2003

Variability of metals in soils in the Sudbury area (Ontario)

Vera Spektor
Wilfrid Laurier University

Your file Votre référence
ISBN: 0-612-80880-7
Our file Notre référence
ISBN: 0-612-80880-7

Variability of Metals in Soils in the Sudbury area

By

Vera Spektor

Bachelor of Science, Moscow State University, Lomonosov, 1999

Master of Science, Moscow State University, Lomonosov, 2001

THESIS

Submitted to the Department of Geography and Environmental Studies

in partial fulfillment of the requirements

for the Master of Environmental Studies degree

Wilfrid Laurier University

2003

Abstract

Industrial development influences the natural and human environment. At the local scale, the most intensive industrial pollution is in the area of factories and industrial centers. Industrial pollution is concentrated in soil and vegetation (then, using water systems and trophic chains it may enter all ecosystem components). The industrial pollution of the Sudbury region includes mostly sulfur dioxide and heavy metals.

The main goal of this study was to examine spatial variability in metal distribution in soil for the Sudbury area. Objectives of the work were to describe metal distribution depending on geographic factors such as topographic location, vegetation cover, distance from the source of pollution and influence of metals on human's health.

For reaching the goal of the work a sampling methodology was developed. Samples of the litter layer, and the A and B soil horizons were taken from different locations to study the distribution of heavy metals in the area. The studies also included short botanical descriptions. All samples were later tested using X-ray fluorescent analysis.

Results allowed the conclusion that metal concentrations vary according to the soil horizons and vegetation and topography of surrounding areas. Emission levels from the single source of main pollutants are still high due to which all surrounding ecosystems are still under a strong environmental stress. High levels of metals in surrounding agricultural areas have increased the potential negative influence on human health.

Acknowledgements

Many people have contributed their time and assistance to the creation of this thesis. At first I would like to thank my advisors Dr. Michael English and Dr. Scott Slocombe for their guidance, support, time and quick response for all my concerns and questions. Also I would like to thank Dr. Graeme Spiers, Dr Peter Beckett, Dr. David Pearson and Andriy Cheburkin for their advise and recommendations about the study area.

I would like to thank Merrin Macrae for her help during the field season and support, to Roger Palmini for his support and help with statistical analyses and all members of CFI lab for their support, chocolate and cookies.

Special thanks to my family for their huge moral and financial support. This degree is for you!

Table of Contents

List of Figures

List of Tables

Chapter 1. Introduction

Industrial environmental pollution of ecosystems from the non-ferrous smelting industry is a serious problem for many countries due to the release of metals into the environment. Metal contamination in northern temperate areas is poorly understood and delineation of the extent of the contamination is not well documented. Though plants and animals depend on some metals as micronutrients, certain forms of some metals can be toxic and therefore pose a risk to the health of animals and people. For example, recent cases of human illness due to metal contamination of soils by atmospheric pollution have been documented in Ontario in the Wawa and Port Colborne areas (Gunn, 1995)

Given the number of smelters that are or have been operating in Canada, the problem of soil metal contamination is probably widespread. Metal contamination is a major problem in northern regions of Canada and Russia, as (a) these regions host most of the major northern industrial smelters, and (b) northern ecosystems are highly sensitive areas that lack the capacity to recover from disturbances quickly. The scientific community and policy-makers are interested in these environments in order to repair past damage due to industrial pollution and to prevent future degradation of northern landscapes and communities (Golubeva, 1999)

As a result of the movement of pollutants high in the atmosphere, pollution by smelters has global implications. Thus, the implications of management of the smelting industry go far beyond the local or regional level.

Sudbury, Ontario is an area that has been strongly impacted by the smelting industry. As such, this area has been the focus of the research community (tracking metals in the environment and re-vegetation programs) and government (policy decisions and management) for approximately 40 years. Extensive research has also been conducted in Russia (Kola Peninsula, Norilsk) on the effects of smelters and industrial pollution on the natural and human environment.

Many problems have been associated with pollution by the smelting industry in these areas, for example: pollutants in the environment impact natural terrestrial and aquatic ecosystems, agricultural practices, and city planning and housing. Thus, a thorough understanding of the accumulation and storage of metals in the environment can assist city planners in designating spaces in communities for specific land uses (*i.e.* by evaluating how 'safe' they are for agriculture, housing, playgrounds, and wildlife). Monitoring programs have been in place for approximately 30 years in Ontario (Ontario Ministry of the Environment, 2001). However these programs, like many monitoring programs, are limited by cost and other logistical problems. Consequently, it is necessary to focus monitoring programs on specific representative areas, and monitor these areas as efficiently and consistently as possible. Given the high potential for variability in rates and patterns of deposition of the metals, a quantitative examination of their spatial distribution in the environment is warranted.

1.1 Goal and objectives of the thesis

The overall goal of this thesis is to examine spatial variability in the accumulation of metals surrounding a point source in Sudbury, Ontario and make recommendations for future monitoring programs (*i.e.* where to sample to obtain the most representative results).

The specific objectives of the work are to

1) Describe how the distribution of metals in soils changes with distance from a point source (smelter);
2) Describe the distribution of metals accross different types of landscapes that are representative of the Sudbury area (*e.g.* coniferous forest, deciduous birch forest, and forested and grassed hill slopes).
3) Describe the distribution of metals with depth in the soil profile in different environments. Pollutant deposition rates within the Sudbury area have been drastically reduced in the past 25 years; SO_2 emissions have been reduced by 90 percent (Gunn, 1995b). An examination of surface soils alone may not be representative of the true concentrations of pollutants in the soil, as many metals may have been translocated downwards in soils or removed by erosion.
4) To evaluate spatial variability of metals within a given site.

Through the examination of variability both within and among different landscapes in the region, this thesis will provide a model for metal variability in the Sudbury area.

1.2 Outline of thesis

This thesis comprises five chapters. The second chapter provides a literature review on metal contamination in the environment, background information about the metals examined in the thesis and the relationship between human health and metal contamination. The third chapter describes the study site area and all stages of the field and laboratory work including methods that were used. The fourth chapter shows all data that were collected, examined and used during this research. The final chapter discusses the results, linking physical and management issues. Conclusions and recommendations are presented.

Chapter 2. Influence of non-ferrous industries on the environment in Northern Countries

This chapter reviews background literature on metal influences on the environment and their relation to human health. This chapter concentrates on the importance and danger of the metals, understanding of soil-vegetation cover as indicators of ecosystem health, and presents two case studies.

There is agreement among Arctic countries that one of the most serious environmental problem for this large region is pollution from heavy metals, and radioactive elements (AMAP, 2000). The influence of copper-nickel smelters and impact on the environment of Russia (Kola Peninsula and Norilsk) and Canada (Sudbury area) will be discussed.

2.1 Smelting and pollution

To produce nickel, copper or any other metal from ore it is necessary to employ extraction technologies. During the different stages of processing, many environmental pollutants are produced. The main ore products from mining concerns in the Sudbury area are nickel and copper. Other elements extracted include: cobalt, platinum, palladium, osmium, iridium, rhodium, ruthenium, zinc, lead, arsenic and some other elements. Almost all minerals in the ore are sulfured (Winterhalder, 1995). For sulfide ore processing flash smelting is the most commonly used technology today, but at the same time electric smelting is used for more complex material. Both of these processes use dry concentrates. Electric smelting requires a roasting step to reduce sulfur. Sulfur dioxide is a major air pollutant from roasting and smelting. Sulfur dioxide releases can be as high as 4 tonnes of sulfur dioxide per tonne of nickel produced (World Bank Group, 1998).

Sudbury mining history began in 1888, when the first roast yard and smelter were set up. Roasting was normally the first step for the Sudbury ore. The ore was heated in air to a temperature at which much of the sulfur was oxidized, and then combusted to form sulfur dioxide. Ore was next burned for approximately 2 months or more using wood and then it was sent to a smelter (Hutchinson, 1997; Winterhalder, 1995).

Levels of emissions from the area have dropped due to new technology and new scrubbers that are used. According to data from different sources, after the new smelter (SuperStack) started to operate in 1972 emissions of sulfur dioxide dropped for 60 percent (Gunn, 1995a). Emissions before 1973 were at least 24 000 tonnes per year. As recorded by the Ministry of the Environment (1982), between 1973 and 1981, after the "SuperStack" (new smelter) started to operate, around 15 000 tonnes of particular matter were released into the atmosphere each year. By the year 1995 emissions had dropped by 90 percent from their level in 1973, to 1500 tonnes of particulate matter per year.

2.2 Importance and danger of metals

Metals and mining are part of everyday life. Without provision of metals from the mining industry it would be impossible for the economies of much of the world to continue as they do. Many metals are found in everyday products, and they are fundamental for new and old technologies. Metals are also an important element in normal flora and fauna development, however high concentrations can be toxic.

Human activity has modified the various metal cycles on a regional and global basis. Of 108 elements known, 84 belong to the group of metals, 17 to nonmetal and 7 to the metalloids. Of the ten most abundant elements in the earth's crust, seven are metals: aluminum, iron, calcium, sodium, potassium, magnesium and titanium.

Most of the above elements can be found in the soils of mining areas or industrially developed areas. In the atmosphere these elements are represented by particles, that is why they mainly deposit on the ground surface.

In most of the mining areas, soil has a very low pH level due to the effects of acid rain. Acid rain lowers soil pH, and that increases ability of soil to hold more metals. For the Sudbury area soil pH was low for many decades which means that metals can migrate through the profile. During the last 20 years the soil pH was elevated by liming the area, but still soil continues to be acidic.

The precipitation of solids such as carbonates, oxides, phosphates, sulfides and some others limits metal solubility. The solubility of heavy metals in soil has strong associations with organics. The solubility of metals in soil can be increased by lowering the pH level of soil (Solomon, 1995). Copper, nickel and zinc can adsorb into fine grain soil material and be moved this way though the aquatic system, but not really in the atmosphere. At the same time for copper, zinc, magnesium biogenic accumulation plays an important role (Alekseenko, 1990).

The elements that will be examined in this work are chosen according to the operation of the smelter and levels of pollution from the Sudbury area.

Copper (Cu)

Copper has been known and used for more than ten thousand years. Copper can be easily extracted from ores.

Copper is one of several metals that are essential to life (Merian, 1991), despite being as inherently toxic as non-essential heavy metals, exemplified by lead and mercury. Copper is toxic to many bacteria, that is why for many years copper pipes have been used in homes.

Different soil qualities influence the uptake of copper by the roots of plants. It is assumed that exchange reactions and the nitrogen content of the soil are important factors for the passive transport of copper. Some mosses and plants are capable of accumulating copper. Some pines may contain several hundred ppm (parts per million) of copper (Merian, 1991).

Copper, a natural element, has been a part of organisms' development. It combines organic compounds in an organism to create biologically active materials such as enzymes and protein. Biotransformation, electron transfer, oxidation and reduction, tissue respiration cannot work without copper. Copper is one of the most important nutrients for human health as well as the growth of animals and plants (Alekseenko, 1990; Luoyang Copper, 2001). But at the same time high concentrations of copper can be toxic to all living forms.

Nickel (Ni)

Nickel is spread widely in the environment. Divalent nickel compounds are relatively nontoxic for plants, fish, birds and mammals. Nickel carbonyl is an extremely toxic vapor, which is absorbed upon inhalation. Nickel carbonyl, $Ni(CO)_4$, is an important organic compound from the viewpoint of toxicology. It can penetrate cell membranes and traverse the blood - brain barrier (Merin, 1991).

Nickel is one of the important elements in everyday technical life. It is used in changes of physical characteristics of other elements and products. For example combination of nickel and chromium metal increases resistance to heat. It is an important additive to steel for increasing anticorrosion quality (Tylkina, 1972; Dric, 1997). Nickel enters groundwater from dissolution of rocks and soil, from biological cycles and from the industrial sector and waste disposal. Acid rain has a pronounced tendency to mobilize nickel from soil and to increase concentrations in groundwater, increasing potential toxicity for microorganisms, plants and animals (Merian, 1991). Nickel compounds in soil can be taken up by plant roots and accumulate in a human's body from agricultural products.

Zinc (Zn)

The toxicity of zinc and most zinc-containing compounds is generally low; nevertheless, industrial waste can contain harmful concentrations of zinc for the environment. The toxicity of zinc to plants is generally low and is only observed in soils, on waste stockpiles, on dumping grounds, etc. Some sensitive species could show zinc toxicity at soil levels of about 300 mg/kg. Zinc is used in many areas of our everyday life including dry cell batteries, electroplating, cable wrapping and plastic. It plays an important role as an essential trace element in all living systems from bacteria to humans. Its supply to plants depends mainly on the geological origin of the various soils (Merian, 1991).

Chromium (Cr)

Chromium is an element found in many minerals which are widely distributed in the earth's crust. When looking at global cycles it seems that chromium compounds are immobilized, but emissions into the atmosphere or into water may be sustainable (Merian, 1991).

The quantities of chromium in the soil that are dangerous for plants depend largely on its biological availability to them. It is toxic by inhalation of dust, one of the first signs of chromium poisoning by inhalation is the loss of the smell sense. In plants chromium can cause root damage (Hawley, 1971; Merian, 1991)

Chromium is widely used in scientific research connected with nuclear power or high temperature studies (Hawley, 1971). Combination of chromium with steel increases its heat-resistant quality (Dric, 1997). The uptake of chromium (III) from the soil depends upon the species of plant.

Manganese (Mn)

Manganese is supposed to be a non-toxic element, but an excess of manganese in plants causes chlorosis (Merian, 1991). However, the tolerance of most plants is very high (in some cases up to 2000 mg/kg). In other cases, manganese salts are apparently potent mutagens (Bowen, 1979). It accumulates in some floral species. Manganese from dust deposits and rainfall accumulates in the upper soil horizon. It seems to be an essential trace element for all organisms. It exists in soil, plants and animals almost independently from human activity. Small amounts of the element are important as a nutrient to plants (Merian, 1991). In many cases manganese can replace magnesium in soil. Significant amounts of the element in the system can cause changes in the bones of man and mammals.

Zirconium (Zr)

Zirconium is a generally non-toxic element and concentration limits that can cause problems are not yet evaluated (Merian, 1991). It is classified as the 20^{th} most common element.

According to the parts of the body where zirconium accumulates mostly it could be a reason for liver and lung cancer in some way (Merian, 1991). Pure zirconium is highly resistance to heat and corrosion that is why it widely used in space technologies, medical equipment and other areas (Hawley, 1971).

Normally zirconium does not accumulate in food chains and is very slow to be taken up by plants, even if the amount of the element in soil is high (Merian, 1991). In humans, zirconium is mostly accumulated in fat, blood, liver, lungs and brain (Los Almos, 1997).

Yttrium (Y)

Yttrium is stable in water and oxidizes easily in moist air. Radioactive isotopes of Yttrium (^{90}Y and ^{91}Y) appear in the environment as a product of nuclear fission (Los Almos, 1997).

Yttrium is used to increase the stability of copper-nickel steel against oxidation and it is also used in laser instruments (Dric, 1982). The main pattern for the element to accumulate in different living systems is to replace calcium. That is how it could accumulate in different systems (Merian, 1991).

Rubidium (Rb)

Rubidium is one of the most electropositive and alkaline elements. It reacts spontaneously in air and violently with water, setting fire to the liberated hydrogen. That is why it must be stored under kerosene or similar liquid. It forms amalgams with mercury. Some of the common rubidium compounds are: rubidium chloride, rubidium monoxide and rubidium copper sulfate (Hawley, 1971).

Rubidium is used in photoelectric cells, vacuum tubes and high speed lamps. The largest portion of metallic rubidium is used however for research purposes. It can cause serious skin burns. Rubidium salts such as rubidium chloride or rubidium bromide are used in medicine as pain killers or tranquilizers (MedlinePlus, 2002).

2.3 Accumulation of heavy metals from air by vegetation and soil

Heavy metals are those which have atomic masses greater than 50 (Tylkina, 1971). It is a large group of metals in which we have elements which are important, such as Zn, Cu, Mn, Fe, Co, and Mo. High concentrations of these metals are often found near smelters. Several elements are toxic for vegetation cover and are ranked in order from the most to least toxic elements: Cu, Ni, Cd, Zn, Pb, Hg, Mo (Alekseeva – Popova, 1991)

Heavy metals are common soil contaminants. In addition to natural occurrence, different amounts of metals can get into soil by dry or wet atmospheric deposition. Their degree of mobility and activity are influenced by many soil parameters, such as temperature, pH, soil solution and moisture. They are also influenced by the initial chemical form of the metal and the type of plants and animals in the system (Ross, 1994).

McBride (1989) suggested that the most valuable way to assess the mobility of metals in soil was through understanding soil properties and the conditions that affect the residency of metals in soil. The main problem is the potentially massive number of influential factors and their interaction in soil.

Generally the trace metal input to soil from parent rock is low and only likely to produce potentially toxic metal concentrations locally in areas of oxide-rich deposits. At the same time precipitation and adsorption are the main physical-chemical processes, that control concentration of metals in soil solution (Brummer and Tiller., 1983).

Chemicals from soil can be transported back into the atmosphere, ground water and vegetation cover (Connel, 1997). These connections are illustrated in Figure 2.1.

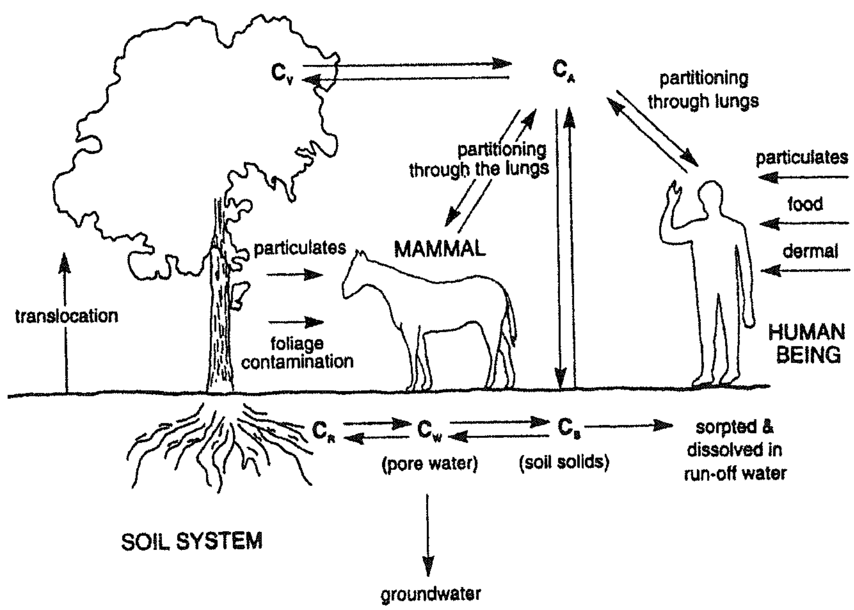


Figure 2.1 Distribution patterns of contaminants in ecosystems

Where: *Vegetation (Cv) ↔Atmosphere (Ca) ↔ Soil solids (Cs) ↔ Pore Water (Cw) Roots (Cr) ↔Pore water (Cw) ↔ Soil solids (Cs) → Sorpted and dissolved in run-off water* (Source: Connell, 1997).

When metal particle sediments migrate from air to vegetation cover, they partly accumulate as a cover and partly build up inside the vegetation cells. The mechanics of this process have not been well studied yet, but it is possible to highlight a few factors that play a role in this process: (a) structure of leaves, specifics of their shape and physiological factors; (b) factors of surrounding environment (wind, precipitation, pH, humidity and others); (c) physical and chemical characteristics of pollution elements. Aerosols and metal particles can be accumulated by leaf cells from air distribution (Little, 1972).

Mechanisms of leaves accumulating metal ions are complex and include passive diffusion and active transport. Soluble metals and their combinations contacting with leaves can partly accumulate in them and move from the leaves to the roots of the plant. There are some examples in the literature that Fe, Cu and Zn can be transported from leaves to other parts of the plant (Beavington, 1976). Carlson (1975) and Foy (1978) showed that after 24 hours of nickel accumulation from air, 24 percent was found in the plant and after 16 days the amount was 57 percent. Leaves are more sensitive to nickel than roots, because smaller concentrations, in most cases, can stop development and growth processes.

The main pollutants in mining and smelter areas are sulfur dioxide and heavy metals. Acid rains accompanied by heavy metals may cause changes in the soil system (Hutchinson, Whitby, 1986). Organic and mineral soil particles have negative charge sites on them. That is why cations (positive charged ions) become attached to the negatively charged site. Plant roots absorb cations for nutrition and growth. Roots deposit an equal amount of hydrogen ions into the soil solution, due to which it becomes more acid (Madison, 2002). High concentrations of metals in the soil can slow root development and do not allow new species of plants to grow or develop. High concentrations of Ni and Cu in soil around smelters are one of the reasons for slow development and degradation of vegetation cover and soil (Hutchinson, 1992).

Many researchers show that increasing concentrations of metals in air and soil cause changes in flora, due to degradation of the most sensitive species. As a result only a few species survive in areas that receive elevated concentrations of smelter emissions. The surviving species are mostly local ones, more resistant to metal pollution or have become resistant over time to elevated concentrations of metals. It should be mentioned that resistant vegetation species collect significant masses of the metals in question. As an example Hutchinson (1981) report resistant species located close to INCO smelters (Table 2.1).

Table 2.1 Vegetation species resistant to high levels of emissions

Vegetation species		**Element**
Agrostis stolonifera	Red top	Cu
Agrostis tenuis	Bent-grass	Zn, Cd
Festuca ovina	Sheep Fescue	Zn, Pb, Cd
Holdus lanatus	Velvet grass	Cd
Deschampsia caespitosa	Tufted Hair Grass	Cu, Ni, Al, Zn, Co

Plants can develop resistance, especially to elements that are the main pollutants in an area. That is why some local vegetation species can be resistant to a group of elements, as shown in Table 2.1. Such research was carried out in Sudbury by Hutchinson, (1981) who demonstrated that adaptation to one metal can cause resistance to some others that are also present in high concentrations.

2.4 Vegetation as an indicator of ecosystem health

Different combinations of vegetation species can represent different environmental conditions, such as natural surrounding or environment under industrial pressure. Different intensities of metal pollution have different influences on vegetation cover. These influences can be divided into two types: high concentrations of toxic elements during a short time and low levels of pollution over a long time.

When comparing the sensitivity of vegetation and human physiology to pollution, vegetation is more sensitive to pollution. The effects of pollution on vegetation can be seen earlier than changes on a human physiological level. That is the reason why in many countries special standards and levels of pollution have been established in order to protect vegetation (Golubiatnicon, 1998).

Vegetation damage under industrial influence can be divided into "unnoticeable", chronic and serious (Aleksandrov, 1999). With low levels of pollution, damage to vegetation is mostly noticeable at the physiological and biochemical level. Chronic effects are noticeable with long term pollution; it should also be mentioned that combinations of different metals can be more dangerous and cause a more serious degradation or mutation than each of the elements can independently.

2.4.1 Lichen-indication

Many different types of vegetation can be used as indicators and accumulators of pollution based on their different reactions to different levels of pollution. It could be lichens, mosses, grasses, trees and so on. In such cases we are talking about biological monitoring.

Studying metal pollution levels by analyzing lichens was developed in the second part of the twentieth century. Field research conducted on the influence of air pollution on lichens has tried to discover what the dependence is between lichen morphology and various factors regarding local pollution. Lichens are used widely for biological monitoring because of their high sensitivity to air pollution (Beckett, 1995; Hutchinson, 1978). The reasons for this are:

- No vegetative cover which makes it impossible to control the amount and quality of gases and water they accumulate
- Changes in pH levels that could cause lichen death

Various species of lichens react to air pollution differently than vascular plants. By understanding how sensitive various lichen species are to metal pollution scientists can delineate areas of low to moderate to severe metal contamination by mapping the spatial distribution of lichen species. For example *Cetraria nivalis* and *Cetraria islandica* are two species that have very high tolerance levels for metal contamination. These differences allow scientists to mark different levels and areas of pollution for the interested area (Becket, 1995).

The influence of air pollution on vegetation can be seen first at the physiological level as for example damaging of leaf cells. Visible symptoms appear depending on the stage of cell degradation. Under long term pollution effects, these changes become more and more noticeable. For example, pines of the northern Russian tundra which have been under the influence of smelters for many years have developed the following changes (Golubeva, 1999):

- Chlorosis (yellow marks) and necrosis (black marks)

- Shorter life cycle of needles
- Faster die-back of tree crowns
- Needleless tree crowns
- Slower growing of branches and stems
- Changes in needle size
- Changes in the structure of young trees, growing as bushes or elfin wood

The type of metal pollutants, their concentrations, and accumulation, combined with the physiological system of the plant in question produce different reactions.

2.5 Soil Stress and reclamation

Intensive land use has caused soil contamination and stress all over the world. The stressed soil ecosystem would reduce the ability of the soil to perform such functions as decomposing the litter horizon (Weil, 2000). For Sudbury, soil metal contamination was first recognized at the government level in 1969, when control orders from the Ontario government were first applied against smelters (Pearson, 1995). Due to the poor environmental conditions in the area a land reclamation program was established to protect the surrounding environment of the Sudbury region. At the beginning of the program, nickel and copper concentrations in soil were more than 1000 ppm (McIlveen, 1994). For reduction of pollution levels different techniques were used. That was one of the first steps before it was possible to establish a reclamation program. One of the first goals of the reclamation program was to increase the soil pH level, which allowed later seeding of grasses and plant trees. For this purpose limestone was spread all over the restoration area, and a few weeks later a high-phosphorus fertilizer was applied. Only after this treatment to Sudbury soils was it possible to seed grasses. Most of the work was done by scientists and local volunteers. In approximately 15 years since the end of the 1970s about 3070 ha of bare land were seeded. At the same time mining companies were running re-vegetation program for their tailing areas (Gunn, 1996).

2.6 Influence of metals on humans

Metals are necessary and important in small concentrations in the human body. At the same time all elements can be toxic to humans after they reach a certain level of concentration. If an organism's uptake of a metal is greater than its ability to get rid of it, the metal will accumulate. Heavy metals tend to accumulate in storage compartments. For example, cadmium accumulates preferentially in the kidneys, mercury in the liver, and lead in the skeleton. The accumulation can continue throughout the organism's life and is the major cause of chronic toxicity. The strongest effect metals have is on infants. In contrast to organic pollutants, metals accumulate in protein tissues and bone rather than in fat (AMAP, 1999).

Humans have used metals for many centuries. For example, many succumbed to lead poisoning in the Roman Empire, because of drinking from lead vessels. Mining is one occupation where metal poisoning is a serious health problem due to the fine dust into which metals have adsorbed that workers inhale (Merian, 1991). The tiny particles of metals could be inhaled deep into the lungs, and may even be absorbed directly into the bloodstream. The body's immune system may mistake these particles for bacteria and start to attack them. That causes damage of healthy cells and increases risk of lung cancer, asthma, heart attack and many others (Eco-usa.net, 2002).

2.7 "Case studies" in some areas of Russia

The Kola Peninsula and Norilsk were chosen as case studies because their smelting operations use the same kind of ore deposits as Sudbury. Norilsk is a large center of nickel and copper smelting similar to Sudbury, but the technologies that they currently use are the same as those used during the 1960's in Sudbury. They represent areas where long - term emissions have the strongest influence on the environment from smelting operations and that is why these areas are of interest to scientists.

2.7.1 Specifics of industrial pollution on the Kola Peninsula

The Kola Peninsula is the most industrially developed area in the Russian North. The natural resources of copper - nickel ore and phosphates of the area are rich and complex. Most of the industry in the area is based on these complex deposits.

On a local level, industrial pollution became noticeable in the 1930s. The level of pollution increased as smelters were built. Today pollution impacts more or less the entire peninsula. Air pollution from the smelters has defoliated vegetation cover, acid deposition has changed pH levels of soil, water and all natural conditions of the area. Every year approximately 20-30 tons of sulfur are deposited per square kilometer (Kasimov, 1995).

The main polluter in this area is the "Severo-nickel" smelter that emits trace metals, sulfur dioxide, mineral dust, and many other gases which are easily distributed by wind. Annual emissions from the smelter operation total about 42 millions tons of sulfur dioxide, 150 tons of nickel, and approximately the same amount of copper and other metals (Golubeva, 1999a, b).

Industrial pollution influences not only vegetation, but also soil. Concentrations of the main pollutants (nickel, copper and cobalt) in vegetation and soil decrease with increasing distance from the source of pollution. As vegetation accumulates metals from the soil, various plant species can be used as an indicator of pollution levels.

Since 1946 forest degradation is visibly noticeable up to 6 km from the smelters. Pine tree growth does not exist within 17 km of the smelter (Kulik, 1994). When smelters switched from local to Norilsk ore, which is rich with sulfur, ecosystem degradation increased (Kasimov, 1995). Snow cover concentrations of nickel in 1966 were 30-1000 times more than background concentrations (Kulik, 1994). The background concentrations for copper were 30 mg/kg and for nickel 15 mg/kg (Spektor, 2001).

Between 1970 and 1973 no vegetation and top soil horizons were observed within 5-6 km of the smelter. Only on the edges of these areas, in spots protected from pollution by elevation, is there still some vegetation noticeable. Pollution traces can be seen at distances up to 80- 90 km now, with such noticeable pollution indicators in vegetation as necroses and chlorosis (Spektor, 2001).

2.7.2 Specifics of industrial pollution for Norilsk area, Russia

Norilsk, with a current population of over 200 000 people, is the centre of non – ferrous metallurgy and one of the largest cities above the Arctic Circle. Significantly rich deposits of coal and copper–nickel occur here and are the base for smelter production.

Norilsk as a city is quite young and depends on smelters which have operated since 1936 (Riashenseva, 1996).

The Norilsk area is one of the most environmentally damaged areas in Russia. Official government data state the environmentally damaged area around smelters and Norilsk reaches 7000 square kilometers (Russia, 1998), and vegetation degradation as the result of smelter operation is noticeable in an area five times greater. The main pollutants are sulfur dioxide and heavy metals which are spread by air streams, and waters which have been damaged by the acid mine tailings (Kasimov, 1995).

This environmental situation has a historical beginning. Smelters started to operate in 1935, when the main aim was to produce as much nickel and copper as possible and to spend as little money as possible. For more than twenty years from 1936 till 1956 it was a "GULACK" – a prison for political prisoners and a residence for prison facilitators. Then during the end of the 1950s and beginning of the 1960s it shifted from a prison complex to a free settlement. At the end of the sixties, rebuilding and reconstruction of smelters began, together with development of new significant deposits of ore rich in sulfur. Thus, mining continued to increase pollution levels, and further degradation of surrounding ecosystems. Tamarack forests were destroyed at a distance of 120 kilometers south-south-west from the source. At the same time it should be noted that the town was built between the various smelters, whereby no matter what direction the wind is blowing the town is constantly down-wind from one or more smelters. In addition, the building of the water reservoir also increased ecosystem degradation by changing the water table.

Generally, before the beginning of the 1970s nobody talked about the degradation of the area, which is why the first official record of forest degradation was not made until 1968

(Voropbieva, 1998). But when the pollution was at its maximum level in the mid-1990s, there was no money for developing and changing technologies, such as scrubbers. Currently, only hard large particles can be trapped (Savchenko, 1996).

Landscape degradation in the area is the result of vegetation, soil and permafrost damage (melting) from chemical pollutants and mechanical pollutants.

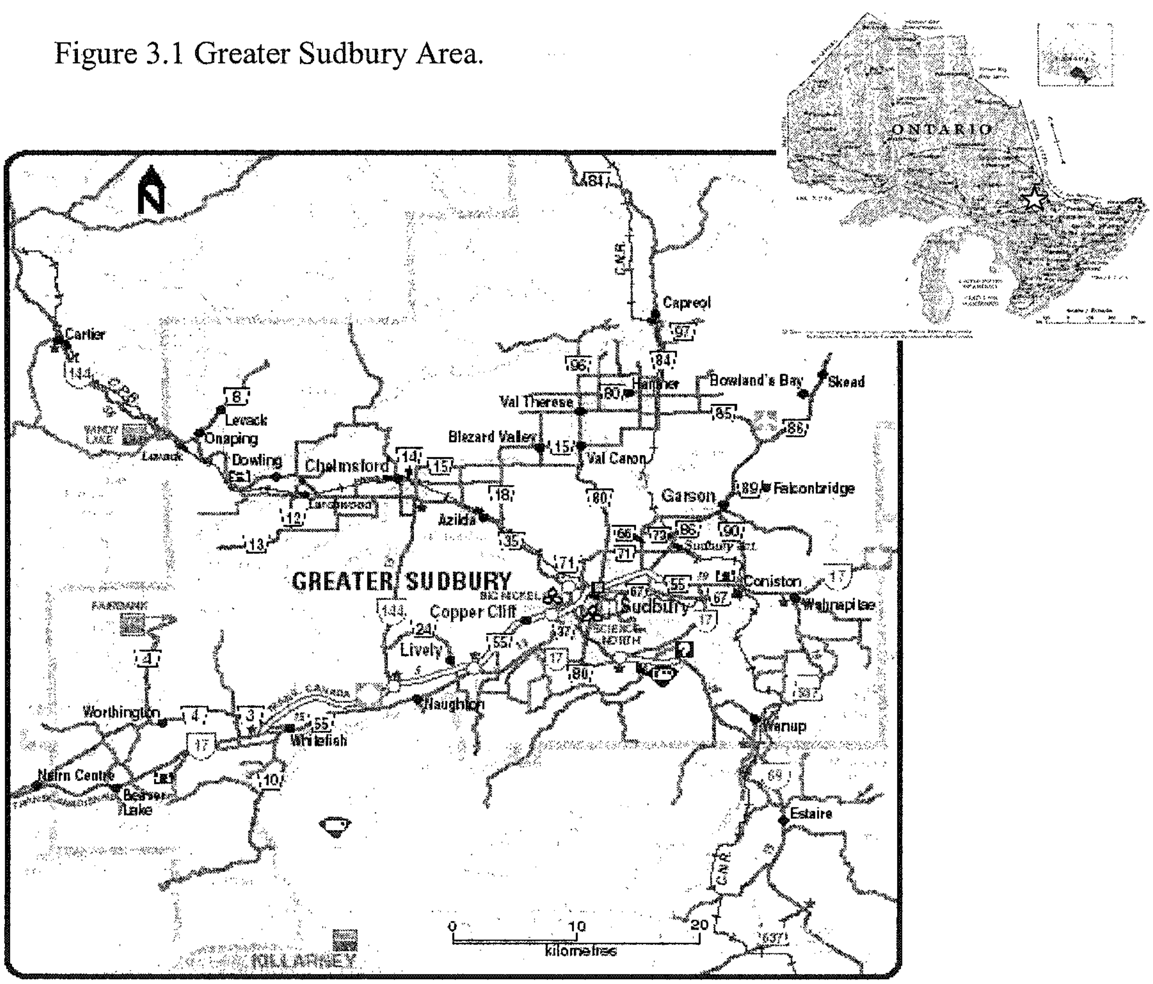
Since new rich ore deposits started to be developed in the 60s, the amount of sulfur dioxide pollution has increased. At least 43 percent of sulfur dioxide is spread from smelters into the surrounding environment (Kasimov, 1995). It causes tremendous change in soil systems. In the town and surrounding territories industrial soils are prevalent. These soils don't have a top soil horizon (litter). In tests of soil profiles in the area, concentrations of heavy metals are extremely high. Levels of copper are around 3000-4000 mg/kg, and nickel concentrations are 500-2000 mg/kg, which is a hundred times more then background metals concentrations in soil for this area. Metal concentrations in this range are mostly in the 5-10 km zone from the sources of pollution.

Chapter 3. Study site and methodology

3.1 Study Area

The Sudbury area is located near the southern edge of the Precambrian Canadian shield, just northeast of Lake Huron (Figure 3.1) [$46^0 00'$ N - $47^0 30'$ W; $79^0 30'$ N - $81^0 30'$ W]. The Sudbury area hosts the largest known concentrations of nickel on the surface of the planet. A generally thin veneer of sandy glacial sediments covers the bedrock and supports a thin soil and widespread forest. Today the majority of landscapes can be described as rock knobs or ridges of rolling hills and valleys (Pearson, 1995).

Figure 3.1 Greater Sudbury Area.



Source: MTO, 2002.

3.2 History of the Study Area

The first settlement of the Sudbury district was at Wanapitie Post, a Hudson Bay trading post in 1822 (Costescu, 1974). The main economic activity for the area for the first hundred years was an intensive lumber industry which exploited a significant forest cover of pines. This industry created stress to vegetation cover in the region, as well to the ecosystem as a whole.

In 1883, ore deposits were discovered in the region (Freeman, 1980). Prior to 1928, ores were mined by various small companies. In 1928, three large companies merged to form the International Nickel Company Ltd (INCO), now one of the two mining companies in the area. The other large corporation operating since 1928 in Sudbury is Falconbridge Nickel Mines Ltd (LeBourdais, 1953).

The provincial government of Ontario became concerned about metal concentrations in the local landscape in the 1960s when the results of degradation became more visibly noticeable. Since the 1960s government direction to reduce levels of pollution from 2.5 millions tonnes of sulfur dioxide per year to a much lower level were made (Gunn, 1995). INCO Ltd responded by building a single smelter and constructing an emissions stack at a greater height. This "SuperStack" was built in 1972, and concentrations of sulfur dioxide in the Sudbury area dropped immediately. After the construction of the new elevated stack pollutants were spread over a larger area from the single source. A re-vegetation program was started and was initiated by first liming the area and planting different grasses species (Gunn, 1995). Today Sudbury is still impacted by the atmospheric pollution of INCO Ltd but at lower concentrations.

3.3 Geology

The Sudbury area is unique to Precambrian shield geology. The Sudbury basin lies near the junction of three major geologic subdivisions of the Canadian Shield, the Superior, Southern, and Grenville provinces. The Sudbury structure also lies along the "line of Junction" of two major fault systems, the east to northeast-trending Murrey system of the north shore of Lake Huron, and the north-northwest-striking Onaping system of the Superior province and the Cobalt plain (Lumbers, 1963). The area is surrounded by older rocks. Granites and related rocks of the Superior province occur to the north and west, while Huronian and pre-Huronian metasediments and metavolcanics surround territory on the south and east (French, 1972).

3.4 Climate

The Sudbury area experiences a continental climate. The average daily temperature in the month of January is -12.3^{0}C, increasing to 19.8^0 C in July, the warmest month of the year. Precipitation is uniformly distributed throughout the year (Freeman and Hutchinson, 1980; Gunn, 1995). Total annual precipitation averages 656 mm of rain and about 247 mm of snow (water equivivalent) (Environment Canada, 2002).

3.5 Soil

The dominant soils in the region are podzols (Gillespie, 1982). In podzolic soils, organic acids form in surface organic horizons and leach basic elements such as calcium, magnesium from the upper layers and then deposit them in soil horizons immediately below and than iron and aluminum are mobilized by the process of cheluviation (Canadian Soil Survey Committee 1978). This process is enhanced under coniferous and mixed conifer-deciduous forests compared to grassed areas.

Podzols are easily identified, and are characterized by their dark organic surface layer, a white to ash-gray leached horizon immediately below, followed by yellowish-brown or reddish-brown subsoil (Figure 3.2). These soils are typically found on well-drained sandy tills in the area.

Litter
Ah
Ae
Bf/Bfh
C

Figure 3.2: Example of the Podzol soils

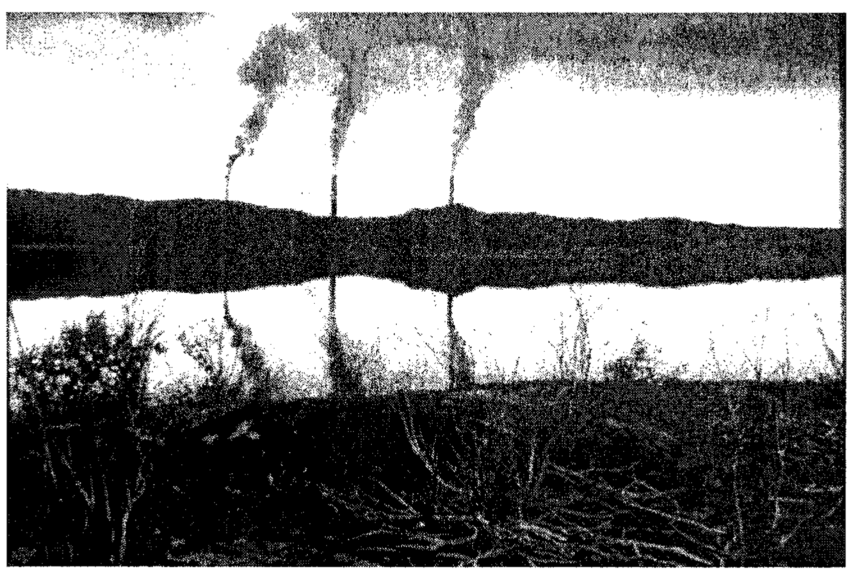
Reduction in vegetation cover brought about by mining activities early in the 20th century caused widespread soil erosion in the region for many years (Winterhalder, 1984). By the time restoration efforts began in the 1970s, most of the fine soil particles had eroded away, leaving behind coarse soils. Moreover, erosion has left the remaining soil deficient in phosphorus, nitrogen, and possibly calcium, magnesium and manganese. Soil pH in the region ranges from 2.0-4.5 (Gunn, 1995). Because of the cation-poor bedrock in the area, soils are naturally acidic. This is exacerbated by acid deposition in the area as the elevated load of hydrogen ion elevates cation exchange. Current restoration efforts in this region have a target soil pH of >5.0 (Pearson, 1995).

3.6 Vegetation

Sudbury is located in a forest zone that is transitional between the boreal, coniferous forest to the north and the deciduous forest to the south. Due to the intensive lumbering practices in the 1800s, the pre-settlement forest probably consisted of a mosaic of white *(Pinus strobis)* and red pine (*Pinus resinosa*) in the uplands and white cedar swamps in the lowlands. The upland forest may have also contained a mixture of northern hardwoods like sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) (DeLestard, 1967).

Following decades of pollution (mainly acid rain) from smelting, the Sudbury area was devoid of vegetation in many areas (Figure 3.3), and simply had exposed bedrock on the landscape.

a.



b.

Figure 3.3(a,b): Vegetation under environmental stress. Sudbury, Ontario (source: Vera Spektor, 1999)

The current vegetation in the area is a result of extensive restoration operations. But also due to the new stack and emission reduction the area is not receiving the same pollutant load which has enabled the vegetation to successfully grow. Vegetation in the area comprise hardy grass species, sparse willow and birch, and coniferous stands (Beckett, 1999).

3.7 Selection of Study Sites

This thesis contributes to research previously and current conducted by researchers at Laurentian University in Sudbury, Ontario.

A total of five study sites were selected for the project by using a stratified sampling method. The sites differed in their distance from the smelter, topography, and vegetation cover. Four study sites were selected on the two most representative landscapes in the

Sudbury area: small topographically flat woodlots and hillslopes which were sampled on the aspect facing INCO smelter.

Two sites were chosen at 15 km and 25 km from the INCO smelter, and the fifth site was located 35km from the smelter (Figures 3.4 and 3.5) at the Onaping falls Conservation Area. At each of the 15 km and 25 km locations one site was chosen on a topographically flat area and one on a hillslope. Within each site, four plots (5 x 5 meters) were selected for sampling. Samples were collected at five locations within each plot. A total of 105 locations were sampled in the study. The five sites are described below.

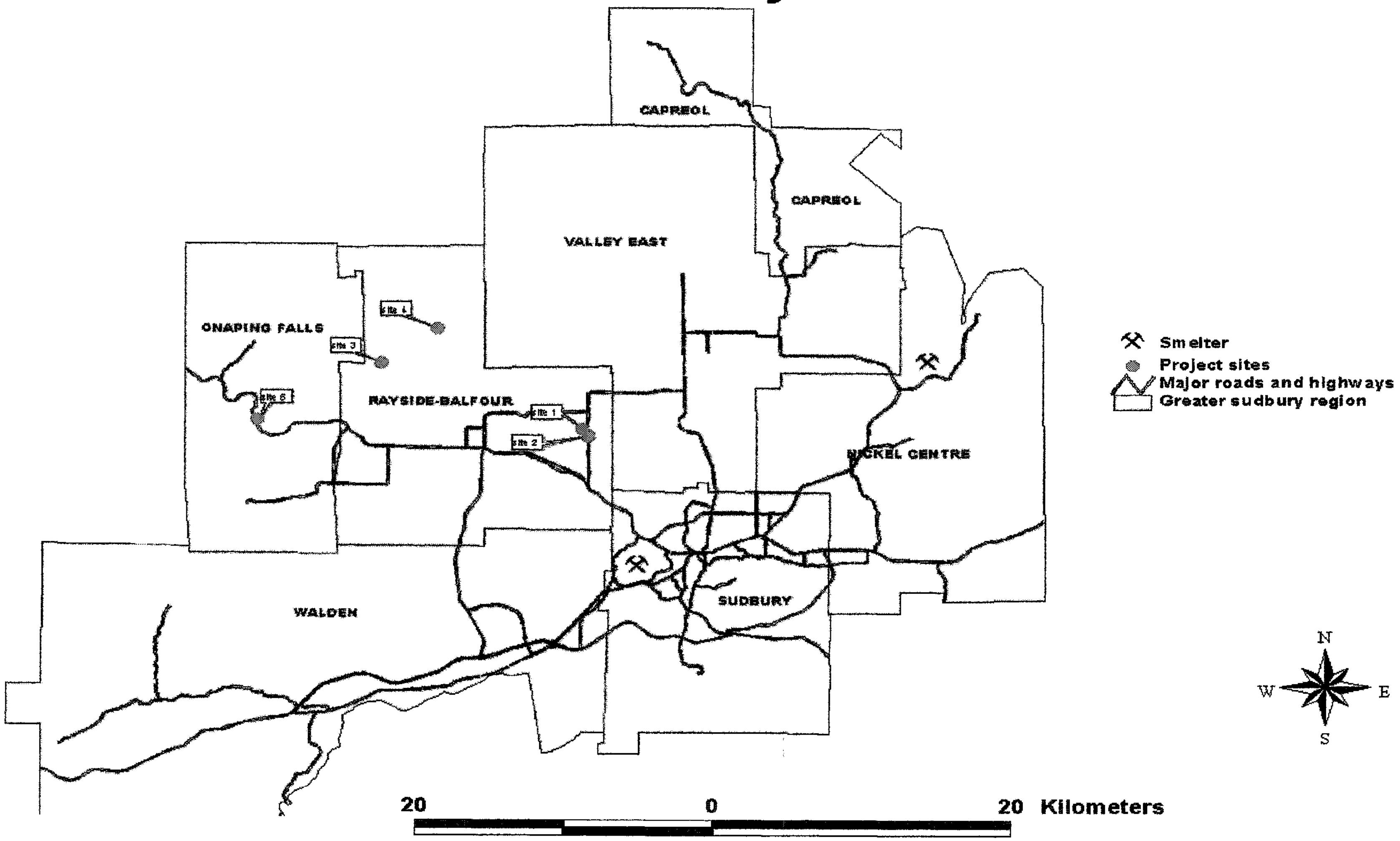
Study Site 1

Site 1 is 15 km from the INCO smelter (the pollution source). This site is located between agricultural fields and residential housing. The sampling site is located in the middle of a balsam fir (*Abies balsamea*) forest, with birch (*Betula papyrifera*) saplings (Figure 3.6).

Figure 3.6 Site 1

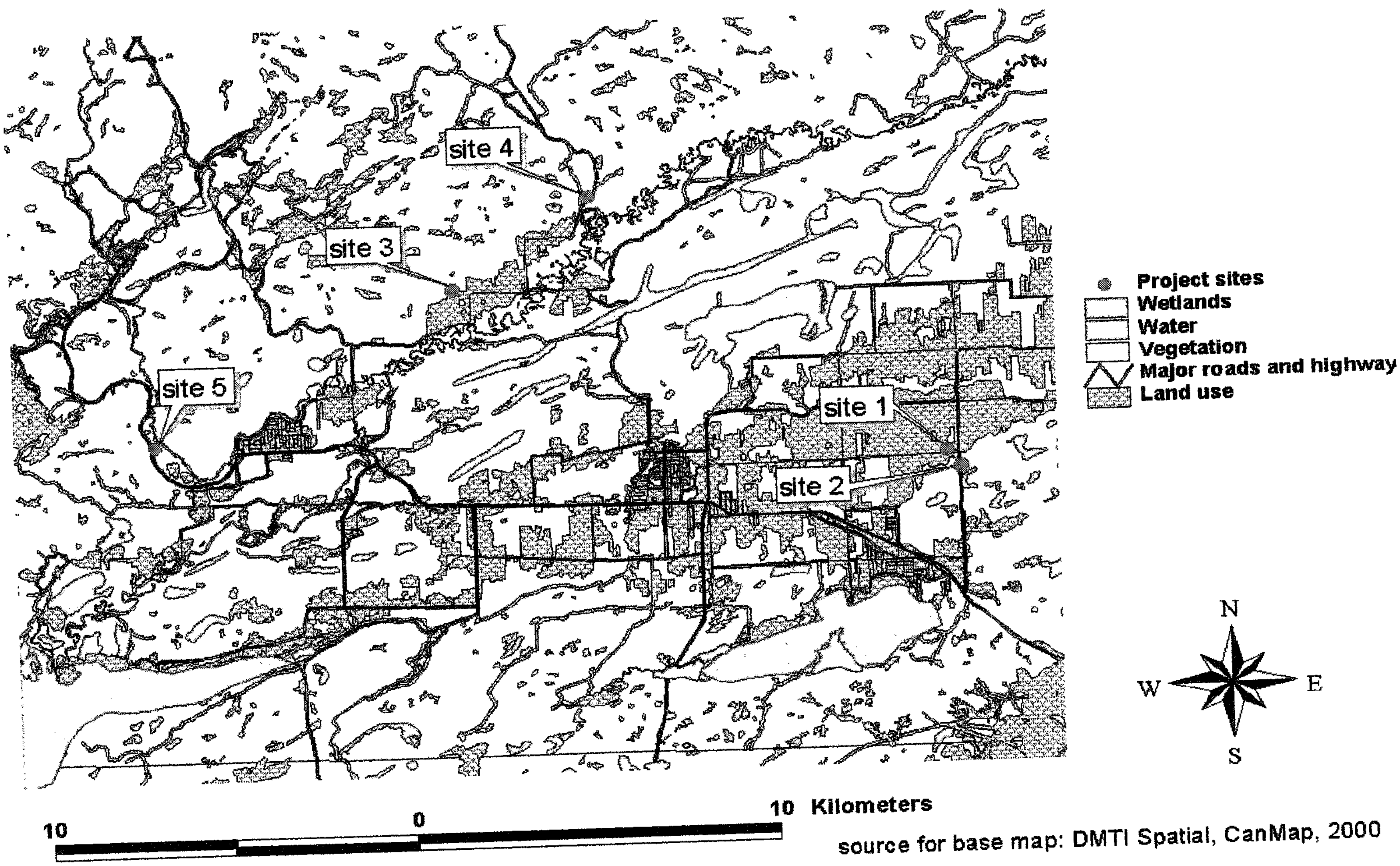
The plots were located approximately 100 m away from a secondary road. The canopy in the woodlot is very dense, and soils at this site are well developed. The 4 plots inside the site spanned a 1 km^2 area, and were at least 75 m apart.

Figure 3.4 Distribution of study sites in the Greater Sudbury area



source for base map: DMTI Spatial, Can Map, 2000

Figure 3.5 Distribution of the study sites



source for base map: DMTI Spatial, CanMap, 2000

Study Site 2

Site 2 is also located 15 km from the INCO smelter, but is located on a 30^0 hillslope facing to INCO smelter. Site 2 is located 1 km away from Site 1. The vegetation cover at Site 2 was dominated by birch (*Betula*) forest, shrubs and grasses (Figure 3.7).

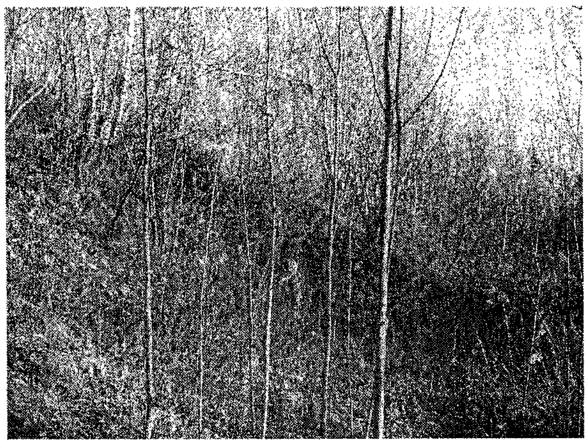


Figure 3.7 Site 2

At site 2 plots were located at the top of the hillslope, at the bottom of the hillslope, and halfway up the hillslope. Four pits (one site) were on the top, eight pits (2 sites) were in the slope and eight pits (2 sites) at the bottom of the hill.

Study Site 3

Site 3 is located approximately 25 km from the smelter on a flat surface. Vegetation at Site 3 is mainly birch (*Betula*) forest (Figure 3.8).

Figure 3.8 Site 3

The site is located close to a secondary road and rural residences. Soils at this site had a well developed A horizon (more than 0.08 m), and all 20 sampling profiles had extensive worm burrows.

Study Site 4

Site 4 was also located 25 km from the smelter, but was on a hillslope. The hillslope was steeper (15^{o}) than the hillslope at Site 2. This site is characterized by birch forest, and is part of a moraine. Consequently, the site was rocky. Site 4 is located next to the secondary road (Figure 3.9).

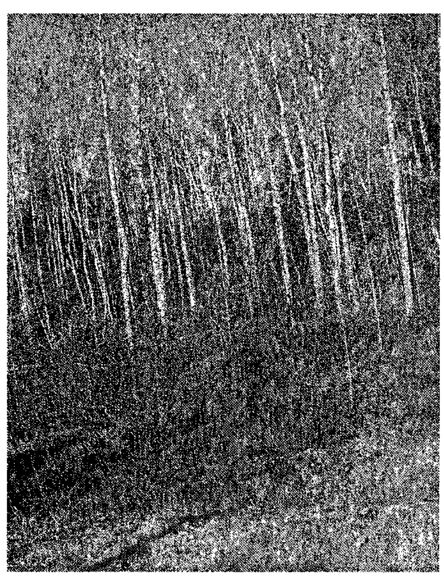


Figure 3.9. Site 4

Study Site 5

Site 5 is located the farthest away from the smelter (35 km) inside the Onaping Falls Conservation Area. This site was chosen as a site with possible lower concentrations than the other sites as a result of its distance from the pollution source. The site is located close to a highway. Vegetation at Site 3 is mainly birch (*Betula*) forest and the site is used as a place for picnicking and is next to a parking lot (5 – 7 m).

3.8 Field Sampling and Laboratory Work

Samples were collected at all five sites over two days (October 5- October 6) in the fall of 2001. The sampling dates followed a dry period, and no rain fell during the sampling dates. Therefore, samples collected during the sampling days are not expected to differ due to environmental conditions.

At each of the five sites, four plots (5m x 5m) were delineated and within each plot, 5 pits were dug to a depth of approximately 0.30 m. A visual description of each pit was recorded (Appendix 1), and samples were collected for chemical and physical analysis from the litter layer, and A and B horizons. Soil horizons were only visually differentiated according to the main horizons (Litter, A and B). Soil samples were collected from the center of the A and B horizon. Due to the variation in the litter layer samples were taken from the entire horizon. Samples were collected using the existing protocol of the Ontario Ministry of Environment and Laurentian University (Graeme Spears, Pers. Comm., 2001). According to this protocol samples collected for chemistry were placed each in double bagged Ziploc baggies with a label and transported to the laboratory at Wilfrid Laurier University. Samples were also collected in soil tins (175 cm^3) for moisture, textural analysis and bulk density using standard techniques.

3.9 Sample Preparation for Chemical and Physical Analyses

Samples collected in pre-weighted soil tins were weighed the same day that they were collected. At the laboratory, soil tins were placed in a drying oven for 24 hours at 105^0C. Dried samples were re-weighed.

$$\text{Moisture \%} = (W_d - W_w)/W_w \tag{1}$$

where W_w is wet soil weight, and W_d is the dry soil weight.

Given the known volume of each soil tin, soil bulk density was determined. It was calculated for most of the soil horizons and for each of the soil profiles. The values of bulk density are presented in Table 4.1. The calculation was determined using

$$W_d\ (g)/\ Vol\ (ml) = \rho_b (g/cm^3) \tag{2}$$

Where $\mathbf{W_d}$*, the dry weight soil has been divided by the volume of soil tin and* $\boldsymbol{\rho_b}$ *is the bulk density.*

Samples collected for chemical analysis were air dried for four weeks at room temperature. The fully dried samples were disaggregated and twigs, rocks and stones were removed. The remaining soil sample was passed through a 2mm sieve (stainless steel sieve number 10 mesh). A sub-sample of the portion less then 2mm was ground with a mortar and pestle (or mechanical grinder for litter) until it passed through a 350 μm sieve (stainless steel sieve number 45 mesh). The sieve and mortar and pestle were cleaned between samples. The processed soil sample was then stored in plastic containers and sent to Laurentian University for X-ray fluorescence spectrometry analysis.

Concentration of elements stored per unit of soil volume were expressed using

$$C_s = [C] * \rho_b \tag{3}$$

where C_s *is the mass of chemical* **C** *in kg* m^{-3} *of soil,* **[C]** *is the concentration of chemical* **C** *in mg* kg^{-1}*, and* ρ_b *is the bulk density of the soil in kg* m^{-3}.

For geochemical analysis the EMMA instrument which is a small desk-top XRF system was used. The excitation X-ray beam is focused from a concave LiF monochromator. In the miniprobe mode, an X-ray beam 0.1 x 0.5 mm is used and focused on a rotating sample holder contained approximately ten grams of sample. With a 1000s analysis time, the samples are rotated more than 400 times per analysis in order to provide accurate average concentrations per sample. The results presented in these theses were obtained using this configuration.

The X-ray tube is usually operated at a voltage of 50 kV and a current of 15 mA, because monochromatic X-ray radiation is used for excitation (17.44 keV). A low background is achieved and detection limits are better that with conventional X-ray instruments (Cheburkin and Shotyc, 1996). The instruments were calibrating using international certified standards reference soil and geological material from NIST, USGS and BCR. All samples were dried at 105^0C prior to analysis.

Chapter 4. Results

4.1 Emissions history

The history of the Sudbury smelters started in 1885. Levels of emissions were not recorded at that time. In the middle of the 1960s the environmental situation of the Sudbury region was taken seriously. Vegetation and soil degradation were so serious that the region was used during astronaut training to present to them a "moon landscape" (Winterhalder, 1995). Records of emissions appeared in the middle of the 1970s. By 1995 levels of emissions had dropped by approximately 90 percent. That was done according to orders from the Ontario Ministry of Environment.

One of the first steps to reduce local level of emissions was to increase the height of the smelter's stack in the 1970s, in order to reduce the concentration of pollution closer to Sudbury. The Stack allowed emissions to be spread across longer distances.

Elements dispersed from the stack distribute differently in the atmosphere. For heavy metals, distribution is generally restricted to within 80 km from the emission source (Golubeva, 1999a). Topography of the area plays an important role. For example, natural barriers such as mountains can effectively reduce emissions by long range transport of the atmospheric pollutants emitted from a smelter. It is difficult to say what the exact distance for metal distribution is, but according to previous research in Russian high latitudes the highest level of emissions was recorded within 5 km of the source (Norilsk, Russia). After 30 kilometers, elevated metal concentrations drop significantly (Golubeva 1999a, Golubeva 1999b).

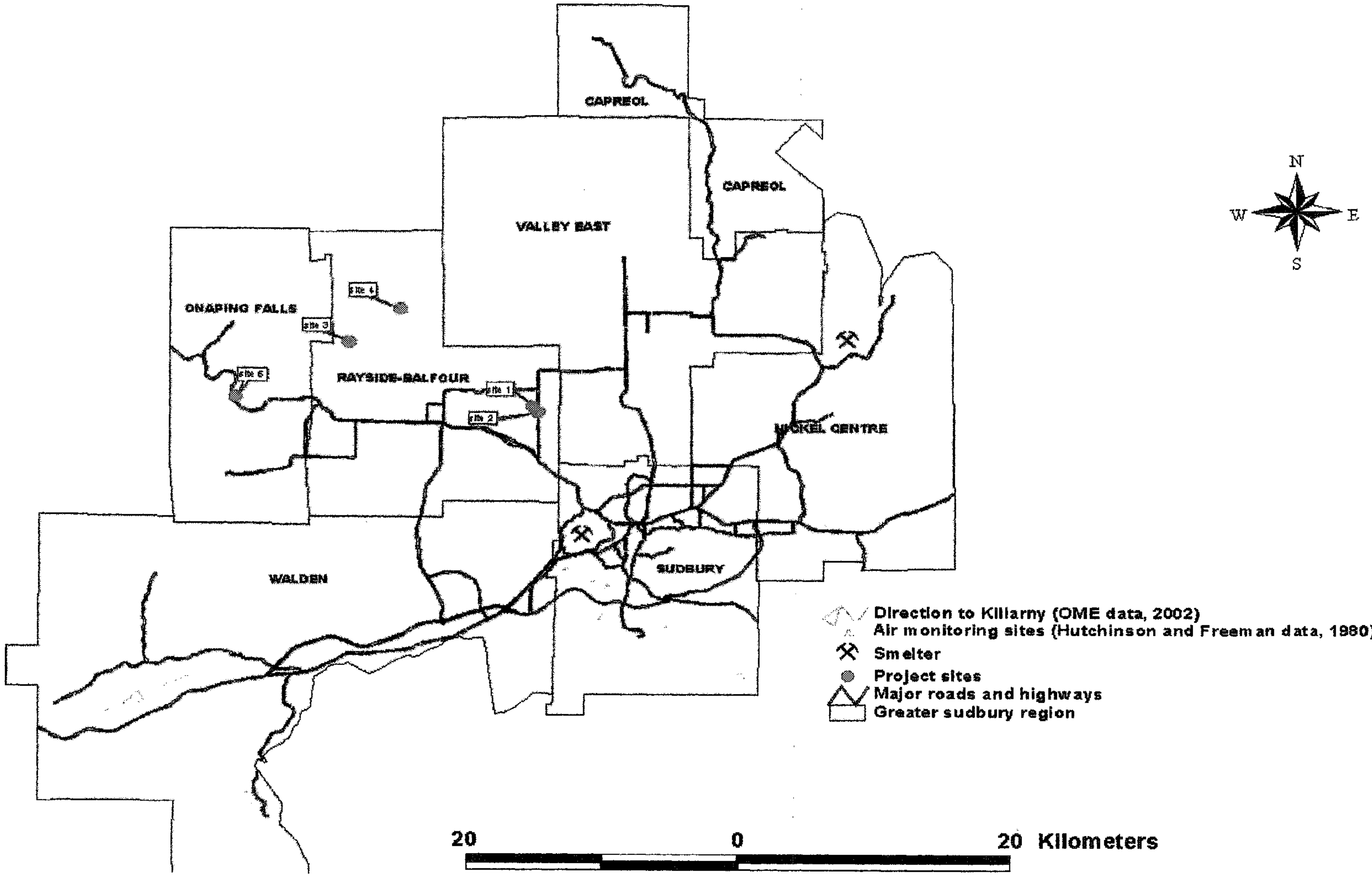
There are few atmospheric deposition data and few soil data available about metal concentrations in the Sudbury area, but there is an ongoing study being conducted by the

Ontario Ministry of Environment and Laurentian University that is in progress. In this work, data from different sources were used. Some of the data were taken from articles and data available from the Ontario Ministry of Environment (Hutchinson and Freeman, 1980; Ontario Ministry of Environment, 2001). The geographical distribution of data collected from the literature referred to in this study is presented on the map (Figure 4.1).

4.2 Physical characteristics of soil

Due to the physical conditions of the area such as duration of winter, low mean annual temperatures, and some environmental issues (depth of the Canadian Shield is variable in this part, as pollution in the Sudbury area killed off significant areas of vegetation and as a result, in elevated areas where soil was thin, the rooting system that binds the soil is no longer effective, and erosion displaces the soil) soil development is slower than in the areas to the south. Due to all these factors, litter material does not accumulate and decompose as fast as in more southern regions, and therefore less organic material for soil development enters the system. During winter all life processes slow down, and for Sudbury this is approximately 6 months a year. For all study sites litter, *A,* and *B,* and in some cases *C* horizons were easily distinguishable with respect to horizon boundary. However the *A* and *B* horizons are distinguishable but not well developed with respect to depth for the average middle latitude soil profile. For most soil pits the depth to the *C* horizon was not more than 30 cm. In the different vegetation zones, horizons were developed differently. Horizon development varies from site to site and is in part attributable to vegetation and to physical attributes of site such as slope, drainage, parent material

Figure 4.1 Location of all available sites



source for base map: DMTI Spatial, CanMap, 2000 aspect and depth of parent material. For example, the litter layer in the soil profiles situated in the wooded areas was approximately 5 cm in thickness and for some other profiles where trees are not as prominent the litter layer is normally about 1cm in thickness.

Most of the "*A*" horizons have the same thickness of around 8-10 cm, and the rest of the profiles belong to the "*B*" horizon. In some profiles, it was possible to reach the "C" horizon, but it was not the aim of this research (Figure 4.2).

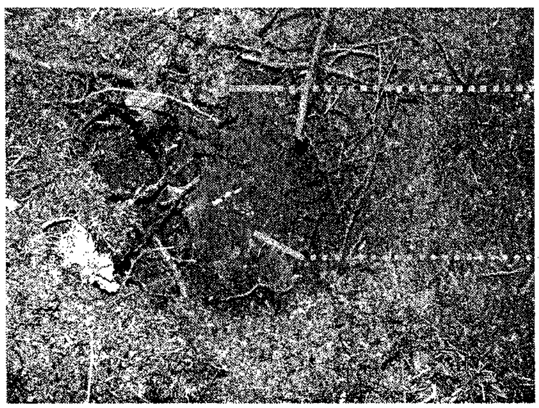


Figure 4.2 Soil profile from site 1

The soil texture for "A" horizons was mainly sand, while for "B" horizons, in most cases, there was sand or in some cases clay. The Litter layer is composed of the dominant vegetation species. In all cases the sampled soil horizons were in the unsaturated zone and in many cases all soil horizons were moist.

The bulk density calculations are discussed in chapter 3 and result for bulk density for soil horizons *A* and *B* are presented in tables Table 4.1 and 4.2

Table 4.1 Site average bulk density values for examined soil horizons

Site	Site 1	site 1	site 2	site 2	Site 3	site 3	Site 4	Site 4	site 5	site 5
Horizon	A	B	A	B	A	B	A	B	A	B
Bulk den kg/m^3	*0.702*	*1.241*	*0.871*	*1.105*	*0.958*	*1.475*	*0.738*	*1.052*	*0.579*	*0.699*
Standard deviation	**0.062**	**0.028**	**0.337**	**0.066**	**0.061**	**0.054**	**0.292**	**0.198**	*n/a*	*n/a*

Table 4.2 Plot average bulk density values for examined soil horizons

Plots	horizon	Bulk density kg/m^3
	Site 1	
plot 1	A	0.681
plot 1	B	1.250
plot 2	A	0.712
plot 2	B	1.220
plot 3	A	0.815
plot 3	B	1.275
plot 4	A	0.689
plot 4	B	1.221
	Site 2	
plot 5	A	1.044
plot 5	B	1.129
plot 6	A	0.776
plot 6	B	0.990
plot 7	A	0.712
plot 7	B	0.998
plot 8	A	0.844
plot 8	B	1.073
	Site 3	
plot 9	A	0.911
plot 9	B	1.448
plot 10	A	0.896
plot 10	B	1.539
plot 11	A	1.008
plot 11	B	1.445
	Site 4	
plot 12	A	1.017
plot 12	B	1.470
plot 13	A	0.814
plot 13	B	1.149
plot 14	A	0.743
plot 14	B	1.303
plot 15	A	0.557
plot 15	B	0.928
plot 16	A	0.780
plot 16	B	0.879
	Site 5	
plot 18	A	0.579
plot 18	B	0.699

Standard deviation values are not available for site 5 in Table 4.1 due to the small number of samples. It is apparent that there is some difference in bulk densities between different soil horizons. The difference in bulk density between "*A*" and "*B*" horizons for average values is approximately double, except for sites 2 and 5. For a more detailed look Table 4.2 presents differences inside each site. Bulk densities for "*A*" horizon vary mostly in site 2 and 4, which represent hill slopes. The main difference is between the top and the bottom part of the hill slope. What is possible to see from the site 4 data, where the bulk density of the *B* horizon on the top is $1.470\ kg/m^3$ and on the bottom is $0.879\ kg/m^3$. Minimum differences between the values are from the 5^{th} site, next to the waterfalls.

4.3 Chemistry of soil

All collected soil samples were analyzed for 19 elements: copper, nickel, arsenic, zinc, chromium, iron, manganese, zirconium, yttrium, potassium, calcium, gallium, titanium, thorium, lead, rubidium, bromine, selenium and strontium (Appendix 2). In this table, most of the concentrations are in parts per million (ppm), which is equivalent to mg/kg and the remaining are in percent abundance. Because of equipment calibration, we have to concede the lowest level of determination (LLD levels) for each element. Results lower or equal to the LLD are not accurate. LLD levels are one of the reasons why in this research eight elements are selected for further examination. These eight elements are the dominant pollutants emitted from the smelter and include: nickel, copper, yttrium, zinc, rubidium, magnesium, zirconium and chromium. These elements were chosen because of their concentration variability and potential to impact the environment (Table 4.3).

Table 4.3 Criteria for element selection

Element	Criteria
Copper	Main pollutant in the area
Nickel	Main pollutant in the area
Yttrium	Can be toxic
Zinc	Can be toxic and even more in combination with other elements
Rubidium	Has a natural radioactive isotope
Magnesium	Concentration variability
Zirconium	Radioactive, poison
Chromium	Toxic by inhalation

Source: Merian (1991), Hawley (1971), Pearson (1995), Gunn (1995).

The remaining eleven elements are not examined in this work. The general distribution pattern for each site and each element is presented in Appendix 3. Graphs in Appendix 2 show the distribution of the 19 elements through the soil horizon with standard statistical characteristics such as minimum, maximum and standard deviation ranges. These values for the 8 selected metals can be also seen in Table 4.4. The general pattern in the data is that manganese, chromium, nickel, copper and zinc have higher concentrations in the litter horizon and than decrease to the B horizon. In contrast rubidium, yttrium and zirconium have lower concentrations in the litter horizon and increases in the A and B horizons. For site 3 and 4 concentrations of this elements in soil does not change with depth.

Table 4.4 Summary data for all study sites

	element	Cr	Mn	Ni	Cu	Zn	Rb	Y	Zr
	LLD	50	30	5.0	3.0	2.0	1.0	2.5	5.0
site #	horizon	concentration in ppm							
site I	Litter	60.1	379.2	168.6	126.5	93.5	37.4	6.2	115.9
Mean	A	44.4	242.8	143.1	123.9	42.3	50.5	9.9	196.5
	B	45.3	222.0	34.1	11.8	29.3	53.8	11.0	223.4
site I	Litter	90.0	852.6	430.6	360.2	179.3	53.0	11.5	202.2
Maximum	A	78.2	1064.8	293.4	338.5	114.5	56.2	11.3	223.9
	B	60.1	321.5	53.5	25.5	35.3	59.3	13.2	248.7
site I	Litter	0.0	201.1	98.7	65.1	47.7	21.0	2.0	45.7
Minimum	A	22.8	150.5	92.8	64.0	23.5	41.5	7.1	149.7
	B	29.7	175.1	20.7	5.5	23.7	46.3	7.4	187.2
site I	Litter	19.2	142.5	72.1	63.6	31.5	7.3	2.2	38.2
Stdeviation	A	12.5	191.2	47.2	54.1	21.2	3.6	1.2	19.8
	B	9.7	35.7	8.1	6.1	3.8	2.8	1.6	18.3
site II	Litter	87.4	1300.6	307.5	250.2	303.3	22.0	4.7	72.1
Mean	A	104.5	1463.4	218.9	194.2	151.6	46.3	10.6	187.0
	B	116.0	1504.2	75.6	48.3	134.4	43.9	10.6	197.6
site II	Litter	186.6	2507.3	606.4	575.3	530.0	38.6	11.4	136.3
Maximun	A	180.9	2549.9	483.0	447.9	250.2	58.4	11.7	273.3
	B	164.5	2489.8	116.9	89.6	217.8	60.0	12.1	276.1
site II	Litter	0.0	452.9	137.4	55.1	149.3	5.5	0.0	7.7
Minimum	A	56.3	375.9	56.0	18.4	63.0	36.1	9.7	129.3
	B	58.3	477.0	46.4	12.9	71.6	33.8	9.6	139.0
site II	Litter	38.0	576.1	131.2	160.6	121.5	11.4	3.6	46.1
Stdeviation	A	31.4	602.2	112.1	113.0	48.1	5.2	0.6	46.4
	B	31.1	673.7	21.0	19.1	41.9	5.8	0.8	51.4
site III	Litter	76.8	212.5	54.9	29.2	110.3	39.2	7.5	172.5
Mean	A	44.8	158.1	34.6	21.6	31.7	46.7	9.6	220.9
	B	45.1	173.1	21.2	6.2	24.9	34.2	6.4	145.4
site III	Litter	122.4	363.4	72.4	43.8	287.2	49.5	11.0	249.7
Maximum	A	56.7	211.9	49.7	29.6	41.1	52.9	14.0	266.5
	B	62.9	210.3	29.2	11.8	35.0	47.6	13.0	243.5
site III	Litter	56.4	137.4	40.5	21.9	43.8	7.9	0.0	20.5
Minimum	A	27.8	121.0	27.1	14.2	26.5	40.8	7.0	169.3
	B	31.3	149.4	13.1	2.8	18.6	11.3	1.6	29.1
site III	Litter	17.6	55.0	9.2	5.7	60.8	11.7	3.2	63.1
Stdeviation	A	7.7	20.3	6.0	4.5	4.1	3.1	1.6	28.0
	B	8.9	16.9	4.1	2.3	3.8	11.5	3.2	66.6
Site IV	Litter	131.0	1382.2	153.2	88.5	198.6	58.9	8.7	191.9
Mean	A	44.3	578.1	104.5	94.5	84.4	52.4	7.5	166.3
	B	81.8	396.8	48.1	37.1	83.8	51.4	6.1	133.6
site IV	Litter	277.3	2360.1	223.9	149.0	385.7	72.8	11.7	295.4
Maximum	A	74.8	1245.0	242.0	249.9	182.9	65.5	10.1	262.9
	B	116.5	1912.5	149.2	119.0	152.5	81.6	10.1	291.0
site IV	Litter	71.4	869.7	90.7	52.6	122.6	28.9	3.7	66.6
Minimum	A	0.0	163.1	45.5	46.0	42.1	13.5	0.0	18.4
	B	44.8	207.6	34.8	14.1	29.4	27.7	2.7	32.9
Site IV	Litter	42.9	404.5	33.2	30.8	59.1	10.5	2.1	54.5
Stdeviation	A	23.3	285.1	44.1	44.6	34.6	12.6	2.9	67.3
	B	21.0	356.4	24.2	26.5	25.8	15.3	2.4	73.0

Table 4.4 Summary data for all study sites (continued)

	element	Cr	Mn	Ni	Cu	Zn	Rb	Y	Zr
	LLD	50	30	5.0	3.0	2.0	1.0	2.5	5.0
site #	horizon	concentration in ppm							
site V	Litter	80.1	1458.8	90.6	62.2	181.1	47.2	7.9	206.3
Mean	A	38.61	641.82	56.68	54.4	84.8	43.6	5.9	172.7
	B	66.2	289.1	38.1	19.9	91.5	49.4	8.2	217.5
site V	Litter	96.2	1793.5	101.5	75.9	212.9	51.0	9.5	247.9
Maximum	A	62.3	837.8	70.7	70.6	101.4	65.5	9.0	274.5
	B	92.5	307.3	49.3	29.7	112.7	56.2	10.0	276.0
site V	Litter	45.9	1236.4	82.4	52.6	143.5	39.8	5.1	115.8
Minimum	A	18.2	468.2	43.9	41.0	57.4	9.1	0.0	34.0
	B	46.1	252.1	27.5	13.3	80.8	39.0	5.0	129.7
site V	Litter	23.5	245.4	8.9	10.3	35.7	5.1	1.9	61.6
Stdeviation	A	20.8	163.9	11.3	10.7	17.8	22.3	4.0	96.7
	B	17.7	22.7	10.1	7.3	13.7	6.5	2.0	53.5

4.4 Background concentration for the area

Understanding background concentration of metals in soil is very important since natural metal concentrations are elevated due to natural deposits. Background readings have to be taken within the Sudbury basin, but outside of the area where metals from the smelters are deposited. Without this knowledge it is difficult to discuss the impact of smelter pollution on the soils. For this area, because of the mining and smelting activity, existing concentrations of metals in soil are higher than in areas without mining activity and without significant metal deposits. That is why background concentrations for the metals in soil should be used from the Sudbury basin area, where natural background concentrations of metals are elevated. For the Sudbury area, background concentration data for metals in soil data were obtained from the Ontario Ministry of Environment, and from metal contamination studies that were completed in the Sudbury area by other researches. Background concentrations for nickel in soil were used from McIlveen (1995), copper and zinc concentration data were found in Hutchinson (1997), and in Dudka (1995). The background concentrations were calculated using average values for a number of sites from the Sudbury basin area that were distant from the source of pollution. Available data for background concentrations in soil for metals in the Sudbury area are presented in Table 4.5.

Table 4.5 Background concentration for Sudbury, ON

Element	Concentrations From Ontario Ministry of Environment (ppm)	Concentrations From Previous Research (ppm)
Copper (Cu)	85	25
Nickel (Ni)	43	10
Yttrium (Y)	-	-

Zinc (Zn)	160	40
Rubidium (Rb)	-	-
Manganese (Mn)	~22000	-
Zirconium (Zr)	-	-
Chromium (Cr)	71	-

Source: (McIlveen 1995, Hutchinson 1997, Dudka 1995, Ontation Ministry of Environment, 2000)

Background concentration for Zirconium, Yttrium and Chromium are not available for the Sudbury basin in the literature.

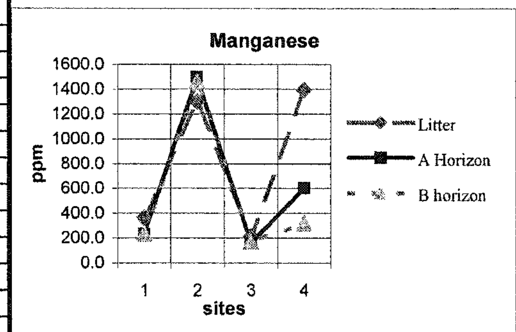
4.5 Variability among sites

To examine patterns of metal distribution for the study area it is important to quantify the distribution of each element within each site. This can assist in defining the spatial distribution of metals, their accumulation and potential movement through the soil profile. For this purpose, all available data were sorted according to the profiles and basic statistical calculations were used to identify changes and variable ranges within each site and each profile.

The first four sites were chosen because of their different topography and vegetation cover; the first two sites are both located next to actively cultivated lands. The first site is a flat area with coniferous vegetation. The second site is a hill slope with mainly deciduous vegetation cover. These landscapes are the most representative landscapes for the area. Sites 3 and 4 have the same topography as sites 1 and 2 respectively, except for the agricultural influence. A descriptive statistical summary for these sites is presented in Table 4.6.

Table 4.6 Descriptive statistical summary of the study sites

Manganese					
	site 1	site 2	site 3	site 4	site 5
Litter	328.9	1149.0	208.3	1556.9	1398.1
Litter	412.4	1301.5	152.0	1371.3	
Litter	425.6	767.7	255.1	1179.9	
Litter	284.1	1984.0	234.4	1466.0	
Mean	**362.7**	**1300.6**	**212.5**	**1393.5**	
maximum	**425.6**	**1984.0**	**255.1**	**1556.9**	
minimum	**284.1**	**767.7**	**152.0**	**1179.9**	
st deviation	**67.7**	**508.0**	**44.6**	**161.3**	
A Horizon	394.2	833.3	151.3	414.4	641.8
A Horizon	222.6	1792.7	145.9	724.8	
A Horizon	193.8	1893.0	155.7	503.9	
A Horizon	171.4	1470.2	168.3	633.4	
A Horizon	178.0	1493.1	170.3	732.0	
Mean	**232.0**	**1496.4**	**158.3**	**601.7**	
maximum	**394.2**	**1893.0**	**170.3**	**732.0**	
minimum	**171.4**	**833.3**	**145.9**	**414.4**	
st deviation	**92.8**	**414.0**	**10.7**	**139.5**	
B horizon	322.1	1297.3	169.2	320.5	289.1
B horizon	214.7	1920.9	181.4	345.4	
B horizon	213.4	1825.9	166.7	277.0	
B horizon	197.8	812.3	171.0	341.1	
Mean	**237.0**	**1464.1**	**172.1**	**321.0**	
maximum	**322.1**	**1920.9**	**181.4**	**345.4**	
minimum	**197.8**	**812.3**	**166.7**	**277.0**	
st deviation	**57.3**	**513.9**	**6.5**	**31.3**	



Chromium					
Litter	56.7	71.4	79.3	159.2	78.4
Litter	51.2	124.2	84.2	118.7	
Litter	67.5	86.1	70.1	126.5	
Litter	64.7	68.0	73.6	131.6	
Mean	**60.0**	**87.4**	**76.8**	**134.0**	
maximum	**67.5**	**124.2**	**84.2**	**159.2**	
minimum	**51.2**	**68.0**	**70.1**	**118.7**	
st deviation	**7.5**	**25.7**	**6.2**	**17.6**	
A Horizon	47.2	82.0	41.6	35.3	38.6
A Horizon	45.8	128.2	50.0	41.1	
A Horizon	41.7	124.9	45.2	41.4	
A Horizon	36.9	82.8	43.0	63.2	
Mean	**42.9**	**104.5**	**45.0**	**45.3**	
maximum	**47.2**	**128.2**	**50.0**	**63.2**	
minimum	**36.9**	**82.0**	**41.6**	**35.3**	
st deviation	**4.6**	**25.5**	**3.7**	**12.3**	
B horizon	54.4	100.4	47.3	86.8	66.2
B horizon	45.1	140.0	44.1	96.0	
B horizon	46.4	125.2	47.0	75.9	
B horizon	36.5	93.9	41.3	70.8	
Mean	**45.6**	**114.9**	**44.9**	**82.4**	
maximum	**54.4**	**140.0**	**47.3**	**96.0**	
minimum	**36.5**	**93.9**	**41.3**	**70.8**	
st deviation	**7.3**	**21.5**	**2.8**	**11.3**	

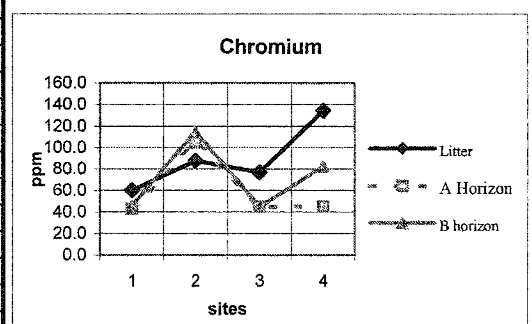
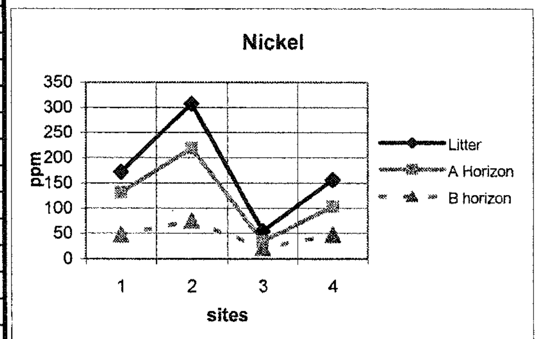


Table 4.6 Descriptive statistical summary of the study sites

Nickel					
Litter	235.6	377.7	49.9	177.6	90.6
Litter	164.8	173.3	54.6	178.3	
Litter	147.5	222.4	59.9	141.0	
Litter	139.6	456.5	55.0	128.4	
Mean	**171.9**	**307.5**	**54.9**	**156.3**	
maximum	**235.6**	**456.5**	**59.9**	**178.3**	
minimum	**139.6**	**173.3**	**49.9**	**128.4**	
st deviation	**43.7**	**132.1**	**4.1**	**25.5**	
A Horizon	174.7	293.6	32.3	84.6	56.7
A Horizon	110.6	183.1	34.1	123.2	
A Horizon	111.8	225.2	40.2	119.7	
A Horizon	128.4	173.8	30.1	86.7	
Mean	**131.4**	**218.9**	**34.2**	**103.6**	
maximum	**174.7**	**293.6**	**40.2**	**123.2**	
minimum	**110.6**	**173.8**	**30.1**	**84.6**	
st deviation	**30.0**	**54.6**	**4.3**	**20.7**	
B horizon	94.4	70.4	18.6	42.4	38.1
B horizon	28.5	77.1	22.1	39.1	
B horizon	37.5	81.0	22.8	47.1	
B horizon	32.1	74.9	21.8	63.0	
Mean	**48.1**	**75.8**	**21.3**	**47.9**	
maximum	**94.4**	**81.0**	**22.8**	**63.0**	
minimum	**28.5**	**70.4**	**18.6**	**39.1**	
st deviation	**31.1**	**4.4**	**1.9**	**10.6**	



Copper					
Litter	215.1	390.8	28.6	101.8	61.2
Litter	128.2	118.6	31.7	115.8	
Litter	95.5	108.7	30.8	76.8	
Litter	99.2	382.6	25.9	65.9	
Mean	**134.5**	**250.2**	**29.2**	**90.1**	
maximum	**215.1**	**390.8**	**31.7**	**115.8**	
minimum	**95.5**	**108.7**	**25.9**	**65.9**	
st deviation	**55.7**	**157.8**	**2.6**	**22.8**	
A Horizon	132.6	214.0	18.2	78.5	54.4
A Horizon	85.4	233.2	23.1	100.1	
A Horizon	101.8	194.1	23.8	116.2	
A Horizon	113.9	127.0	18.5	80.2	
Mean	**108.4**	**192.1**	**20.9**	**93.8**	
maximum	**132.6**	**233.2**	**23.8**	**116.2**	
minimum	**85.4**	**127.0**	**18.2**	**78.5**	
st deviation	**19.9**	**46.2**	**3.0**	**17.9**	
B horizon	66.5	37.8	4.3	34.7	19.9
B horizon	9.9	59.4	8.1	46.1	
B horizon	8.6	59.8	5.3	23.3	
B horizon	14.2	38.5	6.8	45.9	
Mean	**24.8**	**48.9**	**6.1**	**37.5**	
maximum	**66.5**	**59.8**	**8.1**	**46.1**	
minimum	**8.6**	**37.8**	**4.3**	**23.3**	
st deviation	**27.9**	**12.4**	**1.7**	**10.9**	

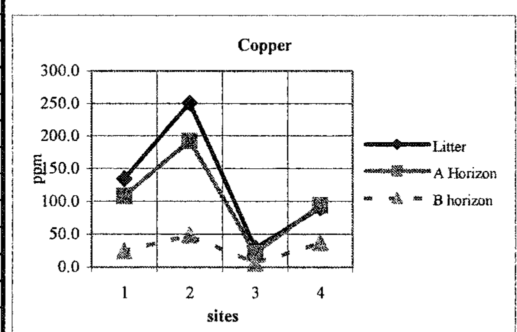
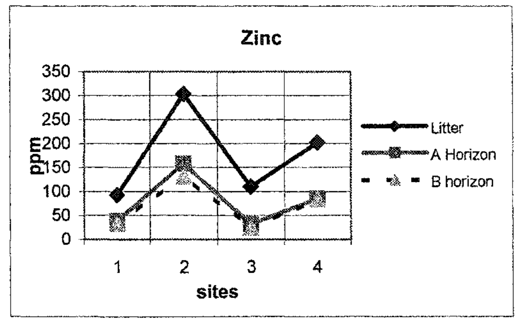


Table 4.6 Descriptive statistical summary of the study sites

Zinc					
Litter	102.4	225.8	82.8	216.4	169.4
Litter	73.7	274.3	135.7	212.0	
Litter	86.8	392.0	109.8	158.8	
Litter	107.7	321.2	113.1	222.3	
Mean	**92.7**	**303.3**	**110.3**	**202.4**	
maximum	**107.7**	**392.0**	**135.7**	**222.3**	
minimum	**73.7**	**225.8**	**82.8**	**158.8**	
st deviation	**15.4**	**70.8**	**21.7**	**29.4**	
A Horizon	58.9	119.4	30.7	68.1	84.8
A Horizon	35.3	174.3	31.4	125.8	
A Horizon	33.5	142.6	35.7	68.5	
A Horizon	28.6	196.9	29.4	80.3	
Mean	**39.1**	**158.3**	**31.8**	**85.7**	
maximum	**58.9**	**196.9**	**35.7**	**125.8**	
minimum	**28.6**	**119.4**	**29.4**	**68.1**	
st deviation	**13.5**	**34.2**	**2.7**	**27.3**	
B horizon	49.7	137.3	25.1	85.8	91.5
B horizon	29.6	148.7	26.3	117.7	
B horizon	27.0	145.5	24.4	58.4	
B horizon	27.3	99.2	23.4	77.7	
Mean	**33.4**	**132.7**	**24.8**	**84.9**	
maximum	**49.7**	**148.7**	**26.3**	**117.7**	
minimum	**27.0**	**99.2**	**23.4**	**58.4**	
st deviation	**10.9**	**22.8**	**1.2**	**24.7**	



Rubidium					
Litter	40.0	25.7	28.1	59.0	48.7
Litter	39.4	27.6	32.0	66.0	
Litter	38.2	14.5	48.5	59.3	
Litter	35.0	20.1	48.3	52.0	
Mean	**38.1**	**22.0**	**39.2**	**59.1**	
maximum	**40.0**	**27.6**	**48.5**	**66.0**	
minimum	**35.0**	**14.5**	**28.1**	**52.0**	
st deviation	**2.2**	**5.9**	**10.7**	**5.7**	
A horizon	46.8	48.2	44.3	52.0	43.6
A horizon	51.9	43.8	43.8	57.7	
A horizon	51.8	49.7	48.6	57.8	
A horizon	49.5	43.4	48.8	39.6	
Mean	**50.0**	**46.3**	**46.4**	**51.7**	
maximum	**51.9**	**49.7**	**48.8**	**57.8**	
minimum	**46.8**	**43.4**	**43.8**	**39.6**	
st deviation	**2.4**	**3.1**	**2.7**	**8.6**	
B horizon	51.7	43.9	46.1	35.6	49.4
B horizon	55.3	42.4	27.2	53.6	
B horizon	53.2	48.3	28.7	50.6	
B horizon	53.1	40.4	35.1	65.5	
Mean	**53.3**	**43.7**	**34.3**	**51.3**	
maximum	**55.3**	**48.3**	**46.1**	**65.5**	
minimum	**51.7**	**40.4**	**27.2**	**35.6**	
st deviation	**1.5**	**3.4**	**8.6**	**12.3**	

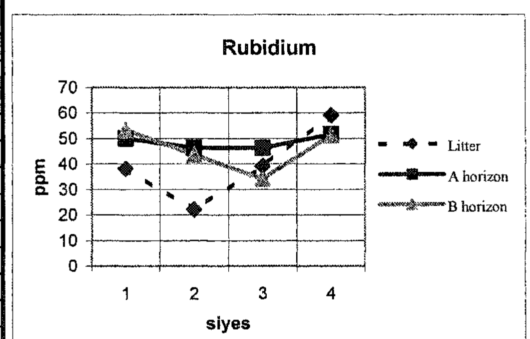
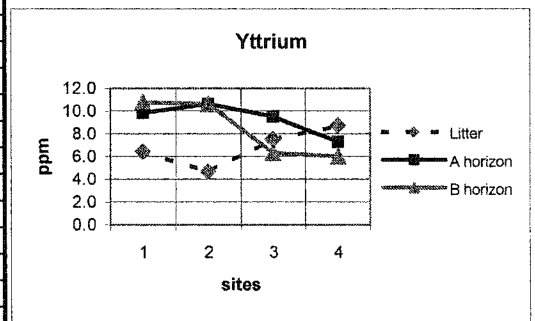
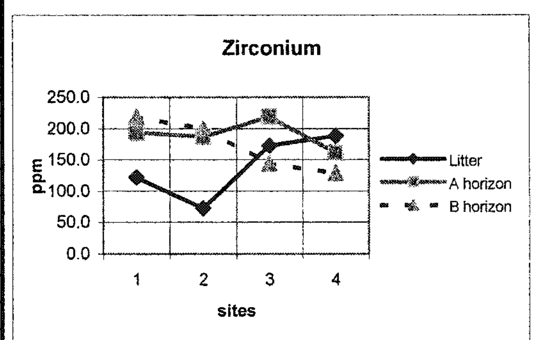


Table 4.6 Descriptive statistical summary of the study sites

Yttrium					
Litter	7.9	5.4	4.0	9.2	7.9
Litter	6.3	7.5	6.3	9.4	
Litter	6.5	1.8	10.0	8.2	
Litter	4.9	4.1	9.8	8.1	
Mean	**6.4**	**4.7**	**7.5**	**8.7**	
maximum	**7.9**	**7.5**	**10.0**	**9.4**	
minimum	**4.9**	**1.8**	**4.0**	**8.1**	
st deviation	**1.2**	**2.4**	**2.9**	**0.7**	
A horizon	9.6	11.1	8.2	9.0	5.9
A horizon	10.5	10.4	8.7	9.7	
A horizon	10.2	10.4	10.9	6.6	
A horizon	9.0	10.5	10.2	3.8	
Mean	**9.8**	**10.6**	**9.5**	**7.3**	
maximum	**10.5**	**11.1**	**10.9**	**9.7**	
minimum	**9.0**	**10.4**	**8.2**	**3.8**	
st deviation	**0.7**	**0.3**	**1.2**	**2.7**	
B horizon	11.1	10.2	9.4	4.3	8.2
B horizon	12.0	11.4	5.6	6.2	
B horizon	10.0	10.7	4.9	5.6	
B horizon	10.0	10.1	5.3	7.8	
Mean	**10.8**	**10.6**	**6.3**	**6.0**	
maximum	**12.0**	**11.4**	**9.4**	**7.8**	
minimum	**10.0**	**10.1**	**4.9**	**4.3**	
st deviation	**1.0**	**0.6**	**2.1**	**1.4**	



Zirconium					
Litter	143.9	90.2	109.6	227.2	217.7
Litter	120.8	94.6	140.6	206.3	
Litter	119.9	35.1	222.2	167.2	
Litter	104.1	68.5	217.5	152.8	
Mean	**122.2**	**72.1**	**172.5**	**188.4**	
maximum	**143.9**	**94.6**	**222.2**	**227.2**	
minimum	**104.1**	**35.1**	**109.6**	**152.8**	
st deviation	**16.4**	**27.2**	**56.2**	**34.3**	
A horizon	183.3	220.3	195.0	191.7	172.7
A horizon	199.2	155.3	212.0	208.6	
A horizon	208.1	141.5	235.1	176.6	
A horizon	183.7	230.9	233.3	68.9	
Mean	**193.6**	**187.0**	**218.8**	**161.5**	
maximum	**208.1**	**230.9**	**235.1**	**208.6**	
minimum	**183.3**	**141.5**	**195.0**	**68.9**	
st deviation	**12.2**	**45.1**	**19.1**	**63.1**	
B horizon	204.0	218.8	217.2	78.9	217.5
B horizon	236.2	155.5	138.6	155.5	
B horizon	214.3	178.7	101.7	93.7	
B horizon	218.1	247.3	118.7	188.1	
Mean	**218.1**	**200.1**	**144.0**	**129.1**	
maximum	**236.2**	**247.3**	**217.2**	**188.1**	
minimum	**204.0**	**155.5**	**101.7**	**78.9**	
st deviation	**13.4**	**40.9**	**51.1**	**51.5**	



It is assumed that the areal deposition of metals at sites 1 and 2 is similar to, and representative of, surrounding lands located into the northwest "air shed" of Sudbury smelting activities and at a similar distance from the pollution sources. It is recognized that much of the surrounding land is under active cultivation, and therefore pesticides, herbicides and fertilizers are added to the soil. These additions contain metals thus there is a good chance that agricultural land which is under cultivation has even higher concentrations of certain metals.

The topography of sites 1 and 2, respectively, is the same as the topography of sites 3 and 4 in a general way. Sites 3 and 4 are located in the non-industrial areas and are not surrounded by rural lands, thus not subject to the influence of pesticides, fertilizer and herbicides. They are located in the same direction from the source as previous sites, but at a greater distance. The main pollutants for these sites are emissions from the Sudbury smelters. Site 3 is a flat area with mainly deciduous vegetation cover, while site 4 is a hill slope with the same type of vegetation. As can be seen on the graphs in Table 4.6, topographically flat sites accumulate less metal than hilly sites. For example mean concentrations for manganese for site one and three are only *362 ppm* and *21 2 ppm* respectively, while for sites 2 and 4 they are *1300 ppm* and *1393 ppm* respectively.

Site 5 is the furthest site from the pollution source in the northwest direction. This site is a topographically flat area in the recreation zone located within 5-7 m of a parking lot. It is a possibility that at this location emissions from cars from the nearby highway and the parking lot elevated metal concentrations in the soil. For example, concentrations of nickel and copper for site 4 are *49.9 ppm, 28.6 ppm* and for site 5 are *90.6 ppm and 61.2 ppm* respectively.

4.5.1 Statistical variability among sites

To identify metal variability among sites statistical analyses were performed. A statistical *t*-test was selected since all of the data are normally distributed. A two sample difference test shows whether samples belong statistically to the same population or not, initially assuming they are from two independent populations. The test is applied to determine whether the two samples are significantly different. The null hypothesis is that means are the same, and the alternative hypothesis is that they are different (McCrew, 1993). In this regard, samples were taken from sites with varying topography and also with varying distance from the point source. If sample differences are found to be significant then it can be concluded that the samples were taken from different populations, whereas if the sample difference is found to not be significant then the samples were taken from a single population.

It is expected that with increased distance from the point source, elemental concentrations in soil will decrease. It is also expected that sites situated on steeper slopes, due to runoff, will contain decreased concentrations.

In this case a *t*-test was done for all 5 sites, and a summary of significant pairs is presented in Table 4.7 and all results are presented in Appendix 6. All sites were compared to each other for 8 selected metals. The test was also done for all soil horizons. Testing was done for difference in concentrations of some metals in all soil horizons across sites. Using alpha values 0.05 and with p value less than 0.2, the *t*-test is considered to be significantly different and helps us in understanding correlations between sites and changes in metal distribution.

Table 4.7 Metals with out significantly different concentrations in soil horizons across sites

	SITE 1	*SITE 2*	*SITE 3*	*SITE 4*	*SITE 5*
SITE 1					
LITTER		1	6	7	8
A					
B					
SITE 2					
LITTER			2	2	6
A					
B	Y				
SITE 3					
LITTER	Rb, Y, Zr	Cr		6	5
A	Y, Cr	Rb			
B	Cr				
SITE 4					
LITTER	Ni	Mn	Zn, Y		12
A	Cu,Rb,Cr		Zn, Cr		
B	Cu, Ni, Rb	Cu	Zn,Y		
SITE 5					
LITTER	Y, Zn,Cr	Y, Mn	Cr	Zn,Y,Zr,Mn	
A	Rb, Cr	Rb,Zr,Mn	Rb, Cr	Rb,Zn,Zr,Cr	
B	Cu,Rb,Zn,Mn	Zn	Rb, Zn, Y	Cu, Ni, Zr, Mn	

The table above represents a matrix in which numbers represent the number of different pairs which are not significantly different; and elements are listed for each horizon. From the results of the test for zinc, significance differs with distance, for example pair 1 – 3, and with topography, as in pairs 1-2 or 3-4. However, site five is not significantly different in the same manner for top horizons, and varies at lower horizons.

For yttrium, results differ with distance, as shown between pairs of sites 2-4 and 3-5. Only hill slope sites 2-4 are significantly different, while the topographically flat sites are statistically the same.

For rubidium results differ within distance for A and B horizon for sites 1-3, 2-4. Clearly the difference can be seen with different topography of sites. Such as sites 1-2 and 2-4, which are significantly different for all horizons.

Zirconium has a significant difference with distance and topography for all horizons and mostly all sites. Pairs 1-2, 3-4 have a significant difference, which is mainly the topography. At the same time sites 1-3, 2-4, and 1-5 have the same topography but vary with the distance from the source, and they are significantly different.

Results of the test for copper reveal that sites are significantly different according to the distance, as sites 1-3 and 3-5 have *p*-values less then 0.07. Sites 1-2 and 3-4 are significantly different, and have different topography.

For nickel all sites are significantly different except for sites 1- 4 only for the *B* horizon and as well as a pair of sites 4 – 5. Therefore the sites vary according to the distance and topography, but only for the top soil horizons.

For manganese most of the sites are different. They vary according to topography and distance. But sites 2 – 4 which are the hill slopes are the same for the Litter horizon, but vary for the rest of the profile. Sites 4 – 5 vary only for the *A* horizon.

Chromium has a significant difference according to the sites topography such as sites 1-3 and 2-4, but is mostly the same according to the distance distribution for the sites with the same topography.

4.5.2 Variability within sites

The metals are distributed differently with depth in the soil profile. The relative proportion of selected metals by weight is illustrated in Figures 4.3 (a, b, c) – 4.7.

a. b. c.

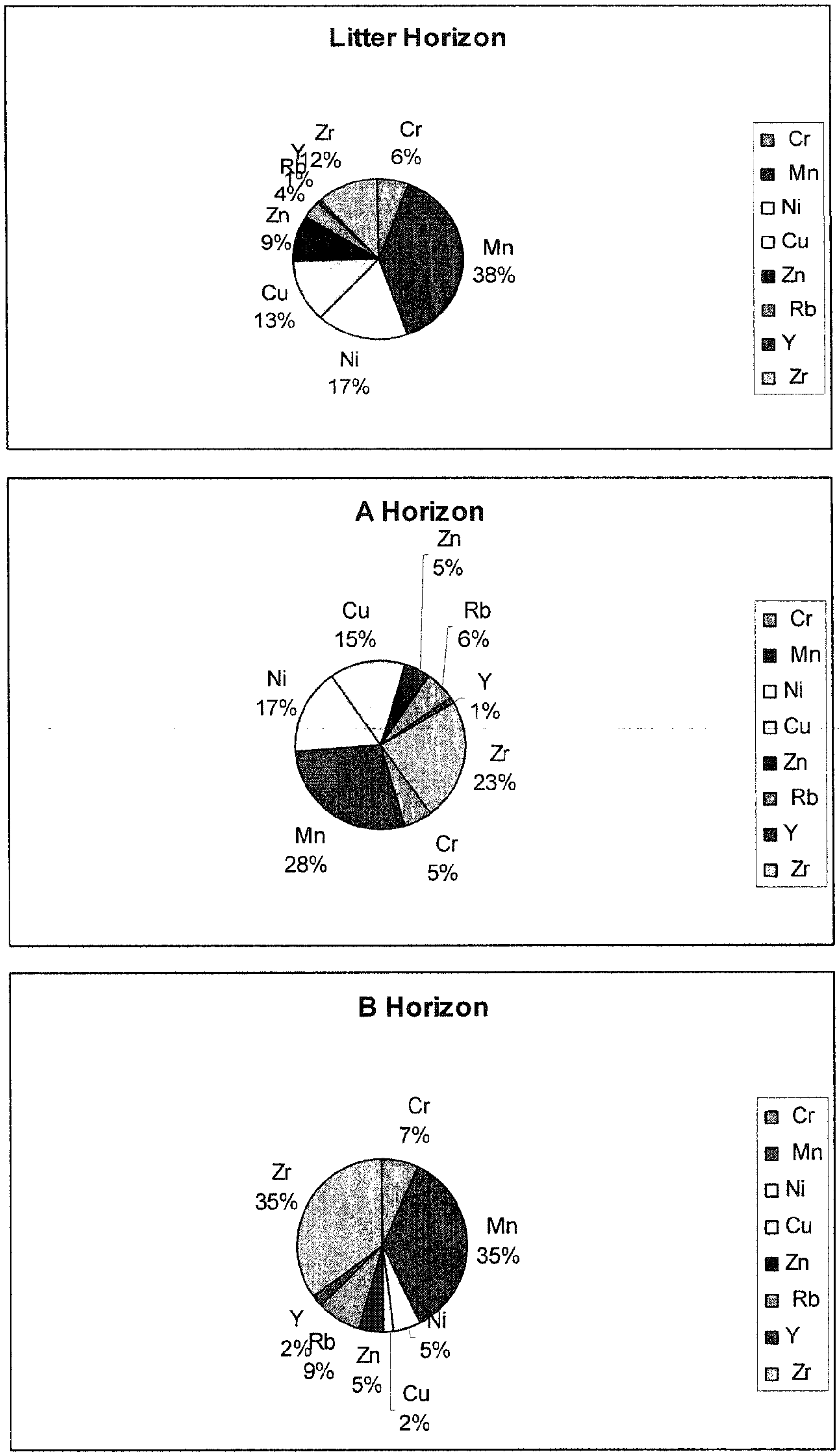


Figure 4.3 (a,b,c) Relative proportion of selected metals in profile, site 1, according to mean concentrations

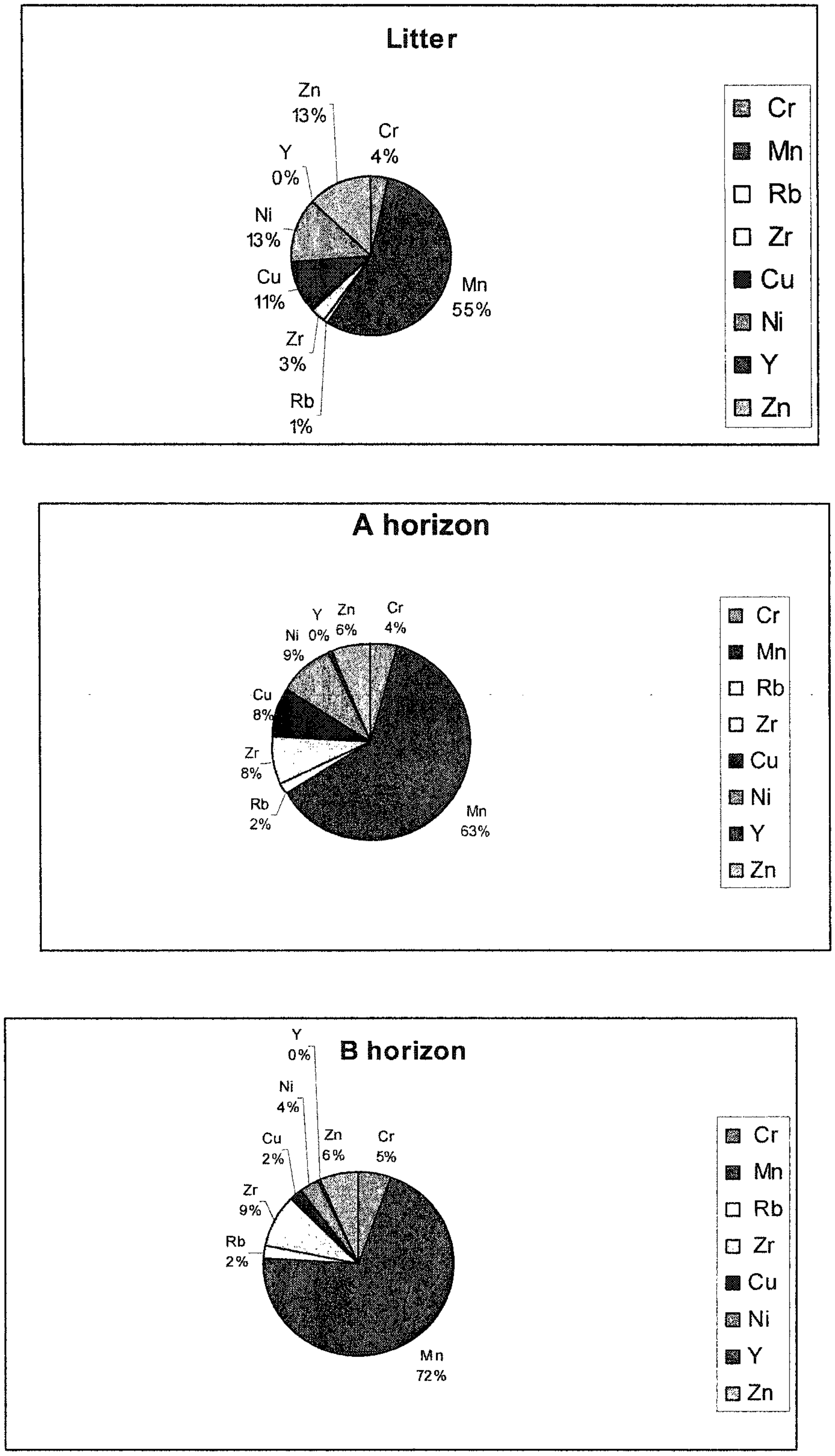


Figure 4.4 Relative proportion of selected metals in profile, site 2 according to mean concentrations

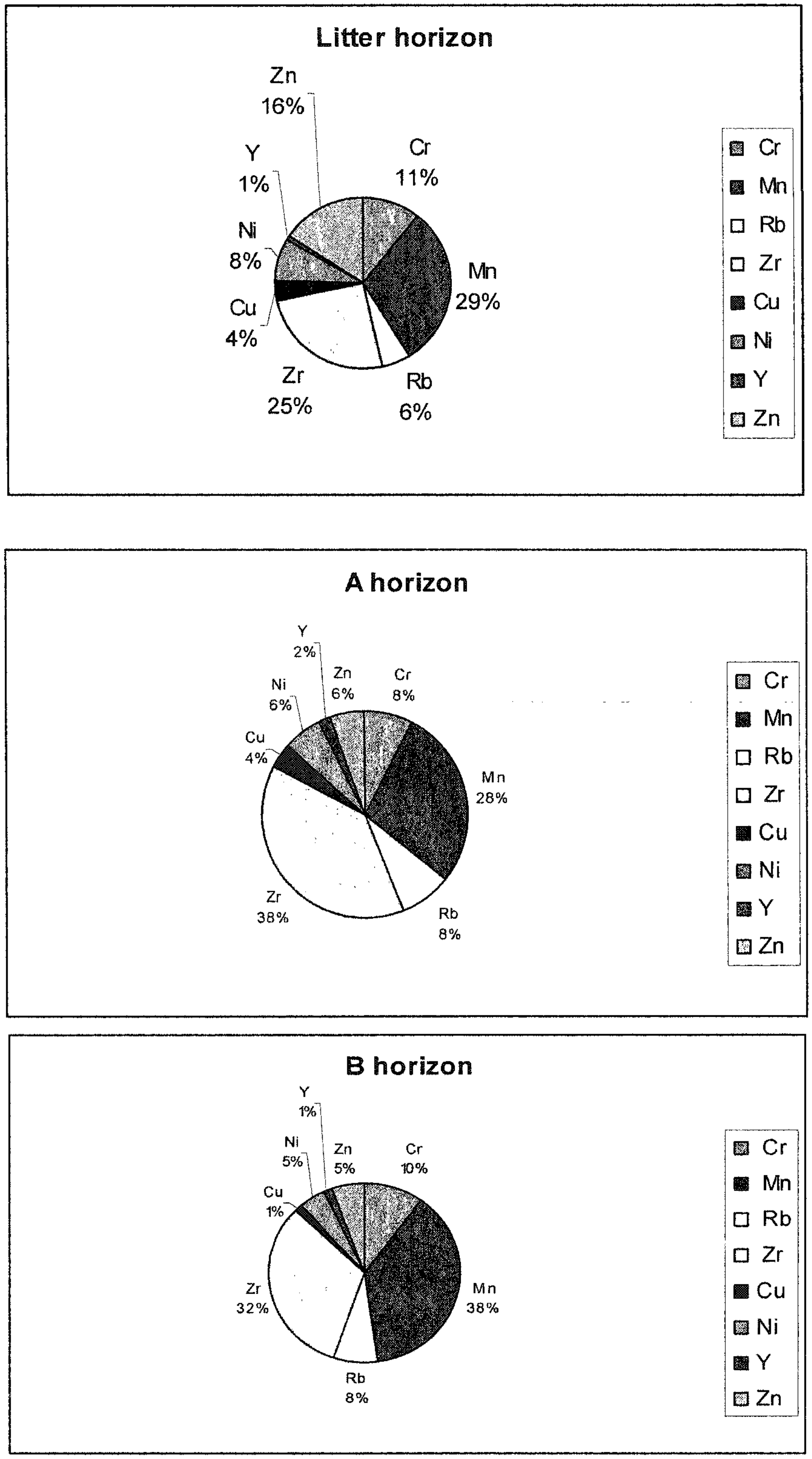


Figure 4.5 Relative proportion of selected metals in profile, site 3 according to mean concentrations

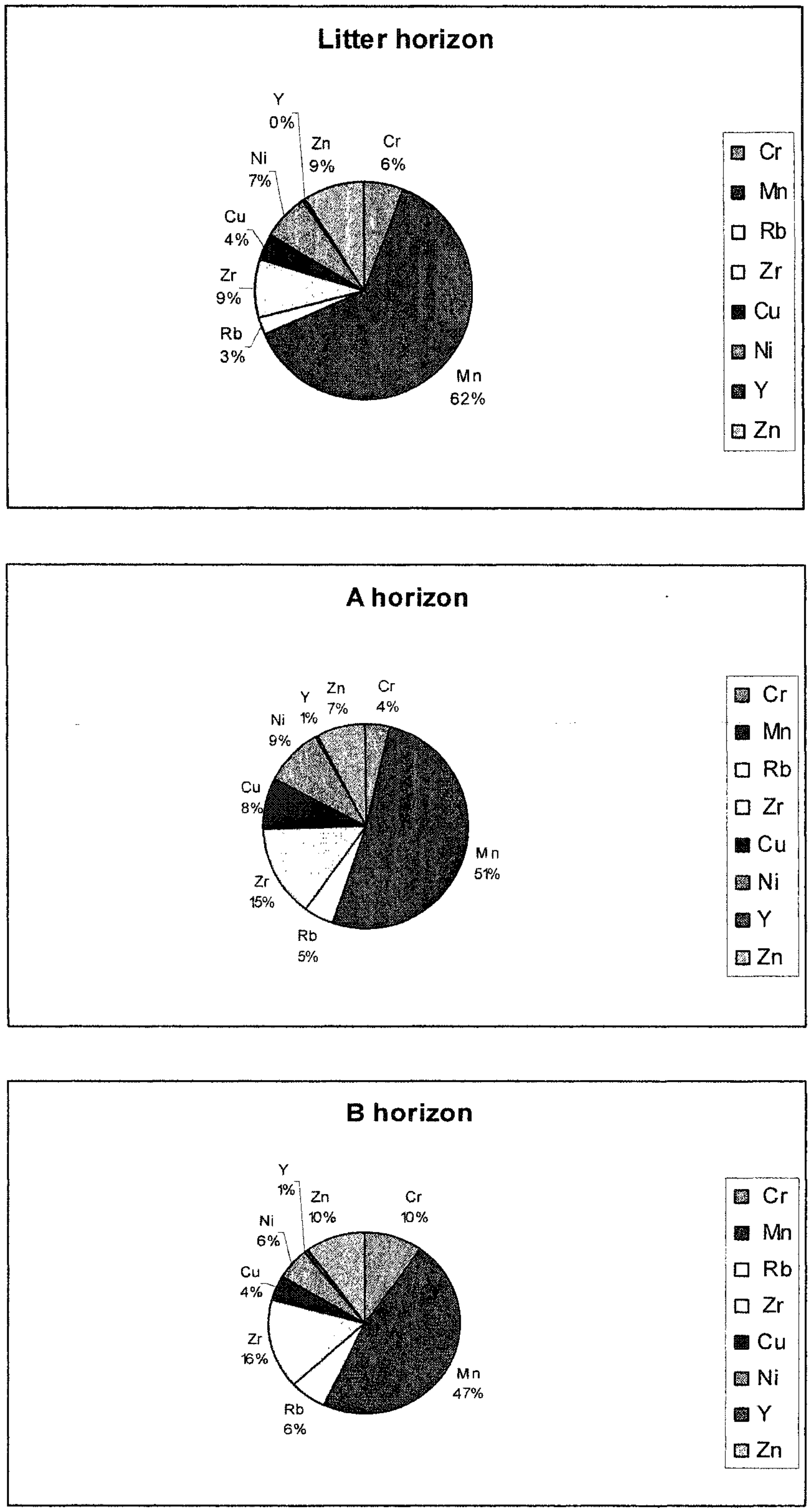
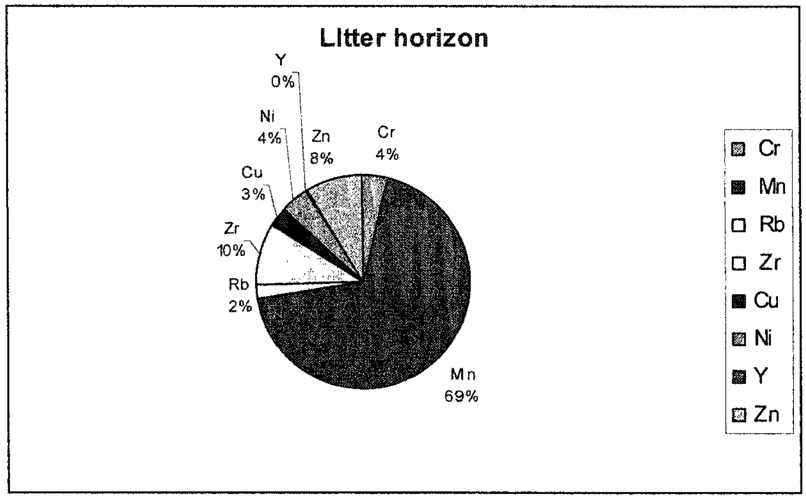
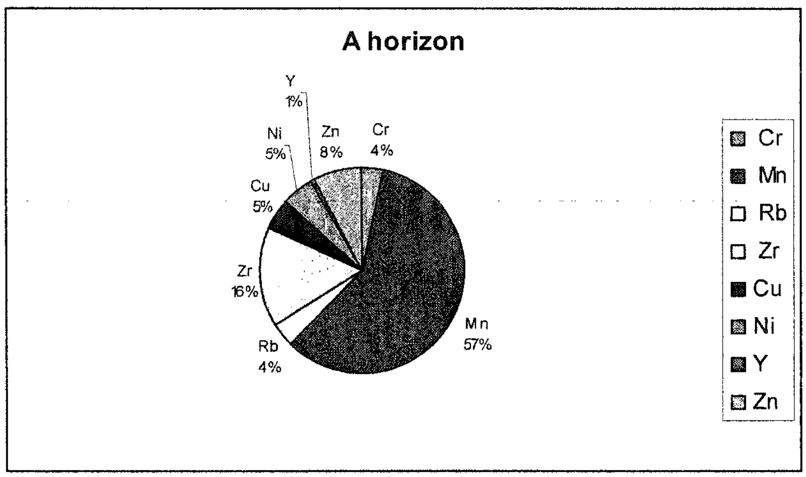


Figure 4.6 Relative proportion of selected metals in profile, site 4 according to mean concentrations





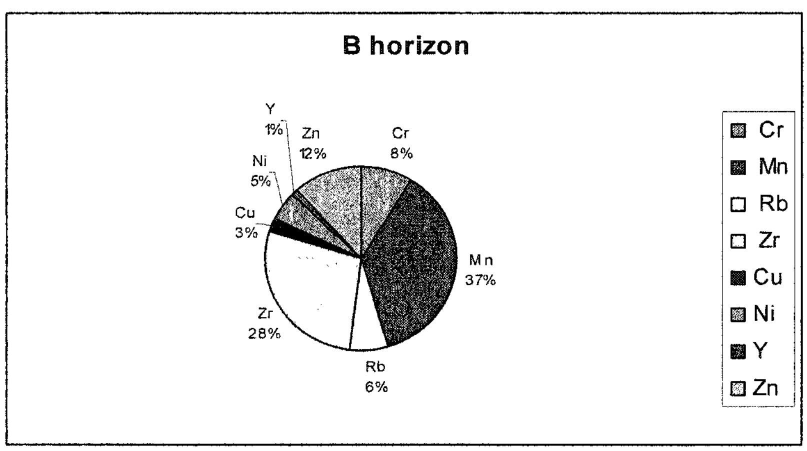


Figure 4.7 Relative proportion of selected metals in profile, site 5 according to mean concentrations

For site 1 the metals have different patterns of distribution in the soil profile. Such metals as copper, nickel and zinc have a drop in concentration; manganese and chromium stay at the same level; while zirconium and rubidium increase in concentration with the depth in the soil profile. For site 2 as for site 1 zinc, nickel, and copper drop in concentration from surface to depth; chromium and yttrium stay at the same level; while zirconium, rubidium and manganese increase in concentration in the soil profile with depth. For site 3 zinc, nickel, copper, zirconium and chromium drop in concentration with increasing depth; while yttrium stays at the same level; rubidium and manganese increase in concentrations. Site 4 can be characterized by a decrease in concentrations of manganese with depth, while copper and nickel decrease in concentration from the A to the B horizons; concentrations of yttrium are at the same level; such metals as chromium, zirconium, zinc and rubidium increase in concentration. For site 5 metals such as chromium, zinc, nickel, copper, zirconium and rubidium show an increase in concentrations with depth; concentration of manganese drops; while concentration of yttrium stays at the same level.

4.5.3 Variability with distance

Concentrations of elements may vary with distance from the point source. Most of the emissions from smelters in Russia are deposited within 5-10 km from the source, in most of the areas (Spektor, 2001). In the Sudbury area, distribution of emissions has changed since construction of the "SuperStack". Areas next to the source of pollution could be protected form the deposition of metals by natural factors (changes in elevation). This kind of "shade" was found in the Russian Arctic (Golubeva, 1999). Some areas next to the smelters which should receive most of the pollution receive hardly any; one of these areas was protected by a hillslope. Some sites that were distant from the smelter received most of the emissions (Golubeva, 1999).

In the Sudbury area the deposition of metals extends a considerable distance, due to the stack height (381m). What must also be taken into account is that the height of the INCO stack was elevated in the 1970s, which also affects the deposition of elemental pollution from the source.

Chapter 5. Discussion

5.1 Introduction

This chapter will discuss the background concentrations of metals in soil and the distribution of elements according to distance, topography and vegetation cover.

5.2 Use of the background concentrations

Background metal concentrations for soil were not sampled in this current work but are derived from the literature (Dudka, 1995; Hutchinson, 1997; McIlveen, 1995). The reported background concentrations of metals in soil (Table 4.5) are lower than metal concentrations found in the studied sites (see below). It is important to collect a representative number of metal concentration data for soils of the region in order to make some spatial assessment of the change in soil chemistry.

Comparing known background concentrations (McIlveen 1995; Dudka, 1995) of copper (25 ppm), to the results from site 1 – the mean concentration is approximately 5 times higher than background, for site 2 the difference is more than 10 times; average concentration at site 3 is approximately equivalent to background levels; the site 4 mean concentration increases by a minimum of 3 times over background levels and the mean copper concentration at site 5 is equivalent to the reported background levels.

Nickel background concentration is 10 ppm (Hutchinson, 1997; Dudka, 1995), and the average concentration of nickel at site 1 is 160 ppm; average concentration at site 2 is 36 times background levels; the mean concentration at site 3 is elevated above background levels by 3 times; for site 4 mean soil values is 12 times greater and site 5, which is 35 km from the INCO stack has nickel concentrations 5-6 times higher that background.

5.3 Dependence on topography

In these studies we have two main topographic features: flat areas and hill slopes. Sites 1 and 3 can be described as topographically flat, while sites 2 and 4 are hill slopes with SSW aspect. Sites 1 and 2 and sites 3 and 4 are located 15 and 25 km, respectively, from the point source (INCO). For understanding the difference between sites, percent difference of metals concentrations between sites was calculated using the formula:

$$\%\ difference = (Litter\ 2 - Litter\ 1)/\ litter\ 1 * 100 \quad (4)$$

Table 5.1 Percent difference of elements concentrations between sites

(Sites that belong to the same population are shown by asterisk)

(*Site/elem.*	*Cr*	*Mn*	*Ni*	*Cu*	*Zn*	*Rb*	*Y*	*Zr*
Litter 1	60.1	379.2	168.6	126.5	93.5	37.4	6.2	115.9
Litter 2	87.4	1300.6	307.5	250.2	303.3	22.0	4.7	72.1
% difference	**45.5%**	**242.9%**	**82.3%**	**97.8%**	**224.3%**	**-41.2%**	**-24.1%**	**-37.8%**
A 1	44.0	242.8	143.1	123.9	42.3	50.5	9.9	196.5
A2	104.5	1463.4	218.9	194.2	151.6	46.3	10.6	187.0
% difference	**137.2%**	**502.7%**	**53.0%**	**56.7%**	**258.3%**	**-8.3%**	**6.9%**	**-4.8%**
B1	45.3	222.0	34.1	11.8	29.3	53.8	11.0	223.4
B2	116.0	1504.2	75.6	48.3	134.4	43.9	10.6	197.6
% difference	**155.8%**	**577.4%**	**121.6%**	**311.1%**	**359.2%**	**-18.4%**	**-3.6%**	**-11.5%**
Litter T-test	**0.018**	**0.000**	**0.001**	**0.004**	**0.001**	**0.000**	**0.262***	**0.000**
A t-Test	**0.000**	**0.000**	**0.002**	**0.016**	**0.001**	**0.017**	**0.330***	**0.000**
B t-Test	**0.000**	**0.000**	**0.045**	**0.056**	**0.094**	**0.000**	**0.670***	**0.000**
Litter 3	76.8	212.5	54.9	29.2	110.3	39.2	7.5	172.5

Litter 4	131	1382.2	153.2	88.5	198.6	58.9	8.7	191.9
% difference	**70.5%**	**550.4%**	**179%**	**203%**	**80%**	**50.2%**	**16%**	**11.2%**
A 3	44.8	158.1	34.6	21.6	31.7	46.7	9.6	220.9
A 4	44.3	578.1	104.5	94.5	84.4	52.4	7.5	166.6
% difference	**-1.1%**	**265.6%**	**202%**	**337.5%**	**166.2%**	**12.2%**	**-21.8%**	**-24.5%**
B 3	45.1	173.1	21.2	6.2	24.9	34.2	6.4	145.4
B 4	81.8	396.8	48.1	37.1	83.8	51.4	6.1	133.6
% difference	**81.3%**	**129.2%**	**126.8%**	**498.3%**	**236.5%**	**50.2%**	**-4.6%**	**-8.1%**
Litter T-test	**0.000**	**0.000**	**0.000**	**0.003**	**0.501***	**0.003**	**0.243***	**0.000**
A t-Test	**0.969***	**0.000**	**0.000**	**0.000**	**0.501***	**0.066**	**0.230***	**0.000**
B t-Test	**0.000**	**0.015**	**0.001**	**0.000**	**0.365***	**0.005**	**0.601***	**0.000**

Table 5.1 illustrates the percent difference of various metal concentrations between sites 1 and 2; and 3 and 4. There are notable differences in the litter horizon between site 1 and 2 for copper, nickel, manganese and zinc. For both A and B horizons chromium, nickel, copper, manganese and zirconium have notable differences. *T*- tests were conducted to determine if the metal concentrations between the flat and hill slope sites located at similar distances from the INCO stack were statistically different. These tests show that all elements for all horizons are significantly different, except yttrium for the *B* horizon. Sites 3 and 4 elements belong to different populations except zinc and yttrium according to the *t* – test.

It is assumed that hill slope values increase due to a combination of topography and vegetation which impose a natural barrier for pollution. Similar observations have been made in Russia (Golubeva, 1999; Spektor 2001). Sites on the flat area do not have this accumulation barrier, except large trees. An interesting fact is that percentage differences are highest in the B horizon comparing to *A* horizon (Table 5.1). This may indicate that metal concentrations were higher in the past; perhaps at this time combination of a vegetation, high deposition levels (pre SuperStack at INCO) which has changed over time was more efficient at trapping metals.

Site 5 has the same topographic character as sites 1 and 3, and also has a potential influence from car emissions at Onaping Falls, the recreational use area. The table below represents a *t*-test which was done for comparing differences among the 3 topographically flat areas (sites 1, 3 and 5) (Table 5.2).

Table 5.2 T-test for sites 1, 3 and 5 and mean concentration of elements in ppm *(Sites that are not significantly different, which belong to the same population, are shown by asterisk)*

	Sig. (2 Tailes)		
	Sites		
element	1-3	1-5	3-5
CR	0.500*	0.461*	0.931*
MN	0.075	0.016	0.135
NI	0.172	0.179	0.033
CU	0.073	0.143	0.005
ZN	0.601*	0.077	0.990*
RB	0.776*	0.783*	0.950*
Y	0.311*	0.988*	0.489*
ZR	0.328*	0.282*	0.280*

Mean concentrations of elements in ppm

element	site 1	Site 3	site 5
CR	45	45	40
MN	240	160	650
NI	120	34	60
CU	100	20	45
ZN	42	60	110
RB	47	34	45
Y	7	6	6
ZR	180	170	190

Manganese, nickel and copper are metals that are significantly different for all sites, and their levels in soil are varying. All data for this table is summarized from appendix 6.

5.4 Variability depending on different types of trees

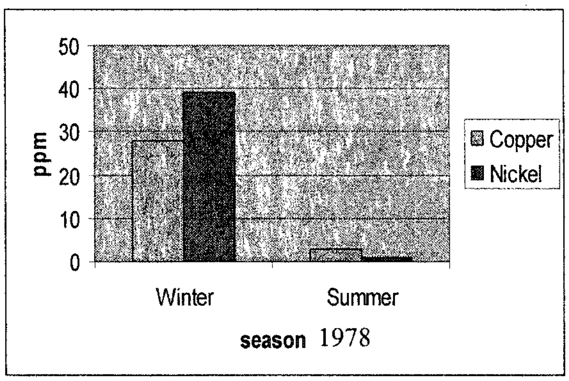
In this research, study sites had two types of tree cover: coniferous and deciduous. Sites 2 to 5 have deciduous species, and site one, coniferous vegetation. Differences in vegetation may play a role in trapping metals in atmospheric distribution. It is reported that deciduous trees can accumulate more pollution from the air than coniferous trees, just by the structure of their leaves (Golubeva, 1999). During the fall, the accumulated pollution would be moved into the litter horizon from the deciduous species. During the winter, when the importance of vegetation trapping metals in atmospheric deposition is minimized, most pollution accumulates in snow and then during melt time it potentially collects in the soil body. Snow accumulating on the canopy has the same effect as snow falling directly on the surface, as the residence time in the canopy is minimized due to the amount that the canopy is able to hold. For understanding the influence of vegetation on metals variability further research is needed.

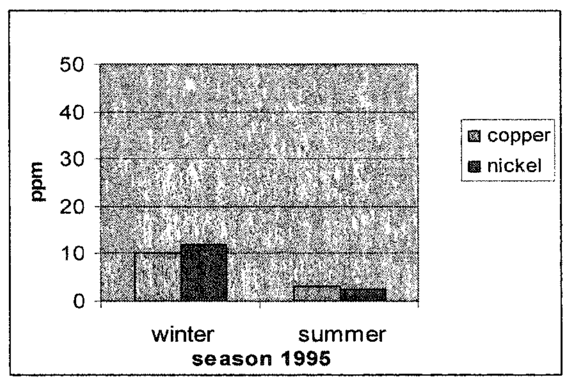
5.5 Deposition of elements and their dependence over time

Winter atmospheric deposition of copper and nickel at Killarney Provincial Park (100 kilometers southwest from Sudbury) was collected in snow tubes by the Ontario Ministry of the Environment in 1978 and 1995. Soil samples were collected during the summer season.

Changes in atmospheric deposition concentrations during different seasons for 1978 and 1995 are represented in Figure 5.1. According to the available data collected from the site concentrations of copper dropped from 28 ppm in 1978 to 10 ppm in 1995 and nickel concentrations changed from 39 ppm in 1978 to 12 ppm in 1995. It is difficult to identify summer atmospheric deposition rates at Killarney Provincial Park. In the summer season soil samples were taken, it is difficult to differentiate atmospheric deposition rates from metals that accumulated in soil before. Due to that, only winter atmospheric deposition rates can be used.

Figure 5.1 Dependence of metal concentrations over time





5.6 Assumption behind metal deposition calculations.

From previous research it is possible to establish a pattern of metal deposition in the area. Hutchinson and Freeman (1980) monitoring air samples for copper and nickel over a summer season provides summer deposition rates. Deposition of metals during the summer season was determined using collectors. During the same years of collection, winter metal deposition data from the Ontario Ministry of Environment (2002) from Killarney Park was sampled from the snow pack. Annual precipitation recorded at Sudbury (Ontario Ministry of Environment, 2002) indicates snow (water equivalent) is 250 mm and rain fall is 650 mm.

With this data it is possible to calculate deposition of copper and nickel in 1 m^2 of snow for years 1978 and 1995 at Killarney Park. All calculations were done using equation (4):

$$D = C\ (mg/L) * 250\ (L/m^2), \tag{4}$$

Where $\boldsymbol{D}$ (mg/m^2) is the deposition; $\boldsymbol{C}$ mg/L is the concentration of metal in snow multiplied by the area (m^2) of the snow volume (Table 5.3).

Table 5.3 Deposition of metals in snow (Ontario Ministry of Environment data)

	In snow 1978	Deposition	In snow 1995	Deposition
Copper	28 mg/l	7 g	10 mg/l	2.5 g
Nickel	40 mg/l	10 g	12 mg/l	3 g

For the snow free period the Hutchinson and Freeman (1980) air monitoring data are used. These data were collected soon after the SuperStack was built. It is documented that all pollution from the smelter SuperStack was reduced 90 percent by 1995 due to installation of scrubbers (Freeman, 1980).

The available data for winter deposition indicates extremely high atmospheric concentrations of copper and nickel at Killarney Park approximately 100 km to the southeast of Sudbury. The published daily emissions of copper and nickel from the SuperStack (Hutchinson and Freeman, 1980) are 0.9 and 0.7 tonnes/day. The atmospheric loading recorded at Killarney Park is equal to 10 and 7 g/m^2 for copper and nickel (OME, 2002). If it is assumed that the copper and nickel snow pack concentrations are the same within the

100 km area of the SuperStack, the general winter loading are $7.1*10^{-5}$ mg/m^2 and $5*10^{-5}$ mg/m^2 respectively. These values are much higher than the published values of Hutchinson and Freeman (1980). As such the winter values from Killarney for copper and nickel are discounted in the following calculations. It is assumed therefore that winter deposition of copper and nickel will approximate the summer concentrations published by Hutchinson and Freeman (1980).

The distribution of atmospheric collectors enabled Hutchinson and Freeman to calculate nickel and copper deposition within a 60 km radius from the SuperStack. The deposition for nickel was estimated to be 42 percent and copper, 40 percent from total SuperStack emissions. Recorded one day emissions of copper and nickel from the stack in June 1977 were 0.9 t / day and 0.7 t / day respectively (table 5.4). The daily mass of copper and nickel deposited outside the 60 km distance was determined by subtracting the daily mass deposited within 60 km range to SuperStack.

Table 5.4 Deposition of elements in the area

For 1977	**Stack**	**Within the 60 km area**	**In greater that 60 km**
Copper	0.9 t/ day	0.37 t/day	0.53 t/day
Nickel	0.7 t/day	0.29 t/day	0.41 t/day
For 1995 (Scrubbers)	**Stack**	**Within the 60km area**	**In greater that 60 km**
Copper	0.09 t/day	0.037 t/day	0.053 t/day
Nickel	0.07 t/day	0.029 t/day	0.041 t/day

From these data it is possible to calculate the amount of copper and nickel that was deposited in 1977 - 1995 and 1996-2001 in the 60 km area from the smelter.

$$C_{t/19eyars}=D * \sum_{days} \quad (5a)$$

$$C_{t/6eyars}=D' * \sum_{days} \quad (5b)$$

Where $C_{t/19years}$ is the total amount deposited in 19 years, ***D*** is the deposition of the metal (mg/m^2/day) before scrubbers multiplied by the total number of days in 19 years; $C_{t/6years}$ total amount deposited in 6 years, ***D*** is the deposition of the metal (mg/m2/day) after emissions were reduced multiplied by the total number of days in 6 years., which was calculated using published data from Freeman and Hutchinson (1980).

Prior to scrubber installation the total copper mass dispersed into the atmosphere with in 60km radius of Sudbury for 19 years (1977-1995) is *2566* t or *220* mg/m^2. For the remaining 6 years (1996-2002) total deposition of copper was *81* t or *7* mg/m^2. Thus the total deposition for the 25 year period is *227* mg/m^2 for copper. For the entire 19 year period *2011* t or *178* mg/m^2 of nickel was deposited within 60 km of the SuperStack. For the remaining 6 years *63.51*t or *5.5*mg/m^2 of nickel were deposited in the 60km area from the SuperStack, therefore the total deposition of nickel for the 25 years period is 2074t or 183mg/m^2.

5.6.1 Deposition of metals according to wind direction

Another method of calculating air deposition rates of metals depend on prevalent wind direction. According to the wind direction data for the Sudbury area (Appendix 5), it is possible to calculate the percentage of total time the wind blows from different directions. Predominant south and south-east winds directed smelter pollution over the study sites for approximately 20% of the year (OME, 2002). As such the study sites receive the equivalent of 2.5 months of direct pollution from the smelter. For the remaining 80% of the year the study sites receive reduced amounts of pollution. The Hutchinson and Freeman (1980) air monitoring sites received approximately the same proportion of the direct wind (20 percent) from the smelter as the study sites from the work. According to the published data (Hutchinson and Freeman, 1980) it is possible to identify high and lower levels of deposition for the area within 60 km from INCO. It is assumed that the Hutchinson and Freeman data showing enhanced and reduced periods of pollution, are related to periods when they are receiving direct wind blowing deposition from the smelter and indirect deposition respectively. To calculate the deposition rates the following formulas were used

$$Z * 9.5(\text{month}) = \text{low level of pollution} \quad (6)$$

$$Z' * 2.5(\text{month}) = \text{high level of pollution}$$

*Where **Z** and **Z'** (mg/(m^2/ month) are rates of deposition (Freeman and Hutchinson, 1980)*

The deposition collectors used by Freeman and Hutchinson (1980) are located at distances of 10, 20, 30 and 60 km from the INCO smelter sites (Figure 4.1). The soil study sites from this research were located at distances of 15, 25 and 35 km from the INCO smelter. Results can be seen in table 5.5.

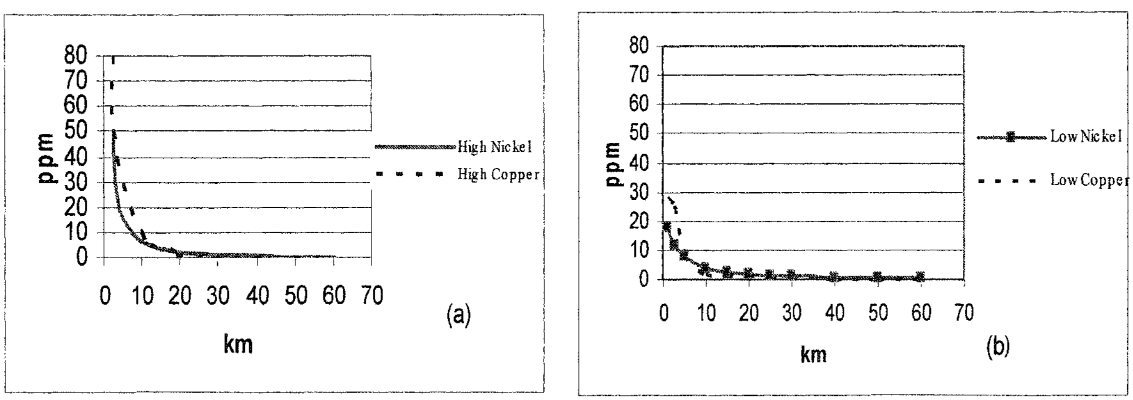


Figure 5.2 Assumed Deposition rates for copper and nickel at Hutchinson and Freeman sites (source Freeman and Hutchinson 1980).
[(a) Prevalent wind blows directly to the smelter sites; (b) Prevalent wind do not blow directly to the study sites]

Table 5.5 Atmospheric deposition of copper and nickel according to Freeman and Hutchinson Data

Nickel mg/m²

Site	Low levels	High levels	1978	1978-1995
15km	19	12.5	31.5	598.5
25 km	17.1	5	22.5	427.5
35 km	4.75	1.25	6	114

Site	1996	1996-2001
15km	3.15	18.9
25 km	2.25	13.5
35 km	0.6	3.6

Copper mg/m²

Site	Low levels	High levels	1978	1978-1995
15km	19	12.5	31.5	598.5
25 km	9.5	7.5	17	323
35 km	4.75	2.5	7.25	137.75

Site	1996	1996-2001
15km	3.15	18.9
25 km	1.7	10.2
35 km	0.72	4.32

To differentiate the mass of a metal that potentially deposits on soil from air, the actual metal mass accumulated in the soil of metal was calculated using equation (7) from the data.

$$Lx = Cx * \rho x \qquad (7)$$

Where $\mathbf{Lx}$ *– mass of a metal accumulated in soil mg/m³,* $\mathbf{C_x}$ *– concentration of the element in mg/kg multiplied by* $\boldsymbol{\rho_x}$ *- bulk density of the profile mg/m³ .*

The actual mass of copper and nickel in soil were calculated for each site *A and B* horizons. Bulk density values for the Litter horizon are not available. All results of these calculations are presented in table 5.6

Table 5.6 Mass of a metal accumulated in soil (mg/m^3)

Site.	Bulk density	Ni mg/kg	Total in soil(mg/m^3)	Soil horizon(mg/m^3)	Cu mg/kg	Total in soil(mg/m^3)	Soil horizon(mg/m^3)
A 1	0.702	143.1	100.5	8.04	123.9	87.0	6.96
A 2	0.871	218.9	190.7	15.2	194.2	169.1	13.52
A 3	0.958	34.6	33.2	2.65	21.6	20.7	1.65
A 4	0.738	104.5	77.0	6.16	94.5	69.7	2.78
A 5	0.579	56.68	32.8	2.62	54.4	31.5	1.26
B 1	1.241	168.6	209.2	8.36	126.5	156.9	6.27
B 2	1.105	307.5	339.8	13.59	250.2	276.5	11.04
B 3	1.475	54.9	80.9	3.23	29.2	43.1	1.72
B 4	1.052	153.2	161.2	6.44	88.5	93.2	3.72
B 5	0.699	90.6	63.3	2.53	62.2	43.5	1.74

This table represents how many milligrams of the element are in one cubic meter of selected soil horizon, and exactly how many mg of metal in each horizon, according to the horizon's depth and bulk density.

From the published data it was calculated that atmospheric deposition of copper is 227 mg/m^2 and for nickel it is 180 mg/m^2 over 25 years. According to this information it is possible to calculate approximate amounts of copper and nickel that were deposited in the study site transect with 35 km of a single source (INCO) using Table 5.7. Using Hutchinson and Freeman deposition rates it was assumed that approximately 100 percent of metals were deposited within 35 km. According to this assumption it is possible to determine the percent of the total deposition rate at each distance, as shown in Table 5.7

Table 5.7 The percent of the total deposition rate at each distance

	15km deposition	% of total	25 km deposition	% of total	35 km deposition	% of total
Copper	2.62	56 %	1.41	30 %	0.6	13 %
Nickel	2.62	52 %	1.87	37 %	0.48	10 %

Using the percent values from Table 5.7 it is possible to calculate the amount of copper and nickel that were deposited at each study site distance by multiplying the total deposition for each metal by the relevant percent value, results can be seen in Table 5.8.

Table 5.8 Deposition values for each distance

	15 km % rate	Deposition mg/m^2	25 km % rate	Deposition mg/m^2	25 km % rate	Deposition mg/m^2
Copper	56 %	127.12	30 %	68.1	13 %	29.5
Nickel	52 %	93.6	37 %	66.6	10 %	18

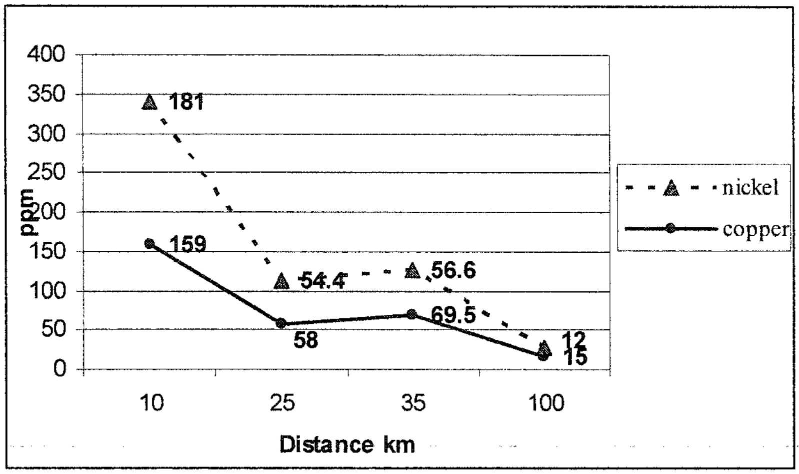
As it can be seen from the Table 5.8, most of the metals are deposited in the first 25 – 35 km from the source. It is possible to say that deposition rates at a distance of 25 km from the SuperStack are mostly the same for copper and nickel, and mean concentrations in soil for sites 3 and 4 are approximately 55 and 45 ppm respectively. That means that most part of the metal emissions are concentrated in soil according to the available data.

As is noticeable from the Table 5.6, sites 2 and 4 (hill slopes) have higher concentrations of copper and nickel than sites 1, 3 and 5. Further from the single source there is a reduced amount of loading ability of underlying surface.

Availability of atmospheric deposition is limited, thus it is difficult to say how concentrations were changing during the 25 years time period. It is possible from the existing data from Killarney Park to state that atmospheric metal concentrations dropped after 19 years, and their level is less than background levels for the area.

To understand the metal correlation between concentrations on metals in soil and distance summer soil data from 1998 at Killarney coupled with the *A* horizon data from this study was used. It is possible to make a transect profile of metals in soil from the source to Killarney located 100 km southwest of Sudbury. For this it is assumed that the concentrations of metals deposited in southwest direction is the same and have been similar over a long period of time. That was done, because our samples were taken in 2001.

Figure 5.3 Cross sectional profile Ni and Cu concentrations in soil (*A* horizon)



The figure above indicates that soil metal concentrations are declining with increase distance from INCO smelter which probably indicates that deposition of elements declined with distance from the source. Although comparisons are not feasible as the fate of metals in the soil here is unknown over long period of time.

5.7 Variability within sites

Copper is reported to be less mobile than nickel in soils. That was proven by different tests that were done in 1994 by a group of scientists (Adamo, 1995). Depending on different behaviors of copper and nickel in soil, their concentration will change over time. Most of the copper is associated with organic forms, while nickel is mostly associated with inorganic forms (Adamo, 1995). That could explain why nickel distributes through the profile faster than copper. For copper to distribute it needs to be connected with organics. This slows the movement downwards. According to the available data from Table 5.6 it is possible to show values for nickel and copper in Table 5.7

Table 5.9 Concentrations of Copper and Nickel according to deposition concentrations (ppm)

Ni	#1	#2	#3	#4	#5	Cu	#1	#2	#3	#4	#5
A	8.04	15.2	2.65	6.16	2.62	**A**	6.96	13.52	1.65	2.78	1.26
B	8.36	13.6	3.23	6.44	2.53	**B**	6.27	11.04	1.72	3.72	1.74
A/B	0.96	1.12	0.82	0.96	1.04	**A/B**	1.11	1.22	0.96	0.75	0.72
A+B	16.4	28.8	5.88	12.6	5.15	**A+B**	13.11	24.56	3.37	6.5	3
Cu/Ni	0.86	0.88	0.62	0.45	0.58	**average**	0.68				
Air/soil Ratio	20	10	78	40	90	**Air/soil Ratio**	40	23	136	89	193

Concentrations of copper are lower than concentrations of nickel, due to its reaction with organic and to a smaller degree of non-organic forms. Historical emissions in the area were acidic. Due to these acid depositions soil pH was very low. Such soil conditions in the A horizon might have been conducive to moving a greater mass of nickel and some amount of copper into the B horizon. Copper moves slower in the soil profile according to the ratio between *A* and *B* soil horizons. That could be an affect of acid soils and different behavior of metals in more acidic environment. The uptake of metals by vegetation is controlled by mycorrhiza. In infertile soils, nutrients taken up by the mycorrhiza fungi can lead to improved plant growth and reproduction. In certain environmental conditions, such as low pH values, the function of mycorrhiza may be impeded due to elevated concentrations of metals such as monomeric aluminum which are more soluble at low pH's. In this manner uptake of trace elements and nutrients by trees may be reduced resulting it degradation. Smelter emissions of copper are higher than emissions of nickel (see Table 5.4), so it is logical to assume that sites will be receiving more copper than nickel. In the soil, the ratio of the mass of copper to nickel decreases with the distance from the INCO smelter, except for site 5, where the influence of the recreation area and car emissions may play a role. The average copper / nickel ratio was calculated as 0.68 for all 5 sites. From the literature this ratio in the air is 1.28. It is possible to expect the same value in soil, however this is not what is observed for the study sites. The ratio between concentrations of metals in the air for 25 years and concentration of metals in soil shows that most of the elements do not deposit into the soil from air. Nickel has twice the ratio of deposition from air into soil than copper. Residence time of metals in the air increases with distance. Concentrations of metals in the air are reduced in topographically elevated sites.

Zinc is another serious pollutant in the area. High concentrations of zinc accumulate in Litter horizon for the first three sites. Concentration of this element drops there after, but there is mostly no difference in the concentrations between A and B horizons. Some elements have an increase of element concentrations with the depth of the profile. The reason for this is that these elements are more mobile than others, or hypothetically, because pollution has historically been higher. For example, Zirconium reaches maximum concentrations at the bottom of profile. All element signatures for site 2 can be seen in Figure 5.8, and for other sites in Appendix 4.

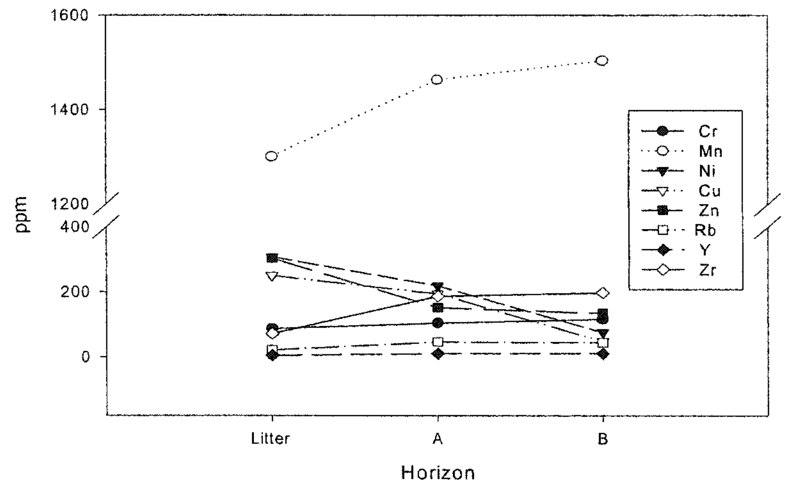


Figure 5.4 Average distributions of elements through the profile, site 2

On the other hand manganese has an unusual and unpredictable signature in distribution through the profile for the different sites. This element is not emitted from the smelter now, and shows increase of concentrations in soil further from the smelter. In the closer sites, this element could be altered due to pollutants from the smelter.

Such elements as Rubidium and Yttrium are more or less equally distributed, with a small increase at the bottom of the profile. It is possible that these metals were emitted in the early days of the smelter.

Chapter 6. Conclusions and recommendation

The results of this research show that metal contamination is a serious ongoing problem for the Sudbury area, even now after 20 years of reclamation and re-cultivation. Levels of some metals in the Sudbury region, as evidenced in the metal data in this research exceed background concentrations by several folds within 50 km of the source.

For reaching the goal of the study which was presented in Chapter 1, different methodologies and techniques were applied. According to the time limit for the field work, sample collection was done in the most efficient way for representing the surrounding environment. All data were analyzed according to the objectives of this study.

It is possible to conclude that concentrations of metals in the Litter, the *A* and the *B* horizons of soil drops with distance from the source, except for manganese, for which concentrations remained elevated with distance. Concentrations of nickel and copper were reduced with distance from the source, but at a distance of about 50 km they remain higher than the background levels. Atmospheric deposition of elements is higher than the amount accumulated in soil. That means that a certain portion of metals originally deposited have moved out or have never accumulated in the soil.

Background concentrations that were used in this work were not determined at the same time as samples were extracted in autumn 2002. It is acknowledged that use of background concentrations extracted from the literature has certain drawbacks. Although there is information published about the area (Hutchinson, 1997; Bagatto, 1991; Gann, 1995; Beckett, 1984), little has been published about background concentration, loading and deposition of metal concentrations.

Concentration of elements deposited in soil appeared to depend in part on topography. It was established that sites with different elevations located in close proximity have significantly different accumulations of metals; it is assumed that they receive the same amount of metals from the atmosphere.

Unfortunately all field work was done in a season when it was mostly impossible to identify vegetation cover except for trees. That is why bio-indication was not applied. At the same time birches are the dominant vegetation now, and most of the sites had deciduous types of vegetation. Where deciduous species dominate the litter horizon are deeper and better developed. This is normal for soil development under different dominant vegetation cover.

Distribution of elements through the soil profile varied, but the general pattern is that most elements accumulate in the A horizon and litter, and concentrations drop in the B horizon. According to the reduction of the pollution over time from the smelter, it was expected that elements would filter through the profile. But even 25 years after the main reduction of pollution it is difficult to say how these elements filtrate in the profile. Due to the northern location of these sites, processes are relatively slower (plant growth, organic decomposition) than in southern areas, and it could take longer to see the effect of distribution of elements through soil profiles. Concentrations of elements accumulated in the Litter and the *A* soil horizons are high. It will take years before all elements are relocated or removed from the profile. It is quite difficult to make any prognosis for the exact time that will be needed to remove high concentrations of pollutants from the system. According to the data that was calculated emissions from the smelter for copper are still 90 kg/day and for nickel 63 kg/day. These amounts were calculated assuming that all emissions were reduced by 90 percent by 1995. So we can see from the numbers above that the mass of copper and nickel being emitted from the stack is quite high. Until the concentrations that are emitted from the smelter drop, the influence on the surrounding environment will stay at the same level.

The model for metal variability in the area is that higher concentrations are closer to the source and on the hill slopes than on the topographically flat areas. Most of the agricultural facilities are located in areas with high levels of metal concentrations. Just because of their location next to the source of pollution all agricultural products would get high concentration of elements that are in the surrounding systems. Afterwards all these components by way of trophic chains will accumulate in animals and humans.

It is important to look not only at the main pollutants of the area but also at other elements that have a significant toxic effect to the surrounding environment.

The main concern is not about any particular element but about their combined effect on the environment. Even if each of them individually exceeds the background level just by a little bit, all of them combined can cause series environmental degradation for the surrounding ecosystems. That is why it is incorrect to analyze each element individually. Most of the elemental levels analyzed in this work are higher than the background concentrations.

Recommendations

One of the main recommendations is that for further research it is most necessary to calculate background concentrations. This concentration will represent recent and exact values.

Selecting a bigger study site for sampling would give a better picture of metal concentration and distribution. It could be necessary also to sample worms as possible vectors of change in elements from different horizons and soil types.

Monitoring should be done for a longer time and some areas probably sampled more than once during different seasons, to understand the influence of climate and vegetation for variability and accumulation of metals.

Medical surveys could be done and hair could be tested for amount of metals in the human body. This could give an idea about human toxicity and areas of the region with high risk of certain disease.

Bibliography

Adamo P., Dudka S., Wilson M.J., McHurdy M.J., 1995. *Chemical and mineralogical forms of Cu and Ni in contaminated soils from the Sudbury mining and smelting region, Canada.* Environmental pollution, pp. 11-19.

Agency for Toxic Substances and Disease Registry web page. Agency for Toxic Substances and Disease Registry Public Health Statement. Retrieved October 15 from World Wide Web: http://www.cla.sc.edu/geog/hrl/sctrap/toxfaqs/nickel.htm

Aleksandrov, 1999. *Environmental chemistry.* St. Petersburg, Russia, p.74 - 99.

Alekseenko V.A., 1990. *Forest Ecosystems and atmosphere pollution.* Leningrad, Nauka (Science), pp. 45-155.

Alekseeva – Popova N.V., 1991. Vegetation stability of different vegetation species. Leningrad, Nauka (Science).

AMAP 1999. *Assessment report: Arctic pollution issue.* AMAP, Norway, Oslo, p.100.

AMAP 2000. *Assessment report: Arctic pollution issue.* AMAP, Norway, Oslo, p. 100

Amiro, B.D., and G.M. Courtin, 1981. *Patterns of vegetation in the vicinity of an industrially disturbed ecosystem, Sudbury, Ontario, Canada.* Canadian journal of Botany 59: p. 1623-1639

Andres M.G. 1984. *Thanes estuary: pollution and recovery. Pp.99-107.* In P.J. Sheeham and al. (ed). *Effects of pollutants on ecosystem level.* John Willey and Sons.

Bagatto, G and J.D. Shorthouse. 1991. *Accumulation of copper and nickel in plants tissue and in insect gall of rawbuch blueberry vaccinium angustifolium near an ore smelter at Sudbury, Ontario, Canada.* Canadian journal of Botany 69: 1483-1490

Bagatto, G., Shorthouse, J.D. 1991. *Biotic and abiotic characteristics of ecosystems on acid metallic-ferrous mine tailings near Sudbury, Ontario.* Canadian journal of Botany. Vol. 77, num. 3: pp. 410-425

Beckett P.J., 1984. *Using plants to monitor atmospheric pollution.* Laurentian University. Rev. 16, pp. 50-57

Becket P., Chapter 6 *Lichens: Sensitive indicators of improving air quality* in: Gunn G. (ed), 1995: *Restoration and recovery of industrial region,* Springer – Verlag, New York, pp. 81-92

Bennett B.G., 1983. *Exposure of man to environmental selenium – an Exposure Commitment Assessment*. Science Total Environ. Vol. 31, pp. 117-127

Berlend M.E., 1989. Environmental cartography, Nauka (Science) Moscow, p.110

Birch N.J., 1998. *Handbook of toxicology of Inorganic Compounds* pp.397-403, Marcel Decker, New York - Basel

Bowen, H.J.M. 1979. *Environmental chemistry of the elements*. Academic Press, New York.

Boyle E.A., 1987. *Evolution of anthropogenic lead in ocean. Sixth international conference on heavy metals in the environment*, New Orleans, Proceeding Vol.1, pp.9-11. CEP Consultant Ltd, Edinburgh.

Braddy N.C., 1974. *The nature and properties of Soil.* MacMillan Publisher Co., Inc, New York, pp.50-311.

Bradshow, A.D. 1983. *The restoration of the ecosystems.* Journal of Appl. Ecol. 20: pp. 1-17

Brummer, G.M., Tiller, H.C, Hurms, U and Clayton P.M. 1983. *Absorption - desorption and/or precipitation – dissolution processes of zinc in soil.* Geoderma, 31, pp. 337-354

Canadian soil survey committee, subcommittee on soil classification. 1978. The Canadian system of soil classification. Agric. Publ. 1646. Department of Agriculture. Ottawa.

Card K.D. and Hutchinson R.W. 1972. *Sudbury structure: its regional geological settings.* The Geological Association of Canada, special paper #10, p.67-78

Cheburkin A.K., Shotyl W., 1996. *An energy dispersive miniprobe multielement analyses for direct analysis of Pb_4 after trace elements and picks*. Journal of analytical chem..: Vol. 354, pp. 688 – 691

Connell, 1997. *Basic concepts of environmental chemistry*. Luwis publishers, New York, p. 399, 404-407, 459-465.Daubermire, R.F. 1974. *Plant and environment. A textbook of plant toxicology.* 3rd edition J. Wiley and Sons. Toronto

DeLestard, L.P.G., 1967. *A history of the Sudbury Forest District*. Dist. His. Series No. 21. Ont. Dept. Lands and Forests, Toronto., 90pp

Dric M.E. (ed.), 1997. *Characteristics of elements*. Encyclopedia, Vol. 2, pp. 49-57, 191-204, Moscow, Metallurgy.

Dric M.E., Roxlin L.L., Gureeva C.E., Dederovich L.E., 1982. *Influence of Yttrium amounts on different metal combinations under stress*. Metallurgy of ferrous metals, p. 231.

Dudka S., Ponce-Hermamdez R., Hutchinson T.C., 1995. *Current levels of total element concentrations in the surface layer of Sudbury's soils*. The science of total environment. Vol. 162, pp. 162-171.

Dudka S., Ponce-Hernandez R., Tate G. and Hutchinson T., 1996. *Forms of Cu, Ni and Zn in soils of Sudbury, Ontario and the metal concentrations in plants*. Water, Air and Soil pollution, Vol. 90, pp. 531-542

Eco-usa.net: Toxics. Retrieved web page: revised September, 2002 form World Wide Web: http://www.eco-usa.net/

Emery ,T., in Sigel, H (ed) 1987. *Metal ions in biological system*., Marcel Dekker, New York.

Environment Canada (September 27, 2002): Canadian climate normal 1971-2000 for Sudbury, Ontario. Retrieved October 10, 2002 from Environment Canada on World Wide Web: http://www.msc-smc.ec.gc.ca/climate/climate_normals/index_e.cfm

Evangelou, V.P., 1998. *Environmental soil and water chemistry: principles and applications*. New York : John Wiley, p. 564

Freedman, B and T.C. Hutchinson. 1980. *Long tern effects of smelting pollution at Sudbury, Ontario on forest community composition*. Canadian journal of botany 58: p.2123-2140

Freedman, B and T.C. Hutchinson. 1980. *Pollutant inputs from the atmosphere and accumulation in soils and vegetation near nickel – copper smelter at Sudbury, Ontario, Canada*. Canadian journal of botany Vol. 58, pp. 208-132

Freedman, B. 1989. Environmental ecology: the impact of pollution and other stresses on ecosystem structure and function. Academic Press, San Diego, California.

French B.M., 1972. Shock-metamorphic feathers in Sudbury structure, Ontario. Geological Association of Canada, special paper #10, p. 19

Golubeva E, 1999 (a). Identification methods of environmental health in changed ecosystems. Geography, MSU.

Golubeva E, Kapitsa A., Spektor V., Tutubalina O., 1999 (b). *Metal contamination of surrounding environment, Norilsk, Russia*. MSU-Geography, Russia. pp. 44-55.

Golubiatnicov LL., Denisenko E.A., Svirezhev Y.M., 1998. *Model of the total exchange carbon flux for terrestrial ecosystems.* Ecological modeling. Vol.108, pp.265-276

Gundermann D., Hutchinson T., 1995. *Changes in soil chemistry in 20 years after the closure of a copper –nickel smelter near Sudbury, Ontario, Canada.* Journal of Geochemical exploration, Vol.52, pp. 231-236

Gunn J. (editor). 1995. *Restoration and recovery of and industrial region.* Springer-Verlag, New York.

Gunn J., Keller W., Negusanti R, Potvin R., Beckett P., Winterhalder K., 1995. *Ecosystem recovery after emission reductions: Sudbury, Canada. Water, air and soil pollution*, vol. 85, pp. 1783-1788.

Haneklaus, S., Vogel, W and Schrug, F., 1994. *Determination of environmental elements in contaminated soils by aqua region extraction and X-ray fluorescence spectroscopy.* Trans. 15^{th} World congress of soil science. Acapulco, Mexico. Vol. 3a; p 509-516

Hawley G., 1971. *The condensed chemical dictionary.* Litton education publishing, Inc. pp. 964

Hester, R.E. and Harrison R.M., 1994. *Mining and its environmental impact. Issued in environmental science and technology.* Royal Society of Chemistry, London, UK

Hollowey, G.T., 1917. *Report of the Ontario Nickel commission.* Legeslative Assembly of Ontario. Toronto.

Hossner, L.R., 1988. *Reclamation of Surface mined lands.* CRC Press Inc., Boca Raton. FL.

Hutchinson T., 1973. *Oil spills and vegetation.* Final repost, 1973 for Arctic Land Use Research program .Can, Dept. Int. Affairs and Northern development, Ottawa.

Hutchinson T., 1981. *Recovery of Arctic and sub-Arctic vegetation nine summers after crude and diesel oil spills.* Canada. Northern Affairs Program pp.18

Hutchinson T and Whitby K., 1986. The use of native and agricultural plant species to re-vegetate northern mine tailings. Canada: Minister of Supply and Services, Canada, p.50

Hutchinson T.C, Meema K. (eds.), 1985. *Effects of atmospheric pollutants on forest, wetland and agricultural ecosystems.* Institute of Environmental studies. University of Toronto, Springer-Veirlog. Toronto, Ontario, Canada.

Hutchinson T.,1992

Hutchinson T., Symingon M.S., 1997. Persistence of metal stress in a forested ecosystem near Sudbury, 66 years after closure of the O'Donnell roast bed. Journal of geochemical exploration, Vol. 58, pp. 323-330.

Kasimov N, 1995. Eco-geochemistry of urban landscapes, Russia. Moscow, MSU p.50-84

Kulik V., 1994. *Concentration of heavy metals in snow, Norilsk*. PhD theses, Geological academy, Moscow, Russia

Lerner R.G,. Trigg G.L, *Encyclopedia of Physics, Second Edition* (VCH Publishers, inc., 1990), pp. 1366-1367

Los Alamos National Laboratory's Chemistry Division Presents Periodic Table of the Elements (December, 1997). Table of Elements: Thorium from World Wide Web: http://pearl1.lanl.gov/periodic/elements/90/html

Luets, J. and W.J. Kelly., 1993. *Cleaning the air of Los Angeles*. Science America Vol. 256: p. 32-39

Luoyang Copper (Group) Co., Ltd: (August, 2002). *Products*. From World Wide Web: http://www.ly-copper.com/e-tyhj.html

Madison F.W, Dickas A.B., T. May, 2002. *Wisconsin's sensitivity to acid rain: the role of geologic material; and soils*. Department of agricultural journalism, University of Wisconsin-Madison. From the World Wide web: http://www.uwex.edu/ces/pubs/pdf/G3305_3.PDF

McIlveen W.D., Negusanti J.J., 1995. *Nickel in the terrestrial environment*. The science of total environment, Vol. 148, pp. 109-138.

McBride, M.B., 1985. *Sorption of Copper (II) on aluminum Hydroxide as affected by phosphate*. Soil. Sci. Soc. Am..Journal, Vol. 49, pp. 843-846.

McGrew J.C., Monroe C.B., 1993. *An introduction to statistical problem solving in geography*. Wm. C. Brown Publishers, Dubuque, Iowa, pp. 153-165

MedlinePlus Encyclopidia (September 2002). *MedlinePlus Health information*. Retrieved October 29, 2002 from MedlinePlus Encyclopedia on the World Wide Web http://www.nlm.nih.gov/medlineplus/encyclopedia.html

Merrian, E., 1984. *Introduction of environmental chemistry and global cycles of chromium, nickel, cobalt, beryllium, arsenic, and selenium, and their derivates*. Toxicol. Environ. Chem. 8, pp. 9-38.

MTO, 2002. *Road map for Sudbury, Ontario*. The official road map of Ontario Online from World Wide Web: www.mto.gov.on.ca/english/traveller/map.htm

Newland L. W., 1982. *The handbook of Environmental chemistry, Vol. 3, part B, Anthropogenic compound.,* Springer- Verlag, Heidelberg pp. 45-57.

Nishimura, H (editor), 1989. *How to conquer air pollution – a Japanese experience.* Elsevier, Amsterdam

Nriagu J.O., Wong H.K.T., Lawson G., Daniel P., 1998. *Situation of ecosystem with toxic metals in Sudbury basin, Ontario, Canada.* The science of the total environment, Vol. 223, pp. 99-117.

Ontario Ministry of Environment. Fall 1982. *Sudbury environmental study – an analysis of the impact of smelter emissions on atmospheric dry deposits in the Sudbury area: Sudbury environmental study airborne particulate matter network results* SES 005/82.

Ontario Ministry of Environment. September 2001, *Metals in soil and Vegetation in the Sudbury area, Ontario*. Report No. SDB-045-3511-2001, pp.18.

Pan Analytical (May 24, 2002).*Pan Analytical X-ray Fluorescence instruments*. Retrieved September 2002 from World Wide Web: http://www.analytical.philips.com/products/xrf/

Pas-Gonzales A., Toboada Castro M.T., and Vioira S.R., 2001.*Geostatistical analysis of heavy metals in a one- hectare plot under natural vegetation in a separation area.* Canadian journal of soil science vol. 81:p. 469-479

Peterson, P.J., Girling, C.A., Benson ,L.M. and Ziev, R., Chapter 8: *Metalloids in*: Lepp, N.W.(ed), 1981: *Effect on heavy metal pollution on plant.*, Vol.1, p. 213,299-322

Pearson, D., Pirblado, J., Chapter 1: *Geological and geographical* settings in: Gunn G. (ed), 1995: *Restoration and recovery of industrial region,* Springer – Verlag, New York, pp 5-17.

Ripley, E.A., Redman R.E., and Crowder, A.A., 1996. *Environmental effects of mining.* St. Lucie Press, Delrey Beach, Fla.

Rodered G.P. Toxic effect in Plant Organisms, in: Grandjean, P (ed), 1984: *Biological effects on Organic - lead compounds*, pp.63-96. CRC Press, Boca-Raton, Florida.

Romenskaia N. 1983. Soil - Textbook. Moscow. Nauka (Science), p. 250

Ross S.M. (ed), 1994. *Toxic metals in soil-plant system*. John Willey and Son, p.469

Riashenseva N.N. (ed), 1996. *History of Norilsk mining area*. Non-Ferrous metallurgy journal, Moscow, Russia Vol. 6 p. 40

Riashenseva N.N. (ed), 1996. *History of Norilsk mining area*. Non-Ferrous metallurgy journal, Moscow, Russia, Vol. 7 p. 40

Solomons W., Foerstner U., Maders P. (eds.), 1995. *Heavy metals: Problems and solutions*. Springer-Verlag, Berlin, Heidelberg, Germany, pp. 3-31.

Spektor V., 1999. *Photos of the Sudbury area*. Sudbury

Spektor V., 2001. *Influence of copper – nickel smelter on the northern environment, Russia.* MS Thesis, Moscow State University, Lomonosov, Moscow, Russia.

Spiers G, 2001. Canada, *Personal communication,* Laurentian University, Ontario.

Stevenson, F.J. and A. Fitch, 1981. *Reaction with organic meter. In copper in soil and plants.* Edit by J.F. Loneragan, A.D. Robson and R.D. Graham. Academic press, New York.

Tylikina M.A, Savickiy E.M., 1971. *Nickel – Rhenium combinations*. Ferrous Metallurgy, USSR, p. 220.

Vet B., 2002. MSC, Environment Canada, unpublished data.

Vorobieva E.S. (editor), 1998. *Satellite methods of geo-ecology*, Atlas. Moscow, MSU, pp. 91-94

Winterhalder, K. 1984, *Environmental degradation and rehabilitation in the Sudbury area*. Laurentian Univ. Rev. 16(2): 15-47.

Winterhalder, K. Chapter 2: *Early history of human activities in trhe Sudbury area and ecological damage to the landscape* in: Gunn G. (ed), 1995: *Restoration and recovery of industrial region,* Springer – Verlag, New York, pp 18-32.

World Bank Group, 1998. *Nickel smelting and refining. Pollution prevention* Abatement Handbook, July, pp. 349-352

Appendix 1 - Field sampling sheet

date	site	GPS coordinates	Picture	samples

topographic location

Vegetation description

Soil profile

Human influence:

Special notes:

Appendix 2 - Chemical analyses of data

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
		%	%	%	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
LLD		**0.1**	**0.1**	**0.01**	**50**	**30**	**0.01**	**5.0**	**3.0**	**2.0**	**1**	**5.0**
1	1a lit	1.2	1.2	0.17	61	324	1.6	430.6	360.2	158.8	9.7	13.5
2	1a A	1.7	0.7	0.23	41	205	1.6	169.0	132.4	42.4	9.7	10
3	1a B	2.1	0.9	0.28	46	321	1.9	53.5	22.2	35.3	11.3	4
4	1b lit	1.4	1.1	0.18	77	356	1.4	176.4	146.6	112.4	8.9	6.1
5	1b A	1.8	0.8	0.25	50	237	1.8	181.5	123.5	41.9	9.9	7
6	1b B	2.0	0.9	0.27	60	238	1.7	40.8	16.5	34.3	12.3	0
7	1c Lit	1.6	0.9	0.2	67	321	1.5	120.5	93.6	74.2	9.0	5.2
8	1c A	1.8	0.8	0.23	47	218	1.6	128.8	107.2	50.9	9.6	7
9	1c B	2.2	0.9	0.27	45	241	1.9	31.6	8.0	31.4	11.3	0
10	1d lit	1.3	1.0	0.18	0	397	1.4	157.0	136.8	76.8	9.5	7.5
11	1d A	1.1	1.7	0.14	56	1065	1.2	231.4	178.8	114.5	6.6	8.9
12	1e lit	1.8	1.0	0.23	62	384	1.7	214.7	175.1	91.2	10.7	13.5
13	1e Ao	1.4	0.9	0.19	78	247	1.5	293.4	338.5	89.9	7.8	11
14	1e A	2.0	0.8	0.23	42	247	1.7	162.8	120.9	44.7	9.3	6.5
15	2a lit	1.4	0.9	0.19	58	426	1.4	131.2	110.6	56.2	9.8	10
16	2a A	2.1	0.8	0.25	41	233	1.8	117.4	107.4	40.1	10.0	0
17	2a B	2.3	0.9	0.26	52	237	1.8	33.0	12.6	31.7	11.5	9
18	2b lit	1.6	0.8	0.24	56	280	1.6	136.0	110.4	47.7	9.9	6.7
19	2b A	1.9	0.7	0.25	31	229	1.8	139.7	128.0	39.0	9.0	10
20	2b B	2.2	0.9	0.28	44	233	1.7	38.8	17.6	34.0	11.0	0
21	2c lit	1.3	0.9	0.15	60	390	1.3	170.5	111.9	104.6	8.8	5.6
22	2c A	1.8	0.7	0.23	42	212	1.6	94.8	93.5	33.9	10.3	11
23	2c B	2.1	0.8	0.23	36	205	1.7	20.7	9.9	25.9	11.6	0
24	2d B	2.0	0.8	0.25	39	206	1.6	26.2	6.4	26.8	9.8	0
25	2d A	2.0	0.8	0.25	49	211	1.7	149.6	110.6	36.8	10.1	10
26	2d Lit	1.5	0.9	0.2	59	307	1.4	166.7	131.3	71.8	8.3	6.0
27	2e Lit	1.1	1.6	0.15	40	853	1.2	233.2	179.9	104.4	6.9	6.7
28	2e A	1.8	0.7	0.23	43	184	1.6	112.9	85.7	35.2	9.8	9
29	2e B	1.9	0.8	0.26	52	185	1.6	27.1	10.2	32.8	11.3	0
30	3a B	2.1	0.9	0.26	54	245	1.6	29.6	5.5	28.3	12.2	0
31	3a Lit	1.4	0.9	0.18	90	307	1.3	118.0	69.3	92.0	8.0	6.7
32	3a A	2.0	0.8	0.25	54	251	1.7	117.8	90.1	33.7	9.8	8
33	3b Lit	1.3	1.1	0.17	57	494	1.4	195.3	127.3	102.5	8.8	7.8

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	0.7	**2**	**1.0**	**1.5**	**2.5**	**5.0**	**2.5**	**3**
1a lit	3.0	5.3	28.6	99.3	3.9	55.9	42.2	3.8
1a A	2	3.1	47.3	248.8	10.9	202.3	31.3	0.0
1a B	0	3.0	54.5	291.4	12.0	224.4	11.6	0.0
1b lit	1.6	4.2	36.2	174.7	7.7	120.3	23.4	3.1
1b A	1	2.7	51.0	262.1	11.0	208.2	29.6	3.3
1b B	0	2.0	55.1	291.5	12.8	246.9	11.4	0.0
1c Lit	0.8	3.1	45.3	226.9	9.8	172.9	20.7	3.1
1c A	1	2.9	46.7	252.3	11.0	197.4	25.8	0.0
1c B	0	2.4	57.4	308.9	13.1	231.9	9.3	3.0
1d lit	1.4	4.2	39.0	179.3	7.7	147.0	25.7	0.0
1d A	1.8	3.7	47.5	212.1	8.0	159.1	31.5	0.0
1e lit	3.3	5.6	38.6	165.1	6.2	114.4	46.8	4.4
1e Ao	1	3.6	51.0	265.3	10.7	223.6	27.6	0.0
1e A	1.0	2.9	41.5	199.4	7.1	149.7	22.4	0.0
2a lit	1	2.6	53.0	275.6	11.5	202.2	27.2	3.2
2a A	0	1.7	55.1	304.8	11.3	218.3	10.5	0.0
2a B	1	3.3	46.3	238.3	9.9	187.2	25.8	0.0
2b lit	1.8	4.1	27.5	114.5	3.7	59.7	21.9	0.0
2b A	1	2.6	56.2	264.6	11.3	201.0	32.6	3.6
2b B	0	1.8	59.3	312.5	12.1	248.7	12.0	0.0
2c lit	1.8	3.7	43.0	161.3	6.3	113.0	23.4	0.0
2c A	0	1.9	48.6	246.3	9.6	182.9	25.3	0.0
2c B	0	1.8	53.2	298.2	13.2	208.8	10.7	0.0
2d B	0	1.8	52.0	294.4	11.4	247.6	10.7	0.0
2d A	2	1.9	55.1	271.5	10.2	204.7	28.9	3.1
2d Lit	1.9	3.6	43.3	197.9	6.6	137.7	25.3	0.0
2e Lit	1.6	5.8	27.9	119.3	3.3	75.2	21.9	0.0
2e A	0	2.8	51.1	267.3	10.3	201.8	23.0	0.0
2e B	0	0.0	56.4	281.1	11.3	243.6	11.3	0.0
3a B	0	0.0	55.9	301.1	12.0	232.3	9.8	0.0
3a Lit	1.2	2.9	37.4	185.2	6.3	122.5	15.2	0.0
3a A	1	2.1	50.9	274.9	10.8	201.4	27.4	3.7
3b Lit	1.8	3.5	36.6	164.5	6.1	105.7	25.1	0.0

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
34	3b B	2.0	0.8	0.25	58	262	1.7	42.3	16.0	31.3	11.1	0
35	3b A	1.9	0.7	0.23	53	202	1.7	121.0	106.5	37.0	9.5	11
36	3c Lit	1.4	1.0	0.16	54	555	1.3	145.4	93.8	78.0	9.2	6.6
37	3c B	2.0	0.7	0.26	47	177	1.5	29.7	7.9	24.1	11.0	0
38	3c A	1.8	0.6	0.25	54	196	1.5	101.9	118.4	34.5	11.5	8
39	3d B	2.0	0.8	0.23	37	223	1.6	40.5	7.2	25.3	12.0	0
40	3d Lit	1.5	0.9	0.21	68	341	1.5	131.2	74.4	80.6	8.5	5.5
41	3d A	1.8	0.7	0.25	26	192	1.6	104.1	64.0	36.9	11.1	6
42	3e Lit	1.2	0.9	0.16	68	431	1.3	147.9	112.9	80.9	8.4	5.6
43	3e B	2.0	0.8	0.25	33	207	1.5	38.3	6.2	30.9	11.5	0
44	3e A	2.0	0.7	0.25	52	157	1.5	92.8	95.4	31.7	11.5	10
45	4a Lit	1.2	1.0	0.12	87	249	1.1	131.2	65.1	116.0	7.3	4.6
46	4a A	1.7	0.7	0.23	23	152	1.4	139.0	124.8	27.6	10.7	9
47	4a B	2.0	0.8	0.26	56	198	1.4	36.9	5.6	23.7	11.9	0
48	4b Lit	1.4	0.9	0.16	71	256	1.2	98.7	69.8	89.9	8.4	5.9
49	4b A	1.9	0.7	0.25	41	161	1.5	128.6	111.1	37.4	11.1	11
50	4b B	2.0	0.7	0.24	30	200	1.4	37.6	25.5	29.5	10.1	0
51	4c A	1.7	0.6	0.2	26	152	1.4	138.0	120.9	26.2	7.6	8
52	4c Lit	1.2	0.8	0.17	65	260	1.3	137.2	112.6	65.9	9.2	5.8
53	4c B	2.0	0.7	0.24	30	175	1.5	27.4	14.6	27.3	10.6	0
54	4d Lit	1.5	0.9	0.18	34	201	1.3	111.1	111.3	87.7	8.0	8.5
55	4d A	1.9	0.7	0.24	40	198	1.6	128.3	133.0	30.6	10.0	9
56	4d B	2.1	0.9	0.24	50	221	1.6	25.7	8.0	25.3	11.8	0
57	4e Lit	1.0	2.1	0.11	67	455	1.0	219.8	137.0	179.3	5.4	5.2
58	4e A	1.6	0.6	0.22	37	151	1.4	152.2	110.9	23.5	8.9	9
60	5a Lit	1.3	0.7	0.19	56	640	2.2	308.1	328.2	149.3	8.0	17.6
61	5a Ao/a	2.0	0.8	0.32	72	376	3.3	483.0	407.3	86.4	6.9	34
62	5a B	2.0	0.8	0.3	58	477	2.5	85.0	20.1	89.8	9.8	6
63	5a Dark	1.8	0.5	0.43	133	2964	7.6	102.4	44.2	98.7	9.7	12
64	5b Lil	0.9	1.9	0.08	51	1492	1.1	355.0	279.2	339.8	4.2	6.6
65	5b A	1.8	0.7	0.32	76	438	3.1	440.1	353.8	79.3	8.1	27
66	5b B	1.9	0.7	0.29	84	650	2.9	52.6	28.6	99.7	12.0	8
67	5b Dark	2.5	0.7	0.39	146	1881	5.9	104.5	83.5	101.5	12.4	11
68	5c lit	1.4	1.0	0.22	81	893	2.3	405.0	437.5	216.9	9.2	11.3
69	5c A	2.1	0.8	0.34	56	647	2.6	56.0	31.0	115.5	12.0	6
70	5c Dark	1.8	0.6	0.36	90	1289	4.9	39.4	27.6	167.8	10.9	5

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
3b B	0	0.0	52.8	285.7	11.8	214.1	11.6	0.0
3b A	2	2.5	55.0	266.3	10.5	191.4	29.2	3.1
3c Lit	1.2	2.5	38.1	190.7	6.6	124.5	19.3	0.0
3c B	0	0.0	53.1	293.1	10.2	222.4	10.5	0.0
3c A	1	2.1	51.4	260.0	10.3	202.9	26.0	0.0
3d B	0	0.0	53.3	295.6	11.4	216.4	8.5	0.0
3d Lit	0.7	2.6	41.7	208.1	7.5	137.3	17.8	0.0
3d A	1	0.0	50.0	271.0	10.6	223.9	18.9	0.0
3e Lit	1.5	3.0	37.4	173.1	5.8	109.3	19.5	0.0
3e B	0	0.0	54.8	294.6	9.1	227.1	10.6	0.0
3e A	1	0.0	52.2	277.8	9.9	217.1	23.1	0.0
4a Lit	0.8	2.4	32.1	163.9	3.6	85.4	16.3	0.0
4a A	1	1.9	50.6	270.5	9.9	205.2	29.2	0.0
4a B	0	0.0	52.0	307.3	7.4	191.6	9.3	0.0
4b Lit	0.7	3.0	43.1	203.3	6.3	126.5	15.8	0.0
4b A	0	2.2	53.7	270.7	9.6	191.1	27.2	0.0
4b B	0	0.0	54.7	281.3	9.6	206.7	11.4	0.0
4c A	2	3.1	46.1	240.7	8.5	178.5	30.5	0.0
4c Lit	1.4	3.8	41.7	189.7	5.8	131.4	25.3	0.0
4c B	0	0.0	53.0	285.6	9.6	228.1	10.1	0.0
4d Lit	1.4	2.8	37.2	202.7	6.8	131.8	21.0	0.0
4d A	1	2.8	52.3	272.6	9.4	198.6	31.4	0.0
4d B	0	0.0	51.6	312.9	10.7	219.4	9.9	0.0
4e Lit	1.2	3.6	21.0	97.8	2.0	45.7	14.4	0.0
4e A	1	2.5	46.9	244.7	7.7	167.2	26.4	0.0
5a Lit	3.4	4.9	29.3	134.2	6.0	118.2	56.0	5.5
5a Ao/a	2	5.4	46.3	199.8	10.7	222.1	103.4	10.8
5a B	0	3.2	45.5	233.5	9.6	276.1	11.0	0.0
5a Dark	0	0.0	36.3	74.8	10.8	124.1	17.9	8.5
5b Lil	2.9	3.7	7.4	51.1	0.0	23.9	27.0	0.0
5b A	3	4.2	48.7	199.8	11.2	228.4	86.5	9.0
5b B	0	2.9	48.1	220.3	9.6	240.7	12.8	0.0
5b Dark	1	2.1	55.5	137.1	11.1	180.5	20.7	7.0
5c lit	4.0	5.7	27.7	120.5	5.8	105.6	65.0	4.6
5c A	1	2.4	48.8	226.2	10.2	272.5	14.8	3.2
5c Dark	0	0.0	42.6	133.1	9.0	182.9	14.5	0.0

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
71	5d Lit	1.5	1.0	0.29	74	1656	4.5	434.7	477.9	222.2	12.4	13.6
72	5d A	2.0	0.5	0.43	127	1830	6.0	108.9	64.1	203.7	10.0	10
73	5d B	2.1	0.7	0.36	84	966	3.9	49.3	26.6	154.3	12.8	0
74	5e A	1.9	0.6	0.36	79	876	4.4	380.1	447.9	111.9	7.2	29
75	5e Lit	1.1	1.0	0.2	96	1064	2.8	385.7	431.5	200.9	8.5	13.8
76	5e B	2.0	0.5	0.49	128	2261	6.3	95.0	72.2	217.8	13.2	8
77	6a Lit	1.4	0.7	0.26	95	1245	3.4	202.3	137.1	177.1	8.5	12.4
78	6a A	2.0	0.6	0.39	116	1485	4.7	200.5	213.7	152.9	9.9	23
79	6a B	1.8	0.4	0.43	148	2132	6.7	70.0	41.8	124.9	10.6	10
80	6b Lit	0.9	2.1	0.13	87	916	2.2	184.5	91.5	530.0	4.7	4.9
81	6b A	1.9	0.6	0.44	124	1969	5.9	146.1	119.9	173.0	9.6	13
82	6b A/B	2.1	0.6	0.5	165	2347	7.8	69.6	53.1	167.7	11.0	11
83	6c Lit	1.3	1.2	0.26	128	1212	3.6	185.1	140.3	309.7	7.9	9.8
84	6c A	2.0	0.6	0.44	134	2032	6.4	243.5	218.9	207.0	8.6	18
85	6c A/B	2.0	0.5	0.44	144	1676	5.6	56.8	52.0	170.0	11.5	6
86	6d Lit	1.6	0.8	0.4	187	1704	5.5	137.4	105.9	176.7	11.4	12.1
87	6d A	2.0	0.7	0.46	155	1784	5.6	186.5	165.4	184.2	10.1	16
88	6d A/B	1.8	0.6	0.43	137	1704	6.0	91.1	66.2	135.1	11.1	8
89	6d un. Water	1.9	0.6	0.47	130	1964	6.5	97.3	73.3	163.9	13.5	8.2
90	6e Lit	1.5	0.9	0.3	124	1431	4.2	157.3	118.0	177.9	8.5	9.7
91	6e A	2.0	0.6	0.42	111	1693	5.7	138.9	109.2	154.3	10.8	11
92	6e A/B	2.1	0.6	0.42	112	1553	5.4	99.2	69.0	151.5	10.1	6
93	7a Lit	1.2	2.5	0.05	48	453	0.9	191.5	55.1	432.1	2.1	0.0
94	7a A	2.3	0.4	0.5	181	2550	7.6	204.3	198.7	159.7	10.1	22
95	7a A/B	2.2	0.5	0.5	143	2324	7.1	68.9	56.5	119.5	12.6	8
96	7b Lit	0.8	3.0	0.07	56	550	1.1	212.6	81.7	523.8	1.1	4.5
97	7b A	2.0	0.6	0.39	112	1915	6.0	263.6	266.8	146.3	10.3	21
98	7b A/B	1.9	0.4	0.43	136	1882	6.1	67.8	52.3	133.0	11.4	9
99	7e A	1.5	0.4	0.36	107	1679	4.7	195.6	185.6	124.2	10.2	15
100	7e A/B	2.2	0.4	0.46	144	2490	7.3	58.9	54.0	103.1	11.8	12
101	7e Lit	0.8	2.7	0.09	100	556	1.4	208.9	84.3	463.1	4.2	0.0
102	7d Lit	1.6	1.3	0.22	116	1169	3.4	222.2	150.5	194.6	9.0	8.8
103	7d A	2.0	0.5	0.36	113	1529	4.7	258.6	210.0	106.5	9.2	17
104	7d A/B	2.4	0.6	0.38	131	1766	5.7	74.0	55.1	97.7	11.9	10
105	7e Lit	1.3	1.7	0.18	111	1110	2.6	276.6	171.7	346.1	7.0	8.5
106	7e A	1.7	0.6	0.36	112	1599	5.0	203.7	156.3	176.1	6.6	15

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
5d Lit	3.0	8.1	38.6	109.0	9.8	128.3	114.3	10.3
5d A	1	3.2	49.6	105.4	11.5	172.3	33.5	4.1
5d B	0	2.1	43.7	179.2	11.5	250.0	59.1	5.2
5e A	3	3.0	47.6	145.4	11.7	206.4	82.0	7.6
5e Lit	3.9	5.0	25.4	84.2	5.3	75.0	71.1	4.6
5e B	1	0.0	47.7	102.2	10.5	168.1	19.6	6.2
6a Lit	1.1	2.3	31.3	98.8	8.5	114.7	30.6	3.8
6a A	2	2.7	47.8	149.3	9.8	189.3	37.7	0.0
6a B	0	3.2	34.9	94.6	9.9	159.2	17.9	8.3
6b Lit	1.1	4.0	10.7	45.2	2.2	25.7	13.7	0.0
6b A	1	4.7	41.3	96.4	10.5	147.1	23.9	5.9
6b A/B	1	6.8	37.5	81.0	10.9	139.0	13.6	8.6
6c Lit	1.6	3.8	24.4	66.1	5.5	79.5	22.7	4.5
6c A	2	5.0	42.9	87.3	10.1	130.1	39.1	7.0
6c A/B	0	3.8	45.0	113.9	12.0	170.8	17.2	6.8
6d Lit	0.9	3.7	36.0	98.7	11.4	136.3	24.1	5.4
6d A	2	5.0	40.7	110.5	10.7	160.4	32.9	5.4
6d A/B	1	4.4	38.2	95.6	12.0	148.2	17.9	5.0
6d un. Water	0.0	3.7	40.7	110.1	13.0	165.7	17.6	3.7
6e Lit	1.1	3.6	35.9	87.7	9.9	116.9	23.9	4.7
6e A	1	3.6	46.4	96.6	11.0	149.8	24.5	4.2
6e A/B	1	4.0	44.0	115.3	10.0	171.9	18.5	4.8
7a Lit	1.0	3.6	6.1	40.0	0.0	7.8	7.6	0.0
7a A	1	3.0	58.4	72.8	10.9	139.8	30.4	8.1
7a A/B	0	2.6	47.0	79.0	12.1	147.4	13.3	7.9
7b Lit	0.7	3.5	5.6	44.5	0.0	10.4	7.9	0.0
7b A	1	3.1	52.7	88.4	9.8	137.5	45.0	6.3
7b A/B	0	2.8	45.2	88.1	10.6	156.7	12.6	4.2
7e A	1	4.4	36.1	85.5	10.0	146.0	36.0	5.9
7e A/B	1	3.3	48.5	76.1	10.7	141.0	14.7	7.3
7e Lit	2.0	3.3	8.2	50.4	0.0	20.9	10.2	0.0
7d Lit	1.2	3.6	33.9	84.2	6.1	88.5	26.2	4.3
7d A	1	2.9	55.3	114.3	11.4	154.7	40.9	5.4
7d A/B	1	3.2	60.0	121.7	11.2	166.0	11.9	4.2
7e Lit	1.6	5.0	18.8	58.5	2.9	48.1	25.6	3.2
7e A	2	4.9	46.0	85.0	10.3	129.3	37.1	7.5

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
107	7e A/B	1.6	0.4	0.48	134	1866	6.2	90.9	48.0	209.9	13.0	8
108	8a A	2.0	0.8	0.33	70	636	3.1	56.5	18.4	63.0	11.8	5
109	8a B	1.9	0.7	0.35	81	1126	2.6	113.5	89.6	183.6	9.8	11
110	8a Lit	1.0	2.4	0.06	0	2356	0.9	306.4	201.9	449.2	3.0	4.6
111	8b Lit	1.2	1.2	0.21	85	1732	3.0	507.5	446.2	320.6	8.8	12.4
112	8b A	1.9	0.6	0.39	98	1647	4.5	152.1	143.5	187.0	10.0	17
113	8b B	2.0	0.7	0.35	128	1238	4.6	75.7	33.0	103.6	12.1	8
114	8c Lit	1.4	0.8	0.25	91	1317	3.2	439.4	327.1	227.6	11.4	13.7
115	8c A	1.7	0.6	0.37	86	1576	4.1	268.0	192.7	196.0	9.2	16
116	8c B	1.8	0.7	0.38	91	1107	4.3	46.4	37.0	139.0	11.3	0
117	8d Lit	1.3	1.0	0.22	88	2007	2.6	422.8	362.7	291.7	9.2	14.6
118	8d A	1.8	0.7	0.34	96	2046	3.3	158.0	123.8	250.2	9.4	12
119	8d B	2.0	0.7	0.3	81	518	2.8	54.5	12.9	71.6	10.3	5
120	8e Lit	0.9	1.5	0.15	76	2507	2.1	606.4	575.3	317.1	7.0	12.5
121	8e A	1.8	0.6	0.31	65	963	3.5	234.6	256.0	154.4	8.4	19
122	8e B	2.0	0.9	0.34	76	497	3.1	116.9	49.8	82.6	11.3	6
123	9a Lit	0.9	1.3	0.11	56	229	0.8	41.2	29.2	99.9	8.1	0.0
124	9a A	1.7	0.7	0.23	37	167	1.1	34.6	22.8	27.7	11.2	0
125	9a A bottom	1.6	0.8	0.26	51	159	1.1	30.1	14.2	33.1	12.2	0
126	9a Loam	1.8	0.8	0.22	44	168	1.4	24.7	4.6	31.2	11.8	0
127	9b Lit	1.1	0.9	0.19	72	203	1.0	53.7	28.9	59.9	7.6	0.0
128	9b A	1.6	0.7	0.23	37	142	1.2	44.0	26.6	27.3	10.8	0
129	9b C	1.8	0.8	0.22	57	158	1.2	19.3	2.8	18.6	9.9	0
130	9c Lit	1.3	1.0	0.14	72	199	0.9	47.2	24.7	83.9	7.8	0.0
131	9c A	1.6	0.7	0.16	39	121	1.1	28.0	23.1	34.3	9.2	0
132	9c B	1.9	0.8	0.23	57	178	1.2	26.0	4.4	24.2	11.3	0
133	9d Lit	1.1	1.4	0.13	110	240	1.0	61.0	38.2	111.6	7.3	0.0
134	9d A	1.8	0.8	0.24	44	164	1.2	31.9	22.0	26.5	12.5	0
135	9d B/c	1.7	0.8	0.29	38	194	1.3	13.1	5.9	26.7	11.6	0
136	9e Lit	1.1	1.0	0.12	87	171	0.9	46.7	21.9	58.8	9.6	0.0
137	9e A	1.5	0.7	0.24	57	138	1.1	28.4	20.3	28.8	12.0	0
138	9e B/c	1.8	0.9	0.26	45	166	1.3	14.0	3.2	23.3	10.4	0
139	10a Lit	0.5	1.6	0.05	72	150	0.6	53.6	30.2	287.2	1.9	0.0
140	10a A	1.7	0.8	0.22	55	145	1.2	33.2	20.3	32.7	10.8	0.0
141	10a B	1.9	0.9	0.23	40	149	1.2	20.4	5.3	32.7	11.0	0
142	10b Lit	1.2	0.9	0.16	122	171	1.1	60.3	38.3	77.3	8.1	0.0

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
7e A/B	0	2.2	42.2	87.4	10.1	159.8	26.0	6.5
8a A	1	3.7	40.9	230.6	9.7	273.3	13.4	3.4
8a B	1	2.8	45.8	195.2	11.2	270.3	22.2	0.0
8a Lit	2.3	2.8	5.5	47.7	0.0	7.7	20.3	0.0
8b Lit	4.0	5.2	23.2	77.3	5.0	63.7	71.2	6.7
8b A	1	3.1	43.9	146.6	10.3	216.7	30.1	6.8
8b B	1	0.0	39.7	151.7	10.7	212.0	23.1	5.6
8c Lit	3.7	4.5	27.8	105.3	6.8	117.0	72.8	6.4
8c A	2	2.8	42.8	136.8	11.2	204.6	46.5	5.4
8c B	1	2.6	33.8	170.4	9.6	239.3	13.7	3.6
8d Lit	2.7	4.4	30.0	109.8	5.8	120.5	63.4	5.8
8d A	2	3.2	43.7	177.5	11.1	233.8	27.6	0.0
8d B	1	3.6	45.9	242.6	9.8	268.9	10.5	3.8
8e Lit	4.3	4.4	14.2	64.1	2.8	33.7	67.2	5.2
8e A	2	3.3	45.7	183.4	10.1	226.3	46.2	4.4
8e B	1	5.2	42.1	228.0	10.3	269.1	15.4	3.1
9a Lit	0.8	2.4	25.0	173.5	3.1	103.9	7.8	0.0
9a A	0	2.7	44.3	283.9	7.0	184.6	15.4	0.0
9a A bottom	0	2.7	40.8	284.4	7.9	196.3	12.7	0.0
9a Loam	0	0.0	46.0	300.0	11.3	238.7	7.1	0.0
9b Lit	0.9	2.9	31.7	195.0	4.2	126.3	12.6	0.0
9b A	1	2.8	44.2	268.1	7.2	186.1	17.9	0.0
9b C	0	0.0	46.0	310.7	8.2	225.5	9.2	0.0
9c Lit	0.0	1.9	30.7	198.3	5.4	134.8	12.7	6.7
9c A	1	2.4	46.2	285.0	7.8	169.3	16.3	0.0
9c B	0	0.0	47.1	319.7	9.1	240.6	10.0	0.0
9d Lit	0.6	2.6	23.6	147.2	3.2	84.5	10.0	0.0
9d A	1	2.7	44.7	298.1	9.1	191.0	14.9	0.0
9d B/c	0	0.0	44.6	305.8	8.9	217.6	9.0	0.0
9e Lit	0.0	1.6	29.6	197.0	3.9	98.3	9.0	0.0
9e A	1	3.1	43.0	262.0	7.9	224.1	15.0	0.0
9e B/c	0	0.0	46.9	314.6	8.6	186.1	8.4	0.0
10a Lit	0.0	1.8	7.9	56.7	0.0	20.5	4.5	0.0
10a A	0.6	2.6	44.2	275.9	8.6	226.4	14.3	0.0
10a B	0	0.0	46.0	312.6	12.3	216.2	8.8	0.0
10b Lit	0.0	2.5	33.0	198.1	5.8	122.7	14.2	0.0

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
143	10b A	1.7	0.7	0.19	43	125	1.2	36.9	25.8	38.5	11.5	0
144	10b B/C	1.9	0.9	0.26	56	198	1.4	23.5	6.2	35.0	13.2	0
145	10c Lit	1.3	0.9	0.16	75	137	1.0	57.5	28.2	74.0	9.1	0.0
146	10c A	1.7	0.8	0.23	51	157	1.3	40.2	27.1	30.5	11.9	0
147	10c B/C	2.1	0.8	0.23	45	176	1.4	23.0	6.3	22.3	11.2	0.0
148	10d Lit	1.3	0.9	0.16	69	146	1.1	49.6	26.3	61.5	8.8	0
149	10d A	1.7	0.8	0.25	51	152	1.3	43.8	29.3	37.3	11.2	0
150	10d B	1.9	0.8	0.24	34	164	1.3	18.4	10.1	24.2	11.4	0.0
151	10e Lit	0.9	1.4	0.11	83	156	0.9	52.1	35.5	178.8	6.7	0
152	10e A	1.6	0.8	0.22	28	161	1.3	49.7	29.6	41.1	12.4	0
153	10e B/C	1.8	0.8	0.23	37	158	1.4	21.8	6.0	23.1	12.6	0.0
154	11a Lit	0.8	1.7	0.09	77	363	0.8	70.8	43.8	203.6	3.4	0
155	11a A	1.8	0.8	0.25	49	162	1.4	33.7	18.3	35.5	11.4	0
156	11a B/C	2.3	1.0	0.26	49	210	1.7	23.8	11.8	27.1	12.6	0.0
157	11b Lit	1.0	1.0	0.13	64	252	0.9	50.3	22.5	105.0	5.9	0
158	11b A	1.9	0.8	0.24	51	158	1.4	34.9	17.7	28.9	10.6	0
159	11b B/C	2.0	0.9	0.23	50	164	1.4	19.7	6.7	24.0	11.3	0.0
160	11c Lit	1.3	0.8	0.18	59	186	1.1	50.4	28.4	54.0	8.9	0
161	11c A	1.9	0.8	0.23	48	170	1.4	39.1	24.4	36.0	13.9	0
162	11C B	1.9	0.9	0.22	63	157	1.4	29.2	6.2	26.3	12.6	0.0
163	11d Lit	1.3	0.9	0.14	80	255	1.1	72.3	29.5	80.9	8.3	0
164	11d A	1.9	0.8	0.26	40	154	1.4	30.2	19.6	28.8	12.8	0
165	11d B/C	1.9	0.8	0.24	33	184	1.4	22.7	5.6	25.2	13.1	0.0
167	11e Lit	1.0	1.0	0.12	70	220	1.0	55.6	29.7	105.3	6.0	0
168	11e A	1.8	0.7	0.22	43	150	1.4	31.3	15.4	31.0	11.2	0
169	11e B	2.0	0.9	0.23	40	157	1.4	22.6	3.3	23.5	12.3	0.0
170	12a Lit	1.1	1.0	0.13	61	236	0.9	53.3	26.6	121.8	5.9	0
171	12a A	1.5	0.7	0.24	36	212	1.3	27.1	17.4	29.4	11.9	0
172	12a B	2.0	0.9	0.23	49	171	1.3	19.5	4.7	23.0	10.8	0.0
173	12b Lit	1.0	1.1	0.1	97	256	0.9	72.4	28.1	136.0	5.7	0
174	12b A	1.9	0.7	0.24	43	196	1.4	34.7	22.1	30.7	12.0	0
175	12b B	1.9	0.9	0.29	49	189	1.4	19.7	5.2	21.3	13.1	0.0
176	12c Lit	1.0	1.3	0.11	91	279	0.9	59.7	27.3	179.2	5.3	0
177	12c A	1.9	0.7	0.22	53	153	1.3	27.4	18.2	27.9	11.3	0
178	12c B	1.9	0.9	0.26	43	158	1.4	18.5	8.1	23.7	13.7	0.0
179	12d Lit	1.4	1.0	0.17	57	227	1.0	49.2	24.1	84.5	9.1	0

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
10b A	0	2.6	45.0	271.1	8.7	181.4	15.4	0.0
10b B/C	0	0.0	47.6	311.1	13.0	243.5	9.8	0.0
10c Lit	0.7	2.2	33.0	215.1	6.6	144.4	12.7	0.0
10c A	0	2.8	42.2	283.8	9.3	237.0	16.0	0.0
10c B/C	1.0	2.2	33.2	198.5	7.5	130.5	11.9	0.0
10d Lit	1	2.6	43.3	277.2	10.1	217.3	15.4	0.0
10d A	0	0.0	46.1	300.3	9.8	230.8	8.3	0.0
10d B	0.0	2.3	19.6	115.6	2.8	173.0	8.9	0.0
10e Lit	1	3.3	42.7	259.9	9.2	198.1	18.4	0.0
10e A	1	0.0	46.7	311.4	9.4	214.0	10.7	0.0
10e B/C	0.0	2.3	11.3	81.7	1.6	29.1	5.8	0.0
11a Lit	0	0.0	48.8	298.4	9.8	220.2	17.5	0.0
11a A	1	0.0	52.9	338.5	14.0	266.5	8.9	0.0
11a B/C	0.0	1.9	24.0	149.3	3.3	116.6	8.5	0.0
11b Lit	1	2.3	46.9	301.3	11.0	230.3	15.1	0.0
11b A	1	0.0	47.2	318.3	10.7	216.6	9.6	0.0
11b B/C	0.7	2.4	36.6	214.0	7.5	152.0	14.4	0.0
11c Lit	1	2.0	48.9	296.9	10.2	207.7	15.6	0.0
11c A	0	0.0	50.3	328.1	10.5	247.8	8.8	0.0
11C B	0.0	2.7	31.5	177.8	5.4	112.0	13.0	0.0
11d Lit	1	2.2	49.3	295.2	9.2	215.7	16.6	0.0
11d A	1	0.0	48.5	311.9	9.7	236.3	12.1	0.0
11d B/C	0.7	1.7	23.3	151.2	4.0	91.2	10.2	0.0
11e Lit	1	0.0	48.7	297.1	9.9	237.3	16.1	0.0
11e A	0	0.0	51.7	335.6	10.6	251.6	10.2	3.1
11e B	0.6	1.7	29.5	173.4	3.8	85.8	7.9	0.0
12a Lit	1	0.0	47.7	273.0	8.8	204.2	14.4	0.0
12a A	0	0.0	48.9	326.6	9.2	221.2	7.2	0.0
12a B	0.6	2.4	22.6	145.2	3.9	67.5	8.1	0.0
12b Lit	1	0.0	48.5	313.8	10.4	249.7	14.5	0.0
12b A	0	1.0	46.3	322.4	11.3	205.5	8.5	0.0
12b B	0.6	2.2	20.4	133.8	2.6	54.4	6.4	0.0
12c Lit	1	2.5	47.5	290.4	10.0	232.2	15.8	0.0
12c A	0	0.0	48.7	315.3	10.4	251.7	9.0	0.0
12c B	0.8	2.1	34.2	207.5	5.7	125.1	11.1	0.0
12d Lit	1	0.0	49.5	294.3	9.5	200.6	12.5	0.0

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
180	12d A	1.9	0.8	0.22	35	171	1.3	32.6	16.2	28.2	9.9	0
181	12d B	1.9	0.8	0.22	31	166	1.4	28.0	6.0	22.8	11.4	0.0
182	12e Lit	1.5	0.8	0.18	61	173	1.2	40.5	23.5	43.8	9.6	0
183	12e A	1.7	0.7	0.24	51	164	1.3	35.8	23.8	31.2	12.2	0
184	12e B	1.9	0.9	0.28	42	189	1.6	19.9	9.7	26.0	12.6	8.0
185	13a Lit	1.1	1.2	0.23	277	870	1.7	177.9	128.7	179.7	10.0	14
186	13a A	1.8	0.7	0.44	35	210	2.0	54.6	58.9	64.0	14.1	6
187	13a B	1.8	0.7	0.52	96	262	3.6	43.2	43.6	87.5	14.5	4.9
188	13b LIT	0.8	1.0	0.17	105	1245	1.4	172.1	92.1	188.6	7.0	8
189	13b A	1.6	0.6	0.34	31	163	1.5	45.5	46.0	44.8	12.7	0
190	13b B	1.8	0.7	0.36	82	208	2.4	36.9	14.1	81.3	10.3	4.3
191	13c Lit	1.0	1.2	0.2	156	1392	1.7	169.1	91.0	196.7	9.7	9
192	13c A	1.6	0.6	0.35	44	376	1.6	102.6	93.0	58.5	12.4	0
193	13c B	1.6	0.7	0.37	68	263	2.6	43.1	25.1	80.2	11.4	8.5
194	13s Lit	1.0	1.5	0.17	120	1918	1.5	179.7	90.6	260.7	8.3	11
195	13d A	1.7	0.9	0.49	67	737	3.3	94.3	94.7	95.7	14.1	6
196	13d B	1.5	0.8	0.53	116	534	4.4	53.1	66.3	82.8	12.6	5.3
197	13e Lit	1.0	1.5	0.2	137	2360	1.6	189.4	106.9	256.2	8.4	11.6
198	13e A	1.8	0.7	0.4	0	585	2.0	126.2	100.1	77.4	13.6	4
199	13e B	1.7	0.8	0.37	72	337	2.6	35.6	24.5	96.9	14.7	4.4
200	14a Lit	1.4	1.1	0.33	149	1005	1.9	139.2	85.1	170.7	9.7	10
201	14a A	1.7	0.6	0.39	39	400	1.7	87.5	85.8	84.0	11.0	0
202	13a B	1.7	0.7	0.4	70	256	3.1	37.9	23.2	109.7	14.9	10.1
203	14b Lit	1.3	1.2	0.4	93	2040	1.9	223.9	140.8	242.0	9.8	12
204	14b A	1.7	0.9	0.44	52	944	2.2	120.8	95.1	110.0	12.4	0
205	14b B	1.7	0.9	0.51	112	384	3.5	39.1	38.5	110.2	13.8	6.2
206	14c Lit	1.3	0.9	0.27	105	995	1.7	145.0	90.9	152.5	8.4	8.2
207	14c A	1.8	0.9	0.34	65	727	2.0	114.8	66.6	129.4	12.2	6
208	14c B	1.8	0.7	0.53	112	335	3.8	37.0	57.7	152.5	17.5	4
209	14c Grey	1.7	0.6	0.38	28	165	1.2	7.6	16.3	30.8	12.1	7.3
210	14d Lit	1.1	1.4	0.24	135	1350	2.0	187.9	113.4	250.5	10.1	16.4
211	14d A	1.6	0.7	0.38	49	308	2.4	125.9	100.6	122.6	14.8	4
212	14d B	1.7	0.8	0.43	78	303	2.9	34.8	19.1	100.2	12.3	9.8
213	14e Lit	1.5	1.1	0.29	111	1466	2.0	195.7	149.0	244.5	10.5	12.0
214	14e A	1.9	1.0	0.41	0	1245	2.4	167.2	152.3	182.9	11.5	6
215	14e B	1.5	0.9	0.49	108	449	4.1	46.7	92.1	115.8	12.8	5.3

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
12d A	0	0.0	49.6	316.5	11.0	250.9	10.5	0.0
12d B	0.7	2.2	41.6	240.0	7.9	197.6	14.9	0.0
12e Lit	1	0.0	48.1	278.1	10.4	200.6	14.0	0.0
12e A	0	0.0	48.9	310.4	10.8	251.0	9.6	0.0
12e B	0.6	3.9	44.1	167.0	5.1	97.7	45.9	3.0
13a Lit	1	0.0	61.2	220.0	8.8	211.8	31.3	5.1
13a A	1	6.0	55.2	207.7	7.6	200.4	17.8	4.5
13a B	0.9	4.1	31.5	134.6	3.7	79.1	29.9	0.0
13b LIT	0	0.0	55.1	208.7	8.4	295.4	26.0	3.0
13b A	1	3.7	50.4	232.2	8.2	216.9	9.5	0.0
13b B	1.8	3.9	42.7	153.5	4.4	112.5	30.6	3.4
13c Lit	1	2.3	56.9	226.9	8.3	174.6	49.4	4.0
13c A	0	6.3	47.4	214.2	10.1	200.3	12.7	5.0
13c B	1.7	3.4	27.7	111.4	2.7	32.9	29.0	0.0
13s Lit	1	4.0	58.0	205.3	11.4	205.3	34.4	4.8
13d A	1	5.0	57.7	199.5	9.8	150.5	18.4	4.8
13d B	1.5	4.2	31.5	116.0	4.4	59.8	36.4	0.0
13e Lit	0.6	2.1	63.7	205.8	9.3	248.7	45.3	3.4
13e A	1	4.5	49.2	226.2	9.4	190.3	9.7	3.4
13e B	0.6	4.0	44.4	183.0	6.5	110.5	35.6	3.4
14a Lit	1	2.8	71.1	220.5	9.7	265.0	35.4	3.4
14a A	1	4.9	54.0	232.9	9.4	223.7	10.5	3.8
13a B	2.4	3.6	48.1	147.0	4.7	78.4	51.8	2.8
14b Lit	1	2.1	66.7	211.0	10.1	169.2	41.6	4.2
14b A	1	5.3	63.4	221.1	10.0	181.6	15.6	4.1
14b B	0.7	3.4	49.7	169.1	5.9	156.8	40.7	4.7
14c Lit	1.5	1.9	66.2	199.7	9.2	231.6	34.0	3.3
14c A	1	6.3	65.2	209.2	10.1	216.8	16.7	4.1
14c B	1	0.0	64.9	225.3	9.0	291.0	10.0	0.0
14c Grey	1.3	3.6	41.5	137.9	5.3	86.6	42.8	4.2
14d Lit	1.4	4.6	58.2	189.6	8.5	182.5	59.2	4.0
14d A	0	4.6	51.8	231.9	9.6	249.5	9.5	0.0
14d B	1.1	3.5	55.5	164.9	7.6	146.5	51.1	3.9
14e Lit	0.0	2.4	67.7	211.7	9.4	183.4	60.0	5.0
14e A	1	4.7	53.9	246.5	9.6	171.7	14.1	4.7
14e B	0.9	4.4	49.8	184.3	4.1	104.9	28.0	3.2

		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
216	15a Lit	1.3	1.1	0.22	105	1372	1.6	127.1	72.4	157.4	9.3	12
217	15a A	1.6	0.5	0.31	38	259	1.5	73.3	107.2	42.1	11.3	0
218	15a B	2.1	0.7	0.41	72	235	2.8	49.7	23.9	73.0	15.6	7.7
219	15b Lit	1.0	1.0	0.15	85	1167	1.5	170.1	139.9	164.7	6.4	11.9
220	15b A	1.0	0.6	0.17	0	324	1.8	242.0	249.9	77.1	10.5	0
221	15b B	1.9	0.7	0.32	85	228	2.1	46.8	21.1	44.3	13.6	4.8
222	15c Lit	1.4	1.3	0.21	156	1164	1.7	141.5	59.2	147.2	8.6	10
223	15c A	2.1	0.8	0.35	63	714	2.5	121.0	88.9	93.6	11.0	0
224	15c B	2.1	0.7	0.36	101	355	2.6	55.3	32.7	72.9	11.9	0.0
224	16e A	1.9	0.7	0.38	48	497	1.7	62.3	56.5	44.1	13.0	9
225	15d Lit	1.5	1.2	0.19	116	1202	1.7	114.4	59.5	175.2	9.5	4
226	15d A	1.9	0.7	0.29	58	683	2.0	100.0	78.8	85.6	11.0	0.0
227	15d B	1.9	0.6	0.34	55	320	2.3	47.9	20.9	72.3	12.2	5
228	15e Lit	1.2	1.3	0.15	170	994	1.3	152.0	53.0	149.2	6.3	0
229	15e A	1.8	0.8	0.25	67	425	1.9	73.6	58.0	50.7	11.2	0.0
230	15e B	1.9	0.7	0.29	66	248	2.1	35.9	17.9	29.4	11.4	15
231	16a Lit	1.4	1.5	0.28	146	1457	2.1	135.5	80.4	205.8	10.2	4
232	16a B	1.8	0.7	0.44	45	1913	2.3	149.2	119.0	82.1	10.4	5.2
233	16a B	1.8	0.7	0.39	102	433	3.1	46.8	36.9	66.0	10.8	9
234	16b Lit	1.4	1.2	0.24	158	1433	1.8	143.4	68.3	204.0	10.5	0
235	16b A	1.7	0.6	0.39	45	863	1.9	89.4	93.7	72.5	12.6	5.0
236	16b B	1.9	0.7	0.44	70	302	3.1	35.0	24.2	83.6	12.8	10
237	16c Lit	1.4	1.1	0.26	139	1075	2.1	137.1	74.0	152.7	9.2	0
238	16c A	1.8	0.7	0.42	66	693	2.4	93.8	97.8	81.2	13.7	0.0
239	16c B	1.9	0.7	0.37	90	286	2.7	36.8	26.1	80.2	12.9	10
240	16d Lit	1.4	2.5	0.11	96	2131	1.0	119.2	52.6	385.7	3.7	0
241	16d A	1.8	0.7	0.33	75	831	2.0	90.0	71.5	87.1	12.6	4.4
242	16d B	1.9	0.6	0.36	63	361	2.4	59.3	22.9	76.8	11.4	4
243	16e Lit	1.3	1.3	0.21	120	1234	1.6	106.8	54.4	163.3	9.2	5.5
245	16e B	1.9	0.7	0.42	56	324	2.5	40.4	29.0	61.1	13.2	4
246	18a Lit	1.0	0.9	0.2	71	1155	1.3	90.7	57.1	122.6	8.0	0
247	18a A	1.5	0.6	0.27	30	468	1.6	43.9	41.0	80.2	11.0	0.0
248	18a B	1.8	0.7	0.4	46	252	2.3	27.5	13.3	80.8	13.2	5
249	18b Lit	0.9	1.6	0.12	46	1793	0.9	94.3	75.9	210.4	2.0	0
250	18b A	1.6	0.7	0.34	62	629	2.5	70.7	70.6	99.8	11.9	4.7
251	18b B	1.6	0.7	0.32	69	302	2.3	29.1	17.7	83.6	13.1	6

	Se	Br	Rb	Sr	Y	Zr	Pb	Th
15a Lit	1	2.4	71.0	206.0	11.7	206.2	46.6	4.4
15a A	1	5.8	63.2	207.9	8.4	262.9	11.3	0.0
15a B	1.3	6.2	29.3	128.3	3.6	58.1	37.2	2.8
15b Lit	3.1	8.2	35.6	105.7	4.0	66.6	59.7	3.1
15b A	0	3.2	62.3	252.6	7.2	176.6	13.0	5.6
15b B	0.0	3.8	44.9	189.5	4.5	77.8	19.1	2.1
15c Lit	1	3.2	72.8	239.0	7.6	153.9	36.4	0.0
15c A	0	6.0	63.9	242.6	8.2	211.9	13.5	4.0
15c B	1.3	3.5	41.7	182.4	3.6	56.2	23.3	2.3
16e A	1	2.5	65.5	230.1	7.2	162.0	45.7	3.3
15d Lit	1	4.9	57.5	224.5	11.5	236.2	13.1	4.6
15d A	0.7	4.3	33.9	185.5	2.2	69.8	17.4	0.0
15d B	1	2.2	60.2	280.8	6.1	111.9	24.4	0.0
15e Lit	0	2.6	59.5	236.2	6.4	173.0	10.5	5.0
15e A	0.6	3.2	47.7	176.7	3.4	72.8	30.8	2.6
15e B	1	2.6	76.8	213.8	10.1	164.7	49.0	5.5
16a Lit	0	7.1	56.2	220.4	8.1	126.2	14.5	4.1
16a B	0.6	3.8	46.4	153.2	3.7	71.7	26.1	0.0
16a B	1	3.1	68.3	194.8	9.2	228.2	42.6	5.3
16b Lit	1	7.5	56.1	204.3	8.9	175.7	14.2	2.9
16b A	1.0	3.6	54.2	175.0	6.5	78.3	29.9	3.0
16b B	1	3.9	81.6	210.7	9.1	187.9	33.6	5.8
16c Lit	0	6.7	59.7	214.8	9.9	166.3	11.9	5.9
16c A	0.0	2.7	13.5	116.5	0.0	18.4	8.5	0.0
16c B	1	2.8	69.5	223.6	8.2	214.9	27.9	0.0
16d Lit	1	5.4	59.2	210.4	9.9	188.2	13.7	0.0
16d A	1.2	3.6	42.9	189.1	5.4	106.2	18.6	2.7
16d B	1	6.8	62.0	215.8	8.9	237.8	14.6	0.0
16e Lit	0.8	4.6	28.9	124.6	3.7	107.8	15.4	0.0
16e B	1	5.2	52.3	223.7	8.7	224.9	27.3	3.3
18a Lit	0	7.0	54.8	235.9	8.3	263.2	15.4	0.0
18a A	0.7	3.0	9.1	59.5	0.0	34.0	11.8	0.0
18a B	1	7.9	53.2	208.0	8.1	223.0	39.0	5.3
18b Lit	1	7.1	51.0	233.7	8.9	219.4	14.2	4.3
18b A	0.6	3.3	34.9	144.7	3.6	121.9	24.6	2.2
18b B	1	3.3	56.2	206.2	9.9	276.0	34.9	5.2

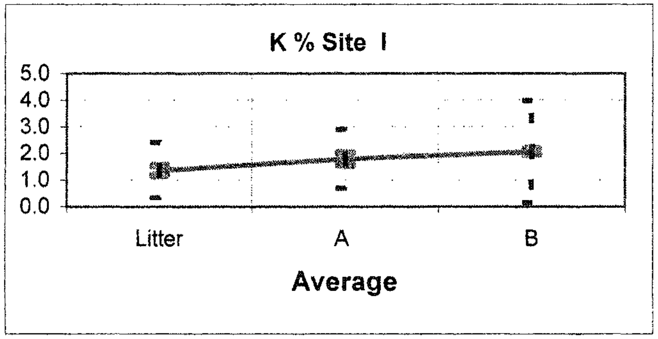
		K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As
252	18c Lit	1.1	1.0	0.22	95	1483	1.4	101.5	52.6	212.9	10.1	5
253	18c A	1.5	0.5	0.37	18	498	1.4	46.3	53.5	57.4	12.1	6
254	18c B	1.6	0.6	0.34	54	302	2.4	49.3	25.2	82.6	12.3	0
255	18a Lit	1.2	0.9	0.26	83	1236	1.7	82.4	56.5	143.5	8.7	5.2
256	18d A	1.5	0.6	0.37	23	776	1.7	60.0	50.8	85.2	12.9	7
257	18d B	1.7	0.8	0.35	69	283	2.7	36.9	13.7	112.7	12.5	5
258	18e Lt	1.2	0.9	0.25	96	1322	1.9	84.3	63.8	157.7	11.1	0
259	18e A	1.6	0.7	0.34	60	838	2.3	62.5	56.1	101.4	12.1	7
260	18e B	1.6	0.7	0.33	92	307	2.3	47.7	29.7	97.7	13.4	4.6
	AVERAGE	1.6	0.9	0.3	73.6	691.6	2.3	110.7	83.7	108.5	10.3	5.7
	MAX	2.5	3.0	0.5	277.3	2964.3	7.8	606.4	575.3	530.0	17.5	34.1
	MIN	0.5	0.4	0.1	0.0	121.0	0.6	7.6	2.8	18.6	1.1	0.0

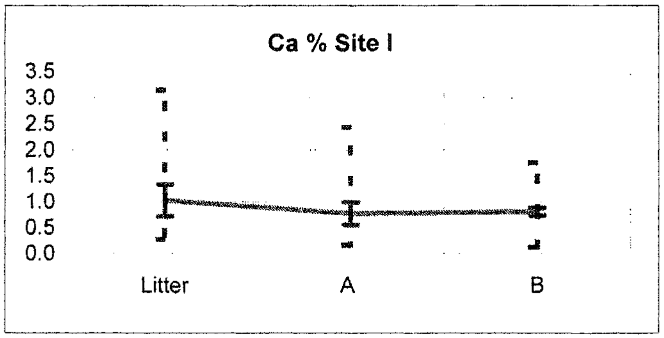
	Se	Br	Rb	Sr	Y	Zr	Pb	Th
18c Lit	1	7.6	47.8	218.1	7.9	247.9	14.0	3.2
18c A	1	3.7	57.0	206.8	9.0	274.5	28.3	0.0
18c B	1	9.1	48.5	227.6	10.0	230.1	11.4	3.9
18a Lit	0.6	5.1	39.8	164.2	5.1	115.8	28.7	4.0
18d A	1	5.4	51.6	223.7	8.9	242.5	34.3	3.8
18d B	1	6.9	50.2	233.1	8.3	228.7	14.6	3.9
18e Lt	1	0.0	50.1	321.1	9.5	242.2	8.4	0.0
18e A	1	2.6	65.5	250.6	7.9	190.9	26.5	0.0
18e B	0.0	4.5	39.0	157.6	5.0	129.7	27.7	3.2
AVERAGE	0.9	3.0	44.8	201.6	8.2	169.7	23.5	2.2
MAX	4.3	9.1	81.6	338.5	14.0	295.4	114.3	10.8
MIN	0.0	0.0	5.5	40.0	0.0	7.7	4.5	0.0

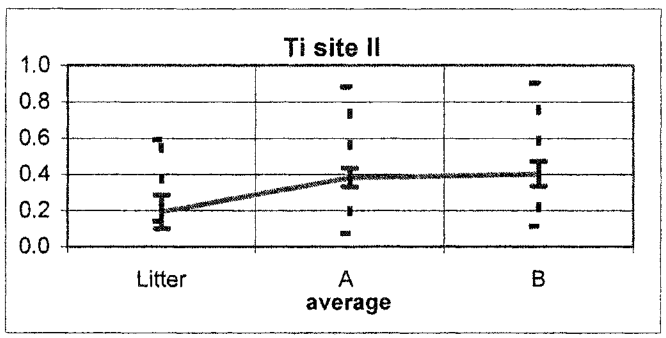
Appendix 3 - Depth distribution of each element

(19 elements)

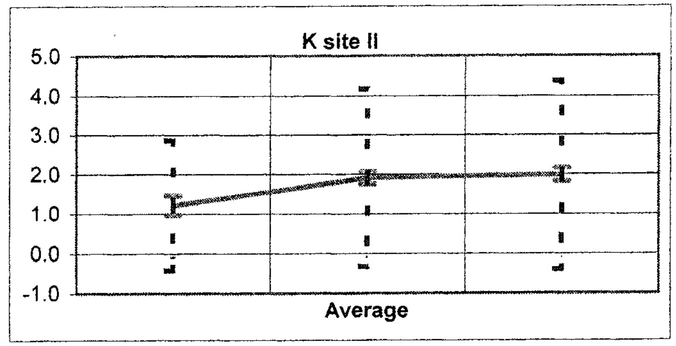
—— stdeviation ---- max/min

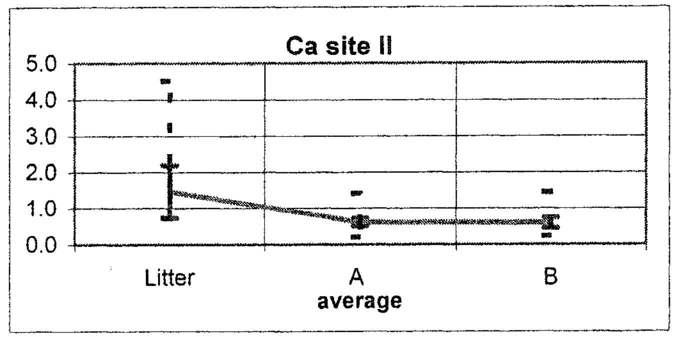


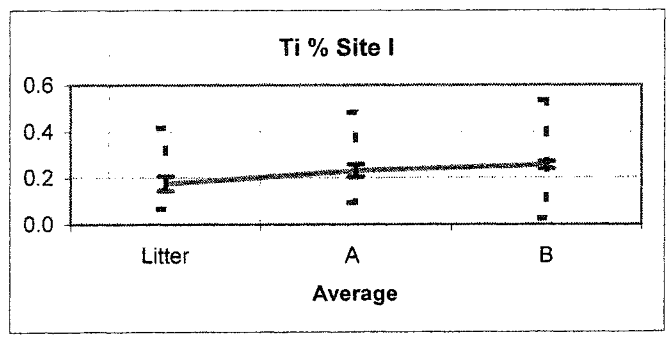


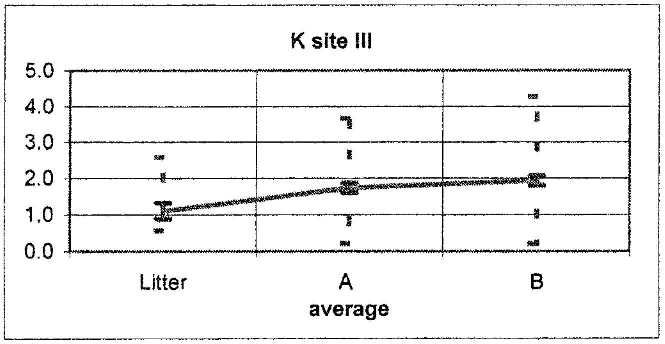


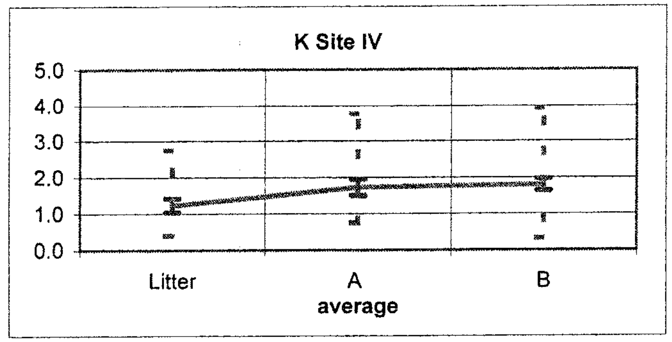
—— stdeviation ---- max/min

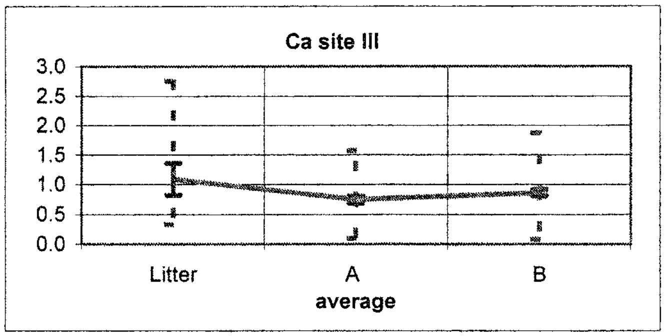


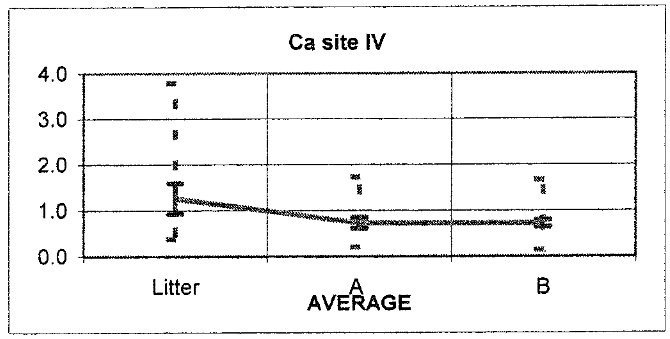


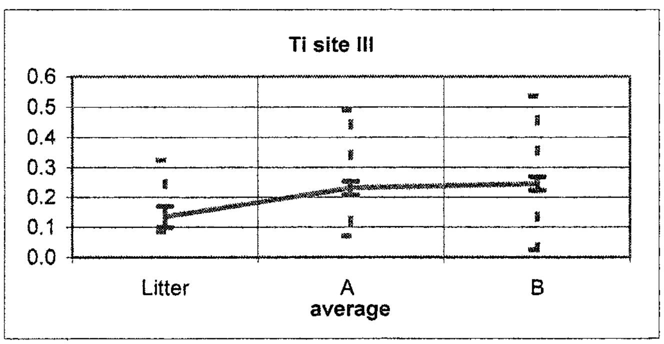


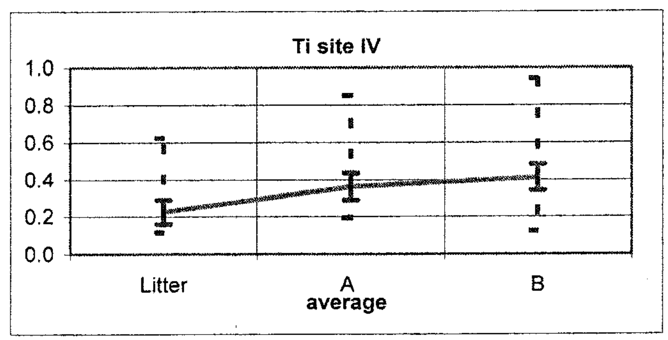




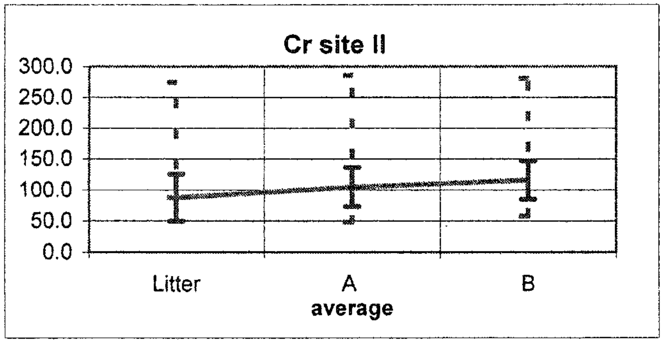


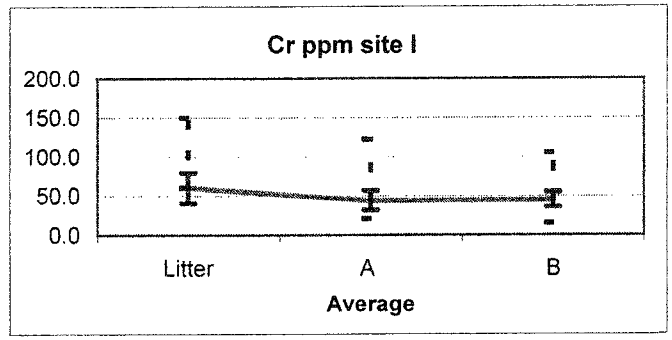


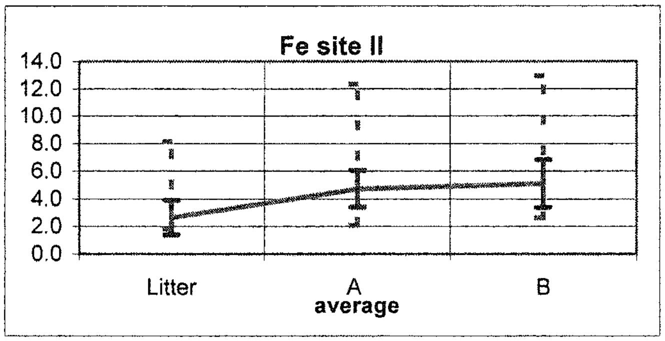


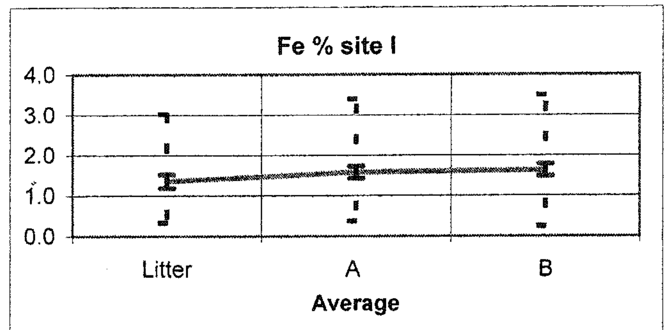


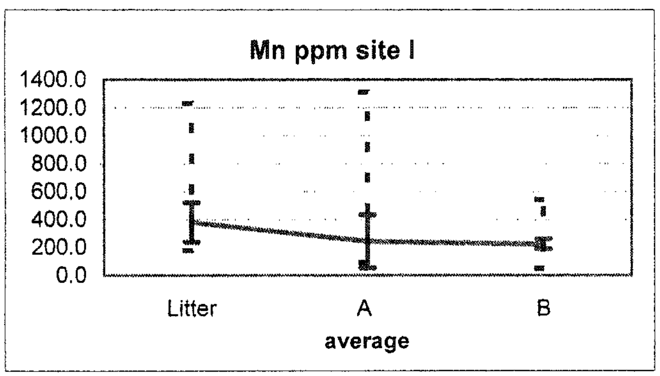
—— stdeviation - - - - max/min

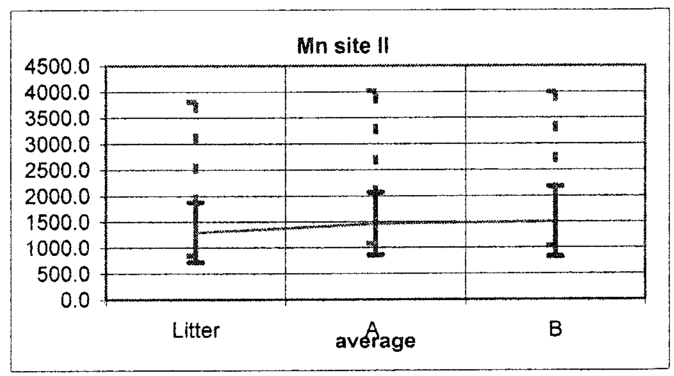




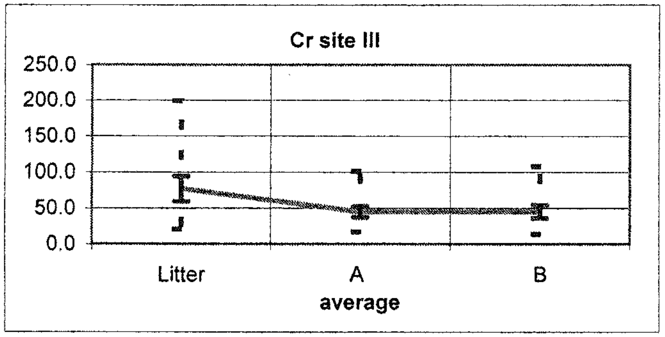


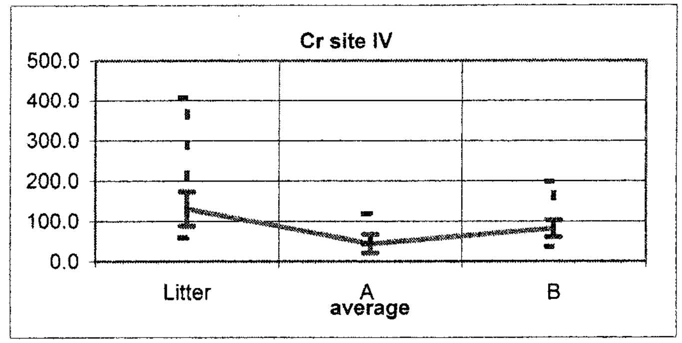


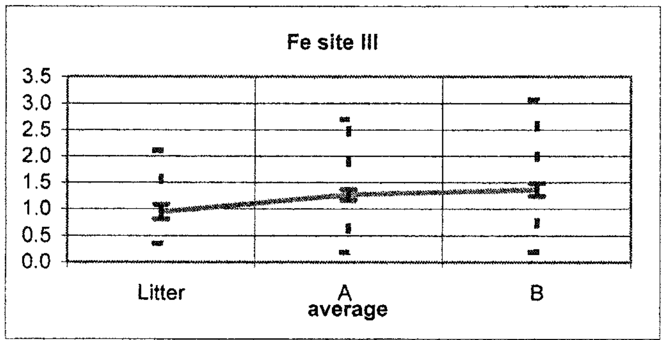


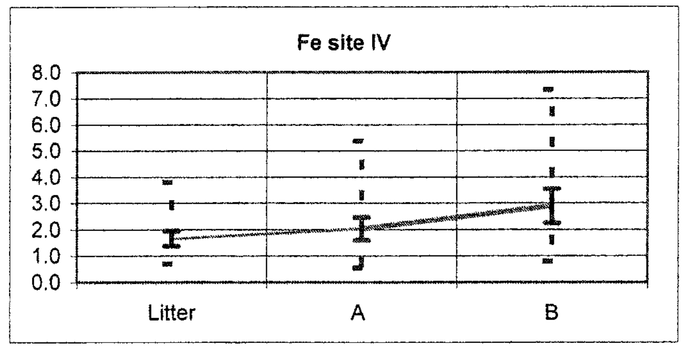


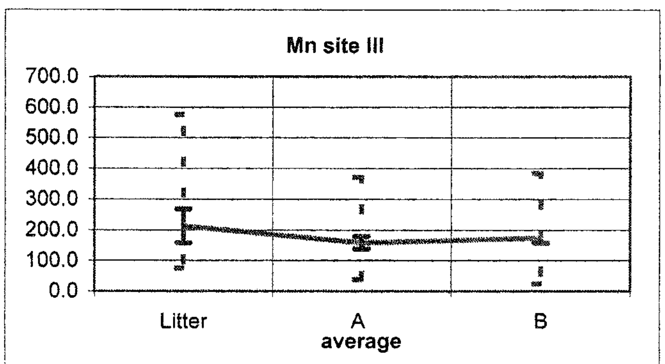
—— stdeviation ---- max/min

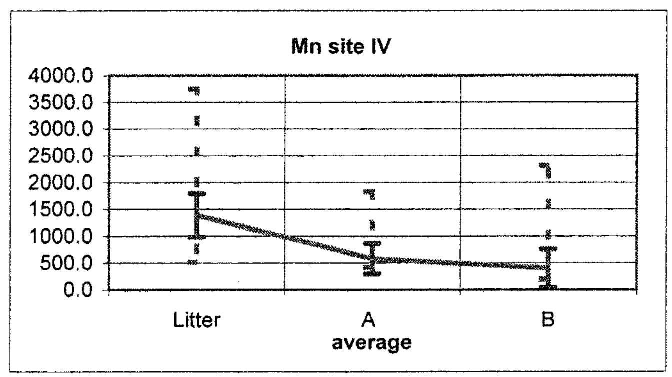




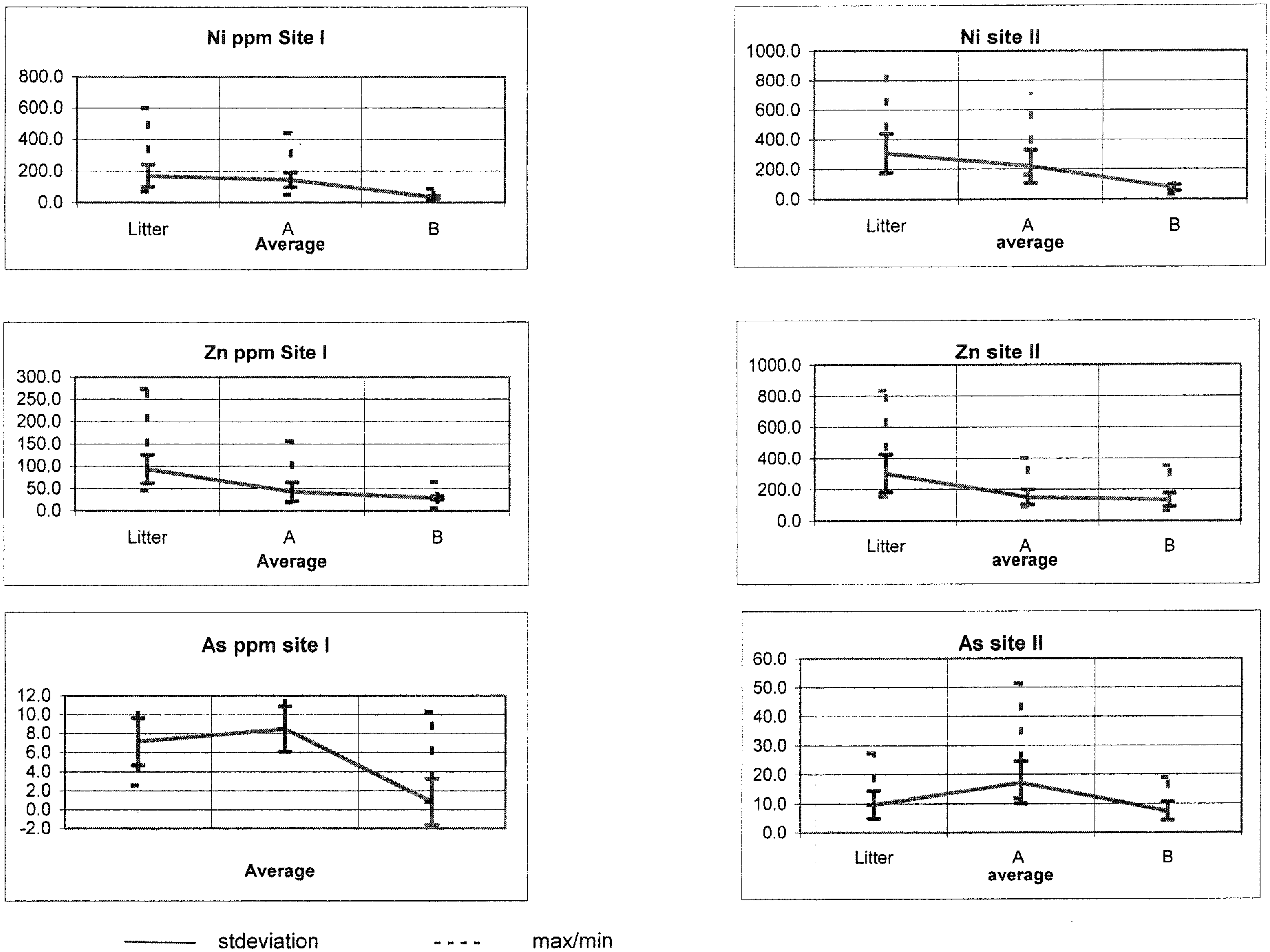


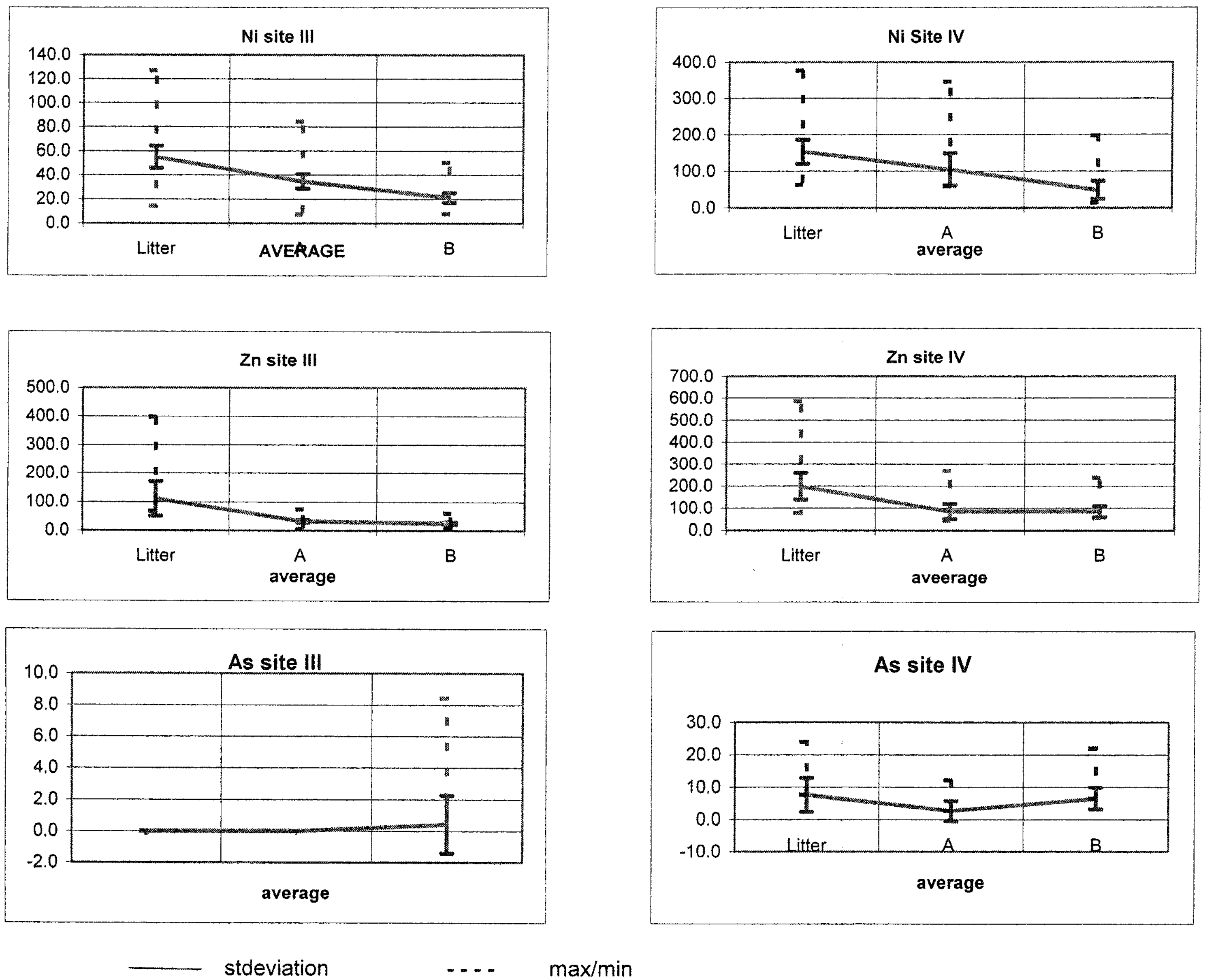


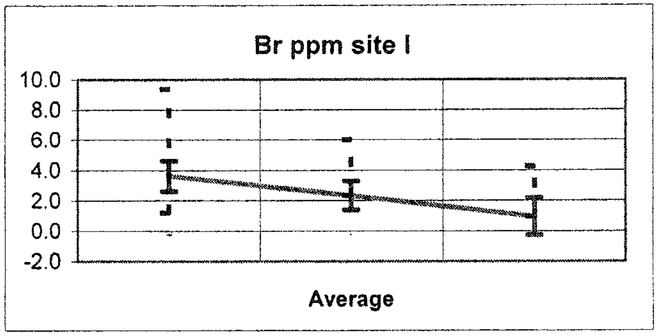


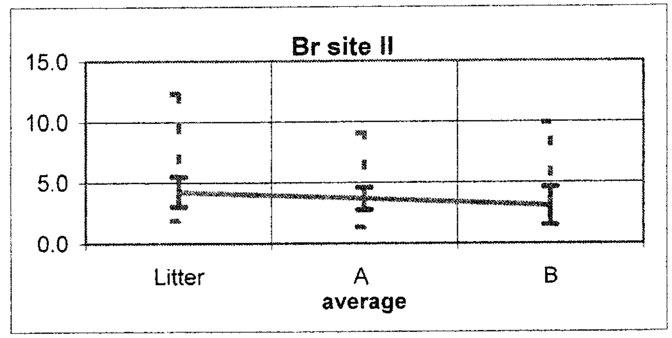


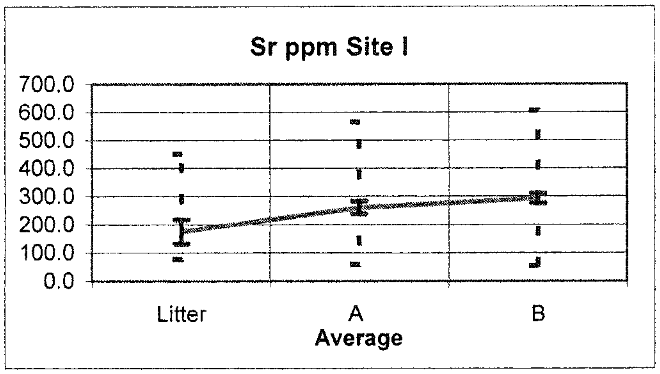
——— stdeviation - - - - max/min

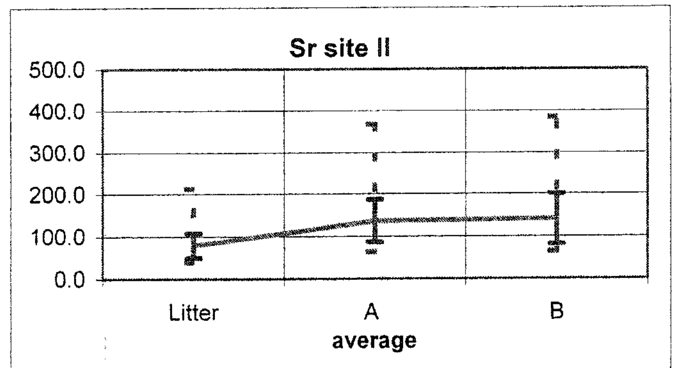

Ni ppm Site I
800.0
600.0
400.0
200.0
0.0
Litter
A
B
Average
Ni site II
1000.0
800.0
600.0
400.0
200.0
0.0
Litter
A
B
average
Zn ppm Site I
300.0
250.0
200.0
150.0
100.0
50.0
0.0
Litter
A
B
Average
Zn site II
1000.0
800.0
600.0
400.0
200.0
0.0
Litter
A
B
average
As ppm site I
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
Average
As site II
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Litter
A
B
average
stdeviation
max/min

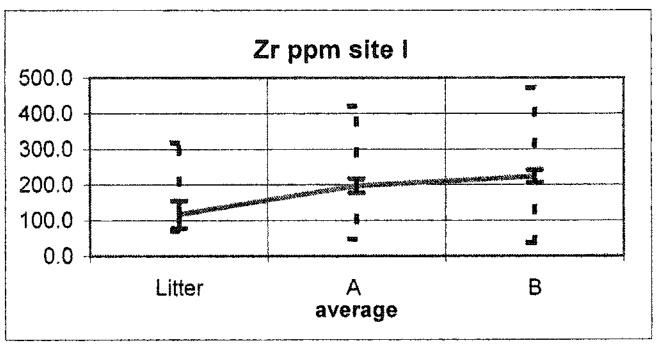

Ni site III
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Litter
AVERAGE
B
Ni Site IV
400.0
300.0
200.0
100.0
0.0
Litter
A
average
B
Zn site III
500.0
400.0
300.0
200.0
100.0
0.0
Litter
A
average
B
Zn site IV
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Litter
A
aveerage
B
As site III
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
average
As site IV
30.0
20.0
10.0
0.0
-10.0
Litter
A
B
average
stdeviation
max/min

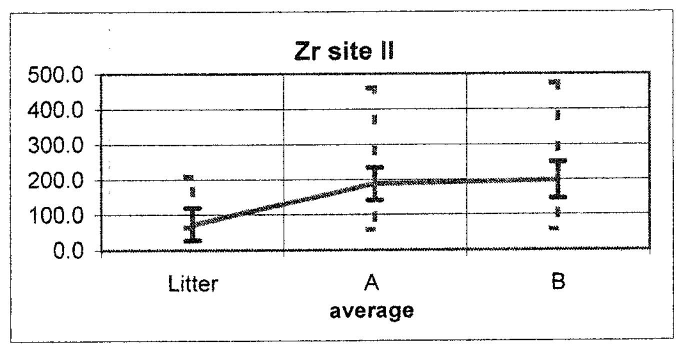




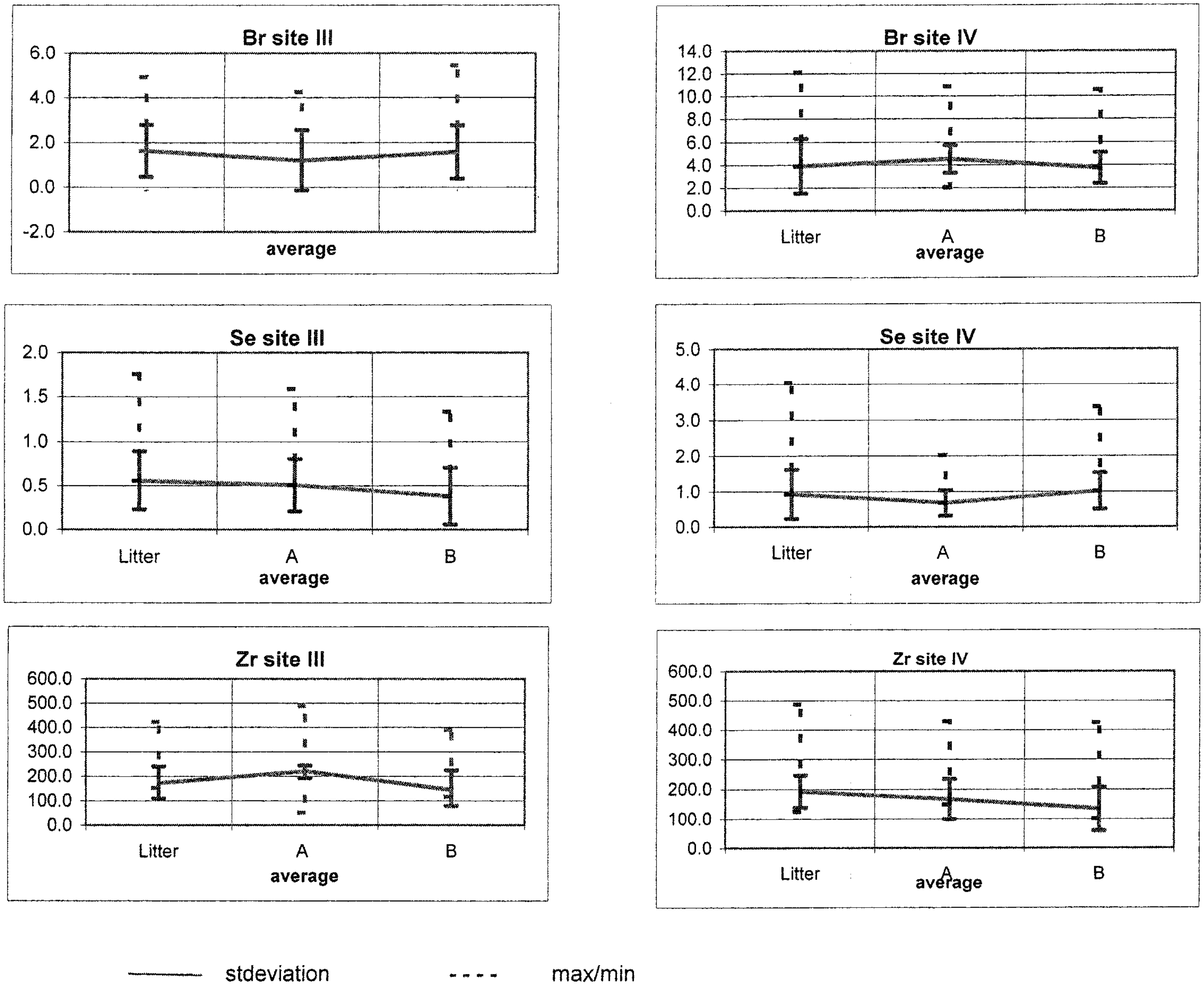


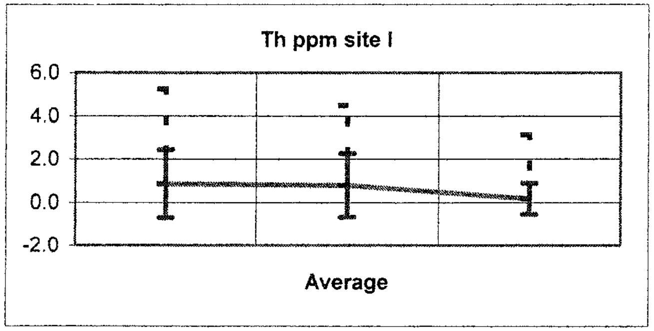


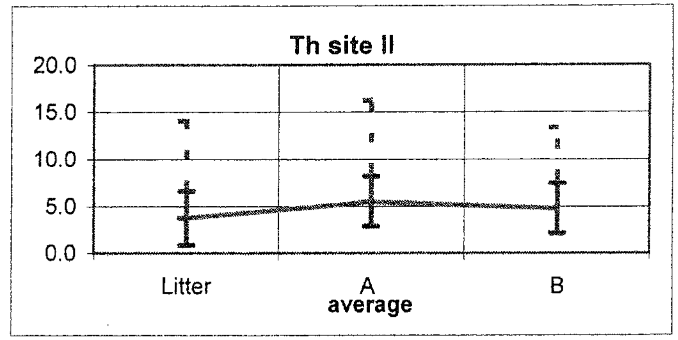


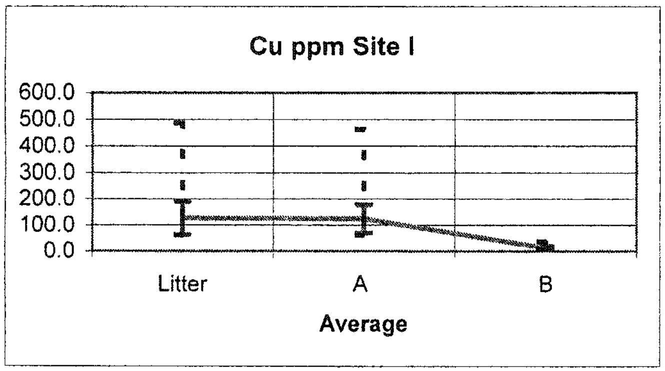


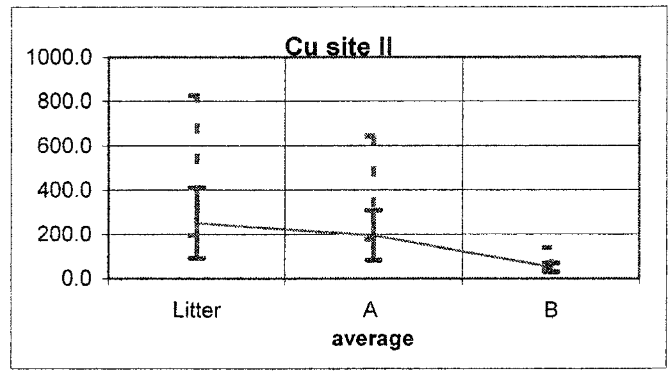
——— stdeviation - - - - max/min

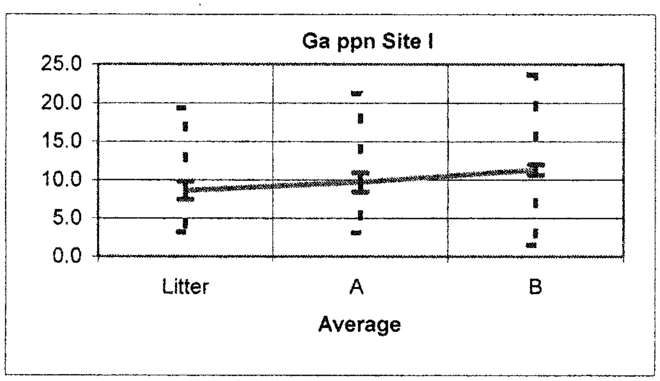

Br site III
6.0
4.0
2.0
0.0
-2.0
average
Br site IV
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Litter
A
B
average
Se site III
2.0
1.5
1.0
0.5
0.0
Litter
A
B
average
Se site IV
5.0
4.0
3.0
2.0
1.0
0.0
Litter
A
B
average
Zr site III
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Litter
A
B
average
Zr site IV
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Litter
A
B
average
stdeviation
max/min

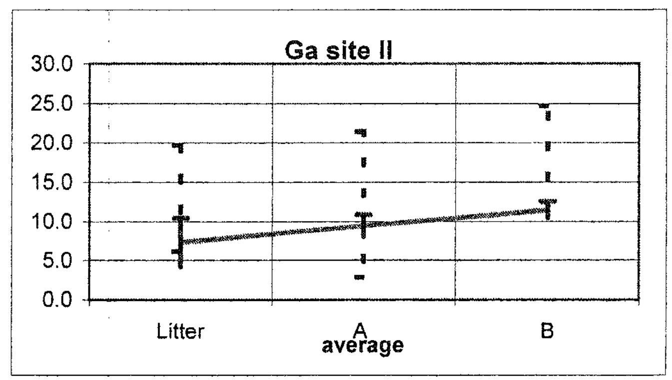




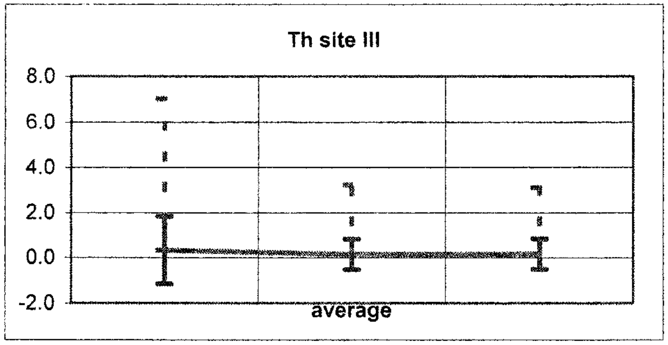


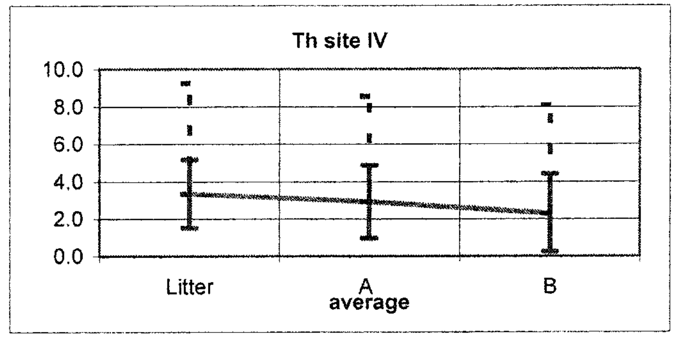


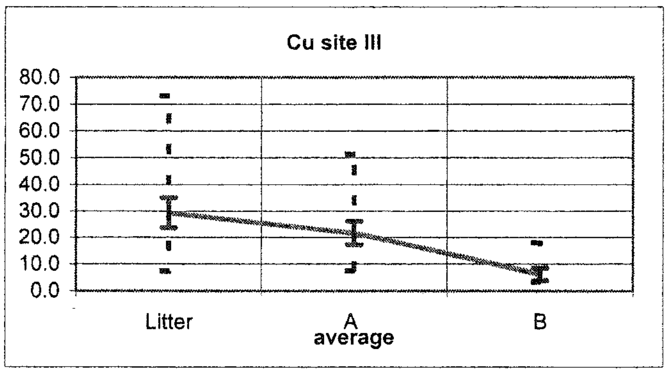


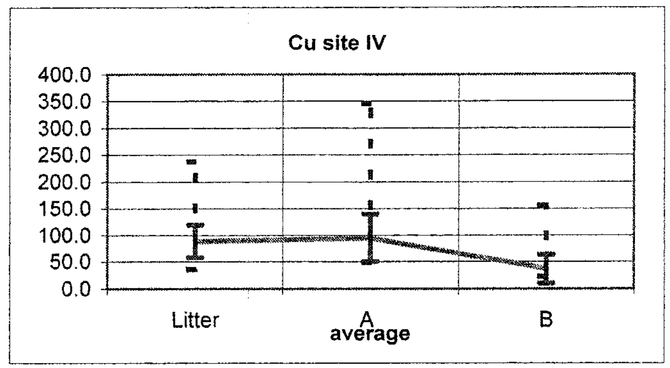


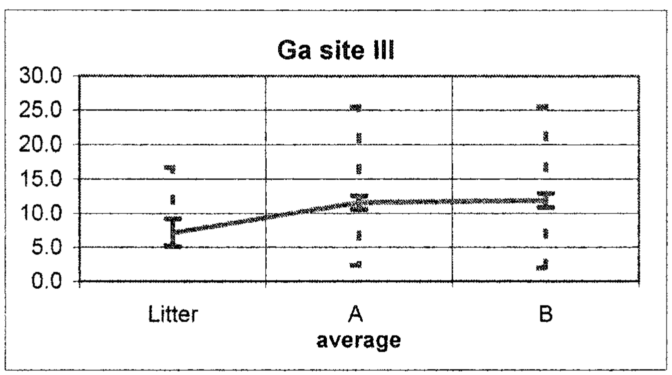
——— stdeviation - - - - max/min

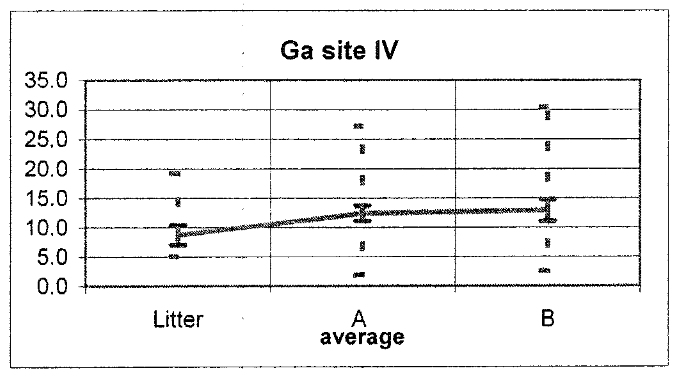




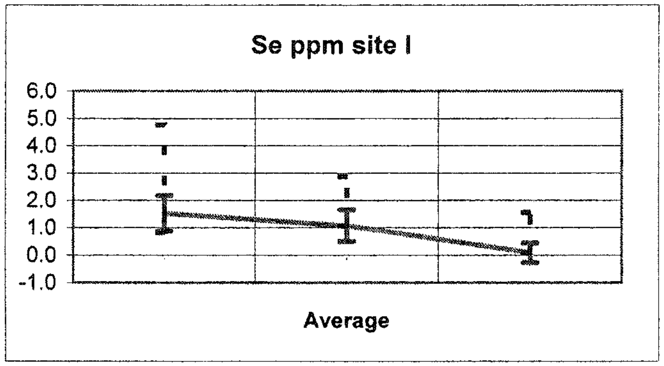


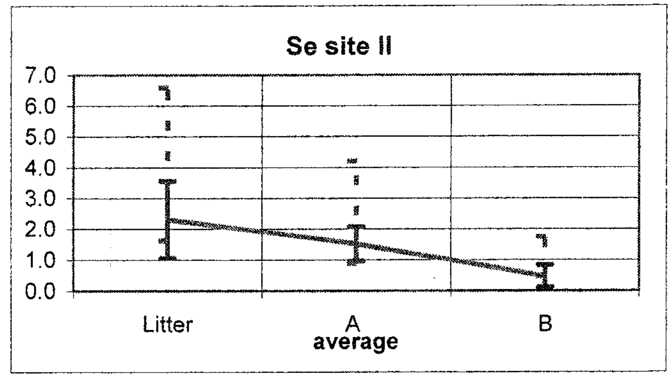


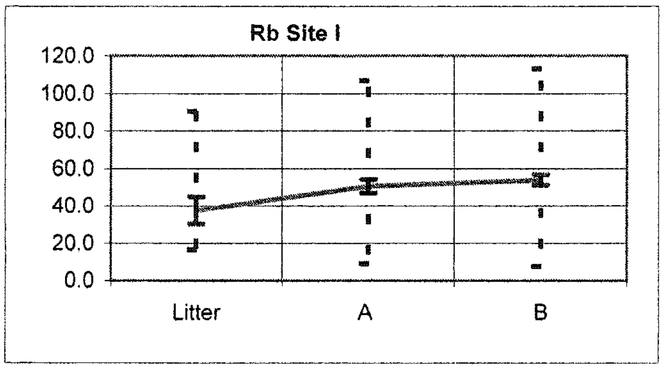


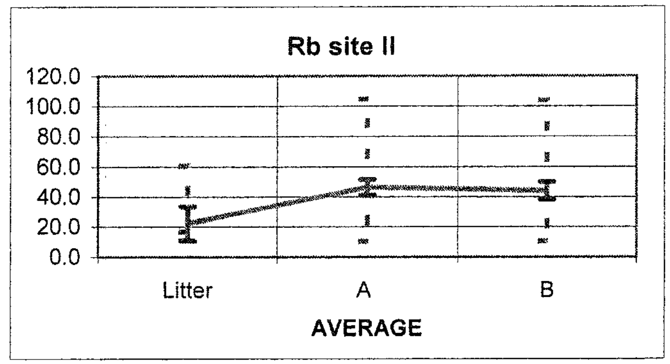


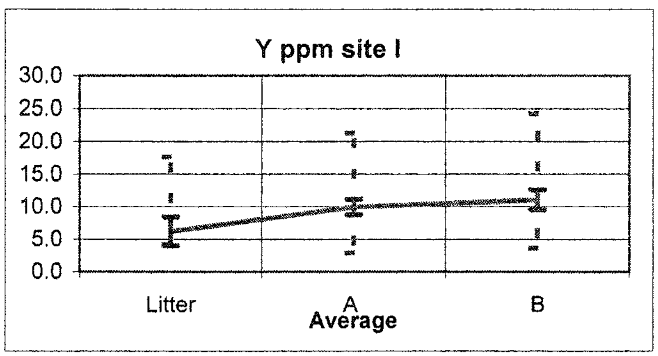
——— stdeviation - - - - max/min

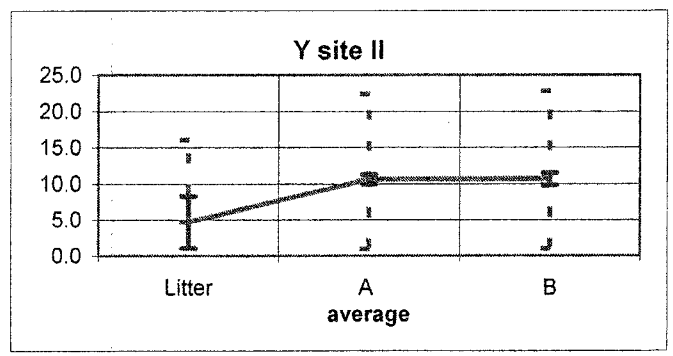




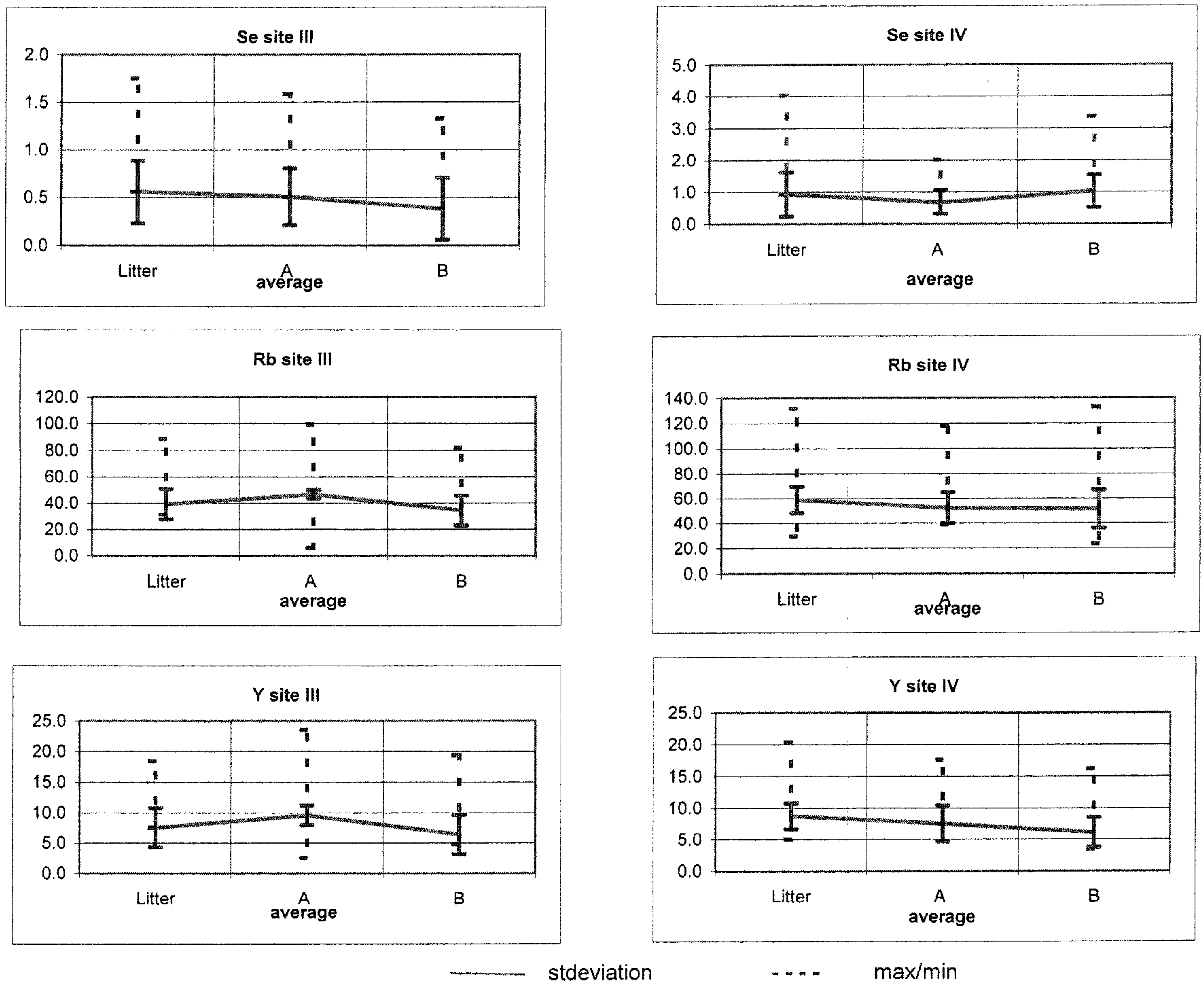


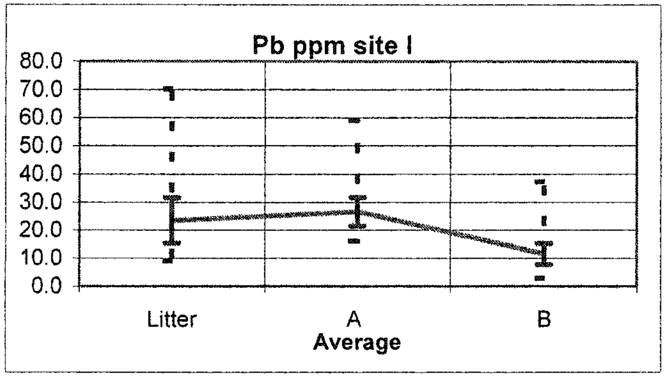


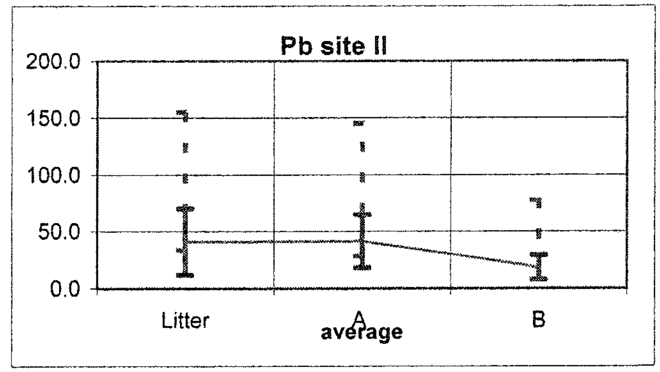




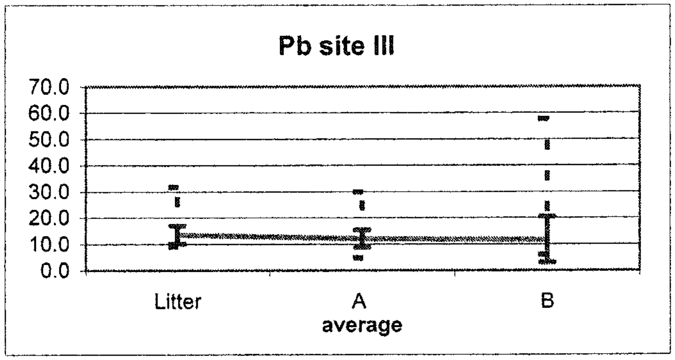
——— stdeviation - - - - max/min

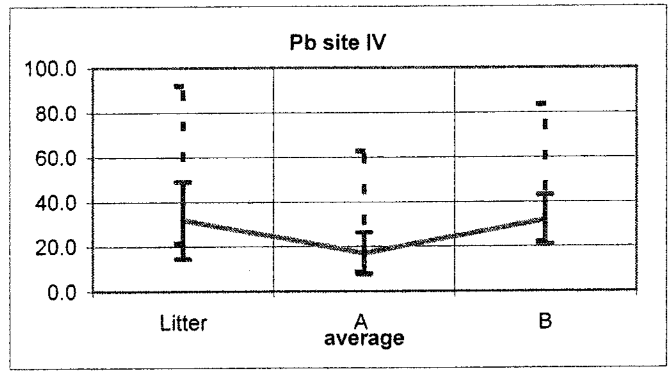

Se site III
2.0
1.5
1.0
0.5
0.0
Litter
A
B
average
Se site IV
5.0
4.0
3.0
2.0
1.0
0.0
Litter
A
B
average
Rb site III
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Litter
A
B
average
Rb site IV
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Litter
A
B
average
Y site III
25.0
20.0
15.0
10.0
5.0
0.0
Litter
A
B
average
Y site IV
25.0
20.0
15.0
10.0
5.0
0.0
Litter
A
B
average
stdeviation
max/min





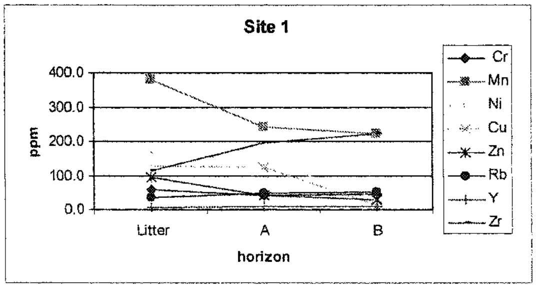
——— stdeviation   - - - - max/min

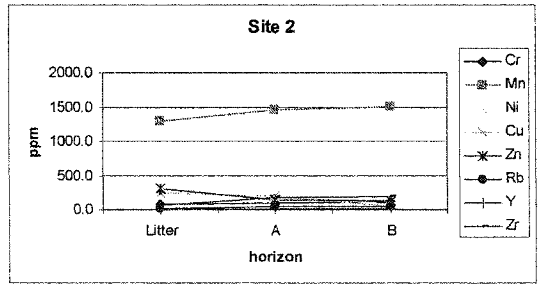


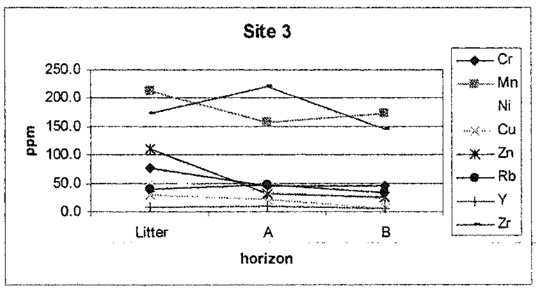


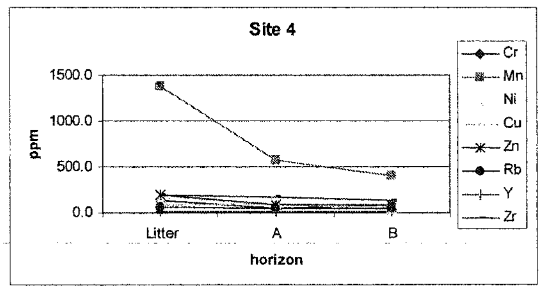
—— stdeviation ---- max/min

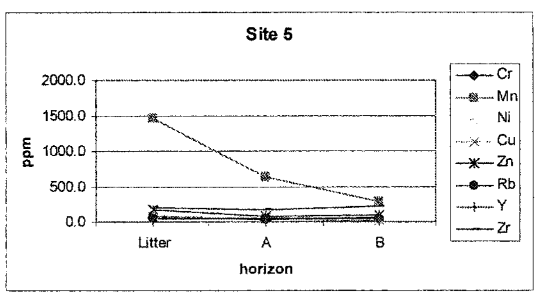
Appendix 4 - Distribution of elements within site


Site 1
400.0
300.0
200.0
100.0
0.0
ppm
Litter
A
B
horizon
Cr
Mn
Ni
Cu
Zn
Rb
Y
Zr

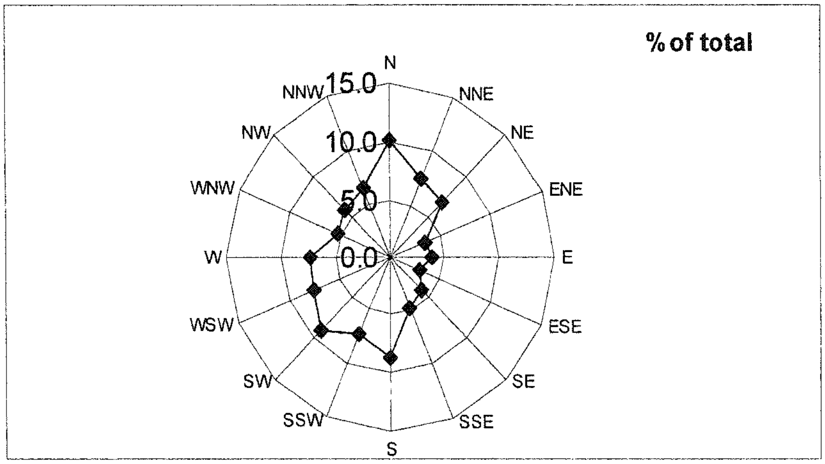

Site 2
2000.0
1500.0
1000.0
500.0
0.0
ppm
Litter
A
B
horizon
Cr
Mn
Ni
Cu
Zn
Rb
Y
Zr

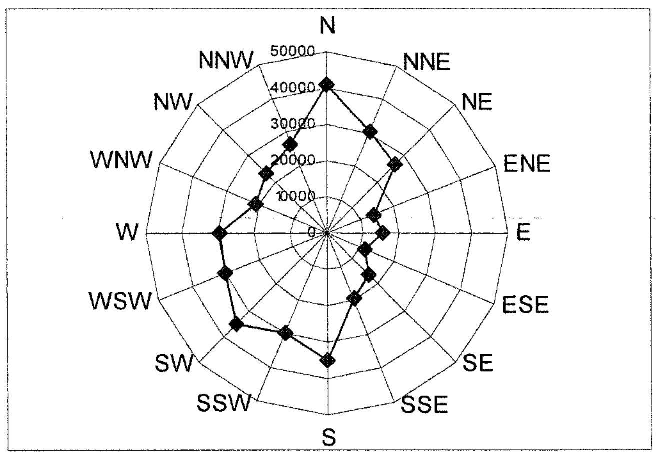

Site 3
250.0
200.0
150.0
100.0
50.0
0.0
ppm
Litter
A
B
horizon
Cr
Mn
Ni
Cu
Zn
Rb
Y
Zr


Site 4
1500.0
1000.0
500.0
0.0
ppm
Litter
A
B
horizon
Cr
Mn
Ni
Cu
Zn
Rb
Y
Zr


Site 5
2000.0
1500.0
1000.0
500.0
0.0
ppm
Litter
A
B
horizon
Cr
Mn
Ni
Cu
Zn
Rb
Y
Zr

Appendix 5 - Wind direction data area





wind direc	amount	% of total
NNE	30297	7.5
NE	26755	6.6
ENE	13775	3.4
E	15480	3.8
ESE	11362	2.8
SE	16058	4.0
SSE	19354	4.8
S	34924	8.6
SSW	29750	7.3
SW	35708	8.8
WSW	30210	7.5
W	29595	7.3
WNW	21029	5.2
NW	23651	5.8
NNW	26320	6.5
N	41048	10.1
total	**405316**	**100.0**

Appendix 6 - Statistical *t* – Test results

T-Test Zn (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	122.165	20	46.799	10.465
	SITE_2	72.128	20	46.086	10.305
Pair 2	SITE_1	122.165	20	46.799	10.465
	SITE_3	172.466	20	63.076	14.104
Pair 3	SITE_1	122.165	20	46.799	10.465
	SITE_4	188.368	20	53.382	11.936
Pair 4	SITE_1	143.912	5	62.266	27.846
	SITE_5	217.662	5	59.096	26.429
Pair 5	SITE_2	72.128	20	46.086	10.305
	SITE_3	172.466	20	63.076	14.104
Pair 6	SITE_2	72.128	20	46.086	10.305
	SITE_4	188.368	20	53.382	11.936
Pair 7	SITE_2	90.200	5	42.121	18.837
	SITE_5	217.662	5	59.096	26.429
Pair 8	SITE_3	172.466	20	63.076	14.104
	SITE_4	188.368	20	53.382	11.936
Pair 9	SITE_3	109.560	5	20.644	9.232
	SITE_5	217.662	5	59.096	26.429
Pair 10	SITE_4	227.160	5	46.364	20.735
	SITE_5	217.662	5	59.096	26.429

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.337	.146
Pair 2	SITE_1 & SITE_3	20	-.391	.088
Pair 3	SITE_1 & SITE_4	20	.494	.027
Pair 4	SITE_1 & SITE_5	5	-.104	.868
Pair 5	SITE_2 & SITE_3	20	-.303	.195
Pair 6	SITE_2 & SITE_4	20	.341	.141
Pair 7	SITE_2 & SITE_5	5	-.264	.668
Pair 8	SITE_3 & SITE_4	20	-.581	.007
Pair 9	SITE_3 & SITE_5	5	.575	.311
Pair 10	SITE_4 & SITE_5	5	.053	.932

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper			
Pair 1	SITE_1 - SITE_2	50.037	53.464	11.955	25.016	75.059	4.186	19	.001
Pair 2	SITE_1 - SITE_3	-50.301	92.069	20.587	-93.390	-7.212	-2.443	19	.024
Pair 3	SITE_1 - SITE_4	-66.203	50.720	11.341	-89.941	-42.465	-5.837	19	.000
Pair 4	SITE_1 - SITE_5	-73.750	90.187	40.333	-185.732	38.232	-1.829	4	.141
Pair 5	SITE_2 - SITE_3	-100.338	88.669	19.827	-141.837	-58.840	-5.061	19	.000
Pair 6	SITE_2 - SITE_4	-116.240	57.399	12.835	-143.104	-89.377	-9.057	19	.000
Pair 7	SITE_2 - SITE_5	-127.462	81.121	36.278	-228.187	-26.737	-3.513	4	.025
Pair 8	SITE_3 - SITE_4	-15.902	103.636	23.174	-64.405	32.601	-.686	19	.501
Pair 9	SITE_3 - SITE_5	-108.102	50.156	22.430	-170.379	-45.825	-4.819	4	.009
Pair 10	SITE_4 - SITE_5	9.498	73.144	32.711	-81.322	100.318	.290	4	.786

T-Test Zn (B Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	218.141	18	30.540	7.198
	SITE_2	193.631	18	49.832	11.746
Pair 2	SITE_1	218.141	18	30.540	7.198
	SITE_3	148.017	18	67.453	15.899
Pair 3	SITE_1	218.141	18	30.540	7.198
	SITE_4	118.261	18	67.149	15.827
Pair 4	SITE_1	203.964	5	52.586	23.517
	SITE_5	217.510	5	53.513	23.932
Pair 5	SITE_2	197.601	19	51.428	11.798
	SITE_3	145.370	19	66.560	15.270
Pair 6	SITE_2	197.601	19	51.428	11.798
	SITE_4	123.348	19	68.922	15.812
Pair 7	SITE_2	218.824	5	52.103	23.301
	SITE_5	217.510	5	53.513	23.932
Pair 8	SITE_3	145.370	19	66.560	15.270
	SITE_4	123.348	19	68.922	15.812
Pair 9	SITE_3	217.208	5	19.911	8.904
	SITE_5	217.510	5	53.513	23.932
Pair 10	SITE_4	78.946	5	33.965	15.189
	SITE_5	217.510	5	53.513	23.932

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	-.007	.978
Pair 2	SITE_1 & SITE_3	18	.053	.836
Pair 3	SITE_1 & SITE_4	18	.265	.287
Pair 4	SITE_1 & SITE_5	5	.189	.760
Pair 5	SITE_2 & SITE_3	19	.098	.689
Pair 6	SITE_2 & SITE_4	19	.205	.401
Pair 7	SITE_2 & SITE_5	5	.597	.288
Pair 8	SITE_3 & SITE_4	19	-.161	.511
Pair 9	SITE_3 & SITE_5	5	.272	.658
Pair 10	SITE_4 & SITE_5	5	-.220	.722

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	24.510	58.631	13.819	-4.647	53.667	1.774	17	.094
Pair 2	SITE_1 - SITE_3	70.124	72.569	17.105	34.036	106.212	4.100	17	.001
Pair 3	SITE_1 - SITE_4	99.879	65.977	15.551	67.070	132.689	6.423	17	.000
Pair 4	SITE_1 - SITE_5	-13.546	67.555	30.212	-97.427	70.335	-.448	4	.677
Pair 5	SITE_2 - SITE_3	52.231	80.017	18.357	13.664	90.798	2.845	18	.011
Pair 6	SITE_2 - SITE_4	74.253	77.096	17.687	37.094	111.412	4.198	18	.001
Pair 7	SITE_2 - SITE_5	1.314	47.444	21.218	-57.595	60.223	.062	4	.954
Pair 8	SITE_3 - SITE_4	22.022	103.228	23.682	-27.733	71.776	.930	18	.365
Pair 9	SITE_3 - SITE_5	-.302	51.773	23.154	-64.587	63.983	-.013	4	.990
Pair 10	SITE_4 - SITE_5	-138.564	69.412	31.042	-224.750	-52.378	-4.464	4	.011

T-Test Zn (A Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	122.165	20	46.799	10.465
	SITE_2	72.128	20	46.086	10.305
Pair 2	SITE_1	122.165	20	46.799	10.465
	SITE_3	172.466	20	63.076	14.104
Pair 3	SITE_1	122.165	20	46.799	10.465
	SITE_4	188.368	20	53.382	11.936
Pair 4	SITE_1	143.912	5	62.266	27.846
	SITE_5	217.662	5	59.096	26.429
Pair 5	SITE_2	72.128	20	46.086	10.305
	SITE_3	172.466	20	63.076	14.104
Pair 6	SITE_2	72.128	20	46.086	10.305
	SITE_4	188.368	20	53.382	11.936
Pair 7	SITE_2	90.200	5	42.121	18.837
	SITE_5	217.662	5	59.096	26.429
Pair 8	SITE_3	172.466	20	63.076	14.104
	SITE_4	188.368	20	53.382	11.936
Pair 9	SITE_3	109.560	5	20.644	9.232
	SITE_5	217.662	5	59.096	26.429
Pair 10	SITE_4	227.160	5	46.364	20.735
	SITE_5	217.662	5	59.096	26.429

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.337	.146
Pair 2	SITE_1 & SITE_3	20	-.391	.088
Pair 3	SITE_1 & SITE_4	20	.494	.027
Pair 4	SITE_1 & SITE_5	5	-.104	.868
Pair 5	SITE_2 & SITE_3	20	-.303	.195
Pair 6	SITE_2 & SITE_4	20	.341	.141
Pair 7	SITE_2 & SITE_5	5	-.264	.668
Pair 8	SITE_3 & SITE_4	20	-.581	.007
Pair 9	SITE_3 & SITE_5	5	.575	.311
Pair 10	SITE_4 & SITE_5	5	.053	.932

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper			
Pair 1	SITE_1 - SITE_2	50.037	53.464	11.955	25.016	75.059	4.186	19	.001
Pair 2	SITE_1 - SITE_3	-50.301	92.069	20.587	-93.390	-7.212	-2.443	19	.024
Pair 3	SITE_1 - SITE_4	-66.203	50.720	11.341	-89.941	-42.465	-5.837	19	.000
Pair 4	SITE_1 - SITE_5	-73.750	90.187	40.333	-185.732	38.232	-1.829	4	.141
Pair 5	SITE_2 - SITE_3	-100.338	88.669	19.827	-141.837	-58.840	-5.061	19	.000
Pair 6	SITE_2 - SITE_4	-116.240	57.399	12.835	-143.104	-89.377	-9.057	19	.000
Pair 7	SITE_2 - SITE_5	-127.462	81.121	36.278	-228.187	-26.737	-3.513	4	.025
Pair 8	SITE_3 - SITE_4	-15.902	103.636	23.174	-64.405	32.601	-.686	19	.501
Pair 9	SITE_3 - SITE_5	-108.102	50.156	22.430	-170.379	-45.825	-4.819	4	.009
Pair 10	SITE_4 - SITE_5	9.498	73.144	32.711	-81.322	100.318	.290	4	.786

T-Test Y (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	6.385	20	2.411	.539
	SITE_2	4.683	20	3.600	.805
Pair 2	SITE_1	6.385	20	2.411	.539
	SITE_3	7.530	20	3.227	.721
Pair 3	SITE_1	6.385	20	2.411	.539
	SITE_4	8.722	20	2.116	.473
Pair 4	SITE_1	7.936	5	2.631	1.177
	SITE_5	7.940	5	1.698	.759
Pair 5	SITE_2	4.683	20	3.600	.805
	SITE_3	7.530	20	3.227	.721
Pair 6	SITE_2	4.683	20	3.600	.805
	SITE_4	8.722	20	2.116	.473
Pair 7	SITE_2	5.362	5	3.497	1.564
	SITE_5	7.940	5	1.698	.759
Pair 8	SITE_3	7.530	20	3.227	.721
	SITE_4	8.722	20	2.116	.473
Pair 9	SITE_3	3.956	5	.919	.411
	SITE_5	7.940	5	1.698	.759
Pair 10	SITE_4	9.220	5	1.253	.560
	SITE_5	7.940	5	1.698	.759

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.233	.322
Pair 2	SITE_1 & SITE_3	20	-.512	.021
Pair 3	SITE_1 & SITE_4	20	.325	.162
Pair 4	SITE_1 & SITE_5	5	.191	.759
Pair 5	SITE_2 & SITE_3	20	-.269	.252
Pair 6	SITE_2 & SITE_4	20	.386	.093
Pair 7	SITE_2 & SITE_5	5	-.749	.145
Pair 8	SITE_3 & SITE_4	20	-.340	.142
Pair 9	SITE_3 & SITE_5	5	.314	.607
Pair 10	SITE_4 & SITE_5	5	-.809	.098

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	1.702	3.838	.858	-9.4E-02	3.498	1.983	19	.062
Pair 2	SITE_1 - SITE_3	-1.145	4.919	1.100	-3.448	1.157	-1.041	19	.311
Pair 3	SITE_1 - SITE_4	-2.338	2.641	.590	-3.573	-1.102	-3.959	19	.001
Pair 4	SITE_1 - SITE_5	-4.0E-03	2.847	1.273	-3.539	3.531	-.003	4	.998
Pair 5	SITE_2 - SITE_3	-2.847	5.442	1.217	-5.394	-.301	-2.340	19	.030
Pair 6	SITE_2 - SITE_4	-4.040	3.401	.760	-5.631	-2.448	-5.312	19	.000
Pair 7	SITE_2 - SITE_5	-2.578	4.899	2.191	-8.661	3.505	-1.177	4	.305
Pair 8	SITE_3 - SITE_4	-1.192	4.420	.988	-3.260	.876	-1.206	19	.243
Pair 9	SITE_3 - SITE_5	-3.984	1.658	.741	-6.042	-1.926	-5.374	4	.006
Pair 10	SITE_4 - SITE_5	1.280	2.809	1.256	-2.208	4.768	1.019	4	.366

T-Test Y (B Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	10.858	18	1.887	.445
	SITE_2	10.663	18	.846	.199
Pair 2	SITE_1	10.858	18	1.887	.445
	SITE_3	6.441	18	3.310	.780
Pair 3	SITE_1	10.858	18	1.887	.445
	SITE_4	5.708	18	2.337	.551
Pair 4	SITE_1	11.106	5	2.832	1.266
	SITE_5	8.242	5	2.041	.913
Pair 5	SITE_2	10.645	19	.826	.189
	SITE_3	6.370	19	3.232	.741
Pair 6	SITE_2	10.645	19	.826	.189
	SITE_4	5.838	19	2.341	.537
Pair 7	SITE_2	10.236	5	.796	.356
	SITE_5	8.242	5	2.041	.913
Pair 8	SITE_3	6.370	19	3.232	.741
	SITE_4	5.838	19	2.341	.537
Pair 9	SITE_3	9.414	5	1.665	.745
	SITE_5	8.242	5	2.041	.913

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	.204	.416
Pair 2	SITE_1 & SITE_3	18	.264	.289
Pair 3	SITE_1 & SITE_4	18	-.339	.169
Pair 4	SITE_1 & SITE_5	5	.203	.743
Pair 5	SITE_2 & SITE_3	19	-.238	.326
Pair 6	SITE_2 & SITE_4	19	-.142	.561
Pair 7	SITE_2 & SITE_5	5	.362	.550
Pair 8	SITE_3 & SITE_4	19	-.265	.273
Pair 9	SITE_3 & SITE_5	5	-.804	.101

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	.194	1.904	.449	-.752	1.141	.433	17	.670
Pair 2	SITE_1 - SITE_3	4.417	3.349	.789	2.752	6.083	5.596	17	.000
Pair 3	SITE_1 - SITE_4	5.150	3.466	.817	3.427	6.873	6.305	17	.000
Pair 4	SITE_1 - SITE_5	2.864	3.137	1.403	-1.031	6.759	2.042	4	.111
Pair 5	SITE_2 - SITE_3	4.275	3.521	.808	2.578	5.972	5.293	18	.000
Pair 6	SITE_2 - SITE_4	4.807	2.591	.594	3.559	6.056	8.089	18	.000
Pair 7	SITE_2 - SITE_5	1.994	1.904	.852	-.370	4.358	2.342	4	.079
Pair 8	SITE_3 - SITE_4	.532	4.464	1.024	-1.619	2.684	.520	18	.610
Pair 9	SITE_3 - SITE_5	1.172	3.522	1.575	-3.202	5.546	.744	4	.498

T-Test Y (A Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	9.821	20	1.165	.260
	SITE_2	10.610	20	.626	.140
Pair 2	SITE_1	9.821	20	1.165	.260
	SITE_3	9.512	20	1.663	.372
Pair 3	SITE_1	9.833	19	1.195	.274
	SITE_4	7.485	19	2.878	.660
Pair 4	SITE_1	9.604	5	1.902	.851
	SITE_5	5.860	5	3.956	1.769
Pair 5	SITE_2	10.610	20	.626	.140
	SITE_3	9.512	20	1.663	.372
Pair 6	SITE_2	10.635	19	.632	.145
	SITE_4	7.485	19	2.878	.660
Pair 7	SITE_2	11.076	5	.623	.279
	SITE_5	5.860	5	3.956	1.769
Pair 8	SITE_3	9.465	19	1.695	.389
	SITE_4	7.485	19	2.878	.660
Pair 9	SITE_3	8.232	5	1.760	.787
	SITE_5	5.860	5	3.956	1.769
Pair 10	SITE_4	9.014	5	1.080	.483
	SITE_5	5.860	5	3.956	1.769

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	-.408	.074
Pair 2	SITE_1 & SITE_3	20	.051	.830
Pair 3	SITE_1 & SITE_4	19	.203	.404
Pair 4	SITE_1 & SITE_5	5	-.536	.352
Pair 5	SITE_2 & SITE_3	20	-.386	.092
Pair 6	SITE_2 & SITE_4	19	.056	.819
Pair 7	SITE_2 & SITE_5	5	.216	.727
Pair 8	SITE_3 & SITE_4	19	-.228	.349
Pair 9	SITE_3 & SITE_5	5	.498	.393
Pair 10	SITE_4 & SITE_5	5	.980	.003

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper			
Pair 1	SITE_1 - SITE_2	-.789	1.531	.342	-1.505	-7.3E-02	-2.305	19	.033
Pair 2	SITE_1 - SITE_3	.308	1.981	.443	-.619	1.236	.696	19	.495
Pair 3	SITE_1 - SITE_4	2.348	2.883	.661	.958	3.737	3.550	18	.002
Pair 4	SITE_1 - SITE_5	3.744	5.229	2.338	-2.748	10.236	1.601	4	.185
Pair 5	SITE_2 - SITE_3	1.098	1.991	.445	.166	2.029	2.466	19	.023
Pair 6	SITE_2 - SITE_4	3.149	2.911	.668	1.746	4.553	4.716	18	.000
Pair 7	SITE_2 - SITE_5	5.216	3.870	1.731	.411	10.021	3.014	4	.039
Pair 8	SITE_3 - SITE_4	1.980	3.657	.839	.217	3.743	2.360	18	.030
Pair 9	SITE_3 - SITE_5	2.372	3.438	1.537	-1.897	6.641	1.543	4	.198
Pair 10	SITE_4 - SITE_5	3.154	2.906	1.300	-.454	6.762	2.427	4	.072

T-Test Rb (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	38.145	20	8.116	1.815
	SITE_2	21.999	20	11.444	2.559
Pair 2	SITE_1	38.145	20	8.116	1.815
	SITE_3	39.214	20	11.707	2.618
Pair 3	SITE_1	38.145	20	8.116	1.815
	SITE_4	59.062	20	10.744	2.402
Pair 4	SITE_1	40.014	5	8.563	3.830
	SITE_5	48.696	5	5.568	2.490
Pair 5	SITE_2	21.999	20	11.444	2.559
	SITE_3	39.214	20	11.707	2.618
Pair 6	SITE_2	21.999	20	11.444	2.559
	SITE_4	59.062	20	10.744	2.402
Pair 7	SITE_2	25.680	5	11.363	5.082
	SITE_5	48.696	5	5.568	2.490
Pair 8	SITE_3	39.214	20	11.707	2.618
	SITE_4	59.062	20	10.744	2.402
Pair 9	SITE_3	28.088	5	3.620	1.619
	SITE_5	48.696	5	5.568	2.490
Pair 10	SITE_4	58.980	5	3.424	1.531
	SITE_5	48.696	5	5.568	2.490

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.347	.134
Pair 2	SITE_1 & SITE_3	20	-.381	.097
Pair 3	SITE_1 & SITE_4	20	.385	.093
Pair 4	SITE_1 & SITE_5	5	-.310	.612
Pair 5	SITE_2 & SITE_3	20	-.337	.147
Pair 6	SITE_2 & SITE_4	20	.205	.385
Pair 7	SITE_2 & SITE_5	5	-.540	.348
Pair 8	SITE_3 & SITE_4	20	-.298	.201
Pair 9	SITE_3 & SITE_5	5	.361	.550
Pair 10	SITE_4 & SITE_5	5	.284	.643

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	16.146	11.507	2.573	10.761	21.531	6.275	19	.000
Pair 2	SITE_1 - SITE_3	-1.069	16.593	3.710	-8.835	6.697	-.288	19	.776
Pair 3	SITE_1 - SITE_4	-20.917	10.681	2.388	-25.916	-15.919	-8.758	19	.000
Pair 4	SITE_1 - SITE_5	-8.682	11.571	5.175	-23.049	5.685	-1.678	4	.169
Pair 5	SITE_2 - SITE_3	-17.215	18.928	4.232	-26.073	-8.357	-4.067	19	.001
Pair 6	SITE_2 - SITE_4	-37.063	13.996	3.130	-43.614	-30.513	-11.843	19	.000
Pair 7	SITE_2 - SITE_5	-23.016	15.113	6.759	-41.781	-4.251	-3.405	4	.027
Pair 8	SITE_3 - SITE_4	-19.848	18.099	4.047	-28.319	-11.378	-4.904	19	.000
Pair 9	SITE_3 - SITE_5	-20.608	5.435	2.430	-27.356	-13.860	-8.479	4	.001
Pair 10	SITE_4 - SITE_5	10.284	5.647	2.525	3.272	17.296	4.072	4	.015

T-Test Rb (B Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	53.359	18	4.217	.994
	SITE_2	44.024	18	5.987	1.411
Pair 2	SITE_1	53.359	18	4.217	.994
	SITE_3	33.684	18	11.535	2.719
Pair 3	SITE_1	53.359	18	4.217	.994
	SITE_4	49.724	18	15.735	3.709
Pair 4	SITE_1	51.704	5	7.522	3.364
	SITE_5	49.402	5	6.535	2.923
Pair 5	SITE_2	43.925	19	5.835	1.339
	SITE_3	34.231	19	11.461	2.629
Pair 6	SITE_2	43.925	19	5.835	1.339
	SITE_4	50.765	19	15.950	3.659
Pair 7	SITE_2	43.940	5	5.370	2.402
	SITE_5	49.402	5	6.535	2.923
Pair 8	SITE_3	34.231	19	11.461	2.629
	SITE_4	50.765	19	15.950	3.659
Pair 9	SITE_3	46.126	5	1.001	.448
	SITE_5	49.402	5	6.535	2.923
Pair 10	SITE_4	35.564	5	7.491	3.350
	SITE_5	49.402	5	6.535	2.923

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	-.185	.462
Pair 2	SITE_1 & SITE_3	18	-.159	.529
Pair 3	SITE_1 & SITE_4	18	.053	.834
Pair 4	SITE_1 & SITE_5	5	.023	.971
Pair 5	SITE_2 & SITE_3	19	-.140	.567
Pair 6	SITE_2 & SITE_4	19	-.261	.280
Pair 7	SITE_2 & SITE_5	5	.937	.019
Pair 8	SITE_3 & SITE_4	19	-.316	.188
Pair 9	SITE_3 & SITE_5	5	.382	.525
Pair 10	SITE_4 & SITE_5	5	-.281	.647

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	9.335	7.937	1.871	5.388	13.282	4.990	17	.000
Pair 2	SITE_1 - SITE_3	19.675	12.896	3.040	13.262	26.088	6.473	17	.000
Pair 3	SITE_1 - SITE_4	3.634	16.073	3.788	-4.358	11.627	.959	17	.351
Pair 4	SITE_1 - SITE_5	2.302	9.853	4.406	-9.932	14.536	.522	4	.629
Pair 5	SITE_2 - SITE_3	9.694	13.571	3.113	3.153	16.235	3.114	18	.006
Pair 6	SITE_2 - SITE_4	-6.840	18.358	4.212	-15.688	2.008	-1.624	18	.122
Pair 7	SITE_2 - SITE_5	-5.462	2.404	1.075	-8.447	-2.477	-5.081	4	.007
Pair 8	SITE_3 - SITE_4	-16.534	22.386	5.136	-27.323	-5.744	-3.219	18	.005
Pair 9	SITE_3 - SITE_5	-3.276	6.221	2.782	-11.001	4.449	-1.177	4	.304
Pair 10	SITE_4 - SITE_5	-13.838	11.239	5.026	-27.793	.117	-2.753	4	.051

T-Test Rb (A Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	50.013	20	3.660	.818
	SITE_2	46.269	20	5.226	1.169
Pair 2	SITE_1	50.013	20	3.660	.818
	SITE_3	46.376	20	3.097	.693
Pair 3	SITE_1	50.087	19	3.745	.859
	SITE_4	52.382	19	12.594	2.889
Pair 4	SITE_1	46.818	5	3.415	1.527
	SITE_5	43.622	5	22.293	9.970
Pair 5	SITE_2	46.269	20	5.226	1.169
	SITE_3	46.376	20	3.097	.693
Pair 6	SITE_2	46.301	19	5.367	1.231
	SITE_4	52.382	19	12.594	2.889
Pair 7	SITE_2	48.184	5	1.295	.579
	SITE_5	43.622	5	22.293	9.970
Pair 8	SITE_3	46.252	19	3.130	.718
	SITE_4	52.382	19	12.594	2.889
Pair 9	SITE_3	44.262	5	2.157	.965
	SITE_5	43.622	5	22.293	9.970
Pair 10	SITE_4	51.984	5	4.332	1.937
	SITE_5	43.622	5	22.293	9.970

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	-.015	.951
Pair 2	SITE_1 & SITE_3	20	-.142	.551
Pair 3	SITE_1 & SITE_4	19	.177	.468
Pair 4	SITE_1 & SITE_5	5	-.541	.347
Pair 5	SITE_2 & SITE_3	20	-.290	.215
Pair 6	SITE_2 & SITE_4	19	.235	.333
Pair 7	SITE_2 & SITE_5	5	.583	.302
Pair 8	SITE_3 & SITE_4	19	-.228	.347
Pair 9	SITE_3 & SITE_5	5	.486	.406
Pair 10	SITE_4 & SITE_5	5	-.451	.446

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	3.744	6.424	1.436	.738	6.751	2.607	19	.017
Pair 2	SITE_1 - SITE_3	3.637	5.119	1.145	1.242	6.033	3.178	19	.005
Pair 3	SITE_1 - SITE_4	-2.294	12.487	2.865	-8.313	3.724	-.801	18	.434
Pair 4	SITE_1 - SITE_5	3.196	24.309	10.871	-26.988	33.380	.294	4	.783
Pair 5	SITE_2 - SITE_3	-.107	6.804	1.521	-3.291	3.077	-.070	19	.945
Pair 6	SITE_2 - SITE_4	-6.081	12.476	2.862	-12.094	-6.8E-02	-2.125	18	.048
Pair 7	SITE_2 - SITE_5	4.562	21.564	9.644	-22.213	31.337	.473	4	.661
Pair 8	SITE_3 - SITE_4	-6.130	13.653	3.132	-12.711	.451	-1.957	18	.066
Pair 9	SITE_3 - SITE_5	.640	21.327	9.538	-25.841	27.121	.067	4	.950
Pair 10	SITE_4 - SITE_5	8.362	24.555	10.981	-22.127	38.851	.761	4	.489

T-Test Zn (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	92.677	20	32.645	7.300
	SITE_2	303.325	20	121.546	27.179
Pair 2	SITE_1	92.677	20	32.645	7.300
	SITE_3	110.342	20	60.777	13.590
Pair 3	SITE_1	92.677	20	32.645	7.300
	SITE_4	202.368	20	57.969	12.962
Pair 4	SITE_1	102.428	5	34.930	15.621
	SITE_5	169.430	5	40.515	18.119
Pair 5	SITE_2	303.325	20	121.546	27.179
	SITE_3	110.342	20	60.777	13.590
Pair 6	SITE_2	303.325	20	121.546	27.179
	SITE_4	202.368	20	57.969	12.962
Pair 7	SITE_2	225.816	5	69.921	31.270
	SITE_5	169.430	5	40.515	18.119
Pair 8	SITE_3	110.342	20	60.777	13.590
	SITE_4	202.368	20	57.969	12.962
Pair 9	SITE_3	82.824	5	23.597	10.553
	SITE_5	169.430	5	40.515	18.119
Pair 10	SITE_4	216.380	5	38.909	17.401
	SITE_5	169.430	5	40.515	18.119

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	-.019	.935
Pair 2	SITE_1 & SITE_3	20	-.362	.117
Pair 3	SITE_1 & SITE_4	20	-.151	.526
Pair 4	SITE_1 & SITE_5	5	-.468	.427
Pair 5	SITE_2 & SITE_3	20	-.172	.469
Pair 6	SITE_2 & SITE_4	20	-.195	.410
Pair 7	SITE_2 & SITE_5	5	.728	.163
Pair 8	SITE_3 & SITE_4	20	-.171	.470
Pair 9	SITE_3 & SITE_5	5	-.563	.323
Pair 10	SITE_4 & SITE_5	5	-.299	.624

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-210.647	126.466	28.279	-269.835	-151.460	-7.449	19	.000
Pair 2	SITE_1 - SITE_3	-17.665	78.720	17.602	-54.507	19.177	-1.004	19	.328
Pair 3	SITE_1 - SITE_4	-109.691	70.687	15.806	-142.773	-76.609	-6.940	19	.000
Pair 4	SITE_1 - SITE_5	-67.002	64.692	28.931	-147.327	13.323	-2.316	4	.082
Pair 5	SITE_2 - SITE_3	192.983	144.933	32.408	125.152	260.813	5.955	19	.000
Pair 6	SITE_2 - SITE_4	100.957	144.499	32.311	33.329	168.584	3.125	19	.006
Pair 7	SITE_2 - SITE_5	56.386	49.031	21.927	-4.494	117.266	2.572	4	.062
Pair 8	SITE_3 - SITE_4	-92.026	90.895	20.325	-134.566	-49.486	-4.528	19	.000
Pair 9	SITE_3 - SITE_5	-86.606	57.233	25.595	-157.670	-15.542	-3.384	4	.028
Pair 10	SITE_4 - SITE_5	46.950	64.028	28.634	-32.551	126.451	1.640	4	.176

T-Test Zn (B Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	34.081	18	16.030	3.778
	SITE_2	137.323	18	41.118	9.692
Pair 2	SITE_1	34.081	18	16.030	3.778
	SITE_3	24.813	18	3.853	.908
Pair 3	SITE_1	34.081	18	16.030	3.778
	SITE_4	85.595	18	27.363	6.450
Pair 4	SITE_1	49.680	5	25.243	11.289
	SITE_5	91.468	5	13.651	6.105
Pair 5	SITE_2	134.441	19	41.888	9.610
	SITE_3	24.876	19	3.755	.861
Pair 6	SITE_2	134.441	19	41.888	9.610
	SITE_4	85.309	19	26.621	6.107
Pair 7	SITE_2	137.294	5	51.471	23.019
	SITE_5	91.468	5	13.651	6.105
Pair 8	SITE_3	24.876	19	3.755	.861
	SITE_4	85.309	19	26.621	6.107
Pair 9	SITE_3	25.074	5	5.154	2.305
	SITE_5	91.468	5	13.651	6.105
Pair 10	SITE_4	85.754	5	6.813	3.047
	SITE_5	91.468	5	13.651	6.105

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	.424	.079
Pair 2	SITE_1 & SITE_3	18	.133	.599
Pair 3	SITE_1 & SITE_4	18	.077	.761
Pair 4	SITE_1 & SITE_5	5	.988	.002
Pair 5	SITE_2 & SITE_3	19	.086	.728
Pair 6	SITE_2 & SITE_4	19	-.021	.931
Pair 7	SITE_2 & SITE_5	5	.814	.093
Pair 8	SITE_3 & SITE_4	19	.202	.408
Pair 9	SITE_3 & SITE_5	5	.256	.678
Pair 10	SITE_4 & SITE_5	5	.192	.757

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-103.242	37.258	8.782	-121.770	-84.714	-11.756	17	.000
Pair 2	SITE_1 - SITE_3	9.267	15.981	3.767	1.320	17.214	2.460	17	.025
Pair 3	SITE_1 - SITE_4	-51.514	30.627	7.219	-66.745	-36.284	-7.136	17	.000
Pair 4	SITE_1 - SITE_5	-41.788	11.948	5.343	-56.623	-26.953	-7.821	4	.001
Pair 5	SITE_2 - SITE_3	109.565	41.734	9.575	89.449	129.680	11.443	18	.000
Pair 6	SITE_2 - SITE_4	49.132	50.111	11.496	24.979	73.284	4.274	18	.000
Pair 7	SITE_2 - SITE_5	45.826	41.126	18.392	-5.239	96.891	2.492	4	.067
Pair 8	SITE_3 - SITE_4	-60.433	26.124	5.993	-73.024	-47.842	-10.084	18	.000
Pair 9	SITE_3 - SITE_5	-66.394	13.300	5.948	-82.909	-49.879	-11.162	4	.000
Pair 10	SITE_4 - SITE_5	-5.714	14.038	6.278	-23.145	11.717	-.910	4	.414

T-Test Zn (A Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	39.501	20	18.786	4.201
	SITE_2	151.577	20	48.101	10.756
Pair 2	SITE_1	39.501	20	18.786	4.201
	SITE_3	31.845	20	4.091	.915
Pair 3	SITE_1	39.797	19	19.253	4.417
	SITE_4	84.382	19	34.579	7.933
Pair 4	SITE_1	58.878	5	31.300	13.998
	SITE_5	84.802	5	17.834	7.975
Pair 5	SITE_2	151.577	20	48.101	10.756
	SITE_3	31.845	20	4.091	.915
Pair 6	SITE_2	151.430	19	49.415	11.336
	SITE_4	84.382	19	34.579	7.933
Pair 7	SITE_2	119.360	5	49.691	22.222
	SITE_5	84.802	5	17.834	7.975
Pair 8	SITE_3	32.052	19	4.095	.939
	SITE_4	84.382	19	34.579	7.933
Pair 9	SITE_3	30.702	5	3.152	1.410
	SITE_5	84.802	5	17.834	7.975
Pair 10	SITE_4	68.090	5	19.330	8.645
	SITE_5	84.802	5	17.834	7.975

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.027	.909
Pair 2	SITE_1 & SITE_3	20	-.234	.321
Pair 3	SITE_1 & SITE_4	19	.010	.968
Pair 4	SITE_1 & SITE_5	5	-.078	.901
Pair 5	SITE_2 & SITE_3	20	.053	.825
Pair 6	SITE_2 & SITE_4	19	.472	.041
Pair 7	SITE_2 & SITE_5	5	-.123	.844
Pair 8	SITE_3 & SITE_4	19	.019	.939
Pair 9	SITE_3 & SITE_5	5	.417	.485
Pair 10	SITE_4 & SITE_5	5	.070	.911

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-112.076	51.161	11.440	-136.020	-88.132	-9.797	19	.000
Pair 2	SITE_1 - SITE_3	7.656	20.139	4.503	-1.770	17.081	1.700	19	.105
Pair 3	SITE_1 - SITE_4	-44.585	39.410	9.041	-63.580	-25.590	-4.931	18	.000
Pair 4	SITE_1 - SITE_5	-25.924	37.208	16.640	-72.123	20.275	-1.558	4	.194
Pair 5	SITE_2 - SITE_3	119.732	48.059	10.746	97.239	142.224	11.142	19	.000
Pair 6	SITE_2 - SITE_4	67.048	44.987	10.321	45.365	88.731	6.496	18	.000
Pair 7	SITE_2 - SITE_5	34.558	54.814	24.514	-33.503	102.619	1.410	4	.231
Pair 8	SITE_3 - SITE_4	-52.331	34.744	7.971	-69.076	-35.585	-6.565	18	.000
Pair 9	SITE_3 - SITE_5	-54.100	16.765	7.498	-74.917	-33.283	-7.216	4	.002
Pair 10	SITE_4 - SITE_5	-16.712	25.368	11.345	-48.211	14.787	-1.473	4	.215

T- test Cu Litter

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	134.491	20	78.927	17.649
	SITE_2	250.174	20	160.617	35.915
Pair 2	SITE_1	134.491	20	78.927	17.649
	SITE_3	29.243	20	5.684	1.271
Pair 3	SITE_1	134.491	20	78.927	17.649
	SITE_4	90.101	20	30.736	6.873
Pair 4	SITE_1	215.140	5	124.367	55.619
	SITE_5	61.180	5	9.180	4.105
Pair 5	SITE_2	250.174	20	160.617	35.915
	SITE_3	29.243	20	5.684	1.271
Pair 6	SITE_2	250.174	20	160.617	35.915
	SITE_4	90.101	20	30.736	6.873
Pair 7	SITE_2	390.848	5	83.345	37.273
	SITE_5	61.180	5	9.180	4.105
Pair 8	SITE_3	29.243	20	5.684	1.271
	SITE_4	90.101	20	30.736	6.873
Pair 9	SITE_3	28.572	5	6.161	2.755
	SITE_5	61.180	5	9.180	4.105
Pair 10	SITE_4	101.836	5	16.469	7.365
	SITE_5	61.180	5	9.180	4.105

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.279	.233
Pair 2	SITE_1 & SITE_3	20	-.202	.394
Pair 3	SITE_1 & SITE_4	20	.467	.038
Pair 4	SITE_1 & SITE_5	5	.029	.963
Pair 5	SITE_2 & SITE_3	20	-.363	.116
Pair 6	SITE_2 & SITE_4	20	-.288	.218
Pair 7	SITE_2 & SITE_5	5	-.685	.202
Pair 8	SITE_3 & SITE_4	20	.154	.516
Pair 9	SITE_3 & SITE_5	5	-.123	.844
Pair 10	SITE_4 & SITE_5	5	-.156	.802

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-115.683	157.955	35.320	-189.608	-41.758	-3.275	19	.004
Pair 2	SITE_1 - SITE_3	105.248	80.266	17.948	67.682	142.814	5.864	19	.000
Pair 3	SITE_1 - SITE_4	44.390	70.059	15.666	11.601	77.179	2.834	19	.011
Pair 4	SITE_1 - SITE_5	153.960	124.438	55.651	-.551	308.471	2.767	4	.051
Pair 5	SITE_2 - SITE_3	220.931	162.764	36.395	144.755	297.107	6.070	19	.000
Pair 6	SITE_2 - SITE_4	160.073	172.015	38.464	79.567	240.579	4.162	19	.001
Pair 7	SITE_2 - SITE_5	329.668	89.879	40.195	218.069	441.267	8.202	4	.001
Pair 8	SITE_3 - SITE_4	-60.858	30.381	6.793	-75.077	-46.639	-8.958	19	.000
Pair 9	SITE_3 - SITE_5	-32.608	11.667	5.217	-47.094	-18.122	-6.250	4	.003
Pair 10	SITE_4 - SITE_5	40.656	20.066	8.974	15.741	65.571	4.531	4	.011

T-Test Cu (B Horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	26.270	18	44.216	10.422
	SITE_2	48.222	18	19.612	4.623
Pair 2	SITE_1	26.270	18	44.216	10.422
	SITE_3	5.971	18	2.246	.529
Pair 3	SITE_1	26.270	18	44.216	10.422
	SITE_4	38.916	18	28.282	6.666
Pair 4	SITE_1	66.478	5	73.506	32.873
	SITE_5	19.902	5	7.268	3.250
Pair 5	SITE_2	48.305	19	19.063	4.373
	SITE_3	6.165	19	2.341	.537
Pair 6	SITE_2	48.305	19	19.063	4.373
	SITE_4	38.240	19	27.642	6.342
Pair 7	SITE_2	37.844	5	20.731	9.271
	SITE_5	19.902	5	7.268	3.250
Pair 8	SITE_3	6.165	19	2.341	.537
	SITE_4	38.240	19	27.642	6.342
Pair 9	SITE_3	4.320	5	1.336	.597
	SITE_5	19.902	5	7.268	3.250
Pair 10	SITE_4	34.704	5	20.627	9.225
	SITE_5	19.902	5	7.268	3.250

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	.163	.518
Pair 2	SITE_1 & SITE_3	18	-.357	.146
Pair 3	SITE_1 & SITE_4	18	.186	.459
Pair 4	SITE_1 & SITE_5	5	-.070	.911
Pair 5	SITE_2 & SITE_3	19	.154	.529
Pair 6	SITE_2 & SITE_4	19	-.007	.977
Pair 7	SITE_2 & SITE_5	5	-.161	.796
Pair 8	SITE_3 & SITE_4	19	.252	.299
Pair 9	SITE_3 & SITE_5	5	.896	.039
Pair 10	SITE_4 & SITE_5	5	-.601	.284

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper			
Pair 1	SITE_1 - SITE_2	-21.952	45.349	10.689	-44.503	.600	-2.054	17	.056
Pair 2	SITE_1 - SITE_3	20.299	45.066	10.622	-2.111	42.710	1.911	17	.073
Pair 3	SITE_1 - SITE_4	-12.646	47.846	11.277	-36.439	11.147	-1.121	17	.278
Pair 4	SITE_1 - SITE_5	46.576	74.371	33.260	-45.767	138.919	1.400	4	.234
Pair 5	SITE_2 - SITE_3	42.141	18.845	4.323	33.058	51.223	9.747	18	.000
Pair 6	SITE_2 - SITE_4	10.065	33.690	7.729	-6.173	26.303	1.302	18	.209
Pair 7	SITE_2 - SITE_5	17.942	23.047	10.307	-10.675	46.559	1.741	4	.157
Pair 8	SITE_3 - SITE_4	-32.075	27.148	6.228	-45.160	-18.990	-5.150	18	.000
Pair 9	SITE_3 - SITE_5	-15.582	6.099	2.728	-23.155	-8.009	-5.712	4	.005
Pair 10	SITE_4 - SITE_5	14.802	25.662	11.476	-17.061	46.665	1.290	4	.267

T-Test Cu A horizon

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	107.149	19	32.698	7.501
	SITE_2	190.900	19	115.140	26.415
Pair 2	SITE_1	108.410	20	32.321	7.227
	SITE_3	20.924	20	5.839	1.306
Pair 3	SITE_1	109.195	19	33.010	7.573
	SITE_4	94.479	19	44.600	10.232
Pair 4	SITE_1	132.554	5	27.393	12.251
	SITE_5	54.400	5	10.698	4.784
Pair 5	SITE_2	194.154	20	113.010	25.270
	SITE_3	20.593	20	5.916	1.323
Pair 6	SITE_2	194.626	18	117.294	27.646
	SITE_4	96.458	18	45.026	10.613
Pair 7	SITE_2	214.045	4	193.969	96.984
	SITE_5	57.750	4	8.819	4.409
Pair 8	SITE_3	21.065	19	5.964	1.368
	SITE_4	94.479	19	44.600	10.232
Pair 9	SITE_3	18.240	5	8.921	3.989
	SITE_5	54.400	5	10.698	4.784
Pair 10	SITE_4	78.528	5	24.398	10.911
	SITE_5	54.400	5	10.698	4.784

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	19	-.582	.009
Pair 2	SITE_1 & SITE_3	20	.063	.793
Pair 3	SITE_1 & SITE_4	19	.001	.998
Pair 4	SITE_1 & SITE_5	5	-.260	.672
Pair 5	SITE_2 & SITE_3	20	-.371	.108
Pair 6	SITE_2 & SITE_4	18	-.137	.588
Pair 7	SITE_2 & SITE_5	4	.663	.337
Pair 8	SITE_3 & SITE_4	19	.471	.042
Pair 9	SITE_3 & SITE_5	5	-.356	.556
Pair 10	SITE_4 & SITE_5	5	-.285	.642

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-83.751	136.785	31.381	-149.679	-17.822	-2.669	18	.016
Pair 2	SITE_1 - SITE_3	87.486	32.481	7.263	72.284	102.687	12.045	19	.000
Pair 3	SITE_1 - SITE_4	14.715	55.473	12.726	-12.022	41.452	1.156	18	.263
Pair 4	SITE_1 - SITE_5	78.154	31.898	14.265	38.547	117.761	5.479	4	.005
Pair 5	SITE_2 - SITE_3	173.561	115.334	25.789	119.583	227.538	6.730	19	.000
Pair 6	SITE_2 - SITE_4	98.167	131.271	30.941	32.888	163.447	3.173	17	.006
Pair 7	SITE_2 - SITE_5	156.295	188.240	94.120	-143.238	455.828	1.661	3	.195
Pair 8	SITE_3 - SITE_4	-73.414	42.122	9.663	-93.716	-53.112	-7.597	18	.000
Pair 9	SITE_3 - SITE_5	-36.160	16.187	7.239	-56.259	-16.061	-4.995	4	.008
Pair 10	SITE_4 - SITE_5	24.128	29.298	13.102	-12.250	60.506	1.842	4	.139

T-Test Ni Litter

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	171.871	20	77.195	17.261
	SITE_2	307.464	20	131.220	29.342
Pair 2	SITE_1	171.871	20	77.195	17.261
	SITE_3	54.857	20	9.166	2.050
Pair 3	SITE_1	171.871	20	77.195	17.261
	SITE_4	156.335	20	30.692	6.863
Pair 4	SITE_1	235.576	5	126.787	56.701
	SITE_5	90.632	5	7.719	3.452
Pair 5	SITE_2	307.464	20	131.220	29.342
	SITE_3	54.857	20	9.166	2.050
Pair 6	SITE_2	307.464	20	131.220	29.342
	SITE_4	156.335	20	30.692	6.863
Pair 7	SITE_2	377.716	5	48.544	21.710
	SITE_5	90.632	5	7.719	3.452
Pair 8	SITE_3	54.857	20	9.166	2.050
	SITE_4	156.335	20	30.692	6.863
Pair 9	SITE_3	49.948	5	7.605	3.401
	SITE_5	90.632	5	7.719	3.452
Pair 10	SITE_4	177.614	5	7.838	3.505
	SITE_5	90.632	5	7.719	3.452

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.021	.932
Pair 2	SITE_1 & SITE_3	20	-.581	.007
Pair 3	SITE_1 & SITE_4	20	.353	.127
Pair 4	SITE_1 & SITE_5	5	-.301	.622
Pair 5	SITE_2 & SITE_3	20	-.153	.520
Pair 6	SITE_2 & SITE_4	20	-.337	.146
Pair 7	SITE_2 & SITE_5	5	-.207	.739
Pair 8	SITE_3 & SITE_4	20	-.190	.421
Pair 9	SITE_3 & SITE_5	5	-.368	.542
Pair 10	SITE_4 & SITE_5	5	-.843	.073

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-135.593	150.870	33.736	-206.202	-64.984	-4.019	19	.001
Pair 2	SITE_1 - SITE_3	117.014	82.855	18.527	78.236	155.791	6.316	19	.000
Pair 3	SITE_1 - SITE_4	15.537	72.320	16.171	-18.310	49.383	.961	19	.349
Pair 4	SITE_1 - SITE_5	144.944	129.323	57.835	-15.632	305.520	2.506	4	.066
Pair 5	SITE_2 - SITE_3	252.607	132.931	29.724	190.393	314.820	8.498	19	.000
Pair 6	SITE_2 - SITE_4	151.130	144.479	32.307	83.511	218.748	4.678	19	.000
Pair 7	SITE_2 - SITE_5	287.084	50.704	22.676	224.126	350.042	12.660	4	.000
Pair 8	SITE_3 - SITE_4	-101.477	33.662	7.527	-117.231	-85.723	-13.482	19	.000
Pair 9	SITE_3 - SITE_5	-40.684	12.674	5.668	-56.421	-24.947	-7.178	4	.002
Pair 10	SITE_4 - SITE_5	86.982	14.934	6.679	68.439	105.525	13.024	4	.000

T-Test Ni B horizon

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	49.585	18	47.744	11.253
	SITE_2	73.271	18	19.033	4.486
Pair 2	SITE_1	49.585	18	47.744	11.253
	SITE_3	21.286	18	4.173	.984
Pair 3	SITE_1	49.585	18	47.744	11.253
	SITE_4	48.546	18	25.934	6.113
Pair 4	SITE_1	94.356	5	77.939	34.856
	SITE_5	38.100	5	10.129	4.530
Pair 5	SITE_2	75.566	19	21.029	4.824
	SITE_3	21.214	19	4.067	.933
Pair 6	SITE_2	75.566	19	21.029	4.824
	SITE_4	47.928	19	25.347	5.815
Pair 7	SITE_2	70.354	5	19.881	8.891
	SITE_5	38.100	5	10.129	4.530
Pair 8	SITE_3	21.214	19	4.067	.933
	SITE_4	47.928	19	25.347	5.815
Pair 9	SITE_3	18.562	5	5.227	2.338
	SITE_5	38.100	5	10.129	4.530
Pair 10	SITE_4	42.374	5	6.900	3.086
	SITE_5	38.100	5	10.129	4.530

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	.272	.275
Pair 2	SITE_1 & SITE_3	18	-.434	.072
Pair 3	SITE_1 & SITE_4	18	.008	.975
Pair 4	SITE_1 & SITE_5	5	.134	.830
Pair 5	SITE_2 & SITE_3	19	-.278	.249
Pair 6	SITE_2 & SITE_4	19	-.036	.883
Pair 7	SITE_2 & SITE_5	5	-.327	.591
Pair 8	SITE_3 & SITE_4	19	-.137	.575
Pair 9	SITE_3 & SITE_5	5	-.529	.359
Pair 10	SITE_4 & SITE_5	5	-.102	.870

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-23.686	46.337	10.922	-46.729	-.643	-2.169	17	.045
Pair 2	SITE_1 - SITE_3	28.299	49.698	11.714	3.585	53.014	2.416	17	.027
Pair 3	SITE_1 - SITE_4	1.039	54.153	12.764	-25.890	27.969	.081	17	.936
Pair 4	SITE_1 - SITE_5	56.256	77.236	34.541	-39.645	152.157	1.629	4	.179
Pair 5	SITE_2 - SITE_3	54.352	22.501	5.162	43.507	65.197	10.529	18	.000
Pair 6	SITE_2 - SITE_4	27.638	33.515	7.689	11.485	43.792	3.595	18	.002
Pair 7	SITE_2 - SITE_5	32.254	25.091	11.221	1.099	63.409	2.874	4	.045
Pair 8	SITE_3 - SITE_4	-26.714	26.216	6.014	-39.349	-14.078	-4.442	18	.000
Pair 9	SITE_3 - SITE_5	-19.538	13.636	6.098	-36.470	-2.606	-3.204	4	.033
Pair 10	SITE_4 - SITE_5	4.274	12.826	5.736	-11.651	20.199	.745	4	.498

T-Test Ni A horizon

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	131.352	20	40.163	8.981
	SITE_2	218.926	20	112.099	25.066
Pair 2	SITE_1	131.352	20	40.163	8.981
	SITE_3	34.175	20	6.491	1.452
Pair 3	SITE_1	133.275	19	40.306	9.247
	SITE_4	104.464	19	44.135	10.125
Pair 4	SITE_1	174.718	5	37.222	16.646
	SITE_5	56.684	5	11.339	5.071
Pair 5	SITE_2	218.926	20	112.099	25.066
	SITE_3	34.175	20	6.491	1.452
Pair 6	SITE_2	218.102	19	115.109	26.408
	SITE_4	104.464	19	44.135	10.125
Pair 7	SITE_2	293.608	5	197.094	88.143
	SITE_5	56.684	5	11.339	5.071
Pair 8	SITE_3	34.534	19	6.462	1.482
	SITE_4	104.464	19	44.135	10.125
Pair 9	SITE_3	32.260	5	7.458	3.335
	SITE_5	56.684	5	11.339	5.071
Pair 10	SITE_4	84.642	5	33.805	15.118
	SITE_5	56.684	5	11.339	5.071

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.172	.469
Pair 2	SITE_1 & SITE_3	20	.079	.741
Pair 3	SITE_1 & SITE_4	19	-.228	.349
Pair 4	SITE_1 & SITE_5	5	.452	.445
Pair 5	SITE_2 & SITE_3	20	-.043	.858
Pair 6	SITE_2 & SITE_4	19	-.182	.456
Pair 7	SITE_2 & SITE_5	5	.225	.716
Pair 8	SITE_3 & SITE_4	19	.464	.045
Pair 9	SITE_3 & SITE_5	5	.097	.877
Pair 10	SITE_4 & SITE_5	5	-.051	.935

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-87.574	112.399	25.133	-140.178	-34.970	-3.484	19	.002
Pair 2	SITE_1 - SITE_3	97.177	40.176	8.984	78.374	115.980	10.817	19	.000
Pair 3	SITE_1 - SITE_4	28.811	66.200	15.187	-3.096	60.718	1.897	18	.074
Pair 4	SITE_1 - SITE_5	118.034	33.654	15.050	76.247	159.821	7.843	4	.001
Pair 5	SITE_2 - SITE_3	184.751	112.564	25.170	132.069	237.433	7.340	19	.000
Pair 6	SITE_2 - SITE_4	113.638	130.563	29.953	50.709	176.567	3.794	18	.001
Pair 7	SITE_2 - SITE_5	236.924	194.854	87.142	-5.020	478.868	2.719	4	.053
Pair 8	SITE_3 - SITE_4	-69.929	41.533	9.528	-89.948	-49.911	-7.339	18	.000
Pair 9	SITE_3 - SITE_5	-24.424	12.954	5.793	-40.509	-8.339	-4.216	4	.014
Pair 10	SITE_4 - SITE_5	27.958	36.201	16.190	-16.992	72.908	1.727	4	.159

T-Test Mn (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	362.7400	20	148.1978	33.1380
	SITE_2	1300.563	20	576.1219	128.8248
Pair 2	SITE_1	362.7400	20	148.1978	33.1380
	SITE_3	212.4500	20	55.0228	12.3035
Pair 3	SITE_1	362.7400	20	148.1978	33.1380
	SITE_4	1393.533	20	411.5064	92.0156
Pair 4	SITE_1	328.9380	5	54.9220	24.5619
	SITE_5	1398.052	5	252.2832	112.8245
Pair 5	SITE_2	1300.563	20	576.1219	128.8248
	SITE_3	212.4500	20	55.0228	12.3035
Pair 6	SITE_2	1300.563	20	576.1219	128.8248
	SITE_4	1393.533	20	411.5064	92.0156
Pair 7	SITE_2	1148.992	5	420.3799	187.9996
	SITE_5	1398.052	5	252.2832	112.8245
Pair 8	SITE_3	212.4500	20	55.0228	12.3035
	SITE_4	1393.533	20	411.5064	92.0156
Pair 9	SITE_3	208.3380	5	27.0830	12.1119
	SITE_5	1398.052	5	252.2832	112.8245
Pair 10	SITE_4	1556.876	5	585.7273	261.9452
	SITE_5	1398.052	5	252.2832	112.8245

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	-.134	.574
Pair 2	SITE_1 & SITE_3	20	-.244	.300
Pair 3	SITE_1 & SITE_4	20	-.222	.347
Pair 4	SITE_1 & SITE_5	5	.113	.857
Pair 5	SITE_2 & SITE_3	20	-.220	.352
Pair 6	SITE_2 & SITE_4	20	.210	.375
Pair 7	SITE_2 & SITE_5	5	.382	.525
Pair 8	SITE_3 & SITE_4	20	-.058	.807
Pair 9	SITE_3 & SITE_5	5	-.379	.530
Pair 10	SITE_4 & SITE_5	5	-.152	.808

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-937.8235	613.7714	137.2435	-1225.08	-650.5696	-6.833	19	.000
Pair 2	SITE_1 - SITE_3	150.2900	170.2076	38.0596	70.6304	229.9496	3.949	19	.001
Pair 3	SITE_1 - SITE_4	-1030.79	467.2773	104.4864	-1249.49	-812.1005	-9.865	19	.000
Pair 4	SITE_1 - SITE_5	-1069.11	252.0615	112.7253	-1382.09	-756.1383	-9.484	4	.001
Pair 5	SITE_2 - SITE_3	1088.113	590.6632	132.0763	811.6746	1364.552	8.239	19	.000
Pair 6	SITE_2 - SITE_4	-92.9695	633.9327	141.7517	-389.6591	203.7201	-.656	19	.520
Pair 7	SITE_2 - SITE_5	-249.0600	399.0469	178.4592	-744.5422	246.4222	-1.396	4	.235
Pair 8	SITE_3 - SITE_4	-1181.08	418.3393	93.5435	-1376.87	-985.2942	-12.626	19	.000
Pair 9	SITE_3 - SITE_5	-1189.71	263.7311	117.9441	-1517.18	-862.2485	-10.087	4	.001
Pair 10	SITE_4 - SITE_5	158.8240	671.9678	300.5131	-675.5342	993.1822	.529	4	.625

T-Test Mn (B horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	241.5283	18	69.0517	16.2756
	SITE_2	1560.181	18	646.1352	152.2955
Pair 2	SITE_1	241.5283	18	69.0517	16.2756
	SITE_3	172.1850	18	16.8931	3.9817
Pair 3	SITE_1	241.5283	18	69.0517	16.2756
	SITE_4	408.9856	18	384.9658	90.7373
Pair 4	SITE_1	322.1340	5	83.9198	37.5301
	SITE_5	289.1400	5	22.6589	10.1333
Pair 5	SITE_2	1560.181	18	646.1352	152.2955
	SITE_3	172.1850	18	16.8931	3.9817
Pair 6	SITE_2	1560.181	18	646.1352	152.2955
	SITE_4	408.9856	18	384.9658	90.7373
Pair 7	SITE_2	1297.306	5	840.8210	376.0266
	SITE_5	289.1400	5	22.6589	10.1333
Pair 8	SITE_3	173.0658	19	16.8601	3.8680
	SITE_4	402.4874	19	375.1903	86.0745
Pair 9	SITE_3	169.1540	5	17.5533	7.8501
	SITE_5	289.1400	5	22.6589	10.1333
Pair 10	SITE_4	320.4900	5	127.7480	57.1307
	SITE_5	289.1400	5	22.6589	10.1333

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	.165	.514
Pair 2	SITE_1 & SITE_3	18	-.195	.438
Pair 3	SITE_1 & SITE_4	18	-.083	.743
Pair 4	SITE_1 & SITE_5	5	-.073	.907
Pair 5	SITE_2 & SITE_3	18	.099	.695
Pair 6	SITE_2 & SITE_4	18	-.048	.850
Pair 7	SITE_2 & SITE_5	5	.357	.555
Pair 8	SITE_3 & SITE_4	19	.232	.340
Pair 9	SITE_3 & SITE_5	5	.325	.594
Pair 10	SITE_4 & SITE_5	5	-.088	.888

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-1318.65	638.4083	150.4743	-1636.13	-1001.18	-8.763	17	.000
Pair 2	SITE_1 - SITE_3	69.3433	74.2163	17.4930	32.4364	106.2502	3.964	17	.001
Pair 3	SITE_1 - SITE_4	-167.4572	396.7237	93.5087	-364.7433	29.8288	-1.791	17	.091
Pair 4	SITE_1 - SITE_5	32.9940	88.5097	39.5828	-76.9054	142.8934	.834	4	.451
Pair 5	SITE_2 - SITE_3	1387.996	644.6750	151.9513	1067.407	1708.585	9.134	17	.000
Pair 6	SITE_2 - SITE_4	1151.196	767.8299	180.9792	769.3627	1533.028	6.361	17	.000
Pair 7	SITE_2 - SITE_5	1008.166	832.9974	372.5278	-26.1369	2042.469	2.706	4	.054
Pair 8	SITE_3 - SITE_4	-229.4216	371.6444	85.2611	-408.5484	-50.2947	-2.691	18	.015
Pair 9	SITE_3 - SITE_5	-119.9860	23.7358	10.6150	-149.4579	-90.5141	-11.303	4	.000
Pair 10	SITE_4 - SITE_5	31.3500	131.6903	58.8937	-132.1651	194.8651	.532	4	.623

T-Test Mn (A horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	242.8015	20	196.1371	43.8576
	SITE_2	1463.436	20	602.2021	134.6565
Pair 2	SITE_1	242.8015	20	196.1371	43.8576
	SITE_3	157.6345	20	20.6894	4.6263
Pair 3	SITE_1	244.4089	19	201.3763	46.1989
	SITE_4	578.137	19	285.076	65.401
Pair 4	SITE_1	394.1720	5	375.2157	167.8016
	SITE_5	641.8220	5	163.9144	73.3048
Pair 5	SITE_2	1463.436	20	602.2021	134.6565
	SITE_3	157.6345	20	20.6894	4.6263
Pair 6	SITE_2	1489.776	19	606.7519	139.1984
	SITE_4	578.137	19	285.076	65.401
Pair 7	SITE_2	833.2500	5	590.7251	264.1803
	SITE_5	641.8220	5	163.9144	73.3048
Pair 8	SITE_3	157.8895	19	21.2240	4.8691
	SITE_4	578.137	19	285.076	65.401
Pair 9	SITE_3	151.2860	5	19.9601	8.9264
	SITE_5	641.8220	5	163.9144	73.3048
Pair 10	SITE_4	414.350	5	244.871	109.509
	SITE_5	641.8220	5	163.9144	73.3048

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.106	.657
Pair 2	SITE_1 & SITE_3	20	-.227	.337
Pair 3	SITE_1 & SITE_4	19	.134	.583
Pair 4	SITE_1 & SITE_5	5	.494	.398
Pair 5	SITE_2 & SITE_3	20	-.007	.978
Pair 6	SITE_2 & SITE_4	19	.415	.077
Pair 7	SITE_2 & SITE_5	5	.655	.230
Pair 8	SITE_3 & SITE_4	19	.060	.806
Pair 9	SITE_3 & SITE_5	5	-.950	.013
Pair 10	SITE_4 & SITE_5	5	.755	.140

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-1220.63	613.2552	137.1280	-1507.65	-933.6222	-8.901	19	.000
Pair 2	SITE_1 - SITE_3	85.1670	201.8334	45.1313	-9.2940	179.6280	1.887	19	.075
Pair 3	SITE_1 - SITE_4	-333.7284	326.1765	74.8300	-490.9405	-176.5164	-4.460	18	.000
Pair 4	SITE_1 - SITE_5	-247.6500	326.9236	146.2047	-653.5792	158.2792	-1.694	4	.166
Pair 5	SITE_2 - SITE_3	1305.802	602.6934	134.7663	1023.732	1587.871	9.689	19	.000
Pair 6	SITE_2 - SITE_4	911.6384	552.8995	126.8438	645.1494	1178.127	7.187	18	.000
Pair 7	SITE_2 - SITE_5	191.4280	498.9547	223.1393	-428.1061	810.9621	.858	4	.439
Pair 8	SITE_3 - SITE_4	-420.2479	284.5852	65.2883	-557.4136	-283.0822	-6.437	18	.000
Pair 9	SITE_3 - SITE_5	-490.5360	182.9824	81.8322	-717.7387	-263.3333	-5.994	4	.004
Pair 10	SITE_4 - SITE_5	-227.4720	161.9165	72.4113	-428.5179	-26.4261	-3.141	4	.035

T-Test Cr (Litter)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	60.0370	20	20.0945	4.4933
	SITE_2	87.4160	20	38.0035	8.4978
Pair 2	SITE_1	60.0370	20	20.0945	4.4933
	SITE_3	76.8125	20	17.5808	3.9312
Pair 3	SITE_1	60.0370	20	20.0945	4.4933
	SITE_4	133.9895	20	41.6954	9.3234
Pair 4	SITE_1	56.7180	5	32.5257	14.5459
	SITE_5	78.3720	5	20.7506	9.2800
Pair 5	SITE_2	87.4160	20	38.0035	8.4978
	SITE_3	76.8125	20	17.5808	3.9312
Pair 6	SITE_2	87.4160	20	38.0035	8.4978
	SITE_4	133.9895	20	41.6954	9.3234
Pair 7	SITE_2	71.4180	5	18.6785	8.3533
	SITE_5	78.3720	5	20.7506	9.2800
Pair 8	SITE_3	76.8125	20	17.5808	3.9312
	SITE_4	133.9895	20	41.6954	9.3234
Pair 9	SITE_3	79.3400	5	20.1235	8.9995
	SITE_5	78.3720	5	20.7506	9.2800

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	-.268	.254
Pair 2	SITE_1 & SITE_3	20	-.262	.264
Pair 3	SITE_1 & SITE_4	20	.111	.640
Pair 4	SITE_1 & SITE_5	5	-.159	.798
Pair 5	SITE_2 & SITE_3	20	.112	.638
Pair 6	SITE_2 & SITE_4	20	-.095	.692
Pair 7	SITE_2 & SITE_5	5	.901	.037
Pair 8	SITE_3 & SITE_4	20	-.295	.207
Pair 9	SITE_3 & SITE_5	5	.330	.587

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-27.3790	47.5093	10.6234	-49.6140	-5.1440	-2.577	19	.018
Pair 2	SITE_1 - SITE_3	-16.7755	29.9707	6.7017	-30.8022	-2.7488	-2.503	19	.022
Pair 3	SITE_1 - SITE_4	-73.9525	44.2218	9.8883	-94.6489	-53.2561	-7.479	19	.000
Pair 4	SITE_1 - SITE_5	-21.6540	41.2697	18.4564	-72.8970	29.5890	-1.173	4	.306
Pair 5	SITE_2 - SITE_3	10.6035	40.0430	8.9539	-8.1372	29.3442	1.184	19	.251
Pair 6	SITE_2 - SITE_4	-46.5735	59.0110	13.1953	-74.1915	-18.9555	-3.530	19	.002
Pair 7	SITE_2 - SITE_5	-6.9540	9.0031	4.0263	-18.1328	4.2248	-1.727	4	.159
Pair 8	SITE_3 - SITE_4	-57.1770	49.7966	11.1349	-80.4825	-33.8715	-5.135	19	.000
Pair 9	SITE_3 - SITE_5	.9680	23.6560	10.5793	-28.4048	30.3408	.091	4	.931

T-Test Cr (B horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	46.602	18	10.479	2.470
	SITE_2	118.1789	18	30.4037	7.1662
Pair 2	SITE_1	46.602	18	10.479	2.470
	SITE_3	45.2822	18	9.1045	2.1459
Pair 3	SITE_1	46.602	18	10.479	2.470
	SITE_4	83.8794	18	21.1534	4.9859
Pair 4	SITE_1	54.404	5	8.042	3.596
	SITE_5	66.2220	5	17.7368	7.9321
Pair 5	SITE_2	115.9663	19	31.0813	7.1305
	SITE_3	45.0926	19	8.8865	2.0387
Pair 6	SITE_2	115.9663	19	31.0813	7.1305
	SITE_4	84.1947	19	20.6033	4.7267
Pair 7	SITE_2	100.3620	5	36.4510	16.3014
	SITE_5	66.2220	5	17.7368	7.9321
Pair 8	SITE_3	45.0926	19	8.8865	2.0387
	SITE_4	84.1947	19	20.6033	4.7267
Pair 9	SITE_3	47.2840	5	8.9060	3.9829
	SITE_5	66.2220	5	17.7368	7.9321
Pair 10	SITE_4	86.8180	5	19.7006	8.8104
	SITE_5	66.2220	5	17.7368	7.9321

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	18	-.091	.719
Pair 2	SITE_1 & SITE_3	18	.216	.389
Pair 3	SITE_1 & SITE_4	18	.068	.788
Pair 4	SITE_1 & SITE_5	5	.728	.163
Pair 5	SITE_2 & SITE_3	19	.074	.762
Pair 6	SITE_2 & SITE_4	19	.064	.795
Pair 7	SITE_2 & SITE_5	5	.902	.036
Pair 8	SITE_3 & SITE_4	19	-.064	.794
Pair 9	SITE_3 & SITE_5	5	-.378	.530
Pair 10	SITE_4 & SITE_5	5	-.194	.754

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-71.5767	33.0507	7.7901	-88.0124	-55.1409	-9.188	17	.000
Pair 2	SITE_1 - SITE_3	1.3200	12.3062	2.9006	-4.7997	7.4397	.455	17	.655
Pair 3	SITE_1 - SITE_4	-37.2772	22.9572	5.4111	-48.6936	-25.8609	-6.889	17	.000
Pair 4	SITE_1 - SITE_5	-11.8180	13.0971	5.8572	-28.0802	4.4442	-2.018	4	.114
Pair 5	SITE_2 - SITE_3	70.8737	31.6840	7.2688	55.6025	86.1449	9.750	18	.000
Pair 6	SITE_2 - SITE_4	31.7716	36.1753	8.2992	14.3356	49.2075	3.828	18	.001
Pair 7	SITE_2 - SITE_5	34.1400	21.8324	9.7637	7.0315	61.2485	3.497	4	.025
Pair 8	SITE_3 - SITE_4	-39.1021	22.9557	5.2664	-50.1664	-28.0378	-7.425	18	.000
Pair 9	SITE_3 - SITE_5	-18.9380	22.6585	10.1332	-47.0722	9.1962	-1.869	4	.135
Pair 10	SITE_4 - SITE_5	20.5960	28.9551	12.9491	-15.3565	56.5485	1.591	4	.187

T-Test Cr (A horizon)

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	SITE_1	42.8855	20	10.1756	2.2753
	SITE_2	104.4710	20	31.3651	7.0134
Pair 2	SITE_1	42.8855	20	10.1756	2.2753
	SITE_3	44.9520	20	7.3839	1.6511
Pair 3	SITE_1	42.9437	19	10.4510	2.3976
	SITE_4	44.3279	19	23.2661	5.3376
Pair 4	SITE_1	47.2000	5	6.2165	2.7801
	SITE_5	38.6080	5	20.8252	9.3133
Pair 5	SITE_2	104.4710	20	31.3651	7.0134
	SITE_3	44.9520	20	7.3839	1.6511
Pair 6	SITE_2	106.5537	19	30.7710	7.0593
	SITE_4	44.3279	19	23.2661	5.3376
Pair 7	SITE_2	82.0220	5	26.7145	11.9471
	SITE_5	38.6080	5	20.8252	9.3133
Pair 8	SITE_3	44.5347	19	7.3400	1.6839
	SITE_4	44.3279	19	23.2661	5.3376
Pair 9	SITE_3	41.5760	5	5.9040	2.6404
	SITE_5	38.6080	5	20.8252	9.3133
Pair 10	SITE_4	35.3280	5	24.1726	10.8103
	SITE_5	38.6080	5	20.8252	9.3133

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	SITE_1 & SITE_2	20	.202	.393
Pair 2	SITE_1 & SITE_3	20	-.148	.534
Pair 3	SITE_1 & SITE_4	19	-.380	.108
Pair 4	SITE_1 & SITE_5	5	-.206	.739
Pair 5	SITE_2 & SITE_3	20	.232	.326
Pair 6	SITE_2 & SITE_4	19	.069	.777
Pair 7	SITE_2 & SITE_5	5	-.131	.833
Pair 8	SITE_3 & SITE_4	19	.190	.435
Pair 9	SITE_3 & SITE_5	5	.455	.442
Pair 10	SITE_4 & SITE_5	5	-.746	.148

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	SITE_1 - SITE_2	-61.5855	30.9554	6.9218	-76.0731	-47.0979	-8.897	19	.000
Pair 2	SITE_1 - SITE_3	-2.0665	13.4266	3.0023	-8.3503	4.2173	-.688	19	.500
Pair 3	SITE_1 - SITE_4	-1.3842	28.9045	6.6312	-15.3158	12.5473	-.209	18	.837
Pair 4	SITE_1 - SITE_5	8.5920	22.9292	10.2542	-19.8784	37.0624	.838	4	.449
Pair 5	SITE_2 - SITE_3	59.5190	30.5125	6.8228	45.2387	73.7993	8.724	19	.000
Pair 6	SITE_2 - SITE_4	62.2258	37.2646	8.5491	44.2648	80.1868	7.279	18	.000
Pair 7	SITE_2 - SITE_5	43.4140	35.9624	16.0829	-1.2393	88.0673	2.699	4	.054
Pair 8	SITE_3 - SITE_4	.2068	23.0260	5.2825	-10.8913	11.3050	.039	18	.969
Pair 9	SITE_3 - SITE_5	2.9680	18.8868	8.4464	-20.4831	26.4191	.351	4	.743
Pair 10	SITE_4 - SITE_5	-3.2800	42.0590	18.8094	-55.5032	48.9432	-.174	4	.870