Stabilization of shooting range soil by iron amendments under various redox conditions

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Preface/Acknowledgements

The work in this master thesis was done in a joint cooperation between Norwegian Geotechnical Institute (NGI), Norwegian University of Life Sciences (UMB), Norwegian Defence Research Establishment (FFI), Lindum AS and Bioressurs Østlandet AS.

The work was a continuation of Dr Gudny Okkenhaug's previous research on antimony (Sb) and its solubility in the environment.

The objectives and scope of the study was determined by NGI in agreement with the employer Norwegian Defence Estates Agency (NDEA). The *in situ* preparation and sampling was done by the author in cooperation with NGI. The ICP-MS analyses were done by FFI, while the HG-ICP-OES analyses were done at the Institute of Plant and Environmental Sciences (IPM, UMB) by the author and lab technicians. Soil analyses were performed by lab technicians and the author at IPM.

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Abstract

Large amounts of lead (Pb), zinc (Zn), copper (Cu) and antimony (Sb) are yearly deposited in Norwegian shooting ranges. Remediating these heavily contaminated areas for various land use often require depositing the soils at landfills. However, the leaching of metals and Sb may become an environmental problem. Thus soils deposited in Norwegian landfills have to be controlled and classified relative to the Norwegian waste regulation (avfallsforskriften).

Previous research has shown that Fe-amendments to effectively stabilize Pb and Sb in shooting range soils. However, environmental conditions may affect the iron amendments stability and effectiveness when used to stabilize such soils prior landfilling. Reducing conditions can mobilize Fe and contaminants through dissolution and desorption. In this work, Fe-amended shooting range soils were introduced to different water saturation levels (WSL; 50 % and 100 %), leading to various redox conditions. Water saturation levels in the containers aiming for 50 % WSL were monitored by tensiometers, showing that most containers maintained a 40-60 % WSL during the experiment.

The Fe-amendments used in this work was iron grit (Gotthard Meyer, Germany) and CFH-12, a Fe-oxyhydroxide powder (Kemira, Finland) mixed with Limestone from Franzefoss, Norway.

For chemical analyses inductively coupled plasma mass spectrometry (ICP-MS) was used, and hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES) was used for speciation analyses of Sb.

The results showed effective stabilization in soils mixed with 2 % CFH-12, where soil pore water concentrations of Pb, Zn, Cu and Sb were measured below the leaching limits for inert (Pb; (C_0: 150 µg/l, L/S 10: 50 µg/l) Zn; ($C_{0:}$ 1200 µg/l, L/S 10: 400 µg/l) Cu; (C_0: 600 µg/l, L/S 10: 200 µg/l)) and non-hazardous waste (Sb; (C_0: 150 µg/l, L/S 10: 70 µg/l)) waste landfills given in the waste regulations.

Iron grit showed effective stabilization with Pb, Zn and Cu pore water concentrations below the leaching limits for inert waste landfills (batch test). However, the remediation effect was not sufficient for Sb to reach this level.

For soils mixed with 0.5 % CFH-12 and iron grit, iron grit gave the best retention for Pb and Sb in both 50 and 100 % water saturation level (WSL). Soils treated with 0.5 % CFH-12, showed poor retention capacity.

In containers holding 100 % WSL, a strong iron mobilization was observed due to reducing conditions. However, this did not mobilize metals and Sb.

Antimony speciation analysis, conducted by HG-ICP-OES showed that even under reducing conditions, Sb was predominantly found as Sb (V).

Water holding capacity of the soil and soil mixed with amendments was determined by the sandbox method.

Sammendrag

Store mengder bly (Pb), sink (Zn), kobber (Cu) og antimon (Sb) forurenser norske skytebaner hvert år. Etter hvert som disse skytebanene avvikles, må områdene remedieres før de kan bli tatt i bruk. Dette innebærer ofte at jorden blir transportert til et egnet deponi. Men selv på deponier kan metaller og antimon mobiliseres og transporteres fra sigevann til grunnvann. Dette er et miljøproblem. Derfor skal forurensede jordmasser som havner på deponi i Norge klassifiseres i henhold til utlekkingspotensiale i avfallsforskriften.

Tidligere forskning av har vist at jernsorbenter effektivt stabiliserer Pb og Sb i forurenset jord fra skytebaner. Men ytre miljøpåvirkninger kan redusere effektiviteten til jernsorbenter. Reduserende forhold kan mobilisere jern og andre metaller gjennom dissolusjon. I denne oppgaven ble skytejord tilsatt jernsorbenter og introdusert til forskjellige nivåer av vannmetning. Vannmetning ved 50 og 100 % gav varierende redoxforhold.

Jernsorbentene som ble brukt i forsøket, var nullverdig jern (Fe^0) produsert av Gotthard Meyer, Tyskland, og CFH-12 (Fe-oxyhydroksid) produsert av Kemira, Finland, blandet med kalkstein fra Franzefoss, Norge.

Kjemiskanalytiske teknikker som ble tatt i bruk inkluderte induktivt koblet plasma massespektrometri (ICP-MS) og hydrid generering induktivt koblet plasma optisk emisjonspektrometri (HG-ICP-OES) for spesieringsanalyse av Sb.

Resultatene viser effektiv stabilisering av Pb, Zn, Cu og Sb i jord behandlet med 2 % CFH-12. Alle prøvertakinger i august måned viser porevannskonsentrasjoner lavere enn grenseverdier for utlekking ved inert (Pb; (C_0: 150 µg/l, L/S 10: 50 µg/l) Zn; ($C_{0:}$ 1200 µg/l, L/S 10: 400 µg/l) Cu; (C_0: 600 µg/l, L/S 10: 200 µg/l)) og ordinært (Sb; (C_0: 150 µg/l, L/S 10: 70 µg/l)) avfall, i henhold til avfallsforskriften.

Nullverdig jern viser effektiv stabilisering av Pb, Zn og Cu, med porevannskonsentrasjoner under grenseverdien for ristetest ved deponi for inert avfall. Men effekten for stabilisering av Sb var ikke tilstrekkelig.

I skytejord behandlet med 0.5 % konsentrasjoner av CFH-12 og nullverdig jern, gav nullverdig jern den beste retensjonen av Pb og Sb i begge vannmetninger (50 og 100 %

vannmetning). Jord behandlet med 0.5 % CFH-12 viste porevannskonsentrasjoner av Pb og Sb over grenseverdier satt ved både L/S 10 og C_0.

En sterk mobilisering av jern ble observert i kontainere med 100 % vannmetning. Porevannskonsentrasjonene økte gradvis fra januar til august. Men denne mobiliseringen gav ikke en merkbar økning i porevannskonsentrasjonene av metallene og Sb.

Spesieringsanalysen av Sb ved HG-ICP-OES viste at Sb hovedsakelig foreligger som Sb (V), selv ved reduserende forhold.

Vannmetningen til behandlet og ubehandlet jord ble kontrollert ved å bruke sandbox metoden og tensiometere.

Table of Contents

List of tables and figures

Tables

Figures

Abbreviations

EC - Eletrical conductivity

Eh - Redox potential

Fe^0 - Zero valent iron

FFI - Norwegian Defence Research Establishment (Forsvarets forskningsinstitutt)

HG - ICP - OES - Hydride generation ICP-OES

ICP - OES - Inductively coupled plasma optical emission spectrometry

ICP - MS - Inductively coupled plasma mass spectrometry

mV - Millivolt

NGI - Norwegian Geotechnical Institute

OM - organic matter

DOC - Dissolved organic matter

TOC - Total organic carbon

µS/cm - Micro Siemens per Centimeter

Sb - Antimony

Zn - Zinc

Cu - Copper

Pb - Lead

Ca - Calcium

Mn - Manganese

Fe - Iron

As - Arsenic

FREVAR - Fredrikstad vann-, avløps- og renovasjonsforetak

HCl - Hydrochloric acid

IPM - Institute of Plant and Environmental Sciences

UMB - Norwegian University of Life Sciences

NGU - Norwegian Geological Survey

KLIF - Norwegian Climate and Pollution Agency

NDEA - Norwegian Defence Estates Agency

DOM - Dissolved Organic Matter

SFT - Norwegian Pollution Control Authority

PZC - Point of zero charge

SD - Standard Deviation

WSL - Water saturation level

IBC - Intermediate Bulk Container

1 Goal and scope

In this project the goal was to investigate (1) the stabilization effect of Fe-amendments on lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) in heavily contaminated shooting range soil *ex situ*, and (2) whether water saturation and redox conditions affected the effectiveness of the Fe-amendments and speciation of Sb.

The Fe-amendments used were 0.5 and 2 % zero valent iron granulate (iron grit) and CFH-12 powder (Fe-oxyhydroxide). The CFH-12 was mixed with limestone at 0.25 % and 1% respectively due to a slightly acid reaction of the CFH-12 material.

The choice of amendments was based on results from previous research done by Okkenhaug (2012), where both sorbents showed good effect for stabilizing Pb and Sb.

Soil from a shooting range stop butt was mixed with the Fe based amendments and stored in containers (1 m^3). pH, redox conditions (Eh) and element concentrations in the soil pore water were monitored from January to August.

The water saturation were set at 50 and 100 % for all treatments, and controlled by tensiometer measurements and soil water saturation curves established in the laboratory.

2 Introduction

Shooting ranges worldwide are huge recipients of contamination through use of small arms ammunition. Typical heavy metals used in this ammunition include the metals Zn, Cu, Pb and and the metalloid Sb (which is used as hardener for Pb). These elements are often mobile in soil, and may pose a risk to the environment.
At Norwegian shooting ranges, Pb is the dominant contaminant, and in 2005 approximately 100 tons were deposited. This equals 66% of the total Pb emissions in Norway (Heier et al. 2009). Roughly 73 tons of Cu, 12 tons of Zn and 12 tons of Sb were also deposited. A gradual decrease of Pb deposits has been observed from 2006 - 2010 due to the change to green bullets, i.e. lead-free bullets. However an increase was reported from 2010 - 2011 due a temporary ban on green bullets as they produced toxic fumes (FFI, 2012).

Between 500 and 800 military shooting ranges are used and managed by the Norwegian Defence Estates Agency (NDEA). Several of these are in the process of being abandoned in connection with restructuring process of the military, and a remediation is required before they can be sold and or re-developed for different land-use.

Often, in this remediation process, shooting range soil has to be excavated and disposed of at a landfill. Thus, the mobility of contaminants in the landfill is of interest.

Mineral based remediation is used to stabilize the contaminants, thus prevent leaching inside landfills. By lowering the leaching of heavy metals and metalloids, the contaminated soil can be deposited in landfill sites of reduced hazard level. Leachate limits are defined in the Norwegian Waste Regulation (avfallsforskriften).

A relatively new mineral remediation tool is the use of Fe-oxides. Okkenhaug (2012) found Fe-amendments to be an effective sorbent for stabilizing Pb and Sb in shooting range soil.

In this work the use and effect of Fe-oxides on stabilizing Cu, Zn, Sb and Pb are examined in shooting range soil under 50 and 100 % water saturation. In landfills and shooting ranges variations in redox conditions will occur by natural processes, such as changes in the water saturation level. The variations in redox conditions will affect the stability and solubility of Fe-oxides, and thus it is an important aspect to determine the remediation effect.

3 Background

3.1 Shooting ranges in Norway

Shooting ranges in Norway are prone to heavy metal contamination due to large amounts of ammunition being deposited. According to FFI (2011) and NDEA (2011), total areas of 1360 km^2 are active shooting ranges. These areas are divided between 48 grounds for exercise and shooting ranges. The locations of these exercise areas are displayed in figure 1.

The ammunition deposited consists of large quantities of heavy metals and metalloids, as Pb, Cu, Zn and Sb. The mobility and speciation of these elements are interesting, as the intensive metal contamination in shooting ranges may cause severe effects on the local environment. In 2007 the deposition of ammunition in small arms shooting ranges consisted of 103, 73, 12 and 7 tons of Pb, Cu, Zn and Sb (Heier et al. 2009). According to FFI (2011) a total of approximately 11 million bullets (NATO 7.62 mm rounds) were reported in use in 2010.

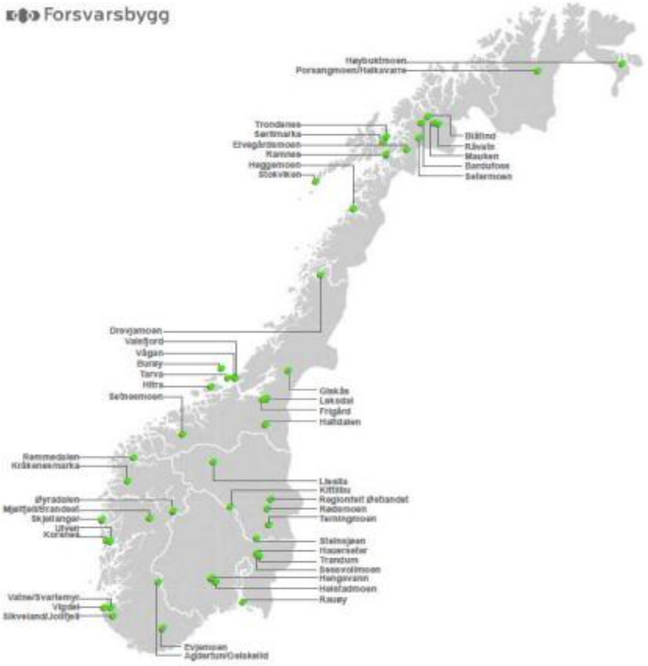

Figure 1. Geographical locations of active shooting ranges used by the Norwegian military (Norwegian Defence Estates Agency, 2011)

In recent years the Norwegian Defence Estates Agency (NDEA) has started remediating their contaminated shooting ranges. They are required by the Norwegian Ministry Defence to assure that the shooting ranges are not posing any risk for the environment. Before any properties are sold, they have to meet the acceptable limits established by The Climate and Pollution Agency (KLIF), a directorate governed by the Norwegian Ministry of Environment (Norwegian Ministry of Defence, 2011).

A common remediation technique used for heavily polluted soils is excavation and landfill deposition. However, the mobility of metals can still be a problem. To safely deposit the contaminated soils in a landfill, the pollutants may need to be stabilized to meet leaching limits of metals and metalloids set by the Norwegian and European landfill regulations.

3.1.1 Shooting range Regimentsmyra, Fredrikstad, Norway

Regimentsmyra shooting range is located outside Fredrikstad in the south eastern part of Norway. The shooting range is controlled and governed by the Norwegian Defence Estates Agency (NDEA). The area is in total 14000 m^2, and consists of 4 areas used for shooting ranges, one area which consists of two pistol ranges, one rifle range, one hand grenade training range and one used for clay pigeon target shooting. The area is a popular recreational area in the eastern parts of Fredrikstad and the shooting ranges are in close vicinity of housing and agricultural areas. Fredrikstad municipality has voiced their interest in taking over the area. Future planning may include a shooting range, though it would be limited to lead-free bullets.

The Fredrikstad area holds like other coastal regions of southern Norway a temperate climate. The last twelve months the temperature was at its lowest in February averaging -1 °C and the warmest in August averaging 16.8 °C. The rainfall varied in 2012 from an average of 140 mm to 5 mm. The annual precipitation for 2011 was 860 mm (Norwegian Meteorological Institute).

The shooting range sampled in this project is shown in figure 2. The stop butt was in close contact with bedrock and may have received surface water runoff from rainfall. The plant growth was sparse in the stop butt itself, however some spruce and pine were found. Especially the pines are worth noting, due to complex and deep root systems able to grow deep into the soil.

Figure 3 shows the bottom of the shooting range stop butt where large amounts of organic material were found in a peat area. In figure 4, surface water is visible and a drainage path leads surface water out of the shooting range into vegetation close by.

Figure 2. The shooting range sampled and treated in this project (Photo: Liland, 2012).

Figure 3. Peat area bordering the impact berm (Photo: Liland, 2012).

Figure 4. Surface water from the shooting range entering vegetation (Photo: Liland, 2012).

3.2 Contamination of shooting ranges

The Norwegian armed forces use different kinds of small arms ammunition relative to needs and specific purposes. However, the most frequently used ammunition is a 7.62 x 51 mm NATO bullet. This ammunition consists of 60 % Pb, 29 % Cu, 8 % Sb and 3 % Zn (Strømseng et al. 2009).

Once the ammunition has been fired, the fate and transport of its constituents is dependent of several factors, such as soil properties, climate, precipitation, vegetation and local topography. To a large extent the contaminants are found in the stop butt, where they may be mobilized and transported to the environment.

The most relevant factors are water saturation and soil properties. For instance redox potentials (Eh) will affect both the mobility and toxicity of metals and metalloids. Ammunitions that have been deposited will with time undergo oxidation and corrosion. This leads to a mobilization of heavy metals and metalloids. Physical fractionation may also take place in the butt, where recently deposited bullets have physically interacted and shattered old bullets. This gives the older bullets a bigger chemically reactive surface, and corrosion may occur at a faster rate (Voie et al. 2006).

Once the metals reach the soil they can be available as particles, or bound through other soil constituents. The distribution is dependent on both physical and chemical factors, for instance pH or redox conditions. Mobilizations are affected by sorption mechanics, hydrolysis, complexation and colloid formation (Heier et al. 2009).

Many shooting ranges are situated close to peatlands where both water and organic matter will influence and increase transport and mobilization. Complexing humic material will be a major pathway of transporting heavy metals into the environment (Heier et al. 2009).
The organic matter with its negative surface will be a possible place for sorption for heavy metals, examples being the cations of Pb, Zn and Cu. Figure 3 shows surface water in the area leading up to the impact berm.

In episodes where big discharges of rainwater happen, a large mobilization of heavy metals will be observed in shooting ranges (Strømseng et al. 2009). As both landfills and shooting ranges are affected by such discharges it is interesting to find out how effective amendments can be at stabilizing heavy metals and metalloids, thus preventing leachate from reaching the groundwater, nearby open water sources or being transported into the environment. Episodes of excessive input of metals into watercourses may cause a threat to exposed organisms in the environment (Strømseng et al. 2009).
According to Conesa et al. (2010), Sb leaching from contaminated soil can be a problem for the environment. It can be relatively mobile, may enter the groundwater, and subsequently accumulate in plants.

3.3 Characterization of antimony (Sb) and metals

The term that is heavy metals is generally used for all metals with a density above 5 g cm^{-3}. They are separated into two groups, being the non-essential and essential heavy metals. As an example both Zn and Cu are essential and needed for biochemical reactions in an organism. However at high concentrations they become toxic. An example of non-essential heavy metals is Pb, an element that is of great environmental concern (McLaren, Cameron, 1996).

Metalloids, like Sb, are elements that hold properties found in both non-metals and metals, or something in between.

3.3.1 Antimony (Sb)

Antimony is a non-essential metalloid in group 15 of the periodic table. Neighboring Arsenic (As), it is chemically similar, and can be found in oxidation states (-III, 0, III, V).

Humic acids found in organic soils are not considered an important sorbent for Sb (Tighe et al. 2005). In more inorganic soils, Sb mobility is limited by Mn and Fe-oxides. By adding limestone to immobilize heavy metals in shooting ranges, Sb may get mobilized due to the pH increase and a following lowered anion exchange capacity. However, the introduction of calcium (Ca) to soil solutions can also cause Sb to precipitate as Ca-antimonate (Okkenhaug, 2012).

The negatively charged oxyanions have been shown to have an affinity for surfaces on clay minerals (Okkenhaug, Mulder, 2011).

Examples of Sb containing minerals are stibnite (Sb_2S_3) and valentinite (Sb_2O_3). Antimony in soil is known to exist primarily as inorganic species.

Compared to some heavy metals, like Pb, little research has been done on Sb in the environment. According to the United States Environmental Protection Agency, Sb is classified as an element that may hold carcinogenic potential, though more research is needed to be done.

In regards to its bioavailability Sb has been shown to bioaccumulate in plants in highly contaminated areas, thus Sb could enter the food chain and become a hazard for humans and other organisms (Okkenhaug et al. 2011).

3.3.1.1 Speciation of antimony (Sb)

In natural systems Sb is occurs as an oxyanion in its pentavalent form, or as the neutral trivalent Sb (III). The most dominant form is Sb (V). Under reducing soil conditions Sb can be found as the inorganic compound antimonite ($Sb(OH)_3$), and under oxidizing conditions Sb (V) is mainly found as antimonate ($Sb(OH)_6^-$). As these species show different properties, the oxidation state becomes an important factor to assess the behavior of Sb in the natural environment.

An example of the change in mobility of Sb relative to its oxidation state is for instance the fact that antimonite ($SbOH_3$) binds well to iron hydroxides over a big pH range, while antimonate ($Sb(OH)_6^-$) adsorbs best at a close to neutral pH.

As the toxicity of Sb is reflected by its oxidation state, and Sb (III) is more toxic then Sb (V) environmental samples require quantitative speciation analysis to determine and assess the toxicity represented by Sb. Toxicity of Sb increases from antimonate (V) to antimonite (III) (Filella et al. 2002).

3.3.2 Lead (Pb)

Lead is a non-essential heavy metal in group 14 of the periodic table. It is well known for its toxicity and ability to bioaccumulate. Lead values in Norwegian soil are considered hazardous waste at 25000 mg kg^{-1}. (SFT, 2009)

The element is a major pollutant in shooting ranges worldwide, where most bullets consists of a core dominated by Pb.

Lead is often mobile in the soil pore water as a divalent cation, Pb (II). But these concentrations can be lowered and controlled by increasing the pH. An increased pH will increase the Pb retention of soil minerals. A common soil treatment to increase the pH, is adding limestone. However, by adding limestone, the Pb (II) adsorbed to minerals can face competition for cation exchange places with divalent calcium. Thus a concentration increase of Pb (II) can be found in soil solutions straight after the utilization of limestone (Klitzke, Lang, 2009).

Increasing concentrations of carbonate (CO_3^-), can immobilize Pb by forming Pb-carbonate ($PbCO_3$). Dissolved organic matter will also affect the behavior of Pb, as it can form complexes. Especially in acidic conditions Pb will be able to form complexes of dissolved organic matter (DOM-complex). This can increase the mobility of Pb in the soil (Weng et al. 2002).

3.3.3 Copper (Cu)

Copper is a heavy metal in the d-block of the periodic table. It is an essential heavy metal needed for biochemical reactions in both plants and humans. But in high concentrations it is considered toxic. According to the Norwegian Climate and Pollution Agency, Cu values above 25000 mg kg^{-1} are considered hazardous waste in soils (SFT, 2009).

The element, like Pb, may form DOM-complexes. Copper found in soil solutions is primarily found as Cu (II). However the element has also been found in monovalent and trivalent oxidation states, though they tend to dissociate to form elementary Cu and Cu (II). The main sorbents for Cu in sandy soil solutions is organic matter present and clay silicates. (Weng et al. 2001) However according to Bes and Mench (2008), most Cu found in soil is associated with Fe and Mn-oxides.

Like many other metals, Cu has increased mobility in acidic conditions. In alkaline conditions Cu may get immobilized by the formation of Cu-carbonate.

3.3.4 Zinc (Zn)

Zinc is another essential heavy metal found in the d-block of the periodic table. Though, like Cu, it becomes toxic in high concentrations. According to Norwegian classification of soil contaminants, Zn is considered hazardous waste at levels of 25000 mg kg^{-1} or above. (SFT, 2009)

Zinc is available monovalent and divalent cations in soil solutions, though most frequently as Zn (II).

The most important sorbents for Zn (II) in soil is organic matter, Fe-hydroxides and clay (Yi et al. 2007).

3.4 Remediation options and classification

One of the great challenges in the 21 century is handling the rapid increase in global population. The dramatic population growth leads to continued pressure on natural resources and the steady state environment. Climate changes leads to worse soil quality for crop production. Industrial pollution affects recreational and housing areas, thus soil remediation becomes even more important. The generally accepted approach now, is to use the concept of risk assessment and management to remediate contaminated land. This means an increased focus on sustainable solutions (Vegter, J.J. 2001).

The idea of sustainable thinking and importance of a healthy environment has led to increased focus on remediation techniques for contaminated soil.

Normally there are three general options available for remediating contaminated land. Excavating the soil and transport it to a landfill, chemically treat it, or isolate it to prevent pollutants reaching the environment. Sometimes a mixture of these techniques is adapted to get the right results.

Contaminated soil remediation techniques can be performed *in situ or ex situ*. An *in situ* technique treats contaminants in place, without removing the soil. *Ex situ* techniques removes the soil for treatment, either on-site or off-site.

Table 1. Norwegian classification of contaminated soil, for lead (Pb), copper (Cu), zinc (Zn) and antimony (Sb). Concentrations are listed in mg kg^{-1} dry weight (SFT, 2009).

Classification	1	2	3	4	5
Condition	Very good	Good	Moderate	Bad	Hazardous waste
Lead (Pb)	< 60	60 -100	100-300	300-700	700-2500
Copper (Cu)	< 100	100-200	200-1000	1000-8500	8500-25000
Zinc (Zn)	< 200	200-500	500-1000	1000-5000	5000-25000
Antimony (Sb)	< 40	40-600	600-3650	3650-7296	>7296

The degree of remediation needed at a contaminated site, is dependent on how heavy the area is polluted. According to the Norwegian Pollution Control Authority (2009) classification 5 is considered hazardous waste (table 1). This degree of soil contamination needs to be removed, irrespective of future use of the area. The landfill accepting the waste has to be an officially approved recipient of hazardous waste. Values available for Sb are proposed by KLIF and developed by NGU (2007).

The future use of contaminated land is important when determining acceptable levels of soil contaminants. For instance, for housing areas, schools etc. the acceptable values in the soil are lower compared to an area designated for future industrial use. Another factor that has to be considered is the soil depth at which the contaminants are found. Acceptable values in surface areas are generally lower compared to contaminants found further down in the soil profile. Topsoil is considered down to a depth of 1 meter and is more rigorously evaluated compared to > 1meter.

3.4.1 Waste regulation

Soils that are excavated and deposited in a landfill have to meet requirements set by the Norwegian waste regulation. Landfill leachate limits are found in chapter 9 appendix 2, and the limits used for Sb, Cu, Pb and Zn are similar to EU's Landfill Directive.

By adhering to the criteria set forward by this directive, contaminated soils are deposited in controlled areas to limit potentially negative effects on the environment. There are three categories of landfills, and acceptable concentrations of leaching decrease from category 1 to 3.

The leachate of pollutants can be a problem in landfills. To determine what landfill contaminated soils can be deposited at the soil must be classified according to leachate limits found in table 2.

- 1: Landfills for hazardous waste
- 2: Landfills for non-hazardous waste
- 3: Landfills for inert waste

Table 2. Threshold limits for Cu, Sb, Zn and Pb leachate in Norwegian landfills (Miljøverndepartementet, 2004).

Element	Inert waste		Non-hazardous waste		Hazardous waste	
	Column test mg/l	Batch test mg/kg	Column test mg/l	Batch test mg/kg	Column test mg/l	Batch test mg/kg
Cu	0,6	2,0	30,0	50,0	60,0	100,0
Sb	0,1	0,06	0,15	0,7	1,0	5,0
Zn	1,2	4,0	15,0	50,0	60,0	50,0
Pb	0,15	0,5	3,0	10,0	15,0	50,0

Threshold limits for column tests are given at L/S 0.1 l/kg. Limit values for batch tests are given through L/S 10 l/kg.

3.5 Iron amendments and remediation

Mineral based remediation is a method where the aim is not to lower the total concentration of contaminants, but rather reduce their mobility and bioavailability through chemical processes. This prevents contaminants from spreading into the environment (water, soil and air).

Previous research has shown that heavy metal contamination in shooting ranges may be stabilized successfully by limestone ($CaCO_3$) and phosphate (PO_4^{3-}). But it has also shown that these amendments may mobilize Sb (Okkenhaug, 2012).

An alternative is Fe-amendments. Iron oxides have been shown to excel at adsorbing both cations and anions, thus reducing their mobility (Kumpiene et al. 2008).

Iron is a natural soil element, and Fe-oxides are products of chemical weathering of minerals (van Loon, Duffy, 2008). While they are found as both Fe-oxides, hydroxides and oxy-hydroxides in soil, they are collectively named Fe-oxides (Cornell, Schwertmann, 2003). In total we know of 16 Fe-oxides, where examples of the most frequently occurring ones are are ferrihydrite (β-FeOOH), lepidocrocite (γ -FeOOH), goethite (α-FeOOH), and hematite (α-Fe2O3) (Miretzky, P. Cirelli, 2010).

Iron amendments are cost efficient and known to adsorb and stabilize heavy metals and metalloids. Their effect has been well documented, and is among the most frequently used amendments (O'day, Vlassopoulos, 2010). By adding Fe-amendments for remediation purposes, there is a reaction between the sorbent and the sorbate. Sorbents are the solid phase fraction reacting with the sorptives. The sorptives, in this case, are the metals and metalloids found in the soil solution that could potentially adsorb to the sorbent. Once the sorptives react with the sorbent they are named sorbates.

Many Fe-oxides have a high specific surface area, making them able to adsorb many heavy metals dissolved as ions (Schwertmann, 1991), and thus reducing the mobility of the contaminants. Vodyanitskii (2008) found this also to be true for metalloids, like Sb.

While Fe is able of adsorbing many metals and metalloids, the adsorbed elements might also be precipitated through creation of insoluble secondary minerals (Kumpiene et al. 2008).

The type of Fe-oxides present varies upon Fe concentration and physical properties. The surface chemistry of the Fe-oxides is however very much dependent on the surface charge.

The surface charge varies with soil pH, due to being influenced by the concentrations of H^+ and OH^- concentrations. If the pH rises and the OH^- concentration in the soil solution increases, the surface charge of Fe-oxides becomes more negative. If the pH drops, the H^+ concentration rises, and the negative charge is lowered. According to McLaren and Cameron (1996), the surface charge of Fe-oxides, clay and aluminosilicates are all affected by the pH variations.

Point of zero charge (PZC) or pHo is considered the pH value a solid holds zero net charge on its surface (Sparks, 1986). If the surrounding environment holds a pH lower than the PZC of the sorbent, it means the solids adsorbing surface could be positively charged, and thus attract anions.

For Fe-oxides the point of zero charge varies between 6.5 and 9.5 pH. This means anions (like antimonate) will adsorb well below PZC. But the divalent cations of Cu, Pb and Zn, will undergo sorption more readily at high pH values.

Once the sorbent and sorbate is connected, they can form two different complexes, inner and outer-spheres. Inner spheres are covalently bound complexes between the sorbents and the sorptives (ion in solution). Outer spheres are electrostatically bound complexes with one or more water molecules between the sorbent and sorptive (Golberg et al. 2000).

3.5.1 Effect of reducing conditions on iron based amendments

By treating the contaminated soil with 50 and 100% water saturation, an aim of the project was to observe the performance of the Fe-amendments in varying soil conditions, with respect to the WSL. The change in water saturation will influence the redox conditions. This is of great interest considering mineral amendments are a possible option for landfill stabilization and *in situ* remediation.

The different levels of water saturation will affect the soil chemistry. The stability of Fe-oxides is for instance reduced in anoxic conditions, and could cause a release of adsorbed heavy metals and metalloids (Kumpiene et al. 2008). The redox conditions in the soil solution will also influence the mobility of metals (Pareuil et al. 2008).

Many microorganisms in soil use redox reactions as a tool for respiration. Redox reactions is a process where electrons are donated, thus an oxidation must be accompanied by a reduction. While many microorganisms use organic material as the electron donor, the lack of organic material and oxygen may cause other specialized microorganisms to use manganese (Mn), Fe or other elements as electron donors. Thus, a reducing soil environment can influence the stability of Fe-oxides. By affecting the stability Fe-oxides, the reduction potential becomes of great interest in evaluating an ongoing mineral remediation process with Fe-amendments.

According to Pareuil et al. (2008) Mn-oxides tend to dissolve more easily under weaker reducing conditions compared to Fe-oxides. This is supported by Kumpiene et al. (2008) where Mn oxides are found to be reduced at higher Eh values compared to Fe oxides. This is interesting as both Mn and Fe-oxides are known to adsorb heavy metals and metalloids, and dissolution may lead to mobilization of heavy metals. Manganese is also energetically preferred by microorganisms as an electron donor compared to Fe.

Varying water saturation levels observed *in situ* could affect the redox conditions and lead to increased mobilization of contaminants. Excessive precipitation (rainfall) or blocked drainage pathways are examples that may influence the water saturation levels and consequentially mobilize metals.

A high Eh value indicates an oxidizing environment and a low Eh value leads to reducing conditions. Measuring the redox potential (Eh) is an important factor in evaluating the remediation process.

Other physical factors measured as part of the evaluation is pH and electrical conductivity (EC).

By combining the information given by pH and Eh – measurements, it is possible to create Porbaix diagrams, explaining the speciation of analytes in the soil solution.

3.6 Water saturation curves

To assess the water saturation level tensiometers were used to monthly control whether 50 % water saturation is achieved. Tensiometers are pipes of plastic with water connecting the soils pores to a porous media at the end of the pipe. Thus unless the soil pore volume is completely saturated they will exhibit a suction to the tensiometer, and this suction is recorded in centibar. The centibar is related to water saturation through a laboratory established saturation curve.

4 Materials and methods

4.1 Soil characteristics

The soils sampled in this study, were taken from Regimentsmyra shooting range, Fredrikstad, Norway. Soil profiles were made and dug out with a digger, see figure 5. The soil was inorganic and the grain size distribution analysis (performed by the laboratory employees at the Department of Plant and Environmental Sciences, Norwegian University of Life Sciences) showed total carbon at respectively 0,94 and 0,91 %, and organic carbon measured at 0,74 %. The low concentration of organic carbon and homogeneity of the soil could be an indication that the masses were not residual, but transported.

Figure 5. Soil profile with a clear view of homogeneity of the soil. (Photo: Liland, 2012)

While the area was largely covered by bedrock and minor surface deposits, there are plenty of shore deposits in the area. (Norwegian Geological Survey, 1990), this could have supported the idea of natural transportation, e.g. glacial or wind sediments. However in the bottom of the soil profile observed in figure 6, there were found large rocks in a layer and above this a geotextile. This supports the notion that the sediments were transported by human activity.

Figure 6. Large rocks and geotextile found in the bottom of the stop butt. (Photo: Liland, 2012)

The groundwater level in the area may have been high, and this could be of importance due to redox conditions in the soil solution. This was a likely scenario concluded from the water table being observed at the ground surface next to the shooting range stop butt, shown in figure 7.

Figure 7. Water table in the open next to the stop butt. (Photo: Liland, 2012)

The soil was classified as a silty sand, available in appendix 3, and grain size distribution is provided in figure 8. However it is worth noting that soil classification systems may vary from nation to nation and silty sand in Norway might not be classified as silty sand in the US or other countries.

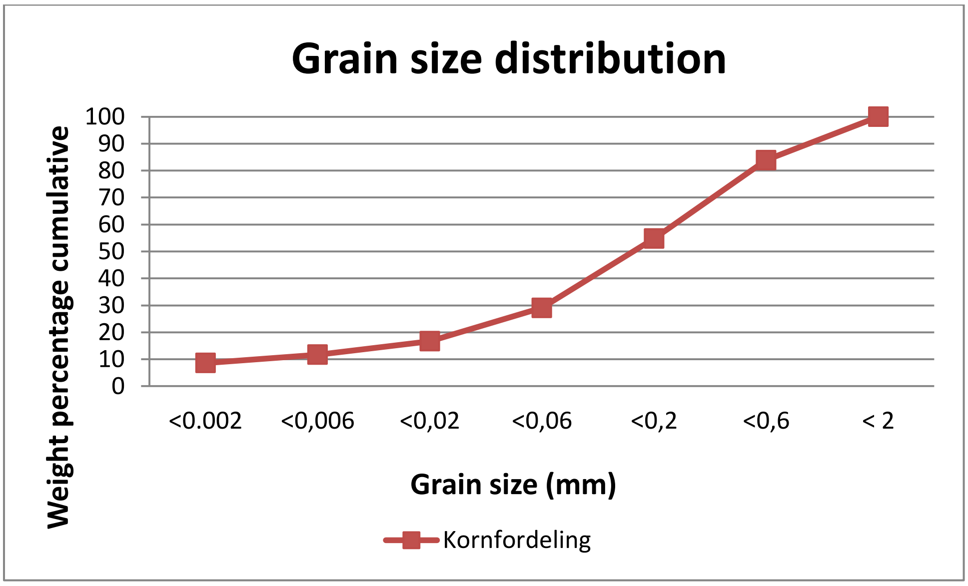

Figure 8. Grain size distribution figure of the soils sampled.

4.2 In situ preparation, sampling and storage

As the soils were to be transported and deposited at a landfill for further treatment, a XRF (x-ray fluorescence gun) was used for representative sampling. The handheld XRF was provided by an external consultancy firm (COWI). After selected areas were controlled with the XRF, a digger was used for excavation. Post excavation the soils were transported by lorry to a landfill for further treatment.

The soils were divided into 14 intermediate bulk containers (IBCs) post treatment before they were driven to a storage facility at FREVAR (Fredrikstad vann-, avløp- og renovasjonsforetak). A digger was used to move the masses and separate the larger rocks from the soil.

Figure 9. Containers during pre-treatment. (Photo: Okkenhaug, 2012)

The chosen facility held a fairly constant temperature and was heated to prevent the freezing of soil water. While a thermometer was not installed, it was generally accepted the temperature was approximately at 15 °C from January to August.

A minor problem with the storage facility was found in the fan from the neighboring facility. To prevent excessive evaporation a tarpaulin was put over the containers.

Once the containers were in place, Rhizon pore water samplers were installed in each container. A total of three samplers per container were installed. By using a steel pipe a preliminary hole was made for the Rhizon samplers. The samplers were however set at the same depth (approximately 30 centimeters). This was done by measuring and marking the steel pipe before the insertion of the Rhizon samplers.

The containers were sampled monthly from January to August with the exception of the month of June. ICP-MS analysis were given as the priority, thus if there was lack of pore water sampled, the sample would go to ICP-MS analysis instead of speciation analysis on ICP-OES.

4.3 Experimental design

4.3.1 Soil amendments and mixing

Before the containers were taken indoors for storage, the Fe-amendments were mixed with the soils. By calculating the amount of each amendment needed to achieve the 0.5 and 2 weight percent values, the amendments were manually added to each bulk of soil before storing it in separate containers. The amendments used were iron grit (Fe^0) and CFH-12 powder (iron oxyhydroxide powder).

As CFH-12 powder holds far less Fe by weight relative to iron grit, it is a factor to keep in mind when evaluating how the amendments will be effective over a period of time. However as CFH-12 is pre-oxidized it should in theory experience quicker and more immediate sorption compared to iron grit.

The soils were mixed with Fe-amendments in 2 % and 0.5 % concentrations, for different containers and saturation levels (50 % and 100 %).

- CFH-12 was added as 2 % and 0.5 % with respectively 1% and 0.25% limestone.
- The iron grit was solely added as 2 % and 0.5 %.

The containers (figure 9) used for soil storage in the experiment, are intermediate bulk containers. They hold a volume of 1 m^3 and are made of plastic with a metal (external) support structure. In the bottom a valve is available to reduce water saturation if needed, however this was never taken in use. The containers were produced by Noreko AS.

4.3.1.1 Iron grit

The iron grit used in this experiment was Cast Iron Grit FG 0300/1000 produced by Gotthard Meyer, Germany. It had a size of 0.3 - 1 mm, dark gray colour, slightly rectangular shape with sharp edges. The Fe content was given at 92 %.

Zero valent iron oxidizes to oxyhydroxides under oxidizing conditions. This creates new sorption sites for heavy metals as Pb, and metalloids like Sb. For the oxidation sequence see equation 1-3 (Kumpiene et al., 2008).

1) $Fe^0 + 2\ H_2O + 0{,}5 \rightarrow Fe^{2+} + H_2O + 2\ OH^-$
2) $Fe^{2+} + H_2O + 0{,}25\ O_2 \rightarrow Fe^{3+} + 0{,}5\ H_2O + OH^-$
3) $Fe^{3+} + 6\ H_2O \rightarrow FeOH_3 + 3\ H_3O^+$

4.3.1.2 Iron oxyhydroxide powder

The ferric oxyhydroxide powder used was the the CFH-12 product from Kemira, Finland. The Fe content is reported at 43 %. It is worth noting this powder was substantially finer grained (powder) compared to the iron grit amendment.

4.3.1.3 Limestone

The limestone added was produced by Franzefoss, Norway (0 – 5 mm size, VK 0/5).

The Fe-oxyhydroxide powder was mixed with limestone to prevent a pH drop which could happen due to the minor acidic reaction from the CFH-12 powder (Okkenhaug, 2012).

However the addition of limestone did not only affect the pH. By adding limestone carbonate (CO_3^{2-}) and calcium (Ca^{2+}) a competition will occur by calcium on minerals that interact with metals and metalloids due to ion exchange. Carbonate can precipitate analytes by forming salts. Calcium may also interact with Sb by forming various Ca-antimonates (Okkenhaug, 2012).

The changes observed in EC are shown in appendix 2. As expected soils treated with CFH-12 and limestone showed far higher EC-values compared to iron grit treated soil or reference. This is due to dissolution of limestone, and the ion concentration increase.

4.4 Pore water sampling and monitoring

The pore water samplers used in the experiment was Rhizon samplers (Rhizosphere Research Products, Wageningen, The Netherlands). The model used was macroRhizon, 9 cm length, 4,5 mm outer diameter, average pore size 0,1 µm.

The samplers were installed in approximately 30 degree angles (eye measurement) in opposite directions. Thus one would sample from all areas of the container.

Redox potentials were measured with a redox meter supplied by the Norwegian Geotechnical Institute. The instrument was a WTW pH3, with a Scholt Blueline 31Rx electrode. The measurements were corrected with a positive value of +214 due to an estimated average temperature of 15 Celsius.

The pH measurements were done at the laboratory of IPM. The pH meter used was an Orion - 1 SA 720. In general, the samples showed little fluctuation during the months of sampling (January to August).

The EC measurements were also done in the laboratory of IPM. The conductivity meter used was a Metrohm, 712 Conductometer. It was at times difficult to get steady readings of the EC-values due to remobilization of precipitation within the sample.

4.4.1 Monitoring of water saturation

The tensiometers used were of the brand Soil Moisture Equipment, produced in Santa Barbara, California, United States. One tensiometer was planted in each of the containers holding 50 % water saturation. The tensiometers showed the matric water potential in centibars, and were manually logged once a month.

4.4.2 Water regime

As an essential aspect of this experiment the containers were saturated at both 100 % and 50 %. This was done to find out the efficiency of the amendments in during changing landfill conditions, or what one could expect in *in situ* remediation projects. By controlling the water saturation the redox potential could be affected. And as redox chemistry is an important factor for both toxicity and mobility of metals and metalloids it was a very interesting aspect of the research.

The containers were filled with a hose provided in the storage facility and the water used for refilling came from the tap water of FREVAR.

The fully saturated containers were filled first, and the time needed to fill these containers was noted. By dividing the time spent filling the 100% saturated containers by two, we had an idea of the volume needed to fill the 50 % containers.

The containers were weekly re-filled by FREVAR. The fully saturated containers were easy the control, but the containers holding 50 % WSL, proved harder to maintain correctly. It was later shown that weekly re-fillings may have been over the top, and could possibly have been reduced to monthly re-fillings.

Whether the refilling worked as intended can be observed from the soil water saturation curves.

It is important to underline that the containers were never re-saturated at the days of pore water sampling. The reason for this was to avoid the chance of pore water sampled not being representative for the respective container.

4.4.3 Extraction procedure of pore water

The pore water was monthly sampled through 50 ml syringes. By setting vacuum to the syringes, and waiting (depending on water saturation and the suction) normally 30 minutes to 2 hours, the pore water was slowly extracted. It could sometimes be necessary to set the samplers and wait 24 hours to get pore water from the most difficult containers. These were normally the containers with 50 % water saturation.

4.5 Analysis

4.5.1 Hydride generation ICP-OES

The speciation analysis was performed by hydride generation on a Perkin Elmer ICP-OES (Optima 5300 DV). The method used in this speciation analysis was taken from Okkenhaug (2012), which is an analytical method derived from Andreae et al. (1981). The principle of the method is measuring the concentrations of Sb (III) and Sb_{TOT} (Sb_{TOT} is the total concentration of all species of Sb). The Sb (V) is estimated by subtracting the Sb (III) from the (Sb_{TOT}). The analysis was done on spectral line 217.582 and 206.836 respectively. Figure 10 shows an illustration of the HG-ICP-OES system used in this speciation analysis.

Table 3. Method parameters for the on-line reduction leading to the speciation analysis.

Parameter	Value
Sample aliquots	2 ml/min
Prereducing agent	5% KI + 5% ascorbic acid
Reaction time	30 minutes
Reducing agent	NaBH4
Acid	10% w/w HCl
Detection	ICP-OES

The advantages of hydride generation ICP-OES is amongst others that it is sensitive, selective and the capacity it has to remove the analyte from the matrix, thus eliminating a lot of possible physical and spectral interferences.

Another factor that promotes speciation analysis is its low detection limits in analytical methods. As Sb normally occur in low concentrations in the natural environment, it is essential to use an analytical method ideal for low detection limits.

Pre-reduction of Sb_{TOT} was done by adding 5% ascorbic acid and 5% potassium iodide in 10% HCl solution pre analysis. This is because Sb (V) has reduced tendency towards hydride generation. Thus Sb_{TOT} has to be reduced to trivalent prior to analysis with HG-ICP-OES (Bowman et al. 1997). According to (Nash et al. 2000) potassium iodide gave 40 % increased signal intensity for Sb (V) with the HG-ICP-OES technique. It also reduced the interference from Cu ions. Figure 11 shows the sample introduction system of HG-ICP-OES. Method parameters for the speciation analysis are available in table 3.

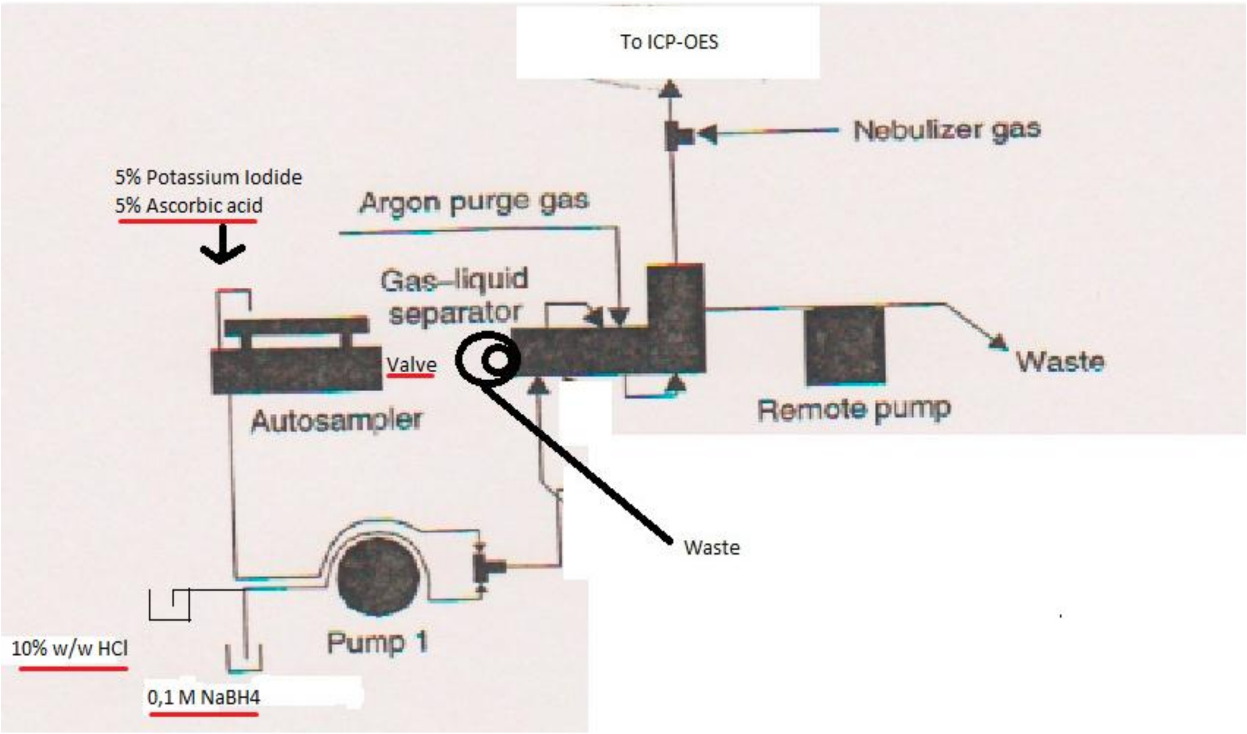

Figure 10. HG-ICP-OES system used for speciation analysis (Modified from Bowman et al. 1997).

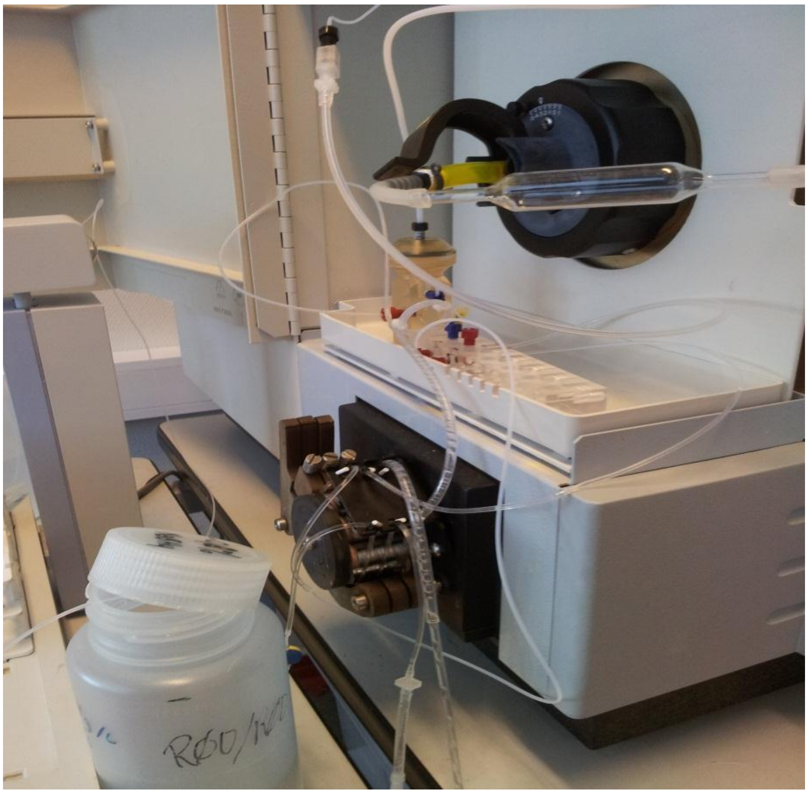

Figure 11. The sample introduction system for HG-ICP-OES. (Photo: Liland, 2012)

Sodium borhydride was used to produce Stibine (SbH_3), which means Sb was available as a hydride in a gaseous phase. The reaction follows equation 4.

1) $NaBH_4 + 3H_2O + HCl \rightarrow H_3BH_4 + NaCl + 8H^+$

The 8 hydrons took part in the production of SbH_3.

An in-house standard (1643e) was copied, and 1643H was used for quality control on Sb_{TOT}. It had a value of 58 ± 0.6 and was analyzed within 1 standard deviation in all reported samplings.

As there were no blank samples available for estimation of limit of quantification (LOQ) and limit of detection LOD, the LOD set for Sb was taken from Okkenhaug (2012) due to the similarity of the experiments. Detection limits for HG-ICP-OES was respectively 0.07 µg/l for Sb (III) and 0.4 µg/l for Sb_{TOT} . All measured concentrations for Sb_{TOT} were above the limit of detection at 0.4 µg/l.

All samples were stored at 4 °C prior to analysis.

4.5.2 Quality assessment

The content of Cu, Pb, SB and Zn found in soils of the respective containers are shown in table 4.

Certified values for Cu, Pb, Sb and Zn are all analyzed within one SD.

Table 4. Content of Cu, Pb, Sb and Zn in shooting range soils from Regimentsmyra.

IBC	Treatment	WSL	Cu mg/kg	Pb mg/kg	Sb mg/kg	Zn mg/kg
1	Reference 1	50 %	222	2370	157	82
2	Reference 2	100 %	299	3894	168	106
3	Iron grit 2%	50 %	285	3613	285	104
5	Iron grit 2%	100 %	303	2504	185	101
6	CFH-12 2%	50 %	285	6983	795	89
7	CFH-12 2%	100 %	244	2873	229	129
8	CFH-12 2%	100 %	309	2091	160	146
9	Iron grit 0,5%	50 %	260	2518	176	132
11	Iron grit 0,5%	100 %	281	2924	192	101
12	CFH-12 0,5%	50 %	300	4564	308	139
13	CFH-12 0,5%	100 %	210	2890	237	81
14	CFH-12 0,5%	100 %	244	11376	183	92
	Average		272	3888	253	108
	SD		±38	±2490	±164	±22
	CRM material (NCS DC73324)*		385	311	59	91
	Certified values		390±14	314±13	60±7	96±6

* Average of two analyzes

4.5.3 Preservation of pore water samples

The pore water samples that was taken for Sb (III) analysis was pre-analysis treated with a 0.5 molar disodium hydrogen citrate ($C_6H_6Na_2O_7$ x 1.5 H_2O) (Sigma – Aldrich, P.A. quality) solution. The reason why citrate was chosen for Sb (III) was to ensure that Sb did not prematurely oxidize into a higher oxidation state. By adding citrate Sb was complex bound in its original state. These citrate-Sb (III) complexes have been found to be highly stabile in various matrixes (Zheng et al., 2001).

The pore water samples that were taken for Sb_{TOT}-analysis was pre-analysis treated with 3% ultrapure (double distilled) HCl (Merck).

By adding hydrochloric acid in the samples taken for Sb_{TOT}, the HCl would not only stabilize Sb in a chloride complex, antimony pentachloride ($SbCl_5$), but also participate later by ensuring the acidic environment needed for $NaBH_4$ reaction with Sb (III) to promote stibine (SbH_3).

4.5.4 ICP – MS

The Norwegian Defence Research Establishment (FFI) performed mass spectrometry analysis over key elements, Sb, Cu, Zn and Pb along with other cations important for soil chemistry like Mn, Fe and Ca. Manganese development however will not be covered in this work.

The analysis was done on an inductively coupled plasma mass spectrometry (ICP-MS, Thermo X-series II Thermon Scientific).

Prior to analysis at FFI, the samples were conserved with 3% Ultrapure HNO_3.

For quality control, certified reference materials (Trace element fortified water, TM 23.4 and TMDA 61.2, Rain-97 og Battle-02, Environment Canada) were analyzed.

All samples were measured within LOQ and LOD at the ICP-MS instrument supplied by FFI (table 5). All samples were stored at 4 °C prior to analysis.

Table 5. Limit of Detection and Limit of quantification values provided by FFI.

	56Fe µg/l	63Cu µg/l	66Zn µg/l	121Sb µg/l	208Pb µg/l	44Ca µg/l
LOD (SD*3)	0,27	0,1	0,1	0,06	0,04	1,44
LOQ (SD*10)	0,92	0,32	0,33	0,19	0,14	4,78

4.6 Establishing experimental soil water saturation curves

From each container with 50% water saturation there was taken a soil sample. This was taken to the soil laboratory at IPM where an experimental soil water saturation curve was established for each container.

There were two major reasons why it was important to monitor the water content in the containers. Firstly, to observe whether the containers that were supposed to hold 50% water saturation actually did hold 50%. Secondly, it was interesting to find out whether the type of amendment added affected the soils ability to retain water.

The soil samples were put into 100 cm^3 steel cylinders (duplicates for each sample), in total 10 cylinders. A rubber band was used to ensure the soil did not fall out during testing.

First the cylinders and the rubber band holding the soil in place were weighed and each cylinder was packed with 140 grams of soil.

Then the cylinders packed with the soil samples were fully saturated and soaked in water while standing in a sandbox. The sandbox (see figure 12) had a drainage pipe in the bottom, and above this the box was filled with fine sand. This sand was used to apply the suction from the drainage on to the samples. On top of the sand there was a thin nylon filter.

After the cylinders had been fully saturated for 24 hours, the surrounding water was removed and the cylinders were weighed. This was done to establish the soils maximum water capacity.

By using the sandbox method the soils ability to retain water at specific suctions was measured. A pressure of 0.01 to 0.1 bar was applied. For method details see Eijkelkamp (2007).

The 1 bar suction to finalize the experimental curve could not be done with a sandbox. Instead a ceramic plate (Soil moisture equipment, Santa Barbara, California, United States) was used. The method was applied according to Eijkelkamp (2012).

After all the suctions needed had been applied to the soil samples, the soils were dried before a final weighing (as dry weight).

A total of 5 experimental curves were established, one for each container holding 50% water saturation. By plotting the suction measured in the containers through tensiometers, it was possible to read off the water content through these experimental curves at all months of sampling.

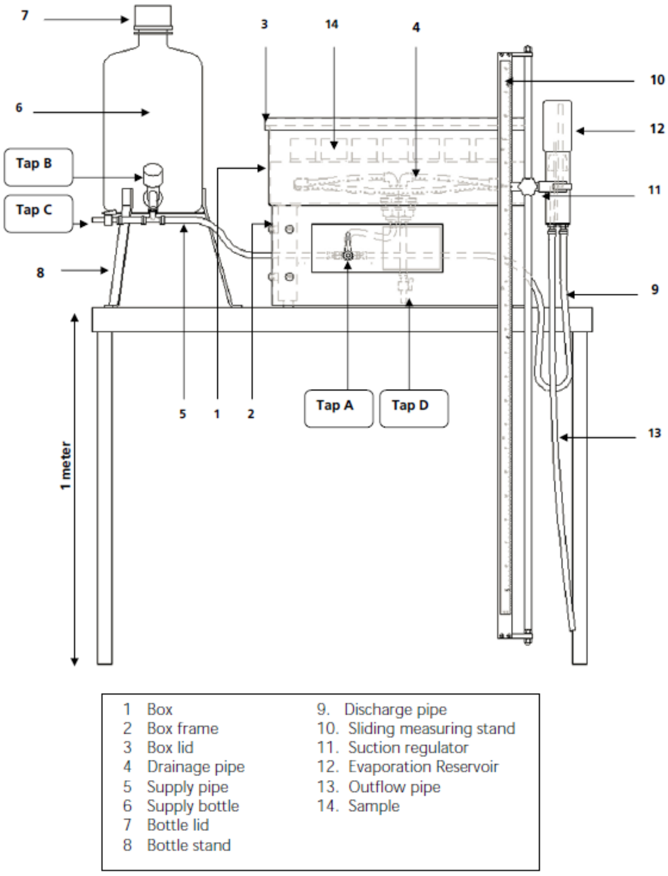

Figure 12. The sandbox and its components (Eijkelkamp, 2007).

5 Results

5.1 Water holding capacity experiment

The containers holding 50 % water saturation are shown in figure 13. The line in each chart represents the water saturation curve established in the laboratory. The monthly values represent the suction measured by tensiometers, and is related through the experimental line to percentage water filled pore space. January values were excluded from the charts, as they would all be 50 %. In figure 13 the monthly saturation development is available for all containers with 50 % WSL. In general the water saturation level results indicate all containers staying within range of 50 % saturation, with the exception of container 3.

For container 1, the reference, all months show a water saturation of 55 – 57 %, with the exception of March and April with respectively 45 and 41 %. In container 3 (2 % iron grit) no months were above the 50 % mark, and this was the container holding the lowest water saturation percentage throughout all months of sampling. April was the extreme month, dropping as low as 30 %. For container 6, all months showed water saturation levels at 50 % or above. It peaked in April with 57 % saturation. The soil treated with 0.5 % iron grit, container 9, had fairly stable saturation from January to August, with suction values between 50 and 61 %. Container 12 had stable saturation in all measurements with saturation never exceeding 55 % and never below 52 %.

The soil water saturation comparison figure indicates that the different amendments will influence the soils ability to retain water. The soil treated with 2 % CFH-12 showed the best ability to retain water up to a suction of 0.75 bar. However 2 % iron grit treated soil showed reduced water holding capacity, especially at low suctions. The containers treated with 0.5 % Fe-amendments show similar saturation development at all suctions. It is worth noting that the untreated reference soil showed the best ability to retain water at suctions between 0.8 and 1 bar.

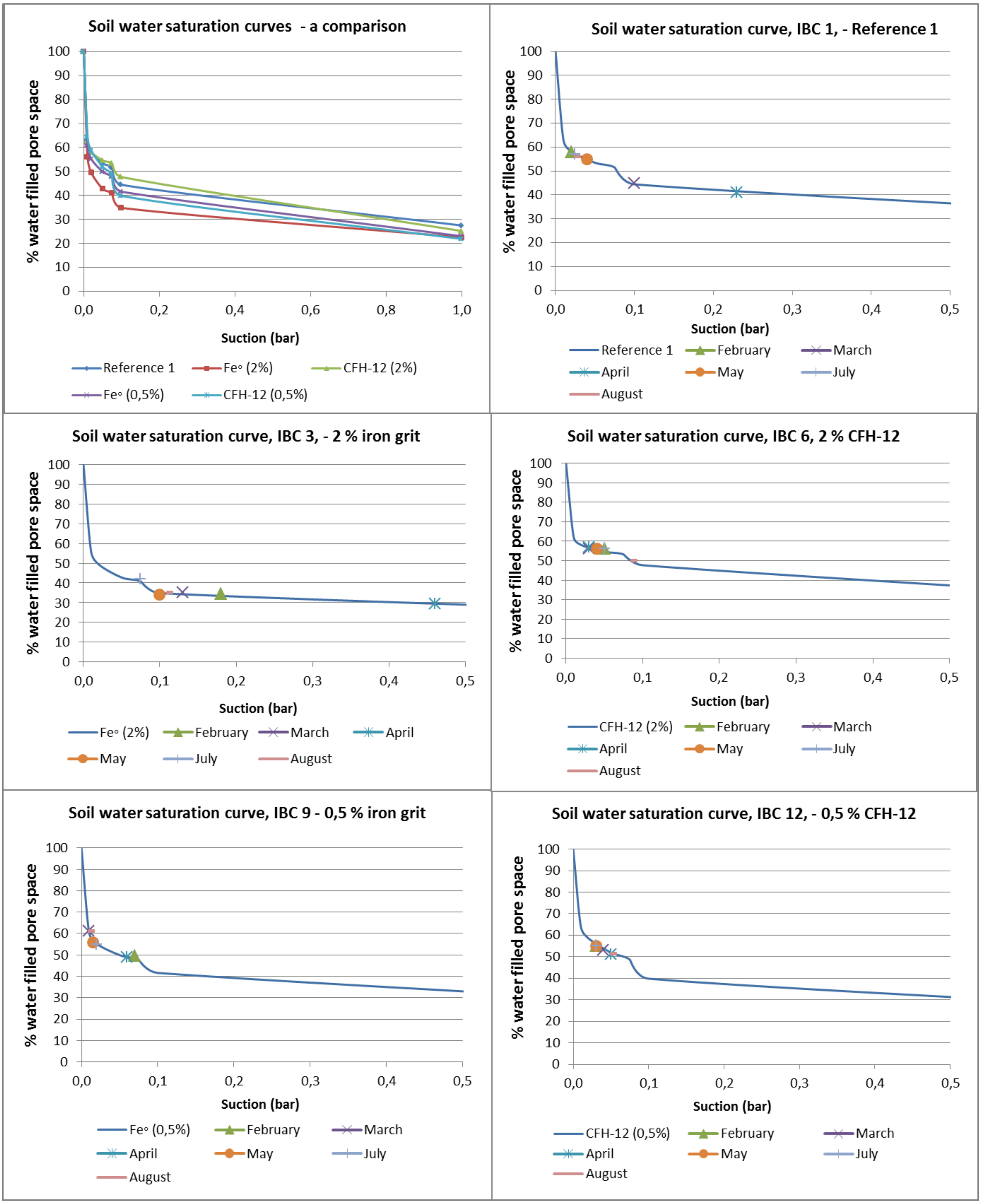

Figure 13. Soil water saturation curves for container 1,3,6,9,12 and an experimental laboratory curve comparison. Suctions were measured between January and August, with the exception of June.

5.2 Eh and pH development in all containers

The developments of pH are shown in figure 14 for both saturation levels. Containers holding 50 % WSL showed pH-values between 6 and 6.9. The soil treated with CFH-12 and limestone showed, as expected, in general higher pH-values compared to the iron grit treated soil and the soil reference. Due to lack of pore water, only one sample was available for 2 % iron grit. The container with 0.5 % iron grit showed a pH as low as 5.5 in February. However a gradual increase was observed from February to August with a final pH measurement of 6.9.

In the 100 % saturated soil all treatments and reference soil showed higher pH-values compared to 50 % saturation. Surprisingly, the highest pH observed in August was the soil treated with 0.5 % iron grit, with a pH of 6.9. Soils treated with 2 % CFH-12 and 1% limestone, show stable pH-measurements between 6.6 and 6.9 for all months of sampling. From the monthly measurements it is clear that soils treated with CFH-12 and limestone showed a higher initial pH-value. This was most likely due to the addition of limestone where $CaCO_3$ enters solution as Ca (II) and CO_3^{2-}, and carbonate will through the bicarbonate buffering system prevent any major pH-changes (Økland and Økland, 2006). While antimonate adsorbs best at pH < 7, and Pb, Zn and Cu adsorbs best > 7, it is reason to conclude the best pH for multi-element adsorption would be around 6-7. This was the pH-range achieved for most soils during all months of sampling.

The incomplete oxidation of iron grit produces alkalinity (Okkenhaug, 2012) (equation 1 and 2), and this could have been a possible explanation to the very high August pH observed for 0.5 % iron grit treated soil in 100 % WSL (figure 14).

Eh-measurements for both 50 and 100 % WSL are shown in figure 15. The redox potentials were measured right after the pore water was sampled. In containers holding 50 % WSL, the reference soil showed high Eh-measurements throughout all months of sampling. January and August Eh-measurements are measured at 400 mV. A gradual decrease was observed for 0.5 % iron grit and CFH-12 treatments. However for 2 % iron grit, only January and February measurements are available due to lack of pore water.

In fully saturated containers, the reference soil showed a decrease in Eh, with a January measurement of 400 mV and August measurement at 250 mV. CFH-12 2 % treatments and 0.5 % iron grit showed similar developments of Eh. However the strongest reducing conditions were found in 0.5 % iron grit treated soil. The Eh-values in January dropped from 260-270 mV, to an August value between 20-70 mV. Soils treated with 2 % iron grit and 0.5 % CFH-12 showed a strong decline in Eh-values measured, and 0.5 % CFH-12 is the only treatment that showed higher Eh values in January compared to the reference soil. A possible explanation of the low Eh values in iron grit treated soils is the oxygen consumption from the iron grit oxidation reaction sequence, equation 1-2. This promotes reducing conditions and the lack of oxygen could stop the iron grit of being fully oxidized towards FeOH$_{3.}$

It is underlined that the redox measurements did include some uncertainty. However they gave an indication of the redox conditions and changes over time.

5.2.1 pH development for all containers, 50 and 100 % WSL

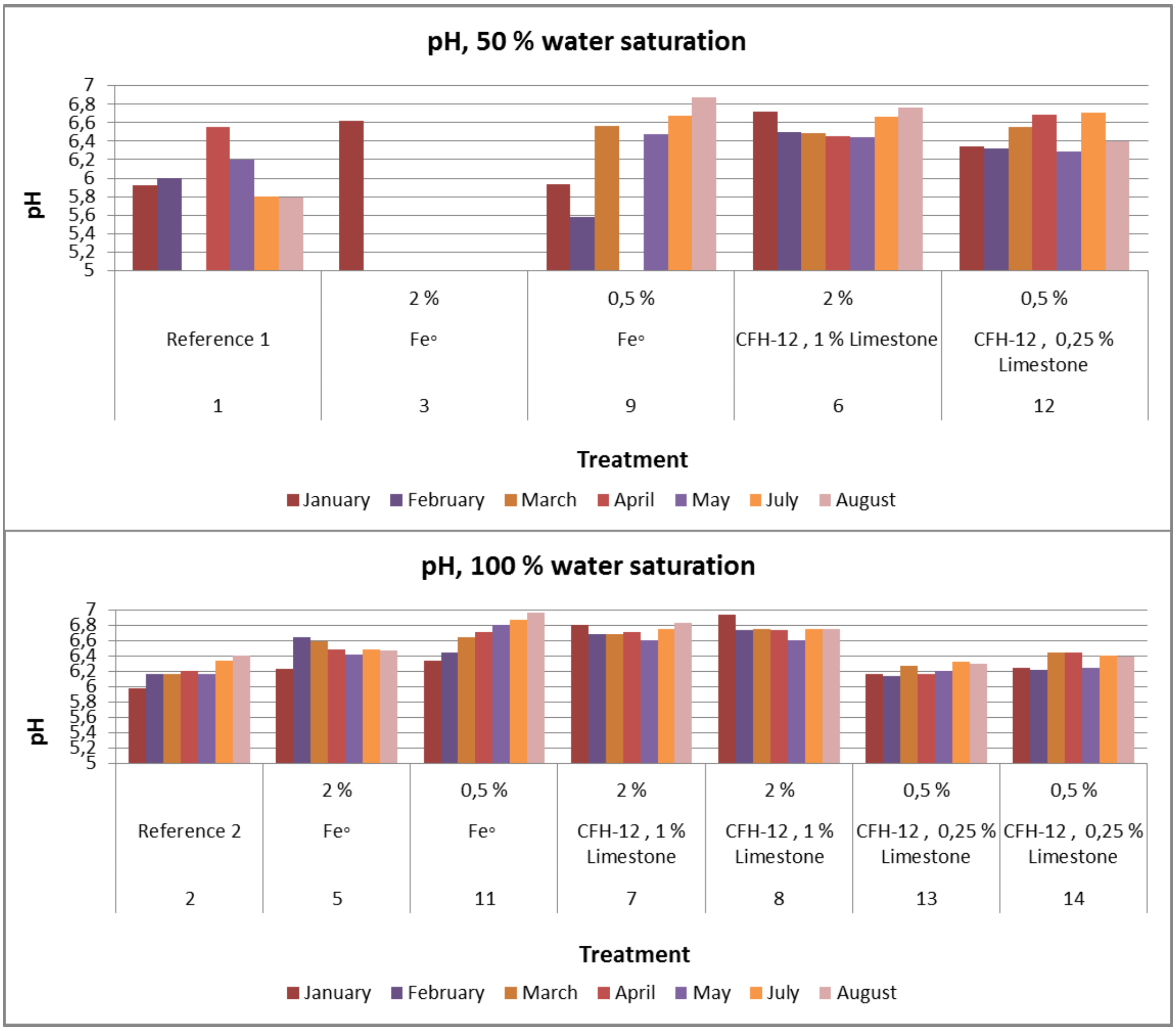

Figure 14. pH-measurements sampled from January to August, with the exception of June, for all ICBs, at both 50 and 100 % WSL. Missing bars in 50 % WSL indicate lack of pore water that month.

5.2.2 Eh development for all containers, 50 and 100 % WSL

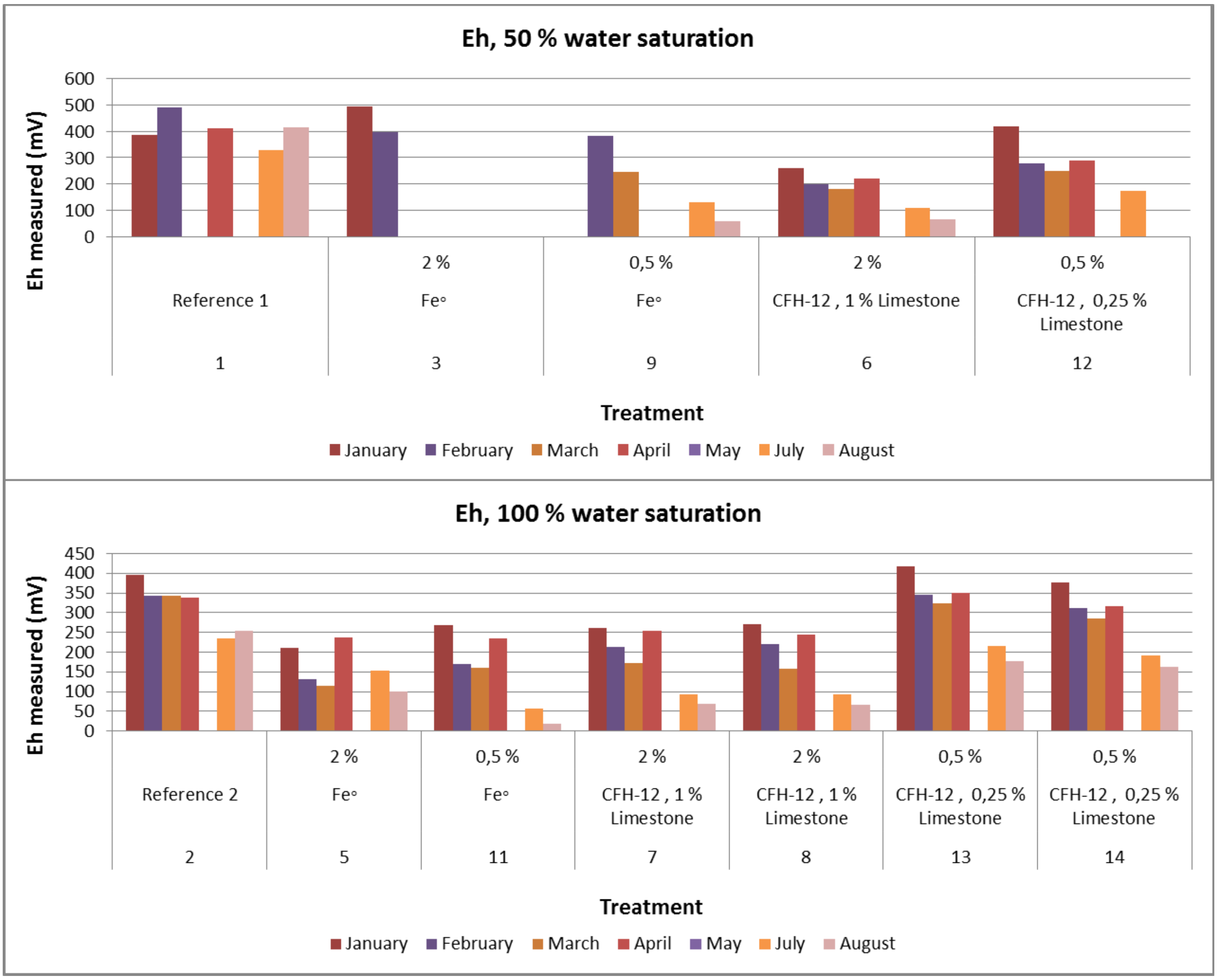

Figure 15. The Eh-development measured from January to August in all containers, with the exception of June. Missing bars in 50 % WSL indicate lack of pore water that month.

5.3 Metals and antimony (Sb)

The results reported were from pore water samples taken from January to August, with the exception of June. Figures include concentrations of Fe, Pb, Zn, Cu and Sb at 50 and 100% water saturation level for both 0.5 and 2 % concentrations of iron grit and CFH-12. One container with untreated soil was used as reference for both water saturation levels.

Reported concentrations are average values from 2 or 3 samples and concentrations are given in µg/l (unless stated otherwise). For 50 % water saturation lack of pore water and malfunctioning pore water samplers gave too few replicates to calculate standard deviations (SD).

5.3.1 Iron (Fe) development in pore water

50 % WSL

Iron concentrations are shown in Figure 16. The untreated soil in reference 1 had as expected very low Fe concentrations, with the exception of a January value of 18.7 mg/l. However in February this was reduced to 115 µg/l. At 50 % saturation, Fe was shown to gradually mobilize for both 0.5 % treatments and 2 % CFH-12. For the soil treated with 2 % CFH-12 the increase in pore water concentrations of Fe was high, moving from 44 mg/l in January to 357 mg/l in August. The amendment of 2 % iron grit showed very low Fe concentrations with January concentrations of 466 µg/l and August being analyzed at 105 µg/l. The highest pore water concentration of Fe measured in 50% WSL, was done in container 6, treated with 2 % CFH-12. This container showed a solid gradual increase during all months of sampling and the August concentration peaked at 357 mg/l.

100 % WSL

In containers holding 100 % WSL, the reference soil showed a gradual increase in Fe pore water concentration. The reference soil peaked in August at 58 mg/l. However, a large mobilization of Fe was observed in pore water for all amendments. Between the different amendments, the 2 % iron grit treatment had the lowest Fe concentrations. Though the pore water concentration of Fe measured in fully saturated soil was far higher compared to the concentration analyzed in the containers holding 50 % WSL. The 2 % CFH-12 mixed soil, showed the highest Fe concentration with August concentrations of 293 mg/l and 268 mg/l for container 7 and 8.

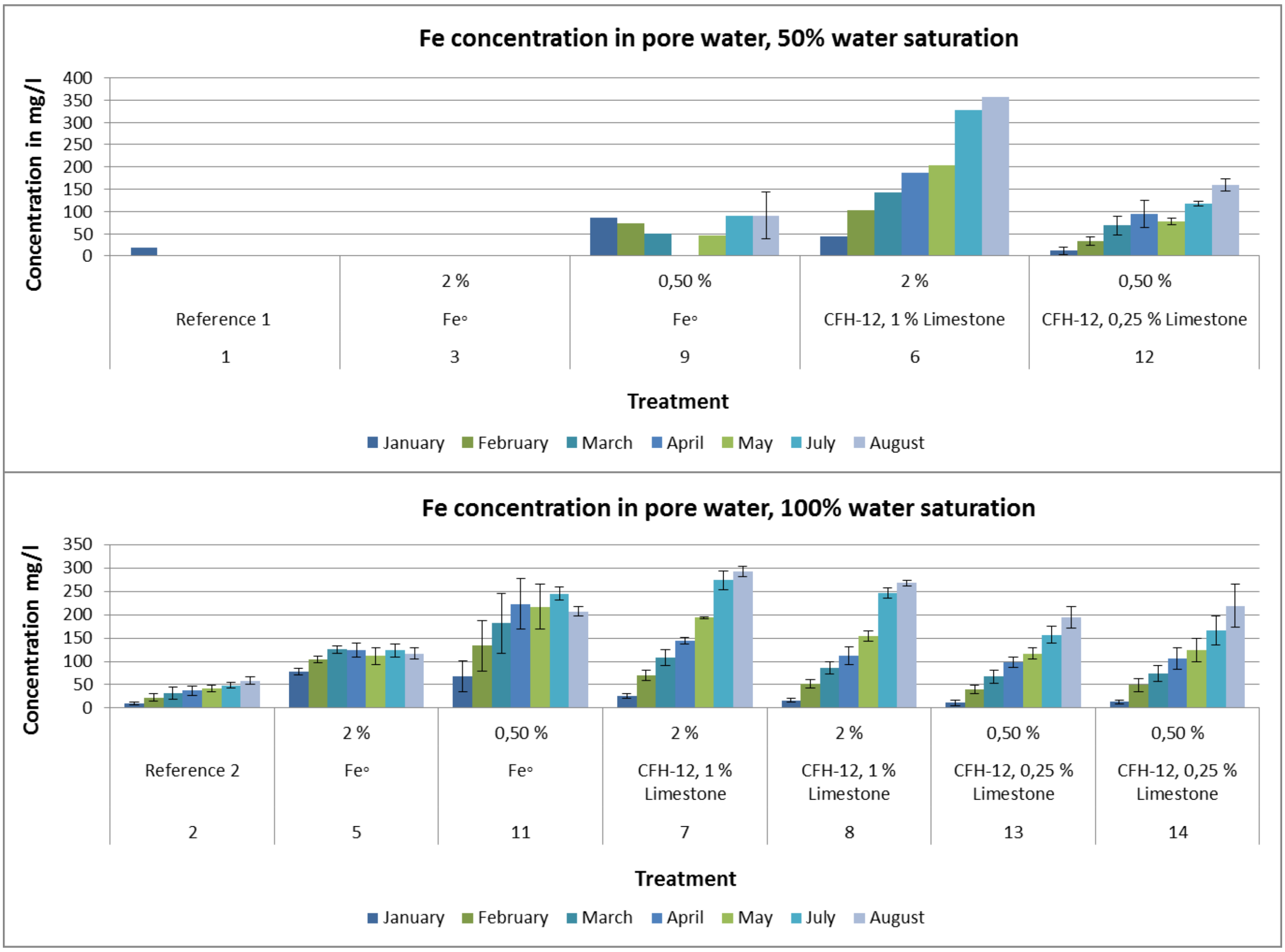

Figure 16. Pore water concentrations of Fe in 50 and 100 % WSL. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

5.3.2 Lead (Pb) development in pore water

50 % WSL

Pore water concentrations for Pb are shown in figure 17. Reference 1, showed an increase in Pb concentration from 1125 µg/l in January to 1701 µg/l in August. Concentrations of 0.5 % iron grit was far more effective compared to 0.5 % CFH-12. The 0.5 % iron grit treated soil showed a gradual development from concentrations of 167 µg/l in January to 35 µg/l in August. The soil mixed with CFH-12 showed a development from 888 µg/l in January to 181 µg/l in July. While 0.5 % concentrations of CFH-12 were not as effective as 0.5 % iron grit, there was still a clear decline in pore water concentrations of Pb.

Lead concentrations were low for both 2 % iron grit and 2 % CFH-12 treated soil. The containers holding soil mixed with 2 % iron grit showed a slight increase from 22 µg/l in February to 35 µg/l in August. Soil treated with CFH-12 (2 %) showed a decrease from 37 µg/l in February to 13 µg/l in August.

100 % WSL

In containers holding 100 % WSL, Pb pore water concentrations in the reference soil, decreased from January to August, to nearly 50 % of the initial concentration. January showed a concentration of 1262 ± 95 µg/l and in August the value was a reported 678 ± 74 µg/l.

Iron grit at 0.5 % concentration in container 11 showed much better retention compared to 0.5 % CFH-12. Iron grit 0.5 % had a reduction from a 338 ± 132 µg/l to 10 ± 2 µg/l in July, however a mobilization was observed in August reaching 368 ± 613 µg/l, though this value is debatable. The average was made of a triplicate being 1076 µg/l, 20 µg/l and 8 µg/l.

The soil treated with 0.5 % CFH-12 showed a strong gradual decline from January to August. Both container 13 and 14 were treated with 0.5 % CFH-12, and their developments were similar. Both January measurements exceeded the reference soil from January with values respectively 1518 ± 1107 µg/l and 1264 ± 1075 µg/l. While the large standard deviation values indicated some uncertainty, the soils showed a steady decline in concentrations to 440 ± 476 µg/l and 288 ± 433 µg/l in August.

Strong pore water reductions for both 2 % amendments are shown for container 5, 7 and 8.

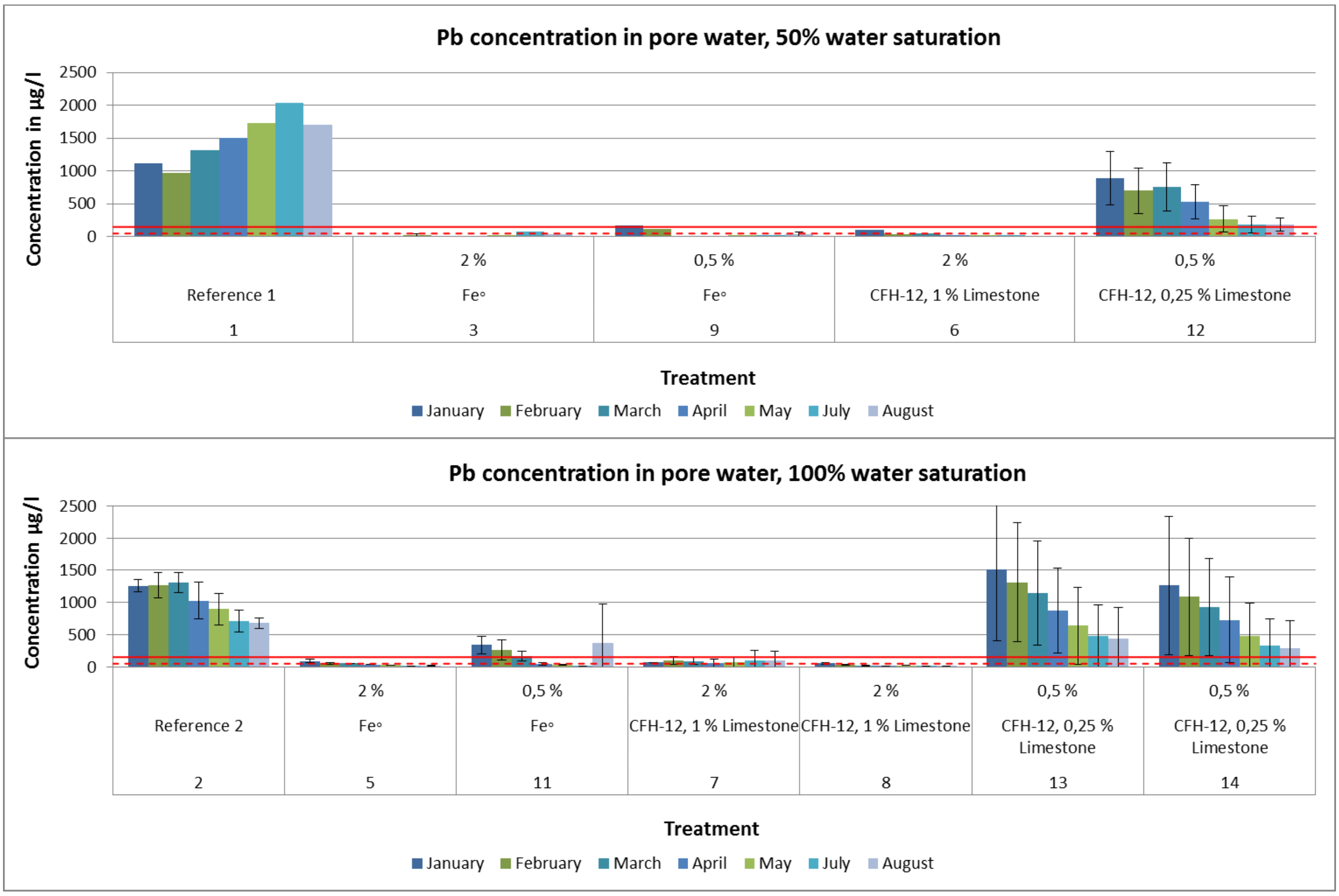

Figure 17. Pore water concentrations of Pb in 50 and 100 % WSL. Solid red line, C_0, column test, limit value for inert waste leachate. Fragmented red line, L/S 10, batch test, limit value for inert waste leachate. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

5.3.3 Zinc (Zn) development in pore water

50 % WSL

Pore water concentrations for Zn are shown in figure 18. In containers holding 50 % WSL, Zn reference values increased from 783 µg/l in January to 1267 µg/l in August. Iron grit concentration of 0.5 % was far more effective compared to 0.5 % CFH-12. The 0.5 % iron grit treated soil showed a pore water concentration development from 176 µg/l in January to 33 µg/l in August. This was a lower concentration than observed from the 2 % iron grit treated soil, and a bit higher than what is observed from the 2 % CFH-12 treatment.

Soil treated with 0.5 % CFH-12 showed a January concentration of 759 µg/l, nearly comparable to reference values. However, increasing retention was observed the remaining months, and in August pore water samples showed Zn concentrations of 141.

It is clear that 2 % concentrations of iron grit and CFH-12 were effective, all though not as effective as for Pb. Measured concentrations in iron grit 2 % were stable throughout the months of sampling. Treatment of 2 % CFH-12 showed a gradual decline in concentrations from 134 µg/l in January to 17 µg/l in August.

100 % WSL

Zinc concentrations in pore water of the reference soil decreased substantially from January to August. January samples showed a pore water concentration of 970 µg/l to 367 µg/l in August. The soil treated with 0.5 % iron grit showed low concentrations as well and July measurements were comparable to 2 % CFH-12 treated soil. However, both 0.5 and 2 % iron grit showed a mobilization in August. Container 13 and 14, treated with 0.5 % CFH-12, showed a gradual decrease in pore water concentrations from January to August. But they were not comparable to reductions in 0.5 % iron grit. January values were close to equal from what the reference soil showed, and in August the final concentrations were measured at 129 ± 50 µg/l and 268 ± 52 µg/l.

In soils treated with 2 % CFH-12 (container 7 and 8) good retention was achieved. The concentrations measured in these containers were the lowest compared to all other treated soils. Both containers showed similar pore water concentration development, and comparable SD-values. Soils treated with 2 % iron grit and CFH-12 showed the best remediation effect from January to August.

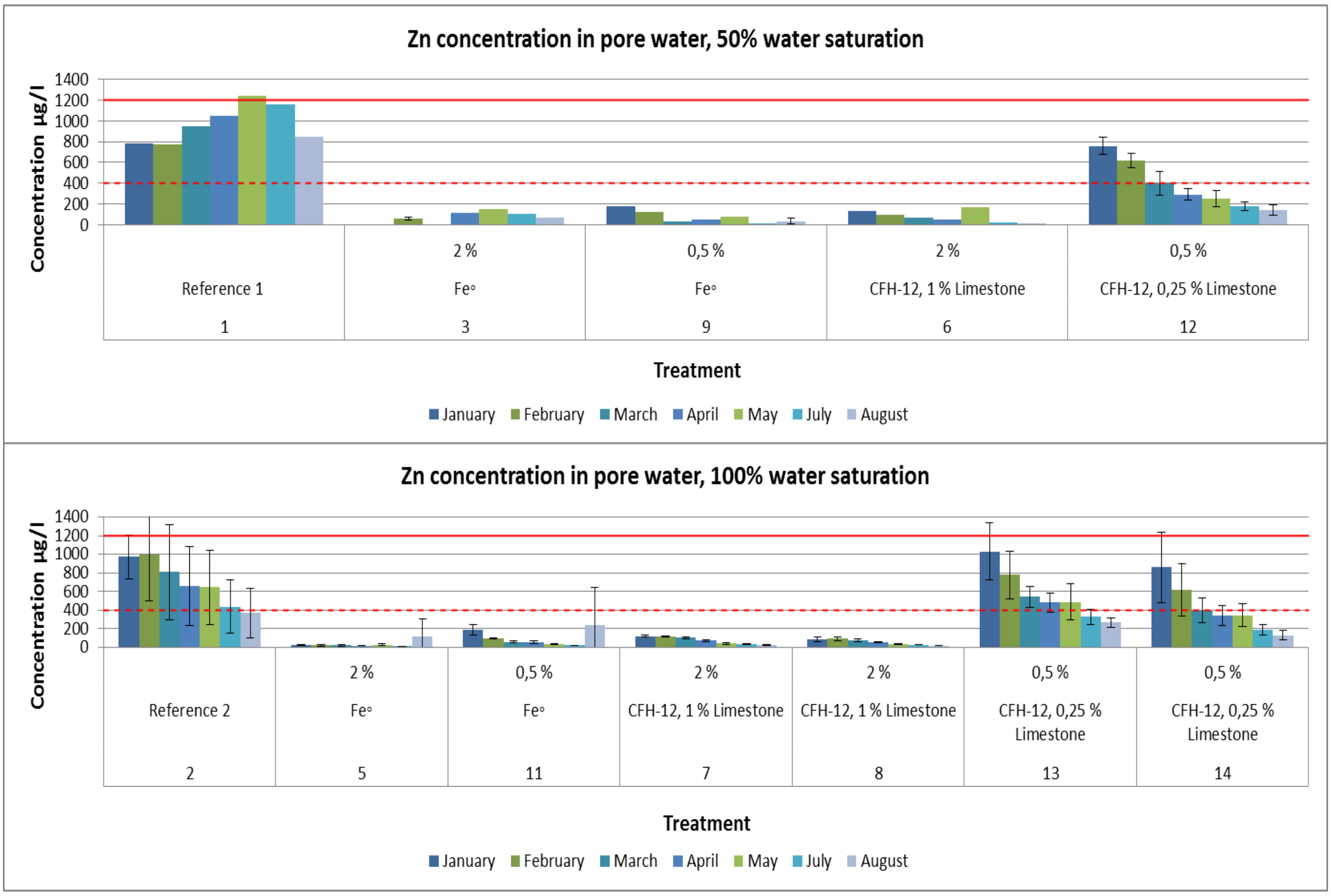

Figure 18. Pore water concentrations of Zn in 50 and 100 % WSL. Solid red line, C_0, column test, limit value for inert waste leachate. Fragmented red line, L/S 10, batch test, limit value for inert waste leachate. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

5.3.4 Copper (Cu) development in pore water

50 % WSL

Pore water concentrations for Cu are listed in figure 19. Reference 1 showed a steady increase of the Cu concentrations in pore water from 74 µg/l in January to 522 µg/l in August.

Pore water samples analyzed from 0.5 % iron grit treated soil, showed similar low concentrations from both 2 % treatments, however a spike was observed in August with an average value of 412 ± 691 µg/l. The August samples from container 9, consists of three measurements of 2 µg/l, 13 µg/l and 1209 µg/l. The extreme value seems to be an outlier.

The container with 0.5 % CFH-12 treated soil showed a steady decline in concentration from January to August, with concentrations moving from 141 µg/l to 8 µg/l. But there were a sudden mobilization in March. An average of 1036 ± 1756 µg/l from a triplicate of 20 µg/l, 3064 µg/l and 25 µg/l was analyzed. This is possibly another outlier.

Copper concentrations were generally low for 2 % concentrations of both iron grit and CFH-12. Values from January to August were stable between 15 µg/l and 9 µg/l for 2 % iron grit and 30 µg/l and 1.0 µg/l for 2 % CFH-12. LOQ for Cu was given at 0.32 µg/l by FFI.

100 % WSL

Copper concentrations showed a decrease in the reference soil from January to August and nearly reached the concentrations from the amended soils.

For container 11, the soil treated with 0.5 % iron grit, a sudden spike was observed in May, with a concentration of 160 ± 164 µg/l. The triplicate consisted of three samples measured at 1 µg/l, 328 µg/l and 151 µg/l. It could be that the lowest value is not representative for the soil water concentration.

Soils treated with 0.5 % CFH-12 (container 13 and 14) showed both lower concentrations of Cu and better development than observed from Pb, Zn and Sb. However, it was only the May, July and August measurements that were close to the effect observed from the other amendments.

The lowest Cu pore water concentrations were measured from the container treated with 2 % iron grit. CFH-12 2 % concentrations performed well, and had a very low August concentration of Cu, however container 7 showed an increase in Cu from January to March before a sudden drop in April.

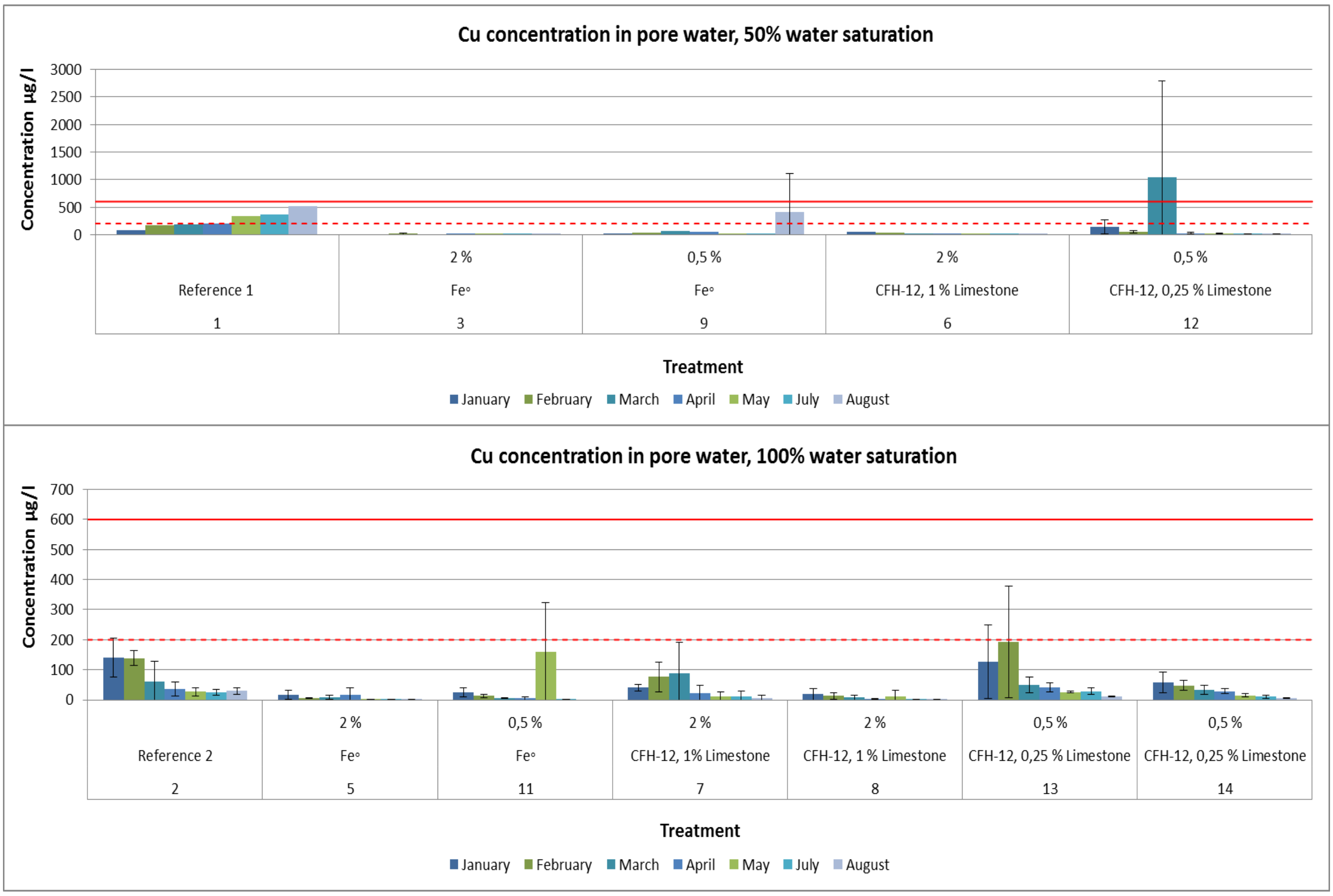

Figure 19. Pore water concentrations of Cu in 50 and 100 % WSL. Solid red line, C_0, column test, limit value for inert waste leachate. Fragmented red line, L/S 10, batch test, limit value for inert waste leachate. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

5.3.5 Antimony (Sb) development in pore water

50 % WSL

Pore water concentrations for Sb are shown in figure 20. In containers holding 50 % WSL, Sb showed similar development for all treated soils. Reference values increased from 372 µg/l in January to 539 µg/l in August. Iron grit concentration of 0.5 % showed to perform better than 2 % iron grit concentrations, with January concentrations at respectively 31 µg/l and 72 µg/l, and August concentrations at 35 µg/l and 85 µg/l. The soil treated with 0.5 % CFH-12 does not show the same strong gradual reduction observed with Zn and Pb. There is however a reduction from January, 146.7 µg/l to 89.2 µg/l in August. Iron grit and 2 % CFH-12 were the most effective. The soil with the lowest pore water concentrations, were the soil treated with 2 % CFH -12. The January concentrations in this container showed an average of 12 µg/l and August showed 13 µg/l.

100 % WSL

Antimony development in 100 % WSL showed a decrease in the reference soil pore water concentration from January to August. The soil treated with iron grit 0.5 % showed substantially lower concentrations compared to 0.5 % CFH-12 treated soils.

January measurements for 0.5 % CFH-12 showed a small and steady decline, but August analyzes were measured at 100 µg/l. Thus not as effective compared to the retention from 2 % concentrations of CFH-12 that showed August concentrations of respectively 13 ± 6 µg/l and 8 ± 1 µg/l in container 7 and 8.

Container 7 and 8 with 2 % CFH-12 treatment were the most stable and high adsorbing throughout all months of sampling. However, low pore water concentrations were analyzed for 2 % iron grit treated soil as well.

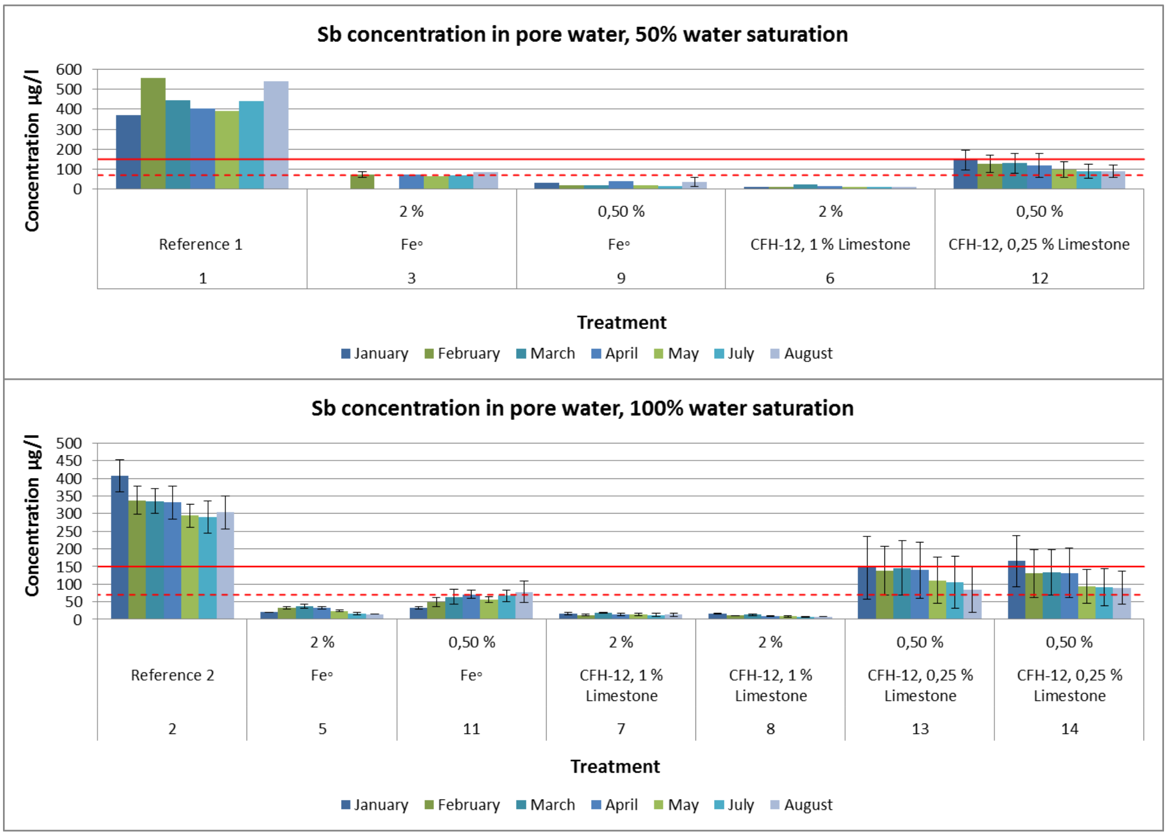

Figure 20. Pore water concentrations of Sb in 50 and 100 % WSL. Solid red line, C_0, column test, limit value for non-hazardous waste leachate. Fragmented red line, L/S 10, batch test, limit value for non-hazardous waste leachate. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

5.3.6 Speciation of antimony (Sb)

5.3.6.1 Speciation of Sb in soil pore water, 50 % water saturation

There were problems getting enough pore water from the containers with 50 % water saturation, and container 3 (2 % iron grit) could not be represented in the speciation analysis. The pore water that was sampled was given priority to ICP-MS analysis. The month of April, no ICP-OES analysis was performed, thus these values will be missing from all charts. The results from speciation analysis on Sb_{TOT} and Sb(III) are shown in figure 21. It is clear that the dominant species of Sb remains in its pentavalent state. Pore water concentrations of Sb_{TOT} on ICP-MS and HG-ICP-OES showed less than 20 % variation for 76 % of the samples.

The reference soil showed a large decrease in Sb (III) concentration from January to August. The likely oxidation of Sb (III) to Sb (V) is supported by Eh-measurements between 400 – 500 mV, indicating oxidizing conditions. The speciation analysis of 2 % CFH-12 treated soil showed Sb (III) concentrations as low as 0.493 µg/l. Measurements in May, July and August showed concentrations at respectively 1 µg/l, 2 µg/l and 2 µg/l. Container 12 treated with 0.5 % CFH-12 showed a gradual increase in Sb(III) from January to August, while 0.5 % iron grit decreased from January to July, before a sudden spike in August. This could be due to an outlier, as the value consisted of two samples, with 0.4 µg/l and 54 µg/l.

The concentration of Sb (V) (available in percentage of Sb_{TOT}), is shown in Figure 22. The reference soil showed an increase in Sb (V) concentration. While January concentrations of Sb (V) were close to 90 % of Sb_{TOT}, an increase was observed for the remaining months, and in August close to 100 % of all Sb was present as Sb (V).

For soils treated with 0.5 and 2 % CFH-12 Sb was prevalent in its pentavalent state, most likely as the oxyanion $Sb(OH)_6^-$, with reported values between 85 – 97 %. These results are supported by Filella et al. (2002). They found that Sb (V) tend to be the dominant species in oxic soil conditions. For 0.5 % iron grit both January and August measurements show Sb (V) reported as low as 65% of Sb_{TOT}. While the reduction potential was not controlled in January (lack of pore water), the Eh measured in August for 0.5 % iron grit showed 59 mV, indicating a reducing environment. This could have explained the low concentration of Sb (V). This is supported by the soil water saturation curve for container 9 (figure 13). In August the WSL was 61 %, thus above the 50 % WSL.

5.3.6.2 Speciation of Sb in soil pore water, 100 % water saturation

Speciation analysis of Sb showed that for all treatments Sb is dominant in its pentavalent state, despite the possible ongoing reduction. However, results from Filella et al. (2002) showed that Sb (V) is frequently observed under anoxic conditions.

A small reduction took place where August samples are shown, and this was most likely due to an increasing reducing environment. This was confirmed by the Eh-measurements (figure 15).

Pore water concentrations of Sb_{TOT} on ICP-MS and HG-ICP-OES showed less than 20 % variation for 83 % of the samples.

The reference soil showed a strong mobilization of Sb (III) from January to August. In container 11, 13 and 14 a gradual increase is observed in Sb (III) concentrations from January to August, these observations correlate well with the measurements of stronger reducing conditions. The lowest concentrations of Sb (III) are found in soils treated with 2 % CFH-12.

The iron grit treated containers had the lowest measured Sb (V) concentration in January (figure 22), with Sb (V) analyzed as 62.9 and 57.6 % of the Sb_{TOT} in the 0.5 and 2 % treated soils respectively. However, an increase of Sb (V) was observed the remaining months.

While there were slight monthly variations, Sb is predominantly available as Sb (V) in all treatments with the exceptions of iron grit treated soil. Both the CFH-12 amended soils and reference 2 show Sb (V) fractions in August between 80-98 % of Sb_{TOT}.

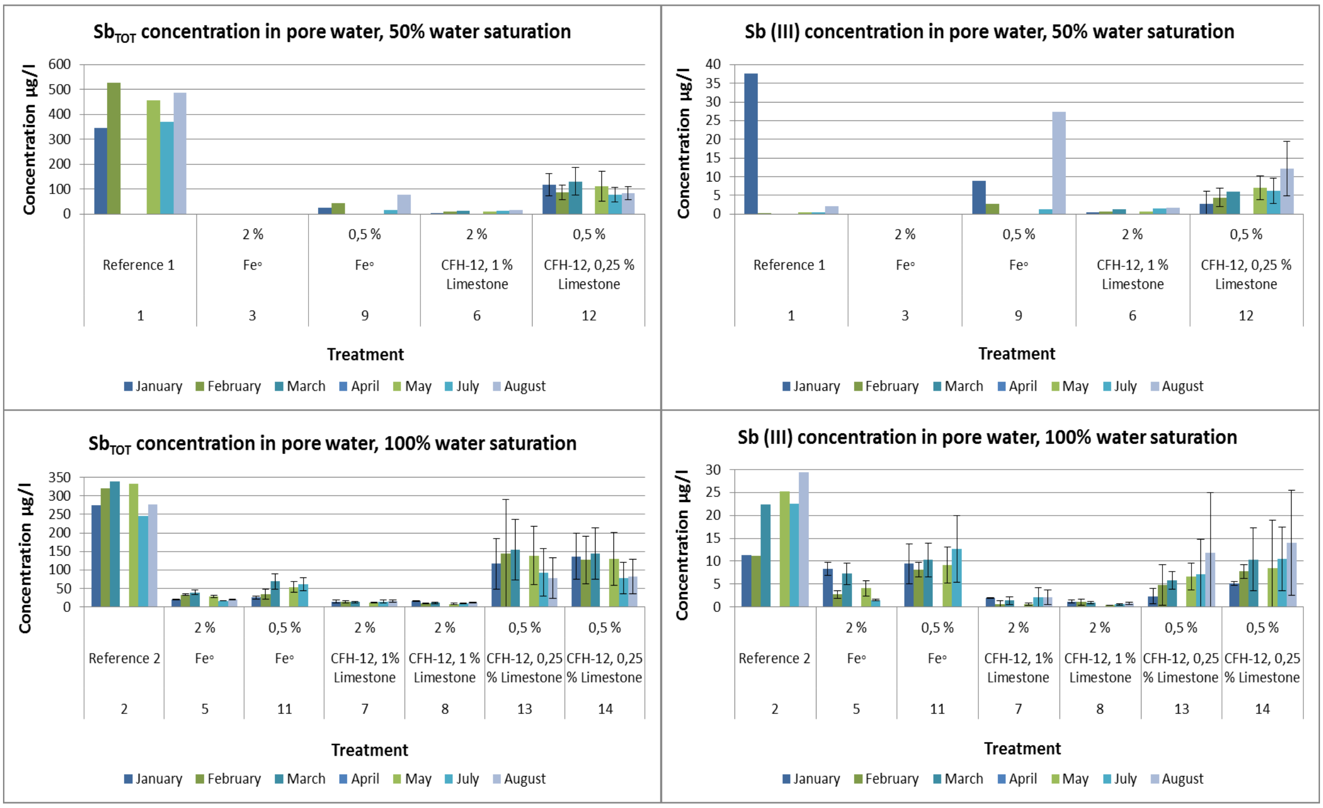

Figure 21. Sb$_{TOT}$ and Sb (III) concentrations in 50 and 100 % WSL. Error bars represent the SD calculated from the triplicates. Samples were taken between January and August, with the exception of June.

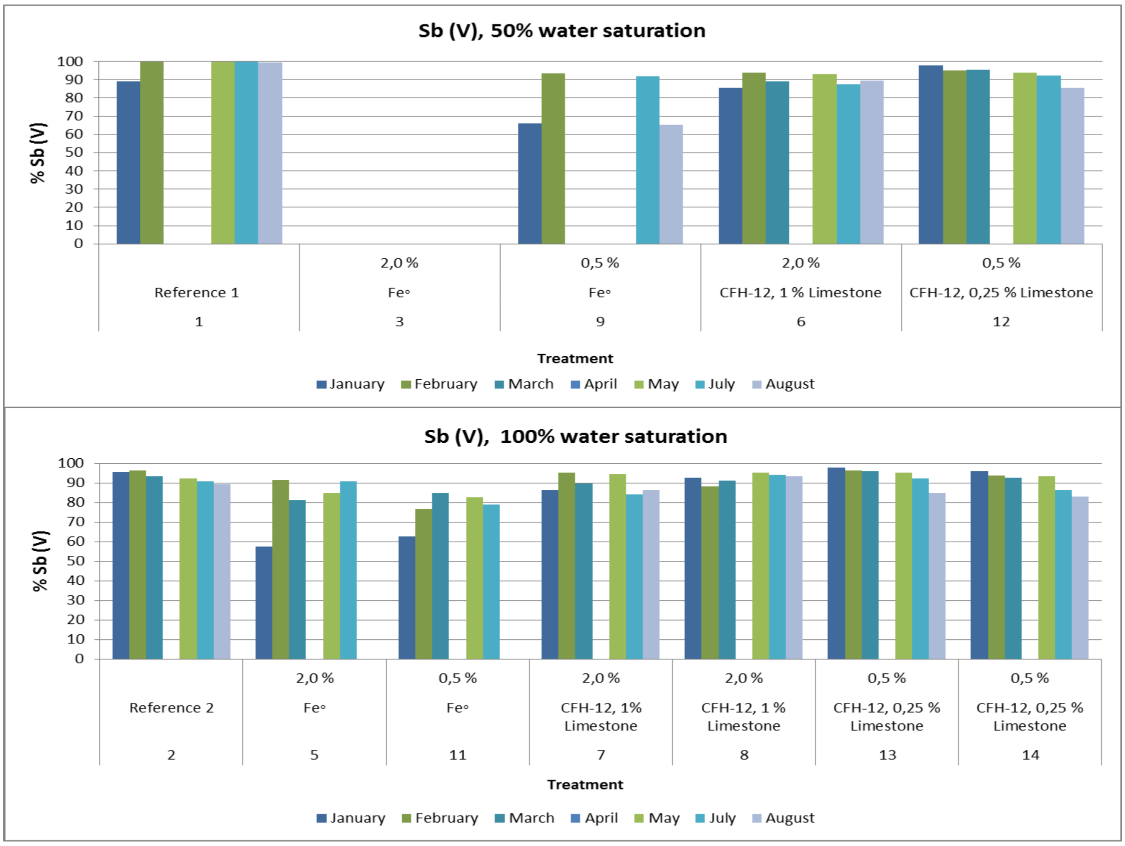

Figure 22. Pentavalent antimony estimated as a percentage from Sb$_{TOT}$.

6 Discussion

6.1 Water saturation level influence on Fe-amendments

A comparison of the experimental soil water saturation curves is available in figure 13. It is clear that the different amendments affect the soils ability to retain water. The soil treated with 2 % iron grit holds the lowest amount of water at all suctions tested. The soil amended with 2 % CFH-12 displays the opposite effect, and between 0.01 – 0.8 bar it shows the best water retention. These differences are most likely due to the particle size distribution of the amendments. While the CFH-12 powder are increasing the fine particular fraction of the soil, the iron grit holds particle size up to 1 mm and will increase the sand fraction of the soil. Generally an increase of the fine particles in soil will increase the soils ability to retain water. This is due to a higher specific surface (Børresen, 2004).

6.2 Effect of water saturation levels on redox conditions and iron mobility

The mineral stability of Fe is of great interest, as a mobilization of Fe in pore water may affect the heavy metals and metalloids adsorbed to the Fe-oxides. Iron's properties as a redox sensitive element (Appelo, Postma, 2005) is observed in figure 16, where the gradual increase in Fe concentration is substantial, especially for fully saturated soils. The Fe pore water concentration increase correlates well with the development of stronger reducing conditions observed, thus a reduction of Fe (III) to Fe (II) takes place. According to Schwertmann (1991), the main path of Fe dissolution is the process of reduction, where the rate of Fe dissolution is determined by pH and Eh.

From literature Fe dissolution has been documented between +100 to +300 mV at pH 6-7 (Gotoh and Patrick, 1974). This is in accordance with the Pourbaix diagram of Fe (figure 23). It is clear from this diagram that the pH and Eh values measured in this project, around 5.6 – 6.9 and + 400 to + 20 mV, Fe should predominantly be found as Fe (II). This will to some extent explain the huge Fe mobilization from January to August.

The Eh and pH-developments in our study (figure 15 and Figure 14) showed that all treated soils in most months are within reported range for Fe dissolution. However, our results showed that the Fe mobilization did not affect the amendments effect on retaining Pb, Sb, Zn and Cu. Considering the monthly development of Pb, Zn, Cu and Sb, (figure 17,18, 19 and 20), the pore water concentrations are decreasing even under strong Fe dissolution. This can be explained by the large amounts of Fe in the soil matrix readily available for sorption of metals and Sb in the pore water. Antimony may precipitate as antimonate tripuhyite ($FeSbO_4$) or schafarzikite ($FeSb_2O_4$) (Okkenhaug, 2012).

In container 9, (treated with 0.5 % iron grit) holding 50 % WSL, a small increase of Fe in pore water was observed from January to August (figure 16). While the container showed an Eh-value of +59 mV in August, that should indicate a substantial mobilization of Fe in pore water, the pH increased from January to August (pH 6.9). From figure 23, it is indicated that Fe under these environmental conditions may include precipitates of Fe-hydroxides. This could be an explanation of why a larger Fe pore water concentration was not observed in the pore water.

Both CFH-12 treated soils, in 50 % WSL, showed a gradual increase of Fe concentration in pore water from January to August. A possible explanation of the higher Fe mobilization observed in CFH-12 soils compared to iron grit treated soils, could be due to the formation of precipitates with the iron grit oxidation products, lowering the Fe measured in pore water.

The Fe pore water mobilization was larger in 2 % CFH-12 soils compared to 0.5 % CFH-12, possible due to the higher Fe concentration in soil.

In containers holding 100 % WSL, a strong increase of Fe pore water concentration was observed for the reference soil and all amendments. The reference soil showed a gradual concentration increase, however as expected a larger mobilization was observed in the soils treated with Fe-amendments.

Soil treated with 0.5 % iron grit showed higher concentrations of Fe in pore water compared to the 2 % iron grit treatment. This was likely due to stronger reducing conditions observed in the former, with Eh-values of +19 and +101 for 0.5 and 2 % respectively.

The largest mobilization observed at both WSLs, were the August pore water concentrations of 357 mg/l and 293 mg/l for container 6 and 7. Both treated with 2 % CFH-12. However, relative to the total mass of Fe added as amendments, only 0.54 % and 0.43 % of this was found mobile in in the pore water for container 6 and 7 respectively.

The anaerobic conditions promoted by fully saturated soils, can lead to Sb release due to reductive dissolution of Fe-oxides (Casiot et al. 2007). However, the strong sorption of Sb (V) in our results may be due to the PZC of Fe-oxides. Below PZC the surface charge of Fe-oxides will turn more positive, thus a greater affinity for oxyanion adsorption. The PZC of Fe-oxides will vary between 6.5 – 9.5 pH, and a pH below PZC will promote antimonate adsorption. The pH-range measured in all months of sampling at 5.6 - 6.9 indicates strong sorption for Sb (V), and this is supported with the high concentration of Sb (V) in this study, even at reducing conditions.

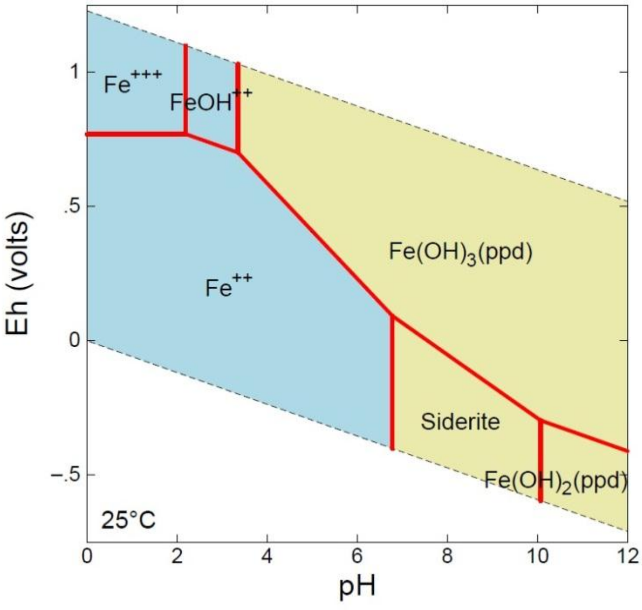

Figure 23. Pourbaix diagram of Fe. Fe^{2+} : Bicarbonate ($HCO3^-$) activity: 10^{-3} . (Source: Geochemistry Workbench).

6.3 Effect of Fe-amendments on Pb, Zn, Cu and Sb pore water concentrations

In figure 24 the remediation effect is shown for all treatments at both 50 and 100 % WSL. The effect is calculated as the ratio between the concentrations in pore water in treated soil and the reference concentrations observed at every sampling point. In addition the pore water concentrations are compared to leaching limits for Norwegian landfills (Table 6). The values based on batch tests are given in µg/l, calculated from the threshold limits (given in mg/kg) provided by the Norwegian Ministry of Environment (Miljøverndepartementet,2004) (table 2).

Table 6. Leachate limits estimated for Cu, Sb, Zn and Pb in µg/l.

Element	Inert waste		Non-hazardous waste		Hazardous waste	
	Column test µg/l	Batch test µg/l	Column test µg/l	Batch test µg/l	Column test µg/l	Batch test µg/l
Cu	600	200	30000	5000	60000	10000
Sb	100	6	150	70	1000	500
Zn	1200	400	15000	5000	60000	5000
Pb	150	50	3000	1000	15000	5000

Concentrations given for both column test and batch test are estimated from waste regulation thresholds provided by Miljøverndepartementet (2004).

In general the 2 % concentrations of iron grit and CFH-12 showed to be more stable and better retention for Cu, Zn, Pb and Sb, for both 50 and 100 % WSL. Soils treated with 0.5 % iron grit were more effective compared to 0.5 % CFH-12. In some cases, like Zn and Sb in 50 % WSL, 0.5 % iron grit performed more or less equal to the effect observed from 2 % amendment concentrations. However, 0.5 % CFH-12 treated soils showed the worst retention for Pb, Zn, Cu and Sb in fully saturated soils.

For Pb, Zn and Cu, the development of the reference pore water for both saturation levels were, as expected, in accordance with changes in pH-levels. A decrease in pH increases the mobilization of these element, and pH < 4.5 the elements are prone to leaching (McLaren, Cameron, 1996), (Calmano et al. 1994). Copper, Zn and Pb are not considered redox sensitive, and pH variations are more likely to influence leaching. In general, while antimonate adsorbs well at a pH < 7, Pb (II), Cu (II) and Zn (II) will adsorb more strongly to Fe-oxides in a more alkaline pH-range.

The results show that CFH-12 2 % amendments undergo a slower initial adsorption compared to 2 % iron grit. This is surprising as iron grit has to undergo a three step oxidation sequence (equation 1-3), while CFH-12 is already pre-oxidized.

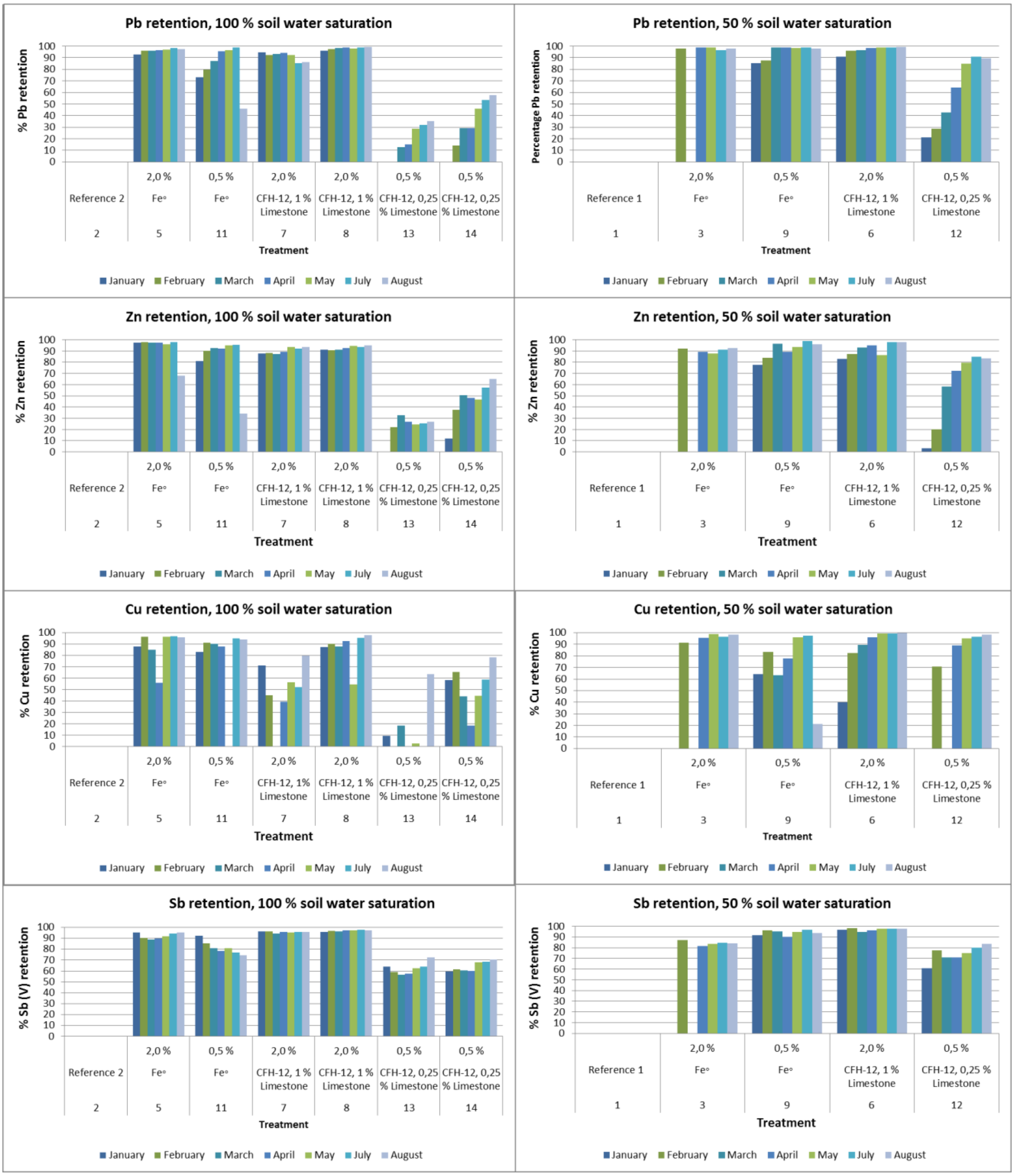

Figure 24. Remediation effect of Pb, Zn, Cu and Sb is shown at both 50 and 100 WSL.

6.3.1 Lead (Pb) in pore water

In containers holding 50 % WSL, the reference soil showed a strong increase of Pb in pore water concentrations from January to August. All months of sampling showed pore water concentrations above the leaching limits (batch- and column tests) for inert waste landfills. Mixing the soil with 0.5 % iron grit lowered the Pb pore water concentrations substantially, and after 6 months a 98 % remediation effect was observed (Figure 24). For soil treated with 0.5 % CFH-12, a gradual increase in retention was observed from January to August, and analyses showed a remediation effect of 89 %. The improved remediation effect over the 6 months may be due to the increased contact time between Pb and the sorbent. Furthermore, both iron grit and CFH-12 in 2 % concentrations showed good remediation effect in August of 98 % and 99 % respectively. Soils mixed with 0.5 and 2 % iron grit, and 2 % CFH-12 showed Pb pore water concentrations below the leaching limits for inert waste landfills.

For untreated shooting range soil holding 100 % WSL (Reference 2), a decrease in pore water concentrations of Pb was observed from January to August. However, all observations were above the leaching limit for inert waste landfills. Containers with 0.5 % CFH-12 treated soils showed a low remediation effect of 35 % and 58 % in August with Pb pore water concentrations above the leaching limits for inert waste. The soils mixed with 2 % CFH-12, showed excellent remediation effect (up to 99 %) in both containers (7 and 8). Only in August a different remediation effect was observed. While the effect in container 8 was excellent, showing retention of 99 %, container 7 showed a weaker remediation effect of 86 %. While pore water concentrations of Pb in container 8 were below both the leaching limits for inert waste landfills, the concentrations found in container 7 were below $C_{0,}$ but above L/S 10. The reason for this variation between similarly treated soils is not known.

Soils mixed with iron grit showed a good retention effect for Pb from January to July with pore water concentrations below the leaching limits. The elevated Pb concentration observed in August (container 11) was likely an outlier.

The very good retention of Pb in soils treated with CFH-12 and limestone could be due to formations of Pb-carbonates. Increasing pH and higher concentration of CO_3^{2-} will favor immobilization and precipitation of Pb (Patterson et al. 1977).

6.3.2 Zinc (Zn) in pore water

Untreated soil with 50 % WSL (Reference 1), showed a gradual increase of Zn pore water concentrations over time, and concentrations analysed in August were above leaching limits for batch tests (inert waste landfills) (400 µg/l), but below the limits for column test (C_0 : 1200µg/l). The soil mixed with 0.5 % CFH-12 showed a lower remediation effect compared to 0.5 % iron grit, with 83 % and 96% respectively. The 0.5 % concentration of iron grit showed similar remediation effect from both 2 % concentrations. In containers holding 100 % WSL, Zn concentration in the reference soil decreased from January to August, with August analysed below L/S 10. The soils mixed with 0.5 % CFH-12 showed a gradual decrease in pore water concentrations from January to August reaching concentration levels below the leaching limit for inert waste landfill. The soil treated with 0.5 % iron grit, showed good retention from January to July, with an observed remediation effect of July at 96 %, however a mobilization took place in August with remediation effect decreasing to 34 %. This could possibly be an outlier. Soils treated with 2 % CFH-12 (container 7 and 8) showed similar development and good remediation effects of 94 and 95 % respectively. However, despite variations in the pore water concentrations between the different treatments, all treated soils were analysed below the leaching limits for inert waste landfills.

6.3.3 Copper (Cu) in pore water

Untreated soil with 50 % WSL (Reference 1), showed a gradual increase in of Cu pore water concentration over time, and in August pore water concentrations were above L/S 10 (200 µg/l), but below C_0 (600 µg/l) for inert waste leachate limits. Soils treated with 0.5 % concentrations of iron grit and CFH-12 showed similar development from January to July with 98 % and 96 % remediation effect respectively. However, a mobilization was observed for iron grit in August, leading to a remediation effect of 21 %. This could be due to the strong reducing conditions observed for this soil (figure 15). Soils mixed with 2 % concentrations of iron grit and CFH-12 show strong retention of Cu, and August showed remediation effect of 98 and 99 % respectively.

In soils with 100 % WSL, container 2 (reference 2) showed a gradual decrease in pore water concentrations of Cu from January to August. Pore water samples from all months were analysed below L/S 10 and C_0. A gradual decrease was observed for CFH-12 as well, and in August the remediation effect was similar to the effect of 2 % amendment concentrations.

Soil treated with 2 and 0.5 % iron grit showed a remediation effect of 96 % and 98 % in August, but a mobilization was observed in May for 0.5 % iron grit. This observation is not represented in the remediation effect figure as it ruined the scale. Pore water concentrations analysed in August of container 7 and 8, containing soils treated with 2 % CFH-12, showed good retention with a remediation effect of respectively 80 % and 98 %. The reason for this variation between these two containers is uncertain. All pore water concentrations of Cu in treated soils (100 % WSL) were analysed below L/S 10 and C_0.

Soils treated with CFH-12 and limestone, may precipitate Cu-carbonates (Kumpiene et al. 2008), thus the retention of 97 % and 99 % Cu, in container 6 and 8 (2 % CFH-12, 1 % limestone), could be due to higher pH, immobilization and precipitation.

6.3.4 Antimony (Sb) in pore water

In untreated soil with 50% WSL (Reference 1), a gradual increase was observed of Sb pore water concentrations from January to August. All the pore water samples were above the leaching limits for non-hazardous waste landfills, for both batch test (L/S10=70 µg/l) and column test (C_0=150 µg/l), see Figure 20. The best Sb retention was observed for 2 % CFH-12 treated soil with a remediation effect up to 98 % (Figure 24). Soil treated with 0.5 % CFH-12 showed substantially lower remediation effect with pore water concentrations above the leaching limits for non-hazardous landfills.

The soil mixed with 0.5 % iron grit showed, surprisingly, better retention then the soil mixed with 2 % iron grit, with remediation effects of 94 % and 84 % respectively. The August pore water concentrations of 0.5 % iron grit were below L/S 10, while the August concentrations for 2 % iron grit were above L/S, but below C_0.

In containers holding 100 % WSL, the reference soil showed a gradual decrease in Sb concentration, but still far above the leaching limits for non-hazardous waste landfills. Similar to the 50% WSL, the 2 % iron grit or CFH-12 treated soils, showed an excellent Sb retention with remediation effects up to 95 % (iron grit) and 97 % (CFH-12). These soils treated with 2 % amendment were below the leaching limits for non-hazardous waste landfills. Soils treated with 0.5 % CFH-12 showed inadequate retention and the month of August with the lowest pore water concentrations were still exceeding the leaching limits. Soil mixed with 0.5 % iron grit showed similar August remediation effect as 0.5 % CFH-12.

In containers treated with CFH-12, limestone was added to counteract the acidity produced from CFH-12 reaction with the soil (Okkenhaug, 2012). The limestone supplies the soil solution with calcium (Ca^{2+}) and carbonate (CO_3^{2-}). It is clear that the soils treated with limestone show a substantially higher Ca (II) concentration compared to the reference and iron grit treated soils. The development of Ca (II) concentration in pore water is given in appendix 1.Calcium can interact with Sb and form Ca-antimonate. Figure 25 shows a stability diagram of $Ca_{1.13}Sb_2O_6(OH)_{0.26}*0.74H_2O$, which has the lowest Ca-antimonate solubility found in literature with a log K = -12.5 (Cornelis et al. 2011). The measured concentrations of Ca and $Sb(OH)_6^-$ in pore water in both untreated and treated soil are superimposed. The figure indicates that the pore water in the reference soil and soil treated with CFH-12 mixed with limestone may be saturated with respect to Ca-antimonate.

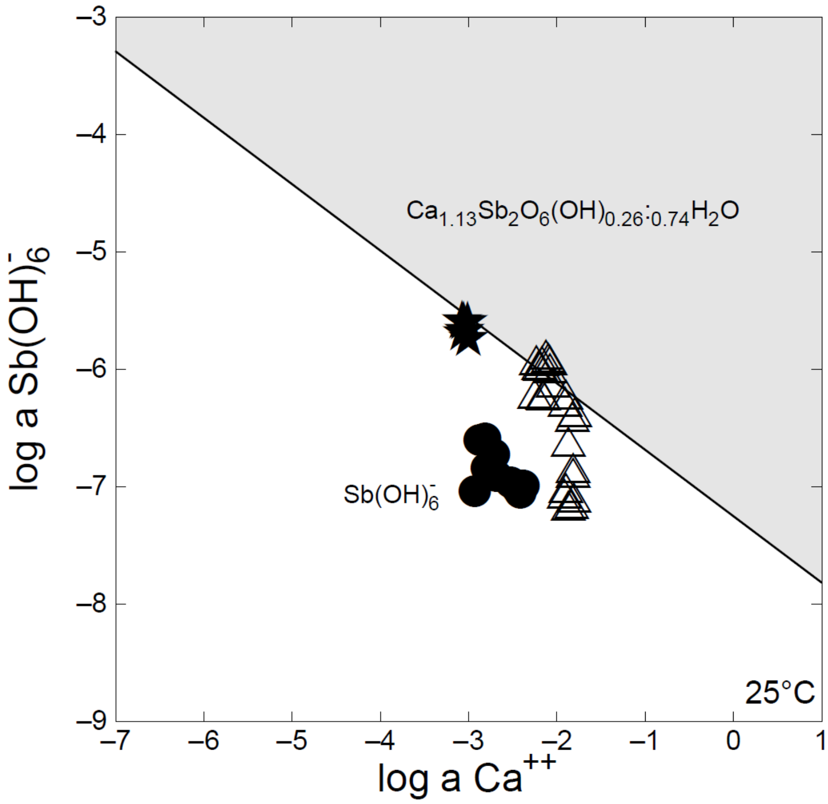

Figure 25. Stability diagram $Sb(OH)_6^-$ 100 % WSL, T = 25 °C, P = 1,013 bars, a [H_2O] = 1, Eh (volts) = 4, pH = 6, Suppressed Sb_2O_4. Black star = observation of reference. Black dot = iron grit treatment. Open delta = CFH-12 treatment.

6.3.5 Speciation of antimony (Sb) in pore water

Antimony is normally found trivalent or pentavalent, as the neutral antimonite ($Sb(OH)_3$) and the oxyanion antimonate ($Sb(OH)_6^-$) in environmentally relevant soil systems. As the oxidation state of Sb will influence the mobility and toxicity (Mitsunobu, 2006), the quantitative speciation analysis was of great interest. The speciation analysis showed little difference between the containers holding 50 and 100 % WSL, and the dominant species of Sb for both saturation levels was Sb (V). Antimony (V) was relatively stable in the soil solution, despite changes in redox conditions. This is similar to the results found by Mitsunobu et al. (2006), where Sb (V) was found to be a stable species under strongly reducing conditions.

In containers holding 50 % WSL, the reference soil showed a large decrease in Sb (III) concentration from January to August. This is likely due an ongoing oxidation of Sb in an oxic environment. A small concentration increase was observed in August, though the reason for this is unknown. Eh-measurements showed an Eh of +400, not indicating reducing conditions. In soils mixed with 0.5 % CFH-12 or iron grit, an increase was observed for Sb (III) in August. This was likely due to stronger reducing conditions, and is confirmed by the Eh-measurements for this month (figure 15). The lowest Sb (III) concentrations were found in 2 % CFH-12 treated soil. In the reference soil the dominant Sb species was Sb (V), and May, July and August concentrations showed Sb (V) fractions of 99 %. Soils mixed with CFH-12 showed Sb (V) as the dominant species as well, with 89 and 86 % of Sb_{TOT}. However, the soil mixed with 0.5 % iron grit showed low Sb (V) concentrations in January and August. The January values could have been due to a slow oxidation process of the iron grit material (equation 1-3), thus a lower initial adsorption of Sb. The dramatic increase of Sb (V) in the month of February could be due to antimonite undergoing an oxidation as surface complex of amorphous Fe-oxides (Olive, 2006) and (Okkenhaug, 2012). This is a favorable detoxifying process, where the oxidation reduces the toxicity of Sb (Belzile et al. 2001). The August mobilization of Sb (III) is probably due to the development of stronger reducing conditions. The reduction of Sb (V) observed in August for 0.5 % iron grit treated soil, could be due to a pH related mobilization of Sb. Container 9, showed a pH of 6.9 in August. Antimonate does not undergo adsorption as strong as antimonite and desorption is a possible path of mobilization for Sb in alkaline environments, thus can increase Sb leaching. Another explanation is the stronger reducing conditions measured (figure 15). Low Eh-values indicate a reducing environment, thus Sb can be found in its trivalent state.

Sorption of Sb (V) is generally more pH dependant compared to Sb (III), where the maximum sorption occurs below pH < 7. The pH measurements found through all months of sampling (figure 14), shows a pH between 5.6 and 6.9 for all treatments in both saturation levels. Thus the soil environment was well suited for antimonate adsorption. Antimonite adsorbs well and forms inner sphere complexes over a large pH-range (Wilson et al. 2010).

While Sb can in theory adsorb to both clay and organic matter. Antimony adsorption to DOC was not included in this study due to a very inorganic soil and previous research has shown that humic acid is not an important sorbent at neutral to alkaline environments (Tighe et al. 2005). Clay adsorption is likely formed as outer-sphere complexes, thus the bindings are weak compared to the irreversible covalently bonded inner-sphere complexes formed on surfaces of Fe-oxides (Olive, 2006). This can to some extent explain the stability from antimonate in iron oxide amended soils.

The results indicate that iron grit treated soils are slower at oxidizing Sb (III) to Sb (V) compared to CFH-12 treated soils.

6.4 Sources of error

A search was done to find background levels of Cu, Pb, Zn and Sb through Geochemical Atlas and Norwegian Geological Surveys online database, however the data files was either corrupt, incomplete or simply lacking. Not taking the background levels of the analytes into account, could in some cases lead to an overestimation of the contaminants. However it is reason to believe this is not a relevant problem in this paper, as shooting range concentrations of heavy metals and metalloids are so extreme it is unlikely any natural occurring concentrations would have influenced the results to a noticeable degree.

Sources of error could also take place in the laboratory analysis, especially for ICP-MS as these analyses were done by an external institute (FFI) and beyond control of the author. It was also confirmed by FFI that they suspected a possible sample contamination with regards to certain Cu values. Consequently two extreme Cu values were excluded from the data due to this information.

Due to lack of pore water in containers with 50 % WSL, no Sb speciation analysis could be carried out on container 3 holding 2 % iron grit. Furthermore, the minimal amount of pore water sampled in container 1,3,6,9 made it impossible to carry out analysis on triplicates, thus no SD could be determined. Longer extraction times of the pore water samplers in the containers holding 50 % WSL, may have given higher amount of pore water. This could have given better information about chemical variations in the pore water.

The soil samples taken for creating the experimental soil water saturation curves should ideally come from undisturbed soils (Eikjelkamp, 2007). This was not possible in this project and soil samples were taken post treatment.

The tap water used to refill the containers to maintain 100 and 50 % WSLs were not analyzed for background contaminants. However, the water was municipal drinking water, and it is assumed to have low metal and Sb concentrations.

Due to incorrect installation of the porewater samplers in container 10 (all 3 samplers) and 6 (2 samplers), no pore water could be extracted.

7 Conclusions

The objectives of this work were to determine the effect of Fe-amendments on stabilizing Pb, Zn, Cu and Sb in shooting range soil, under various redox conditions. A secondary goal was to investigate if the redox conditions affected the solubility of the sorbents and speciation of Sb.

The results showed that the best remediation effect was achieved in soils mixed with 2 % CFH-12 or iron grit, with a substantial better retention compared to 0.5 % amendment concentration. Soils treated with 2 % CFH-12 showed retention > 95 % for Pb, Cu, Zn and Sb, in both WSLs. Iron grit showed a retention for most soils > 92 %. The remediation effect for soil mixed with 0.5 % iron grit was better than the effect observed for 0.5 % CFH-12.

Soils treated with 2 % CFH-12 showed pore water concentrations below the leaching limits for inert waste landfills for all elements and both investigated WSLs. Soils mixed with 2 % iron grit showed pore water concentrations below the same leaching limits (inert waste) for Pb, Cu and Zn. However, for Sb (50 % WSL) concentrations were found above the leachate limit for non-hazardous waste. Pore water concentrations measured in soils treated with 0.5 % CFH-12 were above leachate limits for Pb and Sb, thus this concentration level of the CFH-12 amendment is not sufficient to stabilize leachate within established limits. The soils mixed with 0.5 % iron grit showed pore water concentrations generally below the leachate limits, however some variations was found between the WSLs.

Antimony was found predominantly as Sb (V), also at the lowest Eh-observations. Thus variations in redox conditions due to changing soil water saturation, will not contribute to a substantial reduction of Sb (V) to the more toxic Sb (III).

Pore water concentrations of Fe increased through all months of sampling (especially in 100 % WSL), thus an ongoing Fe dissolution was occurring. However, the increasing dissolution of Fe did not affect the stabilization of Pb, Zn, Cu, and Sb.

The type of Fe-amendment used affected the soils ability to retain water. An increase was observed for CFH-12 and a decrease for iron grit, possible due to changes in the grain size distribution.

This work shows that amendment with Fe based sorbents of shooting range soil prior landfilling may by an effective method to reduce the mobility of metals and Sb and to comply with leaching limits for ordinary landfills.

Based on the results it is reason to conclude that the best Fe-amendment to stabilize shooting range soil in landfills is 2 % concentrations of CFH-12 mixed with 1 % limestone. If iron grit is to be used to stabilize shooting range soils, the concentration should be higher than 0.5 %. For CFH-12 the concentration should be substantially higher than 0.5 %, as the results indicated that this amount of amendment was not sufficient to stabilize the shooting range soil satisfactory.

8 Further work

Continued work should include a more detailed study on the solubility of Fe-oxides under specific redox conditions. This should include a mineralogical study as there are many Fe-oxides and dissolution behavior can be different between the minerals.

Similar work should be continued to find the ideal concentration of CFH-12. Soils treated with 2 % showed the best retention of all treatments, while 0.5 % showed generally the worst. Soils mixed with 0.5 % CFH-12 showed strong gradual decreases in pore water concentrations, especially of Pb, Zn and Sb. This increased retention with increased reaction time, could mean 0.5 % CFH-12 is sufficient for remediation work extending over the 6 months.

As the Fe-amendments are a possible *in situ* remediation option, they should undergo toxicity tests before they are used actively in the environment.

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Appendix

Appendix 1

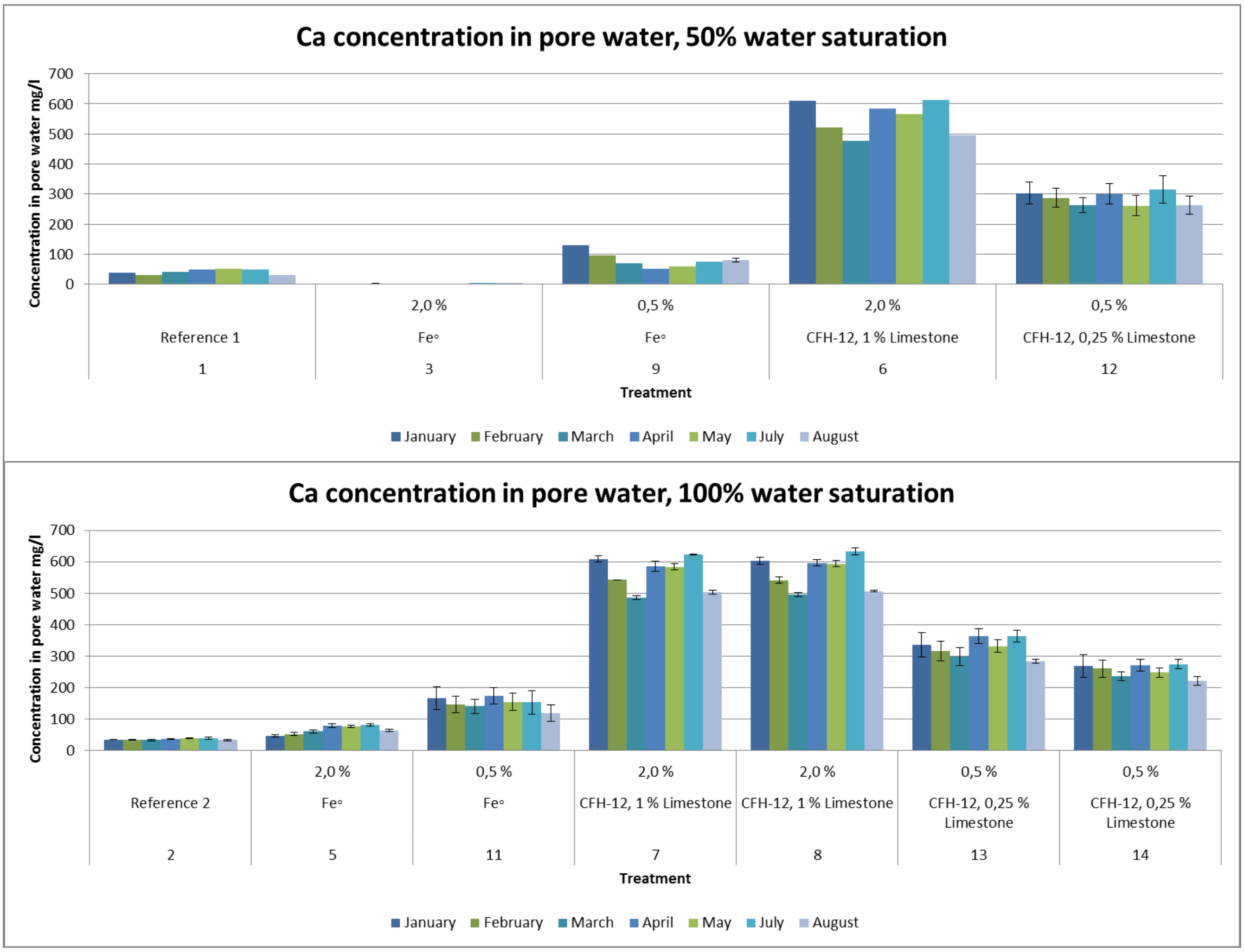
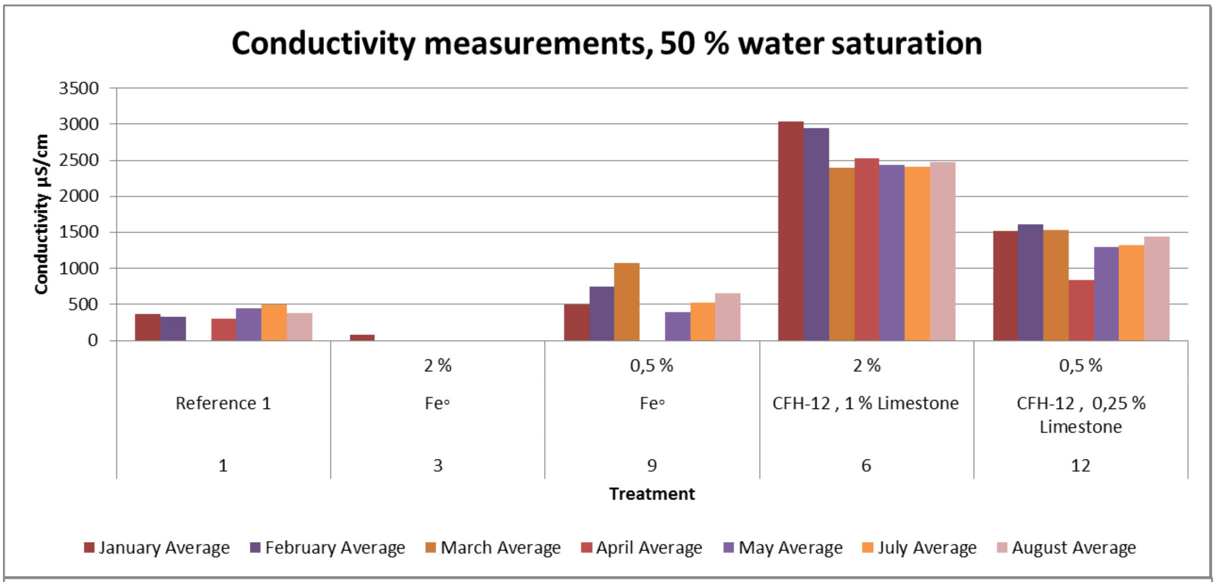


Figure 26. Pore water concentrations of Ca in 50 and 100 % WSL. Error bars represent SD where triplicates were available. Missing bars in 50 % WSL indicate lack of pore water that month.

Appendix 2



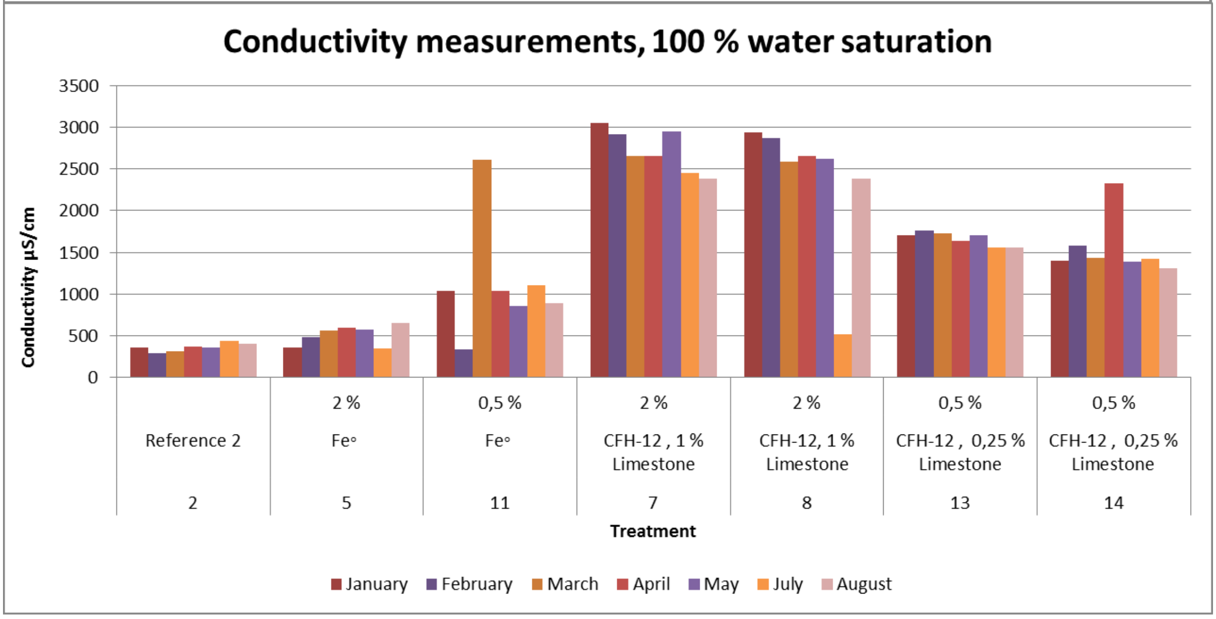


Figure 27. Conductivity measurements in pore water measured from January to August, with the exception of June, for all ICBs, at both 50 and 100 % WSL. Missing bars in 50 % WSL indicate lack of pore water that month.

Appendix 3

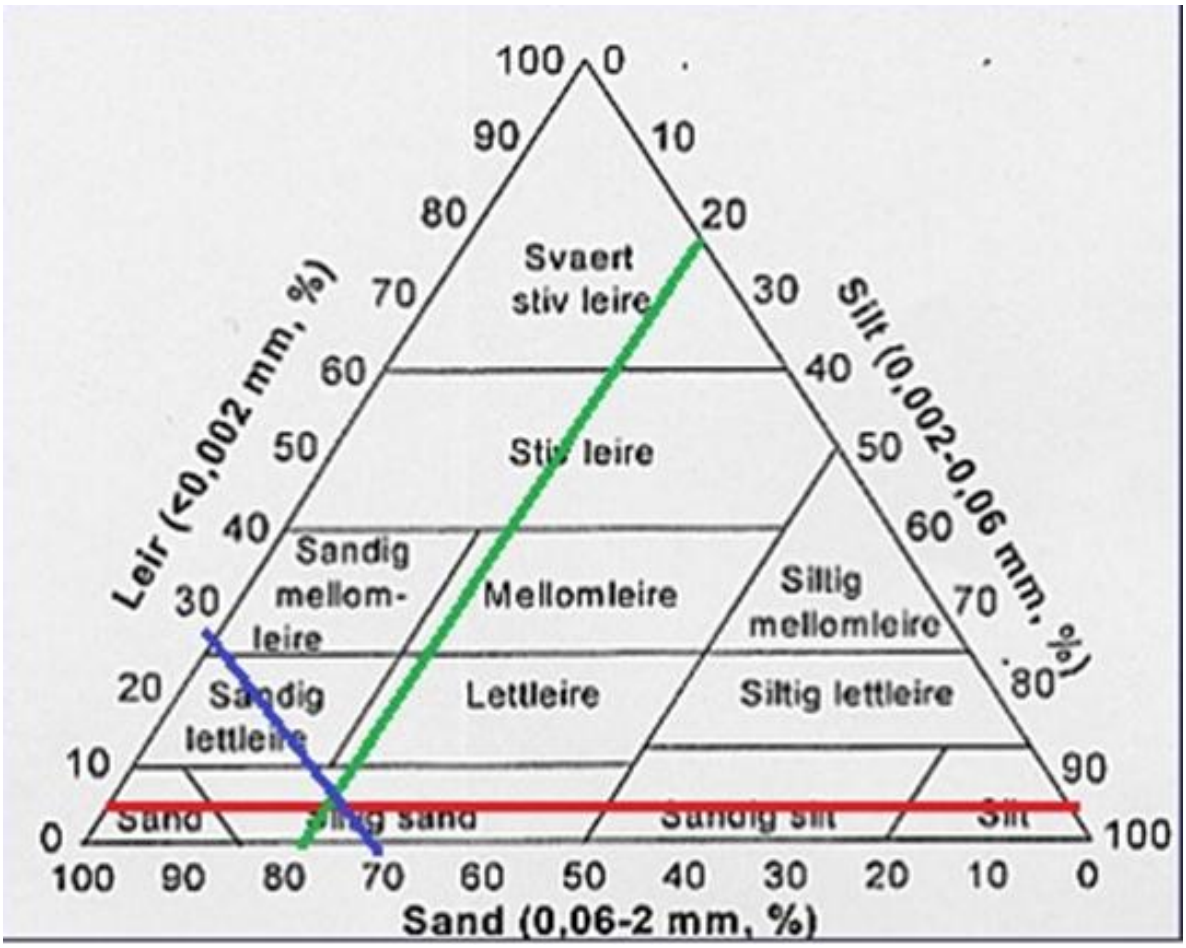


Figure 28. Soil classification texture triangle. The intersection between red, blue and green line represent the soil classification (silty sand).

Appendix 4

Table 7. Raw data ICP-MS – January

FFI-ID	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-1 13.02.2012 16:09:32	1a	39990	4274	120,4	1025	459,9	1433
12-2 13.02.2012 16:14:23	1b	39900	33190	27,28	540,8	284,6	816,4
12-3 13.02.2012 16:19:15	2a	35070	9134	122,3	739,3	424,3	1219
12-4 13.02.2012 16:24:05	2b	36430	13880	85,29	1213	355,1	1195
12-5 13.02.2012 16:33:48	2c	36010	8356	212,8	967,9	442,3	1371
12-6 13.02.2012 18:39:47	5a	50470	76840	6,277	27,22	18,21	114,3
12-7 13.02.2012 16:43:29	5b	42680	85120	11,67	19,01	21,24	93,2
12-8 13.02.2012 16:48:19	5c	46700	71660	33,86	31,06	20,37	68,37
12-9 13.02.2012 16:53:09	6b	611100	44100	44,43	133,7	11,92	103,2
12-10 13.02.2012 16:57:58	7a	622600	28800	50,86	116	12,69	64,49
12-11 13.02.2012 17:02:48	7b	604700	27350	29,37	128,5	16,35	66,21
12-12 13.02.2012 17:07:40	7c	603700	19640	40,32	116,1	18,35	66,96
12-13 13.02.2012 17:12:32	8a	613100	20490	26,66	116,9	16,32	55,2
12-14 13.02.2012 17:17:23	8b	606700	13510	11,43	69,11	17,83	43,14
12-15 13.02.2012 17:22:14	8c	592500	16150	15,77	79,3	15,13	58,3
12-16 13.02.2012 17:27:05	9b	126700	95990	13,04	136,2	21,83	131,5
12-17 13.02.2012 17:36:48	9c	132700	74170	40,07	214,9	39,24	203,3
12-18 13.02.2012 17:41:38	11a	140800	72420	20,95	217,1	35,04	473,7
12-19 13.02.2012 17:46:28	11b	149700	98400	39,81	221,7	28,57	330
12-20 13.02.2012 17:51:18	11c	207600	31740	10,54	123	32,45	210,2
12-21 13.02.2012 17:56:08	12a	337200	8298	47,62	697,6	119,8	416,7
12-22 13.02.2012 18:00:57	12b	263600	20650	286,9	722,3	116,9	1106
12-23 13.02.2012 18:05:48	12c	308600	5551	88,64	855,7	203,4	1141
12-24 13.02.2012 18:10:40	13a	347400	16540	66,37	787,3	88,75	900
12-25 13.02.2012 18:15:32	13b	370500	5888	47,26	926,2	101,9	857,6
12-26 13.02.2012 18:20:23	13c	294000	10400	266,5	1373	249,6	2796
12-27 13.02.2012 18:25:14	14a	266100	14400	97,71	1292	239,9	2496
12-28 13.02.2012 18:30:05	14b	235400	8527	30,37	604,8	95,36	518,3
12-29 13.02.2012 18:34:56	14c	306900	16350	46,66	682	161,7	778,7

Appendix 5

Table 8. Raw data ICP-MS – February

FFI-ID	NGI-merking						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-52 23.02.2012 11:16:43	1a	33620	43,99	183	960	610,1	1330
12-53 23.02.2012 11:21:34	1b	28200	185,9	154,1	589,2	506,4	622,8
12-54 23.02.2012 11:26:25	2a	34590	17240	135,6	623	359,7	1217
12-55 23.02.2012 11:31:16	2b	35500	32040	115,3	1551	293	1096
12-56 23.02.2012 11:36:06	2c	34290	18270	164,2	804,4	361,5	1487
12-57 23.02.2012 11:40:57	3a	2812	43,46	5,217	75,06	70,52	8,745
12-58 23.02.2012 11:45:47	3b	2990	415	36,18	47,33	87,19	46,61
12-59 23.02.2012 11:50:37	3c	960,1	21,59	3,279	60,69	59,5	12,85
12-60 23.02.2012 11:55:27	5a	56810	100300	3,364	31,83	30,09	53,23
12-61 23.02.2012 12:10:02	5b	47220	113100	4,245	15,07	37,32	43,72
12-62 23.02.2012 12:14:53	5c	55470	99810	6,451	15,89	32,54	57,84
12-63 23.02.2012 12:19:45	6a	522600	102200	29,49	97,38	11,31	37,19
12-64 23.02.2012 12:24:35	7a	544000	81380	119,9	125,3	10,45	62,29
12-65 23.02.2012 12:29:26	7b	543300	70710	22,94	110,2	11,74	59,64
12-66 23.02.2012 12:34:15	7c	541900	58430	85,47	116,7	16,04	170,5
12-67 23.02.2012 12:39:07	8a	547900	60830	26,16	113,3	10,79	32,63
12-68 23.02.2012 12:43:58	8b	549800	44950	7,065	85,31	10,15	28,37
12-69 23.02.2012 12:48:49	8c	530700	49800	7,215	78,97	10,89	30,99
12-70 23.02.2012 12:53:40	9a	86790	63150	18,43	93,22	13,83	52,82
12-71 23.02.2012 12:58:31	9c	104300	84880	36,79	154,6	26,9	185
12-72 23.02.2012 13:03:22	11a	136800	154400	18	98,42	64,69	436,7
12-73 23.02.2012 13:17:57	11b	126400	174600	9,997	92,82	44,63	165
12-74 23.02.2012 13:22:49	11c	177000	72760	9,336	101	38,19	171,4
12-75 23.02.2012 13:27:39	12a	313500	30150	21,33	682	96,32	304,4
12-76 23.02.2012 13:32:30	12b	254500	43640	52,8	542,2	108,4	829,1
12-77 23.02.2012 13:37:20	12c	295600	25250	72,64	628,2	174,9	961,9
12-78 23.02.2012 13:42:10	13a	307300	43870	398	489,2	89,89	800,5
12-79 23.02.2012 13:47:01	13b	353100	28580	36,42	878,3	106,8	755,3
12-80 23.02.2012 13:51:53	13c	293500	45670	143,4	960,9	218,3	2383
12-81 23.02.2012 13:56:45	14a	267900	54890	67,1	944,5	198,7	2140
12-82 23.02.2012 14:01:36	14b	230800	33730	37,98	426,9	63,23	507,5
12-83 23.02.2012 14:06:27	14c	284900	60350	38,72	493,3	129,9	618

Appendix 6

Table 9. Raw data ICP-MS – March

FFI-merking	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-107 29.03.2012 11:46:36	1a	43890	33,37	208,6	1184	473,4	1946
12-108 29.03.2012 11:51:27	1b	37440	149,4	148,6	710,9	413,6	698,7
12-109 29.03.2012 11:56:18	2a	34750	22720	26,13	473,7	357,9	1160
12-110 29.03.2012 12:01:09	2b	34980	45830	19,32	1399	295,7	1286
12-111 29.03.2012 12:05:59	2c	31820	26620	137,3	547,8	354,3	1476
12-112 29.03.2012 12:10:50	5a	65070	124800	15,08	28,39	36,67	53,85
12-113 29.03.2012 12:15:41	5b	56400	134000	1,848	14,46	43,9	47,74
12-114 29.03.2012 12:20:30	5c	62980	116900	10,19	16,53	33,04	55,21
12-115 29.03.2012 12:35:06	6a	477400	141800	18,6	65,19	23,79	46,49
12-116 29.03.2012 12:39:57	7a	481000	125000	27	101	18,63	55,19
12-117 29.03.2012 12:44:48	7b	486600	107100	26,08	115	18,06	58,68
12-118 29.03.2012 12:49:39	7c	491800	91780	207,5	91,74	19,36	159,1
12-119 29.03.2012 12:54:29	8a	498100	101500	16,78	93,74	16,02	31,07
12-120 29.03.2012 12:59:20	8b	502400	76940	2,457	63,71	11,32	18,34
12-121 29.03.2012 13:04:10	8c	489700	80240	3,164	62,76	11,55	18,05
12-122 29.03.2012 13:09:02	9a	70090	49360	65,39	33,13	21,09	15,73
12-123 29.03.2012 13:13:53	11a	141000	219100	7,722	65,71	83,52	242
12-124 29.03.2012 13:18:44	11b	119300	218500	6,616	54,33	66,1	150,3
12-125 29.03.2012 13:23:35	11c	163100	107000	3,168	60,64	42,17	103,9
12-126 29.03.2012 13:28:26	12a	279500	82120	19,99	272,9	82,88	343,9
12-127 29.03.2012 13:43:01	12b	235400	77890	3064	499,5	124,7	1022
12-128 29.03.2012 13:47:52	12c	273800	44630	25,32	420,6	181,6	915
12-129 29.03.2012 13:52:43	13a	309900	80420	35,79	409,3	88,66	669,4
12-130 29.03.2012 13:57:33	13b	322800	53360	34,19	613,5	116	678
12-131 29.03.2012 14:02:23	13c	267700	67850	78,75	603,6	233,1	2079
12-132 29.03.2012 14:07:13	14a	233000	79050	49,81	553,7	199	1794
12-133 29.03.2012 14:12:04	14b	224500	55280	20,69	317,8	70,53	404,3
12-134 29.03.2012 14:16:56	14c	252700	87560	31,36	320,6	127,8	579,9

Appendix 7

Table 10. Raw data ICP-MS – April

FFI-ID	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-157 24.04.2012 16:17:02	1a	51360	41,38	242,5	1260	402,2	2055
12-158 24.04.2012 16:22:11	1b	45230	52,5	164,5	829,5	402,7	947,8
12-159 24.04.2012 16:27:20	2a	39810	29460	24,3	400	372	1024
12-160 24.04.2012 16:32:29	2b	36890	48980	19,16	1150	280,9	739,6
12-161 24.04.2012 16:37:38	2c	35900	32810	61,85	428,7	342,2	1314
12-162 24.04.2012 16:42:46	3c	1510	40,18	8,604	113,4	74,59	15,3
12-163 24.04.2012 16:47:54	5a	79840	114300	2,057	16,56	29,73	37,35
12-164 24.04.2012 16:53:02	5b	73610	141500	42,67	22,02	35,75	37,58
12-165 24.04.2012 17:08:32	5c	86980	118400	1,466	16,93	35,78	33,25
12-166 24.04.2012 17:13:41	6a	583400	187600	7,71	54,26	14,4	22,47
12-167 24.04.2012 17:18:50	7a	582500	152200	6,134	78,57	11,29	16,62
12-168 24.04.2012 17:23:58	7b	572700	143600	4,776	55,16	15,12	36,96
12-169 24.04.2012 17:29:07	7c	606000	137300	53	78,41	16,84	128,4
12-170 24.04.2012 17:34:15	8a	591400	132500	3,509	56,98	10,55	15,71
12-171 24.04.2012 17:39:24	8b	593400	97450	2,669	47,89	9,25	8,364
12-172 24.04.2012 17:44:34	8c	608100	106100	1,826	47,04	8,296	7,524
12-173 24.04.2012 17:49:43	9a	41600	283,7	33,64	13,38	37,39	6,364
12-174 24.04.2012 17:54:52	9c	60740	1518	56,73	82,94	41,99	23,24
12-175 24.04.2012 18:00:01	11a	177800	264600	1,618	51,38	83,52	69,34
12-176 24.04.2012 18:05:09	11b	146000	243100	1,351	40,99	70,02	31,41
12-177 24.04.2012 18:20:39	11c	199300	162300	10	69,55	60,21	40,31
12-178 24.04.2012 18:25:48	12a	328400	126600	10,69	247,7	68,19	244,3
12-179 24.04.2012 18:30:56	12b	262400	93300	35,26	273,3	101,9	606,2
12-180 24.04.2012 18:36:05	12c	310800	64960	22,41	351,6	182,7	753,4
12-181 24.04.2012 18:41:13	13a	368000	108900	37,51	363,4	77,76	444,4
12-182 24.04.2012 18:46:21	13b	387500	85890	28,23	532,7	112,5	541,4
12-183 24.04.2012 18:51:30	13c	338400	99520	59,41	551,6	230	1629
12-184 24.04.2012 18:56:40	14a	268100	114900	36,1	463,1	204,7	1485
12-185 24.04.2012 19:01:49	14b	256000	79940	20,4	258,7	66,29	232,7
12-186 24.04.2012 19:06:58	14c	292500	122900	29,17	301,1	125,2	464,7

Appendix 8

Table 11. Raw data ICP-MS – May

FFI-ID	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-368 08.06.2012 10:28:23	1a	52490	24,77	246,6	1334	401,7	2205
12-369 08.06.2012 10:33:28	1b	51740	34,27	174,4	1140	377,7	1271
12-370 08.06.2012 10:38:34	2a	40490	34840	19,8	395,6	327,7	907
12-371 08.06.2012 10:43:40	2b	37610	49080	18,21	1106	262,4	647,8
12-372 08.06.2012 10:48:45	2c	38440	43260	42,27	430,5	293,6	1138
12-373 08.06.2012 10:53:50	3c	1475	37,15	4,63	151,3	63,47	22,3
12-374 08.06.2012 10:58:54	5a	78290	103000	0,52	17,53	21,02	29,49
12-375 08.06.2012 11:03:59	5b	72250	132200	0,876	35,91	24,42	26,27
12-376 08.06.2012 11:19:17	5c	81500	99380	1,417	30,1	26,2	23,43
12-377 08.06.2012 11:24:23	6a	566200	204300	1,752	172,7	9,043	20,22
12-378 08.06.2012 11:29:28	7a	584300	192700	2,745	49,23	10,42	19,42
12-379 08.06.2012 11:34:34	7b	575700	195900	2,671	43,92	14,24	34,02
12-380 08.06.2012 11:39:38	7c	594700	192700	29,53	32,31	17,13	158,6
12-381 08.06.2012 11:44:42	8a	585100	161500	1,58	33,48	9,224	18,15
12-382 08.06.2012 11:49:48	8b	595300	158300	1,171	38,76	9,166	17,5
12-383 08.06.2012 11:54:54	8c	604600	142200	33,79	38,26	6,577	18,94
12-385 08.06.2012 12:00:00	9a	58860	44050	8,869	110,6	15,55	26,36
12-386 08.06.2012 12:05:06	9c	61300	48840	18,9	48,39	25,86	31,62
12-387 08.06.2012 12:10:12	11a	160900	266600	1,366	31,1	65,6	29,51
12-388 08.06.2012 12:15:16	11b	125600	214700	328,1	36,8	53,01	43,71
12-389 08.06.2012 12:30:36	11c	179600	170200	151,3	28,25	49,4	24,99
12-390 08.06.2012 12:35:42	12a	254700	70330	7,714	183,6	60,57	43,13
12-391 08.06.2012 12:40:47	12b	230700	85480	25,59	232,6	92,91	334,3
12-392 08.06.2012 12:45:52	12c	298000	78780	16,34	341,3	137,4	425,3
12-393 08.06.2012 12:50:58	13a	334000	129700	24,86	299,6	56,54	228,9
12-394 08.06.2012 12:56:02	13b	351600	104800	22,99	471,7	92,5	363,6
12-395 08.06.2012 13:01:07	13c	313800	117000	30,27	689,8	183,5	1330
12-396 08.06.2012 13:06:13	14a	239800	133300	20,65	483	147,7	1067
12-397 08.06.2012 13:11:19	14b	240000	95710	9,301	282,2	56,55	144,4
12-398 08.06.2012 13:16:25	14c	266800	143000	14,53	266,7	78,53	240,2

Appendix 9

Table 12. Raw data ICP-MS – July

FFI-ID	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-995 29.08.2012 10:30:57	1a	48460	17,42	278,4	1164	453,7	2294
12-996 29.08.2012 10:36:02	1b	48730	163,4	458,9	1159	427,8	1790
12-997 29.08.2012 10:41:07	2a	43290	41360	19,34	261,3	342,6	783,8
12-998 29.08.2012 10:46:12	2b	35890	50670	19,65	765,5	261,3	520,8
12-999 29.08.2012 10:51:17	2c	40180	53160	34,4	282,1	267,7	830,1
12-1000 29.08.2012 10:56:21	3A	3694	317,2	13,71	102,5	68,12	74,26
12-1001 29.08.2012 11:01:25	5a	82210	118000	0,514	10,69	13,45	8,394
12-1002 29.08.2012 11:16:44	5b	77560,15	139300	0,931	10,08	19,01958	10,62258
12-1003 29.08.2012 11:21:50	5c	85855,51	113600	0,834	9,931	18,47587	14,86743
12-1004 29.08.2012 11:26:56	6a	612872,8	327600	1,981	23,58	10,22277	19,88597
12-1005 29.08.2012 11:32:01	7a	623024,1	295400	2,65	39,38	7,668359	14,81515
12-1006 29.08.2012 11:37:07	7b	625280	273000	1,724	31,29	11,1717	16,77029
12-1007 29.08.2012 11:42:11	7c	622306,3	255500	30,81	33,3	16,66009	278,1108
12-1008 29.08.2012 11:47:16	8a	622614	257000	1,439	29,41	7,122597	10,35597
12-1009 29.08.2012 11:52:22	8b	641583,6	234200	0,958	25,58	6,081342	4,36404
12-1010 29.08.2012 11:57:27	8c	638815	248000	0,882	30,52	6,574784	12,65091
12-1011 29.08.2012 12:02:33	9a	74268,66	93170	4,585	8,93	5,497623	17,40807
12-1012 29.08.2012 12:07:39	9c	74432,72	89160	13,02	15,7	22,59986	25,21817
12-1013 29.08.2012 12:12:43	11a	132479,8	260500	0,935	19,76	76,01677	11,9504
12-1014 29.08.2012 12:28:02	11b	132134,9	240200	0,707	16,2	76,20506	9,96253
12-1015 29.08.2012 12:33:07	11c	195840,7	235700	1,89	23,03	48,91409	7,815195
12-1016 29.08.2012 12:38:13	12a	331316,3	113500	7,019	145,4	55,37683	52,92306
12-1017 29.08.2012 12:43:18	12b	262656,9	124100	18,98	158,3	85,9971	198,9511
12-1018 29.08.2012 12:48:22	12c	348942	115700	14	226,8	125,914	309,0827
12-1019 29.08.2012 12:53:27	13a	362881,3	177700	42,05966	246,1832	41,2763	147,2261
12-1020 29.08.2012 12:58:32	13b	384654,1	140600	18,77	404,3	88,60063	271,5273
12-1021 29.08.2012 13:03:38	13c	346062	153200	25,46	327,9	186,0486	1036,458
12-1022 29.08.2012 13:08:44	14a	264960,9	172200	15,31	252,5	151,6037	804,6748
12-1023 29.08.2012 13:13:49	14b	268416,9	132700	6,08	140,4	52,22034	54,05203
12-1024 29.08.2012 13:18:55	14c	293415,4	194100	8,895	166,8	69,77688	133,7477

Appendix 10

Table 13. Raw data ICP-MS – August

FFI-ID	NGI-ID						
		44Ca	56Fe	63Cu	66Zn	121Sb	208Pb
12-1274 29.08.2012 13:24:00	1a	28620	163,3542	247,3353	844,7645	589,4804	1964,167
12-1275 29.08.2012 13:39:18	2a	36270	50730	16,99	204,7	356,5837	684,8584
12-1276 29.08.2012 13:44:24	5a	68410	113800	1,957	335,8	14,65649	9,206407
12-1277 29.08.2012 13:49:29	6a	495700	357000	0,984	17,05	12,64481	13,07583
12-1278 29.08.2012 13:54:33	7a	498400	300600	1,273	23,73	6,804059	5,537523
12-1279 29.08.2012 13:59:37	8a	504800	267600	0,847	22,14	8,199586	4,437437
12-1280 29.08.2012 14:04:42	9a	87110	99590	1,956	4,152	16,96704	4,192845
12-1281 29.08.2012 14:09:47	11a	110400	207500	12240	702,2	101,101	1075,626
12-1282 29.08.2012 14:14:54	12a	273000	148300	3,577	98,68	53,637	65,78489
12-1283 29.08.2012 14:20:00	13a	285700	220600	9,854	239,1	32,24427	115,0743
12-1284 29.08.2012 14:25:06	14a	211200	214200	8,44	186	138,4032	776,5515
12-1285 29.08.2012 14:30:11	1b	35190	1866	796,3711	843,8737	487,8599	1439,733
12-1286 29.08.2012 14:35:17	2b	30560	57140	38,16831	673,8947	288,8765	596,2951
12-1287 29.08.2012 15:00:48	3b	4883	59,32012	8,621	79,24	90,68201	25,09703
12-1288 29.08.2012 15:05:53	5b	59620	129600	0,621	8,575	15,09052	12,48044
12-1289 29.08.2012 15:10:59	7b	505300	296600	0,83	20,84	13,87541	7,27723
12-1290 29.08.2012 15:16:04	8b	507500	261700	0,706	14,18	7,299925	3,680595
12-1291 29.08.2012 15:21:09	9b	81370	138700	1209,367	37,44006	60,29266	3356,103
12-1292 29.08.2012 15:26:13	11b	100600	196700	0,96	15,93	89,62891	19,74178
12-1293 29.08.2012 15:31:19	12b	228100	175100	10,23	130,5	116,1878	251,1972
12-1294 29.08.2012 15:36:26	13b	289600	174600	10,77	327,7	63,7644	217,6135
12-1295 29.08.2012 15:41:32	14b	216600	176200	3,981	96,55	43,9986	20,57003
12-1296 29.08.2012 15:46:38	2c	35430	67380	34,02124	224,5696	267,093	754,1588
12-1297 29.08.2012 15:51:43	3c	3992	149,9478	10,26	51,13	78,56562	44,3169
12-1298 29.08.2012 15:56:48	5c	66500	105700	0,831	8,364	14,43089	26,17488
12-1299 29.08.2012 16:12:08	7c	510600	281300	15,93	27,87	17,97007	266,3548
12-1300 29.08.2012 16:17:12	8c	510500	274400	0,518	21,44	8,537491	9,787256
12-1301 29.08.2012 16:22:18	9c	73090	34570	23,9	56,56	26,45404	65,02023
12-1302 29.08.2012 16:27:22	11c	148200	217200	2,581	8,627	43,50169	8,405861
12-1303 29.08.2012 16:32:27	12c	287000	156600	9,567	192,5	97,85602	224,8331
12-1304 29.08.2012 16:37:30	13c	278000	189300	11,93	237,2	155,1029	985,4557
12-1305 29.08.2012 16:44:31	14c	238200	267700	7,08	103,8	85,79992	66,26185

Appendix 11

Table 14. Raw data HG-ICP-OES – January

	Sb-TOTAL			Sb 3+		
Line		Sb 217,582	Sb 206.836		Sb 217,582	Sb 206.836
		µg/L	µg/L		µg/L	µg/L
Sample	vask	-0,22344	-0,59878	vask	0,14144	0,12376
	1a	424,046	425,222	1a	8,43158	8,45218
	1b	268,422	267,932	1b	66,9732	67,5036
	2a	412,09	412,188	2a	16,27	16,27
	2b	353,486	353,878	2b	17,884	17,884
	2c	56,3667	55,7944	5a	6,716	6,716
	5a	19,7686	19,5164	5b	9,212	9,212
	5b	19,845	19,5608	5c	9,04464	9,0486
	5c	19,2545	19,2157	6b	0,49302	0,63954
	6b	3,44544	2,97792	7a	1,84734	1,5642
	7a	10,752	10,3872	7b	2,10474	1,58796
	7b	14,8521	14,4894	7c	1,88892	1,83546
	7c	17,6088	17,2684	8a	1,10088	1,485
	8a	15,4882	15,2152	8b	0,95256	1,00352
	8b	17,244	17,217	8c	1,46804	1,2936
	QC	54,504	54,72	9b	8,68672	8,68672
	8c	15,0423	15,106	9c	8,98072	9,01012
	9b	19,3284	19,7743	11a	13,22886	13,3278
	9c	32,5128	32,6692	11b	4,67346	4,9567
	11a	28,8052	28,75	11c	10,3887	10,19664
	11b	21,8224	21,758	12a	1,01656	0,7857
	11c	25,533	25,407	12b	6,53376	6,54912
	12a	92,3268	92,0918	12c	0,63552	0,52032
	12b	92,61	92,88	13a	2,0634	1,8981
	12c	168,542	167,884	13b	0,8474	1,0469
	13a	72,6714	72,3612	13c	4,1021	3,5625
	13b	81,686	81,8646	14a	4,9077	5,0027
	13c	195,57	194,76	14b	4,7557	4,9761
	14a	198,716	198,246	14c	5,586	5,3162
	14b	75,4538	75,388			
	14c	136,135	136,135			
	1643H	58,0224	58,4544			

Appendix 12

Table 15. Raw data HG-ICP-OES – February

	Sb-TOTAL				Sb 3+		
Line			Sb 206.836				Sb 206.836
			µg/L				µg/L
		1643H	57,8442				
Sample	1	1a-feb	575,382		1	1a-feb	0,40964
	2	1b-feb	476,952		2	1b-feb	0,06272
	3	2a-feb	310,488		3	2a-feb	9,67064
	4	2b-feb	271,116		4	2b-feb	15,42912
	5	2c-feb	377,298		5	2c-feb	8,19868
	6	5a-feb	34,3944		6	5a-feb	1,88748
	7	5b-feb	34,0272		7	5b-feb	3,57888
	8	5c-feb	30,90566		8	5c-feb	2,69376
	9	6a-feb	9,556604		9	6a-feb	0,56256
	10	7a-feb	10,78302		10	7a-feb	0,00576
	11	7b-feb	12,79245		11	7b-feb	0,4032
	12	7c-feb	15,9717		12	7c-feb	1,3632
	13	8a-feb	9,792453		13	8a-feb	0,4136
	14	8b-feb	8,189623		14	8b-feb	1,6826
	15	8c-feb	8,360377		15	8c-feb	0,9776
	16	9a-feb	56,38679		16	9a-feb	0,46624
		1643H	58,35849		17	9c-feb	5,0854
	17	9c-feb	28,92453		18	11a-feb	7,71652
	18	11a-feb	49,58491		19	11b-feb	9,97152
	19	11b-feb	32,08491		20	11c-feb	6,72336
	20	11c-feb	23,34906		21	12a-feb	3,30464
	21	12a-feb	62,66038		22	12b-feb	7,19256
	22	12b-feb	75,9434		23	12c-feb	2,66168
	23	12c-feb	118,8679		24	13a-feb	9,93784
	24	13a-feb	54,5566		25	13b-feb	1,6652
	25	13b-feb	65,4434		26	13c-feb	2,944
	26	13c-feb	311,7925		27	14a-feb	9,52936
	27	14a-feb	188,9375		28	14b-feb	6,91288
	28	14b-feb	61,3		29	14c-feb	6,72888
	29	14c-feb	130,1875				

Appendix 13

Table 16. Raw data HG-ICP-OES – March

	Sb-TOTAL		Sb 3+	
Line		Sb 217,582		Sb 217,582
		µg/L		µg/L
Sample	2a-mar	367,6875	2a-mar	27,2872
	2b-mar	295,625	2b-mar	24,066
	2c-mar	355,5	2c-mar	15,5916
	5a-mar	37,78125	5a-mar	6,0642
	5b-mar	45,0625	5b-mar	9,8964
	5c-mar	32,81875	5c-mar	5,6916
	6a-mar	11,69375	6a-mar	1,3266
	7a-mar	12	7a-mar	0,7182
	7b-mar	12,5625	7b-mar	1,1196
	7c-mar	15,2375	7c-mar	2,2896
	8a-mar	12,74375	8a-mar	1,20704
	1643h	58,85	8b-mar	0,58696
	8b-mar	9,1625	8c-mar	0,98624
	8c-mar	10,30625	11a-mar	13,3952
	11a-mar	88,625	11b-mar	11,20744
	11b-mar	71,5625	11c-mar	6,0996
	11c-mar	46,25625	12a-mar	4,49696
	12a-mar	85,3125	12b-mar	6,85584
	12b-mar	116,75	12c-mar	6,5688
	12c-mar	192,625	13a-mar	6,5228
	13a-mar	93,0625	13b-mar	3,69656
	13b-mar	123,3125	13c-mar	7,20176
	13c-mar	248,5	14a-mar	18,2252
	14a-mar	214,375	14b-mar	5,90824
	14b-mar	75,8125	14c-mar	6,88344
	14c-mar	140		

Appendix 14

Table 17. Raw data HG-ICP-OES – May

	Sb-TOTAL		Sb 3+	
Line		Sb 217,582		Sb 217,582
		µg/L		µg/L
Sample	1a may	456,2075	1a may	0,5
	2a may	402,6765	2a may	24,7955
	2b may	263,771	2b may	25,654
	2c may	333,1995	2c may	25,3106
	5a may	26,3389	5a may	3,36798
	5b may	30,56	5b may	5,99148
	5c may	24,64855	5c may	2,92842
	6a may	10,09435	6a may	0,73161
	7a may	10,15165	7a may	0,4
	7b may	11,0175	7b may	0,69482
	7c may	13,25025	7 cmay	0,71344
	8a may	9,362925	8a may	0,4
	8b may	7,011225	8b may	0,4
	8c may	8,635785	8c may	0,4
	11a may	67,4149	11a may	12,7106
	11b may	53,47065	11b may	9,9372
	11c may	38,7351	11c may	4,8853
	12a may	61,8372	12a may	3,90432
	12b may	95,8438	12b may	7,17556
	12c may	179,0075	12c may	10,2508
	13a may	76,5438	13a may	5,84962
	13b may	112,992	13b may	4,19067
	13 c may	226,944	13c may	9,9297
	14a may	204,288	14a may	20,2653
	14 b may	62,544	14b may	0,4
	14c may	121,632	14c may	4,51341

Appendix 15

Table 18. Raw data HG-ICP-OES – July

	Sb-TOTAL		Sb 3+	
Line		Sb 217,582		Sb 217,582
		µg/L		µg/L
Sample	1 a july	378,432	1a july	0,4
	1b july	364,128	1b july	0,4
	2a july	287,424	2a july	19,008
	2b july	218,784	2b july	23,4828
	2c july	229,152	2c july	25,344
	5a july	16,3584	5a july	1,44342
	5b july	16,4448	5b july	1,42362
	5c july	17,328	5c july	1,62558
	6a july	11,7024	6a july	1,50975
	7a july	9,8496	7a july	0,82863
	7b july	13,4016	7b july	1,11771
	7c july	18,0192	7c july	4,5619
	8a july	10,08	8a july	0,73598
	8b july	9,58656	8b july	0,4214
	8c july	9,03936	8c july	0,44002
	9a july	9,35616	9a july	0,46648
	9c july	23,2896	9c july	2,22068
	11a july	75,6576	11a july	18,4044
	11 b july	64,8384	11b july	15,0822
	11 c july	42,1344	11c july	4,39138
	12 a july	50,5056	12a july	2,4451
	12 b july	75,8016	12b july	7,1246
	12 c july	108,096	12c july	8,99444
	13 a july	37,632	13a july	3,19186
	13 b july	77,904	13b july	2,45196
	13 c july	162,816	13c july	15,8956
	14 a july	126,816	14a july	18,1692
	14 b july	47,0815	14b july	4,62168
	14 c july	60,6807	14 c july	8,78238

Appendix 16

Table 19. Raw data HG-ICP-OES – August

	Sb-TOTAL		Sb 3+	
Line		Sb 217,582		Sb 217,582
		µg/L		µg/L
Sample	1a aug	532,89	1a aug	0,55872
	1b aug	443,693	1b aug	3,56281
	2a aug	328,2335	2a aug	22,7465
	2b aug	262,052	2b aug	32,7957
	2c aug	242,57	2c aug	32,9218
	5a aug	20,04545	5a aug	1,65579
	5b aug	18,23095	5b aug	1,52775
	5c aug	19,77805	6a aug	1,62475
	6a aug	15,38505	7a aug	0,71004
	7a aug	11,75605	7b aug	1,65967
	7b aug	15,70975	7c aug	3,8367
	7c aug	18,67025	8a aug	0,99078
	8a aug	12,5296	8b aug	0,63798
	8b aug	11,5364	8c aug	0,57918
	8c aug	10,76285	9a aug	0,4
	9a aug	21,8504	9b aug	54,2528
	9b aug	136,2785	11a aug	19,306
	11a aug	90,21885	11b aug	18,2182
	11 b aug	83,83945	12 a aug	4,11012
	12 a aug	55,91525	12b aug	18,1986
	12 b aug	103,9995	12c aug	14,21
	12 c aug	92,8069	13a aug	4,41196
	13 a aug	35,4305	13b aug	3,95802
	13 b aug	60,4133	13 c aug	27,027
	13 c aug	140,0985	14a aug	26,9379
	14 a aug	134,4245	14b aug	5,3658
	14 b aug	44,14875	14 c aug	9,57132
	14 c aug	69,2098		