



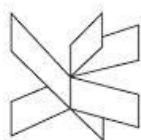
Analysis of lead contaminated soil and remediation proposal in a shooting range



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ABSTRACT

Construction Industry faces the challenge of contaminated soil. Viborg shooting range is lead contaminated as a consequence of the using of lead ammunition.

Lead soil contamination is characterized by means of the preliminary study and the analyses of the level of pollution, the 3-D distribution, as well as the distribution of the contamination depending on the soil grain size.

Lead removal test is developed in order to study the feasibility of soil washing techniques, using physic separation combined with chemical extraction testing two different chelant agents such as EDTA and GLDA.

Lead removal proposal is based on the results of the test and the analysis of the literature. The goal of the remediation proposal is to find an eco-friendly and cost-effective solution, that being technically possible ensures that the cleaned soil can be returned to the site.

ACKNOWLEDGEMENTS

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Finally, I would like to thank deeply my Master colleagues their support and the good atmosphere created during the course. It does not end here friends.

ACRONYMS

APC	Amino Polycarboxylate Chelant
AAS	Atomic Absorption Spectrometer
CE	Chemical Extraction
CO	Cleaning Objective
CoC	Contaminant of Concern
DMS	Dense Media Separation
DU	Decision Unit
DW	Deionized Water
EDDS	Ethylenediamine-N
EDTA	Ethylenediaminetetraacetic acid
EK	Electro Kinetic
GLDA	Glutamic acid-N
GSR	Green And Sustainable Remediation
HIMS	High Intensity Magnetic Separation
ISM	Incremental Sample Methodology
LIMS	Low Intensity Magnetic Separation
RDA	Royal Danish Army
RSD	Relative Standard Deviation
SS	Standard Solution
TCLP	Toxicity Characteristics Leaching Procedure
XRF	X-Ray Fluorescence

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1. INTRODUCTION

1. BACKGROUND

Nowadays cities continue growing. In the past, the surrounding land of the cities was mostly occupied by factories. Decades before environmental laws were more lax with waste from factories, thus most of these sites are contaminated. Soil contamination is a widespread problem in Europe. Therefore, the construction industry faces the challenge of decontaminating soils.

Since 1972 European countries are concerned about with the "European Charter Soil" sensitive to soil contamination, which until then was considered an infinite load capacity. Therefore, restoration techniques of contaminated soils are considered modern and continue evolving to become more effective and eco-friendly.

This dissertation is focused in the analysis of the lead contamination and the evaluation of possible solutions in a military shooting range in Viborg, Denmark.

The contamination is caused by lead ammunition. Lead pollution is very dangerous because of its effects on living organisms, its accumulation in the food chain and the contamination of the water suppliers. Therefore, it is important the analysis of the contamination compared with the reference levels.

Lead removal from the soil is a technology under develop. This dissertation proposes a remediation procedure applied on a real place tacking into account the characteristics and the location of the shooting range because it has finished firing activities.

2. DISSERTATION AIMS AND OBJECTIVES

This dissertation consists in the analysis of the lead contaminated soil and the proposal of an accurate remediation methodology using a real place.

The objectives of this dissertation are the evaluation of the lead contamination compared with the reference levels and the proposal of the best removal method according to the cleaning objectives. The analysis of the removal methods considers the technique, economic and environmental impact. Some of the remediation techniques will be assessed with decontamination tests in order to verify their efficiency.

Finally, this dissertation aims to contribute to the protection of the environment through the study and improvement of the cleaning methods selection.

3. RESEARCH METHODOLOGY

This dissertation is divided in two phases. Firstly, there is a diagnostic of the lead contamination and secondly, the proposal of an accurate remediation technique. Each phase is divided in different activities.

The following flow-chart shows the methodology followed during this final dissertation.

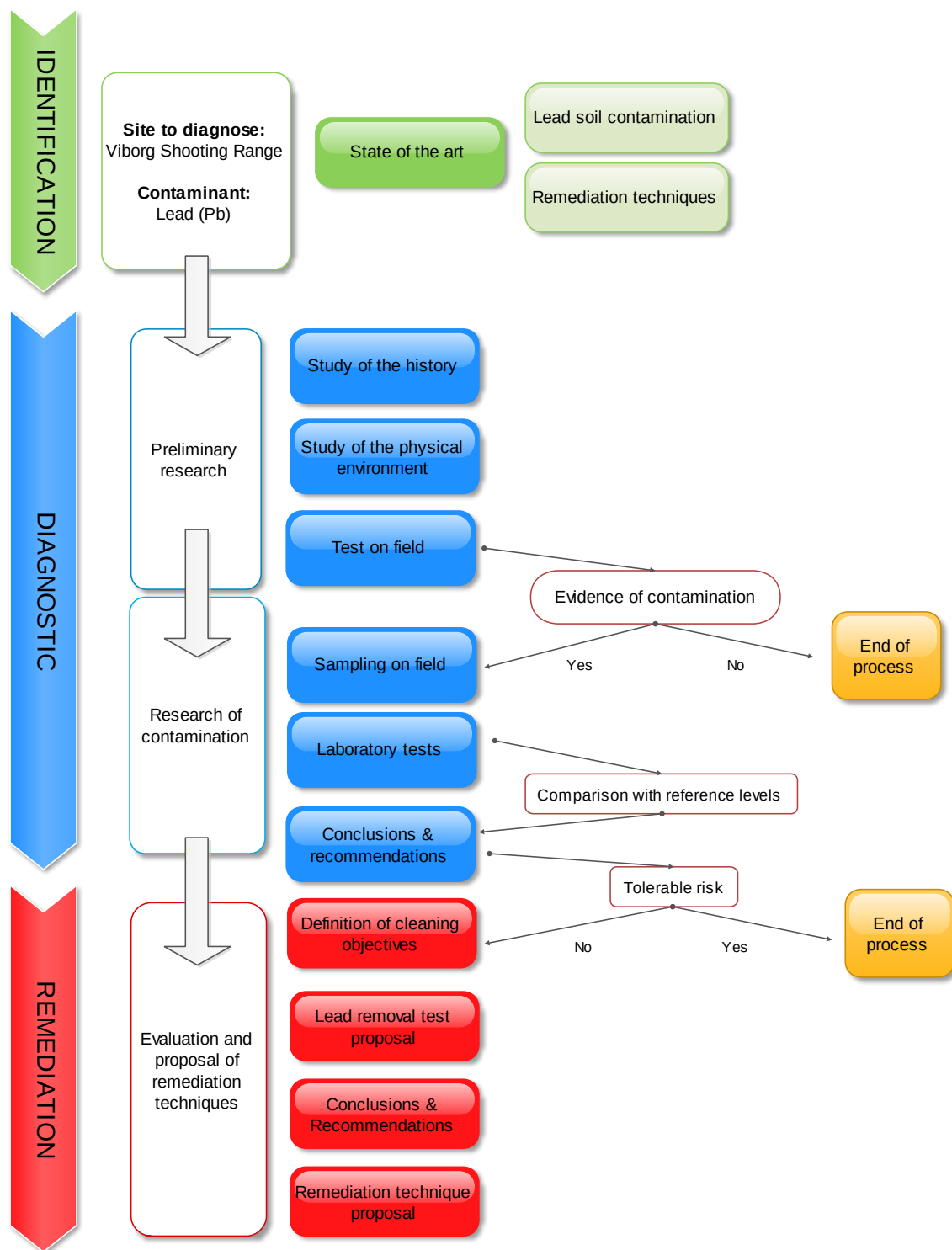


Figure 1- Methodology

3.1. DIAGNOSTIC OF LEAD CONTAMINATION

This phase is divided in two: Preliminary study and research of the contamination.

The preliminary study consists in the research of the history and physic environment and the results of test done on field.

The research of the contamination consists in the description of the sampling on field, done following the Incremental Sample Methodology, laboratory test and measurements, the comparison with reference levels in order to evaluate the results of the laboratory data and, finally, the conclusions and recommendations.

3.2. LEAD REMOVAL TEST AND REMEDIATION PROPOSAL

The second phase is a proposal of the remediation methodology testing some of the currently techniques of remediation.

The remediation proposal has an objective being an eco-friendly solution, economic choice and technically accurate option.

The remediation proposal is based on the lead removal test. The lead removal test is done in order to demonstrate the efficiency of new remediation techniques on a real case.

The remediation proposal finally suggests a remediation technology. This proposal is based on a comparison of different methodologies from the technical, economic and environmental point of view. It is not only a theoretical analysis. Remediation techniques are tested in order to demonstrate their efficiency. The remediation technology selection has the following activities:

- Definition of cleaning objectives
- Lead removal tests
- Effectiveness comparison
- Conclusions and recommendations
- Proposal of technical remediation

4. LIMITATIONS & SCOPE

This dissertation is focused in a real shooting range located in Viborg, Denmark. The analyses and the proposal are focused in lead although there are more pollutants present in the soil.

This academic work is included in the European Master in Construction Engineering requirements. Therefore, as an academic work there are some limits.

4.1. ACADEMIC LIMITATIONS

The main limitation has been the time schedule. 4 months are not enough time to develop as deep as is needed the topic.

The number of words has limited the document. The information managed has been summarized and not detailed as the author would like.

Topic development has required many chemistry concepts which are specific to environmental engineering, not civil engineering. This point has not been a limitation, it has been a challenging personal development.

4.2. ECONOMIC LIMITATIONS

VIA University Collage granted 9.000 dkk to develop the lead removal test. The budget spent in materials has been 4.000 dkk including the EDTA chelant agent, lead kits for the spectrometer and lead nitrate. 5.000 dkk were not enough money to perform the lead content analysis in the column test fluid because there are 180 samples and each cost 1.000 dkk. It means that the test has to be done for free and find a free lab according to the time schedule has been hard. Finally, a lamp for the AAS has been purchased using the remaining money for CPH Business school laboratory in order to use it. GLDA has been acquired free because Akzo Novel is interested in the results obtained in this final dissertation.

4.3. TECHNICAL LIMITATIONS

The availability of the measuring equipment has been the main technical limitation. VIA University collage has not equipment to measure the lead in soil or lead in a chelant solution. The X-Ray Fluorescence equipment has depended on NIRAS in the case of lead content in the soil. The equipment used to measure the lead in a chelant solution, Atomic Absorption Spectrometer, has depended on CPH Business School. The lack of electricity during weeks in VIA Geolab has been a limitation. Without electricity there were no access to the Geolab and as a consequence the tests were delayed.

5. REPORT OUTLINE

This final dissertation is presented in order to fulfil the requirements of the European Master in Construction Engineering. This work represents 20 credits ECTS. The work was developed in VIA University Collage in Horsens, Denmark.

This dissertation consists in an evaluation of the lead contamination in shooting range in Viborg and a proposal of the cleaning method.

The first chapter included is a literature review (State of the art), written in order to understand the lead contamination, the sampling methodology and the currently methods of cleaning including the efficiency experiments.

Furthermore, the goal of this dissertation is to find an environmental friendly and effective remediation technique applied in a real case. As a consequence, some remediation procedures are tested in the lab.

Finally this dissertation proposes a remediation procedure applied to Viborg shooting range based on the literature and the lead removal test developed.

This report is divided in different and independent documents. Each of them can be read separately and together as part of a complete document. The documents are:

- State of the art
- Preliminary study
- Research of the contamination is divided in two documents:
 - o Sampling on field report that includes all the activities done in situ like the test on field and the sampling.
 - o Lead contamination laboratory report that includes the results of the contamination tests, the analysis of the information and finally, the conclusions and recommendations
- Lead removal test
- Conclusions, which includes the proposal of the remediation.

2. STATE OF THE ART

1. INTRODUCTION

Contaminated soil is a recent concept and develop countries have a recent sensibility to them. Therefore remediation techniques of contaminated soils are considered modern and continue evolving to become more effective and eco-friendly.

This dissertation will be focused in the analysis of the lead contamination and the search of possible solutions in a shooting range in Viborg, Denmark.

This document aims be a clear idea of the current state in the field of lead contaminated soils in shooting ranges. This paper is a summary of technical concepts and legal terms of lead-contaminated, current state of research and the techniques used for soil remediation.

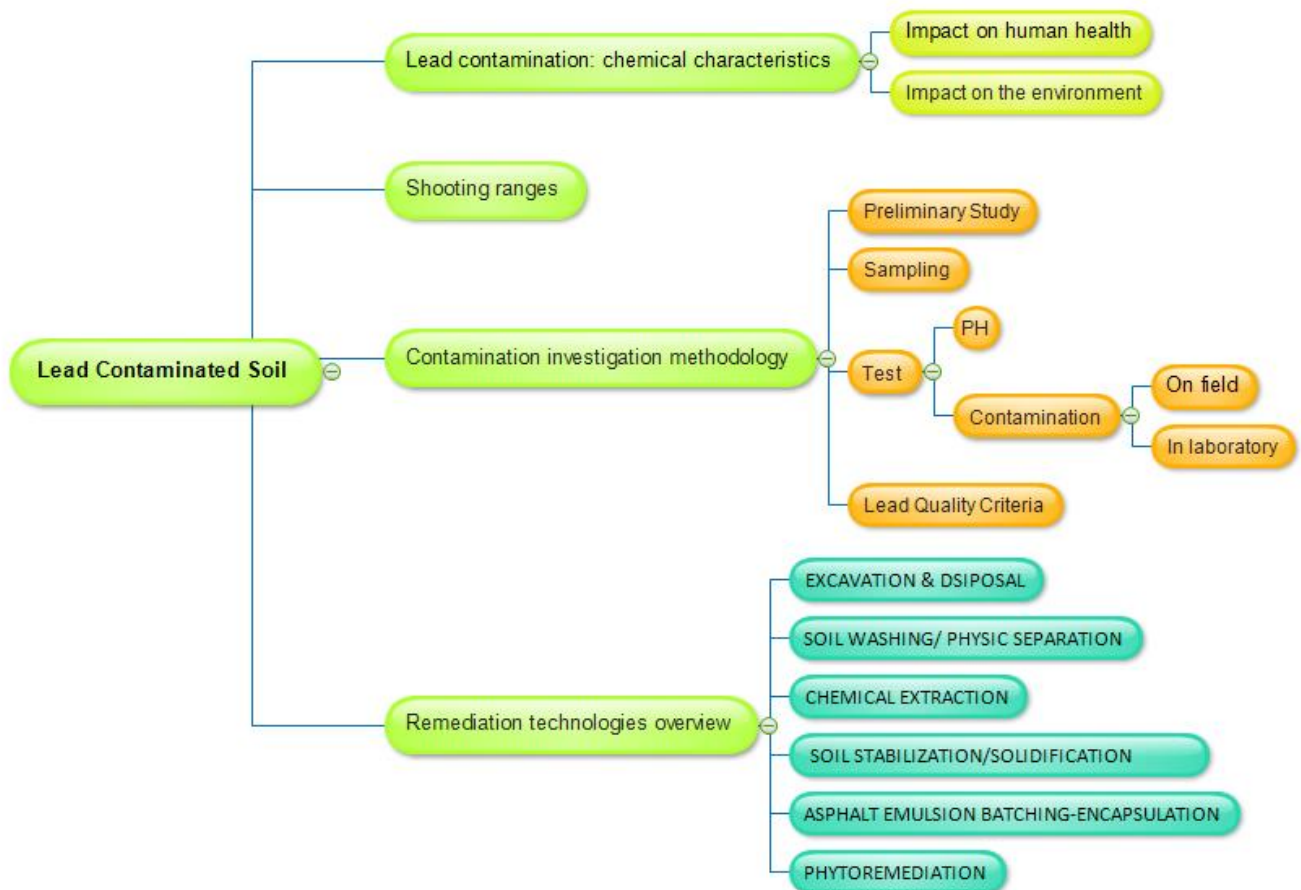


Figure 2- State of the art map

2. LEAD SOIL CONTAMINATION

Soil is a general word to describe the material on the surface of the underlying geological materials. Soil contamination is caused when the soil has an elevated concentration of chemical caused by human activities, (Vegter et al., 2002).

Soil is considered contaminated when the concentration is over, the Quality Soil Criteria. This standard depends on different legislation of the countries. European and Danish quality soil criteria are based on toxicity.

Shooting ranges are lead contaminated places because the composition of the ammunition. The distribution of lead and other metals contaminants is essentially caused by the firing activities at the range, (Sanderson et al., 2012).

Lead is a heavy metal known as Pb. Lead does not perform any biological function and is highly toxic. Lead origin is in the crustal, generally not as a pure element but as sulfides, silicates, carbonates, oxides and hydroxides structures.

1

H

hydrogen

(1.007, 1.008)

2

He

helium

4.003

3

Li

lithium

(6.941, 6.961)

4

Be

beryllium

9.012

11

Na

sodium

22.99

12

Mg

magnesium

(24.30, 24.31)

19

K

potassium

39.10

20

Ca

calcium

40.08

21

Sc

scandium

44.96

22

Ti

titanium

47.87

23

V

vanadium

50.94

24

Cr

chromium

52.00

25

Mn

manganese

54.94

26

Fe

iron

55.85

27

Co

cobalt

58.93

28

Ni

nickel

58.69

29

Cu

copper

63.55

30

Zn

zinc

(65.38, 65.40)

31

Ga

gallium

69.72

32

Ge

germanium

72.64

33

As

arsenic

74.92

34

Se

selenium

(78.96, 79.00)

35

Br

bromine

(79.90, 79.91)

36

Kr

krypton

83.80

37

Rb

rubidium

85.47

38

Sr

strontium

87.62

39

Y

yttrium

88.91

40

Zr

zirconium

91.22

41

Nb

niobium

92.91

42

Mo

molybdenum

95.94(2)

43

Tc

technetium

98.00

44

Ru

ruthenium

101.1

45

Rh

rhodium

102.9

46

Pd

palladium

106.4

47

Ag

silver

107.9

48

Cd

cadmium

112.4

49

In

indium

114.8

50

Sn

tin

118.7

51

Sb

antimony

121.8

52

Te

tellurium

127.6

53

I

iodine

126.9

54

Xe

xenon

131.3

55

Cs

caesium

132.9

56

Ba

barium

137.3

57-71

lanthanoids

72

Hf

hafnium

178.5

73

Ta

tantalum

180.9

74

W

tungsten

183.8

75

Re

rhenium

186.2

76

Os

osmium

190.2

77

Ir

iridium

192.2

78

Pt

platinum

195.1

79

Au

gold

197.0

80

Hg

mercury

200.6

81

Tl

thallium

(204.3, 204.4)

82

Pb

lead

207.2

83

Bi

bismuth

209.0

84

Po

polonium

85

At

astatine

86

Rn

radon

87

Fr

francium

88

Ra

radium

89-103

actinoids

104

Rf

rutherfordium

105

Db

duabium

106

Sg

seaborgium

107

Bh

bohrium

108

Hs

hassium

109

Mt

meitnerium

110

Ds

darmstadtium

111

Rg

roentgenium

112

Cn

copernicium

113

Nh

nihonium

114

Fl

flerovium

115

Nh

nihonium

116

Lv

livermorium

57

La

lanthanum

138.9

58

Ce

cerium

140.1

59

Pr

praseodymium

140.9

60

Nd

neodymium

144.2

61

Pm

promethium

62

Sm

samarium

150.4

63

Eu

euporium

152.0

64

Gd

gadolinium

157.3

65

Tb

terbium

158.9

66

Dy

dysprosium

162.5

67

Ho

holmium

164.9

68

Er

erbium

167.3

69

Tm

thulium

168.9

70

Yb

ytterbium

173.1

71

Lu

lutetium

175.0

89

Ac

actinium

90

Th

thorium

232.0

91

Pa

protactinium

231.0

92

U

uranium

238.0

93

Np

neptunium

94

Pu

plutonium

95

Am

americium

96

Cm

curium

97

Bk

berkelium

98

Cf

californium

99

Es

einsteinium

100

Fm

fermium

101

Md

mendelevium

102

No

nobelium

103

Lr

lawrencium

Figure 3- Lead position in the Periodic table of the elements, (International Union of Pure and Applied Chemistry, 2013)

Table 1-Lead general chemical properties

GENERAL PROPERTIES	Name	Pb, plumbum
	Atomic Number	82
	Standard Atomic Weight	207.2
	Element Category	Post-transition metal
	Group, period, block	Group 14 (carbon group), Period 6, P-Block
	Atomic Radius	154 pm
	Covalent Radius	147 pm

Lead contamination is caused by intact bullets and bullet fragments. Lead is in contact with air and water and as a metal is corrode, (Hudson et al., 1999). Lead in the soil is easily decomposed from metallic form to mineral lead. The decomposition depends on the combination of different environmental aspects like soil PH, organic matter content, soil leaching rate and ligands. The decomposition process transforms 4-8% of bullets in low organic matter soil and 15-6% in high organic matter soil in the 20-25 years, (Lin et al., 1994).

Lead bullets in shooting ranges experience a process of chemical transformation. The surface of the bullets is weathered and below transformation in the soil. The process is divided in two-steps. Firstly the oxidation of metallic lead process achieved by hydration and finally, there is the carbonation mechanism because of water and carbon dioxide. If lead bullets are air exposed, Lead oxide forms easily on their surfaces, and then carbon dioxide and water allow the transformation of lead carbonates from PbO. Lead carbonate or lead oxide can keep on the skin of the bullets or can flow into the soil by way of natural process like rain and wind, (Cao et al., 2003).

Lead in the soil is fairly immobile in the profile, (Lin et al., 1994). On the one hand, controlled by the mineral soil characteristics like the saturation level with metal absorption sites, soil structure and the microbial activity, the vertical flux of lead to groundwater should be higher than predicted from the measured solubility and mobility rates in surface soil. On the other hand, it is improbable that lead will come in the groundwater in the form of a large pulse, except if the total lead is stored firstly in deeper soil layers for example as an effect of incomplete mechanical removal operation of lead shots, earlier being immediately spread into groundwater, or the lead adsorption capacity of soil is changed abruptly for example by a decrease of soil PH. Therefore, even a large pulse of lead would delay when passing through surface and mineral soils, and the final product to ground water would develop into a gradual flux at very low levels of lead, (Turpeinen et al., 2000).

The relationship between the pH of the soil and the solubility of the contaminants has been deeply studied in order to reduce lead mobility in the soil, (Cappuyns & Swennen, 2008)(González-Núñez et al., 2012). Lead bioavailability is controlled by physical, chemical and biological process and their interaction, (Ernst, 1996).

2.1. LEAD CONTAMINATION IMPACT ON HUMAN HEALTH

Lead is a heavy metal considered as a cumulative toxicant because its effects on human health (neurological, haematological, gastrointestinal, cardiovascular and renal systems), according to the World Health Organization. Children and pregnant woman are particularly sensible to the neurotoxic effect of Lead, (World Health Organization, 2010).

According to the World Health Organization, the exposure to lead produces mild mental retardation and cardiovascular disease. Lead in human anatomy is spread to the brain, liver, kidney and bones. It is stored in the teeth and bones, where it accumulates over time, (World Health Organization, 2010).

The International Agency for Research on Cancer (IARC) in 1987 considered lead and inorganic lead compounds causes cancer to humans. A lot of epidemic studies have been published since that time proving this relationship, (World Health Organization International Agency for Research on Cancer, 2006)(World Health Organization, 2010). The most types of cancer caused by lead are lung cancer, stomach cancer and gliomas, (Steenland & Boffetta, 2000).

There is a direct relation between lead levels in blood and lead present in soil and dust. The exposure is direct because the soil is breathed in as a dust, (Hardison et al., 2004).

2.2. LEAD CONTAMINATION IMPACT ON THE ENVIRONMENT

Lead contamination produces effects on the environment, affects both animals and plants. Lewis et al. demonstrated that wild-life is lead poisoned in a shooting range. Lead contamination affects wild birds and mammals. Birds are much more affected than mammals, (Lewis et al., 2001).

Animals that live near the firing range have high levels of lead in their tissues. Although the study is not made clear exactly how exposure to lead, but based on the large number of fragments and lead bullets that are on the ground, animals would eat them by mistake thinking they are berries, (Lewis et al., 2001).

Another way, in which animals may absorb lead, is when they eat plants. These plants are able to absorb lead from soil, increasing the amount of lead inside. Studies leads to the hypothesis that high levels in plants depend on the absorptive capacity of the plant regardless of the species. Besides to plants, elevated lead levels were found in tadpoles and earthworms. The two organisms are a potential route for the lead to move up to higher in the food chain, these being the connection between the soil lead content and the secondary consumers in the trophic chain, (Labare et al., 2004).

Plants absorb lead during the growing up. This is the principle on which phytoremediation is based on.

3. SHOOTING RANGES

Shooting range is a facility specialized for firearms practice. Shooting ranges have a configuration with a firing line, a range floor, a target line, an impact berm, lateral berms and an over flight area.

The classification of the shooting ranges is based on the distance between the target line and the firing line. Basic small-arms ranges have between 15 and 90 meters of distance and long-range rifle up to 600 meter, (USA Army, 1997), (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

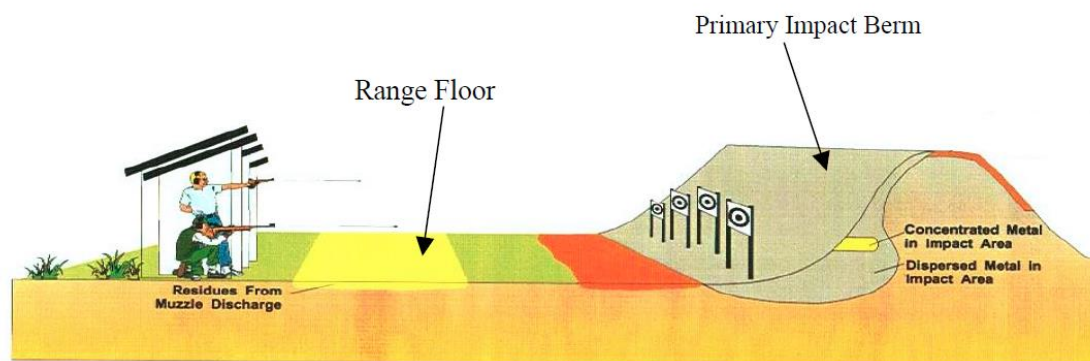


Figure 4- Cross section of a Typical Static Rifle and Handgun Range, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003)

The classification is different when the life of the shooting range is over. Finishing process of shooting ranges classifies them depending on the risk assessment. This risk assessment considers the type of land use, location or distance to residential areas, and generic properties of the site like accessibility, (Sorvari et al., 2006).

Shooting ranges have been studied, and the results conclude that soil lead pollution in the surface are significantly high, being over the average background lead concentration by 10–10 000 times. The top lead concentration (up to 4.84%) is located in the impact berm, that has the maximum collection of

bullets, (Cao et al., 2003). The bullet suffer abrasion because the contact with soil particles in the impact berm, (Hardison et al., 2004).

In a shooting range, the distribution of lead and the related pollutants is related to the firing activities. Movement in the soil profile is associated to the amount of bullets, soil properties like pH and climatic conditions (temperature and rainfall). Lead weathering is favourable with high temperature and rainfall, as the same time that low moisture limits the generation of potentially soluble corrosion products. Organic matter is an important factor that influences bullets transformation in the soil, (Sanderson et al., 2012).

3.1. DANISH SHOOTING RANGES

The first shooting ranges have been built and used within the Royal Danish Army. The first civil rifle club, the current “De Danske Skytteforeninger” was founded in 1861, (Amternes Videncenter for Jordforurening, 2004).

The Danish shooting ranges classification has the following categories according to the type of weapon and the field length: Pistol shooting range, Salon rifle shooting range, Short range trajectory and long distance path.

The following figure shows the Danish shooting range configuration.

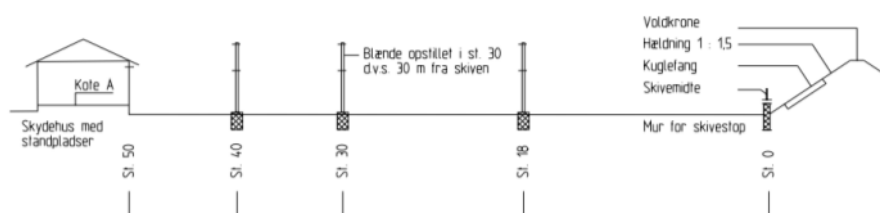


Figure 5-Danish shooting range profile, (Amternes Videncenter for Jordforurening, 2004)

Denmark has around 1900 outdoor shooting ranges, as the following picture shows, (Amternes Videncenter for Jordforurening, 2004).

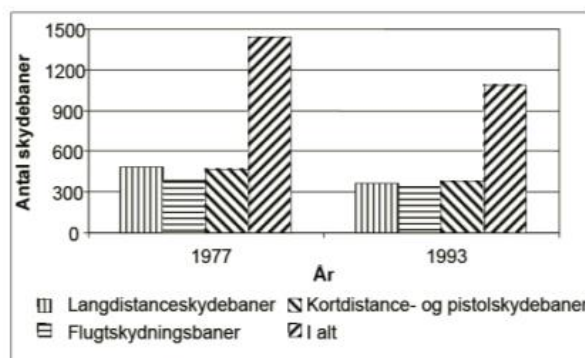


Figure 6-Number of shooting ranges in Denmark, (Amternes Videncenter for Jordforurening, 2004)

4. LEAD CONTAMINATED SOIL INVESTIGATION METHODOLOGY

Shooting ranges are characterized analysing factors like, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003):

- The Contaminants of Concern (CoCs) adding to lead at the range.
- The horizontal and vertical profile of the lead pollution and other contaminants in the range.
- The concentration levels of these pollutants over the contaminated zone.
- Environment that are affected like soil, groundwater, surface water, air, sediment.
- If the polluted zones are bounded to positions where bullets were deposited or if there has been movement of the concerning pollutants.
- If movement has occurred, the presumable migration trajectory.
- Potential and present environmental or human exposure pathways.

The answer at these questions needs a step-by-step procedure. Firstly, a preliminary study is needed. It has to include the history of the range, location and all the collected information available. Secondly it is necessary to study the contamination. This phase consist in the sampling and testing in the laboratory. Finally, the results should be compared with the quality soil criteria.

4.1. PRELIMINARY STUDY

This is the first step in the lead contaminated soil investigation. This step includes the collection of information including the history of the shooting range. There are some important information like the period of time of use, type of ammunition and the manage history of the range. The amount of bullets can be calculated by the number of targets used per year. The removal, relocations, additions or extractions of soil is also important information, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

4.2. SAMPLING METHODOLOGY

According to Danish legislation, it is appropriate to take samples at smaller intervals. Heavy metal soil contamination is strongly embedded in the soil so samples should be taken at smaller intervals around the level that is expected to be contaminated, (Danish Enviromental Protection Agency, 2002).

Currently, there are different Soil sampling methodologies. In the case of soil polluted with heavy metals, the most accurate sampling methodology is the Incremental Sampling Methodology (ISM). "ISM is a structured composite sampling and processing protocol that reduces data variability and provides a reasonably unbiased estimate of mean contaminant concentrations in a volume of soil targeted for sampling. ISM provides representative samples of specific soil volumes defined as decision units (DU) by collecting numerous increments of soil (typically 30–100 increments) that are combined, processed, and subsampled according to specific protocols", (ITRC, 2012).

4.3. TEST

The goal of soil test is to characterize and report lead contamination in the soil. Test can be carried out on field or in the laboratory.

- CONTAMINATION

On the one hand, the tests must identify potential pollutants, quantify the pollution, have a detection limit that corresponds to acceptance criteria (the detection limit must not be no higher than 1/10 of the

acceptance criteria) and have an tolerable exactitude (usually a 10-20 % of standard deviation), (Danish Enviromental Protection Agency, 2002).

According to Danish legislation, the method to measure the contamination is the X-ray fluorescent. X-ray fluorescent values are either obtained using directly on the soil portable field equipment, or in the laboratory, after the samples of soil have been collected. This method is accurate because it is metal specific, (Danish Enviromental Protection Agency, 2002).

- SOIL PH:

On the other hand, as has been explained before there is a strong relationship between the pH of the soil and lead solubility. There are several methods to determine soil PH. Soil pH determination procedure in Denmark is the electrometric method that consist in the pH of a prepared suspension of soil. An example of this method is the test BS 1377-3:1990, (Dansk Standard, 2007).

5. LEAD CONTAMINATION QUALITY CRITERIA

According to the Survey of lead and lead compounds, (Boyd et al., 2014) in Denmark the concentration of lead in unpolluted areas is generally in range of 4-20 mg Pb/kg with an average of 11 mg Pb/kg soil. Besides in polluted urban areas, e.g. typical lead concentrations may be around 200 mg/kg with maximum values that exceed even 1650 mg Pb/kg, (Jensen et al., 1996), (Boyd et al., 2014).

Danish legislation defines different soil quality criteria: Quality criteria, Acceptance criteria and Cut-off criteria. Quality criteria is based in public health reasons, Acceptance criteria is based on a site specific risk assessment and depend on the use of the land and Cut-off criteria is used for immobile and slowly degradable substances, (Danish Enviromental Protection Agency, 2002).

Quality criteria for soil in areas with very sensitive land use are based on chronic harmful effects and are 40 mg/kg dry weight , (Danish Enviromental Protection Agency, 2002).

Criteria for necessary Lead contamination cut off are 400 mg/kg DW and is based on chronic harmful effects, (Danish Enviromental Protection Agency, 2002).

6. REMEDIATION TECHNOLOGY OVERVIEW

Currently many techniques are available in finishing shooting ranges but the most common is soil excavation combined with disposal. The Risk management options are limited in Nordic countries, (Sorvari et al., 2006).

According to the literature, the choice depends on site properties, costs, period of time allowed for remediation, availability of the land, and, use in the future of the land, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

The following chart shows the classification of the remediation techniques:

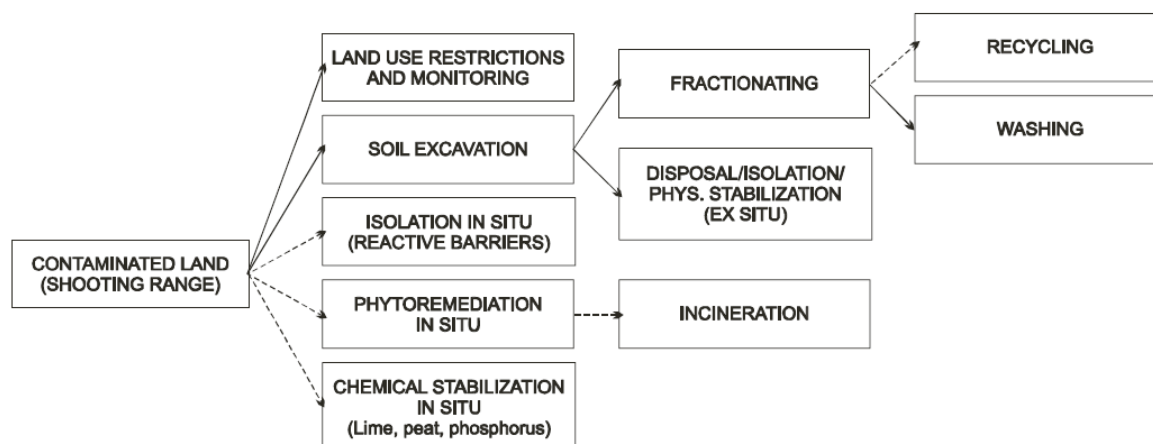


Figure 7- Existing and potential (dash line) risk management options for Finnish shooting ranges (potential methods=methods under study), (Sorvari et al., 2006).

The election of the most accurate remediation technique depends on many factors. The management options, once the shooting range is closed, depend on cost-efficiency balance.

Green and Sustainable Remediation (GSR) aims to remove contaminants from a contaminated system, and to minimize the environmental footprint of the remediation process at the same time, (USA EPA, 2008)

Recent research show the environmental approach of the remediation techniques, (Sorvari et al., 2006)(Kim et al., 2013).

6.1. EXCAVATION & DISPOSAL

As has been said before, this procedure is the most common. It is the most simple. Contaminated soil is excavated, loaded and transported to an accurate landfill. Soil is considerate hazardous waste during the managing process, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003). Contaminated soil can be disposal with and incineration and finally ash stabilization, (Sorvari et al., 2006).

Prices of 450-800 DKK per tonne (60-108 €/tonne) ,including the tax of waste, should be expected for disposing of soil polluted by heavy metals at landfill sites, depending on location and level of pollution. In Denmark, the soil which is heavily polluted by heavy metals can be deposited at landfills or sent to the municipality at a cost of approximately 1000 dkk/tonne (134.12 €/tonne), (Danish Enviromental Protection Agency, 2002).

Table 2- Advantages and disadvantages- Excavation and disposal, (Sorvari et al., 2006)

EXCAVATION & DISPOSAL

ADVANTAGES

Technically simple method

Short term solution

Common used

DISADVANTAGES

Lead removed permanently from range

The soil needs hazardous waste management

Environmental impact: loss of habitat and biota, emissions...

Expensive solution

6.2. SOIL WASHING/ PHYSICAL SEPARATION

Soil washing procedure is an extraction technique of soil contaminants by water application. Sometimes the water contains an additive (surfactants (detergents) and solvent (alcohol)) to promote the solubility of the contaminant.

Soil washing process applies mineral processing technologies and recovering contaminants procedures. The process is dust-free, and in the shooting ranges, the recovered metal is considered scrap metal that can be recycled, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Soil washing can be applied in situ, soil flushing or ex situ, soil washing. Effectiveness is highly dependent on the type of soil.

In situ soil flushing consists in the application of washing solution to the unexcavated polluted area by sprinkling or flooding in order to extract contaminants from the soil, (Abumaizar & Smith, 1999).

Ex situ soil washing technique has four phases: soil excavation, physical separation, chemical extraction and waste water treatment, (Kim et al., 2013). Physical separation phase and chemical extraction phase can be developed individually or a combination of both, (Dermont et al., 2008).

The following diagram shows the different combinations proposed by the authors, (Dermont et al., 2008):

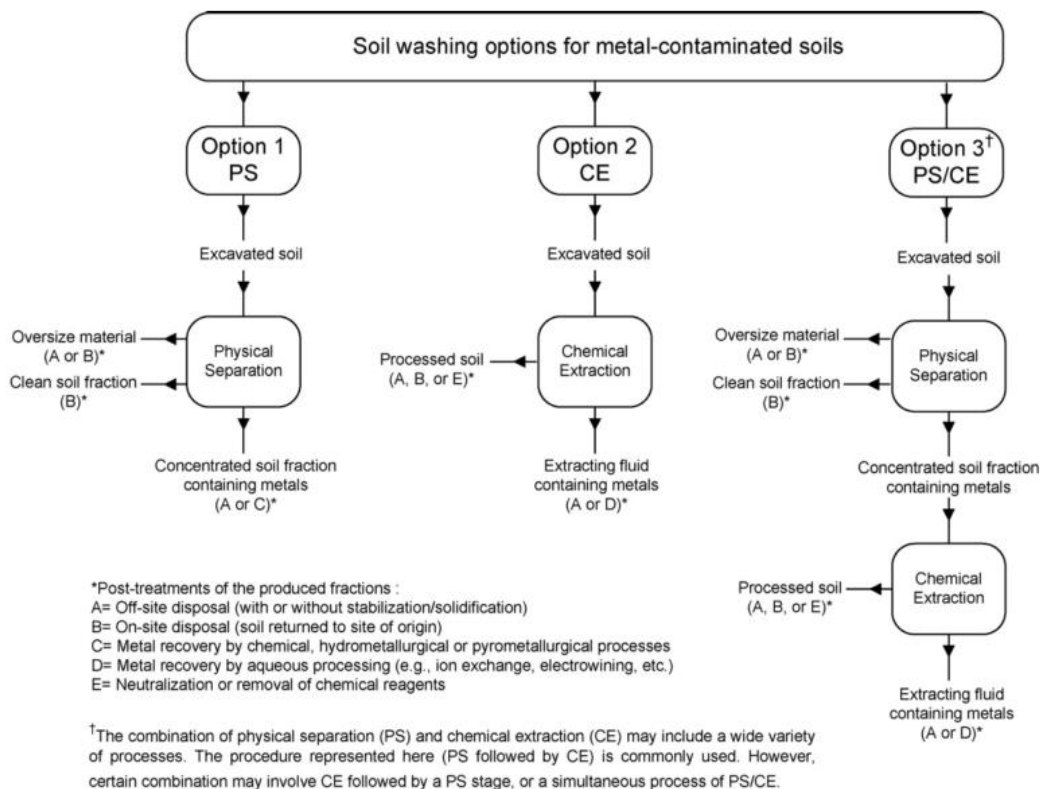


Figure 8- Schematic diagram of typical options used washing processes, (Dermont et al., 2008)

Physical separation can be done by different procedures: mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, electrostatic separation and attrition scrubbing. Chemical extraction will be developed separately.

The following table is an abstract of physical separation types, (Dermont et al., 2008):

Table 3-Physical separation types, (Dermont et al., 2008)

Operation Unit	Basic principle	Description	Comments	Typical technologies implemented
Mechanical Screening	Particle size	Mechanical screening uses size exclusion through a physical barrier to provide suitable dimensions for treatment	Widely used. Fine screens are fragile	- Vibrating grizzly - Barrel trammel - Vibrating or gyratory screens
Hydrodynamic Classification	Settling velocity	Separation of the particles by difference of settling velocity or by centrifugal force into a water flow. Often used for size separation	Widely used. Difficult when clay and humid soils are present	- Hydrocyclones, elutriators - Mechanical classifiers (screw classifier)
Gravity Concentration	Density of particles	Separation of high density from low density minerals or particles in a slurry of water and soil (relatively high solid content)	Widely used. Difficult when clay and humid soils are present	- Spiral concentrator - Shaking table - Jig - MGS-Mozley - Dense Media Separation (DMS)
Froth Flotation	Hydrophobic properties of the surface of particles	The differences in hydrophobic properties of particle surfaces are exploited to separate certain minerals from soil by attachment to air bubbles injected in a pulp (low solid content)	Widely used. Chemical additives are required	- Flotation in cell - Flotation in column (agitation or nonagitation system)
Magnetic Separation	Magnetic properties of particles	Mineral particles are separated according to their different magnetic susceptibilities	Moderately used. High capital and operating costs.	- Dry - Wet separators using: - High intensity (HIMS) - Low intensity (LIMS)
Electrostatic Separation	Electrical conductivity properties of particles	Separation based on the difference in the surface electrical conductivity of the particles to be separated	Rarely used. Materials must be completely dry.	- Electrostatic separators - Electrodynamic separators
Attrition Scrubbing	Mechanical particle-to-particle scrubbing	Using of high energy agitation of soil slurry (high solid content) to remove coating of particle surface and to disperse soil aggregates	Widely used. Pre-treatment that improves separation process	Various types of scrubbers

The efficiency of physical separation has been researched by different authors. The following table is a summary of these laboratory studies.

Table 4- Physical separation literature, (Dermont et al., 2008)

Example of studies	Study objective	Technologies	Concentration (mg Pb/Kg)	Removal (%)	Reference
Magnetic separation (HIMS) on six soils in the Netherlands (results with soil L)	Use of magnetic separation as stand-alone remediation technique	High intensity magnetic separation (HIMS) with dry and wet separators (63–2000µm)	121	46	(Rikers et al., 1998)
Attrition scrubbing in conjunction with a shaking table on a soil from an Army small arms training range, USA Evaluation	Improvement of density separation (shaking table) by the use of attrition scrubbing Study	Wemco attrition scrubber, Wifley shaking table	40,000	96	(Marino et al., 1997)
Evaluation of physical separation technologies for remediation of six soil (polluted by landfilling of various wastes in Quebec City, QC, Canada (results with soil "A1", 90% of sand)	Study of various physical separation technologies for an integrated soil washing process	Wet magnetic separator (63–2000µm) Attrition scrubbing gravity concentration: shaking table (63–850µm) (850–2000µm)	4,893	61 jtb 67 shaking table	(Dermont et al., 2008)
Gravity separation to remediate two shooting range soils contaminated by Pb-containing shotgun pellets in Finland	Study of applicability of gravity separation to remove bullet fragments	Shaking table, heavy liquid separation (DMS)	24,000	88 DMS 91 DMS+ Shaking table	(Dermont et al., 2008)
Evaluation and analysis of soil washing for seven Pb-contaminated soils from Netherlands	Evaluation of gravity separators in an integrated soil washing process	Shaking table (74–840µm) jig (840–4760µm)	500–2,195	22-93 jig+ shaking table	(Benschoten, 1997)
Froth flotation as a remediation technique for heavily polluted sediment in Belgium	Evaluation of froth flotation as stand-alone remediation technique. The influence of the particle size distribution and metal speciation on the froth flotation efficiency	Denver laboratory cell (grain size: 70%<50µm)	721	60	(Cauwenberg et al., 1998b)(Cauwenberg et al., 1998a)
Froth flotation on a soil in Belgium	Improvement of froth flotation by sulfidisation pre-treatment	Sulfidisation with Na ₂ S, Denver laboratory cell(0-200µm)	142	30 without sulfi. 42 with sulfi.	(Vanthuyne & Maes, 2002)

The last step in the washing process is the treatment of the used water. This process is called dewatering. The extracted soil solutions should be treated with a treatment system to remove contaminants from water with additives for reuse and this represents a significant increase in costs.

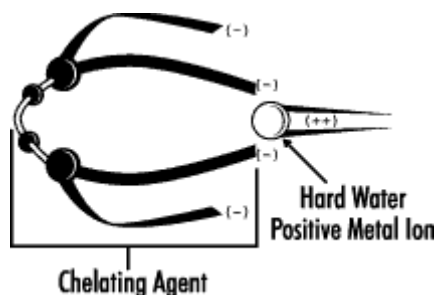
Table 5- Advantages and disadvantages-Soil Washing/physical separation, (Sorvari et al., 2006).**SOIL WASHING & PHYSICAL SEPARATION**

ADVANTAGES	Effective
	Can be done on site with portable equipment
	Cleaned soil can be returned on place
DISADVANTAGES	Hazardous waste-water management
	Ex situ method needs excavation
	Not suitable for peat soil and humus soil
	High Environmental footprint

6.3. CHEMICAL EXTRACTION

Chemical extraction technology is combined with washing technologies. It consists on adding an agent, generally a strong acid in the case of lead, into the water of the soil-washing process to facilitate the dissolution of residual metals into solution after particulate metal removal, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

The agent can be an acid, salt, chelating agent, surfactant and redox agent. The agent selection is based on the metal type, concentration of metal, metal fractionation/speciation, and soil properties, (Dermont et al., 2008). In lead contaminated soil the most common agent is the chelating. Chelating agents are usually flexible organic molecules that can incorporate metal ions into their molecular structure by ligands union. Chele comes from the Greek word to claw.

**Figure 9- Chelant agent effect over the metal ion, (Essential Industries, 2013)**

There are two basic tests in order to determine the effectiveness of washing product: Batch and column. Different chemical products in chemical extraction-washing process have been studied. The following table includes some literature classified by the testing method: Column or batch and the washing agent used, (Abumaizar & Smith, 1999).

Table 6- Soil Washing literature, (Abumaizar & Smith, 1999)(Dermont et al., 2008).

Soil	Washing method	Agents	Concentration (mg Pb/Kg)	Removal (%)	Reference
Artificially contaminated	Column	Na ₂ S ₂ O ₅	204	61	(Abumaizar & Khan, 1996)
Artificially contaminated	Column	HCl EDTA CaCl ₂	500-600	85 100 78	(Abumaizar & Smith, 1999)
Contaminated soil	Batch	EDTA, NTA and citric acid plus reducing reagents: sodium borohydride, Na ₂ S ₂ O ₅ and thiourea dioxide.	21560		
Artificially contaminated	Batch	HCl EDTA CH ₃ COOH CaCl ₂	10-1000	65-100 60-100	
Contaminated soil	Batch	S-carboxymethyl-cysteine (SCMC), N-2 acetamidomindiacetic acid (ADA), Pyridine-2, 6 dicarboxylic acid (PDA)	100	80-100	
Contaminated soil	Batch	EDTA	350	95	
Contaminated soil	Batch	HCl	1000	90	
Contaminated soil	Batch	EDTA	1509-51	85-97	
Artificially contaminated	Batch Column	DI water Na ₂ S ₂ O ₅ and Na ₂ EDTA Na ₂ S ₂ O ₅ and Na ₂ EDTA	742	10 56 100	
Clay Loam Sandy clay	Column	EDTA DTPA	1700	75 89 56-70	(Wasay et al., 2001)
Contaminated by smelting & battery	Batch	EDTA	65200	56	(Dermont et al., 2008)
Urban contaminated by industrial activity	Batch	EDTA	800	76	(Tejowulan & Hendershot, 1998)
Slags and metallurgical waste	Batch	EDTA	64195	44	(Dermont et al., 2008)
Mining and smelting activities	Batch	EDTA	32000	71	(Dermont et al., 2008)
Soil from battery recycling site	Batch	HCl+NaCl	67400	97	(Nedwed & Clifford, 2000)
Fine-grained fraction of industrial soil	Batch	HCl+NaCl	2,730	65	(Djedidi & Drogui, 2005)
Fine-grained soil contaminated by mining activities	Column	HCl+CaCl ₂	16,000	90-95	(Tampouris et al., 2001)
Soil contaminated by smelting and battery recycling operations	Batch	HCl	65,200	35	(Mark et al., 1998)
Soil contaminated with slags and metallurgical wastes	Batch	HCl	64,195	57	(Moutsatsou et al., 2006)

Batch agitation studies are developed in order to identify accurate ranges of concentration of the washing solution. However, soil column studies are performed to reproduce in situ clean-up conditions using a column of contaminated soil with the same objective. Column experiment results are typically better than results obtained in batch tests, (Abumaizar & Smith, 1999).

The agent used in washing techniques has to form stable metal complexes. There are significant considerations in the agent selection for chemical removal from soils, (Dermont et al., 2008):

- Agents have to be able to form highly stable complexes over a wide range of PH.
- The metal complexes formed have to be no absorbable on soil surfaces.
- The agent has to have a low biodegradability in case the reagents are to be recycled for reuse in the process.
- The used agent and metal recovery have to be cost effective.

Recent research shows that the combination of EDTA and acetic acid with electro kinetic (EK) technique can reach an efficiency of 84%. EK remediation is a technique for extraction of pollutants by introducing the electrodes into polluted soils and applying low DC voltage gradient to the electrodes. During EK process, the applied current causes water electrolysis at electrodes and produces a succession of electric effects (electromigration, electroosmosis, and electrophoresis), and in consequence, the contaminants are enriched beside the electrodes and extracted from the soil, (Zhang et al., 2014).

Latest research in Japan develops biodegradable chelant agents in batch tests. In state of using EDTA chelant agent, aminopolycarboxylate chelants (APCs) are used in artificial lead contaminated soil. Biodegradable Chelant Agents are Ethylenediamine-N (EDDS) or Glutamic-N (GLDA). The test had not been developed on real contaminated soil, (Begum et al., 2013). The main advantage of GLDA compared with EDTA is the lower environmental footprint, (Borén et al., 2009).

The environmental assessment of soil washing technique combined with chemical extraction has been studied recently. The results of this research are a calculation of the environmental footprint, including greenhouse gas (GHG) emissions, energy consumption, water consumption, and critical air contaminant productions. The results demonstrates soil washing technology is the most effective technique to remediate heavy metal-polluted soil although the process consumes basically chemicals and water to extract pollutants and has its own environmental risk. Especially, the acid-based chemical extraction process should be avoided in order to improve the sustainability of soil washing processes, (Kim et al., 2013).

Soil washing is a technology under study in Denmark. Soil washing of full-scale experience in Denmark started in 2000 with the support of the Environmental Protection Agency Technologic Group. The washing plant was located in Germany and 6 different contaminated soils were cleaned and tested using washing techniques by physical separation and chemical extraction. Unfortunately, the German company experimented bankruptcy during the project development and the results are incomplete the few obtained were successful in removing pollutants. Soil washing is a promising technology under develop in Denmark, (Lindskov et al., 2000).

Soil washing process requires at least two different tanks. The first one is called Leaching tank and the second one, the precipitation tank. After the two tanks a clarifier process is needed. The dewatering process finishes with the process of solids, (USA Army, 1997). The following figure shows the flow chart used in real commercial cases, (Zech Umwelt GmbH, n.d.).

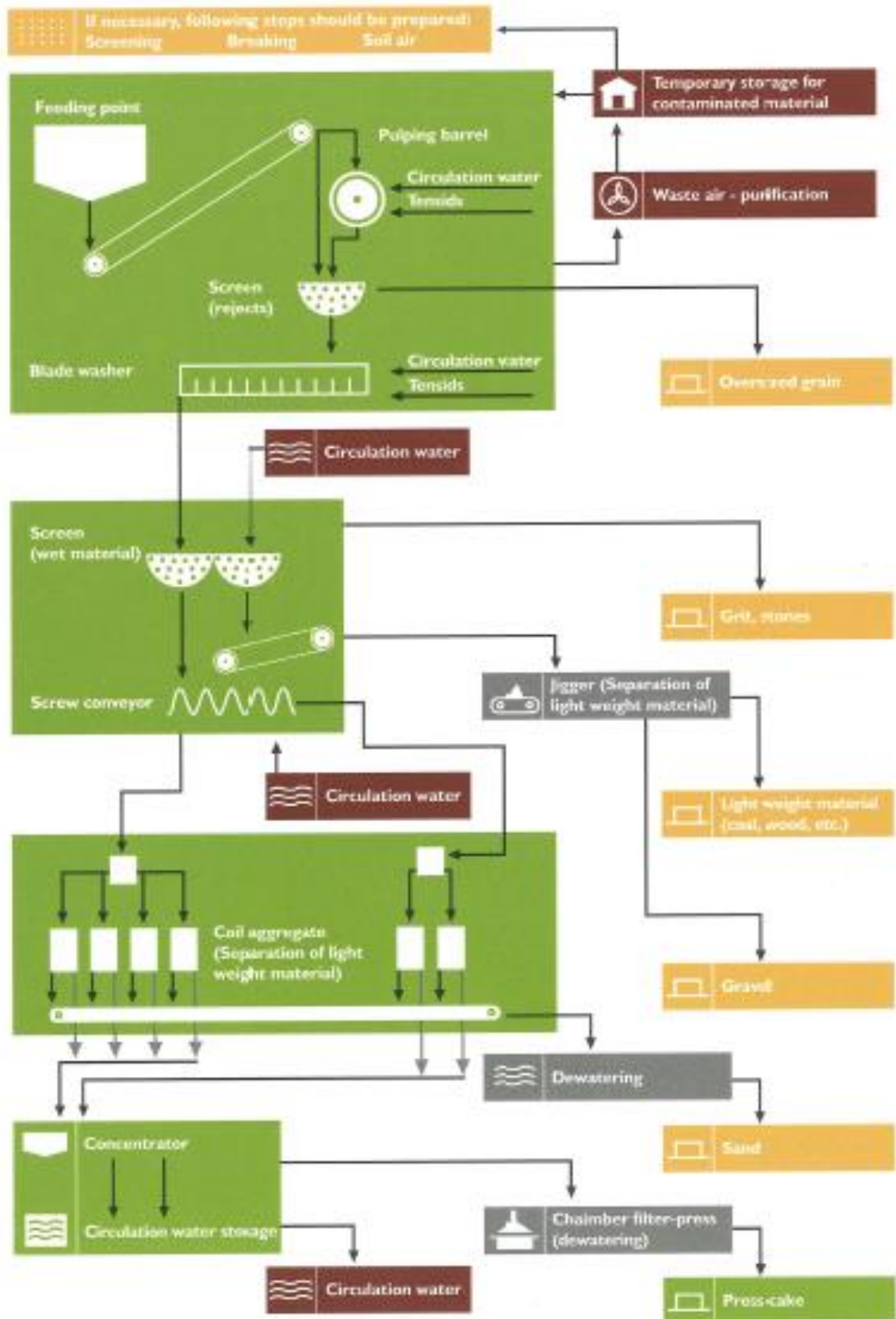


Figure 10- Flow Chart Soil Washing, (Zech Umwelt GmbH, n.d.)

Table 7- Advantages and disadvantages- Chemical extraction, (Sorvari et al., 2006).**CHEMICAL EXTRACTION****ADVANTAGES**

Low costs
Possibility to recover and recycle lead
Cleaned soil can be returned on place

DISADVANTAGES

Hazardous waste-water management
Depending on the agent, not suitable for peat soil and humus soil
Needs excavation
Depending on the agent, high environmental footprint

6.4. SOIL STABILIZATION/SOLIDIFICATION

Soil stabilization is also called soil solidification. This technology has been used to modify the hazardous property of shooting range soil. The solution is based in a long-term management or the control the solubility of metals for groundwater protection. Stabilization process has been used to express some unique procedures which metal-bearing waste can be managed to take away hazardous properties. Lately, Stabilization and Solidification are considered with an important difference between them, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Soil solidification's aim is to limit the spread of lead pollution by leaching. Soil solidification final product is monolithic block of waste. Solidification is the adding of pozzolanic material to a waste in order to reduce permeability and surface area. Pozzolanic material is generally alkaline material that increases the solubility of metals. The most common pozzolanic material used in soil solidification is cement. Cement addition or a cement-based mixture, limits the mobility or solubility of the contaminants. This technique can be applied in situ or ex situ. The process in situ consists in the injection of cement-based agent into the contaminated soil. The process ex situ consists in the excavation of the contaminated soil, machinery to mix the soil with cement-based agent, and put the mixture in the area again. The solidifying agents most common are Portland, gypsum, modified sulphur cement, and grout, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Soil stabilization consists in the adding of chemical products in order to reduce the solubility of the contaminants. This technology is based in the theory that soil pH controls metal solubility. Common stabilization products are phosphates, sulphates, hydroxides (Lime), and carbonates.

Recent research evaluates the effectiveness of eggshell and calcined eggshell on lead immobilization in a shooting range soil. The 5% addition of eggshell and calcined eggshell strongly decreases lead contamination around 69% and increases soil PH. Eggshell and calcined-eggshell amplifies activities of alkaline phosphatase up to 3.7 times higher than in the control soil. The use of eggshell corrections have potential as an integrated remediation strategy that makes possible lead immobilization and soil biological restoration in shooting range soils, (Ahmad et al., 2012).

Capping is an immobilisation method that consists in the placing of a physical barrier between the soil and the environment. The material used in capping is asphalt or concrete. Capping is containment method that has effect on the use of the land, (Vegter et al., 2002).

Table 8- Advantages and disadvantages- Soil Stabilization, (Sorvari et al., 2006)

SOIL STABILIZATION	
ADVANTAGES	Low costs (possibility to use waste materials)
	Technically simple
	No need excavation
DISADVANTAGES	Ecological risks not fully eliminated, treatment needs to be renewed periodically
	No information on irreversibility of contaminant binding in due course (not a permanent solution?)
	Lime verified as unsuitable for acidic forest soils

Table 9-Advantages and disadvantages- Soil Solidification

SOIL SOLIDIFICATION	
ADVANTAGES	Can be done in situ or ex situ
	Technically simple, similar to soil improvement techniques
	Low cost
DISADVANTAGES	Hazardous waste management
	Needs excavation

6.5. ASPHALT EMULSION BATCHING-ENCAPSULATION

Asphalt-based emulsions have been used widely in the construction industry to stabilize soils in order to control dust. This technology minimize the migration of the contaminants because the erosion. There are patents of modified emulsions used to encapsulate heavy metals like lead. These emulsions reduce the leaching process avoiding groundwater contamination. The final product is a material that decreases infiltration and it is resistant to erosion process, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

In July 2000, USEPA classified encapsulation technologies as a recycling for RCRA characteristic wastes, because the final product is a commercial one. Final product is non-hazardous construction material that can be applied in the construction of new roads or structural fills. On military firing ranges, the soil can be topically treated or mixed and compacted, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Table 10- Advantages and disadvantages- Asphalt emulsion batching-Encapsulation

ASPHALT EMULSION BATCHING-ENCAPSULATION	
ADVANTAGES	Final product with economic value
	Final product used in new roads or structural fills.
	No hazardous waste
DISADVANTAGES	Needs excavation
	No metal recovery

6.6. PHYTOREMEDIATION

Phytoremediation technology is called also bioremediation. It consists in the treatment using plants. This solution avoids the excavation of the contaminated soil.

This technology has been studied in other countries. In Nordic countries only in Finland and the Pine tree and there is no study done in Denmark, (Turpeinen et al., 2000).

There are different phytoremediation techniques, (Ali et al., 2013):

- Phytoextraction: This technique consists in the bioaccumulation of the contaminant in harvestable biomass, like leaves. There are studies about different plants using as bio extractors of lead contaminant.
- Phytofiltration: Sequestration of contaminants from polluted water using plants.
- Phytostabilization: This technique uses the roots of the plants limiting the mobility and bioavailability of soil contaminants.
- Phytovolatilization: This technique converses pollutants to volatile form and their subsequent release to the atmosphere.
- Phytodegradation, Rhizodegradation and Phytodesalation are techniques with no use in lead contaminated soil.

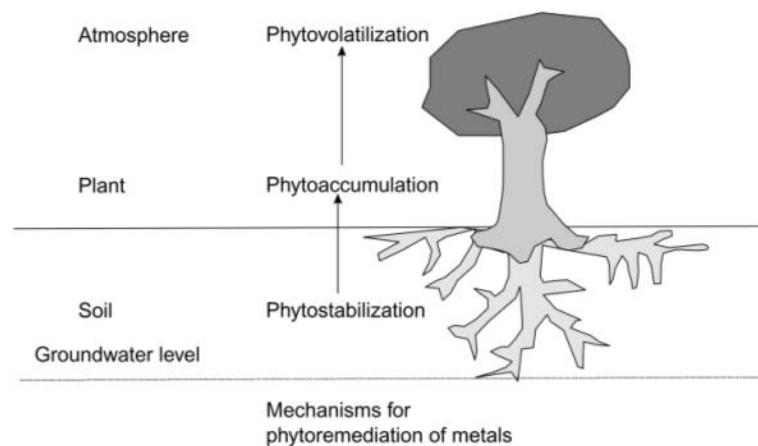


Figure 11-Phytoremediation mechanisms for metal uptake, (Mulligan et al., 2001)

Phytoextraction is the most common of phytoremediation techniques. It is accurate in large areas because the cost-effectiveness balances (Ali et al., 2013)

Phytoremediation techniques take into account the following aspects: lead bio-availability, limits of the plants and the re-vegetation of the area. (Ernst, 1996)

The following table shows the literature of phytoextraction in lead contaminated soil using different plants. The efficiency of the methodology is measured using different units.

Table 11-Phytoextraction literature

Plant	Accumulation in plants-Efficiency	Reference
<i>Thalpi caerulescens</i> <i>Armeria calminare</i>		(Ernst, 1996)
<i>Amaranthus Cruentus</i>		(Opeolu et al., 2005)
<i>Tagetes minuta</i> L. <i>Bidens pilosa</i> L.	380.5 $\mu\text{g/g}$ -1 DW 100.6 $\mu\text{g/g}$ -1 DW	(Salazar & Pignata, 2014)
Charophytes: <i>Chara aculeolata</i> and <i>Nitella opaca</i>	21657.0 $\mu\text{g/g}$ at 10mg/L Pb	(Sooksawat et al., 2013)
<i>Allium fistulosum</i> (green onions) and <i>Pteris cretica</i> cv <i>Mayii</i> (moonlight ferns)		(Cho et al., 2009)
Sunflower: <i>Tithonia diversifolia</i> and <i>Helianthus annuus</i>	87.3-71.3 mg/Kg	(Adesodun et al., 2009)
Natural zeolites (<i>Mirabilis jalapa</i> L.) charged with ammonium or carbon dioxide	960 mg/Kg	(Lai et al., 2012)
Boreal forest- Pine tree (<i>Pinus sylvestris</i>)	30%	(Turpeinen et al., 2000)
Alfalfa (<i>Medicago sativa</i>) Beets (<i>Beta vulgaris</i> var. <i>Cicla</i>) Amaranth (<i>Amaranthus hybridus</i>)	51% 58% 43 %	(Valencia, 2013)

Table 12- Advantages and disadvantages- Phytoremediation, (Sorvari et al., 2006)

PHYTOREMEDIATION

ADVANTAGES

- Technically simple method
- Economic solution
- No need soil excavation
- Positive environmental impact
- Accurate in large areas

DISADVANTAGES

- Long term solution
- Experimental method-No Danish experience

7. CONCLUSIONS

Soil in shooting ranges is heavily contaminated by lead and its combinations. Lead contamination is very dangerous for human health and the environment because its effects and the accumulation in the food chain.

The analysis of the contamination follows a step by step methodology. Firstly a preliminary study should be developed, secondly an analysis of the contamination and a comparison with the reference levels establish in legislation. The analyses of the contamination should be focused in the spatial and grain size distribution of the pollutants.

The solution of heavily polluted shotgun firing ranges, that are usually extend into densely vegetated, wooded forest areas, is challenging. The bullet recovering is time-consuming, technically hard and high-priced. Lamentably, no one of the tested alternative technologies have been demonstrated totally appropriated for Finnish situation yet, (Sorvari et al., 2006). Research into new techniques, new products with minimal environmental and economic impacts should be developed.

Nowadays the remediation techniques can be grouped into Excavation & disposal, physical separation, chemical extraction, stabilization, encapsulation and phytoremediation.

According to the GSR principles, excavation & disposal, stabilization and encapsulation are no considered remediation technologies because the pollutants are not removed and the problem is moved to another place or another time. As a consequence only phytoremediation and soil washing are considered remediation techniques.

Phytoremediation techniques still in develop. There are not many studies in Nordic countries. This remediation technique is more popular in tropical and sub-tropical countries. Phytoremediation experiments take years to be developed. The effectiveness of phytoremediation is not tested following standards, so there is no comparison possible.

The most effective technology removing heavy metals from soil is soil washing by the combination of physical separation and chemical extraction.

On the one hand, Chemical extraction using EDTA as a chelant agent is proved the most common and effective washing technique after excavation & disposal, (Dermont et al., 2008). On the other hand, this technique has a high environmental footprint, (Kim et al., 2013).

Regarding with effectiveness experiments in washing techniques, there are two type of washing tests: batching and column. Batch agitation studies are developed in order to determine accurate ranges of concentration of chelant agent in the washing solution. However, Soil column studies are performed to reproduce in situ clean-up conditions using a column of contaminated soil with the same goal. Column experiment results are in generally better than results obtained in batch tests, (Abumaizar & Smith, 1999).

New biodegradable chelant agents have been tested on artificial contaminated soils using batch test, (Begum et al., 2013). These new biodegradable chelant agents have not been tested on real contaminated soil using a column test.

Soil washing is a promising technology under develop in Denmark. Environmental Protection Agency finances full scale projects and companies develop new strategies. As a consequence, soil washing has to be tested in pilot and full scale to prove the feasibility of this technology in Denmark.

3. PRELIMINARY STUDY

1. INTRODUCTION

The present document is the first phase during the analysis of lead contamination and evaluation of possible solutions in a military shooting range in Viborg, Denmark.

Preliminary study includes the collection of information including the history of the shooting range. There are some important information like the period of time of use, type of ammunition and the manage history of the range. The amount of bullets can be calculated by the number of targets used per year. The removal, relocations, additions or extractions of soil is also important information, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003)

2. LOCATION

The shooting range is located in Viborg, Denmark. The owner of this shooting range is the Royal Danish Army. The following pictures show the location of the shooting range.

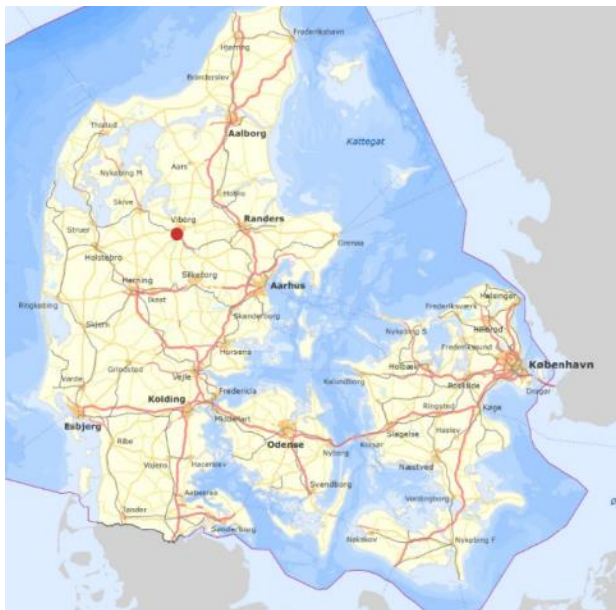


Figure 12-Viborg location, (Danmarks Miljøportal, n.d.)



Figure 13-Viborg Shooting range location, (Danmarks Miljøportal, n.d.)



Figure 14-View of the shooting range, (Danmarks Miljøportal, n.d.)

3. FIRING RANGE DESCRIPTION

The military area is divided in two adjacent shooting ranges. There is one of 200-300 m and another of 50 m length shooting range. The first one is a long distance path shooting range and the short one, a pistol shooting range, according to the Danish classification, (Amternes Videncenter for Jordforurening, 2004).

Viborg firing range is backed by concrete retaining walls. These structures are built in order to prevent shots going outside of the firing line. The shooting range is surrounded by berms constructed by earthworks.

4. HISTORY

The history of the shooting range is linked to the history of the Viborg.

The city Vibjerg has a Viking origin. Viborg was a religious and commercial meeting place for the whole of Jutland. The city was one of Denmark's most important cities until the 1200s. Viborg's location gave the city great strategic importance in politics and religion during the Middle Age. Since 1800 the city has turned into industrial activity. Today, the industry's largest trade comes from iron and steel industry, but the service sector has become even more important, (Danish Centre for Urban History, n.d.).

Viborg has a rifle shooters club since 1860. The original impetus behind the formation of rifle in Denmark was the national revival after the war three years from 1848 to 1850 and the lost war in 1864. During the World War I and II the club stopped the activities. Especially during the occupation weapons were handed over to police. After the war ended in 1945 had the Viborg County Rifle club like any other rifle across the country start from scratch again, (Viborg Historie, n.d.). The history of the civil shooting clubs and the shooting ranges is linked, (Amternes Videncenter for Jordforurening, 2004).



Figure 15- Viborg County Rifle Shooters club in 1918, (Viborg Historie, n.d.)

According to the Environmental Ministry, the shooting range was built in 1900 by the regiment of the “Prince’s life” and refurbished in 1947, (Miljøministeriet Naturstyrelsen, 2010).

The Shooting World Championship of 1914 was developed in Viborg, according to the International Shooting Sport Federation, ISSF. The competition was in this categories 300m free rifle 3x40, 50m free pistol, 300m army rifle, (ISSF, 2012). Probably the competition was developed in the shooting range.

Nowadays the surrounding area of the shooting range is used for walking and public recreation because there is a footpath net across the forest.

The following pictures show the evolution of the shooting range since 1945 until 1996. The area surrounding the shooting range has been reforested.



Figure 16- General View 1945, (Danmarks Miljøportal, n.d.)



Figure 17-General View 1954, (Danmarks Miljøportal, n.d.)



Figure 18-General View 1996, (Danmarks Miljøportal, n.d.)

5. PERIOD OF USE

The shooting range is closed nowadays. The information about the time used as a shooting range is catalogued by secret because it is a military area. Unfortunately this final dissertation cannot develop deeply the present point and the possible consequences according to the literature studied.

According to the Environmental Ministry, the shooting range was built in 1900 by the regiment of the “Prince’s life”, (Miljøministeriet Naturstyrelsen, 2010).

The information obtained on the net, suggest that the shooting range has been used until the end of the twenty century. The following picture shows a shooting training in 1997 obtained from the net, (Jensen, 2011).



Figure 19- Shooting training 1997, (Jensen, 2011)



Figure 20-Shooting training, 1997, (Jensen, 2011)

6. TYPE OF AMMUNITION

The shooting range has been used in military training. Just as the previous point, the information about the type of ammunition and the shots per year is secret.

Taking into account when was the shooting range built, the type of ammunition has changed since the construction time.

According to the literature, the weapons used in Danish shooting ranges in 1900 were rifle, salon rifle and “Bagladerriflen” model 1867. Up to the present, several shooting categories has been added, so currently the weapons used in Danish Shooting ranges are, (Amternes Videncenter for Jordforurening, 2004):

- Gun/ rifle and light machine gun
- Salon gun, rifle and pistol indoor
- Gun
- Revolver
- SMG

Visual inspection of the shooting range provides that the ammunition used is a wide range of pistol, rifle and shotgun.

On the one hand, lead ammunition for civil use is banned in Denmark since 2000, (Avery & Watson, 2009). On the other hand the military use of lead ammunition is out of this regulation so the use is permitted, (Hansen et al., 2004).

As a conclusion, lead ammunition has been used for more than a century in Viborg Shooting range.

7. REMOVALS OF SOIL

The shooting range has a sand layer over the natural soil. This layer has around 30 cm of thickness. This layer has been removed several times during the range history. According to the information recovered in NIRAS, the soil has been removed in order to level the surface.

According to the environmental ministry the shooting range was refurbished in 1947. The impact berms were added in order to make the shooting range safer, (Miljøministeriet Naturstyrelsen, 2010).

Visual inspection of the shooting range shows that the long-rifle shooting range has been reduced longitudinally and there is more vegetation than in the short-pistol shooting range.

8. CHARACTERISTICS OF THE AREA

The surrounded area is a reforested zone, the “Viborg Plantage”. The forest has two different areas: deciduous forest and coniferous forest, (Miljøministeriet Naturstyrelsen, 2010). “Viborg Plantage” is built on the classical way as a plantation with long straight lines.

The following picture shows the reforested area and the Viborg shooting range.

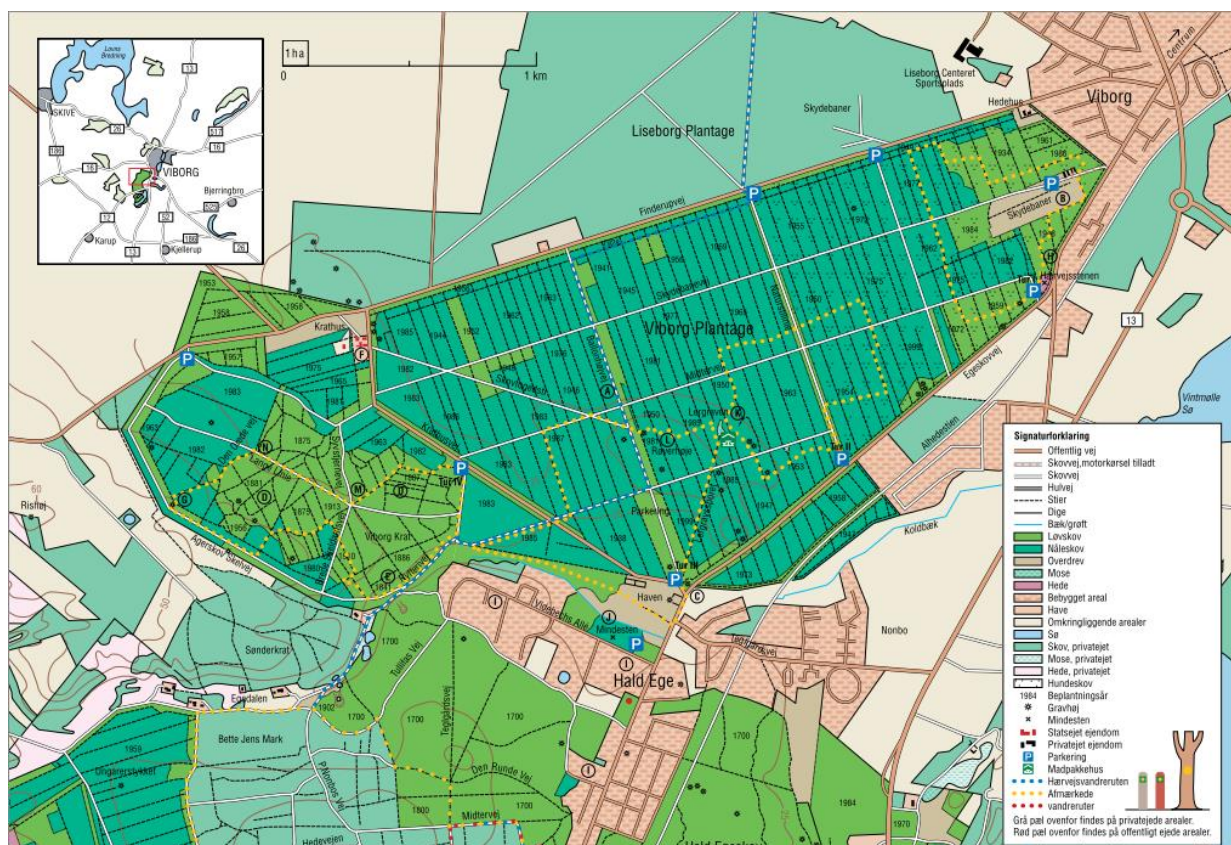


Figure 21- Viborg reforested area and the shooting range(B), (Miljøministeriet Naturstyrelsen, 2010)

The research about the age of Viborg groundwater describes the area surrounding the shooting range. The research was done analysing the chloroform in specific drilling locations. According to this research, the age of the groundwater is ranged between 19 and 21 years. The following figures show the drilling location and section and the potential ground water flux, (Urban and Environmental Planning, 2007).

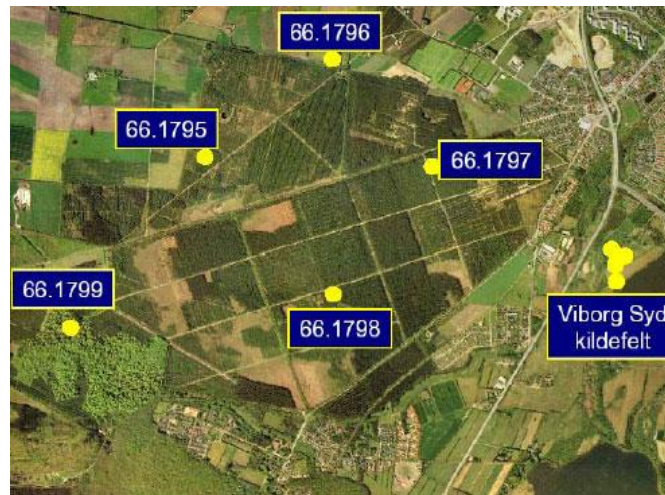


Figure 22-Drilling locations to determine the age of ground water, (Urban and Environmental Planning, 2007)

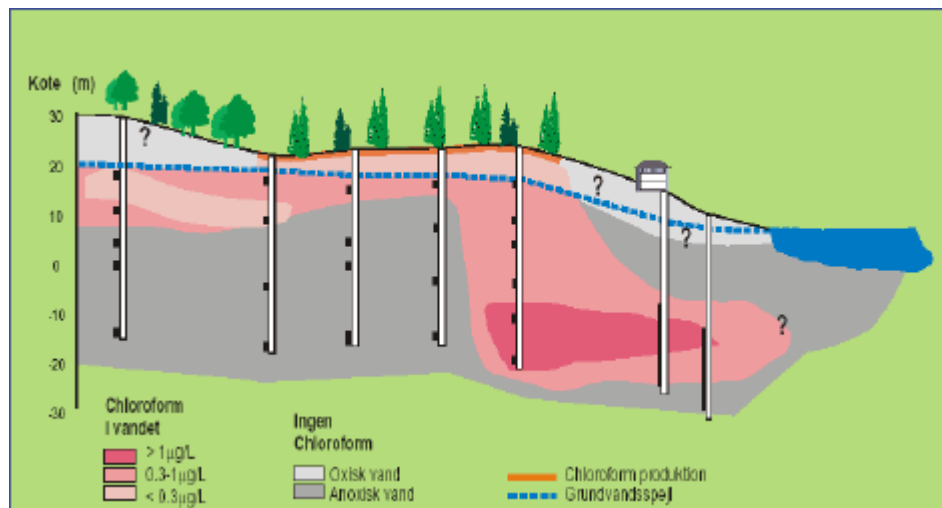


Figure 23-Profile showing the extension of the ground water from the west to the east, (Urban and Environmental Planning, 2007)

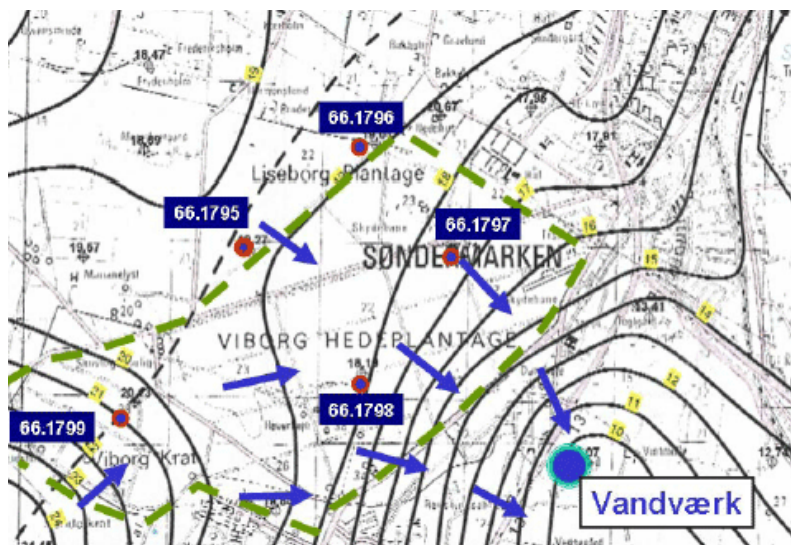


Figure 24-Potential Ground water field and flux, (Urban and Environmental Planning, 2007)

9. CONCLUSIONS

According to the little and dispersed information obtained of the origin, history and situation of the shooting range, some conclusions can be reached.

The shooting range of Viborg has been used since 1900. The maintenance and manage of the shooting range has depended on the Royal Danish Army since it was built. The range has been extensive used with ammunition composed by lead for military training in spite of the banned in the civil use.

The military area is divided in two adjacent shooting ranges. There are one of 200-300 m (long distance path shooting range) and another of 50 m length shooting range (pistol shooting range).

The field is located in a reforested area by deciduous and coniferous forest. As a consequence, the area is likely to be affected because the amount of biomass, specially primary and secondary consumers in the trophic chain.

The main conclusion of this preliminary study is that lead contamination is expected in the shooting range soil. As a consequence, the study of pollution levels should continue through collecting samples in the field and subsequent analysis in the laboratory. The contamination should be compared with the reference levels established by the Danish legislation. The evaluation of the pollutants should be focused in the 50 m shooting range because it has been used for a longer time and it is supposed to be more contaminated.

In addition, if there is contamination once the comparison is done, a remediation proposal should be done in order to restore the area. The objective of this remediation proposal depends on the future use of the land and the legislation.

4. FIELD SAMPLING REPORT

1. INTRODUCTION

This field report is part of the final dissertation on contaminated soil in a military shooting range. The report includes the methodology and the results of the test made in situ. Moreover, this report contains a description of the methodology used, which consists in taking samples, and all the data about the collecting.

This report is included in the diagnostic phase, which is made in collaboration with other student, Martí Burcet. The application of incremental sampling methodologies is the topic that Martí is focused on.

Royal Danish Army (RDA) wants to evaluate the pollutant of the shooting range. RDA has contracted for this purpose the Danish company NIRAS. And, as a consequence, this final dissertation is made in collaboration with NIRAS.

2. BACKGROUND

The contamination is caused by the heavy metals of bullets and shells. Heavy metal pollution is very dangerous because of its effects on living organisms, its accumulation in the food chain and the contamination of the water suppliers.

Viborg shooting range was built in 1900. It has been used for military training by the RDA. The range has been extensive used with ammunition composed by lead. The field is located in a reforested area by deciduous and coniferous forest.

Lead contamination is expected in the shooting range soil. As a consequence, the study of pollution levels should continue through collecting samples in the field and subsequent analysis in the laboratory.

3. LOCATION

The shooting range is located in Viborg, Denmark. The owner of this shooting range is the Royal Danish Army. The following pictures show the location of the shooting range.

The military area has two adjacent shooting ranges. There is one shooting range of 200-300 m length and another one of 50 m. The evaluation of the pollutants is focused in the short range because it has been extensively used.



Figure 25- Location Viborg, (Danmarks Miljøportal, n.d.)



Figure 26-Location shooting range, (Danmarks Miljøportal, n.d.)



Figure 27-General View of the shooting range, (Danmarks Miljøportal, n.d.)

The shooting range has two concrete structures in the middle as bridges and there is a third one in the target area. These structures have a layer of polyurethane and a metallic net. And they are designed to retain misfires.

The shooting range is surrounded by berms in the borders. There is a communication area between the two shooting ranges.

4. TEST ON FIELD

The first step on the research of the soil contamination is performing a test on field. The test is justified, firstly, in order to confirm the presence of pollution, and secondly, to have a first approach of the pollution data. The results of this approach are useful to prioritize the sampling and assess the boundaries.

4.1. METHODOLOGY

The test performed is X-ray Fluorescence (XRF) in-situ. This technique is based on nuclear technology. XRF is X-ray secondary emission from a material that has been bombarding with gamma rays. The tool used to measure the concentration of contamination is a handheld XRF. The test gives a quick profile of the pollutants of the soil. The following picture shows the XRF used in the test on field.



Figure 28- Handheld XRF used in the testing

4.2. RESULTS

This XRF test provides data of the concentration of metals like lead, iron and zinc. The following table shows the results of this first approach and the figure shows the location of the discrete points.

Table 13- Field XRF test results

ITEM NUMBER	METALS CONCETRATION (ppm)		
	LEAD-Pb	IRON-Fe	ZINC-Zn
1	289	141	67
2	458	621	148
3	193	161	31
4	1.203	1.701	220
5	1.820	4.433	513
6	169	3.501	74
7	87	3.724	36
8	77	5.231	49

ITEM NUMBER	METALS CONCENTRATION (ppm)		
	LEAD-Pb	IRON-Fe	ZINC-Zn
9	86	2.134	25
10	205	4.626	54



Figure 29-XRF test results

4.3. CONCLUSIONS

Once this test is completed, there are some conclusions to be taken into account in the sampling process:

Firstly, there is lead contamination, as it was logical to predict in a military shooting range. There is also iron and other metallic elements pollution.

Secondly, the most lead polluted area is the target zone and the less contaminated the shooting area, as it was also logical to predict. The most contaminated area should be analysed deeply and carefully. However, the iron contamination is higher in the target area and in the shooting one than in the central part, where lower values of pollution have been founded.

Thirdly, the distribution is not homogeneous in the shooting range. It is interesting to analyse the longitudinal and transversal lines of the shooting range more deeply.

Finally, the levels of lead contamination in all the cases are over the legal limit for human toxicology 40 ppm, (Jesper L. Bak, 1998). In the target area the values are really high, over one thousand.

However, the XRF test has been done in the surface of the shooting range. The information about the concentration depending on the depth, as a vertical profile, is very important for the future evaluation of the possible solutions and the contamination of the groundwater. As a conclusion, samples in different levels should be taken.

5. SAMPLING METHODOLOGY

In order to compare methodologies of sampling, different types of samples were collected: discrete, composite and incremental.

In order to have a representative estimation of the contaminated soil, the methodology used is the Incremental Sample Methodology (ISM). This technique is based on taking multiple samples in an area called Decision Unit (DU). ISM is statistically more accurate than discrete sample. ISM has two phases: field sampling and laboratory subsampling. This report consists in the field sampling.

The picture shows the process of collecting samples inside the DU. ISM consists in collecting samples composed of a minimum of 30 increments (Sample & Approaches, 2008).

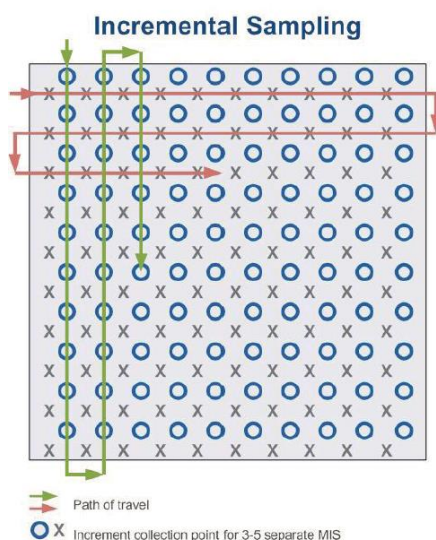


Figure 30-Incremental Sampling Methodology,(ALS Environmental)

5.1. TOOLS

The following pictures show the tools used in the collecting sample process. The selection of the tools depends on the density of the soil. The picture on the right shows the tool used in most of the cases.



Figure 31-Available extraction tools



Figure 32-Extraction tool used in the ISM

5.2. CAUTION

The samples have to reproduce, as more accurate as possible, the characteristics of the shooting range. On the one hand, in order to preserve soil properties all the collected samples are kept in plastic bags. Plastic bags preserve the humidity conditions of the soil during the transportation from the shooting range to the laboratory. The picture below shows the samples once collected.



Figure 33- Collected samples in plastic bags

On the other hand, because of the toxicity of the contaminant, some cautions were taken like washing hands after the sampling and do not eat or drink during the process.

6. SAMPLE AREAS-DECISON UNIT

Depending on the methodology applied for the collecting it takes place the division of the areas and profiles.

Firstly it takes place the collection of samples based on the ISM previously described. The collecting process is made in squares. Moreover, some composite samples are collected in squares.

The shooting range is divided into small areas. The following picture shows the division. It is the same division as the one that NIRAS uses in its report in order to have the same nomenclature. The code includes the number of the square.



Figure 34-Sample areas

Secondly to analyse the profiles, discrete samples are collected. The longitudinal and cross profiles of the shooting range are the series A and B. Series A is the longitudinal one and Series B is the transversal one.

7. SAMPLES

The table below shows the information about the samples collected:

Table 14- Soil sample series

SERIES	Method	Selection	Randomness	Schema	Nº	Increments	Numeration	DU	Code
A	<i>Discrete</i>	<i>Systematic</i>	-	1 per meter	65	1	00_64	108-111&113-121	A XX
B	<i>Discrete</i>	<i>Systematic</i>	-	1 per meter	8	1	00_07	114	B XX
B	<i>Discrete</i>	<i>Systematic</i>	-	1 per meter	9	1	07_16	109	B XX
107	<i>ISM</i>	<i>Systematic random</i>	-	14x4	1	56	-	107	107-C (14x4)
107	<i>Composite</i>	<i>Systematic</i>	-	5x1	1	5	-	107	107-C (5x1)
107	<i>ISM</i>	<i>Simple random</i>	2 dices x2	5x1	1	5	-	107	107-R (5x1)
107	<i>Discrete</i>	<i>Simple random</i>	2 dices x2	1x1	1	1	-	107	107-R (1x1)
111	<i>ISM</i>	<i>Systematic random</i>	-	6x6	10	36	01_10	111	111-C (6x6) XX
111	<i>ISM</i>	<i>Simple random</i>	1 dice x4	5x1	10	5	01_10	111	111-R (5x1) XX
111	<i>Discrete</i>	<i>Simple random</i>	2 dices x2	1x1	10	1	01_10	111	111-R (1x1) XX
112	<i>ISM</i>	<i>Systematic random</i>	-	14x4	1	56	-	112	112-C (14x4)
112	<i>Composite</i>	<i>Systematic</i>	-	5x1	1	5	-	112	112-C (5x1)
112	<i>ISM</i>	<i>Simple random</i>	2 dices x2	5x1	1	5	-	112	112-R (5x1)
112	<i>Discrete</i>	<i>Simple random</i>	2 dices x2	1x1	1	1	-	112	112-R (1x1)
116	<i>Discrete</i>	<i>Systematic</i>	Depth analysis	1x1	5	1	0-10_40-50	116	S 116 XX-YY
TOTAL SAMPLES					125				

8. PICTURES REPORT



Figure 35-General view of the shooting range



Figure 36- General view of the shooting range



Figure 37- View from the point of shot view



Figure 38- View of the ground with the presence of bullets



Figure 39- View of the shot point from the target



Figure 40- View of the shot point



Figure 41- View of the longitudinal profile (series A) from the target point



Figure 42- View of the target pool, Decision Unit number 112



Figure 43- Detail of the sticks used to name the decision units



Figure 44- Collecting of a composite sample according to ISM



Figure 45- Decision unit after the sample collecting



Figure 46- Sample identification using a code



Figure 47- Sample collecting



Figure 48- Sample collecting

5. LEAD CONTAMINATION LABORATORY REPORT

1. INTRODUCTION

This report is part of the final dissertation on contaminated soil in a military shooting range. The report includes the methodology and the results of the test made in the VIA geo-laboratory.

The most important point of this report is the information about the contamination and its distribution. Therefore, this report contains a description of the methodology used. Which consists in drying, dividing and analysing soil samples, and all the data about the tests done. Lead soil contamination data is compared with the lead quality criteria establish in Danish legislation.

This report is included in the diagnostic phase, which is made in collaboration with other student, Martí Burcet. His part is focused in the comparison between different sampling methodologies.

2. METHODOLOGY

2.1. INCREMENTAL SAMPLE METHODOLOGY

As was explained in the sampling report, the methodology followed is the Incremental Sample Methodology (ISM). ISM is a representative methodology that reduces sampling error, (ITRC, 2012).

According to the recommendations, the laboratory is divided in two phases: processing and analyses. The Laboratory processing includes the following steps: moisture determination (%), Drying, particle size selection and reduction and finally Analytical Subsampling. Once the sub sampling has finished, the soil sample is ready for the Laboratory Analyses.

The following figures represent the sample processing an analysis flow chart, (ITRC, 2012).

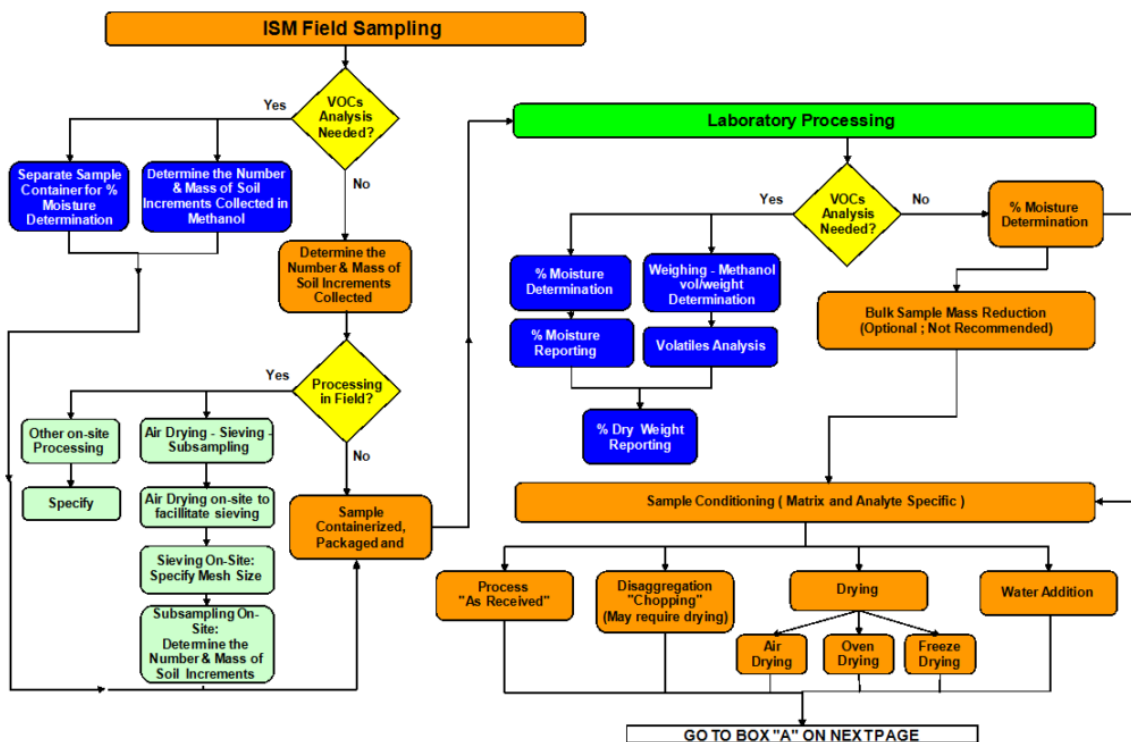


Figure 49- ISM sample processing & analysis flow chart 1,(ITRC, 2012)

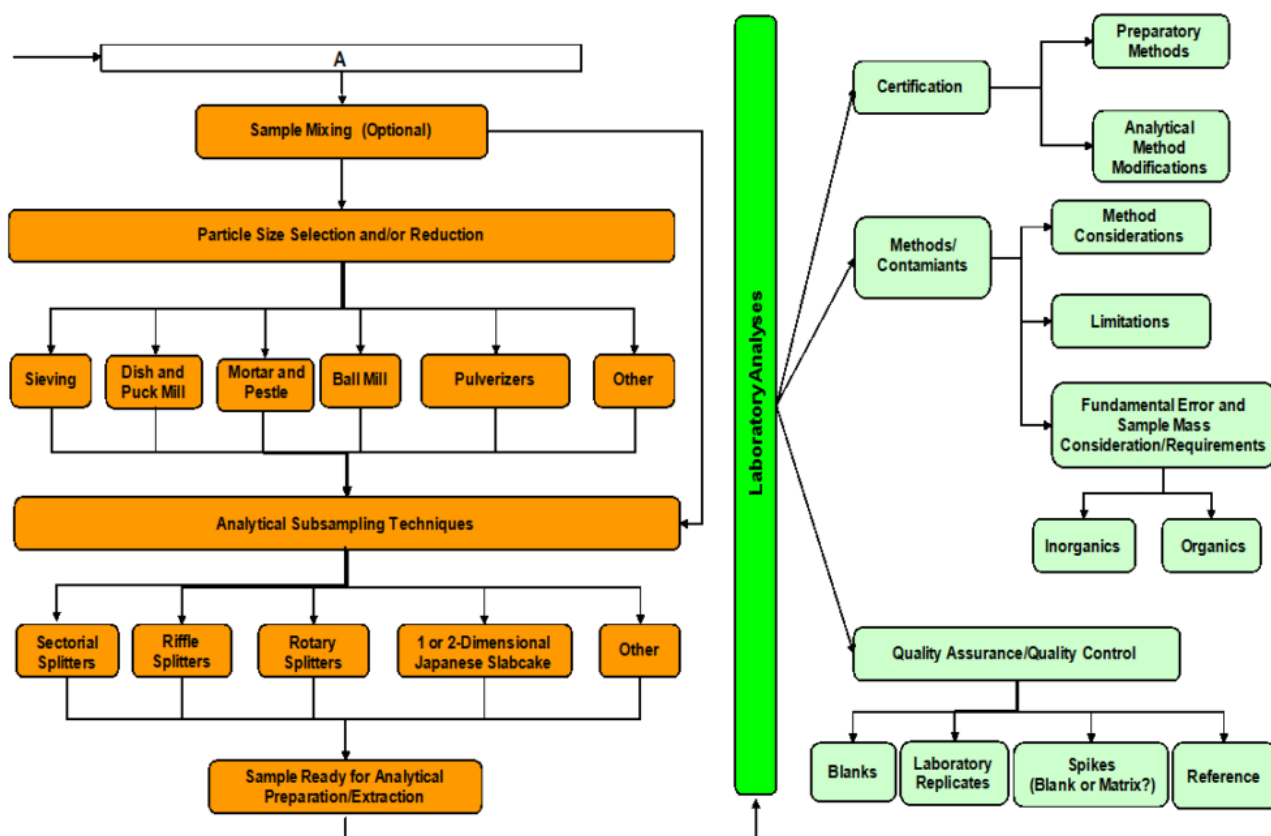


Figure 50- ISM sample processing & analysis flow chart 2,(ITRC, 2012)

2.2. WEIGHT

The first lab processing begins measuring the weight of the samples. Soil samples have been transported in sealed plastic bags. Therefore moisture conditions are maintained. The measuring of the weight is done before the air drying process starts.

Soil samples weight data is useful in order to calculate the moisture content, mass losses. The tool used is in the Geo Laboratory of VIA University Collage.

2.3. AIR-DRY

The second step in lab processing is the air-dry process. Air-dry process is done in order to reduce soil heterogeneity (particles aggregation because water suction) and facilitate further mechanical process (sieving, grinding and sub-sampling).

Soil samples are distributed on trays and dried for a week. The process is done in the Geo Laboratory of VIA University Collage and therefore uses the air conditions of this one.

Figures 58 and 59 show the air-dry process, (Figure 58- Air-dry process, Figure 59- Soil samples during Air-dry process).

2.4. DISAGGREGATION

The third step is the disaggregation. This process is done in order to reduce soil agglomerates and in consequence reduce grouping and segregation errors. Disaggregation process is needed sometimes even after air-dry one and before sieving, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Figures 60, 61 and 62 show the process, (Figure 60- Soil Sample 112-C-01, Figure 61- Soil sample disaggregation process, Figure 62- Soil sample before disaggregation process)

2.5. GRANULOMETRY

The size selection and the contamination analysis in all the fractions is an important information in order to select the Physical separation as a remediation technique, (Mulligan et al., 2001).

Moreover the recommendations followed recommend to analyse the particles with a size smaller than two millimetres (<2mm) and the “fines” particle size fraction (<250 µm), (Sample & Approaches, 2008).

The size selection is done using sieves of the series ASTM. Before and after the size separation the weight is measured. The size selection is developed on part of the soil samples, the composite ones.

The figures from 63 to 66 show the size selection process, (Figure 63- Granulometry, Figure 64- Granulometry division,

Figure 65- Samples after granulometry division, Figure 66- Big particles (>2mm) and bullets).

2.6. SUB-SAMPLING

According to the recommendations, sub-sampling is the last step of the laboratory processing, (Sample & Approaches, 2008), (ITRC, 2012).

In the VIA Geo Lab the sub-sampling is carried out with a sectorial splitter (rotary riffle splitter and a riffle splitter).

The figures 67, 68 and 69 shows the samples and the instruments used in sub-sampling, (Figure 67- Soil sample, Figure 68. Sub-sampling and Figure 69- Sub-sampling)

2.7. X-RAY FLUORESCENCE

XRF is the laboratory analyses process. X-Ray Fluorescence is based on nuclear technology. XRF is X-ray secondary emission from a material that has been bombarded with gamma rays.

According to the literature the XRF instrument is accurate to monitor toxic metal in soil samples. This technique is recognized by the EPA, OSHA, NIOSH, and common used by researchers and commercial laboratories, (Wainner & Harmon, 2001).

The XRF analyses are developed in the NIRAS laboratory in Aarhus.

Figures from 70, to 73 shows the XRF instrument, (Figure 70- XRF Test, Figure 71- XRF Test, Figure 72- XRF Test, Figure 73- XRF Test)

3. SAMPLE SERIES

As described in the Field sampling report, the shooting range is divided by small areas and profiles.

Firstly it takes place the collection of samples based on the ISM previously described. The collecting process is made in squares called decision units. Moreover, some composite samples are collected in squares.

The shooting range is divided into small areas. The following picture shows the division. It is the same division as the one that NIRAS uses in its report in order to have the same nomenclature. The code includes the number of the square.



Figure 51-Sample areas

Secondly to analyse the profiles, discrete samples are collected. The longitudinal and cross profiles of the shooting range are the series A and B. Serie A is the longitudinal one and Serie B is the transversal one.

According to the field sampling, the following table is a summary of the sample series.

Table 15- Soil Sample series

SERIES	Method	Selection	Randomness	Schema	Nº	Increments	Numeration	DU	Code
A	Discrete	Systematic	-	1 per meter	65	1	00_64	108-111&113-121	A XX
B	Discrete	Systematic	-	1 per meter	8	1	00_07	114	B XX
B	Discrete	Systematic	-	1 per meter	9	1	07_16	109	B XX
107	ISM	Systematic random	-	14x4	1	56	-	107	107-C (14x4)
107	Composite	Systematic	-	5x1	1	5	-	107	107-C (5x1)
107	ISM	Simple random	2 dices x2	5x1	1	5	-	107	107-R (5x1)
107	Discrete	Simple random	2 dices x2	1x1	1	1	-	107	107-R (1x1)
111	ISM	Systematic random	-	6x6	10	36	01_10	111	111-C (6x6) XX
111	ISM	Simple random	1 dice x4	5x1	10	5	01_10	111	111-R (5x1) XX
111	Discrete	Simple random	2 dices x2	1x1	10	1	01_10	111	111-R (1x1) XX
112	ISM	Systematic random	-	14x4	1	56	-	112	112-C (14x4)
112	Composite	Systematic	-	5x1	1	5	-	112	112-C (5x1)
112	ISM	Simple random	2 dices x2	5x1	1	5	-	112	112-R (5x1)
112	Discrete	Simple random	2 dices x2	1x1	1	1	-	112	112-R (1x1)
116	Discrete	Systematic	Depth analysis	1x1	5	1	0-10_40-50	116	S 116 XX-YY
Total samples					125				

4. RESULTS

4.1. WEIGHT- MOISTURE CONTENT

The moisture content is an important data in order to characterised the contaminated soil, (Tampouris et al., 2001).

Moreover, moisture content is an important information in order to select remediation techniques such as dry or wet screening in size separation, (USA Army, 1997).

The moisture content of soil samples is calculated using the weight of the samples before and after drying. In this case, the samples were dry in the air conditions of the geo lab. Soil samples were not processed in the oven.

The following table shows the result of the calculation of the moisture content in the composite sample 111-C(6x6)XX from the replicate 5 to the 10. The moisture content is 3.58 % and the Relative Standard Deviation (RSD) is 4.9 %. The results can be considered as a good approximation.

Table 16-Moisture calculation in sample 11-C(6x6)XX

Sample	Wet Weight [g]	Dry weight [g]	Water weight [g]	Moisture [%]
111-C (6x6)05	1905	1835.5	69.5	3.65
111-C (6x6)06	1859	1787.5	71.5	3.85
111-C (6x6)07	1752	1690.5	61.5	3.51
111-C (6x6)08	1807	1745.5	61.5	3.40
111-C (6x6)09	1618	1558.5	59.5	3.68
111-C (6x6)10	1603	1548.5	54.5	3.40
Average	1757.33	1712.83	1694.33	3.58

4.2. MATRIX DENSITY

The information of density is important if the physical method of remediation used is the density separation, (Marino et al., 1997).

Moreover density is used to calculate the weight of the contaminated soil in case of the excavation.

In this report, matrix density estimation is calculated in dry and wet conditions. The volume used is the volume of sample extraction. The sample tool has a conic volume of 41.55 cm³ (diameter of 2.3 cm and 10 cm of height). This is the volume in bank conditions. The figure number 4 shows the tool used in the sampling campaign.

The weights of the A and B series are used because all of them were sampled using the same tool. The following table has the results of Matrix Density calculations.



Figure 52- Sample Tool used

	Weight	Matrix density
Wet	56.32 g	1.36 g/cm ³
Dry	54.30 g	1.31 g/cm ³
Volume	41.55 cm ³	

Table 17- Matrix Density

4.3. GRANULOMETRY

The grain size selection is developed on the sample 111C-(6x6)10. As explained before, the relevant particles are with diameter smaller than 2mm.

The meshes serial used is ASTM: 4mm, 2mm, 1mm, 0.5mm, 250 μ m, 125 μ m and 75 μ m. The procedure consist in the colocation of the meshes form the biggest to the smallest aperture. Soil sample is introduced in the meshes in the big aperture, and sieved in a vibrator platform for 3 minutes. All the retained material is weighted. The soil sample was divided in two parts depending on the size: particles with size between 250 μ m and 2 mm and the particles smaller than 250 μ m.

The following tables represent the result of the passing grain size developed in the Geo Lab.

Passing grain size curve

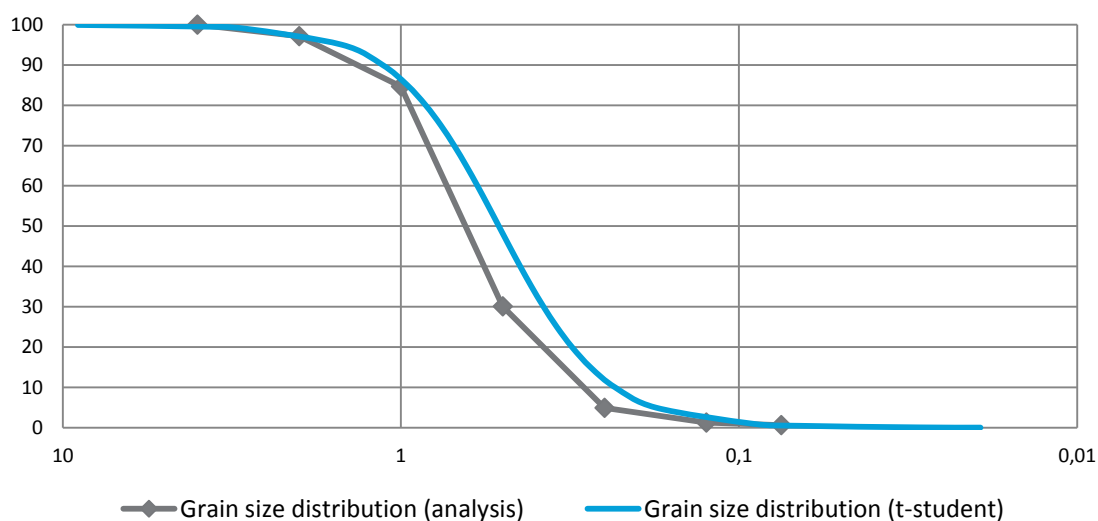


Figure 53-Passing grain size curve

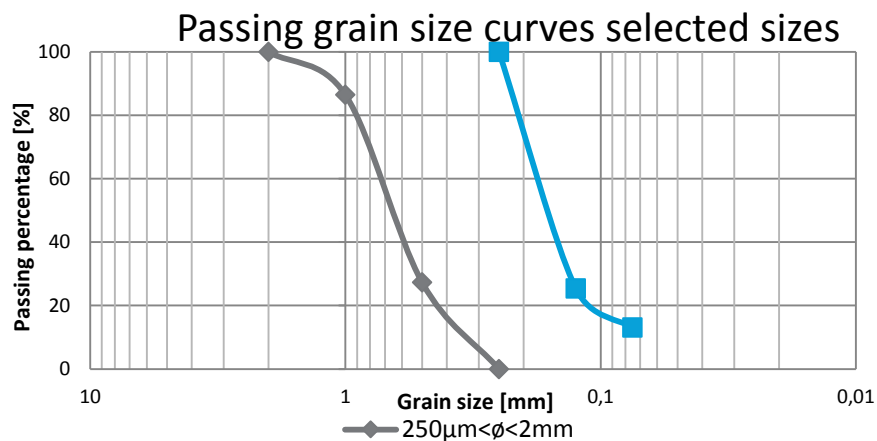


Figure 54-Passing grain size curve selected sizes

4.4. X RAY FLUORESCENCE SPECTROSCOPY

The XRF is the instrument used to identify the lead concentration in soil samples. The test was developed the 2nd of April in the NIRAS laboratory in Aarhus. The XRF analysing machine chosen was the same as was used during the sample collection, the model Handheld Thermo Scientific Niton XRF spectrometer. In this case, the instrument is assembled to a structure and connected to a computer.

The results are given in parts per million [ppm] which is equivalent to milligrams per kilogram (mg/kg). Consequently, the results are given in relative concentration, not in total values.

The analysis procedure consists in the placement of the sample in the middle of the instruments surface and in direct contact with the XRF analyser. Following the NIRAS recommendations, the time of measurement is 30 seconds. On the other hand, in order to compare the precision between 30 seconds and 60 seconds, both times are tested in the same point.

The following tables show the results of the lead concentration and its error. The appendix of this report shows the full results of metal concentrations.

Table 18- Results of lead concentration (ppm)

CODE	Weight	Pb	Pb Error	CODE	Weight	Pb	Pb Error	CODE	Weight	Pb	Pb Error
A00	52	2968.84	63.24	A37	55	124.49	13.74	A00_BIS	52	2466.93	57.98
A01	47	2370.62	60.05	A38	51	110.89	12.74	A10_BIS	51	408.45	23.13
A02	60	1696.02	46.57	A39	59	96.91	12.3	A20_BIS	66	386.22	22.66
A03	64	1063.87	36.81	A40	65	92.23	12.05	A30_BIS	60	138.79	14.23
A04	70	978.96	35.37	A41	56	97.16	12.45	A40_BIS	65	162.62	15.62
A05	63	694.25	30.76	A42	69	105.69	13.5	A50_BIS	69	78.98	11.36
A06	49	615.29	28.2	A43	71	92.58	11.9	A60_BIS	41	67.53	10.6
A07	52	753.48	31.16	A44	46	65.47	10.52	B00	47	440.09	25.21
A08	63	401.02	24.53	A45	66	84.07	11.32	B01	66	433.65	23.35
A09	63	360.71	22.13	A46	65	97.92	12.28	B02	63	711.26	30.91
A10	51	471.8	24.8	A47	37	104.21	12.38	B03	71	475.21	24.98
A11	64	433.2	23.56	A48	63	87.06	11.8	B04	51	491.69	25.13
A12	63	419.6	23.41	A49	53	86.8	11.65	B05	54	657.42	29.07
A13	51	355.77	21.4	A50	69	84.08	12	B06	56	573.22	27.37
A14	61	277.1	19.5	A51	43	72.47	10.88	B07	61	640.9	28.46
A15	55	301.4	19.67	A52	58	61.84	10.02	B08	53	601.3	28.24
A16	66	387.21	23.07	A53	58	53.55	9.87	B09	51	478.8	25.16
A17	69	228.07	17.65	A54	59	51.12	9.86	B10	38	310.74	20.67
A18	59	227.03	17.36	A55	57	48.72	9.35	B11	60	531.03	26.16
A19	55	224.93	17.23	A56	61	38.6	9.24	B12	57	624.9	28.68
A20	66	257.87	18.69	A57	52	50.51	9.91	B13	56	922.17	34.3
A21	67	196.38	16.43	A58	40	61.49	10.25	B14	54	724.41	30.66
A22	52	325.81	20.87	A59	47	69.37	10.7	B15	61	627.96	30.02
A23	53	200.15	16.5	A60	41	72	10.79	B16	48	483.57	24.28
A24	63	202.29	16.64	A61	47	69.9	10.79	B00_BIS	47	409.96	23.15
A25	62	255.42	18.55	A62	49	66.32	10.67	B04_BIS	51	646.74	28.71
A26	45	182.46	15.93	A63	41	86.15	11.78	B08_BIS	53	606.95	28.03
A27	42	194.87	16.51	A64	50	45.98	9.01	B12_BIS	57	536.01	26.46
A28	58	179.95	15.86	A00_60"	52	2509.93	59.4	B16_BIS	48	453.24	24.35
A29	47	147.74	14.92	A10_60"	51	397.5	22.71	B00_60"	47	416.53	23.27
A30	60	126.9	13.42	A20_60"	66	385.87	22.61	B04_60"	51	625.64	28.47
A31	63	152.62	14.91	A30_60"	60	147.29	14.51	B08_60"	53	632.05	28.57
A32	61	98.1	12.32	A40_60"	65	166.69	15.81	B12_60"	57	561.93	27.19
A33	60	171.08	15.67	A50_60"	69	83.69	11.55	B16_60"	48	451.04	24.34
A34	50	132.65	13.95	A60_60"	41	56.4	9.92				
A35	65	119.09	13.73								
A36	52	98.09	12.9								

Table 19-Results of lead concentration (ppm)

CODE	Weight	Pb	Pb Error	CODE	Weight	Pb	Pb Error	CODE	Weight	Pb	Pb Error
S116(0-10)	98	210.52	17.02	111-R(5X1)01	273	172.66	17.06	111-C(6X6)01_250<Φ<2	174	213.87	16.84
S116(10-20)	171	91.94	12.19	111-R(5X1)02	222	278.93	19.33	111-C(6X6)02_250<Φ<2	191.5	290.88	19.5
S116(20-30)	116	73.56	11.15	111-R(5X1)03	290	238.91	18.14	111-C(6X6)03_250<Φ<2	200	380.34	22.27
S116(30-40)	137	0	9.41	111-R(5X1)04	249	257.42	21.74	111-C(6X6)04_250<Φ<2	205.2	206.15	16.82
S116(40-50)	169	0	9.08	111-R(5X1)05	141	205.62	16.89	111-C(6X6)05_250<Φ<2	194.1	272.54	19.03
S116(0-10)_BIS	98	256.39	18.71	111-R(5X1)06	314	316.44	22.66	111-C(6X6)06_250<Φ<2	188	314.76	20.28
S116(10-20)_BIS	171	236.3	17.79	111-R(5X1)07	260	278.96	19.55	111-C(6X6)07_250<Φ<2	178.1	325.75	20.86
S116(20-30)_BIS	116	74.52	10.88	111-R(5X1)08	285	304.36	20.14	111-C(6X6)08_250<Φ<2	181.8	589.46	27.47
S116(30-40)_BIS	137	0	9.36	111-R(5X1)09	262	231.25	17.87	111-C(6X6)01_250<Φ<2BIS	174	262.31	18.59
S116(40-50)_BIS	169	0	8.97	111-R(5X1)10	251	233.05	17.82	111-C(6X6)02_250<Φ<2BIS	191.5	220.11	17.14
107-C(5X1)	262	3760.93	69.3	111-C(6X6)01<250µm	83.1	769.79	32.6	111-C(6X6)03_250<Φ<2BIS	200	333.64	21.07
107-C(5X1)_BIS	262	3659.51	71.5	111-C(6X6)02<250µm	81.3	784.87	33.17	111-C(6X6)04_250<Φ<2BIS	205.2	187.54	15.9
107-C(5X1)_BIS2	262	6287.03	99.83	111-C(6X6)03<250µm	75.2	661.85	30.16	111-C(6X6)05_250<Φ<2BIS	194.1	303.93	20
107-R(1X1)	58	16892.9	189.01	111-C(6X6)04<250µm	64.2	614.12	29.07	111-C(6X6)06_250<Φ<2BIS	188	384.74	22.47
107-R(5X1)	267	2818.92	62.18	111-C(6X6)05<250µm	78.2	783.15	32.82	111-C(6X6)07_250<Φ<2BIS	178.1	314.58	20.47
107-R(5X1)_BIS	267	3967.08	75.85	111-C(6X6)06<250µm	74.7	840.56	34.22	111-C(6X6)08_250<Φ<2BIS	181.8	354.64	21.35
107-R(5X1)_BIS2	267	3367.38	67.62	111-C(6X6)07<250µm	64.4	818.11	33.7	111-C(6X6)09A_250<Φ<2	162.6	238.93	17.85
112-C(5X1)	222	4850.24	83.22	111-C(6X6)08<250µm	87.1	801.57	33.2	111-C(6X6)10A_250<Φ<2	148.7	281.74	19.44
112-R(1X1)	49	2478.18	58.81	111-C(6X6)09<250µm	75.7	712.2	31.6	111-C(6X6)09A_250<Φ<2_60"	162.6	284.55	19.44
112-R(5X1)	222	3480.2	70.44	111-C(6X6)10<250µm	60.3	1025.25	38.34	111-C(6X6)09A_250<Φ<2BIS	162.6	269.5	18.64
111-R(1X1)01	74	198.56	16.58	111-C(6X6)09<250µm_60"	75.7	732.77	32.05	111-C(6X6)10A_250<Φ<2BIS	148.7	303.49	19.97
111-R(1X1)02	59	166.68	15.26	111-C(6X6)01<250µmBIS	83.1	686.61	30.32	111-C(6X6)09A_250<Φ<2BIS2	162.6	262.08	18.63
111-R(1X1)03	59	296.4	19.81	111-C(6X6)02<250µmBIS	81.3	762.69	31.92	111-C(6X6)09A_250<Φ<2BIS3	162.6	233.14	17.64
111-R(1X1)04	64	243.14	18.13	111-C(6X6)03<250µmBIS	75.2	50.33	26.01	111-C(6X6)09A_250<Φ<2BIS4	162.6	251.02	18.15
111-R(1X1)05	63	177.31	16.11	111-C(6X6)04<250µmBIS	64.2	783.66	33.31	111-C(6X6)09B_250<Φ<2	164.3	179.8	15.82
111-R(1X1)06	68	164.65	15.42	111-C(6X6)05<250µmBIS	78.2	755.36	32.27	111-C(6X6)10B_250<Φ<2	148.3	258.46	18.75
111-R(1X1)07	77	263.41	19.26	111-C(6X6)06<250µmBIS	74.7	794.41	34.87	111-C(6X6)09B_250<Φ<2_60"	164.3	262.89	18.69
111-R(1X1)08	78	187.1	16.14	111-C(6X6)07<250µmBIS	64.4	799.27	34.5	111-C(6X6)09B_250<Φ<2BIS	164.3	291.68	19.62
111-R(1X1)09	81	236.82	17.96	111-C(6X6)08<250µmBIS	87.1	791.63	33.19	111-C(6X6)10B_250<Φ<2BIS	148.3	242.82	17.86
111-R(1X1)10	38	222.59	18.07	111-C(6X6)09<250µmBIS	75.7	913.12	35.19	111-C(6X6)09B_250<Φ<2BIS2	164.3	203.9	16.43
				111-C(6X6)10<250µmBIS	60.3	845.74	35.8	111-C(6X6)09B_250<Φ<2BIS3	164.3	341.21	21.26
				111-C(6X6)09<250µmBIS2	75.7	746.73	32.83	111-C(6X6)09B_250<Φ<2BIS4	164.3	347.2	21.24
				111-C(6X6)09<250µmBIS3	75.7	783.6	33.47				
				111-C(6X6)09<250µmBIS4	75.7	691.16	30.64				

Table 20-Results of lead concentration (ppm)

CODE	Weight	Pb	Pb Error	CODE	Weight	Pb	Pb Error
111-R(1X1)01_BIS	74	195.61	16.5	111-C(6X6)09C_250<Φ<2	163.1	237.48	17.84
111-R(1X1)05_BIS	63	241.6	18.02	111-C(6X6)10C_250<Φ<2	146.5	205.08	17.08
111-R(1X1)10_BIS	38	193.37	16.22	111-C(6X6)09C_250<Φ<2_60"	163.1	282.54	19.45
111-R(5X1)01BIS	273	218.29	17.38	111-C(6X6)09C_250<Φ<2BIS	163.1	344.72	21.25
111-R(5X1)02BIS	222	236.92	17.73	111-C(6X6)10C_250<Φ<2BIS	146.5	286.85	19.48
111-R(5X1)03BIS	290	194.36	16.47	111-C(6X6)09C_250<Φ<2BIS2	163.1	362.42	22.01
111-R(5X1)04BIS	249	305.62	20.13	111-C(6X6)09C_250<Φ<2BIS3	163.1	373.52	22.42
111-R(5X1)05BIS	141	249.21	18.29	111-C(6X6)09C_250<Φ<2BIS4	163.1	211	16.79
111-R(5X1)06BIS	314	251.87	18.73	111-C(6X6)09D_250<Φ<2	163.4	317.84	20.71
111-R(5X1)07BIS	260	226.16	17.74	111-C(6X6)10D_250<Φ<2	147.5	212.78	16.83
111-R(5X1)08BIS	285	290.12	19.87	111-C(6X6)09D_250<Φ<2_60"	163.4	283.41	19.33
111-R(5X1)09BIS	262	229.01	17.64	111-C(6X6)09D_250<Φ<2BIS	163.4	258.03	18.46
111-R(5X1)10BIS	251	231.03	17.82	111-C(6X6)10D_250<Φ<2BIS	147.5	293.18	19.46
111-R(5X1)01BIS2	273	207.66	16.99	111-C(6X6)09D_250<Φ<2BIS2	163.4	266.12	18.77
111-R(5X1)02BIS2	222	267.71	18.87	111-C(6X6)09D_250<Φ<2BIS3	163.4	243.71	18.03
111-R(5X1)03BIS2	290	242.91	18.41	111-C(6X6)09D_250<Φ<2BIS4	163.4	245.3	18.1
111-R(5X1)04BIS2	249	247.28	18.25	111-C(6X6)10RIFLE_250<Φ<2	156.3	439.3	23.78
111-R(5X1)05BIS2	141	184.16	16.03	111-C(6X6)10RIFLE_250<Φ<2BIS	156.3	300.86	19.74
111-R(5X1)06BIS2	314	254.36	18.59	OUTSIDE(1X1)01		54.79	10.81
111-R(5X1)07BIS2	260	223.14	17.38	OUTSIDE(1X1)02		33.21	8.43
111-R(5X1)08BIS2	285	361.86	21.97	OUTSIDE(1X1)_60"		47.4	9.32
111-R(5X1)09BIS2	262	234.96	17.95				
111-R(5X1)10BIS2	251	215.07	17.16				
111-R(5X1)01BIS3	273	203.58	17				
111-R(5X1)02BIS3	222	285.11	19.68				
111-R(5X1)03BIS3	290	183.7	15.8				
111-R(5X1)04BIS3	249	243.4	18.25				
111-R(5X1)05BIS3	141	158.47	17.22				
111-R(5X1)06BIS3	314	256.18	18.49				
111-R(5X1)07BIS3	260	221.16	17.5				
111-R(5X1)08BIS3	285	284.79	19.54				
111-R(5X1)09BIS3	262	227.29	17.83				
111-R(5X1)10BIS3	251	307.26	20.37				

5. LEAD QUALITY CRITERIA

As explained in the State of the art, according to the Survey of lead and lead compounds, in Denmark the concentration of lead in unpolluted areas is generally in range of 4-20 mg Pb/kg with an average of 11 mg Pb/kg soil. Besides in polluted urban areas, e.g. typical lead concentrations may be around 200 mg/kg with maximum values that exceed even 1650 mg Pb/kg, (Boyd et al., 2014), (Jensen et al., 1996).

As explained in the State of the art, Danish legislation defines soil Quality criteria and Cut-off criteria. Quality criteria is based in public health reasons and Cut-off criteria is used for immobile and slowly degradable substances. Quality criteria for soil in areas with very sensitive land use is 40 mg/kg. Criteria for necessary Lead contamination cut off is 400 mg/kg dry weight, (Danish Enviromental Protection Agency, 2002).

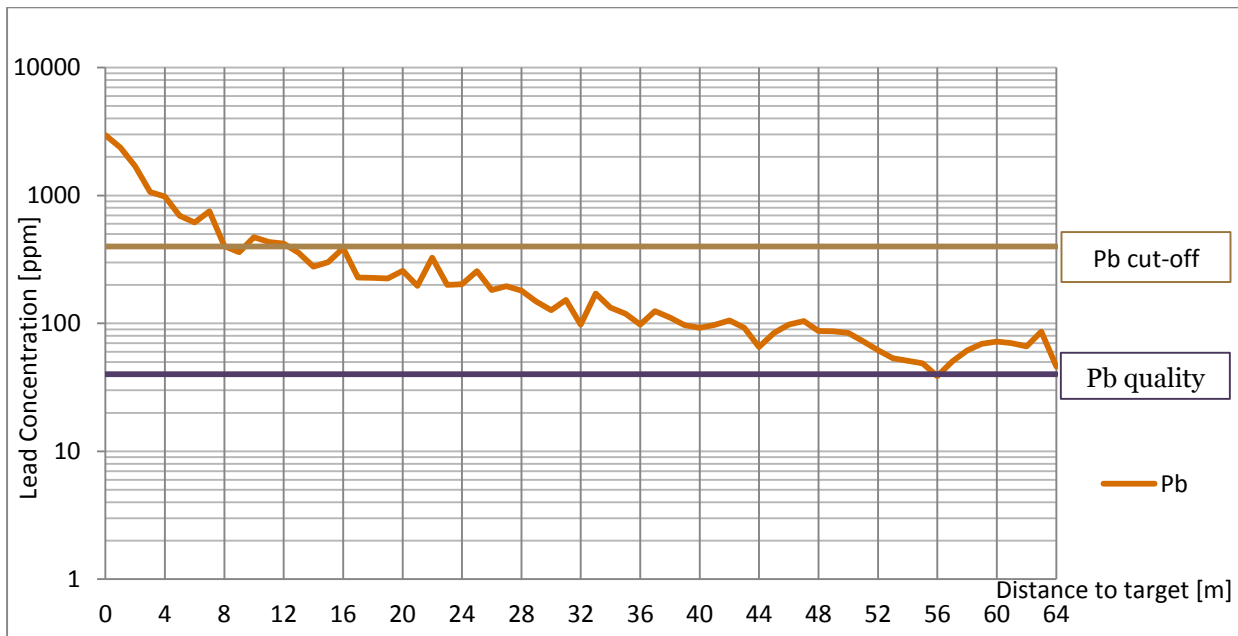
6. ANALYSIS OF LEAD CONTAMINATION

The shooting range has been divided in three different profiles, the series: A-Longitudinal profile, B-Transversal profile and S-Vertical Profile.

6.1. LONGITUDINAL PROFILE

The longitudinal profile of the shooting range is represented by the sample series A. Series A is composed by 65 soil samples. XRF analyses were developed over the whole series. Lead concentration results are shown in the following figure. The data is plotted in a log scale in order to see clearly the exponential tendency and compared with the cut-off and quality lead levels. The concentration has a range of values between 2900 mg/Kg and 45 mg/Kg. The target or impact area is he most polluted in the field.

Table 21- Longitudinal profile Sample Serie A



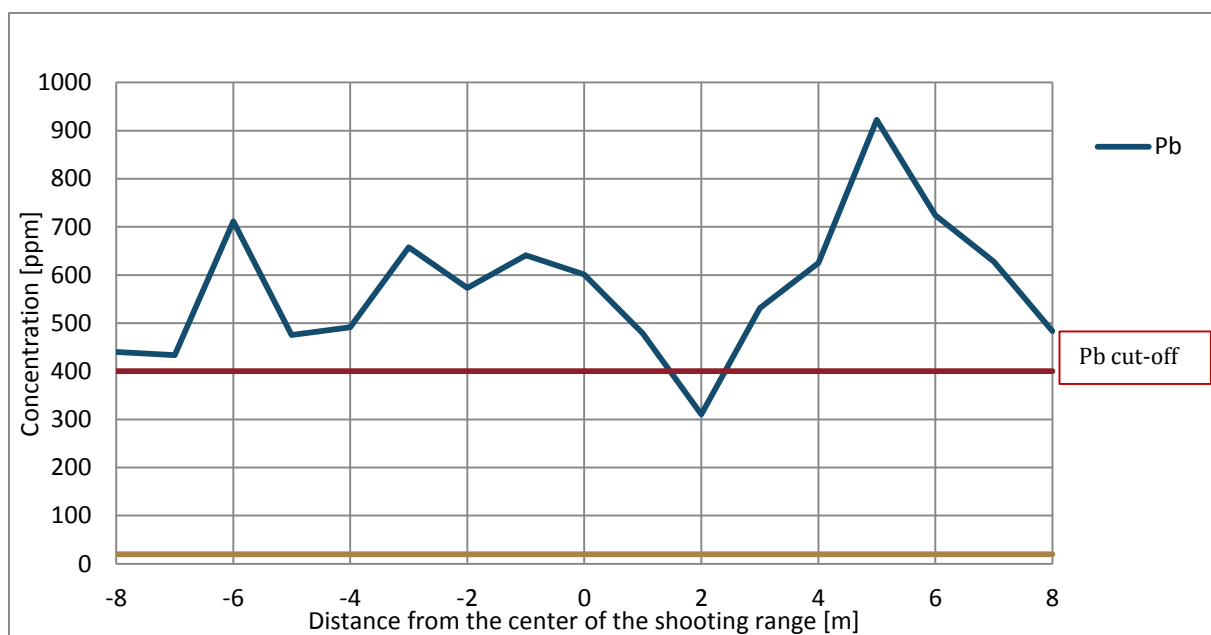
Some conclusions are extracted analysing the profile graph. Firstly, the most contaminated area is the impact area. The distribution of the lead concentration satisfies expectations, (Hardison et al., 2004). Secondly, the first twelve meters are over the lead cut-off criteria (400 ppm). Finally, in all the cases the concentration level is over the quality criteria (40 ppm).

6.2. TRANSVERSAL PROFILE

The transversal profile of the shooting range is identified by the sample series B. Series B is composed by 17 soil samples. The whole series were analysed during 30 seconds. The soil samples B00, B04, B08, B12 and B16 were tested both periods 30 and 60 seconds. The results show no significant difference between the two time periods.

Similarly to the longitudinal profile, lead concentration results are plotted in the following table. The values have an average of 572 mg/Kg.

Table 22-Transversal Profile

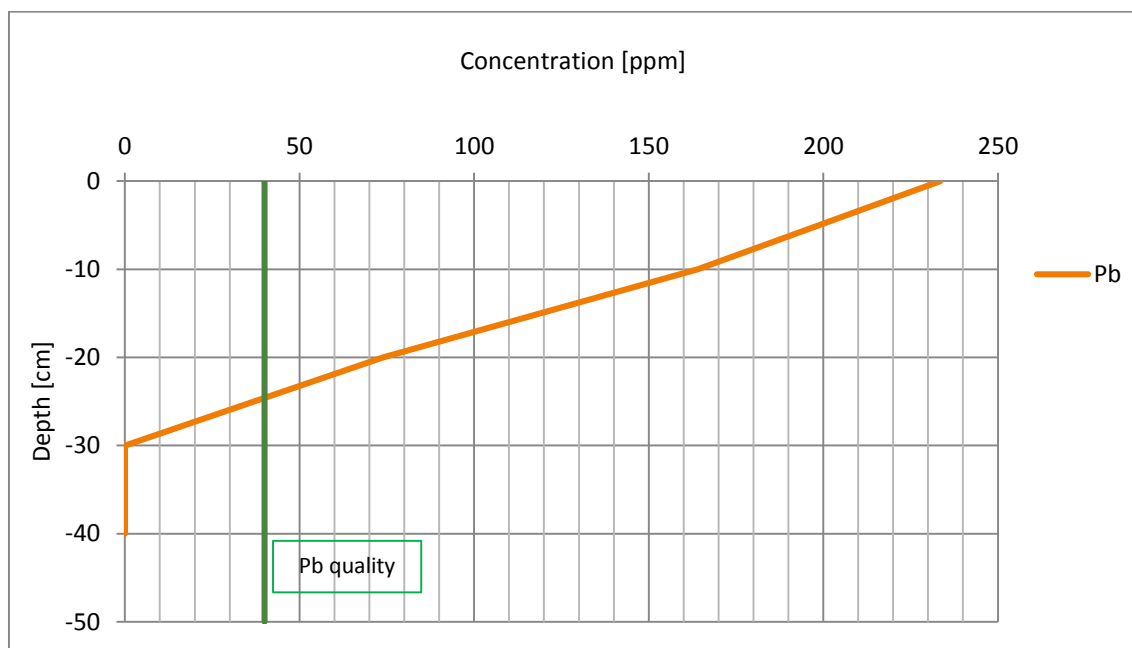


In this case conclusions are not as clear as the longitudinal profile. The endpoints are less polluted and the central part is the most contaminated.

6.3. VERTICAL PROFILE

The vertical profile of lead contamination is represented by the sample series S116. Soil samples were collected every 10 cm. The results of the lead concentration according to the depth are plotted in the table below.

Table 23-Vertical Profile



Same ways as above, some conclusions are extracted. Firstly, the tendency of diminution of lead concentration with depth is clear. Secondly, the concentration is under the lead quality criteria (40 ppm) around 25 cm of depth. Finally, these results are the representation of the lack of lead mobility in the soil.

As explained in the State of the Art of this project, lead is fairly immobile in the soil depending on the environmental conditions, PH..., (Lin et al., 1994).

6.4. OUTSIDE

One discrete sample was collected outside of the shooting range in order to know the extension of the contamination.

Table 24- Outside Shooting range lead concentration results

CODE	LEAD CONCENTRATION (ppm)
OUTSIDE(1X1)01	54.79
OUTSIDE(1X1)02	33.21
OUTSIDE(1X1)_60"	47.4

The results of the lead concentration in this point are over the lead quality criteria (40 ppm) with an average of 45,13 ppm and cannot be used as a reference of the clean soil in the area.



Figure 55-Outside reference point

6.5. MAP OF DISTRIBUTION

The following map represents the lead contamination distribution in the shooting range. The target area is the most polluted, represented by warm colours, (Borcet Rodríguez, 2014).

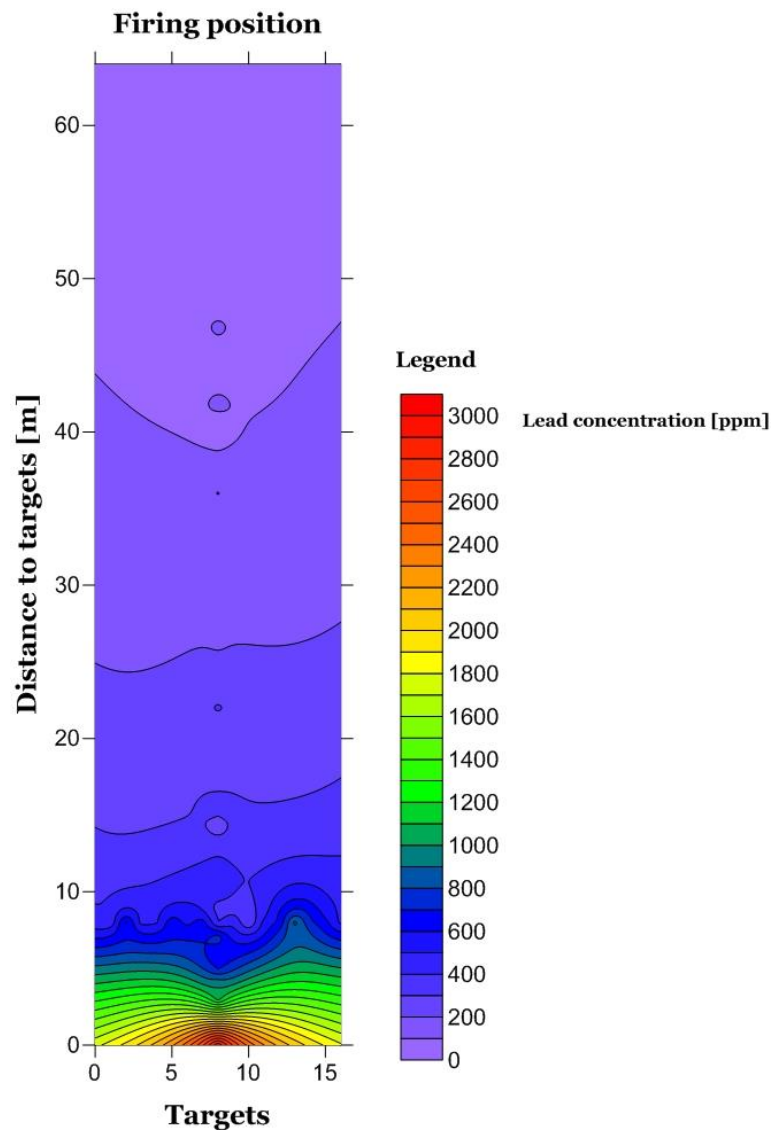


Figure 56- Lead Contamination Map in the Shooting range, (Borcet Rodríguez, 2014)

6.6. GRAIN SIZE

Lead contamination analysis is developed on soil particles selected by size. The following tables have the XRF results according to the grain size separation. Two ranges of sizes were analysed: $<250\ \mu\text{m}$ and $250\ \mu\text{m} < \phi < 2\text{mm}$.

Table 25- Pb concentration $<250\ \mu\text{m}$

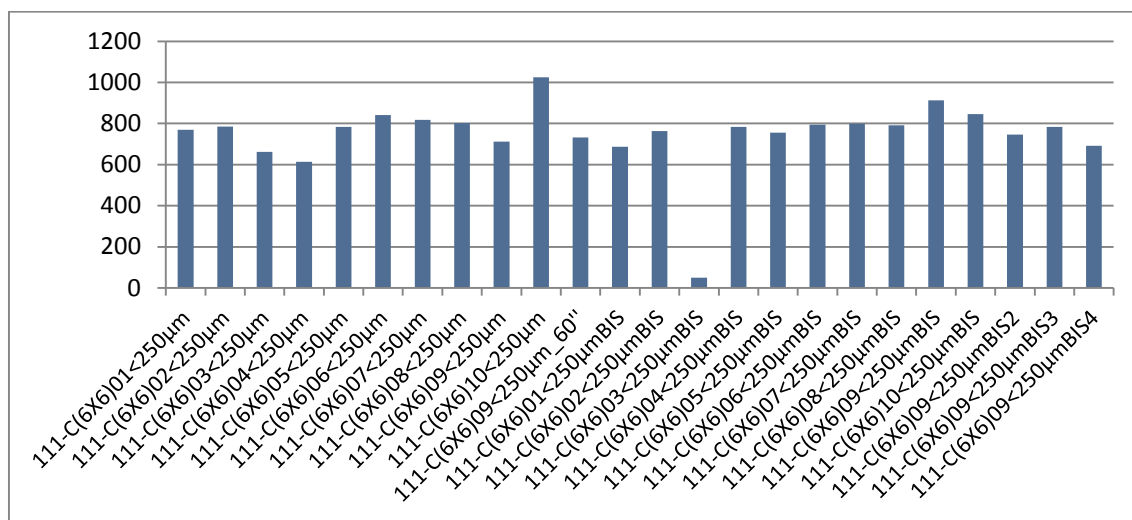
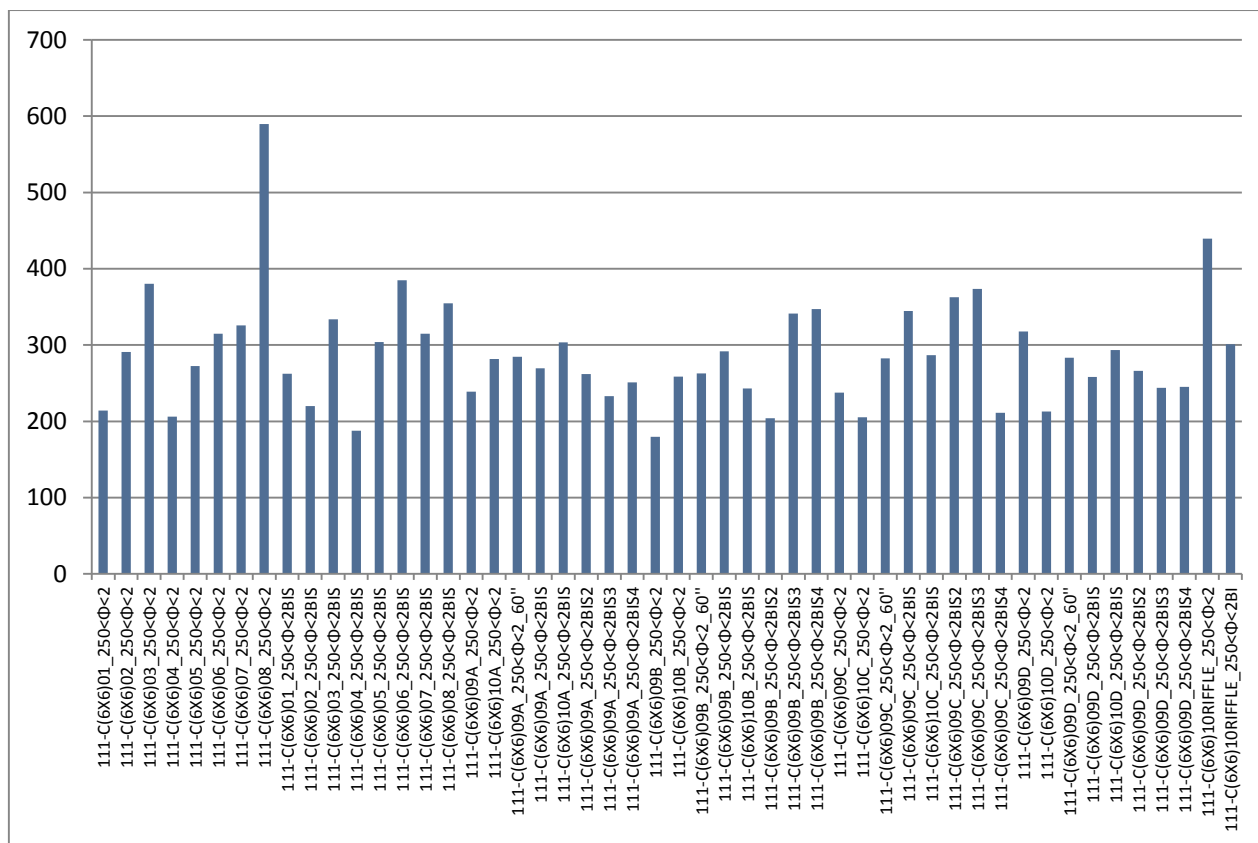


Table 26-Pb concentration $250\ \mu\text{m} < \phi < 2\text{mm}$



The first conclusion according to the results is that the most contaminated is the smallest size (<2mm). The results are twice higher than in the next range of size. The smallest size in all the cases is over the cut-off criteria (400 ppm). In both cases of grain size, lead concentration is above the quality criteria (40 ppm).

7. CONCLUSIONS AND RECOMENDATIONS

7.1. CONCLUSIONS

The shooting range is highly lead contaminated. This is the obvious conclusion that confirms the field results.

The soil is considered contaminated because all the samples are over the quality criteria stablish in Danish standards (40 ppm). All the samples collected have been useful to characterise lead distribution in the space and the grain size.

The concentration has a range of values between 2900 mg/Kg and 45 mg/Kg. Target area is the most contaminated in the shooting range. The concentration is over the cut-off lead criteria 400 ppm with a maximum value of 2.900 mg/Kg.

Lead contamination is concentrated in the smallest grain size (<250 µm) with values around 800 mg/Kg.

Lead pollution is concentrated in the first 25 cm of depth. According to that, lead is considered immobile in the soil.

Soil samples analysed contain gross contamination such as bullets, bullet fragments and shells.

Outside the shooting range lead concentration is also above the quality criteria (40 ppm) with 45.3 ppm. As a result, the data can not be used as a reference of clean soil.

7.2. RECOMMENDATIONS

Lead concentration in Viborg shooting range is above the quality criteria of 40 mg/kg and in most of the cases above the cut-off criteria of 400 mg/Kg. The concentration has a range of values between 2900 mg/Kg and 45 mg/Kg. The main recommendation is to reduce the risk of lead exposure. The risk is considered intolerable according to the Danish Standards.

Lead contamination is concentrated in the smallest grain size (<250µm). Consequently, physical separation as a first treatment step is recommended in order to separate the most concentrated part, the organic matter, the no polluted soil fraction and the rest of bullets. However, a deeper analysis of lead contamination versus soil grain size should be developed.

Because of the lead pollution concentrated the first 25 cm of the vertical profile, the remediation proposal may be concentrated in this first soil layer.

Remediation process may be considered in a larger area than the shooting range field, because the lead contamination is spread outside the shooting range. Moreover, a deeper analysis of lead concentration in the surroundings is also recommended.

8. PICTURES REPORT



Figure 57- Bagged soil sample arrived at the Geo Laboratory.



Figure 58- Air-dry process



Figure 59- Soil samples during Air-dry process



Figure 60- Soil Sample 112-C-01



Figure 61- Soil sample disaggregation process



Figure 62- Soil sample before disaggregation process



Figure 63- Granulometry



Figure 64- Granulometry division



Figure 65- Samples after granulometry division



Figure 66- Big particles (>2mm) and bullets



Figure 67- Soil sample



Figure 68. Sub-sampling



Figure 69- Sub-sampling



Figure 70- XRF Test



Figure 71- XRF Test



Figure 72- XRF Test



Figure 73- XRF Test

6. LEAD REMOVAL TEST REPORT

1. INTRODUCTION

This report is part of the final dissertation about lead contaminated soil in a shooting range in Viborg, Denmark. One of the objectives of this dissertation is to propose a remediation technology applied to a real case. The analysis of the different remediation techniques includes a cleaning test. This report includes the objectives, methodology, results and conclusions of the cleaning test.

The goal of this dissertation is to find an environmental friendly and effective remediation technique applied in a real case following the Danish standards.

As previously mentioned in the state of the art, the most eco-friendly remediation technology is the Phytoremediation. Phytoremediation tests take years to develop because plants are tested during the growing up. Furthermore plants take a long time to grow up in a Nordic Country. Therefore, Phytoremediation technology cannot be tested during this final dissertation.

Chemical extraction is the most effective remediation technology, but its environmental footprint is very high. New biodegradable chelant agents are tested in washing techniques. Chemical extraction usually is combined with Physical separation in washing techniques in order to make the cleaning more effective.

The objective of the test is to evaluate the effectiveness of the most common agent EDTA compared with a new biodegradable chelant, GLDA, combined with a Physical separation. Lead removal test reproduces in bench-scale the performance of the full-scale process in order to study the treatability of Viborg soil.

2. BACKGROUND

The shooting range is located in Viborg, Denmark. The soil is highly lead polluted as has been demonstrated in this dissertation. Field and laboratory test has proved lead contamination, as was explained in the Field sampling report and contamination laboratory report.

Lead contamination is over the quality criteria established in Danish legislation. All the samples analysed were over the quality criteria located in 40 ppm. Target area is the most contaminated in the shooting range. The concentration is over the cut-off lead criteria of 400 ppm.

Lead contamination is concentrated in the smallest grain size (<250 μm) and the first 25 cm of depth. Soil samples analysed contain gross contamination such as bullets and shells.

Outside the shooting range lead concentration is also over the quality criteria (40 ppm).

3. CLEANING OBJECTIVES

The cleaning objectives are established in the Danish legislation, as was explained before. The cleaning objectives are the same values as the ones used to compare the lead pollution. The objective of this test is to reduce lead contamination under the lead quality criteria level.

Danish legislation defines different soil quality criteria and Cut-off criteria. Quality criteria are based in public health reasons and Cut-off criteria are used for immobile and slowly degradable substances. Lead Quality criteria is 40 mg/kg dry weight and contamination cut off is 400 mg/kg DW, (Danish Environmental Protection Agency, 2002).

The cleaning objective is to reach the quality criteria of 40 ppm.

4. METHODOLOGY

The lead removal test is done following the methodology of a column test. The column test consists of passing a fluid through the soil and analyse the washing effluent and the soil.

The figure below represents the column test methodology that the test follows. The pump pumps a flow of 1.2 ml/min of washing solution through a soil column of 1.9 cm of diameter. After the washing process the effluent and the cleaned soil are analysed.

In order to have data about the lead removal, lead content in soil is analysed before and after the washing process. The methodology is the same followed in the contamination analyses, using the XRF of NIRAS.

In order to have information about in which washing step lead is removed, the effluent is collected and analysed in 3 washing steps. The methodology to analyse the effluent is using the UV/VIS spectrophotometer and the Atomic Absorption Spectrometer (AAS), (Dansk Standard, 1982).

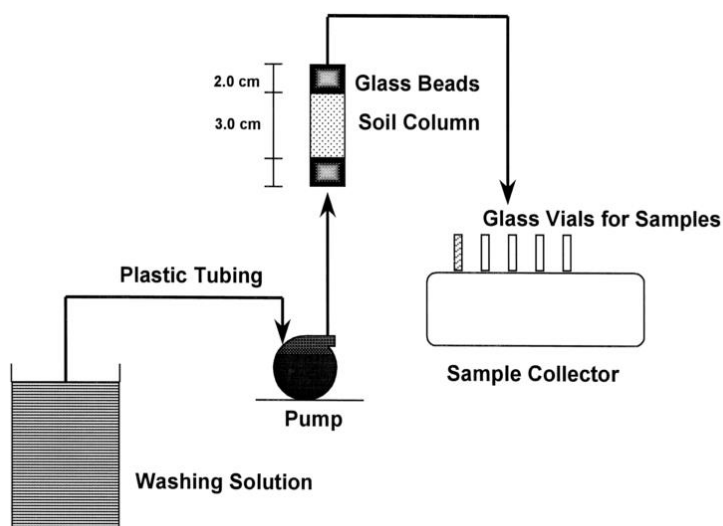


Figure 74- Column test methodology, (Abumaizar & Smith, 1999)

4.1. COMBINATIONS AND VARIABLES

On the one hand, there are 3 different cases to evaluate depending on the product used in the washing: DI water, EDTA, GLDA. The chelant agents EDTA and GLDA are evaluated using two different concentrations. Literature resources are used to select chelant agent concentrations.

On the other hand, the evaluation will be developed over natural soil or Physical separated soil.

The soil Physical separation is in 3 different sizes. The determination of the sizes depends on the grain size lead contamination analyses. The size analysis developed in the contamination laboratory report is a first approach. In order to select properly the different sizes to clean, a deeper size contamination analysis is needed.

The removal of the lead is analysed in 3 different washing steps. Finally, 3 replicates are needed in order to achieve statistically accurate information. The following table represents the combinations and the code used.

Table 27- Variables and Combinations

WASHING PRODUCT		Natural soil (NS)	Size Selected (SS)		
			$\varnothing < 150 \mu\text{m}$ Small (S)	$150 \mu\text{m} < \varnothing < 500 \mu\text{m}$ Medium (M)	$500 \mu\text{m} < \varnothing < 2\text{mm}$ Large (L)
DI water		NS-DIW-REP _x -W _x	S-DIW-REP _x -W _x	M-DIW-REP _x -W _x	L-DIW-REP _x -W _x
EDTA	0.01 M	NS-ED1-REP _x -W _x	S-ED1-REP _x -W _x	M-ED1-REP _x -W _x	L-ED1-REP _x -W _x
	0.05 M	NS-ED5-REP _x -W _x	S-ED5-REP _x -W _x	M-ED5-REP _x -W _x	L-ED5-REP _x -W _x
GLDA	0.01 M	NS-GL1-REP _x -W _x	S-GL1-REP _x -W _x	M-GL1-REP _x -W _x	L-GL1-REP _x -W _x
	0.05M	NS-GL5-REP _x -W _x	S-GL5-REP _x -W _x	M-GL5-REP _x -W _x	L-GL5-REP _x -W _x

CODE: AA-BBB-REP_x-W_z

AA: NS: Natural soil, S: Small size, M: Medium Size, L: Large Size

BBB: DIW: Deionized Water, EDTA0.01 M, EDTA 0.05M, GLDA0.01M, GLDA0.05M

REP_x: Replicate Number 1, 2 or 3.

W_z: Wash Number 1, 2 or 3.

5. GRAIN SIZE CONTAMINATION ANALYSIS

Grain size contamination analysis is needed in order to select Physical separation as a remediation technology.

The first approach of grain size contamination analysis was developed previously in the Contamination Analysis Report. Two ranges of sizes were analysed: under 250 μm and between 250 μm and 2mm. The size under 250 μm has an average of lead concentration of $690,69 \pm 32,62$ ppm. The size between 2mm and 250 μm has a lead concentration of $279,39 \pm 19,23$ ppm. The most contaminated is the smallest size (<250 μm). The results are double than in the next range of size. The smallest size in all the cases is over the cut-off criteria (400 ppm). In both cases of grain size, lead concentration is over the quality criteria (40 ppm).

However, deeper analysis is needed to select the grain size to clean. Lead concentration and grain size have to be compared including the cleaning objectives. Depending on the results it can be established a limit size for cleaning; selecting a fraction of soil in the washing is not necessary or delimiting same ranges of contamination.

For this purpose two soil samples have been sieved and analysed. The contamination analyses have been done over the samples C-107-C01 and 112-01-4x14. The contamination analyses have been done as in the Contamination Analysis Report, using the XRF NITON in the NIRAS office in Aarhus. The results are showed in the figures below.

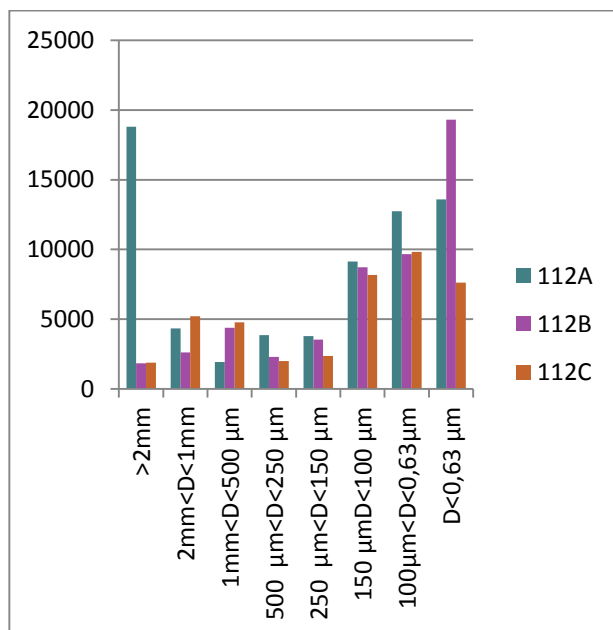


Figure 75-Lead Concentration (ppm) Vs Grain size in sample 112

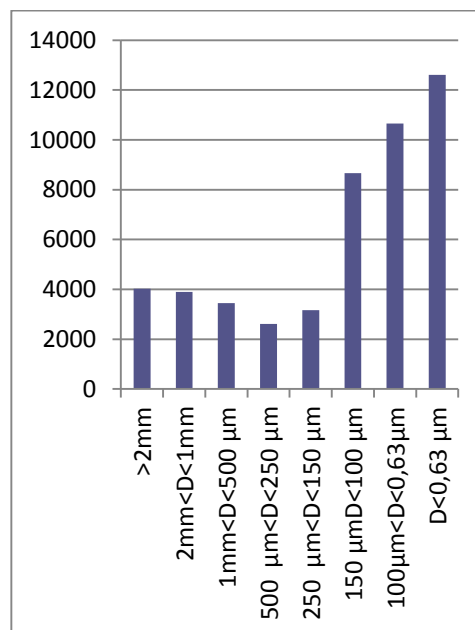


Figure 76-Average of Lead Concentration in sample 112

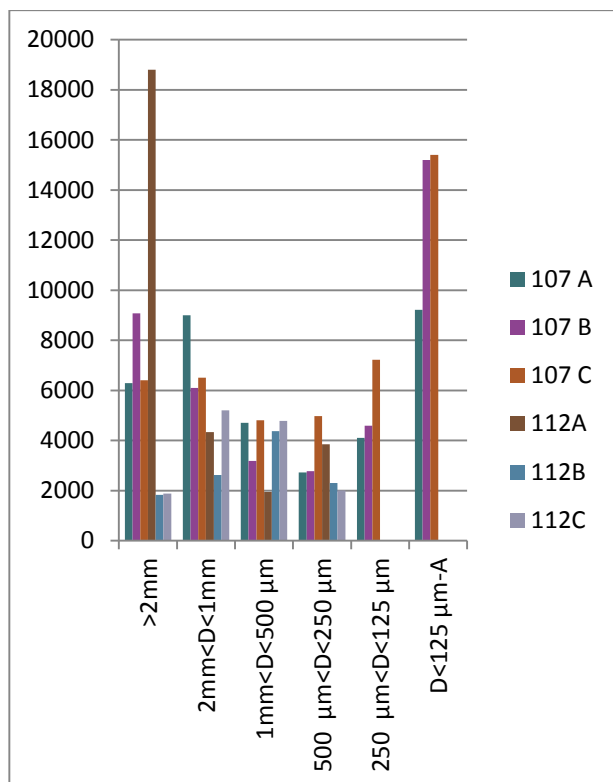


Figure 77-Lead Concentration (ppm) Vs Grain size sample C-107

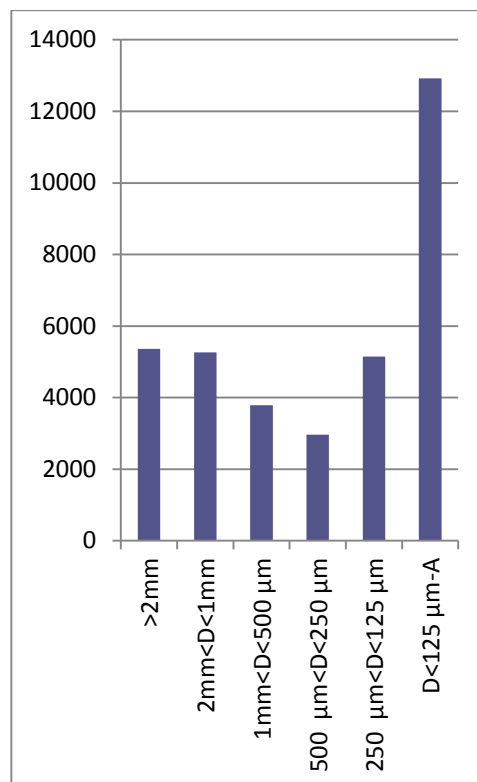


Figure 78-Average of lead Concentration in sample C-107

Lead concentration is in all the cases over the quality criteria established in Danish legislation (40 and 400 ppm). There is not clean fraction, so all of them should be considered. The smallest grain size is the most contaminated. The values are almost near twice higher than those found in the other range of grain size. The minimum level of contamination is located in the grain size between 250 µm and 500 µm.

For this reason, the size limits for the column test are located in bigger than 500 µm (LARGE), between 500 µm and 150 µm (MEDIUM) and smaller than 150 µm (SMALL). This grain size separation in a column test is comparable with Physical separation process in a real scale soil cleaning.

6. PH ANALYSIS

6.1. PH METHODOLOGY

The pH is an indicator of the amount of $[H^+]$ in the solution is formed by putting a certain amount of distilled water in contact with a quantity of soil. Therefore, the pH is used as an indicator of the concentration of hydrogen ions in the soil. The pH is represented in a logarithmic scale ($pH = -\log [H^+]$).

The effectiveness of the chemical extraction depends on the pH of the soil. Chemical extraction is based in the pH reduction in order to increase lead mobility.

Soil pH is analysed following the procedure of the ISO 10390:2005 about Soil quality-determination of PH. The procedure consists in a preparation of a suspension using 5 ml of soil, sample 112C01-4X14 and 5 times of demineralized water. The suspension is shaken during 1 hour and waited 1 hour. The analysis should be done before a period of 3 hours.

The pH meter used is the PH/Cond 340i/SET of the Geo lab of VIA University Collage. The pH meter is calibrated using the control solutions before starting.

The test is done over the sample 112-C-01-4x14. The test is done over three different replicates of the same sample. The pH is measured twice per replicate in order to have statistically accurate information.

6.2. RESULTS AND INTERPRETATION

The following table show the results of the pH Analysis.

Table 28- Soil pH results

SAMPLE	pH
112C01-4X14-R1	2,01
112C01-4X14-R1bis	1,96
112C01-4X14-R2	1,99
112C01-4X14-R2bis	2,00
112C01-4X14-R3	2,03
112C01-4X14-R3bis	2,17

When the soil has a high hydrogen concentration, it is considered as basic, however, when having a low concentration it is considered acidic. The soil pH value is usually between 4 and 9.

In this case the pH has an average of 2.02. According to this value, the soil is denominated acidic.

7. WASHING SOLUTION

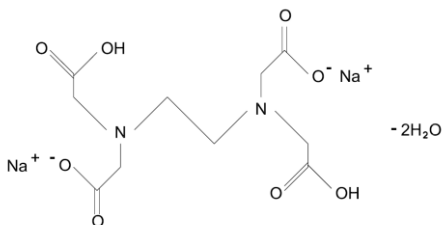
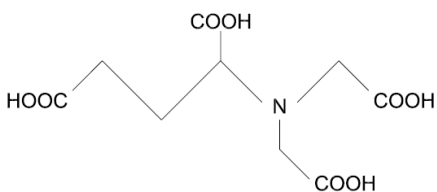
The column test uses 2 different chelating agents to wash the soil, EDTA and GLDA. In order to make comparison, deionized water is used.

EDTA is the most common chelant agent used in chemical extraction. Its effectiveness has been tested since the decade of the 90. GLDA is a new biodegradable chelant agent.

The main advantage of GLDA compared with EDTA is the low environmental footprint, as was explained in the State of the Art.

The following table shows the main data of the chelating agents.

Table 29-Chelant agents

	EDTA	GLDA
Chemical name	<i>Ethylenediaminetetra-acetic acid disodium salt dihydrate</i> , EDTA-Na ₂	<i>Glutamic acid, N, N-diacetic acid</i> GLDA-H ₄
Structure		
Chemical formula	C ₁₀ H ₁₄ N ₂ Na ₂ O ₈ ·2H ₂ O	GLDA-Na ₂
Company	VWR Chemicals	Akzo Nobel
Market product	EDTA disodium salt dihydrate TECHNICAL 1kg	Disolvine GL-47-S
Physical form	Powder	Liquid
Molecular Mass	372.24	351.1

7.1. WASHING SOLUTION VOLUME

The washing volume is given by the literature. The washing volume is measured in pore volume. The Pore Volume is calculated following this equation, (Wasay et al., 2001):

$$V_p = \frac{f}{100} * \pi * r^2 * h$$

Where V_p is the pore Volume (ml or cm³) of the soil column r (cm) of radius and h (cm) of height and f porosity.

The total washing volume used in the lead removal test takes into account the saturation volume. The saturation volume is calculated using the porosity.

Finally, the washing volume is 150 ml. There are 3 steps to analyse in the washing process.

7.2. CHELANT AGENTS EFFICIENCY

Chelant agent efficiency is compared with deionized water removal. The following figure shows the expected efficiency in the DI water.

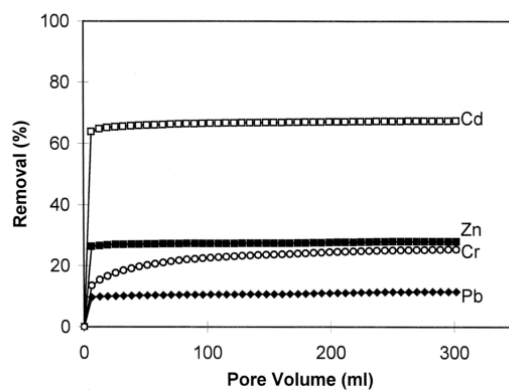


Figure 79-DI water efficiency Vs Pore Volume, (Abumaizar & Smith, 1999)

The following figure shows Lead removal efficiency versus the Pore Volume from recent research on contaminated soil, (Wasay et al., 2001). According to the literature, in the case of EDTA, the Maximum Efficiency is with 20 V_p .

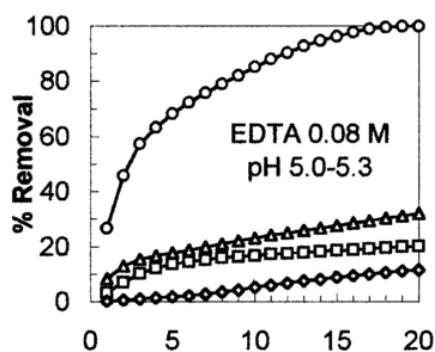


Figure 80-Lead Removal (o - Pb) using EDTA Vs Pore Volume, (Wasay et al., 2001)

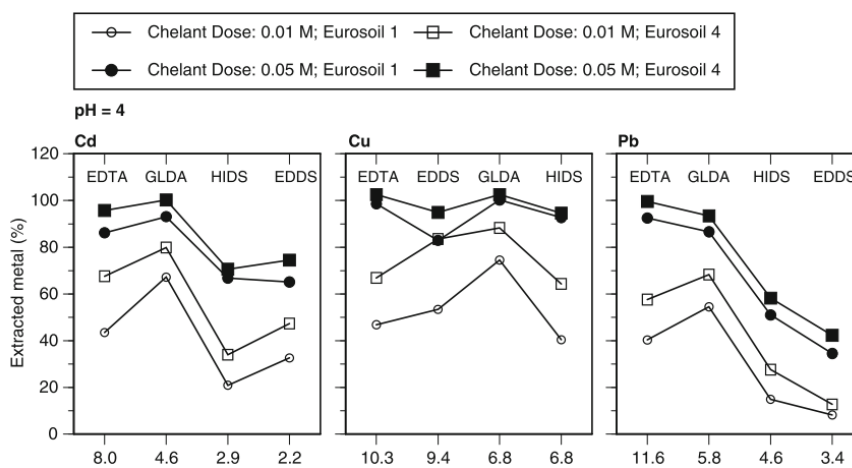


Figure 81- Metal extraction using EDTA and GLDA

According to the literature, the lead removal expected in the case of the EDTA is in a range of 60-100% of effectiveness. Moreover, the GLDA lead removal expected is a range of 40-100 %. Removal efficiency of DI water is very low in a column test.

7.3. CHELANTING AGENTS ENVIRONMENTAL FOOTPRINT

The main objective is to find an eco-friendly solution for lead contaminated soil. Soil washing evolution should be in the way of reducing the environmental impact.

The environmental impact is measured by the environmental footprint. The following figure shows the foot print of the chelant agents used in the lead removal test. GLDA causes less environmental impact. The reason is that GLDA is composed by renewable raw materials and is easily biodegradable.

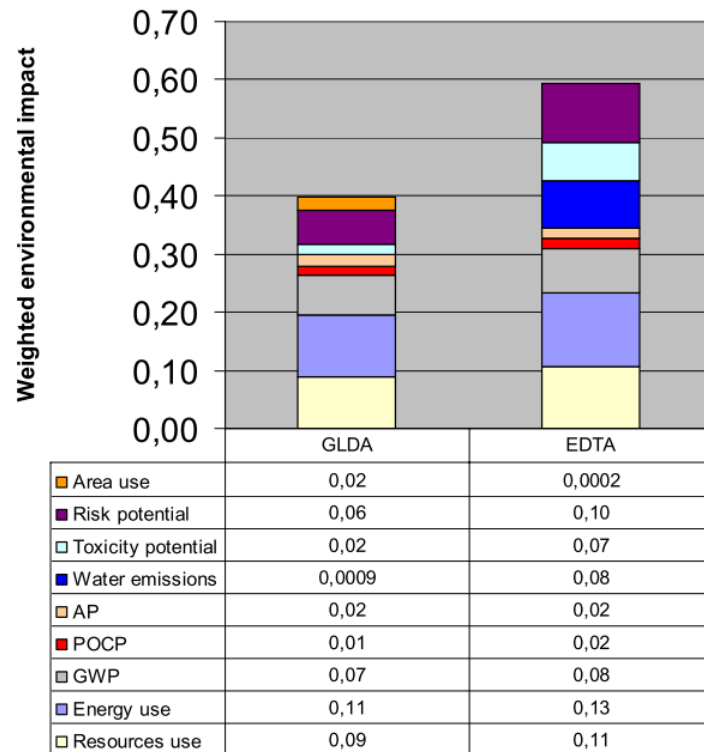


Figure 82-Environmental impact of chelating agents, (Borén et al., 2009)

8. LEAD REMOVAL TEST PREPARATION

8.1. CONFIGURATION

The column test is built in the geo lab in VIA University College. The test is carried on according to the literature, as was shown before, (Abumaizar & Smith, 1999).

The column test uses the Pump Master Flex LS 7524-55 to make the cleaning fluid pass through the contaminated soil. The accurate tubing size for the flow is L/S14. The soil is collected in 20 ml syringes and there are glass beads to make the flow homogenous. The output fluid is collected in 100 ml glass columns. Then 30 ml are collected using plastic sample collectors.

The 20 ml syringes are filled with 2cm of glass beads, 5 cm of contaminated soil and other 2 cm of glass beads.

According to the literature, the ratio between soil and solution is 1:5 (w:v), (Tejowulan & Hendershot, 1998). The volume of soil is 15,7 cm³. The density in dry conditions is 1,31 g/cm³. Each syringe has 20,5 grams of soil.

The three replicates can be done at the same time because the pump can be used with three tubing.

8.2. MATERIALS

The materials used to develop the lead removal test are:

- PUMP: Master flex LS 7524-55
- PLASTIC TUBING: L/S 14
- GLASS BEADS: 0.5mm
- SOIL SAMPLE: Collected in plastic syringe 20 ml.
- SAMPLE COLLECTOR: 100ml
- PLASTIC SAMPLE COLLECTORS: 30 ml

8.3. SOIL SAMPLE PREPARATION

Contaminated soil is collected in 20 ml plastic syringes. According to the number of tests and the replicates, the total number of syringes is 60.

The sample used in the column test is the S-01-116. The sample is divided using the sub-sampling machine, the same one used before in the Contamination Analysis Report.

The following table shows the calculation of soil sample needed in the column test. The percentages used are obtained from the Granulometry.

Table 30-Soil Sample calculation

TYPE OF SOIL	Nº	Grams/Syringe	Weight proportion	%	Sample
Natural Soil	15	20	300	100	300
Small Size Selected Soil <150 µm	15	20	300	2.5	12.000
Medium Size Selected Soil 500 µm>D>150 µm	15	20	300	40	750
Large Size Selected Soil 2mm >D>500 µm	15	20	300	35	860
TOTAL	60				13.910 g

The column test is done over the same soil sample collected in the Field Sampling Report.

The sample S-01-116 has a total weight of 20,5 kg in wet conditions. The bag is divided in 8 identical parts of 2,5 Kg. One of these parts is divided again in 8 parts of 312,5 grams. The Natural Soil sample is one of these parts. The rest is grain size selected and combined in order to have the same size samples.

The contaminated soil used in the column test is firstly dried. Secondly divided and finally is sieved according to the large, medium and small fractions considered.

8.4. VERIFICATION

Before the test starts, it is necessary to verify the system operation and components. Firstly, is necessary to determine whether the UV/VIS spectrophotometer can be used in the presence of chelant agents. Secondly, is necessary to verify that the system does not absorb lead. Finally, all the devices used have to be calibrated.

Verification process uses a solution of lead and Hydrochloric. A little 3 grams piece of lead is solved in 100 ml of 10 % HCl, Technigrade from Applichem and deionized water to have one litre. This lead and 1% HCl solution is called Standard Solution (SS).

In order to known if the spectrometer can be used in a presence of chelant agents, different EDTA solutions are used combined with the SS. Lead solutions are tested before and after adding EDTA. If the results show the same concentration of lead, it means that the spectrometer is accurate in a presence of lead. The UV/VIS spectrophotometer is the Hach Lange model present in the geo lab in Via University.

The following table shows the result of the different solutions of the SS-EDTA and the lead content.

Table 31-Verification test results using SS

HCl	EDTA	comment	Lead
%	M		mg/l
1,00	0	Standard Solution	Over Range
0,5	0		Over Range
0,1	0		0,818
0,1	0		0,906
0,1	0		0,928
0,1	0		1,24
0,1	0		1,11
0,1	0		1

HCl	EDTA	comment	Lead
0,1	0,05	NO SOLVE	
0,1	0,02	NO SOLVE	
0,1	0,01	NO SOLVE	
0,1	0,005	NO SOLVE	
0,1	0,0025	NO SOLVE	
0,01	0,0025		-0,011
0,01	0,0025	Under measuring range	0,01
0,05	0		0,522
0,05	0,005	Under measuring range	0,021

According to the results, the SS is too acid and the EDTA cannot be solved on it. Another solution is needed to verify the using of the UV/VIS spectrophotometer.

The new solution called Standard Solution 2 is made using Lead nitrate ($\text{Pb}(\text{NO}_3)_2$). In this case the pH was controlled during the procedure. The following table shows the results of the Standard Solution 2 combined with EDTA.

Table 32-Verification test using the second Standard Solution

$\text{Pb}(\text{NO}_3)_2$	EDTA	Lead mg/l	PH
1mg/l	0 M	1,55	1,62
1mg/l	0,05 M	0,013	3,62

According to the results, the UV/VIS spectrophotometer cannot be used in order to measure the washing effluent of the column test when chelating agent is used. The washing effluent when using a chelating agent should be analysed using an Atomic Absorption Spectrometer. Subsequently, the measuring process cannot be done in VIA University Collage. The only washing effluent that can be analysed using the UV/VIS spectrophotometer is the deionized water.

Otherwise, once the column test is built is necessary to verify that the system does not absorb lead. On this purpose the first Standard Solution is used with clean sand. Two different sands are used: silica sand from de Geo lab and another one that comes from the Concrete lab. SS is pumped through the clean sand and the washing effluent is analysed. Lead concentration before and after the washing process has to be similar if the system does not absorb lead. If the results after the washing are significantly low compared with the results before, the column test absorbs lead. The SS is used in two washing process. The first washing is not the most accurate because it can be interferences due to the humidity of the sand and the water inside the tubing. The second washing is done complete with the SS and there is not interference with water. The following tables show the results before and after the column test with the SS.

Table 33-Absortion Verification-Lead content in the SS before the column test

HCl (%)	Lead (mg/l)
0,1	0,818
0,1	0,906
0,1	0,928
0,1	1,24

HCl (%)	Lead (mg/l)
0,1	1,11
0,1	1,00

Table 34-Absortion Verification-Lead content after the column test

		HCl 0,1 (%)	Lead (mg/l)
Geo lab sand	1st Wash	75 ml	1,46
	2nd Wash	75 ml	1,38
Concrete lab sand	1st Wash	75 ml	0,203
	2nd Wash	75 ml	0,986

The results before the washing using the SS are an average of Lead Content of 0,991 mg/l and a deviation of 0,14 mg/l. The results after the washing process, especially after the second washing are 1,38 mg /l and 0,986 mg/l.

According to the results the system does not absorb lead. The results after the washing process are within the expected margin. The main conclusion is that the column test assembled in the Geo Lab can be used with fluids that contain lead.

9. LEAD REMOVAL TEST DEVELOPMENT

The Deionized Water situation and the EDTA in both concentrations were developed without any problem.

The case of the smallest grain size and GLDA in both concentrations were failures. In the case of S-GLDA0.01M during the first washing step the pressure inside the syringes was so high, that in the replicate number one and two the connection between syringe and the tubing from the pump went out. During the second washing step the cover was left in the replicate number 3. In the case of GLDA 0.05M the failure happened during the first washing step. The fine particles are light and during the washing process they make a separation between the bottom glass beads and the soil. The fine particles on the top can pass through the glass beads, mixing them. But finally the system is blocked.

There is no explanation for the failure. The flux and the glass beads were exactly the same quantity so there is not a problem with the weight of the soil and the glass beads. The separation between glass beads and the soil took place in all the cases of the small size. But only in the case of the GLDA they mixed with the glass beads trying to get away of the syringe. Therefore, the GLDA and small size cases should be considered for further research.

10. RESULTS

According to the methodology, the analysis is done over the washing effluent once the washing solution has passed through the contaminated soil.

10.1. VISUAL APPROACH

The first approach to the results is the visual inspection of the washing effluent. The input liquid is transparent in all the cases. The turbidity of the washing effluent is higher with the washing agents EDTA and GLDA than with the deionized water. The case of the GLDA presents the highest turbidity with a total black liquid in the first washing step in both concentrations. This difference in the turbidity suggests that the chelant agents have more ability of cleaning than the deionized water and in the same manner GLDA has more cleaning power than EDTA. The darkness of the GLDA is justified by the organic matter. GLDA reacts with the organic matter and turns it into a very dark liquid.

10.2. ANALYSES OF WASHED SOIL-XRF RESULTS

The washed soil is analysed using the XRF before and after the washing.

Lead content before and after the soil washing process is showed in the following table, as the same the lead removal is calculated and represented by a percentage. The total data extracted using the XRF are included in the Appendix 2 of this final dissertation.

Table 35-Lead Content before and after soil washing and % of removal

CODE	Pb (ppm)	REMOVAL %	CODE	Pb (ppm)	REMOVAL %
NS	323,3		M	236,0	
NS-DIW-REP1	237,0	26,7	M-DIW-REP1	272,4	-15,4
NS-DIW-REP2	220,5	31,8	M-DIW-REP2	389,0	-64,8
NS-DIW-REP3	219,8	32,0	M-DIW-REP3	221,9	6,0
NS-ED1-REP1	52,5	83,8	M-ED1-REP1	64,8	72,6
NS-ED1-REP2	55,3	82,9	M-ED1-REP2	64,5	72,7
NS-ED1-REP3	61,8	80,9	M-ED1-REP3	62,1	73,7
NS-ED5-REP1	52,5	83,8	M-ED5-REP1	60,9	74,2
NS-ED5-REP2	78,5	75,7	M-ED5-REP2	55,1	76,7
NS-ED5-REP3	124,9	61,4	M-ED5-REP3	62,1	73,7
NS-GL1-REP1	138,4	57,2	M-GL1-REP1	90,1	61,8
NS-GL1-REP2	110,9	65,7	M-GL1-REP2	83,8	64,5
NS-GL1-REP3	111,4	65,5	M-GL1-REP3	95,2	59,7
NS-GL5-REP1	103,3	68,1	M-GL5-REP1	73,1	69,0
NS-GL5-REP2	87,2	73,0	M-GL5-REP2	84,8	64,1
NS-GL5-REP3	68,9	78,7	M-GL5-REP3	109,1	53,8
S	1055,4		L	231,8	
S-DIW-REP1	465,7	55,9	L-DIW-REP1	210,1	9,4
S-DIW-REP2	511,4	51,5	L-DIW-REP2	114,5	50,6
S-DIW-REP3	550,6	47,8	L-DIW-REP3	148,3	36,0
S-ED1-REP1	216,3	79,5	L-ED1-REP1	86,7	62,6
S-ED1-REP2	159,2	84,9	L-ED1-REP2	73,0	68,5
S-ED1-REP3	147,6	86,0	L-ED1-REP3	73,3	68,4
S-ED5-REP1	151,1	85,7	L-ED5-REP1	128,6	44,5
S-ED5-REP2	160,2	84,8	L-ED5-REP2	215,3	7,1
S-ED5-REP3	172,1	83,7	L-ED5-REP3	63,1	72,8
S-GL1-REP1			L-GL1-REP1	66,7	71,2

CODE	Pb (ppm)	REMOVAL %	CODE	Pb (ppm)	REMOVAL %
S-GL1-REP2			L-GL1-REP2	79,5	65,7
S-GL1-REP3			L-GL1-REP3	71,5	69,2
S-GL5-REP1			L-GL5-REP1	66,7	71,2
S-GL5-REP2			L-GL5-REP2	138,5	40,2
S-GL5-REP3			L-GL5-REP3	109,7	52,7

10.3. ANALYSES OF THE WASHING EFFLUENT-UV/VIS SPECTROPHOMETER RESULTS

According to the verification process of the measure system, the spectrometer is used in the case of the deionized water. Output Deionized Water were analytically analysed using the spectrometer of mass present in the VIA Geolab. The following figure shows the low results of the removal in the different soil cases.

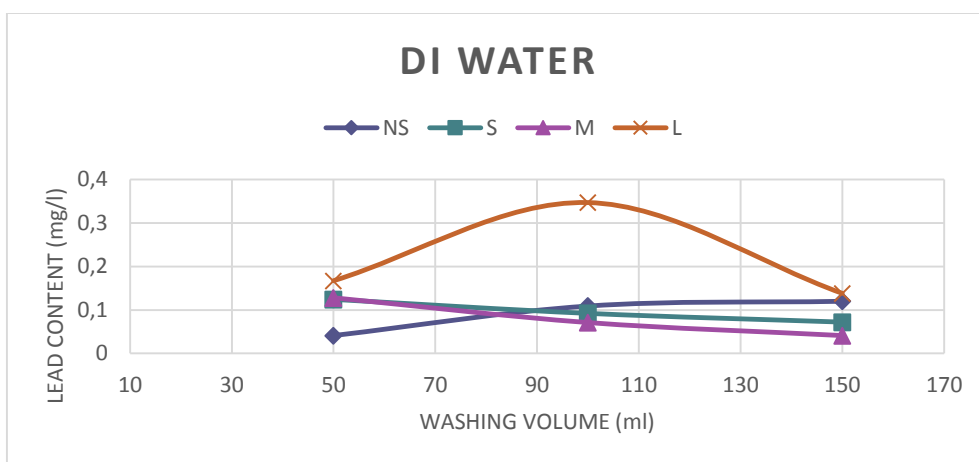


Figure 83-DI Water and different soils lead removal

Lead in water is justified by the dissolution of the smallest fraction, and there is no relevant lead concentrations washing with DI Water.

10.4. ANALYSES OF THE WASHING EFFLUENT-ATOMIC ABSORPTION SPECTROMETER

Unfortunately, the results of the washing effluent using the AAS could not be on time because the availability of the laboratory depends on CPH Business Lab, located in Hillerød.

The test using the AAS will be performed the 1st and 2nd of September and presented in front of the panel. As a consequence, by the moment there is no discussion of lead removal versus washing step.

11. DISCUSSION OF THE XRF RESULTS

11.1. DI WATER

The following table shows the results of the Deionized water over the different soil types. Deionized Water has not cleaning properties. According to the literature, the deionized water removal is the fraction of the lead that is weakly bound to the soil particles and readily available for mobilization, (Abumaizar & Smith, 1999).

Table 36-DI Water lead removal (%)

	SOIL	REMOVAL
DI WATER	NS	30,2
	S	51,7
	M	-24,7
	L	32,0

The case of the medium size soil has a negative result because there is not lead removal in that case and although 3 readings were taken, the XRF has a significant error range. The main conclusion is that lead is immobile in the soil structure, so the lead will not be affected by the rainfall and transported to the groundwater. The same conclusion is obtained by the results of the UV/VIS spectrophotometer.

11.2. EDTA

The following table shows the results of lead removal in the two different molar concentrations. EDTA in both concentrations show very good lead removal results. There is no difference in the lead removal efficiency when the molar concentration changes. The lead removal in the soils without size selection is 74% in both concentrations.

Table 37-EDTA Lead removal (%)

	SOIL	REMOVAL		SOIL	REMOVAL
EDTA 0,01M	NS	73,6	EDTA 0,05M	NS	73,6
	S	83,5		S	84,7
	M	73,0		M	74,9
	L	66,5		L	41,5

11.3. GLDA

The following table shows the GLDA results of the lead removal. Similarity to the case of EDTA, there is no more lead removal when the molar concentration increases. In the case of the Natural soil there is a difference of 10% of lead removal when the concentrations change from 0.01M to 0.05M.

Table 38-GLDA Lead removal (%)

	SOIL	REMOVAL		SOIL	REMOVAL
GLDA 0,01M	NS	62,8	GLDA 0,05M	NS	73,3
	S	0,0		S	0,0
	M	62,0		M	62,3
	L	68,7		L	54,7

11.4. NATURAL SOIL

The following figures show the lead content in the Natural soil before and after the washing process and the washing solution efficiency. The initial value of lead concentration is 323 mg/Kg. In the case of the water there is no significant lead removal effect.

The Cleaning Objective (CO) is nearly reached in the case of EDTA with a molar concentration of 0,01 M. GLDA shows worse cleaning effect compared with the EDTA. There is not impact on the lead content when the molar concentration of the chelant agent changes.

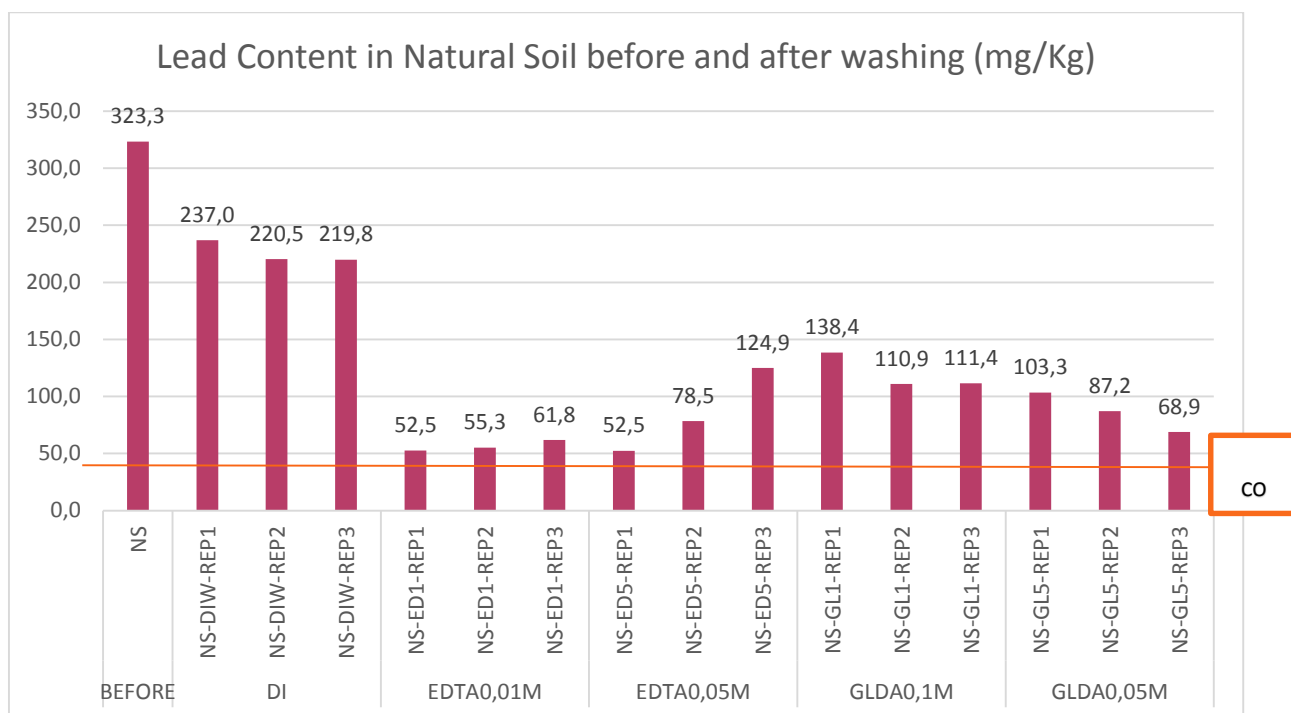


Figure 84-Lead Removal in Natural Soil before and after washing

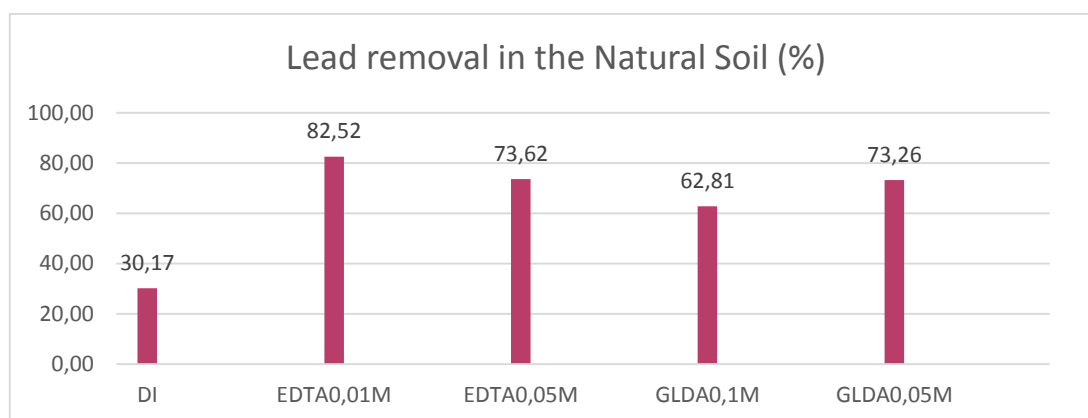


Figure 85-Lead removal efficiency in the Natural Soil

11.5. SMALL GRAIN SIZE

The following figure shows the results of lead content in the soil before and after the washing process. There is no information about the GLDA because were the cases failed during the column test.

The initial value of lead is over the Cut of Criteria of 400 mg/Kg 1055 mg/Kg. The CO is not reached in any washing agent. However, the removal using the EDTA is 84%. The lead content after the soil washing is located between the Cut-Off criteria and the CO. In the case of the DI Water, the Cut-Off criteria is not reached, although the removal is close to 50%. The lead removal in the case of DI water represents the dissolution of fine precipitates.

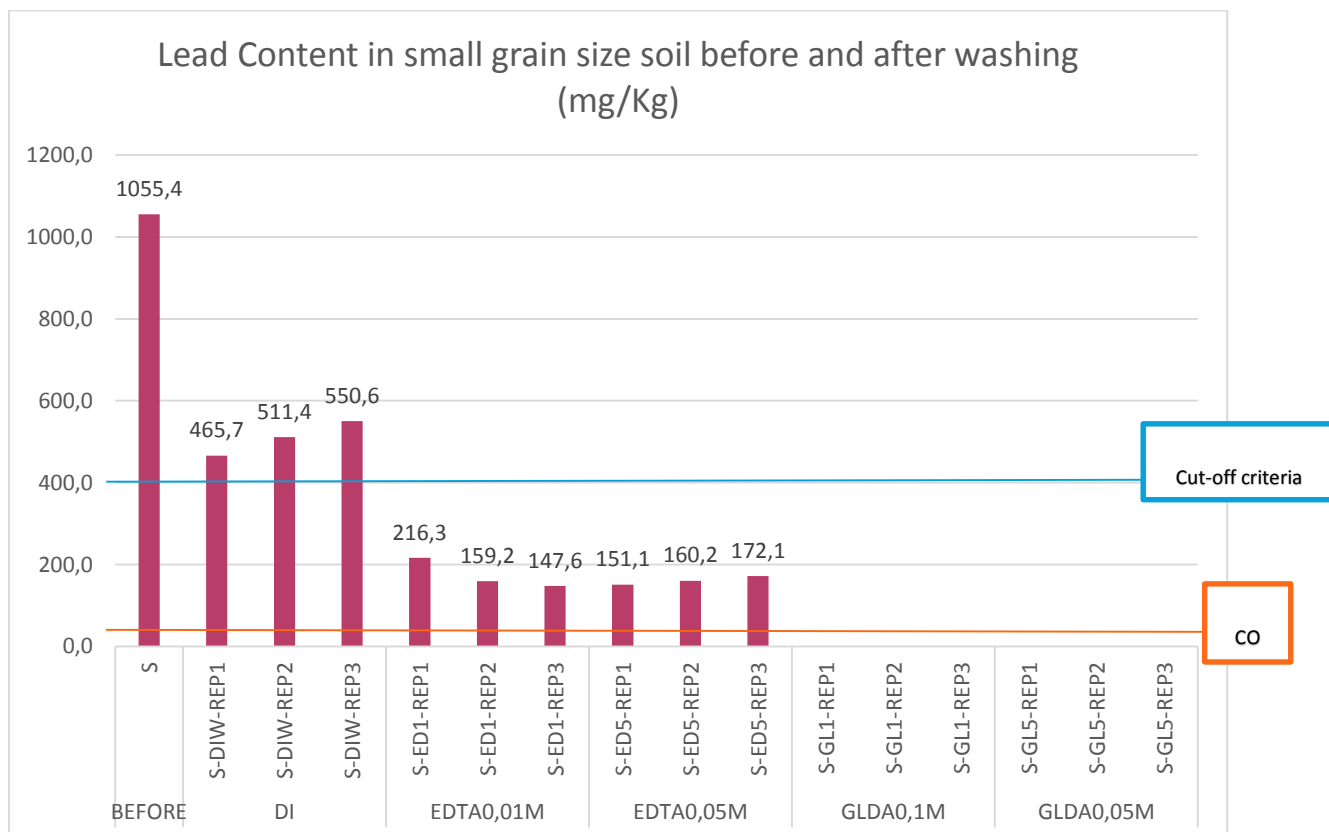


Figure 86-Lead content in small grain soil size before and after washing

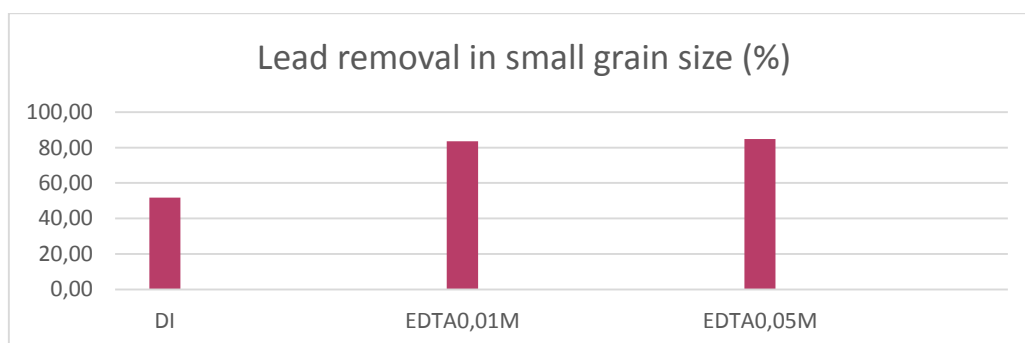


Figure 87-Lead removal efficiency in small grain size

11.6. MEDIUM GRAIN SIZE

Lead removal in medium size is represented in the following figures by the lead content before and after the washing process and the lead removal effectiveness.

In the case of the DI water there is not removal. As it was been explained before, the DI water has not cleaning properties, there is the lead that is weakly bound to the soil particles and readily available for mobilization.

The maximum lead removal is obtained using the EDTA independently of the molar concentration (73 and 75% of lead removal). GLDA has removed lead from soil, but shows less efficiency compared with EDTA with a 11 % of difference.

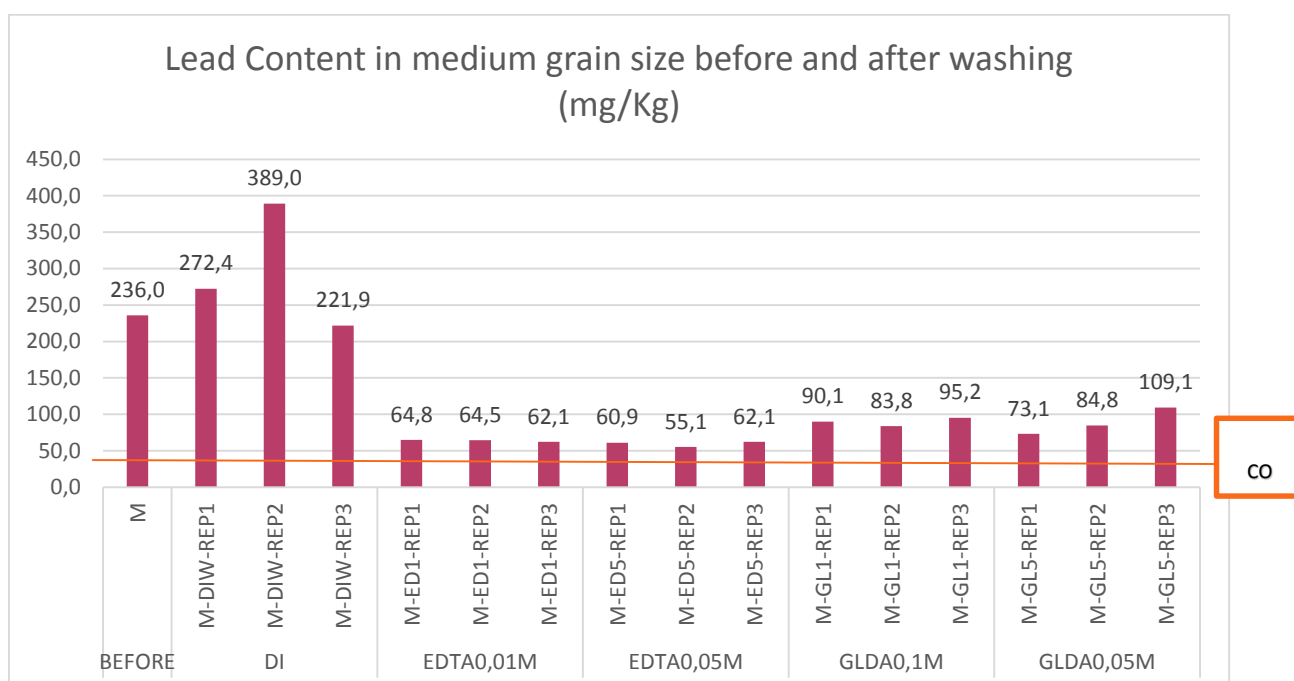


Figure 88-Lead Content in medium size soil grain before and after washing

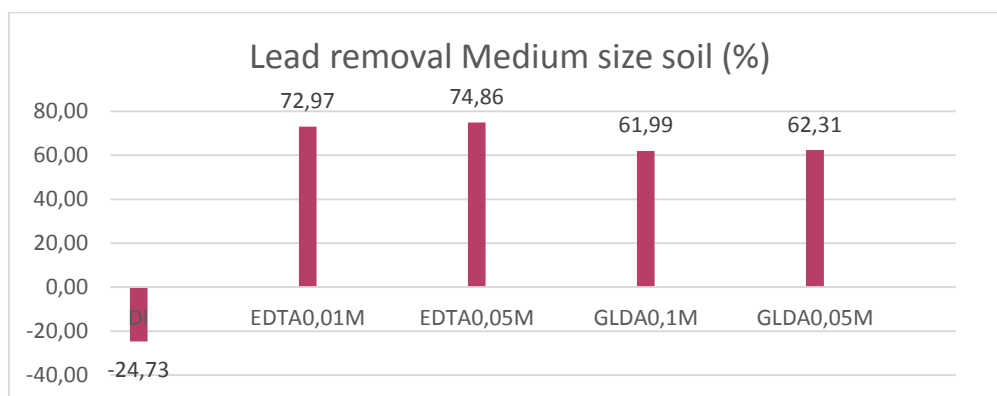


Figure 89-Lead removal efficiency in medium size grain soil

11.7. LARGE GRAIN SIZE

Lead removal efficiency and lead content before and after washing are represented in the following figures. CO has not been reached in any case. In this case GLDA shows better cleaning results (69%) than EDTA (66%). Also, there is less efficiency when the molar concentration of the chelant agent increases in both washing solutions. In the case of the EDTA 0.05 M, there is a huge difference between the 3 replicates. This situation has not been repeated in other cases.

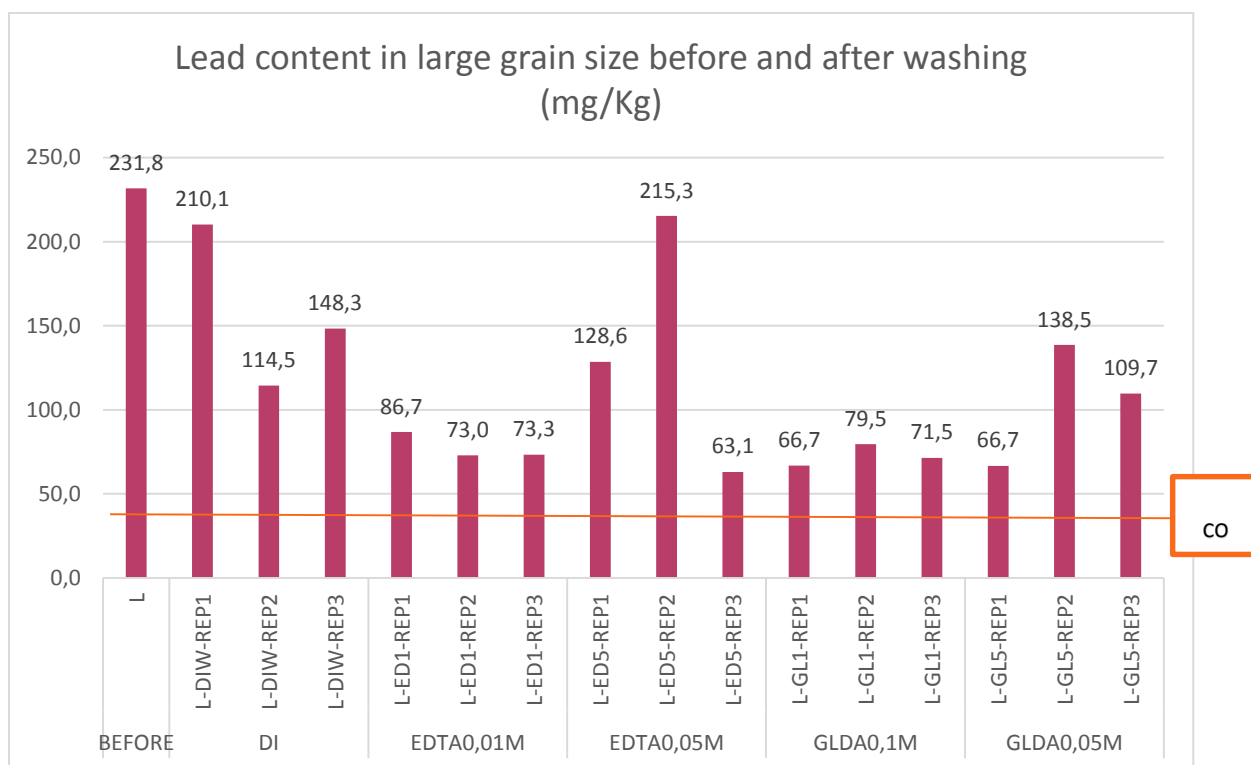


Figure 90-Lead content in large grain size before and after washing

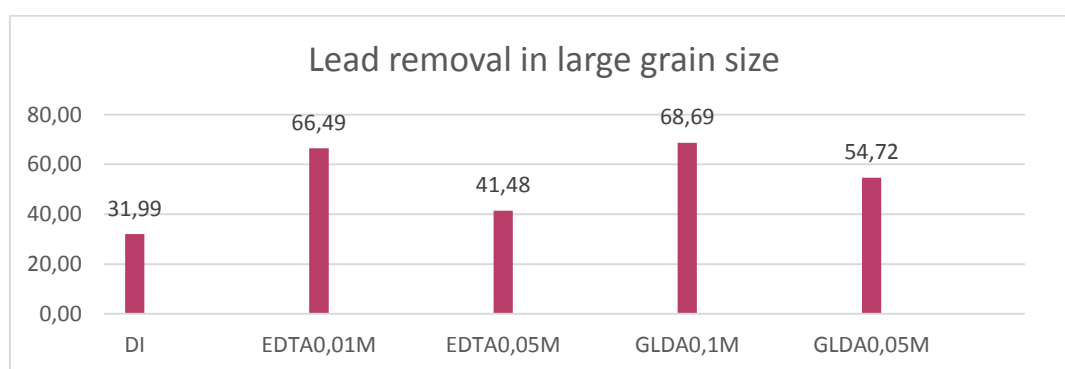


Figure 91-Lead removal efficiency in large grain size

11.8. COMPARISON

Lead removal efficiency in all the washing solutions and soil types, is represented in the figure below. Both chelant agents have lead removal effect. EDTA is the washing agent that has more efficiency (71,4%). GLDA has less lead removal effect, but positive anyway (64%). There is no lead removal significant difference when the molar concentration of the chelant agent increases from 0.01M to 0.05M. Even the difference is negative, it means that the high molar concentration has less lead removal efficiency. The following table summarizes the lead removal efficiency obtained in the column test.

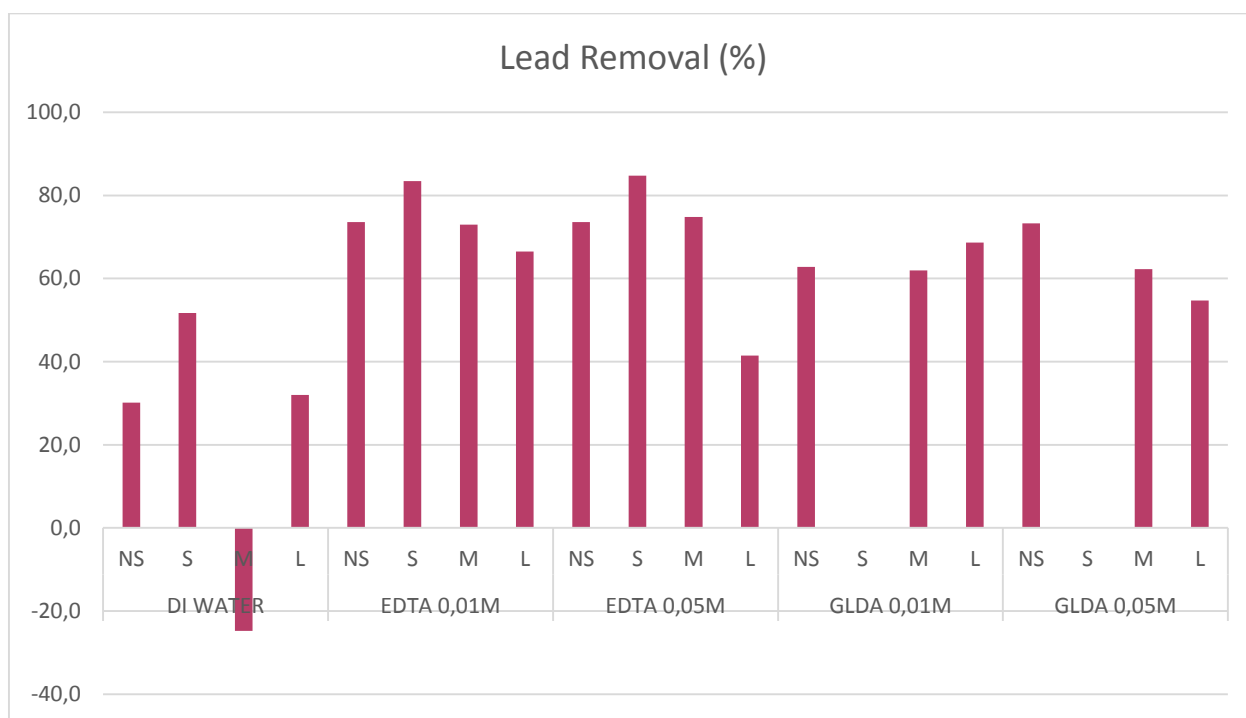


Figure 92-Lead Removal depending on the soil washing agent

Table 39-Lead removal efficiency (%)

	SOIL	REMOVAL			SOIL	REMOVAL	
DI WATER	NS	30,2	22,3				
	S	51,7					
	M	-24,7					
	L	32,0					
EDTA 0,01M	NS	73,6	74,1	GLDA 0,01M	NS	62,8	64,5
	S	83,5			S	0,0	
	M	73,0			M	62,0	
	L	66,5			L	68,7	
EDTA 0,05M	NS	73,6	68,7	GLDA 0,05M	NS	73,3	63,4
	S	84,7			S	0,0	
	M	74,9			M	62,3	
	L	41,5			L	54,7	

12. CONCLUSIONS

Lead removal test is done with the objective of cleaning the contaminated soil according to the Danish standards. The experiment is done in order to test in bench-scale the feasibility of washing techniques in Viborg shooting range soil. Depending on the results of the lead removal test, the remediation proposal full-scale is designed.

Soil washing combines physical separation and chemical extraction. Physical separation is tested using different grain sizes in the washing process. Chemical extraction using organic chelants is one of the currently techniques in remediation.

The effectiveness of the chelant agents and the different grain sizes are tested using a column test according to the literature. The washing agents EDTA and GLDA are compared with the deionized water using two different concentrations 0,01M and 0,05M. EDTA is widely used in soil washing and GLDA has been developed recently.

According to the results of the washed soil in the column test, chelant agents really remove lead from soil. The chelant agent that shows more effectiveness is the EDTA. EDTA has a lead removal average of 71% compared with the 64 % obtained in the GLDA case.

On the one hand, EDTA is more effective in Viborg shooting range soil and also it is cheaper compared with the GLDA. On the other hand, the difference of efficiency is only 7% and GLDA is more eco-friendly. As a consequence, a balance with environmental and economic impact faced with the effectiveness should be considered in order to select the accurate chelant agent. GLDA behaviour in the smallest soil should be continued study in order to answer the failure during the process.

The cleaning objective of 40 mg/Kg has not been reached, but in the case of the soil without division and the medium grain size has been nearly reached (55 mg/kg).

In the case of the smallest grain size which is the most polluted soil fraction (1055 mg/Kg), the cut off criteria has been reached by 80% of removal. As a consequence the smallest fraction cannot be refused and directly disposal. The amount of disposal soil can be reduced if all the soil fractions are treated.

Unfortunately the analyses over the washing steps could not been done by the moment. There is no information about the removal depending on the washing step. As a result, there is no discussion about the washing volume and lead removal. Also there is no extrapolation of the removal in order to reach the cleaning objective.

13. PICTURES REPORT



Figure 93- pH meter PH/Cond 340i/SET



Figure 94-Soil and DI Water mixture used in the pH test

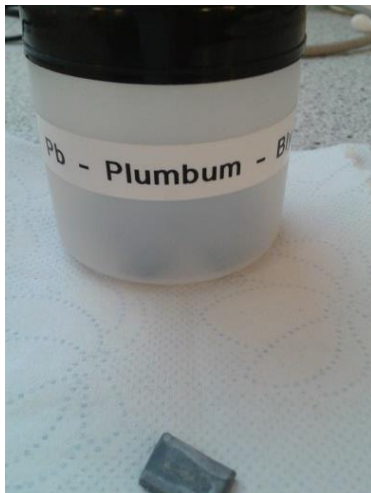


Figure 95-Piece of lead used to prepare the Standard Solution



Figure 96-Standard Solution



Figure 97-Clean sand used in the Verification process



Figure 98-Clean Sand from the concrete Lab



Figure 99-Syringe filled with clean sand



Figure 100-Verification test



Figure 101-Verification test



Figure 102-Lead Kit for the UV/VIS spectrophometer



Figure 103-Lead Kit



Figure 104-Column test

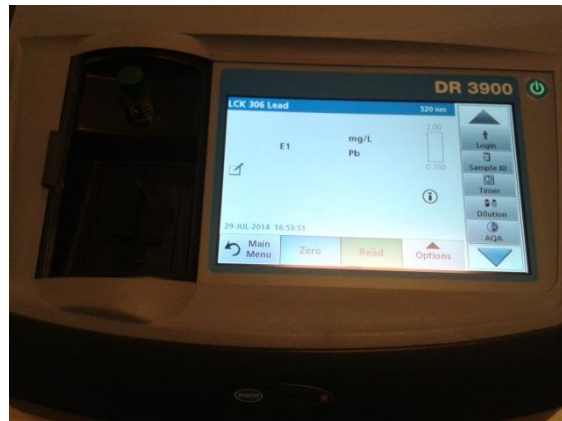


Figure 105- UV/VIS spectrophometer display

7. CONCLUSIONS & REMEDIATION PROPOSAL

1. INTRODUCTION

The main objective of this final dissertation is to carry out an analysis of lead contamination and a proposal of remediation in a real place. Remediation proposal is based in the analysis of the literature done in the State of the Art, the field sampling report, the Contamination Analysis report and the lead removal test developed. The results of the lead removal test are full scale applied.

The goal of this final dissertation is to find an eco-friendly, cost-effective and technically available remediation technique.

The remediation proposal is focused on lead contamination even though the soil is contaminated by more metallic elements. The proposal of remediation is specific to the case of Viborg Shooting range. However, this remediation procedure can be applied in other cases. The remediation proposal covers all the contaminated area.

The results of the lead removal test developed are considered in the remediation proposal. Lead removal test reproduces in bench-scale the performance of the full-scale process.

2. VIBORG SHOOTING RANGE

Viborg shooting range was built in 1900. The range had been used by the Danish Royal Army for military training. Lead ammunition has been used since the construction time.

The military area is divided in two adjacent shooting ranges. There is one of 200-300 m (long distance path shooting range) and another of 50 m length shooting range (pistol shooting range).

The shooting range is located in a reforested area by deciduous and coniferous forest. As a consequence, the area is likely to be affected because of the high amount of biomass, especially primary and secondary consumers in the trophic chain.

3. LEAD CONTAMINATION

Viborg shooting range is lead contaminated. Lead Contamination Analysis has been done over the small firing range because it has been used for a longer period of time and more widely. It is considered contaminated because the lead content in the soil is above the quality criteria established in Danish legislation (cut-off: 400 mg/Kg, quality criteria: 40 mg/Kg).

The contamination is spread all over the field. The lead contamination has a range between 2900 mg/Kg and 45 mg/Kg. The values have an average of 572 mg/Kg, over the Danish cut-off criteria of 400 mg/Kg. The pollutants are concentrated in the impact berm. The pollution is located in the soil layer located in the first 25 cm of depth.

Outside the shooting range boundaries the lead content in the soil is above the quality criteria of 40 mg/Kg.

4. LEAD REMOVAL TEST

Lead removal test is developed in order to extract the lead from the contaminated soil. According to the available technologies and their evolution, soil washing is selected as a remediation procedure. Soil washing using chelant agents combined with physical separation is the most effective and current technique to extract heavy metals from soil. The evolution of this technique is in the direction of reducing the environmental footprint as the same time that increases the cost-effective balance. For this reason, a column test using two different chelant agents combined with physical separation is developed.

On the one hand, EDTA is the most common and widely chelant agent used to extract heavy metals from the soil. On the other hand, GLDA is a new biodegradable chelant agent which has not been tested on a real polluted soil. The Environmental footprint of GLDA is lower than the EDTA one.

The soil is tested with the natural distribution of the soil and in three different grain sizes. The small grain size is smaller than 0.150 mm, the medium size is located between 0.150 mm and 0.5mm and finally, the large size is between 0.500 mm and 2 mm. The soil bigger than 2mm is considered gravel and not polluted.

The column test has the Danish quality criteria of 40 mg/Kg of lead concentration in the soil as a cleaning objective. The results of the lead removal test show the effectiveness of the chelant agents over the different soils. EDTA is the most effective (71%) chelant agent compared with GLDA (64 %). The cleaning objective was nearly reached in the Natural Soil and the medium grain size. The removal in the smallest grain size, which is the most polluted, has reached 80 %.

5. REMEDIATION PROPOSAL METHODOLOGY

Lead removal from Viborg soil according to GSR principles, is the goal of the remediation proposal.

The proposal is a full scale plan based on soil washing ex situ techniques. As a consequence, soil washing needs to be carried in a soil washing plant. For this reason, site foundation process is the first step of the remediation proposal. Soil washing procedure is a combination of two different cleaning methods: physical separation and chemical extraction. Soil washing techniques are always linked with waste water management.

Cleaning objective is to reach the quality standards establish in Danish legislation and return the cleaned soil to the shooting range.

In order to reduce the environmental footprint of soil washing, the recycling of chemicals, the metal recovery and the using of renewable energy are taken into consideration.

The treatment process is a closed-loop that ensures the return of the cleaned soil, lead recovery and recycling of the washing solution. The remediation proposal is a process divided in 4 steps: Site foundation, Physical separation, Chemical extraction and finally, waste water treatment. The following figure shows the step by step process.

The washing plant should be designed with all the elements according to the tonnes of the treating soil, in order to will not have neck of bottles during the process.

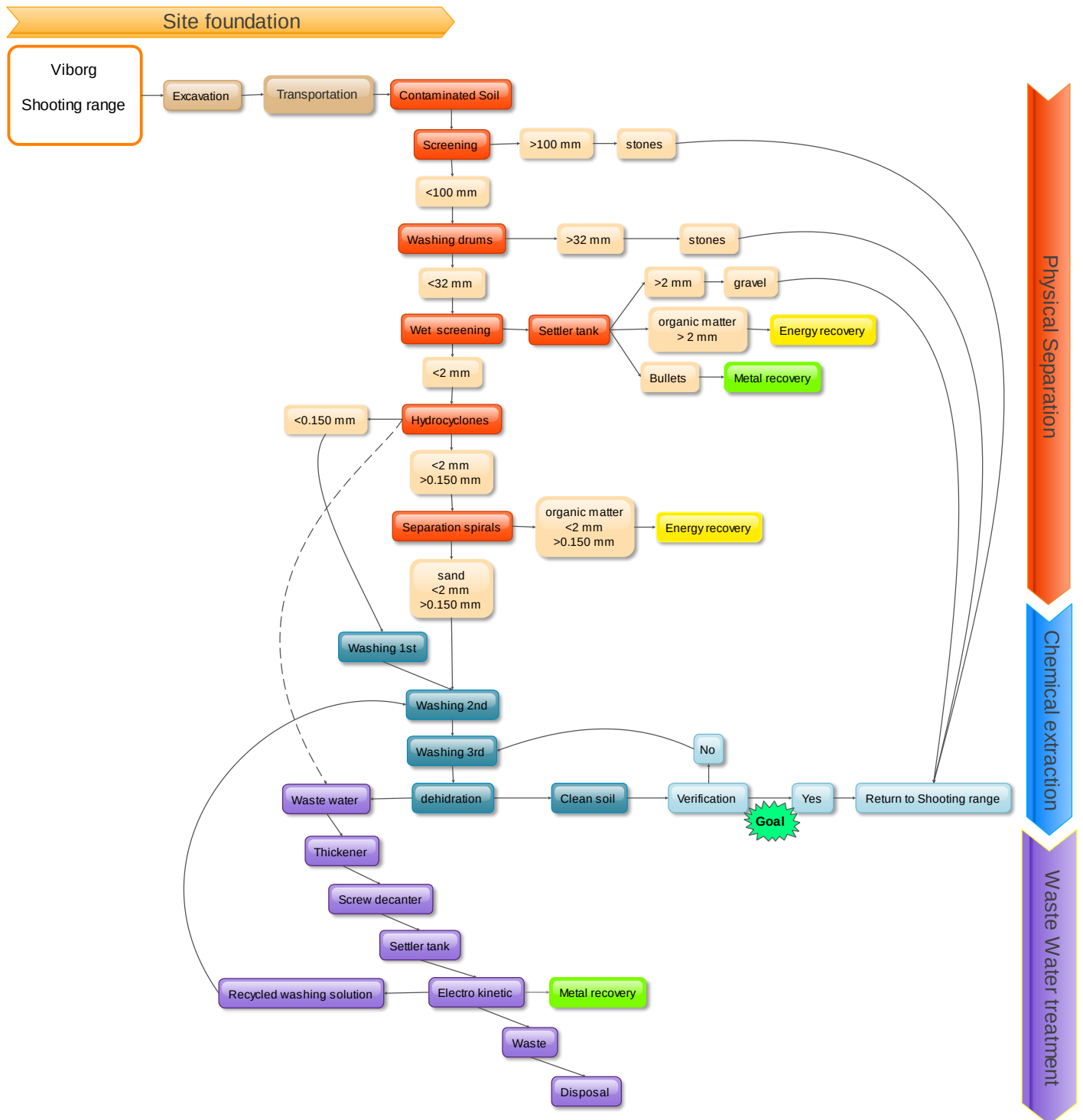


Figure 106 Soil Washing process flow chart

5.1. SITE FOUNDATION

Site foundation is the first phase in the remediation proposal. This phase includes the activities of excavation and transportation to the washing plant.

There is not soil washing plant in Denmark, as a consequence, the contaminated soil has to be transported to Germany, Netherlands or UK. The cost of this phase is not considered in the estimation.

5.2. PHYSICAL SEPARATION

The second phase in the soil washing process is the Physical separation. The goal of this phase is to remove the oversize stones and gravel from the process.

This technology is accurate to separate the rest of the organic matter, bullets and shells present in the shooting range. It is also called lead shot separation.

Several successive processes are needed to reach the physical separation: Screening, Washing drums, wet screening by a settler tank, hydrocyclones and separation spirals.

Firstly, screening is done in order to separate the oversize stones (>100 mm). Secondly, the soil is disaggregated and the stones over 32 mm removed from the process in the washing drums.

The next step is the wet screening done in the settler tank. Oversize gravel (>2mm) and organic matter are removed from the process. Bullets and shells are removed as well and recover the metal in a recycling process. The removal is developed due the weight of the soil compounds. As a consequence, lead is returned to the industrial market for recycled lead.

Finally, hydrocyclones and separation spirals extract the smallest fraction of the soil (<0.150 mm). The smallest fraction of the soil is the most contaminated. Lead removal test has shown the reducing of lead content by washing in this soil fraction. As a result, this soil fraction should be included in the washing process and not directly disposal.

The organic matter is removed from the process depending on the size. Organic matter can be used in energy recovery as biomass. Subsequently, the process can be more efficient from the economic point of view.

The result of the process is the separation between the smallest soil fraction and the sandy soil. Waste water is produced in the hydrocyclones which is treated later.

5.3. CHEMICAL EXTRACTION

The third phase of the washing process is the Chemical Extraction (CE).

CE process has some requirements to achieve. Firstly, CE has to remove lead from the soil reaching the cleaning objective. Secondly, CE has to be developed using the minimum number of washing cycles. Thirdly, CE has to cause lead selectively dissolution without alteration of soil properties. Finally, CE has to be cost effective.

The process is divided in three different washing steps. According to the lead removal test, a washing solution using a molar concentration of chelant agent of 0.01 would be suitable. All soil fractions are washed. The smallest soil fraction is washed 3 times, however, the sandy soil is washed 2 times. Smallest fraction needs more washing time because the initial lead concentration is higher. Lead removal test has

reached a decontamination efficiency ranged between 64 and 71 %. That values could be improve if the washing volume increases. Unfortunately there is no enough information about the removal depending on the washing step to prognosticate if that increase would be suitable for Viborg soil.

5.4. WASTE WATER TREATMENT

The last phase in the washing process is the waste water treatment. The management of the effluents containing lead is an important phase in the design of the washing process. The waste water management is a phase which the chelant agent is recycled and the metal recovered in order to reduce the cost of the process.

On the one hand, chelant agent regeneration is indispensable to avoid the release of chelant agent into the environment. On the other hand, washing solution should be recycled in order to reduce treatment cost.

According to the literature there are different procedures for chelant agent regeneration and the removal of lead from the washing solution, (Dermont et al., 2008):

- Metal precipitation and chelant agent regeneration by adding chemical agents
- Electro-chemical procedure
- Ion exchange resin
- Nano-filtration
- Degradation of chelant agent via oxidation and metal recovery by absorption

In EDTA solutions the agent can be recovered by evaporation, acidification of the evaporation residue washing solution and finally, filtration. Recycled EDTA is suitable for reuse in the washing after its transformation into sodium salt by adding an alkaline agent, (Di Palma et al., 2003).

Despite all the proposals offered by the literature, has not been commercialised or tested on a pilot-scale, (Voglar & Lestan, 2012).

Unfortunately, there is no information about GLDA regeneration in the literature.

Washing solution recycled in reincorporate to the process in the second washing step and the solid waste disposal.

5.5. COST ESTIMATION

The cost estimation is based on the market prices and the literature. According to the literature the price of Soil washing: 300-500 dkk/tonne soil, (Lindskov et al., 2000).

The tonnes of soil are calculated based on the surface contaminated and the soil density.



Figure 107-Lead contaminated area considered, (Danmarks Miljøportal, n.d.)

Lead contaminated area has a surface of approximately 21.000 m². The surface considered is based on the contamination boundaries.

According to the lead contamination laboratory report, lead contamination is located in the first 25 cm of soil layer deepness. As a consequence, the total soil volume considered in bank conditions is 5.250 m³, considering that the swelling coefficient is 20 % the polluted volume is 6300 m³.

If soil density is 1.36 g/cm³ (t/m³), the total weight of the contaminated soil is 8.568 tones. The total cost is calculated with total tonnes multiplied by 500 dkk/tonne. The total cost is 4.284.000 dkk (600.000 €)

This cost does not include the soil excavation and transportation, it is only the cost of the soil washing procedure including the treatment of waste water.

Taking into account that the excavation and disposal is estimated in 1000 dkk/tonne, washing process is only profitable if the transportation cost is less than 500 dkk/tonne.

All the prices have been taken from the literature, (Danish Environmental Protection Agency, 2002).

6. AREA RESTORATION

The area must be restored if firing activities have finish and the shooting range is closed. The restoration of the area is needed after finishing the work of soil excavation and processing in the washing plant. The restoration of the area depends on the future use of the land. However, some activities are common like demolition of the structures and berm reconstruction.

The concrete structures used to collect misfires should be demolished in order to restore the area. The structures are made of reinforced concrete and cover by a layer of polyurethane. The polyurethane, iron and the stone parts should be separated and disposal separately.

The berm reconstruction includes the earthworks needed to recover the original surface. Unfortunately there is no information about the area before the shooting range was built.

Finally, considering that the field is located in a reforested area, the reconstruction of the landscape could be mimicking the presence of the shooting range.

7. ENVIRONMENTAL, QUALITY AND HEALTH & SECURITY MANAGEMENT

The remediation process must follow an environmental and quality management. The Environmental plan should include the relation of the possible environment aspects affected by the works and the procedure to control.

The Quality management includes the design of a quality plan and also the monitoring of it. The quality plan should include the specifications, the documents of control, test procedures, and everything needed to reach the cleaning objectives according to the standards. Quality control objectives should provide accurate, precise, and complete data enough to identify conditions under which lead is removed from contaminated soil, (Interstate Technology and Regulatory Council Small Arms Firing Range Team, 2003).

Health and Security Management (HSM) is always needed in works related with removals of soil and industrial processes. HSM is indispensable in the case of lead processing because the associated hazards. Prolonged exposure to dust containing lead has serious health hazards. As a consequence, Soil excavation, transportation, and treatment operations must be provided by procedures to minimize dust generation like water spray, covers or foam coating. Monitoring must determine the dust and lead concentrations in air in the breathing area, in work zones, and at the shooting range surrounding.

8. CONCLUSIONS

The remediation proposal of Viborg lead contaminated soil is described by the activities included in this chapter. The remediation proposal is focused on lead contamination although the shooting range contains other metallic pollutants like iron or copper.

Soil washing ex situ is the technology suggested to remove lead from the soil. The goal of the process is to reach the Danish quality criteria of 40 mg/Kg. The process has four main activities: Site foundation, Physical separation, Chemical extraction and, finally, Waste water management.

Soil washing using chelant agents effectively remove lead from soil. The removal by EDTA and GLDA is ranged between 64 to 71%. A molar ratio of 0,01M of chelant agent has been found the most effective.

The chelant agent more efficient is the EDTA, but the efficiency has a difference of 7%. The balance between the environmental and the economic impact should be developed deeply according to the objectives and the market prices.

The remediation proposal cost has been estimated around 4.284.000 dkk (600.000 €) according to the literature. This cost does not include the soil excavation and transportation, it is only the cost of the soil washing procedure including the treatment of waste water. Taking into account that the excavation and disposal is 1000 dkk/tonne, the washing process is only profitable if the transportation cost is less than 500 dkk/tonne.

The restoration of the area depends on the future use of the field, however, some common activities are propose like the demolitions of the structures, reconstruction of the berms and reconstruction of the landscape.

All the activities involved in the remediation proposal must follow a quality, environmental and HSM plan.

9. FURTHER RESEARCH

Shooting ranges are lead contaminated areas. The finishing of the firing activities must be followed by the restoration of the area. Human activities should not influence either the environment or the cycle of the elements. Restoration techniques should be eco-friendly and cost-effective.

On the one hand, phytoremediation technologies should be developed in Nordic countries. Considering that these countries are concerned about nature, phytoremediation techniques may have acceptance by the population despite slow plant growth in northern latitudes. Research would be required by using different plants.

On the other hand, soil washing techniques should be deeply developed in Denmark. The effectiveness of this technology need to be improved, making it more cost-effective, at the same time that reduces the environmental footprint.

New biodegradable chelant agents combined with different physical separation should be tested depending of the characteristics of the contaminated soil. GLDA has not been tested on real contaminated soils except the present project, and this chelant agent needs to be tested on different situations included the regeneration during the waste water management. GLDA behaviour in the smallest soil should be continued study in order to answer the failures during the process.

Viborg firing range soil should be studied from other points of view. Lead is not the only pollutant present in the soil. The chelating agent effect over the Iron or Copper is an open door for future researchers.

Furthermore, the chelating agent impact on the microbiological properties of the soil should be evaluated for the re use of the soil in the area, especially if the area is reforested. The surface of the soil particles could absorb the chelant agent and remain after the washing process.

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APPENDIX 1

CONTAMINATION READINGS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
2	A00	52	0	6.32	96.88	8.1	64.06	5.21	0	11.36	20.81	4.17	0	26.25	2968.84	63.24	0	8	0	72.92	0	10.88	280.37	25.4	0	70.33	156.27	26.76	0	49.49	0	91.29	6969.46	219.93	0	80.28
3	A01	47	0	7.65	487.56	15.18	52.02	5.11	0	10.6	23.08	4.27	0	25.69	2370.62	60.05	0	7.85	0	70.18	0	11.89	337.11	29.1	0	69.31	149.01	28.68	0	54.23	0	89.54	5735.91	212.61	214.11	69.37
4	A02	60	0	5.98	78.25	7.13	42.56	4.27	0	9.88	18.32	3.66	0	19.58	1696.02	46.57	0	6.82	0	54.32	0	9.75	229.69	22.39	0	61.34	127.4	23.99	0	44.81	0	77.03	4864.49	179.07	85.23	51.6
5	A03	64	0	6.18	117.43	7.86	40.27	4.11	0	8.88	15.17	3.31	0	15.93	1063.87	36.81	0	5.68	0	43.01	0	8.91	139.65	18.01	0	60.72	98.97	22.23	0	44.28	0	78.6	5355.59	186.35	89.19	50.72
6	A04	70	0	6.06	117.22	7.81	36.86	3.99	0	9.85	17.69	3.54	0	15.04	978.96	35.37	0	6.01	0	41.04	0	10.12	154.1	18.72	0	60.96	65.12	20.34	0	47.3	0	78.39	5092.13	181.98	134.78	54.66
7	A05	63	0	6.32	98.24	7.58	35.42	4.01	0	9.59	16.76	3.5	0	14.15	694.25	30.76	0	5.66	0	35.92	0	9.91	98.79	16.14	0	64.52	42.24	19.67	0	48.35	0	71.7	4350.42	173.07	102.03	52.97
8	A06	49	0	6.1	98.45	7.32	32.44	3.78	0	8.93	13.76	3.18	0	12.56	615.29	28.2	0	5.28	0	33.17	0	9.61	75.19	14.12	0	59.79	44.5	18.93	0	48.7	0	67.91	3782.4	157.32	137.08	54.37
9	A07	52	0	5.97	66.79	6.67	38.24	4.02	0	9.73	25.12	3.84	0	14.65	753.48	31.16	0	5.26	43.94	24.59	0	9.43	122.4	17.12	0	62.59	85.36	21.56	0	45.76	0	75.48	4951.73	179.48	133.63	54.87
10	A08	63	0	6.55	78.55	7.38	47.13	4.6	0	9.86	16.6	3.57	0	12.31	401.02	24.53	0	5.41	0	28.7	0	10.48	100.47	16.9	0	68.76	64.61	22.37	0	51.93	0	68.84	3739	166.44	0	78.23
11	A09	63	0	6.04	56.59	6.4	45.04	4.28	0	10.7	40.78	4.55	0	11.09	360.71	22.13	0	5.16	27.06	17.54	0	9.79	99.27	15.98	0	65.89	69.61	20.81	0	45.71	0	64.91	3747.93	157.95	104.67	52.36
12	A10	51	0	6.1	54.78	6.25	37.73	3.96	0	9.68	24.07	3.74	0	11.96	471.8	24.8	0	5.39	0	28.91	0	9.02	79.07	14.21	0	54.82	60.82	19.79	0	43.93	0	67.71	3742.41	155.88	126.41	54.81
13	A11	64	0	6.12	117.17	7.68	44.42	4.17	0	9.82	18.44	3.49	0	11.59	433.2	23.56	0	4.81	0	27.31	0	9.31	72.73	13.84	0	60.07	61.4	19.59	0	46.97	0	67.25	3710.57	153.6	0	69.66
14	A12	63	0	6.01	61.51	6.45	46.1	4.25	0	9.08	21.67	3.56	0	11.49	419.6	23.41	0	5.16	30.48	18.55	0	8.97	70.73	13.8	0	61.58	57.8	19.78	0	49.25	0	62.81	3350.45	147.4	0	70.41
15	A13	51	0	5.87	61.31	6.37	48	4.27	0	9.18	22.42	3.56	0	11.04	355.77	21.4	0	4.8	0	24.9	0	9.01	103.88	15.57	0	57.69	50.74	18.83	0	46.36	0	72.91	4775.3	172.63	0	67.67
16	A14	61	0	6.09	116.97	7.76	34.57	3.86	0	9.38	16.96	3.39	0	9.99	277.1	19.5	0	4.39	0	22.84	0	9.33	52.25	12.71	0	63.51	49.23	19.51	0	48.91	0	75.85	5265.65	185.82	104.9	52.91
17	A15	55	0	5.96	101.57	7.19	34.25	3.73	0	8.75	17.28	3.26	0	9.68	301.4	19.67	0	4.27	0	22.55	0	8.77	83.13	14.29	0	57.58	64.83	19.6	0	43.18	0	61.36	3778.28	153.4	0	65.9
18	A16	66	0	6.24	89.7	7.27	37.24	4.02	0	9.12	15.08	3.3	0	11.63	387.21	23.07	0	4.93	52.71	18.82	0	9.63	86.69	15.26	0	64.1	76.14	21.63	0	51.4	0	77.04	5182.99	186.53	106.46	52.94
19	A17	69	0	6.09	141.69	8.16	31.84	3.69	0	9.1	18.43	3.4	0	9.54	228.07	17.65	0	4.65	0	20.97	0	8.87	53.25	12.63	0	63.26	56.79	19.64	0	47.88	0	73.76	4843.52	176.15	120.12	53.07
20	A18	59	0	6.03	112.32	7.49	43.26	4.09	0	9.44	14.84	3.24	0	9.18	227.03	17.36	0	4.27	0	20.05	0	8.57	42.77	11.57	0	57.31	80.14	20.53	0	43.22	0	66.71	4419.42	166.17	101.22	51.24
21	A19	55	0	5.87	61.48	6.2	30.34	3.57	0	9.21	16.78	3.29	0	8.9	224.93	17.23	0	4.22	0	19.43	0	8.63	59.85	12.74	0	57.79	51.66	18.67	0	44.09	0	67.62	3801.52	154.06	0	68.07
22	A20	66	0	5.89	70.69	6.62	43.02	4.13	0	8.88	21.49	3.51	0	9.28	257.87	18.69	0	4.84	0	21.56	0	8.96	63.58	13.34	0	60.87	61.07	19.8	0	44.48	0	68.15	4125.79	163.17	83.4	49.84
23	A21	67	0	6.02	99.7	7.24	36.15	3.85	0	8.76	19.18	3.37	0	9.07	196.38	16.43	0	4.36	0	19.49	0	8.46	48.34	11.97	0	56.61	43.37	18.45	0	43.89	0	65.7	3925.62	158.26	0	70.75
24	A22	52	0	6.21	129.19	8.02	47.8	4.33	0	9.5	19.17	3.49	0	10.62	325.81	20.87	0	4.97	0	23.76	0	9.62	62.79	13.38	0	63.68	33.78	18.13	0	47.76	0	78.42	5314.85	184.99	118.07	52.81
25	A23	53	0	5.89	49.91	5.99	38.76	3.93	0	8.95	21.22	3.47	0	8.83	200.15	16.5	0	4.55	25.27	13.32	0	9.04	92.39	14.96	0	58.72	48.31	18.71	0	45.59	0	71.73	4651.31	171.01	0	69.95
26	A24	63	0	6.12	137.93	8.1	51.86	4.41	0	9.22	28.35	3.81	0	9.15	202.29	16.64	0	4.78	0	19.48	0	8.8	117.2	16.39	0	56.44	80.75	20.66	0	44.44	0	83.27	6144.77	195.99	0	70.25
27	A25	62	0	6.05	95.44	7.23	50	4.38	0	9.63	25.92	3.78	0	9.56	255.42	18.55	0	4.84	0	21.18	0	9.3	142.52	17.9	0	59.6	86.4	21.4	0	49.11	0	85.56	6542.83	203.38	102.72	52.56
28	A26	45	0	5.97	97.57	7.27	50.61	4.38	0	9.08	18.12	3.35	0	9.29	182.46	15.93	0	4.54	0	17.79	0	9.28	119.06	16.62	0	60.61	72.24	20.46	0	48.32	0	76.59	5210.23	181.45	87.73	49.66
29	A27	42	0	5.98	82.18	6.96	49.6	4.39	0	9.42	17.76	3.4	0	8.82	194.87	16.51	0	4.47	0	19.05	0	9.33	121.35	16.92	0	62.07	59.5	19.92	0	49.13	0	92.12	7313.52	216.27	139.05	55.9
30	A28	58	0	6.11	70.78	6.67	54.26	4.51	0	9.51	19.51	3.48	0	9.39	179.95	15.86	0	4.55	0	18.49	0	9.25	131.71	17.37	0	61.5	76.02	20.63	0	45.98	0	79.06	5573.89	187.76	0	71.91
31	A29	47	0	6.28	140.63	8.43	62.6	4.89	0	9.31	19.09	3.48	0	9.35	147.74	14.92	0	4.83	0	17.49	0	9.75	85.44	15.1	0	64.13	54.82	19.92	0	47.45	0	96.29	8672.56	238.41	127.19	57.41
32	A30	60	0	5.84	62.77	6.28	42.11	4.02	0	8.23	15.98	3.1	0	7.89	126.9	13.42	0	4.05	0	15.48	0	8.98	55.06	12.4	0	58.19	38.9	17.9	0	44.94	0	73.3	4775.11	171.85	0	69.22
33	A31	63	0	6.24	163.26	8.69	47.73	4.33	0	9.78	22.11	3.65	0	8.85	152.62	14.91	0	4.47	0	17.38	0	9.09	75.99	14.05	0	56.55	52.55	19.36	0	48.13	0	78.97	5531.39	188.74	0	69.77
34	A32	61	0	6.04	76.35	6.77	51.87	4.43	0	9.27	20.31	3.48	0	8.05	98.1	12.32	0	4.56	0	14.18	0	9.47	62.68	13.26	0	62.19	49.16	18.92	0	45.14	0	66.78	4434.03	168.25	135.81	54.34
35	A33	60	0	6.04	89.09	7.13	46.25	4.27	0	8.95	19.56	3.43	0	9.27	171.08	15.67	0	4.72	18.89	12.53	0	9.66	65.52	13.58	0	62.63	62.22	20.08	0	48.7	0	79.36	5985.88	196.53	167.66	58.51
36	A34	50	0	6.03	86.89	6.97	39.68	4	0	8.71	14.95	3.15	0	8.31	132.65	13.95	0	4.69	0	16.56	0	9.38	46.38	11.97	0	60.45	28.79	17.76	0	48.08	0	73.96	4804.54	175.06	90.77	49.83
37	A35	65	0	6.15	76.76	7.02	57.12	4.72	0	9.65	25.41	3.83	0	8.97	119.09	13.73	0	4.98	0	15.87	0	9.37	63.04	13.67	0	65.79	34.05	18.85	0	49.47	0	79.41	4993.23	183.1	105.97	53.01
38	A36	52	0	6.45	94.41	7.5	52.74	4.64	0	10.46	20.92	3.76	0	8.41	98.09	12.9	0	5.2	0	15.41	0	9.53	52.49	12.86	0	61.05	35.19	19.3	0	51.3	0	86.96				

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
40	A38	51	0	5.89	58.8	6.19	36.11	3.81	0	8.88	20.67	3.43	0	8.37	110.89	12.74	0	3.77	0	14.47	0	8.7	44.37	11.61	0	58.89	26.77	17.22	0	48.04	0	75.38	5092.65	178.24	181.68	57.67
41	A39	59	0	6.16	143.68	8.22	43.74	4.15	0	10.06	22.79	3.7	0	7.88	96.91	12.3	0	4.85	0	14.13	0	9.4	34.59	11.12	0	62.88	0	24.77	0	46.19	0	75.06	4963.44	177.9	141.8	55.56
42	A40	65	0	6.06	73.42	6.66	40.25	4.03	0	9.49	27.53	3.83	0	7.71	92.23	12.05	0	4.34	0	13.89	0	9.18	32.68	10.86	0	60.41	0	24.81	0	46.05	0	68.03	4158.58	163.84	117.24	52.3
43	A41	56	0	6.1	94.93	7.4	69.61	5.05	0	9.98	28.11	3.94	0	8.73	97.16	12.45	0	4.54	0	14.19	0	8.56	34.1	11.05	0	59.75	31.13	18.11	0	48.15	0	82.91	5863.35	194.93	76.98	49.62
44	A42	69	0	6.56	104.31	8	67.39	5.25	0	10.4	16.57	3.59	0	8.9	105.69	13.5	0	4.76	0	15.64	0	10.31	42.3	12.69	0	70.05	33.95	19.92	0	50.98	0	94.49	6954.82	223.06	139.24	60.22
45	A43	71	0	6.01	131.78	8.35	155.21	7.04	0	9.24	17.31	3.29	0	7.98	92.58	11.9	0	4.17	0	13.52	0	8.72	32.39	10.61	0	55.12	0	25.2	0	44.07	0	70	4346.69	164.56	119.43	51.78
46	A44	46	0	6.05	84.43	6.92	42.23	4.08	0	9.51	16.46	3.34	0	7.74	65.47	10.52	0	4.07	0	12.26	0	8.95	33	10.98	0	63.18	0	25.46	0	45.09	0	70.58	4461.83	168.79	113.29	51.76
47	A45	66	0	5.89	78.87	6.61	35.89	3.76	0	8.88	19.96	3.36	0	7.88	84.07	11.32	0	4.06	0	13.19	0	9.01	31.55	10.51	0	58.85	0	24.28	0	43.1	0	64.61	4244.21	161.12	0	68.61
48	A46	65	0	6.15	117.02	7.64	42.26	4.08	0	9.58	17.24	3.38	0	7.51	97.92	12.28	0	4.5	0	14.16	0	9.15	40.44	11.51	0	61.6	0	24.9	0	46.31	0	71.03	4578.78	170.78	103.5	51.23
49	A47	37	0	6	59.23	6.22	46.55	4.19	0	9.51	24.39	3.66	0	7.58	104.21	12.38	0	3.75	0	14.07	0	8.46	40.22	11.08	0	53.18	33.28	17.52	0	44.27	0	70.78	4801.53	172.56	108.45	50.82
50	A48	63	0	6.12	119.05	7.82	61.74	4.77	0	9.54	23.44	3.66	0	7.95	87.06	11.8	0	4.43	0	13.51	0	9.34	44.8	11.95	0	62.08	0	26.25	0	47.18	0	77.04	5518.91	187.85	102.74	51.51
51	A49	53	0	5.99	102.82	7.26	36.01	3.83	0	9.22	21.52	3.52	0	7.46	86.8	11.65	0	4.23	0	13.26	0	8.62	44.75	11.64	0	57.43	32.49	17.69	0	47.8	0	73.85	5059.33	178.48	100.68	50.24
52	A50	69	0	6.23	111.26	7.8	46.95	4.39	0	9.26	24.74	3.76	0	8.38	84.08	12	0	4.78	0	13.74	0	9.32	43.04	12.21	0	65.42	0	27.11	0	45.66	0	75.24	4679.03	178.23	0	71.15
53	A51	43	0	6.07	114.53	7.63	55.51	4.54	0	8.79	17.19	3.26	0	7.17	72.47	10.88	0	4.08	0	12.48	0	9.05	50.09	12.25	0	61.28	26.15	17.38	0	46.42	0	72.34	4416.65	167.53	0	68.92
54	A52	58	0	5.85	56.19	6.06	44.47	4.06	0	8.84	19.1	3.31	0	6.86	61.84	10.02	0	3.72	0	11.59	0	8.87	38.99	11.17	0	59.44	35.83	17.34	0	42.18	0	60.77	3403.43	144.68	73.45	46.16
55	A53	58	0	6.22	159.35	8.48	31.94	3.69	0	9.71	22.33	3.63	0	7.13	53.55	9.87	0	4.43	0	10.84	0	9.3	30.55	10.72	0	62.04	0	23.21	0	44.49	0	71	4747.3	174.25	0	71.58
56	A54	59	0	6.22	106.94	7.56	60.02	4.73	0	8.67	17.62	3.28	0	7.32	51.12	9.86	0	4.88	0	11.53	0	9.24	39.52	11.41	0	58.36	0	25.7	0	46.54	0	71.49	4718.85	174.67	74.09	49.36
57	A55	57	0	5.81	89.81	6.85	40.57	3.92	0	8.15	16.34	3.08	0	7.17	48.72	9.35	0	4.36	0	10.46	0	8.52	26.56	9.86	0	53.71	0	24.48	0	41.31	0	66.95	3953.09	155.19	81.2	47.23
58	A56	61	0	6.74	479.62	13.64	62.61	4.89	0	10.47	27.09	3.97	0	7.86	38.6	9.24	0	4.85	0	11.01	0	9.3	78.36	14.32	0	56.57	0	26.66	0	48.32	0	74.77	4844.02	179.07	164.53	57.96
59	A57	52	0	6.23	91.54	7.26	41.34	4.15	0	9.74	20.14	3.58	0	7.93	50.51	9.91	0	4.25	0	10.93	0	9.15	24.3	10.2	0	58.76	0	25.8	0	46.15	0	61.64	3322.11	149.85	0	70.21
60	A58	40	0	6.04	69.01	6.76	93.99	5.63	0	10.27	34.5	4.16	0	7.84	61.49	10.25	0	4.14	0	11.65	0	8.86	28.41	10.5	0	61.5	0	25.35	0	45.76	0	69.81	4272.13	163.76	0	70.63
61	A59	47	0	5.93	77.19	6.67	46.17	4.18	0	8.94	15.51	3.18	0	6.93	69.37	10.7	0	4.47	0	12.22	0	8.31	34.51	10.52	0	51.86	0	24.27	0	46.25	0	71.4	4626.09	170.02	106.58	50.87
62	A60	41	0	6.04	81.88	6.78	42.48	4.05	0	9.12	19.4	3.39	0	7.43	72	10.79	0	4	0	12.15	0	8.95	30.29	10.41	0	57.43	0	23.39	0	45.39	0	71.77	4285.86	163.91	98.43	50.2
63	A61	47	0	6.01	110.86	7.47	40.4	4	0	9.82	16.9	3.38	0	7.7	69.9	10.79	0	4.36	0	12.1	0	8.69	20.74	9.51	0	55.79	0	24.96	0	46.76	0	70.33	4409.58	166.71	0	63.69
64	A62	49	0	6.04	126.08	7.9	44.72	4.2	0	8.87	13.42	3.1	0	7.68	66.32	10.67	0	4.29	0	12.08	0	8.85	24.82	10.07	0	59.13	0	23.13	0	47.39	0	70.39	4102.97	163.01	91.07	49.05
65	A63	41	0	6.09	98.21	7.25	40.37	4.03	0	9.09	13.18	3.12	0	8.25	86.15	11.78	0	4.62	0	12.74	0	8.94	0	12.74	0	58.74	0	24.17	0	46.89	0	71.45	4431.44	168.6	0	71.91
66	A64	50	0	5.79	59.01	5.96	27.83	3.37	0	7.95	11.82	2.81	0	7.03	45.98	9.01	0	4.03	0	10.81	0	8.11	30.44	10.04	0	54.23	0	23.22	0	43.23	0	60.33	3354.88	141.82	128.89	50.49
67	A00_60"	52	0	6.62	106.07	8.37	41.97	4.52	0	10.89	29.41	4.48	32.48	17.17	2509.93	59.4	0	8.1	93.04	46.47	0	11.73	223.87	23.6	0	74.64	168.57	28.16	0	52.23	0	78.5	5191.12	194.43	88.57	55.24
68	A10_60"	51	0	6.11	144.19	8.21	33.98	3.79	0	9.15	17.68	3.37	0	10.98	397.5	22.71	0	4.8	0	26.94	0	9.18	80.45	14.38	0	59.78	74.59	20.6	0	47.41	0	71.42	4441.35	168.23	75.33	49.42
69	A20_60"	66	0	6.07	121.83	7.85	40.39	4.06	0	9.01	21.87	3.56	0	11.03	385.87	22.61	0	4.97	37	18.1	0	8.94	83.34	14.76	0	59.17	136.07	24.18	0	45.29	0	68.25	4076.2	162.92	115.37	52.8
70	A30_60"	60	0	6	62.81	6.39	50.23	4.35	0	8.9	17.94	3.31	0	8.27	147.29	14.51	0	4.95	0	16.71	0	8.77	68.56	13.44	0	59.3	35.74	17.97	0	47.22	0	76.68	5286.7	182.3	109.94	51.83
71	A40_60"	65	0	6.47	134.65	8.58	108.61	6.25	0	11.1	35.69	4.43	0	9.08	166.69	15.81	0	4.6	0	18.21	0	9.58	32.49	11.3	0	63.2	28.63	18.49	0	48.78	0	90.09	7156.93	218.92	105.48	55.33
72	A50_60"	69	0	6.07	101.8	7.29	40.86	4.01	0	9.17	16.71	3.29	0	8.11	83.69	11.55	0	4.5	0	12.75	0	9.04	54.53	12.51	0	60.65	0	25.43	0	45.35	0	72.31	4773.77	173.61	80.52	48.4
73	A60_60"	41	0	5.96	84.16	6.81	35.55	3.79	0	8.33	13.42	2.99	0	7.3	56.4	9.92	0	4.05	0	11.8	0	8.73	13.3	8.76	0	56.13	0	23.64	0	44.99	0	67.05	3930.58	157.67	182.85	56.86
74	A00_BIS	52	0	6.39	108.11	8.24	43.03	4.49	0	10.59	25.9	4.24	0	24.57	2466.93	57.98	0	7.54	0	67.49	0	11.16	236.42	23.6	0	67.16	141.33	26.19	0	51.41	0	77.48	4910.52	186.5	133.06	57.73
75	A10_BIS	51	0	6.15	143.63	8.26	33.93	3.81	0	9.81	18.94	3.53	0	11.8	408.45	23.13	0	4.78	0	27.01	0	9.46	76.69	14.19	0	59.79	63.34	20.02	0	47.27	0	71.77	4437.34	168.92	0	70.38
76	A20_BIS	66	0	6.13	125.17	7.94	43.32	4.2	0	9.56	21.49	3.61	0	10.72	386.22	22.66	0	4.89	40.53	18.23	0	9.55	98.9	15.68	0	57.62	120.88	23.53	0	48.42	0	67.98	4106.08	163.79	0	71.03
77	A30_BIS	60	0	5.93	62.99	6.43	51.																													

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
78	A40_BIS	65	0	6.35	137.3	8.62	110.76	6.29	0	10.63	33.52	4.28	0	8.98	162.62	15.62	0	4.81	0	18.59	0	9.51	41.11	12	0	64.29	0	26.64	0	50.83	0	91.74	6888.45	214.43	172.53	59.99
79	A50_BIS	69	0	5.97	97.68	7.24	44.41	4.15	0	8.76	17.87	3.29	8.84	5.69	78.98	11.36	0	4.54	0	12.99	0	8.65	32.42	10.71	0	58.57	30.16	17.65	0	47.72	0	71.74	4527.07	169.56	95.06	50.18
80	A60_BIS	41	0	6.01	79.72	6.69	36.29	3.81	0	8.16	15.42	3.07	0	7.48	67.53	10.6	0	4.47	0	11.92	0	8.41	18.86	9.24	0	55.06	0	24.61	0	45.69	0	64.93	3923.72	157.14	191.07	57.24
81	B00	47	0	6.61	97.85	7.74	47.06	4.52	0	9.82	23.8	3.87	0	12.59	440.09	25.21	0	5.35	0	29.78	0	9.75	81.61	15.2	0	62.12	45.65	20.59	0	50.43	0	71.98	4070.34	170.54	104.84	54.03
82	B01	66	0	5.93	106.49	7.38	45.62	4.17	0	9.24	20.37	3.48	0	11.03	433.65	23.35	0	4.63	0	27.05	0	8.52	67.72	13.31	0	58.46	53.52	18.93	0	46.37	0	74.65	5125.32	178.08	0	70.29
83	B02	63	0	6.17	66.57	6.86	54.48	4.69	0	9.89	26.16	3.95	0	14.32	711.26	30.91	0	5.66	39.53	24.35	0	9.64	89.81	15.49	0	62.02	86.37	22.14	0	48.92	0	83.93	5862.21	198.57	113.94	54.69
84	B03	71	0	6.12	78.04	6.93	46.85	4.32	0	9.16	18.48	3.44	0	12.16	475.21	24.98	0	4.94	35.31	19.83	0	9.54	45.03	12.04	0	60.28	53.56	19.53	0	47.28	0	67.16	3960.38	160.84	0	70.09
85	B04	51	0	6.11	172.14	8.8	37.77	3.94	0	8.72	17.19	3.3	0	12.01	491.69	25.13	0	4.67	0	29.34	0	9.75	140.71	18.02	0	65.41	98.17	21.96	0	45.21	0	67.12	3790.12	156.07	0	70.25
86	B05	54	0	6.11	68.16	6.75	56.98	4.66	0	9.66	17.41	3.47	0	13.42	657.42	29.07	0	4.96	44.24	23.04	0	9.72	74.74	14.31	0	64	64.35	20.16	0	43.81	0	83.54	6142.81	198.63	86.27	51.19
87	B06	56	0	6.17	82.13	6.99	35.13	3.89	0	9.21	20.79	3.57	0	13.05	573.22	27.37	0	5.45	35.18	21.6	0	9.36	70	13.87	0	60.53	60.06	19.98	0	46.66	0	83.51	6069.82	198.18	0	74.81
88	B07	61	0	5.8	43.02	5.9	34.18	3.8	0	8.68	13.41	3.12	0	13.43	640.9	28.46	0	5.02	0	32.86	0	8.66	83.77	14.4	0	55.63	50.05	18.88	0	46.56	0	72.51	4423.38	167.84	171.68	57.4
89	B08	53	0	6.1	70.14	6.73	33.1	3.83	0	8.93	17.35	3.39	0	12.85	601.3	28.24	0	5.49	0	32.36	0	9.3	109.28	16.51	0	63.62	64.49	20.55	0	46.41	0	67.67	3709.63	157.65	110.61	52.55
90	B09	51	0	6.29	145.68	8.43	41.81	4.14	0	9.86	18.37	3.55	15.04	8.59	478.8	25.16	0	5.09	0	29.25	0	9.17	81.03	14.69	0	64.5	55.25	19.89	0	49.13	0	63.01	3558.37	153.27	87.95	50.05
91	B10	38	0	6.15	55.77	6.3	32.41	3.79	0	9.22	18.13	3.44	0	10.4	310.74	20.67	0	5.14	0	24.33	0	9.82	84.02	14.96	0	66	0	25.65	0	47.94	0	70.86	4155.49	166.22	88.05	51.08
92	B11	60	0	6.03	81.84	6.97	41.56	4.1	0	9.49	17.73	3.45	0	12.63	531.03	26.16	0	4.76	50.45	20.99	0	9.64	58.14	13.07	0	64.51	41.7	18.77	0	48.58	0	65.24	3764.93	156.21	99.11	51.29
93	B12	57	0	6.18	88.9	7.21	37.73	4.02	0	9.75	19.15	3.58	0	13.2	624.9	28.68	0	5.34	56	22.96	0	9.5	87.02	15.08	0	61.44	61.36	20.28	0	48.55	0	72.38	4381.05	170.27	85.6	50.22
94	B13	56	0	6.18	91.64	7.27	42.85	4.19	0	10.02	23.11	3.8	0	15.02	922.17	34.3	0	5.45	0	39.74	0	9.38	67.65	13.73	0	62.23	43.38	18.91	0	46.78	0	70.41	4461.87	170.37	87.97	50.58
95	B14	54	0	6.08	65.52	6.67	47.85	4.39	0	9.26	19.46	3.53	0	13.74	724.41	30.66	0	5.1	36.5	24.11	0	9.3	78.29	14.31	0	56.7	49.85	19.47	0	48.59	0	74.8	5219.71	184.78	132.58	55.47
96	B15	61	0	6.39	55.52	6.67	37.59	4.19	0	9.94	19.88	3.74	0	14.02	627.96	30.02	0	5.77	0	34.98	0	10.46	58.03	13.8	0	66.08	52.65	21.18	0	49.14	0	70.09	4003.6	170.25	103.42	55.45
97	B16	48	0	5.93	79.75	6.7	42.67	4.01	0	8.45	17.53	3.22	0	12	483.57	24.28	0	4.69	0	28.38	0	8.95	66.16	13.06	0	57.39	52.37	18.4	0	42.47	0	65.53	3831.97	152.71	118.49	51.05
98	B00_BIS	47	0	6.13	104.54	7.49	50.23	4.4	0	9.82	22.9	3.7	0	11.47	409.96	23.15	0	5.05	0	27.18	0	9.06	69.9	13.6	0	56.58	50.33	19.21	0	45.88	0	66.17	4185.68	164.08	111.68	51.5
99	B04_BIS	51	0	5.93	46.41	6.12	46.61	4.29	0	9.81	20.11	3.6	15.01	9.28	646.74	28.71	0	4.97	0	33.37	0	9.64	218.49	21.54	0	62.31	92.78	21.82	0	47.51	0	72.59	4495.78	169.73	93.51	51.13
100	B08_BIS	53	0	6.03	81.13	7.01	47.15	4.33	0	9.36	17.66	3.44	0	13.15	606.95	28.03	0	5.06	37.36	22.14	0	9.04	134.71	17.61	0	58.21	74.98	20.83	0	44.23	0	69.08	4376.68	168.67	91.37	50.65
101	B12_BIS	57	0	6.15	96.02	7.32	38.03	4	0	9.27	19.85	3.52	0	12.71	536.01	26.46	0	5.12	0	30.82	0	9.81	58.89	13.1	0	61.47	41.17	18.81	0	46.59	0	67.61	3846.52	158.73	100.4	50.9
102	B16_BIS	48	0	6.12	86.52	7.07	42.26	4.14	0	9.17	18.31	3.42	0	11.7	453.24	24.35	0	4.78	0	28.44	0	9.51	64.63	13.45	0	61.24	49.12	19.29	0	47.13	0	66.94	4074	162.61	0	66.93
103	B00_60"	47	0	6.12	108.49	7.55	46.58	4.26	0	9.25	22.89	3.63	0	11.74	416.53	23.27	0	4.97	0	27.27	0	9.01	62.58	13.14	0	59.16	36.06	18.2	0	44.23	0	68.47	4256.21	165.08	93.06	50.32
104	B04_60"	51	0	5.99	46.12	6.16	47.9	4.35	0	9.22	24.54	3.73	16.76	9.35	625.64	28.47	0	5.5	40.06	22.49	0	9.21	223.27	21.86	0	61.57	103.97	22.55	0	45.56	0	70.41	4476.17	170.46	105.79	52.54
105	B08_60"	53	0	6.12	73.59	6.83	47.61	4.35	0	9.33	17.06	3.4	0	13.29	632.05	28.57	0	4.97	0	32.75	0	8.98	138.52	17.72	0	54.23	83.89	21.34	0	45.14	0	71.1	4393.02	168.93	91.92	51.15
106	B12_60"	57	0	6.17	90.07	7.22	36.48	3.96	0	8.91	17.9	3.39	13.75	8.93	561.93	27.19	0	5.19	0	31.39	0	9.55	62.42	13.25	0	57.13	52.72	19.63	0	47.44	0	66.14	3907.18	160.71	153.2	55.64
107	B16_60"	48	0	6.12	83.8	7.04	43.75	4.2	0	9.65	17.14	3.44	0	12.01	451.04	24.34	0	5.13	0	28.51	0	9.42	67.98	13.74	0	62.48	46.74	19.09	0	44.74	0	65.39	4004.53	161.54	104.81	51.65
108	S116(0-10)	98	0	6.01	104.04	7.46	52.2	4.46	0	9.23	18.2	3.39	0	9.82	210.52	17.02	0	4.36	22.69	13.64	0	9.35	69.54	13.65	0	59.01	58.06	19.6	0	46.67	0	73.94	4905.92	176.98	91.19	50.73
109	S116(10-20)	171	0	6.22	117.26	7.85	61.85	4.81	0	9.3	22.54	3.61	0	8.45	91.94	12.19	0	4.69	0	13.87	0	9.07	184.69	20.12	0	62.97	0	26.47	0	48.94	0	76.84	5274.27	185.17	137.05	55.69
110	S116(20-30)	116	0	6.08	67.33	6.48	30.56	3.65	0	9.16	12.65	3.11	0	7.58	73.56	11.15	0	4.65	0	12.93	0	8.01	62.95	13	0	55.73	0	24.91	0	47.4	0	76.28	5032.36	180.55	147.19	55.57
111	S116(30-40)	137	0	5.88	42.44	5.76	43.88	4.1	0	9.2	20.45	3.43	0	6.87	0	9.41	0	4.18	0	7.1	0	8.97	0	11.45	0	54.61	0	22.95	0	46.1	0	56.51	2796.6	133.29	81.33	47.55
112	S116(40-50)	169	0	5.95	31.05	5.43	40.35	3.99	0	9.05	15.42	3.19	0	6.68	0	9.08	0	4.21	0	6.79	0	8.66	0	11.21	0	53.81	0	24.58	0	46.74	0	52.93	2477.81	126.41	0	65.54
113	S116(0-10)_BIS	98	0	6.14	129.48	8.08	61.11	4.79	0	9.83	24.01	3.75	0	9.51	256.39	18.71	0	4.64	0	21.57	0	9.46	80.85	14.58	0	61.31	63.59	20.04	0	45.21	0	74.98	5230.38	183.89	103.24	52.03
114	S116(10-20)_BIS	171	0	5.91	144.03	8.18	42.25	4.07	0	8.61	15.35	3.15	0	9.74	236.3	17.79	0	4.67	0																	

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
115	S116(20-30)_BIS	116	0	6.02	55.35	6.07	35.68	3.79	0	8.16	8.9	2.72	0	6.98	74.52	10.88	0	3.8	0	12.75	0	8.92	71.44	13.54	0	58.35	0	24.14	0	43.37	0	73.96	5564.03	186.25	123.25	53.17
116	S116(30-40)_BIS	137	0	5.95	33.23	5.64	46.11	4.26	0	8.51	16.78	3.22	0	6.98	0	9.36	0	4.56	0	7.52	0	8.75	13.51	8.99	0	57.49	0	26.34	0	47.23	0	75.48	4952.47	179.51	0	73.65
117	S116(40-50)_BIS	169	0	6.02	90.76	6.9	38.11	3.85	0	8.88	17.85	3.27	0	6.46	0	8.97	0	4.68	0	6.97	0	8.07	0	11.31	0	55.88	0	23.82	0	43.28	0	58.95	3127.01	139.46	0	62.88
118	107-C(5X1)	262	0	5.96	40.02	6.56	30.16	3.95	0	9.94	16.77	3.82	34.48	19.46	3760.93	69.3	0	8.4	283.4	55.28	0	10.87	348.94	27.38	0	63.78	361.85	34.42	0	44.9	0	78.37	5703.02	194.66	109.65	58.77
119	107-C(5X1)_BIS	262	0	6.48	61.12	7.54	53.32	5	0	10.81	21.11	4.22	37.49	20.21	3659.51	71.5	0	8.9	166.95	56.2	0	11.79	256.85	25.05	0	69.17	276.07	33.03	0	51.85	0	83.68	5306.14	196.62	121.32	59.88
120	107-C(5X1)_BIS2	262	0	6.94	85.89	9.15	53.54	5.52	0	13.23	27.11	5.22	59.66	27.87	6287.03	99.83	0	11.89	212.06	78.01	0	13.75	441.63	34.29	0	78.88	491.66	44.62	0	61.96	0	103.31	7313.74	245.78	182.54	70.8
121	107-R(1X1)	58	0	8.08	63.82	11.9	49.21	6.96	0	16.33	22.13	6.94	119.8	51.69	16892.9	189.01	0	19.92	441.24	147.19	0	20.81	1164.8	63.42	0	106.49	1669.3	88.83	0	79.02	0	129.22	8279	304.89	268.4	96.9
122	107-R(5X1)	267	0	6.45	64.97	7.41	50.51	4.8	0	10.96	25.88	4.33	39.97	18.01	2818.92	62.18	0	8.18	0	71.68	0	11.2	244.2	24.06	0	64.53	230.04	30.62	0	52.79	0	81.37	5584.16	199.12	111.51	57.14
123	107-R(5X1)_BIS	267	0	6.56	143.09	9.58	48.81	4.96	0	11.64	29.91	4.78	46.19	21.56	3967.08	75.85	0	9.45	103.45	59.03	0	12.1	271.38	26.23	0	71.92	341.36	36.64	0	56.79	0	87.32	5828.59	209.79	146.64	63.11
124	107-R(5X1)_BIS2	267	0	6.5	105.05	8.35	51.94	4.87	11.89	7.75	19.99	4.22	0	28.39	3367.38	67.62	0	8.2	0	77.69	0	11.18	237.88	23.81	0	65.86	261.12	31.77	0	50.23	0	86.43	5981.46	205.24	124.21	58.14
125	112-C(5X1)	222	0	6.55	68.79	8	50.85	5.04	0	11.55	21.17	4.47	45.25	23.3	4850.24	83.22	0	9.42	0	96.17	0	12.46	323.24	28.17	0	74.69	302.64	34.63	0	52.28	0	86.11	5662.43	205.58	125.98	60.51
126	112-R(1X1)	49	0	6.61	57.96	7.16	42.05	4.51	0	10.64	20.37	4.05	27.59	16.86	2478.18	58.81	0	7.21	0	68.01	0	11.48	233.76	23.82	0	71.06	110.06	24.86	0	50.22	0	86.68	6069.75	209.19	154.16	62.36
127	112-R(5X1)	222	0	6.58	88.66	8.17	40.92	4.6	0	11.16	20.77	4.26	31.66	19.82	3480.2	70.44	0	8.77	166.71	55.43	0	12.36	277.64	26.07	0	69.65	207.62	30.45	0	53.58	0	89	6289.62	215.72	187.57	65.37
128	111-R(1X1)01	74	0	6.09	88.33	7.01	39.27	3.99	0	8.86	19.22	3.39	0	8.33	198.56	16.58	0	4.55	0	18.95	0	9.37	85.43	14.81	0	64.51	29.62	17.81	0	48.24	0	70.79	4436.26	168.96	105.24	52.1
129	111-R(1X1)02	59	0	5.99	63.06	6.46	58.33	4.63	0	9.97	22.1	3.65	0	8.38	166.68	15.26	0	4.33	0	18.17	0	8.73	58.67	12.7	0	56.6	31.87	17.64	0	45.68	0	65.9	4007.82	159.72	120.12	52.3
130	111-R(1X1)03	59	0	6.08	102.65	7.38	48.57	4.32	0	8.49	16.13	3.19	0	10.11	296.4	19.81	0	4.58	0	22.65	0	8.74	34.23	10.82	0	55.73	37.2	18.19	0	45.51	0	60.29	3437.14	148.63	98.09	50.11
131	111-R(1X1)04	64	0	5.85	61.27	6.47	63.84	4.81	0	9.36	23.4	3.62	0	10.06	243.14	18.13	0	5.06	0	20.85	0	8.81	72.13	13.52	0	52.78	31.73	17.57	0	44.99	0	69.54	3973.32	158.95	113.58	51.73
132	111-R(1X1)05	63	0	6.3	125.98	8.11	57.13	4.71	0	9.94	17.11	3.48	0	9.21	177.31	16.11	0	4.68	0	18.81	0	9.69	54.16	12.98	0	65.46	34.87	18.77	0	49.25	0	63.1	3687.62	157.48	120.9	54.26
133	111-R(1X1)06	68	0	6.06	92.16	7.18	43.16	4.16	0	9.2	15.46	3.27	0	8.21	164.65	15.42	0	4.76	0	18.12	0	8.93	32.5	11.01	0	61.98	34.83	18.3	0	47.57	0	76.51	4971.09	179.89	97.81	52.06
134	111-R(1X1)07	77	0	6.03	63.84	6.6	40.97	4.15	0	9.04	16.73	3.34	0	10.57	263.41	19.26	0	4.74	0	22.32	0	9.89	55.03	12.93	0	61.9	0	27.13	0	47.73	0	65.99	3681.57	157.44	0	72.64
135	111-R(1X1)08	78	0	6.01	73.35	6.64	35.07	3.81	0	9.52	16.23	3.34	0	9.41	187.1	16.14	0	4.67	0	19.19	0	8.89	69.62	13.64	0	60.73	41.1	18.38	0	44.58	0	62.92	3538.62	150.88	110.77	51.36
136	111-R(1X1)09	81	0	5.88	52.19	6.15	44.72	4.21	0	9.24	16.03	3.29	0	9.05	236.82	17.96	0	4.53	0	20.5	0	9.74	64.91	13.39	0	59.93	44.23	18.74	0	45.76	0	68.97	4100.85	162.78	130.06	53.75
137	111-R(1X1)10	38	0	6.3	130.54	8.25	40.09	4.16	0	9.88	20.09	3.65	0	10.33	222.59	18.07	0	4.84	0	21	0	9.77	78.64	14.83	0	64.54	50.57	20.18	0	48.55	0	73.32	4868.76	182.35	0	73.23
138	111-R(5X1)01	273	0	6.69	109.11	8.22	43.02	4.5	0	10.14	16.36	3.61	0	10.38	172.66	17.06	0	5.29	0	20.26	0	10.82	39.32	12.75	0	72.25	0	29.2	0	51.09	0	81.28	5104.01	196.93	120.75	58.74
139	111-R(5X1)02	222	0	6.07	98.37	7.31	47.95	4.3	0	9.53	16.84	3.38	0	10.01	278.93	19.33	0	4.87	0	22.59	0	8.84	86.92	14.76	0	60.97	31.79	17.81	0	47.15	0	73.92	4760.19	174.37	96.28	50.41
140	111-R(5X1)03	290	0	6.17	93.1	7.24	51.23	4.45	0	9.21	23.68	3.66	0	9.31	238.91	18.14	0	4.53	0	21	0	8.67	54.26	12.67	0	60.21	50.24	19.34	0	47.44	0	75.78	5503.74	189.35	428.06	77.32
141	111-R(5X1)04	249	0	6.9	57.16	7.38	45.77	4.94	0	11.62	18.06	4.07	0	11.68	257.42	21.74	0	5.61	0	25.38	0	11.53	62.93	15.55	0	74.44	38.49	23.51	0	59.73	0	82.49	4305.39	193.82	0	85.07
142	111-R(5X1)05	141	0	6	74.38	6.69	38.67	3.97	0	8.35	20.48	3.39	0	9	205.62	16.89	0	4.8	0	19.5	0	9.2	46.03	12.01	0	61.33	0	26.09	0	45.73	0	70.78	4385.08	168.05	111.35	51.58
143	111-R(5X1)06	314	0	6.79	51.71	6.93	56.64	5.08	0	11.29	19.16	3.96	14.35	8.4	316.44	22.66	0	5.93	0	26.25	0	10.81	54.65	14.35	0	76.18	46.39	22.05	0	51.81	0	80.54	4787.82	193.06	117.99	58.58
144	111-R(5X1)07	260	0	6.13	79.07	6.93	46.56	4.31	0	9.5	19.41	3.52	0	9.89	278.96	19.55	0	4.79	0	22.69	0	8.88	113.26	16.49	0	58.27	68.49	20.5	0	44.57	0	75.12	4703.77	175.67	187.36	59.7
145	111-R(5X1)08	285	0	6	69.23	6.63	42.61	4.12	0	8.91	17.02	3.3	0	10.86	304.36	20.14	0	4.39	0	23.77	0	9.32	80.6	14.42	0	60.29	54.5	19.46	0	48.29	0	79.5	5366.83	185.27	121.8	53.62
146	111-R(5X1)09	262	0	6.03	73.86	6.69	30.7	3.67	0	9.01	20.21	3.47	0	10.11	231.25	17.87	0	4.59	0	21.06	0	8.79	67.85	13.44	0	57.42	0	26.39	0	48.39	0	70.89	4629.61	173.05	98.01	50.83
147	111-R(5X1)10	251	0	6.14	124.36	7.84	37.49	3.92	0	9.15	16.15	3.29	0	9.97	233.05	17.82	0	4.38	0	20.72	0	9.34	66.32	13.53	0	62.42	39.06	18.36	0	45.64	0	74.15	4635.59	172.48	150.53	56.1
148	111-C(6X6)01<250	83.1	0	7.05	419.77	13.32	72.8	5.38	0	11.58	31.25	4.43	0	15.37	769.79	32.6	0	5.52	0	37.64	0	10.12	123.46	17.98	0	69.13	107.43	23.94	0	50.78	0	109.19	9590.06	257.01	373.22	79.56
149	111-C(6X6)02<250	81.3	0	7.5	638.24	16.15	83.38	5.75	15.7	8.23	32	4.58	0	15.15	784.87	33.17	0	5.65	0	39.11	0	10.15	149.39	19.42	0	66.44	102.48	23.91	0	52.7	0	107.5	9487.41	257.47	221.3	68.22
150	111-C(6X6)03<250	75.2	0	6.8	366.93	12.51	77.37	5.49	0	11.1	33.37	4.41																								

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
152	111-C(6X6)05<250	78.2	0	7.27	509.76	14.46	76.15	5.47	0	11.45	29.63	4.34	0	15.21	783.15	32.82	0	5.72	0	37.94	0	9.98	149.18	19.27	0	67.09	108.1	23.91	0	49.56	0	100.31	8201.97	237.27	135.98	59.8
153	111-C(6X6)06<250	74.7	0	7.11	537.12	14.91	77.66	5.56	0	11.29	32.6	4.46	0	15.55	840.56	34.22	0	6.31	0	39.49	0	10.87	142.65	19.27	0	74.68	100.26	23.77	0	51.16	0	108.31	9889.93	262.12	234.47	68.79
154	111-C(6X6)07<250	64.4	0	6.99	355.9	12.5	76.68	5.51	0	10.94	30.45	4.33	20.5	10.84	818.11	33.7	0	5.72	0	39.35	0	10.06	160.48	19.96	0	69.29	100.26	23.71	0	52.67	0	102.87	8686.35	245.39	245.27	68.93
155	111-C(6X6)08<250	87.1	0	7.14	454.96	13.75	69.16	5.26	0	10.09	33.08	4.3	0	15.43	801.57	33.2	0	5.77	0	38.61	0	10.56	147.72	19.17	0	66.48	101.88	23.58	0	51.15	0	100.2	8396.77	240.12	200.86	64.61
156	111-C(6X6)09<250	75.7	0	7.18	474.42	14.11	78.2	5.58	0	10.96	34.21	4.47	0	13.86	712.2	31.6	0	5.69	0	36.72	0	10.83	119.44	17.78	0	66.62	93.19	23.33	0	52.58	0	103.6	8681.39	246.05	140.06	61.27
157	111-C(6X6)10<250	60.3	0	7.57	582.92	15.77	80.41	5.76	0	11.65	34.4	4.65	17.78	11.82	1025.25	38.34	0	6.28	0	44.88	0	10.42	158.25	20.26	0	69.71	121.8	25.58	0	56.54	0	125.98	12729.89	301.98	252.62	73.03
158	111-C(6X6)09<250	75.7	0	7.63	742.75	17.24	77.27	5.56	0	11.67	29.74	4.39	0	14.96	732.77	32.05	0	5.99	0	37.67	0	10.47	123.54	18.09	0	69.99	97.4	23.73	0	53.73	0	113.74	10391.37	268.95	372.01	78.8
159	111-C(6X6)01<250	83.1	0	6.38	166.38	9.09	68.69	5.15	0	10.39	26.06	4	0	14	686.61	30.32	0	5.43	0	35.33	0	10.24	125.19	17.66	0	65.86	94.52	22.66	0	51.24	0	92.38	7715.57	226.83	217.44	63.8
160	111-C(6X6)02<250	81.3	0	6.65	263.36	10.8	68.04	5.13	0	10.96	31.16	4.29	0	15.13	762.69	31.92	0	5.86	0	36.83	0	9.64	155.43	19.12	0	62.02	87.53	22.21	0	50.36	0	99.91	8598.82	239	165.39	60.68
161	111-C(6X6)03<250	75.2	20.04	12.61	38.16	15.34	0	10.8	0	26.63	0	9.06	0	18.71	50.33	26.01	0	22.76	0	31.03	0	58.62	90.7	51.99	489.7	268.48	239.75	111.94	0	239.41	0	227.83	6758.76	533.53	0	214.9
162	111-C(6X6)04<250	64.2	0	7.45	552.53	15.19	76.61	5.57	0	11.04	32.25	4.43	0	15.4	783.66	33.31	0	6.14	0	38.21	0	10.62	122.43	18.06	0	67.61	89.53	23.25	0	52.29	0	116.75	10750.72	274.9	220.28	68.4
163	111-C(6X6)05<250	78.2	0	6.99	339.45	12.18	75.84	5.46	0	10.05	32.55	4.27	0	15.3	755.36	32.27	0	5.84	0	37.86	0	10.69	128.91	18.24	0	68	109.87	23.99	0	50.62	0	105.12	9091.22	249.63	180.67	64.03
164	111-C(6X6)06<250	74.7	0	7.29	371.18	13.28	66.67	5.46	0	12.3	34.32	4.8	0	15.59	794.41	34.87	0	6.75	0	40.5	0	10.15	142.38	19.91	0	70.79	111.36	26.02	0	55.67	0	113.06	9335.26	266.64	179	67.95
165	111-C(6X6)07<250	64.4	0	7.65	699.47	17.34	78.81	5.8	0	11.49	31.7	4.54	0	15.96	799.27	34.5	0	5.61	0	39.81	0	11.42	162.47	20.79	0	71.61	83.88	23.91	0	56.77	0	122.72	10848.71	283.6	247.42	74.38
166	111-C(6X6)08<250	87.1	0	6.78	326.61	12.05	71.06	5.34	0	10.84	29.12	4.26	19.99	10.7	791.63	33.19	0	5.64	0	38.86	0	9.96	148.17	19.26	0	64.81	137.81	25.77	0	52.94	0	104.47	9028.42	250.09	174.4	63.73
167	111-C(6X6)09<250	75.7	0	6.82	342.4	12.18	75.34	5.42	0	10.48	30.34	4.24	16.95	10.96	913.12	35.19	0	5.96	0	41.01	0	10.21	138.78	18.69	0	68.58	127.6	24.94	0	53.67	0	106.96	9965.92	260.07	346.69	76.37
168	111-C(6X6)10<250	60.3	0	7.57	539.09	15.59	78.17	5.83	0	11.62	30.22	4.54	0	16.15	845.74	35.8	0	6.12	0	41.88	0	10.77	131.18	19.21	0	69.61	90.13	24.59	0	55.78	0	118.49	10487.11	281.66	269	74.93
169	111-C(6X6)09<250	75.7	0	7.9	888.36	18.99	80.36	5.74	0	10	27.71	4.14	0	15.3	746.73	32.83	0	6.05	0	38.17	0	10.17	133.16	18.78	0	65.76	111.27	24.78	0	52.44	0	120.65	12040.89	293.24	261.67	73.25
170	111-C(6X6)09<250	75.7	0	7.57	617.62	16.05	76.36	5.59	0	11.58	28.61	4.37	0	15.82	783.6	33.47	0	5.9	0	39.07	0	10.4	123.4	18.28	0	70.84	86.95	23.34	0	52.83	0	119.01	10798.08	276.94	241.78	71.35
171	111-C(6X6)09<250	75.7	0	6.91	367	12.43	70.01	5.23	0	10.69	28.42	4.15	16.08	9.9	691.16	30.64	0	5.9	0	35.46	0	10.03	123.18	17.61	0	65.39	85.83	22.43	0	52.78	0	99.73	8547.39	239.73	151.66	59.57
172	111-C(6X6)01_250	174	0	6.04	126.09	7.77	46.37	4.17	0	8.84	13.56	3.08	10.1	6.58	213.87	16.84	0	4.25	25.2	13.55	0	8.23	47.84	11.65	0	53.17	36.44	17.51	0	43.93	0	60.04	2955.67	136.2	117.32	51.13
173	111-C(6X6)02_250	191.5	0	5.86	48.42	5.95	33.37	3.72	0	8.59	13.9	3.09	0	10.47	290.88	19.5	0	4.42	0	23.22	0	9.46	60.14	13.07	0	63.6	49.06	18.67	0	43.64	0	63.29	3509.15	149.16	101.1	50.56
174	111-C(6X6)03_250	200	0	6.06	42.72	6.01	57.17	4.61	0	9.66	26.16	3.8	13.11	7.87	380.34	22.27	0	4.97	27.34	17.62	0	9.4	59.73	12.98	0	58.26	71.08	20.16	0	44.14	0	77.51	5483.72	186.48	238.72	63.22
175	111-C(6X6)04_250	205.2	0	5.94	69.09	6.71	68.63	4.97	0	9.6	22.85	3.64	0	9.65	206.15	16.82	0	4.28	0	19.71	0	9.13	50.4	12.32	0	62.31	0	25.9	0	49.25	0	65.85	3858.01	157.28	107.78	51.38
176	111-C(6X6)05_250	194.1	0	5.99	33.8	5.71	55.72	4.55	0	9.09	16.92	3.3	0	10.51	272.54	19.03	0	4.45	0	22.5	0	9.09	67.5	13.42	0	58.93	49.03	18.89	0	48.24	0	72.92	4990.96	177.73	188.88	58.87
177	111-C(6X6)06_250	188	0	6.04	124.77	7.83	49.12	4.31	0	8.84	21.35	3.47	0	10.65	314.76	20.28	0	5.06	26.94	16.13	0	9.48	64.44	13.36	0	62.45	50.47	18.75	0	41.98	0	68.77	4439.85	167.16	97.6	50.28
178	111-C(6X6)07_250	178.1	0	6.16	159.59	8.65	52.15	4.47	0	8.98	16.29	3.29	0	10.86	325.75	20.86	0	4.94	0	24.62	0	8.81	68.45	13.62	0	59.26	52.67	19.22	0	46.11	0	87.81	6965.96	210.81	103.27	53.49
179	111-C(6X6)08_250	181.8	0	5.99	45.64	5.98	33.37	3.78	0	8.89	18.23	3.38	0	12.84	589.46	27.47	0	5.68	61.27	22.12	0	9.61	86.4	14.88	0	61.61	85.99	21.3	0	47.12	0	77.24	5788.38	191.89	141.95	56.38
180	111-C(6X6)01_250	174	0	5.96	57.09	6.24	49.33	4.31	0	7.96	15.32	3.06	0	9.7	262.31	18.59	0	4.37	0	21.74	0	8.69	56.45	12.52	0	57.32	30.59	17.35	0	44.52	0	68.59	4340.7	165.58	293.9	66.38
181	111-C(6X6)02_250	191.5	0	5.76	43.37	5.84	49.03	4.28	0	8.9	14.09	3.11	0	9.21	220.11	17.14	0	4.75	0	20.01	0	9.04	56.37	12.39	0	55.03	39.95	17.98	0	47	0	63.71	3751.44	153.17	87.38	49.18
182	111-C(6X6)03_250	200	0	6.04	39.36	5.99	68.12	4.99	0	10.17	24.05	3.8	0	10.71	333.64	21.07	0	4.72	0	24.74	0	8.81	70.91	13.77	0	58.42	53.82	19.31	0	45.62	0	64.41	3806.72	157.06	0	68.3
183	111-C(6X6)04_250	205.2	0	5.79	32.72	5.6	62.85	4.72	0	8.72	13.85	3.06	0	8.79	187.54	15.9	0	4.51	0	18.85	0	8.61	61.68	12.71	0	54.4	34.93	17.48	0	45.46	0	61.76	3495.06	147.62	84.87	47.58
184	111-C(6X6)05_250	194.1	0	6.06	106.67	7.45	44.35	4.17	0	9.45	23.47	3.65	0	10.39	303.93	20	0	4.48	32.34	16.08	0	9.31	59.18	12.94	0	59.51	69.94	20.16	0	46.2	0	76.81	5450.9	185.67	200.3	59.98
185	111-C(6X6)06_250	188	0	6.1	83.65	7.05	52.5	4.48	0	8.76	17.7	3.33	12.64	7.88	384.74	22.47	0	4.41	0	24.39	0	9.34	82.14	14.69	0	63.8	79.28	20.97	0	47.36	0	72.62	4918.66	177.58	77.75	48.8
186	111-C(6X6)07_250	178.1	0	5.96	162.02	8.7	59.75	4.71	0	9.92	18.71	3.53	0	10.69	314.58	20.47	0	5.1																		

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
189	111-C(6X6)10A_25	148.7	0	6.15	43.22	5.97	52.49	4.48	0	9.46	21.77	3.59	0	9.86	281.74	19.44	0	4.38	0	23.15	0	9.26	71.82	13.78	0	57.73	35.9	18.05	0	44.81	0	77.94	5425.86	186.42	88.69	51.58
190	111-C(6X6)09A_25	162.6	0	6.06	99.65	7.23	33.77	3.77	0	9.09	22.27	3.56	0	9.78	284.55	19.44	0	4.81	0	22.39	0	9.4	61.97	13.15	0	60.91	55.77	19.34	0	47.66	0	71.7	4837.57	175.7	315.94	68.81
191	111-C(6X6)09A_25	162.6	0	5.76	50.57	5.97	40.03	3.94	0	8.14	13.43	2.97	0	9.78	269.5	18.64	0	4.23	0	22.01	0	8.89	53.02	12.21	0	57.48	49.77	18.51	0	46.18	0	62.73	3594.29	149.33	0	66.04
192	111-C(6X6)10A_25	148.7	0	5.88	45.45	5.98	52.81	4.45	0	9.21	21.99	3.55	0	9.92	303.49	19.97	0	4.87	0	22.91	0	8.57	65.17	13.17	0	56.16	48.05	18.64	0	44.68	0	75.59	5194.11	180.9	124.56	53.14
193	111-C(6X6)09A_25	162.6	0	5.9	63.03	6.4	46.64	4.22	0	8.68	15.45	3.18	0	10.03	262.08	18.63	0	4.5	0	21.65	0	8.15	47	11.75	0	55.92	27.18	17.18	0	45.84	0	72.88	4638.95	170.79	100.54	50.64
194	111-C(6X6)09A_25	162.6	0	5.9	100.85	7.26	42.11	4.05	0	9.29	25.2	3.69	0	9.7	233.14	17.64	0	4.6	23.98	14.11	0	8.89	49.32	12.09	0	59.87	36.11	17.77	0	45.49	0	68.13	4591.82	169.51	0	70.97
195	111-C(6X6)09A_25	162.6	0	5.88	65.66	6.4	43.88	4.1	0	9.19	20.23	3.45	0	9.68	251.02	18.15	0	4.75	22.75	14.45	0	8.97	71.09	13.61	0	59.63	72.37	20.04	0	46.03	0	69.26	4553.21	168.21	148.68	54.34
196	111-C(6X6)09B_25	164.3	0	5.95	47.99	5.93	34.44	3.78	0	8.85	13.03	3.07	0	8.74	179.8	15.82	0	4.75	20.66	12.69	0	9.35	36.65	11.21	0	59.5	51.36	18.9	0	43.82	0	59.68	3087.1	140.91	0	69.72
197	111-C(6X6)10B_25	148.3	0	6.05	55.9	6.31	49.21	4.37	0	8.96	15.09	3.21	0	10.17	258.46	18.75	0	4.69	0	22.07	0	9.19	68.45	13.6	0	59.43	42.27	18.59	0	47.26	0	71.36	4768.71	175.25	105.12	52.33
198	111-C(6X6)09B_25	164.3	0	6.07	77.33	6.71	36.8	3.87	0	9.37	15.65	3.29	0	9.44	262.89	18.69	0	4.68	0	22.05	0	9.03	50.38	12.33	0	61.22	59.75	19.47	0	44.43	0	76.2	5462.69	185.49	115.82	53.11
199	111-C(6X6)09B_25	164.3	0	5.9	49.21	6.11	54.91	4.51	0	8.6	15.15	3.16	0	10.35	291.68	19.62	0	4.76	0	23.04	0	8.47	61.58	13.02	0	59.33	59.93	19.49	0	46.89	0	66.12	4052.98	160.37	98	50.13
200	111-C(6X6)10B_25	148.3	0	5.89	39.22	5.67	42.31	4.04	0	8.61	11.72	2.96	0	8.94	242.82	17.86	0	4.52	0	20.65	0	9.17	53.33	12.42	0	62.02	33.39	17.56	0	47.08	0	68.6	3833.46	154.94	93.01	49.69
201	111-C(6X6)09B_25	164.3	0	5.8	32.17	5.42	37.04	3.83	0	8.47	14.12	3.04	0	8.99	203.9	16.43	0	4.22	25.77	13.28	0	9.35	51.68	12.2	0	59.48	52.69	18.74	0	45.86	0	57.79	3567.97	148.97	130.82	53.08
202	111-C(6X6)09B_25	164.3	0	6.35	260.25	10.37	44.17	4.2	0	9.45	18.97	3.48	0	11.16	341.21	21.26	0	4.49	0	24.56	0	9.18	67.2	13.54	0	59.96	45.2	18.73	0	46.95	0	84.74	6368.69	201.55	131.84	54.75
203	111-C(6X6)09B_25	164.3	0	5.99	110.85	7.52	39.43	3.97	0	9.14	20.42	3.49	0	11.17	347.2	21.24	0	4.61	0	25.11	0	8.71	66.78	13.38	0	59.11	55.92	19.15	0	44.93	0	77.62	5211.43	181.07	129.6	54.2
204	111-R(1X1)01_BIS	74	0	5.94	80.95	6.83	36.74	3.89	0	9.45	21.39	3.56	0	9.42	195.61	16.5	0	4.87	0	19.05	0	8.96	73.79	13.76	0	56.69	31.77	17.78	0	48.03	0	68.96	4262.84	165.27	169.38	57.43
205	111-R(1X1)05_BIS	63	0	5.97	59.39	6.32	45.68	4.21	0	9.02	17.77	3.33	0	9.68	241.6	18.02	0	4.58	0	21.3	0	9.63	45.8	12.03	0	63.01	36.6	18.12	0	47.22	0	67.5	3935.49	158.44	106.78	50.75
206	111-R(1X1)10_BIS	38	0	5.92	46.35	5.89	42.03	4.05	0	8.3	19.19	3.3	0	8.44	193.37	16.22	0	4.29	0	18.44	0	8.6	59.68	12.79	0	58.43	32.78	17.67	0	45.59	0	62.38	3453.63	148.27	113.19	51.23
207	111-R(5X1)01BIS	273	0	6.26	177.18	8.91	38.61	3.99	0	9.32	19.07	3.46	0	8.91	218.29	17.38	0	4.56	0	20.48	0	9.63	55.64	12.82	0	62.48	0	26.4	0	46.84	0	68.66	4144.92	164.19	103.08	51.21
208	111-R(5X1)02BIS	222	0	5.85	90.74	7.04	45.55	4.17	0	8.32	15.57	3.12	0	9.59	236.92	17.73	0	4.52	0	20.7	0	9.33	58.19	12.89	0	64.44	25.98	17.2	0	45.62	0	65.04	3889.18	156.43	87.21	49.12
209	111-R(5X1)03BIS	290	0	6.19	121.73	7.81	42.63	4.13	0	9.31	21.06	3.54	0	8.87	194.36	16.47	0	4.45	0	19.52	0	9.25	49.04	12.26	0	61.11	0	25.89	0	44.94	0	71.69	4661.42	173.43	109.57	51.65
210	111-R(5X1)04BIS	249	0	6.16	104.51	7.37	35.08	3.83	0	8.58	13.32	3.07	0	9.66	305.62	20.13	0	4.79	0	23.38	0	9.44	44.48	11.93	0	61.34	50.02	19.1	0	46.43	0	68.56	4423.82	168.43	134.73	53.83
211	111-R(5X1)05BIS	141	0	5.85	82.46	6.88	42.54	4.1	0	9.21	17.48	3.36	0	9.36	249.21	18.29	0	4.55	0	21.63	0	9.03	48.39	12.28	0	63.04	49.34	18.87	0	43.13	0	69.42	4204.31	164.01	141.68	54.92
212	111-R(5X1)06BIS	314	0	6.26	146.93	8.42	41.14	4.12	0	9.64	17.19	3.43	0	10.23	251.87	18.73	0	4.93	0	22.21	0	9.05	63.49	13.37	0	59.93	44.48	19.07	0	48.54	0	80.33	5922.48	196.59	115.26	54.12
213	111-R(5X1)07BIS	260	0	6.01	56.87	6.31	43.26	4.18	0	8.98	17.02	3.32	0	9.23	226.16	17.74	0	4.52	0	20.3	0	8.6	59.95	12.86	0	54.61	36.93	18.46	0	48.85	0	70.3	4519.19	171.71	80.05	49.88
214	111-R(5X1)08BIS	285	0	6	73.76	6.77	42.22	4.14	0	9.15	20.91	3.54	0	10.24	290.12	19.87	0	4.66	0	23.55	0	9.05	80.32	14.44	0	59.07	49.91	19.42	0	49.89	0	87.33	6457.7	204.52	139.55	56.41
215	111-R(5X1)09BIS	262	0	5.94	112.06	7.6	49.28	4.35	0	8.99	15.73	3.24	0	9.29	229.01	17.64	0	4.4	0	20.72	0	8.88	67.68	13.49	0	58.94	40.21	18.31	0	44.05	0	66.97	4208.68	164.17	0	69.23
216	111-R(5X1)10BIS	251	0	6.17	108.02	7.49	34.91	3.83	0	8.76	16.28	3.24	0	9.81	231.03	17.82	0	4.7	0	20.75	0	9.16	75.44	14.04	0	59.62	36.76	18.3	0	47.95	0	72.53	4903.19	177.69	156.56	56.49
217	111-R(5X1)01BIS2	273	0	6.03	75.79	6.82	51.62	4.45	0	9.1	22.61	3.58	0	9.85	207.66	16.99	0	4.52	0	19.81	0	9.33	41.98	11.59	0	57.87	0	26.13	0	45.71	0	75.78	4969.55	178.76	164.43	56.88
218	111-R(5X1)02BIS2	222	0	5.98	85.21	7.04	62.36	4.77	0	9	16.7	3.28	0	9.5	267.71	18.87	0	4.44	0	21.8	0	9	81.99	14.36	0	59.02	0	25.6	0	46.2	0	66.13	4077.44	161.25	89.67	49.97
219	111-R(5X1)03BIS2	290	0	6.2	106.79	7.64	60.24	4.78	0	9.47	25.03	3.76	0	9.94	242.91	18.41	0	5.14	0	21.35	0	9.71	45.2	12.18	0	63.19	43.07	18.96	0	47.33	0	67.2	4126.69	165.15	271.86	66.4
220	111-R(5X1)04BIS2	249	0	6.15	164.17	8.6	39.23	3.98	0	8.67	16.55	3.23	0	9.87	247.28	18.25	0	4.75	0	21.39	0	9.37	57.52	12.82	0	60.88	41.67	18.46	0	46.19	0	66.61	4092.76	161.53	82.59	49.32
221	111-R(5X1)05BIS2	141	0	5.97	65.64	6.53	52.36	4.45	0	9.51	17.22	3.38	0	9.14	184.16	16.03	0	4.57	0	18.43	0	8.97	39.46	11.45	0	60.27	39.73	18.23	0	44.6	0	63.61	3881.81	157.97	153.99	55.42
222	111-R(5X1)06BIS2	314	0	6.09	71.89	6.75	58.06	4.66	0	9.2	15.56	3.27	0	9.62	254.36	18.59	0	4.71	28.65	14.96	0	8.83	79.39	14.22	0	57.59	0	25.88	0	47.3	0	69.93	4511.98	170.49	88.04	50.18
223	111-R(5X1)07BIS2	260	0	6.02	72.23	6.59	39.03	3.97	0	8.85	16.53	3.25	0	8.75	223.14	17.38	0	4.49	0	20.31	0	9.44	84.78	14.6	0	58.61	55.63	19.18	0	43.14	0	72.14	4611.5	171.17	87.06	49.66
224	111-R(5X1)08BIS2	285	0	6.18	123.2	7.87	37.75																													

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	CODE	Weight	Mo	Mo Error	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error
226	111-R(5X1)10BIS2	251	0	5.99	103.53	7.32	28.8	3.56	0	8.88	18.31	3.35	0	9.7	215.07	17.16	0	4.41	0	20.27	0	8.55	71.24	13.59	0	55.54	58.48	19.5	0	46.65	0	68.3	4057.72	161.15	91.09	49.79
227	111-R(5X1)01BIS3	273	0	6.17	90.54	7.36	78	5.32	0	10.34	22.69	3.77	0	9.39	203.58	17	0	4.93	0	20.02	0	9.02	48.24	12.37	0	62.67	43.73	19.02	0	47.61	0	74.54	4755.08	176.33	0	70.86
228	111-R(5X1)02BIS3	222	0	6.12	81.83	6.97	47.77	4.33	0	9.43	20.27	3.53	0	10.26	285.11	19.68	0	5.21	0	22.99	0	9.75	60.64	13.23	0	62.98	38.97	18.54	0	46.76	0	66.68	4356.34	168.49	259.03	65.19
229	111-R(5X1)03BIS3	290	0	6	91.14	6.97	35.15	3.77	0	8.66	13.29	3.04	0	9.08	183.7	15.8	0	4.36	19.74	12.64	0	8.57	44.35	11.49	0	55.77	30.25	17.33	0	45.94	0	62.22	3709.96	152.53	135.24	53.49
230	111-R(5X1)04BIS3	249	0	6.12	91.8	7.15	37.83	3.95	0	9.25	21	3.55	0	9.96	243.4	18.25	0	4.7	0	21.4	0	9.64	53.07	12.87	0	67.7	41.91	18.66	0	45.41	0	67.86	3793.89	157.2	108.31	51.78
231	111-R(5X1)05BIS3	141	0	6.92	74.42	7.62	29.79	4.12	0	10.56	15.07	3.7	12.8	7.47	158.47	17.22	0	5.57	0	20.03	0	10.84	39.73	13.15	0	71.98	0	30.7	0	54.37	0	71.79	3551.23	172.68	0	84.69
232	111-R(5X1)06BIS3	314	0	6.01	65.45	6.43	34.93	3.8	0	9.52	17.76	3.41	0	10.31	256.18	18.49	0	4.59	0	21.54	0	8.51	67.1	13.31	0	57.26	55.47	19.26	0	45.94	0	63.06	3732.62	154.08	82.19	48.61
233	111-R(5X1)07BIS3	260	0	6.06	107.17	7.49	39.73	4.03	0	9.09	14.08	3.18	0	9.36	221.16	17.5	0	4.72	0	20.54	0	9.23	53.56	12.54	0	59.17	27.96	17.61	0	44.94	0	71.56	4466.42	170.06	109.03	52.59
234	111-R(5X1)08BIS3	285	0	5.86	78.37	6.79	32.91	3.74	0	9.73	14.86	3.32	0	10.65	284.79	19.54	0	4.74	0	23.02	0	8.42	61.06	12.88	0	55.33	37.46	18.17	0	44.8	0	69.02	4321.82	166.44	74.21	48.17
235	111-R(5X1)09BIS3	262	0	6.06	78.04	6.89	44.03	4.21	0	9.75	21.64	3.64	0	9.83	227.29	17.83	0	4.82	36.97	14.62	0	9.04	59.96	13.03	0	58.42	31.85	18.13	0	47.11	0	81.54	5622.42	191.17	106.14	53.05
236	111-R(5X1)10BIS3	251	0	5.97	79.93	6.91	44.9	4.22	0	8.85	14.66	3.19	0	10.31	307.26	20.37	0	5.39	0	23.97	0	8.97	105.58	15.97	0	60.69	43.26	18.85	0	47.91	0	69.99	4682.31	176.32	1140.88	113.84
237	111-C(6X6)09C_25	163.1	0	5.93	29.75	5.51	46.89	4.25	12.43	6.76	15.99	3.41	0	9.68	237.48	17.84	0	4.43	0	20.56	0	9.66	49.58	12.29	0	63.15	32.89	17.77	0	47.42	0	67.76	4073.74	160.77	0	70.17
238	111-C(6X6)10C_25	146.5	0	6.02	40.85	5.85	32.86	3.78	0	8.87	15.82	3.26	0	9.54	205.08	17.08	0	4.98	24.7	13.75	0	9.79	50.14	12.76	0	68.67	40.86	18.93	0	47.19	0	61.9	3281.87	147.88	0	70.74
239	111-C(6X6)09C_25	163.1	0	6.22	225.01	9.76	51.02	4.42	0	8.96	18.77	3.38	0	10.35	282.54	19.45	0	4.96	26.49	15.52	0	9.37	72.13	13.72	0	55.8	49.87	18.89	0	45.11	0	83.28	6383.15	200.91	104.77	52.94
240	111-C(6X6)09C_25	163.1	0	6.2	171.47	8.81	54.41	4.52	0	9.5	22.42	3.62	0	10.86	344.72	21.25	0	5.08	0	24.78	0	8.79	73.39	13.81	0	57.95	63.32	19.8	0	48.4	0	86.15	6860.61	207.68	180.14	59.74
241	111-C(6X6)10C_25	146.5	0	5.84	61.14	6.41	52.53	4.44	0	8.89	19.56	3.41	0	9.97	286.85	19.48	0	4.64	42.99	15.94	0	8.52	55.33	12.52	0	56.86	51.75	18.91	0	44.03	0	66.56	4032.32	160.24	85.54	50.39
242	111-C(6X6)09C_25	163.1	0	6.33	234.23	10.05	57.79	4.69	0	9.75	22.93	3.71	0	11.52	362.42	22.01	0	4.83	33.21	17.58	0	9.23	83.23	14.63	0	59.2	35.93	18.25	0	46.93	0	93.46	7688.44	222.29	193.18	61.33
243	111-C(6X6)09C_25	163.1	0	6.46	331.56	11.56	43.07	4.2	0	8.88	19.94	3.48	0	11.03	373.52	22.42	0	5.19	0	25.8	0	9.49	83.61	14.94	0	65.31	55.82	19.77	0	47.83	0	102.48	9415.56	246.76	165.42	60.52
244	111-C(6X6)09C_25	163.1	0	5.79	41.1	5.7	35.56	3.79	0	8.98	21.49	3.48	0	9.11	211	16.79	0	4.2	0	19.39	0	8.84	47.21	11.83	0	58.71	29.57	17.32	0	45.78	0	57.35	3164.88	141.33	0	68.66
245	111-C(6X6)09D_25	163.4	0	6.45	252.7	10.31	49.12	4.4	0	9.49	17.63	3.43	0	10.28	317.84	20.71	0	4.88	0	24.38	0	9.67	73.2	14.13	0	61.88	53.4	19.42	0	45.44	0	88.36	6970.12	212	112.28	55.47
246	111-C(6X6)10D_25	147.5	0	6.15	64.75	6.36	43.76	4.08	0	8.8	14.36	3.12	0	9.13	212.78	16.83	0	4.81	0	19.56	0	8.78	57.95	12.74	0	61.31	57.78	19.11	0	45.07	0	68.32	3869.16	155.12	0	68.26
247	111-C(6X6)09D_25	163.4	0	5.94	115.71	7.6	40	3.99	0	8.81	17.97	3.32	0	10.16	283.41	19.33	0	4.63	0	22.68	0	8.9	61.96	13	0	58.44	46.35	18.56	0	45.69	0	69.8	4568.3	169.66	0	67.74
248	111-C(6X6)09D_25	163.4	0	6.08	97.77	7.23	53.16	4.43	0	9.04	19.19	3.39	0	9.86	258.03	18.46	0	4.82	0	21.54	0	8.78	53.38	12.31	0	57.26	41.29	18.07	0	44.3	0	71.98	4694.42	171.25	118.6	52.29
249	111-C(6X6)10D_25	147.5	0	5.84	37.33	5.7	52.01	4.38	0	9.4	15.7	3.27	0	10.17	293.18	19.46	0	4.74	0	22.61	0	8.77	58.35	12.56	0	56.15	42.34	18.07	0	45.71	0	59.25	3250.82	142.77	109.93	50.91
250	111-C(6X6)09D_25	163.4	0	5.97	115.34	7.58	46.2	4.21	0	8.88	22.16	3.5	0	9.46	266.12	18.77	0	5	0	21.76	0	9.39	60.59	12.84	0	56.22	46.06	18.4	0	44.24	0	66.36	3973.79	158.45	152.15	55.27
251	111-C(6X6)09D_25	163.4	0	5.95	47.69	5.93	36.35	3.83	0	8.51	20.22	3.38	0	9.73	243.71	18.03	0	4.86	0	21.41	0	8.76	58.68	12.77	0	59.62	44.01	18.37	0	45.27	0	64.94	3785.57	154.62	0	71.08
252	111-C(6X6)09D_25	163.4	0	6.03	43.94	6.04	70.18	4.99	0	9.27	18.05	3.38	0	9.8	245.3	18.1	0	4.65	0	21.07	0	8.6	52.38	12.32	0	58.6	38.88	17.99	0	44.62	0	70.91	4577.14	169.92	116.95	52.04
253	111-C(6X6)10RIFF	156.3	0	5.94	53.34	6.11	28.64	3.56	0	8.9	15.29	3.22	0	11.6	439.3	23.78	0	4.9	34.64	18.91	0	9.68	77.86	14.24	0	60.4	77.1	20.65	0	46.01	0	67.42	4260.65	164.63	0	70.83
254	111-C(6X6)10RIFF	156.3	0	5.93	46.32	5.97	52.09	4.39	0	9.1	24.04	3.61	0	10.29	300.86	19.74	0	4.56	44.11	16.14	0	9.19	61.4	12.98	0	61.06	46.26	18.54	0	48.57	0	71.97	4784.11	172.81	225.68	60.32
255	OUTSIDE(1X1)01		15.27	4.88	145.12	8.89	40.48	4.35	0	10.67	21.78	3.91	0	7.88	54.79	10.81	0	5.18	0	13.13	0	9.81	26.86	11.04	0	64.02	0	25.95	0	52.37	0	96.08	7134.15	229.05	0	73.19
256	OUTSIDE(1X1)02		0	6.22	147.6	8.07	34.34	3.68	0	8.28	14.37	3.02	7.98	5.14	33.21	8.43	0	4.77	11.87	6.91	0	8.61	0	12.28	0	59.74	0	22.97	0	41.47	0	71.53	5207.06	177.57	0	58.89
257	OUTSIDE(1X1)_60"		0	6.19	155.35	8.28	34.73	3.74	0	8.82	14.78	3.12	0	7.26	47.4	9.32	0	4.17	0	10.48	0	9.01	15.4	9.08	0	58.21	0	24.5	0	43.19	0	72.9	5257.97	180.09	0	63.35

APPENDIX 2

LEAD REMOVAL TEST READINGS

[illegible]

CODE	Reading No	Time	Type	Duration	Units	Sequence	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error	Cr	Cr Error	V	V Error	Ti	Ti Error	Sc	Sc Error	Ca	Ca Error	K	K Error	S	S Error
S-ED5-REP2	81	13/07/2014 19:53	Soil	32,16	ppm	Final	856,06	17,62	64,41	4,93 <LOD	10,21	27,33	3,95 <LOD	9,26			151,7	14,96 <LOD	4,37 <LOD	17,13 <LOD	8,49	125,09	17,13 <LOD	59,56	58,44	19,65 <LOD	50,07 <LOD	110,71	10559,35	260,26	156,08	60,65 <LOD	45,03 <LOD	21,57 <LOD	257,01 <LOD	27,87 <LOD	339,82 <LOD	531,29 <LOD	33,72													
	82	13/07/2014 19:54	Soil	30,52	ppm	Final	411,87	12,41	69,39	4,95 <LOD	10,05	29,77	3,95 <LOD	8,59			156,48	14,79 <LOD	4,48 <LOD	17,15 <LOD	9,1	147,78	17,96 <LOD	58,74	69,89	19,68 <LOD	47,25 <LOD	105,6	9954,8	247,24	221,57	63,41 <LOD	26,14 <LOD	35,76 <LOD	778,98 <LOD	20,13 <LOD	848,54 <LOD	1275,04 <LOD	83,76													
	83	13/07/2014 19:55	Soil	32,37	ppm	Final	534,74	14,07	74,02	5,15 <LOD	10,05	30,25	4 <LOD	9,11			159,86	15,11 <LOD	4,62 <LOD	17,51 <LOD	9,12	141,89	17,78 <LOD	56,97	64,95	19,59 <LOD	47,14 <LOD	106,85	9693,71	246,31	145,44	58,19 <LOD	31,51 <LOD	17,93 <LOD	208,94 <LOD	27,64 <LOD	285,95 <LOD	593,62 <LOD	62,9													
	84	13/07/2014 19:56	Soil	32,51	ppm	Final	511,45	13,62	64,7	4,81 <LOD	9,9	24,11	3,71 <LOD	8,98			164,18	15,13 <LOD	4,77 <LOD	17,99 <LOD	9,11	124,05	16,75 <LOD	58,93	70,58	19,6 <LOD	44,93 <LOD	101,02	9066,25	235,78	131,72	56,28 <LOD	36,95 <LOD	12,87	147,34 <LOD	27,27 <LOD	266,37	737,15	141,62 <LOD	780,45 <LOD	30,91											
S-ED5-REP3	85	13/07/2014 19:57	Soil	32,7	ppm	Final	561,16	14,12	63,57	4,75 <LOD	10	29,55	3,93 <LOD	8,26			158,53	14,77 <LOD	4,24 <LOD	17,31 <LOD	8,38	131,67	17,01 <LOD	57,23	70,04	19,48 <LOD	43,51 <LOD	97,67	8585,91	228,54	149,54	56,66 <LOD	46,35 <LOD	13,69	240,62	140,02 <LOD	27,6 <LOD	306,65	678,23	431,5 <LOD	33,56											
	86	13/07/2014 19:58	Soil	32,31	ppm	Final	873,42	17,58	69,44	5,02 <LOD	9,87	27,29	3,87 <LOD	9,52			182,59	16 <LOD	4,52 <LOD	18,33 <LOD	9,36	111,46	16,3 <LOD	61,47	58,8	19,26 <LOD	46,77 <LOD	112,13	11265,97	265,4	205,1	63,2 <LOD	44,06 <LOD	24,09 <LOD	291,24 <LOD	23,23 <LOD	297,76	1026,94	565,59 <LOD	70,45												
M	87	13/07/2014 19:58	Soil	30,66	ppm	Final	656,41	15,16	73,34	5,04 <LOD	9,52	26,81	3,75 <LOD	9,12			175,17	15,44 <LOD	4,52 <LOD	17,77 <LOD	9,3	122,76	16,6 <LOD	60,74	45,04	18,05 <LOD	47,7 <LOD	103,66	9898,73	244,82	212,8	62,02 <LOD	28,13 <LOD	1,42 <LOD	37,43 <LOD	55,85 <LOD	847,4 <LOD	36,81 <LOD	63,86													
	88	13/07/2014 19:59	Soil	31,75	ppm	Final	73,84	6,59	43,84	4,08 <LOD	8,38	19,3	3,29 <LOD	9,88			243,93	17,87 <LOD	4,7 <LOD	20,55 <LOD	8,94	114,39	16,15 <LOD	61,22	50,91	18,63 <LOD	44,58 <LOD	65,16	3935,74	156,17	90,45	48,6 <LOD	31,71 <LOD	15,64 <LOD	179,26 <LOD	3,21 <LOD	141,62 <LOD	780,45 <LOD	30,91													
M-DIW-REP1	89	13/07/2014 20:00	Soil	31,9	ppm	Final	77,9	7,81	43,82	4,77 <LOD	11,36	25,8	4,37 <LOD	10,89			238,24	20,62 <LOD	5,88 <LOD	24,14 <LOD	12,23	92,09	17,82 <LOD	82,04	89,11	26,4 <LOD	60,15 <LOD	79,25	4143,12	186,97	132,43	62,91 <LOD	23 <LOD	11,43 <LOD	140,31 <LOD	18,47 <LOD	60,6 <LOD	631,41 <LOD	24,74													
	90	13/07/2014 20:01	Soil	37,87	ppm	Final	42,15	5,89	37,42	3,96 <LOD	9,7	13,38	3,24 <LOD	9,43			225,96	17,72 <LOD	4,39 <LOD	20,2 <LOD	9,38	91,73	15,23 <LOD	59,92	61,12	20,04 <LOD	44,79 <LOD	65,23	3579,82	153,53	87,22	50,38 <LOD	39,42 <LOD	11,71	200,4	88,9 <LOD	15,54	271,76	157,36	1644,79	393,33 <LOD	1035,2										
M-DIW-REP2	91	13/07/2014 20:02	Soil	33,86	ppm	Final	320,28	11,2	44,5	4,18 <LOD	9,28	19,43	3,46 <LOD	10,09			334,18	20,88 <LOD	4,28 <LOD	24,6 <LOD	8,78	172,76	19,4 <LOD	61,49	98,24	21,53 <LOD	46,46 <LOD	100,73	9607,46	245,09	174,01	59,82 <LOD	33,53 <LOD	15,09	235,33	138,06 <LOD	21,9	395,09	196,16	519,99	196,16	519,99	307,59 <LOD	28,36								
	92	13/07/2014 20:03	Soil	30,79	ppm	Final	72,49	6,16	36,49	3,63 <LOD	8,17	16,67	3,03 <LOD	7,48			140,52	13,35 <LOD	4,11 <LOD	15,06 <LOD	8,46	52,6	11,54 <LOD	53,24	33,65	15,96 <LOD	40,46 <LOD	46,45	1785,1	102,55	164,43	51,51 <LOD	101,55 <LOD	4,11 <LOD	224,16 <LOD	46,58 <LOD	425,5 <LOD	21,87 <LOD	36,1													
M-DIW-REP3	93	13/07/2014 20:03	Soil	30,97	ppm	Final	245,99	10,01	50,83	4,37 <LOD	9,19	19,4	3,43 <LOD	10,53			342,47	21,03 <LOD	4,83 <LOD	24,79 <LOD	9,01	187,43	19,93 <LOD	59,3	113,73	22,15 <LOD	45,07 <LOD	97,2	8751,68	232,51	201,56	61,4 <LOD	104,43 <LOD	21,11 <LOD	354,42 <LOD	10,32 <LOD	64,54 <LOD	1313,85 <LOD	59,63													
	94	13/07/2014 20:04	Soil	30,52	ppm	Final	80,11	6,56	43,32	3,97 <LOD	8,78	18,95	3,28 <LOD	9,89			341,6	20,3 <LOD	4,56 <LOD	23,74 <LOD	8,52	159,61	17,95 <LOD	54,56	104,9	20,76 <LOD	41,46 <LOD	79,05	6524,2	194,82	200,9	58,01 <LOD	117,52 <LOD	47,66 <LOD	656,23 <LOD	134,43 <LOD	899,08 <LOD	1315,98 <LOD	11438,02													
M-DIW-REP3	95	13/07/2014 20:05	Soil	31,64	ppm	Final	139,31	7,98	43,26	4,05 <LOD	7,61	14,07	2,95 <LOD	11,12			427,25	23,02 <LOD	5,13	43,06	18,48 <LOD	9,21	213,39	20,86 <LOD	61,47	121,17	22,23 <LOD	44,36 <LOD	97,28	9507,86	239,1	244,24	64,13 <LOD	13,87 <LOD	20,27	325,87	201,39 <LOD	12,59 <LOD	539,32 <LOD	936,65 <LOD	89,67											
	96	13/07/2014 20:06	Soil	30,16	ppm	Final	123,02	7,7	47,7	4,22 <LOD	9,06	16,69	3,28 <LOD	10,6			398,19	22,35 <LOD	4,78	27,52	17,69 <LOD	8,99	215,56	21,03 <LOD	60,94	128,03	22,72 <LOD	45,17 <LOD	91,04	8072,14	221,57	171,14	58,37																			
M-ED1-REP1	97	13/07/2014 20:07	Soil	32,48	ppm	Final	54,53	5,85	36,32	3,68 <LOD	8,29	16,22	3,01 <LOD	9,23			284,05	18,51 <LOD	4,48 <LOD	21,92 <LOD	8,62	112,73	15,55 <LOD	57,19	84,67	19,49 <LOD	41,25 <LOD	70,65	4893,63	168,09	112,14	49,54 <LOD	49,23 <LOD	11,45 <LOD	72,02 <LOD	6,13 <LOD	265,81 <LOD	588,25 <LOD	61,49													
	98	13/07/2014 20:08	Soil	30,22	ppm	Final	23,69	5,04	45,02	3,97 <LOD	8,32	16,1	3,06 <LOD	8,82			194,59	15,59 <LOD	4,33 <LOD	17,86 <LOD	8,27	94,83	14,43 <LOD	56,61	45,16	17,06 <LOD	43,51 <LOD	62,42	3678,46	145,77 <LOD		57,56																				
M-ED1-REP2	99	13/07/2014 20:08	Soil	30,71	ppm	Final	86,77	6,57	38,41	3,72 <LOD	7,99	17,52	3,07 <LOD	8,56			186,97	15,23 <LOD	4,28 <LOD	18,02 <LOD	7,93	73,63	13 <LOD	53,65	45,22	16,93 <LOD	41,87 <LOD	58,62	3306,61	137,77 <LOD		65,92 <LOD	102,29 <LOD	20,45 <LOD	344,21 <LOD	46,09 <LOD	314,2 <LOD	901,6 <LOD	46,34													
	100	13/07/2014 20:09	Soil	30,56	ppm	Final	70,32	6,4	38,16	3,84 <LOD	8,22	7,56	2,64 <LOD	7,41			66,06	10,32 <LOD	3,83 <LOD	11,93 <LOD	8,49	68,1	13,15 <LOD	56,54	49,44	18,18 <LOD	46,13 <LOD	79,27	6214,36	194,21	141,68	54,35 <LOD	144,16 <LOD	9,32 <LOD	511,77 <LOD	27,75 <LOD	1197,8 <LOD	1803,04 <LOD	110,35													
M-ED1-REP3	101	13/07/2014 20:10	Soil	31,67	ppm	Final	46,56	5,52	39,3	3,7 <LOD	8,23	17,83	3,08 <LOD	6,99			55,99	9,3 <LOD	3,65 <LOD	10,91 <LOD	8,01	46,64	11,21 <LOD	54,64 <LOD	22,54	44,7	29,1 <LOD	50,83	2456,9	118,32 <LOD		58,84 <LOD	68,04 <LOD	19,33 <LOD	221,56 <LOD	305,18 <LOD	641,33 <LOD	33,53														
	102	13/07/2014 20:11	Soil	30,41	ppm	Final	55	5,87	35,79	3,67 <LOD	8,45	13,02	2,94 <LOD	7,04			72,28	10,47 <LOD	4,01 <LOD	12,17 <LOD	8,36	63,68	12,72 <LOD	58,38	49,45	17,5 <LOD	42,29 <LOD	67,51	4724,99	166,69	120,58	50,62 <LOD	22,19 <LOD	58,65 <LOD	696,38 <LOD	154,97 <LOD	999,7 <LOD	1237,4 <LOD	87,93													
M-ED1-REP3	103	13/07/2014 20:12	Soil	30,6	ppm	Final	24,73	4,95	44,65	3,88 <LOD	8,75	19,95	3,24 <LOD	7,08			70,84	10,07 <LOD	3,57 <LOD	11,89 <LOD	8,16	54,34	11,69 <LOD	56,11	29,55	15,55 <LOD	40,78 <LOD	63,23	4109,27	151,33	135,08	50,33 <LOD	207,64 <LOD	40,57 <LOD	286,49 <LOD	14,38 <LOD	620,24 <LOD	1314,67 <LOD	11437,81													
	104	13/07/2014 20:12	Soil	30,54	ppm	Final	58,47	5,93	39,13	3,76 <LOD	7,81	15,64	2,96 <LOD	7,03			57,23	9,53 <LOD	3,86 <LOD	10,82 <LOD	7,99	39,2	10,8 <LOD	57,46	24,87	15,67 <LOD	41,52 <LOD	54,92	2742,42	126,93 <LOD		61,27 <LOD	104,95 <LOD	1,8 <LOD	60,83 <LOD	90,9 <LOD	144,56 <LOD	36,94 <LOD	30,78													
M-ED1-REP3	105	13/07/2014 20:13	Soil	30,83	ppm	Final	69,45	6,18	40,66	3,8 <LOD	8,16	16,11	3,01 <LOD	7,73			65,51	10,02 <LOD	4,04 <LOD	11,36 <LOD	8,08	51,12	11,43 <LOD	51,47	28,67	15,76 <LOD	40,63 <LOD	56,65	3043,95	132,44 <LOD		59,39 <LOD	90,58 <LOD	2,54 <LOD	130,55 <LOD	7,09 <LOD	319,02 <LOD	647,6 <LOD	36,78													
	106	13/07/2014 20:15	Soil	30,48	ppm	Final	30,38	5,21	40,12	3,81 <LOD	8,15	17,28	3,09 <LOD	7,54			76,03	10,65 <LOD	4,11 <LOD	12,2 <LOD	8,15	84,81	13,83 <LOD	54,92	34,51	16,43 <LOD	41,81 <LOD	72,38	5396,78	176,62	100,38	49,03 <LO																				

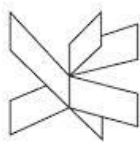
CODE	Reading No	Time	Type	Duration	Units	Sequence	Zr	Zr Error	Sr	Sr Error	U	U Error	Rb	Rb Error	Th	Th Error	Pb	Pb Error	Se	Se Error	As	As Error	Hg	Hg Error	Zn	Zn Error	W	W Error	Cu	Cu Error	Ni	Ni Error	Co	Co Error	Fe	Fe Error	Mn	Mn Error	Cr	Cr Error	V	V Error	Ti	Ti Error	Sc	Sc Error	Ca	Ca Error	K	K Error	S	S Error
L-ED1-REP3	153	13/07/2014 20:51	Soil	32,32	ppm	Final	48,91	5,64	30,16	3,43 <LOD	7,93	10,29	2,7 <LOD	7,03			60,09	9,76 <LOD		4,11 <LOD	11,42 <LOD	7,97	33,02	10,13 <LOD	51,87	33,6	16,21 <LOD		39,6 <LOD	42,25	1301,51	89,74 <LOD	59,42 <LOD	40,46 <LOD	13,97 <LOD	147,39 <LOD	24,93	526,76	267,55 <LOD		266,6 <LOD		31,08									
	154	13/07/2014 20:52	Soil	31,24	ppm	Final	50,26	5,74	41,66	3,85 <LOD	7,94	13,65	2,87 <LOD	7,67			77,13	10,66 <LOD		4,04 <LOD	12,56 <LOD	8,32	52,14	11,61 <LOD	53,2	36,13	16,37 <LOD		43,08 <LOD	59,68	3344,82	139,46	106,19	48,46 <LOD	61,38 <LOD	22,26 <LOD	227,35 <LOD	44,63 <LOD	359,95 <LOD		866,88 <LOD		41,55									
	155	13/07/2014 20:53	Soil	33,18	ppm	Final	29,5	5,08	31,85	3,47 <LOD	8,5	14,88	3,01 <LOD	7,23			69,53	10,21 <LOD		4,12 <LOD	12,11 <LOD	8,29	41,38	10,9 <LOD	56,8	23,75	15,39 <LOD		41,44 <LOD	55,94	3221,88	136,43 <LOD	64,92 <LOD	40,24 <LOD	4,73 <LOD	88 <LOD	15,43 <LOD	207,81 <LOD		436,61 <LOD		22,35										
	156	13/07/2014 20:54	Soil	31,72	ppm	Final	33,75	5,08	20,91	2,98 <LOD	7,79	9,92	2,64 <LOD	7,22			74,94	10,39 <LOD		4,11 <LOD	12,29 <LOD	7,98	49,52	11,2 <LOD	51,8	25,3	15,15 <LOD		39,54 <LOD	48,56	2365,08	116,23 <LOD	53,51 <LOD	25,09 <LOD	16,01 <LOD	113,77 <LOD	21,45 <LOD	139,44 <LOD		580,16 <LOD		1173,89										
L-ED5-REP1	157	13/07/2014 20:54	Soil	32,07	ppm	Final	30,57	5,14	36,58	3,65 <LOD	8,41	14,78	2,99 <LOD	7,39			75,47	10,54 <LOD		4,11 <LOD	12,58 <LOD	7,81	48,7	11,29 <LOD	52,11	45,54	16,81 <LOD		41,75 <LOD	57,5	3085,51	133,58	66,16	43,83 <LOD	40,3 <LOD	14,31 <LOD	153,12 <LOD	16,81 <LOD	275,12 <LOD		487,11 <LOD		27,6									
	158	13/07/2014 20:55	Soil	30,32	ppm	Final	105,83	7,01	35,91	3,66 <LOD	8,15	17,17	3,08 <LOD	7,24			105,73	12,05 <LOD		4,11 <LOD	14,07 <LOD	8,46	54,91	11,99 <LOD	55,95	51,7	17,4 <LOD		40,06 <LOD	73,01	5501,34	178,02	103,77	49,53																		
L-ED5-REP2	159	13/07/2014 20:56	Soil	30,28	ppm	Final	44,59	5,41	25,52	3,18 <LOD	8,14	16,6	3,03 <LOD	8,06			162,98	14,16 <LOD		3,79 <LOD	16,62 <LOD	7,82	34,54	10,15 <LOD	53,62	27,72	15,38 <LOD		39,68 <LOD	49,24	2105,49	110,15	73,13	43,16																		
	160	13/07/2014 20:57	Soil	30,33	ppm	Final	101,77	6,84	30,16	3,4 <LOD	7,39	14,18	2,82 <LOD	7,81			116,98	12,46 <LOD		3,88 <LOD	14,13 <LOD	8,02	61,59	12,14 <LOD	49,96	59,45	17,65 <LOD		40,48 <LOD	72,04	5099,94	169,86 <LOD	65,25																			
L-ED5-REP3	161	13/07/2014 20:57	Soil	31,95	ppm	Final	38,09	5,29	30,58	3,39 <LOD	7,87	11,46	2,74 <LOD	9,03			199,63	15,5 <LOD		4,04 <LOD	18,31 <LOD	8,25	48,28	11,09 <LOD	51,26 <LOD		21,54 <LOD	39,21 <LOD	52,57	2648,23	122,56 <LOD	63,88 <LOD	23,92 <LOD	17,76 <LOD	216,18 <LOD	19,42 <LOD	246,7 <LOD		287,43 <LOD		23,23											
	162	13/07/2014 20:58	Soil	30,52	ppm	Final	66,13	6,14	35,99	3,67 <LOD	8,45	16,6	3,12 <LOD	8,76		23,4	238,89	17,13 <LOD		4,19	13,69 <LOD	7,72	53,57	11,72 <LOD	52,86	33,1	16,19 <LOD		42,34 <LOD	57,84	3345,39	140,1	78,34	45,58 <LOD	102,1 <LOD	38,15 <LOD	270,74 <LOD	2,86 <LOD	167,79 <LOD		1749,82 <LOD		66									
	163	13/07/2014 20:59	Soil	31,62	ppm	Final	31,46	5,17	35,73	3,62 <LOD	8,43	17,03	3,1 <LOD	8,91			207,3	15,9 <LOD		4,06 <LOD	18,88 <LOD	8,2	50,41	11,41 <LOD	53,46	33,7	16,15 <LOD		43,88 <LOD	51,28	2669,83	124,33	121,4	48,89 <LOD	31,08 <LOD	2,17 <LOD	110,44 <LOD	5,07 <LOD	232,18 <LOD		786,77 <LOD		35,02									
	164	13/07/2014 21:00	Soil	32,63	ppm	Final	42,1	5,39	33,35	3,5 <LOD	7,5	8,58	2,53 <LOD	6,72			64,2	9,85 <LOD		4,18 <LOD	11,02 <LOD	7,93	42,38	10,78 <LOD	53,44	26,95	15,51 <LOD		40,67 <LOD	49,21	2214,54	113,37	82,05	44,73 <LOD	39,61 <LOD	5,1 <LOD	99,61 <LOD	16,38	593,73	276,77 <LOD		185,84 <LOD		30,88								
L-GL1-REP1	165	13/07/2014 21:00	Soil	32,63	ppm	Final	45,04	5,43	25,95	3,22 <LOD	7,78	11,48	2,72 <LOD	6,59			59,32	9,59 <LOD		4,06 <LOD	11,25 <LOD	7,86	60,22	11,93 <LOD	49,54	30,75	15,68 <LOD		40,56 <LOD	57,98	3186,64	134,97	81,39	45,66 <LOD	40,5 <LOD	10,67 <LOD	158,67 <LOD	23,9 <LOD	262,42 <LOD		264,54 <LOD		22,46									
	166	13/07/2014 21:01	Soil	30,24	ppm	Final	36,58	5,15	17,78	2,86 <LOD	7,79	11,96	2,76 <LOD	6,46			65,72	9,9 <LOD		3,85 <LOD	11,15 <LOD	8,17	35,74	10,38 <LOD	55,17	36,78	16,22 <LOD		40,91 <LOD	47,26	1977,38	107,71 <LOD	59,72																			
	167	13/07/2014 21:02	Soil	30,21	ppm	Final	32,19	5,1	24,85	3,18 <LOD	8,3	18,29	3,13 <LOD	7,28			72,59	10,33 <LOD		3,89 <LOD	11,76 <LOD	8,06	40,15	10,55 <LOD	50,61	27,38	15,44 <LOD		40,49 <LOD	53,77	2660,14	124,07	67,72	44,23																		
	168	13/07/2014 21:03	Soil	30,77	ppm	Final	33,92	5,18	36,18	3,6 <LOD	7,79	7,57	2,51 <LOD	6,78			55,19	9,3 <LOD		4 <LOD	10,9 <LOD	8,33	42,28	10,85 <LOD	55,27 <LOD		22,02 <LOD	38,01 <LOD	43,34	1428,02	92,07 <LOD	57,01 <LOD	72,98 <LOD	1,24 <LOD	53,13 <LOD	79,45 <LOD	426,61 <LOD		23,07 <LOD		34,68											
L-GL1-REP2	169	13/07/2014 21:03	Soil	31,98	ppm	Final	41,94	5,36	29,82	3,37 <LOD	6,9	6,17	2,29 <LOD	6,61			72,41	10,27 <LOD		4,05 <LOD	11,64 <LOD	7,97	37,11	10,23 <LOD	49,84 <LOD		22,28 <LOD	40,99 <LOD	46,81	1850,15	104,17	75,72	44,1 <LOD	34,85 <LOD	20,22 <LOD	195,13 <LOD	28,28	519,4	312,26 <LOD		577,23 <LOD		39,69									
	170	13/07/2014 21:04	Soil	33,97	ppm	Final	34,91	5,09	26,47	3,21 <LOD	7,83	11,38	2,71 <LOD	6,45			81,73	10,62 <LOD		3,88 <LOD	12,33 <LOD	8,3	31,54	9,86 <LOD	52,2	37,17	15,88 <LOD		39,47 <LOD	37,01	1256,64	86,23 <LOD	54,52 <LOD	27,39 <LOD	6,13 <LOD	66,07 <LOD	14,79 <LOD	128,78 <LOD		262,76 <LOD		14,7										
L-GL1-REP3	171	13/07/2014 21:05	Soil	30,22	ppm	Final	25,47	4,87	29,53	3,32 <LOD	7,64	10,07	2,62 <LOD	7,54			78,58	10,5 <LOD		3,91 <LOD	12,29 <LOD	7,55	29,83	9,65 <LOD	50,4	48,73	16,57 <LOD		37,69 <LOD	41,57	1605,65	96,49 <LOD	62,88																			
	172	13/07/2014 21:06	Soil	30,02	ppm	Final	42,52	5,48	46,68	3,97 <LOD	8,78	13,4	2,96 <LOD	7,43			78,14	10,6 <LOD		4,28 <LOD	12,2 <LOD	7,8	49,11	11,15 <LOD	50,53	28,16	15,41 <LOD		40,19 <LOD	54,05	2592,95	121,59 <LOD	62,75																			
L-GL5-REP1	173	13/07/2014 21:06	Soil	30,12	ppm	Final	35,39	5,16	26,62	3,25 <LOD	8,18	13,41	2,88 <LOD	6,22			51,4	9,12 <LOD		4,12 <LOD	10,48 <LOD	8,33	32,98	10,13 <LOD	54,84	29,53	15,7 <LOD		42,85 <LOD	40,27	1322,08	89,32 <LOD	58,9																			
	174	13/07/2014 21:07	Soil	30,22	ppm	Final	37,07	5,29	31,23	3,44 <LOD	7,62	7,82	2,52 <LOD	7,36			94,25	11,45 <LOD		4,18 <LOD	13,21 <LOD	7,7	45,51	11,05 <LOD	53,63	25,37	15,7 <LOD		42,31 <LOD	49,34	2508,81	120,92	65,39	42,63																		
	175	13/07/2014 21:08	Soil	31,97	ppm	Final	33,93	5,13	25,14	3,19 <LOD	8,01	14,62	2,92 <LOD	6,72			68,78	10,12 <LOD		4,13 <LOD	11,47 <LOD	8,01	29,29	9,71 <LOD	52,28 <LOD		22,04 <LOD	40,54 <LOD	47,76	2082,01	110,33 <LOD	58,83 <LOD	36,01 <LOD	10,84 <LOD	134,8 <LOD	5,04 <LOD	222,1 <LOD		452,82 <LOD		25,13											
	176	13/07/2014 21:09	Soil	30,59	ppm	Final	59,18	5,81	24,84	3,18 <LOD	8,45	14,49	2,97 <LOD	7,32			70,93	10,22 <LOD		3,92 <LOD	11,87 <LOD	8,39	44,6	10,99 <LOD	53,89	25,26	15,46 <LOD		41,08 <LOD	54,16	2764,67	126,1 <LOD	65,15 <LOD	127,92 <LOD	40,31 <LOD	112,11 <LOD	3,02 <LOD	178,27 <LOD		1859,18 <LOD		68,08										
L-GL5-REP2	177	13/07/2014 21:09	Soil	30,43	ppm	Final	33,49	5,27	31,44	3,51 <LOD	7,7	9,91	2,66 <LOD	7,3			72,96	10,56 <LOD		4,19 <LOD	12,16 <LOD	8,43	54,34	11,91 <LOD	53,02	49,44	17,43 <LOD		41,15 <LOD	56,35	2770,99	128,8 <LOD	65,31 <LOD	11,08 <LOD	1,19 <LOD	61,11 <LOD	91,43 <LOD	1000,85 <LOD		1237,39 <LOD		82,34										
	178	13/07/2014 21:10	Soil	30,31	ppm	Final	26,32	4,91	28,92	3,31 <LOD	8,05	20,61	3,18 <LOD	7,13			56,08	9,37 <LOD		4,06 <LOD	10,48 <LOD	7,83	45,26	10,91 <LOD	52,09	32,53	15,9 <LOD		39,97 <LOD	47,8	2177,22	111,85	63,95	42,44																		
L-GL5-REP3	179	13/07/2014 21:11	Soil	30,42	ppm	Final	35,31	5,29	42,14	3,84 <LOD	7,82	15,53	2,94 <LOD	8,02			148,72	13,75 <LOD		4,25 <LOD	16,19 <LOD	7,95	33,32	10,01 <LOD	50,89	24,22	15,28 <LOD		39,53 <LOD	49,59	2480,36	119,72 <LOD	65,3 <LOD</																			



Analysis of lead contaminated soil and remediation proposal in a shooting range



APPENDIX 3 AAS RESULTS



VIA University
College

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MASTER OF SCIENCE IN EUROPEAN

CONSTRUCTION ENGINEERING

Horsens, Denmark

LEAD REMOVAL TEST

AAS RESULTS

0. INTRODUCTION

The following document is part of the Final Dissertation. This appendix contains the results obtained in the Atomic Absorption Spectrometer. This appendix is delivered after the deadline because the availability of the equipment was out of the period.

The information contained in this document is important in order to design a better remediation proposal. By the moment, this remediation proposal was based only in the results of the soil before and after washing. Henceforth information of each washing step is included in the remediation proposal.

1. METHODOLOGY

Atomic Absorption Spectrometer (AAS) was used following the methodology establish in Danish standard, (Dansk Standard, 1982) in order to measure the lead content in the washing effluent of the column test.

Absorption spectroscopy involves the measurement of the fraction of light of a given wavelength which passes through a sample. The sample does not emit light by itself, so it must include a radiation source.

Most sources produce light at wavelengths not desired for the desired addition (The exception to this general characteristic is radio frequency sources and lasers.) The passage of light through a monochromator or filter the wavelength selected for analysis.

For the analysis, two measures of the amount of light absorbed are made. In the first light quantity (a chosen wave length) reaching the transducer, when a target is placed is measured. It is called white intensity P_0 , as the concentration is analysed material is zero.

The final measure is obtained by comparing the measurement of samples or calibration standards to the extent of the target. P is called the intensity measured with the samples or standard. The comparison is always done involves P / P_0 relationship with both intensities measured under the same instrument conditions: wavelength, geometry, etc., (Robledo & Castaño, 2012).

The AAS used is the Thermo Scientific ice 3000 Series present in CPH Business School in Hillerød. The measurements took place the 1st, 2nd and 3rd of September.

Five different calibration curves were prepared, one for each washing agent. The combination with EDTA and the nitric acid of the calibration procedure reacted. For this reason, the calibration solution of EDTA in both concentrations had not nitric acid.

The samples were measured in order to know if the results are in the range of the instrument and if dilution is needed. Then, samples were filtered and diluted when was necessary.

The AAS takes three measurements and reports the average of them. Three replicates per washing step and three measurements gives statistically accurate results.

2. RESULTS

AAS readings and dilution of the samples are showed in the following table.

Table 1-AAS Readings and sample dilutions

CODE	AAS Lead (mg/l)	Nº TIMES CALCULATED	Nº TIMES USED	ADDING ML	AAS Lead (mg/l)	Corrected concentration
NS-ED1-REP1-W1		0	6	8,333	10,6688	64,0128
NS-ED1-REP1-W2		0	1		5,9564	5,9564
NS-ED1-REP1-W3		0	1		3,324	3,324
NS-ED1-REP2-W1	1,226	6,13	6	8,3333	12,1299	72,7794
NS-ED1-REP2-W2		0	1		7,3094	7,3094
NS-ED1-REP2-W3		0	1		3,9234	3,9234
NS-ED1-REP3-W1			6	8,333	11,7389	70,4334
NS-ED1-REP3-W2			1		6,9958	6,9958
NS-ED1-REP3-W3			1		4,1337	4,1337
L-ED1-REP1-W1			6	8,333	11,2567	67,5402
L-ED1-REP1-W2			1		11,7746	11,7746
L-ED1-REP1-W3			1		7,7122	7,7122
L-ED1-REP2-W1	1,128	5,64	6	8,333	11,5743	69,4458
L-ED1-REP2-W2			1		8,6063	8,6063
L-ED1-REP2-W3			1		5,135	5,135
L-ED1-REP3-W1			6	8,333	9,163	54,978
L-ED1-REP3-W2			1		7,3827	7,3827
L-ED1-REP3-W3			1		5,5665	5,5665
M-ED1-REP1-W1			6	8,333	10,6868	64,1208
M-ED1-REP1-W2			1		7,3223	7,3223
M-ED1-REP1-W3			1		4,359	4,359
M-ED1-REP2-W1	1,211	6,055	6	8,333	13,2081	79,2486
M-ED1-REP2-W2			1		7,1847	7,1847
M-ED1-REP2-W3			1		3,857	3,857
M-ED1-REP3-W1			6	8,333	13,4416	80,6496
M-ED1-REP3-W2			1		7,1507	7,1507
M-ED1-REP3-W3			1		3,7802	3,7802
S-ED1-REP1-W1			10	5	19,0176	190,176
S-ED1-REP1-W2			2	25	16,4586	32,9172
S-ED1-REP1-W3			1		16,953	16,953
S-ED1-REP2-W1	1,712	8,56	10	5	20,7607	207,607
S-ED1-REP2-W2	0,362	1,81	2	25	12,0509	24,1018
S-ED1-REP2-W3			1		13,2637	13,2637
S-ED1-REP3-W1			10	5	17,9647	179,647
S-ED1-REP3-W2			1		18,336	18,336
S-ED1-REP3-W3			1		9,1344	9,1344
NS-ED5-REP1-W1			6	8,333	14,937	89,622
NS-ED5-REP1-W2			1		17,1429	17,1429
NS-ED5-REP1-W3			1		2,9841	2,9841

CODE	AAS Lead (mg/l)	Nº TIMES CALCULATED	Nº TIMES USED	ADDING ML	AAS Lead (mg/l)	Corrected concentration
NS-ED5-REP2-W1	0		6	8,333	7,7422	46,4532
NS-ED5-REP2-W2	0,412	2,06	2	25	14,79	29,58
NS-ED5-REP2-W3			1		4,8313	4,8313
NS-ED5-REP3-W1			6	8,333	10,9763	65,8578
NS-ED5-REP3-W2	0,396	1,98	2	25	14,5208	29,0416
NS-ED5-REP3-W3			1		6,0584	6,0584
L-ED5-REP1-W1			5	10	12,4867	62,4335
L-ED5-REP1-W2			1		7,9083	7,9083
L-ED5-REP1-W3			1		4,3946	4,3946
L-ED5-REP2-W1	1,027	5,135	5	10	15,7963	78,9815
L-ED5-REP2-W2	0,268	1,34	1		15,4987	15,4987
L-ED5-REP2-W3	0,196	0,98	1		11,0477	11,0477
L-ED5-REP3-W1			5	10	12,8033	64,0165
L-ED5-REP3-W2			1		6,0831	6,0831
L-ED5-REP3-W3			1		3,7681	3,7681
M-ED5-REP1-W1			6	8,333	16,11	96,66
M-ED5-REP1-W2	0,111	0,555	1		6,3101	6,3101
M-ED5-REP1-W3			1		3,5736	3,5736
M-ED5-REP2-W1			6	8,333	13,9398	83,6388
M-ED5-REP2-W2			1		5,8526	5,8526
M-ED5-REP2-W3			1		3,4437	3,4437
M-ED5-REP3-W1			6	8,3333	13,5844	81,5064
M-ED5-REP3-W2			1		5,2349	5,2349
M-ED5-REP3-W3			1		3,1105	3,1105
S-ED5-REP1-W1			15	3,333	19,3119	289,6785
S-ED5-REP1-W2			1		13,9349	13,9349
S-ED5-REP1-W3			1		8,2866	8,2866
S-ED5-REP2-W1	1,776	8,88	15	3,333	18,1017	271,5255
S-ED5-REP2-W2			1		15,7478	15,7478
S-ED5-REP2-W3			1		9,3182	9,3182
S-ED5-REP3-W1			15	3,333	17,4379	261,5685
S-ED5-REP3-W2			1		14,7044	14,7044
S-ED5-REP3-W3			1		8,6143	8,6143
NS-GL1-REP1-W1			6	8,333	10,9659	65,7954
NS-GL1-REP1-W2			1		10,1569	10,1569
NS-GL1-REP1-W3			1		6,8898	6,8898
NS-GL1-REP2-W1	1,166	5,83	6	8,333	10,7478	64,4868
NS-GL1-REP2-W2			1		9,0601	9,0601
NS-GL1-REP2-W3			1		5,5745	5,5745
NS-GL1-REP3-W1			6	8,333	11,1115	66,669
NS-GL1-REP3-W2			1		9,5325	9,5325
NS-GL1-REP3-W3			1		6,1055	6,1055
L-GL1-REP1-W1			3	16,667	14,187	42,561
L-GL1-REP1-W2			1		5,7856	5,7856

CODE	AAS Lead (mg/l)	Nº TIMES CALCULATED	Nº TIMES USED	ADDING ML	AAS Lead (mg/l)	Corrected concentration
L-GL1-REP1-W3			1		3,4793	3,4793
L-GL1-REP2-W1	0,64	3,2	3	16,667	13,6716	41,0148
L-GL1-REP2-W2			1		5,698	5,698
L-GL1-REP2-W3			1		3,7037	3,7037
L-GL1-REP3-W1			3	16,667	13,6633	40,9899
L-GL1-REP3-W2			1		6,0324	6,0324
L-GL1-REP3-W3			1		3,8246	3,8246
M-GL1-REP1-W1	0,942	4,71	5	10	14,0195	70,0975
M-GL1-REP1-W2			1		4,6634	4,6634
M-GL1-REP1-W3			1		4,6145	4,6145
M-GL1-REP2-W1			5	10	14,3711	71,8555
M-GL1-REP2-W2			1		4,6045	4,6045
M-GL1-REP2-W3			1		4,655	4,655
M-GL1-REP3-W1			5	10	13,7889	68,9445
M-GL1-REP3-W2			1		7,1024	7,1024
M-GL1-REP3-W3			1		4,2051	4,2051
NS-GL5-REP1-W1	0,837	4,185	4	12,5	17,7151	70,8604
NS-GL5-REP1-W2			1		7,9942	7,9942
NS-GL5-REP1-W3			1		6,7577	6,7577
NS-GL5-REP2-W1			4	12,5	18,1947	72,7788
NS-GL5-REP2-W2			1		6,7031	6,7031
NS-GL5-REP2-W3			1		5,516	5,516
NS-GL5-REP3-W1			4	12,5	19,2575	77,03
NS-GL5-REP3-W2			1		7,0645	7,0645
NS-GL5-REP3-W3			1		5,5814	5,5814
L-GL5-REP1-W1	0,814	4,07	4	12,5	14,9908	59,9632
L-GL5-REP1-W2			1		6,9318	6,9318
L-GL5-REP1-W3			1		5,8212	5,8212
L-GL5-REP2-W1			4	12,5	17,5935	70,374
L-GL5-REP2-W2			1		8,0887	8,0887
L-GL5-REP2-W3			1		6,6769	6,6769
L-GL5-REP3-W1			4	12,5	15,1895	60,758
L-GL5-REP3-W2			1		8,2197	8,2197
L-GL5-REP3-W3			1		7,5225	7,5225
M-GL5-REP1-W1	0,982	4,91	5	10	18,2658	91,329
M-GL5-REP1-W2			1		7,219	7,219
M-GL5-REP1-W3			1		5,9837	5,9837
M-GL5-REP2-W1			5	10	16,1344	80,672
M-GL5-REP2-W2			1		6,4702	6,4702
M-GL5-REP2-W3			1		5,7543	5,7543
M-GL5-REP3-W1			5	10	16,6959	83,4795
M-GL5-REP3-W2			1		6,5347	6,5347
M-GL5-REP3-W3			1		5,629	5,629

3. DISCUSSION

The results obtained from the AAS are combined with the XRF results. The total lead removal was calculated by the difference of lead before and after washing obtained using the XRF. Lead removal by step in percentage is represented in the following figures in all the cases depending on the washing volume.

3.1. EDTA 0.01 M

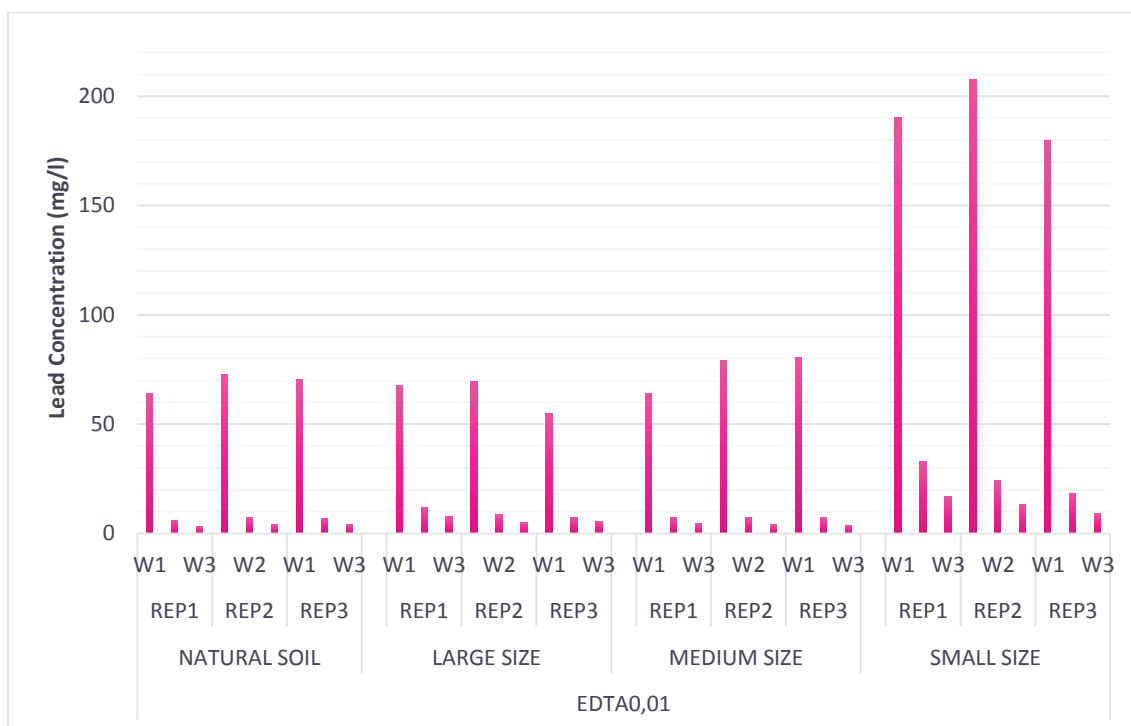


Figure 1-AAS results using EDTA 0.01M

The maximum removal in all the soil cases using EDTA 0,01 M is developed during the first washing step. The relation between the washing steps is 10:1 (W1:W2) and 20:1 (W1:W3) and 2:1 (W2:w3).

All the replicates have the same tendency. The lead removal curve obtained has the same shape than the literature studied:

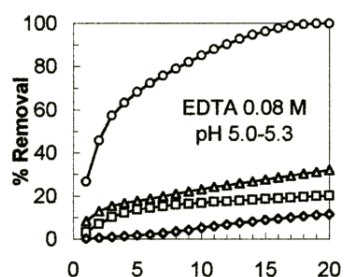


Figure 2-EDTA Lead removal, (Wasay et al., 2001)

3.2. EDTA 0.05M

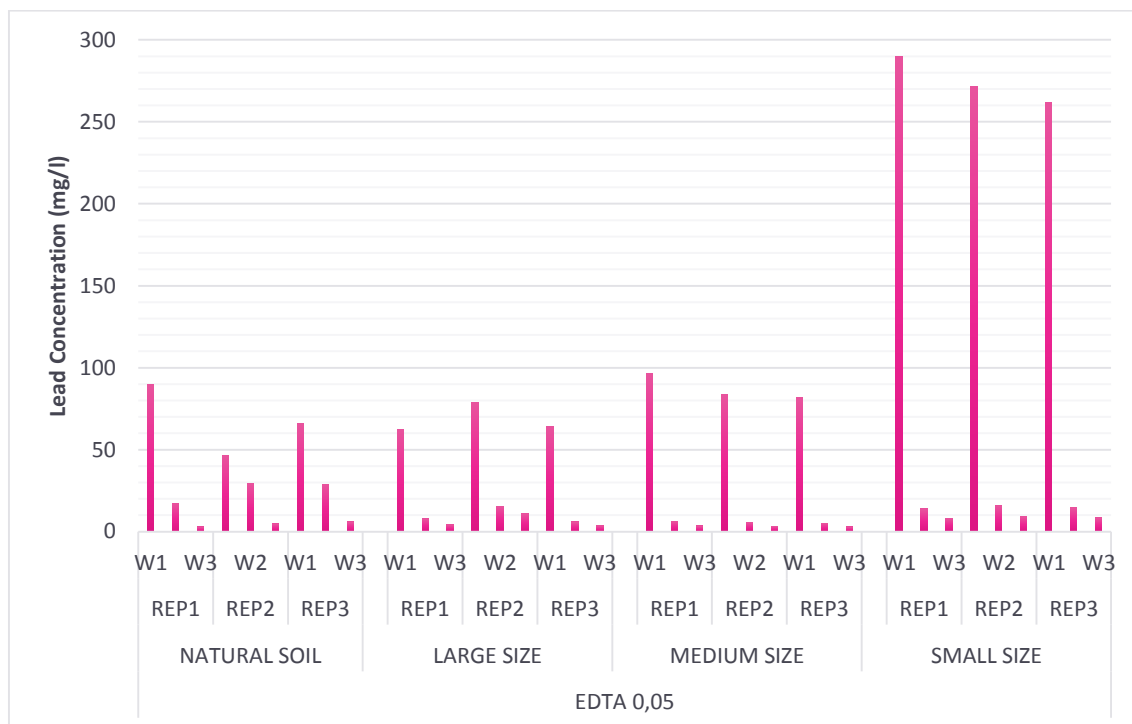


Figure 3-AAS results using EDTA 0.05M

Using EDTA 0.05M like a washing solution obtains same results than the 0.01M ones as to compare the washing step. The maximum of lead removal is obtained during the first washing step. All the lead removal curves have the same tendency. However, the dispersion of the results in the case of the Natural and Large soil are significant.

3.3. GLDA 0.01M

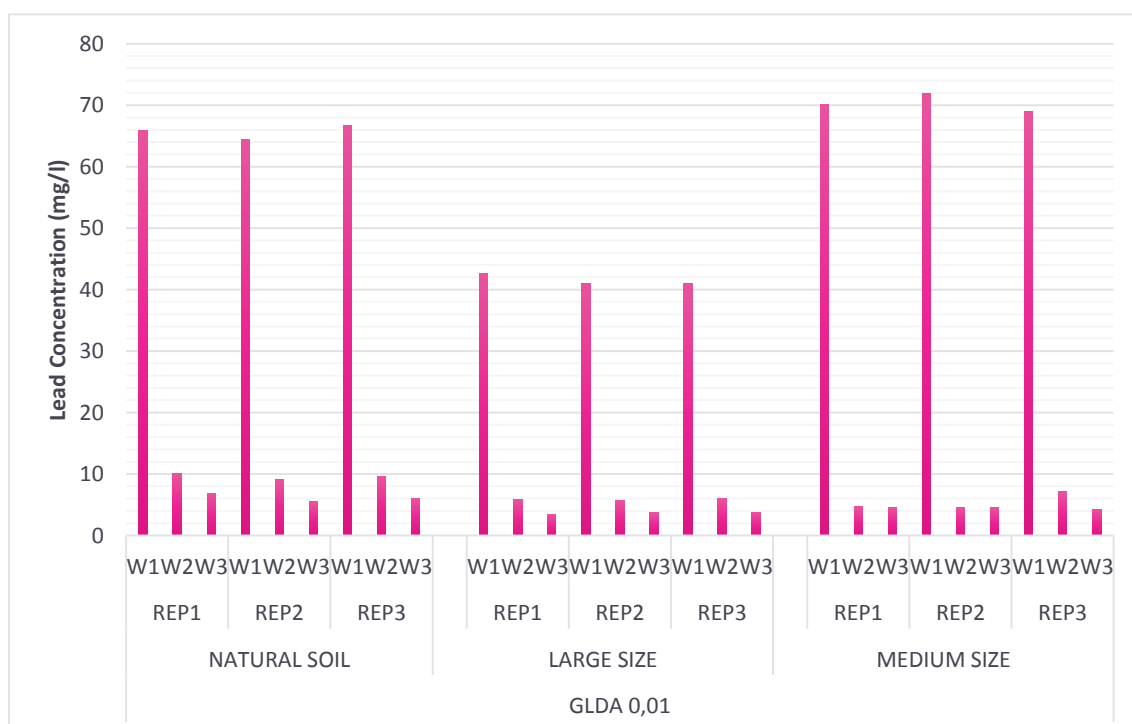


Figure 4-AAS results using GLDA 0.01M

GLDA shows the same tendency than EDTA. The maximum lead removal is developed during the first washing step. GLDA lead removal curve's growth is most sustained when the washing volume increases. The three replicates have the same tendency and the results have no significant dispersion.

3.4. GLDA 0.05M

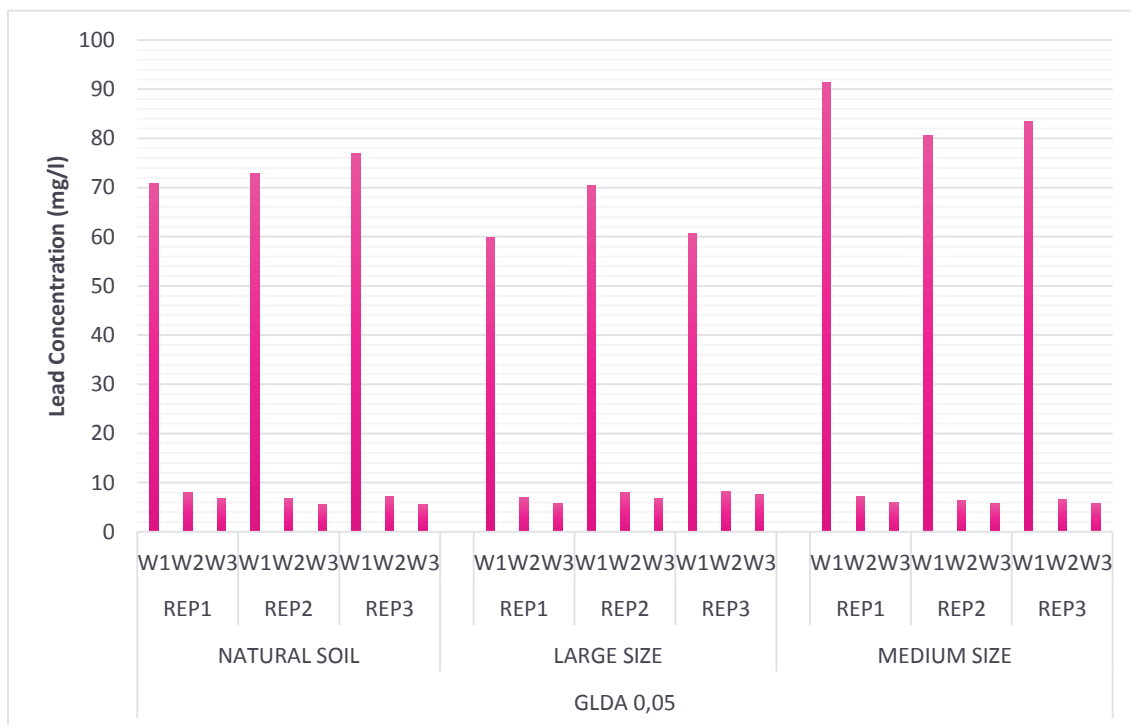


Figure 5-AAS results using GLDA 0.05M

GLDA with 0.05 of molar ratio is a similar situation than the GLDA 0.01M. The maximum lead removal is obtained during the first washing step.

4. XRF-AAS RESULTS COMPARISON

XRF and AAS are used to measure lead in the soil and in the washing solutions. Both methods are comparable calculating the lead removed.

On the one hand, lead removed in XRF is calculated using the results before and after the washing process. The concentration is expressed in mg /Kg DW. The amount of soil used is 20 grams, so removed lead expressed in milligrams is easily calculated.

On the other hand, lead removed in the soil is present in the washing effluent and measured by AAS. The amount of lead expressed in milligrams present in the washing effluent is calculated by the concentration mg/l and the washing volume used of 50 ml each washing step.

The following graphs show the removed lead using both methods. There is a difference between them, at the same time that suggest the same tendency.

The difference represents the accuracy of the methodology. The same tendency allows a direct relation between both results.

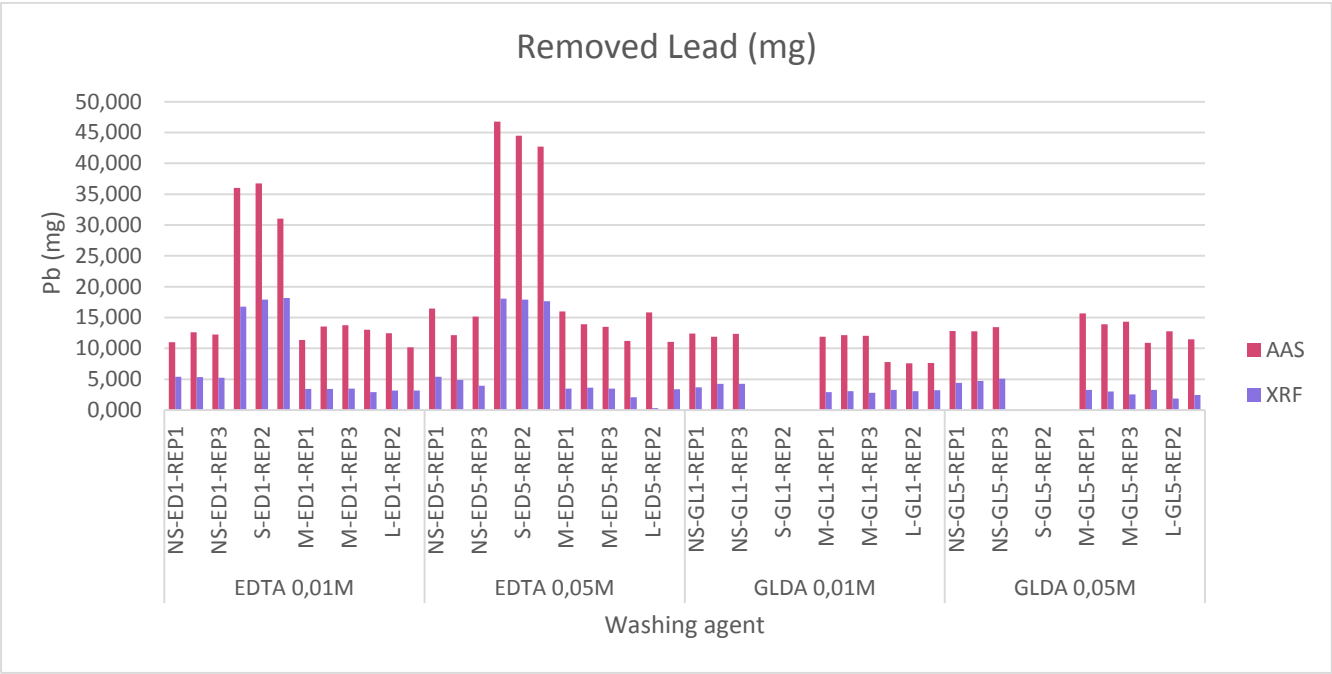


Figure 6-Pb removed calculated using AAS and XRF results

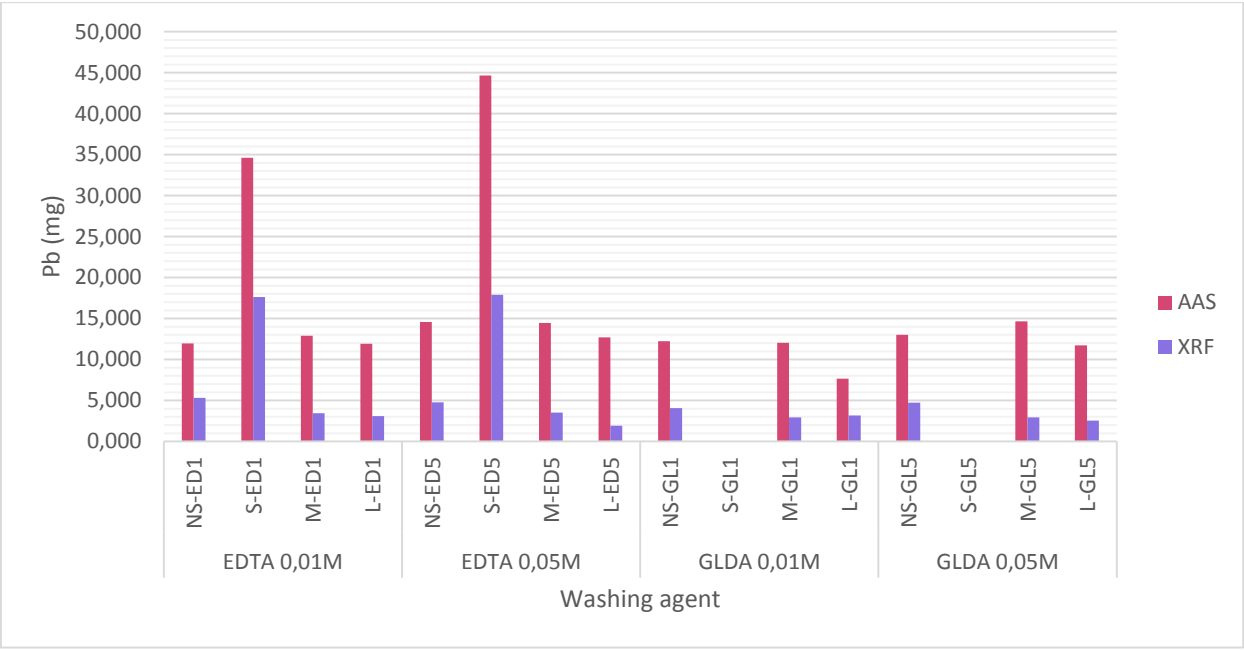


Figure 7-Pb removed calculated using AAS and XRF results

5. CONCLUSIONS

The main conclusion obtained with the AAS is that the first washing step is the most important. Lead removal during the first step is 10 times the second step and 20 times the third one.

Lead removal proposal should be based in only one washing step, because the relation between lead removal and washing volume is profitable only in that washing phase.

Cleaning objective was nearly reached during this first step. Washing procedure in full scale can be developed using one washing step in order to save washing solution.

50 ml of washing solution in 20.5 grams of soil contained in the syringes, is the relation between washing solutions and dry weight contaminated soil used. The application in full scale would be as follows.

The contaminated soil was estimated in 8.568 tonnes, so the washing volume needed would be around 21.000 m³.

6. PICTURES REPORT



Figure 8-AAS



Figure 9-AAS



Figure 10-AAS burner switched off



Figure 11-AAS burner working

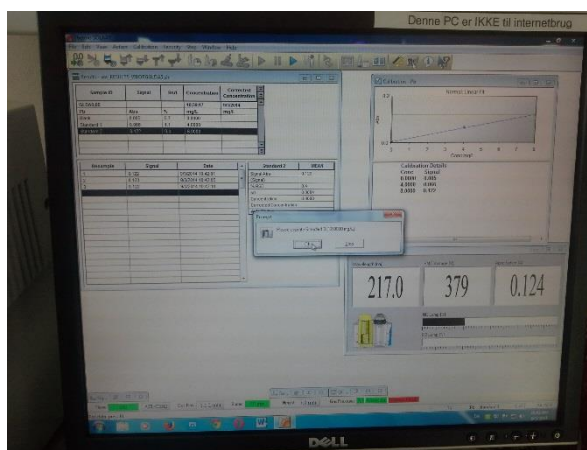


Figure 12-AAS Display



Figure 13-Calibration solutions

7. REFERENCES

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Wasay, S., Barrington, S. & Tokunaga, S., 2001. Organic acids for the in situ remediation of soils polluted by heavy metals: soil flushing in columns. *Water, Air, and Soil Pollution*, pp.301–314. Available at: <http://link.springer.com/article/10.1023/A:1005251915165> [Accessed August 4, 2014].

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