

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES



ATMOSPHERIC METAL DEPOSITION IN SUBARCTIC NORWAY BASED ON  
PEAT BOG CORES

DIPLOMA THESIS

FRANK BOAHEN

SUPERVISOR OF THE THESIS: Ing. Hana Šillerová, Ph.D.

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## DIPLOMA THESIS ASSIGNMENT

B.Sc. Frank Boahen

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Thesis title

**Study of atmospheric metal deposition in subarctic Norway based on peat bog cores**

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### Objectives of thesis

The main objective of the thesis is to determine the concentration of selected metal(loid)s (As, Cd, Cr, Cu, Ni, Pb, Zn etc.) and also Pb isotope composition in two peat cores from Northern Norway in order to study differences in the metals concentration with respect to the depth and distance from the Russian Ni-ore smelter. Moreover the Pb isotope analysis will provide an information on the origin of this metal in the local environment.

### Methodology

The sampling of the peat cores will be realized in August 2016. The samples will be transported to the laboratory in Prague, dried, homogenized and decomposed totally in a mixture of acids (HNO<sub>3</sub>, HCl, HF). The liquid samples will be filtered (0.45µm) and analysed for a selected metal content (Ni, Cu, Zn, Cr, Pb, etc.) by Mass Spectrometry with Inductively Coupled Plasma (ICP-MS). Obtained data will be evaluated with respect to the metal concentration, distance of each sampling site from the Ni-ore smelter and depth of the peat core. Pb isotope composition will be compared with the isotope composition of potential sources.

## The proposed extent of the thesis

60

## Keywords

peat, Norway, lead, isotopes

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## Recommended information sources

Reimann, C., de Caritat, P., Niskavaara, H., et al., 1998. *Geoderma* 84, 65-87.  
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Souter, L., Watmough, S.A., 2016. *Sci. Tot. Environ.* 541, 1031-1040.

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## The Diploma Thesis Supervisor

Ing. Hana Šillerová, Ph.D.

## Supervising department

Department of Environmental Geosciences

## Advisor of thesis

Ing. Anna Kunčíková

Electronic approval: 12. 4. 2017

**prof. RNDr. Michael Komárek, Ph.D.**

Head of department

Electronic approval: 12. 4. 2017

**prof. RNDr. Vladimír Bejček, CSc.**

Dean

Prague on 18. 04. 2017

## DECLARATION

I hereby declare that the present Diploma Thesis entitled “Atmospheric metal deposition in subarctic Norway based on peat bog cores” is my own work and the literature and other sources, which I used, are stated list of references which are attached to this work.

In Prague, 18<sup>th</sup> of April 2017

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Frank Boahen

## ABSTRACT

The subarctic Norway- Russia area is known to be contaminated with metals and metalloids due to emissions from mining and metallurgical industry in Russia. Peat core from ombrotrophic bogs provide information on atmospheric metals and metalloids deposition, since they are exclusively fed by atmospheric inputs. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentration of selected elements (Cd, Cr, Cu, Ni, Pb, Zn and As) and Pb isotope composition ( $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) in peat core from 3 ombrotrophic bogs in Norway close to the Russia border. Measured average concentrations of Cu, Cr, Ni, Zn and As were higher in comparison with Norwegian pollution control authority report 1999 threshold values, however Pb and Cd concentrations were below that of the Norwegian authority threshold value on soil quality. From Pb isotope analysis, combustion of gasoline from Norway and Russia were identified as major source of Pb pollution in the area.

Keywords: Peat, Pb isotope, metal contamination, source of Pb.

## ABSTRAKT

Oblast na pomezí Norska a Ruska je známa díky relativně vysoké kontaminaci kovy a polokovy, pocházejícími z těžby a zpracování rudy a z hutního průmyslu na ruské straně. Rašelina z mokřadů poskytuje velmi přesnou informaci o znečištění ovzduší a depozici kovů a polokovů v průběhu času. A to díky tomu, že jediným zdrojem kovů v ombrotrofních rašelinách je atmosferický spad. Hmotnostní spektrometrie s indukčně vázaným plazmatem (ICP-MS) byla použita ke stanovení koncentrace vybraných prvků (Cd, Cr, Cu, Ni, Pb, Zn a As) a zároveň k stanovení izotopových poměrů Pb ( $^{206}\text{Pb}/^{207}\text{Pb}$  a  $^{208}\text{Pb}/^{206}\text{Pb}$ ) k určení zdroje znečištění olovem v rašelině ze 3 norských ombrotrofických mokřadů v blízkosti ruských hranic. Oproti norské zprávě o úrovni znečištění z roku 1999 jsme zaznamenali nárůst koncentrace Cu, Cr, Ni, Zn a As, nicméně koncentrace Pb a Cd byla nižší oproti norskému povolenému limitu pro tyto prvky v půdě. Z izotopových poměrů olova bylo určeno jako největší zdroj znečištění dané oblasti spalování benzínu v obou zemích.

**Klíčová slova:** Rašelina, izotopy olova, znečištění kovy, zdroj Pb.

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## 1. INTRODUCTION

Anthropogenic activities like mining and smelting have adverse effects on the environment through the accumulation of metals and metalloids such as Pb, Zn, and As (Vanek et al., 2005). These metals and metalloids released can have a negative impact on human health due to their toxicity and/or carcinogenicity, persistent and bioaccumulation characteristics (Pacyna and Pacyna, 2001). Anthropogenic activities are known to have increased the local, regional and world fluxes of metals and metalloids to the atmosphere. This situation has caused governments worldwide to agree on a legally enforce policy document such as Convention on Long-range Transboundary Air Pollution, instituted by the United Nations Economic Commission for Europe with the aim of controlling metals and metalloids emissions ( Ilyin et al., 2013). Significant fraction of metals and metalloids emitted into the atmosphere are often transported long range, deposited by precipitation or as aerosols, and stored in either aquatic or terrestrial ecosystems (Bao et al., 2015). In this regard, regular monitoring of atmospheric metal deposition has become very necessary with basic importance of assessing air pollution and its adverse effects on the aquatic and terrestrial ecosystems, and related risk on human health (Meyer et al., 2015, Steinnes et al., 2011).

The subarctic Norwegian-Russian border area is contaminated with metals (especially Ni and Cu) and SO<sub>2</sub> mainly due to high emissions from three nickel smelting industries at towns of Nikel, Monchegorsk and Zapolyarny in the north-west Russia (Reimann et al., 2001). Additionally, the researchers stated these Russian smelters are the world's largest point source of SO<sub>2</sub> and metal emissions (Reimann et al., 2001). The nickel smelting industry has resulted in severe damage to the terrestrial ecosystem from air pollution as revealed by satellite imagery, covering an area of 5000 km<sup>2</sup> in 1988. These smelters accounted for 300000 t SO<sub>2</sub>, 1900 t of Ni, 1100 t Cu and 94 t of V<sub>2</sub>O<sub>5</sub> emissions yearly (De Caritat et al., 2001, Lappalainen et al., 2007). On the other hand, at the Norway side close to Russia border, the smelting activity from iron ore mine at Bjornevatn and iron mill at Kirkenes are known to be minor sources of atmospheric pollution (De Caritat et al., 2001). High levels of Cr in terrestrial moss around the vicinity of Kirkenes have also been reported (Ayras et al., 1997).

Peat bogs are ecosystems, which receive all chemical constituents from direct deposition from the atmosphere or through uptake from the atmosphere by vegetation. As a result, records on peat bogs provide essential information on atmospheric deposition of metal and metalloids (Bao et al., 2015). Hence in this thesis, chemical composition analysis of peat core samples will reflect atmospheric input/deposition in the studied area.

The main aims of this thesis work is to use Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) firstly to determine the concentration of selected metals and metalloids (Ni, Cu, Zn, Cr, As, Cd, Pb etc.) in peat core samples at 3 different sites from Norway close to the Russia border, and secondly apply Pb stable isotope composition analysis to trace sources of the metal pollution.

## **2. AIMS OF THE THESIS**

The main aims of this thesis are the use of ICP-MS:

- (a) To determine the concentrations of selected metals(loid)s ( Ni, Cd, As, Cu, Zn, Cr, Pb etc.) in peat core samples to assess the extent of metal pollution in 3 different sampling sites at Norway, close to the Russia border
- (b) For Pb stable isotope composition analysis to trace the source of metal pollution.

### **3. LITERATURE REVIEW**

#### **3.1 Peatland and types**

Peat consists of an accumulated dead organic material formed in situ (formed in the original place without any transport) under waterlogged conditions (Schumann and Joosten, 2008). The organic material is derived from mosses of genus *Sphagnum* and several other non-moss species (Joosten and Clarke, 2002). The *Sphagnum* derived peat are found in arctic, subarctic and boreal regions, whilst reed/sedge peat and forest peat are found in temperate regions, through to mangrove and swamp forest peat in the humid tropics ( Montanarella et al., 2006). Peatlands can be divided into two broad types, namely, fens and bogs, a classification which is based on genesis, vegetation and hydrological functioning (Blais et al., 2015., Rausch, 2005).

The fens which are also referred to as minerotrophic peatlands have their mineral composition fed by waters percolating through mineral soils (Rausch, 2005). According to Komarek et al. (2008), the fens are not only fed by atmospheric precipitation, but as well from groundwater, hence disrupting the continuity of the atmospheric deposition.

Bogs or ombrotrophic peatlands have their surface vegetation exclusively nourished by nutrients from wet and dry deposition from the atmosphere, since they are isolated from the groundwater and surface runoff (Pratte et al., 2013). For this reason, bogs are useful indicators for valuable information pertaining to atmospheric inputs of metals and metalloids. Most of the metals deposited on the peat bogs are assumed to be sequestered by the living or organic matter which are immobile, thus providing a reliable information on the changing deposition and also the contents of elements in the air ( Bao et al., 2012).

#### **3.2 Metal retention and biogeochemistry of bogs**

Bogs have been used by researchers to study the atmospheric metal pollution records because they are exclusively fed by atmospheric inputs. As a result they have advantage of recording more directly the atmospheric deposition than other continental archives like lake sediments. But they have similar atmospheric record potential to ice

cores, but bogs have principally two advantages. The first one is, bogs are more wide spread geographically and the second advantage been that they are easier to access and sample (Blais et al., 2015). Because bogs have poor nutrient conditions, in the northern hemisphere, their vegetation is dominated by *Sphagnum* species and other bryophytes. Because these plants lack roots, metal uptake is only through atmospheric deposition. Additionally, the *Sphagnum* mosses have imbricate leaves, spirally arranged at branches to provide large surface area to intercept/trap metals from the atmosphere. These leaves are one cell thick with hyaline cell to provide high cation exchange capacity sites for strong binding of metals. During decomposition the fraction of metal binding humic substances increase. Humic substances have good metal binding capacities (Blais et al., 2015, Rausch, 2005). As a major constituent of organic matter, humic substances possess acid functional groups of high degree of heterogeneity in proton dissociation which results in high specific adsorption potential for dissolved solids such as metals and polar organic molecules. They bind to cations by both specific and non-specific (ion exchange) mechanisms. In addition, complexation, surface adsorption and chemisorption are other means the peat takes up metals. Complexation occurs either by inner sphere complex formation (chelation) or outer sphere complex formation (the inner hydration sphere is retained and electrostatically ions are bound together) (Lofts et al., 2002, Brown et al., 2000). Humic carboxylic -COOH and phenolic -OH groups are greatly behind humic-metal complexes formation. The strength of metal-humic complexes depends on the pH of the bog water, ionic strength, and affinity of metal ions to bind the functional groups present in the peat (Boruvka and Drabek, 2004. Silamikele et al., 2011).

Lead (Pb) is known to be immobile in bogs from studies on stable and radioactive Pb isotopes (Allan et al., 2013). However, some studies have shown that Pb concentration is affected by diagenetic remobilization and distribution processes especially in saturated peat (Allan et al., 2013). Zinc is very often accompanied by Pb in sulphide minerals (including galena) and coals. Contrary to Pb, Zn exhibits different behaviour in bogs. That is, it can be mobile as a result of bioaccumulation, redistribution by plants and pH conditions (Allan et al., 2013). From Rausch et al. (2005), Cd is mobile in peat cores from Finnish bogs, and that Cd is affected by post depositional processes, meanwhile Co was immobile.

According to Scouter and Watmough, (2005), some studies have concluded that metals are not retained equally because of various speculative processes occurring in the peatland. Such speculative factors as decomposition rates and variations in vegetation type can determine the suitability of peat cores as far as their use as environmental archives is concern. From the authors, some studies findings have also shown that, rapid downwash and smearing of contaminants after deposition by rain is a phenomenon that can occur on the surface layers, and the effect is stronger on Zn and Ni as compared to Pb and Cu. Also the behaviour of metals such as Cu, Ni and Co in peat cannot be generalised, further more metal mobility varies among peatlands.

Acrotelm (surface layer) and catotelm (underlying layer) are two layers in bogs, each with distinct physicochemical and biological characteristics. The acrotelm is relatively biologically active, aerated with high hydraulic conductivity. On the other hand, the underlying layer possesses low biological activity coupled with permanent anaerobic condition as well as low hydraulic conductivity. The water table in bogs are found above the catotelm. Atmospheric deposition (wet and dry) containing metals are taken up by living moss above the high water table. Excess water moves laterally through the acrotelm, elements are captured above the high water table due to the high binding capacity of moss. Conversely, with decomposition process, metals may be released from organic phase. Acidic conditions generated from the decomposition process are the cause of low pH of bog pore waters, leading to the increase in solubility of several metal compounds. However, inorganic precipitation can immobilize released metals. Electron activity (pE) regulates the oxidation state of solutes. It controls the speciation of dissolved metals and sulphur in peat waters. Metals are likely to precipitate as oxides, hydroxides or even sulphates in oxidation conditions above the water table, while those reduced are likely to precipitate as sulphides. Water table decline in peatlands in summer periods is known to influence metal release during the re-wetting periods. An increased metal mobility is as a result of oxidation of S stored in peat to sulphate, the sulphate is further converted to sulphuric acid during the re-wetting periods when exposed to air. (Benoit et al., 1998, Scouter and Watmough, 2015).

### **3.3 Bogs as continental archives of atmospheric inputs**

The extent of metals emission into the environment especially atmospheric fluxes has been assessed commonly through geological archives. Among the geological archives

used for the study of environmental changes (both natural and human influenced) is peat bogs (De Vleeschouwer et al., 2010). The peat bogs are known to store inputs from fluxes of another reservoir, mainly the atmosphere (Cortizas et al., 2002). The peat bogs are able to build up time record from the environmental changes. It is able to in some cases, well preserved the amount of element accumulated without post-depositional remobilisation (Cortizas et al., 2002). The records from peat bogs is closely linked to concentration variations of elements in the atmosphere resulting from significant climate changes, and anthropogenic emissions from mining and metallurgy (Cortizas et al., 2002). Theoretically, modelling from recorded data can be used to reconstruct original signal in case of post depositional occurrence, but that is when the post depositional process is understood. Peat bogs cover local, regional, global and temporal time scales (ranging from tens to thousands of years). They represent an ideal record keeping environmental material for understanding both natural and human influenced processes impacts on the ecosystem. Essentially, as continental geochemical archives, they have wider global distribution as compared to ice cores, as the two are the only archives with exclusive records on atmospheric deposition (Cortizas et al., 2002).

The European continent is a region that has contributed to greater fraction of atmospheric pollution globally in the past 50 years (De Vleeschouwer et al., 2010). The elevated levels of metal in atmosphere presently as compared to prehistoric levels have manifested in studies conducted in the northern hemisphere, particularly in Europe. The levels have increased due to anthropogenic activities principally from mining and metallurgical processes, transport emissions and later coal burning (Allan et al., 2013). Lead remains probably the most widely analysed metal in peat profiles, on the other hand, Ni, Cu, Zn, Hg, Co and Cd have also been analysed in peat profiles. Concentrations of these metals are deemed to reflect the historical changes of atmospheric deposition (Scouter and Watmough, 2016). Peat cores have been used to record Pb emissions in Europe (De Vleeschouwer et al., 2010). The use of Pb and other trace metal to determine archaeological problems using peat cores from bogs has become an important tool to providing a detailed and reliable means of chronology of metal pollution, in situations where other means like archaeological and historical evidences are deficient or insufficient (De Vleeschouwer et al., 2010). Studies on peat bogs in Europe have provided results of Pb contamination, which reflect the historical

records of lead sulphide mining (De Vleeschouwer et al., 2010). As an example, Pb mining in Iberian Peninsula more than three thousand years ago has been determined in Swiss bog, also Pb and antimony (Sb) atmospheric pollution from the Roman period has been documented from peat in Faroe Islands. Peat core from Lindow bog in Manchester, United Kingdom was used as archive of paleo-pollution and archaeology (De Vleeschouwer et al., 2010). Concentration, enrichment factors and isotope composition analysis have showed that atmospheric Pb pollution started 3500 -3000 years back, reflecting the beginning of Phoenicians trading in ternary leaded-bronze in southern Spain (Cortizas et al., 2002) . This has been observed by data in ombrotrophic peat bogs and lake sediments in Sweden, Scotland, Switzerland and Spain. The records reflected a combination of global, regional and local situations. In Sweden and Scotland, the medieval period is seen as the cradle of atmospheric lead pollution. Further, it is recorded that atmospheric pollution began in Scotland compared to Eastern Canada. Also in Loch Ness, a decrease in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio by 1170-1230 AD ( in the year of our Lord) is seen as direct relation to medieval mining and smelting in mainland Europe, while in recent times, high values is recorded in areas close to heavily populated and industrialized (Cortizas et al., 2002). Pollution in Sweden has been traced to continental Europe and British Islands. The north-south gradient at least for the last 2000 years is attributed to atmospheric circulation promoting long-range transport of pollutants (Cortizas et al., 2002).

In Germany, peat bogs from the Harz Mountains recorded highest Pb concentrations in samples from medieval times, as a reflection of local mining (Weiss et al., 1999). In addition, the decreased in lead emissions during Roman Empire and its increase from the beginning of the industrial revolution in the nineteenth century is clearly evident in peat bog deposits in Sweden, United Kingdom, Switzerland and the Netherlands (Weiss et al., 1999). Lead historical reconstruction using peat core from bogs and also from lake sediments has combined concentration measurements, enrichments factors and isotope composition of the deposited lead, from different locations. Interpretation of results from concentration analysis is hindered by changes in matrix properties (ash content, mineral phases present, bulk density, etc.) and in such instance, quantification of both natural and human influenced activities cannot be directly determined from the concentration variations. A solution to this is to calculate the enrichment factors by normalizing the Pb to conservative element ratios of the



individual samples to Pb to conservative element of a reference. Conservative element refers to Al, Ti, Zr, and Sc that accounts for natural variations. But this technique has been identified to have its limitations. This is because assumption that a homogeneous background of Pb to conservative element ratio is not always the case (Cortizas et al., 2002). More recently, isotope composition analysis of accumulated Pb is employed to determine enrichment as well as sources of Pb pollution (Cortizas et al., 2002).

### **3.4 The adverse impacts of smelting activity on the environment globally**

Metallurgical processes negatively affect the environment. This is because they result in the release of heavy metals which accumulate in soils in the vicinity of the processing industries (Vanek et al., 2005). These heavy metals are ubiquitous, toxic and persistence with significant risk to humans and ecosystem (Luo et al., 2015).

Over the last two decades, significant progress have been made to assign the major sources of anthropogenic activities that lead to the release of trace metals such as Cd, Pb, Hg into the environment in Europe and other parts of the world. High temperature processes, like coal and oil combustion in electric power stations together with heat and industrial plants, gasoline combustion, roasting and smelting of ores in non-ferrous metals smelters, melting operations in ferrous foundries etc. have been identified as causes of emission of trace metals into the atmosphere, the aquatic and terrestrial ecosystems. In effect, each industrial activity mentioned above, release one or more trace metal into the ecosystem. First annual quantitative determination globally of 16 trace metals emission from industry was conducted in the beginning of 1980, on air, soil and water samples. Major source of atmospheric emission of metals such as As, Cd, Cu, In, Sb, Zn, Pb, Se was from pyrometallurgical process in the primary non-ferrous metals industries. Additionally, from results in mid 1990s obtained on worldwide emissions of trace metals from major anthropogenic sources into the atmosphere indicated, non-ferrous metal production as the third source of trace metals. From the estimation, As (60%), Cd (73%), In (100%) and Zn (72%). Most of the trace metals are emitted as fine particles, while some are in gas phase, e.g. Hg and Se. These fine particles and gases can be carried by air masses for long distances such as 2000 Km (Pacyna and Pacyna, 2001).

Toxicological effects of metals emanating from the activity of a secondary Pb smelter, which has been in operation for over 200 years at Příbram, Czech Republic was found in three edible mushroom species (*Boletus edulis*, *Xerocomus badius*, *Xerocomus chrysenteron*). Pb isotope analysis has shown that the smelter is the principal cause of contamination of both forest and agricultural soils in the area. Concentration values of Pb and Cd recorded for all the three species of mushroom were higher than both Czech (Czech regulation 53, 2002) and European Union (EC Commission regulation 466/2001) limits. Pb recorded up to 165mg/kg and Cd up to 55 mg/kg, Se was up to 57mg/kg in *Boletus* while in *Xerocomus* Ag recorded up to 190mg/kg. Pb concentration in *Boletus* (widely consumed) was 17 times higher than the Czech limit and 55 times higher than the EU limit, while that of Cd was up to 28 times higher than both the Czech and EU limits (Komárek et al., 2007).

Similarly, a study conducted on a farmland located in the vicinity of a non-ferrous metal smelters at Baiyin of Gansu Province, China, indicated lead and cadmium poisoning in sheep and horses. Recorded concentration values in their blood, hair and tissues were higher than reference values (NRC, 1980) and in control animals. Also the concentrations of Pb, Cd, Zn, and Cu in soils, forages, feed and water were markedly higher than those in control areas (Liu, 2003).

Additionally, a research conducted at southeastern Missouri (USA) on accumulation of metals in three species of fish (*Camptostoma oligoleptis*, *Lepomis megalotis*, *Hypentelium nigricans*) collected from a downstream of active lead/ zinc mine and ore beneficiation indicated high levels of Pb in the blood and liver of all the three species (Schmitt et al., 2007).

According to Allert et al, 2009, Crayfish (*Orconectes hylas*) did not only have high metal accumulation but also decreased in density (lower survival) and lower biomass at mining sites than reference and downstream sites.

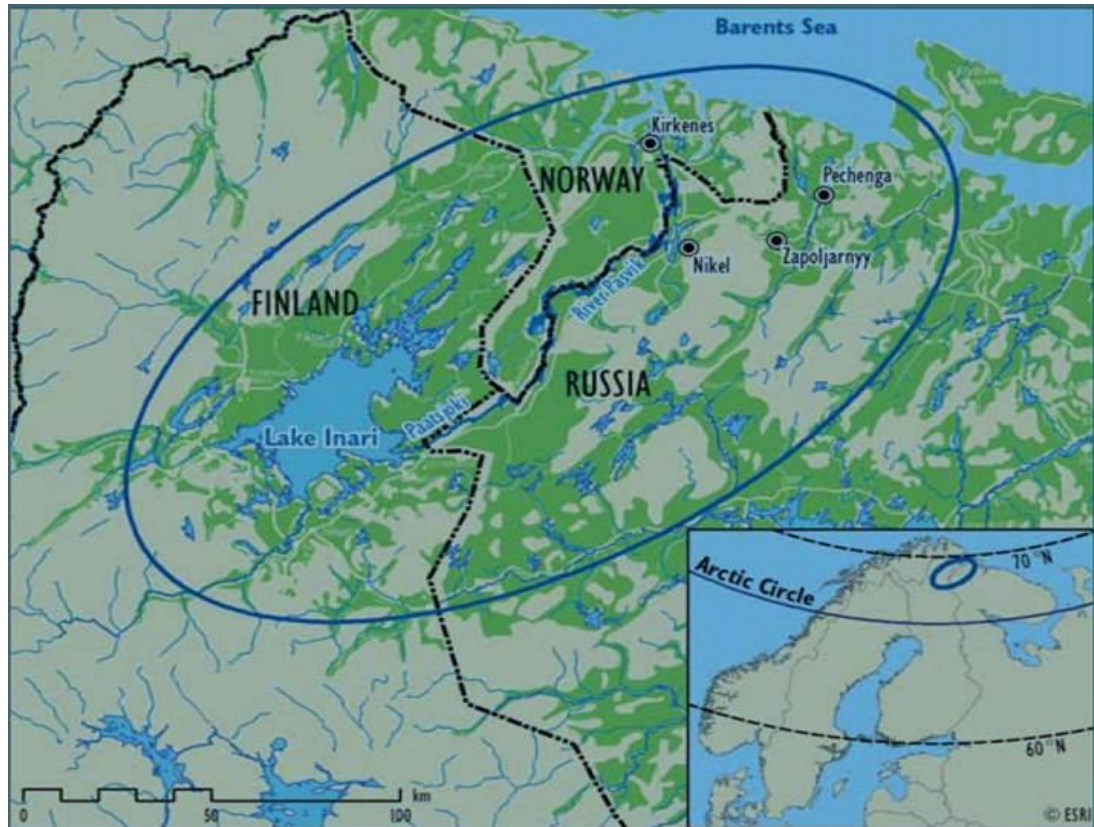
Water bodies around the vicinity of a lead/Zn smelter in the following areas in China, the junction of Yunnan, Guizhou and Sichuan provinces, West-central Hunan province, Central Guangxi province, northern Guangdong and the region of Liaoning province near Bohai were polluted from activities of the smelter. Research data indicated that concentration levels of heavy metals in water bodies have gone beyond

the water criteria V (GB 3838-2002, China). Major metals involved are Pb, Zn and Cd. The research also revealed that soils in proximity to the Pb/Zn smelter were significantly polluted by Pb, Cd, and to a smaller extent by Zn and Cu. The levels of these metals exceeded criteria III (GB 19618-1995, China). Most of these soils are no longer useful for agricultural purpose. Crops around the area have accumulated high levels of Cd, Pb and Zn. Rice had accumulated significantly Cd. Pollutants accumulated most in leaf vegetables followed by bulb vegetables, then root vegetables followed. Pb and Cd being the main pollutants are known to have caused high lead content in blood of children, arthralgia (pain in the joint) osteomalacia (softening of the bones) and excessive Cd in urine. Cd is an extremely toxic pollutant, as it is classified as 1B carcinogen. High levels of Pb in children can cause ataxia (loss of coordination of the muscles) coma, convulsions and even death (Zhang et al., 2012, ATSDR, 2010, 2012).

The activity, biomass, diversity and community composition of soil microorganisms were affected by a copper smelter in China. The experiment demonstrated long term effects from nearly 20 year heavy metal accumulation near a copper smelter. The findings reflected how heavy metals could affect the activity and community composition of soil microorganisms. The activity and community composition of soil microorganisms are closely related to soil fertility and environmental quality. Alkaline phosphatase (enzyme) activity in the soil was also greatly lower near the smelter. A direct correlation was observed between the enzyme activity and distance from the smelter. Significant decrease of enzymes were recorded in soils 200m away from the smelter. Also the findings of the research revealed, soil phosphatase activeness increased with decrease heavy metal content (Wang et al., 2007).

### 3.5 State of the environment in the vicinity of the Finland-Norway-Russia border area

#### 3.5.1. Description of the area



**Figure 1.** Finland-Norway-Russia border area, showing the locations of industrial activities (Sandanger et al., 2013).

It is an area consisting of north-western corner of the Euro-Siberian taiga, where it meets the barren, tundra coast of the Barents Sea. Although, there are several smaller rivers and lakes scattered in the upland forest and vegetation free mountainous areas, the river Pasvik (Pas) and lake Inari are the 2 main freshwater bodies dominating the area ( Sandanger et al., 2013). The climate of the area is sub-oceanic along the coast in the northern parts and in the southern parts it is continental. Annual mean temperature at Kirkenes is  $-2^{\circ}\text{C}$ ,  $-1.1^{\circ}\text{C}$  in areas around river Paz, and then it is between  $-1^{\circ}\text{C}$  and  $0^{\circ}\text{C}$  at Lake Inari (1971-2000). The climatic condition is determined by the Gulf Stream (Stebel et al., 2007).

The northern-western parts during summer are cool and winters mild, while the central parts have warm summers and cold winters usually. Easternmost areas have

climatic conditions similar to the central, but relatively cold winters (Reimann, et al., 2001). Several different natural vegetation zones are identified, it ranges from subarctic tundra along the coast in the north to subarctic birch forest through to boreal forest in the south (De Caritat et al., 2001).

Waterlogged areas have nutrient deficient bogs and ferns which are dominated by peat mosses (*Sphagnum spp*) dwarf shrubs, graminoids and also herbs such as *Betula nana*, sedges (*Carex spp*), cotton grasses (*Eriophorum spp*) and cloudberry (*Rubus chamaemorus*) (Stebel et al 2007). Precipitation is relatively low, with a long term annual average between 350mm and 450mm. The highest precipitation figures are in July and August, representing 60mm per month. In the winter, precipitation ranges between 20-30mm per month. The soil is usually covered by snow for (the yearly precipitation occur mostly in the form of snow) 7 months per year usually from middle of November to late May (Niskavaara et al., 1996, Stebel et al., 2007).

The prevailing wind direction in the area are to the north and north eastern towards the Barents Sea. That is the prevailing wind direction are from south to the north (Niskavaara et al., 1996, Reimann et al., 1996).

The geological composition of the area is complex, since it consists of different numerous bedrock types. There are numerous alkaline intrusions, the biggest ones are found in Russia (Khibiny and Lovozero) and east of Apatity. The different rock types have different trace element contents, as a result there are significant differences in the natural element composition in local dust (De caritat et al., 2001, Riemann et al., 2001).

Eastern parts of Norway, northern Finland, and the north-western parts of Russia consist of bedrock of over 1,900million years old granulite that extends from the western parts of the Kola Peninsula, through Finland into Norway. A large granite-gneiss complex consisting of granites, granodiorites, amphibolites, gneisses of different composition and a greenstone zone of volcanic origin extends from the Kola Peninsula through the northern Inari and eastern Utsjoki area, and expand further to Norway. Basaltic and komatitic vulcanites are the composition of the greenstone zones in each country. It comprises several ore deposits including the nickel ore deposit at Zapoljarnyi. Additionally, up to 1000 million year old sedimentary rocks such as sandstones and conglomerates are found in the northern parts of Norway and Russia.

Till is the dominant mineral soil in the area, having mineral formation that reflect the local bedrock. It has particle size ranging from boulder to clay fractions. An estimate of 10 percent of the surface area on the hill and fell tops is peatland. The peat bogs in the northern areas are made usually of aapa, palsa and hilltop bogs (Stebel et al., 2007).

### **3.6 Communities, job opportunities and impacts of industrial activities in the area.**

The area has 3 border municipalities of Pechenga in Russia, Sor-Varanger in Norway and Inari in Finland. The administrative towns of these municipalities are Nikel for Pechenga in Russia, Kirkenes for Sor-Varanger in Norway and Ivalo for Inari in Finland. The Russian municipality has the largest population with 45,100 inhabitants (2000 census), followed by Sor-Varanger with 9,500 and finally Inari with 7,120 inhabitants (2004 census). Sor-Varanger and Pechenga are primarily mining and metallurgy centres. Majority of the working population in Pechenga is employed by the Pechenganikel Ni-Cu industry. In Norway, Kirkenes and Bjoerbevann used to be the towns where the Iron mill and Iron mine were located respectively. However, industrial activities at the Norway end stopped in 1996. Presently, in Sor-Varanger, business activity is much diversified: ship repairing, harbour development, agriculture and commerce. Meanwhile, in comparison to most parts of Europe, the Finland part is almost pristine, since the human activities is limited to fishery, reindeer-herding and forestry (Niskavaara et al., 1996, Reimann et al., 2001, Stebel et al., 2007).

In effect the industrial activity is confined to the Norway-Russia border. The smelters located in Nikel and Zapoljarnji in Russia have been in operation since 1932 and 1955 respectively to process local ores. From 1971, Cu and Ni ores were processed from Norilsk in central Siberia, which had high content of sulphur. SO<sub>2</sub> emissions annually from the smelter was around 400 million kg in the late 1970s. In the beginning of 2000s emissions began to decline to 100-150 million kg annually. Apart from the sulphur deposition, heavy metals are also a threat to the environment especially Ni and Cu being the main metal pollutants in the area. 555 tonnes and 335 tonnes respectively were the highest annual Ni and Cu emissions in 1978. Not only SO<sub>2</sub> emissions have gone down, but as well heavy metals. In the beginning of 2000s, the annual Ni and Cu

emissions from the smelter in Russia was reported to be 350 and 180 tonnes respectively (Lappalainen et al., 2007).

Although annual SO<sub>2</sub> emissions from the smelter has decreased over the past 30 years, there is still instances where SO<sub>2</sub> concentrations have exceeded the Norwegian threshold values, for example, at Svanik and Karpdalen. Air concentrations of Ni, Cu and other toxic substances have not exceeded the European and Norwegian targets values, but on the contrary, concentrations of Ni, Cu, Co have increased considerably in other ecosystem after 2004 (Sandanger et al., 2013).

This increase is shown in freshwater systems in the area. In lakes Barsajarvi, St. Valvatnet and Langvatnet situated at Norway in the border area, water concentrations of Ni have increased from 2005. High to extreme high concentrations of Cu and Ni in lake sediments were recorded in 2010 study within distance 20km from the Russia smelters, also elevated levels of Pb, Co, Hg, As, Cd were recorded from the study. Ni, Cu, As and Hg recorded increasing concentrations from sub-surface to surface sediments in lakes at distances of 20-60km from the smelter. This is an indication of changes in atmospheric deposition in the nearby Norway areas (Rognerud et al., 2013).

2004-2006 regional lake survey showed a sharp elevated levels of Ni and Cu in the upper part of the sediment profile. Soil samples recorded elevated levels of metal concentrations within distance of 30-40 km from the smelters. Plants such as grasses and dwarfs shrubs had high heavy metal concentrations, a reflection of the accumulation of metals in the litter and organic layer of the soil. A Norwegian survey conducted from 1997-2010 showed a result of Ni and Cu increase within that period. Metal analysis conducted on edible berries on the Finnish-Russian and Norwegian border revealed elevated concentration values of Ni and Cu, significantly with highest levels determined near the smelters. Cloudberries from Sor-Varanger analysed in 2008 showed Cu, Ni, Cd and Mn were higher in the vicinities close to the smelter (Nikel) than far away areas. This result reflects emissions from the smelter was adversely affecting the environment (Sandanger et al., 2013).

Pollution of the air from the nickel smelter has caused drastic changes in the soil properties and plants uptake of elements in the forest of the Norwegian –Russian border areas. These changes have led to differences in the cation exchange capacity

and acidity of the soil. Decreased cation exchange capacity, total and active acidity in the organic horizon close to the smelter is due to significant loss of organic matter from severe leaching of hydrolysable humus compounds and also small amounts of litter falls. On the contrary, an increase in soil acidity and cation exchange capacity with increasing distance from the smelter is related to an increase in organic matter content from annual inputs of litter fall due to intense needle loss and death of lichen and mosses. The activity of the smelters in Russia has also affected the terrestrial animals. It has resulted in changes in biodiversity in most polluted areas due to lack of vegetation and also from soil contamination. Studies on invertebrates in dwarf shrub pine forest at different distances from the smelter source, showed results that demonstrated diversity of invertebrates was reduced with decreased distance from the smelter source. The results also showed decreased in soil fauna biomass with decreasing distance from the source. Metal accumulation in small mammals depend on the trophic level of the mammal in question. Highest amount of accumulated metals were found on the liver of the common shrew (*Sorex araneus*) from a study. The shrew *Sorex* stands on the second trophic level, where it consumes invertebrates living in the soil and litter. The research showed the highest accumulated metals were Zn, Pb, and Ni from the Norwegian side of the border. With an increasing in distance from the emission source, heavy metal accumulation decreased accordingly (Lystad, 2002).

From Steinnes et al., 2011, atmospheric metal deposition in mosses at the Norway-Russia border has significantly increased consistently in the last 25 years, meanwhile there is decreasing trend in the Norway- Finland border in the same period. The heavily polluted areas around the smelters was lichen “desert”. The most common lichens found on birch stems in the area were *Hypogymnia physodes* and *Melanohalea olivacea*.

These epiphytic lichens are pollution sensitive, as such their degree of coverage is used to assess the extent of pollution load (Stebel et al., 2007).

A study by Moiseenko and Kudryavtseva, 2001 to determine trace metal accumulation and fish pathologies in areas affected by mining and metallurgical enterprise in Kola Region Russia, indicated maximum Ni accumulation up to 51 µg/g dry weight was observed in the kidneys of white fish collected from lakes near copper-nickel smelters, while the brown trout and char fishes had Ni accumulation in the liver, kidney,



muscles and skeleton. Additionally, Cu accumulation was identified in the kidneys, liver, skeletons and muscles of char fish. The findings from Moiseenko and Kudryavtseva, (2001), further observed elevated concentrations of Cu, Sr and Ni in water bodies around the areas impacted by the smelters from Russia.

Elevated metal concentrations especially Ni, Cu and Cd has been recorded in Lake Kuetsjarvi (water, sediment and whitefish) at a distance of 5-100 km to the smelters. The concentration decreased with increasing distance to the smelters. The study showed that majority of metal emitted and runoffs are deposited close to the pollution source and only moderate quantities of the heavy metals are transported at further distances (Amundsen et al., 2011).

### **3.7 Lead profile**

#### **3.7.1 Chemical and physical properties of lead**

Lead is a chemical element in group 14, period IV of the periodic table (Petrucci et al., 2002). The chemical symbol of lead is Pb, derived from the Latin word *plumbum* with atomic number of 82 (Burns, 2010). It is a metal, possessing the general physical properties associated with metals. That is, a conductor of both electricity and heat, but not as good conductor as compared to copper and aluminium. Lead is silvery in colour when newly cast, but becomes dull grey to bluish as its surface oxidizes in the presence of air. Lead has a metallic lustre, though dull one, with low melting point of 327<sup>0c</sup> relative to most metals. Metallic lead has density of 11.3g/cm<sup>3</sup>, which is high compared to metals like iron (7.8g/cm<sup>3</sup>), copper (8.9g/cm<sup>3</sup>) and aluminium (2.7g/cm<sup>3</sup>) (Thornton et al., 2001). The high density of lead is due to its high atomic number of 82 and relative atomic mass of 207, an indication of how dense and closely the atoms are arranged. The high density of lead has been useful in its application as shield against sound, vibrations and radiation. Lead is very ductile and also malleable. It undergoes large plastic deformation before it breaks. The tensile strength of pure lead is around 12-17 MPa, which is much lower than that of other common metals, such as, Copper as cast is 10 times stronger, aluminium as cast is 6 times stronger. (Thornton et al., 2001). The high malleability, ductility, low melting point and high resistance to corrosion properties of lead have culminated in its widespread use in different

industrial applications such as in the automobile, paint, ceramics, plastics etc. Subsequently, this has led to significant increase of the metal in biological systems as well as in inert environment (Flora et al., 2012).

Inorganic lead has three oxidation states: Namely 0, II and IV oxidation states. Pb (0) oxidation state, is the familiar bluish-grey metal which rarely exist in nature, Pb(II) oxidation state, represent the most frequent form in the environment and Pb(IV) oxidation state, does not occur naturally, it is formed rarely except under extreme oxidizing stress (Petrucci et al, 2002). Pb (IV) is the oxidation state of lead in most organolead compounds (Burns, 2010). Conversely, Pb (II) classically forms lead salts responsible as lead ores throughout the world (Petrucci et al., 2002). The common most formed lead ores are PbS (galena), PbSO<sub>4</sub> (anglesite) and PbCO<sub>3</sub> (cerussite) (Witkowski and Parish, 2001). Generally, lead is less reactive than iron and tin, but more reactive than copper. Metallic lead is extremely corrosion resistant (that is, it is not easily attack by water or air). When exposed to air or water, lead salts are formed, which produce a protective film on the surface of the beneath metal, resulting in slowing/completely stopping of the corrosion. Many of the lead salts have low solubility in water particularly lead sulphate, lead carbonate and lead chromate. This protective property of lead salts is particularly useful in the chemical industry. However, notable exceptions are lead acetate, lead nitrate and lead chloride which are very soluble and thus do not offer protection. These characteristic physical and chemical properties of lead have resulted in its widespread use by humans (Thornton et al., 2001, Burns, 2010).

### **3.7.2 Sources of lead to the environment**

#### **3.7.2.1 Natural sources of lead to the environment**

Like other metals, lead occurs naturally in small concentrations in rocks and soils. The average concentration of lead in the Earth crust is estimated to be approximately 16mg/kg (Thornton et al., 2001). Even though lead is naturally occurring chemical, it usually does not exist in elemental form. In the earth crust, it exists mainly as galena (PbS) or in a lesser extent as anglesite (PbSO<sub>4</sub>) or cerussite (PbCO<sub>3</sub>). These minerals are mostly found together with zinc, copper, and iron sulphides and also gold, silver,

bismuth and antimony minerals. Trace concentrations of lead occurs in coal (3-111ppm), crude oil (0.31ppm) and wood (20ppm). Some lead concentrations in some ores are copper ores (11,000ppm), lead and zinc ores (24,000ppm) and gold ores (6.60ppm). Silicon, sodium, potassium, calcium and aluminium represent the most abundant metals and metalloids in the Earth crust. The various processes from which these rocks were formed, together with the atomic size and chemical behaviour of the metals, influence which metals to be most associated with what type of rock (EPA, 2001a, Thornton et al., 2001).

Lead is found in significant amounts in certain sedimentary rocks, namely black shales, shales, granites, and sandstones at levels ranging from 1-150 ppm, the highest amount is usually present in black shales. Lead concentrations in these rocks is on average estimated to be 12-30ppm. On the contrary, other rocks such as limestone, basalts, and igneous ultramafic rocks, only contain lead in trace proportions, with mean concentrations around 1-9 ppm. In some countries, elevated concentrations of lead have been found to be an indication of lead deposits. This abnormal concentrations of lead is associated with lead deposits in areas, where they crop out of the surface and are subjected to weathering process, followed by dispersion or distribution of the component base metal, including lead into the overlying soils. Volcanic activity and weathering process are major natural sources of lead mobility from the earth lithosphere to the atmosphere and biosphere. The atmospheric emission of lead from volcanic activity in 1983 is estimated to be 540-6000 tonnes. Through weathering of rocks, lead is released to soils and aquatic ecosystems, which eventually becomes available to the biota. The mineral composition of a soil usually is similar to the parent bedrock. As a result soils formed from lead rich rocks through natural process such as weathering will have high concentration of lead. 18.6-29.5million kg per year is the estimated global natural release of lead to the atmosphere. But the figure is small compared to the anthropogenic flux of lead to the atmosphere. Other minor natural sources of lead emission into the environment particularly the atmosphere is windblown dust, sea spray, biogenic material, erosion, meteorite dust and forest fires. (ATSDR, 2007, Thornton et al., 2001 UNEP, 2010).

### **3.7.2.2 Anthropogenic sources of lead to the environment**

Human activities have greatly influenced the biogeochemical cycle of lead globally. In 2004, 3,150,000 tonnes of lead were extracted from the earth crust through human activity and brought into societal circulation (UNEP, 2010). Significant amount of this ended up as metal extractive residues or was mobilised as impurities to assist in the extraction of other minerals like coal and lime. A total of 400,000- 1,000,000 tonnes of such mobilised lead were disposed of together with waste from mining, base metal production and from use of coal into the environment (UNEP, 2010). Multiple sources of lead to the environment have been identified: Petrol, industrial processes, paint, solder in canned foods and water pipes. Therefore the relative contribution of these sources is complex and may differ between areas and populations (Tong et al., 2000).

Ore tailings (i.e. material discarded during lead production but still contain a small proportion of ore) from mines have very high concentrations of lead are major source of lead to the soil (Alloway and Ayres, 1997). The lead ore tailings emitted to the soil was estimated amount of 130, 000 - 390, 000 t of lead per year out of global emissions to the soil of 808, 000 - 1,893, 000 t per year in 1983 (Nriagu and Pacyna, 1988). Soils close to lead mines, houses painted with lead paint, orchards treated with arsenate, heavy automobile traffic mostly contain high concentrations of lead (Tiwari et al., 2013). In lead smelting areas, metallurgical activity dominates as the major source of lead in soil through atmospheric deposition. The lead particles are carried in the air, and deposited to accumulate in the topsoil layer, also can be mobilised in the deeper soils (Ettler et al., 2004). Significant quantities of lead are also directed to the landfills and waste dumps from discarded lead products. Studies in Denmark and the Netherlands concluded that about 10% of lead products ended up in the landfills (UNEP, 2010). Ammunition used for hunting is also a major source of direct lead release to the soil. The ammunitions are lost to the environment during shooting and accumulate. It is estimated ammunition may increase the lead content of soils in some countries (UNEP, 2010).

Non-ferrous metal production, and also coal combustion are other major sources of lead to the atmosphere (Tiwari et al., 2013, UNEP, 2010, Tong et al., 2000). Lead from contaminated soils can re-enter the atmosphere as the surface of the soil is disturbed by wind or other mechanical processes. This situation has been identified as

important source of atmospheric lead in different parts of United States of America (Li et al., 2010). Additionally, lead smelting, lead acid batteries production, waste management through incineration are other sources of lead to the atmosphere (Li et al., 2010).

Lead may be present in natural water sources in small quantities as a result of its dissolution from soils and rocks minerals (mainly from geogenic origin) (Thornton et al., 2001, WHO, 2011). Generally, the concentration of Pb decrease from rain water (usually acidic, about 20ug/l Pb) to freshwater (generally neutral, about 5ug/l Pb) to sea water (alkaline, below 1 ug/l) (Thornton et al., 2001). However, the solubility of most Pb compounds are low, hence high concentrations of lead in water are rare. Conversely, high concentrations of Pb in rivers can be as 10 times more in areas of Pb mineralisation than in unmineralised areas with background Pb levels below 10ug/l (WHO recommended limit for drinking water) (Thornton et al., 2001). Principally household plumbing systems in which the pipes, solder fittings may contain lead are significant sources of lead in tap water (WHO, 2011). Polyvinyl chloride (PVC) pipes has lead compounds which can be leached to drinking water to induce high lead concentrations. Lead crystals (lead glass) and ceramic containers can also leach lead into drinking water and food (Tchounwou et al., 2012, WHO, 2011). In general lead is immobile in soil. The downward movement of metallic lead and inorganic lead compounds from soils to groundwater by leaching is very slow under most natural conditions (UNEP, 2010).

### **3.8 Toxicity of lead**

The route of lead exposure to humans occur mainly through inhalation of lead contaminated dust particles, ingestion of lead contaminated food substances and drinking water and also degradation of household paints ( Shamma et al., 2009, Tchounwou et al., 2012 ). The effect of lead is dependent on factors like age, genetic characteristics, nutritional status, tobacco smoking, alcohol consumption and overall health status. Children below 6 years are the most susceptible to lead exposure at even low levels (Tiwari et al., 2013). The toxicological effects of lead in humans include:

## **Neurotoxicology**

This is usually found in settings involving occupational exposures. In adults it can lead to ataxia (loss of full control bodily movements), memory loss and at highest levels coma and eventual death. The overt effects on the nervous system include weakness of the waist and fingers caused by nerve compression.

**Reproductive effects-** High lead exposure is also known to have adverse effects on the reproductive health in both males and females. In women, lead toxicity can cause sterility, miscarriage, stillbirth, and neonatal morbidity and mortality. In men, decreased sperm count and decreased sperm density have been associated with lead toxicity (Juberg, 2000).

**Cardiovascular effects** - Lead toxicity can result in acute and chronic damage to the vascular and cardiac systems. Possible fatal consequences include, cardiovascular illness and hypertension. Additionally, cerebrovascular accidents, peripheral vascular disease and ischemic coronary heart disease are possible diseases that can result from lead intoxication.

**Effects on the Kidney and Liver** - Exposure to high level of lead (>60ug/dL) can cause renal and liver dysfunction (Assi et al., 2016).

**Effects on the mental development and Intelligent Quotient** –It has been shown that lead can impair mental development of young children even at low levels.

**Effects on biochemical process-**Another adverse effects of lead in the human system is the syntheses of haem (a vital constituent of red blood cells) in children and adults. Lead inhibition of haemoglobin synthesis has caused anaemia in children. Lead also reduces life span of circulating erythrocytes (both in children and adults) by increasing the fragility of cell membranes. The resulting effect cause 2 types of anaemia, haemolytic anaemia which is associated with acute high level of lead exposure, and frank anaemia which is due to blood level elevation for prolonged periods.

**Effects on the bone** – The primary location of lead storage in the human body are the bones. Stable lead isotope analysis have showed the bones contribute around 40- 70% of lead released into the blood stream. Lead intoxication of the bone directly or indirectly alters the bone cell function through changes in the circulating levels of

hormones responsible for matrix formation, matrix mineralisation and bone resorption under the control of both systemic and local factors Lead toxicity in bones has also shown to have interfered with essential cell processes such as cell division, motility and even cell death in bone cells (Flora, 2010., Pounds et al., 1991, Renner, 2010).

### **3.9 Pb isotope analysis for tracing the sources of pollution**

Lead is among the common anthropogenic contaminants released into the environment. Determination of Pb concentration alone, does not show evidence of human influenced contamination, even though it represents the first step to evaluating the extent of pollution. Significant amount of Pb may be released into the environment from natural processes. Pb occurs in the environment as 4 main isotopes:  $^{208}\text{Pb}$  (52%),  $^{206}\text{Pb}$  (24%),  $^{207}\text{Pb}$  (23%) and  $^{204}\text{Pb}$  (1%) (Komarek et al., 2008).  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  are radiogenic isotopes, released into the environment from radioactive decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  respectively.  $^{204}\text{Pb}$  is the only primordial stable isotope with constant abundance with time on earth. The percentage abundance of stable Pb isotope in an environmental sample depends mainly on the concentrations of primordial Pb, U, Th and the length of decay process. The isotopic composition ratio of Pb can be expressed in several ways, with the common ones in Earth and environmental sciences being  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$ , and  $^{208}\text{Pb}/^{206}\text{Pb}$  (Komarek et al., 2008).  $^{206}\text{Pb}/^{207}\text{Pb}$  is the most preferred since it can be determined precisely analytically. The abundance of  $^{207}\text{Pb}$  has not changed much with time compared to  $^{206}\text{Pb}$ , since  $^{235}\text{U}$  has already decayed while  $^{238}\text{U}$  is still present in high abundance on the earth (Erel et al., 2001). Old Pb ores have generally shown a low  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio range (1.06-1.10), more recent samples with more radiogenic Pb (released from U and Th decay) have higher  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of  $>1.18$  (Farmer et al., 2001, Bacon, 2002). Therefore, in recent times, stable Pb isotopes have proved helpful as a reliable tracer of pollution sources (combustion of coal and gasoline, industrial activity such as smelting) in different environmental samples, notably in peatbogs, sediments, soils, snow and aerosols. Lead ores have a characteristic isotope composition ratio (signature), which persists (does not change) even after the physical and physicochemical processes of smelting, refining and manufacturing. Each source of Pb has a definite or sometimes overlapping isotopic composition range. In soils for example, Pb isotopic ratios have reflected the mixing of

different sources of Pb, and source identification can be confirmed after all possible sources of Pb have been characterised and their respective Pb isotope composition ratios have been quantified (Komarek et al., 2008).

Recent analytical technology for Pb isotopic ratios measurements are based on the use of Thermal Ionisation Mass Spectrometry (TIMS), Inductively Coupled Plasma Multicollector Mass Spectrometry (MC ICP-MS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In case of ICP-MS, liquid samples are introduced into the Ar plasma where ions are efficiently generated (Porcelli and Baskaran, 2012). This method is the most simple and does not require any special sample pretreatment or matrix separation.



## 4 Methods and Materials

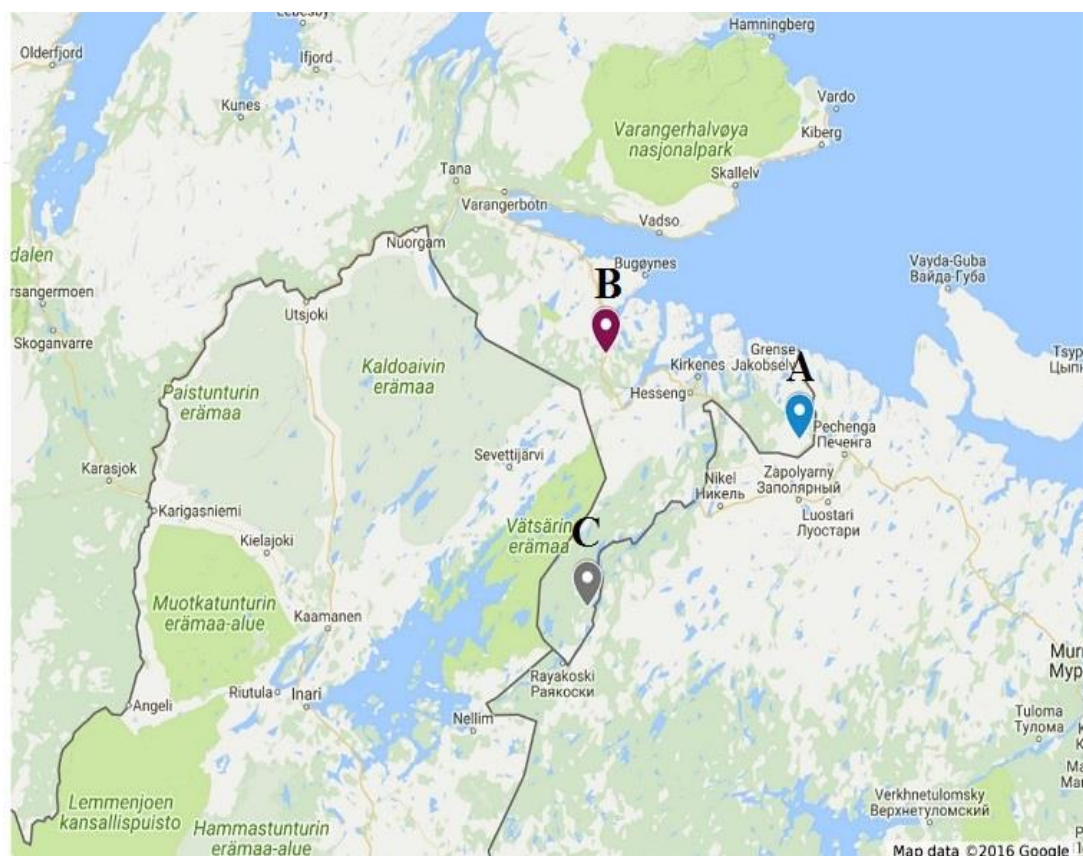
### 4.1 Sampling of the peat cores

Accumulated peat samples were collected from 3 different bog sites in Norway, close to the Russia border. The sampling sites are located at different distances from the smelter in Russia. The Russian smelters are located at towns of Nickel, Zapolyarny and Monchegorsk, close to the Norwegian - Russian border. The sampling sites are denoted as A, B, C as shown in the map below (Figure 2).

Peat cores were sampled by a peat core drill (Ekotechnik, Czech Republic). The sampling head was 0.5m long so the core was successively sampled in 0.5m long sections. Once all the core sections were extracted, they were precisely cut into 5cm slices using a ceramic knife and put into a plastic bag for transportation. In the laboratory, the samples were taken out and dried in a drier (40°C) for 48 hours. In all, 46 peat core samples were collected. Below is the table representing the sampling sites, their coordinates, depth of peat layer and associated numbers (Table 1).

**Table 1.** The coordinates of the 3 sampling sites (A, B, C) with their respective peat depths and designated numbers.

A	69°34'8.508" N	30°49'39.136" E	B	69°46'41.1" N	29°20'10.1" E	C	69°09'13.2" N	29°11'38.5" E
no.	depth (cm)		no.	depth (cm)		no.	depth (cm)	
	1	0-5		19	0-5		38	0-5
	2	5-10		20	5-10		39	5-10
	3	10-15		21	10-15		40	10-15
	4	15-20		22	15-20		41	15-20
	5	20-25		23	20-25		42	20-25
	6	25-30		24	25-30		43	25-30
	7	30-35		25	30-35		44	30-35
	8	35-40		26	35-40		45	35-40
	9	40-45		27	40-45		46	40-50
	10	45-50		28	45-50			
	11	50-55		29	50-55			
	12	55-60		30	55-60			
	13	60-65		31	60-65			
	14	65-70		32	65-70			
	15	70-75		33	70-75			
	16	75-80		34	75-80			
	17	80-85		35	80-85			
	18	85-100		36	85-90			
				37	90-100			



**Figure 2** A map of the 3 sampling sites (A, B, C) at Norway-Russia border

#### 4.2 Pre-treatment of the peat and laboratory analysis

At the laboratory, the fully air dried peat samples were homogenised by grinding with pestle and mortar made of porcelain. After that,  $250 \text{ mg} \pm 0.4$  of the peat samples were weighed using analytical balance RADWAG AS 220. R2 into a teflon vessel (Saville, USA). Acid decomposition of the samples involved the addition of 9 ml of nitric acid ( $\text{HNO}_3$ , 65%) and 3 ml of hydrochloric acid ( $\text{HCl}$ , 34-37%). The vessels were then placed on a hot plate at a temperature of  $150^\circ\text{C}$  overnight with the vessels tightly capped. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 250  $\mu\text{l}$ ) was added to the samples not fully decomposed (traces of residual organic matter could still be seen). The fully decomposed samples (seen as clear liquid) were placed on hot plate with the vessel open to evaporate to dryness. After all the solvents have evaporated, 20ml of 2%  $\text{HNO}_3$  (v/v) was added to each of the sample. Each sample was then filtered (0.45 $\mu\text{m}$  filter)

and stored in a fridge for the ICP-MS analysis of the total metal and metalloid concentration and Pb isotope analysis.

The procedure for the decomposition of the peat samples in this case was a modified version of 3051A method (US EPA) for microwave assisted acid digestion of sediments, sludges, soils and oils.

The concentration of selected metal(loid)s (Cd, Cr, Cu, Ni, Pb, Zn, and As) was determined using an inductively coupled plasma mass spectrometry (ICP-MS, iCAP Q, Thermo Fisher Scientific, Germany). The concentration data in  $\mu\text{g/l}$  were then recalculated to  $\mu\text{g/g}$  (i.e.,  $\mu\text{g}$  of a metal per g of the peat). All the Pb isotope measurements ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) were determined using the ICP-MS. Correction for mass bias was performed by using analyses of SRM 981 (Common lead NIST, USA) after every two samples. We used the following certified values as references: 1.093 and 2.168 for  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  respectively. The samples were diluted to a concentration of approximately  $10^{-3}$  mg/L of Pb to ensure that the detection always remained within the range of the 'pulse' mode. The standard errors for the measurements of the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios in SRM 981 were  $<0.4\%$  RSD and  $<0.4\%$  RSD, respectively.

## **5. Results and Discussion**

### **5.1 Average concentration ( $\mu\text{g/g}$ ) and distribution of selected metals and metalloid in the peat.**

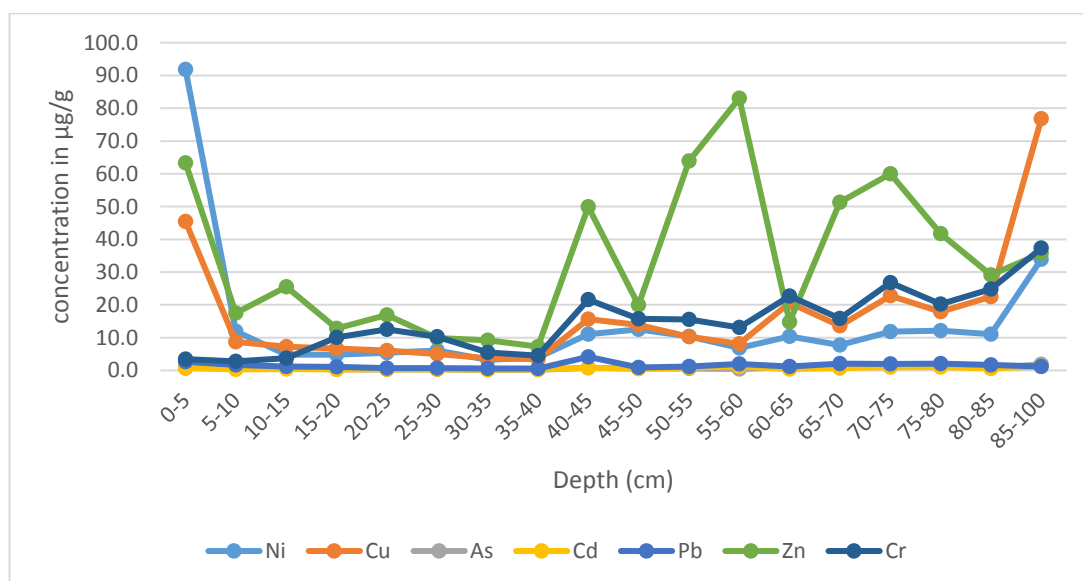
The average concentration data for Ni, Cu, As, Cd, Pb, Zn and Cr at varied peat depth in 3 different sampling sites are summarized in site A (Table 2 and figure 3), site B (Table 3 and figure 4) and site C (Table 4 and figure 5).

The peat cores from 3 ombrotrophic bogs at Norway are meant to study the degree and time trend of atmospheric metal deposition in the vicinity of the Norway- Russia border area. At sampling site A and B, the bogs have ombrotrophic layer extending down to a depth of 100cm, while at sampling site C, the ombrotrophic layer extends down till 50cm depth. These peat cores tightly hold the metals to maintain a temporal metal deposition record. The metals are assumed not to have significantly undergone post depositional redistribution.

In the tables below, the coloured figures represent the maximum and minimum concentration values of the elements. The peat core values (concentrations with depths) in the tables provide information on time- related changes in atmospheric input of the metals and As. The maximum and minimum concentrations of the metals at different peat depths record significant variations in the metal deposition within a temporal time period. The variations in the metal deposition is dependent on factors such as wind conditions, pollutant dispersion conditions, before and after industrial revolution and changes in technology of ore processing etc. can affect the concentration of metals in the peat.

**Table 2. Average concentrations ( $\mu\text{g/g}$ )  $\pm$  standard deviations of metals and As with depth**

Depth/cm	Ni	Cu	As	Cd	Pb	Zn	Cr
0-5	91.8 $\pm$ 0.4	45.5 $\pm$ 1.5	0.7 $\pm$ 0.0	0.7 $\pm$ 0.0	2.6 $\pm$ 0.4	63.3 $\pm$ 1.7	3.4 $\pm$ 0.1
5-10	11.9 $\pm$ 2.2	8.7 $\pm$ 0.3	1.9 $\pm$ 0.2	0.3 $\pm$ 0.1	1.7 $\pm$ 0.1	17.5 $\pm$ 2.0	2.8 $\pm$ 0.1
10-15	4.8 $\pm$ 0.9	7.3 $\pm$ 1.4	0.7 $\pm$ 0.2	0.4 $\pm$ 0.4	1.2 $\pm$ 0.8	25.5 $\pm$ 29.0	3.8 $\pm$ 0.3
15-20	4.8 $\pm$ 1.0	6.6 $\pm$ 2.0	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	1.1 $\pm$ 0.3	12.8 $\pm$ 0.7	10.0 $\pm$ 2.0
20-25	5.4 $\pm$ 0.1	6.1 $\pm$ 0.5	0.3 $\pm$ 0.1	0.4 $\pm$ 0.1	0.7 $\pm$ 0.1	16.9 $\pm$ 7.0	12.5 $\pm$ 0.2
25-30	6.0 $\pm$ 1.5	5.0 $\pm$ 0.6	0.3 $\pm$ 0.1	0.3 $\pm$ 0.0	0.7 $\pm$ 0.2	9.9 $\pm$ 5.7	10.3 $\pm$ 0.3
30-35	3.2 $\pm$ 3.3	3.8 $\pm$ 4.2	0.2 $\pm$ 0.3	0.3 $\pm$ 0.0	0.7 $\pm$ 0.1	9.2 $\pm$ 3.1	5.5 $\pm$ 6.5
35-40	3.9 $\pm$ 0.5	3.4 $\pm$ 0.7	0.2 $\pm$ 0.1	0.3 $\pm$ 0.0	0.6 $\pm$ 0.0	7.3 $\pm$ 0.1	4.5 $\pm$ 1.4
40-45	11.0 $\pm$ 0.1	15.7 $\pm$ 4.6	0.8 $\pm$ 0.1	0.8 $\pm$ 0.4	4.2 $\pm$ 0.0	49.9 $\pm$ 48.1	21.6 $\pm$ 1.3
45-50	12.5 $\pm$ 3.7	13.9 $\pm$ 6.5	0.6 $\pm$ 0.1	0.5 $\pm$ 0.2	0.9 $\pm$ 0.2	20.0 $\pm$ 0.8	15.8 $\pm$ 2.1
50-55	10.4 $\pm$ 0.1	10.3 $\pm$ 1.5	0.6 $\pm$ 0.1	0.9 $\pm$ 0.0	1.2 $\pm$ 0.3	63.9 $\pm$ 12.6	15.5 $\pm$ 0.8
55-60	6.9 $\pm$ 1.4	8.1 $\pm$ 0.1	0.4 $\pm$ 0.2	1.2 $\pm$ 0.4	1.9 $\pm$ 1.1	83.0 $\pm$ 13.3	13.1 $\pm$ 3.4
60-65	10.3 $\pm$ 1.0	20.7 $\pm$ 1.7	1.0 $\pm$ 0.1	0.4 $\pm$ 0.1	1.2 $\pm$ 0.2	14.8 $\pm$ 6.6	22.7 $\pm$ 2.7
65-70	7.7 $\pm$ 3.2	13.6 $\pm$ 9.6	0.9 $\pm$ 0.4	0.7 $\pm$ 0.1	2.1 $\pm$ 0.0	51.3 $\pm$ 1.7	15.8 $\pm$ 6.7
70-75	11.8 $\pm$ 1.7	22.7 $\pm$ 6.9	1.8 $\pm$ 1.2	1.0 $\pm$ 0.6	1.9 $\pm$ 0.1	60.0 $\pm$ 55.3	26.8 $\pm$ 6.2
75-80	12.2 $\pm$ 3.8	17.9 $\pm$ 11.6	2.0 $\pm$ 0.7	1.0 $\pm$ 0.4	2.1 $\pm$ 0.1	41.7 $\pm$ 27.4	20.3 $\pm$ 10.9
80-85	11.1 $\pm$ 2.6	22.5 $\pm$ 5.2	0.7 $\pm$ 0.3	0.6 $\pm$ 0.1	1.7 $\pm$ 0.1	29.1 $\pm$ 13.6	24.8 $\pm$ 4.4
85-100	33.9 $\pm$ 23.2	76.7 $\pm$ 27.3	1.8 $\pm$ 0.7	1.2 $\pm$ 1.1	1.2 $\pm$ 1.0	35.8 $\pm$ 28.7	37.3 $\pm$ 3.1



**Figure 3. Average concentrations ( $\mu\text{g/g}$ ) of metals/metalloid**

From site A (table 2, figure 3), From the depth of 85-100cm with markedly high concentration of 33.9  $\mu\text{g/g}$ , the atmospheric deposition of Ni decreased towards the surface layer, until at depth of 5-10cm, when significantly its concentration increased from 11.9 $\mu\text{g/g}$  to 91.8 $\mu\text{g/g}$ . This concentration represents the highest average concentration of Ni and also the entire selected metal composition in the peat sample under study at sampling site A. This is clear indication of Ni enrichment at the uppermost layer of the peat reflecting recent atmospheric deposition.

Unlike Ni, Zn demonstrated different variations with time. At depth of 85- 100cm, the concentration of Zn was markedly high, but not the highest concentration. The pattern of atmospheric Zn deposition in the peat with time was zigzag towards the surface until the highest concentration of 83.0 $\mu\text{g/g}$  was recorded at depth of 55- 60cm. This figure corresponds to the second highest metal deposition concentration in the peat at sampling A. The concentration of Zn drastically decreased from 83.0 $\mu\text{g/g}$  to 17.5 $\mu\text{g/g}$  at depth of 5-10cm approximately 79%. Emission of Zn into the peat increased again by 72% at depth of 0-5cm from to 17.5 $\mu\text{g/g}$  to 63.3  $\mu\text{g/g}$ . Zn like Ni, showing surface enrichment with conclusion of recent atmospheric settlement.

Highest concentration of Cu recorded 76.7  $\mu\text{g/g}$  corresponding to deeper depth profile of 85-100cm of peat. Cu followed Zn as the next highest average concentration at sampling site A. The concentration of Cu towards the surface profile of the peat did not show significant decrease and increase pattern until the uppermost depth of 5-10cm when it significantly increased from 8.7  $\mu\text{g/g}$  to 45.5  $\mu\text{g/g}$  at depth of 0-5cm. Cu also showing recent atmospheric deposition through surface enrichment in the peat profile.

Cr followed Cu with average concentration of 37.3  $\mu\text{g/g}$  at 85-100cm depth at sampling site A. Cr deposition pattern shows high concentration at the deeper depth, its deposition further decreased towards the surface till the 0-5cm. This surface reduction deposition of Cr is an indication of recent cut in emission.

Pb has average concentration of 4.2  $\mu\text{g/g}$  (45-50cm) following Cr in descending order of average concentration of the elements in the peat sample. Pb also showed surface enrichment in the peat.

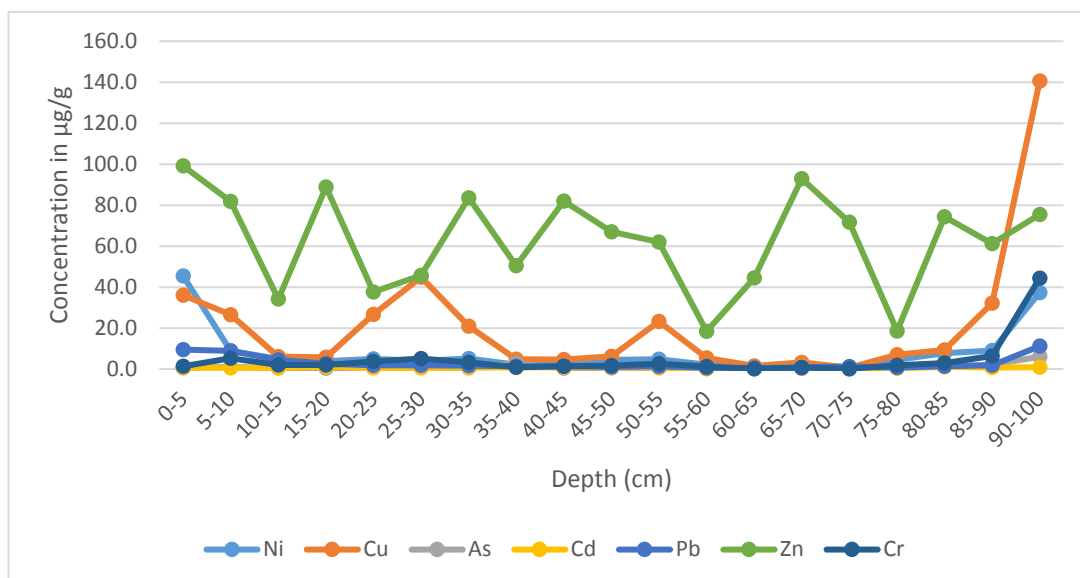
2.0  $\mu\text{g/g}$  at depth of 75-80cm is the highest concentration of As in sampling site A, representing the last but one element in descending order of concentration in sampling

site A. Though not large amount of As has been emitted into the atmosphere (as depicted in the peat) as compared to Ni, Cu and Zn, its concentration pattern towards the surface of the peat profile has being increasing. It also shows surface enrichment.

Cd like As per the data has not recorded high concentrations compared to Ni and Cu. However, its concentration has increased towards the surface of the peat profile. An indication of recent atmospheric deposition. Cd has the least recorded concentration of 1.2 µg/g at depth of 85-100cm. Hence the order of average concentration of the metals and metalloid in sample site A is Ni>Zn>Cu>Cr>Pb>As>Cd.

**Table 3. Average concentrations (µg/g) ± standard deviations**

Depth/cm	Ni	Cu	As	Cd	Pb	Zn	Cr
0-5	45.4 ± 23.8	36.1 ± 15.2	0.6 ± 0.4	0.7 ± 0.4	9.5 ± 1.0	99.1 ± 20.9	1.3 ± 1.2
5-10	8.9 ± 4.4	26.5 ± 12.9	1.1 ± 0.5	0.5 ± 0.3	8.9 ± 1.6	81.8 ± 22.3	5.2 ± 4.2
10-15	5.0 ± 0.1	6.1 ± 0.0	0.6 ± 0.1	0.5 ± 0.1	4.4 ± 2.7	34.1 ± 16.3	2.0 ± 0.9
15-20	3.8 ± 1.3	5.7 ± 1.5	0.4 ± 0.1	1.1 ± 0.4	2.5 ± 0.5	88.9 ± 30.1	2.0 ± 0.5
20-25	4.9 ± 0.2	26.7 ± 0.3	0.7 ± 0.0	0.5 ± 0.2	1.8 ± 0.5	37.6 ± 28.1	3.7 ± 0.2
25-30	4.0 ± 2.7	44.7 ± 28.0	0.6 ± 0.4	0.6 ± 0.5	1.8 ± 0.5	45.6 ± 48.2	5.1 ± 4.5
30-35	5.1 ± 0.6	20.9 ± 2.5	0.6 ± 0.1	0.8 ± 0.8	1.6 ± 0.6	83.5 ± 48.1	3.2 ± 0.3
35-40	2.1 ± 1.4	4.7 ± 3.1	2.5 ± 3.5	0.7 ± 0.5	1.3 ± 0.7	50.4 ± 52.7	0.9 ± 0.7
40-45	3.5 ± 0.9	4.6 ± 1.0	0.4 ± 0.1	0.9 ± 0.1	1.3 ± 0.4	82.0 ± 12.1	1.4 ± 0.2
45-50	4.4 ± 1.3	6.1 ± 2.1	0.6 ± 0.3	0.8 ± 0.2	1.1 ± 0.3	67.0 ± 35.7	1.6 ± 0.5
50-55	4.7 ± 0.4	23.2 ± 6.7	0.6 ± 0.1	0.7 ± 0.3	1.3 ± 0.4	62.0 ± 10.5	2.6 ± 1.7
55-60	2.1 ± 2.5	5.4 ± 6.4	0.3 ± 0.3	0.1 ± 0.0	0.6 ± 0.6	18.4 ± 13.4	1.2 ± 1.6
60-65	0.7 ± 0.6	1.5 ± 0.9	0.1 ± 0.1	0.6 ± 0.4	0.6 ± 0.5	44.5 ± 37.3	0.1 ± 0.1
65-70	2.7 ± 1.6	3.3 ± 1.9	0.2 ± 0.1	1.1 ± 0.1	0.8 ± 0.3	92.9 ± 23.2	0.7 ± 0.8
70-75	0.5 ± 0.2	0.6 ± 0.0	0.1 ± 0.0	0.6 ± 0.1	1.1 ± 1.1	71.6 ± 24.8	0.1 ± 0.0
75-80	4.5 ± 1.4	7.0 ± 1.8	0.7 ± 0.3	0.4 ± 0.1	0.7 ± 0.0	18.5 ± 11.9	1.8 ± 0.6
80-85	7.7 ± 0.1	9.3 ± 0.2	1.3 ± 0.0	1.0 ± 0.4	1.4 ± 0.3	74.3 ± 20.4	2.9 ± 0.1
85-90	8.9 ± 1.8	32.1 ± 5.1	2.2 ± 0.3	0.7 ± 0.2	1.9 ± 0.4	61.3 ± 16.9	6.4 ± 3.0
90-100	37.3 ± 4.5	140.5 ± 9.2	6.0 ± 0.8	0.9 ± 0.0	11.1 ± 1.4	75.4 ± 0.9	44.3 ± 1.3



**Figure 4. Average concentrations ( $\mu\text{g/g}$ ) of metals/metalloid**

From sampling site B (table 3 and figure 4), at high atmospheric deposition of Ni with concentration of  $37.3\mu\text{g/g}$  at deeper depth of 90-100cm, towards the surface layer, its deposition increased to  $45\mu\text{g/g}$ . The deposition pattern reduced to  $8.9\mu\text{g/g}$  denoting 76% decrease. However, the concentration increased from the  $8.9\mu\text{g/g}$  to  $45\mu\text{g/g}$  at upper surface of 0-5cm. This trend of Ni metal deposition from the atmosphere with enrichment at the surface layer of the peat, is an indication of contemporary source still releasing the metal into the atmosphere of the peat ecosystem.

The highest concentration of Cu was  $140.5\mu\text{g/g}$  at depth of 90-100cm. Its concentration decreased to  $6.1$  at depth of 10-15cm after which the concentration began to rise to  $36.1\mu\text{g/g}$  at corresponding depth of 0-5cm showing surface enrichment.

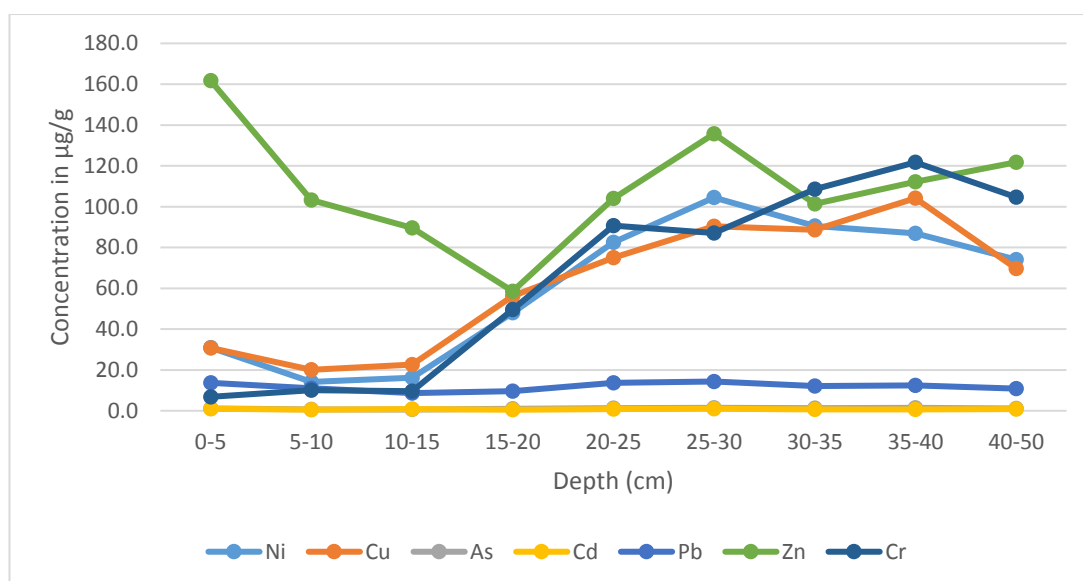
The atmospheric deposition pattern of Zn is wavy in from the data obtained, showing temporal time trend of deposition. From concentration of  $75\mu\text{g/g}$  at 90-100cm depth, the concentration towards the surface shot up at depth of 65-70cm to  $92.9\mu\text{g/g}$ . The wavy pattern of deposition towards the peat surface continues until 10-15cm depth of concentration  $34.1\mu\text{g/g}$ , when the concentration began to show upward trend towards the surface with the highest concentration of  $99.1\mu\text{g/g}$  at the surface of 0- 5cm.



As, Cr, Pb, and Cd, deposition patterns did not show remarkable increase over the time period. However, As, Pb and Cd showed a marginal increase towards the 0-5cm depth. From the data in sampling site B, the order of average concentration of metals and metalloid are Cu>Zn>Ni>Cr>Pb>As >Cd.

**Table 4. Average concentrations ( $\mu\text{g/g}$ )  $\pm$  standard deviation**

Depth/cm	Ni	Cu	As	Cd	Pb	Zn	Cr
0-5	30.9 $\pm$ 12.4	30.8 $\pm$ 2.8	1.2 $\pm$ 0.2	0.9 $\pm$ 0.2	13.6 $\pm$ 1.0	161.7 $\pm$ 3.0	6.8 $\pm$ 2.0
5-10	14.1 $\pm$ 1.4	20.1 $\pm$ 2.5	0.7 $\pm$ 0.0	0.6 $\pm$ 0.1	11.0 $\pm$ 0.1	103.2 $\pm$ 8.6	10.0 $\pm$ 0.9
10-15	16.2 $\pm$ 2.2	22.5 $\pm$ 0.6	0.6 $\pm$ 0.0	0.8 $\pm$ 0.1	8.7 $\pm$ 0.2	89.7 $\pm$ 16.6	9.6 $\pm$ 0.3
15-20	48.1 $\pm$ 2.2	56.1 $\pm$ 1.9	1.0 $\pm$ 0.0	0.6 $\pm$ 0.5	9.6 $\pm$ 0.8	58.6 $\pm$ 23.5	49.6 $\pm$ 2.7
20-25	82.5 $\pm$ 5.2	75.0 $\pm$ 4.8	1.3 $\pm$ 0.0	0.9 $\pm$ 0.2	13.7 $\pm$ 1.5	104.0 $\pm$ 0.7	90.8 $\pm$ 1.6
25-30	104.4 $\pm$ 4.5	90.4 $\pm$ 3.3	1.4 $\pm$ 0.0	1.0 $\pm$ 0.3	14.3 $\pm$ 0.1	135.7 $\pm$ 16.7	87.1 $\pm$ 22.3
30-35	90.5 $\pm$ 9.1	88.6 $\pm$ 9.5	1.3 $\pm$ 0.2	0.7 $\pm$ 0.5	12.1 $\pm$ 0.8	101.4 $\pm$ 7.6	108.5 $\pm$ 23.0
35-40	86.9 $\pm$ 7.0	104.1 $\pm$ 9.5	1.4 $\pm$ 0.3	0.7 $\pm$ 0.3	12.5 $\pm$ 0.3	112.1 $\pm$ 22.2	121.7 $\pm$ 27.3
40-50	74.1 $\pm$ 6.9	69.6 $\pm$ 7.0	1.1 $\pm$ 0.1	0.9 $\pm$ 0.6	10.9 $\pm$ 0.5	121.8 $\pm$ 43.2	104.6 $\pm$ 19.2



**Figure 5. Average concentrations ( $\mu\text{g/g}$ ) of metals/metalloid**

At sample site C, depicted by table 4 and figure 5, Ni, Cu and Zn show similar pattern of deposition with marked surface enrichment. However, As, Cr, Pb and Cd show insignificant increases over the temporal time period. Again Pb and As concentrations showed to a lesser extend surface enrichment.

Zn> Cr>Ni> Cu>Pb> As> Cd, is the arrangement of the average concentration of the metals and metalloid at sample site C.

From results obtained, in all the 3 sampling sites, elevated concentrations of Ni, Cu, Zn, Cr and As were recorded at different depths of the peat. These metals and metalloid concentrations were compared with soil quality threshold values from the Norwegian pollution Control authority report, 1999. The comparison shows higher concentrations for the above mentioned toxic elements. However, concentration values of Pb and Cd were below the threshold values set by the Norwegian authority. Over the years, lot of research have been conducted in the Norwegian-Russian border area with different environmental media to determine qualitatively and quantitatively the toxic elements present, to assess the extent of pollution and the major elements involved. This study using peat cores will also be additional work to assess the extent and also the temporal time trend of pollution in the area. Different environmental samples such as snowpack, terrestrial moss etc. have been used as means to evaluate the pollution levels. Below are some of them and their comparison with findings from this thesis work. Also, different sources of these toxic metals as identified by the different authors would also be mentioned.

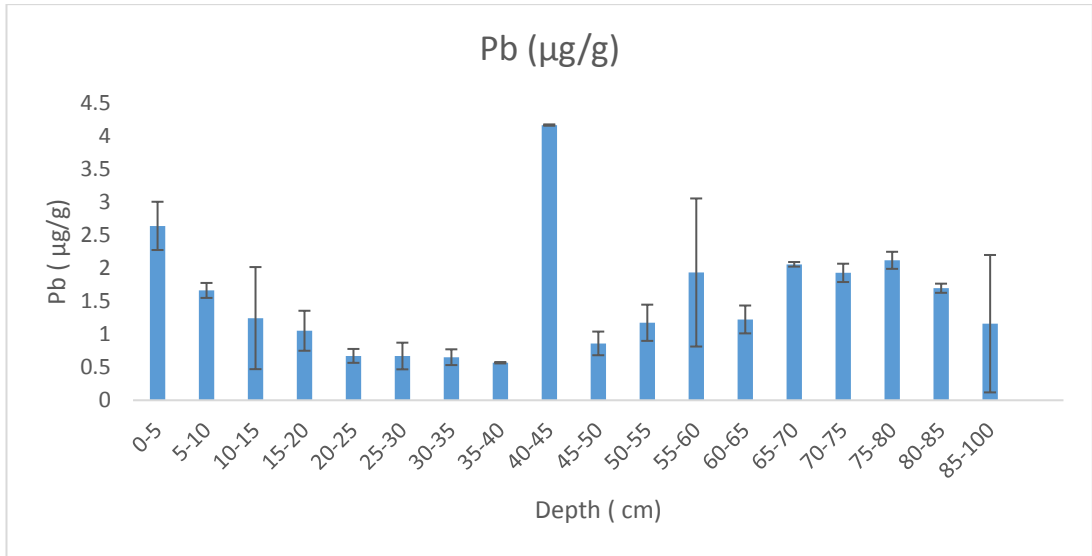
High concentrations of As, Cu and Ni from the findings in this work is supported by Reimann et al., 1996 research on snowpack chemistry in the vicinity of the Norway – Russia border and Frontasyeva and Steinnes, (2004) findings in peat cores from ombrotrophic bogs in the same Norway-Russia border locality . The two research works from the analysis of the authors, attributed the elevated concentrations of these elements (As, Cu, Ni) in the vicinity of the Norway-Russia border to emissions from the Russia smelter. The emission impact of the smelter in Russia is clearly shown in this thesis work by the increasing surface enrichment of these elements in the peat. Again Ni and Cu have been quoted as major airborne pollutants in the Norway-Russia border area emanating from nickel mining and smelting complex based in Russia (Ayras et al., 1997). Cr concentration which is also high from this work is confirmed by Ayras et al. 2007, according to Ayras et al., 1997, Cr concentration can be due to local iron and steel mills industry at Kirkenes in Norway and also combustion of coal. The pattern of Cr deposition reduction towards the surface of the peat in this study at all the 3 sampling sites, indicates reduction in its emission. This collaborate with the

above findings from Ayras et al., 2007. Since the iron and steel mills industries in Kirkenes is no more in full capacity, additionally this industry is intermittently shut down. However, The findings of this thesis in relation to Cr, is inconsistent with findings from Rognerud et al., 2013, who concluded that Cr among other metals are major pollutants released into the atmosphere by the smelter in Russia. Zinc as pollutant in the vicinity of the study area is seen to have diverse sources. These sources are the smelter at Russia, local mines and industries at Norway as well as traffic in the vicinity of the Norway –Russia area (Ayras et al., 1997). This is also consistent with the deposition pattern of Zn enrichment towards the surface of the peat in this study, an indication of the active emission source which in this case more likely to be the smelter and traffic. According to Rognerud et al., 2013, Cr, Zn, Ni, and Cu among others are major constituents of the ore in the Cu-Ni smelter in Russia. From the above named author, these elements are released in larger particles at high temperatures and thus are mainly deposited as dry deposition within short distances around the smelter. These argument tend to support the findings of this thesis work which has recorded high concentrations of Cr, Ni, Cu, and Zn. Hg, Pb, As and Cd are released in minor quantities into the surrounding areas of the smelter located in Russia. But they usually undergo long range transport since they appear in the form of small aerosols (Rognerud et al., 2013).

It must be noted that from the concentration data, some of the concentration values recorded high standard deviation which could have been solved by repetitive decomposition of the samples and finding the average, but that could not be done due to time constraint. This problem arose probably from lack of thorough homogenisation of the sample.

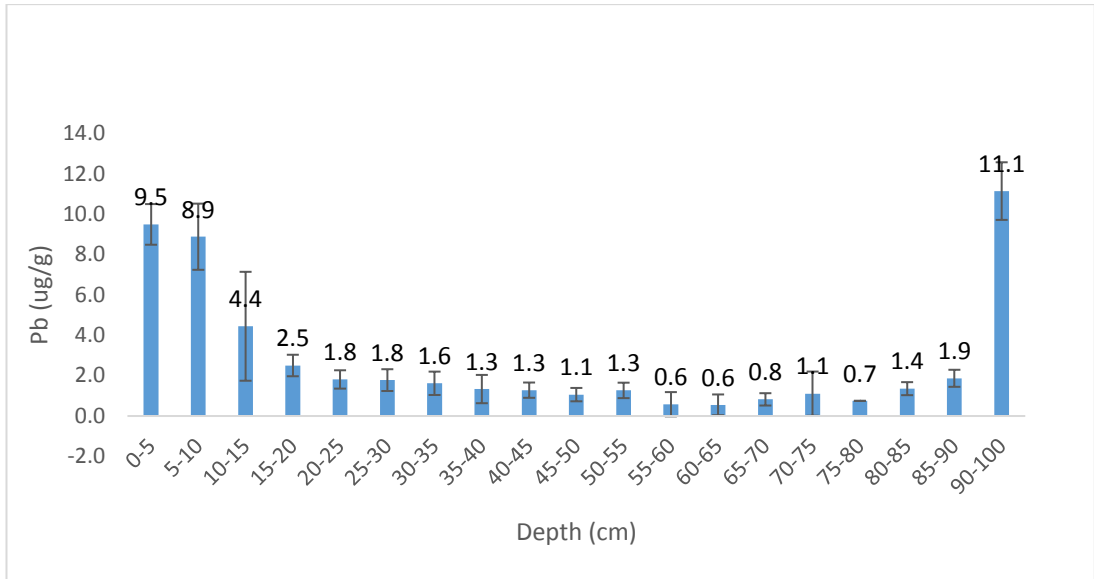
## **5.2 Pb concentration with depth of peat layers.**

The Figures below show the concentration of Pb in peat sample at different peat depths in 3 different sampling sites (A, B and C) from the Ni-ore smelter



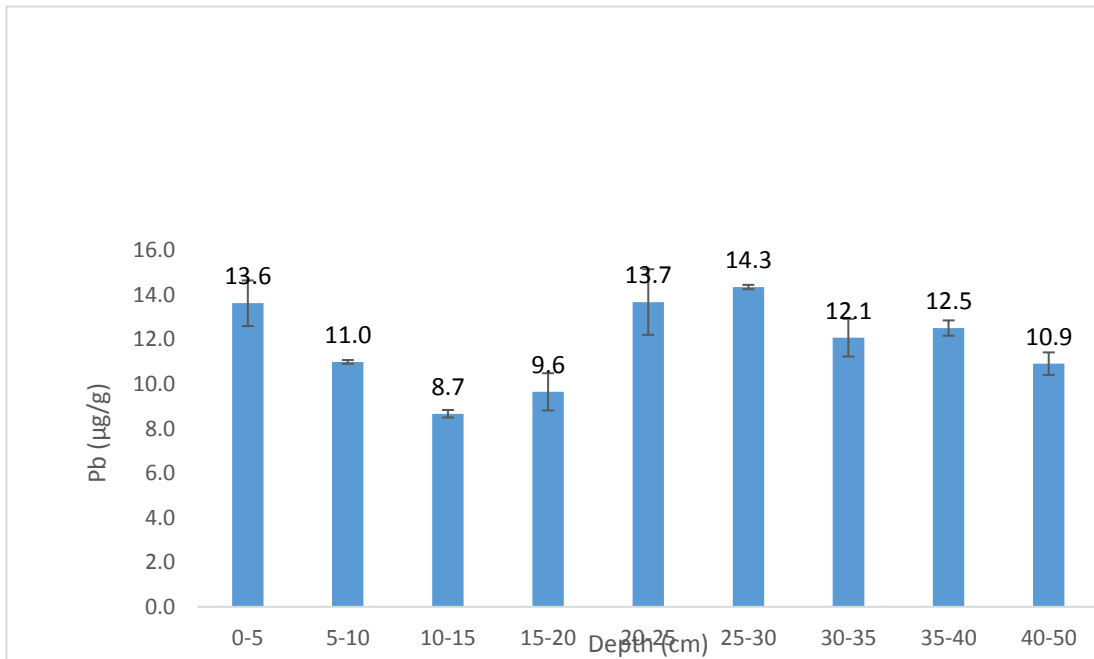
**Figure 3. Average concentration of Pb (µg/g) as a function of depth (cm) sampling site A.**

Figure 3 above, showing the vertical distribution of Pb indicate depth 40-45cm as having the highest concentration of 4.2 µg/g at sampling site A. From this depth, upwardly (toward the surface) the concentration dropped to 0.7ug/g at depth of 20-25cm. However, from the 15-20cm depth, the concentration of Pb showed an upward trend of 1.1µg/g to 1.2ug/g at 10-15cm through to 1.7 µ/g of depth 5-10cm to 2.6 µg/g as the uppermost concentration at 0-5cm. An indication that Pb emission at the sampling site is within short term deposition.



**Figure 4. Average concentration of Pb ( $\mu\text{g/g}$ ) as a function of depth (cm) at sampling site B**

At sampling site B, with corresponding graph 2, the highest concentration of Pb occurred at depth of 90-100cm of value 11,1 $\mu\text{g/g}$ . The concentration of Pb decreased towards the surface layers, till the 30-35cm depth when the concentration started increasing from 1.6 $\mu\text{g/g}$  to 9.5 $\mu\text{g/g}$  at the outermost layer of 0-5cm. The pattern obviously show Pb enrichment in the surface of the peat in this sampling site.



**Figure 5. Average concentration of Pb ( $\mu\text{g/g}$ ) as a function of depth (cm) at sampling site C.**

From the highest concentration of Pb at depth of 25-30cm corresponding to 14,3ug/g, from site C, showed by figure 5, the Pb concentration decreased toward the surface layers till the 5-10cm depth, when it began to soar from 11.0 ug/g to 13.6 ug/g at the outermost layer of 0-5cm.

From the figures and resulting analysis above, the concentration of Pb is increasing towards the surface layers (surface enrichment) in all the 3 sampling sites.

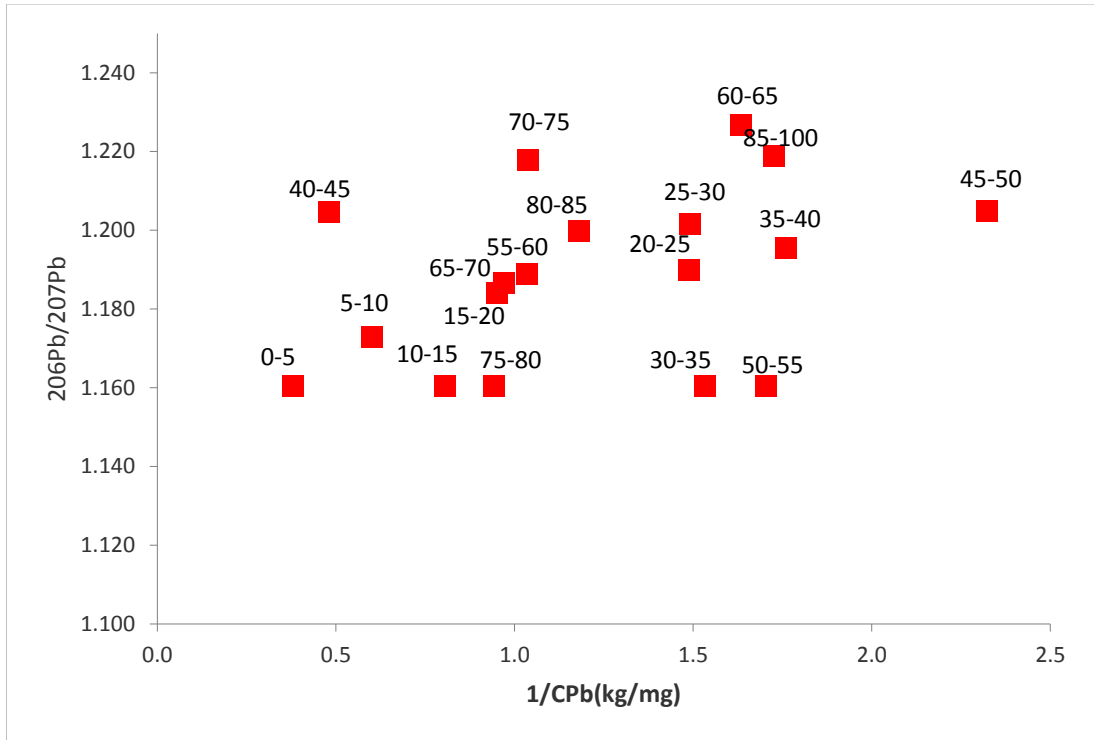
### 5.3. Pb isotope ratio, depth of peat and inverse concentrations of Pb at the 3 sampling sites.

The tables and figures below show the peat depth, the Pb isotope composition ratios ( $^{206}\text{Pb} / ^{207}\text{Pb}$ ,  $^{208}\text{Pb} / ^{206}\text{Pb}$ ).

Source identification becomes the rationale step after assessing the concentration levels of toxic metals (lead) in the study area. The use of stable Pb isotope composition ratio has proven as efficient technique for source apportionment of Pb pollution (Komarek et al., 2008).

**Table 5. Sampling site A**

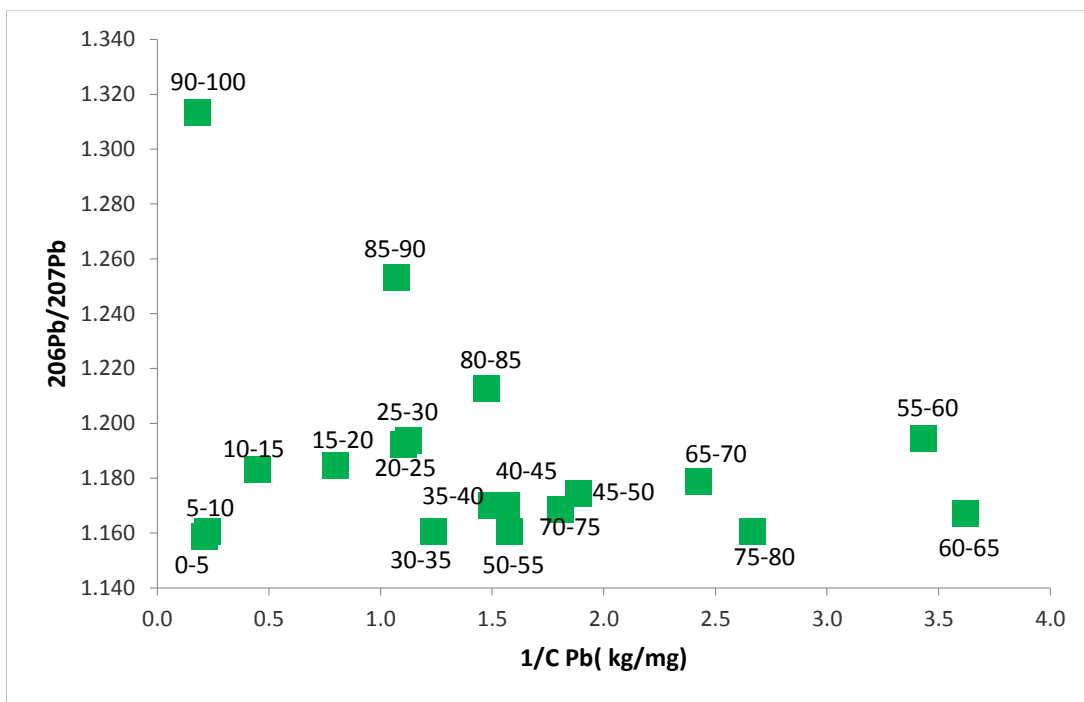
Depth	1/C	$^{206}\text{Pb} / ^{207}\text{Pb}$	$^{208}\text{Pb} / ^{206}\text{Pb}$
0-5	0.379	1.160	2.101
5-10	0.601	1.173	2.087
10-15	0.804	1.160	2.083
15-20	0.950	1.184	2.075
20-25	1.488	1.190	2.071
25-30	1.492	1.202	2.053
30-35	1.533	1.160	2.065
35-40	1.759	1.196	2.063
40-45	0.480	1.205	2.060
45-50	2.322	1.205	2.053
50-55	1.704	1.160	2.067
55-60	1.034	1.189	2.068
60-65	1.634	1.227	2.030
65-70	0.972	1.187	2.075
70-75	1.037	1.218	2.039
75-80	0.944	1.160	2.037
80-85	1.179	1.200	2.057
85-100	1.725	1.219	2.045



**Figure 6. Showing  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio and the inverse concentration of Pb at sampling A.**

**Table 6. Sampling site B**

Depth	1/C	$^{206}\text{Pb} / ^{207}\text{Pb}$	$^{208}\text{Pb} / ^{206}\text{Pb}$
0-5	0.211	1.159	2.099
5-10	0.225	1.160	2.096
10-15	0.450	1.183	2.090
15-20	0.800	1.184	2.088
20-25	1.105	1.192	2.083
25-30	1.125	1.194	2.085
30-35	1.235	1.160	2.075
35-40	1.499	1.170	2.096
40-45	1.564	1.170	2.098
45-50	1.890	1.174	2.110
50-55	1.578	1.160	2.093
55-60	3.432	1.194	2.078
60-65	3.619	1.167	2.101
65-70	2.425	1.179	2.094
70-75	1.806	1.169	2.099
75-80	2.667	1.160	2.074
80-85	1.477	1.213	2.067
85-90	1.071	1.253	2.042
90-100	0.180	1.313	2.009

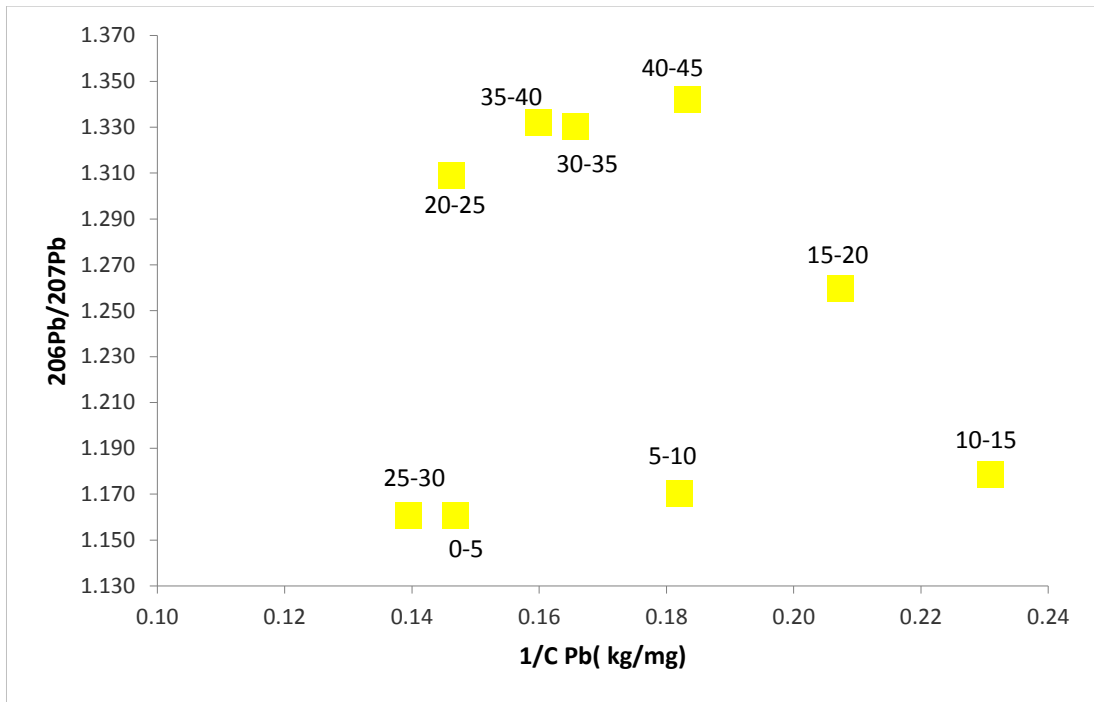


**Figure 7. Showing 206Pb/207Pb ratio and the inverse concentration of Pb at sampling B.**

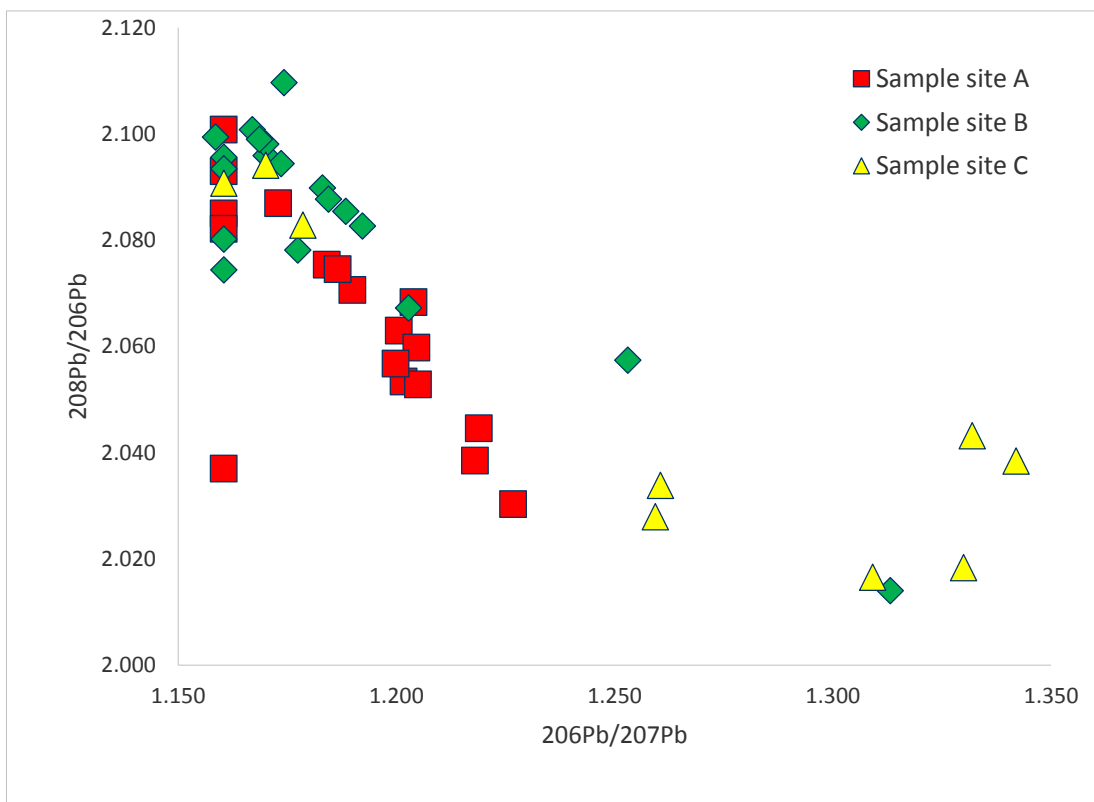
**Table 6. Sampling site C**

Depth	1/C	206Pb / 207Pb	208Pb / 206Pb
0-5	0.147	1.160	2.091
5-10	0.182	1.170	2.094
10-15	0.231	1.179	2.083
15-20	0.207	1.259	2.028
20-25	0.146	1.309	2.017
25-30	0.139	1.160	2.034
30-35	0.166	1.330	2.018
35-40	0.160	1.332	2.043
40-50	0.183	1.342	2.038





**Figure 8. Showing <sup>206</sup>Pb/<sup>207</sup>Pb ratio and the inverse concentration of Pb at sampling C.**



**Figure 9. Showing the ratios of <sup>208</sup>Pb / <sup>206</sup>Pb and <sup>206</sup>Pb / <sup>207</sup>Pb in all the 3 sampling sites.**

The  $^{206}\text{Pb}/^{207}\text{Pb}$  composition ratio serve as the most significant for the analysis of Pb isotopic composition in the peat core and Pb pollution source identification. Major sources of Pb for consideration in the vicinity of the study area and their  $^{206}\text{Pb}/^{207}\text{Pb}$  composition ratio are:

Ni smelter: Ni concentrate  $^{206}\text{Pb}/^{207}\text{Pb}$ - 1.150, Ni slag-  $^{206}\text{Pb}/^{207}\text{Pb}$ -1.14

Gasoline: from both unleaded gasoline station in Kirkenes Norway and Nickel, Russia has  $^{206}\text{P}/^{207}\text{Pb}$  - 1.10. European gasoline of  $^{206}\text{P}/^{207}\text{Pb}$  – 1.12-1.168 (Komarek et al., 2008)

Natural Pb: natural Pb derived from bedrock in Norway-  $^{206}\text{P}/^{207}\text{Pb}$ - 1.22.

In sampling site A, Table 5, the range of  $^{206}\text{Pb}/^{207}\text{Pb}$  composition is 1.16-1.227. With the possible sources of Pb being from the combustion of European gasoline and the bedrock.. Most of the samples recorded  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.160, an indication of European gasoline as a major source of Pb pollution. From figure 6, the surface depth of 0-5cm was an extremely high concentration of Pb. At sampling site B, Table 6, the  $^{206}\text{P}/^{207}\text{Pb}$  composition range was 1.159-1.1313. Again a mixture of Pb sources can be attributed to it, this can be from both the Ni concentrate, the bed rock, and the European gasoline. Again, most of the samples have ratios of 1.160. Reaffirming the combustion of European gasoline as big source of Pb contamination. The surface layers of 5-10cm and 0-5cm from figure 7 are the most contaminated with Pb.

From the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, at sampling site C, table 7, 1.160-1.342. Once again mixing sources of Pb can be ascribed to it. These are European gasoline, the bedrock especially the deeper layers, and Ni concentrate.

From the 3 isotopes plot in figure 9, site A and B are the most Pb polluted area as compared to site C.

## **6. Conclusion**

The use of peat core to determine atmospheric deposition in the highly contaminated Norway- Russia border, revealed high average concentration values associated with Cr, Ni, Zn and As with comparison with soil quality threshold values, from Norwegian pollution control report, 1999. However, Pb though significantly enriched in the source layer and As showed average concentration below the target values. Using Pb isotope composition analysis, mixture of sources were identified as sources, with European gasoline showing as the major source in all the 3 sampling sites.

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