aces.

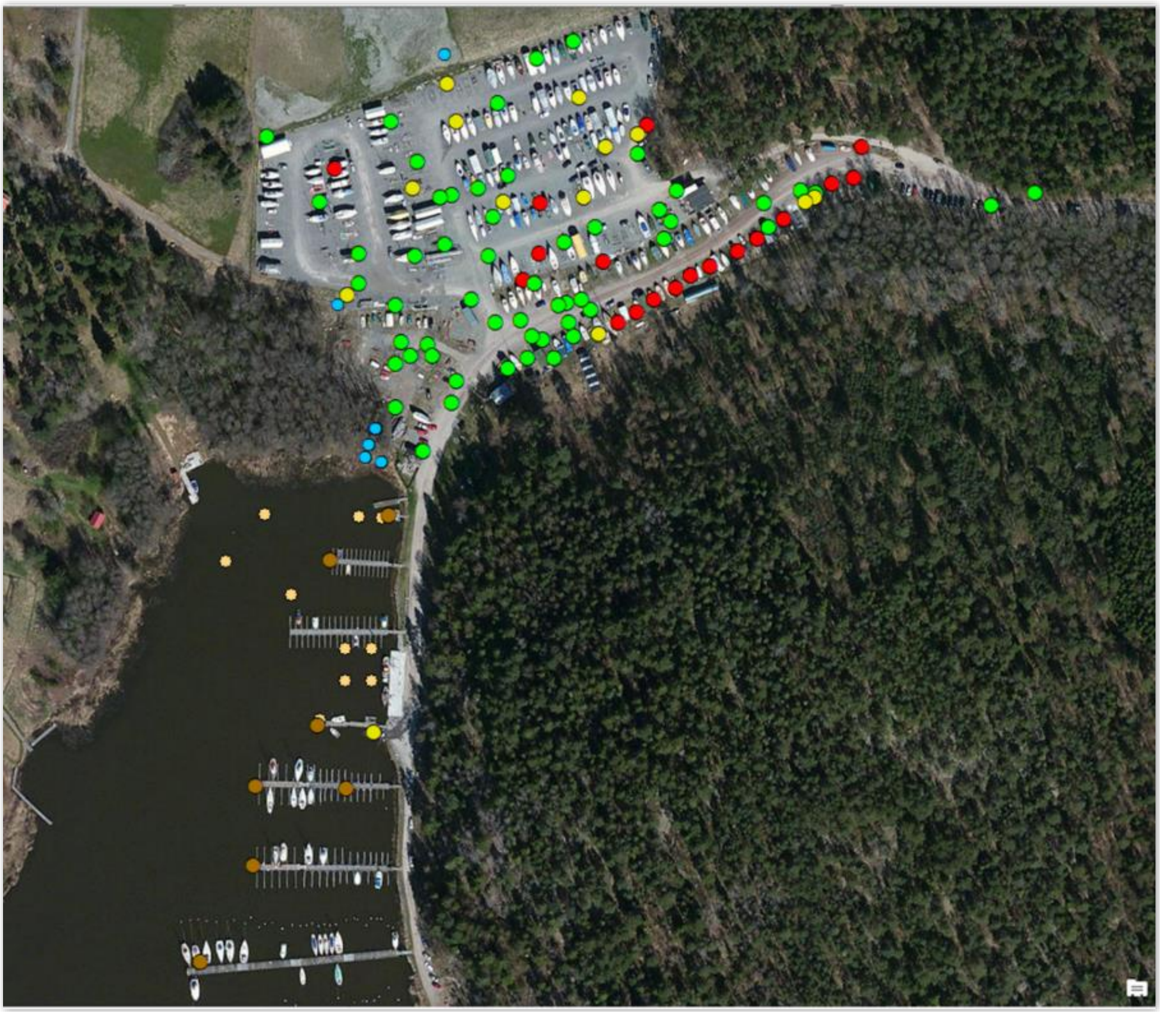
Department of Environmental Science
and Analytical Chemistry

Stockholm
University

XRF-as a tool for monitoring of biocide load in boatyards

Case study on two boatyards in Lake Mälaren

Matz Norling



Master´s thesis 2015:3

Stockholm University
106 91 Stockholm

Abstract

The aim of this study was to assess the suitability of a special application to a Field Portable, handheld X-Ray Fluorescence (FPXRF) analyzer for monitoring of boatyards with focus on biocide load on boat hulls. In addition, the instrument was used for investigating the spatial distribution of contaminants in soil and sediments. Field activities on two boat yards in the lake Mälaren were done from April to October 2014. Lab analysis was finished in January 2015.

I have found the FPXRF analyzer to be a quick, accurate and cost efficient tool for screening of contaminated boatyards. A major usage area is the detection of boat hulls with high levels of old biocide paint. The total levels of contaminants on every boat hull can easily be determined. This information can then be used when approving boats for different types of maintenance procedures or when selecting boats for decontamination activities. The FPXRF can also be used for detection of contaminated soil and sediments. The data can then be used in a risk assessment of the area and conclusions can be drawn on the need for remediation. The investigation of the two boatyards in the Lake Mälaren has shown that high levels of heavy metals are detected in boat hulls, soil and sediments often in par with what have been detected in other boatyards on the east and west coast of Sweden. This is a threat to the Lake Mälaren as it is a source for freshwater and an inland lake system where no biocide-based paints is allowed. Paint recommendations and regulations needs to be communicated to boat owners. To reduce toxic flows to sediments and water from the boatyards, existing hulls need to be tested for contamination and the hulls with the highest risk of releasing heavy metals decontaminated. Boat washers and other cleaning equipment must be made available at a reasonable cost and distance. Surface and ground water flows from contaminated areas needs to be directed and filtered through wetlands or other bio filters.

Sammanfattning

Syftet med denna studie var att undersöka lämpligheten av en ny applikation för en portabel röntgenfluorescensmätare (FPXRF) för övervakning av båtuppläggningsplatser med fokus på metallinnehåll i bottenfärg på båtskrov. Samtidigt undersöktes den spatiala distributionen av metaller i jord och sediment. Undersökningen gjordes på två båtuppläggningsplatser vid Mälaren mellan maj och oktober 2014.

Jag har funnit att FPXRF-utrustningen är snabb, noggrann och kostnadseffektiv vid undersökning av förorenade båtuppläggningsplatser. Ett huvudsakligt användningsområde är att detektera båtskrov med gammal bottenfärg som innehåller höga halter av metaller. Den totala mängden på varje båt kan enkelt bestämmas och denna information kan sedan användas för att godkänna båtar för olika typer av underhållsaktiviteter eller som underlag för ett beslut om bottensanering. FPXRF-utrustningen kan också användas för att detektera förorenade jordar och sediment vid en riskbedömning av båtuppläggningsplatser och ge underlag till beslut om åtgärder.

Undersökningen av båtuppläggningsplatserna har visat att höga halter av tungmetaller, jämförbara med båtuppläggningspaltser på ost- och västkusten, finns i båtskrov, jord och sediment. Detta är ett hot mot Mälaren som är en reservoar för dricksvatten och ett inlandsvatten där giftig bottenfärg inte får användas. Gällande regler måste tydliggöras för båtägare. För att minska flödet av gifter till sediment och vatten måste befintliga båtar undersökas och skrov med höga halter av gifter saneras. Båttvättar måste finnas tillgängliga till en rimlig kostnad och på lämpligt avstånd. Avrinning från förorenade uppställningsplatser måste avledas till våtmarker eller lämpliga biologiska filter.

Statement

This report is the result of my master thesis carried out at Stockholm University at Department of Environmental Science and Analytical Chemistry (ACES).

All maps are provided by ESRI and SLU/Lantmäteriet according to Stockholm university license I2014/00691 and projected in SWEREF99TM using ArcMap 10.2.2. Statistical tests were done using R 3.12.

I made the following contributions to the results presented in this thesis.

- Drawing of all maps
- Coordination with concerned yacht clubs
- Planning and executing of the "Transport in surface water" activity
- Planning and executing of the soil measurements in suspected areas
- Planning and preparation for ground water testing
- Grinding and FPXRF lab measurements of most of the soil and sediments samples
- Preparations for the sediment sampling

Together with Maria Lagerström and Britta Eklund I planned and executed all other soil, ground water and sediment measurements.

Together with Britta Eklund I planned and executed the boat hull measurements.

All chemical analysis was done by Maria Lagerström.

As the investigation was extended to include an additional boat yard and a more detailed analysis in a lab environment the design of the load model, modeling of probable scenarios and estimation of modeling uncertainty specified in the study plan was excluded due to time constraints.

Content

Abbreviations

Al - Aluminum
Ca - Calcium
Cu - Copper
Fe - Iron
FPXRF - Field Portable X-Ray Fluorescence analyzer
ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry
MBK - Märsta Yacht Club/Märsta Båtklubb
Pb - Lead
Rbk - Rosersberg Yacht Club/Rosersberg Båtklubb
Sibk - Sigtuna Yacht Club/Sigtuna Båtklubb
Sn - Tin
TBT – Tributyltin
TPhT - Triphenyltin
Zn - Zink

1 Introduction

Even the old Phoenicians 3000 year ago were aware of the negative impact of biofouling from barnacles and used copper and lead sheeting on the hulls (Lunn, 1974). Biofouling leads to an increase of weight and a lower speed together with high fuel consumption (Yebra et al. 2004). Many biocide paints have shown to harm also other organisms than the target species (Karlsson et al. 2010). Up to now almost no monitoring of boat yards has been done to investigate the environmental status (Schiff et al. 2007).

50% of the boats in the Baltic Sea use some kind of toxic paints to prevent biofouling (Swedish Transport Agency 2010). Based on information from paint manufactures about 90 % of the toxic substances will leak to the water in the first season (Ytreberg, 2012). Most of these toxic substances have a negative impact on marine organisms (Karlsson et al. 2006, 2010).

The levels of metals coming from toxic paint will reach high concentrations in boatyard soils (Turner et al. 2008, Eklund and Eklund 2014). Toxic substances from boat hulls are released to the water and end up in sediments posing a risk to the ecosystems and humans (Hollert et al. 2003; Schiff et al. 2007; Karlsson et al. 2008 and Ytreberg et al. 2010). Eklund et al. (2008) and Turner (2010) have shown that toxic particles are found near boatyards.

Old paint on hulls is dislodged to the soil during maintenance activities (Eklund et al. 2008 and Eklund and Eklund 2014). Paint flakes coming from abandoned boats or from boat maintenance is a risk to human health (Turner et al. 2008; Eklund and Eklund, 2014; Turner et al. 2014). Concentrations above recommended levels for Cu and Zn are commonly found in boatyards (Eklund et al. 2014 and Eklund and Eklund 2014). Up until today just 34 out of a total of about 2500 boatyards in Sweden have been screened giving limited information on the contamination status (Eklund and Eklund, 2012).

To analyze toxic substances on boat hulls, in soil and sediments chemical analytical methods (ICP-OES) can be used or the emerging non-destructive hand held X-ray fluorescence spectroscopy (XRF) method that can be used on-site (Ytreberg et al. 2015 and Turner et al. 2015).

2 Aims and hypotheses

The aim of this Master's thesis is to assess the suitability of a Field Portable, handheld X-Ray Fluorescence (FPXRF) analyzer for monitoring of recreational boatyards with focus on biocide load on boat hulls and spatial distribution of contaminants in soil and sediments.

The hypotheses in this study are:

(1) The FPXRF tool is a cost effective tool for screening of contaminated boatyards.

(2) The FPXRF tool can be used for measuring of sediment, soil and boat hulls.

(3) The recreational boatyards in Mälaren follows the government biocide-based paints regulations

2.1 Delimitations

The study is limited to address the heavy metals Cu, Zn, Sn and Pb that are typical for biocide-based paint. Pb and Sn are no longer used but are still present in soil and sediments. Measuring of Sn is used for addressing the impact of old organic tin compounds in boat hulls, soil and sediments containing e.g. Monobutyltin(MBT), Dibutyltin(DBT), Tributyltenn (TBT), Monofenyltin(MPT), Difenyltin(DPT) and Triphenyltin (TPhT).

3 Background

The toxicity of specific heavy metals like Cu (Copper), Zn (Zinc) and Pb (Lead) are reflected in the requirements stated by Swedish authorities and complying with EU regulations. There are specific limits for sensitive and less sensitive land use and limits for sediments and water. An overview of applicable limits is presented in table 1.

Table 1 Overview of requirements from regulating documents regarding contaminating limits applicable for boatyard screening of soil, sediments and water.

Substance	AA-EQS Lakes Annual mean	AA-EQS Ocean Annual mean	MAC-EQS Lakes Max concentration	MAC-EQS Ocean Max concentration	EQSSed Sediment TS/DW	SL/KM Sensitive Land use TS/DW mg/kg	LSL/MKM Less Sensitiv Land TS/DW
Cu	4 µg/l c) 0,5 µg/l h)	1,3 µg/l c) 0,87 µg/l h) Bal		2,6 µg/l e)	84 mg/kg e)	80 mg/kg d)	200 mg/kg d)
Zn	3-8 µg/l c) 5,5 µg/l h)	3,4 µg/l c) 1,1 µg/l h) Balt		6,0 µg/l e)	340 mg/kg e)	250 mg/kg d)	500 mg/kg d)
Pb	1,2 µg/l a,h)	1,3 µg/l a,h)	14 µg/l a,h)	14 µg/l a,h)	120 mg/kg h) (130 mg/kg Inland)	50 mg/kg d)	400 mg/kg d)
TBT	0,2 ng/l a) b) h)	0,2 ng/l a) b) h)	1,5 ng/l a) b) h)	1,5 ng/l a) b) h)	2ng/kg e) **1,6 µg/kg h)**	1 mg/kg g)	2 mg/kg g)

a) EU 2013/39/EU about changing 2000/60/EG and 2008/105/EG regulating prioritized substances.
b) HVMFS 2013:19. Classification and regulations for surface water, updating ongoing (2014:XX).
c) HVM Dnr 3383-13. Recommendations for chemical classification 2013.
d) Swedish Environmental Protection Agency Report 597**6** Recommended values for contaminated soil 2009.
e) TA3001 Klima- og Forurensningsdirektoratet i Norge Environment standards for water, sediment and biota 2012.
g) Finland (2007)Sum of TBT+TPhT
h) HVMFS 2014:XX Proposed update of b) HVMFS 2013:19

There is today no specific limit for Sn as the requirements are stated for the TBT state values. Limits and guidelines are also missing for all boat hull measurements.

The EU Water Framework directive (WFD) has been implemented in the Swedish legislation and is the base for the requirements of good water status to be reached by 2015 (EU, 2000). To meet these objectives and legislation requirements and to achieve a significant decrease of the continued spread of toxic substances from boat activities, the total complexity of the environmental problem needs to be addressed.

The Swedish basic legislation regarding liability for the remediation of contaminated land and water areas is that any operator who contributed to the contamination may be required to pay for the remediation cost. However, the operator is responsible only for the portion of the remedial action that corresponds to the operators own contribution to the harm. Relevant case law supports that leisure boat clubs are to be regarded as operators and thus liable for any contamination (Langlet et al. 2014). It is an equally important responsibility to prevent damage from ongoing activities in the boatyards. This means yacht clubs have to implement protective measures and take any other actions that are not unreasonable in view of the benefits of the measures compared to the costs (Langlet et al. 2014).

Another factor to understand beside the leakage of paint to water is the transportation of metals to topsoil and ground water. Mainly this relates to adsorption/desorption in surface water. Cu, Zn, Pb and Sn are bound to the soil by surface reactions involving organic matter. Metals can later dissolve and affect surface water metal content many years after the contamination occurred (SEPA, 2006). Adsorptions of metals can often be linked to pH. The mobility of groundwater to surface waters depends on soil hydraulic properties (SEPA, 2006).

4 Material and Methods

This study is based on the investigation of two boat yards using a FPXRF. The measurements were focused on boat hulls, soil, sediments and groundwater. During the activity the FPXRF was evaluated concerning suitability and accuracy. Field activities were done from April to October 2014. Lab analyses were finished in January 2015.

4.1 Field Portable, handheld X-Ray Fluorescence (FPXRF) analyzer

4.1.1 XRF Technology

When the X-rays emitted from an XRF enter the atom structure of the irradiated substance, electrons in the inner shells can be dislodged. If that happen the vacant spot will be filled with an electron from an outer shell. As those electrons have a higher energy level, the energy balance is disrupted. In order to restore the energy level a photon is sent out with a distinct energy spectra for each metal that can be identified by the XRF, see . Depending on the response from the irradiated areas, called x-ray fluorescence, the content of heavy metals can be determined (EPA, 2007).

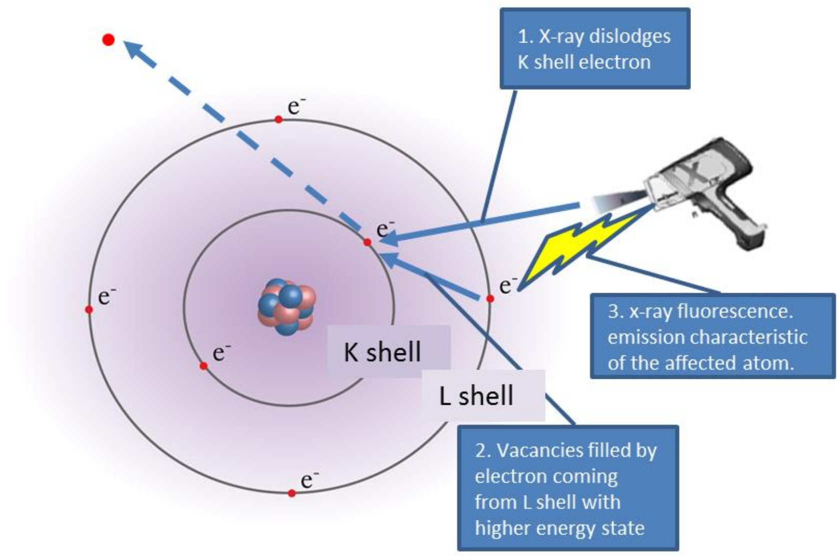


Figure 1 When the X-rays emitted from the FPXRF enter the atom structure electrons in the inner shells can be dislodged. The vacant spot will be filled with an electron from an outer shell. As that electrons has a higher energy level the energy balance is disrupted. In order to restore the energy level a photon is sent out with a distinct energy spectra for each metal.

The XRF technique is also used in industrial quality control and for analysis of geological specimens (Marguri and van Grieken, 2013).

4.1.2 Field Portable XRF, Delta 50 from Olympus

The used FPXRF, Field Portable XRF, is the Delta 50 version from Olympus, capable of generating 50kV. This is a prerequisite for accurate Sn measurements (Ytreberg et al. 2015). After power-up the FPXRF performs a calibration check to make sure the instrument is operating within resolution and stability tolerances. Every 20th soil measurement a blank sample was checked together with two NIST (National Institute of Standards and Technology) samples, one with low content of Cu, Zn and Pb (NIST 2711) and one with high values (NIST 2710). The blank sample was used to monitor for cross-contamination and lab interferences. (EPA 2007). The NIST samples were used for accuracy and performance checks of the FPXRF soil analysis functionality. For hull measurements only the calibration check was used as no reference sample was available. In Figure 2 the FPXRF Delta 50 is shown performing a NIST check in a field environment. In the used FPXRF there was also an added software module used for the detecting of antifouling paint.

Figure 2 The FPXRF Delta 50 performing a NIST check in a field environment

Measurements can be done in two ways using the FPXRF instruments. When operated in the field the FPXRF window, shielded by a disposable Mylar sheet, is placed directly in contact with the soil or hull surface to be analyzed. The soil surface must be as smooth as possible and allowing the probe window a good contact with the soil. Sometime this may require a leveling of the surface to increase the soil density and compactness for better measurement repeatability. Soil moisture should be less than 20 percent (Imansishi et al. 2010) so all measurements were done on days with low humidity and no rain. No soil moisture sensor was used in field.

In a lab environment the samples were prepared (dry freezing and homogenized by grinding) and placed in a plastic bag on top of the window, inside a protective cover, exposing the sample to radiation from the FPXRF source. The measurements are controlled by the InnovX system software in a lab PC, see Figure 3.

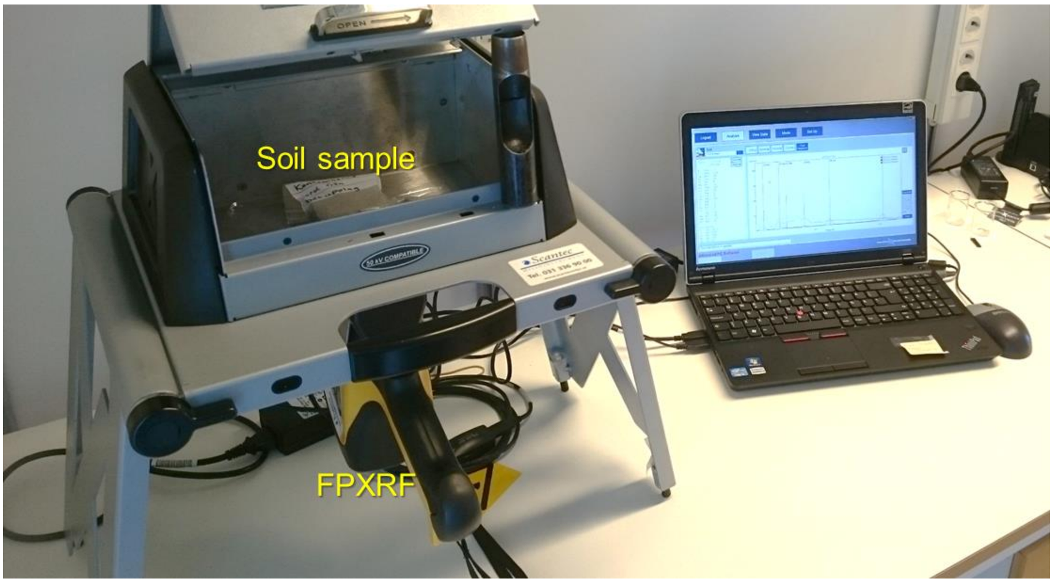


Figure 3 FPXRF work station in a lab environment. A soil sample in a zip bag is situated on top of the FPXRF measuring aperture window in the shielded enclosure.

The Delta 50 was used in two different modes in this study. One for soil and sediment measurements that is supplied by the manufacturer and one mode for hull measurements that has been developed by Britta Eklund, Erik Ytreberg and Lennart Lundgren at Stockholm University. This added functionality is the only non-destructive method that can measure the amount of heavy metals on boat hulls (Ytreberg et al. 2015). For hull measurements the content is presented in µg/cm^2, soil and sediment measurements are presented in ppm (mg/kg). The instrument delivers instant information about Cu, Zn, Pb and Sn content after a completed test cycle. For Sn a confirming lab spectra check is needed (Ytreberg et al. 2015).

4.2 Investigation areas

This screening study was done at two recreational boatyards, Flottvik and Rosersberg in Lake Mälaren, Sweden. Mälaren, belonging to the Northern Baltic Sea River Basin, drains to the Baltic Sea through the Norrström basin, see Figure 4. Mälaren is used as a fresh water resource for most of the Stockholm area along with a number of other cities in the drainage basin.

Figure 4 Flottvik and Roserberg in Lake Mälaren

4.3 Boat hull screening

The FPXRF was used together with an application developed by Stockholm University (Ytreberg et al. 2015) that gives the contamination result in µg/cm^2 instead of the relative figure in percent coming from similar FPXRF measuring equipment. This application makes it possible to calculate the total amount of heavy metals on a boat hull (even old layer of paint is measured). The FPXRF measuring time was set to 30s for all measurements. The aim was to see the distribution and the amount of Cu, Zn, Pb and Sn in the existing paint layers. The measurements were done at Flottvik partly together with representatives from Sigtuna Yacht Club and Sigtuna municipality environment committee. The boat yard master at Märsta Yacht Club was informed in advance and posters were placed at the boat yard.

The FPXRF present the contamination result in µg/cm^2 directly after the 30s measuring period. The data base in the FPXRF can then be downloaded to a lab PC for a more detailed analysis of the energy response in keV, kiloelectronVolt. See example of a spectrum presentation in Figure 5.

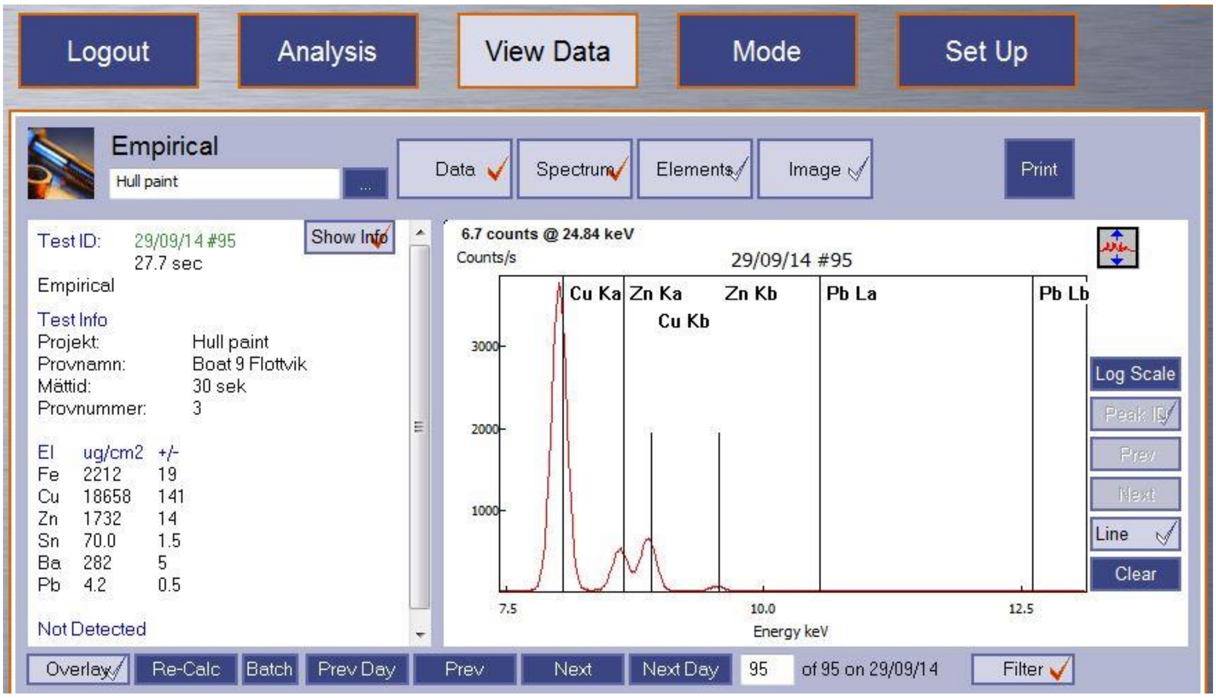


Figure 5 Example of FPXRF presentation on a lab PC. In the left window the contamination load in µg/cm^2 is presented in a similar way as on the FPXRF in the field. In the right hand window the spectrum response is presented in Counts/s as a function of the energy in keV. In the left hand table the Cu, Zn, Pb and Sn content is presented

This presentation is also available on a standalone FPXRF in a field environment. On the right hand the result is presented in graphs showing the response in keV for a beam voltage of 50kV (red curve). Black vertical lines indicate where the response should be for Cu, Zn and Pb. Sn is at a higher energy level and is not visible in this spectra. The elements studied have the following Kα line energy levels;

Cu: 8.046 keV, Zn: 8.637 keV, Pb 10.551 keV, Sn 25.271 keV

Boat hull screening was done in the Flottvik boatyard covering 173 boats from Märsta and Sigtuna yacht clubs. All fiber glass boats in the indicated areas, see Figure 6, were measured. Wood and metal hulls were excluded as the FPXRF has no suitable calibration. One measurement of 30 s was done on every measured boat at the middle of the port side about 20 – 50 cm below the water line. Boat length and type was noted as a basis for a bottom area estimation used when calculating the total contamination load for every vessel.

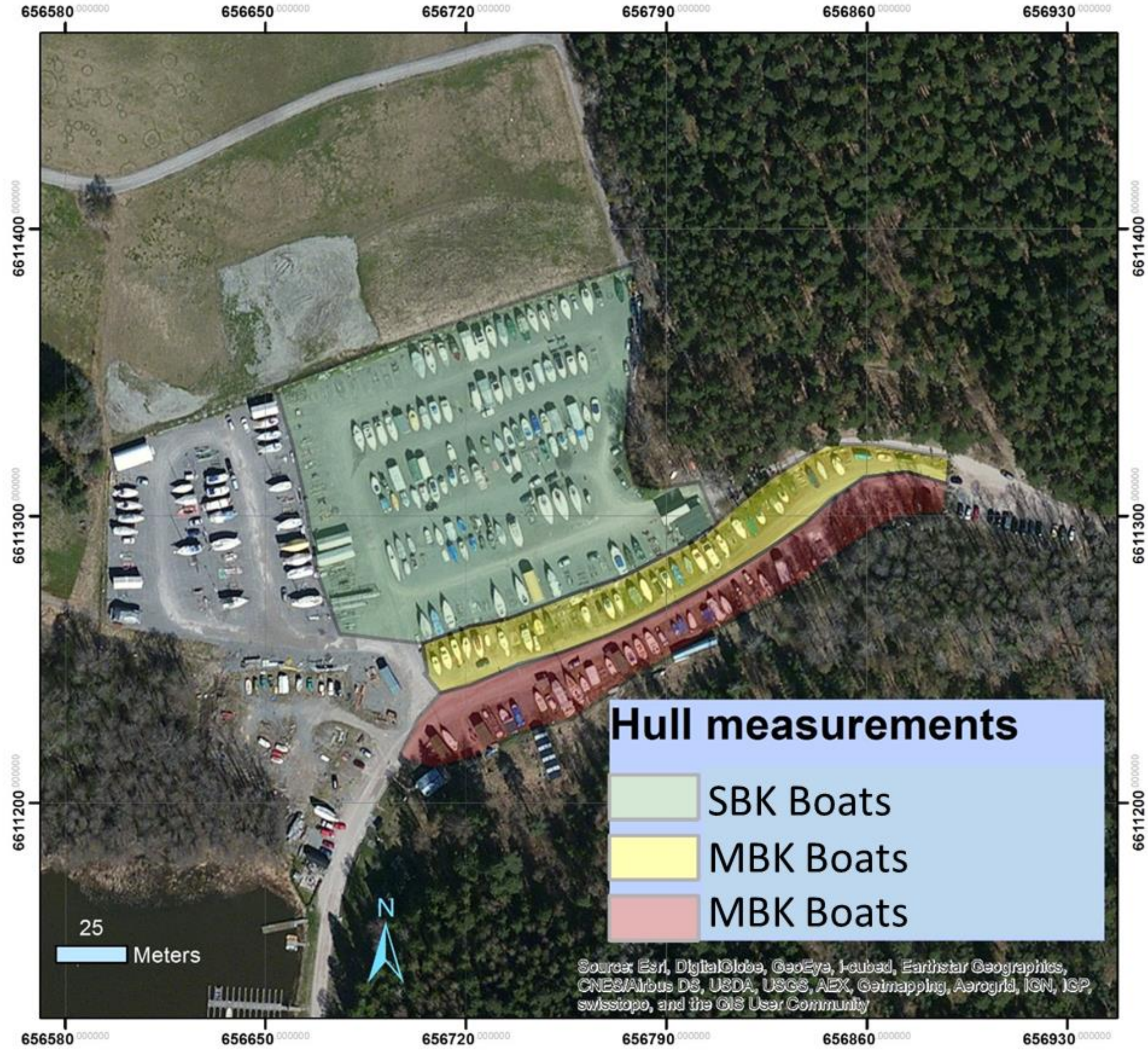


Figure 6 Location of the areas in Flottvik where glass fiber hulls from Sibk and MBK Boat hull were screened with the FPXRF. Red area indicates also the area used for suspected soil measurements.

4.3.1 Vessel bottom area calculation

The estimation of vessel bottom area is based on a paint consumption recommendation from a major manufacturer (Hempel 2014), see Table 2.

Table 2 Paint consumption (l) recommendation from Hempel for two layers of paint used when calculating the hull area.

Längd	6m 20ft	7.5m 25ft	8.5m 28ft	10m 33ft	11.5m 38ft	13m 43ft	14.5m 48ft	16m 53ft	18m 60ft	20m 66ft	23m 76ft
Fenkölad	**1.5l**	**1.5l**	**3l**	**4l**	**5l**	**6l**	**7l**	**8l**	**9.5l**	**11l**	**13l**
750ml	2	2	4	2	0	2	3	1	2	1	1
2.5l	0	0	0	1	2	2	2	3	3	4	5
Långkölad	**2l**	**3l**	**4l**	**5l**	**6l**	**7.5l**	**9l**	**11l**	**13l**	**15.5l**	**19l**
750ml	3	4	2	0	2	0	2	2	1	1	2
2.5l	0	0	1	2	2	3	3	4	5	6	7
Motorbåt	**2l**	**3.5l**	**4.5l**	**6l**	**7l**	**9l**	**10l**	**12l**	**15l**	**18.5l**	**23l**
750ml	3	2	3	2	3	2	0	3	0	2	1
2.5l	0	1	1	2	2	3	4	4	6	7	9

Using the recommended paint figures together with information on coverage for a typical boat paint product of 13m^2 per liter the following corresponding hull bottom area was calculated, see Table 3.

Hull bottom area [m^2] = Recommended paint consumption one layer [l] x Paint coverage [m^2/l]

Table 3 Bottom area in m^2 and paint consumption in liters related to boat length in meters for different boat types.

Length m	Bottom area m2 Sail fin	Long keel	Motor	Paint consumption Sail fin	Long keel	Motor
5	6.5	9.8	9.8	1	1.5	1.5
6	9.8	13.0	13.0	1.5	2	2
7	9.8	19.5	22.8	1.5	3	3.5
8	13.0	22.8	26.0	2	3.5	4
9	19.5	26.0	29.3	3	4	4.5
10	26.0	32.5	39.0	4	5	6
11	29.3	35.8	42.3	4.5	5.5	6.5
12	32.5	39.0	45.5	5	6	7
13	39.0	48.8	58.5	6	7.5	9
14	42.3	52.0	61.8	6.5	8	9.5
15	45.5	58.5	65.0	7	9	10
16	52.0	71.5	78.0	8	11	12
17	58.5	78.0	91.0	9	12	14
18	61.8	84.5	97.5	9.5	13	15
19	65.0	91.0	110.5	10	14	17
20	71.5	100.8	120.3	11	15.5	18.5

4.3.2 Total load calculation

The total load for each boat can then be calculated as shown below.

Total boat load [kg] =

(Cu [$\mu g/cm^2$] + Zn [$\mu g/cm^2$] + Pb [$\mu g/cm^2$] + Sn [$\mu g/cm^2$]) x 10^{-5} x bottom area [m^2]

as 1 $\mu g/cm^2$ = 10000 $\mu g/m^2$= 10 mg/m^2 = 0.01g/m^2= 0.00001 kg/m^2 = 1x10^{-5} kg /m^2

4.3.3 Weighted load calculation

In order to get one single contamination figure for every boat a weighted load per boat was calculated using factors based on the toxicity of Cu, Zn, Pb and Sn. The alternative to use only the added values for Cu, Zn, Pb and Sn will give low attention to Cu relative Zn values and the Sn value will be too small to reflect the toxicity. As there are today no set requirements for the metal content on boat hulls the soil requirements for non-sensitive land use, as presented in Table 1, were used as a basis when defining the factors to use. The factor for Cu is set to 1 and the factor for Zn to 0.4 as the limit for Cu is 200 mg/kg and for Zn 500 mg/kg (200/500=0.4). The limit for Pb is 400 and the factor is set to 0.5 (200/400=0.5). For Sn there is a Finnish directive of 2 mg/kg of TBT for less sensitive land use and a factor 100 relative Cu was chosen. The relation between measured Sn and TBT is still to be detailed. The high figure for Sn also reflects that the Sn value is used to indicate the presence of TBT, considered to give serious disturbances to non-target organisms (Alzieu, 1991). The weighted load for each boat can then be calculated as shown below.

Weighted boat load [kg] = (Cu x 1 [$\mu g/cm^2$] + Zn x 0.4 [$\mu g/cm^2$] + Pb x 0.5 [$\mu g/cm^2$] + Sn x 100 [$\mu g/cm^2$]) x 10^{-5} x bottom area [m^2]

4.4 Soil screening

FPXRF soil screening were carried out in the two boatyards, Rosersberg and Flottvik, through systematic random sampling or focused on suspected contaminated areas. The FPXRF accuracy was evaluated by measuring randomly selected soil samples after sieving and grinding in the lab with the FPXRF. In addition a number of samples were also correlated against ICP-OES measurements. Particle sizes and moisture will affect the measuring precision (EPA, 2007). Imansishi et al. (2010) has shown that the thickness of samples when doing lab measurements should be 6 to 10 mm. To minimize the impact of samples condition soil samples are dry freezed, grinded and sieved.

4.4.1 Sampling strategy

The objective of sampling was to evaluate the FPXRF field performance and investigate different sampling methods. A methodology for selecting of screening spots, defined by SEPA (2009), was used to define the actual measurements.

The Rosersberg boatyard was the first to be screened. Random spots were assigned before going out to the field and were then located with a measuring tape and a compass. All of the available land was divided in 42 squares of 100m2. Then one randomly selected spot in every square was measured with the FPXRF tool. The 42 spots were located with help of a measuring tape and a compass from predefined reference points. The located test spot was then cleared from larger objects and flattened before the actual screening with the FPXRF. Nine randomly selected soil samples were collected from the top soil and from a depth of 10cm placed in zip-bags and brought back to the lab for confirmatory analysis.

The “prior knowledge” method was used in Flottvik when screening of used storage spaces, other spots were randomly chosen in advance. Maps were produced in advance showing exact location for every randomly selected sampling spot together with guidelines how to handle practical problems of sampling. Measurements were done in three ways. Randomly selected in advance covering the total area (95 samples), focused on suspected storage areas identified in situ (18 samples) or focused on small hotspot areas discovered during the screening (31 samples).

The area was smoothed and cleared of larger objects with help of a small garden spade. Sieved soil samples were collected in zip bags from the surface and also from a depth of 5 cm for 10 percent of the spots and brought back to lab for confirmatory analysis. Those samples come from a larger area about 1 dm^2 and 1 cm deep in contrast to the in-situ measurements where only the soil under the FPXRF aperture (collimator) window of 30.5 mm^2 is measured.

The 55 randomly generated spots were located with an improved method comparing with the method used in Rosersberg. A handheld Garmin Montana 650t GPS with EGNOS functionality and showing SWEREF99TM coordinates were used for easier locating of the screening spots. The 18 suspected spots were visually identified and then positioned with a measuring tape to a separation of 10m. An additional soil measurement was also done on a spot just north of the boatyard where the dredged material was stored temporarily. Sieved soil samples (<2mm) were randomly selected and 6 samples were brought back for confirmatory laboratory analysis through acid digestion and subsequent analysis on ICP-OES and with additional XRF measurements in lab.

4.4.2 Total soil load calculation

The total load of metals in the soil in the boatyards was calculated by using a density for sand/soil of 1500 kg/m^3 as used by Eklund et al. (2014) Addressing the soil top layer of 1 cm and using the median top soil random values for Flottvik and Rosersberg the load was calculated as shown below

Total load [kg] = Area [m^2] x Density [kg/m^3] x Median random value [mg/kg] x Depth [m] x 10^{-6}

4.4.3 Soil screening at Rosersberg

The Rosersberg boatyard is situated in the end of a small a bay, Rosersbergsviken, just 6 km southeast of the Flottvik boatyard at a steep bed rock hill. The area has been filled out with rock fill from the construction of the Käppala waste water tunnel. The winter storage area is 3600 m^2 and has been filled with gravel several times during the years. The area is owned by the Swedish government (Statens fastighetsverk) and has been used since the late sixties. In the southern part of the bay there is an outlet from the heavy PCB polluted Oxunda basin (Sigtuna 2014).

The area was screened for soil contaminants as can be seen in Figure 7.

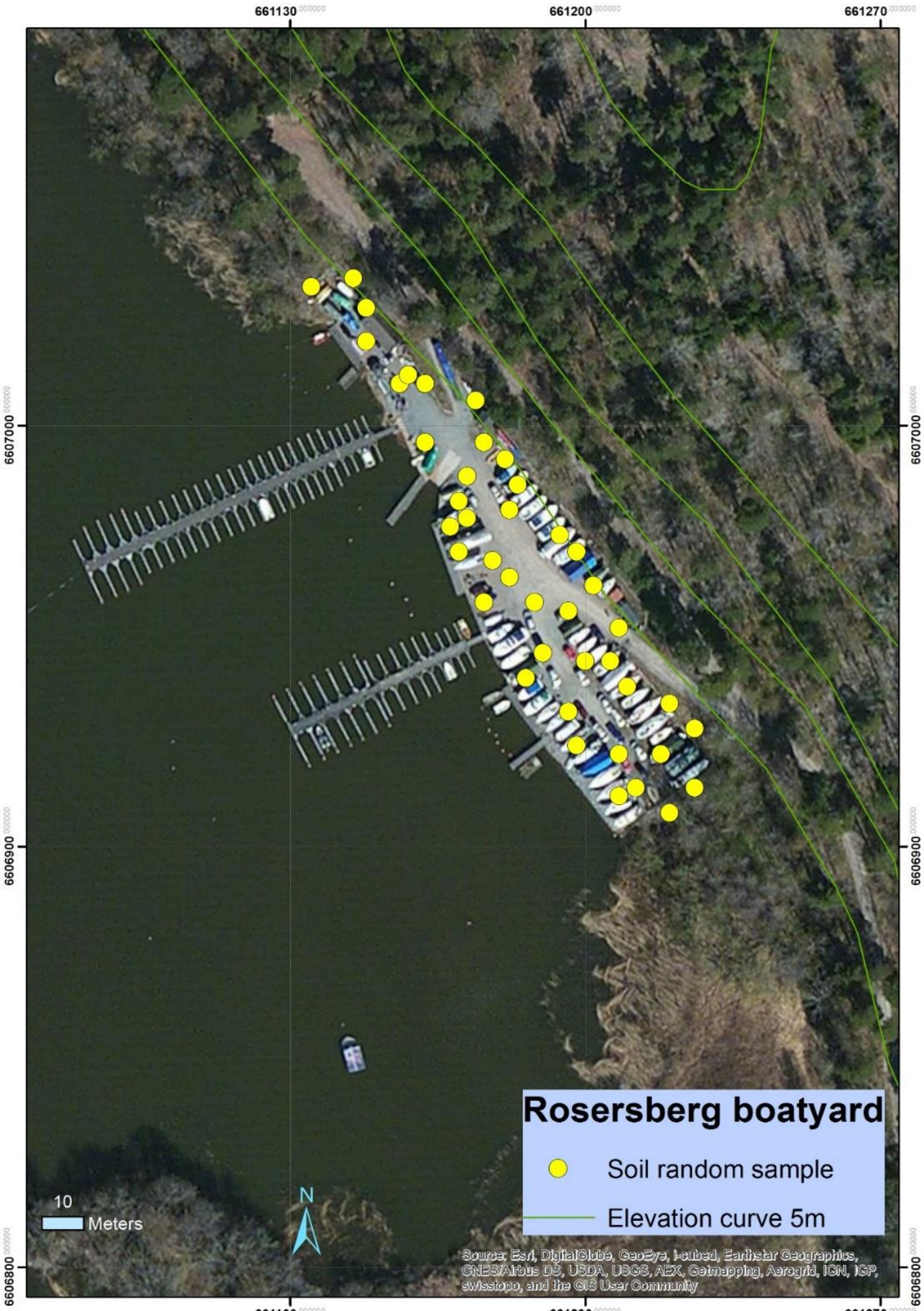


Figure 7 Rosersberg boatyard situation map showing spots where random soil random samples were measured and collected and the 5m elevation curve, see legend box

4.4.4 Soil screening at Flottvik

The Flottvik boatyard is situated in the end of a small a bay, Flottviken, just south of the city of Sigtuna. The area was earlier a marsh on glacier clay at the end of a steep valley but has since then been filled with rock fill from the construction of the Käppala waste water tunnel. The area has been refilled with gravel on top several times. In the southwest part there is some sandy moraine and a steep bed rock hill. The Sigtuna municipality owns the area and has rented it to the two yacht clubs, Sigtuna båtklubb (Sibk) and Märsta båtklubb (MBK). North of the boatyard there is an old waste dump that are draining towards the boatyard through the Rävsta stream that ends up in the marsh south of the boatyard. See Figure 8.

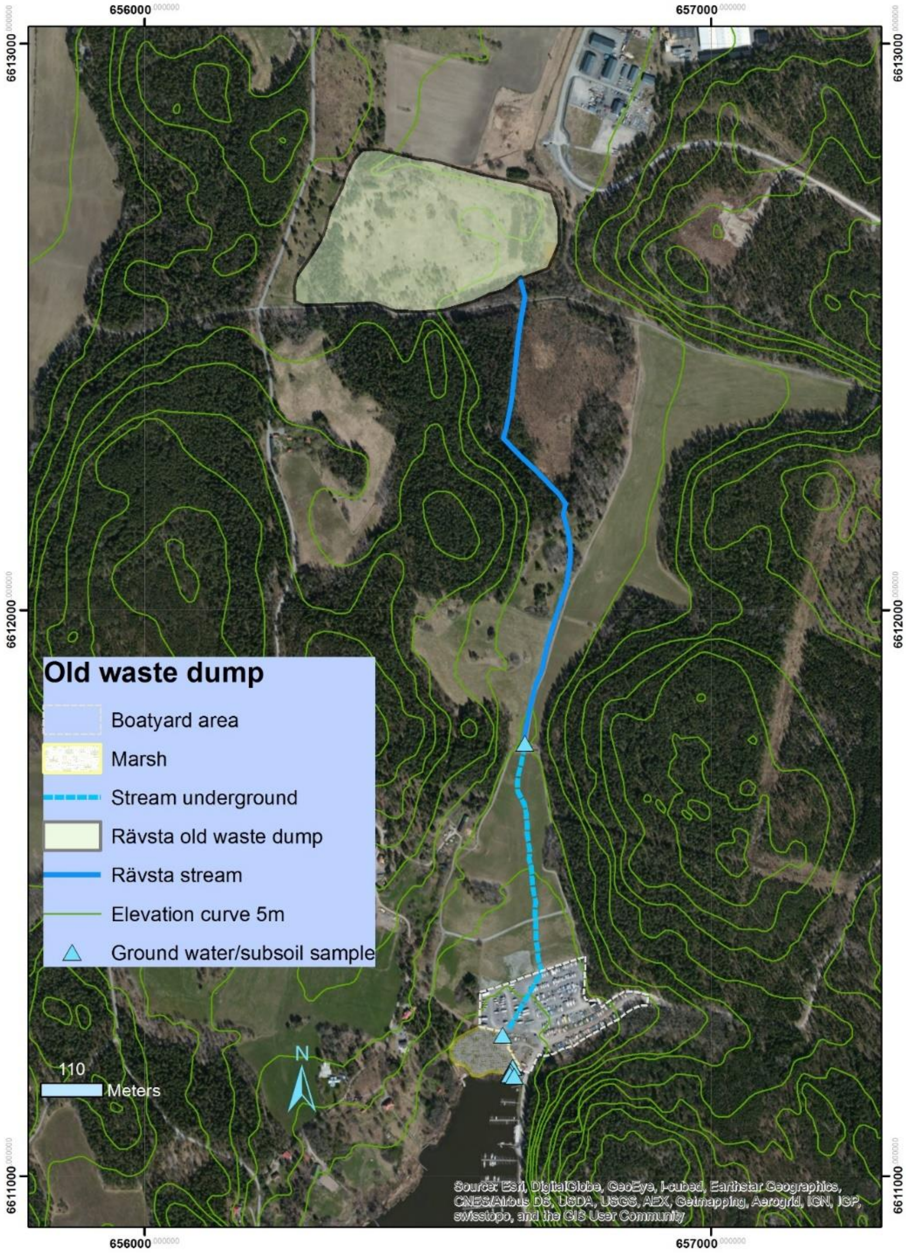


Figure 8 The larger Flottvik area with the old waste dump at Rävsta to the north. Flottvik harbor in the south. Blue line shows the runoff from the waste dump by a small stream. Dotted light blue line shows were the stream goes underground. Blue triangular symbols shows where water and soil samples were collected in the marsh (southwest of the marina close to the lake) and in the stream

The Flottvik boatyard area is divided between Sibk and MBK as can be seen in Figure 9. MBK is situated in the southeast and northwest part, Sibk is in the northeast part. MBK has been there since the beginning of 1965 and are using an area of about 69800 m^2. They are also the sole users of the pier system that houses about 200 boats (MBK, 2014). The total winter storage area for Sibk and MBK is 30000m^2. Sigtuna yacht club moved part of their boats here for winter storage in 2006 from the nearby

Steninge Marina. When their old boat yard in the town of Sigtuna was open to the public and used for other purposes in 2010 the rest of the vessels transferred to Flottvik for winter storage. In 2010 the Flottvik area was also extended with 4500 m^2, shown with black dotted line, in the northern part making winter storage space for the remaining 160 boats. Still they are using the piers in Sigtuna harbor for almost all their boats in summer time. Some boats transfer out in the Baltic Sea area (Sibk, 2014).

Sediments sampling has also been done earlier by Ramböll (2010) and Bjerking (Not available).

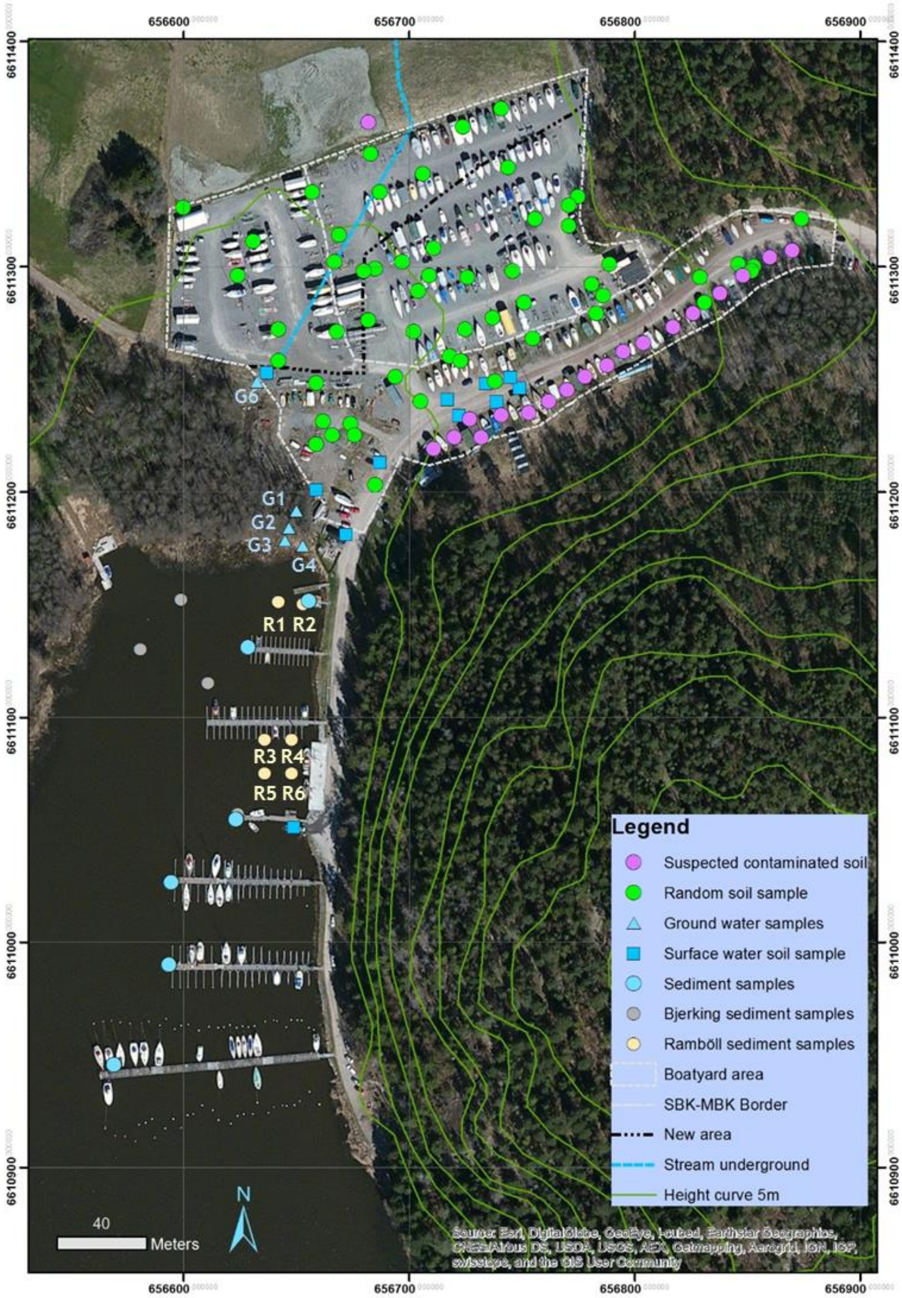


Figure 9 Flottvik boat yard situation map showing where samples from water, sediments and soils were collected, see symbols in the legend box. White dotted line shows the border between Sibk and MBK. Black dotted line where the boat yard was extended to the north in 2010. Green lines are 5m elevation curves. Spots from earlier investigation by Ramböll and Bjerking are shown in gray and yellow

As can be seen in Figure 9 the Flottvik area was sampled and screened for biocide loads in soil, sediments and ground water. The selection of soil measuring spots were done both randomly and focused on suspected spots that had indications on boat maintenance activities like boat cradles and paint residue.

To understand the spatial distribution of contaminants from maintenance activities two hotspots were also measured with 31 spots in a tighter grid. The chosen hotspots showed signs of being used for a long time and were situated in the MBK south area, see Figure 6. In the autumn of 2014 one belonged to an old sailing boat (left) and one to a newer motor cruiser (right). The soil under the boats was sampled in situ with the FPXRF just after the motor cruiser was placed on a trailer and before the sailing boat was returned for winter storage.

4.4.5 Soil sample preparation

Before the samples were measured in the lab, drying, sieving and milling were performed according to recommendations in EPA (2007). Two different methods for drying and grinding were used.

During the investigation of contaminant transport by surface water, all soil samples were transported back to lab for 2 mm sieving and drying in a fume hood before Cryomill grinding and FPXRF measurement. For other soil and sediment lab measurements dry freezing and grinding at room temperature were used and samples were sieved in the field.

4.4.5.1 Grinding procedures

The cryomill grinding method, see Figure 10, was used for samples taken for evaluation of contaminant transport by surface water at Flottvik. Here the sample is placed in small metal containers together with 3 steel balls and then milled at a low temperature of minus 196°C. Program used: PreCool 5Hz, Cryocycle 2, Precool 4min, Grinding 4 min 25Hz and Intermediate period 40s.

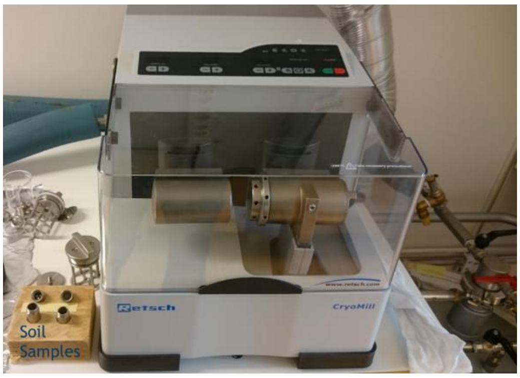


Figure 10 Cryomill grinder with the small metal soil sample containers to the left. To the right are the connection pipes to the nitrogen tank.

In all other subsequent lab measurements a FRITSCH Pulverisette Electromagnetic laboratory micro-pulveriser was used in order to get more material for the FPFXRF measurements as recommended by (EPA 2007) and (Imansishi et al. 2010), see Figure 11. Sediment samples were freeze dried before grinding.

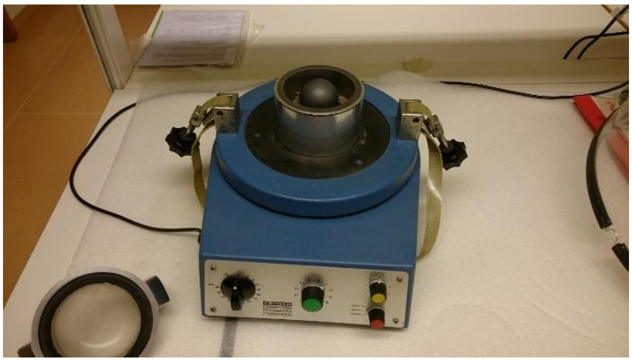


Figure 11 FRITSCH Pulverisette grinder. Soil sample is in the top container with one large metal ball.

4.4.6 FPXRF accuracy

The FPXRF accuracy was addressed by measuring the impact of different plastic containers, measurement time, sieving, grinding, and by randomly select soil samples for confirmatory laboratory analysis with ICP-OES. Totally 21 samples from Flottvik and Rosersberg were freeze dried, milled and digested (9 soil samples from Rosersberg, 6 soil and 6 sediment samples from Flottvik).

- Polypropylene beakers, standard Coop plastic bags and polyethylene zip-bags were tested to see the impact on FPXRF measurements. Two soil samples from Flottvik were sieved to 2mm and divided in the different containers. Every container was then screened in three different positions by the FPXRF in a lab environment.
- FPXRF measuring time was evaluated by measuring on a blank standard and observing the impact on the FPXRF detection limit for Sn soil measurements. 60s and 120s measuring time were used.
- 17 soil samples from Flottvik were tested before and after sieving and grinding. Every sample was screened (Ziam red zip bags) in three different positions by the FPXRF in a lab environment.
- IC-OES analysis was done on randomly selected samples and compared with the results from FPXRF lab measurements. Freeze dried and FRITSCH Pulverisette milled samples were digested according to SS 02 81 50 – 2 (7M HNO_3 125°C in an autoclave, 30 min) followed by analysis on an ICP-OES. The sediment standard PACS-3 was also digested and used as an indicator of the digestion fullness. Another standard solution, NIST 1640a, was used to confirm that the accuracy of ICP-OES quantification was <5%.

4.5 Sediment screening at Flottvik

Sixty sediment samples were collected with a Kajak sediment corer from seven spots on the pier system, see Figure 12. The collected cores were divided in 3 cm thick samples and brought back to the lab in new plastic cans and placed in a refrigerator. After dry-freezing and FRITSCH Pulverisette grinding the FPXRF was used for analysis. Six of the collected samples were also analyzed with ICP-OES.

Figure 12 Kajak sediment sampler together with the plastic slicing tool

4.6 Ground water measurements at Flottvik

To identify the current impact from the old waste dump four ground water samples from the marsh area and two upstream water samples from the Rävsta stream were collected. The stream is collecting the runoff water from the waste dump and runs above the ground until 300m north of the Flottvik boatyard where it goes into an underground pipe and then drains in the marsh area.

Four ground water shafts were dug with a spade to depth of 40 to 100 cm and 30 cm wide the day before the investigation. The water table in each shaft had stabilized to a level of 20 to 6o cm down from the surface at the time the measurements were done. Soil samples were collected from different levels in the ground water shafts and two samples from the stream bed, see Figure 8. For shaft G1 furthest from the shore line the water table were 60 cm down and 6 soil samples were collected at surface level down to a depth of 85 cm. Shaft G2 had the water table at 50 cm and 4 soil samples from 5 to 50 cm. Shaft G3 had the water table at 35 cm and 3 soil samples from 5 to 50 cm. Shaft G4 had the water table at 20 cm and 2 soil samples at 5 and 35 cm. Detailed data is presented in appendix 2. Stream soil samples were collected from the top level in the stream bed. Water samples were collected in the water table and filtered at 0.45 µm to acid cleaned test tubes for later ICP-OES analysis. Soil samples were also brought back to the lab for freeze drying, sieving (2 mm), grinding and then measured with the FPXRF.

4.7 Transport in surface water

Soil and gravel samples were collected on the access road. Spots were chosen that had signs of water flowing, see Figure 9 for spot locations. Samples were collected at the surface and at a depth of 20cm and brought back to the lab for sieving, cryomilling and FPXRF measurements.

5 Result

5.1 Boat hull screening

Screening of 173 boat hulls from MBK and SBK yacht clubs were done in the Flottvik boat yard. The frequency distribution of Cu, Zn, Pb and Sn is presented in Figure 13. The majority of the hulls in the two boatyards have very high levels (>1000 µg/cm^2) of Cu and Zn. For Sn 20% of the boats had levels >100 µg/cm^2 and for Pb 10% had levels >100 µg/cm^2. See appendix 1 for the complete data set.

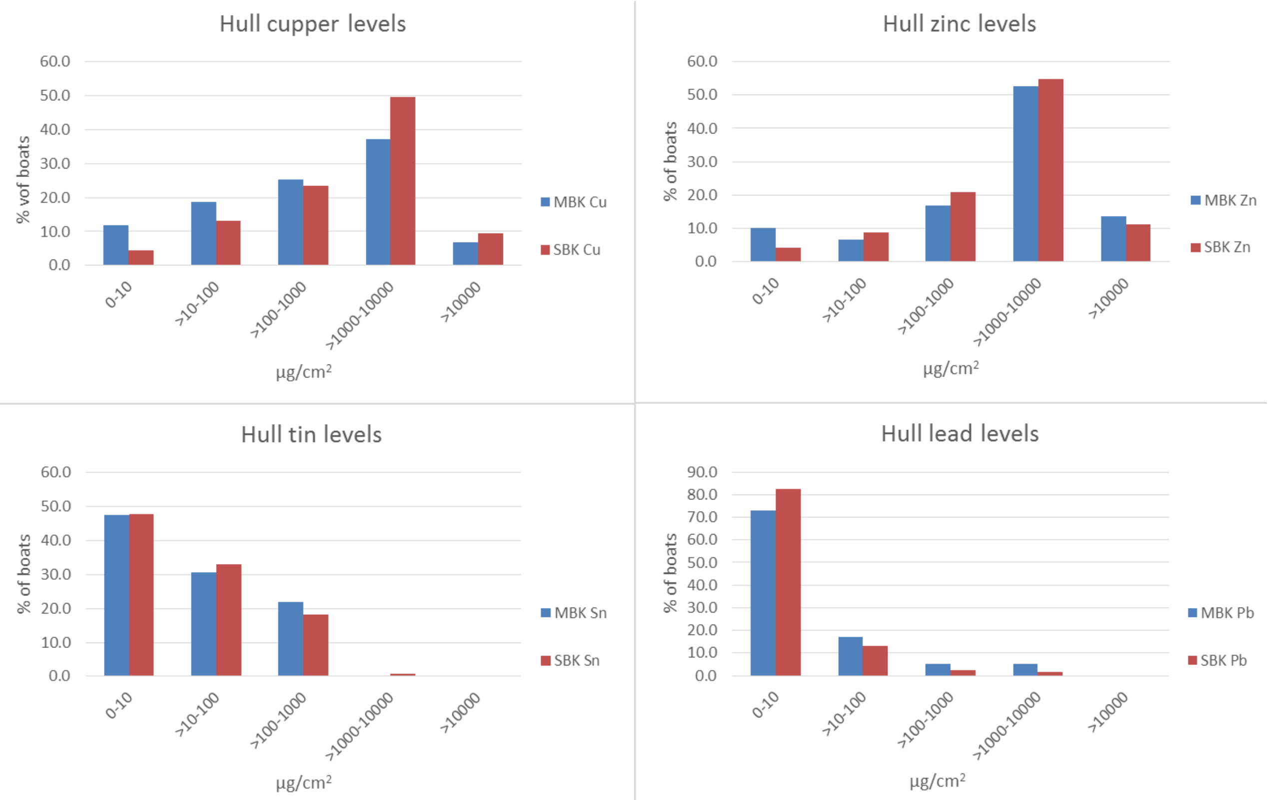


Figure 13 Cu, Zn, Sn and Pb hull contamination levels at Flottvik MBK and SBK boatyards. Bars show the frequency distribution.

The values for copper and zinc range between as not being detected up to 33 000 µg/cm^2 and 29 000 µg/cm^2, respectively. For Pb and Sn the max values are 70 and 66 µg/cm^2 down to as not being detected. Comparing the median values for the different areas, see Table 4, the Cu value for SBK (1472 µg/cm^2) are higher than the values for MBK (835 µg/cm^2). The Pb and Sn values are similar. The high standard deviation values for SBK (Cu 5617 µg/cm^2, Zn 5623 µg/cm^2) and MBK (Cu 6253 µg/cm^2, Zn 5710 µg/cm^2) reflect the high distribution of Cu and Zn as presented in Figure 13.

Table 4 Flottvik hull contamination levels in µg/cm² for SBK and MBK yacht clubs and the combined median value for the Flottvik boatyard.

Flottvik hull levels	Length	Area	Cu µg/cm2	Zn µg/cm2	Pb µg/cm2	Sn µg/cm2
SBK Mean value	9.0	38.1	3588.9	4440.3	46.0	70.0
SBK Median value	**9**	**33**	**1472**	**2770**	**3**	**12**
SBK Max value	14	72	33735	29690	1433	1027
SBK Standard deviation	2	17	5617	5623	294	147
MBK Mean value	7	23	3111	4889	115	59
MBK Median value	**7**	**20**	**835**	**3103**	**5**	**12**
MBK Max value	10	59	29281	25839	2199	776
MBK Standard deviation	1	9	6253	5710	415	118
Flottvik Median value	**8**	**26**	**1318**	**3062**	**3**	**12**

Based on bottom area calculation figures, presented in Table 3, the Cu, Zn, Pb and Sn total contamination content in kg was calculated for every individual boat end then summed for the different yacht club areas, see Table 5.

Cu and Zn are the dominating metals on the screened hulls with higher median values for SBK (Cu 0.55 kg, Zn 0.93 kg) comparing with MBK (Cu 0.18 kg, Zn 0.77 kg). SBK also has the highest MAX values (Cu 19.7 kg, Zn 17.4 kg) compared with MBK (Cu 9.1 kg, Zn 10.7 kg)

Table 5 Flottvik hull levels in kg for SBK and MBK yacht clubs and the combined median value for the Flottvik boatyard.

Flottvik hull levels kg	Cu tot kg	Zn tot kg	Pb tot kg	Sn tot kg
SBK Mean value	1.61	1.74	0.01	0.02
SBK Median value	0.55	0.93	0.00	0.00
SBK Max value	19.74	17.37	0.37	0.35
SBK Standard deviation	2.95	2.59	0.06	0.05
MBK Mean value	0.78	1.14	0.02	0.01
MBK Median value	0.18	0.77	0.00	0.00
MBK Max value	9.10	10.73	0.48	0.25
MBK Standard deviation	1.67	1.68	0.09	0.04
Flottvik Median value	0.35	0.82	0.00	0.00

There is in total 341 kg of Cu, Zn, Pb and Sn contamination on the measured hulls, see Table 6. Zn is the dominating metal (183 kg) and Pb (2 kg) the lowest. Based on the paint manufacture recommendation, the nominal paint consumption is in all 600 liters for giving every boat two layers of paint.

Table 6 Flottvik total hull levels in kg and paint consumption in liters for the different yacht clubs

Flottvik total hull levels in kg and paint consumption in liters for the different yacht clubs							
Yacht club	# Boats	Cu tot kg	Zn tot kg	Pb tot kg	Sn tot kg	Total load kg	Paint l
SBK	114	121.0	135.0	0.9	1.8	258.7	452.5
MBK	59	32.2	48.1	1.1	0.6	82.0	150.0
Flottvik total	59	153	183	2.0	2.4	341	603

To see the distribution of biocide paint on the measured boats individuals, the boats were sorted in 4 quartiles using the individual weighted load figures of every boat, see Table 7. If the weighted value is calculated to be ≤ 0.54 kg then it belongs to the 1st quartile. If the value is >0.54 - ≤1.29 kg then it belongs to the 2nd quartile, value >1.29 - ≤3.24 kg then it belongs to the 3rd quartile and >3.24 kg 4th quartile.

As can be seen in Table 7 there is 43 boats in every quartile except quartile 3 that got 44 boats. The added weighted load in the 1st quartile is 10 kg, in the 2nd quartile 36 kg, in the 3rd quartile 90 kg and in the 4th quartile 328 kg representing 71% of the total weighted load. In the 4th quartile there is also 71% of the total Cu load, 41% of the Zn load, 20% of the Pb load and 79% of the Sn load. The added Cu, Zn, Pb and Sn figure of 187.6 kg in the 4th quartile represent 55% of the of the total load of 341 kg.

Combining the boats in the 3rd quartile and 4th quartile, 87 boats, give 91% the total Cu load, 75% of the Zn load, 25% of the Pb load and 94% of the Sn load. The added Cu, Zn, Pb and Sn values represent 82% of the total load. 86 boats in the 1st quartile and the 2nd quartile represent only 18% of the potential toxic load to soil and water. The difference in paint consumption between the 1st quartile (20%) and 4th quartile (31%) is small. The complete data set for the Flottvik boat yard is listed in Appendix 1.

Table 7 Contaminant load distribution for the measured boats individuals and paint consumption

Contaminant load distribution for the measured boats individuals								
Quartile span	# Boats	Sum Weighted load kg	Cu tot kg	Zn tot kg	Pb tot kg	Sn tot kg	Cu+Zn+Pb+Sn kg	Paint cons. l
1 ≤ 0.54 kg	43	10.1	2.7	8.9	0.9	0.0	12.5	121
2 >0.54 -≤1.29 kg	43	36.3	11.7	36.4	0.6	0.1	48.9	134
3 >1.29 -≤3.24 kg	44	90.5	29.4	61.9	0.1	0.4	91.8	161
4 >3.24 kg	43	328.5	109.4	75.9	0.4	1.9	187.6	187
Total	173	465.5	153.2	183.1	2.0	2.4	340.7	603
	Percent of total							
Quartile	# Boats	Weighted load kg	Cu tot kg	Zn tot kg	Pb tot kg	Sn tot kg	Cu+Zn+Pb+Sn kg	Paint cons. l
1	25%	2%	2%	5%	44%	1%	4%	20%
2	25%	8%	8%	20%	32%	4%	14%	22%
3	25%	19%	19%	34%	5%	15%	27%	27%
4	25%	71%	71%	41%	20%	79%	55%	31%
3+4	50%	90%	91%	75%	25%	94%	82%	58%

5.2 Soil screening

The contamination levels differ highly among the randomly selected spots as can be seen by the high standard deviation figures in Table 8. As a result the mean and median values also differ. The median figure is considered to give a more realistic value and is used for the total load calculation.

The contaminant levels were graded against the regulatory limits (Table 1) and the result is presented in figure 14 and 17. The limits for less sensitive land use for Cu are 200 mg/kg, for Zn 500 mg/kg and for Pb 400 mg/kg. For Sn there is no defined Swedish limit (there is a Finnish TBT limit at 2mg/kg see Table 1).

The Cu median value (Table 8) of the suspected spots was 245 mg/kg and for Zn 863 mg/kg, exceeding the limit for less sensitive land use (Cu 200 mg/kg / Zn 500 mg/kg). For the randomly selected spots in Flottvik 15% had values exceeding the less sensitive land use limit for Cu (200 mg/kg), 40% had values exceeding the limit for Zn (500 mg/kg) and 4% had values exceeding the limit for Pb (400 mg/kg). The corresponding less sensitive land use figures for Rosersberg were 50% for Cu, 50% for Zn and 5% for Pb. The detailed contamination data set is listed in Appendix 2.

Table 8 Mean and median soil contaminant levels in Rosersberg and Flottvik boatyards

Soil Contamination mg/kg	Cu	Zn	Sn	Pb
Rosersberg random soil screening				
Mean random RBK	1564	1583	8	99
Median random RBK	183	455	0	35
Standard deviation	6938	2681	16	220
MAX value	45254	12632	65	1080
Flottvik random soil screening				
Mean random Sibk, MBK	186	1235	5	79
Median random Sibk, MBK	37	356	0	28
Standard deviation	612	2421	8	195
MAX value	4413	12632	50	1080
Flottvik suspected soil screening MBK				
Mean susp MBK	1111	1667	45	253
Median susp MBK	**245**	**863**	14	38
Standard deviation	1997	2031	76	573
MAX value	7358	5689	247	2536
Flottvik and Rosersberg random values				
Mean Sibk, MBK, RBK random	783.1	1386.0	6.4	87.7
Median Sibk, MBK, RBK random	58.0	386.0	0.0	31.3

The existing load in the top soil layer for Cu in Flottvik is 0.6 mg/m2. The load in Rosersberg is 4 times higher, 2.7 mg/m2.

Table 9 Total contaminant load based on median values from random measurements

Soil Contamination Top 1 cm	Cu	Zn	Sn	Pb
Rosersberg total load ($3600m^2$) kg	9.9	24.6	0.0	1.9
Flottvik total load ($30000m^2$) kg	16.7	160.2	0.0	12.5
Rosersberg load mg/m^2	2.7	6.8	0.0	0.5
Flottvik load mg/m^2	0.6	5.3	0.0	0.4

5.2.1 Sampling strategy

The locating procedure used at the Rosersberg boatyard, starting from a number of predefined reference points, has proved to be difficult and time consuming. Together with aerial photos of high resolution the GPS method proved to be a time efficient way of locating the selected spots.

5.2.2 Soil screening at Rosersberg

The measured values for Cu, Zn, Sn and Pb are presented in Figure 14. The data is color-coded according to the limit values for sensitive (green) and less sensitive land use (yellow). Red color indicates values exceeding the limit for less sensitive land use (Table 1). It is clearly visible that the values are higher in the winter storage areas and lower on the access roads. Cu and Zn are exceeding the limits for less sensitive land use in a similar pattern. Pb values are less frequently exceeding the limit for sensitive land use. Sn has high values (>20 mg/kg) in some spots but is mostly not detected.

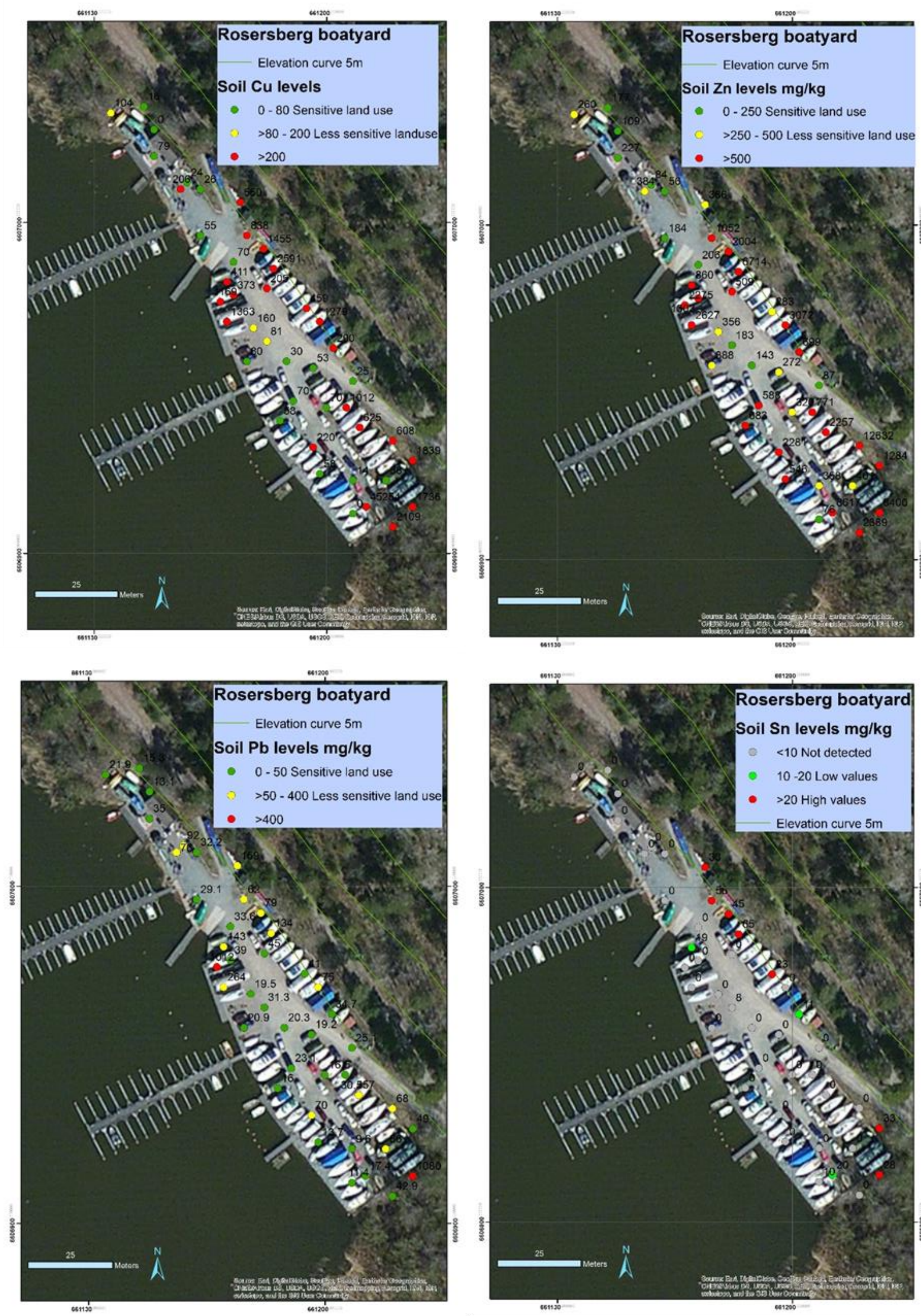


Figure 14 Rosersberg boatyard contamination levels. Actual values are visible for some spots in black figures, complete list is presented in Appendix 2. Contamination values are color coded according to existing regulations as showed in the legend box. For Sn just high and low values are indicated.

The data shows that values on the surface are higher than the values 10 cm down. The distribution of contaminants on surface and 10 cm down is presented in Figure 15. Detailed data set is shown in Appendix 2.

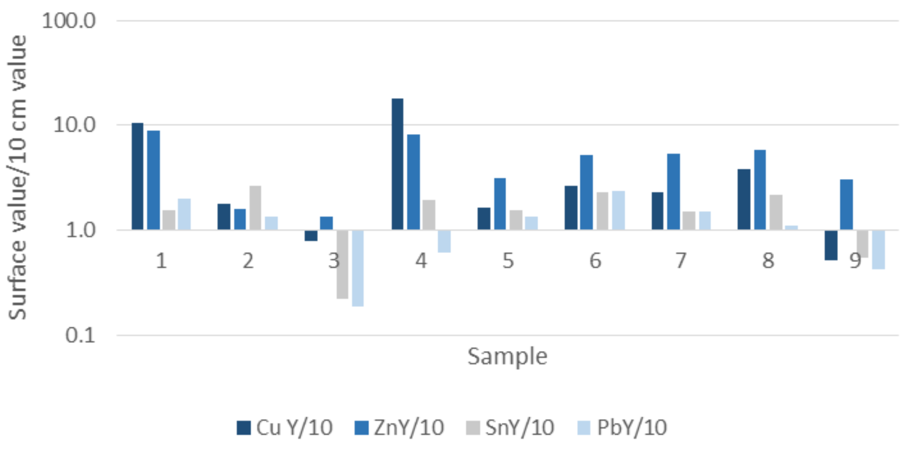


Figure 15 Contamination levels ratio for 9 spots collected on the surface and at a depth of 10cm at the Rosersberg boat yard. Positive bars indicate that higher values at the surface, "negative" bars indicate higher values at a depth of 10cm. Logarithmic Y-axis.

5.2.3 Soil screening at Flottvik

The measured values for Cu, Zn, Sn and Pb are presented in Figure 16. The data is color-coded according to the limit values for sensitive (green) and less sensitive land use (yellow). Red color indicates that it is exceeding the limit for less sensitive land use (Table 1). The soil contaminant levels are higher in the suspected southeast area where boats have been winter stored and maintained from the start of the Flottvik operations. The values are higher in the winter storage areas and lower on the access roads or other support areas. Cu and Zn are exceeding the limits for less sensitive land use in a similar pattern. Pb values are less frequently exceeding the limit for sensitive land use. Sn has high values (>20 mg/kg) in the old storage area.

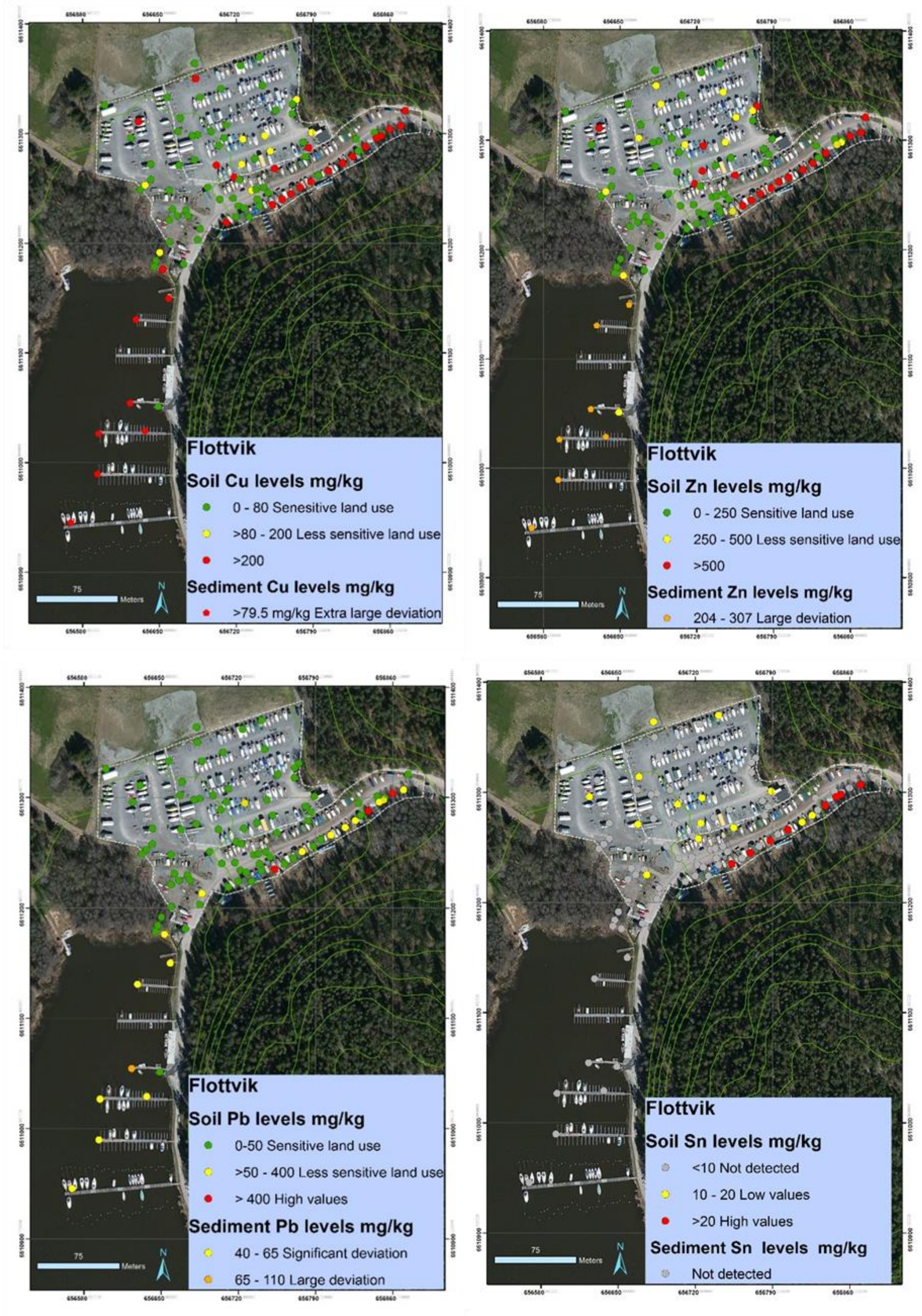


Figure 16 Flottvik Cu, Zn, Sn and Pb contamination levels for soil and sediments. Contamination values are color coded according to existing regulations as showed in the legend box. For Sn just high and low values are indicated.

The lowest values are found in the areas used for transportation only. Red dots indicate areas where contamination levels exceed even less sensitive land use.

5.2.3.1 Distribution of metals in soil beneath chosen boats

The FPXRF results from the spatial distribution of contaminants from boat hull maintenance activities are shown in Figure 17. High contaminant levels were detected within a meter from the centerline. The Cu levels were up to 45 times higher (9051mg/kg) than the limit for less sensitive land use (200 mg/kg). The Zn level (12700 mg/kg) was up to 25 times higher than the limit for less sensitive land use (500 mg/kg).

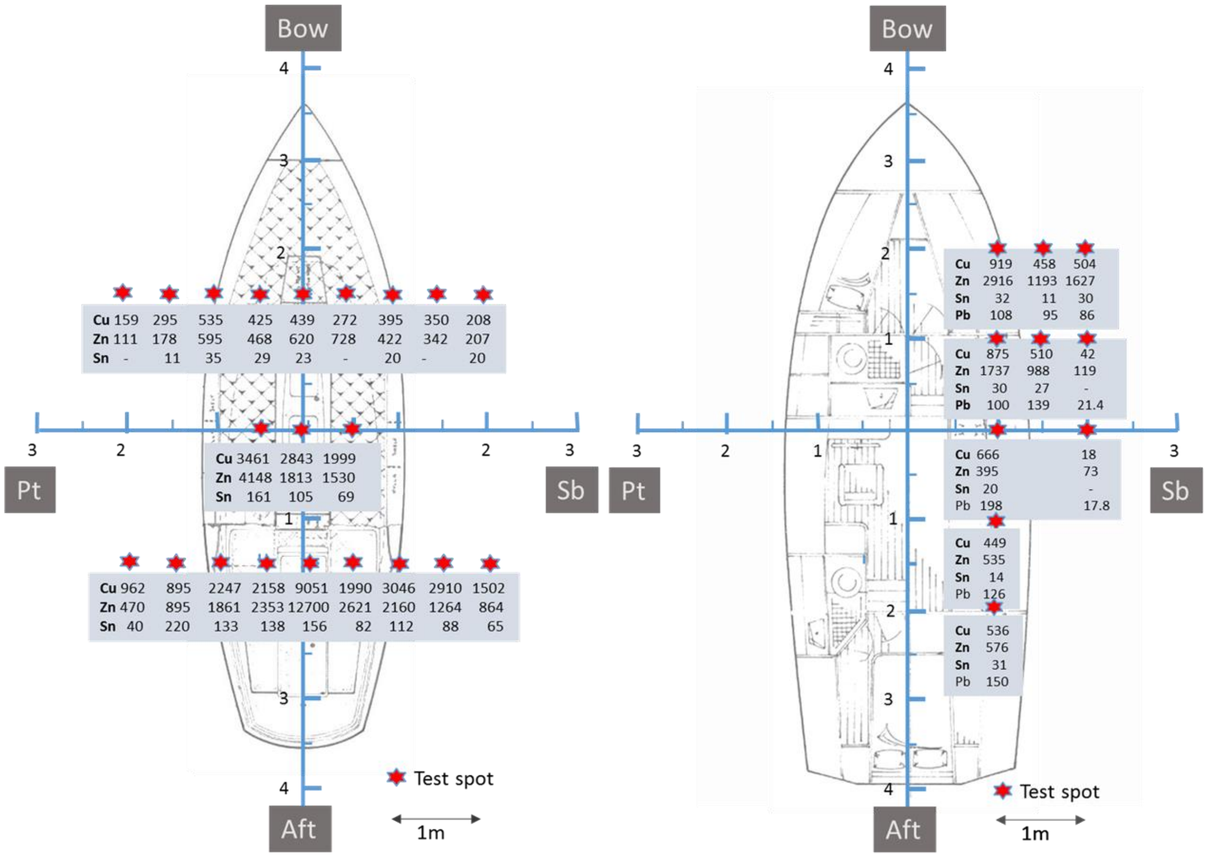


Figure 17 Soil hotspot contamination values in mg/kg TS in two different places where boats are stored in winter time. Distances and levels are shown relating to the two boats that occupy the area in the autumn 2014. Sailing boat to the left, motor boat to the right. Sb = starboard side, Pt = port side. Levels are directly copied from the FPXRF data log and resolution does not reflect accuracy.

For the sailing boat (left) it is shown how the contaminant levels vary from port to starboard with high peak values at the centerline. The sailing boat figures are highest in the aft section while the motor boat (right) figures are highest in the bow section. Hull screen mean values for the motor boat showed Cu 17600 µg/cm^2, Zn 1800 µg/cm^2, Sn 63 µg/cm^2 and Pb 3 µg/cm^2.

5.2.4 FPXRF Accuracy

The suitability of the XRF as a tool for investigating of boatyard soil and the impact on measurements was analyzed for

- Impact of sieving and grinding
- FPXRF measuring time
- Impact of different plastic containers when doing FPXRF lab measurements

5.2.4.1 Impact of sieving and grinding

The mean values from the FPXRF measurements are presented relative the raw soil values in Figure 18 and Figure 19. Error bars show the standard deviation in percent (relative raw values) for the 17 samples. Three high values (outliers) were found among the cryomill Cu data. The cryomill samples were small weighing about 4 to 5g compared with samples from the FRITSCH Pulverisette grinder that were 100 to 200g.

The error bar on “Sieved 2 mm” overlaps the top value for “Raw soil” showing that the impact of sieving versus the removal of larger object when collecting samples on site is small.

A one-way paired analysis of variance on the mean values showed that there are no significant differences between the soil sample preparations for Cu (ANOVA, $F=0.244$; $P>0.05(0.784)$) or for Zn (ANOVA, $F=0.851$; $P>0.05(0.433)$).

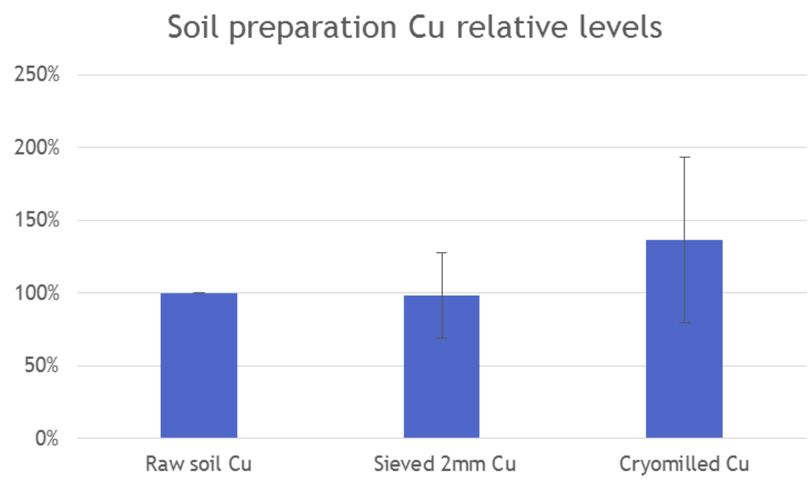


Figure 18 Cu values normalized against raw soil values for the different soil sample preparations. Error bars show standard deviation for 17 samples.

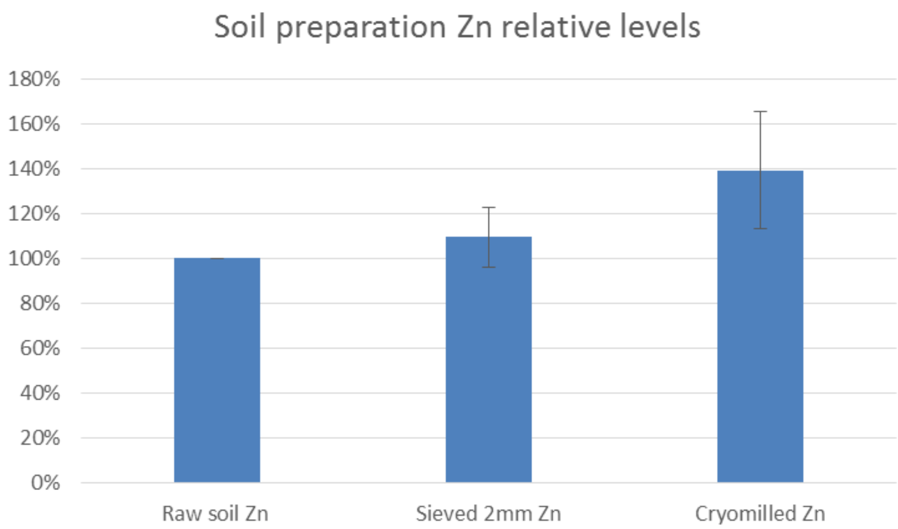


Figure 19 Zn values normalized against raw soil values for the different soil sample preparations. Error bars show standard deviation for 17 samples.

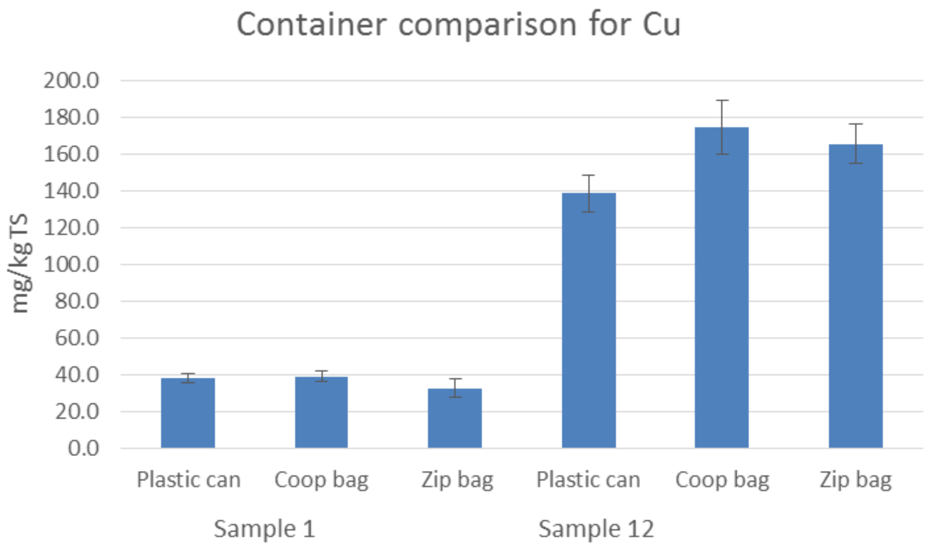
5.2.4.2 FPXRF measuring time

The FPXRF measuring time was changed from 60s to 120s with the result that the detection limit for Sn, calculated by the FPXRF, went from 10 mg/kg down to 7 mg/kg, a reduction with 30%.

5.2.4.3 Impact of different plastic containers

Two soil samples were measured repeatedly 3 times in different containers and the mean values with error bars for Cu and Zn are presented in Figure 20. No replicate test data is available for variance analysis.

Measurement on sample 12 in plastic cans gives a lower value both for Cu and Zn. There is no big difference between Coop plastic bags and zip bags as the error bars overlap. The zip bags were used for the FPXRF accuracy tests and for all other lab tests.



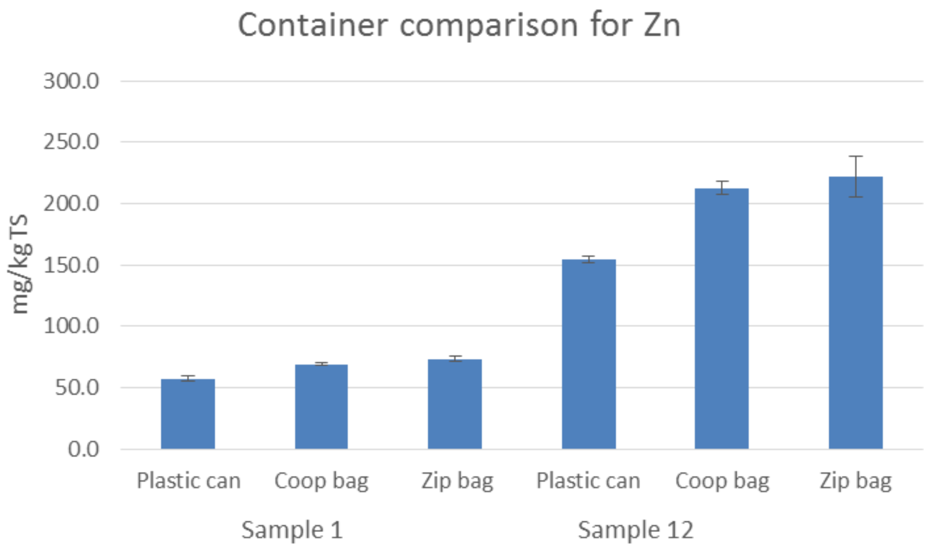


Figure 20 Container comparison made on Cu sample 1 and 12. Error bars show SD from 3 XRF measurements on one sample

5.2.5 FPXRF Confirmatory measurements

Soil samples were brought back to the lab to be measured with both FPXRF and ICP-OES chemical analysis. According to (EPA 2007) the correlation coefficient (r) value ≥ 0.7 indicate screening performance. An r value ≥ 0.9 indicate that the data could potentially meet definitive level data requirements. A slope of 0.9 – 1 indicate that no correction factor is needed.

A correlation analysis of the results from this study showed that values had a good agreement see Figure 21 and Figure 22. The R^2 values for Cu (0,989 in lab and 0.839 in field) together with R^2 values for Zn (0,989 in lab and 0.918 in field) shows that Cu and Zn values measured in the lab and in the field are reliable. R^2 Values for Pb (0,893 in lab and 0.735 in field) are good enough for screening purposes.

Regarding the Sn R^2 values only 4 of the random samples had detectable levels in a field environment making it hard to present a reliable figure. No correction factor is needed for Cu and Zn as the slope values are above 0.9. For Pb a correction factor may be needed and for Sn too few data points exist to determine the slope value.

The small error bars for FPXRF lab measurements shows standard deviation from 3 measurements with the FPXRF for all samples and from 4 samples with the ICP-OES.

The correlation is stronger for the FPXRF measurement done in a lab environment when comparing with the result from the ICP-OES. Cu and Zn show high correlation (0.989) than for Sn (0.853) and Pb (0.893). The correlation for FPXRF in field measurements is highest for Zn (0.918) and low for Sn (0.422). Slope values are high for all Cu and Zn correlation (0.96 – 1.09) and low for Sn (0.21 in field).

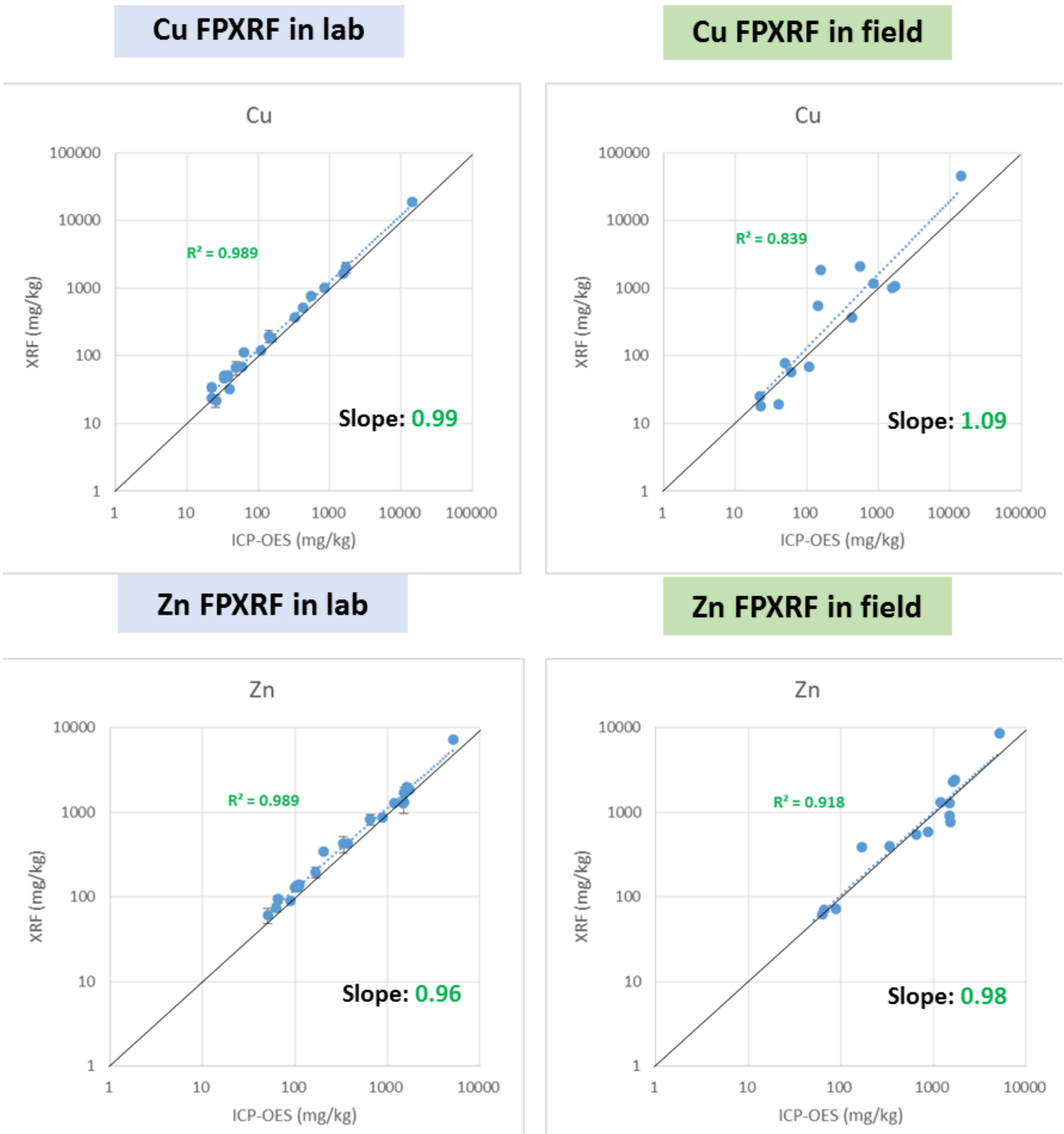


Figure 21 Confirmatory Cu and Zn soil and sediment samples measured with ICP-OES. R^2 is the coefficient of determination equal to the squared value of the correlation coefficient (r). The small error bars for in lab measurements shows standard deviation for 3 measurements with the FPXRF on all samples and from 4 samples with the ICP-OES (Graphs was made by Maria Lagerström).

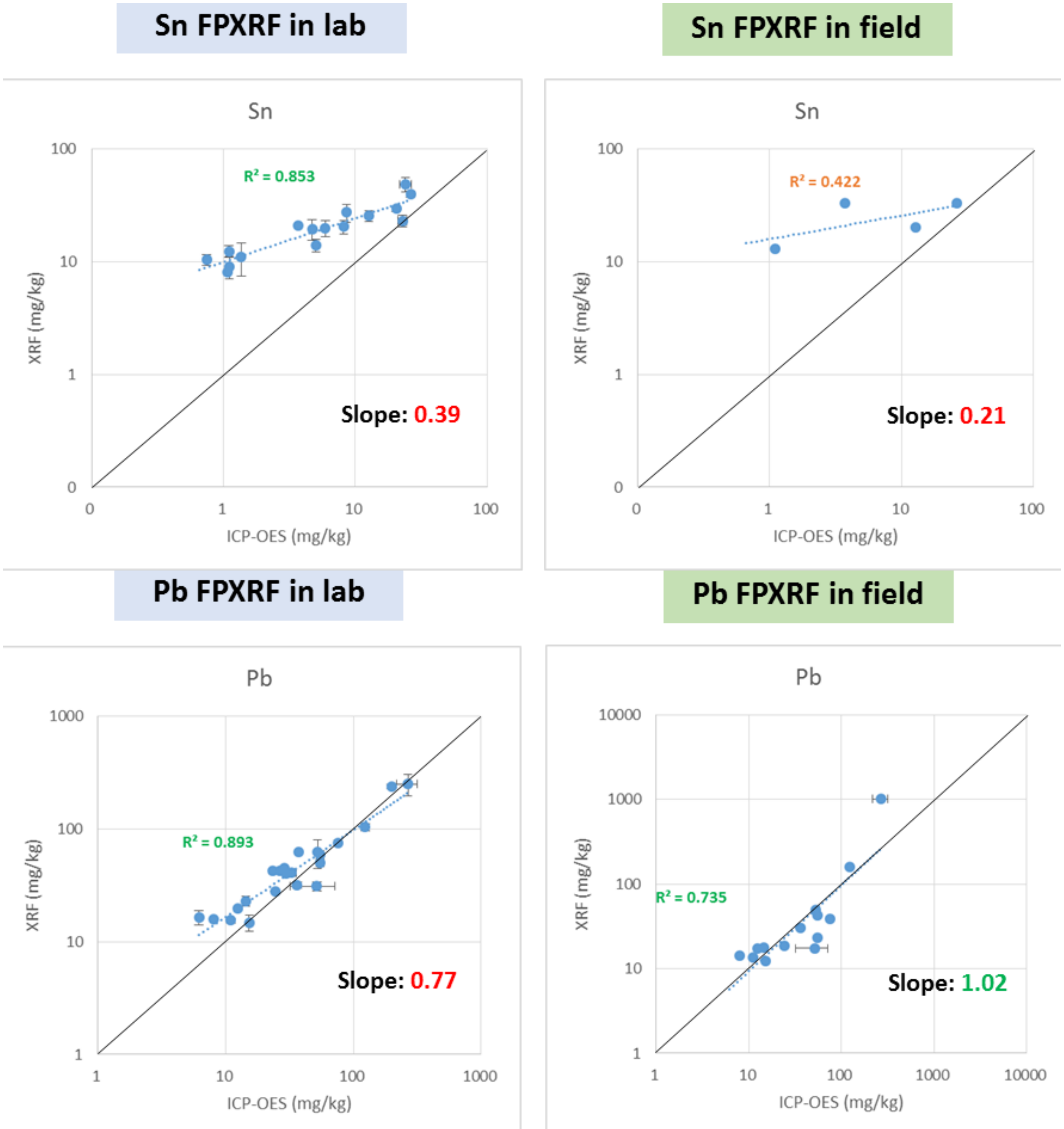


Figure 22 Confirmatory Sn and Pb soil and sediment samples measured with ICP-OES. R2 is the coefficient of determination equal to the squared value of the correlation coefficient (r). The small error bars for in lab measurements shows standard deviation for 3 measurements with the FPXRF on all samples and from 4 samples with the ICP-OES (Graphs was made by Maria Lagerström).

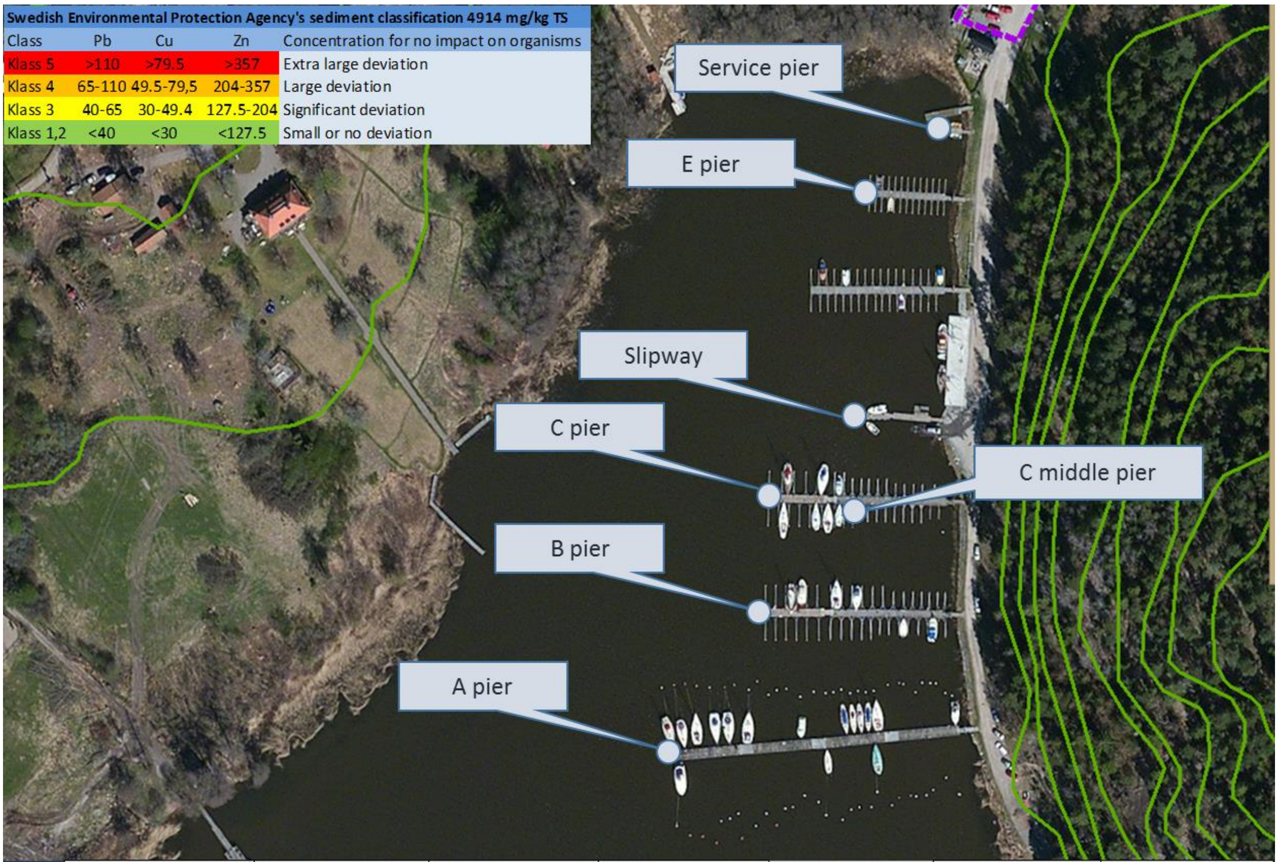
5.3 Sediment screening at Flottvik

The Sediment samples collected with a Kajak sediment corer from selected spots on the pier system is shown in Figure 23. The actual values for different depths are shown in the table at the bottom of the figure. Comparison values for eco toxicological levels of heavy metals from Table 27 of the Environmental Protection Agency Report 4914 (SEPA, 1999). The figures indicate the concentrations over the expected impact on organisms. Color grading is done according to the SEPA (1999) classification presented in Table 10.

Table 10 Swedish Environmental Protection Agency's sediment classification 4914 mg/kg TS

Swedish Environmental Protection Agency's sediment classification 4914 mg/kg TS				
Class	Pb	Cu	Zn	Concentration for no impact on organisms
Klass 5	>110	>79.5	>357	Extra large deviation
Klass 4	65-110	49.5-79,5	204-357	Large deviation
Klass 3	40-65	30-49.4	127.5-204	Significant deviation
Klass 1,2	<40	<30	<127.5	Small or no deviation

High values classified as "significant deviation" up to "extra-large deviation" of Cu, Zn and Pb is detected in the 10 cm topmost layer and values are higher closer to the boat yard. Cu is the dominating metal in all sediment samples with values up to 127 mg/kg. No Sn is detected at the top layer but high concentrations, 18.7 mg/kg, was found at the service pier. The core coming from the slipway area had a Pb figure of 797 mg/kg at 7.5 cm depth.



Swedish Environmental Protection Agency's sediment classification 4914 mg/kg TS				
Class	Pb	Cu	Zn	Concentration for no impact on organisms
Klass 5	>110	>79.5	>357	Extra large deviation
Klass 4	65-110	49.5-79,5	204-357	Large deviation
Klass 3	40-65	30-49.4	127.5-204	Significant deviation
Klass 1,2	<40	<30	<127.5	Small or no deviation

mg/kg TS	Service pier				E pier				Slipway				C middle			
Depth cm	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn
1.5	63.3	127.0	353.7	0.0	49.0	101.3	295.0	0.0	67.0	97.3	237.0	N/D	55.7	83.3	307.0	N/D
4.5	103.0	96.0	286.5	0.0	54.7	101.7	311.7	0.0	50.0	65.0	161.7	N/D	59.7	104.7	362.7	N/D
7.5	77.2	42.0	114.0	10.0	69.3	118.3	377.3	0.0	797.3	57.0	142.3	N/D	80.3	95.0	317.7	N/D
10.5	100.3	80.7	216.7	18.7	60.3	99.3	291.7	0.0	45.0	50.7	128.7	N/D	86.0	89.3	284.0	11.0
13.5					47.6	78.7	228.3	0.0	47.2	53.3	133.0	N/D	53.6	58.0	169.0	N/D
16.5					56.7	80.7	240.0	0.0	48.0	55.3	146.0	N/D	48.6	54.7	158.3	N/D
19.5									47.6	54.3	140.3	N/D	46.9	53.7	150.0	N/D
22.5									46.5	54.7	139.0	N/D	51.0	52.7	149.0	8.0
25.5									42.7	52.0	126.7	8.0	51.3	57.3	171.7	N/D
28.5									50.8	59.0	157.0	N/D	46.2	50.0	143.3	8.0
31.5													41.6	48.3	141.7	N/D

mg/kg TS	C pier				B pier				A pier			
Depth cm	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn
1.5	52.2	87.7	263.0	N/D	60.0	90.0	306.3	N/D	59.0	91.7	282.7	N/D
4.5	55.3	71.7	198.3	N/D	57.3	83.0	258.0	N/D	46.1	89.0	249.0	N/D
7.5	47.8	56.0	150.0	N/D	77.0	84.3	257.7	N/D	61.7	102.3	277.3	N/D
10.5	40.4	52.0	130.7	N/D	64.7	84.0	229.7	N/D	53.2	84.0	195.7	N/D
13.5	45.9	50.3	142.0	N/D	48.7	66.3	177.7	N/D	42.0	54.3	141.7	N/D
16.5	40.9	48.0	132.0	N/D	43.0	48.3	142.0	N/D	40.9	47.7	142.7	N/D
19.5	44.0	48.7	149.0	N/D	46.7	55.0	148.3	N/D	43.0	49.0	142.3	N/D
22.5	47.0	52.7	143.0	N/D	45.2	53.7	155.7	N/D	43.1	51.3	143.3	9.0
25.5	44.9	53.3	142.7	N/D	41.3	50.3	142.3	N/D				
28.5	53.0	62.7	169.0	N/D								
31.5	43.6	50.3	146.0	N/D								

Figure 23 Sediment contamination levels. The color classification is detailed at the box in the upper left corner according to SEPA (1999). In the bottom the contamination for different layers of sediment are shown in mg/kg TS. For Sn there are no specific requirements so green has been used where the amount was under the detection limit for the FPXRF, otherwise yellow was used and N/D means under the detection limit.

5.4 Ground water measurements at Flottvik

The water quality data from samples collected in the four shafts in the marsh below the boatyard and measured with ICP-OES is shown in Figure 24. Low values for Cu were detected in the shafts G1 – G4 and upstream the Rävsta stream. Downstream the value was exceeding the new proposed annual mean of 0.5 µg, see Table 1. For Zn some values were exceeding the proposed new annual mean limit of 5.5 µg.

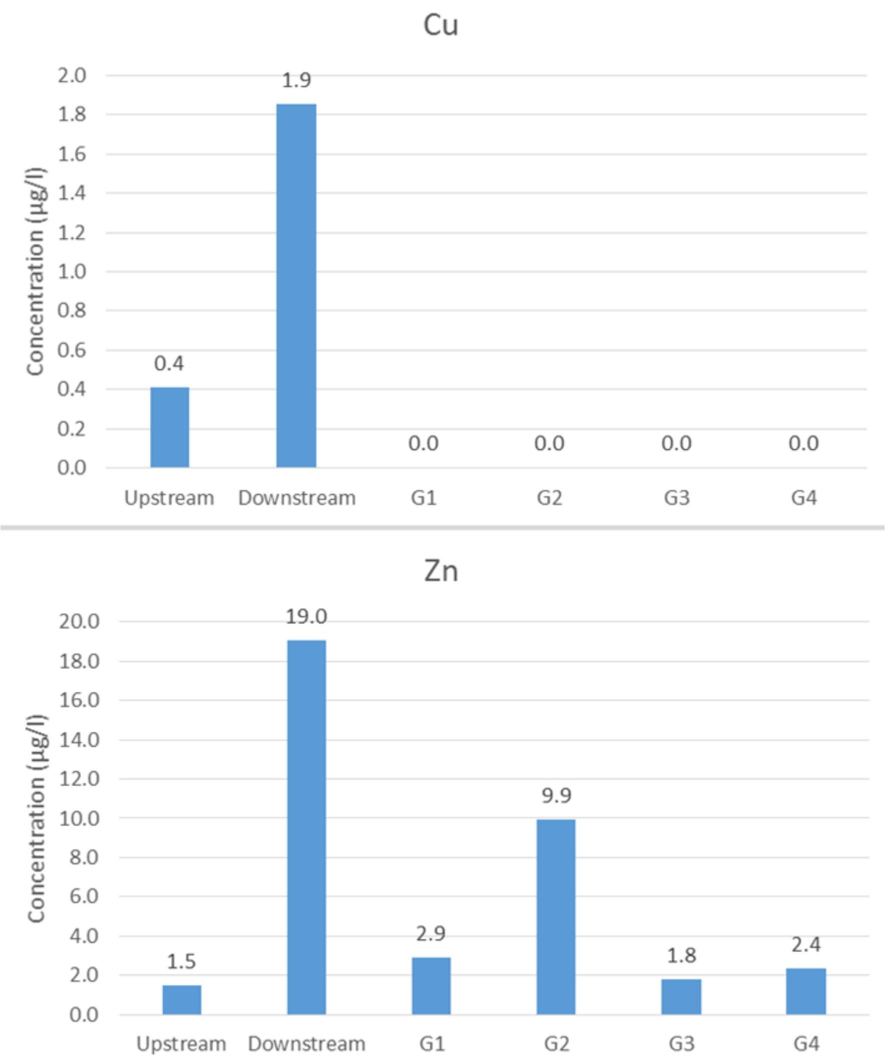


Figure 24 Cu and Zn levels in the ground water and in the Rävsta stream. Groundwater positions G1 – G4 and Rävsta stream test positions are shown in figure 2 and 3. Upstream is closer to the old waste dump.

Contaminant levels in soil samples from the ground water shafts are shown in Figure 25. The Cu and Zn values follow each other in the four profiles. In shaft 1 to 3 the values are lower than the limit for sensitive land use (Cu 80 mg/kg dw, Zn 250 mg/kg dw). Values are higher in the upper levels but still lower than the limit. In shaft 4 there was mostly decomposed reed residues with high Cu and Zn values exceeding the limit for sensitive land use, in the bottom even exceeding the limit for less sensitive land use (Cu 200 mg/kg dw, Zn 500 mg/kg dw). Detailed data set with standard deviation figures from 3 FPXRF measurement are shown in Appendix 2.

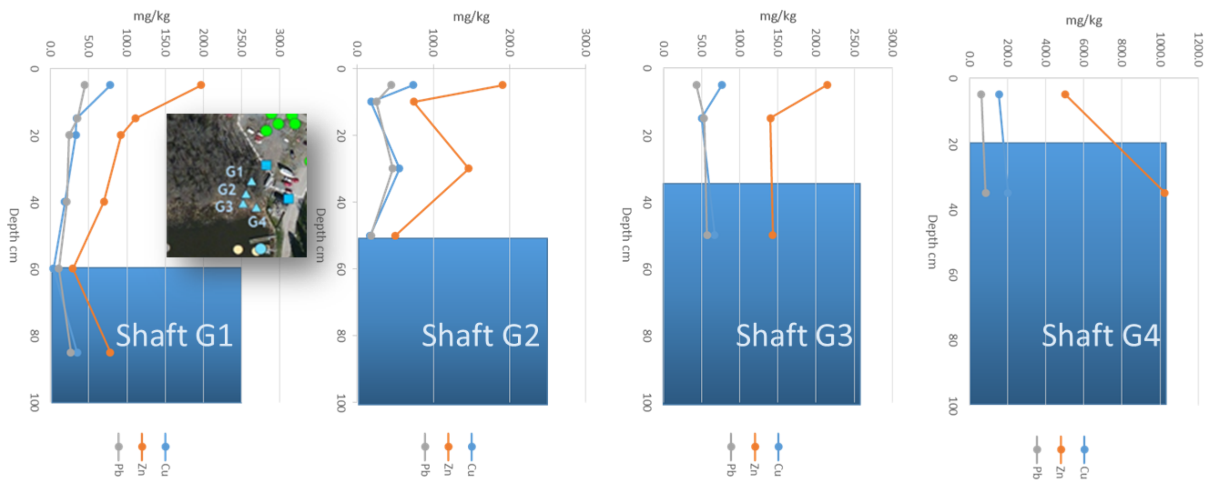


Figure 25 Soil samples from ground water shaft G1, G2, G3 and G4 contaminant figures for Cu and Zn. Note the different scale of the x-axis for shaft 4. Blue area indicates depth below the water table (G1 60cm, G2 50cm, G3 35cm and G4 20cm).

In the soil samples from the stream bed and the dredged material, see Figure 26, the values are much lower than the limits for sensitive land use, Cu 80 mg/kg dw and Zn 250 mg/kg dw. The downstream values are higher than the upstream values.

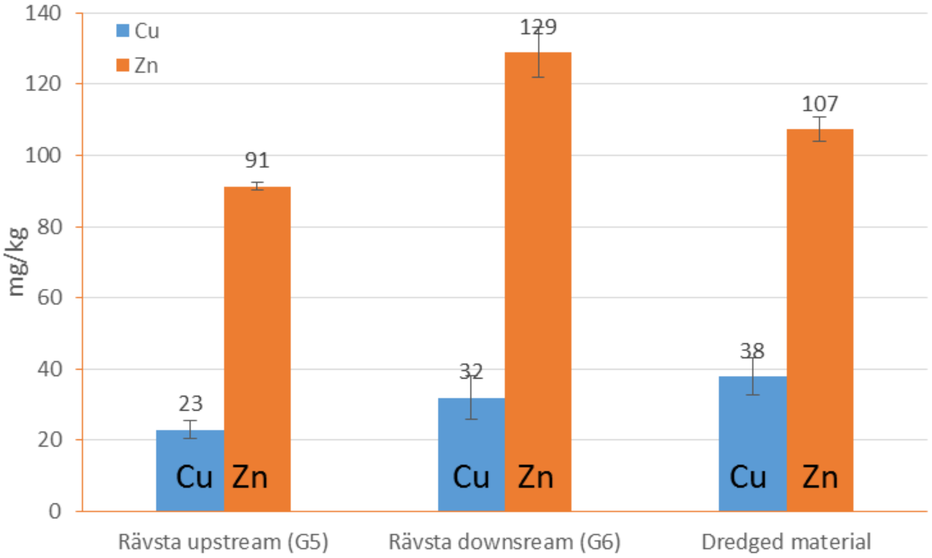


Figure 26 Soil samples from the Rävsta stream bottom north of the boat yard area and from the dredged material old storage area. Error bars show the mean value from 3 different FPXRF measurement.

5.5 Transport in surface water

The contaminant levels along the access road where surface water is flowing are shown in Figure 27. There is no indication in the data that the contamination travels downhill by means of surface water. The trend line for Cu+Zn+Pb indicates a small rise downhill. A linear regression was done on spot 2 – 9 against the distance in meters from spot 2. There was no association between the predictor "Distance" and the added response for Cu, Zn and Pb. The null hypothesis cannot be rejected and there is no significant relationship between "Distance" and Y values. (20 cm data $p = 0.98$. Surface data $p = 0.5$).

Comparing the mean values for all metals in all spots for top soil and 20 cm deep soil the contamination levels are about 1.5 times higher deeper down. Detailed data shown in Appendix 2.

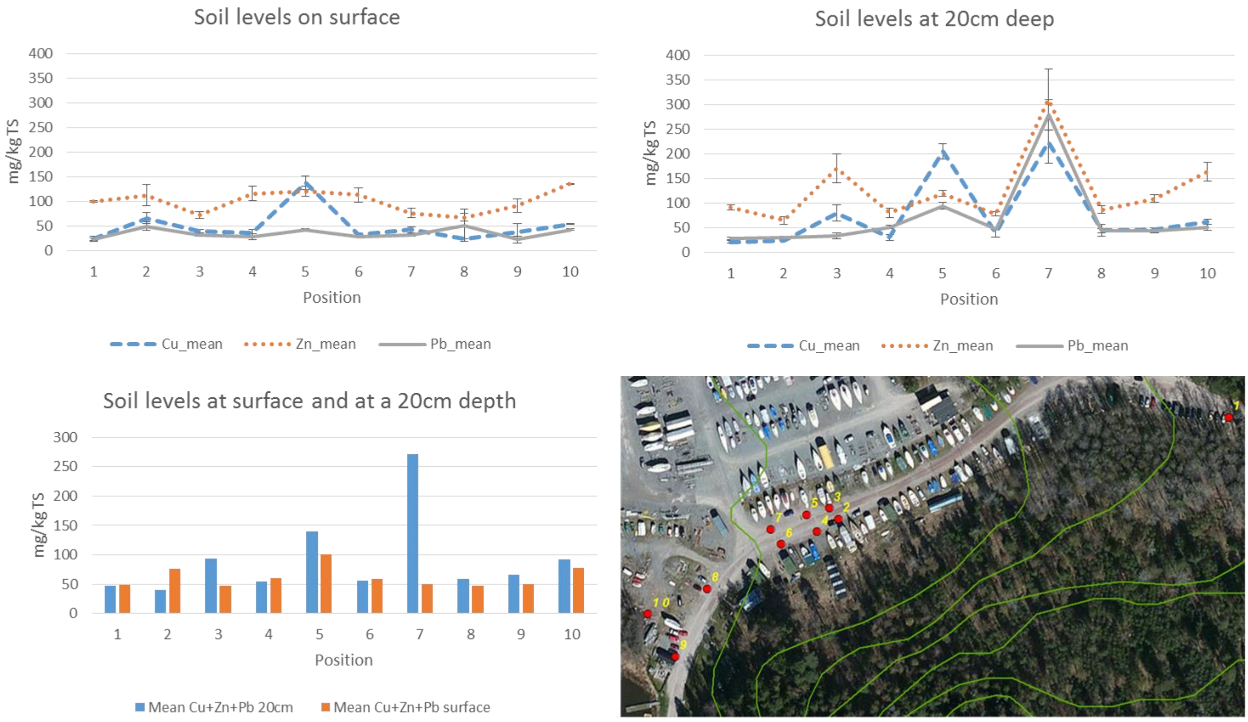


Figure 27 Surface contamination values along surface water flows. Measured spots showed in red. Cu, Zn and Pb values are presented in the graphs below. 20 cm deep figures to the left, top soil figures to the right. Error bars show standard deviation from 3 lab measurements on collected soil.

6 Discussion

Boat hulls, soils, and sediments of the investigated boat yards have proved to be highly contaminated with Cu, Zn, Pb and Sn with concentrations for soil and sediments exceeding guidance values. This is in accordance with the findings of (Eklund & Eklund 2014, and Turner 2010) that metal contamination from boat yard maintenance is an environmental concern. It is also consistent with the findings of Turner et al. (2008) and Turner (2013) that substances coming from sanding and water blasting leads to problems in the environment.

The FPXRF analyzer used in this study, the Delta 50 from Olympus with added functionality for boat hull measurements, has proved to be a quick, accurate and cost efficient tool for screening of metals in boat hulls, soil and sediments. Soil and boat hull screening can be done in situ. Measurements of Cu, Zn and Pb meet accuracy requirements for screening level data, see Figure 21 and Figure 22. Hull screening with a FPXRF is a non-destructive method with no impact on hull finish. Together with data on length and width at the waterline and information about the keel construction the total content of Cu, Zn, Sn and Pb can be estimated for each vessel, see Table 5.

6.1 Screening of boat hulls

When selecting boat hulls for decontamination or approving boats for the use of boat washers an easy to use selecting procedure is needed. A major finding of this screening study is that 25% of the boats are responsible for 70% of the total Cu load and the same group of boats has also 80% of the total Sn load indicating old TBT-based paint, see Table 7. This finding can be used when selecting boat hulls for decontamination. The FPXRF with added functionality (Ytreberg et al. 2015) for quantification of elements in old antifouling paint layers on boat hulls was used to measure the amount of heavy metals in µg/cm^2. Based on this information the total load in kg/hull for all measured boat could be calculated. This is a major advantage of the used FPXRF, comparing with a standard FPXRF that only gives the value in ppm and a calculation of the total load is not possible. This opens up the possibility to introduce detailed requirements on boat hull metal levels.

The FPXRF technique can be used to identify boats with large amounts of old toxic biocide paint that has shown to be harmful to non-target organisms (Eklund et al. 2014). This means that the identified hulls might need to be decontaminated according to existing or other future recommendations. The FPXRF also has a potential for yacht clubs that need to approve boat hulls for the use of different kinds of mechanical cleaning methods in order to minimize leakage of metals to soil and water. This is in line with the findings of Turner et al. (2015) that used a standard FPXRF to measure paint flakes collected from abandoned boats and ships undergoing maintenance and identifying metals that have been banned.

The used FPXRF has proved to be an efficient tool for hull screening. Also Turner et al. (2015) states that the FPXRF technique requires minimal preparation and has a high throughput. An advantage of the used tool is also that it´s non-destructive when measuring the amount of heavy metals on boat hulls. There are today no alternative non-destructive methods available on the market (Eklund et al. 2015).

The FPXRF additional functionality for quantification of elements can be added to similar FPXRF equipment providing the basis for screening of boat hulls on a larger scale. A prerequisite is a 50kV X-ray tube capable to excite heavy elements and detect e.g. the K-lines of Sn.

6.2 Screening of soil

The FPXRF tool can be used to effectively identify boat yard areas that have been contaminated by flaking paint or boat maintenance activities. Screening of the Flottvik and Rosersberg boatyards revealed metal concentrations exceeding guidelines for sensitive land use (80mg/kg) with values up to 500 times for Cu, see Figure 14 and Figure 16. For areas where boats are stored in wintertime the mean values for Cu and Zn are 3 times exceeding the limit for less sensitive land use (Cu 200 mg/kg, Zn 500g/kg) and median values are exceeding the limit.

Good screening performance for Sn is important as Sn is used as an indicator of TBT. Data showed that by increasing the FPXRF measurement time from 60 to 120s, the screening sensitivity of Sn improved with 30%, see Section . More field measurements are needed to address the screening accuracy for Sn as the samples used for confirmatory test were low on Sn content, see Figure 21 and Figure 22.

The selection of soil measuring spots should be done randomly if land use is unknown and focused on suspected spots with boat cradles to find areas with high metal content. Comparing the two strategies used for locating of predefined screening spots a handheld GPS has proved to be more efficient than using a measuring tape. This is consistent with the findings of Amoret et al. (2014) that used random patterns and GPS for soil investigation.

A large area can be covered with 50 to 60 test spots in a single working day. That should be enough to cover a boatyard with up to 500 boats and identify all areas that have contaminant levels exceeding the guideline values. No drying or sieving or other sample preparation is necessary as correlation tests has proved that field performance is good for screening purposes except for Sn where more investigation needs to be done, see Figure 21 and Figure 22. This is in line with the findings of Rees et al. (2014) that also used the FPXRF technique to measure soil contamination from peeling paint on the ground under boat hulls. Usage of the XRF tool for Pb soil measurements has also been investigated by Amoret et al. (2014) and, consistent with our findings, analyses have proved to be accurate and repeatable.

An additional advantage of the FPXRF analyzer is the small disturbance when doing soil measurements, mainly some flattening of the topsoil.

6.3 Screening of sediments

The FPXRF can also be used for detailed analysis of sediments along the pier systems of a marina. Sediments can easily be brought back to lab for freeze-drying and grinding before being measured by the FPXRF to find small to extra-large deviations from recommended values. Similar findings have been reported by Brady et al. (2014) that used XRF and freeze-drying for analysis of metals in sediments. This means that a detailed mapping easily can be done along the pier system and hotspots identified.

This is especially important when planning of dredging activities and selecting what methods should be used to minimize the spreading of heavy metals in the harbor basin. After dredging the same spots can be screened for follow up of the contaminant distribution. If bio-filters are used along the shorefront the efficiency can be checked by screening of dried soil samples from the filters.

6.4 Contamination from boat maintenance

Maintenance areas in boat yards has shown to be highly polluted, see Figure 14 and Figure 16, and restrictions on everyday use must be decided and posted. This is consistent by the findings of Eklund et al (2014) that boatyards are no playing ground for small children.

Detailed screening on two spots used for winter storage and related maintenance activities has shown that very high levels of metals exist in the soil within a couple of meters from the centerline of the boat cradles, see Figure 17. This is probably caused by maintenance work being done without adequate soil protection measures. This makes it clear that stringent rules for maintenance activities need to be implemented giving instructions on how to contain paint residue and how to apply personal safety measures. This finding supports the need to use a canvas when working with paint removal for collecting and later disposal of contaminated paint particles.

6.5 FPXRF cost effectiveness

The FPXRF tool has proved to be a cost effective tool for screening of Cu, Zn, Sn and Pb levels in boat hulls, soil and sediments in contaminated boatyards. The alternative is to use a lab based ICP-OES or similar equipment and brings soil samples or paint flakes back to a lab environment. ICP-OES involve several steps of sample preparation and extraction that are time-consuming and costly (Ytreberg et al. 2015). Lab analysis takes several days and the cost per sample is 340 SEK each for Cu and Zn including soil drying and milling (SLU 2014). For measuring of 100 soil spots, that means an extra cost of 34 000 SEK in addition to other costs for visiting the boatyard. A lab analysis to find old TBT-based paint cost 2500 SEK for each sample. This means that normally only 5 spots in general are checked in a boatyard and no boat hulls (Eklund & Eklund 2012).

The cost for a consultant to do XRF soil measurements in the field is about 2000 SEK for one day plus travelling costs (MRM Konsult AB 2015). This is consistent with the findings of Turner et al. (2015) that the FPXRF technique can do cost efficient measurements of Cu, Pb and Zn in soil. The capital cost of a FPXRF, 400 000 SEK, is typically around five times lower than that of an ICP–MS.

6.5.1 Hull screening

The FPXRF hull screening time used in this study was 30s per measured spot. That means a boatyard with up to 75 boats can easily be screened on a single day even if several shots are done on every boat hull.

A personal observation is that the stabilization time for contamination data presented on the FPXRF, when in field use, indicates that the measuring time can be reduced down to at least 10s. This will enable the screening of several spots on every hull to better reflect the contamination status.

6.5.2 Soil screening

The soil screening FPXRF measuring time used in this study was 120s. That means a boatyard can be screened with high resolution (60 spots) in one day. This made it possible to do a detailed mapping of the investigated boatyards to see differences between storage areas and access roads, see Figure 14 and Figure 16. The locating procedure used at the Rosersberg boatyard, starting from a number of predefined reference points, has proved to be difficult and time consuming and an improved GPS based methodology was used at Flottvik. Together with aerial photos of high resolution the GPS method proved to be a time efficient way of locating the selected spots. For the suspected areas investigation a measuring tape was used to document spot positions as a standard GPS has not the needed spatial accuracy.

As all the measured spots easily can be marked with GPS coordinates comprehensive maps can be produced with tools like Arcmap and Mapinfo. This makes it possible to present data with desired spatial resolution and content to be a base for a risk assessment when planning remedies.

6.6 Screening accuracy

Confirmatory soil samples analyzed both by ICP-MS and XRF demonstrated that the Cu, Zn and Pb measurements meet the guidelines for screening level data and potentially meet definitive level data criteria as defined by EPA (2007).

EPA (2007) also recommends that one sample of twenty should be sent to lab for confirmatory testing. Our findings indicate that the presence of discarded paint particles in the soil, soil structure and moisture will affect the FPXRF measured value to a large extent. This has to be considered when selecting samples for confirmatory analysis. Spots for FPXRF in situ screening and confirmatory sampling must reflect the overall structure and composure of the local area under investigation. This is also pointed out by EPA (2007) that particle size and structure is affecting measurements. As our data shows that good screening performance is possible even in a field environment the need and number of samples for confirmatory analysis can be discussed and adapted to the situation at hand.

Different soil sample preparation procedures in a lab environment show that the measured values of each element is higher for the cryomilled soil samples compared to measuring on raw soil or sieved through 2 mm, see Figure 18 and Figure 19. This is in accordance with findings in EPA (2007) and Imansishi et al. (2010) that the FPXRF is sensitive to particle size. The large standard deviation on the Cryomill data are probably caused by the too small sample size available (5 g), giving a usable thickness of only a few mm covering the FPXRF aperture. For all subsequent lab measurements a room temperature grinder, the FRITSCH Pulverisette grinder, was used. It gives the same particle sizes as the Cryomill grinder but gives 200 g of material and is ten times faster. Lab measurement results for raw and sieved soil are similar proving that good accuracy is possible for soil measurements in the field. Comparing the use of different kinds of containers for lab measurements our result shows that samples should be tested in plastic zip bags rather than in plastic cans, see Figure 20.

6.7 Boatyard findings

Many boats in the Flottvik boat yard have high levels of contaminants. 25% of the boats are responsible for 70% of the total Cu load and the same group of boats also has 80% of the total Sn load indicating old TBT-based paint. This fact might be used to divide the total boat population in categories for cost efficient decontamination reducing significantly the potential risk to soil and water.

Comparing hull contamination values in $\mu g/cm^2$ with another similar study done with the same FPXRF unit in Västerås (Eklund & Ytreberg, 2014) indicate that this is a typical hull contamination situation for boats in Lake Mälaren. The mean bottom area for all measured boats (22 m^2) is similar to the findings of Ambrosson (2008) of 19.75 m^2 indicating that load values in kg can be estimated in other boatyard based on the median values obtained in this study.

In the Rosersberg boatyard only soil was investigated showing high concentrations exceeding guidance values. The difference in soil contaminants between the two boatyards, Flottvik and Rosersberg, is small. The soil in the Flottvik and Rosersberg boatyards are heavily polluted with Cu, Zn and Pb. There are also indications of TBT in the maintenance areas as Sn is present. Comparing with soil findings from 34 boatyards along the Swedish coast (Eklund and Eklund 2014) the Flottvik and Rosersberg all spots median Cu values (69 mg/kg) is lower than the mean median values for the 34 boatyards of 130 mg/kg. Zn values (388 mg/kg) are higher than the mean median value of 180 mg/kg. Pb (33 mg/kg) is lower than the mean median of 150 mg/kg. The reasons for the differences are probably the low number of soil spots measured in the 34 boatyards (mean number = 5) making the values sensitive to area selection and spot location characteristics as paint flakes or soil structure.

The existing load in the top soil layer for Cu in Flottvik is 0.6 mg/m^2. The load in Rosersberg is 4 times higher, 2.7 mg/m^2. The reason might be that Rosersberg having less roads and other areas not used for boat storage in winter time and that a third of the Flottvik area is rather new and has not accumulated that much of contaminants.

The existing load on the measured hulls is 340 kg with a potential to add to the existing soil load of 190 kg. In fact the potential load is higher as 50 boats belonging to Sibk were not screened. Using the average total load figure (Cu+Zn+PB+Sn) of 2 kg/boat means an additional 100kg load to the soil, see Table 7. These values are higher than the findings of Eklund et al. (2014) that calculated the least and worst use of another boatyard to have between 1,800 to 36,500 kg Cu on 12,000 m^2 using a depth of 20cm instead of the 1cm used in this study. That translates to a load of max 0.15 kg/m^2. The differences are probably a result of the few spots (4) used in that calculation making it sensitive to spot selection.

A number of soil hotspots were detected, usually spots where boat hulls have been maintained for a number of years. A detailed check on two hotspots with the FPXRF was done. The first when the boat was in the cradle and a complimentary hull screen showed high contaminant values for the hull (Cu 17600 µg/cm^2, Zn 1800 µg/cm^2, Sn 63 µg/cm^2) indicating that paint residue has accumulated into the ground from the hull. The other screening was done before the boat was in the cradle. The Cu levels in the soil beneath the hulls (9051 mg/kg) were up to 45 times higher than the limit for less sensitive land use and the Zn level (12700 mg/kg) was up to 25 times higher than the limit for less sensitive land use, see Figure 17.

This shows that maintenance activities need to be more regulated with instructions on how to contain paint residue and how to apply personal safety measures (SwAM/HVMFS 2014b). This is also suggested by Turner et al. (2008) and Turner (2010). Accessibilities of Cu, Pb and Zn in contaminated soils are a concern for individuals working in boatyards or visiting (Turner et al. 2009).

Comparing the mean values for metals in top soil spots and 20 cm deep soil spots in Flottvik the contamination levels are about 1.5 times higher deeper down indicating a transport of contaminants from the topsoil. This also corresponds to the findings of Eklund et al. (2014) that concentrations were much lower in the surface compared to the subsurface. Similar measurements in Rosersberg showed that values seem to be higher in the topsoil. However these figures are affected when adding on new gravel so the significance of this finding is probably low and needs further investigation. The samples from Flottvik were taken at an access road that probably has a new top layer more often than the areas where boats are stored. Samples from Rosersberg included boat storage areas.

In Flottvik there is a suspicion that an old waste dump is still leaking contaminants to the boatyard area. As the upstream values in the small stream that runs to Flottvik are lower than the downstream values there is no evidence that the abandoned waste dump is a major source of contamination today. There are probably several connections from the boat yard area to the underground pipe that explains the higher values downstream. The proposed new water quality limit for Cu is 0.5 µg/l and for Zn 5.5 µg/l (SwAM/HVMFS 2014) so the downstream water values (Cu 1.9 µg/l, Zn 19 µg/l) is high. Soil samples from the Rävsta stream bed also show higher metal values downstream indicating that metals is deposited in the stream bed downstream. The water samples taken from the four shafts G1 to G4 in the marsh shows no Cu levels and small Zn levels. This indicates that the marsh area is filtering the stream water reducing the metal level with 50% to 100%. This is also confirmed by the soil samples from the shafts showing metal values around the limit for sensitive land use (Cu 80 mg/kg dw, Zn 250 mg/kg dw). Decomposed reed residues in the shaft closest to the shoreline had even values exceeding the limit for less sensitive land use.

Sediments in the Flottvik harbor show large (x2.5) to extra-large (x4) deviation from recommended values in Table 1. The actual sedimentation rate is not known and thus no dating of the sediment samples was possible. Using a rate of 7 mm/year as measured by Cato et al. (2012) outside Lövsta in Lake Mälaren gives that sediments from a depth of 30 cm shows the contamination values from the boatyard operations in the 1970s. Significant to large deviations for Cu, Zn and Pb is visible down to a depth of 30 cm. Copper shows extra-large deviation (x4) in the upper 10 cm layer. This is probably caused by biocide-containing paint releasing Cu and Zn from boats moored in the pier system and the reason might be that Cu and Zn based paints are still in use by boats from the Flottvik boatyard.

Comparing with an earlier sediment investigation (Ramböll 2010) that listed mean values for Cu and Zn the corresponding figures for the E-pier and Service pier top layer are higher in our investigation, see Figure 9. This is probably due to the dredging activities after the Ramböll sampling in 2010 when tons of sediments were removed and old sediments were spread in the harbor water. The dredging activity was done to enable the use of a sublift vehicle for the launching of vessels. The dredged masses were temporally placed just north of the boatyard and then later transported away from the Flottvik area. Measurements on the temporary storage area showed values under the limit for sensitive land use (Cu 80 mg/kg dw, Zn 250 mg/kg dw).

Altogether the following recommendations should be considered for the Flottvik and Rosersberg boatyards.

Storage areas must be marked as contaminated and not therefore suitable for other activities as contamination figures are exceeding limits for less sensitive land use. A new layer of topsoil should be added in the old storage areas. Information must be given to boat owners using the pier systems that no biocide paint is allowed for boats in the Lake Mälaren. Boat maintenance practices must be established to prevent heavy metals to enter soil, sediments and water. Boat washers must be made available for the yacht clubs situated in the Lake Mälaren. If possible, hulls with high contamination values should be identified and decontaminated.

6.8 Swedish legislation

The first directive for antifouling paints was published by the Swedish Chemical Agency in 1998 and states "For boats with principal berth in the Gulf of Bothnia and in lakes, there are no approved anti-fouling paints. Boats in these waters may only use such paints that do not require approval" (Keml 1998). On their website today (Keml, 2015) there is a clarification stating "There are no approved antifouling paints for pleasure boats with their main mooring in inland waters". This means that no biocide based paint is approved for boats that have their main mooring in the Lake Mälaren and specific for Flottvik and Rosersberg is that all boats renting a mooring in summertime cannot use antifouling paints.

The discussion today also resolves around the use of wash pads with adequate sewage water treatment or using boat washer equipment on boats in the water with or without fresh or old biocide-based paint (SwAM/HVMFS, 2014b). Some yacht clubs e.g. Sticklinge Udde and Bosö yacht club, Lidingö, have already started activities to stop the use of biocide paints and will be relying on mechanical cleaning measures like boat washers or handheld tools during the sailing season. One obstacle today is how to interpret the recommendation from SwAM/HVMFS (2014b) stating that mobile or stationary boat washers may not be used on hulls containing biocide based paint. Clearly the ambition must be to find a way for boat owners, that choose not to use biocide based paint, to have as many alternative cleaning methods as possible.

A yacht club is responsible to prevent damage from an ongoing operations. This means a responsibility to take all relevant precautions that are not unreasonable in view of the involved cost. It is also important to have clear rules for members and also check that they are observed (Langlet et al. 2014). Of the three investigated yacht clubs there is only one, RBK, that provides easy to find information on the homepage about the handling of contaminated boat hulls (RBK 2014). For the other yacht clubs there is no information to be find about the restriction for using biocide-based paints in inland waters under a “wharfs rules/environmental” header.

Information on existing national regulations and specific rules for boatyards must be easy available and communicated to boat owners. Local regulation from the county and municipality level must be established in cooperation with affected yacht clubs.

6.9 Way forward

Clearly the boat owners and yacht clubs have a responsibility to reduce most of the contaminant flow to water and soil (Langlet et al. 2014), especially into Lake Mälaren as it is a source for drinking water. Today efficient methods are available that can be implemented on pleasure boatyards like boat washers, manual scrubbers, boat lifts, hull sheets, silicon paint and ultra sound transmitters. The Swedish Yachting Association provides detailed information of alternative to antifouling paint (SBU 2015). Suitable mechanical methods like rotating boat washers in the water for cleaning of hulls needs to be accessible at a reasonable cost and within a short distance.

Focus should be on how to decrease the heavy metal load from vessels to Lake Mälaren in a cost-efficient way. That means introducing a risk management approach by identifying the majority of vessels that have the possibility to release high amounts of contaminants during washing or other maintenance activities. The new FPXRF boat hull module (Ytreberg et al. 2015) can be used to measure the total contaminant load on every boat and the potential risk can easily be estimated.

According to the findings in Flottvik 25% of the boat hulls contain about 70% of the contaminant load and 50% of the hulls have about 90% of the total load. The investigated boat yard may be regarded as typical and the same distribution can be expected on similar boat yards in the Lake Mälaren.

An easy to use method is needed to identify and classify boat hulls with high levels of metals. This means a single figure should be provided giving a reasonable estimation of the total load. With help of the FPXRF boat hull module the mean Cu, Zn, Pb and Sn load per cm^2 for a number of spots on all fiber glass vessels can be measured. With a good estimation of the bottom hull area based on boat dimensions and type the total amount of contaminants can be calculated. Based on the toxicity of the detected metals and existing regulation limits, factors can be defined and used in the final calculation to produce a single “weighted” value indicating boat hull status. This information will then be the input to the risk management approach where specific limits for different remediation activities are specified.

Half of the vessels might only contain less than 10% of the weighted load meaning they can be certified for using any type of mechanical cleaning, even in the water, at a small cost for the environment and with a subsequent potential for reducing the need of applying biocide boat paint if outside inland waters.

Big boats have larger bottom area and will have a higher total load in kg when comparing with smaller boats that have the same concentration in $\mu g/cm^2$ on the hull. But this is in line with the “polluter pays principle” (Environmental Code, 1998) and they represent a higher risk to the environment. Surely it is more efficient to screen and decontaminate a big vessel with high levels than many small boats.

Load distribution data obtained in this study on Cu, Zn, Sn and Pb levels may be regarded as typical when deciding on limits to be implemented in recommendations/regulations on a local or national level. In my opinion focus should be on the boat population having a high probability to pollute soil and water (high total load) and therefore should be decontaminated. Limits should be defined for a total weighted load per boat as to facilitate screening activities. Limits should also be adapted for boats on the west coast, east coast and inland waters.

The FPXRF can also be used to identify boats that will be allowed to use boat washers in the sea and high water pressure tools without having to install additional water cleaning equipment. For boatyards that only have decontaminated vessels or vessels certified by the FPXRF boat module with a low level of existing biocide paint there is no need for a costly wash pad with cleaning treatments and high maintenance requirements and boat washers can be used.

Soil contamination measurements can be done randomly or focused on suspected spots. For handling of old deposits of heavy metals the adding of a new layer of top gravel on hotspots could be a way forward to protect people that perform maintenance activities or just visit the boat yard. This must then be combined with more stringent rules for maintenance to prevent the contamination of the new top layer. Particles coming from sanding and water blasting of boat hulls must be collected and the ground covered. Højenvang (2003) has shown that with better working methods the contaminant spill to ground can be reduced with 99%. It is therefore important to assess the risk and the remediation need of boatyards with help of a cost-effective screening method and decontaminate vessel with high risk of releasing heavy metals under maintenance activities.

If existing old boat yards are to be used for other purposes, i.e. housing, our findings indicate that a complete decontamination has to be done in all areas where boats with biocide paint have been stored. Other areas can be randomly checked by FPXRF as to identify other hotspots.

As of today only a small number (34) of Swedish boat yards have been investigated (Eklund and Eklund 2014). This means that many old boatyards still have soil hotspots with metal values exceeding existing limits many times. Suspected areas should be screened for heavy metals and properly marked and treated according to the findings.

Moderate levels of heavy metals were measured in the marsh shafts indicating that there is a transport downhill even if this study has found no proof that contaminants travel with surface water. This means that surface water need to be directed to wetlands or bio filters along the shore front in order to reduce the level of heavy metals coming into the sea. This is especially important for the runoff from hard-made surfaces. Blecken (2011) has shown that bio filtration can reduce metals with up to 90% even in cold climates.

7 Conclusion

The FPXRF analyzer used in this study has shown to be a quick, accurate and cost efficient tool for screening of contaminated boatyards.

A major usage area is the detection of boat hulls with high levels of old biocide paint. The total levels of contaminants on every boat hull can easily be determined. This information can then be used when approving boats for different types of maintenance procedures or when selecting boats for decontamination activities.

The FPXRF can also be used for detection of contaminated soil and sediments. Gathered data can be used in a risk assessment of the area and conclusions can be drawn on the need for remediation.

The investigation of the two boatyards in the Lake Mälaren has shown that high levels of heavy metals are detected in boat hulls, soil and sediments often in par with what have been detected in other boatyards on the East and West coast of Sweden. This is a threat to the Lake Mälaren as it is a source for drinking water and an inland lake system where no biocide-based paints is allowed. Paint recommendations and regulations need to be communicated to boat owners.

To reduce toxic flows to sediments and water from the boatyards, existing hulls need to be tested for contamination and the hulls with the highest risk of releasing heavy metals decontaminated. Boat washers and other cleaning equipment must be made available at a reasonable cost and distance. Surface and ground water flows from contaminated areas need to be directed and filtered through wetlands or other bio filters.

8 Acknowledgements

First I would like to thank my supervisor Britta Eklund for all the positive feedback during the project and for sharing most of the field work. Maria Lagerström helped me with most of the soil and sediment sampling and showed me how to handle all the collected data.

Thanks to Marika Wennbom for the Arcmap support, Martin Ogonowski for the R statistic support, Hanna Gustavsson for the Cryomill introduction and Sofia Bejgarn for being a good roommate and my first line of support.

Finally, thanks to my wife Elisabeth Sjöholm for answering all my chemistry questions!

9 References

Alzieu, CL., Sanjuan, J., Deltreil, JP., Borel, M. (1986) Tin contamination in Arcachon Bay: effects on oyster shell anomalies. Mar Pollut Bull 17: 494–498

Ambrosson, J. (2008) MAMPEC-scenarier för Sveriges östkust och västkust. Konsultrapport till KemI 2008-10-08, 48 sid. In Swedish.

Amoret, L., Brad, G., Jill M., Pulsipher, B., Gorton, A., Bisping, L., Brandenburger, J., Pino, C., Martinez, D., Rana, K., Wellman, D. (2014) 100-OL-1 Operable Unit Pilot Study: XRF Evaluation of Select Pre-Hanford Orchards. Pacific Northwest National Laboratory PNNL-23868. 160p.

Blecken, G., Marsalek, J., Viklander, M. (2011) Laboratory Study of Stormwater Biofiltration in Low Temperatures: Total and Dissolved Metal Removals and Fates. Water, Air, & Soil Pollution July 2011, Volume 219, Issue 1-4, pp 303-31

Brady, J., Godwin, A., Wayde, M., Martens, A. and Goonetilleke, A.(2014) Enrichment, distribution and sources of heavy metals in the sediments of Deception Bay, Queensland, Australia. Marine Pollution Bulletin Volume 81, Issue 1, 15 April 2014, Pages 248–255

Cato, I.,Kjellin, B. (2012) Investigation of sediment in Mälaren outside Lövsta/Undersökningar av Mälarens botten utanför Lövsta gamla deponiområde, Hässelby, Stockholms kommun. SGU-rapport: 2012:6 (In Swedish)

Eklund, B., Elfström, M., Borg, H. (2008) TBT originates from pleasure boats in Sweden in spite of firm restrictions. Open Environ Sci 2:124–132

Eklund, D., Eklund, B. (2012) Contamination in Swedish boatyards – overview/Förorening av båtuppläggningsplatser – en sammanställning av utförda undersökningar i svenska kustkommuner. ITM rapport 208, 27 s., 4 bilagor. (In Swedish)

Eklund, B. Johansson, L., Ytreberg, E. (2014) Contamination of a boatyard for maintenance of pleasure boats. Journal of Soils and Sediments, 14:955-967

Eklund, B., Eklund, D. (2014) Pleasure boat yard soils are often highly contaminated. Environmental management. Volume 53, Issue 5 (2014), Page 930-946.

Eklund, B. Ytreberg, E, (2014) Preliminary report from hull measurement in Västerås/Preliminär rapport från mätningar av metallinnehåll I bottenfärger på båtar uppställda på Lögarängen I Västerås 2014-04-10 (In Swedish) 11p.

Environmental Code Miljöbalken 1998:808

EPA (2007) US Environmental Protection Agency. METHOD 6200, FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT Rev 0 2007. 32p.

EU (2000) Water Framework Directive 2000/60/EC of the European Parliament

EU Directive (2013) 2013/39/EU of the European Parliament and of the Council Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Sub- stances in the Field of Water Policy 2013, 12.8.2013. 2011/0429 (COD).

Hempel (2014) Paint Manual SE Interactive

Højenvang, J. (2003) Maintenance analysis/Afvaskning og afslibning af biocidholdig bundmaling i forbindelse med vedligeholdelse af lystbåde på land. Miljöstyrelsen Miljøprojekt Nr. 772 2003. 73s. (in Danish)

Hollert H, Keiter S, König N, Rudolf M, Ulrich M, Braunbeck T (2003) A new sediment contact assay to assess particle-bound pollutants using zebrafish (Danio rerio) embryos. J Soils Seiments 3:197–207

Karlsson J, Breitholtz M, Eklund B (2006) A practical ranking system to compare toxicity of anti-fouling paints. Marine Pollut 52:1661–1667

Karlsson, J., Sundberg, H., Åkerman, G., Grunder, K., Eklund, B., Breitholtz, M (2008) Hazard identification of contaminated sites—ranking potential toxicity of organic sediment extracts in crustacean and fish. J Soils Sediments (2008) 8:263–274

Karlsson J, Ytreberg E, Eklund B (2010) Toxicity of anti-fouling paints for use on pleasure boats and vessels to non-target organisms representing three trophic levels. Environ Pollut 158:681–687

Keml (1998) Swedish Chemical Agency, The use of antifouling products. Decision 1998-02-24 Rev 1998-12-18. In Swedish.

Keml (2015) Antifouling paints and products http://www.kemi.se/sv/Innehall/Fragor-i-fokus/Batbottenfarger-och-antifoulingprodukter/ (2015-05-20)

Imanishi, Y., Bando, A., Komatani, S., Wada, .S., Tsuji, K. (2010) Experimental Parameters for XRF Analysis of Soils. Graduate School of Engineering, Osaka City University Japan. International Centre for Diffraction Data 2010 ISSN 1097-0002

Langlet, D. Eklund, D. Eklund, B (2014) Responsibility for contaminated ground in boatyards with focus on yacht clubs/Ansvar för förorenad mark på båtuppläggningsplatser med fokus på ideella föreningar. ITM-rapport 222. 28s (In Swedish)

Lunn, I., 1974. Antifouling – A Brief Introduction to the Origins and Developments of the Marine Antifouling Industry. BCA Publicatons, Thame, ISBN 0950129917.

MBK (2014) Märsta Yacht Club / Om MBK, Märsta båtklubb http://www.mabk.se/historik/# Retrieved: 20141115. (In Swedish)

Marguí, E., Grieken, R. (2013) X-ray Fluorescence Spectrometry and Related Techniques : An Introduction. Momentum Press. New York,

Ramböl (2010) FLOTTVIKEN, SIGTUNA Investigation before water work permit / Undersökning för Anmälan om vattenverksamhet Stockholm 20100317. 42p (In Swedish)

Rees, A., Turner, A., Comber, S. (2014) Metal contamination of sediment by paint peeling from abandoned boats, with particular reference to lead. Science of the Total Environment 494–495 (2014) 313–319.

RBK (2014) Rosersberg Yacht Club / Om Rosersbergs båtklubb http://rosersbergsbatklubb.se/Klubbens-historia.php Retrieved: 20141115. (In Swedish)

SBU (2015) Swedish Yachting Association / Svenska Båtunionen. http://www.batunionen.com/modules/miljoparm/pages/default.asp?pID=52 (2015-05-20)

Schiff, K., Brown, J.B., Diehl, D., Greenstein, D., (2007). Extent and magnitude of copper contamination in marinas of the San Diego region, California, USA. Mar. Poll. Bull. 54, 322–328.

Sibk (2014) Sigtuna Yacht Club / Om Sigtuna båtklubb http://www.sigtunabk.se/om-sibk/ Retrieved:20141115. (In Swedish)

Sigtuna (2014) High PCB values in fish from Oxundasjön / Mycket höga halter av PCB i fisk från Oxundasjön http://www.sigtuna.se/sv/Pressmeddelanden1/Mycket-hoga-halter-av-PCB-i-fisk-fran-Oxundasjon/ Retrieved: 20150118. (In Swedish)

SLU (2014) Växtnäringsläras analyser och prislista Gäller från 1 febr. 2014.

SwAM/HVMFS (2014a) Swedish Agency for Marine and Water Management 2014:XX Remiss uppdatering HVMFS 2013:19 17s (In Swedish)

SwAM/HVMFS (2014b) Swedish Agency for Marine and Water Management 2014:XX Remiss uppdatering HVMFS 2013:19 17s (In Swedish) Guidelines for bottom washing of recreational boats / Båtbottentvättning av fritidsbåtar Riktlinjer, revised in december 2014. (In Swedish)

Swedish Transport Agency (2010) Investigation on boating 2010—a study about Swedish pleasure boats and how they are used. /Båtlivsundersökningen 2010—en undersökning om svenska fritidsbåtar och hur de används) (In Swedish)

SEPA (2006) Swedish Environmental Protection Agency. Mobility of metals in the ground / Metallers mobilitet i mark. Rapport 5536. 115p. (In Swedish)

SEPA (2009) Swedish Environmental Protection Agency Sampling strategies for contaminated soil / Provtagningsstrategier för förorenad jord RAPPORT 5888 JULI 2009 (In Swedish)

SEPA (1999) Swedish Environmental Protection Agency Environmental quality assessment / Bedömningsgrunder för miljökvalitet – Kust och hav 5p. Tabell 30 i Naturvårdsverkets rapport 4914 (1999) (In Swedish)

SEPA (2013) Swedish Environmental Protection Agency) Environmental objectives http://www.miljomal.se/sv/Environmental-Objectives-Portal/Undre-meny/About-the-Environmental-Objectives/4-A-Non-Toxic-Environment/ (2015-01-17)

Turner, A., Singh, N., Millard, L. (2008a) Bioaccessibility and bioavailability of Cu and Zn in sediment contaminated by antifouling paint residues. Environ Sci Technol 42:8740–8746

Turner, A., Fitzer, S., Glegg, G.A., (2008b). Impacts of boat paint chips on the distribution and availability of copper in an English ria. Environmental Pollution 151, 176–181.

Turner, A., Singh, N., Richards, JP. (2009) Bio accessibility of metals in soils and dusts contaminated by marine antifouling paint particles. Environmental Pollution 157 (2009) 1526–1532.

Turner, A. (2010) Marine pollution from antifouling paint particles. Marine Pollution Bulletin 60 (2010) 159–171

Turner, A. (2013) Metal contamination of soils, sediments and dusts in the vicinity of marine leisure boat maintenance facilities. J Soils Sediments 13:1052–1056

Turner A., Comber S., Rees A., Gkiokas D., Solman K. (2015) Metals in boat paint fragments from slipways, repair facilities and abandoned vessels: An evaluation using field portable XRF. Talanta 131 (2015) 372-378.

Yebra, D.M., Kiil, S., Dam-Johansen, K., 2004. Antifouling technologydpast, present and future steps towards efficient and environmentally friendly antifouling coatings. Progress in Organic Coatings 50, 75–104.

Ytreberg, E., Karlsson, J., Eklund. B. (2010) Comparison of toxicity and release rates of Cu and Zn from anti-fouling paints leached in natural and artificial brackish seawater. Science of the Total Environment 408 (2010) 2459–2466

Ytreberg, E (2012) Dispersion of biocide paint – contributions / Spridning av biocider från båtar – Undersökning av olika källor och dess bidrag, ITM Stockholms universitet. ITM 215 23p

Ytreberg, E., Lundgren, L., Bighiu, M., Eklund, B. (2015) New analytical application for metal determination in antifouling paints. (In press).

Appendix 1 – Boat hull data from Flottvik boatyard

Flottvik hull levels in µg/cm^2 SB: Sailing boat MB: Motor boat

Type	Position	Length m	Cu	Zn	Pb	Sn
SB	SBK	11	21742	13783	10	76
SB	SBK	12	1089	5568	3	1
SB	SBK	13	10510	253	0	5
MB	SBK	10	33735	1654	3	155
MB	SBK	10	1779	18916	11	59
SB	SBK	12	1379	511	0	4
SB	SBK	10	6349	251	0	8
SB	SBK	11	14693	318	0	17
SB long keel	SBK	12	1367	85	0	0
SB long keel	SBK	12	344	4420	1	11
SB	SBK	12	13107	3958	3	30
SB	SBK	12	11405	2239	2	22
SB long keel	SBK	12	23	16	6	0
SB	SBK	10	4000	2895	0	15
MB	SBK	10	4	77	0	91
MB	SBK	10	3474	545	0	8
MB	SBK	10	3718	1560	0	8
SB	SBK	10	3232	9894	4	48
MB	SBK	10	9598	89	0	22
SB long keel	SBK	10	16099	934	2	101
SB	SBK	12	7088	5101	4	34
SB	SBK	10	6574	92	0	0
SB long keel	SBK	11	3554	4654	13	200
SB	SBK	11	1747	6398	3	17
MB	SBK	10	264	1145	0	4
SB	SBK	9	2060	9238	3	29
MB	SBK	10	5491	4318	8	13
SB	SBK	8	2982	76	0	9
SB	SBK	11	1635	23312	12	7
SB	SBK	8	280	328	0	106
SB	SBK	8	2336	4839	0	4
SB	SBK	8	3108	9891	18	5
SB	SBK	9	3115	10643	1	1
MB	SBK	10	1650	1624	0	2
SB	SBK	12	9897	1230	1	15
SB	SBK	10	270	5867	2	17
SB	SBK	8	43	1972	1433	63
SB	SBK	9	992	4166	854	184
SB	SBK	12	349	3322	0	2
MB	SBK	10	4930	29690	15	14
MB	SBK	8	3640	1402	0	0
MB	SBK	8	1356	6640	3	9
MB	SBK	8	31	9251	7	3
MB	SBK	7	945	3515	0	1
MB	SBK	8	166	13772	10	5
SB	SBK	11	983	18607	9	13

Type	Position	Length m	Cu	Zn	Pb	Sn
MB	SBK	10	645	4	0	5
MB	SBK	8	239	11395	14	7
MB	SBK	8	2134	282	0	3
SB long keel	SBK	8	2301	7051	66	103
MB	SBK	6	1206	1029	8	527
MB	SBK	8	11	176	0	8
MB	SBK	8	26	0	0	3
MB	SBK	8	1029	4256	0	84
SB	SBK	10	23398	450	2	63
MB	SBK	6	2861	6830	9	91
MB	SBK	5	99	335	0	29
MB	SBK	7	1448	2596	0	1
MB	SBK	8	28	2474	68	46
MB	SBK	6	2852	118	0	7
MB	SBK	6	92	6694	8	66
MB	SBK	7	906	6872	4	3
SB	SBK	6	969	441	47	111
SB	SBK	8	621	2380	5	6
MB	SBK	5	2072	3407	0	4
MB	SBK	8	2624	4170	29	330
MB	SBK	7	246	15708	14	169
MB	SBK	7	1003	14016	8	284
MB	SBK	6	19	168	0	4
Jolle	SBK	3	1447	747	17	414
MB	SBK	7	618	5645	4	314
MB	SBK	6	924	11591	8	6
MB	SBK	7	47	6855	3	142
MB	SBK	7	24	5545	5	37
SB	SBK	8	2066	4653	6	3
MB	SBK	5	403	456	952	13
MB	SBK	5	7515	6311	4	25
MB	SBK	8	629	3235	4	0
MB	SBK	7	523	1823	2	217
MB	SBK	7	2	24	0	2
MB	SBK	6	27	4901	0	4
SB	SBK	6	37	9402	7	3
SB	SBK	14	3447	9131	9	10
SB long keel	SBK	12	27	4	0	0
SB long keel	SBK	12	13659	470	6	22
SB	SBK	10	15166	3676	8	45
SB long keel	SBK	6	496	594	0	1
SB	SBK	7	3655	1284	0	201
MB	SBK	9	57	143	0	15
MB no paint	SBK	5	1	19	0	0
SB	SBK	9	1497	5823	3	9
SB	SBK	5	817	71	5	32
SB	SBK	6	2666	5411	116	1027
SB long keel	SBK	7	3025	7638	1	564
SB	SBK	12	31347	8340	9	54
SB	SBK	9	7319	100	0	1

Type	Position	Length m	Cu	Zn	Pb	Sn
SB	SBK	10	0	0	0	0
MB	SBK	7	4126	573	0	64
MB	SBK	10	5665	2644	3	7
SB	SBK	11	377	1453	0	242
SB long keel	SBK	12	875	17079	13	4
SB	SBK	13	567	4366	0	39
SB	SBK	10	5098	1981	0	54
SB	SBK	12	531	10102	9	9
SB long keel	SBK	12	2853	737	4	536
MB	SBK	12	2414	4085	0	1
SB	SBK	12	1745	24	0	0
SB long keel	SBK	10	1880	3976	0	421
SB	SBK	10	961	1675	0	24
SB	SBK	12	2	0	0	4
MB	SBK	10	1575	4313	3	5
MB	SBK	8	5128	8001	5	7
MB	SBK	7	1151	111	1314	0
MB	SBK	7	6785	1270	0	10
SB	N upper row	5	7412	25839	10	195
SB	N upper row	5	58	227	2199	58
MB	N upper row	5	1318	3971	107	105
MB	N upper row	6	646	3103	11	185
MB no paint	N upper row	5	2	0	0	4
MB no paint	N upper row	6	2	0	0	1
MB	N upper row	5	4378	7767	13	12
MB	N upper row	5	1910	8660	10	2
MB	N upper row	5	4	11	0	2
SB	N upper row	7	3482	3456	3	249
MB	N upper row	5	1431	5934	12	5
MB	N upper row	5	18	1080	4	0
MB no paint	N upper row	6	3	0	0	0
MB	N upper row	6	29281	10202	8	137
SB long keel	N upper row	8	17	102	1489	3
MB	N upper row	9	51	913	0	42
MB no paint	N upper row	7	1	0	0	0
MB	N upper row	5	16	0	0	6
MB	N upper row	6	5606	20337	10	111
MB	N upper row	6	653	7055	2	8
SB long keel	N upper row	8	22	7838	6	21
SB	N upper row	8	5068	84	0	3
SB	N upper row	7	139	8374	8	22
SB	N upper row	8	13649	3062	5	32
SB	N upper row	7	99	12762	11	3
SB	N upper row	7	835	1650	13	193
MB	N upper row	6	133	4246	3	15
MB	N upper row	7	680	294	0	166
MB	N upper row	6	921	6693	6	7
SB	N upper row	7	2027	775	14	0
SB long keel	N upper row	8	7890	154	639	293
SB long keel	N upper row	7	25413	981	6	122

Type	Position	Length m	Cu	Zn	Pb	Sn
MB no paint	N upper row	9	0	210	0	8
MB	N upper row	7	716	13	0	1
SB	N upper row	8	1148	2920	0	32
SB	N upper row	8	3679	2039	0	25
MB	N upper row	7	32	3167	5	0
MB	N upper row	7	2927	75	0	24
MB	S upper row	8	3527	4515	84	11
SB long keel	S upper row	7	92	11133	5	9
SB	S upper row	8	3	-2	0	0
MB	S upper row	7	917	7934	20	0
MB	S upper row	8	2561	17836	11	7
MB	S upper row	8	1613	2409	8	1
MB	S upper row	10	4815	18338	0	44
MB	S upper row	8	289	2642	0	0
MB	S upper row	6	172	7453	8	3
MB	S upper row	7	122	8125	1	2
MB	S upper row	6	23	6260	0	39
MB	S upper row	7	110	1995	1803	6
MB	S upper row	7	2607	5818	7	61
MB	S upper row	6	906	572	136	50
MB	S upper row	8	27996	2316	7	776
SB	S upper row	7	4457	4561	1	2
MB	S upper row	7	3104	4199	0	47
MB	S upper row	6	47	4225	3	158
SB	S upper row	7	2950	416	0	134
SB long keel	S upper row	7	119	7074	8	19
SB	S upper row	7	5467	16655	97	22

Appendix 2 – Soil data from Rosersberg and Flottvik

Soil contamination values in mg/kg TS

Location	North	East	Cu	Zn	Pb	Sn
Flottvik rand	6611370	656741	14	356	20	12
Flottvik rand	6611362	656724	13	1303	39	0
Flottvik rand	6611350	656683	320	206	34	0
Flottvik rand	6611344	656744	65	1052	62	0
Flottvik rand	6611341	656706	25	2627	264	0
Flottvik rand	6611333	656687	51	2275	1012	0
Flottvik rand	6611333	656657	19	860	143	0
Flottvik rand	6611331	656775	87	184	29	0
Flottvik rand	6611327	656771	77	386	159	0
Flottvik rand	6611326	656600	28	56	32	0
Flottvik rand	6611321	656874	519	384	76	0
Flottvik rand	6611321	656756	27	84	92	0
Flottvik rand	6611318	656771	29	227	35	10
Flottvik rand	6611314	656669	57	109	13	12

Location	North	East	Cu	Zn	Pb	Sn
Flottvik rand	6611311	656631	1060	177	15	0
Flottvik rand	6611308	656711	45	260	22	0
Flottvik rand	6611302	656667	74	183	31	0
Flottvik rand	6611302	656697	14	509	45	0
Flottvik rand	6611301	656789	81	6714	134	12
Flottvik rand	6611301	656846	0	2004	79	0
Flottvik rand	6611300	656853	38	3072	75	8
Flottvik rand	6611299	656685	25	283	41	0
Flottvik rand	6611298	656680	16	699	35	0
Flottvik rand	6611298	656852	733	87	25	50
Flottvik rand	6611298	656746	108	771	31	0
Flottvik rand	6611296	656709	63	272	19	8
Flottvik rand	6611296	656624	17	320	17	14
Flottvik rand	6611295	656726	107	2281	70	12
Flottvik rand	6611295	656829	9	546	14	8
Flottvik rand	6611292	656781	35	2257	57	9
Flottvik rand	6611289	656704	48	12632	68	14
Flottvik rand	6611287	656786	398	143	20	9
Flottvik rand	6611284	656831	31	388	21	0
Flottvik rand	6611284	656751	179	588	23	0
Flottvik rand	6611279	656783	51	683	16	0
Flottvik rand	6611277	656737	37	358	10	0
Flottvik rand	6611276	656682	67	76	11	0
Flottvik rand	6611272	656725	156	401	66	11
Flottvik rand	6611272	656642	32	1284	49	10
Flottvik rand	6611271	656668	14	8617	17	11
Flottvik rand	6611271	656702	459	2389	43	0
Flottvik rand	6611268	656755	4413	8400	1080	13
Flottvik rand	6611260	656718	304	594	22	0
Flottvik rand	6611258	656642	13	51	13	0
Flottvik rand	6611258	656723	35	100	13	13
Flottvik rand	6611251	656694	50	89	28	0
Flottvik rand	6611249	656738	37	62	18	0
Flottvik rand	6611248	656659	22	83	14	9
Flottvik rand	6611240	656705	15	63	19	8
Flottvik rand	6611231	656662	27	78	14	0
Flottvik rand	6611230	656674	18	62	18	0
Flottvik rand	6611225	656666	27	72	14	0
Flottvik rand	6611225	656676	25	71	18	13
Flottvik rand	6611221	656659	31	75	17	0
Flottvik rand	6611203	656685	11	38	10	0
Flottvik susp	6611307	656870	626	1883	175	55
Flottvik susp	6611304	656860	230	1618	412	0
Flottvik susp	6611296	656848	593	420	148	35

Location	North	East	Cu	Zn	Pb	Sn
Flottvik susp	6611288	656838	2584	1831	2536	247
Flottvik susp	6611279	656826	245	5111	127	17
Flottvik susp	6611273	656817	5415	5514	278	14
Flottvik susp	6611266	656804	7358	868	280	151
Flottvik susp	6611262	656795	67	655	16	0
Flottvik susp	6611256	656788	1555	4957	35	221
Flottvik susp	6611251	656778	350	5689	53	0
Flottvik susp	6611245	656770	1210	863	36	66
Flottvik susp	6611240	656762	229	1359	29	0
Flottvik susp	6611235	656753	273	280	552	35
Flottvik susp	6611234	656741	14	74	13	0
Flottvik susp	6611224	656732	21	58	15	0
Flottvik susp	6611232	656727	51	103	24	0
Flottvik susp	6611224	656720	15	62	17	0
Flottvik susp	6611219	656711	235	227	32	0
Flottvik susp	6611364	656682	34	104	38	16
RBK	6606968	661178	160	356	20	0
RBK	6606978	661172	373	1303	39	0
RBK	6606988	661172	70	206	34	0
RBK	6606996	661176	838	1052	62	56
RBK	6606970	661170	1363	2627	264	0
RBK	6606976	661168	1169	2275	1012	0
RBK	6606982	661170	411	860	143	19
RBK	6606996	661162	55	184	29	0
RBK	6607006	661174	550	386	159	33
RBK	6607010	661162	26	56	32	0
RBK	6607010	661156	206	384	76	0
RBK	6607012	661158	24	84	92	0
RBK	6607020	661148	79	227	35	0
RBK	6607028	661148	0	109	13	0
RBK	6607035	661145	16	177	15	0
RBK	6607033	661135	104	260	22	0
RBK	6606964	661182	81	183	31	8
RBK	6606980	661182	205	509	45	0
RBK	6606986	661184	2591	6714	134	65
RBK	6606992	661181	1455	2004	79	45
RBK	6606970	661198	1279	3072	75	0
RBK	6606974	661194	459	283	41	23
RBK	6606962	661202	290	699	35	11
RBK	6606952	661208	25	87	25	0
RBK	6606944	661206	1012	771	31	0
RBK	6606956	661196	53	272	19	0
RBK	6606944	661200	70	320	17	0
RBK	6606932	661196	220	2281	70	0

Location	North	East	Cu	Zn	Pb	Sn
RBK	6606924	661198	58	546	14	0
RBK	6606938	661210	625	2257	57	0
RBK	6606934	661220	608	12632	68	0
RBK	6606958	661188	30	143	20	0
RBK	6606958	661176	80	388	21	0
RBK	6606946	661190	70	588	23	0
RBK	6606940	661186	58	683	16	0
RBK	6606922	661208	14	358	10	0
RBK	6606912	661208	0	76	11	10
RBK	6606922	661218	38	401	66	0
RBK	6606928	661226	1839	1284	49	33
RBK	6606914	661212	45254	8617	17	20
RBK	6606908	661220	2109	2389	43	0
RBK	6606914	661226	1736	8400	1080	28

Soil samples from surface and 10cm/20 cm depth

Boatyard	Depth	Spot	Cu	Zn	Pb	Sn
Rosersberg	Surface	J2	847	1929	71	16
Rosersberg	Surface	F12	199	216	108	33
Rosersberg	Surface	I6	1775	1833	37	21
Rosersberg	Surface	J3	20064	7315	32	24
Rosersberg	Surface	K4	168	1253	56	13
Rosersberg	Surface	E9	1147	2102	221	44
Rosersberg	Surface	G6	132	970	57	12
Rosersberg	Surface	F9	558	1404	77	23
Rosersberg	Surface	H4	81	961	17	12
Rosersberg	10 cm	J2	81	215	36	11
Rosersberg	10 cm	F12	111	136	79	13
Rosersberg	10 cm	I6	2233	1347	200	94
Rosersberg	10 cm	J3	1109	887	52	13
Rosersberg	10 cm	K4	102	404	41	8
Rosersberg	10 cm	E9	430	400	95	19
Rosersberg	10 cm	G6	57	183	38	8
Rosersberg	10 cm	F9	144	238	69	11
Rosersberg	10 cm	H4	155	316	41	22
Flottvik	Surface	1	25	101	23	No values
Flottvik	Surface	2	66	113	50	No values
Flottvik	Surface	3	40	72	32	No values
Flottvik	Surface	4	36	116	28	No values
Flottvik	Surface	5	138	121	42	No values
Flottvik	Surface	6	33	113	29	No values
Flottvik	Surface	7	43	77	32	No values
Flottvik	Surface	8	24	68	52	No values
Flottvik	Surface	9	39	91	23	No values

Boatyard	Depth	Spot	Cu	Zn	Pb	Sn
Flottvik	Surface	10	54	136	43	No values
Flottvik	20cm	1	22	91	28	No values
Flottvik	20cm	2	25	65	30	No values
Flottvik	20cm	3	80	170	33	No values
Flottvik	20cm	4	31	80	52	No values
Flottvik	20cm	5	205	120	95	No values
Flottvik	20cm	6	40	78	48	No values
Flottvik	20cm	7	224	310	279	No values
Flottvik	20cm	8	45	87	44	No values
Flottvik	20cm	9	46	109	44	No values
Flottvik	20cm	10	62	164	51	No values

Data from ground water shaft and Rävsta stream bed

Shaft	Depth (cm)	Cu mg/kg	Zn mg/kg	Pb mg/kg	Cu Std	Zn Std	Pb Std
G1	5	78.3	197.3	45.0	3.8	6.7	0.0
G1	15	34.3	111.0	35.3	4.0	2.6	2.5
G1	20	33.3	92.3	24.6	3.8	7.2	1.9
G1	40	19.0	70.0	21.6	1.0	2.6	2.8
G1	60	4.0	29.3	10.9	6.9	2.5	1.5
G1	85	35.0	78.3	26.6	4.6	4.2	2.2
G2	5	73.3	191.0	45.0	5.0	12.1	3.6
G2	10	18.3	74.3	25.3	4.0	9.1	4.6
G2	30	55.7	146.7	46.7	4.2	4.5	5.5
G2	50	17.0	50.3	18.3	7.1	4.2	1.3
G3	5	76.7	215.0	43.0	1.2	5.2	1.7
G3	15	50.3	140.3	53.3	5.9	10.2	3.5
G3	50	67.3	143.3	57.3	4.0	7.6	0.6
G4	5	154.3	503.0	63.0	3.8	18.5	2.6
G4	35	202.3	1024.3	85.3	13.1	59.5	2.1
G5	5	23.0	91.3	49.0	2.6	1.2	29.4
G6	5	32.0	129.0	30.3	6.1	7.0	1.2