Center for
ARKTISK TEKNOLOGI

Danmarks Tekniske Universitet
Technical University of Denmark

Environmental Impact of Heavy Metals Released from the Landfill in Sisimiut (Greenland)

DTU Course 11427: Arctic Technology

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December 3, 2012

Declaration and Acknowledgements

This project was conducted as group work. During the project period (February - December 2012), the work was equally distributed between the group members. All field and laboratory work was performed together. The data analysis was divided and peer reviewed by the other group member. The results were discussed and the report was written together.

This project would not have been possible without the help and support of a lot of persons, who we would like to thank. Our two supervisors Gunvor Marie Kirkelund (DTU Civil Engineering, Arctic Technology Center) and Lis Bach (DMU) have been of great help with all kinds of questions and problems that occurred during the project, for which we want to thank them. Their help was professional and they kept us motivated during the whole project period. The laboratory and field work was supported by the lab technicians Sabrina Madsen, Thomas Friis and Malene Møller, who were always available for questions and professional assistance. The trip to Greenland was a very special and memorable experience and the organization (Ingrid Vernimmen and Niels Hoedeman) was great.

Finally, we would like to thank the Municipality of Sisimiut (Qeqqata Kommunia) - especially Jacob S. Lundgaard and Hans Holt Poulsen - for supporting this project, being available for questions and letting us work unhindered on the landfill.

Abstract

The impact of the landfill in Sisimiut on the heavy metal concentrations in the aquatic environment was investigated. This was done by analyzing soil, sediment, water, seaweed and blue mussel samples, as well as using passive samplers. Previous studies showed elevated heavy metal concentration close to Greenlandic landfills.

The problematic in this case was that a stream is flowing through the landfill, which was suspected to wash out heavy metals more efficiently. From the samples, the heavy metal concentrations were obtained using ICP analysis following the corresponding laboratory methodology.

Concluding from the results it is clear that the landfill is the reason for elevated heavy metal concentrations in the aquatic environment. Especially the stream is exposed to high concentrations, which are washed into the ocean. In the ocean the heavy metals get quickly diluted, so that only the cove at the landfill is influenced, while after ca. 150 m offshore no significant elevations could be measured. The threshold value for foodstuffs was not exceeded in the mussel samples. Also other pollution sources are close to the landfill and the existence of it is unavoidable. Shielding the stream from the landfill could mitigate the impact on the environment.

Dansk Sammenfatning

Påvirkningen til vandmiljøet af tungmetaller fra lossepladsen tæt på Sisimiut blev undersøgt. Dette blev gjort ved at analysere prøver af jord, sedimenter, vand, tang og blåmuslinger, samt brug af *passive samplers*. Tidligere studier har vist forhøjet koncentration af tungmetaller tæt ved de Grønlandske lossepladser.

I dette tilfælde er problematikken, at et vandløb løber igennem lossepladsen, hvilket giver mistanke om, at tungmetallerne bliver frigivet mere effektivt. Fra prøverne blev tungmetallernes koncentration opnået ved hjælp af ICP analyse, efterfulgt af laboratoriemetoder.

Ud fra resultaterne kan det klart konkluderes, at lossepladsen er grunden til forhøjet koncentration af tungmetaller i vandmiljøet. Vandløbet er især udsat for en høj koncentration, hvilket bliver frigivet direkte ud i havet. I havet bliver koncentrationen af tungmetaller hurtigt udvandet, det vil sige, at kun bugten foran lossepladsen bliver påvirket, mens der 150 m fra kysten, ikke blev fundet nogle signifikante forhøjninger heraf. Grænseværdien for fødevarer var ikke overskredet i prøverne fra blåmuslingerne. Også, andre forureningskilder er til stede tæt på lossepladsen, hvis eksistens er uundgåelig. At afskærme vandløbet fra lossepladsen kunne mindske påvirkningen af vandmiljøet.

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Chapter 1

Introduction

In Greenland, waste was put into landfills without previous treatment over the last decades. Landfills in Greenland consist of a mixture of all kinds of waste, are very simple and do not have any control of leachate and gas. They are normally located close to the ocean, not far away from the settlements [Eisted and Christensen, 2011]. It has previously been shown that heavy metal contents around Greenlandic landfills are increased in fish, mussels, seaweed and sediments [Asmund, 2007]. Heavy metals are bio-accumulative and toxic. High contents in fish and mussels can pose a danger to human health when eaten. Even at low concentrations, repeated intake of contaminated food can become a health risk due to the accumulation of the heavy metals in the body. Furthermore, heavy metal concentrations higher than the limits given for foodstuffs pose a potential threat to the local fishing industry. The fishing industry is Greenland′s most important exporting industry [Statistics Greenland, 2011] and companies such as Royal Greenland A/S stress the pristine fishing grounds, sustainable and environmental friendly fishing [Royal Greenland, 2012].

For tourism, another important industry, Greenland sells a picture of itself of untouched nature [Visit Greenland, 2012]. Landfills close to settlements and potentially contaminated seafood can therefore not only be of disadvantage for locals, but also for tourism.

This project aims to quantify the heavy metal contents in the marine environment close to the landfill in Sisimiut. Samples of mussels, seaweed, sediments and soils were analyzed, as well as deployed passive samplers. The role of the stream running through the landfill was highlighted and suggestions for the reduction of pollution from the landfill were made.

Chapter 2

Background

In this chapter, an introduction to the waste situation in Greenland in general and the landfill in Sisimiut in particular is given. Previous studies on heavy metal releases from landfills and mines are presented and the theoretical background of using passive samplers, in this case diffusive gradients in thin films devices (DGTs), is given.

2.1 Waste situation in Greenland

In Greenland, waste is handled by the municipalities (kommuner). In their research-article *Waste management in Greenland: current situation and challenges* Eisted and Christensen (2011) analyzed the waste situation in Greenland. Greenlandic consumers have nowadays the same opportunities as northern European consumers and have adopted modern comfort and life-style products. That means, the Greenlandic society has also imported waste of similar consistence as European waste and the problem of getting rid of it. Until recently, this waste was just deposited on landfills, without previous treatment. More recently, incinerators have been introduced to burn the combustible waste and hazardous waste is collected separately and exported.

Landfills today are therefore a mixture of all kind of waste from the last decades and have possible heavy metal sources in cars, trucks, heavy machinery and bottom ash from the incineration plants [Eisted and Christensen, 2011]. All over Greenland between 30,000 and 35,000 tons of waste are landfilled yearly, including around 6,000 tons of bottom ash from the incinerators [Eisted and Christensen, 2011]. Compared to European standards landfills are very simple and do not have any control of leachate or gas.

Larger towns with export possibilities, such as Sisimiut, can generate enough metal waste to export it every fifth or tenth year under gaining financial profit. Around 1,000 tons of metal are exported for recycling each year, which equals to around 30 kg per inhabitant and year in Sisimiut [Eisted and Christensen, 2011]. Hazardous waste is including the fly ash from the incinerators and is exported (around 730 tons per year, which equals to 12 kg per inhabitant and year) [Eisted and Christensen, 2011].

Eisted and Christensen (2011) conclude that landfills will be always a main part of Greenlandic waste management, as municipal waste quantities are small and land plentiful. They note however that taking the local conditions and surroundings of a landfill into account could reduce the pollutant loads into the environment at low costs.

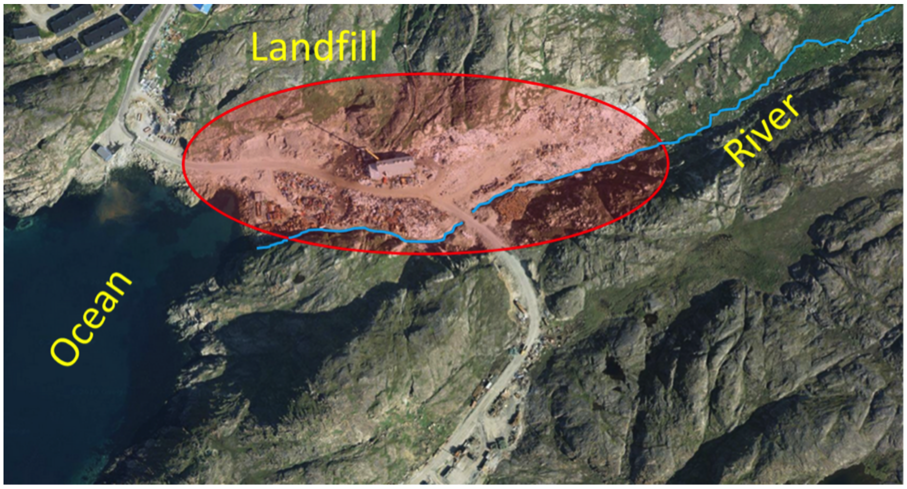

Figure 2.1: Map of the landfill in Sisimiut [Google Earth, 2012]

2.2 The landfill in Sisimiut

The landfill in Sisimiut (figure 2.1) is located just south of the city. It was built in 1981 and has an area of around 25,000 square meters. Already in 1998 it was much bigger than expected when it was built [Robro and Yding, 2000]. On the west it is directly adjacent to the Davis Strait. The incinerator of Sisimiut is placed on its ground. Previous studies about the incinerator have been conducted for example by Simon Challet during the Arctic Technology course in 2011. A stream, the outflow of Spejdersø (Lake Spejder, located within the eastern part of the city), runs through the landfill, uncovered at the moment. As can be seen from the satellite picture (see figure 2.1), large areas of the landfill are uncovered. Figure 2.2 on the left shows the landfill in 2004. A lot of different potential sources of heavy metals could be expected. In 2004, the Municipality of Sisimiut (today Qeqqata) started cleaning up the landfill, so that in the end of 2004, a lot of open metal waste was removed [Kanukoka, 2012], see figure 2.2 on the right.

Figure 2.2: Landfill in 2004, before and after the cleaning [Kanukoka, 2012]

As far as it could be judged from the distance, it was suspected that the run-off during rain events and the washout via the stream are significant contributors to the washout of heavy metals and other pollutants from the landfill into the marine environment.

2.2.1 Recent developments

The following paragraphs are mainly based on interviews with Jacob S. Lundgaard and Hans Holt Poulsen from Qeqqata Kommunia (the Municipality of Sisimiut) in the beginning of August, 2012. Since beginning of August, a waste shredder has been in use, shredding the bulky municipal waste. Since then, the incinerator has been working much better and it is expected to burn the piles of waste that have been accumulated over the last two years within the next five years. The bottom ash coming from the incinerator is distributed over the landfill. The future vision is, to avoid storing municipal waste on the landfill, but instead directly burn it and pile up the bottom ash together with e.g. concrete waste.

Data of the amount or consistency of the waste deposited at the landfill is not available, as only the number of trucks delivering waste is counted and not the waste weight or volume.

Recently, a recycling system for glass and metals has been introduced in Sisimiut. The glass is going to be crushed in the nearby stone pit and then supposed to be used in asphalt production. For the metal waste, final decisions where to store and what to do with it, have not been made, yet.

The municipality is at the moment considering to build a dam before the stream reaches the landfill. This way, the landfill would become less visible and the stream could be diverted, e.g. led through a pipe below the landfill. The costs of piping the stream would be around DKK 6000 per meter of pipe, i.e. around DKK 2.6 mio for the pipe construction alone. Furthermore, local citizens claim to have seen salmon in the stream (which is doubted by the authors of this report, due to the general condition of the stream). These arguments could be used against a pipe construction. This report aims, as stated before, to provide arguments, whether the stream is a major contributor to pollution in the marine environment around the landfill.

Another recent development is the plans of the Government of Greenland to build a three times bigger incinerator in Sisimiut and burn the waste from all settlements between Thule and Nuuk there. Reasons for this plan are that Sisimiut already has a heating net that is connected to the incinerator and a year-long ice free harbour. At the moment, around 25% of the houses, mainly big apartment buildings, are connected to this heating net, while other houses receive their heat via a lot of smaller, separate nets. If these smaller nets were connected, the heat of a bigger incinerator could be distributed all over the city.

The fact, that the city itself anticipates a population increase of around 500-600 inhabitants in the next 10 to 15 years and the creation of the new harbour, which shall attract Canadian fishermen to discharge their catch in Greenland and thus receive direct access to the European market, are additional factors when considering the future of the landfill.

At the moment it can be said that there are a lot plans and visions for the future. However, the realization of them has not or has just started, so that the decisions made in the close future may have huge impact on the way, Sisimiut treats its waste and the landfill influences the environment.

2.3 Previous studies

2.3.1 Cryolite mine in Ivittuut

A previous study, where the concentrations of heavy metals (here: lead and zinc) in the arctic marine environment were measured by analyzing seaweed and blue mussels was carried out in Ivittuut at Arsuk Fjord in South Greenland by Johansen et al. (2010). Here, the pollution was due to cryolite mining from 1854 to 1987. This study found elevated lead and zinc levels in seaweed and blue mussels. The zinc pollution was spread out further in the fjord than the lead pollution. As blue mussels are part of the diet in Greenland and may be collected and eaten, they recommended not to collect mussels on a coastal stretch of around 5 km around Ivittuut, as the maximum residue level for lead in Greenlandic diet items was exceeded. Since the mine is closed since 1987, the heavy metal concentrations in seaweed and mussels are decreasing now.

2.3.2 Four different landfills in Greenland

In the study *Recipientenundersøgelse ved grønlandske lossepladser* (engl.: Investigation of receiving waters around Greenlandic landfills) from the Danish EPA Danmarks Miljøundersøgelser (DMU) in 2007, the marine environment around four Greenlandic landfills was investigated [Asmund, 2007]. The samples of blue mussels, seaweed, fish, sea urchins and sediments were analyzed for the heavy metals mercury, cadmium, lead, zinc, copper, chromium, nickel and arsenic, as well as for other, non-metal pollutants. Table 2.1 gives an overview over the results, only for the planned samples (seaweed, blue mussels, sediment) taken in this project in Sisimiut.

Table 2.1: Results of heavy metal concentration measurements in the marine environment at four Greenlandic landfills [Asmund, 2007]

	Seaweed	Blue mussels	Sediment
Lead (Pb)	clearly elevated	clearly elevated	clearly elevated
Zinc (Zn)	clearly elevated	NO	NO
Copper (Cu)	clearly elevated	NO	clearly elevated in the acid-soluble fraction
Mercury (Hg)	few cases	few cases	few cases
Cadmium (Cd)	NO	NO	NO
Nickel (Ni)	NO	NO	NO
Arsenic (As)	NO	NO	NO

As can be seen, especially concentrations of lead, zinc and copper are elevated around the Greenlandic landfills. It was suspected that the measurements carried out in this project would probably lead to comparable results at the landfill in Sisimiut. Although the heavy metal concentrations were clearly elevated, in contrast to the marine environment at the cryolite mine in Ivittuut none of the samples exceeded the food guidelines. This is also suspected at the landfill in Sisimiut, although of course the local situation (e.g. river washout) could lead to different results.

2.4 Passive samplers (DGTs)

DGT stands for *Diffusive Gradients in Thin films.* These devices will be utilized to measure the heavy metal concentrations in water. They were invented in Lancaster by Bill Davison and Hao Zhang. Based on the manual *DGT for measurements in waters, soils and sediments* [Davison and Zhang, 1993] the theory of DGTs is presented in the next sections.

2.4.1 Operation

The simple device uses a layer of chelex resin impregnated in a hydrogel to accumulate the metals. The resin-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. It is the establishment of a constant concentration gradient in the diffusive layer that forms the basis for measuring metal concentrations in solution quantitatively without the need for separate calibration.

2.4.2 Principles for use in waters

DGTs work by accumulating the component measured for from the solution where the device has been deployed. They are designed to (a) bind selectively only the substances of interest and (b) accurately control the transport of the substances to the device.

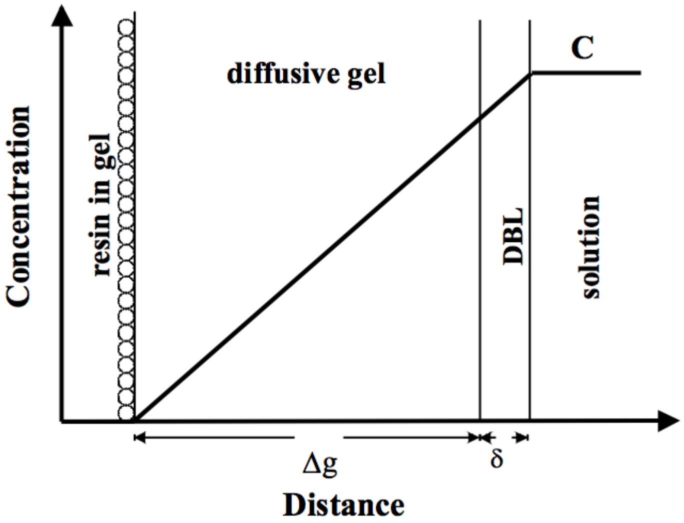

Figure 2.3: Schematic cross-section through a DGT device in contact with solution

The DGT technique is based on a simple device that accumulates solutes on a binding agent after passage through a hydrogel which acts as a well defined diffusion layer (figure 4.1). A binding agent such as a resin, selective to the target ions in solution, is immobilized in a thin layer of hydrogel (binding-gel). It is separated from solution by an ion permeable hydrogel layer (diffusive gel) of thickness Δg. An scheme of the different parts of the DGT is shown in the figure above.

The flux, J ($mol{\cdot}cm^2{\cdot}s^{-1}$), of an ion through the gel is given by Fick′s first law of diffusion (equation 2.1), where D is the diffusion coefficient ($cm^2 \cdot s^{-1}$) and $\frac{dC}{dx}$ ($mol \cdot cm^{-4}$) is the concentration gradient.

$$J = D\frac{dC}{dx} \tag{2.1}$$

Neglecting the boundary layer thickness (δ) due to the fact that it is small compared to the thickness of the diffusive layer (Δg) leads to the next equation:

$$J = D\frac{C}{\Delta g} \tag{2.2}$$

Several techniques can be used to measure the mass bound to the resin. After retrieving the layer, ions are eluted with a known volume, V_e(ml), of an acid solution (here 1 HNO_3 in the case of metals bound to chelex resin). And the concentration C_e was measured using ICP analysis. The mass (M) will be calculated with the next expression:

$$M = \frac{C_e(V_g + V_e)}{f_e} \tag{2.3}$$

considering that f_e is the dilution factor and the experiment is based on immersions of 24h. M can be used to calculate the flux through the known area of the exposed diffusive layer, A (cm^2)

$$J = \frac{M}{A \cdot t} \tag{2.4}$$

Rearranging the Equation 2.2 and Equation 2.4, the concentration of the mass will be expressed as follows

$$J = \frac{M \cdot \Delta g}{D \cdot t \cdot A} \tag{2.5}$$

It is necessary to consider that the diffusion coefficient in the gel can be measured for each temperature and it does not depend on the concentration of other components in the solution.

The expression calculated before is shown assuming a negligible boundary layer thickness. In the case it is not insignificant and the diffusion coefficients in the gel (D_g), filter (D_f) and water (D_g) are all different; the equation should be utilized is:

$$\frac{1}{M} = \frac{a}{C\,A\,t}(\frac{\Delta g}{D_g} + \frac{\Delta f}{D_f} + \frac{\delta}{D_w}) \tag{2.6}$$

2.5 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma spectrometry is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.

The appearance of an ICP-MS is shown as follows.

Figure 2.4: Inductively coupled plasma mass spectrometer

Chapter 3

Methods

The concentration of heavy metals in the marine environment outside the landfill in Sisimiut is investigated by the analysis of:

- Blue mussels
- Seaweed
- Sediments
- Passive Samplers (DGTs)

Seaweed, e.g. brown seaweed (*Fucus vesiculosus*) and blue mussels (*Mytilus edulis*) are suitable indicators for elevated concentrations of heavy metals in an aquatic environment, as they are sessile and accumulate metals from the surrounding waters [Johansen et al., 2010]. Therfore, they are showing a heavy metal pollution over a longer time span. This is a big advantage, as the concentrations of heavy metals in the water could vary over serveral magnitudes, depending on the sources. If for example high loads of heavy metals were flushed into the marine environment during a rain event, seaweed and mussels will show elevated levels even after the rain event.

Blue mussels filtrate the water for food and therefore collect all kinds of pollutants effectively [Asmund, 2007]. As shown above, copper and chromium concentration can be elevated in the sediment close to landfills. By using passive samplers, it is investigated, if they give acceptable results, so that in future those can be used more often in order to reduce the impact of investigations to the environment by removing biota and sediments.

With the concentrations measured from different locations in the ocean near the landfill, the influence of the landfill on the aquatic environment can be visualized and assessed. The measured values can be compared to those of other Greenlandic landfill sites as found in [Asmund, 2007] and to threshold values for mussels intended for eating.

The role of the stream will be investigated by deploying one DGT before it reaches the landfill and one just where it flows into the bay. This investigation could lead to very important conclusions when discussing possible ways of reducing the heavy metal wash out. If found that the stream is the main transport media of the pollutants, putting it into a pipe or covered canal would be one rather simple and effective measure.

Another significant influence of how much heavy metals reach the marine environment is the storage of the waste. Therefore, it will be tried to map different waste categories in the landfill area using GPS. An overview over the situation could lead to some recommendations of how to optimize waste storage in regard to minimizing heavy metal leaching. If possible, the landfill could be divided into different waste category areas and by soil sample analysis, the most heavy metal leaching categories can be identified.

The samples were analyzed by using inductively coupled plasma mass spectrometry (ICP). The laboratory work was conducted during the fall semester 2012 at DTU. The analysis was conducted for the metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni) and zinc (Zn). In the following sections, the used methods to extract the heavy metals from the samples are described.

3.1 Blue mussels

For the sampling of the blue mussels, two nets with around 30 mussels were placed at two locations (S1 and S2) and attached to buoys. The mussels originated from a location in the Second Fjord, around 20 km north of Sisimiut. They were present at their respective sites for the period from the 6^{th} of July to the 12^{th} of August. At location C6, enough mussels were attached to the rocks, so that they could be collected for analysis. For comparison reasons, all mussels had a similar shell length (ca. 4-5 cm). After collection, the blue mussels were opened with a knife. Water was allowed to drip out for 2 minutes, before the meat of the mussels was cut out with a scalpel. For each station, two samples were prepared, containing the meat of around 6-8 mussels. The wet weight was measured and the samples were dried in an oven at 60 °C for 24 hours.

The dried samples were transported back to Denmark, where they were were grinded and homogenized using mortar and pestle. 0.4 g of the samples were put into an autoclave container (in triplicates) and 15 mL of 1:1 HNO_3 (nitric acid) was added. The acid digestion took place in an autoclave at a temperature of 125 °C and a pressure of 1.4 bar during 30 minutes. The cooled samples were then filtrated through a 0.45 μL filter using a vacuum pump. The samples were then filled up to 25 mL with de-ionized water and analyzed in the ICP.

3.2 Seaweed

At several locations along the coast of the landfill and the southern bay shore, seaweed samples were taken. As only the tips of the seaweed were analyzed, they were cut off after collection. The following procedure was equivalent to that of blue mussels.

3.3 Sediment and soil

Sediments are the final sink of many pollutants [Asmund, 2007]. To measure the pollutant deposition coming from the landfill, good results can be obtained, if the samples are taking from a flat zone of active sedimentation. The sediment was collected using a sediment grab. Soil samples were collected by hand. The sediment and soil samples were dried in an oven at 105 °C for 24 hours, after they have been collected.

The dried samples were transported back to Denmark, where the heavy metals were extracted by acid digestion. For this, the samples were homogenized and 1.00 g was put into an autoclave container. 20.00 mL of 1:1 HNO_3 (nitric acid) was added. The digestion took place in an autoclave at a temperature of 125 °C and a pressure of 1.4 bar during 30 minutes. The cooled samples were then filtrated through a 0.45 μL filter using a vacuum pump. The samples were then filled up to 50 mL with de-ionized water and analyzed in the ICP. For each station, triplicates were taken. The same procedure was used to prepare the reference material (DORM-3).

3.4 Passive Samplers (DGTs)

After retrieval of the DGT units, they were rinsed with de-ionized water and stored in a tight plastic bag at 5 °C. In order to retrieve the resin-gel, the unit capsule was broken at the weak point and the filter and the diffusive gel were peeled off. The resin gel was then placed in a long glass tube and 0.6 mL of 1M HNO_3 was added, so that the resin gel is fully immersed in the solution. The extraction was given 24 hours, whereafter 0.4 mL of the sample was taken with a pipette and 4.4 mL of milli-Q water was added. The samples were then analyzed in the ICP.

3.4.1 Modification of the procedure to obtain the concentrations from DGTs in this project

The preparation of the sample to analyze later in the spectrometer consisted firstly of 0.6 ml of HNO_3 (1M) and the resin gel taken from the DGTs, which was already impregnated with the metals. The solution had to be resting for 24 h before being tested.

In the next step a sample of 0.4 ml of the HNO_3 was mixed with 4.6 ml of milli-Q water. This means, the extracted sample only contained 66.7 % of the total ions in the resin gel. This solution was delivered to the technician, who analyzed the sample in order to obtain the concentrations of the different metals in the solution. Notice, the final solution is different to the solution described in the manual according to [Davison and Zhang, 1993] and consequently, the procedure to attain the concentration of the metals in the locations of the DGTs was changed slightly.

In the calculation of the final concentration the next phases were carried out:

- First phase

  Calculate the mass of the metals contained in the solution of HNO_3 & milli-Q water

  $$M_{HNO_3} = \frac{C_{HNO_3}}{(V_{HNO_3} + V_{H_2O})} \tag{3.1}$$

  with:

  M_{HNO_3}, Mass of the metals contained in the solution of the HNO_3 and water

  C_{HNO_3} , Concentration of metals in the solution of the HNO_3 and water

  V_{HNO_3}, Volume of the acid in the solution

  V_{H_2O}, Volume of the water in the solution

- Second phase

  Apply the rule of three to get the masses of the metals in the first solution with the acid and the gel from the DGTs. If the mass contained in 0.4 ml of HNO_3 is known, the mass contained in 0.6 ml is known, too.

  $$M_6 = \frac{M_{HNO_3} \cdot 0.6}{0.4} \tag{3.2}$$

  with:

  M_6, Mass of the metals contained within 0.6 ml of acid

- Third phase

  Divide by the dilution factor (0.8 according to [Davison and Zhang, 1993]) in the acid in order to obtain the mass of metals contained in the DGT (in the gel)

  $$M = \frac{M_6}{f_e} \tag{3.3}$$

with:

M, Mass of the metals accumulated in the DGTs

- Fourth phase

  Calculate the concentration of the metals in the aqueous environment where the DGTs were situated.

  $$C_{DGT} = \frac{M \cdot \Delta g}{D \cdot t \cdot A} \tag{3.4}$$

  where Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.14 mm), D is the diffusion coefficient of metal in the gel (data obtained from [Davison and Zhang, 1993]), t is deployment time (see appendix) and A is exposure area (A=3.14 cm^2).

Chapter 4

Field Work

The field work was conducted between the 30^{th} of July and the 17^{th} of August 2012 in Sisimiut, Greenland.

4.1 Material & Use

The main material used during the field work was pre-ordered and shipped before arriving in Greenland. After the preparation of the material, the locations for the samples were decided and finally set. The DGTs were located in holes which had been shaped into plastic cylinders (figure 4.2). Two DGTs per cylinder were attached, in order to have a spare in case one fell off and to compare their measurements. A rope was used to attach the cylinder to fixed places (buoys with anchors in the ocean, stationary objects on land for the stream) and nylon to attach the DGTs to the cylinders.

Following, Pictures of different items utilized during the field work are shown:

Figure 4.1: Diffusive Gradients in Thin-films, DGT

Figure 4.2: Plastic cylinder with holes to place the DGTs

Figure 4.3: Rope used to attach the objects to fixed spots

Figure 4.4: Nylon to secure the DGTs to the Cylinder

Figure 4.5: Web with stones inside to keep the DGTs below the sea surface

4.2 Work in the Field

The installation of the different devices and the collection of samples were done across several days. In order to get a longer time for the heavy metals to diffuse through the diffusive layer of the DGTs, the first task of the work was to deploy them. In the stream of the landfill, the DGTs were located in three different places: one before the stream reaches the dump, another half through and the last one at the end of the landfill without falling yet into the sea. In all these spots, samples of sediments as well as water samples were taken at the same time.

In figure 4.6, the different work sites are shown. The locations where seaweed was taken are represented with the green marks, the soil spots with the yellow marks, DGTs location in the stream in red and finally, blue-mussels and DGTs in the sea in blue. The spot far from the shore, used as a reference location, is not displayed in this picture (S0 at Qeqertarmiut island).

Besides the spots where the DGTs were located, soil samples were also taken from other places around the landfill to compare the normal properties of the soil in areas not influenced by the dump. The seaweed was taken along the shore; in close places to the mouth of the stream and further areas to get less influenced samples of seaweed.

In order to set the DGTs and take the water samples as well as the sediments in the ocean the assistance of the technicians and supervisors with a boat was necessary for two days. The first day to place the DGTs and the second day almost at the end of the stay in order to take back all the samples and the material.

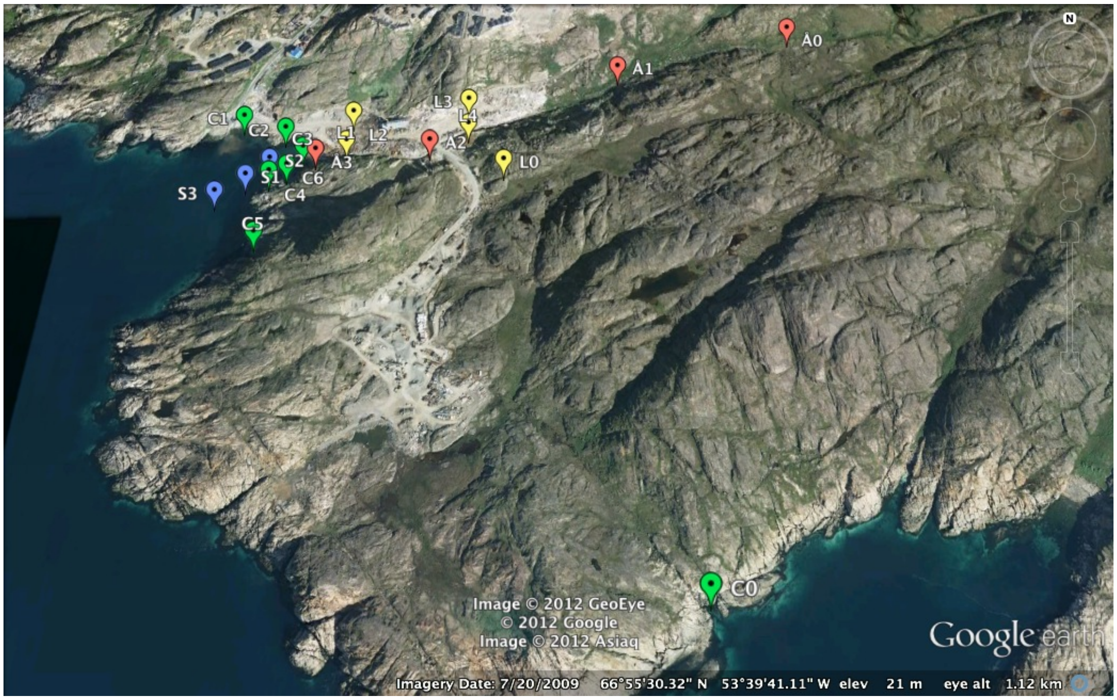

Figure 4.6: Map of the landfill with all sites where samples were taken

Chapter 5

Results and Discussion

5.1 Quality control

In order to ensure that the conducted measurements of the samples deliver reliable results, a reference sample was measured (DORM-3). The results and the comparison to the certificate values are shown in table 5.1. The confidence interval of the certificate values is equal to two times their standard deviation.

Table 5.1: Comparison of the measured heavy metal concentrations and their certificate values [National Research Council Canada, 2007].

	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Certificate value [mg/kg]	6.88	0.29	1.89	15.5	347	1.28	0.395	51.3
Confidence interval [mg/kg]	0.3	0.02	0.17	0.6	20	0.24	0.05	3.1
Sample [mg/kg]	2.10	0.30	1.70	15.82	320.72	1.26	0.43	55.78
Measurement deviation [mg/kg]	-4.78	0.01	-0.19	0.32	-26.28	-0.02	0.03	4.48
Relative error [%]	69.5	3.7	9.8	2.1	7.6	1.4	8.8	8.7

As marked in red, the measurements for arsenic (As) are not precise, maybe due to bad precision of the ICP analysis machine. For the other metals, reasonable good precision could be achieved (Cr, Fe and Zn are just outside of the confidence interval, as marked yellow), indicating that the laboratory work and the ICP were up to standard. Another reference material (MESS-3) has been measured, but since only a very small and not representative sample could be acquired, these measurements were discarded.

5.2 Mapping of the landfill and soil contamination

The present distribution of waste types on the landfill was investigated by site inspection. The result can be seen in figure 5.1.

The eastern part, adjacent to the shore is characterized by metal waste, hereunder ship wrecks, trucks, cars and a variety of smaller metal waste pieces. Next to the incinerator, a recycling station is established and gas cylinders and batteries (car- and ship batteries, some of which are leaking) are stored. In the two large, red marked areas, mixed municipal waste is stored before it is being shredded and burned. The piles of this waste reach up to ca. 5 meters. The bottom ash is disposed closer to the stream and the fly ash is stored just south of the stream, close to the road, before it is getting exported. The fly ash is contained in bags and there has been no indication that these bags could be leaking. On the other side of the road, old, mainly empty oil barrels are

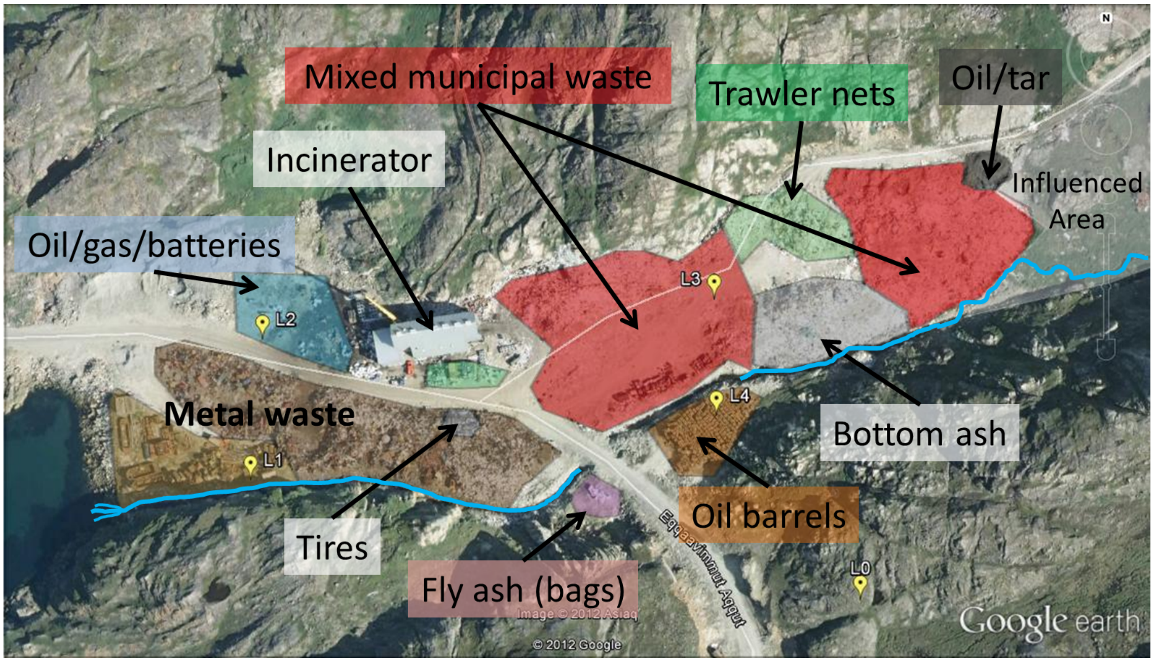

Figure 5.1: Categorization of the waste distribution [Google Earth, 2012]

stored. At the western end of the landfill, a pond containing tar and oil has been established. The environment is evidently influenced by the landfill around 400 meters up the valley towards the east, where pieces of municipal waste can still be found.

Furthermore, it has to be stressed that the above picture is just a snapshot of the situation in August, 2012. As can be seen in figure 5.2, the present landfill is build on a deep layer of older waste. Therefore, the current picture only shows the waste distribution on the top.

In order to get an overview over the contamination of the top soil at different locations of the landfill, several soil samples have been analyzed (see locations L0-L4 in figure 5.1). The results are shown in figure 5.3. The red line indicates the recommended environmental assessment criteria (EAC) for soil (according to the Swiss Federal Order on Soil Pollution [Bundesbehörden der Schweizer Eidgenossenschaft, 1998]), concentrations below these lines should be targeted. These values are legal target values in Switzerland, however, they are applicable for other countries as well and are generally a bit stricter than target values from other countries [Huber et al., 2008].

Figure 5.2: Deep layer of waste below the ground

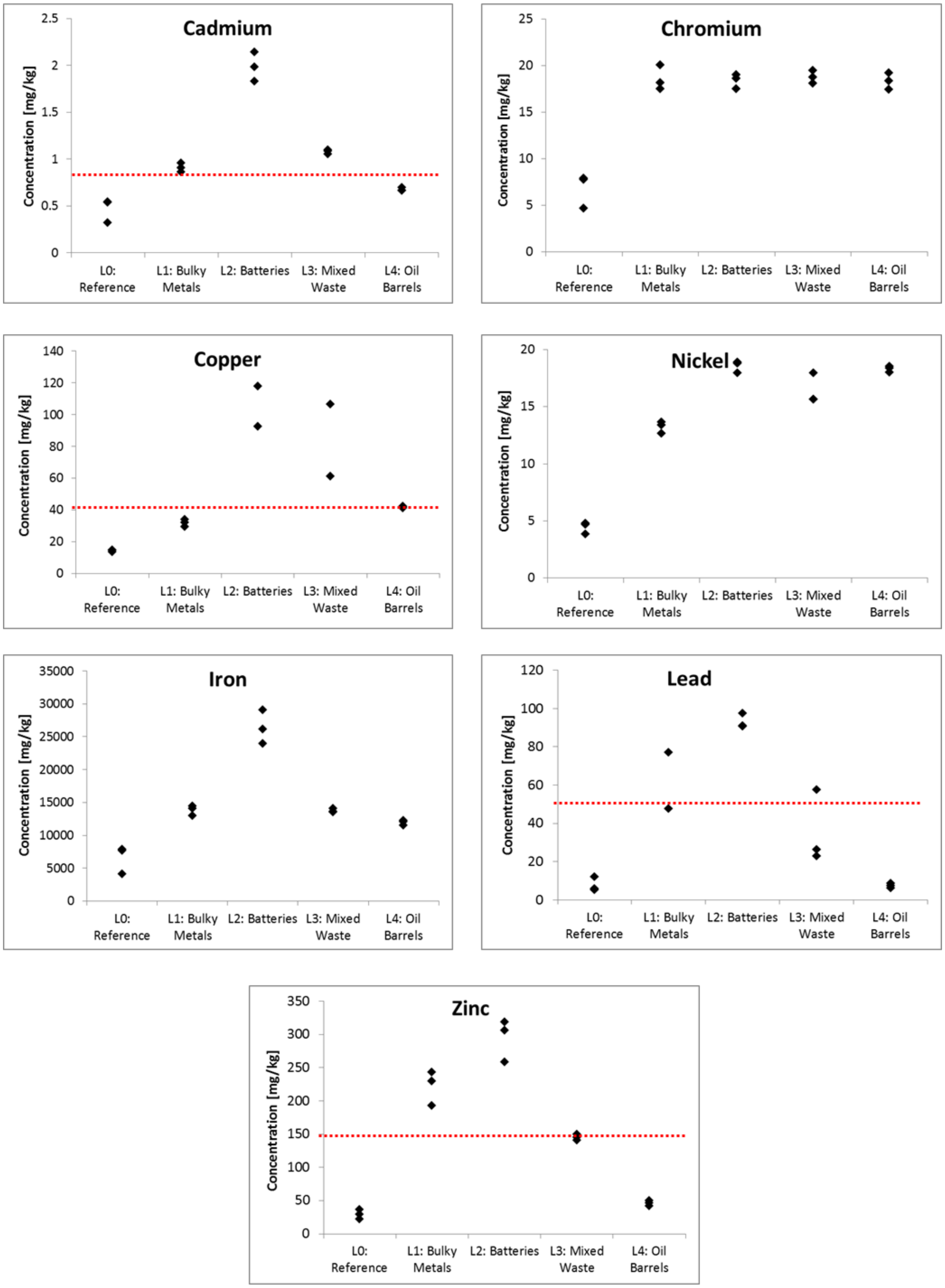

Figure 5.3: Heavy metal concentrations for soil samples at different locations

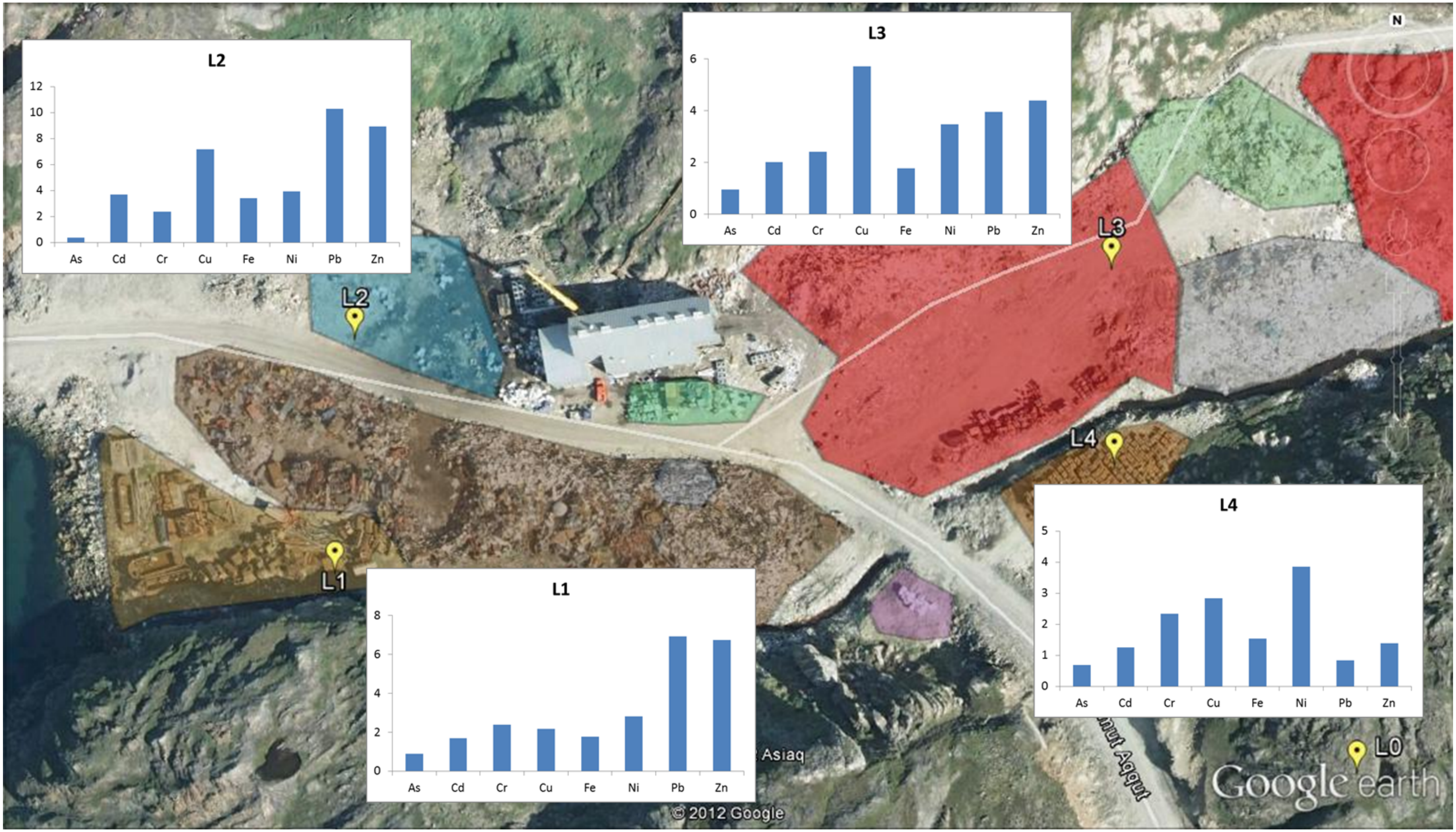

Figure 5.4: Heavy metal concentrations in soil at different locations in relation to the reference site's concentrations [Google Earth, 2012]

As can be seen, the reference site is below the EAC concentrations for all heavy metals. The two samples from the bulky metal and battery areas (L1 and L2) can be considered contaminated with Pb and Zn, with exceedances of around double the target values. All sites have a significant elevation for all tested heavy metals. L2 is consistently showing the highest concentrations. For Cd, the EAC values were exceeded at L1, L2 and L3 and for Cu at L2, L3 and L4. The concentrations of Cr and Ni were below the EAC values at all stations, an EAC value for Fe is not included in the environmental assessment [Huber et al., 2008]. Figure 5.4 shows the average elevation in concentration of the tested heavy metals in relation to the reference site L0. Values above 1 mean that the concentration is higher than at the reference site.

From figure 5.4 it can be observed that L1 (bulky metal waste) with its highly elevated levels (especially for Pb and Zn) and its proximity to the stream could be the source of large loads being washed into the ocean. L3 (mixed municipal waste) could be another source, also located along the stream. Here it has to be noted that the one soil sample cannot give a good picture over the probably very high variation in heavy metal concentrations in the mixed municipal waste area. Although L2 has the highest levels, it is a comparatively small area and located away from stream and ocean. However, as this area is rather small it could be considered to clean it up and/or to remove leaking batteries.

5.3 Stream

The heavy metal concentrations in the stream were analyzed in water and sediment samples as well as DGTs that were deployed. Four sampling locations were chosen. The DGTs were deployed for a period of 11 days. Å1 just before the stream flows into the landfill area, Å2 in the middle of the landfill, after the stream flows out of a pipe that is under-tunneling the road and at Å3, just before the stream flows out of the landfill via a waterfall over rocks into the ocean (see also the map in figure 5.8). While at Å1 the water still looks natural (clear and surrounded by meadows), at Å2 and especially at Å3 the water is colored darkly red and waste from the landfill is floating around or sitting on the stream bed. As another reference, samples at Å0 further upstream were taken. This station is located on the southern tributary stream. The northern tributary stream is the outflow from Spejdersø, while the southern one comes from a swampy area around 500 m south of Spejdersø. The exact coordinates of the locations are shown in table A.1 in Appendix A.

5.3.1 Sediment samples

The heavy metal concentrations measured in sediments are shown in figure 5.5. The yellow line indicates the lower value of the environmental assessment criteria (EAC) for sediments, while the red line indicates the upper (less strict) value [Bignert et al., 2004]. All values above the yellow and especially above the red line indicate therefore polluted sediments. While measuring rather high concentrations at Å0, the concentrations just before the stream reaches the landfill (Å1) are low and then significantly increasing while the river flows further through the landfill (Å2 and Å3). This pattern is followed for all measured heavy metals.

The reason, why Å0 shows elevated concentrations is not clear. It has to be noted that Å0 is located at only one of the tributary streams. While the surroundings at Å0 did not seem to be influenced by the landfill at all, it cannot be excluded that there is a local pollution source, as close by is a path that is used by fishermen and some fishing equipment can be found lying around in the area. To show how the landfill itself influences the pollution in the stream, Å1 is chosen as the reference site.

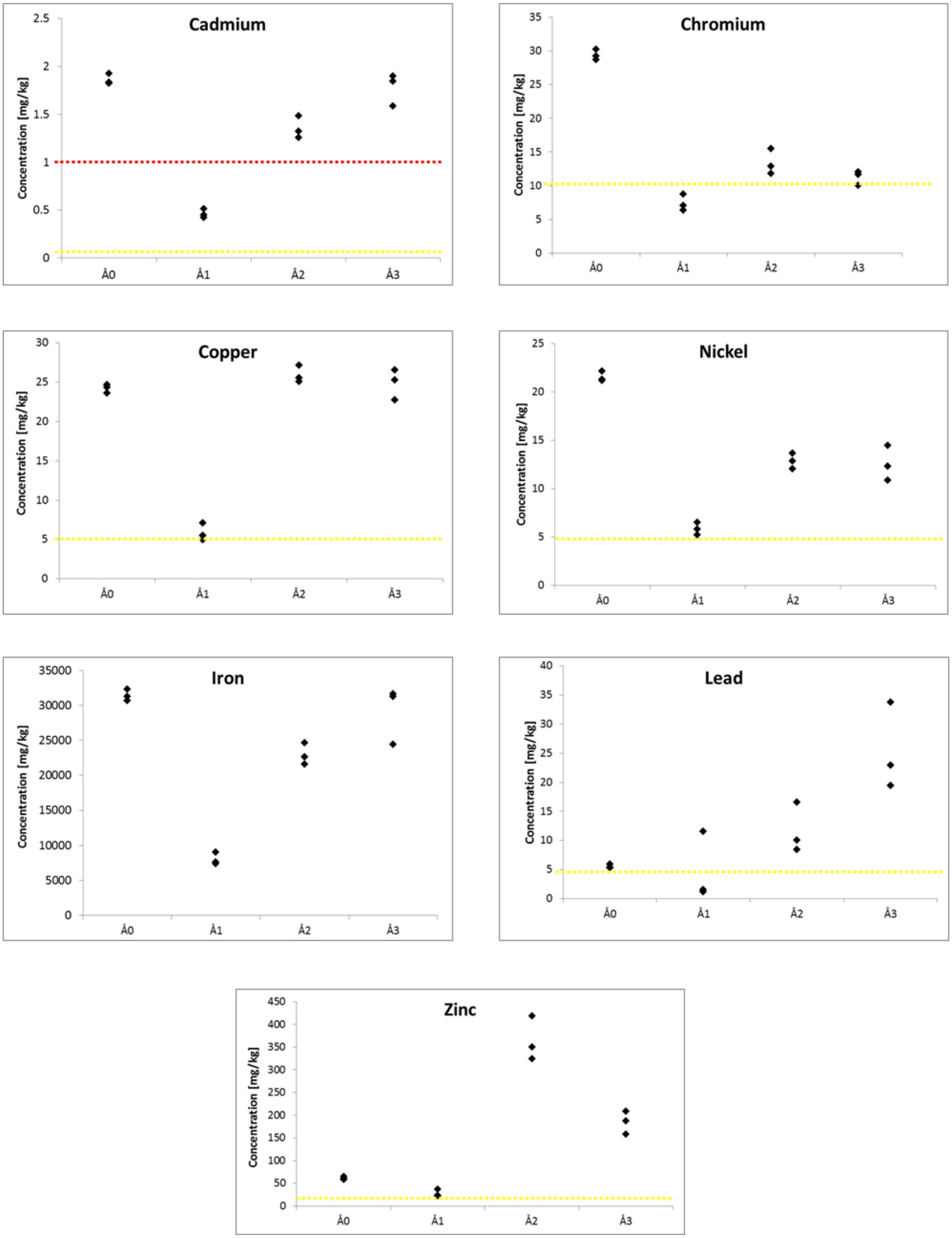

Figure 5.5: Heavy metal concentrations for sediment samples at the sample locations in the stream

As shown in figure 5.5, the lower EAC value is only met for Cr at Å1, indicating that there is a rather high background concentration for all the other metals, maybe from natural or anthropogenic sources. For Cd, all stations except Å1 exceed the upper EAC value. While all heavy metal concentrations are in the magnitude of mg/kg, are the iron concentration in the magnitude of g/kg, around 1000 times higher. This is reasonable, as iron does not only occur in higher concentrations in nature, but also in waste and the water and the sediment of the stream were colored dark brown/red, indicating high iron content.

Generally it can be concluded that the stream's sediment has a background concentration (be it a natural or from other sources) which is then significantly raised by the influence of the landfill.

5.3.2 Water samples

The water samples were taken on the 8^{th} of August 2012 after several days of light rain weather. As they are grab samples, they can only show the concentrations at that particular time and do not integrate pollution over time, such as the mussel, seaweed and sediment samples as well as the passive samplers do. This has to be kept in mind when interpreting the results.

Table 5.2 shows the measured concentrations in the water samples as well as pH and temperature and the EAC values according to the OSPAR convention [Bignert et al., 2004]. The measured pH values show a slightly basic water, being in the range of 6.5 to 8.5 which can be found widely in natural waters and normal temperatures [CRRAPCC, 2002].

Table 5.2: Heavy metal concentrations in water samples of the stream; values of 0 indicate measurements below the detection limit

Station	Cd [μg/L]	Cr [μg/L]	Cu [μg/L]	Fe [μg/L]	Ni [μg/L]	Pb [μg/L]	Zn [μg/L]	pH [-]	Temperature [°C]
OSPAR EAC	0.01 -0.1	1 - 10	0.005 - 0.05		0.1 - 1	0.5 - 5	0.5 - 5		
Å0	0	2.1	8.3	578	4.9	13	38	7.66	8.0
Å1	0	0.9	4.7	328	3.2	9.4	47	7.82	8.5
Å2	0.46	2.9	17	2284	5.5	111	139	7.36	9.0
Å3	0	2.9	4.0	2661	4.6	8.3	100	7.31	9.0

The measured heavy metal concentrations show a similar pattern to the sediment samples: At station Å0 the concentrations were higher than at Å1. Just before the stram enters the landfill (Å1), the concentrations are lower and then getting significantly elevated at stations Å2 and Å3. For Cd the concentrations were below the detection limit for most stations. While for Cr the EAC at Å0 and Å1 can be complied with, the concentrations of Cu, Ni, Pb and Zn are not complying with the criteria. However, it has to be noted, that the given EAC values were developed for ocean waters [Bignert et al., 2004]. Although, as being grab samples and therefore not representing the potentially high variation in concentrations, the water sample analysis confirms the general picture of higher concentrations in and after the landfill compared to when the stream reaches it.

5.3.3 Passive samplers (DGTs)

The average concentrations of heavy metals in the stream for the period of deployment (2^{nd} - 13^{th} of August 2012) could be obtained from the passive sampler (DGT) analysis. The calculation steps are shown in Appendix B.1 and the results can be seen in figure 5.6. The yellow and red lines indicate again the lower and upper EAC value [Bignert et al., 2004]. If a station shows less that one point in the graph, the other measurements were below the detection limit.

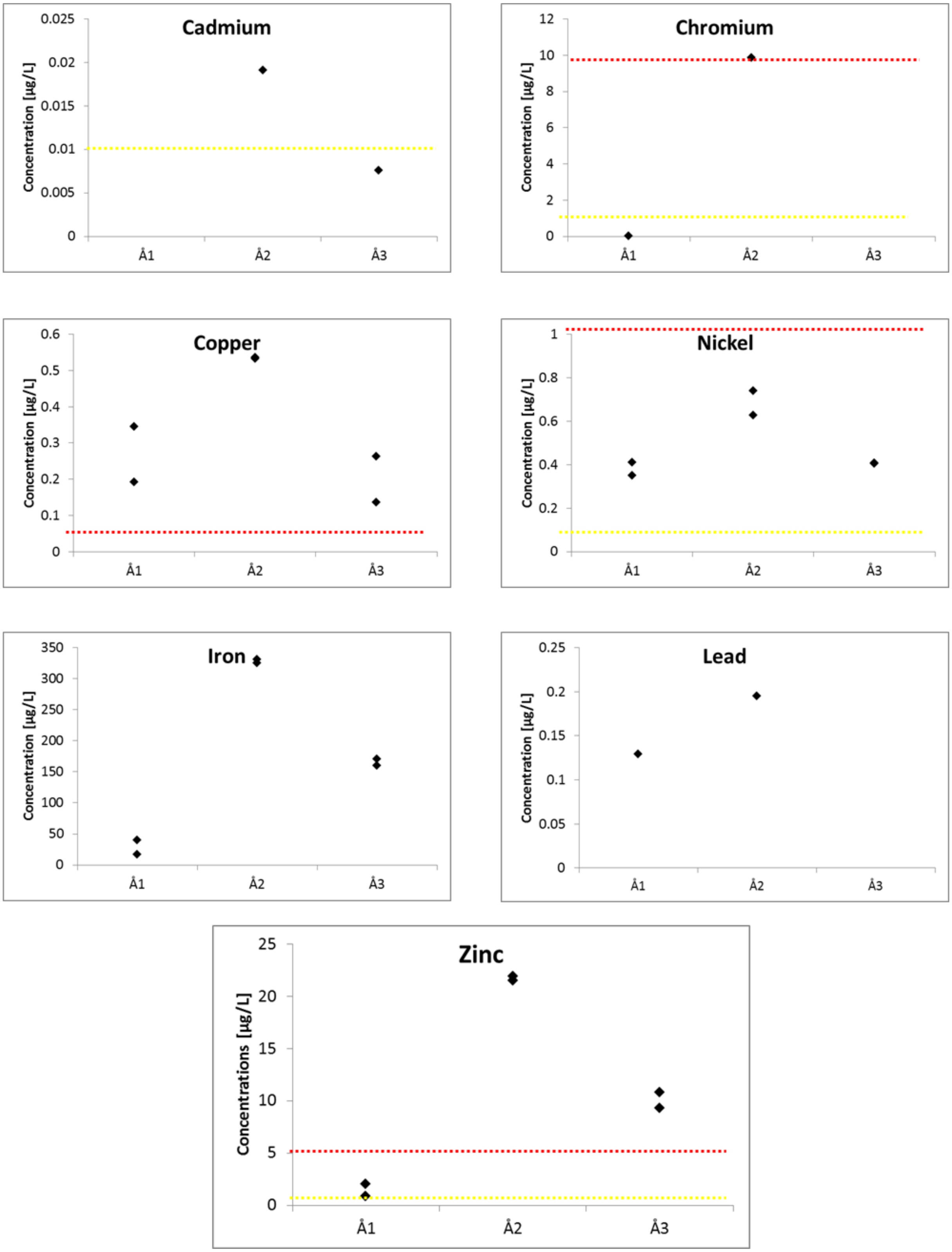

Figure 5.6: Heavy metal concentrations in the stream, obtained from DGTs

For Cu, Fe, Ni and Zn a similar pattern can be observed: Station Å1 shows low concentrations, which are then significantly raised when the stream reached Å2. For Å3 the concentrations are lower again, which is not what was expected. However, this can be explained, as the stream at Å3 was so turbid that the DGT's diffusive layer was blocked with a layer of dirt (see figure 5.7). That means that at Å3 heavy metals were hindered from diffusing through the diffusive layer and could not reach the resin gel. It is suspected that this is the reason, why the measured concentrations for Å3 are below of those for Å2. It is expected that the real concentrations at Å3 are equally high or higher than at Å2 (as seen in the sediment and water samples).

Figure 5.7: Layer of dirt blocking the diffusive layers of the DGT (Å1 on the left, Å3 on the right)

Several samples from the DGT analysis yielded concentrations below detection limit, which was due to the way the resin gels had to be prepared. For the ones, where concentrations could be calculated following conclusions can be drawn: The Cu concentrations are above the EAC value for all locations, while the Ni concentrations are between the lower and upper EAC values. For Zn, the upper EAC value could be reached at Å1, but Å2 and Å3 fail to comply with the criteria.

It can also be noted that compared to the water grab samples, different concentrations were found using the DGTs. For all metals - except Cr - the DGT analysis yielded lower concentrations than the water samples. However, looking at figure 5.8, it can be seen that the relative concentration elevations from the water samples and the DGT analysis give for most metals similar results.

Also for the analysis of the passive sampler results, it can be seen that the landfill influences the water quality in that the concentrations get raised significantly in the stream during its flow through the site. This is shown in figure 5.8, too, where the relative concentrations of the stations Å2 and Å3 are shown in relation to the concentrations at Å1. For all heavy metals, the landfill induces an increase of concentrations of up to 15 times the concentration at Å1 (for Zn at Å2).

5.3.4 Total loads

From the analysis of the passive samplers it is possible to estimate the total yearly load entering the ocean via the stream. This can of course only be a rough estimate, as concentrations and especially discharge vary greatly during the year. The discharge at Å2 was determined to be 57 L/s and at Å3 to be 60 L/s after several days of light rain in the middle of August. Looking at the flow regime of an arctic river, only during approximately 6 months per year there is run-off, the rest of the time the rivers are frozen. In spring a discharge peak is reached due to snow melt. During snow melt, the concentrations of heavy metals in the water will likely be reduced as well, because there is more water to dilute with. Therefore, for this estimate it was decided to approximate the yearly loads by assuming a constant discharge of 60 L/s over 6 months. The average concentrations at Å2 were used, because - as explained above - the measurements at Å3 were disturbed by a layer of pollutants blocking the diffusive layer of the DGTs.

The estimated yearly loads that reach the ocean via the river are shown in table 5.3.

Table 5.3: Heavy metal loads discharged by the stream into the ocean per year

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Total yearly load [kg/a]	0.018	9.20	0.499	306	0.637	0.182	20.3

By far, the biggest load reaching the ocean is iron with over 300 kg/a. This does not necessarily need to pose a big problem, as iron can be found in high concentrations in nature as well. The above analysis showed however that the origin of by far most of this iron is the landfill and therefore an anthropogenic source. A main question is, whether the stream is contributing significantly to the washing out of heavy metals into the marine environment. This is of course very difficult to answer, as it is not known how much the total heavy metal loads from the landfill leaking into the ocean are. It is clear that the stream is raising the contact area between the landfill and the aquatic environment significantly.

A study from a landfill in Austria by Krizek (2009) is taken as a comparision. For two landfills of similar size as the one in Sisimiut a scenario was calculated where the top layer of the landfill was removed (which leads to a similar situation as in Sisimiut). The results showed a total yearly load of Cd transported into the environment of 0.15 kg/a and 0.45 kg/a respectively [Krizek, 2009]. Adjusting these numbers for Sisimiut (snow cover for around 6 months, where much less wind and run-off driven erosion is happening) around 0.08-0.23 kg/a Cd would be expected to be leaving the landfill. This would mean that the stream contributes to 8-23 % of the total Cd load.

The real contribution of the stream to the leaking of heavy metals into the ocean is however impossible to estimate, due to the lack of data (amounts and types of waste on the landfill).

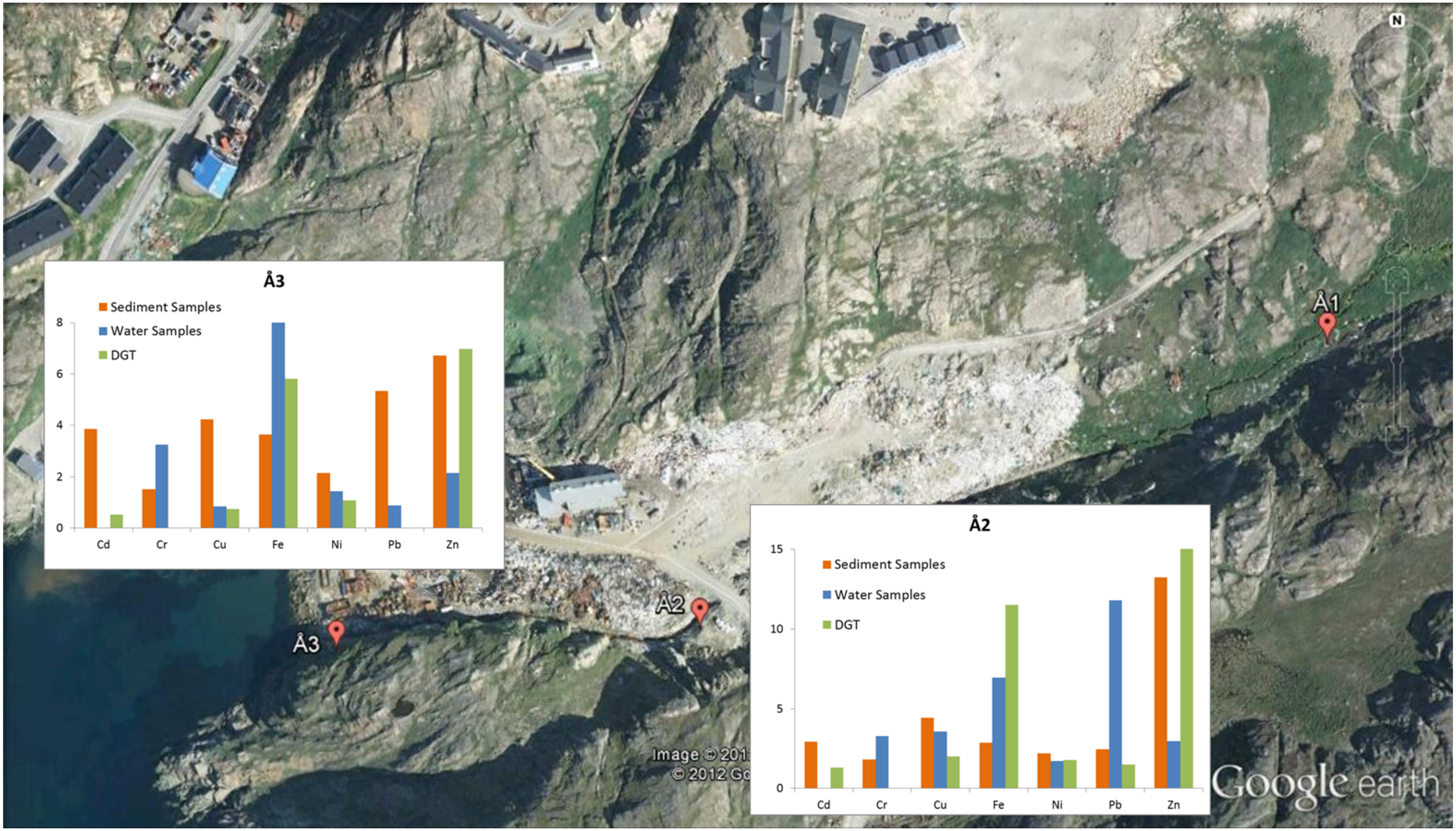

Figure 5.8: Heavy metal concentrations in the stream (sediment and water samples, passive samplers) at different locations in relation to site Å1's concentrations [Google Earth, 2012]

5.4 Ocean

The analysis of heavy metals was also carried out in the ocean, in the bay close to the landfill. The selected locations for the samples are shown in figure 5.12. Sediments, water samples and DGTs were collected at S1, S2 and S3 as well as at S0, which is the reference station far from the stream (this point is not displayed in figure 5.12). The DGTs were deployed for a period of around 9 days. Mussels were taken from a reference site at the Second Fjord approximately 20 km north of the city; and also from S1, S2 and C6. While the mussels at S1 and S2 were moved from the Second Fjord to the sites on the 6^{th} of July and collected again on the 12^{th} of August, the mussels at C6 were collected from local rocks. The exact coordinates are shown in table A.2 in Appendix A, along with the water depths.

5.4.1 Sediment samples

The heavy metal concentrations measured in sediments are shown in figure 5.9. The yellow line is delimiting the lower value of the environmental assessment criteria (EAC) for sediments according to the OSPAR convention [Bignert et al., 2004]. The concentrations of metals increase as the locations are closer to the mouth of the stream and the landfill (S2 is the closest station). In the case of Cr and Cd, the pattern is similar, but a difference has to be noted: The concentration increases from S3 over S1 to S2 as in the rest of the metals; but a high concentration is located at the reference site S0. None of the sediment samples are reaching the upper value of the EAC, but for Cd, Cu and Pb the lower EAC value is reached at all stations. Stations below this value are only S1, S2 and S3 for Cr and S3 for Ni and Pb.

A first reasoning could be that the sediments in the reference location have a richer concentration of Ni, Cr and Cd in background. Another explanation would be that the collection at that point would have an abnormal concentration for those metals. In both cases the site would not be a good reference to compare. The reason why the concentrations increase with the proximity to the mouth of the stream seems logical. The sediments and therefore the metals attached to them are being deposited close to where the stream flows into the ocean and consequently, the concentrations decrease as distance from the landfill decreases.

Notice that Fe has higher levels than the other metals for reasons mentioned in previous sections; there is a high background concentration from natural sources and in waste. Besides, in the closest location this concentration is notably bigger, perceiving the enormous influence of the landfill over the results.

In the results of other studies on Greenlandic landfills (see table 2.1 by [Asmund, 2007]), Pb and Cu showed clear elevation compared to the reference site. This can be confirmed here and Fe can be added to this list. At S3, ca. 150 m offshore, no significant elevation in heavy metal concentrations can be seen, only the values for Cu are slightly elevated.

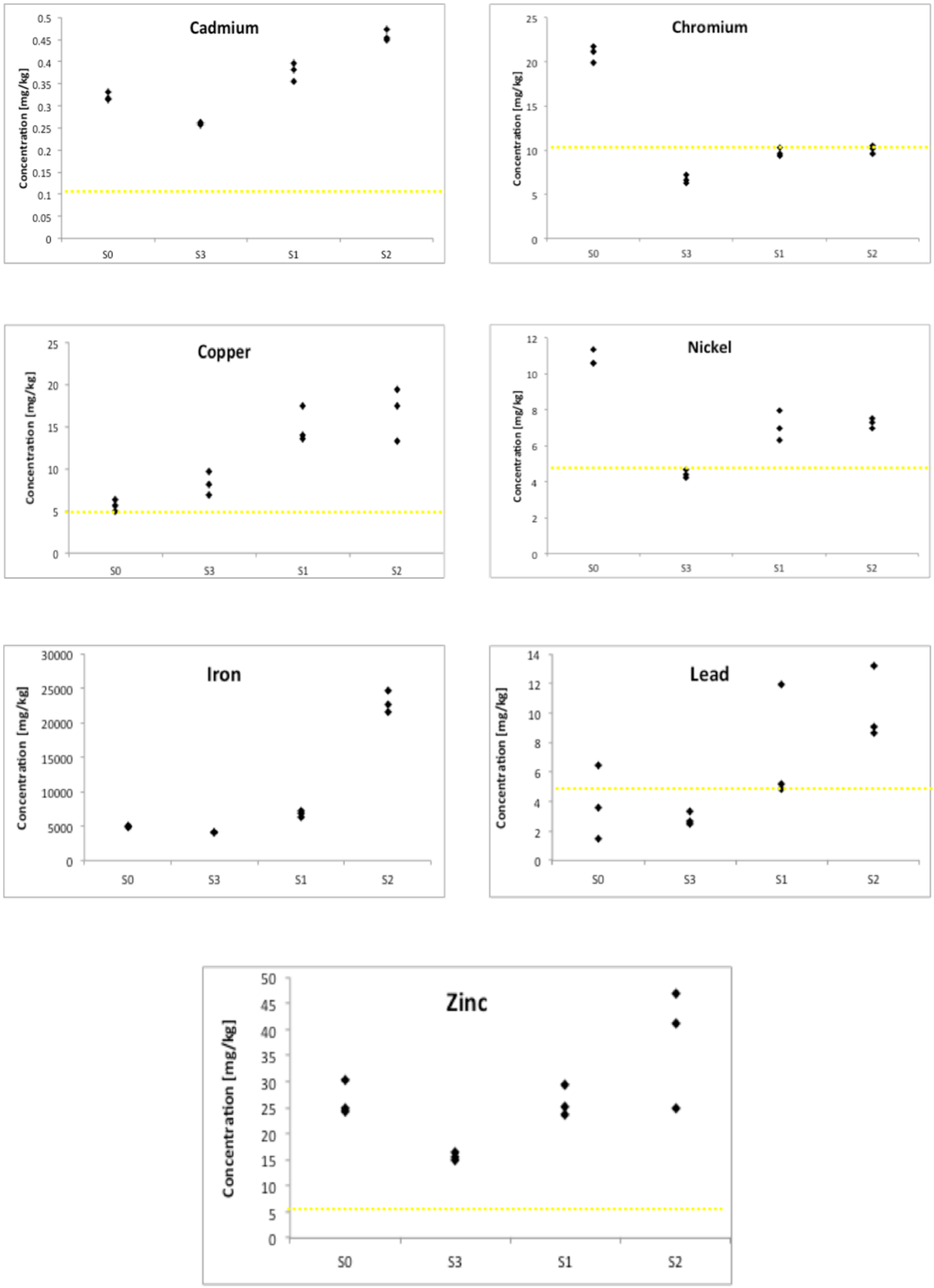

Figure 5.9: Heavy metal concentrations for sediment samples at the sample locations in the ocean

5.4.2 Water samples

In table 5.4 the concentrations of the metals for the different locations are shown. Looking at the results, different patterns are seen for the different cases. The Cr concentrations increase with the proximity to the landfill, but within the range of the lower and upper EAC value. Cu, Ni and Zn show a maximum value at S1, which is not the closest to the landfill. Notice all these metals display higher values of concentration than the EAC values, even the samples taken at S0.
The Fe concentration also increases with proximity to the dump.

In the case of Pb, the concentrations maintain within the lower and upper EAC values, with the anomaly at S1, which presents a concentration of 22.67 $\mu g/L$. Cd presents again the same scenario as Pb but with a smaller concentration of 1.374 $\mu g/L$ and concentrations below the detection limit for the other stations.

Table 5.4: Heavy metal concentrations in water samples of the ocean; values indicated with 0 are below the detection limit

Station	Cd [μg/L]	Cr [μg/L]	Cu [μg/L]	Fe [μg/L]	Ni [μg/L]	Pb [μg/L]	Zn [μg/L]	pH [-]	Temperature [°C]
OSPAR EAC	0.01 -0.1	1 - 10	0.005 - 0.05		0.1 - 1	0.5 - 5	0.5 - 5		
S 0	0	0.642	8.322	195.946	2.752	3.366	20.828	7.64	6.5
S 3	0	0.533	11.237	412.0.46	4.02	2.66	69.574	7.99	6.5
S 1	1.374	1.393	15.33	467.919	6.746	22.677	621.581	7.88	6.5
S 2	0	2.74	5.551	592.275	2.428	4.143	46.258	7.9	6.5

The reason why there is an anomaly in the S1 is uncertain. A first thought could be that the water sample collected was taken from a current in the ocean where the pollution was significantly higher than others at that point. The conclusions for the water samples can only be seen as an indication, as they are only grab samples of a specific point and time. The tide of the ocean, its different currents and changes make it difficult to get a meaningful conclusion. This is why the passive samplers were deployed at the locations. Nevertheless, it is noticeable that values for the places close to the landfill show an elevation of the metal concentrations in comparison to the reference site. It is possible to underpin the general picture of higher concentrations closer to the landfill.

5.4.3 Passive samplers (DGTs)

Figure 5.10 displays the concentrations of the metals in the ocean for the sample locations. Two passive samplers (DGTs) - named A and B - were deployed at each spot to ensure the collection of results. After the corresponding analysis the metals with significant values to show were Cu, Ni, Fe and Zn. For the other metals, the total mass that accumulated in the resin gel was not high enough that the detection limit in the prepared solution could be reached. Notice the plots show data for both DGTs in order to show the incongruity in some of the results.

The graph for Ni gives the best performance regarding to the similarity between the results for both DGTs at the same sites. The calculated concentrations range around the lower EAC value. Cu levels are above the maximum limit according to the EAC value, when the detection limit could be reached. This means that even though the results are not showing an important reliability, the pollution for this metal in the ocean as a consequence of the landfill is an evidence.

The pattern obtained in the analysis of sediment could not be reached: There is no significant increase in concentrations at locations closer to the landfill. Keeping the devices for a longer period of time in the locations would allow them to accumulate more mass and would lead to better

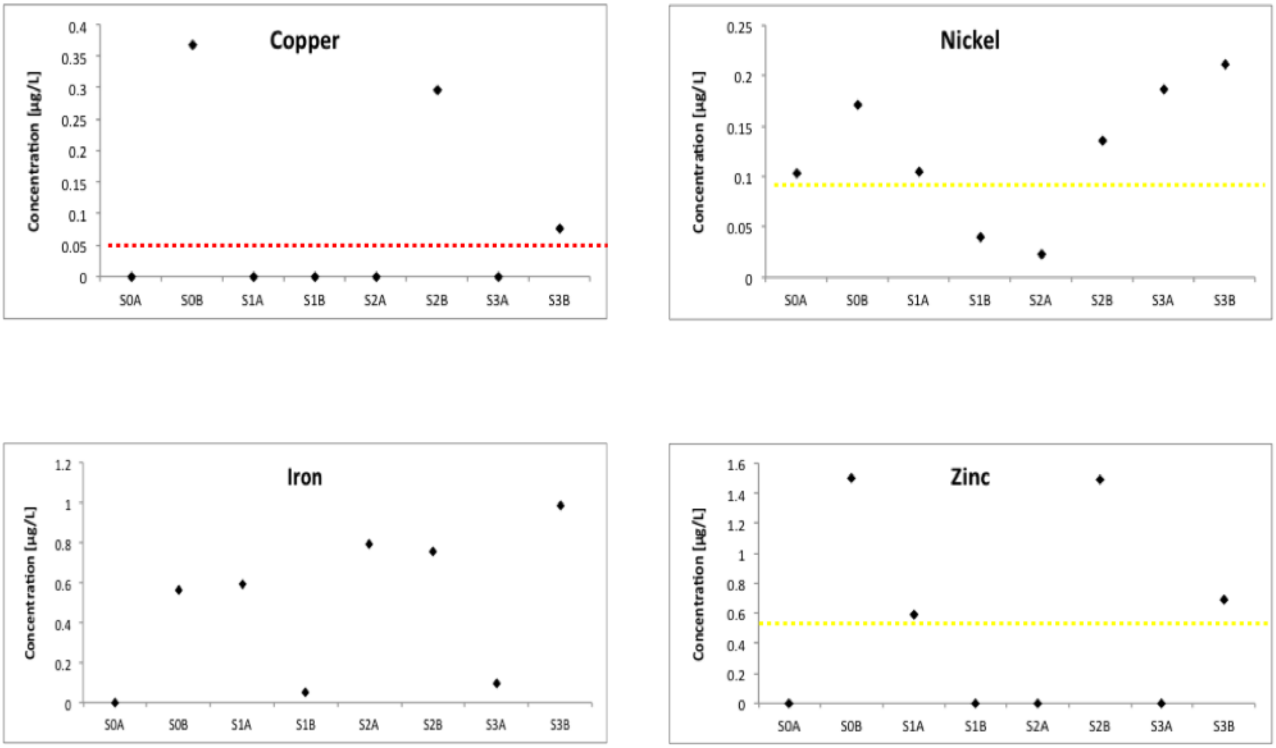

Figure 5.10: Heavy metal concentrations for DGT at the sample locations in the ocean

results, giving a better understanding of the situation.

5.4.4 Blue mussels

Blue mussels were located at S1 and S2 in the bay of the landfill. Some blue mussels were also collected from the rocks on the shoreline (C6). The used reference site is the location, the mussels were moved from (the Second Fjord).

The mussels placed in S1 and S2 present similarity in the results (figure 5.11). Almost the same concentration of each heavy metal is found in both sites; which means that there is not a clear relation between the heavy metal concentration and the proximity to the mouth of the stream, at least when the locations are close to each other.
Comparing the locations with the reference site in the Second Fjord, the mussels close to the landfill show higher concentrations in the bay at the landfill, except for Cr and Zn. This shows that the area is more polluted than other areas further out.
As can be seen, the measured concentrations for Cd and especially Pb are rather spread out, but a general pattern of elevated concentrations for Cd, Cu, Ni, Fe and Pb can be seen. It has to be noted that the mussels at S1 and S2 were only exposed to the environment close to the landfill for a short period of time and this time was enough in order for them to accumulate more heavy metals. If they were exposed for a longer time, a clearer trend could be expected to be found.

For Pb, the measured concentrations at S1, S2 and C6 are clearly elevated compared to the reference site, although the measured values have a high variance. This compares well with earlier findings at Greenlandic landfills (see table 2.1), where Pb was found to be the main elevated heavy metal in mussels.

Within the bay, the C6 location among the rocks shows a lower value of the concentrations than in S1 and S2 for Cd, Cr, Cu and Ni (in average). However, the site displays higher values for Fe, Pb and Zn.

The reasons why there are these differences in the bay could be explained by the way the mussels were placed in the locations. In C6, the mussels were attached to the rocks being immersed by water at high tide only. Contrarily, the mussels in S1 and S2 were totally immersed in the water (deeper waters) hanging on a buoy. While the mussels at C6 were not moved and therefore were exposed to the pollution from the landfill over a longer period, they were also a bit smaller (younger) than the ones at S1 and S2. That they were younger and therefore did not accumulate as much pollutants as the other mussels could explain the obtained results. It is difficult to say without further studies that mussels in the rocks were highly influenced by the metals from the cliff; and the differences in the others metals could be explained by the fact of the differences in the depths of the water.

Food threshold values for Cd and Pb are 1.0 mg/kg and 1.5 mg/kg respectively in several countries [Asmund, 2007]. These were not reached in the sampled mussels, with highest values in the magnitude of 0.1 mg/kg for both metals.

Figure 5.12 shows the relative elevations in heavy metal concentrations in the ocean for sediment, water and mussel samples, as well as for the DGT analysis. Iron and lead at the closest location to the landfill (S2) showed the highest increase.

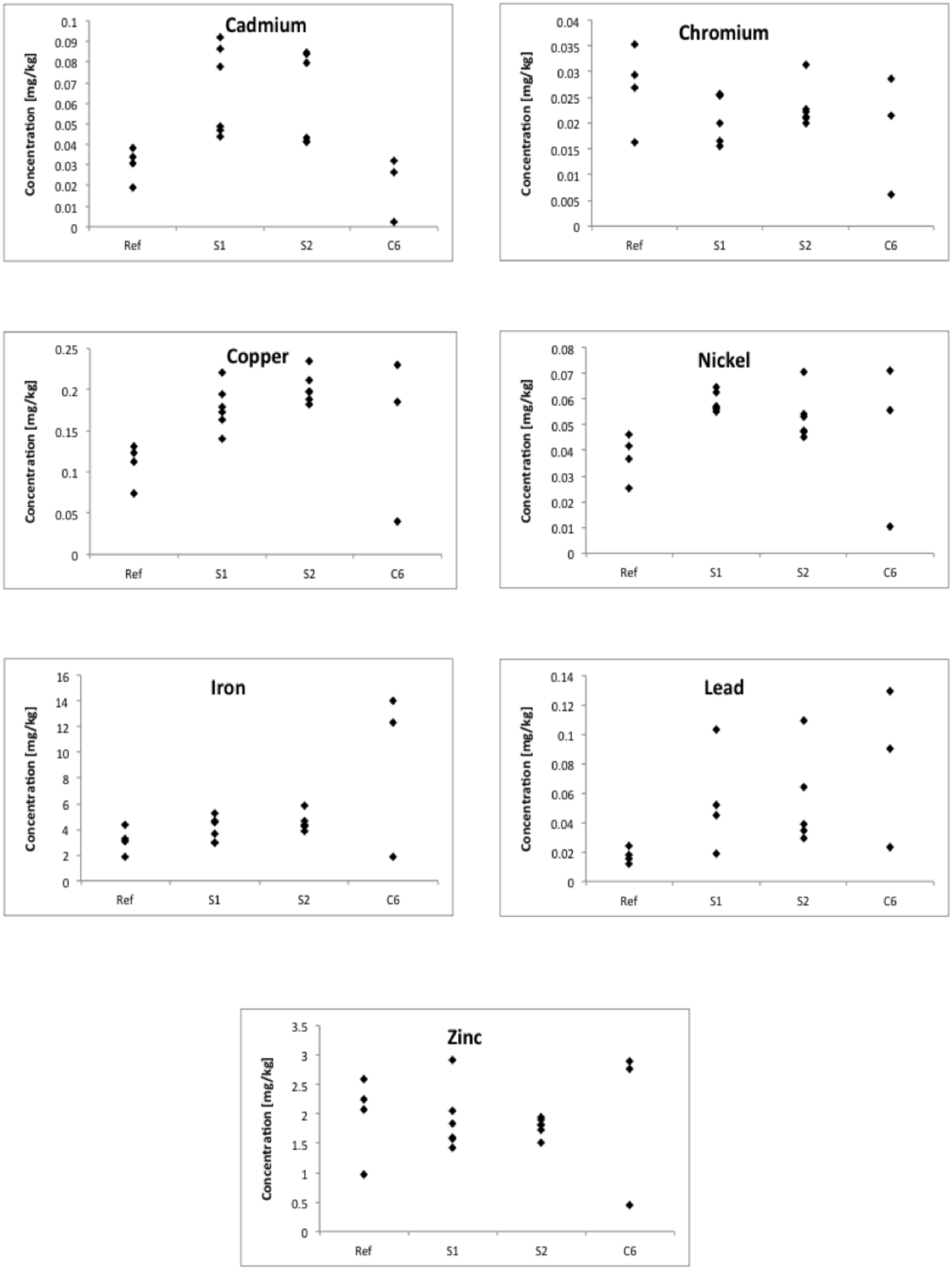

Figure 5.11: Heavy metal concentrations for mussels at the sample locations in the ocean

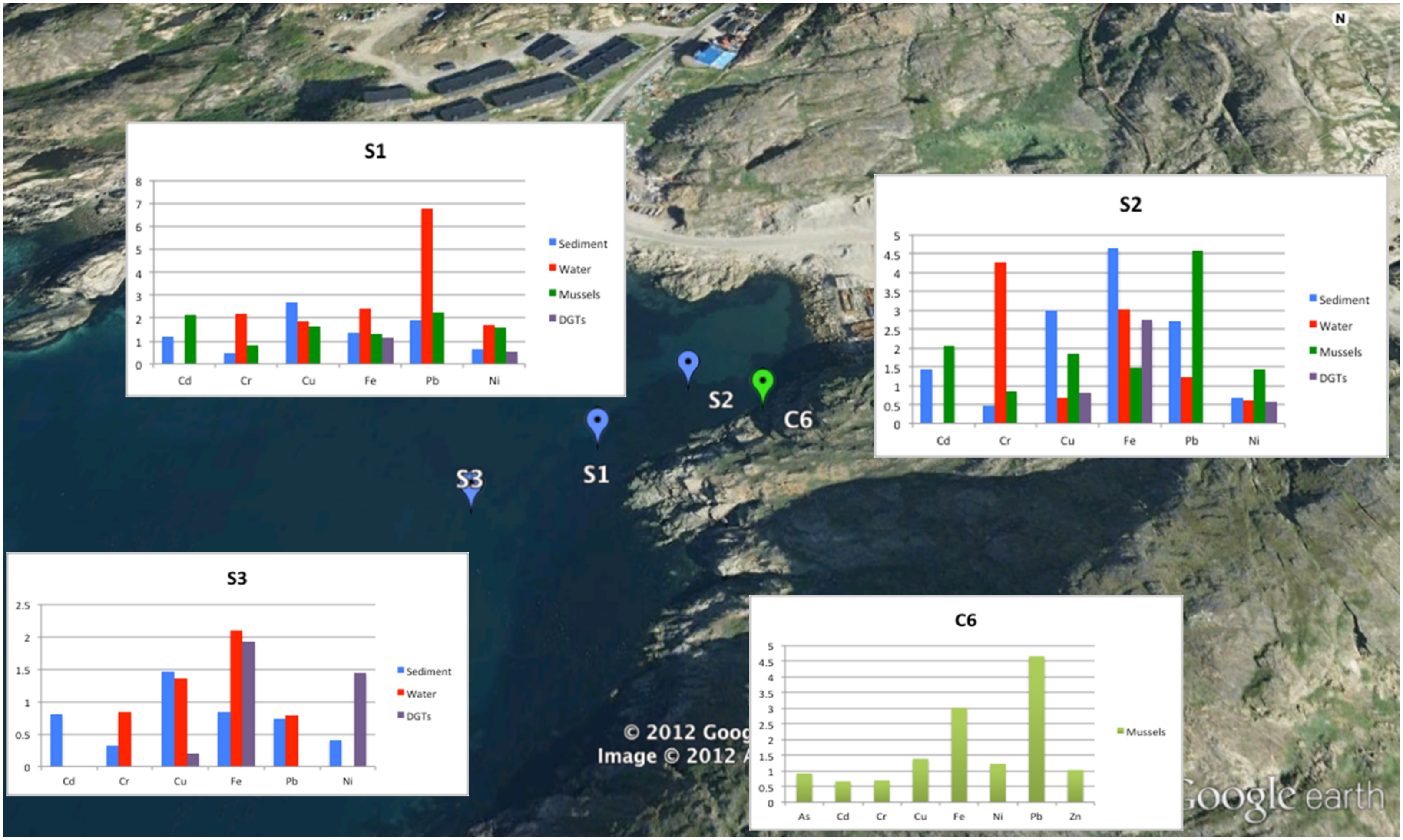

Figure 5.12: Heavy metal concentrations in the ocean (sediment, water samples, passive samplers and mussels) at different locations in relation to site S0's concentrations [Google Earth, 2012]

5.5 Coast

Figure 5.13 shows the measured concentrations in seaweed for the two reference stations S0 and C0 and the sample locations along the coast. It can be observed that for most metals, the levels are not elevated at the stations closer to the landfill (for Cd they are even significantly lower). Exceptions are Fe, where the concentrations at C3 (located directly where the landfill is adjacent to the coast) are significantly higher and to some extend for Pb at C3 as well. Comparing the Zn concentrations at S0 with the locations closer to the landfill a slight increase can be interpreted. Otherwise it can be concluded that the landfill does not seem to influence the heavy metal concentrations in seaweed significantly. The relative elevations of the heavy metal concentrations in seaweed along the coast can be seen in figure 5.14. Compared to previous studies (see table 2.1), where the concentrations in seaweed for Pb, Zn and Cu were observed, these results can only partly confirm that. The exact coordinates of the locations are shown in table A.3 in Appendix A.

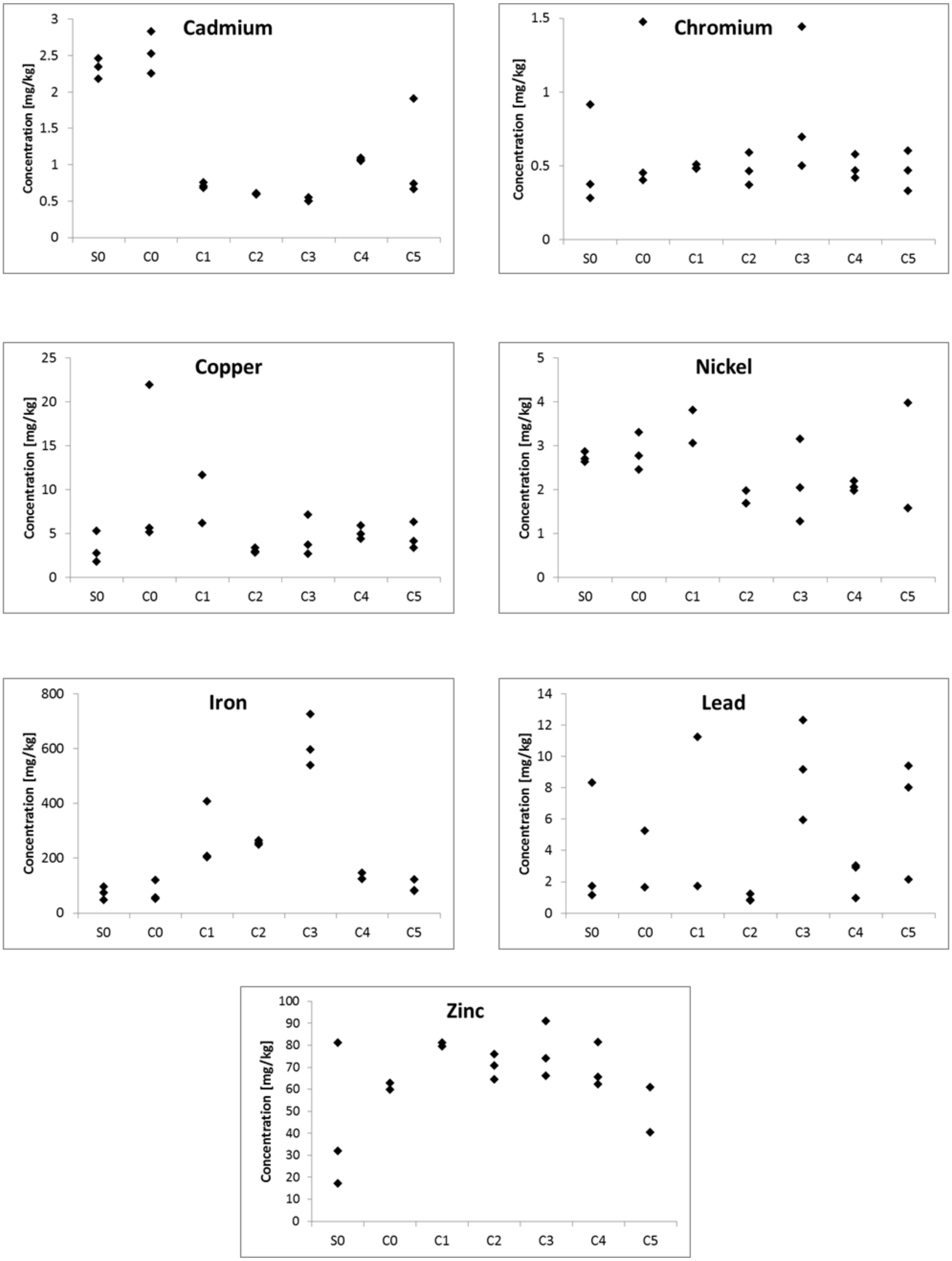

Figure 5.13: Heavy metal concentrations in seaweed samples taken along the coast

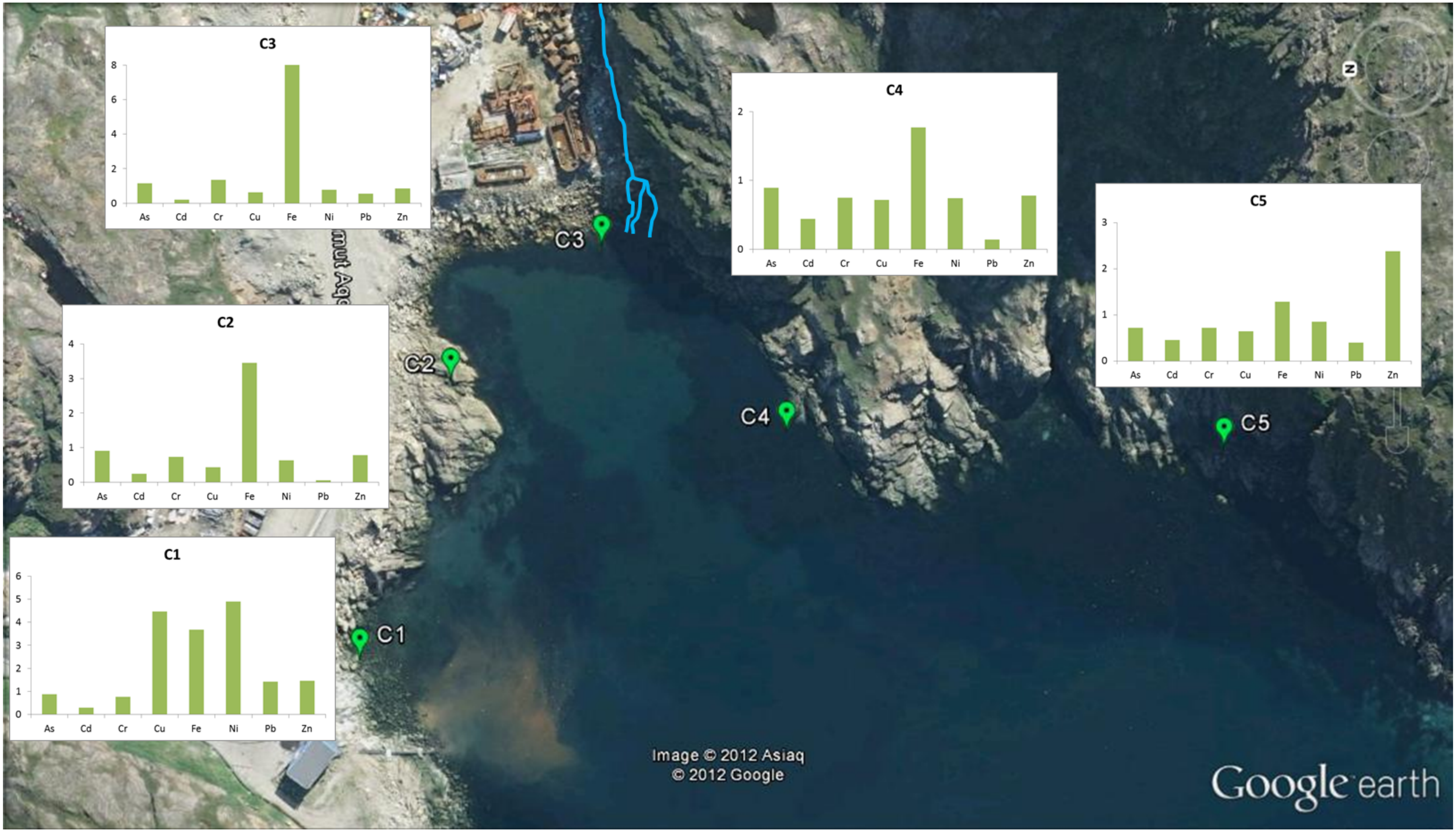

Figure 5.14: Heavy metal concentrations in seaweed for different locations along the coast in relation to the reference sites S0 and C0 (not on map) [Google Earth, 2012]

Chapter 6

Conclusions

The heavy metal pollution in the aquatic environment at the landfill in Sisimiut was investigated by analyzing water, sediment, soil and blue mussel samples as well as using passive samplers (DGTs). Following conclusions can be drawn:

- The soil of the landfill shows highly elevated concentrations, especially for the area where batteries are stored. The areas, where bulky metal waste and mixed waste are stored are the ones closest to the stream and therefore probably the source of the elevated concentrations there. This means that the total loads washed into the ocean could be reduced by only piping the stream from the road (where it is already piped) to the bay (around 180 m).
- The landfill is the main source of heavy metals for the stream. Heavy metal concentrations are increasing from where the stream reaches the landfill until it flows into the ocean. This hypothesis is supported by the results from the DGTs, although at the last location the diffusive layer might have been blocked by a dirt layer. The total loads of heavy metals reaching the ocean was calculated, with iron being the largest amount. It is suspected that the stream could leak the major proportion of metals into the ocean. In general, it should be aimed at to reduce the interface of the landfill and the stream. Therefore, piping the whole river would lead to the least loads. Another measure could be to heighten the bank of the stream, so that rain run-off does not directly flow into it.
- The ocean's aquatic environment is only influenced by the landfill in the bay until a distance of less than 150 m. At station S3 no significant rise of heavy metal concentrations could be found. The concentrations in mussels were elevated for cadmium and lead. Foodstuff threshold values were not reached. The concentrations in the water were lower than in the stream, which is why the DGTs did not accumulate enough metals in order to be analyzed. The influence of the landfill is restricted to the cove. At the same cove, the sewage of Sisimiut is led into the ocean (*"the chocolate factory"*). This means that the bay is already exposed to a lot of pollution of a different matter. Therefore, even if the impacts from the landfill were minimized, the aquatic environment in the cove would still be greatly influenced by anthropogenic waste.
- In seaweed only the iron concentrations close to the mouth of the river and to some extend the lead concentrations showed significant elevations.

It could be shown that the landfill influences the aquatic environment in the area. Especially in the stream concentration were clearly elevated. In the ocean, only a limited area is influenced (less than 150 m from the shore). However, it has to be noted that this project only looked at the heavy metal pollution and other pollutants (e.g. organic chemicals) could show a different behavior.

Using the DGTs in the ocean for such a short period of time gave only poor results, because the concentrations in the ocean water are too low. They should be deployed for a longer time. For the stream the results were reasonable and the devices are easy to use. The preparation of the samples is much faster than e.g. for mussel samples.

The water samples are not as reliable, because they are only a random collection. In order to get good results, a much higher spatial and temporal resolution of sampling would be needed.

The municipality wants to construct a dam before the landfill in order to make it less visible. This could be a good opportunity to divert the stream or put it into a pipe. Then, the heavy metal loads reaching the ocean could be reduced significantly. On the other hand, the influence is only restricted to the cove at the landfill, so that large investments might not be justified.

In case the dam is built, a successive study should be carried out a few years later in order to see whether the heavy metal concentrations could be lowered as expected.

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Appendix A

Locations

In the following tables, the precise location (taken with a hand-held GPS) and nearer descriptions of the sample stations are given.

Table A.1: Locations in the stream

Station	**Location**		**pH**	**Temp**	**Depth**	**Width**	**Notes**
	N	W		°C	m	m	
Å0	66.92984	53.65342	7.66	8.0			Southern tributary
Å1	66.92926	53.65941	7.82	8.5	0.2	0.85	Just before the landfill
Å2	66.92805	53.66595	7.36	9.0	0.2	1.5	After the pipe under the road
Å3	66.92804	53.66967	7.31	9.0	0.4	1.7	Before waterfall into the ocean

Table A.2: Locations in the ocean

Station	**Location**		**pH**	**Surface Temp**	**Depth**	**Notes**
	N	W		°C	m	
S 0	66.93176	53.75012	7.64		12	At Qeqertarmiut (island)
S 1	66.92760	53.67187	7.88		7	Between S2 and S3
S 2	66.92786	53.67115	7.90	6.5	3	Closest to landfill
S 3	66.92734	53.67280	7.99		12	Farthest from landfill
Mussel Ref	67.08178	53.48345				At Anden Fjord

Table A.3: Locations along the coast

Station	**Location**		**Temp**	**Notes**
	N	W	°C	
C 0	66.92221	53.65741	7.0	Ca. 1km south of landfill, next bay
C 1	66.92857	53.67227		Close to the 'chocolate factory'
C 2	66.92836	53.67077		Between C1 and C3
C 3	66.92803	53.67007		At head of landfill
C 4	66.92765	53.67111		Ca. 60m SW of landfill
C 5	66.92670	53.67127		Ca. 160m SSW of landfill
C 6	66.92774	53.67054		Close to C4

Table A.4: Locations at the landfill

Station	**Location**		**Notes**
	N	W	
L 0	66.92773	53.66327	Ca. 100m south of landfill, on top of a hill
L 1	66.92812	53.66862	Bulky metal waste
L 2	66.92861	53.66850	Batteries
L 3	66.92875	53.66453	Mixed municipal waste
L 4	66.92835	53.66451	Oil barrels

Appendix B

Calculations of the heavy metal concentrations

In the following tables the results from the ICP analysis are shown together with the subsequental calculations to obtain the heavy metal concentrations. Values marked in red where taken out from the further analysis, as they were considered outliers (wide out of the range of the two other measured values).

Table B.1: ICP results and calculated heavy metal concentrations for soil samples

Prøve	**afvejet**	**målekolbe**	**As**		**Cd**		**Cr**		**Cu**		**Fe**		**Ni**		**Pb**		**Zn**	
	[g]	**[mL]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**
Dorm 3	0.9731	50	0.0408	2.099	0.0059	0.301	0.033	1.70	0.308	15.82	6.24	321	0.0246	1.26	0.008	0.43	1.086	55.8
L0-1	1.0266	50	0.0000	0.000	0.0066	0.322	0.095	4.63	0.280	13.63	84.9	4136	0.0784	3.82	0.108	5.27	0.449	21.9
L0-2	1.0299	50	0.0094	0.459	0.0112	0.542	0.163	7.91	0.302	14.68	162	7870	0.0966	4.69	0.124	6.00	0.608	29.5
L0-3	1.0216	50	0.0095	0.465	0.0109	0.534	0.158	7.74	0.300	14.66	157	7707	0.0980	4.79	0.247	12.08	0.748	36.6
L1-1	1.0366	50	0.0117	0.562	0.0188	0.907	0.363	17.50	0.660	31.81	291	14024	0.278	13.40	20.369	982	4.007	193.3
L1-2	1.1083	50	0.0090	0.407	0.0191	0.862	0.402	18.14	0.652	29.41	288	12988	0.281	12.67	1.058	47.73	5.084	229.4
L1-3	0.9946	50	0.0051	0.257	0.0190	0.957	0.400	20.09	0.675	33.93	288	14476	0.271	13.64	1.532	77.02	4.841	243.3
L2-1	1.0077	50	0.0022	0.109	0.0431	2.140	0.352	17.46	15.567	772	586	29070	0.381	18.91	1.832	90.89	6.178	306.5
L2-2	1.0272	50	0.0078	0.379	0.0376	1.830	0.391	19.03	2.416	117.60	492	23935	0.369	17.95	2.001	97.39	6.546	318.6
L2-3	1.0073	50	0.0000	0.000	0.0399	1.980	0.375	18.64	1.859	92.29	526	26122	0.379	18.81	1.829	90.77	5.215	258.8
L3-1	0.9985	50	0.0000	0.000	0.0219	1.099	0.362	18.11	1.220	61.09	270	13507	0.312	15.64	0.527	26.37	2.898	145.1
L3-2	1.0398	50	0.0130	0.625	0.0226	1.088	0.405	19.49	39.597	1904	293	14106	0.373	17.93	1.200	57.72	3.107	149.4
L3-3	1.0416	50	0.0143	0.688	0.0219	1.051	0.390	18.72	2.213	106.22	283	13607	0.326	15.63	0.475	22.80	2.939	141.1
L4-1	0.9963	50	0.0083	0.416	0.0133	0.667	0.347	17.42	0.829	41.63	230	11536	0.369	18.51	0.150	7.53	0.988	49.6
L4-2	1.0599	50	0.0000	0.000	0.0141	0.667	0.389	18.34	0.897	42.29	256	12096	0.390	18.38	0.134	6.32	0.883	41.6
L4-3	1.0387	50	0.0113	0.543	0.0145	0.697	0.398	19.17	0.849	40.87	255	12271	0.374	18.01	0.180	8.67	0.971	46.7

Table B.2: ICP results and calculated heavy metal concentrations for mussel samples

Prøve	**afvejet**	**målekolbe**	**As**		**Cd**		**Cr**		**Cu**		**Fe**		**Ni**		**Pb**		**Zn**	
	[g]	**[mL]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**
M0-1	0.477	50	0.040	4.21	0.0191	2.00	0.0162	1.701	0.074	7.76	1.90	199	0.0251	2.63	0.012	1.256	0.96	101.0
M0-2	0.4228	25	0.067	3.94	0.0336	1.99	0.0293	1.731	0.123	7.25	3.22	190	0.0415	2.45	0.016	0.932	2.07	122.6
M0-3	0.4153	25	0.072	4.31	0.0384	2.31	0.0354	2.132	0.132	7.93	4.36	263	0.0461	2.77	0.018	1.099	2.59	156.1
M0-4	0.4122	25	0.066	4.01	0.0308	1.87	0.0269	1.631	0.112	6.78	3.04	185	0.0365	2.21	0.024	1.452	2.25	136.3
S1A-1	0.3924	25	0.098	6.27	0.0776	4.94	0.0156	0.994	0.140	8.94	2.93	187	0.0624	3.98	0.052	3.326	1.41	90.1
S1A-2	0.4289	25	0.112	6.52	0.0923	5.38	0.0199	1.159	0.173	10.06	3.71	216	0.0566	3.30	0.046	2.654	1.60	93.1
S1A-3	0.4104	25	0.108	6.56	0.0862	5.25	0.0165	1.006	0.179	10.91	2.93	178	0.0570	3.47	0.019	1.170	1.58	96.2
S1B-1	0.413	25	0.086	5.23	0.0440	2.66	0.0253	1.534	0.164	9.90	4.70	285	0.0552	3.34	0.501	30.3	1.83	110.6
S1B-2	0.4026	25	0.100	6.23	0.0484	3.01	0.0255	1.583	0.194	12.03	4.56	283	0.0563	3.49	0.103	6.420	2.05	127.1
S1B-3	0.4	25	0.090	5.60	0.0467	2.92	0.0256	1.599	0.220	13.78	5.30	331	0.0646	4.04	6.152	385	2.91	181.7
S2A-1	0.4162	25	0.110	6.62	0.0846	5.08	0.0228	1.371	0.197	11.82	4.63	278	0.0704	4.23	0.202	12.124	1.81	108.7
S2A-2	0.4194	25	0.104	6.20	0.0797	4.75	0.0200	1.193	0.189	11.24	3.88	231	0.0529	3.16	0.039	2.316	1.52	90.4
S2A-3	0.4067	25	0.108	6.67	0.0838	5.15	0.0222	1.363	0.197	12.13	4.28	263	0.0543	3.34	0.029	1.796	1.81	111.0
S2B-1	0.3996	25	0.091	5.70	0.0431	2.70	0.0313	1.959	0.234	14.66	5.90	369	0.0476	2.98	0.110	6.855	1.95	121.7
S2B-2	0.4057	25	0.083	5.14	0.0411	2.53	0.0209	1.287	0.212	13.05	4.37	269	0.0472	2.91	0.035	2.161	1.73	106.7
S2B-3	0.404	25	0.087	5.35	0.0412	2.55	0.0213	1.319	0.183	11.31	4.25	263	0.0452	2.80	0.064	3.970	1.90	117.5
C6-1	0.3523	25	0.075	5.31	0.0267	1.89	0.0215	1.523	0.186	13.18	12.33	875	0.0556	3.94	0.091	6.428	2.76	195.9
C6-2	0.3988	25	0.085	5.33	0.0319	2.00	0.0286	1.790	0.230	14.45	14.01	878	0.0711	4.46	0.130	8.132	2.89	181.0
C6-3	0.0271	25	0.009	8.75	0.0022	2.01	0.0060	5.553	0.040	37.13	1.89	1741	0.0103	9.46	0.024	21.865	0.44	409.9

Table B.3: ICP results and calculated heavy metal concentrations for sediment samples in ocean

Prøve	**afvejet**	**målekolbe**	**As**		**Cd**		**Cr**		**Cu**		**Fe**		**Ni**		**Pb**		**Zn**	
	[g]	**[mL]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**
S0-1	1.0875	50	0.0096	0.443	0.00686	0.316	0.459	21.12	0.106	4.89	106	4853	0.230	10.6	0.033	1.49	0.542	24.9
S0-2	1.0006	50	0.0154	0.772	0.00635	0.317	0.397	19.86	0.126	6.28	99.8	4985	0.227	11.4	0.071	3.55	0.487	24.3
S0-3	1.0166	50	0.0230	1.130	0.00674	0.332	0.441	21.69	0.116	5.69	101	4947	0.215	10.6	0.131	6.43	0.614	30.2
S1-1	1.0361	50	0.0146	0.705	0.00738	0.356	0.194	9.35	0.363	17.52	131	6310	0.164	7.94	0.101	4.87	0.607	29.3
S1-2	1.0008	50	0.0223	1.114	0.00796	0.397	0.206	10.27	0.281	14.02	145	7238	0.140	7.00	0.239	11.93	0.472	23.6
S1-3	1.0919	50	0.0202	0.924	0.00833	0.382	0.209	9.58	0.295	13.52	149	6826	0.138	6.32	0.113	5.19	0.551	25.2
S2-1	0.9934	50	0.0187	0.940	0.00940	0.473	0.203	10.20	0.385	19.37	162	8170	0.150	7.53	0.262	13.18	0.928	46.7
S2-2	0.9968	50	0.0159	0.797	0.00904	0.453	0.192	9.62	0.264	13.26	155	7799	0.139	7.00	0.173	8.67	0.819	41.1
S2-3	1.0466	50	0.0276	1.321	0.00939	0.449	0.221	10.56	0.366	17.50	172	8202	0.153	7.29	0.190	9.10	0.521	24.9
S3-1	1.0115	50	0.0163	0.806	0.00531	0.262	0.145	7.16	0.196	9.69	84.9	4196	0.095	4.68	0.051	2.53	0.312	15.4
S3-2	1.0812	50	0.0175	0.809	0.00564	0.261	0.143	6.63	0.177	8.17	88.9	4113	0.095	4.39	0.057	2.62	0.358	16.5
S3-3	1.0778	50	0.0186	0.863	0.00555	0.257	0.134	6.24	0.147	6.84	89.3	4141	0.091	4.22	0.071	3.31	0.323	15.0

Table B.4: ICP results and calculated heavy metal concentrations for sediment samples in the stream

Prøve	**afvejet**	**målekolbe**	**As**		**Cd**		**Cr**		**Cu**		**Fe**		**Ni**		**Pb**		**Zn**	
	[g]	**[mL]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**	**[mg/L]**	**[mg/kg]**
Å0-1	1.0115	50	0	0	0.0371	1.831	0.581	28.73	0.477	23.57	620	30667	0.431	21.28	0.107	5.29	1.179	58.3
Å0-2	1.0258	50	0	0	0.0394	1.923	0.621	30.29	0.499	24.34	662	32281	0.454	22.12	0.120	5.87	1.233	60.1
Å0-3	1.0781	50	0	0	0.0392	1.819	0.632	29.29	0.531	24.64	675	31292	0.457	21.18	0.116	5.37	1.388	64.4
Å1-1	1.0305	50	0	0	0.0106	0.514	0.181	8.76	0.147	7.11	186	9023	0.134	6.51	0.237	11.52	0.764	37.1
Å1-2	1.051	50	0.0070	0.3346	0.0089	0.421	0.134	6.37	0.105	4.98	155	7356	0.110	5.22	0.033	1.56	0.496	23.6
Å1-3	1.0707	50	0.0141	0.6605	0.0096	0.448	0.151	7.05	0.117	5.49	163	7601	0.124	5.81	0.025	1.17	0.465	21.7
Å2-1	1.0818	50	0	0	0.0272	1.258	0.255	11.77	0.542	25.05	467	21579	0.260	12.01	0.182	8.42	7.003	324
Å2-2	0.9926	50	0.0126	0.6328	0.0262	1.322	0.256	12.88	0.507	25.52	449	22635	0.255	12.82	0.199	10.03	6.953	350
Å2-3	1.0054	50	0	0	0.0299	1.485	0.311	15.47	0.546	27.15	496	24643	0.274	13.64	0.334	16.60	8.405	418
Å3-1	1.0099	50	0	0	0.0320	1.585	0.202	10.02	0.535	26.50	493	24388	0.219	10.85	0.682	33.77	3.190	158
Å3-2	0.9968	50	0	0	0.0367	1.843	0.233	11.67	0.453	22.70	630	31608	0.246	12.32	0.387	19.43	3.727	187
Å3-3	1.0265	50	0	0	0.0389	1.896	0.247	12.02	0.519	25.29	642	31270	0.297	14.45	0.470	22.90	4.281	209

Table B.5: ICP results and calculated heavy metal concentrations for seaweed samples along the coast

Prøve	afvejet	målekolbe	As		Cd		Cr		Cu		Fe		Ni		Pb		Zn	
	[g]	[mL]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]	[mg/L]	[mg/kg]
S0-1	0.4048	25	0.158	9.76	0.0379	2.34	0.0148	0.914	0.044	2.73	1.554	96.0	0.0463	2.86	0.135	8.32	1.31	81.0
S0-2	0.4107	25	0.164	10.01	0.0358	2.18	0.0061	0.373	0.028	1.73	1.223	74.5	0.0443	2.70	0.019	1.14	0.28	17.2
S0-3	0.406	25	0.183	11.25	0.0399	2.46	0.0046	0.282	0.086	5.27	0.774	47.7	0.0426	2.63	0.028	1.70	0.52	31.8
C0-1	0.4002	25	0.129	8.04	0.0360	2.25	0.0064	0.402	0.089	5.58	0.821	51.3	0.0442	2.76	0.026	1.63	0.96	59.7
C0-2	0.357	25	0.123	8.63	0.0360	2.52	0.0065	0.452	0.073	5.14	0.810	56.7	0.0350	2.45	1.148	80.40	0.90	62.8
C0-3	0.0484	25	0.023	12.13	0.0055	2.83	0.0029	1.477	0.042	21.9	0.231	119.1	0.0064	3.31	0.010	5.25	0.55	284.9
C1-1	0.3987	25	0.135	8.49	0.0108	0.679	0.0077	0.480	1.23	76.9	3.230	202.5	0.544	34.1	0.179	11.22	3.65	228.9
C1-2	0.3991	25	0.139	8.69	0.0112	0.702	0.0081	0.510	0.098	6.13	3.310	207.3	0.0607	3.81	0.028	1.72	1.30	81.1
C1-3	0.4187	25	0.153	9.12	0.0127	0.756	0.0081	0.484	0.194	11.6	6.838	408.3	0.0511	3.05	0.947	56.54	1.33	79.5
C2-1	0.3961	25	0.139	8.74	0.0093	0.589	0.0094	0.590	0.044	2.80	3.940	248.7	0.0267	1.69	0.019	1.20	1.20	75.8
C2-2	0.4028	25	0.147	9.15	0.0096	0.596	0.0075	0.466	0.047	2.90	4.270	265.0	0.0271	1.68	0.013	0.82	1.14	70.8
C2-3	0.4175	25	0.155	9.28	0.0101	0.608	0.0062	0.370	0.056	3.36	4.269	255.6	0.0330	1.97	0.013	0.78	1.07	64.3
C3-1	0.402	25	0.180	11.20	0.0080	0.497	0.0081	0.502	0.042	2.62	8.674	539.4	0.0205	1.28	0.147	9.15	1.19	73.9
C3-2	0.3977	25	0.178	11.19	0.0080	0.502	0.0110	0.694	0.059	3.68	11.535	725.1	0.0324	2.03	0.196	12.32	1.05	66.0
C3-3	0.1595	25	0.078	12.27	0.0035	0.549	0.0092	1.443	0.046	7.14	3.809	597.1	0.0201	3.16	0.038	5.95	0.58	90.9
C4-1	0.3952	25	0.140	8.85	0.0172	1.09	0.0091	0.577	0.093	5.90	1.955	123.7	0.0312	1.98	0.048	3.04	1.29	81.3
C4-2	0.4032	25	0.143	8.88	0.0172	1.06	0.0067	0.418	0.079	4.88	2.343	145.3	0.0352	2.18	0.047	2.90	1.06	65.6
C4-3	0.4466	25	0.160	8.93	0.0188	1.05	0.0084	0.470	0.078	4.38	2.223	124.4	0.0368	2.06	0.017	0.93	1.11	62.1
C5-1	0.4281	25	0.118	6.89	0.0126	0.734	0.0080	0.469	0.070	4.07	2.076	121.2	0.0680	3.97	0.137	8.02	1.04	60.7
C5-2	0.4145	25	0.130	7.84	0.0316	1.91	0.0100	0.601	0.104	6.25	1.385	83.5	0.0261	1.58	0.155	9.38	8.94	539.4
C5-3	0.3526	25	0.096	6.78	0.0094	0.667	0.0047	0.330	0.047	3.36	1.140	80.8	0.0222	1.58	0.030	2.13	0.57	40.4

Table B.6: ICP results for water samples in ocean and stream

Prøve	**As** **[mg/L]**	**Cd** **[mg/L]**	**Cr** **[mg/L]**	**Cu** **[mg/L]**	**Fe** **[mg/L]**	**Ni** **[mg/L]**	**Pb** **[mg/L]**	**Zn** **[mg/L]**
Water samples Ocean								
S ref	0.0118	0	0.00048	0.0109	0.050	0.00244	0.00501	0.037
S0	0.0085	0	0.00181	0.0127	0.786	0.00275	0.00661	0.063
S0	0.0079	0	0.00064	0.0083	0.196	0.00405	0.00337	0.021
S1	0.0094	0.00137	0.00139	0.0153	0.468	0.00675	0.02268	0.622
S2	0.0069	0	0.00274	0.0056	0.592	0.00243	0.00414	0.046
S3	0.0116	0	0.00053	0.0112	0.412	0.00402	0.00266	0.070
Water samples Stream								
Å0	0.00388	0	0.00207	0.00829	0.578	0.00494	0.0129	0.038
Å1	0.00427	0	0.00090	0.00469	0.328	0.00319	0.0094	0.047
Å2	0.00650	0.00046	0.00294	0.01672	2.284	0.00547	0.1108	0.139
Å3	0	0	0.00290	0.00396	2.661	0.00458	0.0083	0.100

B.1 Calculations of the concentrations measured by DGTs

Table B.7 shows the measured heavy metal concentrations in the resin-gel-HNO_3-milli-Q solution. The measured values from the blinds were subtracted.

Table B.7: ICP results for DGT analysis

Prøve	**As** [mg/L]	**Cd** [mg/L]	**Cr** [mg/L]	**Cu** [mg/L]	**Fe** [mg/L]	**Ni** [mg/L]	**Pb** [mg/L]	**Zn** [mg/L]
Blind 1	0.00339	0	0.00372	0	0.0202	0.00293	0	0.017
Blind 2	0.00588	0	0.10643	0	0.0156	0.00292	0.0140	0.010
Å1-1	0.00463	0.000187	0.00379	0.002514	0.2354	0.00719	0.0092	0.039
Å1-2	0.00575	0	0.00338	0.004521	0.5330	0.00791	0.0015	0.025
Å2-1	0.00560	0	0.10831	0.006971	4.1916	0.01054	0	0.289
Å2-2	0.00424	0.000245	0.00344	0.007017	4.2658	0.01189	0.0103	0.294
Å3-1	0.00288	0	0.00341	0.00176	2.0632	0.00786	0.0068	0.132
Å3-2	0.00413	0.000097	0.00344	0.003428	2.1979	0.00782	0.0025	0.151
S0-1	0.00501	0	0.00301	0	0.0179	0.00385	0	0.006
S0-2	0	0	0.00361	0.00355	0.0232	0.00446	0.0013	0.028
S1-1	0.00507	0	0.00355	0	0.0235	0.00386	0	0.019
S1-2	0.00207	0	0.00315	0	0.0183	0.00328	0	0.011
S2-1	0.00565	0	0.00275	0	0.0254	0.00312	0.0041	0.005
S2-2	0.00183	0	0.00285	0.002862	0.0250	0.00413	0.0048	0.028
S3-1	0.00733	0	0.00308	0	0.0188	0.00459	0	0.009
S3-2	0	0	0.00323	0.000739	0.0272	0.00482	0	0.020

The calculations were performed as described in Chapter 3.4.1, using f_e of 0.8 and were deployed for a time as shown in table B.8.

Table B.8: Period for which the DGTs were deployed

	Deployed		**Retrieved**		**Total time**
Station	Day	Time	Day	Time	[s]
Å1	02.08.2012	13:30	13.08.2012	11:30	943200
Å2	02.08.2012	14:00	13.08.2012	11:20	940800
Å3	02.08.2012	14:30	13.08.2012	10:30	936000
S 0	03.08.2012	17:40	12.08.2012	11:25	755100
S 1	03.08.2012	17:10	12.08.2012	11:15	756300
S 2	03.08.2012	17:15	12.08.2012	11:15	756000
S 3	03.08.2012	17:25	12.08.2012	11:15	755400

Tabel B.9 shows the used diffusion coefficients according to [Davison and Zhang, 1993].

Table B.9: Diffusion coefficients D used in the DGT calculations in $[10^{-6} cm^2/s]$

	Cd	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Ocean (6.5 °C)	3.47	2.87	3.545	3.48	3.285	4.57	3.46
Stream (9.0 °C)	3.78	3.13	3.86	3.79	3.58	4.98	3.77