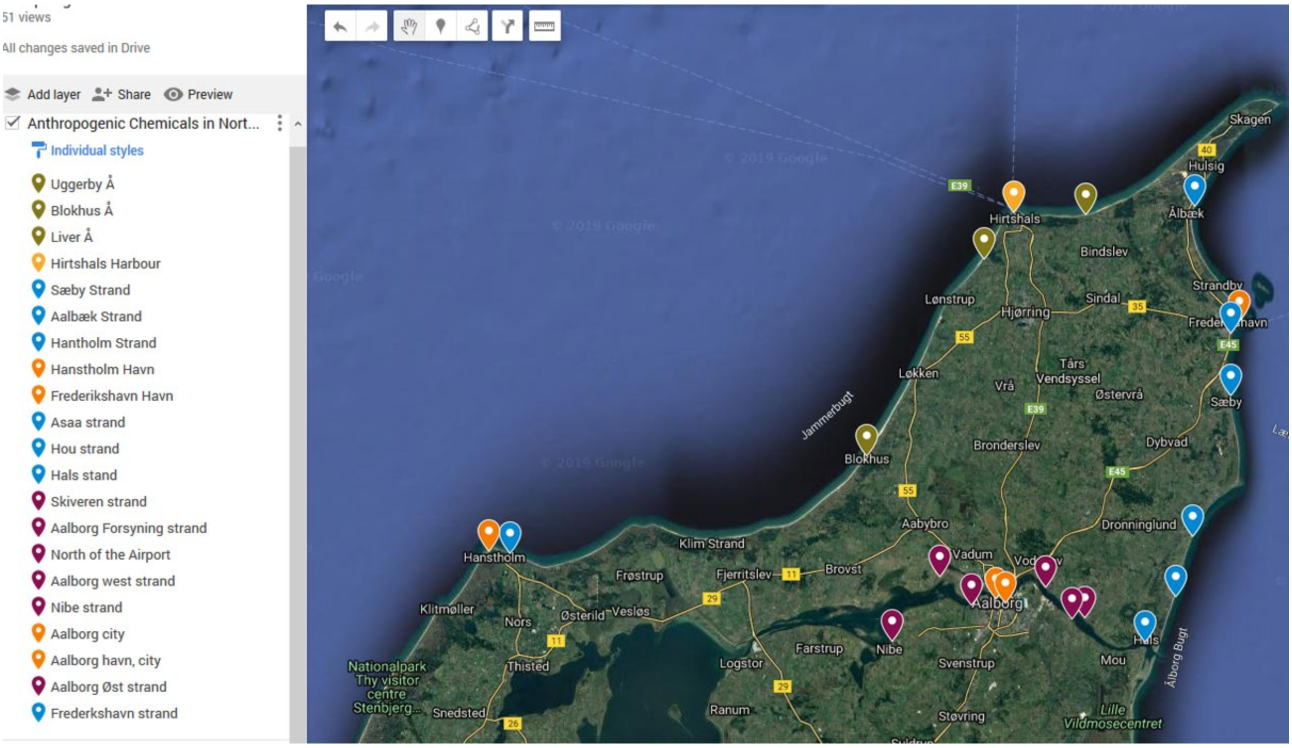


Figure 2. Total selected sampling locations: five harbours (ORANGE), seven beaches(BLUE), three estuaries (OLIVE), six in the Limfjord (PURPLE).

Sampling

All materials used for sampling were made of plastics, to avoid contamination. In total, it is estimated we estimate we collected more than 250 kg of sediment samples. The sampling was different depending on the type of location where we collected the data.

For estuaries, beaches and fjord surface samples were typically collected within the first 1-3 cm of the surface, while core samples normally belong to -20 to -3 cm from surface (Fig. 3). The area on the shore was typically the splash-fringe zone. For each location we would collect have:

- 2 core samples stored in plastic buckets
- Surface sample
- Rizla bags or vials (PHAs, TBTs and flame retardants)
- Punctual measurements of pH, T , oxygen and conductivity

3. In case of harbor locations, the only possibility was to collect the samples inside the harbours on the seabed surface. This was done using a double excavation bucket that will open when touching the seabed and close when being lifted up back to the surface. The bucket is the only tool made in metal, as both the weight and resistance are necessary to hit the bottom, sink and close around a suitable material sample (Fig. 4). We were therefore carefully collecting the material for heavy metals from the center of the sample (not in touch with the surface of the tool), while PHAs and TBTs samples where sourced from the remaining amount. For each harbours location we collected:

- 2 samples stored in platic vials or buckets
- Rizla bags or vials (PHAs, TBTs and flame retardants)
- Water
- Punctual measurements of pH, Temperature, dissolved oxygen and conductivity

Figure 3. Beach sampling images.

Figure 4. Figure 2. Harbour sampling example.

The sampling procedure could be summarized in the following pints:

1. Once arrived at location, write down the GPS coordinates, the name tag of the location, notes and take pictures (always a good role to set for a place where you can see some organic matter, either in form of dark/fine sediments or dark waters).
2. <u>Collect water</u>, 1 bucket (circa 5 Liters), label it.
3. Measure salinity, temperature, pH not it down (Appendix 1).
4. <u>Surface sampling</u>: with large plastic scoop, collect surface sediment/sand into a 3-5 L bucket, label it.

5. In the same area of the surface sample (where you have removed not more than 5 cm thickness of material) or after removing circa the first 2 cm of surface material, proceed with 2 X core sampling. A rubber hammer with a piece of wood between the hammer and the probe was used for piling down the probe. The extracted material was put into a 3L bucket (circa 3 Kg) and labelled.
6. For PHAs, TBT, flame retardants: take 1 core sample and place it in a Rizlan plastic bag , circa 3 x 200 gr (to avoid evaporation and decomposition of compounds), close it with stripes and label it.

All samples correctly labelled are stored in the cold room at AAU at 5°C.

Samples were used for inhouse and external analysis (Fig. 5).

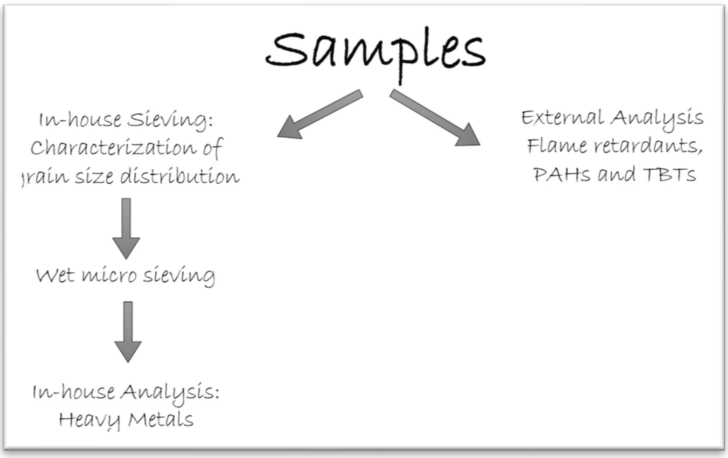


Figure 5. Summary of analysis after sampling.

In-house Sieving

The sieving was necessary in order to obtain the grain size distribution at the different locations (excluding the harbours). The grain size distribution is an important information in relation to heavy metals as literature indicates that heavy metals preferably bond to very fine particles and organic matter. Indeed, grain size (clay and silt), clay mineralogy, organic matter (organic carbon), and pH are the major controls of heavy metal accumulation in coastal sediments. They are typically the dominating factors except near hotspots. Salinity and temperature can be additional controls for sediment concentrations of heavy metals. Both clay content and clay mineralogy affect heavy metal accumulation (studies on sediment profiles from the Wadden Sea, Vadehavet, Denmark). Studies on soils across Denmark show clay mineralogy to be relatively uniform – dominated by illite and kaolinite, and illite and kaolinite was also the dominating clay minerals found in the Wadden Sea studies. Most coastal sediment studies have used either < 63 micrometer (clay + silt), < 20 micrometer (clay + fine silt), or < 2-4 micrometer (clay fraction) as the fractions where most heavy metals are accumulated. Based on this, we designed our sediment separation procedure. The sieving procedure can be summarized in the following pints (Fig. 6):

1. Only if we see evident organic matter or we are dealing with harbor sediments: put 10 gr in one vial, closet and label it. This is then ready for macro-heavy metal analysis (Freeze dry and procedure, in-house analysis).
2. For dry sieving, we put 400 g of wet sediments on trays for air-drying for at least 24 hours (sieving laboratories). We make sure to crush well any aggregates with a spoon and make sure the soil is spread in a thin uniform layer on the tray. After air-drying we pre-sieve 200 gram air-dry sample through a 2 mm (2000 micron) sieve and record [stone + gravel] content.

3. We then take 100 gram of the pre-sieved, air dried soil and put in the automated sieving tower for 20 minutes at 70% of max shaking. Sieving tower set-up, 10 components: 1 mm - 0,5 mm - 0,425 mm - 0,25 mm - 0,2 mm - 0,15 mm - 0,125 mm - 0,075 mm - 0,063 mm – bottom.
4. We then measure content in each sieve. Final check: total amount in the sieves must not deviated from the applied mass (100 g) by more than 1%.
5. Plot the grain-size distribution curve.

6A. If there is more then 5-10% and/or less than 80% fine particles < 200 micrometer, the following procedure (wet plastic sieving) is used:

- 212 micron plastic sieve (net+frame) is collected/prepared and placed above 2L glass or plastic beaker.
- The sieve (net+frame) is fixed on top of a beaker.
- Add soil/sediment to top of 212 micron sieve by plastic spoon; make sure not to spill outside sieve area.
- Do wet sieving using demineralized water and non-metallic soft brush.
- Oven-drying at 60-80 C for required time (at least X hours, based on estimated loss of water 6-8 mL/hours)
- Dried, pre-sieved material is transferred to measurement vial using plastic funnel, circa 10 gr.
- Measurement vial in holder (known weight) is weighed; weight oven-dry sediment sample calculated
- At least 10 gram of oven-dry material is needed for freeze-drying and subsequent heavy metal analyses.
- Label and these two are then ready for macro-heavy metal analysis (freeze dry and procedure).

6B. If less than 5% of the material is below 202 micron, then we conclude there can not be heavy metals in the sediments.

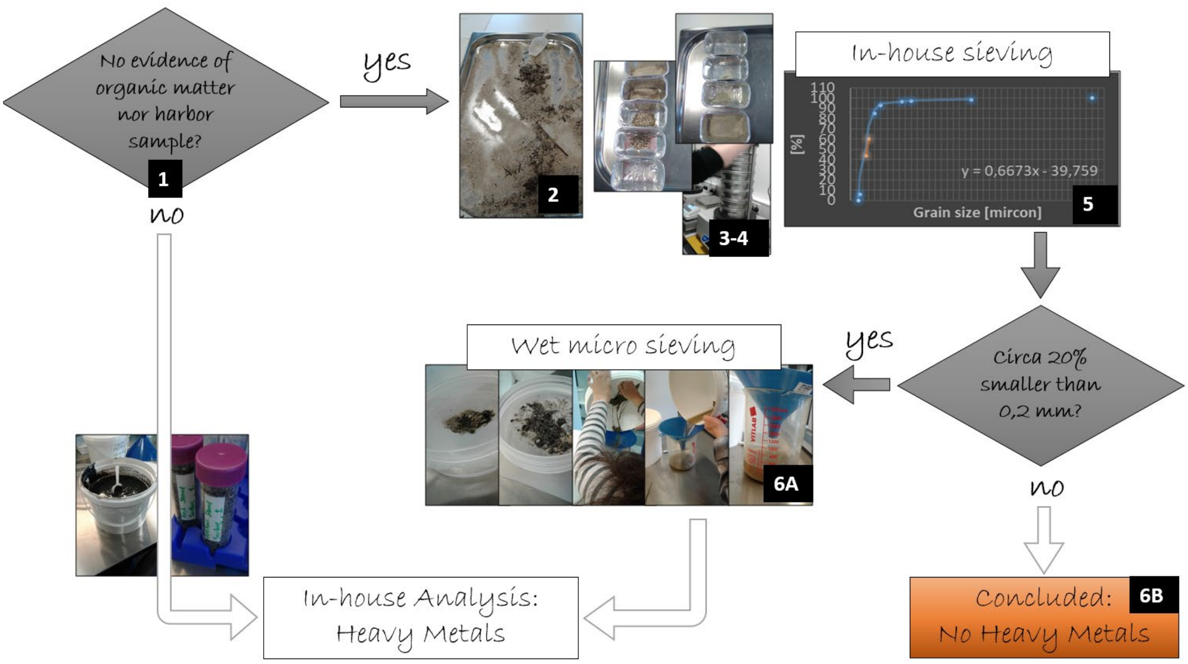


Figure 6. Summary of sieving procedure and decision making related to analysis.

RESULTS

This Chapter will present the results from sieving and the chemical analysis of the samples collected in the 21 selected locations. Because of interruptions and disruptions related to the Covid 19 lockdowns, the seasonal variability was difficult to monitor as planned. Nevertheless, we could collect at least two samples par location, one in the warm season (summer) and the other on the cold season (winter/early spring).

Grain size distribution characterization

The characterization of the samples based on grain size distribution was done for the 7 on the beach, 3 estuaries, 6 on the Limfjord, for a total of 16 locations (Table 1). Harbor locations were characterized by severely dark-brown -black mud of very fine composition and were therefore sent directly to chemical analysis.

The characterization of the sediment´s samples based on grain size distribution, besides providing some information on the gran size distribution present at location, allows to focus on the finest sediments in order to run only heavy metal tests for the location where heavy metals have the chance to be found. In table 1, all result are presented as d50, % of the sediment smaller than 200 µm and % of the sediment smaller than 75 µm**.** The graphics for each location are in Appendix 2.

When possible, we collected both core and surface samples for the same location, but sometimes this was not possible and/or redundant (Table 2). Particularly:

I. The location called “Hals strand” was covered in a thick layer (30 cm and more) of seaweeds. So only a core sample was taken, after removing the seaweed.
II. The location called “North of lufthavn” was aslo covered in a thick layer of decomposing organic matter. That one was removed and the core sample was collected.
III. In Uggerby å we decided to collect only one sample in the wet area of the estuary, where organic matter was visible.
IV. In the location called “Nibe strand”, a layer of organic matter and algae was covering the surface, so we collected one core sample, after removing the surface layer.
V. In Aalborg West there were rocks 10 cm circa below the surface, so we only took a surface sample. Nevertheless we could not appreciate any noticeable differences in color or gran size by eye, between the surface and the core depth.
VI. In Hanstholm strand, we could not see any appreciable difference between the surface layer and the core, so we collected the core sample only.
VII. Frederikshavn strand presented itself with 1-2 cm of shells and algae on the surface. Once that was removed, we collected the core sample for the location.
VIII. Generally, harbours present themselves with polluted mud generally considered not safe to be handled in AAU laboratories.

The 6 locations with more than **4,5 % < 75µm**, based on their grainsize distribution, have the capacity to include heavy metals (together with the harbor locations, Table 3).

The location with the highest d50 is Skiveren vej strand (core and surface) while the one with the lowest is Aalborg Forsyning strand – surface, while Aalborg Forsyning strand – core has a d50 closer to Skiveren vej strand (Fig. 7). This is interesting, considering the two locations are less than 8 km from eachother on the same north shore of the Limfjord. Hals and Blokhus have the finest sands while Hou strand and Aalborg Forsyning have the biggest variation between the d50 of the core and surface samples.

Table 1. Summary of calculated d50 for all locations and % smaller than indicative fractions sizes.

Name of location	d50 [µm]	% smaller than 200	% smaller than 75
Hou Strand Surface	214	36,8	0,0
Hou Strand Core	368	3,9	0,0
Asaa Strand surface	290	5,2	0,0
Asaa Strand core	225	27,1	0,0
Hals Strand core	162	70,4	1,9
Aalborg Forsyning strand surface	135	84,8	5,9
Aalborg Forsyning strand core	399	25,9	0,9
Skrive vej strand surface	447	5,4	0,1
Skrive vej strand core	449	18,2	5,9
North of lufthavn core	234	64,5	16,5
Liverå surface	216	36,9	0,0
Liverå core	221	33,5	0,0
Blokhus strand surface	172	83,5	0,3
Blokhus strand core	182	69,7	0,1
Aalborg East strand surface	249	44,0	17,3
Aalborg East strand core	237	44,9	14,1
Ålbæk strand surface	215	40,6	0,0
Ålbæk strand core	193	57,5	0,0
Uggerby å core	178	75,6	0,0
Nibe strand core	334	9,8	0,1
Aalborg west surface	282	14,9	0,1
Sæby surface	240	35,0	0,0
Sæby core	239	10,2	0,0
Hanstholm strand core	291	32,1	0,0
Fredrikshaven strand core	225	40,3	4,1

Table 2. Pictures of the 7 locations (among 7 on the beach, 3 on estuaries, 6 on the Limfjord) where the collection of both core and surface sample was not possible. The last picture in the bottom right is representative, instead, of harbor locations.

Hals strand	North of lufthavn	Uggerby å	Nibe strand
			
Aalborg West	Hanstholm strand	Frederikshavn strand	Harbors
			

Table 3. Locations where heavy metals are expected.

Location	Type
Hirtshal	harbour
Frederikshavn	harbour
Hanstholm	harbour
Aalborg Havn	harbour
Aalborg City	harbour
Aalborg Ø core	Limfjord
Aalborg Ø surface	Limfjord
Aalborg Forsyning surface	Limfjord
Skrive vej strand core	Limfjord
North of lufthavn core	Limfjord
Fredrikshaven strand core	beach

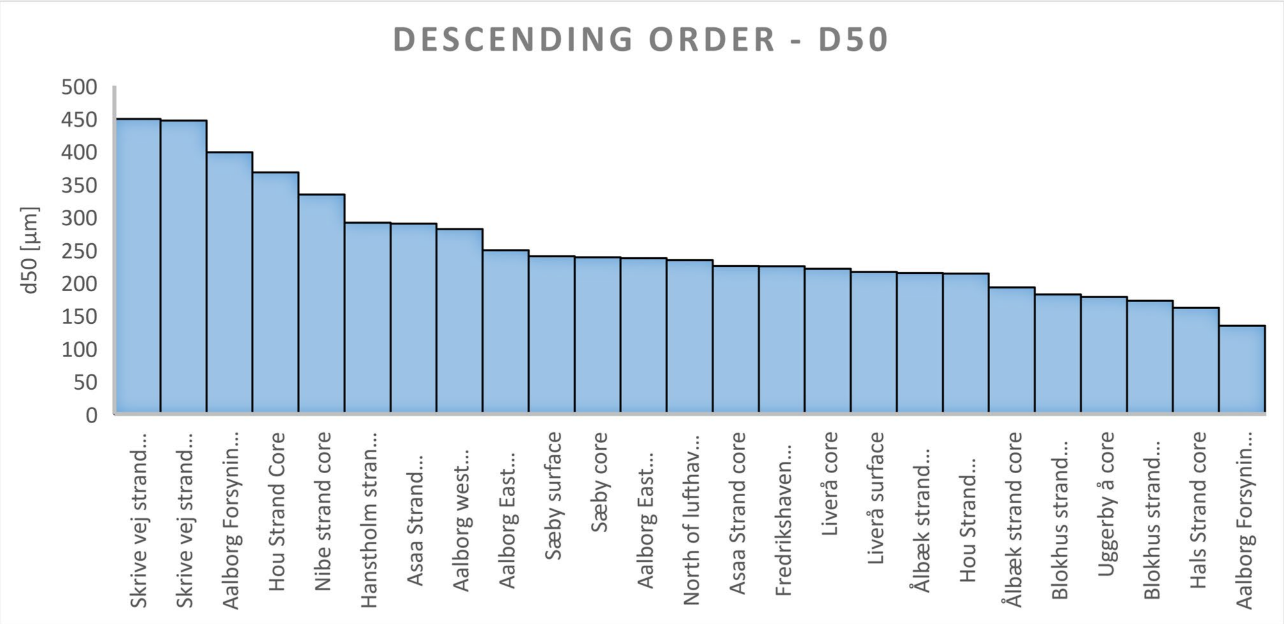


Figure 7. Descendent calculated d50 for all locations.

Core samples and surface samples for the same location present relevant differences only for 5 locations (Fig. 8):

- Asaa strand surface > Asaa strand core
- Ålbæk surface > Ålbæk core
- Hou strand surface < Hou strand core
- Blokhus surface < Blokhus core
- Aalborg Forsyning surface < Aalborg Forsyning core

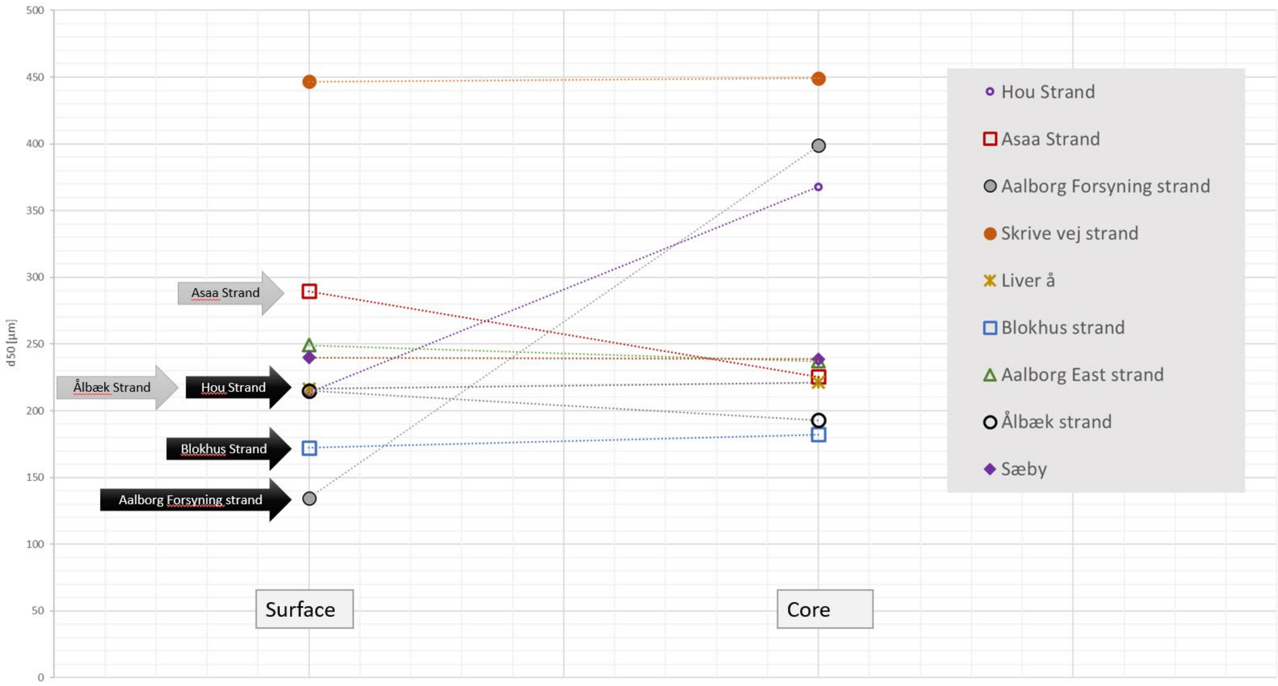


Figure 8. Comparison of d50 between surface and core samples for same locations.

Heavy metals

We have looked for 5 heavy metals in the sediments we have collected: Hg, Cd, Cu, Pb, Zn, Ni. The investigation was performed with ICP. Values for Hg were below instrument detection levels for all locations and therefore are not reported.

Based on the grain size distribution and the literature indication that heavy metals will bound to very fine particles and organic matter, we expect the find heavy metals only in the location in Table 3 (previous chapter). Nevertheless, more location showed the presence of heavy metals. Harbours show higher concentrations and samples needed to be diluted x10 to be within detection limits.

Concentrations in mg/kg are presented in Fig.9-18. Because the concentrations in harbours are much higher than in other locations, graphics are presented separated. Harbour locations present concentrations at least 100 times higher than beaches and estuaries for copper and nickel, while for lead and zinc the concentration in the harbours are circa 10 times higher than the other locations. It must be noted that besides the harbours, Frederikshavn strand, Aalborg North of Lufthavn , Aalborg West and Aalborg Øst, Aalborg forsyning, and Skiveren strand are outliners for Cd, Cu and Ni with values consistently higher than the other locations. These are all the locations in the Limfjord, with the exception of Frederikshavn strand. Nibe Strand, instead, presents lower concentrations than the above. Lead and Zinc are present in similar concentrations both in the Limfjord locations and in the estuaries and beaches.

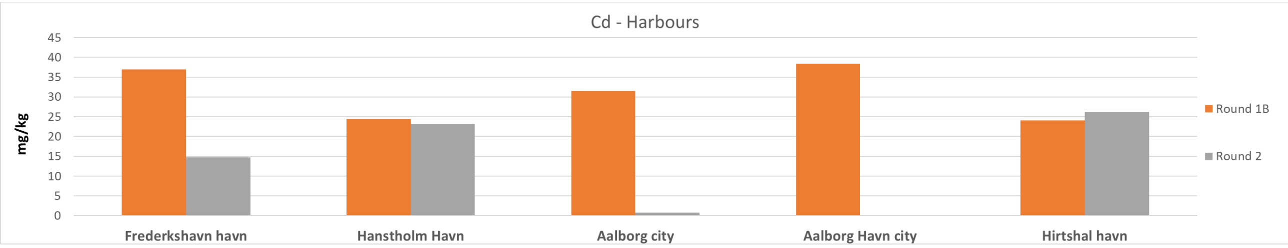
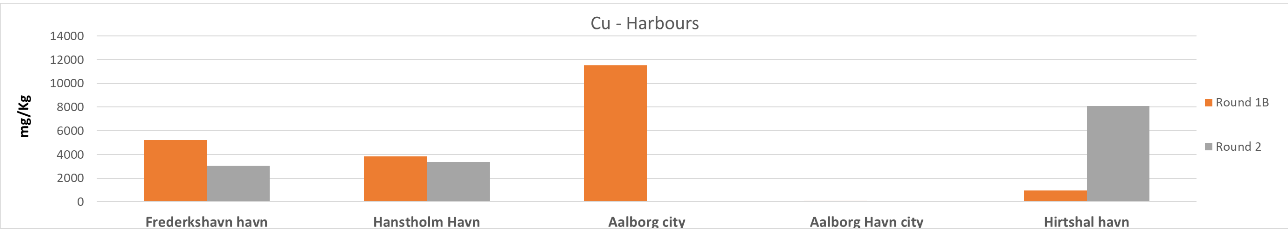


Figure 9



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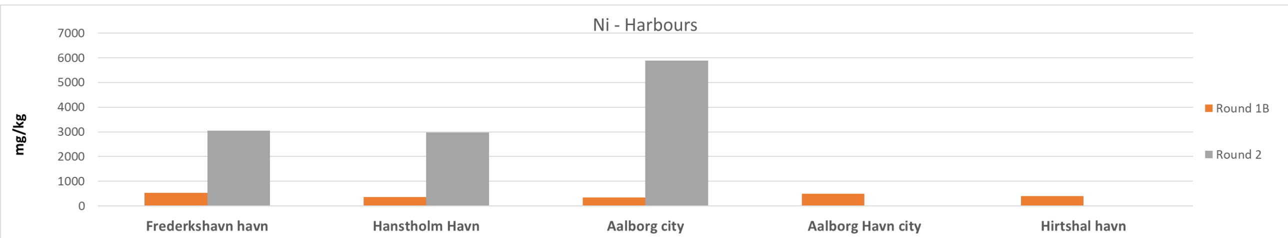

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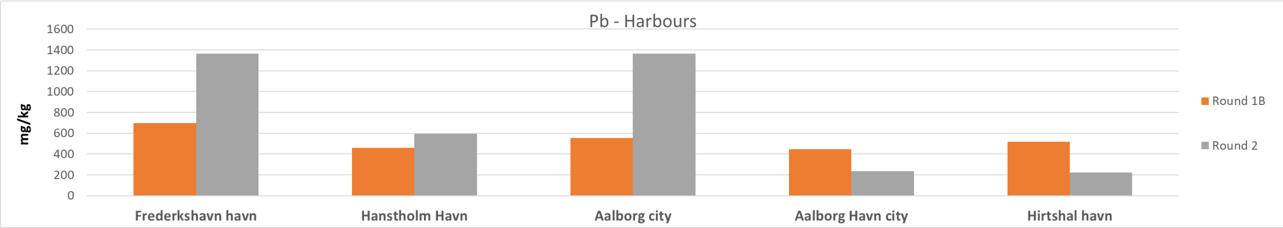

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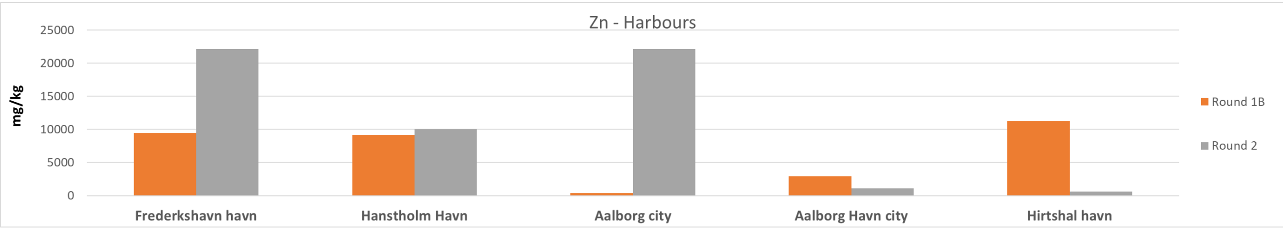

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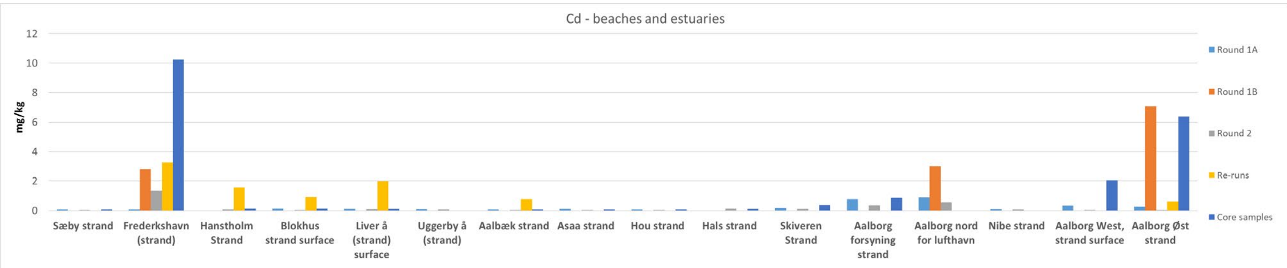

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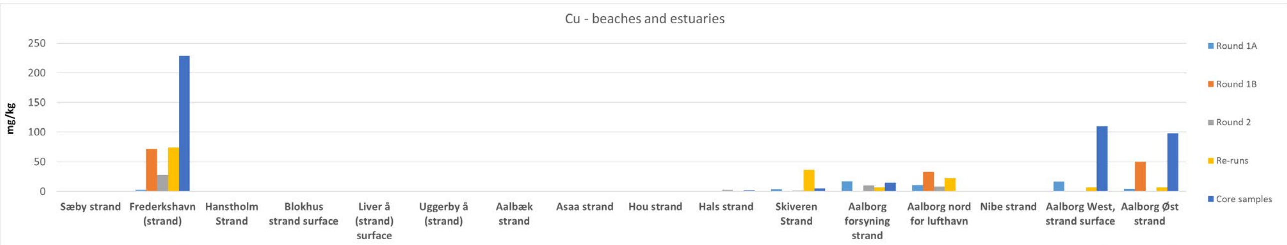

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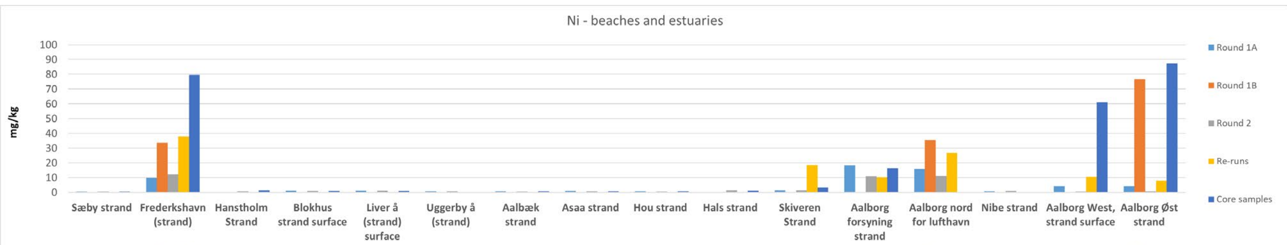

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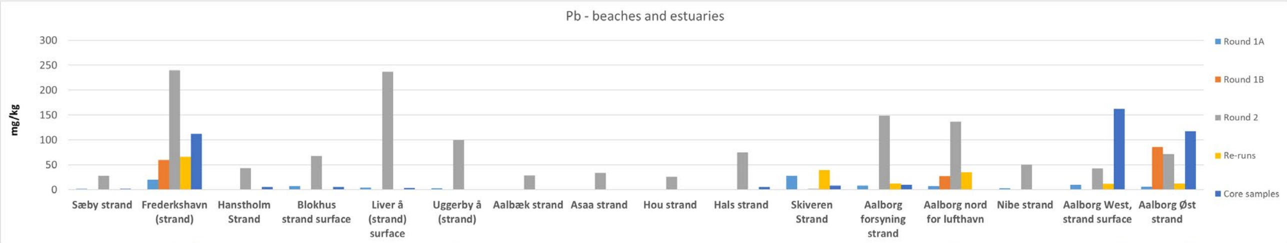

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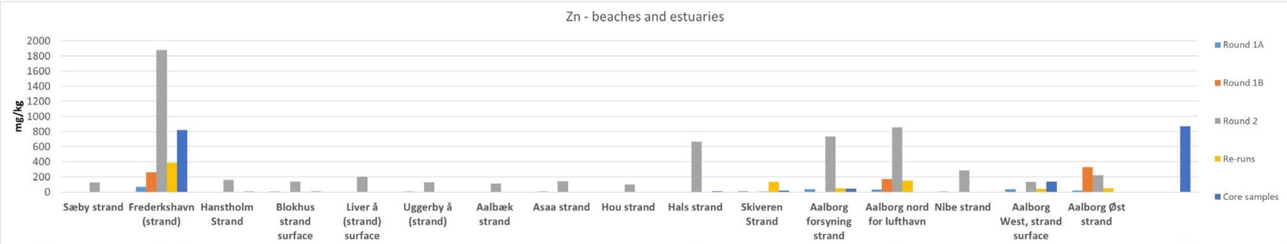


Figure 18

Non negligible amounts of Copper, Nickel lead and Zinc are found in more locations than the ones foreseen based on the grain size distribution. All locations present, in some amounts, one or more of the heavy metals here investigated. Some locations distinguish themselves by the presence of different types of heavy metals and in concentrations higher than literature.

These location are:

1. Skiveren strand,
2. Aalborg forsyning,
3. Aalborg nord of lufthavn,
4. Aalborg Øst strand,
   And (not expected because of grain size distribution):
5. Aalborg West strand surface, Sæby strand core.

Generally, the highest values are related to Zinc and Lead. A comparison with literature shows similar order of magnitude for the values of the most relevant heavy metals, even with appreciable decrease.

The more recent data reported on the "Hazardous and Radioactive Substances in Danish Marine Waters" dates 2004 report values for the North Sea, Skagerrak and Kattegat. While beach and Estuaries are below the values indicated in the report, the Limfjord presented higher concentrations (Table 4).

Table 4. Comparison with values presented in "the Hazardous and Radioactive Substances in Danish Marine Waters"

	North Sea 2003/4	Skagerrak2003/4	Kattegat2003/4	Limfjord 2019/2021
Cu (mg/kg)	5	0	15	50
Pb (mg/kg)	20	10	30	30
Zn (mg/kg)	40	30	100	300
Ni (mg/kg)	15	2	20	35

Seasonal variability trends were not evident. There was at times significant variation between one measurement and the other, but it wasn´t possible to correlate it with temperatures related to seasonal variability. For the same of the samples, some heavy metals showed higher concentrations in warm months while others in winter months (see Appendix 3).

Flame retardants

Flame retardants were included in the study under request of Velux.

We have therefore commissioned the analysis together with the PHAs and TBTs to the Eurofins laboratories. The first time the analysis was made for all 21 locations for the flame retardants in the list in Table 5 (left), with detection levels of 10000 µg/kg. None of the sample resulted above detection levels. In a second moment the 21 samples were sent back again in order to deepen the investigation about selected flame retardants (Table 5, right) and none of them resulted above detection limits and were not repeated. Results of the analysis are in Appendix 5.

Table 5. List of investigated flame retardants.

FLAME RETARDANTS List	
FLAME RETARDANTS PBB/PBDE LA-GC-008.03 – **first round, 10 mg/kg detection limits**	FLAME RETARDANTS – selected **– second round, 0.005 mg/Kg detection limits**
Tribromodphenylether	BDE-28 -Tribromodiphenylether
Tetrabromibiphenylether	BDE-47- Tetrabromodiphenylether
Pentabromobiphenylether	BDE-49 - Tetrabromodiphenylether
Hexabromobiphenylether	BDE-85 - Pentabromodiphenylether
Heptabromobiphenylether	BDE-99 - Pentabromodiphenylether
Octabromobiphenylether	BDE-100 - Pentabromodiphenylether
Nonabromibiphenylether	BDE-138 - Hexabromodiphenylether
Decabromobiphenylether	BDE-153 - Hexabromodiphenylether
Tribromobiphenyl	BDE-154 - Hexabromodiphenylether
Tetrabromibiphenyl	
Pentabromobiphenyl	
Hexabromobiphenyl	
Heptabromobiphenyl	
Octabromobiphenyl	
Nonabromobiphenyl	
Decabromobiphenyl	

Tin, PHAs and TBTs

Tin, PHAs and TBTs results from Eurofins laboratories were polotted and a first comparison with literature has been made. Final comparison will be completed after the second round of analysis. All harbours locations present a considerable amount of anthropogenic pollutants (Fig 19). Additionally, Blokhus and some fjord and beach locations also present important concentrations of PHAs, and Tin.

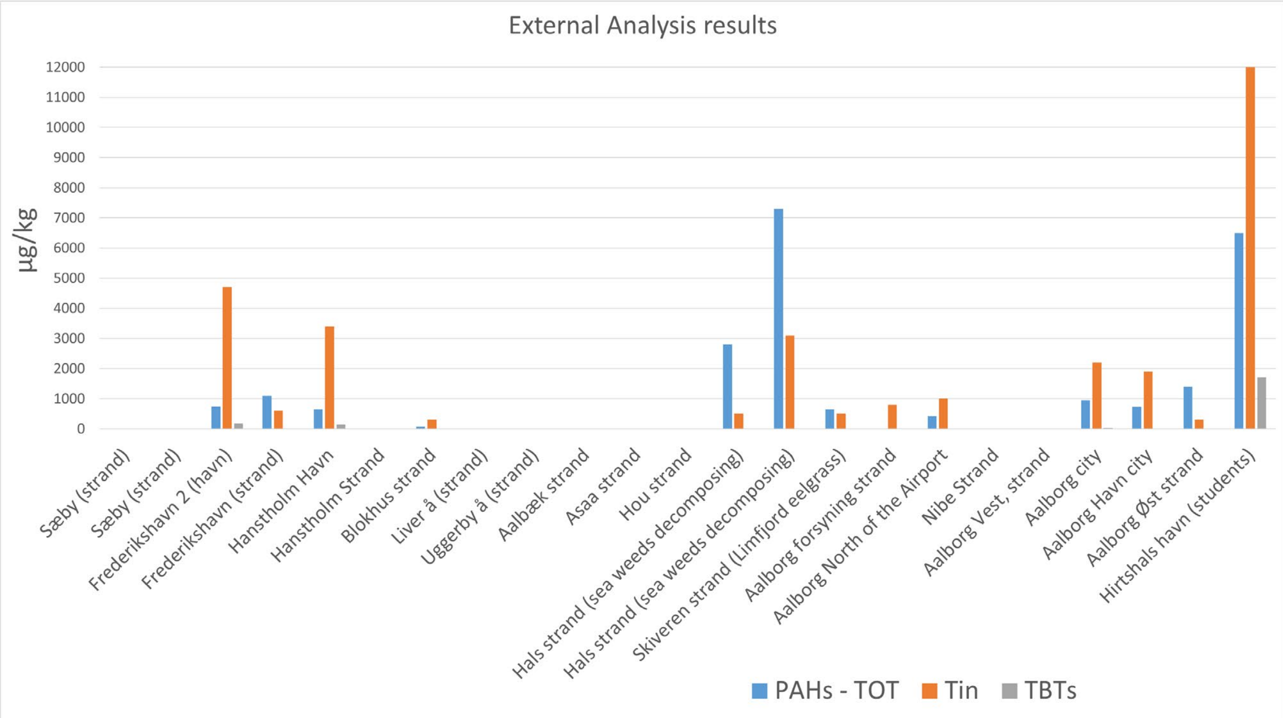


Figure 19. Summary of measured PHAs- TOT, TBTs and Tin in all locations for ROUND 1.

Tin

Tin was measured before and reported in ”*Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 Faglig rapport fra DMU, nr. 585”* but only for groundwater and fresh water. In our analysis, the detection limit was 200 µg/Kg. Tin is present in all harbour locations concentration of circa circa 2000 µg/Kg and above, with Hirtshals reaching 10.000 µg/Kg, more than double the second highest location Fredrikshavn. Fredrikshavn strand also present the presence of Tin. The sampling in Hals produced only core samples, as the beach was covered in seaweeds. These have been nevertheless collected and analysed. Tin was measured in seaweed samples from Hals (Fig. 20). Other location were Tin was measured were Blokhus, Hals strand core, Skiveren vej, Aalborg forsyning, Aalborg north to the Lufthavn, and Aalborg Øst strand.

Tin analysis were not carried out for ROUND 2 as the external laboratory used for this task (Eurofins) did not include them in the same deal as ROUND 1.

PHAs – TOT

In our analysis, detection limits were 10 and 20 µg/Kg.

Generally all harbor locations present PHAs but some locations on the Limfjord do too. Results from ROUND 1 and ROUND 2 are in accordance.

In “Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 - Faglig rapport fra DMU, nr. 585” the highest values were reported in Østersøen, for circa 4000 µg/Kg, followed by Arhus Bugt and the Limfjord. In our measurements we see Hals strand (above 7000 µg/Kg) and Hirtshals (above 9000 µg/Kg for round 2) to have the highest readings (Fig. 21).

TBTs - TOT

In our analysis, the detection limit was 5 µg/Kg.

Results from ROUND 1 and ROUND 2 are in accordance, even if concentration for Hirtshal havn, already very high in ROUND 1, almost reached 1750 µg/kg in ROUND2.

TBTs are present in few locations and only in harbours: Frederikshavn, Hantholm, Hirtshals and is small amounts also in Aalborg City. While the measurements from “Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 - Faglig rapport fra DMU, nr. 585” did not top 60 µg/Kg all the measurements we analysed exceeded this amount considerably (Fig. 22).

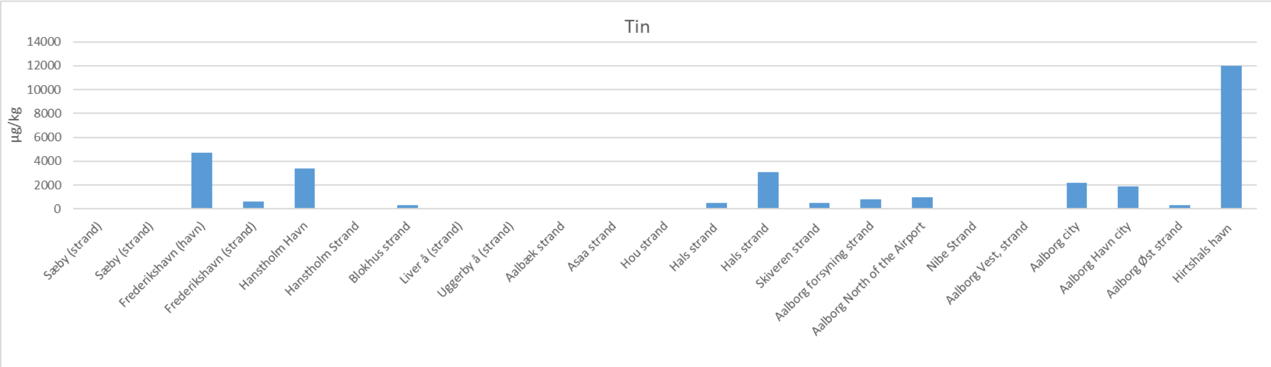


Figure 20. Tin Measurements and screenshot from “Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 - Faglig rapport fra DMU, nr. 585”

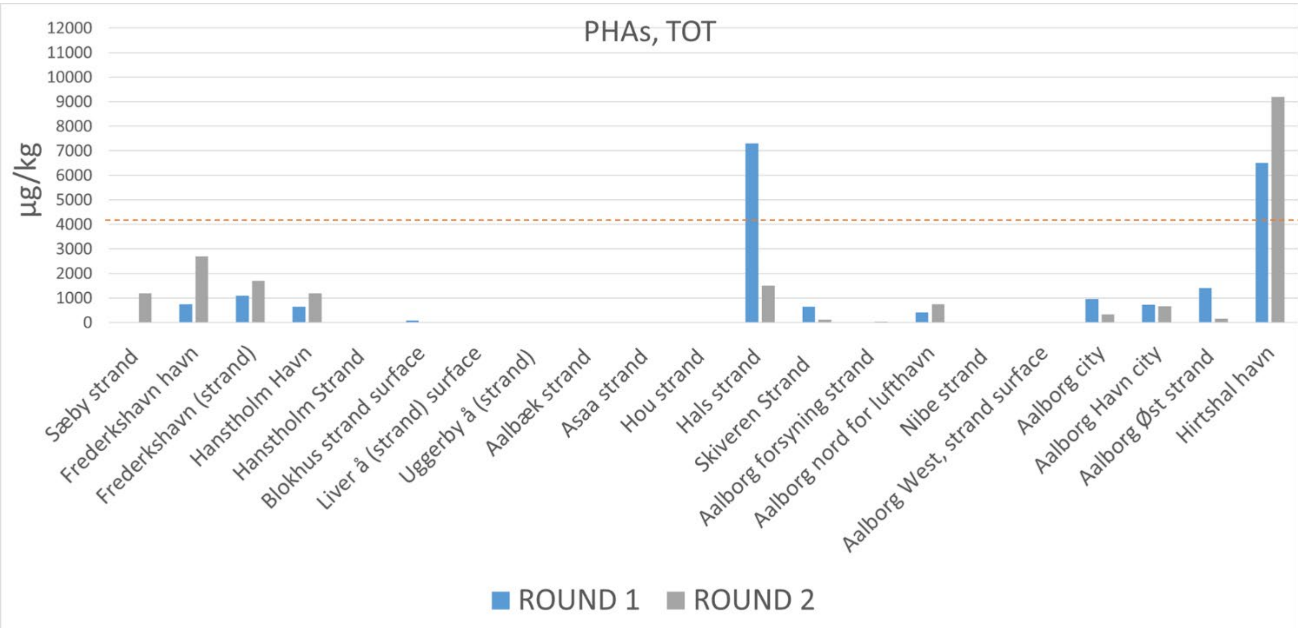


Figure 21. PHAs TOT and comparaison with “Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 - Faglig rapport fra DMU, nr. 585” data. 4000 µg/Kg is marked in both graphics for easier comparison.

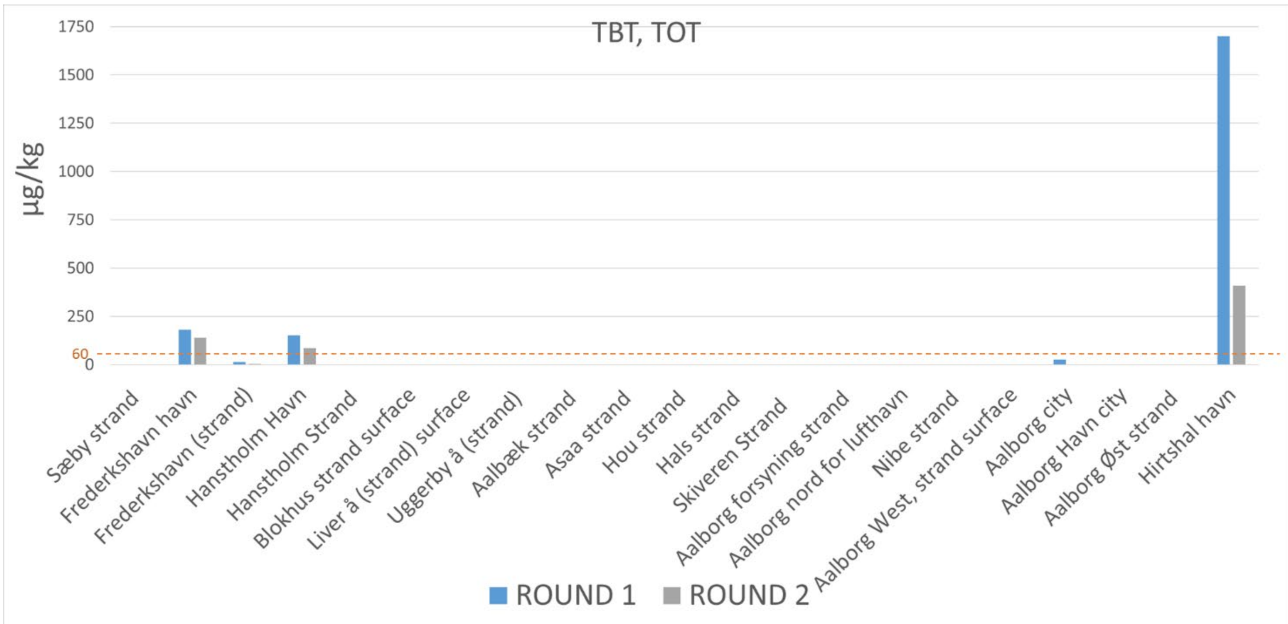


Figure 22. TBTs TOT and comparaison with "Miljøfremmede stoffer og tungmetaller i vandmiljøet Tilstand og udvikling, 1998-2003 - Faglig rapport fra DMU, nr. 585" data. 60 µg/Kg line is marked in both graphics for easier comparison.

Laboratory tests – remediation technology

The tests featured three setups with three different heavy metals in high concentrations: Zn, Cd and Ni. We use synthetic sea water adequately monitored for pH, temperature, conductivity and heavy metal concentrations.

Working principle

The cathodic protection (CP) induced by a current through the steel cathode (Fig. 23), initiates electrochemical reactions precipitating both aragonite ($CaCO_3$) and brucite ($Mg(OH)_2$) referred to as calcareous material. The hypothesis is that in presence of heavy metals, these will be primarily attracted to the cathode. In this way, with the proper engineering, heavy metals can be collected and disposed, avoiding further dispersion in the natural environment.

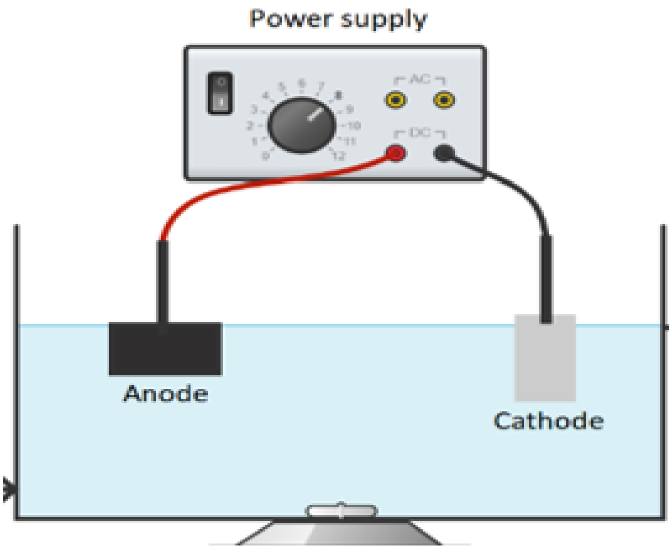


Figure 23. working principale

Setup

The tests run in triplets: each one included a 20 L tank with artificial sea water (Fig. 24, Table 6), one anode (DSA material) and one cathode (non galvanized Iron) with an electric potential of 2.2 V between them. All tests run for 7 days. Water temperature was between 18-22°C. Water conductivity was circa 50-54 mS/cm with no particular trend with the time passing by. Water pH was circa 7.4 . Once the tests were concluded, we dried the cathode at 50°C and carefully scraped some of the deposited material from the surface, only using plastic tools. The cathode was weighted before and after the tests.

- First, we conducted tests with artificial sea water only (blanks) (Fig. 25).
- Second we run the tests with heavy metals in high concentration dissolved in salts in the artificial seawater (Table 7).

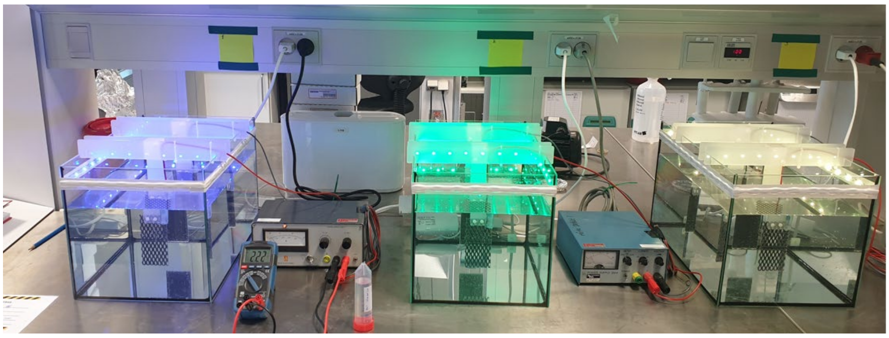


Figure 24. Blanks running in triplets

Table 6. Artificial seawater composition

Chemical	Formula	Fraction	(g)/L
Sodium Chloride	NaCl	0,58490	24,54
Magnesium Chloride	MgCl2-6H2O	0,26460	11,10
Sodium Sulfate	Na2SO4	0,09750	4,09
Calcium Chloride	CaCl2	0,02765	1,16
Potassium Chloride	KCl	0,01645	0,69
Sodium Bicarbonate	NaHCO3	0,00477	0,20
Potassium Bromide	KBr	0,00238	0,10
Boric Acid	H3BO3	0,00071	0,03
Strontium Chloride	SrCl2-6H2O	0,00095	0,04
Sodium Fluoride	NaF	0,00007	0,00

Figure 25. Triplets, blanks – cathodes after test and drying ta 50°C

Table 7. Heavy metal salts used in each batch. One batch = 20 L

Element	Molar mass					
	(g/mol)	(mol/L)	(mg/L)	Chemical	MW (g/mol)	Salt per batch (g)
Cd	112,411	3,7E-04	41,6	CdCl2	183,32	1,36
Ni	58,6934	3,7E-04	21,7	NiCl2.6H2O	237,69	1,76
Zn	65,38	3,7E-04	24,2	ZnCl2	136,3	1,01

The precipitated material on the cathodes looked very different, depending on the heavy metal salt dissolved and trapped (Fig. 26-28). Th reasons for these differences, consistent across triplets of the same kind, is unknown and expertise in the area of chemistry and electrochemistry must be included in further studies.

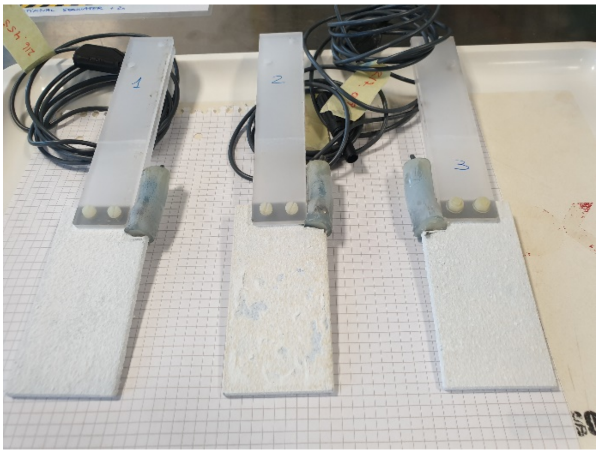


Figure 26. triplets, Zink tests - cathodes after test and drying ta 50°C

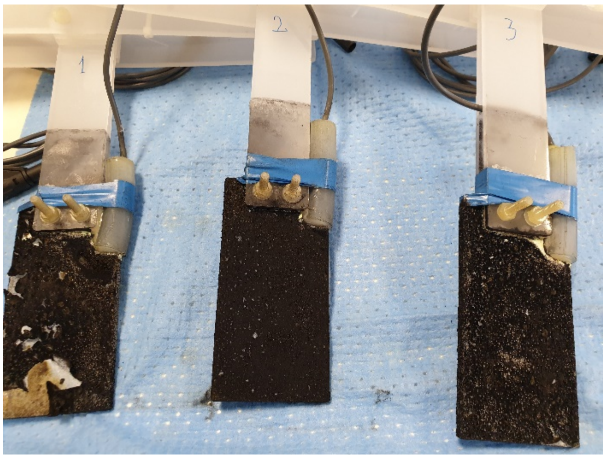


Figure 27. triplets, Nickel tests - cathodes after test and drying ta 50°C

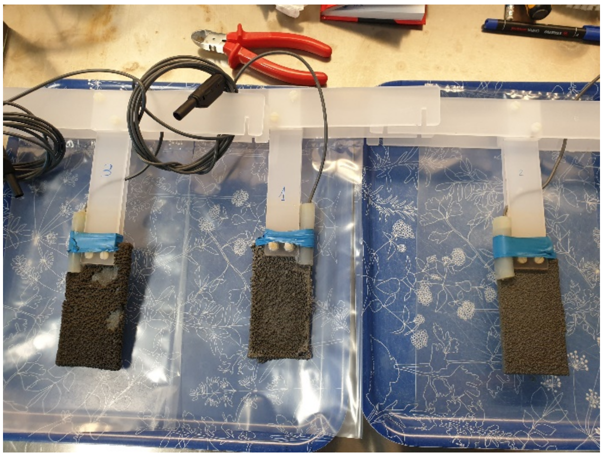


Figure 28. triplets, Cadmium tests- cathodes after test and drying ta 50°C

Trapping of heavy metals

The results show that the proposed remediation technology is capable of trapping heavy metals on the cathode, together with lower quantities of magnesium and calcium that would precipitate in the blanks (no heavy metals dissolved in water). Further analysis is necessary to better understand the process and optimize the technology for maximum efficiency.

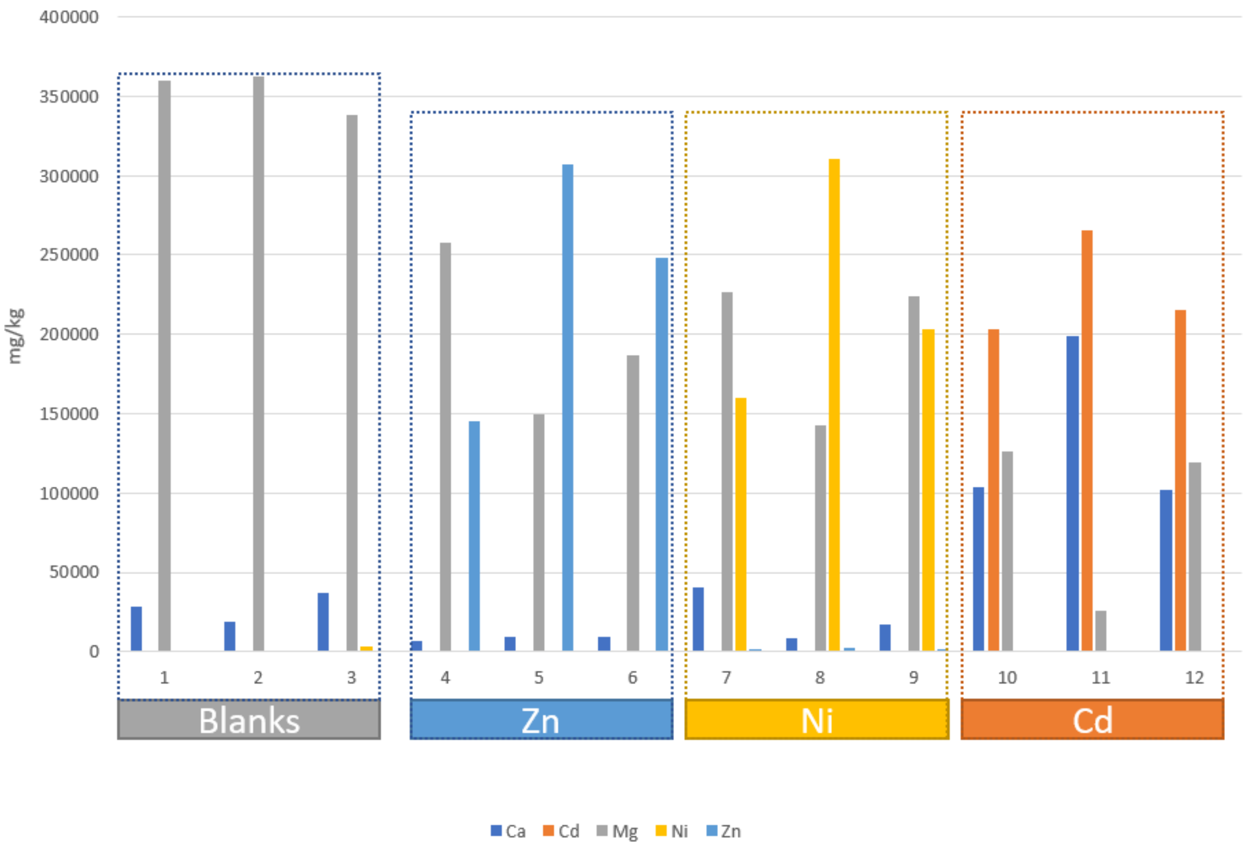


Figure 29. Comparison of the material composition precipitated on the cathode in terms of calcium, Magnesium, Cadmium, Nickel, and Zink.

Conclusions

We have collected samples from 21 locations: 5 harbours, 7 on the beach, 3 estuaries, 6 on the Limfjord. All samples, with exception to the harbour samples, were taken when possible, as surface samples and core samples, for a total of more than 250 Kg of sediments.

One procedure for handling the samples and sieving them was designed, with the purpose of avoiding heavy metal contaminations and characterizing the samples based on their grainsize distributions. Indeed, in literature it was suggested that heavy metals bond with organic matter and/or clays.

All samples with the exception of harbour locations were analysed in house for heavy metals. All samples were also sent to Eurofins laboratories for analysis on flame retardants, PHAs, TBTs, and Tin (Sn).

Heavy metals were expected to be found only in presence of organic matter or very fine gran sizes (clays). Nevertheless, traces of heavy metals were found also in locations that did not feature a suitable grainsize distributions. Comparison with literature levels must be completed.

For heavy metal a big variability was found in the different samples, but could not be linked to temperature and other seasonal variations. For PHAs and TBTs there was good accordance between ROUND 1 and ROUND 2.

Analysis of flame retardants was conducted twice with different detection limits (10 mg/ kg and 0.005 mg/ kg) and never flame retardants were detected in any of the locations in the study.

Tin detection limit was 200 µg/Kg. Tin is present in several sediments from different location at quite high concentrations. Comparison with literature still need to be addressed: there may be a lack of data to compare to.

PHAs detection limits were 10 and 20 µg/Kg. PHAs have been generally found in all harbor locations and also in some locations in the Limfjord. Concentration in harbours can be higher than values in preliminary literature review.

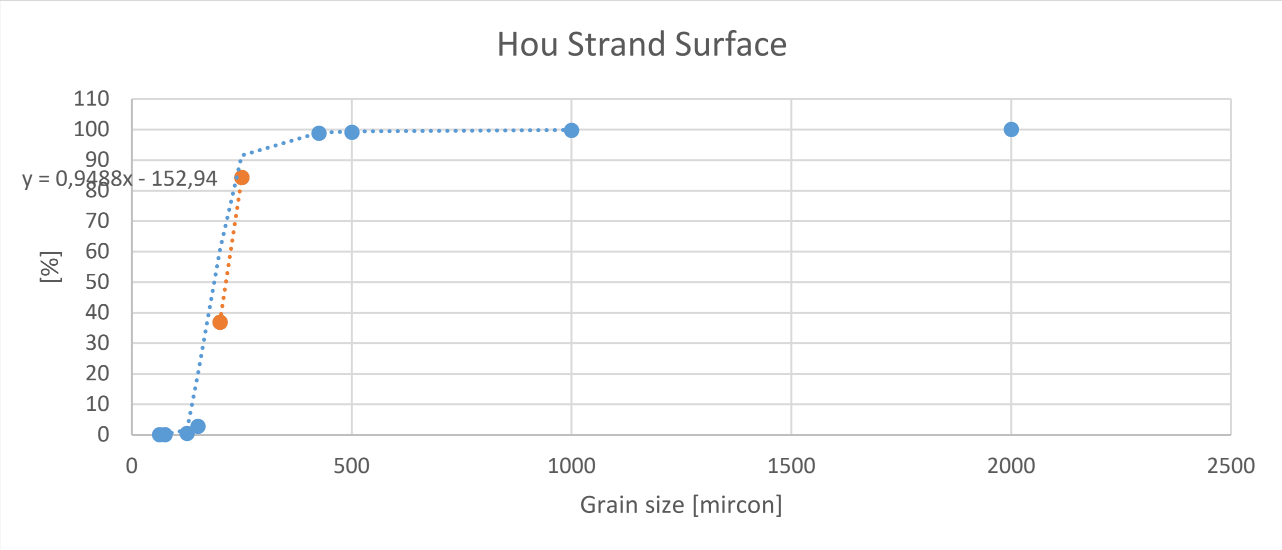
TBTs detection limit was 5 µg/Kg. TBTs are present in few locations and only in harbours but at considerably higher values than the ones encountered in preliminary literature review.

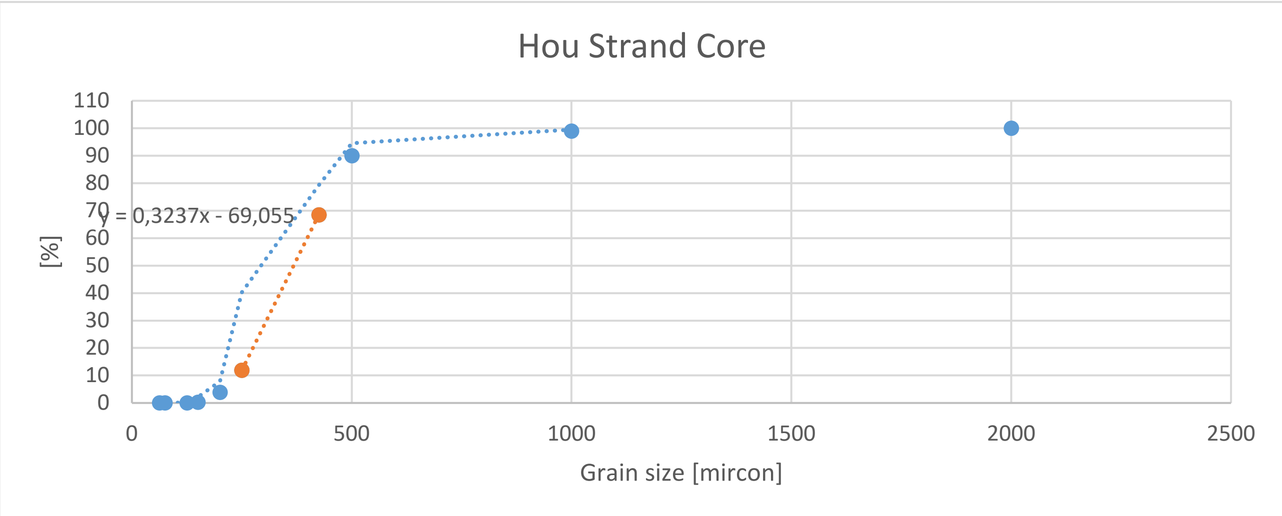
The remediation technology tested in the laboratory demonstrated to be a promising solution to trap heavy metals in contaminated waters. Nevertheless, further analysis is needed to better understand the process. Particularly, further development of this remediation should include chemical and electrochemical experts.

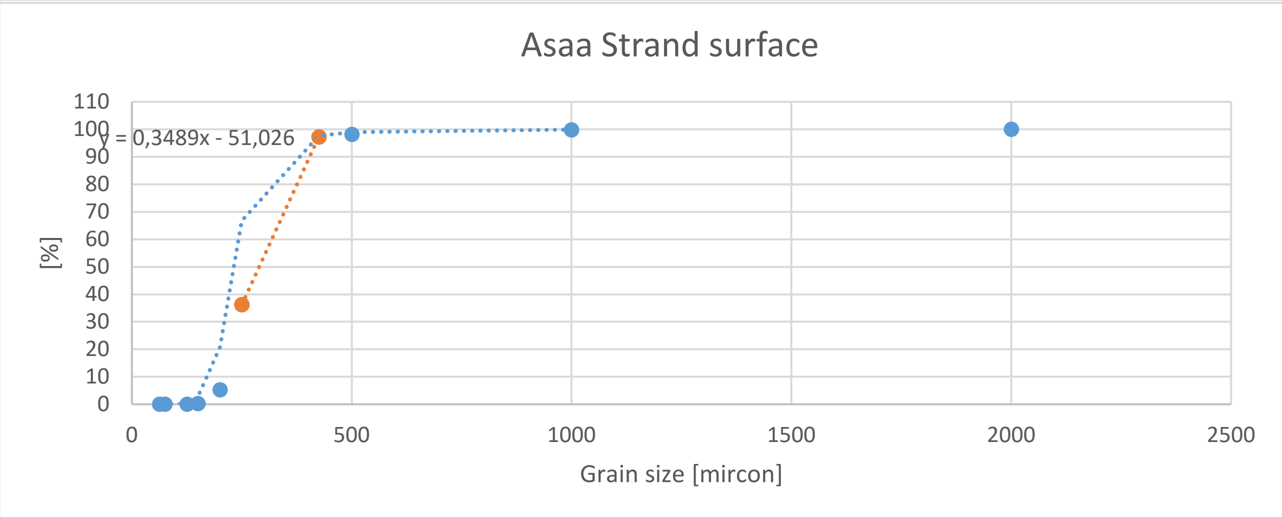
Appendix 1 – (water analysis round 1)

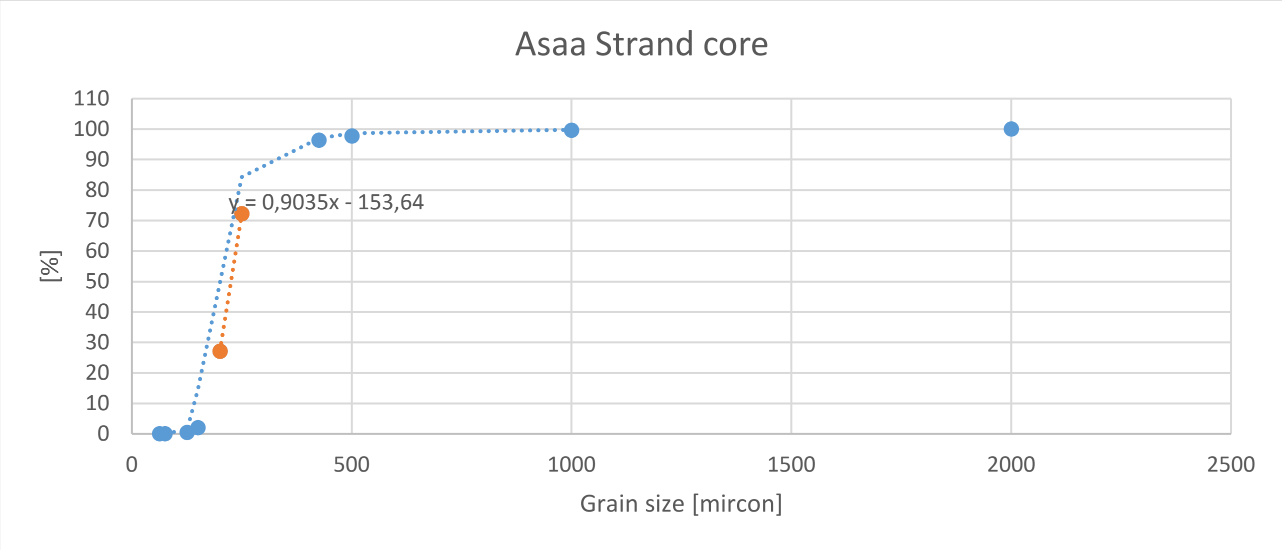
	round 1					date
No.	**location**	**pH**	**temp (C)**	**conductivity (ms/cm)**	**oxigen (mg/l)**	
1	Sæby strand	7.2	4.2	51.0	13.26	05-02-2019
2	Frederikshavn (Havn)	7.92	2.9	46.7	13.24	13-06-2019
3	Frederikshavn (strand)	7.92	3.2	47.6	12.9	05-02-2019
4	Hanstholm Havn	6.896	5.5	50.2	78.7	07-03-2019
5	Hanstholm Strand	8.444	5.8	50.7	104.4	07-03-2019
6	Blokhus strand	7.13	14.4	731	10.15	13-06-2019
7	Liver å (strand)	7.35	19.2	627	9.36	13-06-2019
8	Uggerby å (strand)	7.4	17.1	526	9.68	13-06-2019
9	Aalbæk strand	7.2	19.9	34.4	9.35	13-06-2019
10	Asaa strand	7.4	17.4	35.3	11.16	17-06-2019
11	Hou strand	7.9	16.5	36.9	11.04	17-06-2019
12	Hals strand	7.6	18.2	26.3	9.6	17-06-2019
13	Skiveren strand	7.4	15.4	8.59	9.89	17-06-2019
14	Aalborg fdorsyning strand	7.5	19.5	3.89	10.4	17-06-2019
15	Aaalborg North of the Airport					17-06-2019
16	Nibe strand	8.63	18.9	32.3	9.96	18-06-2019
17	Aalborg Vest, strand	8.132	20.1	39.4	10.93	18-06-2019
18	Aalborg city	8.147	20.1	39.3	9.09	18-06-2019
19	Aalborg Havn city	8.122	20.4	38.0	9.61	18-06-2019
20	Aalborg Øst, strand	8.198	21.9	35.9	10.92	18-06-2019
21	Hirtshal havn (students)					10-04-2019

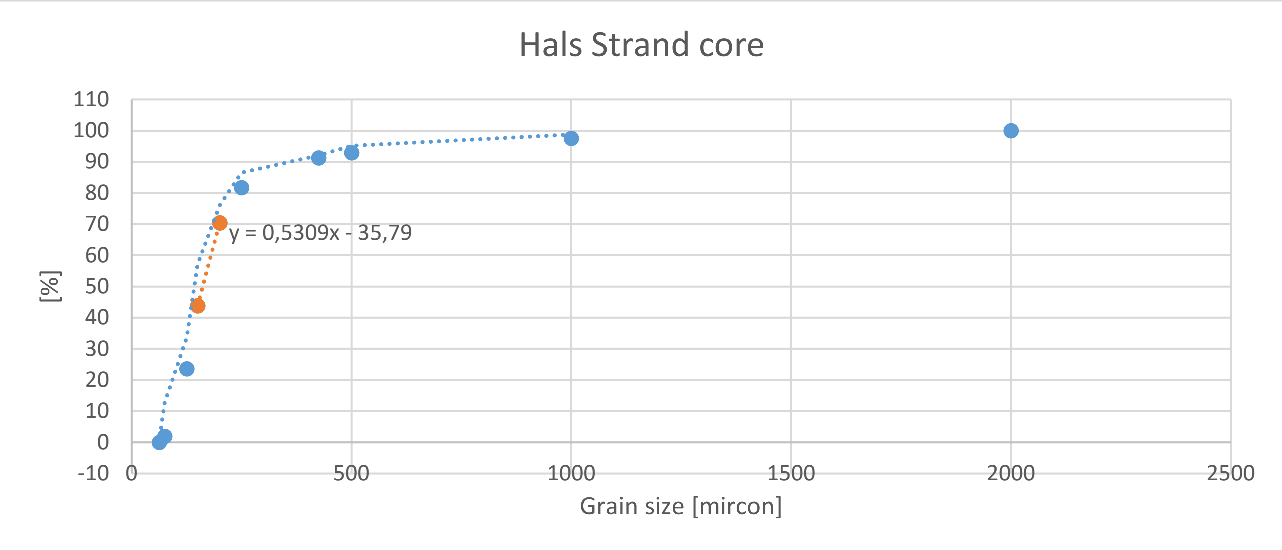
Appendix 2 (grainsize distributions)








Asaa Strand core
y = 0,9035x - 153,64
[%]
110
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Grain size [mircon]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[%]
110
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30
20
10
0
-10
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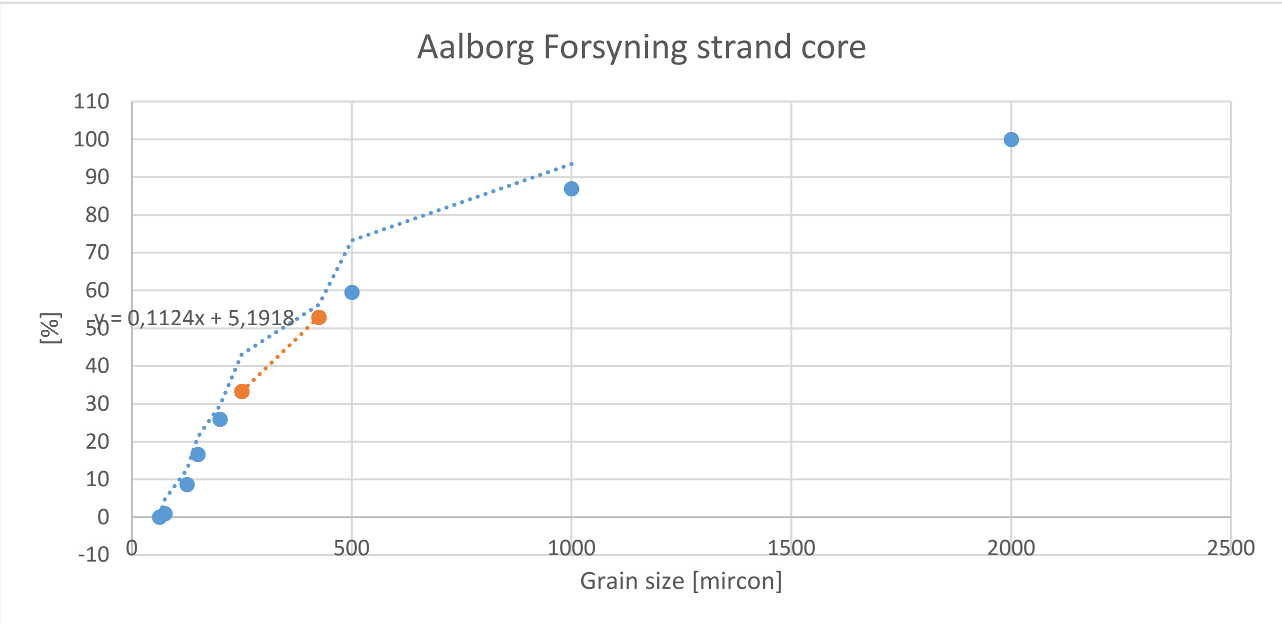
1500
2000
2500
Grain size [mircon]


Aalborg Forsyning strand core
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[%]
110
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70
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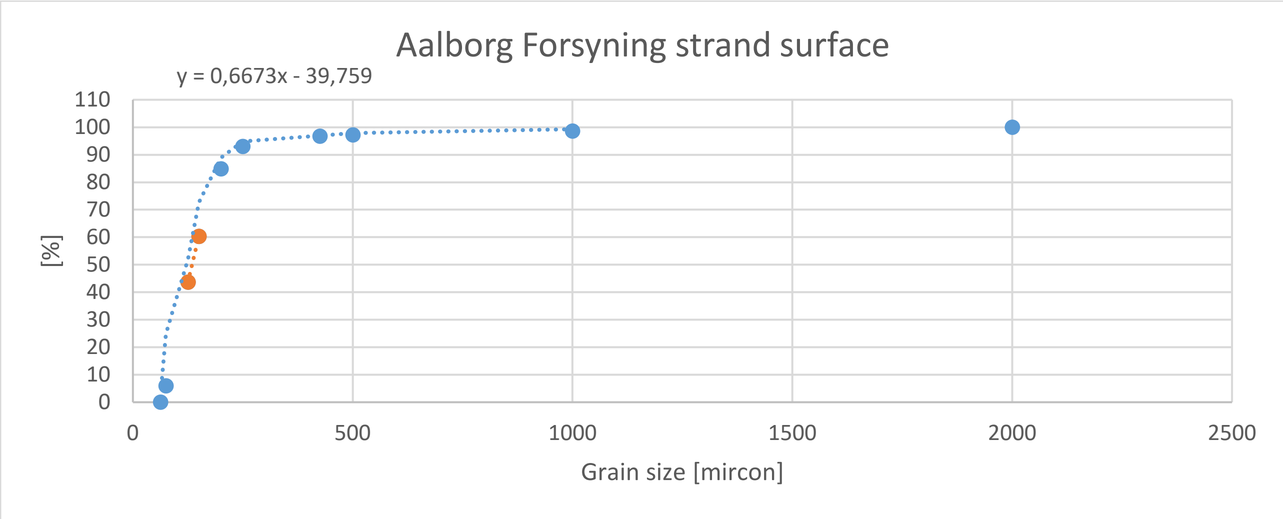
50
40
30
20
10
0
-10
0
500
1000
1500
2000
2500
Grain size [mircon]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10
0
[%]
0
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1000
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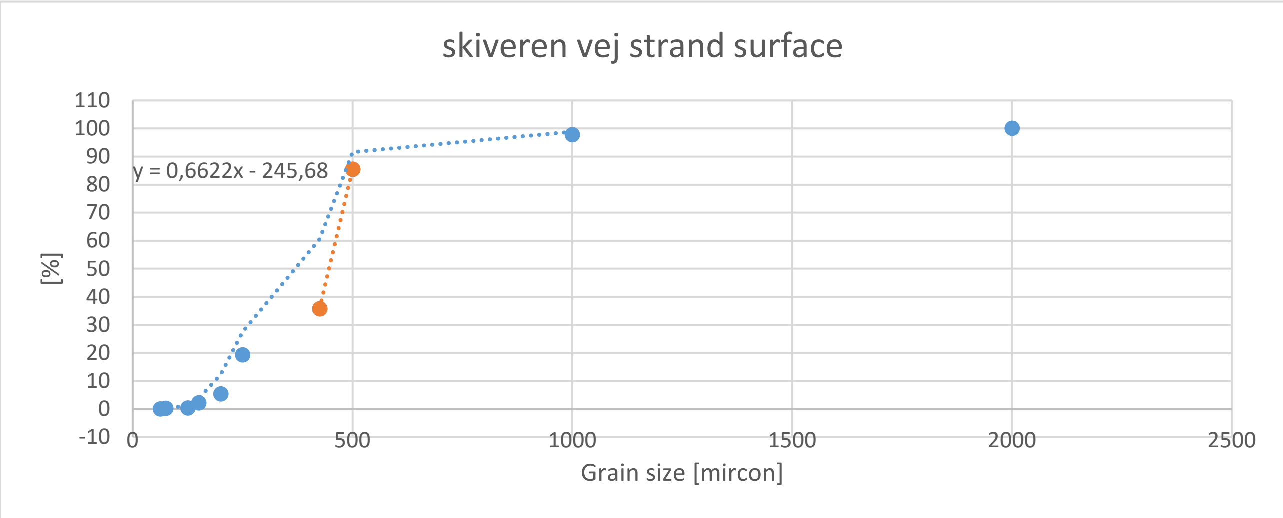
2000
2500
Grain size [mircon]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30
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0
-10
[%]
0
500
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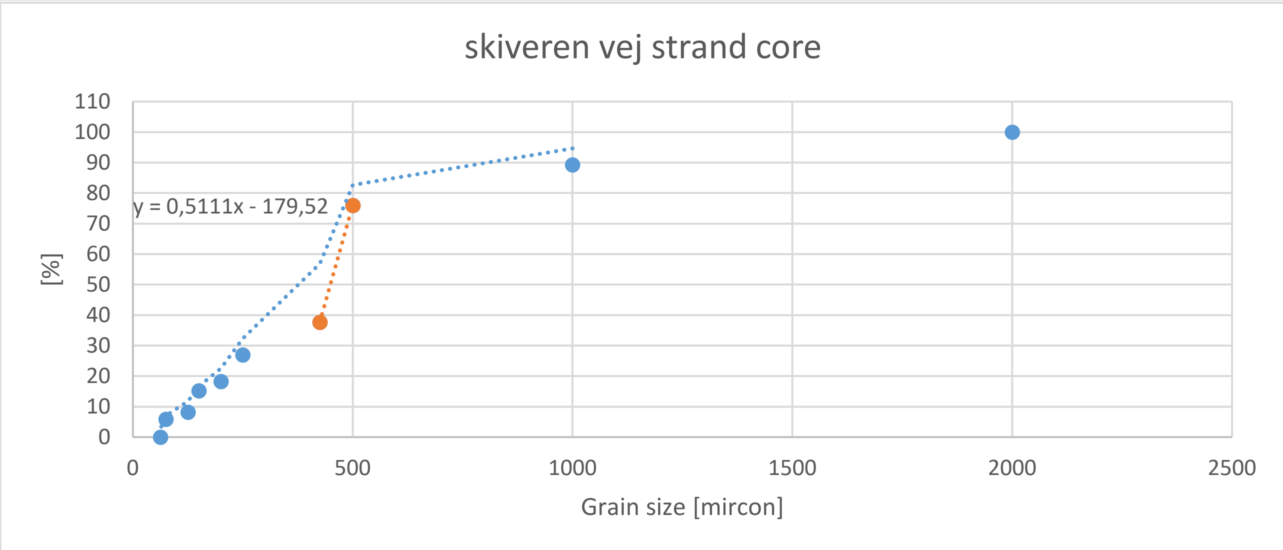
Grain size [mircon]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40
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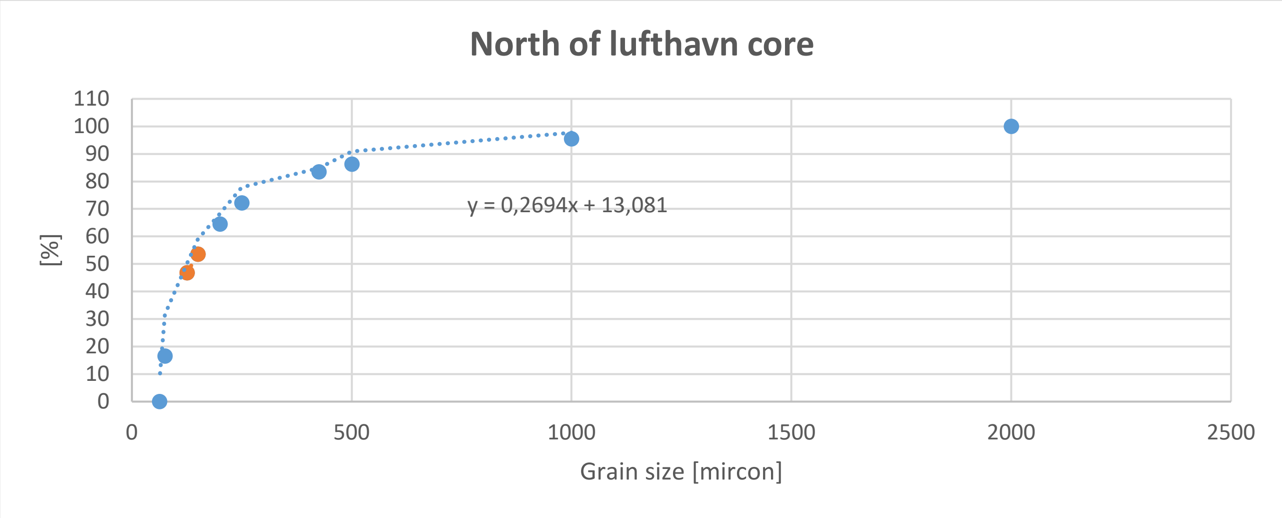
10
0
[%]
0
500
1000
1500
2000
2500
Grain size [mircon]



North of lufthavn core
110
100
90
80
70
60
50
40
30
20
10
0
[%]
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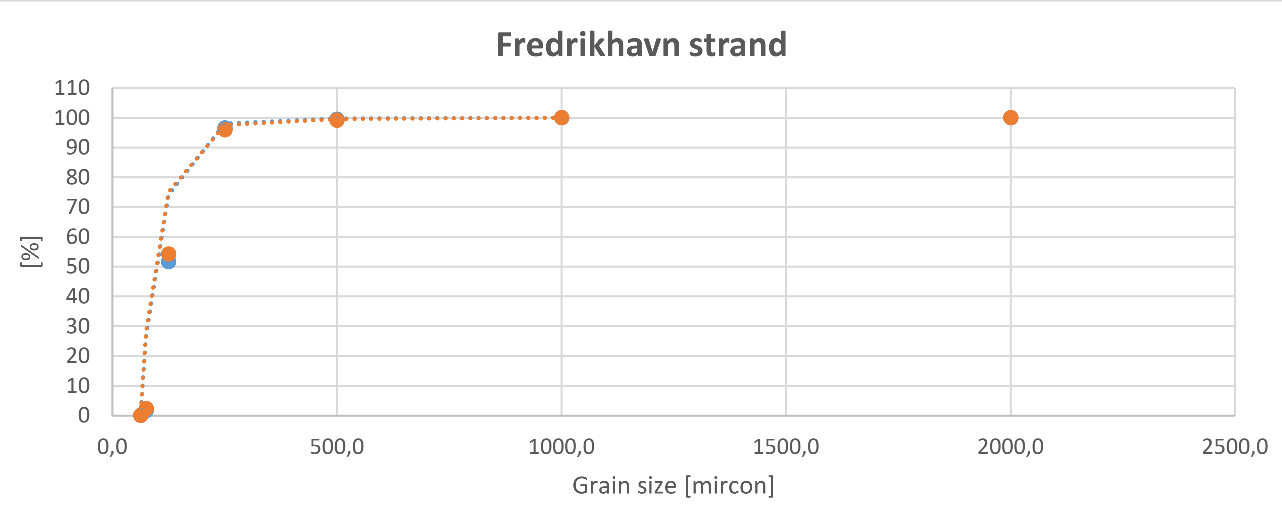
0
500
1000
1500
2000
2500
Grain size [mircon]



Fredrikhavn strand
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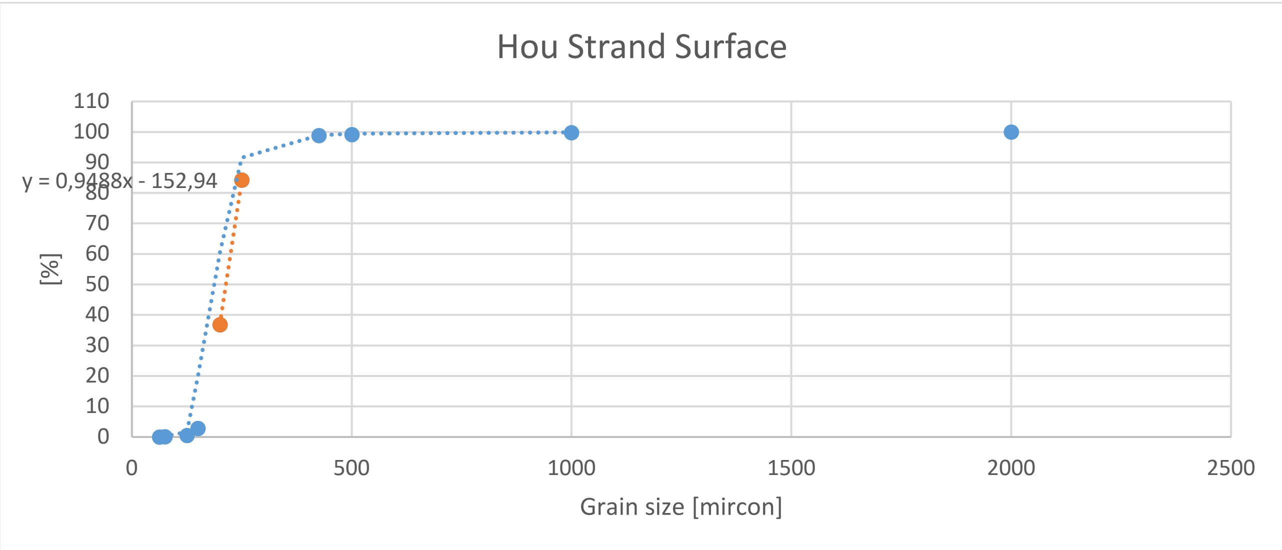
0
[%]
0,0
500,0
1000,0
1500,0
2000,0
2500,0
Grain size [mircon]



Hou Strand Surface
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80
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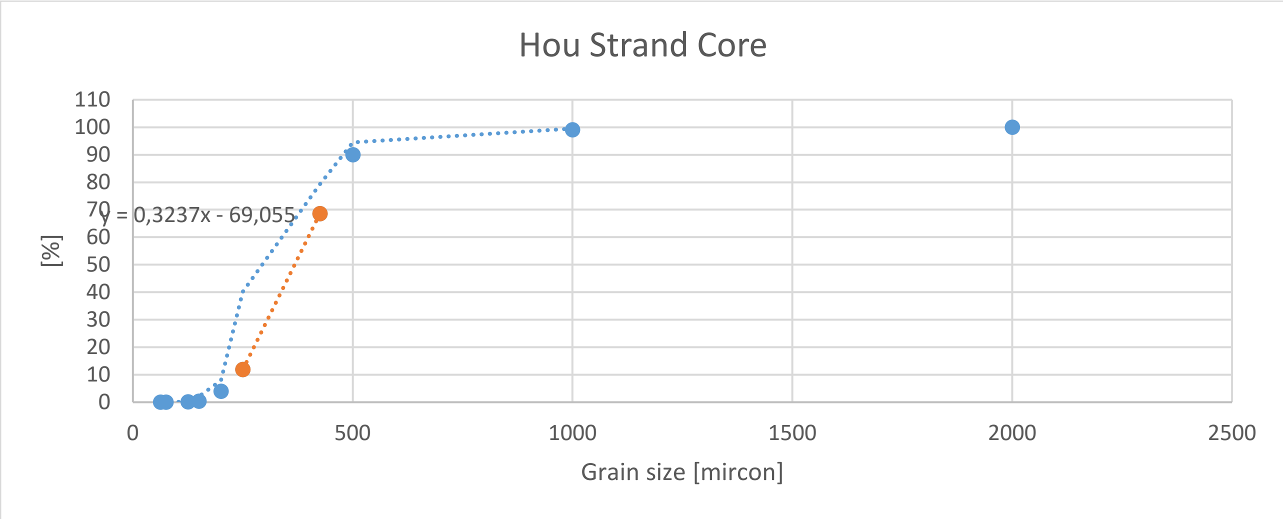
2000
2500
Grain size [mircon]



Hou Strand Core
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80
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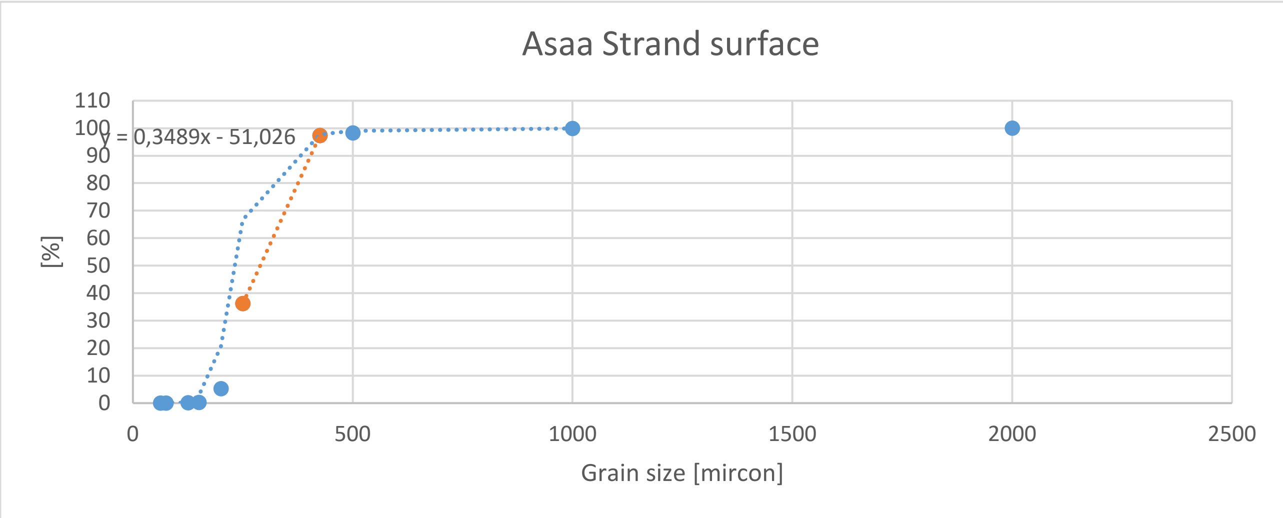
2000
2500
Grain size [mircon]



Asaa Strand surface
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90
80
70
60
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10
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0
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2000
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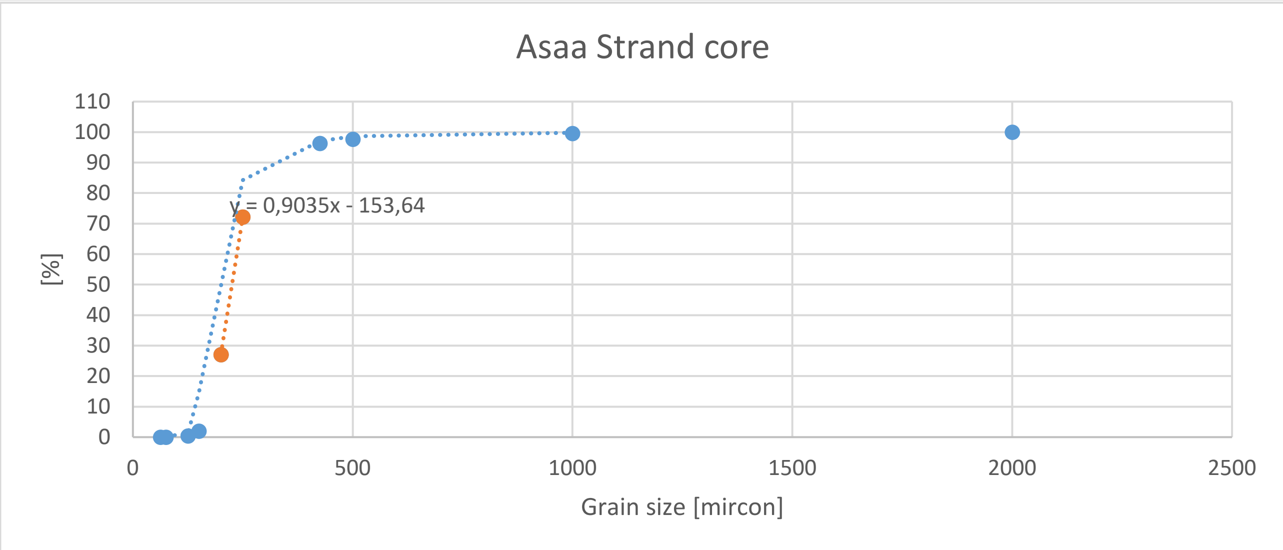
Grain size [mircon]



Asaa Strand core
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100
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70
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[%]
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0
500
1000
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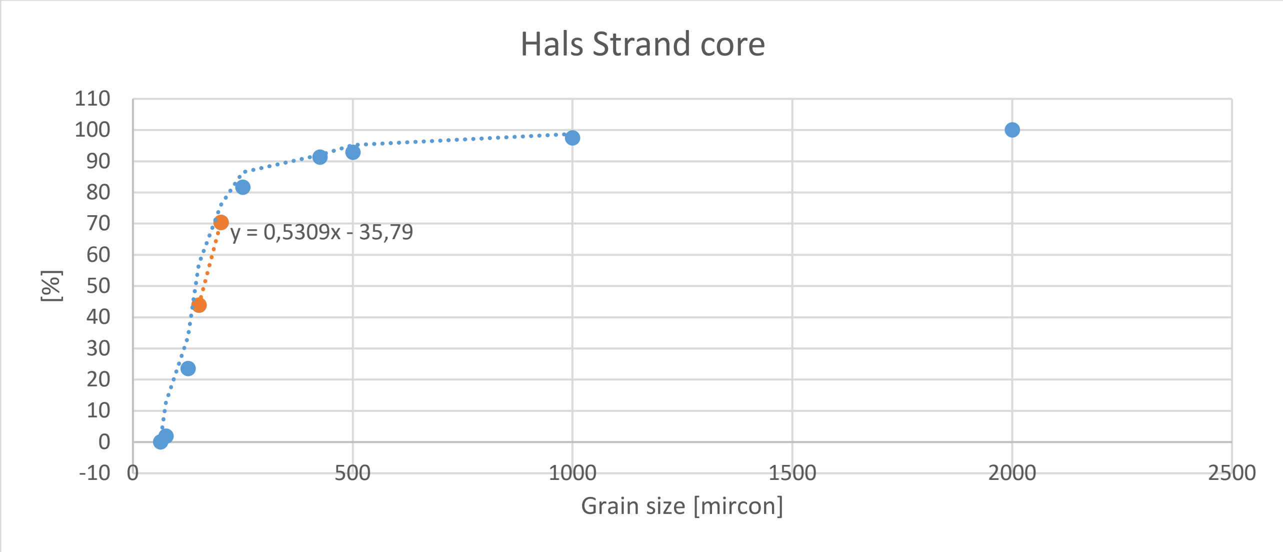
2500
Grain size [mircon]


Hals Strand core
y = 0,5309x - 35,79
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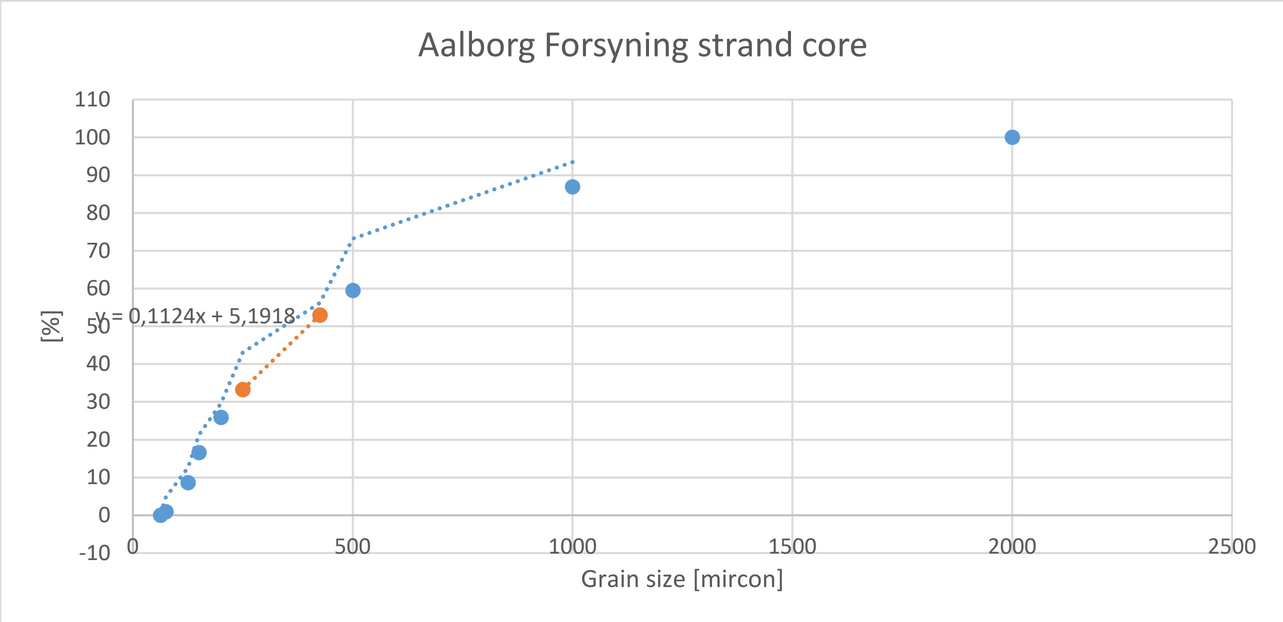
Grain size [mircon]


Aalborg Forsyning strand core
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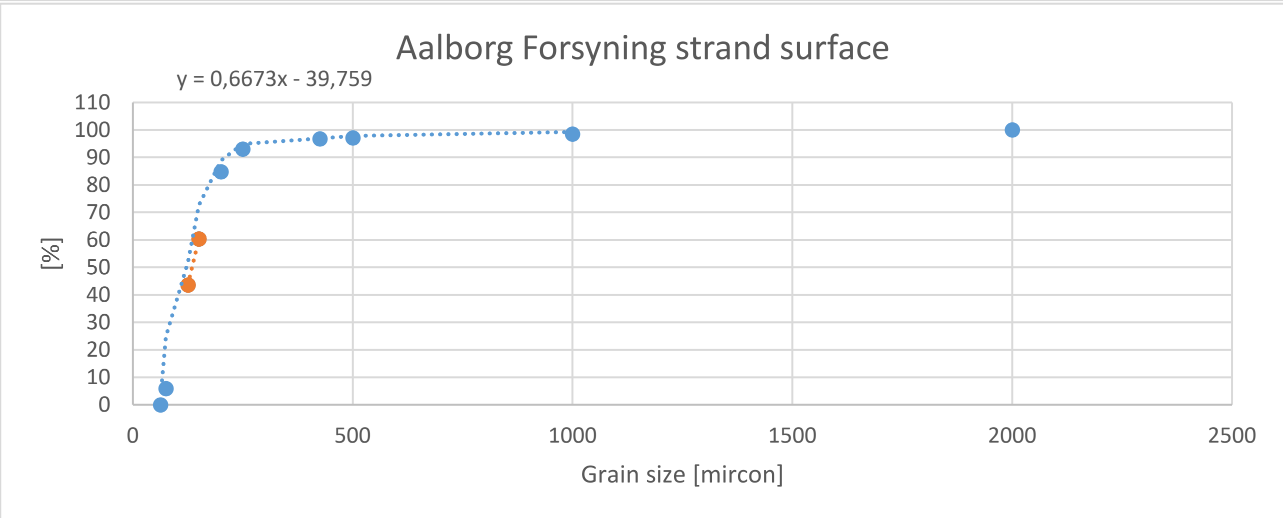
[%]
Grain size [mircon]


Aalborg Forsyning strand surface
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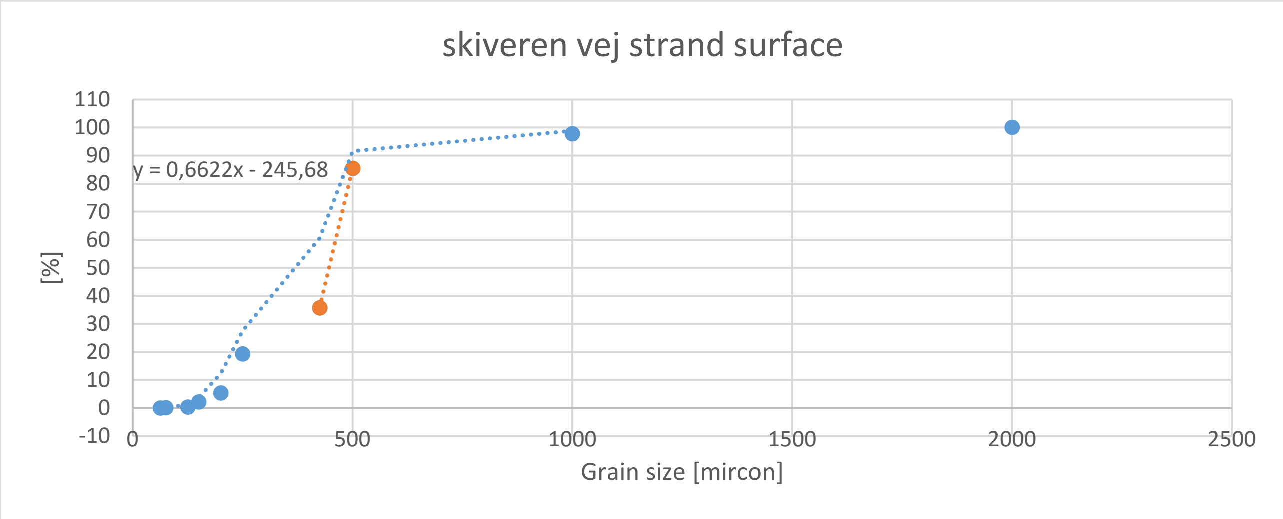
[%]
Grain size [mircon]


skiveren vej strand surface
110
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y = 0,6622x - 245,68
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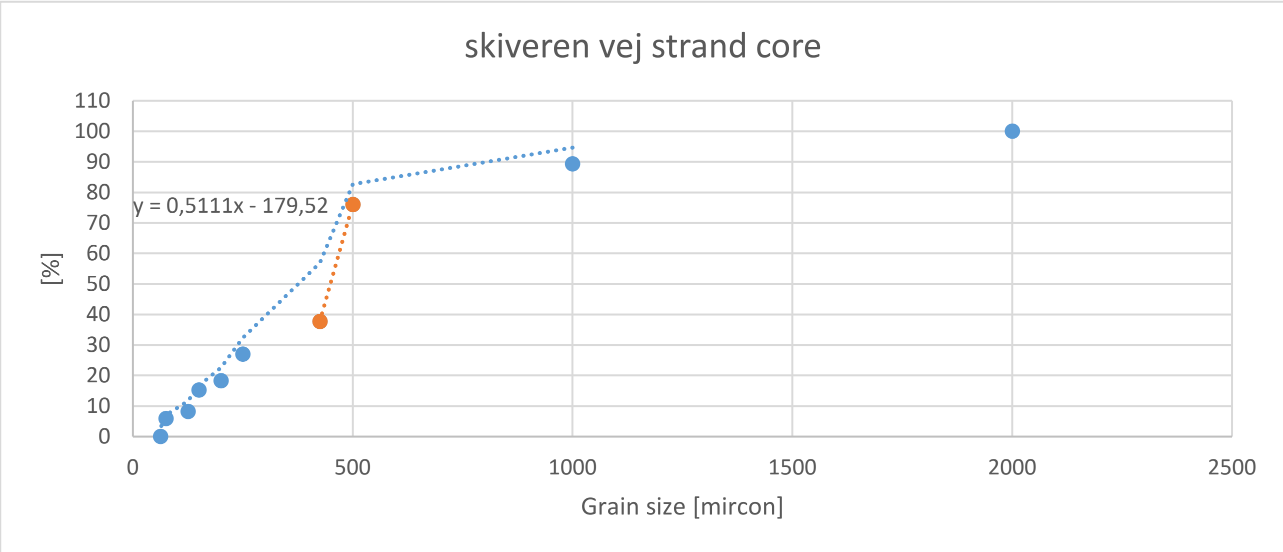
2000
2500
Grain size [mircon]


skiveren vej strand core
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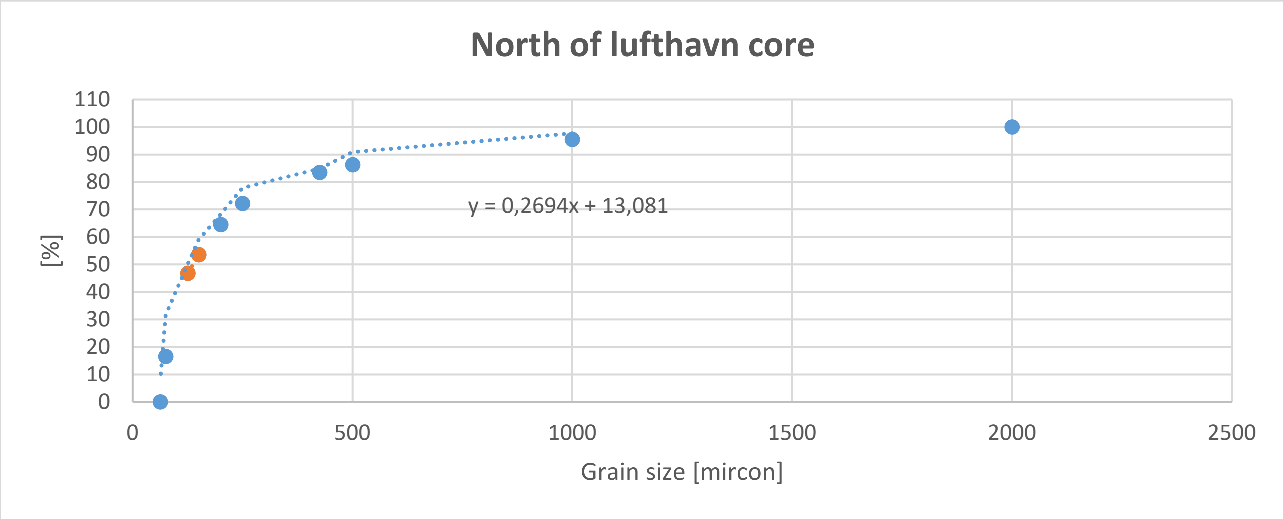
Grain size [mircon]


North of lufthavn core
110
100
90
80
70
60
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30
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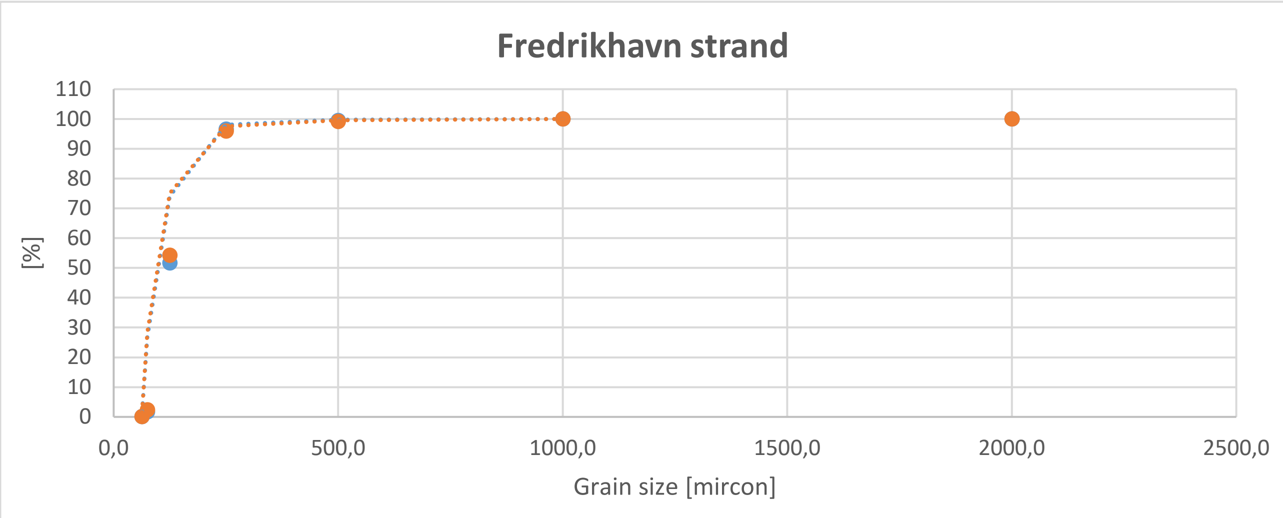
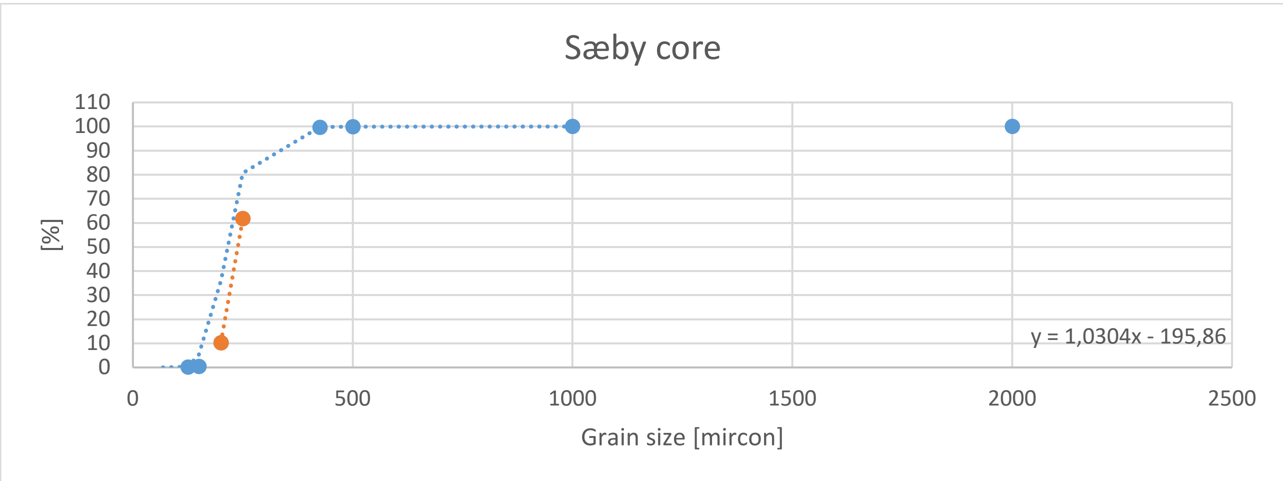
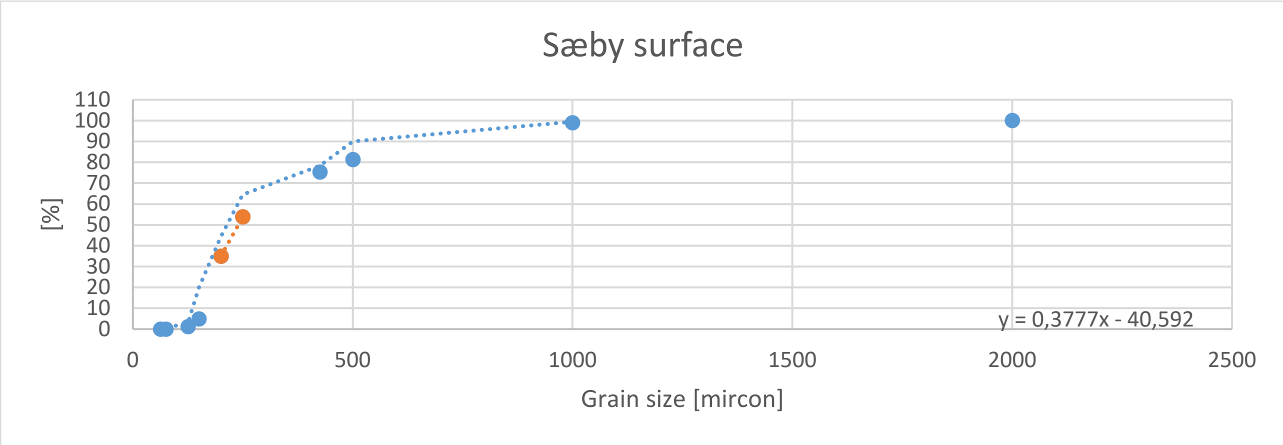
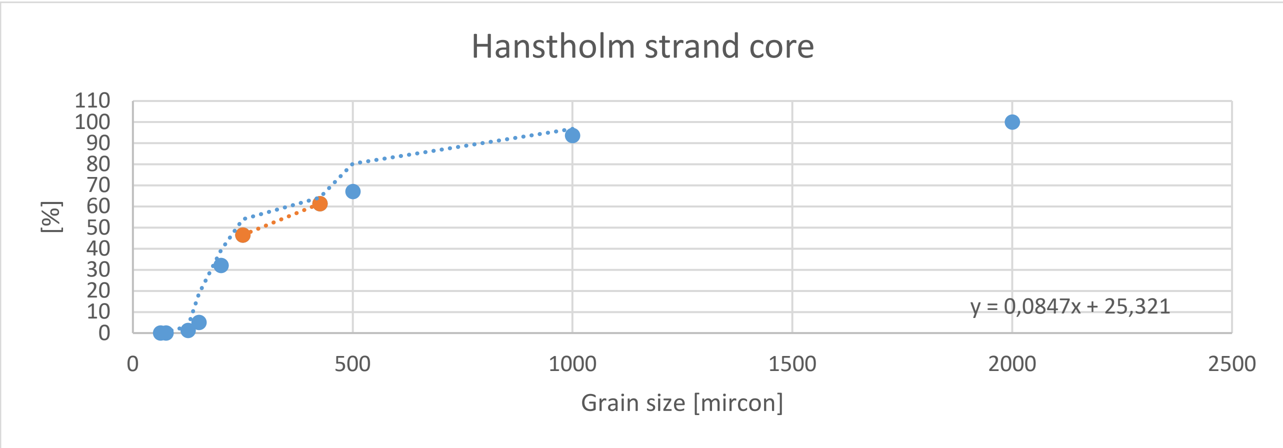
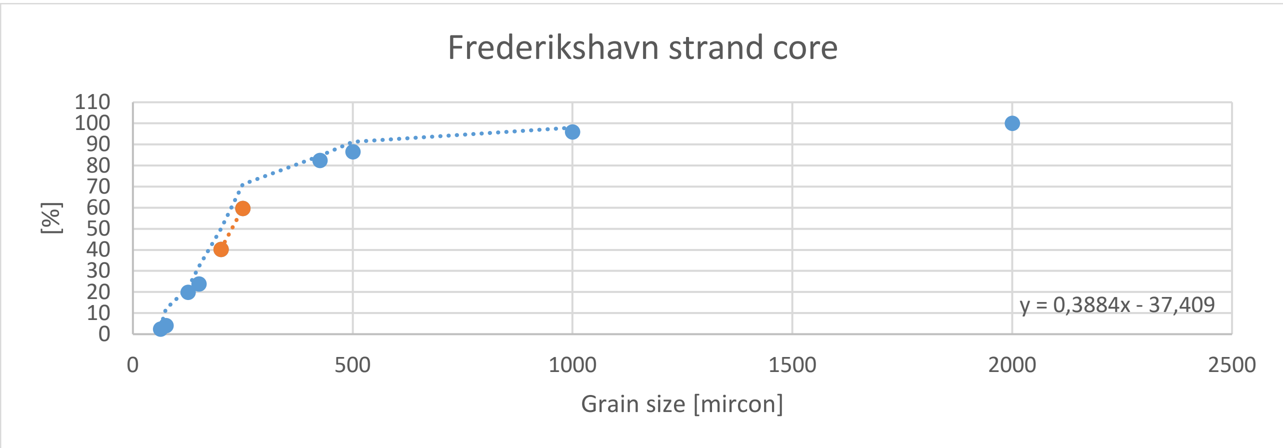
0
[%]
y = 0,2694x + 13,081
0
500
1000
1500
2000
2500
Grain size [mircon]


Fredrikhavn strand
110
100
90
80
70
60
50
40
30
20
10
0
[%]
0,0
500,0
1000,0
1500,0
2000,0
2500,0
Grain size [mircon]


Sæby core
110
100
90
80
70
60
50
40
30
20
10
0
[%]
y = 1,0304x - 195,86
0
500
1000
1500
2000
2500
Grain size [mircon]


Sæby surface
[%]
110
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Grain size [mircon]
y = 0,3777x - 40,592


Hanstholm strand core
[%]
110
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Grain size [mircon]
y = 0,0847x + 25,321


Frederikshavn strand core
[%]
110
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Grain size [mircon]
y = 0,3884x - 37,409

Appendix 3 – selected locations, heavy metals detail

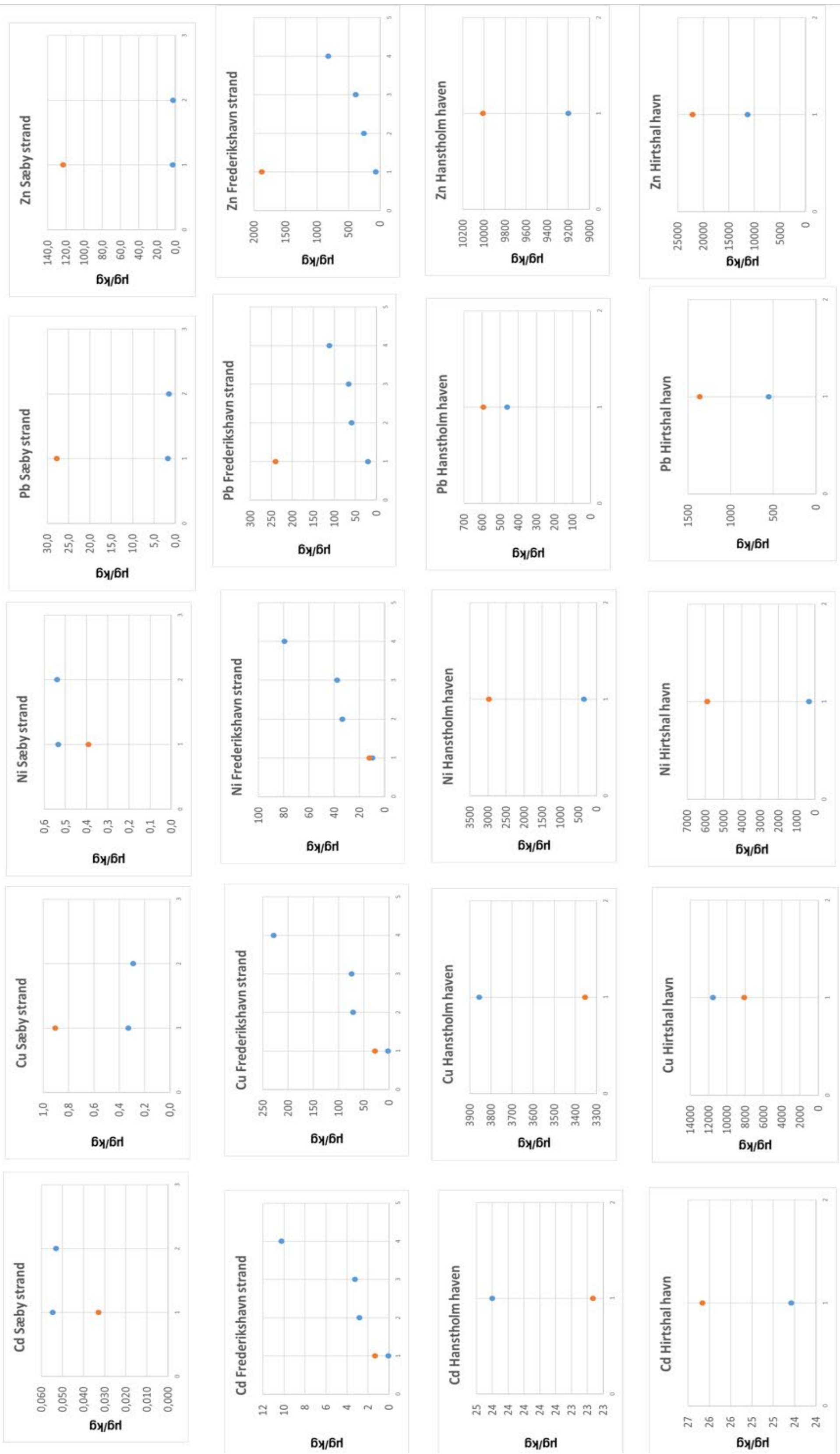


Figure 30. blue dots are sample collected during winter/early spring, orange during summer

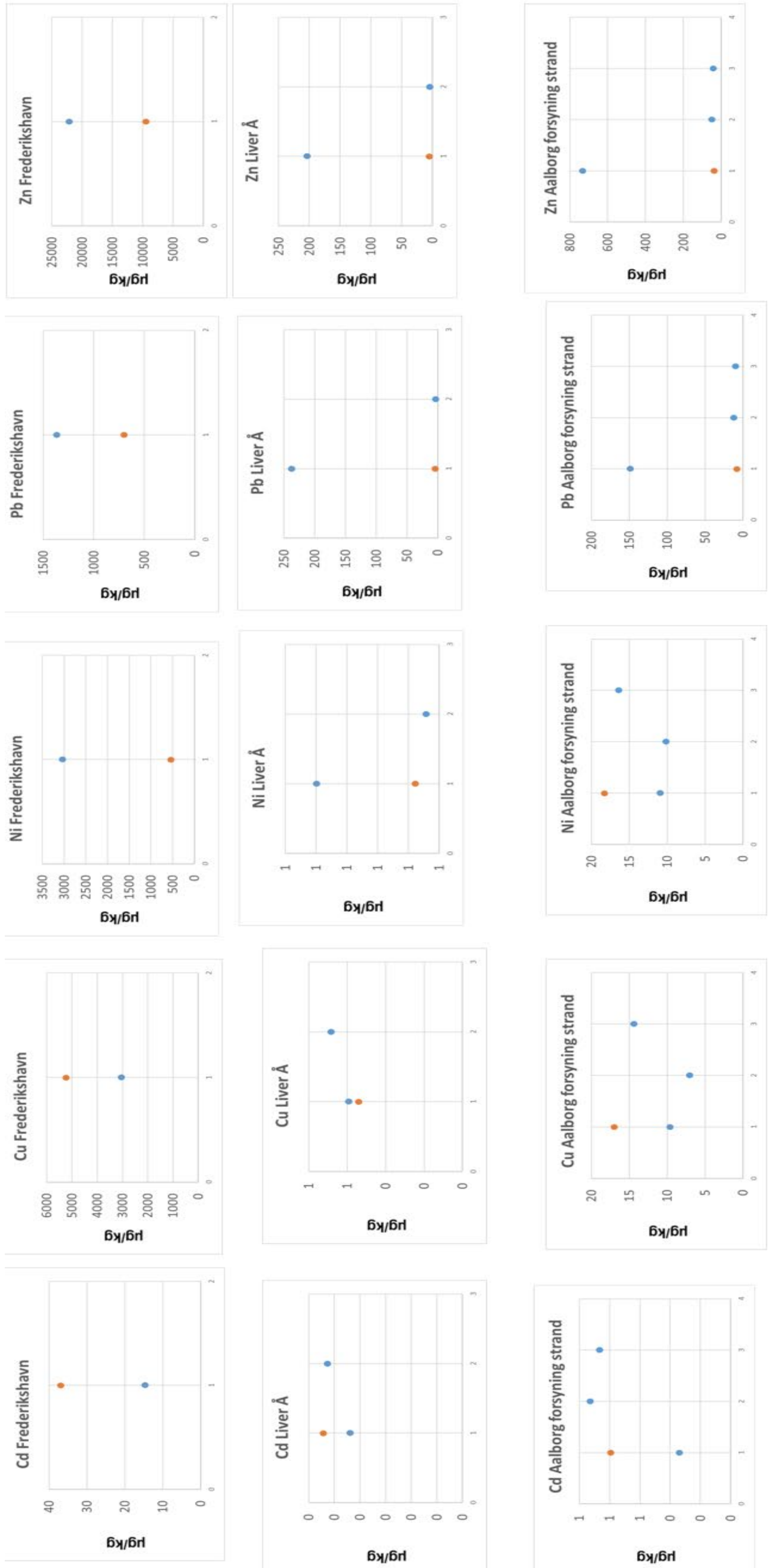


Figure 31. blue dots are sample collected during winter/ early spring, orange during summer

Appendix 4 – heavy metals values round 1

*Table 4. Heavy metal quantities. All results are in ppb in digested sample*must be normalized to g/kg.*

		Cd2265	Cu3247	Hg1849	Ni2316	Pb2203	Zn2025
	sample weight (g)	Cadmium (Cd)	Copper (Cu)	Mercury (Hg)	Nichel (Ni)	Lead (Pb)	Zinc (Zn)
Aalborg nord for lufthavn	0,4981	18,36	214,90	3,22	330,40	154,90	235,7
	0,5906	20,43	240,60	1,44	372,80	173,30	770,6
	0,5626	20,29	233,50	1,31	360,60	170,70	866,7
Aalborg Øst strand	0,6492	7,00	101,90	1,85	111,20	155,20	841,9
	0,5861	6,68	97,41	2,04	103,20	144,10	433,6
	0,554	5,94	90,51	2,04	90,24	132,80	430,1
Skiveren Strand	0,6204	9,19	118,20	1,89	80,09	194,20	392,5
	0,6036	9,23	106,80	1,80	79,20	197,80	547
	0,5509	9,19	108,00	1,77	79,57	224,20	537,1
Aalborg forsyning strand	0,568	17,96	385,70	2,53	418,20	185,10	537,8
	0,6038	19,10	416,70	2,38	440,70	194,00	906
	0,6504	19,93	425,60	2,64	455,80	202,40	955,5
Sæby strand core	0,5966	1,27	6,83	2,02	12,83	37,74	983,6
	0,7216	1,58	8,42	2,10	16,34	42,37	69,77
	0,8223	1,75	9,55	1,96	17,74	46,25	84,68
Sæby strand surface	0,6167	1,35	8,67	2,04	14,47	43,94	94,61
	0,6589	1,43	8,33	2,04	14,10	42,99	73,06
	0,669	1,53	8,82	2,33	14,25	49,71	79,22
Hanstholm Strand core	0,7741	4,31	21,08	2,35	48,09	190,00	78,24
	0,6152	2,82	12,25	2,38	30,98	120,30	198,4
	0,5962	3,27	12,42	2,46	36,76	118,50	141,5
Blokhus strand surface	0,5092	2,75	9,76	2,18	22,45	156,60	152,1
	0,6694	3,71	11,07	1,89	29,70	215,60	118,1
	0,5962	2,88	9,58	2,45	24,92	155,50	152,7
Blokhus strand core	0,7423	3,62	15,86	2,38	27,64	158,20	138,8
	0,5418	3,41	14,11	2,18	23,03	156,80	190,8
	0,6649	3,34	14,59	2,18	25,71	140,40	159,4
Liver å (strand) surface	0,7536	3,27	16,25	2,69	32,42	114,40	165,3
	0,6558	2,84	13,87	2,52	27,91	85,54	127
	0,5842	2,45	13,49	2,33	25,27	87,69	110,2
Liver å (strand) core	0,588	2,48	13,60	2,27	28,57	76,99	103,5
	0,7428	3,08	20,34	2,35	31,75	80,77	107,1
	0,662	3,39	38,09	2,44	27,93	109,40	139,9
Uggerby å (strand) core	0,5783	1,81	8,35	2,66	18,60	51,77	122,9
	0,7802	2,59	11,89	2,29	25,12	76,19	78,6
	0,557	1,74	8,43	2,70	18,19	48,37	109
Nibe strand core	0,6608	2,40	28,21	2,53	21,24	54,03	74,99
	0,6458	2,34	25,23	2,46	19,62	56,25	188,5
	0,5619	2,10	22,39	2,68	17,26	54,21	183,4
Aalbæk strand core	0,7108	1,80	12,03	2,58	17,59	29,47	156,3
	0,7864	1,95	11,76	2,76	19,44	31,97	91,58
	0,6838	1,65	10,95	2,45	16,88	27,44	97,95
Aalbæk strand surface	0,7176	1,66	12,52	2,82	18,68	28,38	84,69
	0,7137	1,67	12,11	2,76	17,75	27,94	89,93
	0,733	1,60	12,21	2,81	17,73	29,45	87,05
Asaa strand core	0,6826	2,08	15,81	3,35	17,81	31,80	90,01
	0,7116	1,93	17,47	2,71	18,89	30,73	113,5
	0,9174	2,00	14,19	2,98	18,11	34,30	103,5
Asaa strand surface	0,7809	3,21	26,93	2,78	29,84	32,26	112
	0,6778	3,01	24,91	3,19	25,59	27,35	213,9
	0,6683	3,01	26,58	3,32	25,23	27,88	198
Hou strand core	0,6712	1,69	16,94	2,94	19,80	32,12	199,4
	0,6599	1,62	22,37	3,06	19,28	31,20	108,5
	0,7017	1,65	34,77	3,03	19,45	30,98	100,8
Hou strand surface	0,5966	1,35	12,26	2,80	16,08	24,09	132,7
	0,6583	1,31	11,32	2,79	15,86	23,33	88,62
	0,5953	1,26	12,29	2,62	15,38	23,79	84,18
Hals strand core	0,5647	2,48	41,57	2,77	25,82	150,40	79,28
	0,6324	3,14	80,31	2,89	32,87	102,40	302,9
	0,7265	3,41	67,65	2,72	35,86	143,30	424,1
Skiveren strand surface	0,95	6,28	127,10	1,66	46,74	835,40	454,1
	0,8276	5,87	64,75	2,26	50,04	920,30	353
	0,6043	4,48	225,80	2,69	34,62	879,50	349,6
Aalborg fdorsyning strand core	0,7829	26,33	461,80	3,22	508,20	283,50	284,8
	0,5911	20,51	341,30	3,57	388,20	227,90	1147
	0,5204	18,04	299,60	3,04	344,30	200,60	892,8
Aalborg West, strand surface	0,5087	6,52	329,00	2,55	87,10	192,40	788,1
	0,7349	8,33	344,90	2,74	117,70	278,80	549
	0,5617	7,13	384,10	2,88	99,77	208,80	787,5

Table 5. Heavy metal quantities in µg/g of sample

	Cadmium (Cd)	Copper (Cu)	Mercury (Hg)	Nickel (Ni)	Lead (Pb)	Zinc (Zn)
Aalborg nord for lufthavn	0,922	10,786	0,161	16,583	7,775	11,830
	0,865	10,185	0,061	15,781	7,336	32,619
	0,902	10,376	0,058	16,024	7,585	38,513
Aalborg Øst strand	0,269	3,924	0,071	4,282	5,977	32,421
	0,285	4,155	0,087	4,402	6,147	18,495
	0,268	4,084	0,092	4,072	5,993	19,409
Skiveren Strand	0,370	4,763	0,076	3,227	7,826	15,816
	0,382	4,423	0,074	3,280	8,193	22,656
	0,417	4,901	0,080	3,611	10,174	24,374
Aalborg forsyning strand	0,790	16,976	0,111	18,407	8,147	23,671
	0,791	17,253	0,098	18,247	8,032	37,512
	0,766	16,359	0,102	17,520	7,780	36,727
Sæby strand core	0,053	0,286	0,084	0,538	1,581	41,217
	0,055	0,292	0,073	0,566	1,468	2,417
	0,053	0,290	0,060	0,539	1,406	2,574
Sæby strand surface	0,055	0,351	0,082	0,587	1,781	3,835
	0,054	0,316	0,077	0,535	1,631	2,772
	0,057	0,330	0,087	0,533	1,858	2,960
Hanstholm Strand core	0,139	0,681	0,076	1,553	6,136	2,527
	0,115	0,498	0,097	1,259	4,889	8,062
	0,137	0,521	0,103	1,541	4,969	5,933
Blokhus strand surface	0,135	0,479	0,107	1,102	7,689	7,468
	0,138	0,413	0,071	1,109	8,052	4,411
	0,121	0,402	0,103	1,045	6,520	6,403
Blokhus strand core	0,122	0,534	0,080	0,931	5,328	4,675
	0,157	0,651	0,101	1,063	7,235	8,804
	0,126	0,549	0,082	0,967	5,279	5,993
Liver å (strand) surface	0,109	0,539	0,089	1,076	3,795	5,484
	0,108	0,529	0,096	1,064	3,261	4,841
	0,105	0,577	0,100	1,081	3,753	4,716
Liver å (strand) core	0,105	0,578	0,097	1,215	3,273	4,401
	0,104	0,685	0,079	1,069	2,718	3,605
	0,128	1,438	0,092	1,055	4,131	5,283
Uggerby å (strand) core	0,078	0,361	0,115	0,804	2,238	5,313
	0,083	0,381	0,073	0,805	2,441	2,519
	0,078	0,378	0,121	0,816	2,171	4,892
Nibe strand core	0,091	1,067	0,096	0,804	2,044	2,837
	0,091	0,977	0,095	0,760	2,178	7,297
	0,093	0,996	0,119	0,768	2,412	8,160
Aalbæk strand core	0,063	0,423	0,091	0,619	1,037	5,497
	0,062	0,374	0,088	0,618	1,016	2,911
	0,060	0,400	0,089	0,617	1,003	3,581
Aalbæk strand surface	0,058	0,436	0,098	0,651	0,989	2,950
	0,058	0,424	0,097	0,622	0,979	3,150
	0,054	0,416	0,096	0,605	1,004	2,969
Asaa strand core	0,076	0,579	0,123	0,652	1,165	3,297
	0,068	0,614	0,095	0,664	1,080	3,987
	0,054	0,387	0,081	0,494	0,935	2,820
Asaa strand surface	0,103	0,862	0,089	0,955	1,033	3,586
	0,111	0,919	0,118	0,944	1,009	7,889
	0,113	0,994	0,124	0,944	1,043	7,407
Hou strand core	0,063	0,631	0,110	0,737	1,196	7,427
	0,061	0,847	0,116	0,730	1,182	4,110
	0,059	1,239	0,108	0,693	1,104	3,591
Hou strand surface	0,057	0,514	0,117	0,674	1,009	5,561
	0,050	0,430	0,106	0,602	0,886	3,365
	0,053	0,516	0,110	0,646	0,999	3,535
Hals strand core	0,110	1,840	0,123	1,143	6,658	3,510
	0,124	3,175	0,114	1,299	4,048	11,974
	0,117	2,328	0,094	1,234	4,931	14,594
Skiveren strand surface	0,165	3,345	0,044	1,230	21,984	11,950
	0,177	1,956	0,068	1,512	27,800	10,663
	0,185	9,341	0,111	1,432	36,385	14,463
Aalborg fdorsyning strand core	0,841	14,746	0,103	16,228	9,053	9,094
	0,867	14,435	0,151	16,419	9,639	48,511
	0,867	14,393	0,146	16,540	9,637	42,890
Aalborg West, strand surface	0,320	16,169	0,125	4,281	9,455	38,731
	0,283	11,733	0,093	4,004	9,484	18,676
	0,317	17,095	0,128	4,441	9,293	35,050

Appendix 5 - (flame retardants)

Flame retardants results, round 1 – no sample above 10 mg/kg detection limit.

		Sæby (strand)	Sæby (strand)	Frederikshavn 2 (havn)	Frederikshavn (strand)	Hanstholm Havn	Hanstholm Strand	Blokhus strand	Liver å (strand)	Uggerby å (strand)	Aalbæk strand	Asaa strand	Hou strand
Tribromo	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tetrabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pentabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Hexabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Heptabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Octabron	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Nonabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Decabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tribromo	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tetrabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pentabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Hexabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Heptabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Octabron	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Nonabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Decabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

		Hals strand (sea weeds decomposing)	Hals strand (sea weeds decomposing)	Skiveren strand (Limfjord eelgrass)	Aalborg forsyning strand	Aalborg North of the Airport	Nibe Strand	Aalborg Vest, strand	Aalborg city	Aalborg Havn city	Aalborg Øst strand	Hirtshals havn (students)
Tribromo	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tetrabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pentabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Hexabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Heptabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Octabron	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Nonabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Decabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tribromo	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tetrabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pentabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Hexabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Heptabro	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Octabron	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Nonabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Decabror	mg/kg	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

Flame retardants results, round 2 – no sample above 0.005 mg/kg detection limit. For some of the samples the reporting limit has been raised due to matrix interference. All results are below the LOD for all samples, but the LOD varies for different samples.

		Sæby (strand)	Sæby (strand)	Frederikshavn 2 (havn)	Frederikshavn (strand)	Hanstholm Havn	Hanstholm Strand	Blokhus strand	Liver å (strand)	Uggerby å (strand)	Aalbæk strand	Asaa strand
BDE-028	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,003
BDE-047	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,008	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,003
BDE-049	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,003
BDE-085	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,004
BDE-099	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,01	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,004
BDE-100	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,006	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,004
BDE-138	mg/kg ts	< 0,0005	< 0,0005	< 0,005	< 0,002	< 0,002	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,003
BDE-153	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,004
BDE-154	mg/kg ts	< 0,0005	< 0,0005	< 0,003	< 0,002	< 0,005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,004

		Hou strand	Hals strand (sea wee	Hals strand (sea weeds	Skiveren strand (Limfjord	Aalborg forsyning s	Aalborg North of th	Nibe Strand	Aalborg Vest, s	Aalborg city	Aalborg Havn city	Aalborg Øst stra	Hirtshals havn (students)
BDE-028	mg/kg ts	< 0,004	< 0,007	< 0,001	< 0,001	< 0,0005	< 0,002	< 0,0005	< 0,0005	< 0,003	< 0,003	< 0,001	< 0,002
BDE-047	mg/kg ts	< 0,005	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,002	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-049	mg/kg ts	< 0,005	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,002	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-085	mg/kg ts	< 0,006	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,001	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-099	mg/kg ts	< 0,006	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,002	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-100	mg/kg ts	< 0,006	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,002	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-138	mg/kg ts	< 0,005	< 0,02	< 0,001	< 0,001	< 0,0005	< 0,001	< 0,0005	< 0,0005	< 0,005	< 0,005	< 0,001	< 0,002
BDE-153	mg/kg ts	< 0,006	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,001	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002
BDE-154	mg/kg ts	< 0,006	< 0,01	< 0,001	< 0,001	< 0,0005	< 0,001	< 0,0005	< 0,0005	< 0,004	< 0,003	< 0,001	< 0,002