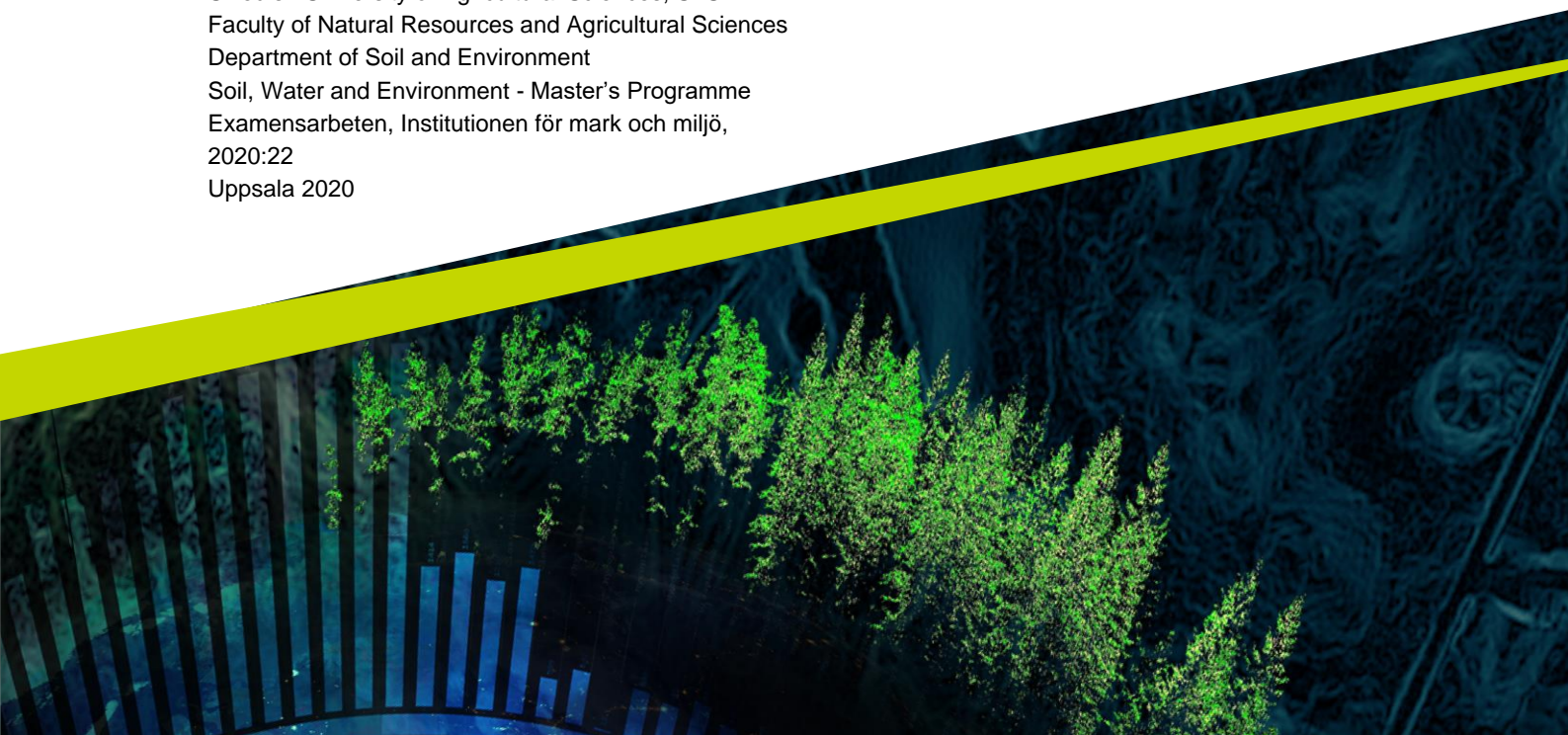# Cobalt and nickel concentrations in the Uppsala clay deposits

– solubility and risk assessment

Ali Reza Sadeghi

Cobalt and nickel concentrations in the Uppsala clay deposits – solubility and risk assessment

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Abstract

Heavy metals create a contamination problem in soils. Examples of heavy metals are Ni, Co, and Cu. Soil environment and minerals existing in the soil such as Fe and Mn oxides affect the presence of these heavy metals.

In this thesis, the cobalt and nickel concentrations of selected soil samples from different locations in Uppsala were determined. Then risk assessment was performed based on two different tools, the Swedish guideline model for contaminated soils and the Threshold calculator. The output from these two methods is being discussed.

The Swedish model provides generic guideline values for different risk objects such as humans, environment, natural sources, and the soil environment. On the other hand, the threshold calculator is focusing particularly on the ecotoxicological threshold concentration of metals. In addition, the toxicity effect on different soil trophic levels is being calculated.

The obtained total concentrations of Co and Ni in the soil samples were compared to the Swedish generic guideline value. If the value exceeds the limitation provided by the Swedish Environmental Protection Agency (SEPA) then a leaching test is required. The leaching test will provide extracted concentrations of Co and Ni in the soil samples. Based on this, the partition coefficient (the K_d value) is obtained.

The value of the partition coefficient (K_d) determines the mobility of metal in the soil environment. Derivation of a site-specific guideline value helps to determine a new guideline value for different risk levels and protection objects based on the SEPA risk assessment tool.

The above is performed by both methods (risk assessment with SEPA- and threshold calculator). One of the advantages of using the Threshold calculator risk assessment tool is that it focuses only on an ecotoxicological threshold concentration of metals. However, the SEPA provides an integrated guideline for the soil environment, human health, groundwater, and surface water. In the report, I explain more about why the threshold calculation is required. The values obtained by SEPA for the soil environment is replaced by values obtained by the threshold calculator. The new guideline values of Co and Ni are used to find the new value of other parameters, which were impossible to determine by the Threshold risk assessment method alone. This way of determining the protection level presents a new way of combining the two tools to get a more accurate picture of the actual risk of heavy metals in contaminated soils.

Keywords: Heavy metal, Soil contamination, Geochemically active fraction, Leaching test. Guideline value, Total concentration. Site-specific guideline value, Sensitive land use, Less sensitive land use.

Popular science summary

Soils have been polluted with different contaminants such as heavy metals, i.e. Ni, Co, Cu, As, etc. A certain concentration of metal may be essential for the soil organisms. However, high concentrations of metals harm the soil and ecosystem and therefore poses an environmental risk for the soil environment. Further, the mobility of heavy metal in the soil environment determines its migration through the soil and on to surface and ground waters. This poses an additional type of environmental risk, which need to be considered in risk assessments.

To reduce the risk associated with cobalt and nickel, certain guideline values have been derived. The guidelines depend on the land use. In the Swedish system, the Swedish Environmental Protection Agency (SEPA) has derived the existing generic guideline values, which relate to sensitive and non-sensitive land use. For sensitive land use the generic guideline value for cobalt and nickel is set at a total concentration of 15 and 40 mg kg^{-1} respectively, while for less sensitive land use the generic guidelines are 35 mg kg^{-1} for Co and 120 mg kg^{-1}.

The main aim of this study is to investigate whether the combination of the SEPA guideline model with the Threshold Calculator is possible and if it could yield meaningful results when deriving site-specific guideline values for Co and Ni. This would help in more correctly estimate the environmental risk of Co and Ni in the Uppsala clays, which are naturally high in these two metals.

This thesis examines which factors that influence the concentration of Co and Ni in the soil, and what factors that influence the environmental risk. Site-specific risk assessment was evaluated with two different tools, using (i) the SEPA Excel sheet method for all types of environmental risk and (ii) the SEPA Excel sheet method complemented with the Threshold calculator to provide the risk for the soil environment.

The main results of this study can be summarized as follows:

a. The adsorption of both Co and Ni to soil particles was strong, as reflected by the K_d values obtained from HNO_3 and $CaCl_2$ extractions.

b. Further, the high K_d value means that the risk of leaching of both Co and Ni to ground- and surface waters was low

c. When using the SEPA method, the site-specific guideline value became higher than the generic guideline value for sensitive land use (KM).

d. With the Threshold calculator, the so-called effective concentration of Co and Ni was high due to high clay content and high CEC value.
e. By combining both risk assessment tools, the health risk was identified as the governing protection object for sensitive land use (KM), whereas protection of soil environment was still more important for less sensitive land use (MKM), although in both cases significantly higher guideline values were obtained compared to when using the SEPA risk assessment tool alone.

Preface

I would like to take this opportunity to express my sincere gratitude to everyone who helped and supported me during this project. I would like to express my appreciation to Ing-Marie Nyström and the rest of Bjerking's staff for their support and taking the sample and analyze every single support to reach my goal in the thesis. I would like to extend my special thanks to my supervisor Jon-Petter Gustafsson as well as Dan Berggren Kleja, especially during this hectic time of the pandemic. Finally, I would like to express gratitude to my lovely family who lives far away yet constantly sending me good wishes. I also greatly appreciate my kind wife and amazing children for their support, contribution, and encouragement, which give extra energy to run and finalize this study.

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Abbreviations

SLU	Swedish University of Agricultural Sciences
SEPA	Swedish Environmental Protection Agency
TOC	Total Organic Carbon
TC	Total Carbon
TIC	Total Inorganic Carbon
KM	Sensitive land use, (Känslig mark)
MKM	Less sensitive land use, (Mindre känslig mark)
EC	Effective concentration
HC	Probability Level
PAF	Potentially Affected Fraction
SSD	Species Sensitivity Distribution

1. Introduction

Soils play an important role in the ecosystem, including organisms, plants, and invertebrates, as well as for water management. From a human perspective, the soil has an important role in the economy and food production (Marsz 2014). For a long time, soils have been polluted with different contaminants. Common inorganic contaminants are heavy metals, i.e. Ni, Co, Cu As. etc. Soil contaminants have become an environmental issue (Lange et al. 2016). A certain concentration of metal is essential for plants and microorganisms in the soil. On the other hand, high concentrations of these metals harm the soil and ecosystem. Increasing the concentrations of metals has a direct negative effect on plants, microorganisms, and indirectly on humans. The mobility of metals constitutes one type of environmental risk. Different factors govern the mobility of contaminants through the soil to surface and ground waters (Giraldo 2018).

Increased metal contamination of a soil can also cause an increasing metal solubility and mobility. Soluble metals are more easily accessible for uptake of metals. The result of this process may affect the quality and quantity of yield, toxicities of animals, and humans (Marsz 2014).

In Sweden, there are about 80.000 polluted land areas. (SGI, 2018). Some of these places are likely to have significant metal leaching, which could have a negative health effect on the environment and people. Risk assessment of the contaminated area is one way to identify and quantify these negative effects, and to make informed decisions. The risks of these pollutants in many cases are associated with spreading and leaching to the local environment. One way to predict the risk for metal mobility within a contaminated area is by using leaching tests. Leaching tests can give a better picture of the leaching than simple calculation models where one often assumes that all contamination is leachable. Increased knowledge of the number of nearby lakes and watercourses to be affected also leads to a better risk assessment (Nyhlén 2004).

1.1. Aim and Delimitation

Bjerking AB is a technical consultancy company, which works with different soil contaminant projects. One of the main issues is about metal concentration in the soil and especially Co and Ni which are common with a high concentration in the clay of Uppsala county.

The main objective of this study is to perform a risk assessment to understand what factors that influence the concentration of Co and Ni in the soil, and what factors that influence the environmental risk. To reach the objective, the total and soluble concentrations of Co and Ni in selected soils has been studied. Different factors e.g soil texture, availability of organic carbon, and pH were evaluated to see if they affected the results. By combining the Swedish EPA guideline model (Naturvårdsverket, 2009) with the Threshold Calculator, we could then develop site-specific guidelines for Co and Ni, that would help in more correctly estimate the environmental risk of Co and Ni in the Uppsala clays (Naturvårdsverket. 2009)

2. Background

2.1. Risk and bioavailability of trace elements

There are different definitions of risk. In different situations and perspectives, the risk could be defined as the feasibility of loss or damage. In the concept of this project, risk means the effect of exposure in contaminants to humans, organisms, plants, and animals (Pierzynski et al. 2005).

European countries have agreed regulatory guidelines for soil contaminants based on risk assessment to protect natural resources e.g. soil, groundwater, groundwater, and humans.

The definition of a high concentration of heavy metal depends on the land use, i.e. industry, agriculture, etc. However, many evidences show that the total concentration of heavy metals is not sufficient to evaluate environmental impact because the total concentration is not directly linked to ecotoxicological risk. Potential mobility and bioavailability are two key factors that can help to evaluate environmental impact (Tashakor et al. 2011).

The threshold value is based on the ecotoxicological risk in the soil environment. If the background concentration exceeds the threshold value, then the concentration is considered as an assessment threshold.

The other term of concentration is called a guideline value. The contaminated area is evaluated based on whether the guideline value is exceeded. There are different values for different land uses, see Table 1.

Total concentration in the soil is the main factor for risk assessment. According to the survey by the EU to highlighted distribution of heavy metal in the European Union. A key finding of survey highlights a different distribution of heavy metal across EU countries (Lee et al. 2011).

Element	Sweden[1]		UK Soil Guideline values (SGV) (mg/kg)[2]	
	Sensitive land use (mg/kg)	Non-sensitive land use (mg/kg)	Residential with home grown produce (mg/kg)	Residential without home grown produce (mg/kg)
Arsenic (As)	10	25	37	40
Cadmium (Cd)	0.8	12	22	150
Copper (Cu)	80	200	N/A	
Chromium (Cr)	80	150	130	200
Mercury (Hg)	0.25	2.5	10[3]	
Molybdenum (Mo)	40	100	N/A	
Nickel (Ni)	40	120	130[3]	
Vanadium (V)	100	200	N/A	
Zinc (Zn)	250	500	N/A	

[1]Naturvårdsverket (2009)
[2]ALS Environmental UK (2020)
[3]Residential

2.2. Heavy metals

Heavy metals in soil systems are considered an important concern in soil and environmental science (Siebecker & Sparks. 2010). There are various definitions of "heavy metal". A general definition is that heavy metals are metals with a density higher than 5 g/cm^3 (Eriksson et al. 2011). The issue of heavy metals is linked to food security and food safety. Similarly, degradation of water quality and the spread of heavy metals to the food chain are two major issues that occur as a result of soil contamination (Toth et al. 2016).

The presence of metals in soils is widespread and metals emanate from both natural and anthropogenic sources.

2.3. Cobalt and nickel in European soils

Cobalt in the soil is from a combination of natural and human activities. Different factors affect the concentration of cobalt in the soil like atmospheric deposition of cobalt, local geology, land use, soil particle, climate, and the age of soil. (Wendling et al. 2009). See Figure 1 and Figure 2 for an overview of the concentration of these two metals in the EU.

2.4. Sources

Magmatic sulfide ores and lateritic silicates are two natural sources of Ni in the soil system. The other potential source of heavy metal, and specifically Ni and Co, are metamorphic rocks. This kind of rock originates from the hydrothermal alteration of ultramafic rock. The presence of Co and Ni in metamorphic rock is because of the exchange capacity of cation e.g. Fe, Mn, and Mg in the octahedral layer at high temperatures and pressures. Weathering of bedrock is another explanation of a natural source of metal such as Ni and Co in the soil. Clay is a product of the weathering process. During the weathering process, other elements such as Co, Ni, and Cr are transferred to clay minerals.

Soil texture is another factor that affects Ni in the soil. Clay-textured soil has more capacity to store more Ni compared to soil with coarser texture. The topsoil has 10- 4000 kg Ni ha^{-1}. The rate of crop uptake is relatively low (2-8 g ha^{-1}) (Hamnér et al. 2013).

The anthropogenic sources include municipal waste, stainless steel industry, ignition of coal, and emission from Ni refinery. The anthropogenic emissions of Ni may be a significant health risk to people and communities surrounding Ni-emission sources (Siebecker & Sparks, 2010).
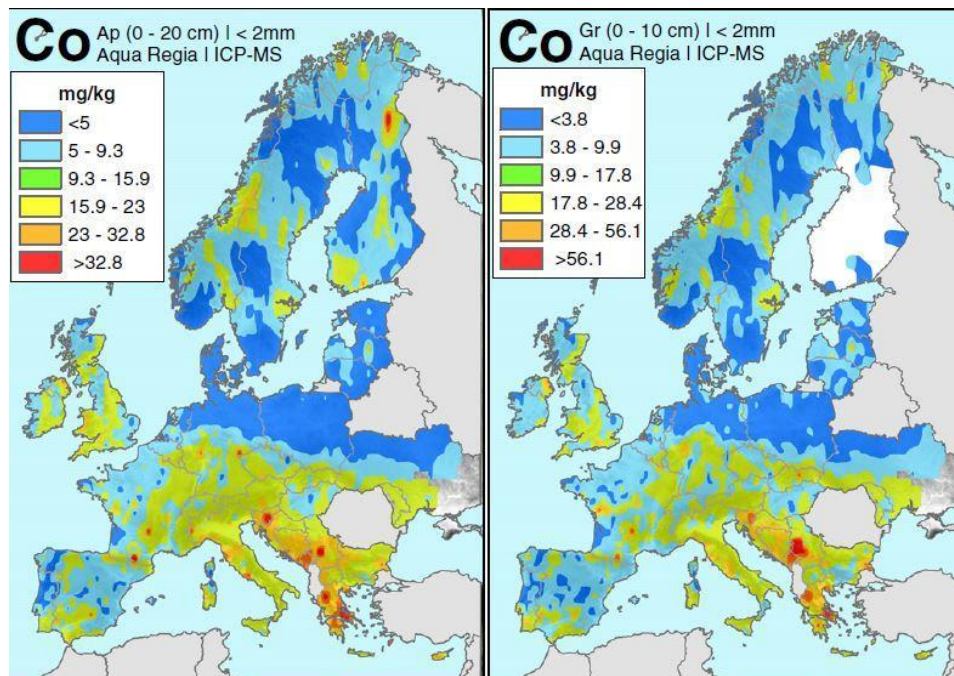
Figure 1. The concentration of Co in European soils. © 2020 Elsevier, Rightslink. Used with permission from Albanese et al. (J. Geochem. Explor. 154, 81-93, 2015).
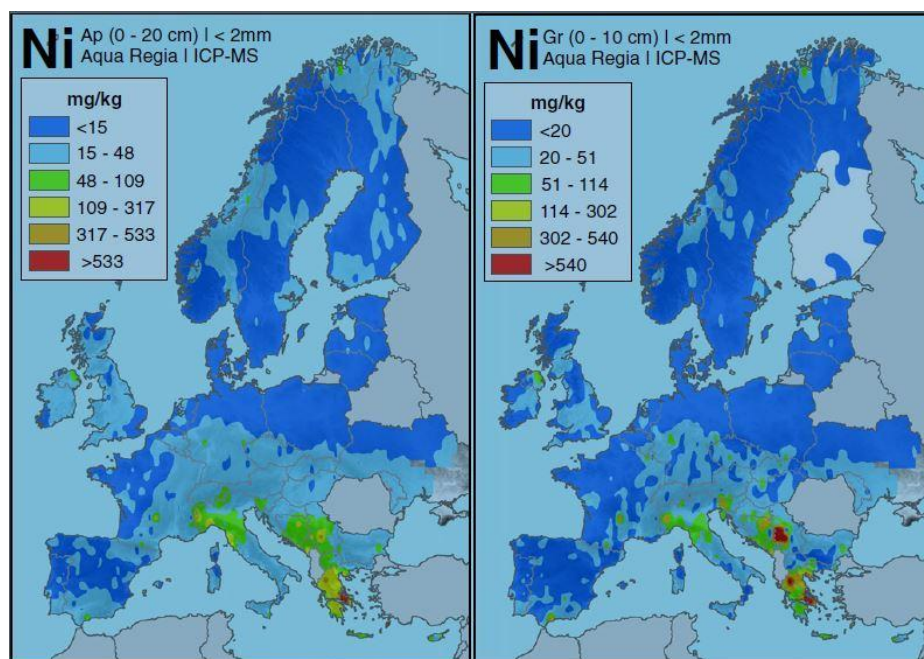
Figure 2. The concentration of Ni in European soils. © 2020 Elsevier, Rightslink. Used with permission from Albanese et al. (J. Geochem. Explor. 154, 81-93, 2015).

2.5. Natural background concentration

The concentration of nickel and cobalt are low in the Earth's crust. Nickel is about three times more common than cobalt. The average concentration of nickel in Gabbro (mafic intrusive igneous) and basalt (mafic extrusive igneous) is 130 mg/kg, in granite 5 mg/kg, in sandstones 2 mg/kg and limestone 5 mg/kg. Like many other metals, much higher values are obtained in sulfur-rich sediments with high organic matter. The adsorption capacity of the metal, especially to clay particles, is indicated by its high concentration in clayey sediments. The metal is weatherable under oxidizing conditions and dissolves rather under weakly acidic conditions. At this condition, nickel is transported into the stream systems via surface and groundwater. The mobility of nickel is limited by nickel's ability is adsorb to iron-manganese hydroxides (limonite), clay particles, and organic matter (Arvidsson et al. 2007).

2.6. Properties of nickel

Nickel is a transition metal that belongs to group 10 of the periodic table (Arvidsson et al. 2007). Nickel is a hard and shiny silver ferromagnetic metal, which can easily be formed. The chemical symbol is Ni and the atomic weight is 58.71 g mol^{-1}. Nickel melts at 1445°C and has low electrical and thermal conductivity. Some properties that distinguish Ni alloys are a high resistance against corrosion, oxidation, and includes good strength properties against high temperatures.

There are five stable Ni isotopes: ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni, where ^{58}Ni is the most abundant (68.077%). Nickel occurs in 4 different oxidation states: $^{+}1$, $^{+}2$, $^{+}3$, and $^{+}4$. Among these, only Ni^{+2} is relatively stable among different pH and redox conditions in the soil (McGrath, 1995).

Nickel belongs to the metal group together with Fe and Co. Nickel is found in nature in association with oxygen, sulfur, silicon, and other substances (Arvidsson et al. 2007).

Hardness, ductility, and highly polishable are the physical characteristics of this element.

Generally, nickel is present as free Ni^{2+} in the soil solution, with contributions also from Ni^{2+} complexes with inorganic and organic matter (Ma & Hooda. 2010)

The concentration of dissolved organic carbon (DOC) is a factor that governs the extent of Ni-organic complex formation. The determination of the total concentration of Ni in solution is commonly <100 µg L^{-1}.

2.6.1. Source of Ni

Ore deposits that contain nickel include laterites and magmatic sulfide deposits. Laterites have two Ni sources: the first one is nickeliferous limonite (Fe. Ni)O(OH) and the second is hydrous nickel silicate (Ni.Mg)$_3$Si$_2$O$_5$(OH). In the magmatic sulfide deposits, the main mineral is pentlandite (Ni.Fe)$_9$S$_8$.

Nickel is an essential element for plants and animals. On the other hand, too high concentrations of Ni can harm both plants and animals (Wuana & Okieimen 2011).

2.6.2. Nickel in Sweden

Geological Survey of Sweden (SGU) conduct mapping surveys in which the concentrations of different metals are determined. Figure 3 shows the concentration if Ni at 75 cm depth of Swedish glacial till soils. The soil texture is an important factor for the spatial variability across Sweden. High concentration occurs at Caledonides rock at the north part and a small part in the south (Andersson et al. 2014).

Figure 3. Concentration of Ni in Sweden, Soil: Till, Depth: 75 cm, No of samples: 2578. (Andersson, et al. 2014).

2.6.3. Use of nickel

More than 80% of the mined nickel is used in various alloy industries. About 60% is used in the production of the stainless-steel sector, 10 percent of nickel is used in nickel plating, 5 percent of Nickel is used for casting and the remaining 5 percent is used for catalysts, batteries (NiMeH), chemicals, welding electrodes, coins, pigments, electronic components, and printing inks (Arvidsson et al. 2007).

2.6.4. Biological effect

Nickel deficiency has not been reported in humans nor has there been any nutritional physiological role described in humans or animals. However, nickel can compete with other metal ions and trace elements in the body, e.g. iron, copper, and zinc, which affect their absorption and turnover either in a positive or in a negative way. It is worth mentioning that nuts are rich in nickel. About 3 percent of the nickel contained in diets is absorbed in the gastrointestinal tract, even at air exposure has been shown uptake. The urine is primarily excreted (Barceloux 1999).

2.6.5. Environmental effects

The largest environmental effects of nickel extraction from sulfide nickel ores are found in Russia. It is the sulfur that is bound to nickel in the sulfide ores that causes significant environmental problems. It is estimated that 1 ton of produced copper produces an equivalent of 1 ton of sulfur; while 1 ton of produced nickel generates 8 tons of sulfur. Nickel functions as a trace element mainly in igneous rocks, partly as a substitute for iron and magnesium (in silicates and oxides) and partly as sulfide-bound together with cobalt, arsenic, and copper. Nickel is mobile in an acidic environment (Barceloux 1999).

The nickel content of foods is usually below 0.5 mg/kg, but soybeans, nuts, and oatmeal may have higher levels of it. The daily intake from food is 150 µg /day for adults and 80 µg day^{-1} for children. Acute nickel poisoning, when taken orally by soluble nickel compounds, can lead to headaches, dizziness, and nausea. The tolerable daily (TDI) intake is estimated to be 12 µg kg^{-1} body weight day^{-1} (U.S. Department of Health and Human Services, 2005).

2.6.6. Mobilization factors

Nickel as a metal has different transport pathways in the environment. Apart from the total Ni content in the soil, natural or anthropogenic sources of Ni and physicochemical properties control the mobility and bioavailability of Ni in the soil and soil solution (Nicholson et al. 2003). The pH value is the most important factor that influences Ni solubility in the soil. Acidic and oxidizing conditions lead to the mobilization of Ni (Andersson et al. 2014). By decreasing pH and the cation

exchange capacity (CEC), the mobility of Ni increases (Ma & Hooda, 2010), while the clay content is of secondary importance (Ma & Hooda, 2010).

2.6.7. Source of soil contamination

Natural and anthropogenic nickel sources determine the extent of accumulation of Ni in the soil profile. Nickel is supplied to the soil mainly as atmospheric deposition and as fertilizer. The nickel is transferred to the atmosphere by burning of fossil fuel and Ni mining (Luo et al. 2009; Nicholson et al. 2003).

2.7. Properties of cobalt

Cobalt is a transition metal that belongs to group 9 in the periodic table. It exists as a silver-gray color. Hardness and lustrous are physical properties of this element. It is a Ni, part of ferromagnetic metals.

Cobalt has just one stable isotope, ^{59}Co, because of that nickel is referred to as a monoisotopic element (Zakir & Shikazono, 2010).

Generally cobalt is present in either +2 or the +3 oxidation state in the environment. In most waters, cobalt is present as Co^{+2} ions (Krupka & Serne, 2002), but exactly as for Ni, some organic and inorganic complexes of Co^{2+} are also expected.

2.7.1. Source of Co

Physical and chemical weathering of naturally occurring minerals is the dominant natural source of Co in the soil (Zakir & Shikazono, 2010). The other source is anthropogenic, i.e. industrial activities, urban waste, sewage and phosphorus fertilizer (Senesi et al. 1999).

2.7.2. Cobalt in Sweden

Figure 4 shows results from the SGU geochemical survey of glacial till soils across Sweden. Again, as for Ni, soil texture is an important factor behind the spatial variations in Sweden. High concentrations occur in the north part of the country. Ultramafic and mafic rocks occur in the north part of Sweden which is one of the natural sources of cobalt. (Andersson et al. 2014)

SGU collected clay (glacial till) samples across Sweden under the geochemical and biogeochemical program. this program aims to evaluate the total natural concentration of nickel over 27000 clay (glacial till) samples and 37000 stream water plant samples. clay (glacial till) is the common soil in Sweden. The natural total nickel concentration in the clay (glacial till) fraction <0.06 mm varies between <2 and 204 mg / kg.
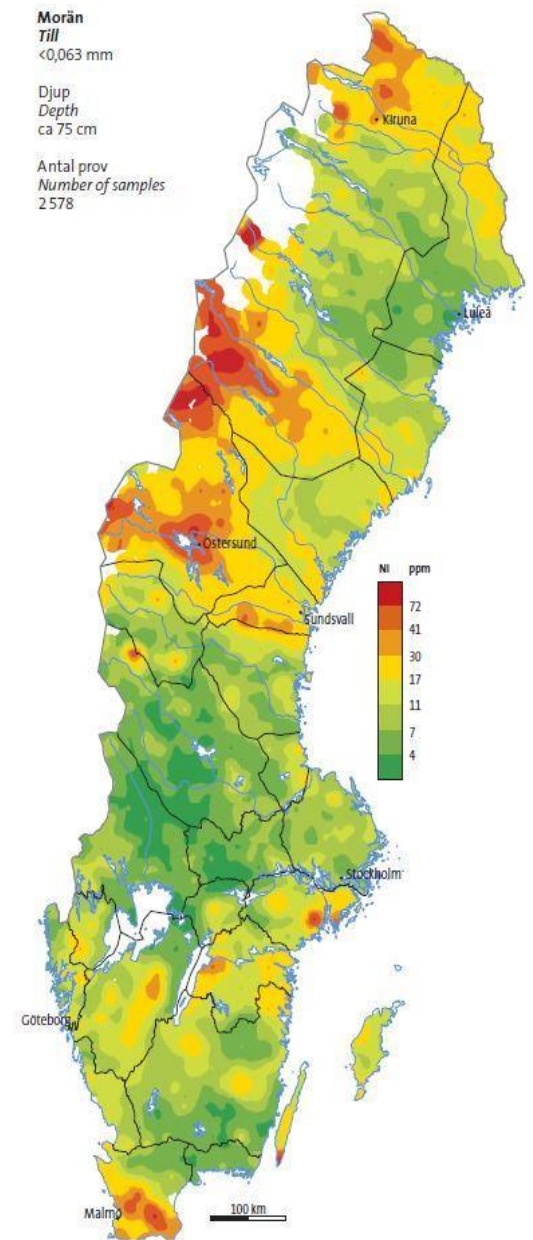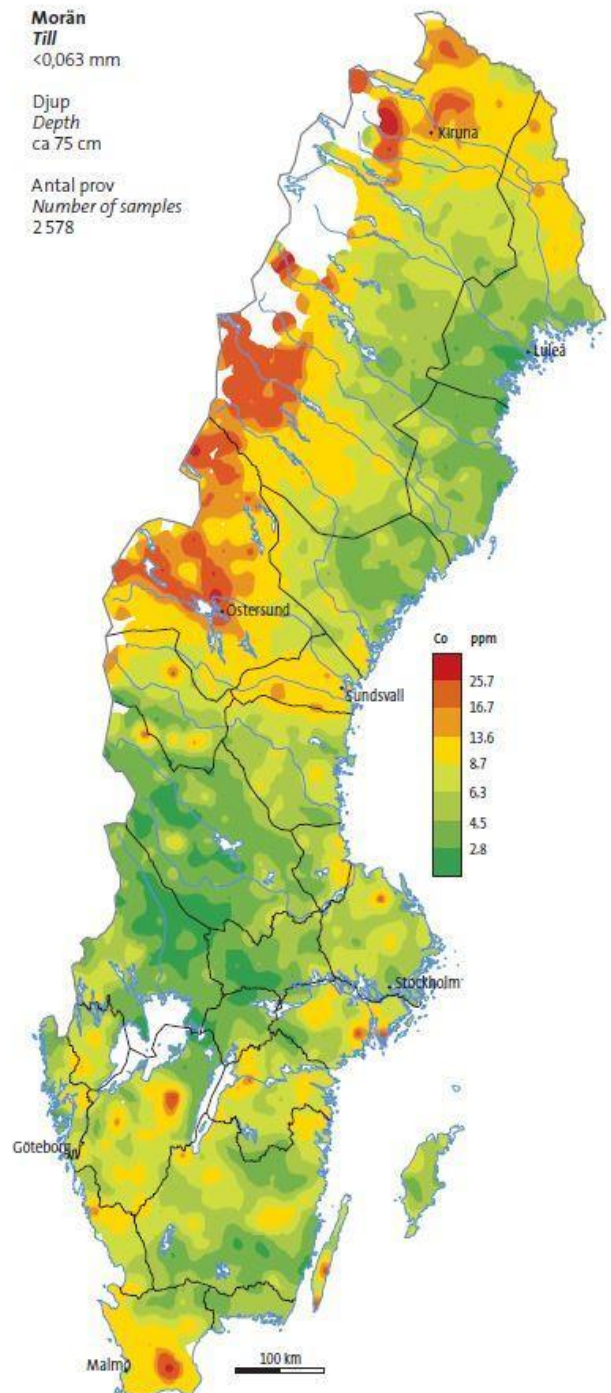

Figure 4. Concentration of Co in Sweden, Soil: Till, Depth: 75 cm, No of samples: 2578. (Andersson et al.2014).

2.7.3. Use of cobalt

Cobalt is used as a desiccant in black ink and is recovered from paper waste. It is included as contaminant in nickel and cement. During the burning of fossil fuels, it spreads. Occupational exposure to cobalt occurs mainly during the manufacturing and processing of cemented carbide. In this regard, the limitation is 0.05 mg/m^3 (Tinnerberg et al. 2009). Cobalt presence and varying levels in the earth's crust. The average Co content estimated about 25-30 ppm in the Earth's crust. Cobalt is essential to humans as it is part of Vitamin B12. Cobalt helps blood formation. It is calculated that the average daily intake through food is 3-14 µg /day for both children and adults (Pourret & Faucon 2017)

2.7.4. Biological and environmental effect

Exposure of cobalt to humans can cause allergic contact eczema. Cobalt-containing dust can cause obstructive pulmonary problems, and the worst case can be pulmonary fibrosis - cemented carbide. Cobalt interferes with the enzyme systems in the body and inhibits the absorption of other essential substances. There is an accumulation in the liver, kidneys, heart, and pancreas and chronic oral exposure can damage, for example, heart, thyroid, and auditory organs. Acute toxic intake produces nausea, vomiting, and colic (Tinnerberg et al. 2009).

Food is the largest source of nickel exposure for humans. (Tinnerberg et al. 2009)

3. Materials and Methods

3.1. General geology and hydrogeology of Uppsala county

Uppsala County is over a flat landscape, with clear traces of the ice sheet's progress about 8000 years ago. The whole area is below the highest coastline. The county is surrounded by Lake Mälaren in the south, Dalälven in the north, and a shallow coast towards the Bothnian Sea in the east. To the west, the agricultural plain turns into upland forests. In the far west, the landscape reaches about 110 meters above sea level, which is the highest of the county.

The bedrock consists mostly of granites, and the most common soil is glacial till (morän). The depth of soil is relatively shallow. The glacial till contains some limestone, particularly in the northeastern part of the county. This is a contributing factor as to why there are no major acidification problems in the county's lakes. Within the plains and in the valleys, the most common soil is clay. The clay layers can be very deep. In Uppsala, the clay depth of some urban areas is more than 100 meters.

The flat terrain with an ongoing isostatic uplift contributes to the formation of shallow lakes. There are about 300 lakes in Uppsala county, many of which are shallow and strongly overgrown. Some of them have been lowered several times to access larger areas of pasture and arable land. The receiving water bodies are sensitive to pollution impacts. A characteristic feature of Uppsala County is that the supply of groundwater is good as there are three large ridges that are excellent aquifers (Länsstyrelsens Meddelandeserie. Miljöskyddsenheten 2017).

3.2. Target area and soil samples

For this thesis, two types of projects have been chosen in collaboration with Bjerking. The environmental department at Bjerking investigates environmental issues in the contamination area, particularly the traces or contamination of metal in the soil. It is common to find a high concentration of cobalt in the Uppsala clay. Both projects are in the city of Uppsala. This study aims to determine the concentration of metals specifically cobalt and nickel. The preliminary evaluation for selection of target area and sampling was built on previous sample analyses on the area and support of the Uppsala county administration board website Geographic Information System (GIS) to identify potential contaminant areas.

The sample extraction from both locations (Fyrislund and Gränby) is carried out by a field technician at Bjerking's geotechnical department. The sample is obtained through the screw drill sampling method, see Figure 5.

Figure 5. Screw drill machine method with drilling track

3.2.1. Fyrislund

Bjerking received an offer to perform a comprehensive environmental and geotechnical investigation on the Fyrislund 6:13 property. The area under investigation is in Fyrislund, Uppsala. See Figure 6 for the approximate study area.

Figure 6. Approximate study area marked with red borderline. Picture from Bjerking's map portal 2020-02-21

The survey is designed for a property to build buildings in one of the other facilities. The location of the drilling points has been chosen from places where potential buildings and other facilities are to be constructed. See Figure 7, for the very early placement of the buildings.

Figure 7. Approximate placement of buildings and/or facilities.

The study area has previously been used as farmland. It is worth noting that the pharmaceutical industry is in the west of the study area, See Figure 8

Figure 8 . Aerial photos of the investigated area at Fyrislund 6:13. Left from 2014/2017 and right 1955/1967. The approximate study area marked in red. Photo from eniro.se.

The industries are not considered as risk zone by county administrative boards. According to the Uppsala county administrative board GIS map, the industries classified as an environmentally hazardous operation with an obligation to review. see Figure 9
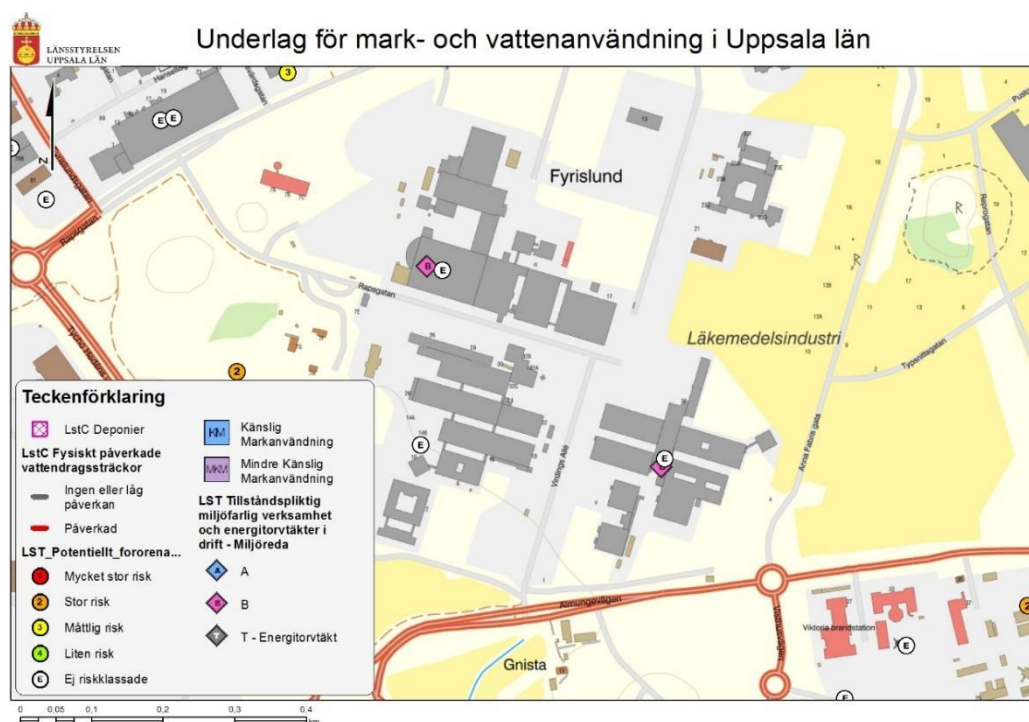
Figure 9. Support from the County Administrative Board's WebGIS for post-treatment support (2020-02-20).

The soil texture sequence in most parts of the property consists of the top layer of humus soil, overlaying cohesion soil above friction soil resting on bedrock. The depth of bedrock has been evaluated at two points based on field estimation, which varies between 6 and 8.5 m. Soil samples for this study were taken from 3 sample points. The screw drill sampling method was used, see Table 2.

Table 2. Fyrislund's soil sample properties

Soil texture			
Project	Fyrislund 6:13		
Test point	BG20001	BG20003	BG20008
Depth	0.0-0.3 m	0.0-0.3 m	0.0-0.3 m
Soil texture	clayey Humus	clayey Humus	clayey Humus

3.2.2. Kvarngärdesskolan

Bjerking received an offer to perform a comprehensive environmental and geotechnical survey of the Gränby 11:3 property. The area under investigation located in Gränby 11:3, the result of this survey will lead to building a school in this area, See Figure 10 for the approximate study area.
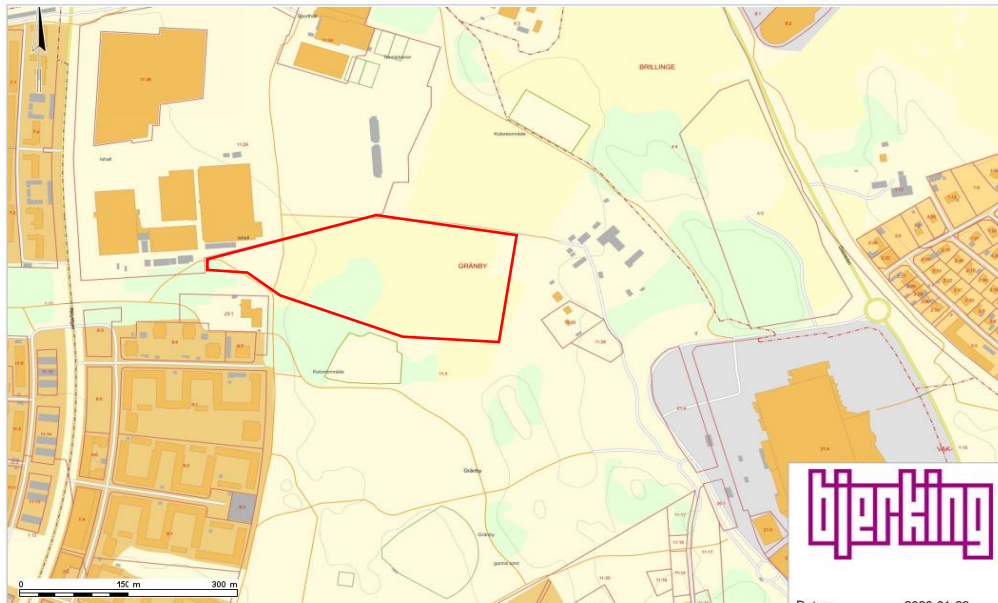
Figure 10. Approximate study area marked with red borderline. Picture from Bjerking's map portal

The area under this project used as pastureland. The soil texture sequence generally consists of the top of a layer of humus soil, overlaying cohesion soil above friction soil resting on bedrock.

3.4. Soil condition/texture

In this study the soil texture was determined by a combination of sedimentation and sieving. The primary evaluation of soil texture has been done in the field. Table 3 provide the soil sample properties.

Table 3. Kvarngärdesskolan's soil sample properties

Soil texture			
Project	Kvarngärdesskolan		
Test point	BG20010	BG20013	BG20016
Depth	0.3-1.5 m	0.3-1.5 m	1.4-2.0 m
Soil texture	Dry Clay	Dry Clay	Dry Clay

3.4.1. Particle size distribution - sedimentation

SIS-CEN ISO/TS 17892-4:2013 was used to determine the particle-size distribution. The first step in this process was to estimate the clay content. The clay

content is a key parameter for risk assessment. In this project, the particle-size distribution was determined at the Bjerking laboratory.

The water content of the soil sample was determined by weighing approximately 40 g soil sample into a crucible, which was oven-dried at 105°C for 24 hours. The difference between the wet and dry weight is the water content of the soil sample:

$$m = m_w \frac{100}{100 + w}$$

where:

m: is the total dry mass (g)

m_w: is the wet mass of soil (g)

w: is water content (%)

In this thesis, hydrometer analyses were used. Once the samples dried, 50 g dry soil sample was placed in a conical flask and dispersed in water. Then the soil sample was put on the centrifuge for at least 3 hours to be sure all material is aggregated. In the end, the suspension was moved to the cylinder and water was added to reach 1000 mL. Before inserting the hydrometer into the suspension, the suspension was shaken for 30 s. Then the hydrometer values were recorded at 0,5, 1, 2, 4, 8, 30, 60, 120, 480 min, and 24 h.

3.5. Total Organic Carbon analyses

The total organic carbon (TOC) analyses method is one of the more practical parameters of risk assessment in this thesis. In order to determine TOC, dried soil samples were prepared. Soil samples were dried at 105°C for 24 hours. The dried sample was sieved to obtain the soil sample fraction smaller than 2 mm. The dried sample was analysed for C and N with the LECO method at the SLU soil chemistry laboratory. TOC determination using a LECO TruMac CN analyser combines two components. Total inorganic carbon (TIC) was determined by loss-on-ignition. 1 g dry soil sample was incinerated at 550°C before analysis using the LECO TruMac CN analyser. After obtaining TIC, the total carbon (TC) was obtained. 1 g dry soil sample was incinerated with pure oxygen at 1350°C. Finally, the TOC was determined by difference between TC and TIC: TOC=TC-TIC.

3.6. Geochemically active fraction

The geochemically active fraction constitutes a method for understanding the mobility of metals in soil (Giraldo 2018). This method is particularly useful for cationic heavy metals. One the most well-known such methods involves HNO_3

extraction (Gustafsson et al. 2003). Once the samples were prepared, 35 mL of 0.1 M HNO_3 was added to 2 g dried soil. The prepared soil sample was shaken for 16 hours in and end-over-end shaker apparatus. Subsequently, samples were put in the centrifuge for 20 min at 2500 rpm. Lastly, a 0.2 µm filter was used to filter the samples. The extracted samples were sent to the ALS laboratory for determination of the total concentration of metals with the W-SFMS-5D method.

3.7. Leaching test

Leaching tests are common for determining the extent of leaching of pollutants from a solid phase e.g. soil to a liquid, usually water (Elert et al. 2006). The ratio of liquid to soil is given as the L / S ratio (liquid / solid), if the L / S ratio is equal to 2, it means that there is twice as much liquid as soil (L / S = 2/1). In a leaching test, the natural leaching processes in the laboratory are accelerated, without altering the mechanisms associated with leaching. However, certain processes that affect the leaching cannot be performed, such as biological processes or transformation of one substance through light, so-called photolytic transformation. In leaching tests, it is also difficult to imitate slow temperature variations, aging processes, and mineral conversion processes since they take longer time than is practically possible to set aside for a leaching test (Thygesen et al, 1992).

In this study, 3.5 g dry weight of soil was suspended in 35 ml 0.01 M $CaCl_2$. The suspensions were then shaken for 16 hours. Afterwards, the sample was centrifuged, and the supernatant was filtered by 0.2 µm filter. Finally, the solution phase sample was sent to the ALS laboratory for determination of dissolved metal concentrations.

Table 4. Generic guideline values for metals according to Swedish EPA

Substance	Unit	Sensitive land use (KM)	less sensitive land use (MKM)
Arsenic. As	mg kg^{-1}	10	25
Barium. Ba	mg kg^{-1}	200	300
Lead. Pb	mg kg^{-1}	50	400
Cadmium. Cd	mg kg^{-1}	0.8	12
Cobalt. Co	**mg kg^{-1}**	**15**	**35**
Copper. Cu	mg kg^{-1}	80	200
Chromium. Cr	mg kg^{-1}	80	150
Mercury. Hg	mg kg^{-1}	0.25	2.5
Nickel. Ni	**mg kg^{-1}**	**40**	**120**
Vanadium. V	mg kg^{-1}	100	200
Zinc. Zn	mg kg^{-1}	250	500

3.8. Risk assessment – Swedish EPA Guideline model

In Sweden, the Swedish EPA guideline conceptual model is used for evaluation of risk and determination of protection objects at a contaminant site. One of the most important protection objects is protection of the soil environment at the contaminant site. There are three main risk objects used to evaluate the risk level for the human, environment, and natural sources (Naturvårdsverket, 2009). In the simplest application of this method, the total concentration of the metal is compared with a generic guideline value, which is defined both for sensitive land use, and for less sensitive land use (Table 4). A drawback with this method is that it is complex. Another drawback is that the bioavailability of contaminants can vary among different soils. A high concentration, although an indicator of risk, may not be a risk for the soil ecosystem because of the low bioavailability of contaminants. To deal with this, site-specific information can be used to refine the guideline value to produce a site-specific guideline.

The partition coefficient (K_d) describes the mobility of metal in the soil environment. It is determined as the ratio of the total concentration in the solid phase to the total dissolved concentration in the solution phase. The K_d value is important when determining the site-specific guideline value using the SEPA risk assessment tool.

3.9. Risk assessment - Threshold Calculator

Recently, other tools for assessing risk assessment have been developed. The threshold calculator is a tool for ecotoxicological risk assessment of metals in soil. This tool assesses the ecotoxicity of metals such as: Cd, Cu, Pb, Mo, Ni, and Zn. It calculates the ecotoxicological threshold values that cause toxic effects for organisms on three different trophic levels: plants, invertebrates, and micro-organisms. Apart from Cd, total concentrations are used to define the toxicological threshold values. The result is corrected for bioavailability by applying different soil factors. The threshold calculator allows calculating the maximum bioavailability by choosing the concentration effect (ECx), the effect level (HCx), and total background concentration of metals. Other parameters required for the risk assessment include:

pH, which is measured in a 0.01 M $CaCl_2$ soil suspension. If pH is determined with another method, there is a possibility to correct to 0.01 M $CaCl_2$.

Organic carbon content (TOC) %, which should be determined on the dry soil sample.

Clay content %, which is determined based on ISO 11277:2009. The sieving and hydrometer method could be applied.

Effective Cation Exchange Capacity (CEC) cmol kg⁻¹: CEC may be estimated based on the above mentioned (pH, clay content, and TOC) parameters from the following relationship:

$$\text{eCEC (cmol}_c \text{ kg}^{-1}) = (30 + 4.4 \times \text{pH}) \times \% \text{Clay}/100 + (-59 + 51 \times \text{pH}) \times \% \text{OC}/100$$

The results are displayed as species sensitivity distributions, see Figure 11.
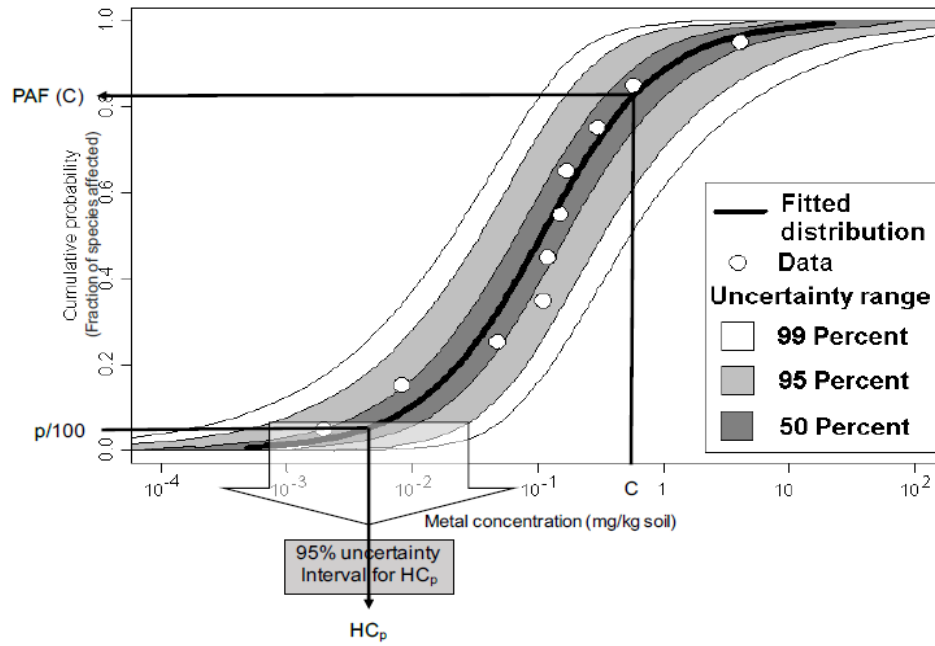
Figure 11. Example of SSD with uncertainties (Oorts, K. 2018 © 2020).

In this project, the threshold calculator was used to determine the ecotoxicological threshold values for Co and Ni, relevant for protection of the soil environment in the SEPA guideline tool for contaminated soils.

4. Results

4.1. Soil sample properties

The basic soil properties that were determined include: total metal concentration determined at the Eurofins laboratory, pH(0.01 M $CaCl_2$) at the SLU research laboratory, total organic carbon (TOC), as determines by the LECO truMac method, the clay content, as determined by hydrometer analyses at the Bjerking soil laboratory, and cation exchange capacity (CEC), which was determined by calculation as described above. Table 5 contains an overview of the soil properties for both projects. At both Fyrislund and Kvarngärdesskolan, the pH ($CaCl_2$) values were found to be close to 7. Total organic carbon (TOC) ranged from 0.87 to 1.97 % at Fyrislund and from 0.53 to 1.39 % at Kvarngärdesskolan. The clay content was about 35% at Fyrislund and about 45% at Kvarngärdesskolan.

Table 5. Soil properties at the studied sites

Parameter	Fyrislund			Kvarngärdesskolan		
	BG20001	BG20003	BG20008	BG20010	BG20013	BG20016
pH ($CaCl_2$)	6.64	7.07	7.02	6.87	7.33	7.40
TOC (%)	1.9	0.9	1.3	1.4	0.7	0.5
Clay content (%)	38	30	36	48	50	42
eCEC ($cmol_c$/kg)	28.0	21.0	25.7	33.0	33.3	28.0

4.2. Total concentration in solid soil samples

In order to determine the total concentration of metals, the soil samples were analysed as a collection soil sample at each soil depth per sample point. 11 metals were included in the analyses' package (total heavy metal concentrations). They were: Arsenic As, Barium Ba, Lead Pb, Cadmium Cd, Cobalt Co, Copper Cu, Chromium Cr, Mercury-Hg, Nickel Ni, Vanadium V, Zinc Zn. The soil samples were sent to Eurofins laboratory to analyze the total concentration.

4.2.1. Kvarngärdesskolan's soil sample

Total concentration

Table 6 shows the total metal concentrations at Kvarngärdesskolan. The cobalt concentration met the generic guideline value for sensitive land use (KM) based on the Swedish Environmental Protection Agency (SEPA). The other elements had values lower the generic guideline value for sensitive land use.

Table 6. Total metal concentrations in mg kg^{-1} - Kvarngärdesskolan.

Project		Kvarngärdesskolan		
Test point		BG20010	BG20013	BG20016
Substance	**Unit**	0.3-1.5 m	0.3-1.5 m	1.4-2.0 m
Arsenic. As	mg kg^{-1}	3.7	3.7	4
Barium. Ba	mg kg^{-1}	110	110	140
Lead. Pb	mg kg^{-1}	21	21	11
Cadmium. Cd	mg kg^{-1}	< 0.20	< 0.20	< 0.20
Cobalt. Co	**mg kg^{-1}**	**15**	**15**	**15**
Copper. Cu	mg kg^{-1}	27	27	32
Chromium. Cr	mg kg^{-1}	41	41	49
Mercury. Hg	mg kg^{-1}	0,062	0.062	0.013
Nickel. Ni	**mg kg^{-1}**	**26**	**26**	**29**
Vanadium. V	mg kg^{-1}	50	50	55
Zinc. Zn	mg kg^{-1}	84	84	75

HNO$_3$ -extracted concentration

The results obtained from extraction with 0.1 M HNO$_3$ are shown in Figure 12 and Figure 13. Cobalt and nickel are both to a large extent dissolved into the HNO$_3$ extract. From the data in Figure 12 and Figure 13, it is apparent that Co had the highest geochemically active fraction in the BG 20016 sample, i.e. more than 80 % of total Co and 50% of total Ni. In the other two points the geochemically active fraction was between 43 and 54% for Co. The Ni concentrations showed lower trend (28% and 24%). However, as the figures show, Ni had consistently a lower geochemically active fraction than Co.

Figure 12. The HNO₃-extracted concentration for Co compared with the total metal concentration.

Figure 13. The HNO₃ -extracted concentration for Ni compared with the total metal concentration

Table 7. The HNO₃ extracted concentration in mg kg⁻¹ - Kvarngärdesskolan

ELEMENT	The total extracted concentration by 0.1 M HNO₃		
Sampling Date	Unit	BG20010	BG20013	BG20016
Arsenic. As	mg kg⁻¹	0.04	0.07	0.08
Barium. Ba	mg kg⁻¹	78.67	62.54	184.23
Cadmium. Cd	mg kg⁻¹	0.16	0.15	0.22
Cobalt. Co	**mg kg⁻¹**	**8.10**	**6.51**	**12.16**
Chromium. Cr	mg kg⁻¹	4.93	5.75	10.48
Copper. Cu	mg kg⁻¹	7.46	8.67	16.45
Molybdenum. Mo	mg kg⁻¹	<1	<1	<1
Nickel. Ni	**mg kg⁻¹**	**7.25**	**6.32**	**14.60**
Lead. Pb	mg kg⁻¹	9.62	8.17	18.66
Vanadium. V	mg kg⁻¹	7.87	9.81	24.38
Zinc. Zn	mg kg⁻¹	23.70	22.53	49.91

4.2.2. Fyrislund's soil sample

Total concentration

Table 8 shows the total concentration of metals at Fyrislund**.** As can be seen from the table, the cobalt concentrations at sample point BG20001 and BG20003 exceeded the generic guideline whereas BG20008 met it concerning sensitive land use. Other elements were lower than generic guideline value for sensitive land use.

Table 8. Total metal concentrations in mg kg⁻¹ - Fyrislund

Project		Fyrislund		
Test point		BG20001	BG20003	BG20008
Substance	**Unit**	0.0-0.3 m	0.0-0.3 m	0.0-0.3 m
Arsenic. As	mg kg⁻¹	2.7	3	3.5
Barium. Ba	mg kg⁻¹	120	110	140
Lead. Pb	mg kg⁻¹	15	16	15
Cadmium. Cd	mg kg⁻¹	0.45	0.38	0.36
Cobalt. Co	**mg kg⁻¹**	**17**	**16**	**15**
Copper. Cu	mg kg⁻¹	31	27	29
Chromium. Cr	mg kg⁻¹	47	41	44
Mercury. Hg	mg kg⁻¹	0.031	0.034	0.024
Nickel. Ni	**mg kg⁻¹**	**32**	**27**	**29**
Vanadium. V	mg kg⁻¹	53	52	54
Zinc. Zn	mg kg⁻¹	100	92	95

HNO₃ extracted concentration

The results obtained from extraction with 0.1 M HNO$_3$ are shown in Figure 12 and Figure 13. Again, a large part of the total Co and Ni was dissolved into the HNO$_3$ extract, at Fyrislund the extracted percentage ranged from 50 to 60 % for Co and 39 to 49% for Ni, and there was no significant difference between Co and Ni in this respect.
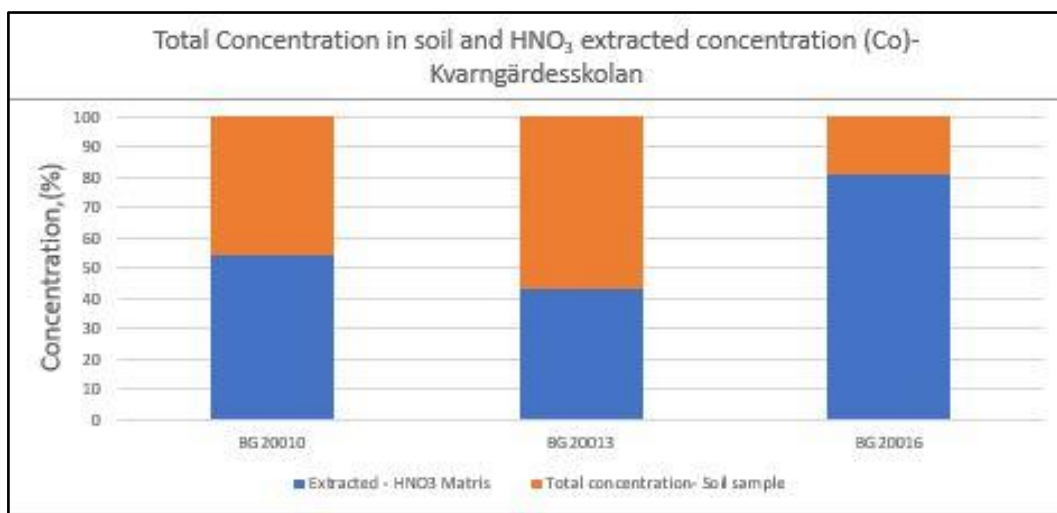

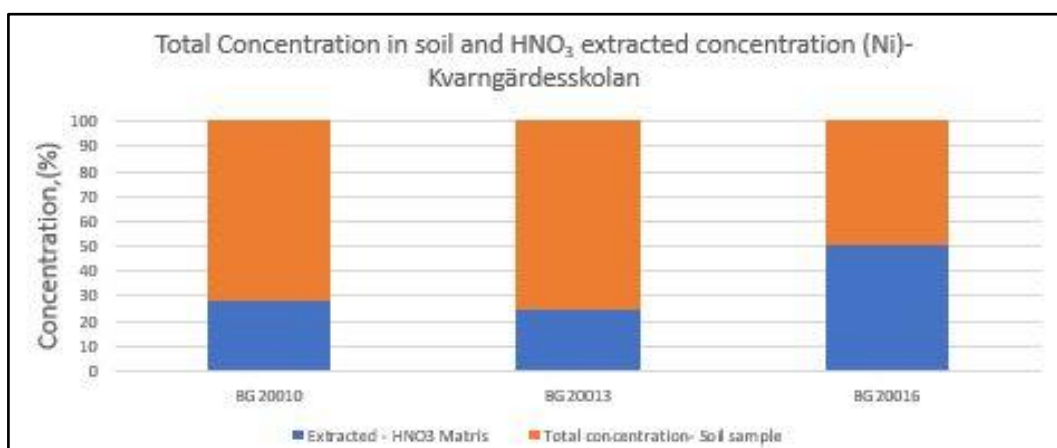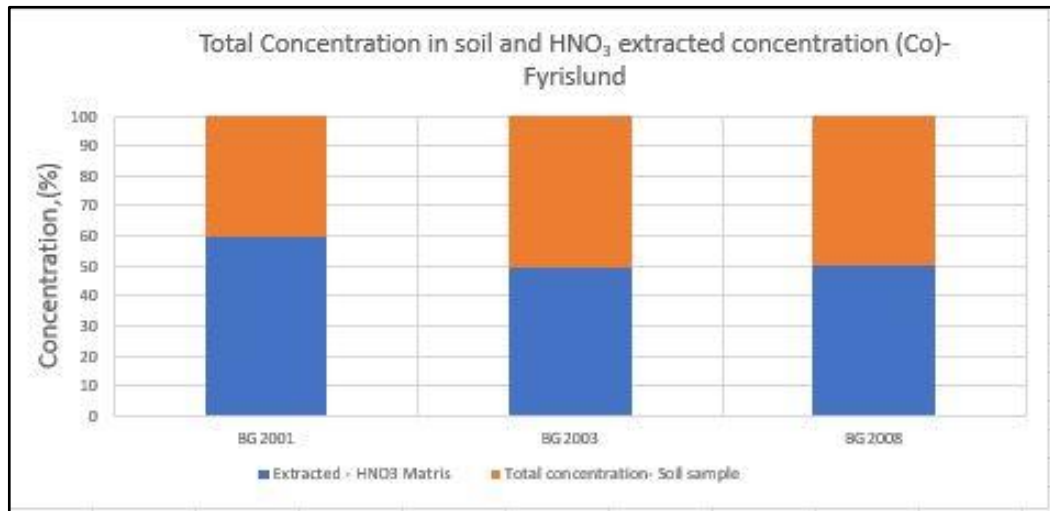*Figure 14. The HNO₃ extracted concentration for Co compared with the total metal concentration*
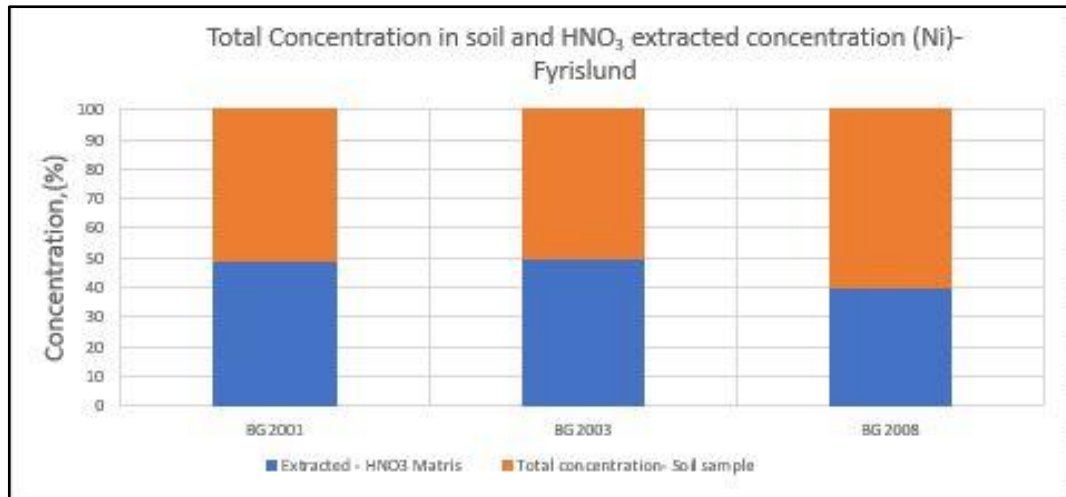
Figure 15. The HNO₃ extracted concentration for Ni compared with the total metal concentration

Table 4. HNO₃-extracted concentrations of metals in mg kg⁻¹

ELEMENT	Unit	BG2001	BG2003	BG2008
Arsenic. As	mg kg⁻¹	0.3	0.2	0.2
Barium. Ba	mg kg⁻¹	94.6	111.2	102.6
Cadmium. Cd	mg kg⁻¹	0.3	0.1	0.2
Cobalt. Co	**mg kg⁻¹**	**10.2**	**7.9**	**7.5**
Chromium. Cr	mg kg⁻¹	5.2	7.4	5.2
Copper. Cu	mg kg⁻¹	21.8	17.4	17.1
Molybdenum. Mo	mg kg⁻¹	<1	<1	0.8
Nickel. Ni	**mg kg⁻¹**	**15.6**	**13.4**	**11.4**
Lead. Pb	mg kg⁻¹	21.3	12.5	15.7
Vanadium. V	mg kg⁻¹	17.5	17.0	13.4
Zinc. Zn	mg kg⁻¹	39.5	34.1	31.1

4.3. Leaching test K_d values

This section presents the solution chemistry. **Error! Reference source not found.** shows the result obtained from the leaching test as a result of 0.01 M CaCl₂ extracted concentration.

Figure 18 presents the 0.01 M CaCl₂-extracted concentration as a function of pH and Figure 19 presents it as a function of total organic carbon (TOC).

Table 5. Results from the leaching test with 0.01 M CaCl₂

Test point		Fyrislund			Kvarngärdesskolan		
Substance	Unit	BG2001	BG2003	BG2008	BG20010	BG20013	BG20016
Aluminium. Al	µg L⁻¹	41.4	5.61	5.02	14.2	12.9	6.54
Arsenic. As	µg L⁻¹	1.10	0.55	0.79	0.55	0.30	0.10
Cadmium. Cd	µg L⁻¹	0.27	0.046	0.099	0.107	0.009	0.012
Cobalt. Co	**µg L⁻¹**	**1.12**	**0.252**	**0.383**	**0.455**	**0.0452**	**0.0496**
Chromium. Cr	µg L⁻¹	1.10	0.76	0.40	0.39	2.17	9.67
Copper. Cu	µg L⁻¹	17.0	7.63	10.7	12.8	2.94	0.71
Iron. Fe	µg L⁻¹	149	3.45	4.15	10.8	5.11	1.43
Manganese. Mn	µg L⁻¹	620	83	171	234	10.7	10.8
Nickel, Ni	**µg L⁻¹**	**6.99**	**2.54**	**3.56**	**3.31**	**0.671**	**0.364**
Phosphorus. P	µg L⁻¹	2170	102	134	148	26.7	17.5
Lead, Pb	µg L⁻¹	0.49	0.056	0.060	0.190	0.106	0.057
Vanadium. V	µg L⁻¹	2.58	1.14	1.38	0.69	0.41	0.15

Zinc. Zn	µg L^{-1}	10.8	3.87	2.56	3.43	2.10	1.84
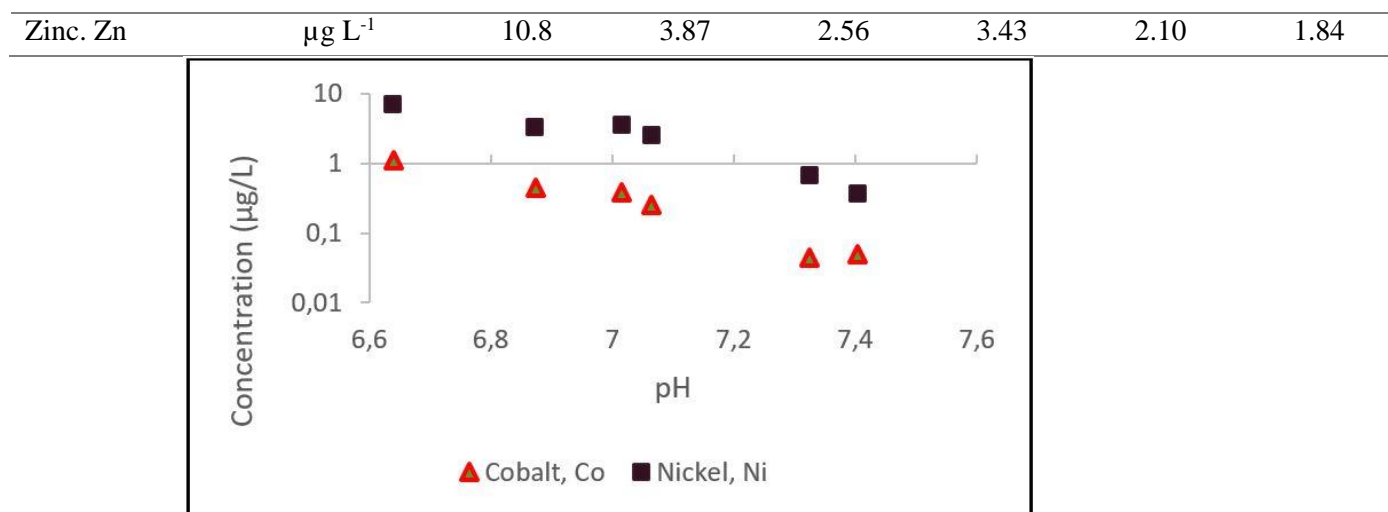
Figure 16. 0.01 M CaCl$_2$-extractable metals at different sites as a function of pH

It is apparent from above figure that both Ni and Co have a negative correlation with pH, which means that by increasing the pH, the total concentration that is determined by extraction CaCl$_2$ decreased.
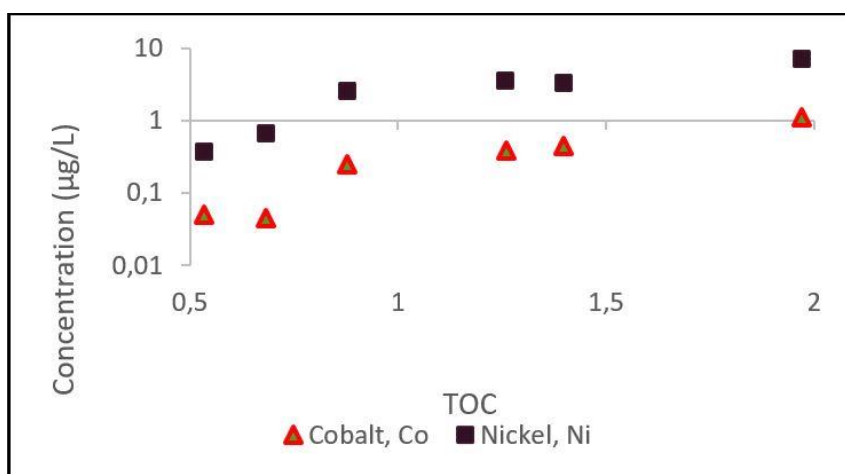
Figure 17. 0.01 M CaCl$_2$-extractable metals at different sites as a function of TOC

Further analysis showed that both Ni and Co have a positive correlation with TOC, which suggests that both bind to finer particles such as an organic matter (Yang et al. 2011). Accumulation of organic matter is often observed near to the surface layer with negative charges. By increasing the TOC, the total concentration determined by extraction CaCl$_2$ is increased.

4.4. Risk assessment – Swedish EPA Guideline model

A reasonable approach of guideline values is to focus on the protection objects that are expected in and around a contaminated area. The guideline value for the protection of the soil environment indicates the level of pollution below which the soil ecosystem is expected to be able to perform the functions according to the type of land use. Some of these functions relate to human activities such as agriculture, animal husbandry, and cultivation of different plants to reduce dusting and erosion. Another function related to the environment is the soil's role for the carbon and nutrients cycle, which enables survival and continued development of the ecosystem.

For certain metals e.g. Ni and Co, it is common that the protection of soil environment is the protection object that governs the final guideline. Determination of the site-specific guideline value is useful to help identify the proper protection object that is valid for a specific site. A key parameter for this is the revised K_d value obtained from leaching tests.

Thus, a scenario was designed with the support of SEPA's Excel calculation tools, where the K_d value was exchanged for the site-specific K_d value determined from the ratio of total metal to the $CaCl_2$-extractable metal concentration. What stands out in the Table 6 is the higher site-specific guideline value for the KM scenario as a result of high K_d value.

Table 6. Estimation of site-specific guideline value with revised K_d value

		Cobalt: mg kg^{-1}	Nickel: mg kg^{-1}
Generic guidelines (SEPA)	Sensitive land use, KM	15	40
Site-specific guideline value		20	70
Generic guidelines (SEPA)	Less sensitive land use, MKM	35	120
Site-specific guideline value		35	120

The Excel tool showed that that the protection of the soil environment was the most important governing factor for both KM (Table 7) and MKM (Table 8). A high clay content in combination with a high CEC in the soil samples might be an explanation. In other words, both Co and Ni strongly adsorb to soil particles as a result of a high clay content and CEC value.

In conclusion, the higher K_d value indicated a low risk of leaching, which turned out to be important for the KM, but not for the MKM, scenario.

Table 7. Governing protection objects of the SEPA risk assessment tool for KM

	KM (mg kg^{-1})		Governing for guideline
Generic guidelines (SEPA)	Co	15	Intake of plants+other sources
Site-specific guideline value	Co	20	Protection of soil environment
Generic guidelines (SEPA)	Ni	40	Protection of groundwater
Site-specific guideline value	Ni	70	Protection of soil environment

Table 8. Governing protection objects of the SEPA risk assessment tool for MKM

	MKM (mg kg $^{-1}$)		Governing for guideline
Generic guidelines (SEPA)	Co	35	Protection of soil environment
Site-specific guideline value	Co	35	Protection of soil environment
Generic guidelines (SEPA)	Ni	120	Protection of soil environment
Site-specific guideline value	Ni	120	Protection of soil environment

Figure 18 shows the partition coefficient value (K_d) and the generic K_d value as a function of pH. As shown in the Figure 18, there was a significant difference between the generic K_d value compared with the obtained site-specific K_d value. Figure 18 presents a positive correlation which means with higher pH values, Ni and Co are more strongly bound to the soil particles. Further, the results of Figure 18 suggest that both Co and Ni have a low rate of leaching through the soil profile.
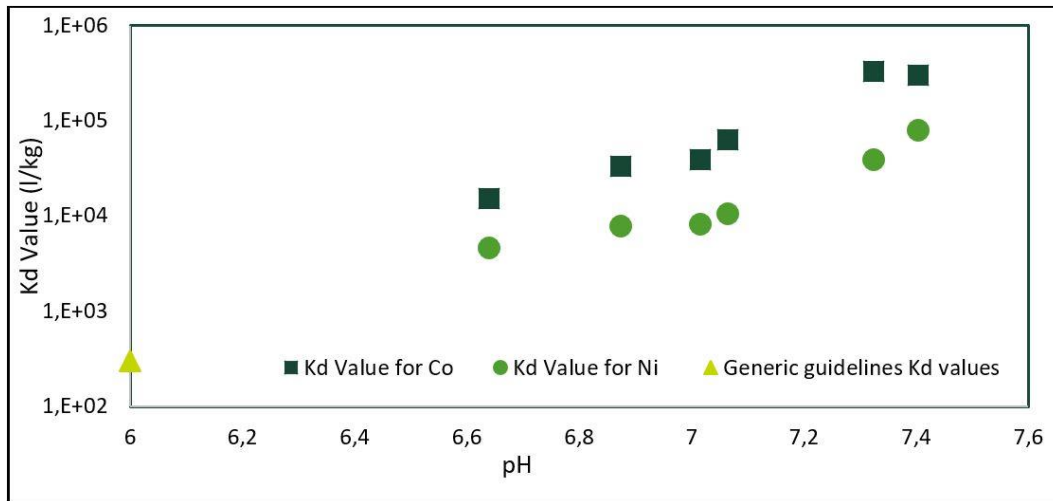
Figure 18. Generic partition coefficient (K_d) and site-specific partition coefficient (K_d) as a function of pH

The partition coefficient (K_d) value as a function of total organic carbon (TOC) is shown in Figure 19.
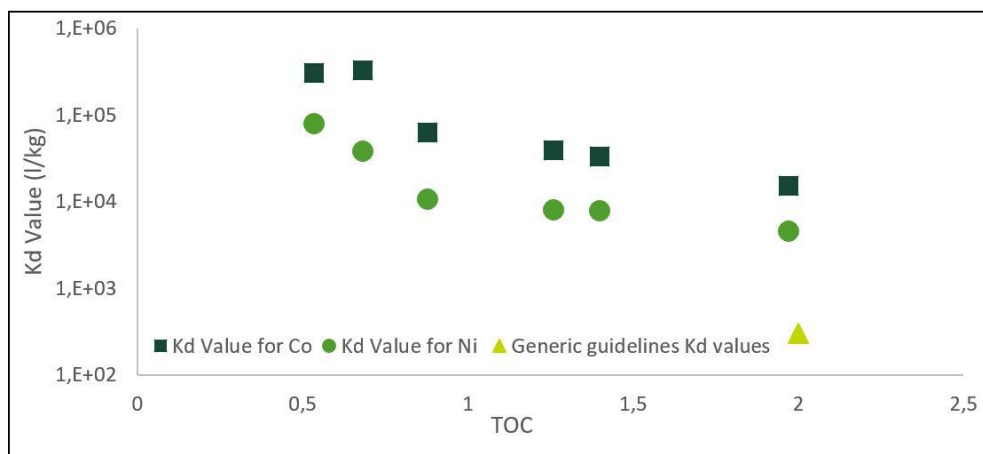
Figure 19. Partition coefficient (K_d) value by the function of TOC and Generic guideline K_d value

The other partition coefficient studied in this thesis is called K_{acc}. Figure 20 shows the ratio of partition coefficient K_d) and the partition coefficient K_{acc}, which is determined as the ratio of the 0.1 M HNO_3-extractable concentration in the solid phase (the geochemically active concentration) to the $CaCl_2$-extractable leaching test concentration, see Figure 20.

According to Gustafsson et al. 2007, the partition coefficients are nearly equal, i.e. $K_{acc} \approx K_d$.
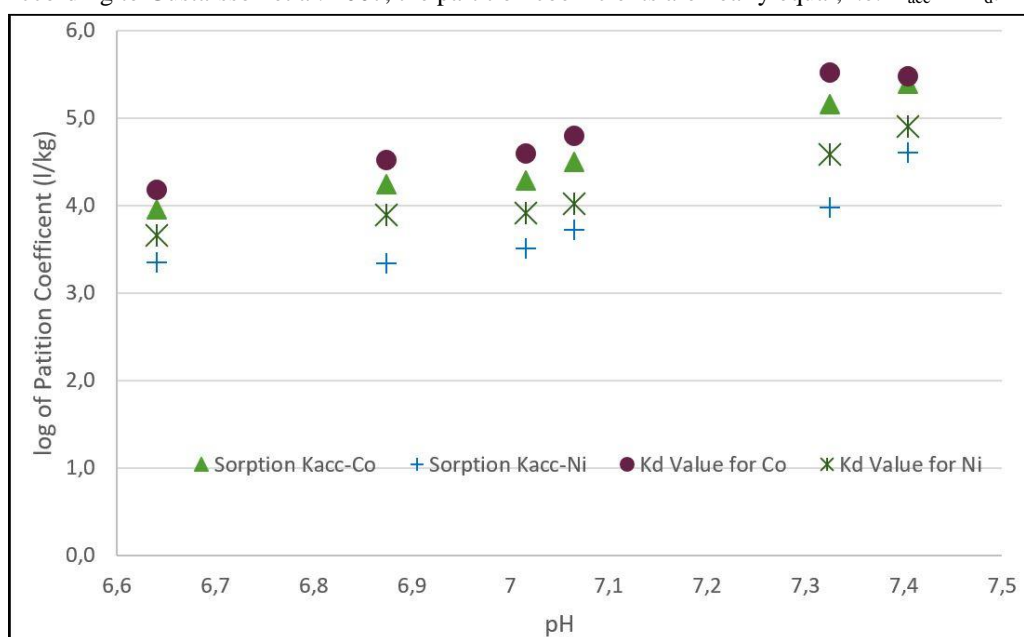
Figure 20. Compare K_d value and K_{acc} with the function of pH

To confirm the protection level obtained by the SEPA risk assessment tool, the Threshold calculator was applied, considering the variation of four soil properties (pH, TOC, clay content, and CEC).

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4.5. Risk assessment -Threshold calculator

First, to understand more about risk assessment using the Threshold calculator as adopted to the Swedish conceptual model, three scenarios with key indicators (Clay content, TOC, and pH) were performed. The result of all three scenarios are shown in Figure 21, 22 and 23. These figures show the effect on the ecotoxicological threshold values when the soil properties, i.e. TOC, pH, and clay content, are varied.

The y axis of these figures shows the effect concentration at x % toxic effect, determined and indicated as EC_x. The EC_{10} value was chosen for this analysis which is usually considered equivalent to NOEC (highest no observed effect concentration). This effect level (EC_{10}) was used for both sensitive and less sensitive land use (KM & MKM) scenarios. However, the protection level (HC_x) is different for the KM and MKM scenarios. For KM protection the HC_{25} level is used, which means protection of 75 % species, while HC_{50} is used to calculate for MKM. The protection level (HC) is calculated based on the species sensitivity distribution (SSD) as estimated by Threshold calculator from the given set of soil properties. In the SSD, EC_{10} values for soil organisms at three different trophic levels are included.
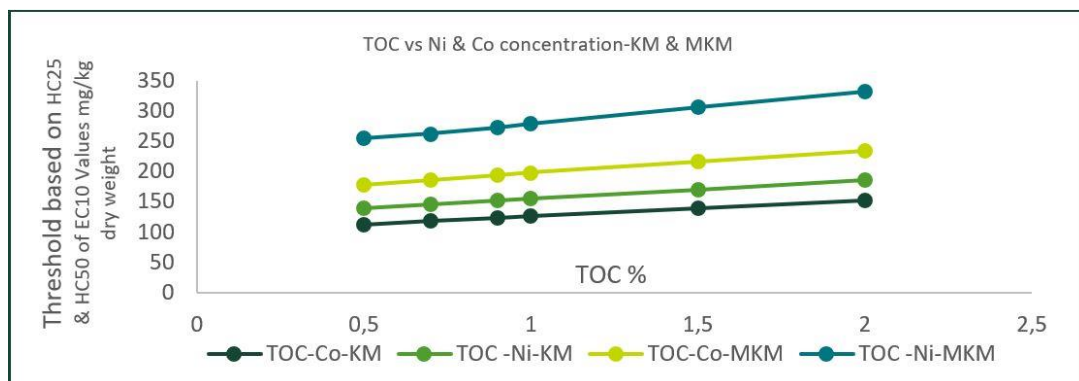
Figure 21. Threshold values as a function of the TOC content (%) using EC_{10} values and protection levels of 75 % (KM) and 50 % (MKM). In this scenario, clay content = 40%, pH = 6.
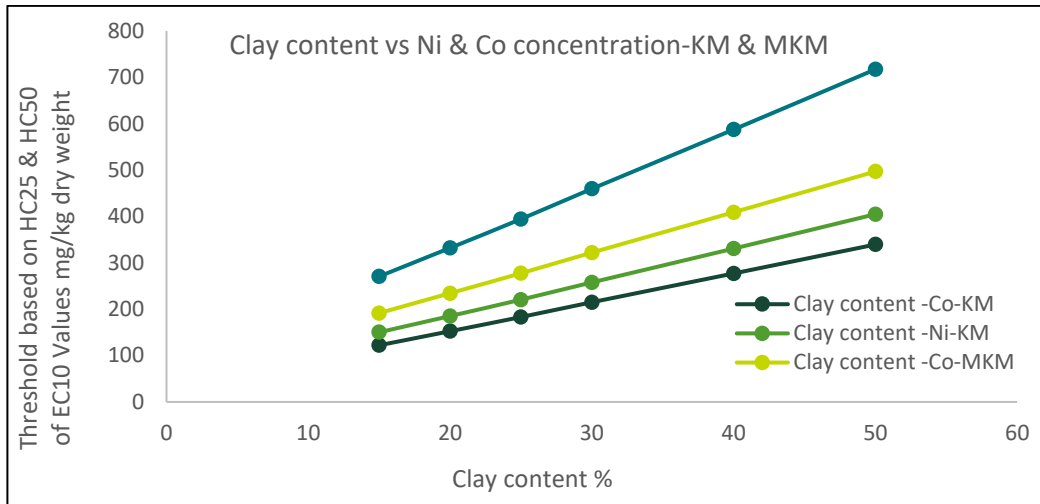
Figure 22. Threshold values as a function of the clay content (%) using EC_{10} values and protection levels of 75 % (KM) and 50 % (MKM). In this scenario, TOC = 2%, pH = 6.
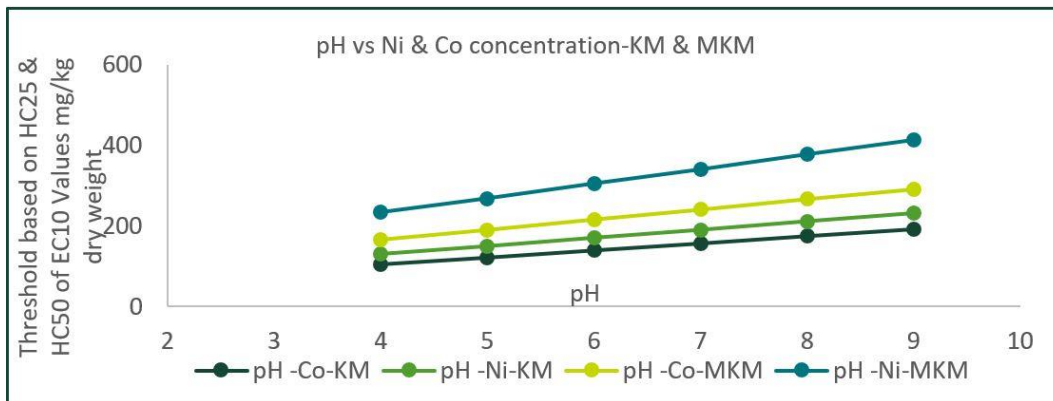
Figure 23. Threshold values as a function of pH using EC_{10} values and protection levels of 75 % (KM) and 50 % (MKM). In this scenario, TOC = 2%, pH = 6, clay content = 40%.

As seen in Figures 21-23, there was a positive relationship between the Co and Ni threshold concentrations to the Clay content, TOC, and to the pH value. Generally, one would expect a positive relationship between clay% and pH, because the more clay, the higher is the weathering rate, which would increase the pH.

According to the Swedish Environment protection agency (SEPA), the pH value in the generic scenarios is expected to range from 5 to 7 and the organic carbon is about 2%. So, the scenarios designed are close to the generic SEPA scenarios as regards pH and TOC, but a higher clay content had to be assumed to match the site-specific soil properties.

The results obtained from the soil sample are summarized in Table 9 and Table 10. There is different information in the tables which helps to understand the specific changes compared to the Swedish conceptual model. Table 8 presents the

EC$_{10}$ (effect level) values based on the HC$_{25}$ (protection level that agreed with KM) for Co and Ni in the soil.

The ecotoxicological thresholds for sensitive land use (KM) and less sensitive land use (MKM), as obtained with the Threshold Calculator, indicate slightly higher values at Fyrislund's soil samples compared to the Swedish guideline values, except for the BG2003 soil sample point. At Kvarngärdesskolan, all the ecotoxicological thresholds were higher than those obtained with the Swedish guideline model. The results were similar for both Co and Ni.

The Threshold calculator-estimated risk is only valid for the protection of the soil environment. However, it considers differences in soil properties not explicitly considered in the SEPA risk assessment tool, and it may be argued that this allows for calculation of a guideline that is more adapted for the specific soil environment. Therefore, to be able to use the best of these two tools I integrated them by replacing the soil environment value in the SEPA tool with the Threshold calculator value, the result is seen in **Error! Reference source not found.**.

When the SEPA tool and the Threshold calculator was combined for this project, the protection of health value now instead became the new governing protection object for sensitive land use (KM). Regarding less sensitive land use (MKM), there was no difference observed concerning the protection object. In other words, the soil environment was still governing the final guideline value. However, the guidelines became higher in all cases.

Table 9. Thresholds (mg kg^{-1}) based on the HC$_{50}$ protection level (=MKM), using EC$_{10}$ values in the Threshold calculator.

	Substance	Fyrislund			Kvarngärdesskolan			Threshold
		BG2001	BG2003	BG2008	BG20010	BG20013	BG20016	
Threshold based on specific soil condition	Cobalt	283.8	205.6	258.2	339.6	343.0	283.8	**246.9**
	Nickel	354.4	259.0	322.8	423.9	428.1	354.4	**309.1**

Table 10. Thresholds (mg kg^{-1}) based on the HC$_{25}$ protection level (=KM), using EC$_{10}$ values in the Threshold calculator.

	Substance	Fyrislund			Kvarngärdesskolan			Threshold
		BG2001	BG2003	BG2008	BG20010	BG20013	BG20016	
Threshold based on specific soil condition	Cobalt	429.5	316.5	392.4	510.4	515.2	429.5	**376.2**
	Nickel	630.2	463	574.9	751.5	758.9	630.2	**550.9**

Table 11. Estimation of guideline value-based to SEPA and re-estimation based on the site-specific value with an exception for the soil environment. The soil environment guideline value estimated by the Threshold calculator.

	Generic guidelines (SEPA)				Site-specific guideline value- Threshold Calculator			
	KM (mg kg^{-1})		MKM (mg kg^{-1})		KM (mg kg^{-1})		MKM (mg kg^{-1})	
	Co	Ni	Co	Ni	Co	Ni	Co	Ni
Soil Environment	15	40	**35**	**120**	247*	309*	**376***	**551***
Health value	**15**	140	720	2400	**22**	**230**	720	2400
Protection of GW	22	**43**	70	140	4600	5600	15000	18000
Protection of SW	240	1200	240	1200	51000	150000	51000	150000

*These values were calculated using the Threshold calculator

The orange color indicates the governing protection object for the soil guideline value

5. Discussion

5.1. Total concentrations

In the current study, the total concentrations of cobalt and nickel were evaluated. The cobalt concentrations were slightly higher than SEPA's general guideline value at Fyrislund, although the BG20008 concentration was similar to SEPA's general guideline value. Regarding nickel, all samples had concentrations lower than the guideline value. Similarly, according to the Geological Survey of Sweden (SGU) 22-27 ppm Ni is the total background concentration at the investigated area, which is close to the obtained values.

Contrary to expectations, I did not find a significant difference between the Co and Ni concentrations for Kvarngärdesskolan's project.

5.2. Geochemically active fraction

The geochemically active fraction extracted by 0.1 M HNO_3 indicates the amount of metal bound to the surfaces of organic matter and iron/aluminum (hydr) oxides, as well as cations bound to clay mineral surfaces. (Gustafsson et al. 2003; Elert et al. 2008).

The extracted values by 0.1 M HNO_3 indicate that both Co and Ni concentration have a high geochemical activity within all samples. Generally, more than half of the amount of Co was HNO_3-extractable, while for Ni slightly less than half was extractable. The geochemically active fraction of Co varied between 50% and 60% for Fyrislund's soil samples. For Kvarngärdesskolan the corresponding figures were 43% to 80%. At Fyrislund, the geochemically active Ni concentration was between 39 and 49% and for Kvarngärdesskolan it ranged from 24 to 40%.

According to these results, a large part of Co and Ni in these soil samples is not strongly bound within primary minerals, but present on the soil surfaces. Instead the high clay content and high pH are two factors that contribute to a strong adsorption (and therefore low solubility) of both Co and Ni, as can be seen from the high K_d value. This confirms the strong adsorbed of Ni and Co into soil particles.

5.3. Leaching test

Most studies in the field of risk assessment have focused on leaching tests. In this thesis, a one-step leaching test was performed to soil samples by ALS Scandinavian laboratory. The method consists of shaking the sample with 1 mM $CaCl_2$ at an L/S ratio of 10 L kg^{-1} for 24 hours. The leached contents obtained are assumed to correspond to leaching in the short term.

Staunton (2004) showed that the distribution coefficient (K_d) value changes factor with chemical factors for Ni. Ni sorption decreased when there were competing cations in the system. This idea is valid mainly for cations with similar chemical properties. In the same survey, the K_d for Ni increased with increased pH, and by increasing at over pH 7; at alkaline pH, a decrease was seen again. The study also has shown that pH changes due to biological activity and seasonal variations can cause significant variations in nickel adsorption and mobility. Therefore, it is difficult to get a good picture of nickel mobility in the soil by solely measuring K_d (Staunton, 2004).

The background electrolyte consists of deionized water with the addition of a low amount of substances that are common in natural water. For example, 0.001 M calcium chloride is prescribed in the leaching test for soil base to ISO / DIS 21268-1. The leaching measured could be higher when e.g. calcium chloride ($CaCl_2$) has been added to the leached solution, compared to water, for these two reasons:

a.   Cations such as Calcium (Ca^{2+}) can compete with heavy metal ions on the surface of the soil particle.

b.   Anion such as Chloride (Cl^-) can form complexes with metal ions and increase their solubility. (Elert m fl. 2006)

c.   The $CaCl_2$ extract generally results in lower pH, which can cause a higher solubility of cationic metals.

Generally, the K_d value expresses the binding strength of a substance. A low K_d value indicates a high risk of leaching to groundwater sources. A high K_d value indicated that a substance is strongly bound to soil particles and as a result, there is little leaching. Clay content, pH, TOC are factors that affect the K_d value. In his study, a high pH value and clay content were observed in all of the soil samples. The increase of the K_d value agreed with the increase of pH. In some cases, Co may be precipitated as $CoCO_3$ (Bangash et al. 1992), although there are no such indications in the current study.

It is interesting to note that all soil samples of this thesis had a high K_d value. This result may be explained by the fact that Co and Ni were strongly bound to soil particles leading to low leaching risk for both Fyrislund and Kvarngärdesskolan. In

this case, the guideline value was recalculated based on the leaching test K_d values. The result indicated the site-specific guideline value for sensitive land use (KM) changed and being higher than generic guideline value, see Table 6.

In this thesis, the $CaCl_2$-extracted concentration had a negative correlation with the pH. This means by increasing the pH, the extracted concentration decreased.
TOC, on the other hand, had a positive correlation. In another word, by increasing the TOC the dissolved concentration increased. The distribution coefficient (K_d) value showed a positive correlation with pH in the studied soil sample. pH is one of the key factors to control the mobility of both Co and Ni. Both elements are easily soluble at low pH, however, both elements are strongly bound to soil/surface particles at high pH (Berggren et al. 2006). This fact confirms the result of HNO_3 extraction as well.
The other interesting point is the partition coefficient called K_{acc}. K_{acc} and K_d in soil samples are 4-5 (log value) showing that both the extraction methods have the same result. It is worth noting that mobilization is relatively low into surface and groundwater.

5.4. Risk assessment

An initial objective of the risk assessment was to evaluate the risk to soil ecosystem. In this thesis risk assessment has shown based on the combination of different biological and chemical factors. In this method, the total metal concentration in the contaminated soil is compared with generic guideline values. Although the total metal concentration is a key indicator for risk assessment there is uncertainty in risk assessment for the soil ecosystem. A high concentration is an indicator of risk, but it need not be a serious risk for the soil ecosystem if the bioavailability of contaminants is lower than in the generic scenario.
Site-specific guideline values for sensitive land use (KM) were higher than generic guideline value, due to the high K_d value. The result of this risk assessment did not show any significant difference to less sensitive land used (MKM). However, the same result observed at both the Fyrislund and Kvarngärdesskolan projects. Risk assessment with Threshold calculator covers three trophic levels for ecotoxicological risk assessment. An initial requirement for this assessment is: effect concentration is 10% which means that 10% of organisms show a response based on the ecotoxicological aspect.

The threshold based on the specific soil condition HC_{25} and HC_{50} of EC_{10} was slightly higher at Kvarngärdesskolan. The clay content at this site was higher than 40%, higher than at Fyrislund. The CEC is the other parameter that control the threshold value.

The TOC value is another factor that influences the thresholds of Co and Ni. But in our samples, the TOC concentration was not high except for BG20001 at the Fyrislund project. The system can resist negative effects better with a high clay content, TOC, and pH.

What is surprising is that by combination of SEPA and Threshold calculator risk assessment's result for this thesis, the protection of health value was introduced as a new guideline value for sensitive land use (KM). Regarding the less sensitive land use (MKM), there was no difference observed about protection objects and still governing for guideline value is the protection of the soil environment, although the actual guideline values increased.

Finally, the critical protection object for the soil samples studied under this thesis may be the health risk concerning sensitive land use (KM) and the soil environment for less sensitive land use (MKM). These conclusions are based on a combination of the Threshold calculator and the SEPA risk assessment tool.

6. Conclusion

The purpose of the current thesis was to determine the concentrations of Co and Ni in the Uppsala clay deposit, especially in the Uppsala county. Two main goals of current study were to study the solubility and risk of this Co and Ni. Soil samples were investigated at two locations, Fyrislund and Gränby (Kvarngärdesskolan), extracting 3 soil samples from each site. Basic soil properties were analysed. The pH value in $CaCl_2$ solution was about 7. The total organic carbon varied between 0.5 and 1.97 %, and the clay content was relatively high at both locations.

This study showed that the total Co concentration was slightly higher than the SEPA generic guideline value at Fyrislund, whereas Ni was slightly lower. For Kvarngärdesskolan, the total Co had the same value as the SEPA generic guideline, whereas Ni was lower.

Extraction with HNO_3 confirmed that both Co and Ni are strongly geochemically active. The extractability was high for Co, and for Ni it was slightly lower but still rather high. The result shows that the adsorption of both Co and Ni to soil particles was strong.

Extraction with $CaCl_2$ indicated low risk of leaching of both Co and Ni and a high K_d value. The high K_d value was used to calculate a site-specific guideline value calculated with the SEPA risk assessment tool. For the KM scenario, the site-specific guideline value became higher than the generic guideline value.

Risk assessment was carried out with two different tools. One using the SEPA risk assessment tool to identify different risk objects, and the second one was the Threshold calculator. The result of the latter showed that high clay content and high CEC value increased the effective concentration. However, the Threshold calculator only calculates the ecotoxicological risk to protect the soil environment.

Combining both risk assessment tools led me to identify the health risk as a governing protection object for sensitive land use (KM), whereas protection of soil environment was still more important for less sensitive land use (MKM), although in both cases significantly higher guideline values were obtained compared to when using the SEPA risk assessment tool only.

These findings provide the following recommendations for further research in order to evaluate of Co and Ni behaviour in the soil:

- Collect more data to understand the concentration of Co and Ni in the clay.
- Investigate additional samples to define the type of clay with a high concentration of Co and Ni.
- Study more closely the effects of soil properties e.g. pH, clay content, TOC, and CEC to understand the role of these factors for the mobility of Co and Ni.

7. References

Albanese, S. Sadeghi, M, Lima, A, Cicchella, D. Dinelli, E. Valera, P. Falconi, M. Demetriades, A. De Vivo, B. (2015). *GEMAS: Cobalt, Cr, Cu, and Ni distribution in agricultural and grazing land soil of Europe*. Journal of Geochemical Exploration, 154:81-93, https://doi.org/10.1016/j.gexplo.2015.01.004

ALS Environmental UK Ltd (2020). Heavy metal guidelines in soil. Technical data sheet. WWW: als_cl_heavy-metals-guidelines-in-soil_uk_feb_17_v2.pdf (alsenvironmental.co.uk)

Andersson, M. Carlsson, M. Ladenberger, A. Morris, G. Sadeghi, M. Uhlbäck, J. (2014). *Geochemical atlas of Sweden*. Geological Survey of Sweden, https://www.sgu.se/en/arkiv/arkiv-mineralnaring/mineral-resources-old/geochemical-mapping/geochemical-atlas/

Arvidsson, S. Berg, Å. Backman, C.M. Åkerhammar, P. Ålinder, C. (2007). *Mineralmarknaden. Tema: Nickel*. (Per.publ.2007:1). Sveriges geologiska undersökning, http://resource.sgu.se/produkter/pp/pp2007-1-rapport.pdf.

Bangash, M.A. Hanif, J. Ali Khan, M. (1992). *Sorption Behavior of Cobalt on Illitic Soil.* Waste Management, 12:29-38, https://doi.org/10.1016/0956-053X(92)90006-5

Barceloux, D.G., Barceloux, D. (1999). *Nickel*. Journal of Toxicology: Clinical Toxicology, 37:2, 239-258, http://doi.org/10.1081/CLT-100102423

Berggren, D. Elert, M. Gustafsson, J.P. Jarvis, N. Norrström, A.C. (2006). *Metallers mobilitet i Mark*. (Rapport 5535. April 2006). Naturvårdsverket, https://www.naturvardsverket.se/Om-Naturvardsverket/Publikationer/ISBN/5500/91-620-5536-4/

Elert, M. Fanger, G. Höglund, L.O. Jones, C. Kemakta Konsult AB. Suer, P. Wadstein, E. (2006). *Laktester för riskbedömning av förorenade områden*. Huvudrapport och underlagsrapport 1a, Rapport 5535. Naturvårdsverket, https://www.naturvardsverket.se/Documents/publikationer/620-5535-6.pdf

Eriksson, J. Dahlin, S. Nilsson, I. & Simonsson, M. 2011. *Marklära*. 1:1 ed. Lund: Studentlitteratur.

European Environmental Agency (EEA). (2010). *The European environment: state and outlook 2010-soil*. Copenhagen: EEA.

Giraldo, J.P.S. (2018). *Application of the Geochemical Fractionation of Metals in Sediments for Environmental Analysis of a Water Reservoir*. Case Riogrande Ii (Antioquia - Colombia). http://dx.doi.org/10.5772/intechopen.76223

Gustafsson, J.P. Pechova, P. Berggren, D. (2003). *Modeling Metal Binding to Soils: The Role of Natural Organic Matter*. Environmental Science and Technology, 37:2767–2774, https://doi.org/10.1021/es026249t

Gustafsson, J.P., Elert, M., Kleja, D.B, Jarvis,N. (2007). *Modeller för spridning av metaller från mark till vatten*. Naturvårdsverket. Rapport 5741, https://www.naturvardsverket.se/Om-Naturvardsverket/Publikationer/ISBN/5700/91-620-5741-3/

Hamnér, K. Eriksson, J. Kirchmann, H. (2013). *Nickel in Swedish soils and cereal grain in relation to soil properties. fertilization and seed quality*. Acta Agriculturae Scandinavica. Section B - Soil & Plant Science. 63(8):712-722, http://doi.org/10.1080/09064710.2013.861507

Kjellin, J. (2004*). XRF-analysis of contaminated soil - a study of error sources and suitable sample preparation*. Uppsala University. Department of Earth science, http://uu.diva-portal.org/smash/get/diva2:159223/FULLTEXT01.pdf

Krupka, K.M. Serne, R.J. (2002). *Geochemical Factors Affecting the Behavior of Antimony. Cobalt. Europium. Technetium and Uranium in Vadose Sediments*. Pacific Northwest National Laboratory, https://doi.org/10.2172/15004491.

Lange, B et al. 2016. *Copper and cobalt mobility in soil and accumulation in a metallophyte as influenced by experimental manipulation of soil chemical factors*. Chemosphere 146:75-84, https://doi.org/10.1016/j.chemosphere.2015.11.105

Lee, S-H. Park, H. Koo, N. Hyun, S. Hwang, A. (2011). *Evaluation of the effectiveness of various amendments on trace metals stabilization by chemical and biological methods*. Journal of Hazardous Materials 188:44 - 51, https://doi.org/10.1016/j.jhazmat.2011.01.046

Luo. L, Ma, Y.B. Zhang, S.Z. Wei, D.P. Zhu, Y.G. (2009). *An inventory of heavy metal inputs to agricultural soils in China*. Journal of Environmental Management 90:2524-2530, https://doi.org/10.1016/j.jenvman.2009.01.011

Länsstyrelsens Meddelandeserie. Miljöskyddsenheten. (2017). *Regionalt program för arbetet med förorenade områden i Uppsala Län 2018–2020*, https://www.lansstyrelsen.se/uppsala/tjanster/publikationer/regionalt-program-for-arbetet-med-fororenade-omraden-i-uppsala-lan-2018-2020.html.

Ma, Y. Hooda, P.S. (2010). Chromium. Nickel and Cobalt. In: Trace elements in soils (ed. P.S. Hooda), pp. 461-479, Wiley, https://doi.org/10.1002/9781444319477.ch19

Marsz, A.M. (2014). *Remediation of metal contaminated soils- Evaluation of long-term effect of zero-valent iron amendments*. SLU. Master's thesis. Department of Soil and Environment, https://stud.epsilon.slu.se/6509/

McGrath, S.P. (1995) Chromium and nickel; in: B.J. Alloway (ed.). *Heavy Metals in Soil.* 2nd edn; Blackie Academic & Professional. London. Chapter 7, pp. 152–178.

Naturvårdsverket. (2009). *Riktvärden för förorenad mark. Modellbeskrivning och vägledning*. Rapport 5976, https://www.naturvardsverket.se/978-91-620-5976-7

Nicholson, F.A. Smith, S.R. Alloway, B.J. Carlton-Smith, C. Chambers, B.J. (2003). *An inventory of heavy metals inputs to agricultural soils in England and Wales*. Science of the Total Environment 311:205–219, https://doi.org/10.1016/S0048-9697(03)00139-6

Nyhlén, E. (2004). *Laktester för riskbedömning av förorenad mark*. SLU. Examensarbete. Institutionen för mark och miljö, https://stud.epsilon.slu.se/11850/

Oorts, K. (2018). *Threshold calculation for metals in Soil. A global tool for terrestrial risk assessment*. Background Document for version 2.0. ARCHE Counsulting. WWW.Arche-consulting.be

Pierzynski, G.M. Sims, J.T. Vance, G.F. (2005). *Soils and environmental quality*. 3rd ed. Boca Raton: CRC Press.

Pourret, O. Faucon, M-P. (2017). Cobalt. In: W.M. White(ed), *Encyclopedia of Geochemistry*, https://doi.org/10.1007/978-3-319-39193-9_271-2

Senesi, G.S. Baldassarre, G. Senesi, N. Radina, B. (1999). *Trace element input into soils by anthropogenic activities and implications for human health*. Chemosphere 39:343–377, https://doi.org/10.1016/S0045-6535(99)00115-0

Siebecker, M. Sparks, D-L. (2010). *Nickel Speciation in Serpentine Soils using Synchrotron Radiation Techniques*. 19th World Congress of Soil Science. Soil solution for a Changing world. Department of Plant and Soil Sciences and Delaware Environment Institute. Newark. DE. USA. 1-6 August 2010. Brisbane. Australia, http://www1.udel.edu/soilchem/Siebecker2010WCSSAbs.pdf

Staunton, S. (2004). *Sensitivity analysis of the distribution coefficient, K_d, of nickel with changing soil chemical properties.* Geoderma, 122:281-290, https://doi.org/10.1016/j.geoderma.2004.01.014

Swedish Geotechnical Institute (SGI). (2018). *Förorenade Områden.* Available at : https://www.swedgeo.se/sv/vagledning-i-arbetet/fororenade-omraden/ (2020.05.26)

Tashakor, M. Wan Yaacob, W.Z. Mohammad, H. (2011). *Speciation and Availability of Cr, Ni and Co in Serpentine Soils of Ranau. Sabah.* Current Research in Geoscience 2(1):4-9, https://doi.org/10.3844/ajgsp.2011.4.9

Tinnerberg, H., Tekavec,V., Jakobsson, K. (2009) *Exponeringsbedömning av förorenande mark i området Rydöbruk. Hylte Kommun. Halland*. Rapport from Arbets- och miljömedicin, Universitetssjukhuset, Lund, https://sodrasjukvardsregionen.se/download/exponeringsbedomning-av-fororenad-mark-i-omradet-rydobruk-hylte-kommun-halland/

Thakali, S., Herbert, E.A., Di Toro, D.M. et al. (2006) *A terrestrial biotic ligand model. 1. Development and application to Cu and Ni toxicities to barley root elongation in soils*. Environmental Science and Technology 40:7085–7093, https://doi.org/10.1021/es061171s

Thakali, S., Herbert, E.A., Di Toro, D.M. et al. (2006) *A terrestrial biotic ligand model. 2. Application to Ni and Cu toxicities to plants. invertebrates. and microbes in soil;* Environmental Science and Technology 40:7094–7100, https://doi.org/10.1021/es061173c

Thygesen, N., Larsen, F., Hjelmar, O. 1992. *Risikoscreening ved nyttiggörelse og deponering af slagger*. Miljøprojekt nr. 203. Vandkvalitetsinstitutet, ATV, Danmark.

Toth, G., Hermann, T., Da Silva, M.R., Montanarella, L. (2016). *Heavy metals in Agricultural soils of the European Union with implications for food safety*. Environment International 88:299-309, https://doi.org/10.1016/j.envint.2015.12.017

U.S. Department of Health and Human Services. (2005). *Toxicological profiler for Nickel.* Public Health Service. Agency for Toxic Substances and Disease Registry. 25th April 2020. https://www.atsdr.cdc.gov/toxprofiles/tp15.pdf

Yang, X., Xiong, B., Yang, M. (2011). *Relationship among heavy metals and organic matter in sediment Cores from lake Nanhu, an urban lake in Wuhan, China.* Journal of Freshwater Ecology 25:243-249, https://doi.org/10.1080/02705060.2010.9665074

Wuana, R.A., Okieimen, F.E. (2011). *Heavy metals in contaminated soils: A review of sources, chemistry, risk and best available strategies for remediation*. International Scholarly Research Notices, 402647, https://doi.org/10.5402/2011/402647

Zakir, H.M., Shikazono, N. (2011). *Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river.* Journal of Environmental Chemistry and Ecotoxicology 3:116-126, https://academicjournals.org/journal/JECE/article-full-text-pdf/971BDF61644