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Contaminated soil: Waste today, resource tomorrow? Coupling hydraulic conductivity and leachability in soil characterization – a lab based study

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Acknowledgments

This thesis concludes my master's degree in Environment and Natural Resources at the Norwegian University of Life Sciences (NMBU). The thesis is part of a larger research and development program, *GEOreCIRC – Georesources in a circular economy*, at the Norwegian Geotechnical Institute (NGI).

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Abstract

Tons of surplus contaminated soil from construction projects are landfilled as waste every year. Lack of appropriate methods to assess and evaluate the leaching and spreading of contaminants from soil prevents a comprehensive risk assessment, and thereby reuse. The purpose of this thesis was to evaluate a newly developed extended up-flow percolation column that enables chemical and physical characterization of contaminated soils in order to assess the true aspects of leaching and spreading. Another objective was to investigate the effect of soil compaction as a physical treatment to reduce leaching and spreading from contaminated soil. Two soils of different origin and with distinct contaminant levels were characterized using the extended up-flow percolation column to meet the objectives of this thesis. To investigate the effect of compaction, one of the soils was characterized at two compaction modes. The results of contaminant leaching were compared with results from a standard batch leaching test and total contaminant concentration analysis. Contaminant spreading was considered using hydraulic conductivity derived from i) the extended up-flow percolation column and ii) empirical formulas. The experimental outcomes demonstrated that the extended up-flow percolation column yielded a more accurate evaluation of leaching and spreading of contaminants. By considering chemical and physical aspects present under field conditions, that are ignored in batch tests and empirical formulas, the extended up-flow percolation column can be used to assess the true risk of reuse for a variety of soils. Physical compaction was not found to reduce the leaching of the elements of concern, but a less extensive contaminant spreading was observed as a result of lowered hydraulic conductivity in the soil.

Sammendrag

Hvert år deponeres store mengder forurenset overskuddsjord fra byggeprosjekter. Gjenbruk av lett forurenset jord er begrenset som følge av mangel på hensiktsmessige metoder for vurdering av utlekking og spredning av forurensninger. Formålet med denne masteroppgaven var å vurdere utlekking og spredning gjennom uttesting av en nylig utviklet metode, *en utvidet kolonnetest*, som muliggjør en kombinert kjemisk og fysisk karakterisering av forurenset jord. Oppgaven undersøkte også effekten av jordkomprimering som en fysisk behandlingsmetode for å redusere utlekking. To forskjellige jordtyper med ulik forurensningsgrad ble karakterisert med den *utvidede kolonnetesten*. Effekten av komprimering ble undersøkt ved å pakke én av jordprøvene inn i den *utvidede kolonnetesten* på høy og lav pakningsgrad. Utlekkingsresultatene ble sammenliknet med utlekkingsresultater fra standardiserte ristetester og analyser av totalkonsentrasjonene av forurensningene. Forurensningspredningen ble vurdert basert på den hydrauliske konduktiviteten i) målt fra de *utvidede kolonnetestene* og ii) med empiriske formler som i stor grad benyttes i dag. Resultatene viste at den *utvidede kolonnetesten* er godt egnet for å evaluere utlekking og spredning av forurensninger. Ved å ta hensyn til viktige kjemiske og fysiske jordparametere som dominerer i felt, og som ikke inkluderes i ristetester og i empiriske formler, kan metoden gi et godt bilde på den faktiske risikoen ved gjenbruk av en rekke ulike jordtyper. Fysisk komprimering ga ingen reduksjon i utlekking av forurensninger, men forurensningsspredningen ble redusert som følge av en lavere hydraulisk konduktivitet i jorda.

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Abbreviations and Acronyms

Ca	Calcium.
C_H	Hazen empirical constant.
Cl^-	Chloride.
C_s	Concentration in the solid phase.
Cu	Copper.
C_u	Uniformity coefficient.
C_w	Concentration in aqueous phase.
DOC	Dissolved organic carbon.
d_{10}	Effective particle size.
e	Pore number.
EC	Electrical conductivity.
E_h	Redox potential.
Fe	Iron.
G_s	Specific gravity.
HCl	Hydrochloric acid.
HCO_3^-	Bicarbonate.
HF	Hydrofluoric acid.
HNO_3	Nitric acid.
H_2O_2	Hydrogen peroxide.
IC	Ion chromatography.
ICP-MS	Inductively coupled plasma mass spectrometry.
ICP-OES	Inductively coupled plasma optimal emission spectrometry.
K	Potassium.
K	Hydraulic conductivity.
K_{exp}	Experimental hydraulic conductivity.
K_d	The partition coefficient.
K_d^*	Dimensionless partition coefficient.
LOD	Limit of detection.
LOI	Loss on ignition.
LOQ	Limit of quantification.
L/S ratio	Liquid to solid ratio.
Mg	Magnesium.

$MgCl_2$	Magnesium chloride.
MINA	Faculty of Environmental Sciences and Natural Resource Management.
n	Porosity.
Na	Sodium.
NAVFAC	Naval Facilities Engineering Command.
n_{eff}	Effective porosity.
NGI	The Norwegian Geotechnical Institute.
NMBU	The Norwegian University of Life Sciences.
NO_3^-	Nitrate.
Pb	Lead.
PMMA	Polymethylmethacrylate.
POC	Particulate organic carbon.
PSD	Particle size distribution.
Q	Discharge.
rpm	Revolutions per minute.
Sb	Antimony.
SO_4^{2-}	Sulfate.
S_r	Degree of saturation.
TIC	Total inorganic carbon.
TOC	Total organic carbon.
V	Soil volume: consists of the volume of solid material (V_s) and the pore volume (V_p). V_p is filled with air (V_a) and water (V_w).
w	Volumetric water content.
Zn	Zinc.
ρ_b	Bulk density.
γ_d	Dry unit weight of soil.
γ_w	Unit weight of water.

1 Introduction – Soil in a circular economy

Worldwide anthropogenic activities have resulted in elevated concentrations of potentially hazardous inorganic contaminants at numerous sites. Many inorganic contaminants are persistent and non-degradable in nature, and accumulation can have a negative environmental impact and lead to adverse effects for humans (Almås & Singh, 2017; Pierzynski et al., 2005, p. 332-343). A complete remediation of contaminated soil is in most situations practically and economically unfeasible. Accordingly, sustainable management practices of our finite soil resources is crucial.

1.1 Low level contaminated soil: Waste today, resource tomorrow

During the last decade, the ideas of circular economy have led to a growing awareness of turning the waste of today into the resources of tomorrow (the Norwegian Environment Agency, 2017c). Circular economy can be defined as a value chain where resources are maintained in a closed loop, in contrast to the traditional take-make-dispose model of linear economy, as shown in Figure 1 (European Commission, 2015; World Economic Forum, n.d.).

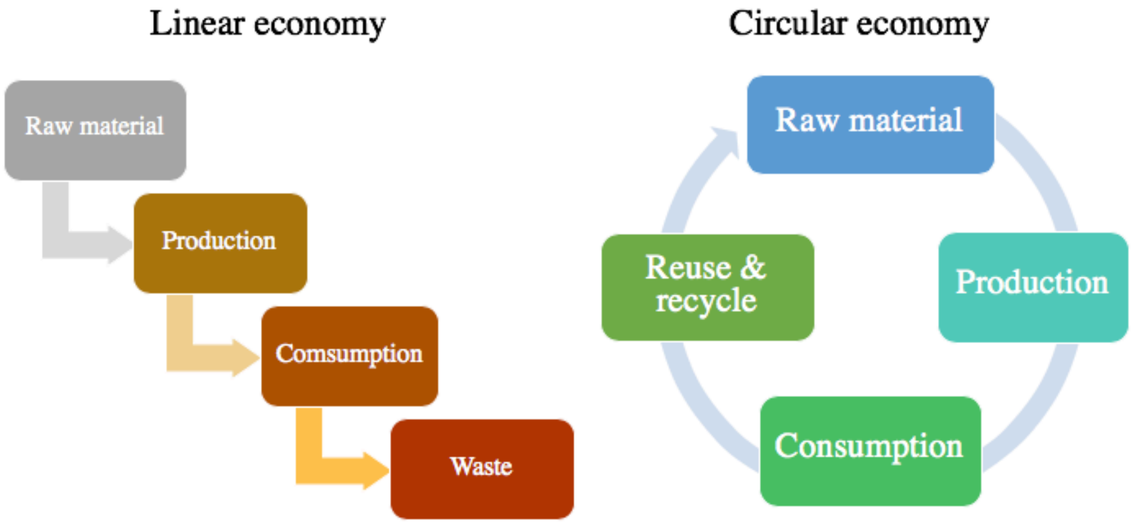

Figure 1. Linear economy vs. circular economy. Materials introduced to the linear economy follow the traditional take-make-dispose model. In the circular economy, materials are recycled and reused in a loop.

Efforts to integrate the ideas of circular economy to soil management are underway on both a local and global scale in order to increase the reusable amount of geomaterial from construction and demolition projects (The European Commission, 2017; the Norwegian Environment Agency, 2017c). However, tons of diverse geomaterial, e.g. low level contaminated soil, are landfilled every year, following the take-make-dispose model. 99 % of all surplus low level contaminated soil in 2016 was landfilled, and Figure 2 shows that low level contaminated soil made up 63 % of the total quanta landfilled waste in 2016 in Norway (The Statistics Norway, 2018a). A large quantity of the landfilled soil was surplus material from construction sites (The Statistics Norway, 2018b).

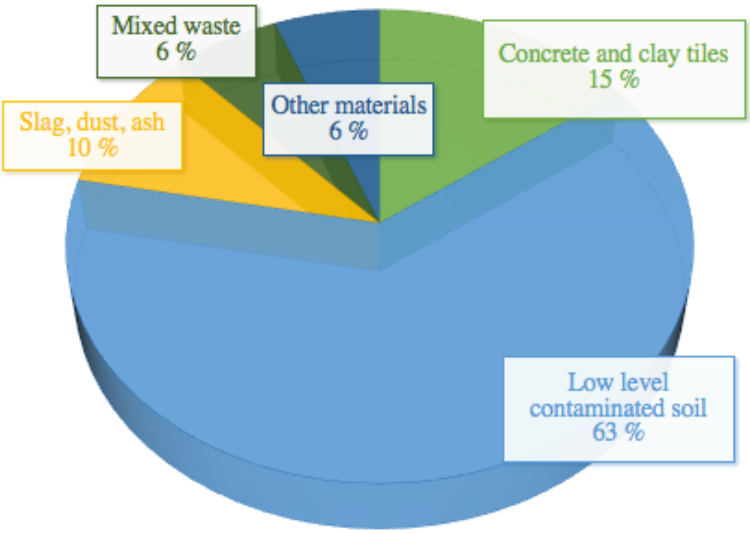

Figure 2. The origin of landfilled waste (non-hazardous) in Norway, 2016. Low level contaminated soil constitutes more than 60 % of the total quanta (The Statistics Norway, 2018a).

Although heavily contaminated soil requires landfilling, landfilling of low level contaminated soil is a non-sustainable solution, mainly due to three factors: Firstly, soil is a non-renewable resource – essential for, among other reasons, food production. Soil forming processes occur over thousands of years, and are dependent on site specific factors such as bedrock, climate and microbiology (Pierzynski et al., 2005, p. 65). Secondly, there are potentially large costs associated with landfilling of low level contaminated soil – especially in larger construction projects. Finally, soil can serve as a valuable geomaterial, e.g. in fundaments and fillings, in other construction projects. Thus, reuse of low level contaminated soil will yield both environmental and economical advantages.

1.2 Legislative frameworks as barriers for reuse?

Reuse of surplus soil is strictly limited by Norwegian guidelines and legislative frameworks, and relocation of surplus low level contaminated soil between different locations is restricted to prevent spreading of contaminants (the Norwegian pollution regulations, § 2-5). If removed from its original location, surplus contaminated soil is to be considered as waste and should be landfilled or treated at an approved waste management facility according to the Norwegian Waste Regulations (2014) (the Norwegian pollution regulations, § 2-5). The Norwegian Environmental Agency can grant exceptions upon individual assessment of the project as long as no negative impacts on human health or the environment can be assured (The Norwegian Environment Agency, 2017b). In particular, the soil must either be considered *clean*, or a risk assessment must prove that the potential leaching and spreading of contaminants associated with reuse is tolerable, as indicated in Figure 3.

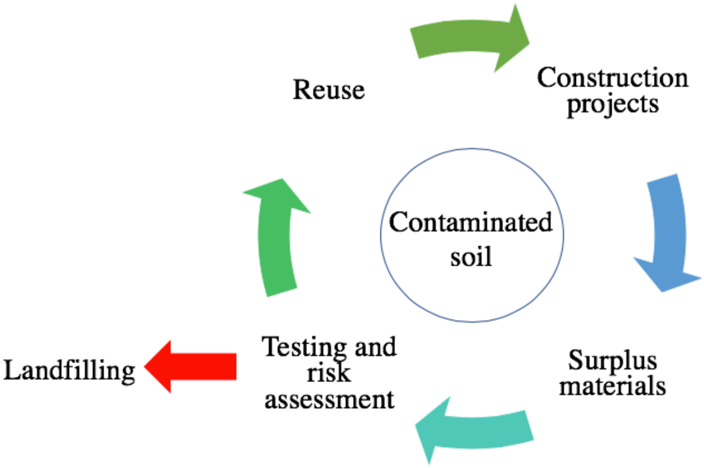

Figure 3. Surplus contaminated soil can be reused as an alternative to landfilling if a risk assessment proves that the potential leaching and spreading from soil is tolerable.

Today, however, there is a lack of appropriate methods to assess and evaluate the risk of soil reuse. This prevents a comprehensive assessment of effects, and complicates policy and decision-making (The Norwegian Geotechnical Institute, 2018). As a consequence, surplus low level contaminated soil from construction sites are landfilled on a precautionary basis. This demonstrates a knowledge gap, demanding development of methods, which can evaluate the risk of soil reuse.

1.3 How to assess the risk of reuse?

The effect of contaminant leaching and spreading are the main concerns when soil reuse is considered. A risk assessment aims to determine the probability and magnitude of impacts from a potential hazard (Pierzynski et al., 2005, p. 475-478). Figure 4 demonstrates a risk assessment in the case of soil reuse. In particular, a risk assessment must examine the potential effect on humans and the environment though identification of a) the potential hazard associated with a contaminated soil, i.e. the total contaminant concentration, and b) the probability of contaminant leaching and spreading (The Norwegian Geotechnical Institute, 2019a).

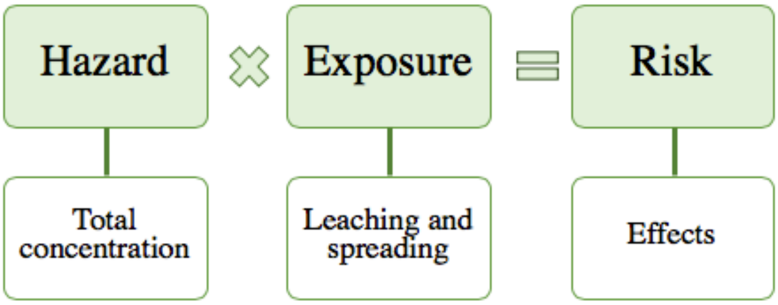

Figure 4. The risk is a function of the hazard and the exposure. For contaminated soil, a risk assessment must include the total contaminant concentrations and the exposure through contaminant leaching and spreading. Adapted from The Norwegian Geotechnical Institute (2019).

Analyzing the total contaminant concentrations in soil is cost-effective and easy, and is performed as a part of the routine environmental engineering surveys of potentially contaminated sites today (The Norwegian Geotechnical Institute, 2018). By ignoring the *exposure*, the analysis overestimates the soil's potential risk if reused. A more accurate way of determining whether the soil can be reused, is through a leaching test. Only a minor fraction of the total contaminant concentration in soil is leachable, and site specific factors, e.g. pH and presence of organic matter, influence the leaching. Standard column and batch tests are among the most commonly used laboratory techniques to investigate the leaching from soils today (Grathwohl et al., 2003).

A physical characterization of soil must be performed to examine spreading of contaminants. The hydraulic conductivity, defined as the ease of a fluid to flow through a geological material (Schwartz & Zhang, 2003, p. 49), is a particularly important parameter. Accordingly, the hydraulic conductivity is a measure of the water movement which in turn affects contact time between water and solids along with contaminant transport (Grathwohl & Susset, 2009; Van der Sloot et al., 1997). Current methods for determining hydraulic conductivity in risk assessments are based on empirical formulas, e.g. Hazen, where the hydraulic conductivity is correlated to a limited number of soil parameters such as the particle size distribution (Schwartz & Zhang, 2003, p. 52; The Norwegian Geotechnical Institute, 2019a). However, these formulas are hampered by several simplifications and limitations.

Development of a cost-effective method that includes both chemical and physical characterization of the contaminated soil could provide a more accurate assessment of the true aspect of leaching and spreading. Recently, an extended up-flow percolation column has been developed as a part of the research project *GEOreCIRC*, at the Norwegian Geotechnical Institute (NGI), meeting this need. This equipment allows for determination of the hydraulic conductivity in soil samples and simultaneously enables contaminant leaching. However, further testing is required to ensure an accurate assessment of the leaching and spreading.

1.4 Compaction as a physical treatment

Remediation refers to several processes that remove, degrade or stabilize contaminants in various medias, e.g. soil (Pierzynski et al., 2005, p. 453-456). Removal or degradation of contaminants lead to a reduced *hazard* associated with reuse, while other treatments, e.g. stabilization, reduces the potential *exposure* by addition of sorbents. The invention of new remediation techniques can lead to a reduction in the amount of soil that is landfilled and entail more reuse.

Soil compaction has multiple benefits, including increased bearing capacity and reduced settlements in construction projects (The Norwegian Public Roads Administration, 2010), stabilization of landfills providing economic benefits in terms of storage capacity, and reduced permeability in landfill barrier materials in accordance with the Norwegian Waste Regulations (2014) (The Norwegian Environment Agency, 2005). Compaction of soil has been suggested as a novel method for physical treatment of the soil (The Norwegian Geotechnical Institute, n.d.). As soil compaction reduces the pore volume, and thereby also reduces the hydraulic conductivity, the spreading of contaminants is assumed to be lowered. However, tests are needed in order to document the effect of soil compaction on the release of contaminants.

2 Overall aim and research objectives

2.1 GEOreCIRC – Georesources in a circular economy

This master thesis takes part in the research project GEOreCIRC, at the Norwegian Geotechnical Institute (NGI). GEOreCIRC's overall aim is to encourage reuse of surplus geomaterial and reduce the quantity that is landfilled. Topics of concern in the project includes identification of legislative and practical barriers that hinder reuse, development methods that improve physical and chemical characterization of materials, and development of tools for risk assessment (The Norwegian Geotechnical Institute, n.d.).

2.2 Thesis aim and research objectives

The overall aim of this master thesis is to secure a sustainable management of georesources by exploring contaminant release from soil. Specifically, the scope of the thesis, is to obtain experience with chemical and physical characterization by the extended up-flow percolation column in order to evaluate the potential reuse of contaminated soils.

Based on the knowledge gaps identified in Section 1 *Introduction*, the objectives of this thesis are to:

(i) Provide an insight into leaching from contaminated soil and briefly evaluate management options.

(ii) Investigate the effect of compaction as a physical treatment to reduce leaching from contaminated soil.

(iii) Compare contaminant transport based on values of the hydraulic conductivity derived from the extended up-flow percolation column and empirical formulas.

(iv) Evaluate the extended up-flow percolation column as a method to simultaneously characterize leaching and determine the hydraulic conductivity of soils.

The objectives will be achieved by the workflow shown in Figure 5 based on analysis of two soils of different origin and distinct contaminant levels: i) an urban low level contaminated soil, and ii) a heavily contaminated shooting range soil. Lead (Pb) and copper (Cu) will be the focus in the urban soil, while antimony (Sb), Pb and Cu will be the elements of concern in the shooting range soil. Total contaminant concentration analysis, and leaching results from a) the extended up-flow percolation column and b) a standard batch test, will be compared for chemically characterization. Possible management practices for each soil will be discussed in relation to existing guideline values. The spreading of contaminants in the groundwater zone will be elucidated based on values of the hydraulic conductivity derived from a) the extended up-flow percolation column and b) empirical formulas. The shooting range soil samples will be analyzed in the extended up-flow percolation column at high and low packing in order to investigate the effect of soil compaction on contaminant release. Lastly, the thesis will evaluate the use of the extended up-flow percolation column as an alternative to established routine measurements.

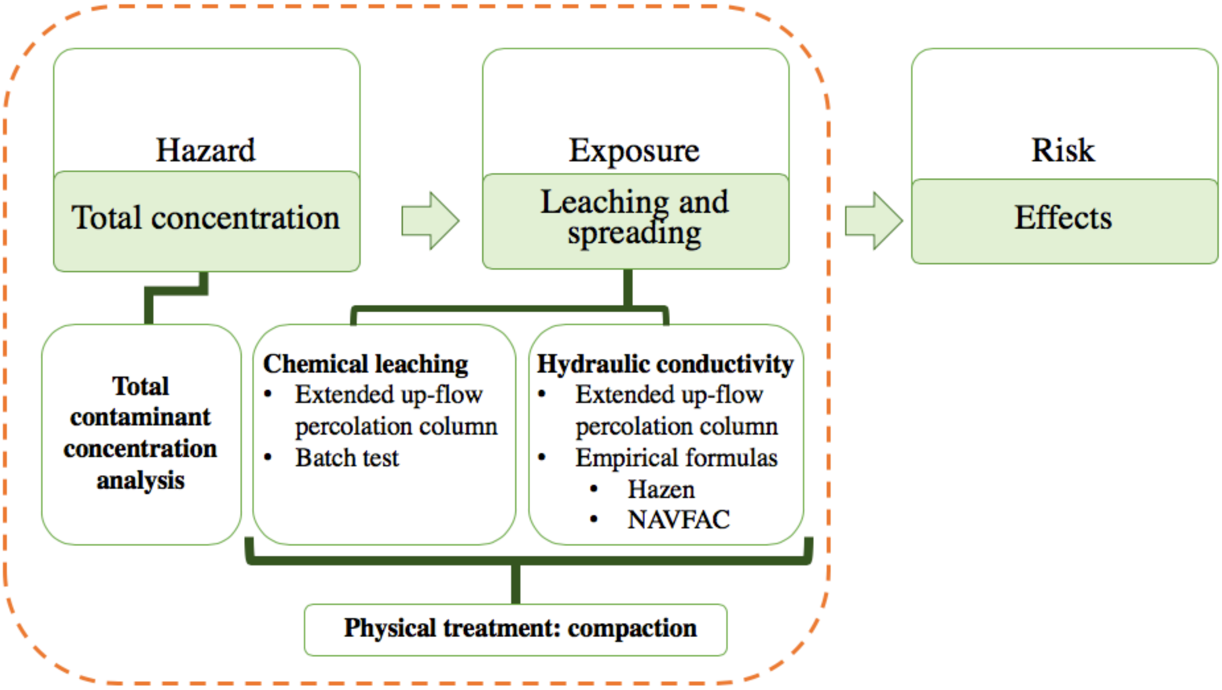

Figure 5. Flowchart showing the thesis context with relation to hazard, exposure and risk of soil reuse. The red box indicates the main focus and methodology of the thesis.

3 Theory

3.1 Soil leaching and retention

Only a minor fraction of the total contaminant concentration in soil is *leachable* in contact with water. As Figure 6 indicates, the leachable fraction is composed of the contaminant present in the pore water, *the actually leached amount*, and *the potentially leachable amount* (Grathwohl et al., 2003). The *actually leached amount* is considered to be the equilibrium concentration between pore water and solids under the current conditions (Grathwohl & Susset, 2009), while the latter represents leaching under worst-case conditions as a result of changes in the soil solution chemistry (Grathwohl et al., 2003).

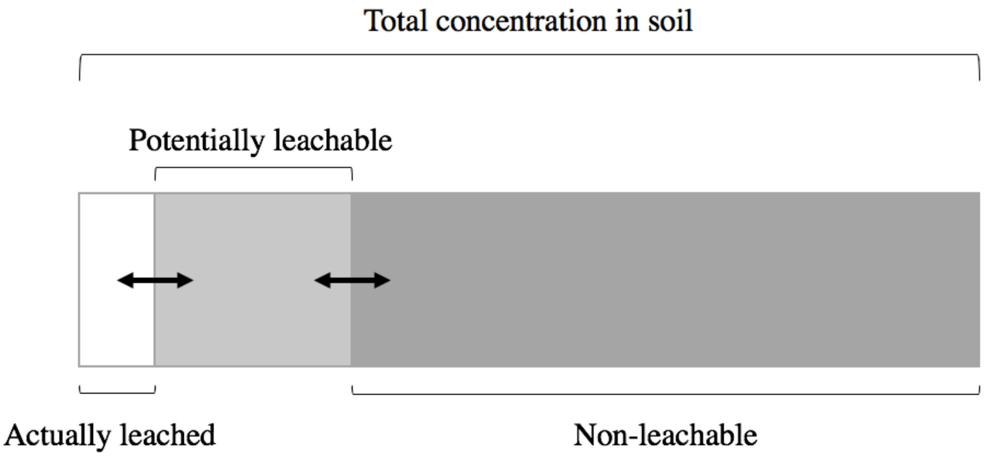

Figure 6. Schematic presentation of the partition of contaminants in soil. Modified from Almås and Singh (2017).

3.1.1 Chemical factors influencing leaching

Some of the major factors influencing leaching are shown in Figure 7, and includes both properties of the solid phase and the soil solution. *Sorption* is a collective term for processes where formation of various bonds results in attachment of a sorbate to a sorbent (Pierzynski et al., 2005, p. 83; Van der Sloot et al., 1997). The sorbate can be retained on the sorbent surface (adsorption), or inside the sorbent matrix (absorption) (Appelo & Postma, 2005, p. 241). Important sorbents include clay minerals, aluminum and iron oxides and hydroxides, and soil organic matter (Pierzynski et al., 2005, p. 83). In contrast to sorbents having a permanent surface charge, the surface charge of amphoteric sorbents changes as a function of pH. At low pH, abundance of H^+ leads to a protonation of the surface causing a net positive charge. As the pH increases, more sites become unprotonated and the net charge becomes negative. Consequently, cation sorption is usually greatest at high pH (McBride, 1994 p. 96; Pierzynski et al., 2005, p. 83). Furthermore, specific bindings dominate between metals and sorbents at near-neutral conditions, while at low pH, metals are bound to sorbents by weaker non-specific bindings (Kim et al., 2015). Presence of complexing agents, inorganic (chloride, sulfate, carbonate) or organic (dissolved organic carbon, DOC), facilitates the mobility of contaminants. Association to complexing agents lowers the interaction between the contaminant and the solid phase, resulting in contaminant concentrations exceeding the equilibrium concentrations (Van der Sloot et al., 1997).

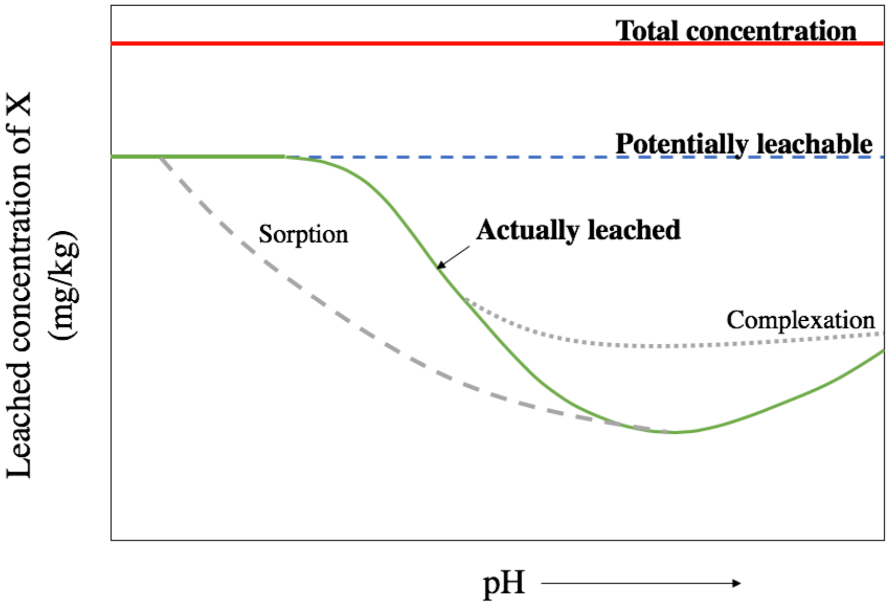

Figure 7. Leaching behavior of metal X as a function of pH and the total concentration (red line). The proportion of the potentially leachable fraction (blue dashed line) that is actually leached (green line) depends on soil solution chemistry such as pH and redox, presence of complexing agents and sorption. Adapted from Van der Sloot and Kosson (2010).

A division can be made between minerals that i) react fast upon contact with water, i.e. readily soluble compounds like halite (NaCl) and ii) react slowly in contact with water, i.e. most metals (Hyks et al., 2009). The former group, characterized by high initial leaching, is controlled by availability (Hyks et al., 2009; Kosson et al., 1996). In the latter group, solubility is a function of pH, complexing agents and co-precipitating species (Appelo & Postma, 2005, p. 119; Kosson et al., 1996).

3.2 Trace metal contamination

The term *trace metal* refers to metals that occur in low concentrations in the environment (Pierzynski et al., 2005, p. 332-343). This group includes copper (Cu) and lead (Pb), whereas the latter has a specific density exceeding 5 g/cm^3 and can be classified as a *heavy metal* (Berkowitz et al., 2014, p. 63). *Oxyanions* are formed by association of a *metalloid*, e.g. antimony (Sb), and one or several oxygen atoms. They commonly have a negative charge (Almås & Singh, 2017).

3.2.1 Lead

Lead (Pb) has high mammalian toxicity, and occurs principally as Pb^{2+} in soil (McBride, 1994, p. 336). The fate of Pb in natural soils is highly influenced by the amount of soil organic matter (Jordan et al., 1997). Anthropogenic activities, including use of Pb gasoline and paint, have resulted in elevated concentrations in many soils (Berkowitz et al., 2014, p. 68; Pierzynski et al., 2005, p. 335). The Norwegian release of Pb was reduced by nearly 90 % from 1995 to 2015. Followed by abrasive blasting, ammunition used at shooting ranges constituted the largest source of Pb emissions in Norway in 2015 (The Norwegian Environment Agency, 2017a).

3.2.2 Copper

Copper (Cu) is essential to all organisms and has moderate mammalian toxicity (McBride, 1994, p. 331). The divalent Cu^{2+} is the dominant form in soil solids and solutions, often complexed to the functional groups of humus (McBride, 1994, p. 331). Major sources of Norwegian emissions of Cu include abandoned mines, electronic products, impregnation and ammunition (The Norwegian Environment Agency, 2010).

3.2.3 Antimony

Antimony (Sb) occurs in a variety of oxidation states. Sb(V), in the form of $Sb(OH)_6^-$ (antimonate), dominates in near-neutral oxic systems. Under reducing conditions, Sb(III) takes form as $Sb(OH)_3$ at near-neutral pH (Filella et al., 2003; McBride, 1994, p. 337). Sb has high mammalian toxicity, and Sb(III) is considered more toxic than Sb(V) (Wilson et al., 2010). As a crucial component in semiconductors, hardener in lead products (e.g. batteries and ammunition) and flame retardants, the global demand of Sb has stimulated an extensive mining of Sb-containing ore minerals the last decades (Johnson et al., 2005; Okkenhaug & Mulder, 2016).

3.3 The partition coefficient

The partition coefficient, K_d, (L/kg) is a measure of the partition of a contaminant between the aqueous and solid phase at equilibrium, and can be defined as

$$K_d = \frac{C_s}{C_w} \tag{1}$$

where C_s is the concentration in the solid phase and C_w is the concentration in the aqueous phase (The United States Environmental Protection Agency, 1999).

Furthermore, a dimensionless partition coefficient, K_d^*, can be defined as

$$K_d^* = K_d \bullet \frac{\rho_b}{n} \tag{2}$$

where ρ_b is the bulk density of soil (g/cm^3), defined as the ratio between the mass of soil and total soil volume, and n is the porosity (%) (see Section 3.5 *Soil porosity and pore number* for more details).

3.4 Guidelines and leaching limits

The Norwegian quality guidelines for contaminated soil

The Norwegian quality guidelines for contaminated soil (TA-2553/2009), given in Table 1, from The Norwegian Environment Agency (2009) cover the acceptable level of the most common contaminants in relation to land use and soil depth. The division between quality class 1 and 2 corresponds to the norm values for contaminated soil. Soil values below the norm value can be considered clean (the Norwegian pollution regulations, 2004). Quality classes for the elements of concern in this thesis are given in Table A.1, Appendix A.

Table 1 *The Norwegian quality guidelines for contaminated soil (TA-2553/2009) from* The Norwegian Environment Agency (2009).

Class	1	2	3	4	5
Quality class	Very good	Good	Moderate	Bad	Very bad
Upper limit is based on	Norm value	Health-based acceptance criteria	Health-based acceptance criteria	Health-based acceptance criteria	“Hazardous waste”

Leaching limits for landfills

Leaching limits for inert, ordinary and hazardous landfills are provided by the Norwegian Waste Regulations (2014). The leaching limits are defined for batch tests (L/S ratio 10) and column tests (L/S ratio 0.1). Limits for the elements of concern in this thesis are given in Table A.2, Appendix A.

3.5 Hydraulic conductivity

The hydraulic conductivity is defined as the ease of a fluid to flow through a geological material, and is a function of both geological properties and flow characteristics of the fluid (Schwartz & Zhang, 2003, p. 49). Today's experimental understanding of hydraulic conductivity is based on the work of the French civil engineer Henry Darcy who studied water flow in porous media in the 1850s. He showed experimentally that water flow in a cylinder at a known discharge (Q) at time (t) is proportional to the cross-sectional area (A) and the difference in stand pipe levels (h), and inversely proportional to the distance (l) which separates the stand pipes (Al-Khafaji & Andersland, 1992, p. 130-137; Schwartz & Zhang, 2003, p. 44-46), as illustrated in Figure 8.

Darcy derived what we today know as *Darcy's law* or *Darcy's equation*

$$\frac{Q}{A} = K\left(\frac{h_1-h_2}{l}\right) \tag{3}$$

where K is the hydraulic conductivity (m/s), Q is the volume of passing water (m^3), A is the column cross-sectional area (m^2) and h_1-h_2/l is the hydraulic gradient, that can be denoted i= -dh/dl (Schwartz & Zhang, 2003, p. 44-46).

Hydraulic conductivity can be determined by several means, including field measurements, empirical formulas and laboratory measurement. The method and formulas used in this master thesis are further described in Section 4 *Materials and Methods*.

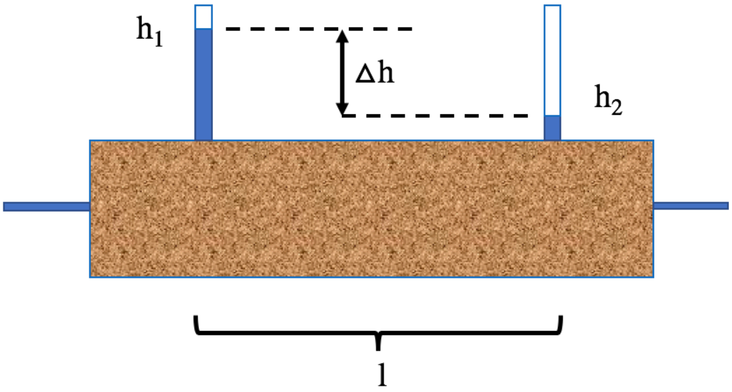

Figure 8. Darcy's experiment. Column with cross-sectional area (A), flow rate (Q), stand pipes levels (h), and distance (l).

3.6 Soil porosity and pore number

The relationship between the solid, liquid and gas phase in soil is illustrated in Figure 9. Total soil porosity (n) is defined as the ratio (%) between pore volume (V_p) in the soil and the total soil volume (V) (Janbu, 1970, p. 44), and is expressed as

$$n = \frac{V_p}{V} \bullet 100\ \% \tag{4}$$

The *effective* porosity (n_{eff}) is defined as the volume of drainable pores, and is of greater interest in a hydrogeological view, as only interconnected pores are conducting water (Schwartz & Zhang, 2003, p. 44).

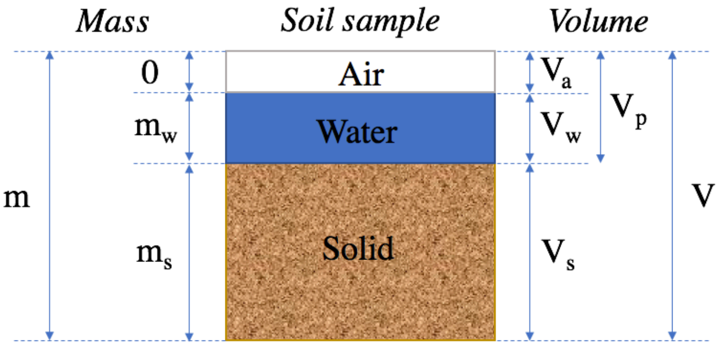

Figure 9. The relationship between mass (m) and volume (V) for the solid (s), liquid (w) and gas (a) phase in soil. Modified from Aarhaug (2003).

The porosity is influenced by the soil compaction, sorting and structural arrangement, as shown in Figure 10. The cubic packing (a) represents the highest theoretical soil porosity of 48 %.

Compaction leads to a reduction in porosity (b) (Schwartz & Zhang, 2003, p. 43). Sorting is described by the uniformity coefficient, $C_u = d_{60}/d_{10}$. When $C_u > 6$, the material is considered to be poorly sorted (Fetter, 2001, p. 74). The porosity decreases in poorly sorted material as smaller particles occupy the free pore space (d). Deviations from spherical particles reduce the porosity as the structural arrangement becomes more complex (Cox & Budhu, 2008; Fetter, 2001, p. 71), as shown in (e) and (f).

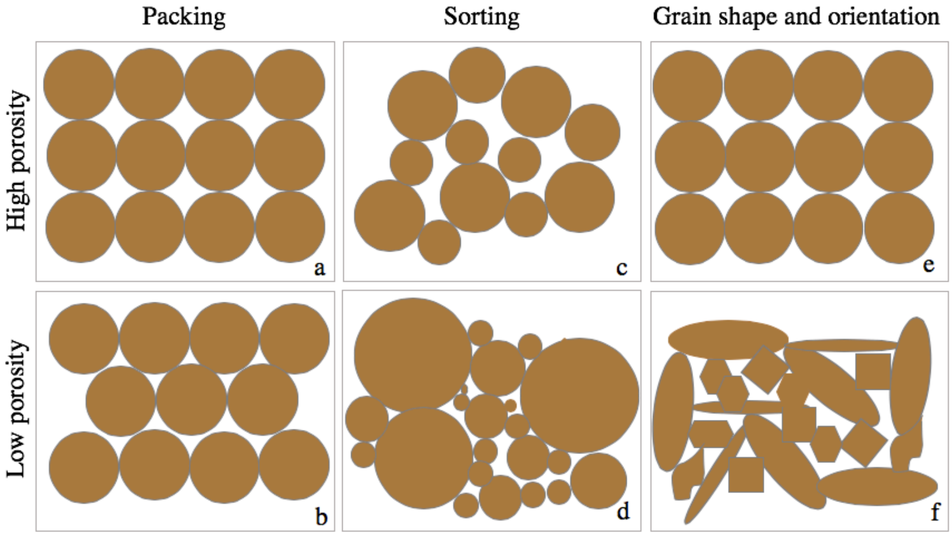

Figure 10. Geological factors influencing porosity can be summarized into compaction, degree of sorting, and the grain shape and orientation.

The pore number (e) is the ratio between the pore volume (V_p) and the volume of solid material (V_s) (Janbu, 1970, p. 45), and can in a partially saturated system be expressed as

$$e = \frac{V_p}{V_s} = \frac{V_a + V_w}{V_s} \tag{5}$$

In geotechnical engineering, the pore volume can be further related to the specific gravity (G_s), the volumetric water content (w) and the degree of saturation (S_r)

$$e = \frac{wG_s}{S_r} \tag{6}$$

where a G_s ranging from 2.6 – 2.8 is assumed for most soils (United States Army, 1999).

In the case of 100 % saturation ($S_r = 1$) (Barnes, 2016, p. 41), where $V_w = V_p$, the pore number can be expressed as

$$e = wG_s \tag{7}$$

Further, the relationship between the pore number, the dry unit weight (γ_d) (kg/m^3) and the specific gravity can be defined as

$$e = \left(\frac{G_s \gamma_w}{\gamma_d}\right) - 1 \tag{8}$$

where γ_w is the unit weight of water (kg/m^3) (Hicks et al., 2018).

4 Materials and methods

Figure 11 summarizes the materials and methods of this thesis.

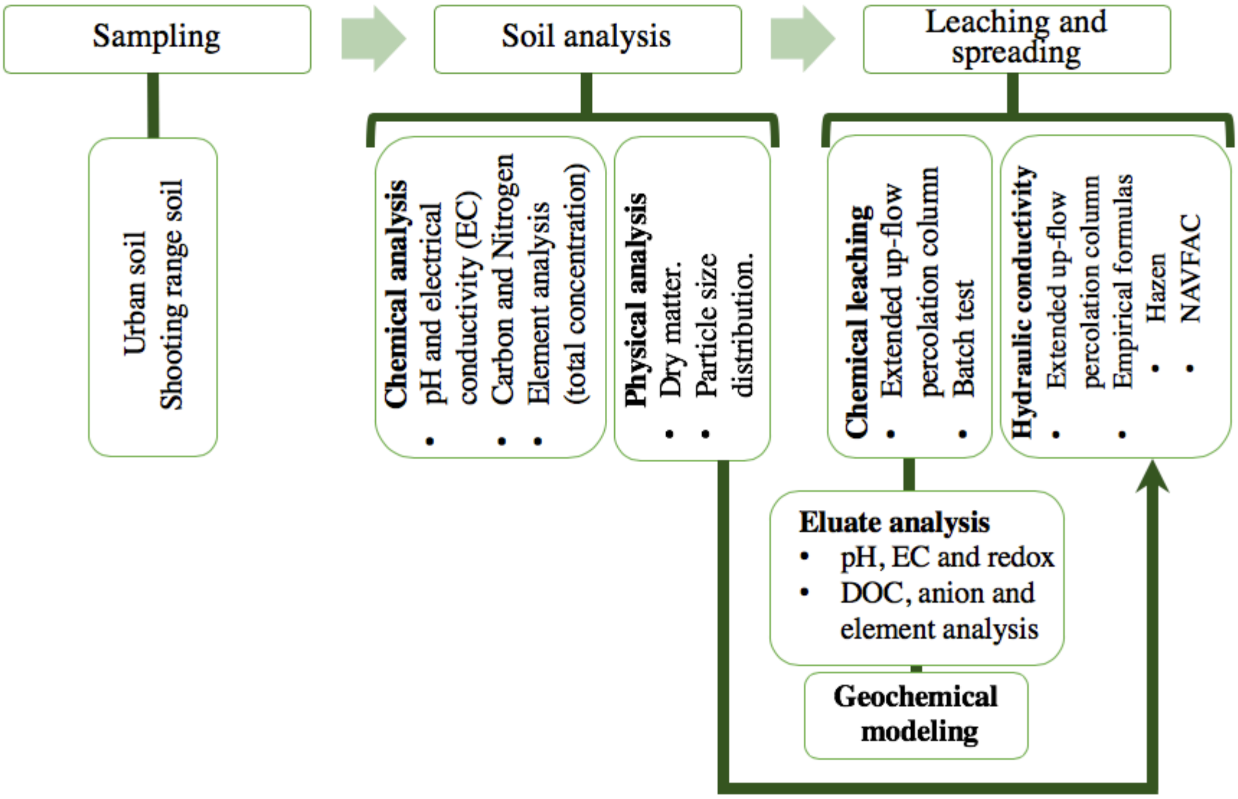

Figure 11. Flowchart summarizing the materials and methods of this thesis.

4.1 Sampling and sample homogenization

4.1.1 Field sites

Top soil (< 15 cm depth) was collected through grab sampling at two contaminated sites. The first soil, *the urban soil*, was sampled in June 2018 from an urban filling in the Oslo region, Norway, which has been affected by local industry from the 19th century until late 20th century. Further details regarding the urban soil are excluded for sake of the property owners. The second soil, *the shooting range soil*, was sampled from a military shooting range at Steinsjøen, Oppland County, Norway (UTM 32, 6717012 N 6053180 E) in June 2010. The sample was taken from a bullet trap which was under operation from 1984 until 2000 (Okkenhaug, 2012) and stored in a cold room (4 °C).

4.1.2 Sample homogenization

After sampling, the soil was homogenized manually in a large plastic pan and sieved (16 mm steel sieve) to remove stones, leaves and roots. A riffle splitter was used to divide the collected soil volume into representative subsamples. Approximately 2 kg of each soil, illustrated in Figure 12, was used for chemical and physical analysis at the NMBU. Soil for the extended up-flow percolation column and batch experiments (Section 4.3 *Extended up-flow percolation column* and Section 4.4 *Batch test*) was sieved through a 4 mm mesh steel sieve. The soil was stored in a cold room (4 °C) after sampling and prior to analyses.

Figure 12. Soil samples after homogenization and sieving (16 mm). Left: The shooting range soil. Right: The urban soil.

4.2 Soil analyses

Soil analyses were performed in triplicates in the Soil Laboratory at the Faculty of Environmental Sciences and Natural Resource Management (MINA) at NMBU, unless stated otherwise.

4.2.1 Sample preparations

Before analyses, the soil samples were filled in paper bags and dried at 40 °C in a drying cabinet for 72 hours prior to sieving (4 mm steel sieve), as described by Krogstad (1992). Prior to total nitrogen (tot-N), total carbon (tot-C) and element analysis (Section 4.2.2 *Soil chemical analysis*), a subsample was grounded in an agat mortar (Mortar Grinder, RM 200, Retsch) for approximately five minutes. Another subsample was sieved through a 2 mm mesh steel sieve prior to particle size distribution analysis (Section 4.2.3 *Soil physical analysis*).

4.2.2 Soil chemical analysis

pH

As a proxy for the soil pH, pH was measured in the liquid phase using a pH-meter (PHM210 Meterlab, Radiometer Copenhagen, Denmark) following mixing and sedimentation of 10 mL soil and 25 mL deionized water, in accordance with Krogstad (1992).

Electric conductivity

10 mL soil and 10 mL deionized water were shaken by hand and centrifugated at 3000 rpm for 10 minutes prior to filtration on a 4-12 μm filter (Schleicher & Schuell 589^2 White Ribbon Filter Paper Circles, ashless, 100, Ø 125 mm). Electric conductivity (EC) in the filtered solutions was measured using an EC meter (Metrohm 712).

Carbon and Nitrogen analysis

Approximately 200 mg of the grounded soil (Section 4.2.1 *Sample preparations*) were analyzed for tot-C and tot-N using LECO Truspec. Loss on ignition (LOI) is described in Section 4.2.3 *Soil physical analysis*. Analysis of total inorganic carbon (TIC) and total organic carbon (TOC) were conducted at the ALS Laboratory Group Norway AS, Oslo (Appendix N).

Element analysis

Approximately 0.3 gram grounded soil (Section 4.2.1 *Sample preparations*) was digested with acid and decomposed in Milestone ultraCLAVE, in order to transform the solid material into solution. Digestion with nitric acid (HNO_3) was performed in triplicates and digestion with hydrofluoric acid (HF) was performed in one replicate in order to investigate the effect of digestion acid on the element recovery. The presence of lead (Pb), antimony (Sb), copper (Cu), zinc (Zn) and iron (Fe) in the solution were identified and quantified using an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8900 QQQ ICP-MS).

Quality assessment of the element analysis

Digestions of the standard reference materials *2709a* and *2702* were carried out for quality control of the element analysis. The standard reference material *2709a* is an agricultural San Joaquin soil, collected in California, US, while *2702* is a marine sediment sampled in the Baltimore Harbor, Maryland, US (National Institute of Standards & Technology, 2009; National Institute of Standards & Technology, 2016). The recoveries of Fe, Cu, Zn and Pb in

2709a from digestion with HNO_3 were 95 %, 88 %, 94 % and 75 %, respectively. Recovery of Sb in *2702* from digestion with HF was 91 %. Green numbers in Table A.3, Appendix B indicate recovery values inside the acceptable interval designated by the lab engineers. High recovery indicate high method accuracy. Low recovery can be explained by i) the various properties of the reference materials, e.g. 2702 is intended for use in marine or fresh water sediment (or similar materials), or ii) the use of other acids or acid combinations in different laboratories.

4.2.3 Soil physical analysis

Dry matter and loss on ignition

Porcelain crucibles were weighed before and after addition of soil, and dried over night at 105 ± 5 °C. After cooling, the crucibles with soil were weighed such that the percentage of dry matter could be determined. Following dry matter determination, the loss on ignition (LOI) was determined by placing the same crucibles with dried soil in a calcinating oven at 550 ± 25 °C for a minimum of three hours. The samples were cooled prior to determining the percentage LOI in accordance with Krogstad (1992). Formulas for dry matter and LOI are given in Appendix C.

Particle size distribution analysis

The particle size distribution in the soil samples was determined by the pipette method, in accordance with Krogstad and Børresen (2015). The method can be conducted with and without pretreatment, i.e. standard and modified method respectively. The pretreatment causes the soil aggregates to break down, and thus modifies the natural particle size distribution in the soil (Gee & Or, 2002). In order to maintain the *natural* particle size distribution in the samples, the modified method was also conducted. Table 2 summarizes the main differences in methodology between the two methods.

Fraction < 2 mm

10 gram of the two soil samples (particle size < 2 mm) were analyzed as listed in Table 2.

Table 2 Short summary of the differences and similarities between the standard method (with pretreatment) and the modified method (without pretreatment).

	Standard method	Modified method
Pretreatment	Hydrogen peroxide (H_2O_2): oxidizes organic material. Hydrochloric acid (HCl): dissolves aggregate forming amorphous compounds. Magnesium chloride ($MgCl_2$): increases the sedimentation velocity.	No pretreatment.
Particle size separation	Sodium pyrophosphate was added to the samples to disperse the material, and deionized water was added prior to pipetting. Based on the temperature and water viscosity, sedimentation time for each fraction (63 µm , 20 µm, 6 µm and 2 µm) was determined from Krogstad and Børresen (2005). The various fractions were pipetted out and transferred to glass beakers.	
Sieving	The remaining soil particles in the samples were transferred to a stack of sieves with following size: 600 µm, 212 µm, 63 µm, from top to bottom respectively. The samples were seived with water and each fraction collected at the different screens were washed into glass beakers.	
Calculation of the weight fraction	The beakers were dried at 105 °C for at least 24 hours, before weighing. The weight fraction was now calculated.	

Source: Krogstad and Børresen (2015).

Fraction 2 – 4 mm

The pipette method is normally used to determine the particle size distribution in materials < 2 mm. As the fraction 2 - 4 mm was included in the column and batch test (Section 4.3 *Extended up-flow percolation column* and Section 4.4 *Batch test*), 10 gram of material < 4 mm was analyzed for each soil. The samples were treated similarly as the samples < 2 mm, with and without pretreatment respectively, before sieving at 2 mm in order to obtain the weight fraction 2 – 4 mm.

Quality assessment particle size distribution analysis

A particle size distribution analysis was performed on an internal laboratory reference soil, *Control A*, in order to examine the quality of the analysis. High recovery was reported for *Control A* in the standard particle size distribution analysis as seen from Table A.4, Appendix D, and values were found inside the control limits. For the modified method, lack of data sets hinders a statistical basis and interpretation. However, as indicated in Table A.5, Appendix D, the recovery of *Control A* was in consistency with the previously conducted analysis without pretreatment. It should be noted that fraction 2 – 4 mm has a lower accuracy than the fraction

< 2 mm as result of difficulties in obtaining a representative sample when only 10 gram soil was analyzed.

4.3 Extended up-flow percolation column

Leaching tests of the contaminated soil were performed using the extended up-flow percolation column. One of the soils was characterized at two compaction modes to investigate the effect of compaction.

Note: *Only* the extended up-flow percolation column was used in this thesis, and must *not* be confused with the standard column (technical specification in CENT/TS 14405 (2006)) used for routine leaching tests today.

4.3.1 Experimental setup

Three identical extended up-flow percolation columns, marked 1, 2 and 3, were used. The columns were made of polymethylmethacrylate (PMMA) (Plexiglas) and with an internal diameter of 50 mm and a height of 45 cm. On each column, three 6 mm PMMA stand pipes, marked A, B, and C, were installed with 7.5 cm intervals. Filters (plastic) inhibited migration of soil particles from the column into the stand pipes. The setup is illustrated in Figure 13.

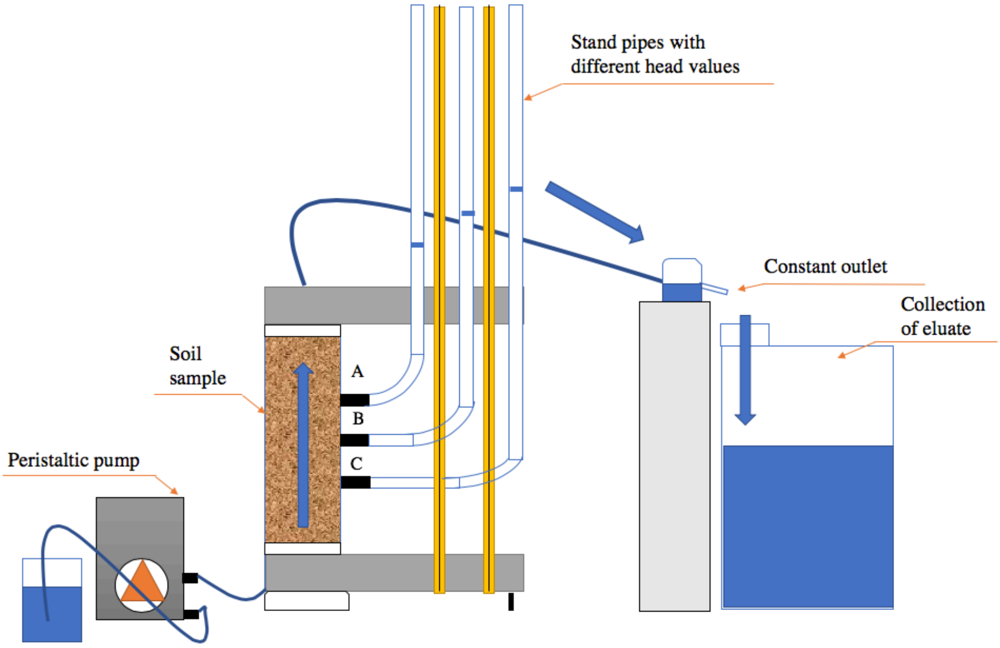

Figure 13. Experimental setup for the extended up-flow percolation columns. The eluent was pumped from the bottom towards the top of the soil column using a peristaltic pump (arrow in the column indicates flow direction). Eluate was collected for chemical analysis. The stand pipes allow the hydraulic conductivity to be calculated.

The top and bottom section, made of teflon, were equipped with grid filters (plastic) for securing water flow and 0.45 µm membrane filters (47 mm diameter, Supor-450, Pall Corporation) for particle retention. Both the top section and bottom section were sealed with O-rings. Filter details and O-ring are shown in Figure 14. A peristaltic pump, connected to the bottom section with tubes, allowed the eluent (Direct-Q, Millipore) to be pumped from a plastic container into the column. The eluent container was capped with parafilm to prevent evaporation and contamination. The top section was connected with tubes to the constant outlet where the eluate was retained before entering the eluate collection bottle.

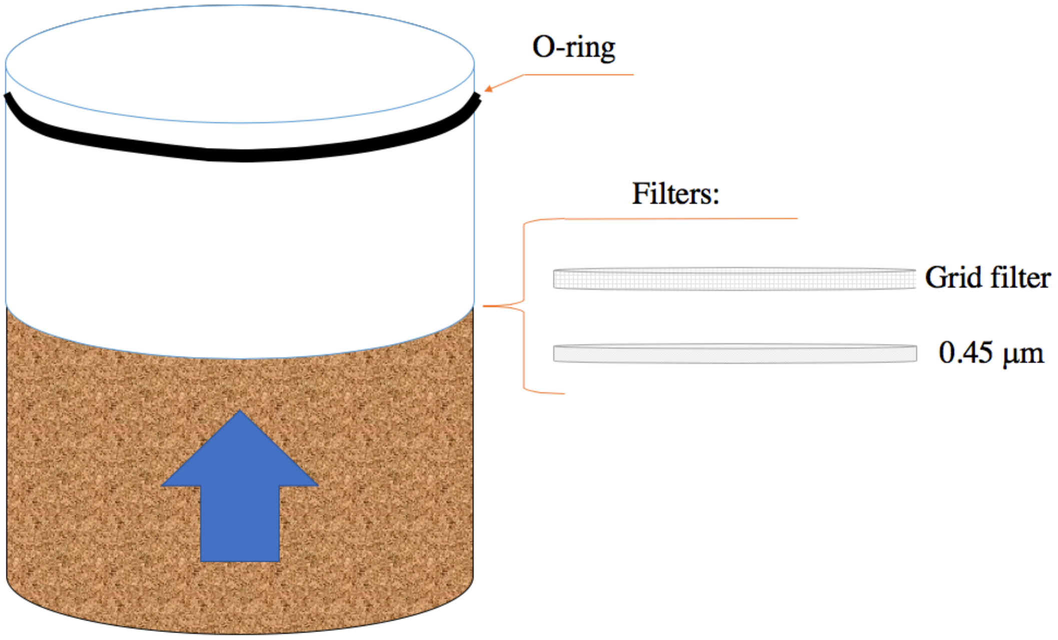

Figure 14. Close-up of top section (white) showing O-ring and filters. Arrow indicates flow direction.

4.3.2 Column packing

Two different compaction modes, high and low packing, were considered for the shooting range soil (particle size < 4 mm). For the urban soil, only low packing was performed. All tests were performed in triplicates. The samples were packed in a specific number of consecutive layers up to a height of approximately 30 cm. A weight (125 gram) was dropped from a height of 23.5 cm along a rod, one single time or three times for each layers, at low and high compaction respectively. Packing specifications are presented in Table 3. After the final layer was packed, the top section was fitted closely to the soil sample in order to avoid open space. The total amount of soil materials (gram) packed in the columns is given in Table A.6, Appendix E.

Table 3 Packing specifications for high and low compaction.

	High compaction	**Low compaction**
Height of soil column (cm)	30	30
Layers	10	6
Height of each layer (cm)	3	5
Number of times the weight was dropped on each layer	3	1

4.3.3 Equilibrium conditions

The extended up-flow percolation columns were saturated with deionized water (Direct-Q, Millipore) within 3 days prior to the test start in order to equilibrate the system. Deionized water was pumped through the column until it reached the top section before the pumps were switched off. A clamp inhibited the water from escaping the column.

4.3.4 Collection of eluates

After the equilibrium period, the peristatic pumps were started and deionized water was pumped into the columns. Optimal flow range was from 10.6 to 13.9 mL/h. The *actual* flow rate was lower, as seen from Table A.6, Appendix E.

Eluates were collected at liquid to solid (L/S) ratio 0.1, 2 and 6 as the fractions were reached. The L/S ratio is a measure of the amount of liquid (L) that has percolated through the column relative to the solid material (S), expressed in L/kg (dry mass). L/S ratio 2 and 6 (and L/S ratio 10 for the highly packed shooting range soil) were collected as accumulated quantities. E.g. L/S 6 constituted the entire eluate volume ranging from the point of which L/S ratio 2 was collected until L/S ratio 6 was reached. Figure 15 illustrates the setup at the lab, represented with the collection of L/S ratio 2 for the lightly packed shooting range soil.

The experiment was conducted at room temperature (~ 20 °C) at NGI geotechnical laboratory. A collection scheme developed at NGI was used in order to collect the eluates at the correct time interval with respect to the L/S ratio. The eluate bottles and constant outlets were capped in order to avoid evaporation, and the pump settings were adjusted when needed. Plastic bottles were changed after each eluate collection. The columns were washed thoroughly and the filters and tubes were changed between each test.

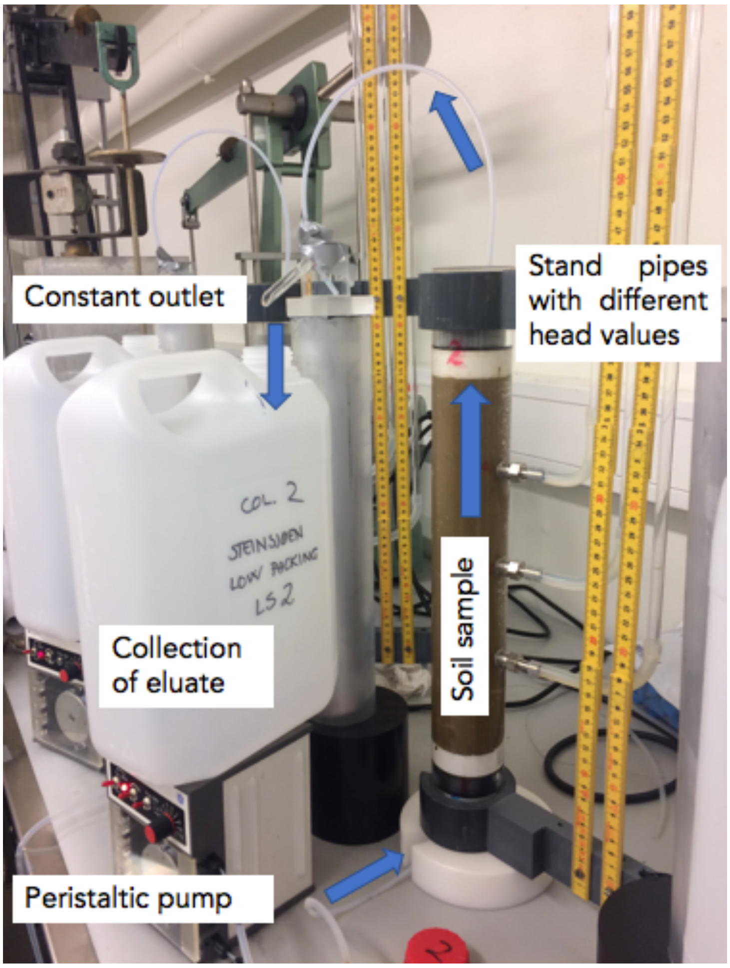

Figure 15. Setup for the lightly packed shooting range soil, L/S ratio 2. Deionized water was pumped into the column using a peristaltic pump, and eluates were collected in plastic containers. The calculation of the hydraulic conductivity from the stand pipes is described in Section 4.6.1 *Calculation of hydraulic conductivity from the extended up-flow percolation columns*.

Sample conservation

Eluates for ICP-analysis (Section 4.5.2 *Element analysis*) were conserved with ultrapure HNO_3 in 15 mL plastic tubes using a ratio 9 mL eluate and 1 mL HNO_3. Eluates for ion chromatography (IC) and dissolved organic carbon (DOC) analysis (Section 4.5.1 *Dissolved organic carbon and anion analysis*) were kept in plastic tubes. All the samples were stored in a cold room (4 °C) at NGI before transport to NMBU for analysis.

4.4 Batch test

A batch test was performed in accordance with Standard EN 12457-2 (2003) in triplicates for the shooting range soil and the urban soil, to compare with the results from the extended up-flow percolation column test.

Soil and deionized water were mixed in L/S ratio 10 and agitated for 24 ± 0.5 hours using an end-over-end shaker (10 rpm) at room temperature. Once the solids had settled (15 ± 5 minutes), the eluate volume needed for chemical analysis was sampled using a 100 mL syringe (BD Plastipak) with a 0.45 μm 7 mm filter attached. Sample conservations were done as described above.

4.5 Chemical analysis of the eluates

The eluates from the extended up-flow percolation columns and the batch tests were subjected to the same chemical analysis. Blanks were collected regularly and analyzed by the same chemical analysis as the eluates. pH and EC were measured in the eluates immediately after sampling at the NGI lab, using a pH meter (WTW Inolab pH level 2) and an EC meter (WTW LF 538, electrode: TetraCon 325). For practical reasons, the redox potential (E_h) was only measured in L/S ratio 6 for the lightly packed shooting range soil, and for L/S ratio 0.1 and 2 for the urban soil, using a redox meter with platinum tip (Orion SA 720, electrode: Hanna Instruments (HI 3230)). The detected values were corrected with 205 mV to establish E_h values.

4.5.1 Dissolved organic carbon and anion analysis

The concentration of DOC in the eluates was measured using Shimadzu TOC-V CPN Total organic carbon analyzer. IC 5000 Ion Chromatograph, Lachat (Zellweger analytics) was used to determine the concentrations of anions (sulfate (SO_4^{2-}), nitrate (as NO_3^--N) and chloride (Cl^-)). Analysis of the standard reference material *ION-96.4*, river water sampled from the Grand River, Ontario, Canada (Environment and Climate Change Canada, 2016), was conducted for quality control. The high recoveries given in Table A.7, Appendix G indicate high method accuracy.

4.5.2 Element analysis

The eluates were analyzed for Fe, Cu, Zn, Sb and Pb by ICP-MS (8900 Agilent QQQ), and macro elements (calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na)) by inductively coupled plasma optical emission spectrometry (ICP-OES) (5110 Agilent synchronous vertical dual view plasma instrument).

Analysis of the standard reference material, *1640a*, consisting of acidified spring water (National Institute of Standards & Technology, 2010), and the internal lab references, *1643h* (Soil Laboratory, n.d.), were carried out for quality control of the metal and Sb analysis. High metal recoveries were reported by the green numbers in Table A.8, Appendix G. High recoveries of *1643h* for the macro elements analysis were also reported, as given in Table A.9, Appendix G.

4.6 Data analysis

4.6.1 Calculation of hydraulic conductivity from the extended up-flow percolation columns

The hydraulic conductivity was calculated at a regular basis through the experiment as

$$K = \frac{QL}{A \bullet \Delta \mathrm{h} \bullet \Delta t} \tag{9}$$

where the volume of collected eluate (Q) was measured as a function of time (t), the cross-section area (A) and the separation distance (l) between the stand pipes were known, and the difference in head (h) was read from the stand pipe levels (Schwartz & Zhang, 2003, p. 44-46). The concept is illustrated in Figure 16.

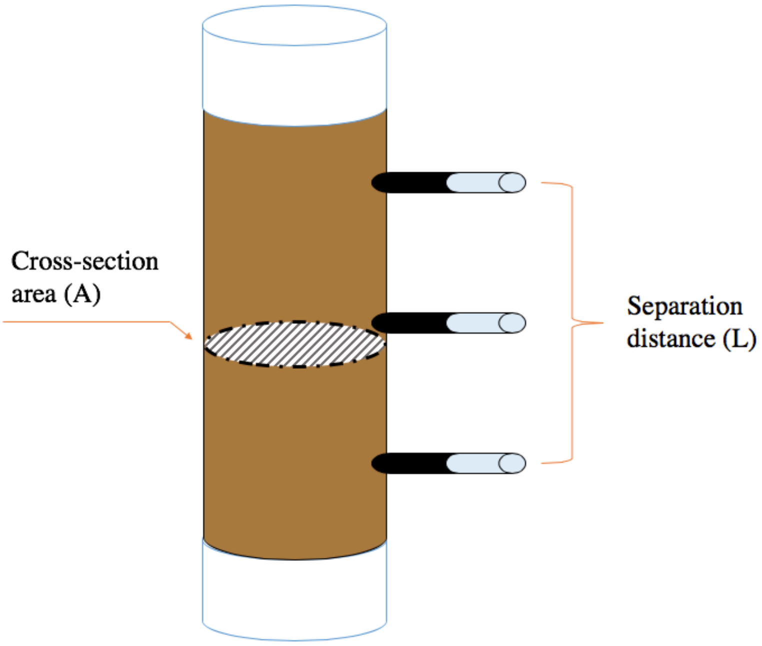

Figure 16. The parameters cross-section area (A) and separation distance (l) in Eq. 9.

4.6.2 Calculation of hydraulic conductivity from empirical formulas

Empirical approaches based on particle size distribution represent an inexpensive and quick alternative to resource demanding field methods and time consuming lab methods during hydraulic conductivity investigations. The formulas used in this thesis are listed in Table 4. Parameters were graphically obtained from the standard particle size distribution, see Figures A.1 and A.2, Appendix L.

Table 4 Formulas for calculation of hydraulic conductivity, limitations and additional information.

Name	Formula		Additional information
Hazen	$K = C_H(d_{10})^2$	(10)	C_H is an empirical constant, set to 0.01157 in this thesis (equivalent to the most used value in Scandinavian literature (Andersson et al., 1984)). A temperature correction factor (0.70 + 0.03 T) where T is the temperature in °C was added (Carrier, 2003). T was set to 20°C in this thesis.
	Limitations		
	$C_u < 5$ $0.1 < d_{10} < 3.0$ mm		
Naval Facilities Engineering Command (NAVFAC)	$K=10^{1.291e-0.6435}(d_{10})^{10^{0.5504-0.2937e}}$	(11)	Eq. 11 is a result of derivations of the relationship between log(K) and log(d_{10}) for a material performed by Chapuis (2004). A calculation of this relationship for the specific materials tested is recommended by Chapuis (2004), but was beyond the scope of this thesis.
	Limitations		
	$0.3 < e < 0.7$ $2 < C_u < 12$ $d_{10}/d_5 < 1.4$ $0.1 < d_{10} < 2.0$ mm		

e is calculated from Eq. 8 assuming a 100 % saturation and a G_s of 2.7. d_{10}, d_{50} and C_u are derived graphically from the particle size distribution.

4.6.3 Geochemical modelling

Geochemical modelling using the software *Visual MINTEQ* version 3.0. was carried out to predict the speciation and solubility of the elements of concerns. The model was operated using the default setting unless stated otherwise. The following was added or specified in the model:

- The results obtained in the chemical analysis was added, including element concentrations, pH and redox potential (E_h).

- The redox couples were included for Fe and Sb in knowledge of the redox potential.
- The charge balance was adjusted to maximum 5 % by adding bicarbonate (HCO_3^-). HCO_3^- is one of the main anions in water, but analysis was not performed due to a limited preservation potential.
- The NICA-Donnan model (with default settings) was specified for complexation with DOC.

It should be noted that Visual MINTEQ assumes thermodynamically equilibrium and the results from geochemical modelling should only be considered as indications.

4.6.4 Statistical data treatment

Blank corrections of the eluate concentrations were performed and negative values caused by blank correction were set to zero. Average values were calculated from three replicates. The statistical software *R,* version 3.3.3 (2016) was used to check for normality of the data by drawing density plots. Some of the distributions deviated from the normal distribution, also in the case of log transformation. Linear regressions were therefore performed based on Spearman's rank order correlation by using Microsoft Excel with the extension *Analysis ToolPak*, version 16.16.3 (2018). Normality was assumed for the data when T-tests (in Microsoft Excel) were performed to test for significant differences. A 95 % confidence interval, $p < 0.05$, was used.

4.7 Data quality

Limit of detection (LOD) is defined as the lowest quantity or concentration than can be distinguished from a blank sample. The limit of quantification (LOQ) is defined as the lowest concentration of a substance that can be quantified with an acceptable uncertainty (Egeland, 2009). Calculated LOD and LOQ values are given for the respective analysis in Appendix B and Appendix G.

5 Results

The results from soil chemical analysis, eluate analysis, physical analysis and hydraulic conductivity are included in this section. The primary focus of the results from the chemical analysis will be on the elements of concern, i.e. Pb, Cu and Sb, and the most important ligands, i.e. DOC. Major sources of the soil compounds are briefly commented in this section. Supporting information and details can be found in Appendices B – O.

5.1 Soil chemical analysis

Table 5 summarizes the basic properties (pH, electrical conductivity (EC), organic content and inorganic content) for the urban soil and the shooting range soil studied in this thesis.

Table 5 The average concentrations of pH, EC (μS/cm), organic content (total organic content (TOC) and loss of ignition (LOI) (%) and total inorganic content (TIC) (%) for the urban soil and the shooting range soil. Standard deviations are based on three replicates. Tot-N, tot-C and dry matter are given in Table A.10, Appendix H.

	pH[a]	**EC** (µS/cm)	**Organic content** (%)		**TIC** (%)
			TOC	LOI	
Urban soil	7.4±0.0	206±18	5.33±0.11	7.7±0.5	0.076±0.016
Shooting range soil	5.2±0.0	50±3	1.12±0.03	2.5±0.1	0.019±0.002

[a]average and standard deviation were calculated directly, without taking considering that the pH is based on a logarithmic scale.

5.1.1 pH and EC

The urban soil had a pH value of 7.4±0.0, given in Table 5, which corresponded to a neutral or slightly alkaline soil. Urban soils tend to have a higher pH than their natural counterparts, as described in the literature (Craul, 1985). The shooting range soil was found to have a pH value of 5.2±0.0, which is in agreement with previously reported pH values for the same soil (Okkenhaug et al., 2013). A slightly acidic pH for the soil is expected from areas dominated by podzol soil and coniferous forest (The University of Oslo, 2011). The EC values of 206±18 µS/cm for the urban soil and 50±3 µS/cm for the shooting range soil indicated unreactive soils of low salinity (Seifi et al., 2010).

5.1.2 Organic and inorganic content

The content of soil organic matter was measured by the total organic content (TOC) and the loss of ignition (LOI) (see Section 4.2.2 S*oil chemical analysis*). LOI is a commonly used estimate for the soil organic matter, but overestimates the soil organic matter relative to TOC due to i) the release of CO_2 from carbonates, and ii) the release of water preserved in clay minerals, when combusted at high temperatures (Bojko & Kabaa, 2014; the Norwegian Geotechnical Institute, 2019b). Higher values of LOI relative to TOC were confirmed for both soils in Table 5.

A high organic content was found in the urban soil (TOC ~ 5.3 % and LOI ~ 7.7 %), as expected from its dark color shown in Figure 12. The organic content in the shooting range soil (TOC ~ 1.2 % and LOI ~ 2.5 %) was consistent with previously reported values from the same shooting range soil (Okkenhaug et al., 2016). The TIC value measured in the urban soil (TIC ~ 0.08 %) can indicate influence from concrete sources in the urban environment (Craul, 1985), which can also increase the buffer capacity of the soil. The TIC value of the shooting range soil (TIC ~ 0.02 %) was low.

5.1.3 Element concentration

Soil digestion

To study the total contaminant concentration in the soil, each soil was digested with HF and HNO_3 as described in Section 4.4.2 *Soil chemical analysis*. Figure 17 shows a linear relationship between the total metal concentrations obtained from digestion with HF and HNO_3. This suggests that both digestion acids achieve satisfactory recovery of the metals. For statistical reasons, the total metal concentration discussed in the following sections are based on digestion with HNO_3 (performed in triplicates) rather than HF (performed in one replicate). The total Sb concentration obtained from digestion with HF was several orders of magnitude larger than the concentrations obtained from digestion with HNO_3 as seen from Figure 17. This was consistent with previously conducted studies evaluating various digestion acids for Sb (Mariussen, 2012; Okkenhaug et al., 2015), suggesting that HF provides a more accurate estimate of how much Sb that is actually present in soil. Therefore, all reported values of Sb in the following sections are based on digestion with HF.

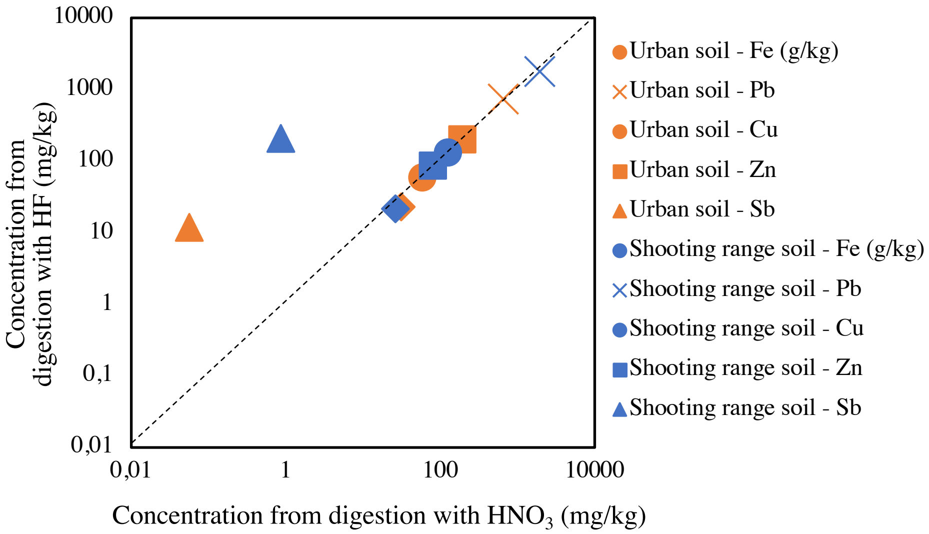

Figure 17. Comparison of the total concentrations of metals and Sb derived from digestion with HF and HNO$_3$ for the urban soil and the shooting range soil. Concentrations are given in mg/kg for all elements except for Fe (g/kg). The dotted line represents a 1:1 relationship. A linear relationship was found for all metals. The total Sb concentration obtained from digestion with HF exceeded by far the total Sb concentration obtained from digestion with HNO$_3$.

Total concentrations

Table 6 summarizes the total concentrations of Pb, Cu, and Sb for the urban soil and the shooting range soil. The total concentrations of Fe and Zn can be found in Table A.11, Appendix H.

Table 6 Total concentrations[a] of Pb, Cu and Sb (mg/kg) in the urban soil and in the shooting range soil. Standard deviations are based on three replicates of digestion with HNO$_3$ for Pb and Cu. Only one replicate of digestion with HF was performed for Sb.

	Pb (mg/kg)	**Cu** (mg/kg)	**Sb** (mg/kg)
Urban soil	660 ± 36	59 ± 4	12
Shooting range soil	1933 ± 58	127 ± 6	210

[a]The soil decomposition at the NMBU lab corresponds to the “environmental available concentration”. For practical reason, termed *total concentrations* in this thesis.

The total concentration of Pb in the urban soil (660 ± 36 mg/kg) was consistent with reported average concentrations of Pb (780 mg/kg) from contaminated sites in Oslo, Norway (Ottesen et al., 2007). Major sources of Pb in urban soils are industrial processes, and remains of Pb based paint and gasoline (Pierzynski et al., 2005, p. 335). The total concentration of Cu (59 ± 4 mg/kg) was in agreement with average concentrations of Cu (60 mg/kg) reported for urban Norwegian soils (Ottesen et al., 2007). The total concentration of Sb was 12 mg/kg, exceeding by far the estimated world average of ~ 0.5 mg/kg (Reimann et al., 2010). The concentrations of Cu and Sb in the urban soil can be attributed to their abundance in several industrial and electrical products (Okkenhaug & Mulder, 2016; The Norwegian Environment Agency, 2010).

The total concentrations in the shooting range soil were 1933 ± 58 mg/kg for Pb, 127 ± 6 mg/kg for Cu and 210 mg/kg for Sb. This was in accordance with concentrations previously reported for soil sampled in the same shooting range bullet trap (Pb ~ 2050 mg/kg, Cu ~ 145 mg/kg, Sb ~ 40 to 671 mg/kg) (Okkenhaug et al., 2013; Okkenhaug et al., 2016). In the shooting range soil, the presence of Pb, Cu and Sb reflects to the chemical composition of the most commonly used ammunition at the shooting range (Voie & Strømseng, 2000). According to Voie and Strømseng (2000), the relative contribution from Pb, Cu and Sb in the shooting range soil would be ~ 1800 mg/kg Pb, ~ 900 mg/kg Cu and ~ 210 mg/kg Sb if only corrosion was considered. With the exception of Cu, these values were in good agreement with the values in Table 6.

5.2 Extended up-flow percolation column

5.2.1 EC, pH and redox potential

Urban soil

Figure 18a shows the EC and pH values measured in eluates from the extended up-flow percolation column filled with urban soil, as a function of L/S ratio. pH values ranged from 8.4±0.0 to 8.5±0.2, and indicates slightly alkaline conditions. The pH values from the extended up-flow percolation column were significantly higher ($p < 0.05$) than the soil pH values (~ pH 7.4) listed in Table 5, suggesting some buffering capacity in the soil over time. The initial EC value was 780±19 µS/cm, and by L/S ratio 2, a near 50 % reduction was measured before the EC values stabilized at 296±36 µS/cm at L/S ratio 6. The measured redox potential (E_h) was ~365 and ~380 mV at L/S ratio 0.1 and 2, respectively, indicating stable and suboxic conditions in the columns.

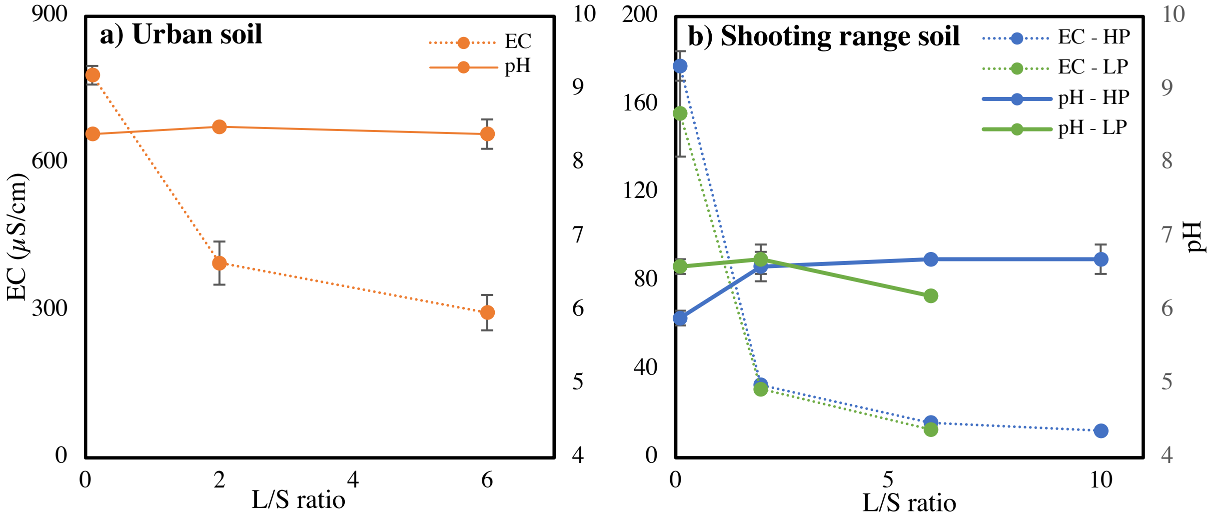

Figure 18. Eluate electrical conductivity (EC) (dashed lines) and pH (solid lines) as a function of the L/S ratio for **a) the urban soil** and **b) the shooting range soil** (high packing (HP) and low packing (LP) included) in the extended up-flow percolation column. Error bars represent standard deviations of three replicates.

Shooting range soil

Figure 18b displays the EC and pH values for the shooting range soils (at the different compaction modes) in the eluates from the extended up-flow percolation column as a function of L/S ratio. For the highly packed shooting range soil, the initial pH measurement was 5.9±0.1, and during column operation the pH reached a stable value of 6.7±0.0 at L/S ratio 6. The initial pH for the lightly packed soil (pH 6.6±0.1) was significantly higher ($p < 0.05$) than for the highly packed soil (pH 5.9±0.1). The lightly packed soil experienced a slight decline in pH towards 6.2±0.0 at L/S ratio 6. A significantly lower ($p < 0.05$) pH value was measured in the lightly packed soil (pH 6.2±0.0) compared to the highly packed soil (pH 6.7±0.0) at L/S ratio 6. The pH values were significantly higher ($p < 0.05$) than for the soil pH (pH ~ 5.2) in Table 5, suggesting some buffering capacity in the soil. The EC values exhibited a similar trend for both compaction modes. Insignificant differences ($p > 0.05$) between the two compaction modes were detected at L/S ratio 0.1 (177±7 µS/cm for high packing and 156±20 µS/cm for low packing). A near 80 % reduction was detected from L/S ratio 0.1 to L/S ratio 2, prior to a stabilization at ~ 12-16 µS/cm at L/S ratio 6, corresponding to normal rain water (Dodson, 2005, p. 37). The measured redox potential (E_h) was ~390 mV and indicated suboxic conditions in the lightly packed column at L/S ratio 6.

5.2.2 Concentrations of DOC and anions

Urban soil

Figure 19 shows leaching of DOC and anions from the urban soil as a function of L/S ratio. The figure suggests that the highest eluate concentration of DOC for the urban soil was detected in the first flush (31±2 mg/L). The DOC concentration was reduced by 60 % during the column operation, and resulted in a final DOC concentration of 13±3 mg/L at L/S ratio 6. The DOC concentration was low compared to what could be expected from the level of organic content (TOC ~ 5.3 %, LOI ~ 7.7 %) in Table 5.

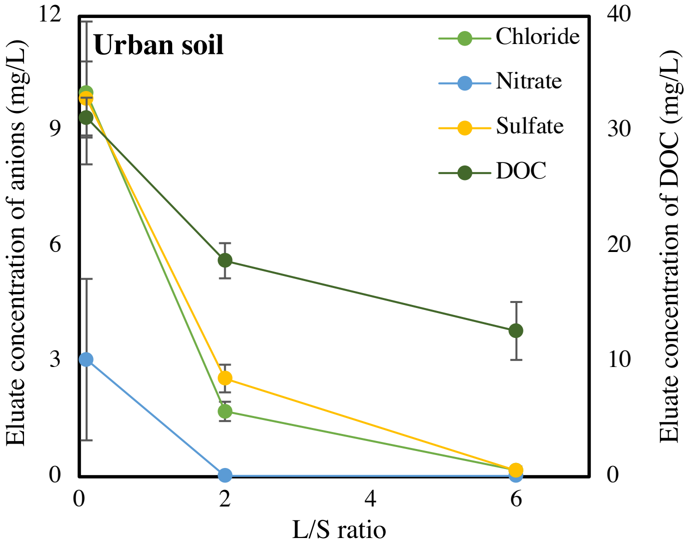

Figure 19. Eluate concentrations (mg/L) of DOC, SO_4^{2-}, Cl^- and NO_3^--N as a function of L/S ratio for the urban soil from the extended up-flow percolation column. Error bars represent standard deviations of three replicates.

Figure 19 indicates that the anions (SO_4^{2-}, Cl^- and NO_3^--N) exhibited a similar release pattern as a function of L/S ratio. The highest concentrations were observed in the first flush ($[Cl^-]$ = 10±2 mg/L, $[SO_4^{2-}]$ = 10±1 mg/L and $[NO_3^-]$ = 3.1±2.1 mg/L), prior to a decline in concentration approaching LOD as the L/S ratio increased. This suggests that the anion leaching was availability controlled (Kosson et al., 1996). The presence of Cl^- can be attributed to the near-coastal sampling location and de-icing products from the adjacent road, while NO_3^- and SO_4^{2-} in urban areas often originate from industry and combustion (Appelo & Postma, 2005, p. 29).

Shooting range soil

The leaching of DOC and anions from the shooting range soil is illustrated in Figure 20 as a function of L/S ratio. Figure 20a shows that the leaching pattern of DOC in the eluates at high and low packing were almost identical until L/S ratios 6. Highest releases of DOC were observed in the first column flush with concentrations of 36±3 mg/L and 37±5 mg/L at high and low packing, respectively. Both compaction modes showed a simultaneous decrease in concentration of ~ 75 % from L/S ratio 0.1 to 2. The concentration at high packing (6.1±1.8 mg/L) was significantly higher ($p < 0.05$) than at low packing (2.4±0.2 mg/L) at L/S 6. A further decrease in DOC concentration was observed for the high packing mode from L/S ratio 6 to 10.

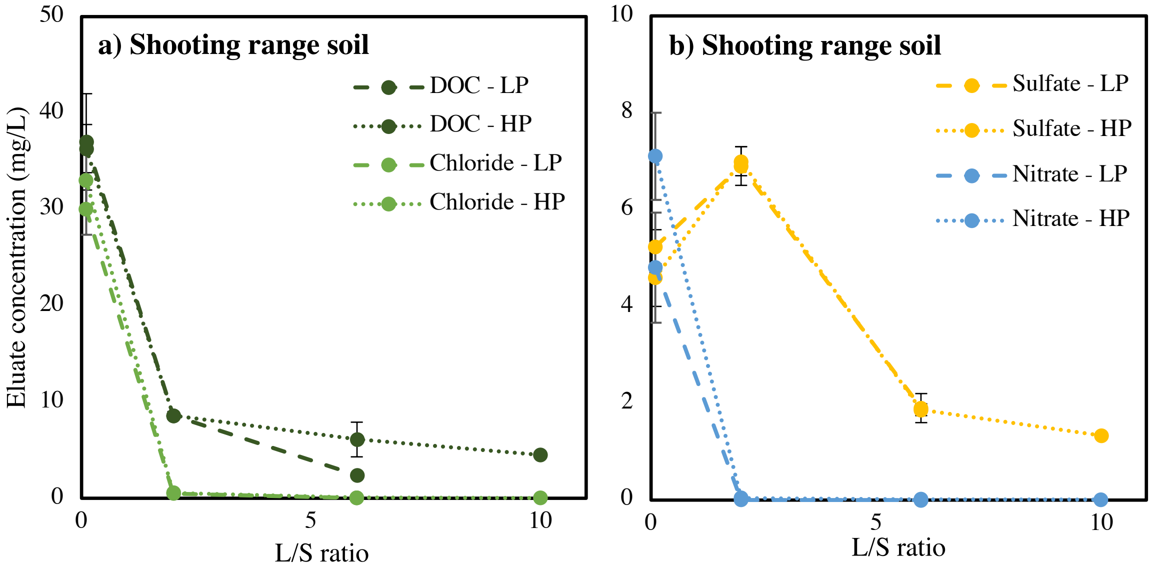

Figure 20. Eluate concentrations (mg/L) of **a) DOC and Cl^-**, and **b) SO_4^{2-} and NO_3^--N** as a function of L/S ratio for the shooting range soil (high packing (HP) and low packing (LP) included). Error bars represent standard deviations of three replicates.

Figure 20 indicates that Cl^- and NO_3^--N exhibited a similar release pattern in which the highest concentrations were observed during the first flush ($[Cl^-]$ = 33±3 mg/L, $[NO_3^-]$ = 7.1±0.9 mg/L), followed by a rapid decline reaching concentrations < LOD at L/S ratio 6. This is typical for highly soluble, availability controlled components in soil (Kosson et al., 1996). SO_4^{2-} showed a delayed flush pattern that yielded a maximum peak concentrations at L/S ratio 2 ($[SO_4^{2-}]$ = 7.0±0.3 mg/L) prior to a decrease towards L/S ratio 6 (and 10). This behavior can reveal a solubility controlled mechanism that most likely can be attributed to dissolution of sulfate minerals. The concentration differences between the compaction modes were overall small for the anions. The concentrations of DOC and anions were low, as expected for a mineral soil with moderate EC and TOC levels (Table 5).

5.2.3 Concentrations of macro elements

Urban soil

Figure 21 shows the eluate concentrations of macro elements as a function of L/S ratio for the urban soil. Figure 21a and b reveal that the highest concentrations of macro elements (Ca, K, Mg and Na) in the eluates were detected in the first flush ([Ca] = 137±5 mg/L, [K] = 43±2 mg/L, [Mg] = 10±0 mg/L, [Na] = 18±1 mg/L), prior to a decrease as a function of L/S ratio. Weathering of minerals contribute to the background concentrations of Ca, K, Mg and Na (Appelo & Postma, 2005, p. 27). Elevated concentrations of Ca can be attributed to the presence of carbonate or concrete in the urban soil, de-icing products from the adjacent road can be a source of Na and Mg, while the near coast location of the sampling site can increase the concentration of Na (Appelo & Postma, 2005, p. 27).

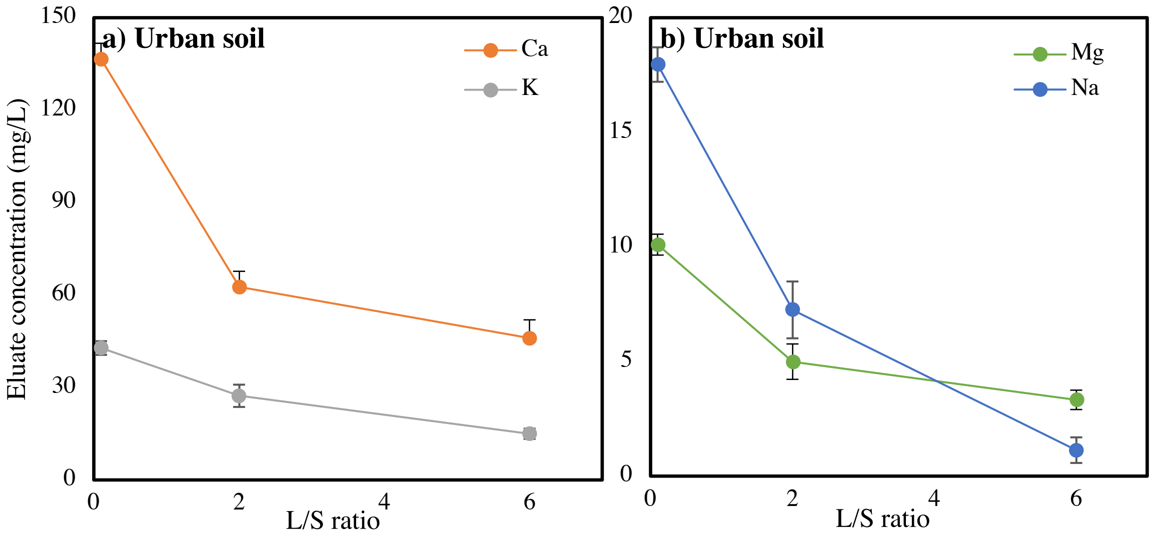

Figure 21. Eluate concentrations (mg/L) of **a) Ca and K**, and **b) Mg and Na** as a function of L/S ratio for the urban soil. The error bars represent standard deviations of three replicates.

Shooting range soil

The eluate concentrations of the macro elements in the shooting range soil are shown in Figure 22 as a function of L/S ratio. Highest concentrations of Na, Mg and K were detected in the first flush, before a sharp decline at L/S ratio 2 was observed. Concentrations are given in Table A.15, Appendix I. The low level of macro elements can be attributed to low base saturation and slow weathering of minerals (Appelo & Postma, 2005, p. 27).

Figure 22b indicates that great concentrations of Ca were detected in the first flush at both compaction modes. The large standard deviations associated with the eluate concentrations of Ca for the highly packed shooting range soil cannot be explained. Statistical analysis was not performed to compare the differences in Ca concentrations between the two compaction modes.

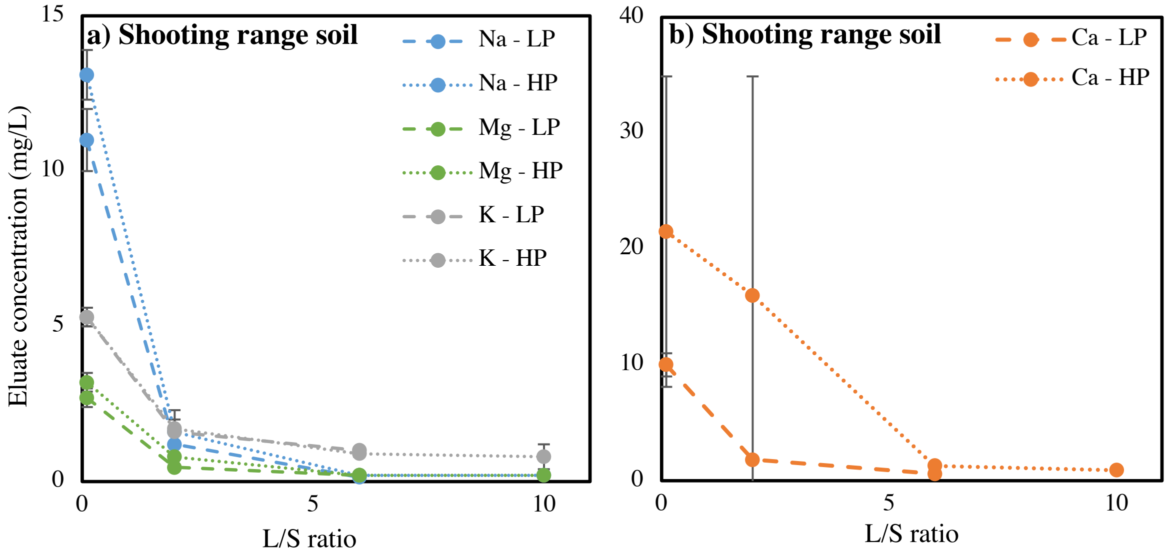

Figure 22. Eluate concentrations (mg/L) of **a) Na, Mg and K** and **b) Ca** as a function of L/S ratio for the shooting range soil (high packing (HP) and low packing (LP) included). The error bars represent standard deviations of three replicates.

5.2.4 Concentrations of metals and Sb

Urban soil

The eluate concentrations of Pb and Cu in the urban soil are shown in Figure 23 as a function of the L/S ratio. The greatest mobilization of Pb was found during the first flush and the initial concentration was 28±8 µg/L. At L/S ratio 6, the final Pb concentration reached 4.5±2.4 µg/L, which corresponded to a near 80 % reduction. Geochemical modeling, Table A.20, Appendix K, indicated that more than 95 % of Pb was complexed to DOC. The concentration of Cu remained relatively stable throughout the experiment, and ranged from 39±5 µg/L at L/S ratio 0.1, to 32±3 µg/L at L/S ratio 2, before reaching a concentration of 37±9 µg/L at L/S ratio 6. Geochemical modeling, Table A.20, Appendix K, indicated that more than 99 % of Cu was complexed to DOC.

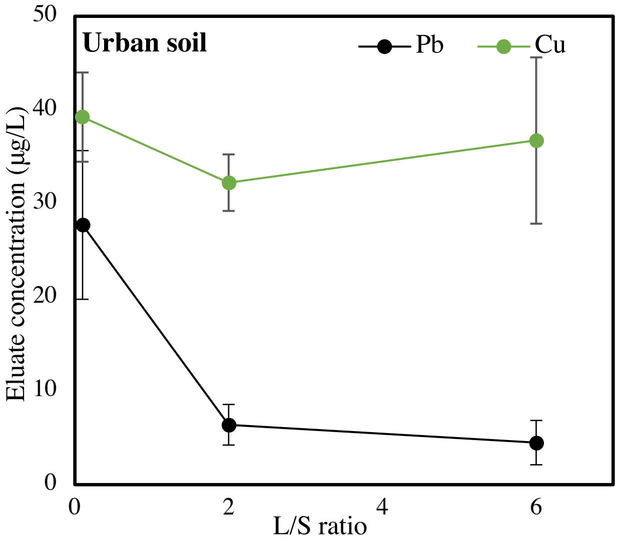

Figure 23. The eluate concentrations (µg/L) of Pb and Cu for the urban soil as a function of L/S ratio. The error bars represent standard deviations of three replicates.

The eluate concentrations of Zn, Fe and Sb are given in Table A.16, Appendix I. Highest concentration of Zn was detected during the first flush, prior to a reduction in concentration of nearly 100 %. This suggests that Zn is a mobile, availability controlled specie (Kosson et al., 1996). The Fe eluate concentrations increased by more than 350 % throughout the test. This could indicate changes in redox conditions during the experiment, although this was not confirmed by redox measurements. The concentration of Sb was highest in the first flush, and showed thereafter a steady decrease as a function of L/S ratio.

Shooting range soil

Figure 24a shows the eluate concentrations of Pb and Cu from the shooting range soil, as a function of the L/S ratio. Highest concentrations of Pb were detected in the first column flush, and yielded 3100±297 µg/L and 2616±343 µg/L for high and low packing, respectively. A rapid decline of ~ 70 % from L/S ratio 0.1 to 2 resulted in concentrations of 813±111 µg/L for high packing and 825±43 µg/L for low packing. The concentrations remained relatively stable thereafter, and the concentration for high packing at L/S ratio 10 was 555±33 µg/L. The reported differences between the two compaction modes were insignificant ($p > 0.05$). Geochemical modeling, Tables A.21 and A.22, Appendix K, indicated that Pb almost exclusively (> 90 %) was complexed to DOC. The initial concentration of Cu at high packing (443±52 µg/L) was significantly higher ($p < 0.05$) than for low packing (326±34 µg/L). The total decline in concentration was ~ 75 % from L/S ratio 0.1 to L/S ratio 6, and resulted in concentrations of 106±5 µg/L for high packing and 86±5 µg/L for low packing. Significantly higher ($p < 0.05$) concentrations were also obtained for high packing compared to low packing at L/S ratio 6. Geochemical modeling, Tables A.21 and A.22, Appendix K, indicated mainly (> 90 %) complexation between DOC and Cu.

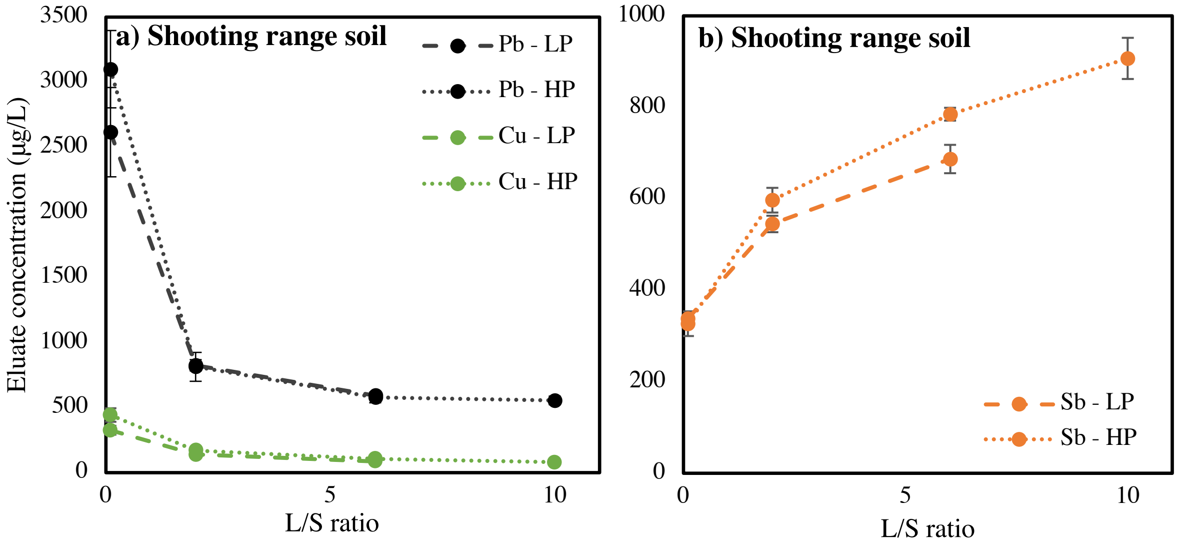

Figure 24. Eluate concentrations (µg/L) of **a) Pb and Cu,** and **b) Sb** as a function of L/S ratio for the shooting range soil (high packing (LP) and low packing (LP) included). The error bars represent standard deviations of three replicates.

Figure 24b shows that Sb yielded the lowest eluate concentrations at L/S ratio 0.1 before a steady increase towards L/S ratio 6 (and further towards L/S ratio 10 for high compaction). The concentration of Sb at low packing (338±8 µg/L) was slightly higher than the concentrations of Sb yielded at high packing (327±27 µg/L) at L/S ratio 0.1. In contrast, the eluate concentration of Sb at high packing was significantly higher ($p < 0.05$) than at low packing for L/S ratio 2 and 6. The total concentration increase of Sb was more than 100 % and 140 % from L/S ratio 0.1 to 6 for low and high compaction respectively. At L/S ratio 10, the concentration was 907±45 µg/L – equivalent to an increase of 177 %. Geochemical modeling indicated that $Sb(OH)_6^-$ was the predominant species (> 99 %) of Sb in the eluates.

The concentration of Zn and Fe are found in Table A.16, Appendix I. A rapid decline in the concentration of Zn was detected after the first flush. The highest concentrations of Fe were observed for L/S ratio 2 for both compaction modes. Changes in concentration of Fe throughout the experiment could indicate variations in redox conditions, although this was not confirmed by redox measurements.

5.3 Batch test

Table 7 summarizes a selection of eluate characteristics from the batch tests for the urban soil and the shooting range soil. Concentrations of Fe, Zn, major elements and anions are given in Table A.18, Appendix J.

Table 7 pH, EC (µS/cm) and concentrations of Pb, Cu, Sb and DOC (mg/kg) in the eluates from batch tests of the urban soil and the shooting range soil. Standard deviations of three replicates are included.

	pH	**EC** (µS/cm)	**Pb** (mg/kg)	**Cu** (mg/kg)	**Sb** (mg/kg)	**DOC** (mg/kg)
Urban soil	7.9±0.1	178±7	2.3±2.8	0.5±0.2	0.1±0.0	97±3
Shooting range soil	6.2±0.1	14±2	3.5±0.4	0.9±0.1	4.8±0.2	81±8

The pH (7.9±0.1) and EC (178±7 µS/cm) level in the urban soil were in the same range as earlier reported for the soil analysis (pH ~ 7.4, EC ~ 206 µS/cm in Table 5), but lower than for the column eluates ($pH_{L/S\ 6}$ ~ 8.5, $EC_{L/S\ 6}$ ~ 296 µS/cm in Figure 18a). The urban soil yielded high DOC concentrations as expected from the TOC level (TOC ~ 5.3 %, LOI ~ 7.7 %) in Table 5. Geochemical modeling, Table A.23, Appendix K, indicated that nearly 70 % of Pb was present as $PbCO_3$, followed by 13 % complexed to DOC, and that 50 % of Cu was complexed to DOC, next to 40 % as $CuCO_3$. Modeling results indicated that Pb, Cu and Fe were oversaturated with respect to several minerals, given in Table A.24, Appendix K.

The pH (6.2±0.1) measured for the shooting range soil in the batch test was lower than the pH measured in the column eluates ($pH_{L/S\ 10}$ ~ 6.7 in Figure 18b), but higher than for the soil analysis (pH ~ 5.2, in Table 5). The EC value (14±2 µS/cm) measured in the batch test was in the same range as the EC value measured in the column eluates ($EC_{L/S\ 10}$ ~ 12 µS/cm in Figure 18b), and lower than for the soil analysis (EC ~ 50 µS/cm in Table 5). Geochemical modeling, Table A.23, Appendix K, indicated that the majority (90 %) of Pb and Cu was complexed with DOC, while Sb was present as $Sb(OH)_6^-$.

5.4 Soil physical analysis and hydraulic conductivity

5.4.1 Particle size distribution

The particle size distribution (PSD) of the soil samples was determined with and without pretreatment, i.e. standard and modified method, as described in Section 4.2.3 *Soil Physical Analysis*. Figure 25 shows the standard and the modified PSD curve for the urban soil and the shooting range soil. The modified and the standard PSD curves were in good agreement for the shooting range soil. Greater deviations between the two methods were found for the urban soil. This suggests that the most pronounce effects of the pretreatment are found for soils high in TOC and TIC (see Table 5), due to oxidation of organic matter and dissolution of aggregates and cementing minerals, e.g. oxides and carbonates (Gee & Or, 2002). For practical reasons, the values derived from the PSD in the following sections are based on the standard method. Both soils can be characterized as poorly sorted *silty sands* based on the particle size distribution (PSD) curve in Figure 25 and calculated uniformity coefficients (C_u urban soil ~ 150, C_u shooting range soil ~ 59) larger than six (Fetter, 2001, p. 74; Statens Vegvesen, 2014).

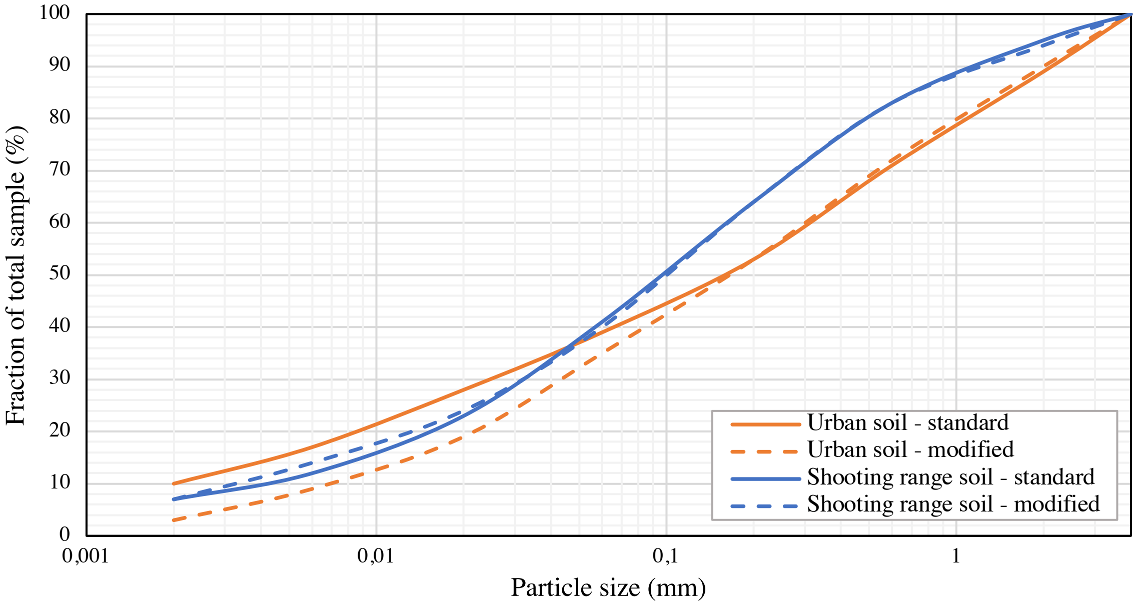

Figure 25. Particle size distributions for the urban soil (orange) and the shooting range soil (blue) showing differences between the standard method (with pretreatment) and the modified method (without pretreatment), marked as solid and dashed lines respectively.

5.4.2 Hydraulic conductivity from the extended up-flow percolation columns

The hydraulic conductivity was experimentally determined using the extended up-flow percolation columns. The development in the hydraulic conductivity as a function of L/S ratio or time is shown in Figure 26 for the urban soil and the shooting range soil. Figure 26a reveals substantial variations between the three replicate columns for the experimental hydraulic conductivity (K_{exp}) in the urban soil over time. At day 8, the values detected in column 2 (~ 2 • 10^{-4} m/s) and column 3 (~ 2 • 10^{-6} m/s) differed by two orders of magnitude. Since column 3 showed the largest deviations, values obtained from column 3 were excluded when determining the average hydraulic conductivity, K_{exp}. The large deviations between the columns can be explained by the high permeability of the material, resulting in minor pressure differences in the stand pipes. Thus, small changes in the stand pipes resulted in large variations in the hydraulic conductivity. This suggests that the extended up-flow percolation column has an upper limit for measurements of the hydraulic conductivity.

Figure 26b displays an overall decreasing trend in hydraulic conductivity over time for the shooting range soil. The largest variation between the three replicate columns was found for the lightly packed shooting range soil. Column 3 experienced large fluctuations prior to a substantial increase during the last week of operation. Minor variations were initially observed between the replicate columns for the highly packed shooting range soil before an increase was detected for column 2 at L/S ratio 6-7. Consequently, column 2 (high packing) and column 3 (low packing) were excluded from the average K_{exp} for the shooting range soil prior to comparisons and further analysis. Problems with overflow from the stand pipes required low flow rates in the highly packed columns. This suggests that the extended up-flow percolation column has a lower limit for measurements of the hydraulic conductivity.

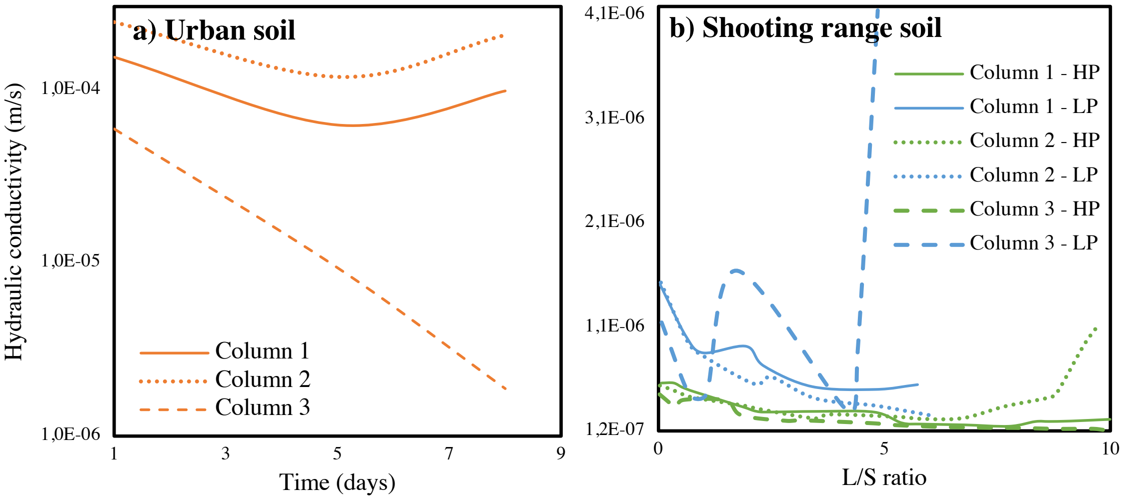

Figure 26. Development in hydraulic conductivity (m/s) for **a) the urban soil** and **b) the shooting range soil** (high packing (HP) (green lines) and low packing (LP) (blue lines) included) as a function of L/S ratio. Note that the hydraulic conductivity for the urban soil is presented in logarithmic scale.

5.4.3 Comparisons experimental and empirical values of the hydraulic conductivity

Table 8 summarizes the soil parameters derived from the standard particle size distribution in Figure 25, that are included in the Hazen and NAVAC equations (directly or as a limitation). The pore number, calculated from Eq. 8, is also included.

Table 8 Parameters derived from the standard particle size distribution and the pore number included in the Hazen and NAVFAC equation.

	d_5 (mm)	**d_{10}** (mm)	**d_{60}** (mm)	**C_u**	**e**
Urban soil	-	0.002	0.3	150	1.8^a
Shooting range soil	-	0.004	0.2	59	0.9^a 0.8^b

^{a}low packing, ^{b}high packing.

The values of K_{Hazen} and K_{NAVFAC}, calculated from Eq. 10 and Eq. 11, respectively, are given in Table A.26, Appendix L. Figure 27 compares the experimental values of hydraulic conductivity (K_{exp}) with values of Hazen (K_{Hazen}) and NAVFAC (K_{NAVFAC}). The largest differences were observed between the K_{exp} and K_{Hazen} for the urban soil. K_{Hazen} provided identical estimates for the highly and lightly packed shooting range soil, while K_{NAVFAC} considers the compaction by including the pore number in the formula. Highest agreement between K_{exp} and the empirical formulas was found for the highly packed shooting range soil.

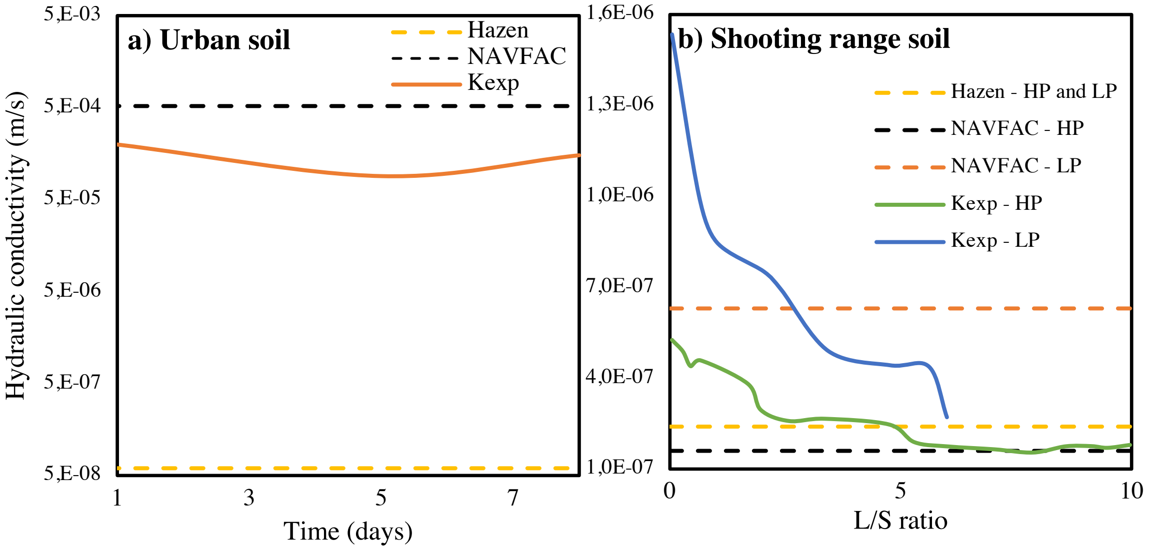

Figure 27. Comparison of hydraulic conductivity (m/s) in **a) the urban soil** and **b) the shooting range soil** (high packing (HP) (green line) and low packing (LP) (blue line) included) with values obtained from the extended up-flow percolation columns (K_{exp}) and empirical formulas (K_{Hazen} and K_{NAVFAC}).

6 Discussion

In this section, the results obtained from the extended up-flow percolation column are discussed with the purpose of investigating how chemical and physical characterization can be used to assess leaching and spreading from contaminated soil. The first part covers an evaluation of the contaminant leaching from the urban soil and the shooting range soil. Leaching from the urban soil is evaluated to assess the risk of reuse by monitoring the leaching behavior of Pb and Cu. Leaching of Pb, Cu and Sb from the shooting range soil is then examined in order to identify the risk of contaminant spreading i) *in situ*, and ii) landfilled. The second part discusses compaction as a physical treatment to reduce leaching and spreading from the shooting range soil. Lastly, a method evaluation investigates advantages and disadvantages from predicting leaching and spreading by i) a batch test combined with empirical approaches for hydraulic conductivity and ii) the extended up-flow percolation column.

6.1 Leaching behavior and evaluation of management practices

6.1.1 The urban soil

Leaching behavior

Only 0.005 % and 0.5 % of the total concentrations of Pb and Cu, respectively, were leached at L/S ratio 6 from the extended up-flow percolation columns. Greatest eluate concentrations were detected for Cu throughout the experiment as seen from Figure 23, despite yielding a ten-folded lower total concentration than Pb (Table 6). Similar observations have been reported in other studies (Okkenhaug et al., 2017; Strømseng et al., 2009).

A visual interpretation of the leaching patterns of different compounds provides information regarding the major mobility controlling factors (Kosson et al., 1996). As shown in Figure 23, a relatively stable concentration of Cu was observed throughout the experiment. The most pronounced leaching of Pb, on the other hand, was observed during the first operation period prior to reaching a stable, but low, concentration level in the eluates. Surface wash-off processes in the early stage of the column operation can explain the substantial mobilization of Pb in the first flush eluates (Delay et al., 2007). Furthermore, the stable leaching patterns indicate that the mobilization of Pb and Cu was solubility controlled. A solubility controlled leaching has been proposed by Kosson et al. (1996) to be typical for percolation dominated systems containing (heavy) metal cations. Solubility is governed by several processes, including sorption, complexation and precipitation/dissolution (Appelo & Postma, 2005; Kim et al., 2015; McBride, 1994).

The pH values remained stable (pH ~8.4-8.5) throughout the experiment, as shown in Figure 18. As stated in Section 3.1.1 *Chemical factors influencing leaching,* cation sorption is greatest at high pH since the surface charge of many sorbents becomes negative (McBride, 1994, p. 96; Pierzynski et al., 2005, p. 83). This suggests that the stable, slightly alkaline conditions in the urban soil favored retention of Pb and Cu. The calculated logarithmic partition coefficients (K_d^*) were 4.8±0.1 for Pb and 3.9±0.6 for Cu. Being directly linked to the partition between solid and aqueous phase, the greater K_d value of Pb compared to Cu indicated a stronger sorption and less mobilization of Pb in the urban soil. Covelo et al. (2006) investigated the preferential sorption of Pb and Cu on different sorbents. They found that Pb was preferentially retained by several soil sorbents at the expense of Cu.

Figure 28 shows the relationship between the eluate concentrations of DOC and Pb, and DOC and Cu. Linear regression analysis demonstrated a high and significant ($R^2 = 0.69$, $p < 0.05$) correlation between DOC and Pb. However, only a weak correlation ($R^2 = 0.11$, $p > 0.05$) was found between the concentrations of Cu and DOC. Geochemical modeling revealed that both Pb and Cu were complexed mainly to DOC. Multiple studies have investigated the complexation between Pb, Cu and organic matter. They are overall demonstrating that the metal concentration in soil solution is highly dependent on the concentration of DOC, as complexation between the metal and DOC prevents interaction between the metal and the soil solid (Tipping et al., 2003). For that reason, the presence of DOC facilitates metal mobility (Bradl, 2004; Jordan et al., 1997).

In addition to DOC, the urban soil contained large amounts of organic matter (TOC ~ 5.3 %, LOI ~ 7.7 %). It can be hypothesized that, since carbon exists in a variety of chemical forms in soil systems, the properties or *forms* of complexation vary between Pb-DOC and Cu-DOC. In particular, Saar and James (1980) found that Pb-DOC complexes precipitated at a lower metal-DOC ratio, compared to equivalent Cu-DOC complexes. This was supported by Heier et al. (2010) who found that Pb in shooting range runoff streams was mainly present as particulate and colloidal high molecular mass species, while Cu was found as colloidal and low molecular mass species. Filtration of eluates on 0.45 µm prior to chemical analysis, as described in Section

4.3.1 *Experimental setup*, removes particulate and high molecular mass colloids in the solution and can exclude a fraction of the Pb in solution. Thus, predicting metal mobility based solely on results from filtrated eluates should be considered with caution. The literature also demonstrates that the stability constants of Cu-DOC complexes are greater than the stability constants of Pb-DOC complexes at equivalent pH (Kim et al., 2015), suggesting that presence of DOC enhances the mobility of Cu relative to Pb. Furthermore, particulate organic carbon (POC) can act as a strong sorbent restricting metal mobility (McBride, 1994, p. 56), with preference for retention of Pb relative to Cu as found by Covelo et al. (2006).

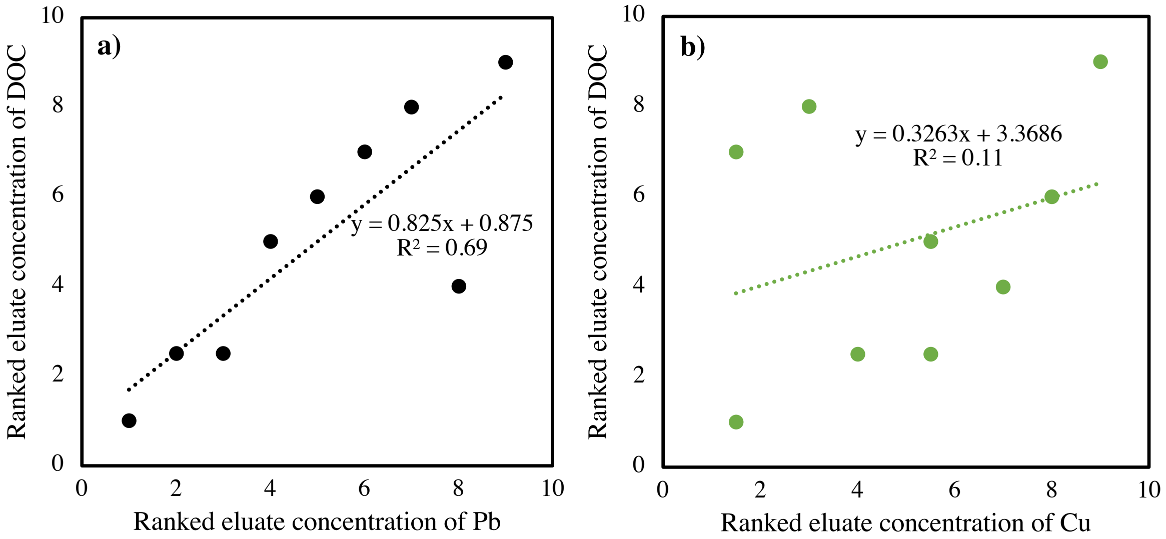

Figure 28. Spearman's rank correlation between **a) the eluate concentrations of DOC and Pb** ($R^2 = 0.69$, $p < 0.05$), and **b) the eluate concentrations of DOC and Cu** ($R^2 = 0.11$) in the urban soil.

The discussion above fails to explain the weak correlation between Cu and DOC in the eluates. The geochemical modeling does not indicate shortage of DOC with respect to Cu, suggesting that DOC is the major mechanism controlling transport of Cu in the urban soil. However, the weak correlation can indicate that several factors control leaching of Cu from the urban soil. These factors were not revealed in this study.

To conclude, the overall low leaching of Pb and Cu in the urban soil can be attributed to the alkaline soil pH which in turn controls the metal sorption capacity. Complexation with DOC increased the mobility of both metals. The high relative abundance of Cu in the eluates compared to Pb can be attributed to three mechanisms: i) greater mobility of Cu-DOC complexes relative to Pb-DOC complexes, ii) preferential sorption of Pb in soil, and iii) a larger fraction of the Cu complexes were included in the analyzed eluates as a result of eluate filtration prior to analysis.

Evaluation of reuse

The substantial total concentrations of Pb (Pb ~ 660 mg/kg, Table 6), detected in the urban soil, resulted in the soil quality being classified as *bad* (quality class 4, Pb 300-700 mg/kg) according to *the Norwegian quality guidelines for contaminated soil (TA-2553/2009)*. Based on the guideline, reuse of the soil could be acceptable as top soil in areas allocated for industrial activity or infrastructure (The Norwegian Environment Agency, 2009). The soil should be classified as waste if removed from its original site. However, by only considering the total concentration, the factors governing Pb and Cu leaching are ignored. The extended up-flow percolation column test demonstrated that a large fraction of the total concentration of Pb and Cu was non-leachable when exposed to percolating water under the prevailing conditions.

As addressed earlier, there is a lack of guidelines and leaching limits covering reuse of contaminated soil. However, the environmental authorities have indicated that the maximum upper leaching limit for reuse should be equivalent to the leaching limit for inert landfills (The Norwegian Geotechnical Institute, 2018; The Norwegian Geotechnical Institute, 2019a). The reported concentrations of Pb (~ 29 µg/L at L/S ratio 0.1) and Cu (~ 40 µg/L at L/S ratio 0.1) from the column tests were found below the leaching limits for inert landfills (150 µg/L for Pb and 600 µg/L for Cu, L/S ratio 0.1, column test), making the urban soil a possible candidate for reuse. This was consistent with the batch test results at L/S ratio 10 for Cu (~ 0.5 mg/kg, leaching limit 2 mg/kg). Pb, on the other hand, exceeded the leaching limit for inert landfill (~2.3 mg/kg, leaching limit 0.5 mg/kg) in the batch test, requiring landfilling as ordinary waste or remediation. Thus, the urban soil represents a borderline case with respect to reuse versus landfilling. If reused, potential changes in site specific parameters controlling leaching, e.g. pH and DOC, must be identified. The lack of agreement between the column and the batch test are discussed further in Section 6.3.2 *Column vs. batch test*.

6.1.2 Shooting range soil

Leaching behavior of Pb and Cu

The cumulative releases of Pb and Cu from the extended up-flow percolation column accounted for 0.2 % and 0.6 % of their respective total concentrations at L/S ratio 6. Figure 24a shows that the most substantial eluate concentrations were detected in the first flush, prior to reaching low and stable eluate concentrations. It was suggested that this effect could be explained by i) surface wash-off processes during the initial column operation period (Delay et al., 2007), followed by ii) a solubility controlled leaching process (Kosson et al., 1996).

The near-neutral pH in the shooting range soil eluates (pH ~ 5.9-6.7) favored sorption of Pb and Cu as addressed for the urban soil (McBride, 1994, p. 96; Pierzynski et al., 2005, p. 83). This was confirmed by the great logarithmic partition coefficients (K_d^*) of 4.2±0.0 for Pb and 3.8±0.0 for Cu. The partition coefficient for Pb was in the same range as reported by Okkenhaug et al. (2016) for the same soil (log K_d(Pb = 2.6-6.2), while the partition coefficient for Cu was found to be lower than the previously reported values from a peatland shooting range soil (log K_d(Cu) ~ 4.2) (Okkenhaug et al., 2017). Several authors (e.g. Xifra Olivé (2006), Okkenhaug et al. (2013)) have reported that residual bullet fragments act as a continuous source of Pb and Cu (and Sb) in shooting range soils. The underlying assumption for determining the partition coefficient is an established equilibrium between the soil solid and soil solution (The United States Environmental Protection Agency, 1999). This assumption is no longer valid in the presence of residual bullet fragments, which continuously supply the soil with contaminants preventing equilibrium to be established.

Suboxic conditions were measured in the column eluates (E_h ~390 mV), indicating favorable conditions for corrosion of residual bullet fragments. The Cu/Pb ratio for the total concentration (~ 0.07) as seen in Table 6, was lower than expected from the bullet fragments (~ 0.5, from Voie and Strømseng (2000)). This suggests that leaching of Cu exceeds leaching of Pb from the shooting range soil in field, prior to the leaching test in this study. A further release of Cu was found in the leaching tests, as confirmed by their cumulative releases (~ 0.2 % and ~ 0.6 % of total concentration of Pb and Cu, respectively). To be more specific, the most commonly used ammunition contains a larger fraction of Pb relative to Cu. However, more Cu is leached relative to Pb from the shooting range over time.

Figure 29 indicates that high and significant correlations were calculated between DOC and the two metals ($R^2 = 0.76$, $p < 0.05$ for Pb, and $R^2 = 0.88$ $p < 0.05$ for Cu). This suggests a DOC facilitated transport. Geochemical modeling also indicated metal complexation with DOC. As discussed earlier, several studies have investigated the complexation between these metal cations and DOC (e.g. Tipping et al. (2003) and Jordan et al. (1997)), the differences between Pb-DOC and Cu-DOC (e.g. Saar and James (1980) and Heier et al. (2010)), and their relative mobility (e.g. Kim et al. (2015)) and sorption (e.g Covelo et al. (2006)). Thus, higher solubility and mobility of Cu-DOC complexes and high sorption of Pb relative to Cu, are hypothesized to explain the higher relative release of Cu compared to Pb.

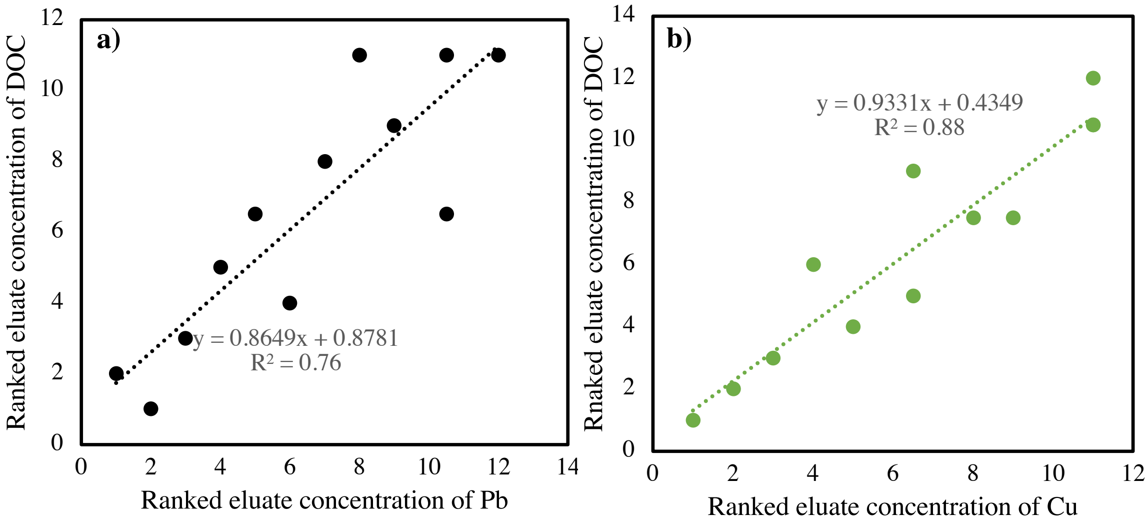

Figure 29. Spearman's rank correlation between the eluate concentration of **a) DOC and Pb** (R^2 = 0.76), and **b) DOC and Cu** (R^2 = 0.88) for the shooting range soil.

Leaching behavior of Sb

The cumulative release of Sb at L/S ratio 6 corresponded to 2 % of the total concentration. The log K_d^* value was 3.1±0.1 and in the range previously reported by Okkenhaug et al. (2013) for the same shooting range soil (log K_d(Sb) ~ 2.4 – 3.9). As for Pb and Cu, it has been proposed that the K_d value of Sb might be inaccurately high due to the presence of residual bullet fragments which constitute a continuous supply of Sb (Okkenhaug et al., 2013; Scheinost et al., 2006). The geochemical modeling indicated that $Sb(OH)_6^-$ was the dominant specie in the eluates. This was consistent with other studies on shooting range soils (e.g. Johnson et al. (2005) and Okkenhaug et al. (2016)).

Figure 24 indicates that the leaching behavior of Sb was significantly different from the metals. A substantial mobilization of Pb and Cu was observed during the first flush, while Sb yielded the lowest concentration in this period. The eluate concentrations of Sb increased as a function of L/S ratio (from ~ 340 µg/L at L/S ratio 0.1 to ~ 690 µg/L at L/S ratio 6). This substantial increase was in contrast with leaching tests performed previously on the same shooting range soil. In particular, Okkenhaug et al. (2013) performed long-term column leaching tests and found that after reaching an initial concentration of ~ 380 µg/L, the concentration of Sb stabilized at ~ 290 µg/L throughout the rest of the experiment. Small variations in the concentration of Sb in the near-neutral pH (pH ~ 5.9 – 6.7) could possibly be attributed to pH. In contrast to the metal cations, the anionic characteristics of Sb results in the strongest sorption to solids at pH < 6 as the sorbents hold a positive surface charge (Okkenhaug & Mulder, 2016; Wilson et al., 2010). The slightly lower pH (pH ~ 5.2 – 6.0) observed in the study of Okkenhaug et al. (2013) could possibly result in an increase in positively charged surfaces, and thus cause an reduced mobilization of Sb relative to this study.

Suboxic conditions (E_h ~ 390 mV) were detected in the column eluates. This suggests that Sb was present mainly as Sb(V) which is the predominant form under oxic conditions (Filella et al., 2003). Sb(V) is the most abundant Sb specie in shooting range soils in general (Okkenhaug & Mulder, 2016). Hockmann et al. (2014) recently found that Sb(III) was present at shooting ranges, but under lower redox conditions than measured in the column eluates (E_h < 50 mV). Furthermore, Scheinost et al. (2006) performed an extended X-ray adsorption fine structure (EXAFS) study on samples from Swiss shooting range soils, and found that Sb(V) and Sb(0) were the only Sb species identified. The former was suggested to be sorbed at Fe oxides, while unweathered bullet fragments was suggested to constitute the latter (Scheinost et al., 2006). Thus, the release of Sb in the shooting range soil is hypothesized to be a result of desorption of Sb followed by oxidation of residual bullet fragments.

Overall, the outcome from the extended up-flow percolation column tests indicated that the greater relative leaching of Cu compared in Pb was explained by higher solubility and mobility of Cu-DOC complexes and higher retention of Pb by soil sorbents. Corrosion of residual bullet fragments along with low sorption capacity of Sb, resulted in substantial leaching of Sb in the form of Sb(V).

Evaluation of possible management practices

The total concentrations of Pb (~ 1933 mg/kg) in the shooting range soil resulted in the soil quality being classified as very bad (quality class 5, Pb 700-2500 mg/kg) according to the *Norwegian quality guidelines for contaminated soils (TA-2553/2009)*. Also, substantial concentrations of Sb were detected. The presence of residual bullet fragments will cause long-term environmental impacts *in situ* as predictions for complete weathering of ammunition varies between 30 to 300 years (Clausen et al., 2011). Additionally, stabilization of shooting range soils *in situ* is challenging due to the distinctly different properties and leaching mechanisms of Pb, Cu and Sb.

The shooting range soil is to be considered as waste if removed from its current location, and requires classification according to the Norwegian Waste Regulations (2014). Concentrations from batch and the extended up-flow percolation column test are given in Table 9 together with leaching limits for inert, ordinary and hazardous landfills. The soil should be landfilled at an ordinary landfill based on the batch test concentrations of Pb. However, the initial column concentration of Pb exceeded the leaching limits for ordinary waste landfill and indicated landfilling as hazardous waste. This was consistent with leaching of Sb, although some of the batch replicates slightly exceeded the upper leaching limit of 5 mg/kg. The inconsistency between the two leaching tests demonstrates that several testes are needed in order to obtain a proper characterization of the shooting range soil prior to landfilling.

Table 9 Concentrations of Pb and Sb from the batch tests (mg/kg) at L/S ratio 10, and the extended up-flow percolation column test (mg/L) at L/S ratio 0.1. Standard deviations of three replicates are included. Leaching limits for inert, ordinary and hazardous landfills for the column and batch tests are also included (the Norwegian Waste Regulations, 2014).

	Pb		**Sb**	
	Column (L/S ratio 0.1) (mg/l)	Batch (L/S ratio 10) (mg/kg)	Column (L/S ratio 0.1) (mg/L)	Batch (L/S ratio 10) (mg/kg)
Shooting range soil	3.1±0.3	3.5±0.4	0.3±0.3	4.8±0.2
Leaching limits[a]				
Inert landfill	0.15	0.5	0.1	0.06
Ordinary landfill	3	10	0.15	0.7
Hazardous landfill	15	50	1	5

[a] from the Norwegian Waste Regulations (2014).

6.2 Evaluation of compaction for reduced risk of contaminant release

6.2.1 Effect on density

The extended up-flow percolation columns were packed with shooting range soil at two compaction modes. The bulk density of the highly packed column and the lightly packed column was calculated to be ~1940 kg/m^3 and ~1880 kg/m^3, respectively. This minor difference in density indicated that the shooting range soil was not very compactable. Greater differences could possibly be expected from a more compactable soil, or by different packing of the columns.

6.2.1 Effect on leaching

Figure 30 compares the cumulative leaching of Pb, Cu and Sb at the two compaction modes. A significantly greater leaching of Sb ($p < 0.05$) was detected from the highly packed columns compared to the lightly packed columns (L/S ratio 2 and 6). Minor differences were found for Cu and Pb. The fact that no reduction in leaching was observed, suggests that the assumed effect of soil compaction on leaching of contaminants may have been overestimated. Possible explanations for these results are discussed in the following paragraphs.

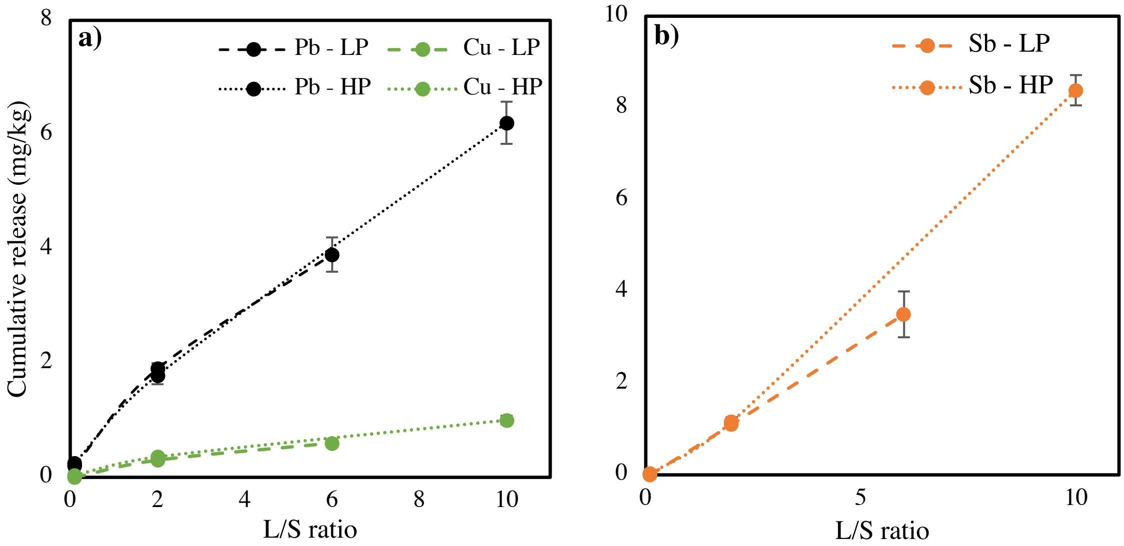

Figure 30. Cumulative releases of **a) Pb and Cu**, and **b) Sb** from the shooting range soil as a function of L/S ratio. Releases from high packing (HP) and low packing (LP) are included. Error bars represent standard deviations of three replicates.

The highly compacted shooting range soil had a greater flow resistance than the soil with light packing, resulting in different operating flow rates for the two compaction modes, see Table A.6, Appendix E. The effect of reduced flow rate due to compaction is not given much attention in the literature. Most examinations have been conducted in order to minimize the test time at the laboratory, i.e. *increase* the flow rate. For instance, Naka et al. (2016) found that flow rates had a negligible effect on the leaching of cation and anion from contaminated soil. Despite testing other materials than soil, other studies have demonstrated that flow rate and contact time have no significant effects on leaching (e.g. López Meza et al. (2010) and Naka et al. (2016)). These findings are consistent with the work of Grathwohl and Susset (2009). They compared theory, percolation tests and field lysimeters of a large data set, and found good agreement between the theory and test methods, even though flow velocity was not included in the theoretical equations. Thus, it is unlikely that the variations in flow rate can have introduced errors which affected the result of leaching from the two compaction modes.

As shown in Section 6.1.2 *Shooting range soil*, leaching of Sb increased as a function of L/S ratio relative to Pb and Cu. This was explained by the corrosion of residual bullet fragments followed by i) formation of highly mobile Cu-DOC complexes, ii) high retention of Pb on solids, and iii) release of Sb as a result of the low anion sorption capacity in soil. The highly packed columns were run for several months to reach the predetermined L/S ratio, compared to the significantly shorter operation period for the lightly packed columns. It is assumed that corrosion requires more time than sorption processes and formation of complexes. Thus, the longer operation period for the highly packed columns could therefore be hypothesized to result in a more pronounce leaching of Sb relative to Cu and Pb.

6.2.2 Effect on spreading

Although soil compaction had no reducing effect on contaminant leaching, the results indicated that soil compaction reduced the hydraulic conductivity in the soil, as seen in Figure 26. To evaluate the effect of spreading, flow in the saturated zone was considered through i) the highly compacted and ii) lightly compacted shooting range soil. The concept of contaminant spreading from a defined body of soil in the saturated zone is illustrated in Figure 31. The annual discharge was calculated from Eq. 3 (using the hydraulic conductivity from the extended up-flow percolation columns in the stable range between L/S ratio 4 and 6), the cross-sectional area was set to 100 m^2, and the hydraulic gradient (i) was set to 10^{-3}. Additionally, the following assumptions were made: i) homogeneous soil characteristics and ii) similar leaching mechanisms as identified in Section 6.1.2 *Shooting range soil*.

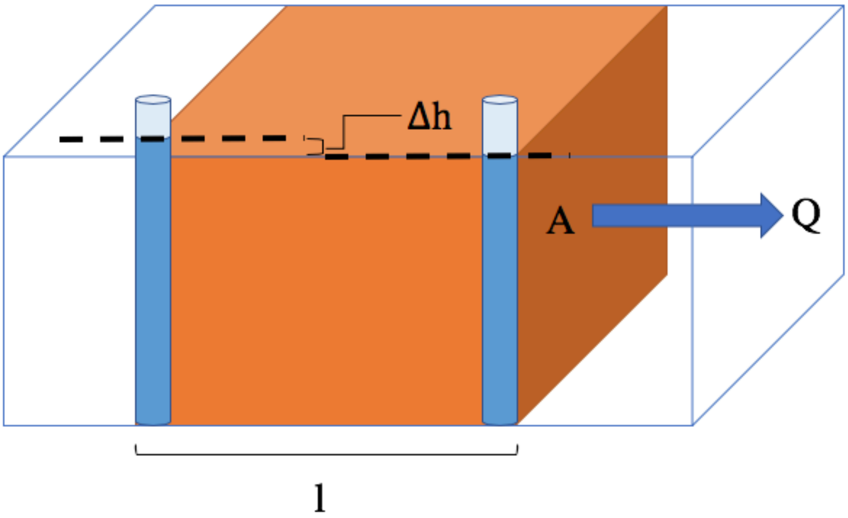

Figure 31. Cross section of a contaminated soil body in the saturated zone. The discharge (Q) was calculated from Eq. 3, the cross-sectional area (A) was set to 100 m^2, the hydraulic gradient ($i = (h_1 - h_2)/l$) was set to 10^{-3}.

Table 10 shows estimated annual discharge and release of Pb, Sb and Cu from the highly and lightly compacted shooting range soil. The lightly compacted soil yielded the greatest annual releases, despite that small leaching differences were observed.

Table 10 Estimate of discharge (m^3/year) and release of Pb, Sb and Cu (mg/year) at high and low compaction based on the case in Figure 31.

	Q (m^3/year)	**Pb** (mg/year)	**Sb** (mg/year)	**Cu** (mg/year)
High compaction	0.6	330	450	60
Low compaction	1.2	720	830	100

Summing up, the results from the extended up-flow percolation column test at two compaction modes do not demonstrate that compaction reduces the leaching from contaminated soil. However, the predicted spreading in the saturated zone demonstrated that high compaction reduces the hydraulic conductivity and thereby also reduces the discharge and release of contaminants from the soil. The results show the need for further investigations related to whether compaction can be used as a method to reduce the risk of contaminant release from soil.

6.3 Method evaluation

There is a broad spectrum of methods that can be used in order to characterize the spreading and leaching of soil contaminants. Figure 11 illustrates that leaching can be determined by using i) the standardized batch test, and ii) the extended up-flow percolation column test, and that hydraulic conductivity can be determined from i) empirical formulas based on particle size distribution, and ii) the extended up-flow percolation column test. Care should be taken when interpreting results from various approaches and methods, and identification of their advantages and disadvantages is crucial when estimating the leaching and spreading of contaminants.

The model in Figure 31 was further used to evaluate the estimate of leaching and spreading obtained from i) the quick and cost-effective methods, i.e. the batch test combined with empirical formula (K_{Hazen} and K_{NAVFAC}), and ii) the time-consuming extended up-flow percolation column (K_{exp}). The results in Table 11 indicate that the quick and cost-effective methods underestimate the releases of Pb and Sb (and to some extent Cu). In particular, the release of Sb from the batch test combined with K_{Hazen} and K_{NAVFAC} accounted for only 70 % and 45 %, respectively, of the estimated release from the extended up-flow percolation column.

Table 11 Discharge (m^3/year), release of Pb, Sb and Cu (mg/year) from the batch test results combined with K_{Hazen} and K_{NAVFAC}, and from the extended up-flow percolation column, based on the case in Figure 31.

Leaching test	**Hydraulic conductivity**	**Q** (m^3/year)	**Pb** (mg/year)	**Sb** (mg/year)	**Cu** (mg/year)
Batch test	K_{Hazen}	0.8	260	360	70
	K_{NAVFAC}	0.5	170	240	40
Column test	K_{exp}	0.6	320	520	50

The strengths and weaknesses of these methods are briefly discussed in the following section.

6.3.1 Empirical formulas vs. the extended up-flow percolation column

The Hazen and NAVFAC formula

The Hazen and NAVFAC formula less accurately predict the hydraulic conductivity since the conditions given in Table 4 with respect to d_5, d_{10}, d_{60}, C_u and e (Table 8) are not satisfied for the shooting range soil. Firstly, the high clay and silt fractions disqualify the use of these formulas as they are developed for sandy materials. The shooting range soil did not meet the criteria set for d_{60}, d_{10} or d_5, whereas the high clay fraction made graphical solutions of d_5 impossible. Secondly, the values of C_u exceeded the upper limit set for both equations. In particular, the formulas should only be used on sorted, uniform soils. Modification can be made for the graphical solution of Hazen when the materials are heterogenic (Brattli, 2009, p. 61), but this was beyond the scope of this thesis. Lastly, only the NAVFAC equation considers the effect of compaction by including the pore number, whereas Hazen predicts identical values of K for the two compaction modes. Thus, the accuracy of the empirical formulas for the shooting range soil should be questioned. Furthermore, it demonstrates that the formulas are limited to sandy, uniform soils, making them unsuitable for accurate predictions of the hydraulic conductivity in most soils. General limitations in the use of empirical approaches to predict the hydraulic conductivity are provided by Carrier (2003).

Extended up-flow percolation columns – experiences and limitations in use

The extended up-flow percolation column was tested to assess whether it can be used to perform routine measurements of the hydraulic conductivity in combination with leaching tests. Suitable methods for testing hydraulic conductivity depend on the material properties. The optimal operation range for the extended up-flow percolation column was found to be in the range of from approximately 10^{-6} to 10^{-4} m/s for two reasons: i) high permeability material (i.e. the urban soil > 10^{-4} m/s) resulted in minor pressure differences in the columns and the variations in head levels were almost undetectable from the stand pipes, ii) low permeability material (i.e. the highly packed shooting range soil < 10^{-6} m/s) resulted in substantial differences in the stand pipes and over flow. However, many soils are expected to have a hydraulic conductivity in this range. This suggests that the extended up-flow percolation column could be relevant despite of its limited operational range.

Another disadvantage of the extended up-flow percolation column, was the observed variation in hydraulic conductivity as a function of time, as shown in Figure 26 and 27. For instance, the outlier for the lightly packed shooting range soil experienced an increased hydraulic conductivity and at the same time a sudden decrease in pressure differences in the stand pipes. This suggests *preferential flow* in the column. Preferential flow in the material can lead to an overestimation of the hydraulic conductivity as the water flows through the path of least resistance (Chapuis, 2012; Chapuis et al., 2015). Figure 26 also reveals that the lightly packed column experienced larger anomalies and outliers than the highly packed material. This can be explained by the increased likelihood of erosion and preferential flow along the column walls in lightly packed columns (Chapuis et al., 2015), especially in the case of poor sorting (Chapuis, 2012).

Air bubbles occasionally leaked into the extended up-flow percolation columns from the joints where the peristaltic pump and tubes were attached. These air bubbles can cause pore blockage, which in turn may change the hydraulic conductivity over time. Based on a visual assessment, the air bubbles had two fates in the columns: i) transported into the stand pipes causing artificial high differences in head (these pipes would often have overflow as a result), or ii) trapped in pores, introducing errors in the calculations of the hydraulic conductivity. In further development of the extended up-flow percolation column, mechanisms to avoid entrapments of air bubbles should be installed. Possible solutions include the use of de-aired water, vacuum pumps or air-traps (Chapuis, 2012).

6.3.2 Column vs. batch test

Column and batch tests are among the most commonly leaching test used today. The major advantage of batch tests, compared to column tests, is the cost-efficiency provided by the design. Contrary to column tests, which allows the examination of leaching as a function of L/S ratio (or time), batch tests aim to evaluate leaching under specified conditions, e.g. pH or redox potential, at one single L/S ratio (López Meza et al., 2008; Van der Sloot et al., 1997). Column tests, on the other hand, are time-consuming but enable investigation of time-dependent release under conditions resembling field scenarios (López Meza et al., 2010; Van der Sloot et al., 1997).

A comparison of the leaching between the extended up-flow percolation column and the batch test was performed at L/S ratio 10. Figure 32 shows that the release of Pb, Cu and Sb from the extended up-flow percolation column was significantly ($p < 0.05$) higher than the results from the batch test. Despite the fact that various studies have compared batch and column leaching tests, there is a lack of consensus regarding the two methods. López Meza et al. (2008) compared the release of Pb, Zn and major cations, from five different waste materials in batch and column tests under different flow regimes and detected no significant difference between the methods (or flow rates). Other studies, however, have found that the cumulative releases from column tests exceed releases from batch tests at high L/S ratios, i.e. 10 (Grathwohl & Susset, 2009; Kalbe et al., 2008; Turner et al., 2009).

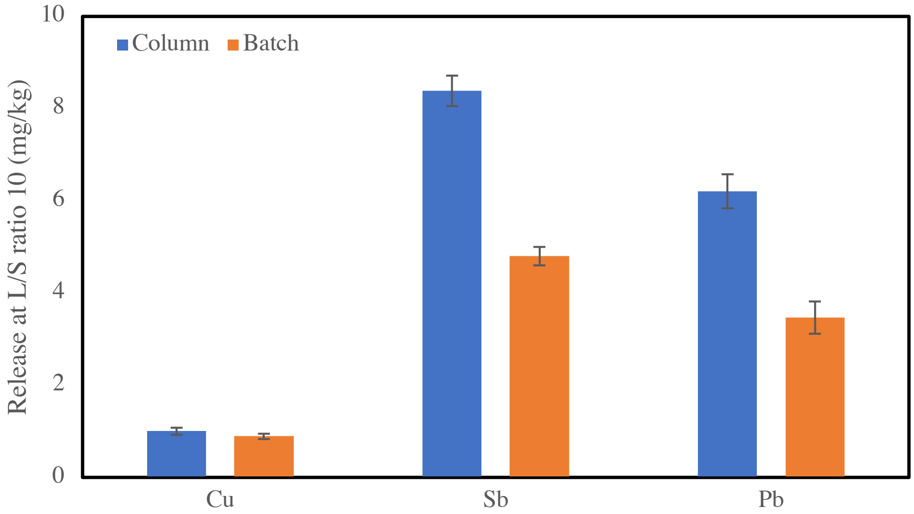

Figure 32. Comparison between release (mg/kg) of Cu, Sb and Pb from the extended up-flow percolation column test (blue) and the batch test (orange). Error bars represent standard deviations of three replicates.

A higher pH was detected in the eluates from the extended up-flow percolation column tests (pH ~ 6.7) compared to the batch test (pH ~ 6.3). This, however, was not suggested to explain the differences in Figure 32 since a higher leaching was detected for metals and Sb. Furthermore, a significantly ($p < 0.05$) higher release of Fe was observed in the batch test (~ 1.0 mg/kg) relative to the column tests (~ 0.1 mg/kg), as seen from Tables A.17 and A.19 in Appendices J and I . In lack of redox measurements in the batch tests, high concentrations of Fe can serve as a proxy for reducing conditions due to dissolution of Fe oxides. Turner et al. (2009) observed lower concentrations of Fe in column than in batch eluates, and suggested that columns are prone to precipitation of secondary minerals, e.g. Fe oxides, which adsorb (or co-precipitates) with other metals. However, this is not in agreement with the elevated concentrations of Sb and Pb detected in the column eluates.

A significantly higher ($p < 0.05$) release of DOC was detected in the batch test eluates (~ 81 mg/kg) compared to the column test eluates (~ 55 mg/kg), as seen from Table A.14 and A.19 in Appendices J and I. This was consistent with Van der Sloot et al. (2003) who reported that batch tests lead to an irreversible mobilization DOC and colloids compared to what would be expected in percolation tests. Also Grathwohl and Susset (2009) suggested that batch eluates are more prone to variability in data as a result of higher mobilizations of DOC. However, based on knowledge of the DOC facilitated mobilization of metals, the significant mobilization of DOC fails to explain the low concentration of metals in the batch eluates.

Section 6.1.2 *Shooting range soil* suggests that the leaching of Pb, Cu and Sb was governed by oxidation of residual bullet fragments. Furthermore, the time-dependent oxidation was in Section 6.2.1 *Effect on leaching* hypothesized to explain the higher leaching of Sb relative to the metals in the highly packed shooting range soil. The same mechanisms are proposed to explain the significant differences in Figure 32. For instance, the extended up-flow percolation column tests were conducted over several months in order to obtain L/S ratio 10, whereas the batch tests were run for a substantially shorter period (24 h). Assuming that the redox reactions in the batch test were limited by time, the low release of contaminants from the batch could be attributed to limited corrosion.

Although the batch test is cost-effective and easy to perform, it underestimates the risk of leaching from the shooting range soil. The time-dependent corrosion of bullet fragments was hypothesized to explain the differences between the column and the batch test results. Clearly, the effect of variations in key release controlling mechanisms, e.g. concentrations of DOC, should be further elucidated to fully understand the differences between the two leaching methods.

6.3.3 Concluding remarks of the method comparison

The extended up-flow percolation column represents a novel, sophisticated leaching equipment that combines measurements of leaching and simultaneously allows for determination of the hydraulic conductivity. Assessments of leaching from the extended up-flow percolation column can be more realistic than from the batch test, as the leaching resembles field scenarios as a function of time. The extended up-flow percolation column considers several geological properties crucial for describing flow in the saturated zone. Thus, it provides a more realistic estimate of the hydraulic conductivity than the empirical formulas, especially when the soil is unable to fulfil the required assumptions that the formulas are based on. Lastly, it should be emphasized that lab methods cannot reflect natural *in situ* conditions since laboratory tests modify the material on a small scale, e.g. particle size and shape, sorting, structure, and on a larger scale, e.g. stratifications and heterogeneity (Al-Khafaji & Andersland, 1992, p. 130-137).

7 Conclusion and recommendations

This thesis provides the first evaluation of the extended up-flow percolation column as a method to assess the leaching and spreading of contaminants, i.e. *the exposure*, from contaminated soil. The results showed that the extended up-flow percolation column considers several field specific factors that influence the release and retention of inorganic contaminants. The extended up-flow percolation column provides a better estimate of the true aspects of contaminant leaching, rather than the use of the total contaminant concentration or batch tests alone. The study also found that the extended up-flow percolation column provides a better estimate of the contaminant spreading in a larger variety of soils than the empirical formulas commonly used today. Thus, the extended up-flow percolation column meets the demands for methods that assess and evaluate the true risk of soil reuse. By including multiple chemical and physical aspects of soil characterization, the extended up-flow percolation columns provides a more accurate evaluation of the contaminant leaching and spreading from soil that better reflects the actual environmental conditions.

Compaction as a physical treatment did not demonstrate any reduced effect on leaching from contaminated soil. On the contrary, a greater leaching was observed for several contaminants when the soil was highly compacted. At the same time, compaction resulted in a lowered soil hydraulic conductivity, and thus a reduced contaminant spreading. It is recommended that the effect of compaction should be investigated further using additional soil samples.

Future research should focus on improving our understanding on spreading and leaching of contaminants from soil, and how this knowledge can be used to increase the amount of reusable soil and thereby secure a sustainable management of our finite soil resources.

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APPENDICES

Appendices

Appendix A Guidelines and leaching limits

Table A.1 *The Norwegian quality guidelines for contaminated soil* (TA-2553/2009) for the components of concern in this thesis, concentrations in mg/kg. From the Norwegian Environmental Agency (2009).

	1	2	3	4	5
	Very good	Good	Moderate	Bad	Very bad
Lead	< 60	60 -100	100-300	300-700	700-2500
Copper	< 100	100-200	200-1000	1000-8500	8500-25000

Table A.2 Leaching limits of inert, ordinary and hazardous waste landfills for selected parameters of concern in this thesis. From the Norwegian Waste Regulations (2014).

	Leaching limits inert waste		**Leaching limits ordinary waste**		**Leaching limits hazardous waste**	
Parameters	L/S = 10, batch test (mg/kg)	L/S = 0.1 column test (mg/L)	L/S = 10, batch test (mg/kg)	L/S = 0.1, column test (mg/L)	L/S = 10, batch test (mg/kg)	L/S = 0.1, column test (mg/L)
Copper (Cu)	2	0.6	50	30	100	60
Lead (Pb)	0.5	0.15	10	3	50	15
Antimony (Sb)	0.06	0.1	0.7	0.15	5	1
Zink (Zn)	4	1.2	50	15	50	60
Chloride	800	460	15000	8500	25000	15000
Sulfate	1000	1500	20000	7000	50000	17000
DOC	500	160	800	250	1000	320

Appendix B Quality assessments soil chemical analysis

Table A.3 Quality assessment for analysis of the total soil concentrations. Green numbers indicate high recovery for the reference materials *2709a* and *2702*. LOD, LOQ and blanks are included.

Quality assessment	**Fe** (g/kg)	**Cu** (mg/kg)	**Zn** (mg/kg)	**Sb** (mg/kg)	**Pb** (mg/kg)
LOD	0.0005	0.13	1.58	0.0006	0.08
LOQ	0.0015	0.42	5.30	0.0020	0.26
Blank	<0.0015	<LOD	<LOD	0.0022	<LOD
Blank	<0.0015	<LOD	<LOD	<0.002	<LOD
Blank	<0.0015	<LOD	<LOD	<0.002	<LOD
Blank	<0.0015	<LOD	<LOD	<0.002	<LOD
Recovery *crm 2709a* (HNO_3)	32	30	97	0.016	13
Recovery *crm 2702* (HF)	47	120	480	5.1	130
Values form *crm 2709a*	3.36±0.07 (%) [a]	33.9±0.5[b]	103±4[b]	1.55±0.06[a]	17.3±0.1[a]
Values from *crm 2702*	-	117±5.6[b]	485.3±4.2[a]	5.60±0.24[a]	132.8±1.1[a]

[a] Certified value, [b] Reference value. Values obtained from the National Institute of Standards & Technology (2009) and National Institute of Standards & Technology (2016) for *crm2709a* and *crm2702*, respectively.

Appendix C Formulas for dry matter and loss on ignition

The dry matter and loss on ignition are calculated as following

$$\%\ \text{dry matter} = \frac{(m3 - m1)}{m2} \bullet 100\ \% \tag{A.1}$$

$$\%\ \text{loss on ignition} = \frac{(m3 - m4)}{(m3 - m1)} \bullet 100\ \% \tag{A.2}$$

where m1 = weight of crucible
m2 = weight of soil sample before drying
m3 = weight of crucible with sample after drying
m4 = weight of crucible and sample after calcination

according to Krogstad (1992).

Appendix D Quality assessment for the particle size distributions

Table A.4 Quality assessment for the standard particle size distribution analysis based on the internal laboratory reference soil, Control A. n=14. A coefficient of variation less than 10 % indicates that the analysis is relatively precise and of high repeatability.

	Clay (%)	**Silt (%)**	**Sand (%)**
Mean	12	39	49
St. deviation	0.9	1.5	1.0
St. deviation * 2 (control limits)	2	3	2
Control A	12 ± 2	39 ± 3	49 ± 2
Coefficient of variation	8	4	2
Recovery Control A	12	38	50

Table A.5 Quality assessment for the modified particle size distribution based on the internal laboratory reference soil, Control A.

	Clay (%)	**Silt (%)**	**Sand (%)**
Control A, run 1	4	47	49
Control A, run 2	3	45	51
Recovery Control A	3	46	51
Recovery Control A	4	46	50

Appendix E Packing specification, the extended up-flow percolation column

Table A.6 Packing specifications for the urban soil, the shooting range soil (high and low packing).

		Urban soil	**Shooting range soil (HP)**	**Shooting range soil (LP)**
Water content	% water content	13.6	1.3	1.3
Packing	Weight wet sample (g)	644.3	900.9	814.7
	Dry weight sample (g)	567.2	889.9	804.7
	Height (cm)	29.8	29.6	28.9
	Void ratio (e)	1.8	0.8	0.9
	Porosity (n)	0.6	0.4	0.5
Flow rate (mL/h)		9.7	5.7	9.4

Appendix F Formulas for calculation of LOD and LOQ

The limit of detection is calculated as following

$$\text{LOD} = 3 \bullet \text{ Standard deviation}_{\text{blank}} \tag{A.3}$$

The limit of qualification is calculated as following

$$\text{LOQ} = 10 \bullet \text{ Standard deviation}_{\text{blank}} \tag{A.4}$$

Appendix G Quality assessments eluate analysis

Table A.7 Quality assessment for IC and DOC eluate analysis. Green numbers indicate high recovery for the reference material *ION-96.4*. Blanks are included in the table.

		Chloride (mg/L)	**Nitrate** (mg/L)	**Sulfate** (mg/L)	**DOC** (mg/L)
Highly packed shooting range soil, L/S 0.1 to 6 + batch tests	Blank	<0.060	<0.020	<0.080	0.64
	Blank	<0.060	<0.020	<0.080	<0.50
	Blank	<0.060	<0.020	<0.080	1.3
	Recovery *crm ION-96.4*	77.4	2.70	81.0	-
	Certified values *ION-96.4*	74±3.8	2.86±0.30	76.3±4.2	-
Highly packed shooting range soil, L/S 10, lightly packed shooting range soil L/S 0.1 to 2	Blank	<0.060	<0.020	<0.080	0.23
	Blank	<0.060	<0.020	<0.080	0.15
	Blank	<0.060	<0.020	<0.080	0.11
	Blank	<0.060	<0.020	0.082	0.32
	Blank	<0.060	<0.020	<0.080	0.92
	Blank	<0.060	<0.020	<0.080	0.13
	Recovery *crm ION-96.4*	-	-	-	4.66
	Certified values *ION-96.4*	74±3.8	2.86±0.30	76.3±4.2	4.67±0.73
Lightly packed shooting range soil, L/S 6 + urban soil	Blank	<0.060	<0.020	<0.080	3.7
	Blank	<0.060	<0.020	0.080	2.8
	Blank	<0.060	<0.020	<0.080	2.9
	Blank	<0.060	<0.020	<0.080	2.0
	Recovery *crm ION-96.4*	73	2.9	78	4.5
	Certified values *ION-96.4*	74±4	2.86±0.30	76.3±4.2	4.67±0.73

Source: Environment and Climate Change Canada (2016).

Table A.8 Quality assessment for the element eluate analysis. Green numbers indicate high recovery for the internal lab reference *1643h* and the reference materials *1640a*. LOD, LOQ and blanks are included.

		Fe (mg/L)	**Cu** (µg/L)	**Zn** (µg/L)	**Sb** (µg/L)	**Pb** (µg/L)
Highly packed shooting range soil + batch test	LOD	0.000	0.012	0.010	0.042	0.115
	LOQ	0.000	0.040	0.035	0.140	0.385
	Blank	<LOD	<0.04	0.049	<LOD	<LOD
	Blank	<LOD	<LOD	0.042	<LOD	<LOD
	Blank	<LOD	<0.04	0.049	<LOD	<LOD
	Blank	<LOD	<0.04	0.049	<LOD	<LOD
	Recovery *1643h*	0.10	23	77	58	19
	Recovery crm *1640a*	0.038	95	57	5.1	12
Lightly packed shooting range soil + urban soil	LOD	0.000	0.158	0.028	0.0006	0.003
	LOQ	0.000	0.527	0.095	0.0019	0.010
	Blank	<LOD	<LOD	<LOD	<0.0019	0.017
	Blank	<LOD	<LOD	<LOD	<0.0019	0.016
	Blank	<LOD	<LOD	<LOD	<0.0019	0.015
	Recovery *1643h*	0.098	23	76	57	19
Values from *1643h*		0.0981±0.014	22.76±0.31	78.5±2.2	58.3±0.61	19.63±0.21
Certified values from *crm 1640a*		0.0365±0.017	85.07±0.48	55.20±0.32	5.064±0.045	12.005±0.040

Source: Soil Laboratory (n.d.) and certified values from National Institute of Standards & Technology (2010).

Table A.9 Quality assessment for macro element eluate analysis. Green numbers indicate high recovery for the internal lab reference *1643h*. LOD, LOQ and blanks are included.

	Ca (mg/L)	**K** (mg/L)	**Mg** (mg/L)	**Na** (mg/L)
LOD	0.03	0.06	0.002	0.020
LOQ	0.10	0.19	0.006	0.067
Blank	<LOD	<LOD	<LOD	<0.067
Blank	<LOD	<0.19	<LOD	<0.067
Blank	<LOD	<LOD	<LOD	<LOD
Recovery *1643h*	32	2.0	8.0	21
Values from *1643h*	32.3±1.1	2.034±0.029	8.037±0.098	20.740±0.260

Appendix H Soil characterization

Table A.10 Total carbon, total nitrogen and dry matter (%) in the shooting range soil and the urban soil. Standard deviations are based on three replicates.

	Tot-C (%)	**Tot-N** (%)	**Dry matter** (%)
Urban soil	3.35±0.02	0.18±0.01	98.9±0.02
Shooting range soil	0.58±0.00	0.06±0.00	99.5±0.03

Table A.11 Total concentration of Cu, Zn, Pb, Sb (mg/kg) and Fe (g/kg). Standard deviations are based on three replicates.

	Cu (mg/kg)	**Zn** (mg/kg)	**Pb** (mg/kg)	**Fe** (g/kg)	**Sb** (mg/kg)
Urban soil					
HNO_3	59 ± 4	193 ± 6	660 ± 36	31 ± 1	0.05 ± 0.02
HF	58	200	730	23	12
Shooting range soil					
HNO_3	127 ± 6	80 ± 1	1933 ± 58	26 ± 0	0.75 ± 0.06
HF	130	86	1800	22	210

Appendix I Eluate analysis from the extended up-flow percolation column

Table A.12 pH and EC (µS/cm) in the eluates from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
	Compaction mode	**0.1**	**2**	**6**	**10**
Urban soil					
pH	LP	8.4±0.0	8.5±0.0	8.4±0.2	-
EC (µS/cm)	LP	780±19	397±44	296±36	-
Shooting range soil					
pH	HP	5.9±0.1	6.6±0.2	6.7±0.0	6.7±0.2
pH	LP	6.6±0.1	6.7±0.2	6.2±0.0	-
EC (µS/cm)	HP	178±7	33±2	16±0	12±0
EC (µS/cm)	LP	156±20	31±2	13±1	-

Table A.13 Eluate concentrations of DOC and anions (mg/L) from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
Concentration (mg/L)	**Compaction mode**	**0.1**	**2**	**6**	**10**
Urban soil					
Cl^-	LP	10±2	1.7±0.3	0.2±0.0	-
NO_3^--N	LP	3.1±2.1	0.0±0.0	0.0±0.0	-
SO_4^{2-}	LP	10±1	2.6±0.4	0.2±0.1	-
DOC	LP	31±2	19±2	13±2	-
Shooting range soil					
Cl^-	LP	30±3	0.5±0.0	0.0±0.0	-
	HP	33±3	0.5±0.1	0.0±0.0	0.0±0.0
NO_3^--N	LP	4.8±1.1	0.0±0.0	0.0±0.0	-
	HP	7.1±0.9	0.0±0.0	0.0±0.0	0.0±0.0
SO_4^{2-}	LP	5.2±0.4	6.9±0.4	1.9±0.3	-
	HP	4.6±0.6	7.0±0.3	1.9±0.1	1.3±0.1
DOC	LP	37±5	8.6±0.2	2.4±0.2	-
	HP	36±3	8.6±0.4	6.1±1.8	4.5±0.0

Table A.14 Cumulative releases of DOC and anions (mg/kg) from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
Concentration (mg/kg)	**Compaction mode**	**0.1**	**2**	**6**	**10**
Urban soil					
Cl^-	LP	1.2±0.3	4.2±0.4	4.9±0.4	-
NO_3^--N	LP	0.4±0.3	0.4±0.3	0.5±0.4	-
SO_4^{2-}	LP	1.2±0.2	5.7±0.2	6.3±0.5	-
DOC	LP	3.6±0.5	37±2	87±15	-
Shooting range soil					
Cl^-	LP	2.7±0.4	3.7±0.5	3.7±0.5	-
	HP	2.6±0.2	3.7±0.0	-	3.8±0.2

NO_3^--N	LP	0.4±0.1	0.5±0.1	0.5±0.1	-
	HP	0.6±0.1	0.6±0.0	-	0.7±0.2
SO_4^{2-}	LP	0.5±0.0	14±1	21±0	-
	HP	0.4±0.1	14±0	-	24±0
DOC	LP	2.3±0.7	20±2	29±1	-
	HP	2.8±0.2	19±1	-	55±1

Table A.15 Eluate concentrations of macro elements (mg/L) from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
Concentration (mg/L)	**Compaction mode**	**0.1**	**2**	**6**	**10**
Urban soil					
Na	LP	18±1	7±1	1±1	-
Mg	LP	10±0	5±1	3±0	-
K	LP	43±2	27±4	15±2	-
Ca	LP	137±5	63±5	46±6	-
Shooting range soil					
Na	LP	11±1	1.2±0.1	0.1±0.1	-
	HP	13±1	1.6±0.4	0.2±0.1	0.2±0.1
Mg	LP	2.7±0.3	0.5±0.0	0.2±0.0	-
	HP	3.2±0.3	0.8±0.4	0.2±0.0	0.2±0.0
K	LP	5.3±0.3	1.6±0.0	1.0±0.1	-
	HP	5.3±0.3	1.7±0.6	0.9±0.1	0.8±0.4
Ca	LP	10±1	1.8±0.1	0.6±0.3	-
	HP	21±13	16±19	1.3±0.1	0.9±0.1

Table A.16 Eluate concentrations of metals and Sb (µg/L) from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
Concentration (µg/L)	**Compaction mode**	**0.1**	**2**	**6**	**10**
Urban soil					
Cu	LP	39±5	32±3	37±6	-
Zn	LP	17±5	0.0±0.1	0.8±1.2	-
Pb	LP	28±8	6.4±2.2	4.5±2.4	-
Fe	LP	42±13	66±16	239±133	-
Sb	LP	6.1±0.6	2.6±0.7	0.9±0.1	-
Shooting range soil					
Cu	LP	326±34	138±8	86±5	-
	HP	443±52	171±21	106±5	81±6
Zn	LP	989±101	189±8	81±10	-
	HP	4435±4133	1911±2304	150±26	66±17
Pb	LP	2616±343	825±43	592±23	-
	HP	3100±297	813±111	578±41	555±33
Fe	LP	42±28	69±24	53±21	-
	HP	20±32	35±42	18±14	6±4
Sb	LP	338±8	545±18	687±31	-
	HP	327±27	597±27	785±14	907±45

Table A.17 Cumulative release of metals and Sb (mg/kg) from the extended up-flow percolation column for the urban soil and the shooting range soil as a function of L/S ratio. High packing (HP) and low packing (LP) included. Standard deviations are based on three replicates.

		L/S ratio			
Concentration (mg/kg)	**Compaction mode**	**0.1**	**2**	**6**	**10**
Urban soil					
Cu	LP	0.01±0.00	0.07±0.01	0.27±0.06	-
Zn	LP	0.00±0.00	0.00±0.00	0.01±0.01	-
Pb	LP	0.00±0.00	0.02±0.01	0.03±0.02	-
Fe	LP	0.01±0.00	0.13±0.03	1.11±0.60	-
Sb	LP	0.00±0.00	0.01±0.00	0.01±0.00	-
Shooting range soil					
Cu	LP	0.0±0.0	0.3±0.0	0.6±0.0	-
	HP	0.0±0.0	0.4±0.0	-	1.0±0.1
Zn	LP	0.1±0.0	0.5±0.0	0.7±0.0	-
	HP	0.4±0.4	3.8±4.0	-	4.4±0.4
Pb	LP	0.2±0.0	1.9±0.1	3.9±0.1	-
	HP	0.2±0.0	1.8±0.2	-	6.2±0.4
Fe	LP	0.0±0.0	0.1±0.0	0.3±0.1	-
	HP	0.0±0.0	0.1±0.1	-	0.1±0.1
Sb	LP	0.0±0.0	1.1±0.0	3.5±0.5	-
	HP	0.0±0.0	1.2±0.1	-	8.4±0.3

Appendix J Eluate analysis from the batch tests

Table A.18 Eluate pH, EC and concentrations from the batch tests (L/S ratio 10) for the urban soil and the shooting range soil. Standard deviations are based on three replicates.

Concentration	**Urban soil**	**Shooting range soil**
pH	7.9±0.1	6.2±0.1
EC (µS/cm)	178±7	14±2
Cu (µg/L)	48±24	89±6
Zn (µg/L)	233±105	408±96
Pb (µg/L)	232±283	346±35
Fe (mg/L)	6±7	0.1±0.1
Sb (µg/L)	5±2	480±20
Na (mg/L)	2.1±0.2	0.5±0.1
Mg (mg/L)	3.4±2.2	0.2±0.0
K (mg/L)	12±1	0.7±0.0
Ca (mg/L)	28±1	1.1±0.2
Cl^- (mg/L)	0.4±0.1	0.5±0.0
NO_3^--N (mg/L)	0.1±0.0	2.0±0.1
SO_4^{2-} (mg/L)	1.4±0.1	0.8±0.1
DOC (mg/L)	9.6±2.3	8.1±0.8

Table A.19 Cumulative releases of metals and DOC (mg/kg) from the batch tests (L/S ratio 10) for the urban soil and the shooting range soil. Standard deviations are based on three replicates.

Concentration	**Urban soil**	**Shooting range soil**
Cu	0.5±0.2	0.9±0.1
Zn	2.3±1.0	4.4±1.1
Pb	2.3±2.8	3.5±0.4
Fe	0.6±0.7	1.0±0.6
Sb	0.1±0.0	4.8±0.2
DOC	97±23	81±8

Appendix K Geochemical modeling

Table A.20 Species distribution of Cu and Pb in the extended up-flow percolation column eluates from geochemical modeling for the urban soil.

L/S ratio 0.1			L/S ratio 2			L/S ratio 6		
Component	% of total concentration	Species name	Component	% of total concentration	Species name	Component	% of total concentration	Species name
Cu^{2+}	1.1	FA1-Cu(6) (aq)	**Cu^{2+}**	1.3	FA1-Cu(6) (aq)	**Cu^{2+}**	0.1	$CuOH^+$, $Cu(OH)_2$ (aq), $Cu(CO_3)_2^{2-}$
	98.9	FA2-Cu(6) (aq)		98.7	FA2-Cu(6) (aq)		0.5	$Cu(CO_3)$ (aq)
Pb^{2+}	0.1	$Pb(CO_3)_2^{2-}$	**Pb^{2+}**	0.1	$PbOH^+$ and $Pb(CO_3)_2^{2-}$		9.3	FA1-Cu(6) (aq)
	0.3	$PbCO_3$ (aq)		0.2	$PbCO_3$ (aq)		90.1	FA2-Cu(6) (aq)
	0.6	FA1-Pb(6) (aq)		0.7	FA1-Pb(6) (aq)	**Pb^{2+}**	0.3	Pb^{2+}, $PbOH^+$, $PbHCO_3^+$, $Pb(CO_3)_2^{2-}$
	99.0	FA2-Pb(6) (aq)		99.0	FA2-Pb(6) (aq)		1.5	$PbCO_3$ (aq)
							1.5	FA1-Pb(6) (aq)
							96.7	FA2-Pb(6) (aq)

Table A.21 Species distribution of Cu and Pb in the extended up-flow percolation column eluates from geochemical modeling for the highly packed shooting range soil.

L/S ratio 0.1			L/S ratio 2			L/S ratio 10		
Component	% of total concentration	Species name	Component	% of total concentration	Species name	Component	% of total concentration	Species name
Cu^{2+}	1.6	Cu^{2+}	**Cu^{2+}**	2.8	Cu^{2+}	**Cu^{2+}**	2.0	Cu^{2+}
	0.8	$CuOH^+$, $CuSO_4$ (aq), $CuCO_3$ (aq), $CuHCO_3^+$, (6)Cu+2D(aq)		1.6	$CuOH^+$, $CuSO_4$ (aq), $CuCO_3$ (aq), $CuHCO_3^+$, (6)Cu+2D(aq)		2.5	$CuOH^+$, $CuCO_3$ (aq), (6)Cu+2D(aq)
	80.3	FA1-Cu(6) (aq)		72.3	FA1-Cu(6) (aq)		78.6	FA1-Cu(6) (aq)
	17.3	FA2-Cu(6) (aq)		23.3	FA2-Cu(6) (aq)		16.9	FA2-Cu(6) (aq)
Pb^{2+}	3.4	Pb^{2+}	**Pb^{2+}**	3.0	Pb^{2+}	**Pb^{2+}**	3.4	Pb^{2+}
	0.7	$PbOH^+$, $PbCl^+$, $PbSO_4$, $PbNO_3^+$, $PbCO_3$,		2.2	$PbOH^+$, $PbSO_4$, $PbCO_3$, $PbHCO_3^+$, (6)Pb+2D(aq)		0.4	$PbOH^+$, $PbSO_4$, $PbCO_3$, $PbHCO_3^+$,
	0.6	(6)Pb+2D(aq)		5.3	FA1-Pb(6) (aq)		3.6	(6)Pb+2D(aq)
	2.3	$PbHCO_3^+$		89.5	FA2-Pb(6) (aq)		6.6	FA1-Pb(6) (aq)
	7.0	FA1-Pb(6) (aq)					86.0	FA2-Pb(6) (aq)
	86.0	FA2-Pb(6) (aq)						

Table A.22 Species distribution of Cu and Pb in the extended up-flow percolation column eluates from geochemical modeling for the lightly packed shooting range soil.

L/S ratio 0.1			**L/S ratio 2**			**L/S ratio 6**		
Component	% of total concentration	Species name	Component	% of total concentration	Species name	Component	% of total concentration	Species name
Cu^{2+}	0.2	Cu^{2+}	**Cu^{2+}**	0.8	Cu^{2+}	**Cu^{2+}**	14.6	Cu^{2+}
	0.1	$CuOH^+$, (6)Cu+2D(aq)		1.0	$CuOH^+$, $CuSO_4$ (aq), (6)Cu+2D(aq)		0.8	$CuOH^+$, $CuSO_4$ (aq), $CuCO_3$ (aq), $CuHCO_3^+$
	68.0	FA1-Cu(6) (aq)		76.7	FA1-Cu(6) (aq)		8.5	(6)Cu+2D(aq)
	31.7	FA2-Cu(6) (aq)		21.5	FA2-Cu(6) (aq)		73.8	FA1-Cu(6) (aq)
Pb^{2+}	0.4	Pb^{2+}	**Pb^{2+}**	1.1	Pb^{2+}		2.3	FA2-Cu(6) (aq)
	0.3	(6)Pb+2D(aq)		1.5	$PbOH^+$, $PbSO_4$, (6)Pb+2D(aq)	**Pb^{2+}**	36.9	Pb^{2+}
	5.4	FA1-Pb(6) (aq)		6.1	FA1-Pb(6) (aq)		2.1	$PbOH^+$, $PbSO_4$, $PbCO_3$, $PbHCO_3^+$
	93.9	FA2-Pb(6) (aq)		91.3	FA2-Pb(6) (aq)		21.5	(6)Pb+2D(aq)
							9.0	FA1-Pb(6) (aq)
							30.5	FA2-Pb(6) (aq)

Table A.23 Species distribution of Cu and Pb in the batch test eluates from geochemical modeling for the urban soil and the shooting range soil.

Urban soil			**Shooting range soil**		
Component	% of total concentration	Species name	Component	% of total concentration	Species name
Cu^{2+}	1.5	Cu^{2+}	**Cu^{2+}**	0.8	Cu^{2+}
	2.6	$CuOH^+$		2.3	$CuOH^+$, (6)Cu+2D(aq)
	1.3	$Cu(OH)_2$ (aq), $CuHCO_3^+$, $Cu(CO_3)_2^{2-}$, (6)Cu+2D(aq)		87.7	FA1-Cu(6) (aq)
	39.7	$CuCO_3$ (aq)		9.2	FA2-Cu(6) (aq)
	52.7	FA1-Cu(6) (aq)	**Pb^{2+}**	2.9	Pb^{2+}
	2.2	FA2-Cu(6) (aq)		0.2	$PbOH^+$, $PbSO_4$ (aq), $PbCO_3$ (aq), $PbHCO_3^+$
Pb^{2+}	4.4	Pb^{2+}		7.5	(6)Pb+2D (aq)
	6.1	$PbOH^+$		13.2	FA1-Pb(6) (aq)
	1.7	$Pb(OH)_2$ (aq), $Pb(CO_3)_2^{2-}$, (6)Pb+2D (aq)		76.2	FA2-Pb(6) (aq)
	68.3	$PbCO_3$ (aq)			
	5.5	$PbHCO_3^+$			
	6.7	FA1-Pb(6) (aq)			
	7.3	FA2-Pb(6) (aq)			

Nomenclature in output for the NICA-Donnan model (adapted from Visual Minteq):

FA1-Metal(aq), FA2-Metal(aq): Organically complexed Metal to dissolved fulvic acid. Sites 1 and 2 refer to carboxylic and phenolic functional groups, respectively.

(8)Metal+2D: Weakly (electrostatically) bound Metal to dissolved fulvic acid.

Note: the FA was assumed to be DOC.

Table A.24 Oversaturation in the batch test eluates from geochemical modeling for the urban soil. Their stability under the present thermodynamic conditions is not considered.

Mineral	**Sat. index**
Cerrusite	0.143
Cuprix Ferrite	12.459
$Fe(OH)_{2.7}Cl_{.3}$ (s)	4.784
$Fe_3(OH)_8$ (s)	1.665
Ferrihydrite	2.358
Goethite	5.067
Hematite	12.535
Hydrocerrusite	0.461
Lepidocrocite	4.187
Maghemite	4.731
Magnesioferrite	5.752
Magnetite	18.485
Siderite	0.488

Appendix L Particle size distribution

Table A.25 Average values for clay, silt and sand fraction based on the standard and the modified particle size distribution.

	Clay (%)	Silt (%)	Sand (%)
Shooting range soil, standard PSD	7	34	59
Shooting range soil, modified PSD	7	33	50
Urban soil, standard PSD	10	29	61
Urban soil, modified PSD	3	32	65

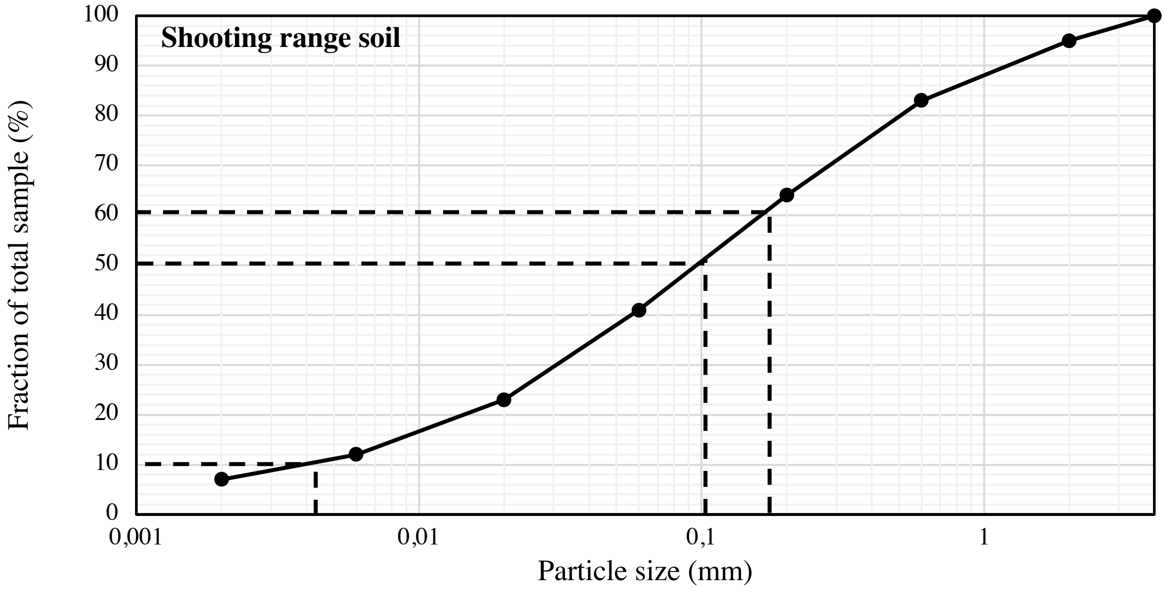

Figure A.1: Graphical solution of d_{10}, d_{50} and d_{60} for the shooting range soil (standard particle size distribution).

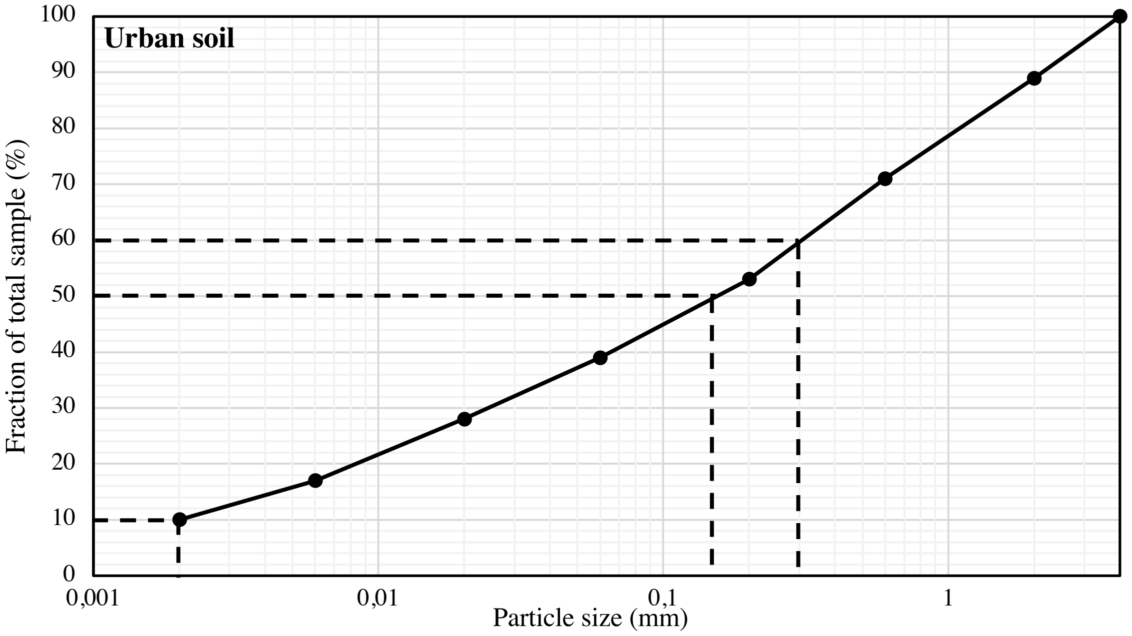

Figure A.2: Graphical solution of d_{10}, d_{50} and d_{60} for the urban soil (standard particle size distribution).

Table A.26 Hydraulic conductivity (m/s) calculated from the Hazen (K_{Hazen}) and NAVFAC (K_{NAVFAC}) formulas for the urban soil and the shooting range soil, based the standard particle size distribution.

	Urban soil	**Shooting range soil**	
	Low packing	High packing	Low packing
K_{Hazen}	$6.1 \bullet 10^{-8}$	$2.4 \bullet 10^{-7}$	$2.4 \bullet 10^{-7}$
K_{Navfac}	$5.2 \bullet 10^{-3}$	$1.6 \bullet 10^{-7}$	$6.3 \bullet 10^{-7}$

Appendix M Hydraulic conductivity from the extended up-flow percolation columns

Table A.27 Hydraulic conductivity (m/s) for the urban soil as a function of time.

Column 1		**Column 2**		**Column 3**	
Day	K (m/s)	Day	K (m/s)	Day	K (m/s)
1	$1.5 \bullet 10^{-4}$	1	$2.4 \bullet 10^{-4}$	1	$5.9 \bullet 10^{-5}$
5	$6.2 \bullet 10^{-5}$	5	$1.3 \bullet 10^{-4}$	5	$9.3 \bullet 10^{-6}$
8	$9.8 \bullet 10^{-5}$	8	$2.1 \bullet 10^{-4}$	8	$1.9 \bullet 10^{-6}$

Table A.28 Hydraulic conductivity (m/s) for the highly packed shooting range soil as a function of L/S ratio.

Column 1		**Column 2**		**Column 3**	
L/S ratio	K (m/s)	L/S ratio	K (m/s)	L/S ratio	K (m/s)
0.07	$5.8 \bullet 10^{-7}$	0.03	$5.6 \bullet 10^{-7}$	0.02	$4.7 \bullet 10^{-7}$
0.33	$5.8 \bullet 10^{-7}$	0.30	$5.2 \bullet 10^{-7}$	0.23	$4.0 \bullet 10^{-7}$
0.53	$5.4 \bullet 10^{-7}$	0.50	$4.8 \bullet 10^{-7}$	0.37	$3.4 \bullet 10^{-7}$
0.79	$5.0 \bullet 10^{-7}$	0.77	$4.4 \bullet 10^{-7}$	0.54	$4.2 \bullet 10^{-7}$
1.89	$3.5 \bullet 10^{-7}$	1.85	$3.7 \bullet 10^{-7}$	1.48	$4.1 \bullet 10^{-7}$
2.10	$3.2 \bullet 10^{-7}$	2.29	$3.3 \bullet 10^{-7}$	1.84	$2.7 \bullet 10^{-7}$
2.31	$3.0 \bullet 10^{-7}$	3.47	$2.4 \bullet 10^{-7}$	2.84	$2.2 \bullet 10^{-7}$
3.53	$3.1 \bullet 10^{-7}$	3.77	$2.8 \bullet 10^{-7}$	3.17	$2.2 \bullet 10^{-7}$
4.77	$3.0 \bullet 10^{-7}$	5.35	$2.5 \bullet 10^{-7}$	4.72	$1.9 \bullet 10^{-7}$
5.39	$2.0 \bullet 10^{-7}$	5.78	$2.4 \bullet 10^{-7}$	5.21	$1.8 \bullet 10^{-7}$
5.83	$1.9 \bullet 10^{-7}$	6.72	$2.4 \bullet 10^{-7}$	6.23	$1.6 \bullet 10^{-7}$
6.77	$1.8 \bullet 10^{-7}$	7.66	$3.6 \bullet 10^{-7}$	7.30	$1.5 \bullet 10^{-7}$
7.78	$1.6 \bullet 10^{-7}$	8.69	$4.5 \bullet 10^{-7}$	7.98	$1.5 \bullet 10^{-7}$
8.34	$2.1 \bullet 10^{-7}$	8.85	$5.1 \bullet 10^{-7}$	8.81	$1.4 \bullet 10^{-7}$
8.64	$2.1 \bullet 10^{-7}$	9.41	$9.4 \bullet 10^{-7}$	9.62	$1.4 \bullet 10^{-7}$
9.12	$2.1 \bullet 10^{-7}$	9.68	$1.1 \bullet 10^{-6}$	9.83	$1.3 \bullet 10^{-7}$
9.99	$2.3 \bullet 10^{-7}$			9.94	$1.3 \bullet 10^{-7}$

Table A.29 Hydraulic conductivity (m/s) for the lightly packed shooting range soil as a function of L/S ratio.

Column 1		**Column 2**		**Column 3**	
L/S ratio	K (m/s)	L/S ratio	K (m/s)	L/S ratio	K (m/s)
0.04	$1.5 \bullet 10^{-6}$	0.05	$1.6 \bullet 10^{-6}$	0.07	$1.2 \bullet 10^{-6}$
0.61	$1.0 \bullet 10^{-6}$	0.65	$9.8 \bullet 10^{-7}$	0.70	$4.6 \bullet 10^{-7}$
0.99	$8.7 \bullet 10^{-7}$	1.04	$8.3 \bullet 10^{-7}$	1.06	$4.8 \bullet 10^{-7}$
1.94	$9.3 \bullet 10^{-7}$	2.14	$5.7 \bullet 10^{-7}$	1.74	$1.7 \bullet 10^{-6}$
2.33	$7.4 \bullet 10^{-7}$	2.50	$6.4 \bullet 10^{-7}$	4.22	$3.0 \bullet 10^{-7}$
3.40	$5.5 \bullet 10^{-7}$	3.47	$4.3 \bullet 10^{-7}$	4.41	$8.9 \bullet 10^{-6}$
4.80	$5.2 \bullet 10^{-7}$	4.76	$3.7 \bullet 10^{-7}$	4.85	$4.2 \bullet 10^{-6}$
5.73	$5.6 \bullet 10^{-7}$	5.49	$3.1 \bullet 10^{-7}$		
		6.00	$2.7 \bullet 10^{-7}$		

Mottatt dato **2018-10-11**
Utstedt **2018-10-17**

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Analyse av faststoff

Deres prøvenavn **R.1.**
Jord

Labnummer N00611779

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) [a ulev]	**87.4**	5.28	%	1	1	ERAN
TIC [a ulev]	**0.068**	0.009	% TS	1	1	ERAN
TOC [a ulev]	**5.28**		% TS	2	1	ERAN

Deres prøvenavn **R.2.**
Jord

Labnummer N00611780

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) [a ulev]	**87.7**	5.29	%	1	1	ERAN
TIC [a ulev]	**0.066**	0.009	% TS	1	1	ERAN
TOC [a ulev]	**5.46**		% TS	2	1	ERAN

Deres prøvenavn **R.3.**
Jord

Labnummer N00611781

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) [a ulev]	**88.5**	5.34	%	1	1	ERAN
TIC [a ulev]	**0.095**	0.012	% TS	1	1	ERAN
TOC [a ulev]	**5.25**		% TS	2	1	ERAN

Deres prøvenavn **S.1.**
Jord

Labnummer N00611782

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) [a ulev]	**98.9**	5.96	%	1	1	ERAN
TIC [a ulev]	**0.019**	0.007	% TS	1	1	ERAN
TOC [a ulev]	**1.11**		% TS	2	1	ERAN

Deres prøvenavn **S.2.**
Jord

Labnummer N00611783

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) $^{\text{a ulev}}$	**98.9**	5.96	%	1	1	ERAN
TIC $^{\text{a ulev}}$	**0.017**	0.007	% TS	1	1	ERAN
TOC $^{\text{a ulev}}$	**1.15**		% TS	2	1	ERAN

Deres prøvenavn **S.3.**
Jord

Labnummer N00611784

Analyse	Resultater	Usikkerhet (±)	Enhet	Metode	Utført	Sign
Tørrstoff (E) $^{\text{a ulev}}$	**98.9**	5.96	%	1	1	ERAN
TIC $^{\text{a ulev}}$	**0.020**	0.007	% TS	1	1	ERAN
TOC $^{\text{a ulev}}$	**1.10**		% TS	2	1	ERAN

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"a" etter parameternavn indikerer at analysen er utført akkreditert ved ALS Laboratory Group Norway AS.
"a ulev" etter parameternavn indikerer at analysen er utført akkreditert av underleverandør.
"*" etter parameternavn indikerer uakkreditert analyse.
Utførende laboratorium er oppgitt i tabell kalt Utf.
n.d. betyr ikke påvist.
n/a betyr ikke analyserbart.
< betyr mindre enn.
> betyr større enn.

	Metodespesifikasjon
1	**Totalt uorganisk karbon (TIC) i jord e.l.** Metode: ISO 10694, EN 13137, EN 15936 Måleprinsipp: Coulometri Rapporteringsgrenser (LOQ): 0,010 % TS
2	**Bestemmelse av total organisk karbon (TOC) i jord, kolometri** Metode: ISO 10694, EN 13137, EN 15936 Måleprinsipp: Kolometri Rapporteringsgrenser: LOR 0.01 % TS Andre opplysninger: TOC er differansen mellom total karbon (TC) og total inorganisk karbon (TIC).

	Godkjenner
ERAN	Erlend Andresen

	Utf[1]
1	Ansvarlig laboratorium: ALS Laboratory Group, ALS Czech Republic s.r.o, Na Harfě 9/336, Praha, Tsjekkia Lokalisering av andre ALS laboratorier: Ceska Lipa: Bendlova 1687/7, 470 03 Ceska Lipa Pardubice: V Raji 906, 530 02 Pardubice Kontakt ALS Laboratory Group Norge, for ytterligere informasjon

Måleusikkerheten angis som en utvidet måleusikkerhet (etter definisjon i "Evaluation of measurement data – Guide to the expression of uncertainty in measurement", JCGM 100:2008 Corrected version 2010) beregnet med en dekningsfaktor på 2 noe som gir et konfidensinterval på om lag 95%.

Måleusikkerhet fra underleverandører angis ofte som en utvidet usikkerhet beregnet med dekningsfaktor 2. For ytterligere informasjon, kontakt laboratoriet.

Måleusikkerhet skal være tilgjengelig for akkrediterte metoder. For visse analyser der dette ikke oppgis i rapporten, vil dette oppgis ved henvendelse til laboratoriet.

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[1] Utførende teknisk enhet (innen ALS Laboratory Group) eller eksternt laboratorium (underleverandør).

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