HEAVY METAL UPTAKE AND ACCUMULATION IN AGRICULTURAL CROPS IN URBAN AREAS OF THE WESTERN CAPE

By

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Declaration

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I, Bonita Joy Sheldon, hereby declare that the work on which this thesis is based is my original work (except where acknowledgements indicate otherwise), and that neither the whole work nor any part of it has been, is being, or is to be submitted for another degree in this or any other Technikon or University.

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ABSTRACT

A research study into heavy metals in the Cape Town area, found significant amounts of potentially toxic metals such as lead, cadmium, chromium and iron leaching into the underground aquifer. A further additional study conducted on a community garden in Khayelitsha, showed that vegetable crops have the tendency to accumulate certain heavy metals if they are present in soil and water resources.

This study was centered around the Philippi Horticultural Area, which is a large significant farming area within the Cape Metropolitan Region. The significance of the study lies in the fact that at least 50% of the local farmers' produce is sold directly to street traders, residents, local supermarket-chains and restaurants. The remainder of the produce is sold at the Epping Market.

The purpose of this study was to investigate heavy metal accumulation in various vegetable crop species taken from some of the local farms in the Phillipi Farming area with the objective to:

- investigate heavy metal accumulation in various vegetable crop species taken from some local farms in the Phillipi Farming area.

- determine the concentrations of heavy metals present in water and soil resource since these will be the primary source of heavy metals to the vegetables.
- determine the soil pH and soil organic matter as these two factors would determine the bio-availability of the heavy metals.
- identify those crops that pose a definite health risk by means of comparing the determined results to the allowed limits. This will enable one to identify problem crop species.

In consultation with statisticians, it was decided that 40 sites should be monitored in order for the results to be statistically valid. Forty sites were then selected in collaboration with the Botany Department at the University of the Western Cape. Samples of soil, water and vegetables were collected and analysed by means of ICP-OES to determine heavy metal concentrations.

A difference was observed between summer and winter soil results, with the winter results being generally higher than that of summer, with the exception of Cu and Cd concentrations. Unlike the soil values that were high during the winter months, the heavy metal concentration in the water sampled at the various dams were generally lower. The results indicated that the heavy metal concentrations in the water was well within the allowed limits.

All of the vegetables sampled accumulated high levels of Fe, Zn and Mn even though the levels were within the allowed limits. This is to be expected because these heavy metals are also regarded as micronutrients. Only the celery accumulated Fe and Zn to the extent that exceeded the allowed limit of 70 mg/kg for both metals. With regard to the soil values during summer, the average Fe concentration is the highest in the soil (609 mg/kg), followed by Zn (25 mg/kg) and then Mn (20 mg/kg). The Fe concentration was the highest in all of the vegetables and this could be due to the fact that the average concentration of this metal in both the soil and the water was relatively high.

The results obtained for the vegetables during winter differed from the summer results. Fe, Mn and Zn concentrations have increased in the cauliflower during winter when comparing the results obtained in summer. Pb, Mn, Zn and Mg concentrations have also increased in the cabbage during winter, while the Mn concentration has almost tripled in the celery and also increased in the lettuce.

Only one roadside plot exhibited Pb contamination in the soil. There was no contamination of the remaining heavy metals at any of the sampling sites, although the soil in most cases can be indicated as the main source of metals available to the vegetables. All the vegetables that were sampled during winter had levels of Pb and Cd that exceeded the allowed limit. The average Ni, Cr, Mn and Cu concentrations in the vegetables were below the allowed limit. Spinach celery and lettuce exhibited a high accumulation tendency of most of the heavy metals tested and can be regarded as good accumulators.

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GLOSSARY OF SYMBOLS

FAO	Food and Agricultural Organisation
WHO	World Health Organisation
SABS	South African Bureau of Standards
AR	Analytical reagent
HPLC	High Performance Liquid Chromatography
PCA	Principal Component Analysis
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Background to the study

One of the major problems facing our world is the threat that heavy metal pollution poses on the environment. These metals have received increasing attention because of the public and scientific awareness of environmental issues which relates to human health. The concern mainly involves the contamination of agricultural soil, crops and water resources because these metals, unlike organic pollutants, cannot be biodegraded (Queirolo et al., 2000: 75). They merely find their way along the food chain and, if eventually consumed, could have a detrimental effect on the health of the consumer in the long run.

A research study by the Department of Soil Sciences, University of Stellenbosch, into heavy metals in the Western Cape, found significant amounts of potentially toxic metals such as Pb, Cd, Cr and Fe leaching into the underground aquifer (WRC Report No 572/1/99). There was uncertainty regarding the source and the factors that contributed to the migration of these heavy metals into this area. Coetzee et al. (2000: 565) sampled from 35 boreholes, situated in the Western Cape area, and identified Cd, Fe, Pb and Mn as potentially hazardous constituents in some areas. This study reported that the mean Pb levels were higher than the maximum levels allowed in all the borehole samples. Studies conducted by the author (Cooke, 1999), on a community Garden in Khayelitsha

(Western Cape), have shown that selected vegetable crops accumulated certain heavy metals. Vegetable crops do not have the ability to excrete unwanted metals. Once these metals are accumulated in excessive amounts, only then are they capable of exerting toxic effects on living organisms.

The very first recorded case of soil and water pollution causing Cd poisoning in people was among the rice farmers in the Jintsu Valley, in the Toyama Prefecture of Japan. Alloway (1995: 141), states that a nearby Cd-Zn mine had been causing extensive pollution of the river water and the paddy soils in the flood plain of the Jintsu Valley for many years. During and after the Second World War, more than 200 elderly women developed skeletal deformations and kidney damage and of the 200, 65 of them had died of heavy metal poisoning. This condition was caused by Cd toxicity. The locally grown rice, as well as the drinking water had been heavily contaminated with Cd. Even the average Cd content in the rice was ten times higher than the local controls.

Studies such as the one mentioned above, are widely reported and documented in other countries, while in South Africa, it has yet to be documented. It is of utmost importance to assess the potential risk of heavy metal translocation to vegetable crops and at the same time provide background data which could inform farmers. It is also important to inform the relevant stakeholders of possible contamination.

1.2 The problem statement

Pollution of the environment by heavy metals such as Pb, Cd, Cu, Ni, and Cr has become a health hazard all over the world. Heavy metals can find their way into the food chain through contaminated resources such as soils and plants, and when consumed by living organisms, can pose a definite health risk to these organisms. Vegetables do not have the ability to excrete unwanted metals, and therefore may accumulate heavy metals in either its above or below ground structures over a period of time.

The purpose of this study is:

- to investigate heavy metal accumulation in various vegetable crop species taken from some local farms in the Phillipi Farming area.
- to determine the concentrations of heavy metals present in water and soil resource since these will be the primary source of heavy metals to the vegetables.
- to determine the soil pH and soil organic matter as these two factors would determine the bio-availability of the heavy metals.
- to identify those crops that pose a definite health risk by means of comparing the determined results to the allowed limits. This will enable one to identify problem crop species.

1.3 Hypothesis

Vegetable crops do not have the ability to excrete unwanted metals and therefore they have the tendency to accumulate these metals if they are present in the natural resources.

1.4 Assumptions

This study is based on the following assumptions:

- The soil in which the crops are grown and the water used for irrigation is possibly contaminated and therefore can contribute to the concentration of heavy metals present in these crops.
- Accumulation of heavy metals through the aerial parts of the plant is negligible.
- The standard methods that will be used for the analysis of these heavy metals are suitable and sensitive.

1.5 Delimitations

- Although the soil characteristics are important when trying to establish the availability of the heavy metals for uptake by plants, only the soil pH and the organic content will be determined. Other soil characteristics such as the physical and chemical conditions, the presence of reactive species and complexing ligands, and the nature and surface area of the soil will not be dealt with in this study.

- Crop selection will be carried out based on availability at the time and will not be restricted to leafy vegetables only.

- This study will not investigate the contamination of vegetables through the aerial parts of the plant.

1.6 Project site

The Philippi Horticultural Area is a large significant farming area within the Cape Metropolitan Region. It has been facing urbanisation pressures along its boundaries as well as erosion from within, because of illegal use of the land. This area is surrounded by small-scale industrial and commercial developments and is divided by lower order public roads. The farming area covers approximately 3000 hectares and is bounded by Vanguard Drive, Lansdowne and Strandfontein Roads. Approximately 80 vegetable farmers occupy this farming area.

The climatic conditions are temperate, with cool wet winters and relatively hot dry summers. The temperatures vary from a minimum of 4°C in the winter months and as high as 38°C in summer. As a result, frost is not a problem and hail is seldom experienced. Mist, on the other hand, is experienced throughout the year.

The rainfall ranges between 550 mm and 1200 mm per annum. Most of the rainfall occurs during the winter months. Very strong south-easterly winds are experienced throughout the year, especially during summer. The farming area has a high water table and in some areas the water table is only 1.5 m below the surface.

Most of the area consists of wind blown sand, surface limestone or grey sands containing organic material. The Philippi Horticultural Area supplies building and foundry sand to the Cape Metropolitain Region and has a high quality glass sand. Horticulture on the other hand, is still the predominant land use in the area and includes the cultivation of shrubs, flowers and vegetables. The cultivation of vegetables is by far dominant.

The vegetables most commonly grown include cabbages, beetroot, potatoes, carrots, spinach and lettuce. At least 50% of the local produce is sold directly to street traders, residents, local supermarket chains and restaurants. The remainder of the produce is sold at the Epping Market – the major public market in Cape Town. Fifty percent of the vegetables such as carrots, cauliflower, lettuce and cabbages sold at the Epping Market, are supplied by the farmers in the Philippi Farming area. Even though there has been a decrease in the production area over the last 25 years, there has not been a decline in the volume of the produce sold at the market.

Local piggeries and compost manufacturers supply manure to farmers. The Philippi Boere Dienste, a co-operative, supplies fertilizer, equipment and other products to farmers.

Water for crop irrigation is supplied by numerous borehole and storage dams. The underground water is pumped into these reservoirs. With a national population growth rate of about 2.8% and the prediction that the population will double in 30 years, South Africa has little option but to ensure the effective use of all available water supplies (Metro South East plan, 1997).

Traditionally, groundwater has formed the main source of supply to the agricultural community. It can be expected that groundwater will continue to be used increasingly, since it is often the cheapest and safest source of potable water supply (Morris, 1997).

1.7 Sources of heavy metals

There are many ways in which heavy metals could be defined. According to one definition, heavy metals are a group of dense chemical elements such as Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni and Zn with a density greater than 3.5 g/ml (Lozet, 1991). Heavy metals can also be defined as metallic elements with a high relative atomic mass number (EPA, 2000). This study focuses on eight of these heavy metals.

There is a continual influx of heavy metal contaminants and pollutants into the biosphere from both natural and anthropogenic sources. A complex variety of processes affect their speciation and distribution. Some of these processes can effectively isolate heavy metals from the biosphere, whereas others can cause their release (Gordon, 1999: 3388).

Geochemical Sources

Heavy metals are natural components of soil and most of them are present in *minimal, insignificant eco-toxilogical concentrations in undisturbed locations* as stated by Alloway (1993: 142). They are also included in the group of elements referred to as 'trace elements' which together constitute less than one percent of the rocks in the earth's crust. These metals occur as 'impurities' isomorphously substituted for various macroelement constituents of the crystal lattice of many primary minerals.

Hydrosphere

These heavy metals do exist in surface waters in colloidal, particulate and dissolved phases although dissolved concentrations are generally low.

Anthropogenic

There are a number of man-made causes including the processing of ores and metals, the industrial use of metal compounds and also the leaching from domestic and industrial waste dumps, mine tailings, contaminated sediments and Pb pipes.

Three main sources are:

i. Extraction and purification by processes such as mining, smelting and refining.
ii. The release from fossil fuels by the combustion of substances such as coal and oil.
iii. Production and use of industrial products containing metals, which is increasing as new applications are found. Industrial applications include agricultural and horticultural materials; sewage sludges; electronics; waste disposal; sports shooting and fishing; warfare and military training and chemical manufacturing.

Several studies have indicated that vegetables grown in heavy metal contaminated soils have higher concentrations of heavy metals than those grown in uncontaminated soil (Guttormensen et al., 1995: 29). Vegetable growing areas are often situated in, or near sources of atmospheric deposits, and thus have an elevated risk of potential contamination. The Philipi Horticultural Area is surrounded by small-scale industrial developments and a network of public roads divides this area. These could be potential sources of heavy metal deposition in the soil and water of the surrounding vegetable farms.

1.7 Toxic Effects of heavy metals

The sensitivity of organisms to metal toxicity varies widely with species of plants and animals and genotypes within species. Many factors can modify the response to the toxic dose of metals. Some plant species are adapted genetically to tolerate high concentrations of certain metals.

Studies confirm that heavy metals can directly influence behaviour by impairing mental and neurological function, influencing neurotransmitter production and utilization and altering of numerous metabolic body processes. Systems in which toxic metal elements can induce impairment and dysfunction include the blood, cardiovascular, detoxification pathways, endocrine, energy production pathways, enzymatic, gastrointestinal, immune, nervous, reproductive and urinary (Kellas & Dworkin, 1996: 187-230). When ingested and inhaled in excessive amounts, heavy metals can affect the liver, brain and lungs, although each metal causes its own characteristic symptoms (Friedman, 1994: 8).

Children appear to be more sensitive to heavy metal exposure than adults, and are consequently the focus of concern. The toxic nonessential metals such as Cd and Pb are characterized as having no demonstrated biological requirements in humans, and exposure is associated with recognizable toxicity. Also, severity of toxicity increases with increases in dosage (Goyer, 1997: 37-50). Today, increasing emphasis is being placed on the carcinogenic effects of metals. Pb and Cd are all proven or suspected causes of certain cancers associated with industrial processes.

A metal is regarded as toxic if it injures the growth or metabolism of cells when it is present above a given concentration. Casdorph and Walker (1995: 95) states that almost all metals are toxic at high concentrations, and some are severe poisons even at very low concentrations. Each metal has an optimum range of concentration, in excess of which the element is toxic. The heavy metals listed in the table to follow are amongst the most prevalent. The health effects of exposure to these metals are also identified.

The toxicity of a metal depends on its route of administration and the chemical compound with which it is bound. The combining of a metal with an organic compound may either increase or decrease its toxic effects on cells. On the other hand, the combination of the metal with sulphur to form a sulphide results in a less toxic compound than the corresponding hydroxide or oxide, because the sulphide is less soluble in body fluids than the oxide.

Table 1.1: Examples of health effects of exposure to heavy metals

HEAVY METAL	*RESULT OF EXPOSURE*
Chromium	Cancer, damage to respiratory organs
Cadmium	Anemia, emphysema, fatigue, hair loss, heart disease, hypertension, kidney and liver damage, lung cancer
Lead	Brain damage, anorexia, anemia, constipation, convulsions, miscarriage
Nickel	Cancer, contact dermatitis, diarrhea, headaches, skin rashes, nausea

Toxicity generally results when an excessive concentration is presented to an organism over a prolonged period of time; when the metal is presented in an unusual biochemical form; or, when the metal is presented to an organism by way of an unusual route of intake.

Cadmium

The pathway of Cd to man is from food, particularly leafy vegetables, grains and cereals. Cd is nutritionally non-essential and toxic and can accumulate in the liver and kidneys. Toxicity involves two organ systems, the renal and skeletal systems and is largely a consequence of the interactions between Cd and essential metals, particularly calcium (Goyer, 1997: 39).

Lead

Novak et al. (2003), states that more Pb has been released into the environment since prehistory than any other metal, and as late as 1990, 50% of the annual worldwide Pb production was still being lost to the atmosphere. It is for this reason that there is a need to be concerned about elevated Pb levels in the environment.

The effect of major concern today, regarding Pb toxicity, is the impairment of cognitive and behavioural development in infants and young children in the general population (Mathee et al., 2002: 181). Studies conducted around the world have established beyond doubt that elevated childhood blood lead levels may lead to detrimental health effects. Even at relatively low levels of blood lead, health effects such as neurobehavioral deficits and poor school performance have been demonstrated. Following the findings of investigations into childhood blood lead levels in South Africa's Cape Peninsula during the late 1980s and early 1990s, there has been ongoing concern for the health of large groups of urban South African children exposed to elevated environmental lead levels (Mathee et al., 2002: 181).

Chromium

Chromium is an essential nutrient that can be toxic in large doses however, the toxicity depends on the oxidation state and the solubility of the metal compound. The target organ of inhaled chromium is the lung, the kidneys, liver, skin and even the immune system may be affected (Burrows, 1993). In epidemiological studies, an association has been found between exposure to Cr by the inhalation route and lung cancer (WHO, 1993).

Copper

Copper is one of the most essential elements for plants and animals, but it can also be toxic if it is present in large concentrations. Acute gastrointestinal effects may result from exposure to Cu in drinking water, although levels at which such effects occur are not defined with any precision (WHO, 1993).

Nickel

Harte (1991: 103) stated that the greatest danger from chronic exposure to Ni is lung, nasal or larynx cancers and gradual poisoning from accidental or chronic low-level exposure. The risk is greatest for those living near metal smelting plants, solid waste incinerators, or old Ni refineries.

Manganese

Biological Mn is considered to be an essential metal important to mitochondrial oxidative processes for all living mammals, but may also be toxic at high concentrations (Röllin et al., 2005: 94). Excessive intake of Mn, either through inhalation or ingestion, may result in pathology, particularly to the central nervous system. Excessive exposure via the inhalation has been shown to cause effects on the lungs and accumulate in the brain, causing irreversible brain disease (Röllin et al., 2005: 94).

Zinc

Zinc belongs to the group of trace metals potentially most hazardous to the biosphere. Most of the concern about excessive Zn concentrations in soils relates to its possible uptake by crops and consequent adverse effects on the crops themselves and on livestock and human diets. Zn is required in the human diet and is not toxic in moderate amounts, however, excesses will cause metal poisoning similar to that of Pb (Alloway, 1995: 301).

Iron

Iron is physiologically essential for life, but biochemically dangerous. Toxicity attributable to excess Fe can occur chronically because of excessive accumulation in the body from contaminated food sources. Iron toxicity can have a direct effect on the *gastrointestinal tract and can cause death* due to widespread cellular dysfunction (Hardman, 1995: 1324).

Even though some of the metals covered in this study are essential for plants and animals, they have the ability to bioaccumulate and become toxic at higher concentrations.

1.9 The review of the related literature

Contamination of food and feed crops cultivated in West Berlin was systematically investigated by the Heavy Metal Measurement Survey conducted by the Berlin Department of Urban Development and Environmental Protection from 1979-1990 (Senate Administration for Town development and environmental protection Berlin, 1991). Tests were conducted at allotment gardens, house yards, horticulture and agricultural areas at various locations. Heavy metal contents were analysed in 140 kinds of food and feed crops.

This study revealed a clear indication that levels exceeding the index values in crops in the allotment gardens and house yards, occur in all parts of the city. The distribution of contamination corresponds in most locations, with the spatial distribution of Pb and Cd soil contamination. Table 1.2 reflects the number of sites exceeding the Index values.

Table 1.2: **Number of tested sites exceeding index values of heavy metals in vegetable crops (Senate Administration for Town development and environmental protection Berlin, 1991).**

CROP	*NO. OF TESTED SITES*	*LEAD*	*CADMIUM*
Wheat	10	1	1
Rye	221	37	28
Kale	1258	3	23
Leaf Celery	1254	56	108
Savoy Cabbage	8	1	1
Spinach	9	-	-
Head Lettuce	40	-	3
Ice-berg Lettuce	6	-	1
Parsley	59	1	8

Pb and Cd levels of all tested feed crops were evaluated individually and tested in their form of consumption. The results were compared with the medium and element-specific Foodstuff Index Values. Crops were categorised according to the Feed Crop Limit Value Regulations. Table 1.3 reflects the index and limit values for Pb and Cd in food and feed crops.

Table 1.3: Index values for Pb and Cd in feed crops (Senate Administration for Town development and environmental protection Berlin, 1991).

CROP TYPE	*LEAD*	*CADMIUM*
Wheat	0.30	0.10
Rye	0.40	0.10
Potato	0.25	0.10
Leafy vegetables	0.80	0.10
Kale	2.00	0.10
Spinach	0.80	0.50
Root vegetables	0.25	0.10

The Institute of Environmental Protection at Katowice, Poland, (Global Report 1990/91:132-133) measured the exposure of the local population to two toxic metals, Pb and Cd, by the consumption of vegetables grown in the metal contaminated soils of the region.

To estimate the average weekly intake of Pb and Cd through vegetable consumption by the local population, a study was conducted covering 431 vegetable plots in the Katowice region on the basis of a random sample of the most commonly consumed vegetables from each plot. Carrots, parsley, celery, red beets and potatoes were selected from each plot. Approximately 30-50 vegetable samples were picked per sampling site and then washed, dried, ground and mineralised. The metal content of each vegetable was then measured.

The sample results reflected that vegetable leaves are more readily exposed to metal contamination than roots. Thus, the highest concentrations were found in celery leaves and parsley leaves, followed by celery roots, carrot roots, red-beet roots, parsley roots and potatoes.

Compared to the maximum concentration limits recommended by the Food and Agricultural Organisation of the United Nations (FAO) and the World Health Organisation (WHO), of the 3 mg/week for Pb and 0.4 - 0.5 mg for Cd, the estimated Pb intake of the local population all exceeded the allowed limit. Cd intake is almost twice the maximum allowable limit for all districts. Cd can disturb kidney functions, and some studies indicate a cancerous effect.

A similar study, by Bosnir and Puntaric (1997), was conducted in the Zagreb Home Gardens in Croatia. From November 1995 to February 1996, 81 samples of brassicas (savoy cabbage, Swiss chard, lambs'-lettuce, cabbage, leeks, parsley, dandelion, lettuce, spinach, Brussels sprout, kohlrabi and celeriac) were obtained from Zagreb home gardens.

Samples were thoroughly cleaned, homogenised and digested. Pb quantification was performed by flame Atomic Absorption Spectrometry. The concentration of Pb was determined in 81 samples of brassicas obtained from five locations in the Zagreb area. The results obtained from the analysis in µg/kg are given in table 1.4.

Table 1.4: Lead concentrations (µg/kg) in brassicas from Zagreb home gardens, November 1995 – February 1996, Bosnir and Puntaric (1997).

CITY AREA	*NO OF SAMPLES*	*MEAN*	*MEDIAN*	*RANGE*
South	17	834	903	504-1134
South West	12	789	976	289-1290
North	19	421	175	19-1871
East	23	329	391	26-551
West	10	301	260	78-867
Total	81	541	454	19-1871

The average Pb concentration was 541 µg/kg. The highest mean Pb concentration, which was 834 µg/kg, was recorded in the southern part of the city.

Pb concentrations exceeding the allowed limit of 10 ppm were found in 12 samples out of 81 vegetable samples. The greatest portion of samples with high Pb concentrations was found in the south-western part of the city. In the southern and northern areas, 4 out of 17 and 3 out of 19 samples exceeding the allowed limit of Pb concentrations were recorded, respectively. In the northern part of the city, the highest measured Pb concentration of 18.71 ppm was found, whereas none of the samples from the eastern and western suburbs showed a Pb concentration exceeding the allowed limit. This study concluded that the Pb contamination in the city of Zagreb was within the acceptable levels

A similar case of large-scale environmental pollution by certain metals occurred in the village of Shipham in Somerset, UK, where Zn was mined. Large-scale expansion of the village occurred and most of the new houses were built on the site of the old mines (Alloway, 1995: 141). Geochemical and soil surveys were carried out and revealed that there were very high concentrations of Zn, Pb and Cd in the soils of the village. In view of the possible health effects of this pollution, a survey was carried out in order to monitor heavy metal contamination.

The survey concluded that the average Cd concentration of almost 1000 vegetable samples was 0.25 mg/kg, which was nearly 17 times higher than the national average of 0.015 mg/kg of Cd. They also found that the highest Cd concentrations were in leafy vegetables such as spinach, lettuce and other vegetables belonging to the brassica family. The most contaminated vegetables contained 15 to 60 times more Cd than those grown in ordinary soils. Salim et al. (1995: 831-849) also found that all edible parts of tested vegetables such as spinach, parsley and cauliflower contained higher concentrations of Cd than the maximum allowed limit.

All of the above mentioned studies have shown that crop species have the ability to accumulate heavy metals if present in soil and water resources. Crop species also differ with respect to heavy metal uptake and their transport to edible tissues. Below is a table of relative heavy metal accumulation in certain vegetable crop species based on data from a related study. This study reflects the trend of vegetable crops to accumulate heavy metals and groups them into high accumulators and low accumulators (Davis & Calton-Smith, 1980).

Cd reaches variable concentrations in different plant organs of varying species. Certain vegetable crop species such as tomato, corn, soybeans and oats accumulate more Cd in roots than in the aerial parts of the plant. On the other hand, carrots, lettuce and potatoes accumulate more in the leaves (Kabata-Pendias & Pendias, 1992; Sauerbeck, 1991). A study done by Stalikas, et al. (1997: 21) indicated that plants grown in Zn-and Cu-contaminated soils accumulate a great proportion of metals in their roots. The highest accumulation of Pb was reported to have occurred in leafy vegetables (Kabata-Pendias & Pendias, 1992: 365). Rahlenbeck et al. (1999: 31) stated that in general, vegetables with soft leaves (kale, lettuce, silver beet) had higher concentrations of metals than others such as carrots or cabbage.

Table 1.5: Relative metal accumulation - Cd and Pb in edible portions, Cu, Ni and Zn in leaves (Davis and Calton-Smith, 1980).

METAL	*HIGH ACCUMULATIONS*	*LOW ACCUMULATIONS*
Cd	Lettuce, spinach, celery, cabbage	Potato, maize, french bean, peas
Pb	Kale, ryegrass, celery	Some barley, potato, maize
Cu	Sugar beet, certain barley crops	Leek, cabbage, onion
Ni	Sugar beet, ryegrass, mangold, turnip	Maize, leek, barley, onion
Zn	Sugar beet, mangold, spinach, beetroot	Potato, leek, tomato, onion

Itanna (2002: 295-302) determined heavy metal concentration of leaf samples of cabbage, swiss chard and lettuce sampled from two areas namely, Peacock Park and Kera in Addis Ababa. The results indicated that cabbage was the least accumulator of heavy metals, whereas lettuce and swiss chard grown at Kera had higher concentrations of metals when compared to that of the Peacock Park. In a few cases, Cr, Fe and Pb in these vegetables have surpassed maximum permitted concentrations, while Cu deficiency was observed in cabbage. This study concluded that metal uptake difference by the leafy vegetables is attributed to plant differences in tolerance to heavy metals. Vegetables from Kera consisted of higher metal concentrations than from Peacock Farm because the river irrigating this area was more contaminated.

Secer et al. (2002: 196-211) conducted a study in the Gediz River Region in order to determine trace element and heavy metal concentrations in fruits and vegetables. To study the pollution status, vegetables such as tomato, pepper, bean, purslane, cowpea and fruits such as apple, plum, pomegranate, walnut, watermelon, peach, cherry, grape and leaf samples were taken from 12 different places being irrigated from the Gediz River. The amounts of trace elements (Fe, Mn, Zn, Cu, B) and heavy metals (Co, Ni, Cr, Cr, Pb, Cd) were measured in these samples. These parameters were compared with published standards. Trace element and heavy metals pollution levels arising from natural and industrial wastes were recorded in some vegetables, fruits and leaf samples at all sampling places. The leaves of vegetables and fruits contained more trace elements and heavy metals than the edible parts.

A study done by Golueke (1995: 29) on the effect of Pb and Cd on vegetables has shown that the uptake of heavy metals by vegetable crops increased with an increase in the concentration of these metals in the water used for irrigation. This study also showed that the uptake of heavy metals decreased with an increase in the concentration of metal ions in the applied water, and that the uptake of these metals was higher in plants treated with Cd than those treated with Pb. A study done by Salim, et al. (1995: 831-849) confirmed results obtained by Clarence Golueke.

Liu et al. (2004) states that the accumulation effect is strongly affected by the crop's physiological properties, the mobility of the metals, and the availability of the metals in soils. Another paper by Golueke (1998) stated that the significance of accumulation rests in the fact that uptake of heavy metals by plants is partly a function of the mobility of the metals. Thus, the extent of metal uptake declines with the loss of mobility and vice versa. In addition to the concentration of heavy metals in the dissolved form, the extent of its availability will decrease with a drop in pH. Stalikas et al. (1997) states that the uptake of metals from the soil depends on their soluble content in it, soil pH, plant species, fertilisation and soil type. Alloway (1984), Jackson (1991) and Xue (1991) also states that the soil pH is a key variable influencing the bioavailability of metals for uptake by plants. This deals with the process of adsorption and desorption.

A publication by the Water Research Commission (WRC Report No 572/1/99) and Bahemuka and Mubofu (1999: 64) reports on an investigation of the availability of heavy metals as a result of various soil characteristics. Listed below are some of the most important characteristics, which may be relevant to this study.

1.10 Chemical characteristics

1.10.1 pH

pH is the primary variable affecting the uptake of heavy metals because it controls all the chemical processes in the soil. These chemical processes include complexation, dissolution/precipitation, reduction/oxidation, adsorption and hydrolysis (WRC Report No 572/1/99). For metal cations, high pH favours sorption and precipitation as carbonates, oxides and hydroxides.

Although the pH of the soil is the primary variable, there are instances where well-buffered soils can resist pH changes. Soils have several buffering mechanisms, which can somehow cause buffering to varying extents. Even with these buffering mechanisms, the soil pH can differ due to localised variations within the soil. Soil pH usually increases with depth in humid regions where bases are leached down the profile and can decrease with depth in arid environments where evapouration causes salts to accumulate in the surface horizon (Alloway, 1995).

Heavy metals are more mobile under acid conditions and with an increase in pH, they become less available for uptake.

1.11 Physical characteristics

1.11.1 Soil Type

Soil properties such as surface area, particle size, structure, mineralogy, organic and mineral coatings affect the capacity for adsorption of solutes. Soils have underlying minerals coupled to certain inorganic and organic species. These species posses a heterogeneous collection of adsorption sites. In most cases, the surface charge is actually negative and therefore there is greater tendency of adsorption of cationic species such as the heavy metals.

The grain size distribution of gravel, sand, silt and clay provides a basis for classifying soil by texture. Texture and surface area are closely related so that as particle size decreases, the surface area per unit mass increases, resulting in an increase of adsorption capacity. Finer textured soils are less permeable and will therefore have a longer contact time for sorption of dissolved species than coarser-textured soils.

1.11.2 Soil organic matter

The mobility of heavy metals in soils and also their bioavailability, is somehow associated with the percentage of organic matter present in the soil (Jackson, 1991; Hogue & Neilsen, 1996). All soils contain organic matter, although the amount of organic material and the type can vary considerably. The organic matter and the type of functional groups present in these organic materials will indicate the capacities for cations and thus, heavy metal exchange.

The structure of soil determines the surface area exposed and will have an effect on water velocity. Structure in this case refers to the degree of aggregation of the primary soil particles into structural units. The presence of aggregated soil increases the potential for bypass flow in the macropores between the aggregates, reducing the contact time for sorption.

Based on the above-mentioned studies, it is clear that various factors will play an important role in the subsequent accumulation of heavy metals in the vegetable crops. One of the most important factors to focus on in this study, would be the soil characteristics where both the physical and the chemical aspects are considered.

This study was confined to the investigation of the accumulation of eight metal elements in vegetable crops. These metal elements included metals such as Cu, Zn, Mn, Pb, Ni, Cr, Fe and Cd. This selection of metal elements covers some of the most toxic metals such as Pb and Cd and some of the microneutrients required for normal and healthy growth of crops.

The source of contamination was investigated and thus the soils in which the vegetables are grown as well as the water used for irrigation were tested. It is of utmost importance to relate the concentrations of heavy metals found in the soil and water resources to the concentrations found in the various vegetables as the contamination could be attributed to high concentrations in either one or even both. The results obtained from the analysis of the soil, water and vegetable samples was compared to the allowable limits as specified by professional bodies such as South African Bureau of Standards (SABS) and other Health Organisations.

One particular point that comes across in most of the articles is that most leafy vegetables are known to accumulate heavy metals in large concentrations. It was therefore a point to consider during crop selection. Crop selection was done on a seasonal basis and on the basis of availability.

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 *Introduction*

In consultation with statisticians at Stellenbosch University, it was decided that 40 sites should be monitored in order for the results to be statistically valid. The selection of the 40 sites was done in collaboration with the Botany Department at the University of the Western Cape.

Only high purity water was used during sample preparation and analysis. The acids, as well as the standards used, were obtained from Merk-Saarchem laboratories and were analytical reagent grade. Prior to use, all glassware, sampling containers and plastic containers for the storage of the ultra pure water were soaked overnight in 0.1 M nitric acid and thoroughly washed with laboratory-grade detergent and water. It was then rinsed with water, soaked for a few days in a mixture of dilute nitric acid and hydrochloric acid, followed by rinsing with water and ultra-pure water. This was done to ensure that the containers were free of possible contaminants.

A gravity convention oven, with thermostatic control capable of maintaining 70 °C ± 5 °C was used to remove the moisture in both soil and vegetable samples. The soil was completely dried within 24 hours, while the vegetable samples required 3 days before they were free of moisture. In order to determine soil organic matter, higher temperatures were required and therefore a Protolab muffle furnace was used. Digestion of soil samples was carried out on a standard laboratory hotplate, while the vegetable samples were first milled to a powder by means of a Retsch-PM 400 ball mill and then digested using a Milestone-MLS 1200 Mega microwave oven. According to the EPA method, the water samples did not require any sample preparation. Preliminary analyses (refer to page 35) showed that the digestion of the water samples yield statistically similar results when compared to analysing the water samples without any sample preparation. It was therefore decided not to digest the water samples.

All samples (soil, water and vegetable) were analysed by a Spectroflame Spectro Modula ICP capable of multi-element analysis. The data obtained was converted to actual concentrations.

Samples of soil, water and vegetables were collected at each of the sites during summer and winter in order to determine the effect of seasonal change on heavy metal uptake.

2.2 Sampling

The water, soil and vegetable samples were all treated differently, as is described below.

2.2.1 Water sampling

Water samples were collected in 2.5 L plastic containers which were soaked in dilute nitric acid for two weeks and rinsed with high purity water prior to use. This was done in order to avoid any possible external contamination. The plastic containers were initially rinsed with the borehole water before the actual collection.

The pH and temperature were measured in the laboratory on the same day of sampling. For calibration, buffers of pH 4.00 and 7.00 were used. It was necessary to preserve the water samples for storage so that it could be used for analysis at a later stage. This was done by means of acidification with suprapure nitric acid to below a pH of 2. The acidified samples were kept for approximately 16 hrs before they are prepared for analysis (EPA Method 200.7: 47-49).

2.2.2 Soil sampling

Composite soil samples were collected at each site by combining small portions of soil from various locations within the plot. Soil was sampled to a depth of approximately 12 cm (EPA Method 200.7: 47-49). At this depth, the soils sampled will cover the average root system of the vegetables. Unused, clear sampling bags were used for the collection of soil samples.

For the purpose of illustrating Pb deposition from the exhaust fumes of vehicles passing the roadside plots, soil samples were collected at a distance of 5 m, 10 m, 20 m and 30 m from the road.

The pH of the soil was potentiometrically measured in the supernatant suspension of a 1:5 soil/liquid mixture. This liquid was a 0.01 M $CaCl_2$ solution. 20 g of soil was weighed and to this 100 mL of $CaCl_2$ was added.

2.2.3 Vegetable sampling

Composite samples of vegetables were collected in appropriately labeled brown paper bags simultaneously with the soil samples at the same locations. Cabbage, lettuce, carrots, leeks, spinach, cauliflower and celery were collected based on availability at the selected site at the time. Vegetable samples were also collected at roadside plots. These vegetables were rinsed thoroughly with de-ionized water in order to remove all traces of soil and dust particles to ensure that there is no external contamination.

2.3 Sample preparation

2.3.1 Liquid samples

No preparation was needed for the liquid samples (EPA Method 200.7: 47-49). A B-Tech student (Dube, 2001) carried out a preliminary study by comparing the differences between results when liquid samples were analysed with sample preparation (digestion) and without sample preparation. This study showed that there was *no statistically significant difference* between the two sets of results.

2.3.2 Soil samples

Soil samples were initially sieved with a 2 mm sieve. The soil was mixed thoroughly to achieve homogeneity and then dried in an oven (Gravity convention oven, *with thermostatic control capable of maintaining* 70 °C ± 5 °C) until all the moisture was removed. Once cooled, 1.0 g of the dried soil was accurately weighed using an analytical balance capable of weighing to the nearest 0.0001 g and transferred to a 50 mL Phillips beaker. To this, 4.0 mL of 1:1 nitric acid and 10 mL of 1:4 hydrochloric acid were added. A watchglass was used to cover the beakers containing the samples. The samples were then heated to approximately

85 °C and gently refluxed for approximately 30 minutes. Once again, only slight boiling was allowed. After 30 minutes, the sample was cooled, transferred to a 100 mL volumetric flask, and diluted to the mark with de-ionized water. The sample at this stage was ready for analysis (EPA Method 200.7: 47-49).

2.3.3 Vegetable samples

The vegetables were dried in an oven at 70°C for 3 days, until free of all moisture. After grinding the dried vegetables by means of a ball mill, 0.1 g of each sample was weighed out accurately and transferred to the reaction vessel. 2 mL of the 30% hydrogen peroxide and 5 mL of nitric acid were added to the contents of the vessel. The vessels were then placed in the carousel and digestion proceeded by means of a temperature programme. The digestion was carried out in a Milestone-MLS 1200 Mega microwave oven capable of accommodating 6 digestion vessels, using the programme as outlined in table 2.1.

Table 2.1: Programme for vegetable samples:

STEP	*POWER*	*DURATION*
1	250 W	1 min
2	0 W	2 min
3	250 W	5 min
4	400 W	5 min
5	600 W	5 min

After digestion, the samples were cooled, transferred to a volumetric flask and made up to the mark with de-ionized water.

2.4 Reagent preparation

2.4.1 Ultra pure water

Normal tap water was purified using a Millipore apparatus for reverse osmosis. This process was followed by ion exchange also referred to as the Milli-Q system. The Milli-Q system consists of a pre-filter, a charcoal absorption column and 2 mixed-bed ion-exchange columns. After the de-ionisation of the tap water, the water was then passed through the micro-filter to remove the particulate matter. The unused water in the ion-exchange unit was automatically circulated every hour for 1 minute. This ultra pure, HPLC grade water was used during all experimental procedures.

2.4.2 Standard Stock Solutions

1000 ppm standard stock solutions were used during the preparation of calibration standards. These stock solutions were obtained from Saarchem and were all AR grade.

2.4.3 Mixed Calibration Standards

Mixed calibration standards were prepared by combining appropriate volumes of the stock standard solutions in 500 mL volumetric flasks. The standards were grouped into 3 categories (Cu, Cd and Mn, Cr and Zn and Fe, Ni and Pb) according to the EPA method (EPA Method 200.7: 47-49). 20 mL of 1:1 nitric acid and 20 mL of 1:1 hydrochloric acid were added to the flask, followed by the appropriate standard solutions and diluted to the mark with the ultra pure water. These freshly prepared standards were then transferred to the acid cleaned polyethylene bottles for storage.

2.4.4 Blanks

Three types of blank solutions were prepared and required during the analysis.

1. A calibration blank was used in order to establish the analytical calibration curve.
2. A laboratory reagent blank was used to assess possible contamination from the sample preparation procedure.
3. A rinse blank was used to flush out the instrument uptake system and nebulizer between standards and samples in order to reduce memory effects.

2.4.4.1 Calibration blank

The calibration blank was prepared by diluting a mixture of 20 mL of 1:1 nitric acid and 20 mL of 1:1 hydrochloric acid to 500 mL with ultra pure water.

2.4.4.2 Laboratory reagent blank

The laboratory reagent blank contained all the reagents in the same volumes used in processing the samples. The laboratory reagent blank was carried through the entire preparation procedure and analysis scheme. The final solution contained the same acid concentrations as sample solutions for analysis.

and the selection of lines is infinitely variable, background correction can readily be made and it is less expensive.

2.6 Calibration

Calibration standards were prepared by combining appropriate volumes of the stock standard solutions in 500 mL volumetric flasks.

20 mL of 1:1 nitric acid and 20 mL of 1:1 hydrochloric acid were added to the stock standards and then diluted to 500 mL mark with ultra pure de-ionized water These stock solutions were then diluted to the appropriate concentrations needed for the analysis of the various samples.

Table 2.2: Wavelength selection for metal analytes (nm):

ELEMENT		*QUANTITATION LINE (nm)*
Cadmium	(Cd)	226.502 nm
Copper	(Cu)	324.754 nm
Iron	(Fe)	259.940 nm
Manganese	(Mn)	257.610 nm
Lead	(Pb)	220.353 nm
Zinc	(Zn)	213.856 nm
Chromium	(Cr)	205.552 nm
Nickel	(Ni)	231.604 nm

These wavelengths provided the sensitivity needed to carry out analysis and was corrected for spectral interferences.

2.7 Analysis

ICP Method

A variable speed peristaltic pump was used to deliver both standard and sample solutions to the nebulizer. The concentration of heavy metals was then determined by means extrapolation from a calibration curve.

2.8 Soil organic matter

The soil samples were first oven dried in order to remove the excess moisture.
1 g of each soil sample was weighed out accurately into a crucible. The weight of the soil + crucible was recorded. A muffle furnace was heated to 500 °C and these crucibles containing the soil samples were then placed in the furnace for 2 hours and then cooled in a dessicator for approximately 1 hour (Storer, 1984).

2.9 pH

The pH of the soil and water samples were measured using a pH meter.

2.10 Statistical Analysis

Descriptive statistics were applied to the data sets, in order to determine the relationship that exists between the soil, water used for irrigation and the vegetable crops. The boxplot is a descriptive technique for summarising data. The "box" indicates the middle 50% of the observations, while the "whiskers" stretch from the minimum to maximum non-outlying values. Observations further than 1.5 times the box size are indicated separately as outliers. The median (middle value) is indicated by a horizontal line inside the box.

The boxplot is a useful summary of the data, indicating location (median), spread (box size and whisker length) and symmetry. A 95% confidence interval is constructed for the median value. In pair wise comparisons of boxplots, the median values differ statistically significantly at a 5% significance level if the notches do not overlap.

The notches perform a task similar to a *t*-test for testing differences in location. If the confidence intervals were calculated for mean values, the notches would correspond to the *t*-tests. In boxplots, however, the median is represented, instead of the mean. The median is a more robust measure of location, i.e. it will not be influenced by outliers to the same extent as mean values (McGill et al., 1978).

Principal Component Analysis (PCA) was used to study variable patterns as well as sample grouping and trends. In 1971, Gabriel introduced the PCA biplot as a graphical technique for displaying both the samples and variables of multivariate data (Gabriel, 1971). PCA is a powerful pattern recognition technique that can be viewed as a projection method where the intension is to preserve as much as possible of the variance in the original data set (Voutsa et al., 1996: 329). The S-Plus 2000 software was used to compile the statistics, namely the boxplots, analysis of covariance and PCA analysis.

2.11 Quality control

Certified reference material (lake sediment sample) was used in order to determine the accuracy and precision of the total digestion procedure. The reference material was treated and prepared in the very same way as the soil samples (International Atomic Energy Agency Lab/243 15 December 1979).

Fe, Al, Mn and Zn were determined because these were the only metals which formed part of the certified reference material information sheet along with other analytes which were not part of this study. The obtained and certified values of Fe, Al, Mn and Zn did not differ significantly, at 95 % in all the runs.

Procedural blanks were determined with each batch of samples and were below 1 % of the sample values.

In order to ensure further quality control measures, standards of known concentration were analysed as samples. This was carried out after every 10 samples of either soil, vegetables or water analysed.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Introduction

Analysis was performed on the soil, water and vegetable samples that were collected during the last week in August 2000 (winter) and the last week in February 2001 (summer). Sample collection was done just before harvesting. During winter, 39 water samples and 44 soil samples were collected, while during summer, 38 water and 41 soil samples were collected. One dam did not contain water during winter and two dams were empty during summer. There are therefore no results available for these dams. The collected samples had to undergo preparation before they were ready for analysis.

In order to determine the relationship that exists between the soil, water used for irrigation and the vegetable crops, descriptive statistics were applied to the data sets. Boxplots were also to summarise and indicate the location (median), spread and symmetry of the data. Principal component analysis was another statistical technique used in order to study variable patterns as well as sample grouping and trends.

The heavy metal concentrations in the soil, water and vegetable samples were compared to allowed limits specified by the SABS for soil and underground water, WHO (1993) and Plant Analysis Handbook (Jones et al., 1991) in the case of the vegetable samples.

3.2 Determination of heavy metal concentration in soil and water

3.2.1 Comparison of soil and water by means of descriptive statistics

The soil and water sampled during summer and winter were analysed in order to determine the concentrations of the selected metals. The minimum, maximum and mean concentrations during summer and winter were used to illustrate the concentration ranges, within a data set of a particular metal, between metals relative to each other and between summer and winter seasons. Boxplots were used to summarise the data and to illustrate differences between summer and winter results. The soil values were compared to the maximum metal and inorganic content permissible in soil as specified by SABS. It was not possible to obtain allowable limits for Fe and Mn in soil in South Africa because it has not been documented. The water values on the other hand were compared to the maximum allowed limit for ground water also specified by SABS.

Table 3.1: Minimum and maximum concentration ranges for soil in mg/kg. Median in parentheses.

	Fe	*Ni*	*Pb*	*Mn*	*Cu*	*Cd*	*Zn*	*Cr*
Concentration range	161 - 4626	2 - 8	5 - 63	1 - 55	1 - 25	0.1 - 2	4 - 50	2 - 19
Mean summer	609 (566)	3 (3)	14 (15)	20 (21)	9 (9)	2 (2)	25 (25)	9 (9)
Mean winter	820 (624)	5 (5)	26 (25)	22 (21)	8 (7)	1 (1)	30 (32)	9 (10)
Allowed limit	-	15	56	-	100	2	185	80

Table 3.1 illustrates the concentration ranges of each of the eight metals in soil, as well as the average concentrations during summer and winter. These average values (determined from 40 soil samples collected during summer and winter) were compared to the allowed limits also illustrated in the table.

A difference was observed between summer and winter soil results, with the winter results being generally higher than that of summer, with the exception of Cu and Cd concentrations illustrated in figure 3.1 and shown in table 3.1. Fe, Ni and Pb were determined as 609 mg/kg, 3 mg/kg and 14 mg/kg during summer respectively. During winter, their concentrations increased to 820 mg/kg, 5 mg/kg and 26 mg/kg respectively. Similarly, Mn and Zn levels were determined as 20 mg/kg and 25 mg/kg respectively during summer and increased during winter to 22 mg/kg and 30 mg/kg (Table 3.1). Fe exhibited the greatest increase in comparison to the rest of the heavy metals. The higher concentration of heavy metals in the soil during winter could be attributed to the fact that the seasonal rainfall could have resulted in a degree of enrichment of heavy metals in the soil. During winter, the water table tends to rise thus concentrating the heavy metals in the surface soils. The variation between the concentrations of heavy metals in the soil was much greater for Fe, Pb, Mn and Zn when compared to the rest of the heavy metals. The average concentration of Cr in the soil was 9 mg/kg during both seasons. The heavy metal that was present in the highest average concentration during summer and winter was Fe at 609 mg/kg and 820 mg/kg respectively. Stalikas (1997: 21) stated that the high Fe concentration in the soil could be due to the presence of great amounts of ferrous oxyhydroxides in the soil system. The lowest concentration of heavy metals present in the soil during both seasons was Cd and Ni at 2 mg/kg and 3 mg/kg during summer and 1.39 mg/kg and 4.85 mg/kg during winter respectively. Pb was the only heavy metal that was present in the soil at a concentration that exceeded the allowed limit of 56 mg/kg. This Pb contamination was apparent at only 1 of the 40 sites. This Pb contaminated site was alongside a main road that usually has a high traffic density. This could have contributed to Pb deposition. The rest of the heavy metals did not exceed the allowed limit.

The boxplot is a descriptive technique for summarising data. The "box" indicates the middle 50% of the observations, while the "whiskers" stretch from the minimum to maximum non-outlying values. Observations further than 1.5 times the box size is indicated separately as outliers. This is illustrated in Figure 3.1. The median is indicated by a horizontal line inside the box.

The boxplot is a useful summary of the data, indicating its location (median), spread (box size and whisker length) and symmetry. A 95% confidence interval is constructed for the median value. In pairwise comparisons of boxplots, the median values differ statistically significantly at a 5% significance level if the notches do not overlap.

The boxplots (Figure 3.1) show that the results for Ni, Pb, and Cd in the soil had differed significantly between summer and winter, while the results for the rest of the metals were similar during both seasons.

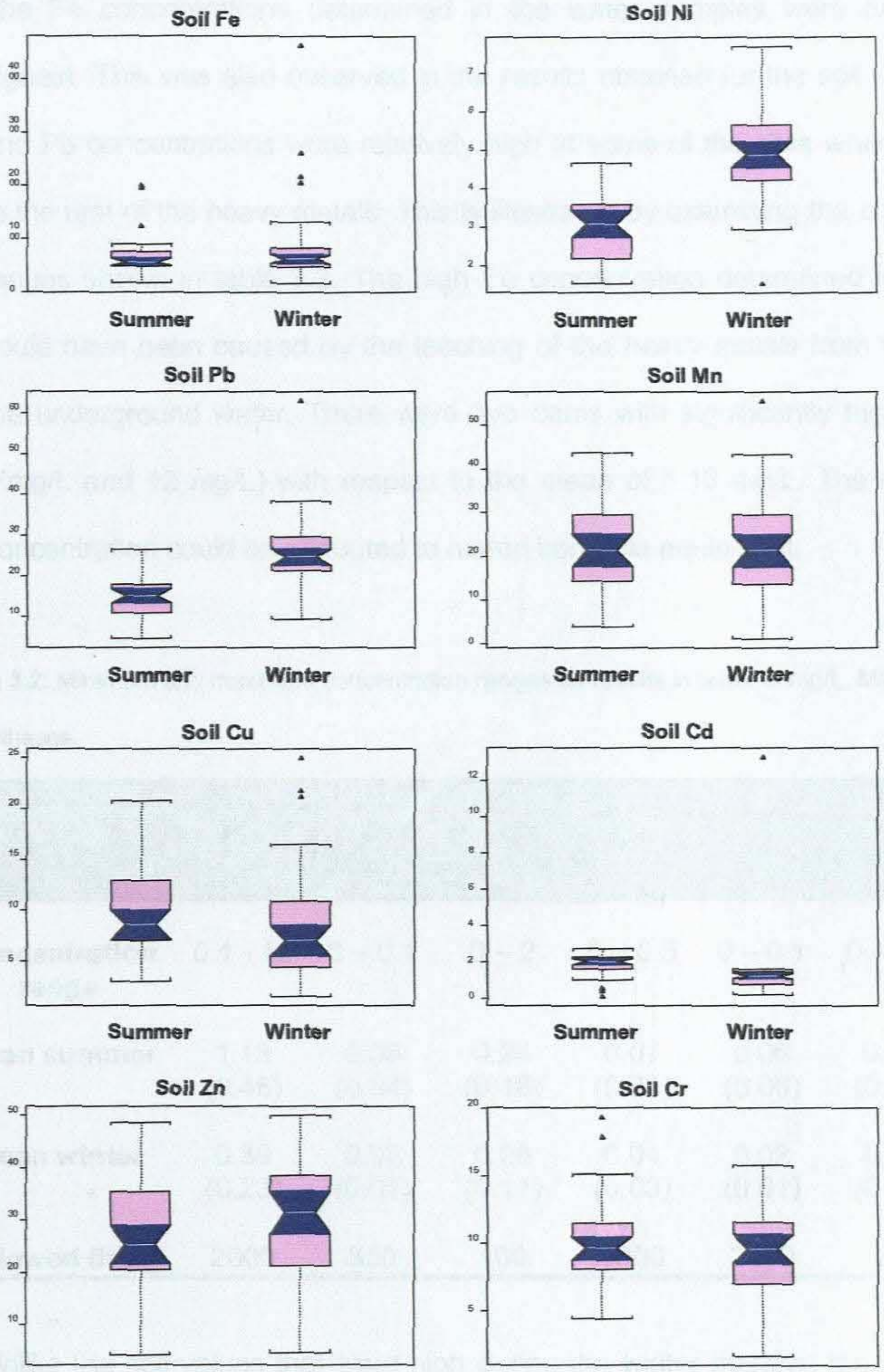

Figure 3.1: *Boxplots of heavy metal concentrations in soil during summer and winter*

The Fe concentrations determined in the water samples were amongst the highest. This was also observed in the results obtained for the soil samples. Fe and Pb concentrations were relatively high at some of the sites when compared to the rest of the heavy metals. This is illustrated by examining the concentration ranges shown in table 3.2. The high Fe concentration determined in the water could have been caused by the leaching of the heavy metals from the soil into the underground water. There were two dams with significantly high Fe levels (7mg/L and 12 mg/L) with respect to the mean of 1.13 mg/L. The elevated Fe concentration could be attributed to rusted borehole equipment.

Table 3.2: *Minimum and maximum concentration ranges for results in water in mg/L*. Median in parentheses.

	Fe	*Ni*	*Pb*	*Mn*	*Cu*	*Cd*	*Zn*	*Cr*
Concentration *range*	0.1 - 12	0 – 0.1	0 – 2	0 – 0.5	0 – 0.1	0 – 0.1	0 – 0.3	0 – 0.2
Mean summer	1.13 (0.46)	0.06 (0.04)	0.24 (0.16)	0.07 (0.04)	0.06 (0.06)	0.03 (0.03)	0.03 (0.02)	0.01 (0.01)
Mean winter	0.39 (0.23)	0.02 (0.01)	0.26 (0.11)	0.04 (0.03)	0.02 (0.01)	0.01 (0.01)	0.05 (0.03)	0.01 (0.02)
Allowed limit	2000	350	100	1000	2000	20	10	500

Unlike the soil values that were high during the winter months, the heavy metal concentration in the water sampled at the various dams were generally lower, as can be observed in table 3.2. This contradiction could be attributed to the fact that the winter rainfall would cause the dams to fill and as a result cause the dilution of the heavy metals already present in the dams. Pb and Zn, however were the exceptions. The average Pb concentration during summer was 0.24 mg/L and increased to 0.26 mg/L during winter, similarly, the average Zn concentration was 0.03 mg/L during summer and increased to 0.05 mg/L during winter. Cr was the heavy metal that was present in the lowest average concentration at 0.01 mg/L during both seasons. Cr also remained constant during both seasons in the soil and water samples. The concentration of all the heavy metals in the water samples were well within the allowed limits specified for borehole water by SABS.

The boxplots (Figure 3.2) show that the results for Ni, Cu, and Cd in the water had differed significantly between summer and winter with Cu having the largest difference. The results for the rest of the metals were similar during both seasons.

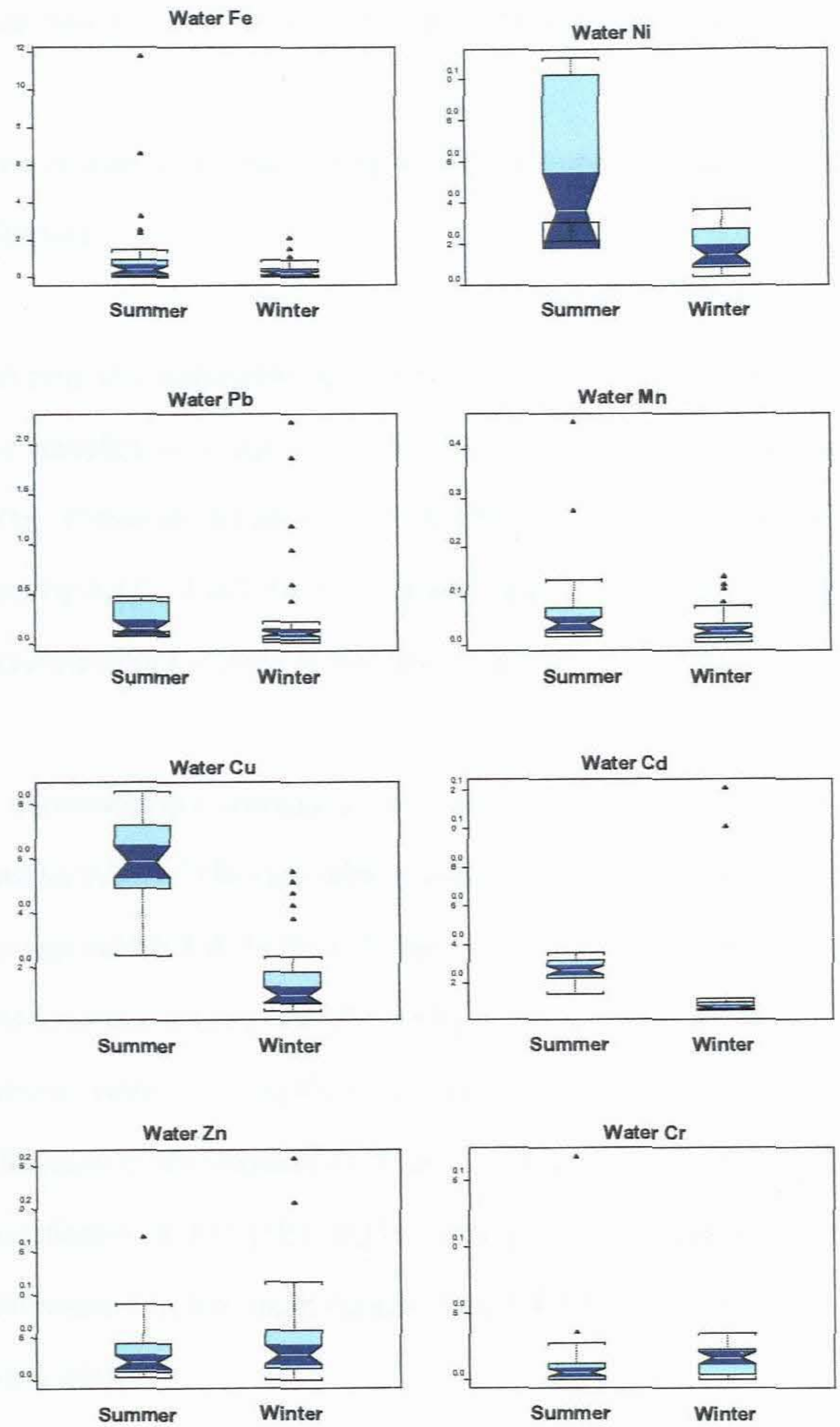

Figure 3.2: Boxplots of heavy metal concentrations in water during summer and winter

3.3 Determination of heavy metal concentration in vegetables

3.3.1 Comparison of summer and winter results by means of descriptive statistics

After analyzing the vegetable samples collected during summer and winter, descriptive statistics were applied to the data, as was the case for the water and soil samples. These values were then compared to the permissible levels in food as reported by WHO, FAO (Codex Alimentarius Commission, 1994) and levels for the micronutrients reported in the Plant Analysis Handbook.

The Fe concentration displayed in table 3.3 exceeded all other metal concentrations in all of the vegetable samples. The Fe concentration in spinach and celery was particularly high (123 mg/kg for both). Zn was the second highest accumulated metal, ranging from 29 mg/kg to 72 mg/kg. The Ni, Pb, Cd and Cr concentrations were not significantly different, when comparing the values obtained for each of the vegetables. The spinach had accumulated a significantly high concentration of Mn (101 mg/kg during summer and 181 mg/kg during winter) with respect to the mean concentration (60 mg/kg during summer and 62 mg/kg during winter).

Table 3.3: Average metal concentration of vegetables during summer in mg/kg. Allowed limit in parenthesis.

	Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
Carrots	85	3	6	14	11	1	3	46
	(300)	**(5)**	**(0.5)**	**(200)**	**(15)**	**(0.03)**	**(5)**	**(250)**
Leeks	91	3	5	7	7	1	3	40
	(300)	**(5)**	**(0.5)**	**(65)**	**(10)**	**(0.03)**	**(5)**	**(550)**
Cabbage	76	2	5	17	5	0.9	3	29
	(200)	**(5)**	**(0.5)**	**(200)**	**(15)**	**(0.03)**	**(5)**	**(200)**
Spinach	123	2	7	60	8	0.9	4	66
	(200)	**(5)**	**(0.5)**	**(250)**	**(25)**	**(0.03)**	**(5)**	**(100)**
Cauliflower	44	2	5	17	3	0.8	3	22
	(200)	**(5)**	**(0.5)**	**(250)**	**(15)**	**(0.03)**	**(5)**	**(250)**
Celery	123	3	8	12	11	0.9	4	72
	(70)	**(5)**	**(0.5)**	**(300)**	**(8)**	**(0.03)**	**(5)**	**(70)**
Lettuce	108	7	6	18	10	1	4	60
	(500)	**(5)**	**(0.5)**	**(90)**	**(10)**	**(0.03)**	**(5)**	**(100)**

The Cu concentration was the highest in the carrots (11 mg/kg) and the celery (11 mg/kg). Generally, the leafy vegetables such as lettuce, celery and spinach had higher concentrations of metals than the less sensitive species, such as carrots and leeks. This was also observed in a study done by Rahlenbeck, et al. (1999:31) and Davis (1980). Cu, Pb and Zn concentrations were slightly higher when compared with previously reported data for similar vegetables by

Bahemuka and Mubofu (1999: 65). The Cd concentrations, on the other hand was significantly higher in similar vegetables reported by Bahemuka (1999: 65).

The heavy metal concentration for the vegetables sampled during winter are generally lower than the results obtained for summer. The Mn concentration in most of the vegetables was, however, higher during winter. The carrots and leeks exhibited the lowest accumulation tendency for Fe, Pb Mn and Zn at 40 mg/kg, 4 mg/kg, 8 mg/kg and 21 mg/kg for carrots and 46 mg/kg, 4 mg/kg, 7 mg/kg and 19 mg/kg for leeks respectively, when compared to the rest of the vegetables. Kabata-Pendias (1992:365) reported that the highest accumulation of Pb occurred in leafy vegetables. A similar trend can be observed in this study, with the exception of cabbage. The Pb concentration in the cabbage was also high at 7 mg/kg. During both seasons, Fe appears to be the most abundant of the elements in the analysed samples. It is well known that some vegetable species show particular preference to Fe uptake, this being especially true for celery and spinach (Stalikas, 1997: 21). A similar trend was also observed in this study.

Table 3.4: Average metal concentration of vegetables during winter in mg/kg. Allowed limit in parenthesis.

	Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
Carrots	40	1	4	8	7	0.4	3	21
	(300)	**(5)**	**(0.5)**	**(200)**	**(15)**	**(0.03)**	**(5)**	**(250)**
Leeks	46	1	4	7	4	0.3	2	19
	(300)	**(5)**	**(0.5)**	**(65)**	**(10)**	**(0.03)**	**(5)**	**(55)**
Cabbage	75	2	7	26	5	0.5	3	43
	(200)	**(5)**	**(0.5)**	**(200)**	**(15)**	**(0.03)**	**(5)**	**(200)**
Spinach	95	2	6	62	10	0.5	3	120
	(200)	**(5)**	**(0.5)**	**(250)**	**(25)**	**(0.03)**	**(5)**	**(100)**
Cauliflower	67	1	5	25	5	0.4	2	45
	(200)	**(5)**	**(0.5)**	**(250)**	**(15)**	**(0.03)**	**(5)**	**(250)**
Celery	73	2	8	35	7	0.6	3	48
	(70)	**(5)**	**(0.5)**	**(300)**	**(8)**	**(0.03)**	**(5)**	**(70)**
Lettuce	94	1	5	26	8	0.6	4	53
	(500)	**(5)**	**(0.5)**	**(90)**	**(10)**	**(0.03)**	**(5)**	**(100)**

All the vegetables sampled at the forty sites have a concentration of Pb higher than Cd. This is in agreement with the findings of a study conducted by Queirolo et al. (2000), who states that this is a normal situation for plants.

3.3.2 Comparison of heavy metal concentrations in vegetables during winter

A graphical representation of the average heavy metal concentration in the various vegetables was used to illustrate trends and draw comparisons between the various vegetables

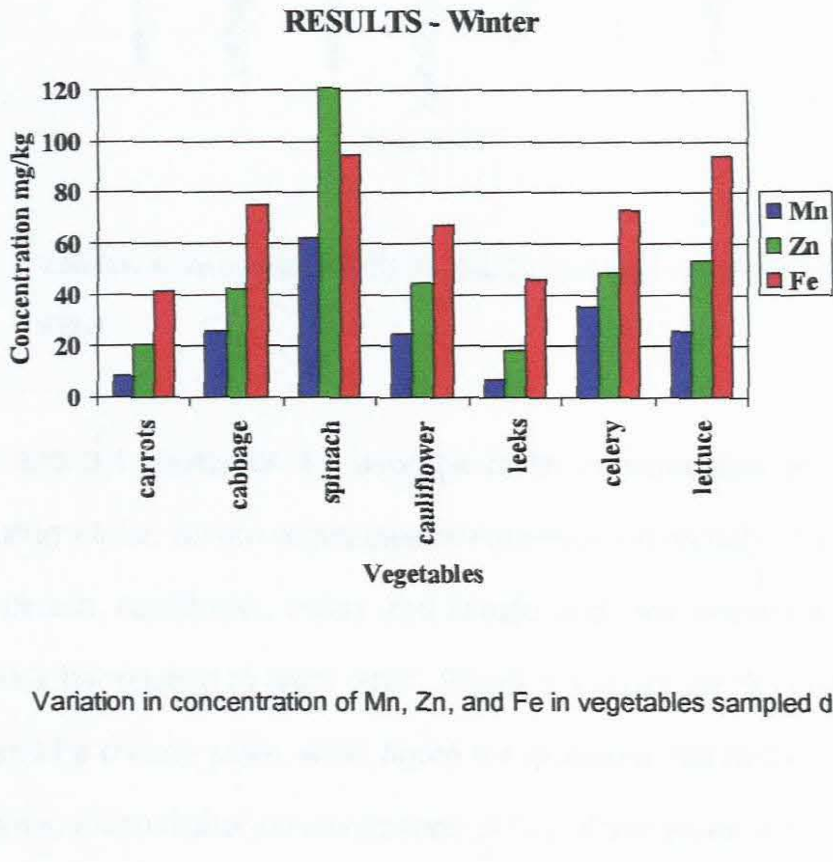

Figure 3.3: Variation in concentration of Mn, Zn, and Fe in vegetables sampled during winter

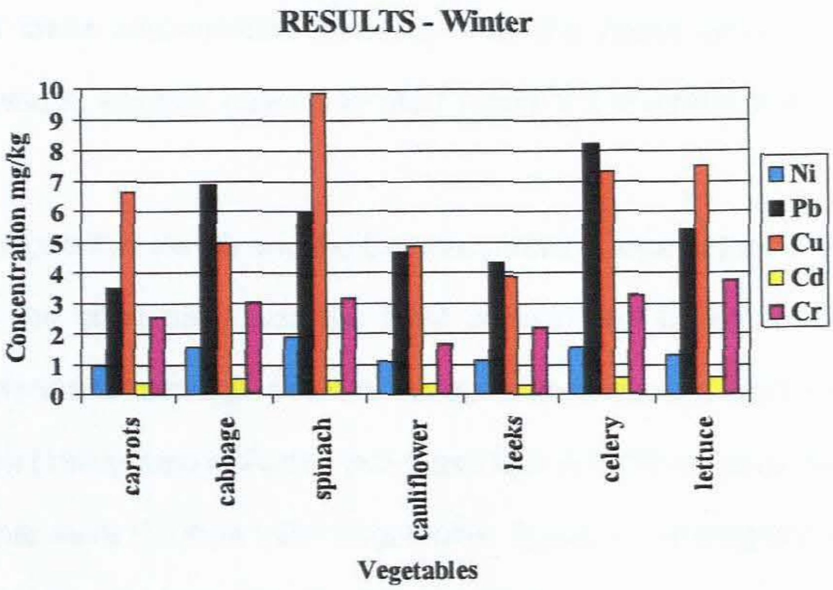

Figure 3.4: Variation in concentration of Ni, Pb, Cu, Cd, and Cr in vegetables sampled during winter

Figure 3.3 and 3.4 represent the average metal concentration in vegetables sampled during winter. Seven vegetables are represented namely, carrots, leeks, cabbage, spinach, cauliflower, celery and lettuce and their heavy metal content displayed as a bar relative to each other. Figure 3.3 illustrates the concentration of Mn, Zn and Fe on one scale, while figure 3.4 illustrates the rest of the metals. Fe is present in much higher concentrations in five of the seven vegetables than the rest of the heavy metals. The Fe concentration in the vegetables ranges from 40 mg/kg to 95 mg/kg. The concentration of Fe in almost all cases is greater than that of Zn and Mn. *The spinach seems to exhibit a high accumulation tendency* for Fe, Mn and Zn, at 95 mg/kg, 62 mg/kg and 120 mg/kg respectively, whereas leeks and carrots seem to exhibit a low accumulation tendency for Fe, Zn and

Mn. In general, the below ground vegetables such as the carrots and the leeks exhibited a lower accumulation tendency than the above ground vegetables (cabbage, lettuce, spinach, cauliflower etc.). Figure 3.3 illustrates this tendency.

Figure 3.4 shows that the Pb and the Cu concentration exceed that of Ni, Cd, and Cr. Cd, on the other hand was the least accumulated heavy metal. Lettuce, spinach, celery and cabbage seem to be good accumulators of Cd. Davis and Calton-Smith (1980), also indicated that these four vegetables have the tendency to accumulate more Cd than other vegetables. Spinach, once again, exhibited a high accumulation tendency for Cu, Pb and Ni in comparison to the rest of the vegetables. The leeks, cauliflower and carrots exhibited the lowest accumulation tendencies. Cabbage, lettuce and celery are generally somewhere between the two extremes with respect to accumulation tendencies.

3.3.3 Comparison of heavy metal concentration in vegetables during summer

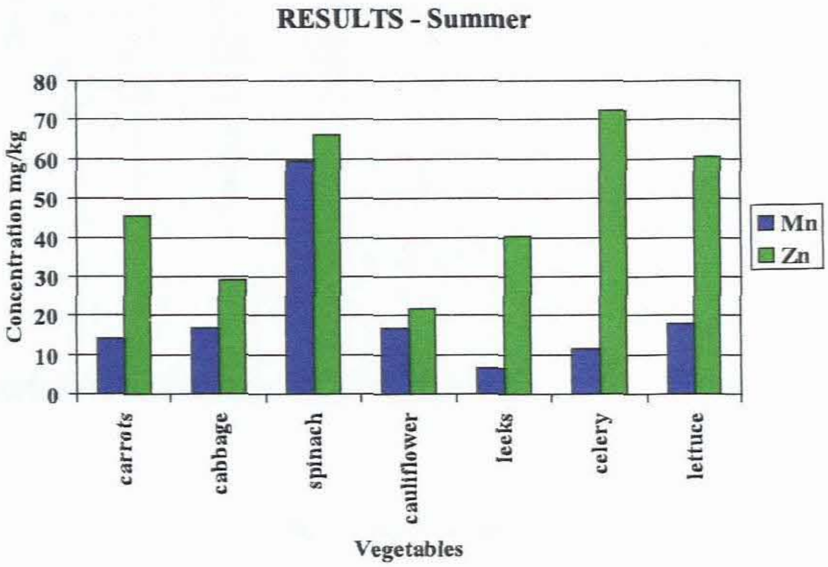

Figure 3.5: Variation in concentration of Mn and Zn in vegetables sampled during summer

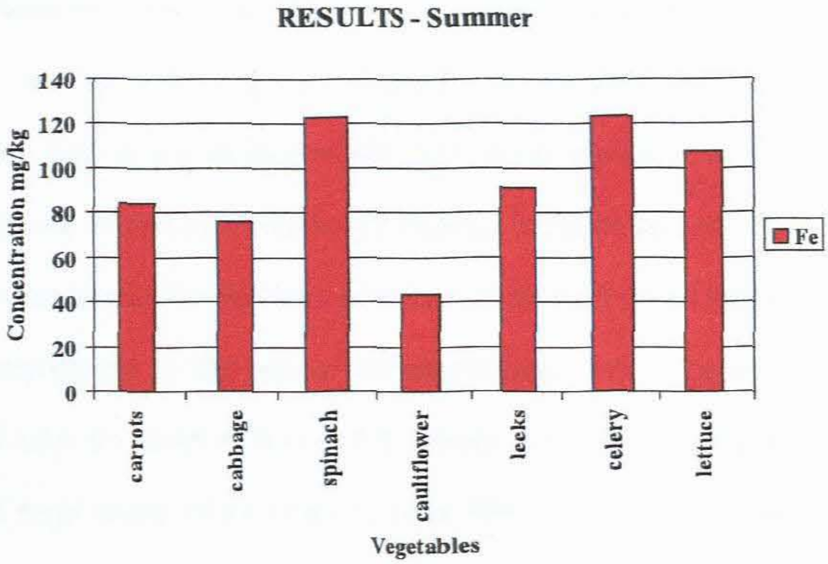

Figure 3.6: Variation in concentration of Fe in vegetables sampled during summer

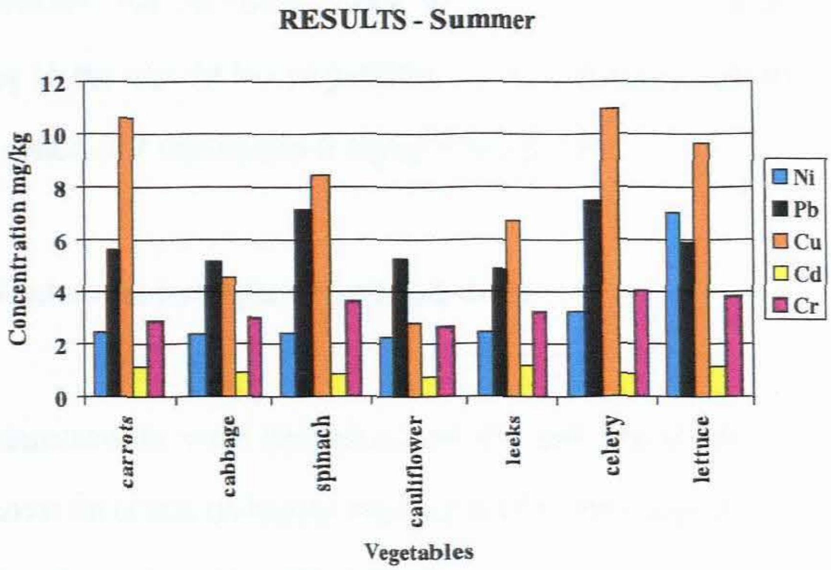

Figure 3.7: Variation in concentration of Ni, Pb, Cu, Cd and Cr in vegetables sample during summer

Figures 3.5, 3.6 and 3.7 represent the average metal concentration in vegetables sampled during summer. Figure 3.5 shows celery as the highest accumulator of Zn (72 mg/kg) followed by spinach (66 mg/kg), which accumulated a high levels of Zn and Mn (60 mg/kg). Spinach, celery and lettuce Zn concentration ranged from 61 to 72 mg/kg. Spinach accumulated Mn at 60 mg/kg, which exceeded the Mn concentration in the rest of the vegetables by far. The Mn concentration in the rest of the vegetables was all below 20 mg/kg. A similar trend can be seen in figure 3.6, where the celery, spinach and lettuce accumulated high levels of Fe ranging from 108 to 123 mg/kg. Figures 3.5, 3.6 and 3.7 show that cauliflower, on average, had the lowest accumulation tendency during summer, which was not the case during winter. The Ni concentration in figure 3.7 seems to be fairly consistent in most of the vegetables except for celery and lettuce. The Ni concentration at 7 mg/kg in the lettuce exceeds Ni concentration in the rest of the vegetables by far. Pb levels are the highest in spinach and celery at 7 mg/kg and 8 mg/kg respectively.

3.4 Physical measurements of soil and water

Physical measurements were carried out on the soil and water samples since they could have an effect on heavy metal uptake by the vegetables as reported earlier in this study. Comparisons between summer and winter, and soil and water results can also be made.

Table 3.5: *Physical measurements of soil and water samples*

	pH	*Organic Matter*	*Temperature*
Soil			
Range	5.31 – 7.9	1.0 – 72.9 %	-
Mean Summer	7.2	4.6 %	
Mean Winter	7.0	7.6 %	
Water			
Range	2.2 – 8.7	-	21 - 28
Mean Summer	6.9	-	
Mean Winter	7.7	-	

The pH of the water ranged from acidic at around 2.2 to fairly basic at around 8.7. The pH of the soil ranged from 5.31 to 7.9, with most of the sampled sites having a pH above 7. This would imply that the heavy metals present in the soil would be less available for uptake. The mobility and bioavailability of heavy metals in soils are associated with the percentage of organic matter present in the soil with a decrease in availability expected with an increase in organic content. The soil organic matter ranged from 1.0 % to 72.9 %.

In an attempt to determine how the heavy metals in the soil, and water as well as the pH of the soil and the organic matter present in the soil influence the heavy metal uptake of the vegetables, an analysis of covariance was performed. The model fitted (for each heavy metal) allowed for different heavy metal levels in the different vegetable types. The relationship between the soil heavy metal values, water heavy metal values, pH and organic matter on the one hand and the vegetable heavy metal values on the other hand forms a regression equation.

The results from this equation indicated that uptake relationships were only identified for Fe (p=0.0002), Mn ($p < 0.0001$) and Cd (p=0.0004) where the soil pH, metal in the soil and the organic matter had a statistically significant influence on the metal in the vegetable. A statistically significant uptake relationship implies that the predictor variables have a significant influence on the heavy metal content of the vegetable. P-values of less than 0.05 indicates that there is a statistically significant uptake relationship. There was no statistically significant relationship between the Zn (p=0.32), Cu (p=0.56), Pb (p=0.38), Ni (p=0.87) and Cr (p=0.25) levels in the vegetables and the predictor variables (pH and organic matter).

3.5 The inter-relationships between variables

The Principal Component Analysis biplot was introduced by Gabriel in 1971 as graphical technique for displaying both the samples and variables of multivariate data. In 1996 Gower & Hand proposed a new approach to biplot methodology, viewing biplots as the multivariate analogues of scatterplots. In these displays, only the sample points are plotted while each variable is represented by a biplot axis. Since the biplot axes are fitted with scale markers in the original units of measurement, orthogonal projection of a sample onto the axis facilitates inferring the value of the original variable for that sample point. PCA is a powerful pattern recognition technique that can be viewed as a projection method where the intension is to preserve as much as possible of the variance in the original data set (Voutsa, Grimanis & Samara, 1996: 329).

In this study the values differ widely between the different heavy metals. Therefore, the data was scaled to have zero mean and unit standard deviation. Since a PCA biplot aims to represent as much of the variation in the data in 2 dimensions, the quality of display represents the proportion of variance displayed in the graphical representation.

Apart from the quality of the display, Gower & Hand (1996) also defines a measure of how well each variable is represented in the graphical display. The adequacy of representation of each variable varies between 0 and 1, with a higher adequacy indicating a better representation. Although angles between the biplot axes should be interpreted with caution, smaller angles are indicative of larger correlation between the variables.

3.5.1 Inter-relationship between the heavy metal concentration in soil sampled during summer and winter

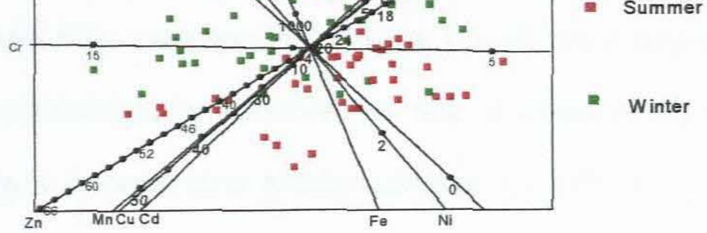

Figure 3.8: PCA biplot of heavy metals in soil during summer and winter

PCA was used to compare the heavy metal concentration of the soil samples with each other and the seasons in which they were sampled. Figure 3.8 illustrates an overlap of data with slight separation between summer and winter values. The overlapping of data points indicates that the results obtained for both seasons were relatively similar. The winter data is more scattered across the graph indicating that the concentration of a particular metal from sampling site to sampling site and from metal to metal differed to a greater extent during this season. There is virtually no clustering of data within each season, which means that there are no similarities between heavy metal concentrations in the soil samples. Although the data for summer is also scattered, it does however exhibit a smaller spread. The PCA plot indicates seasonal variation in heavy metal concentration in the soil.

3.5.2 Inter-relationship between the heavy metal concentration in water sampled during summer and winter

Principal component analysis was also used in the case of the dams to compare the heavy metal concentration of the water samples with each other, and the seasons in which they were sampled. Figure 3.9 shows a degree of separation between data obtained during summer and data obtained during winter. The data obtained during summer shows greater variation as indicated by the scattering with a very large spread. More than 50 % of the summer values differ largely when comparing the heavy metal concentrations of the water samples to each other.

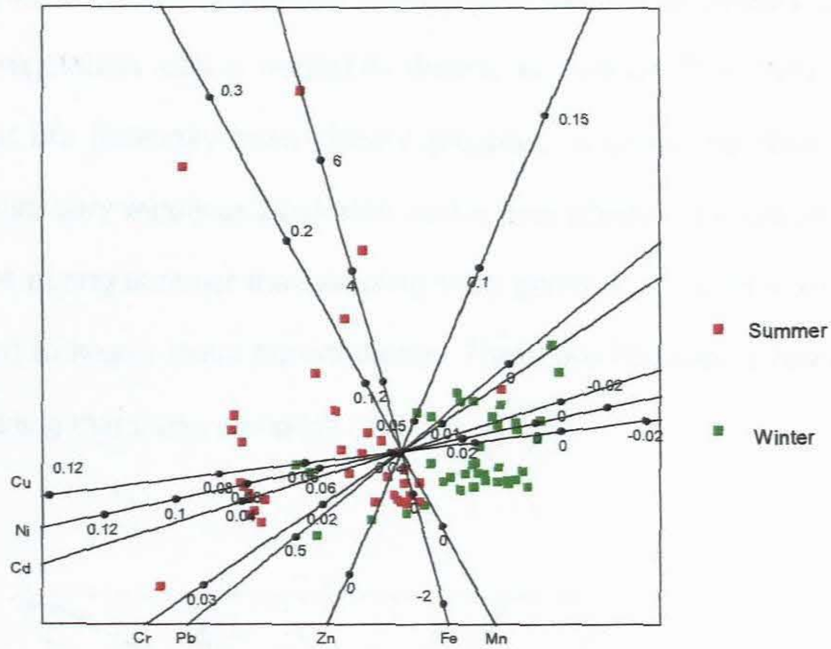

Figure 3.9: PCA biplot of heavy metals in water during summer and winter

There is a cluster present in both the summer and winter data. These clusters represent values that are similar. This means that the concentration of heavy metals in those water samples relative to each other are similar. The data obtained during winter on the other hand have a much smaller spread, indicating less variation between data when compared to that of summer. Similar to the PCA plot of heavy metal concentration in the soil, this PCA plot also indicates seasonal variation in heavy metal concentration in the water.

3.5.3 Inter-relationship between the heavy metal concentration in vegetables sampled during summer and winter

Figure 3.10 shows separation between the summer and winter data collected for the vegetables with a negligible degree of overlap. The data collected during winter are generally more closely grouped, whereas the data collected during summer vary widely as illustrated by the data points in the graph. The conclusion is that during summer the sampling sites generally differed from each other with regard to heavy metal concentration. There are however a few clusters present indicating that those sampling sites are similar.

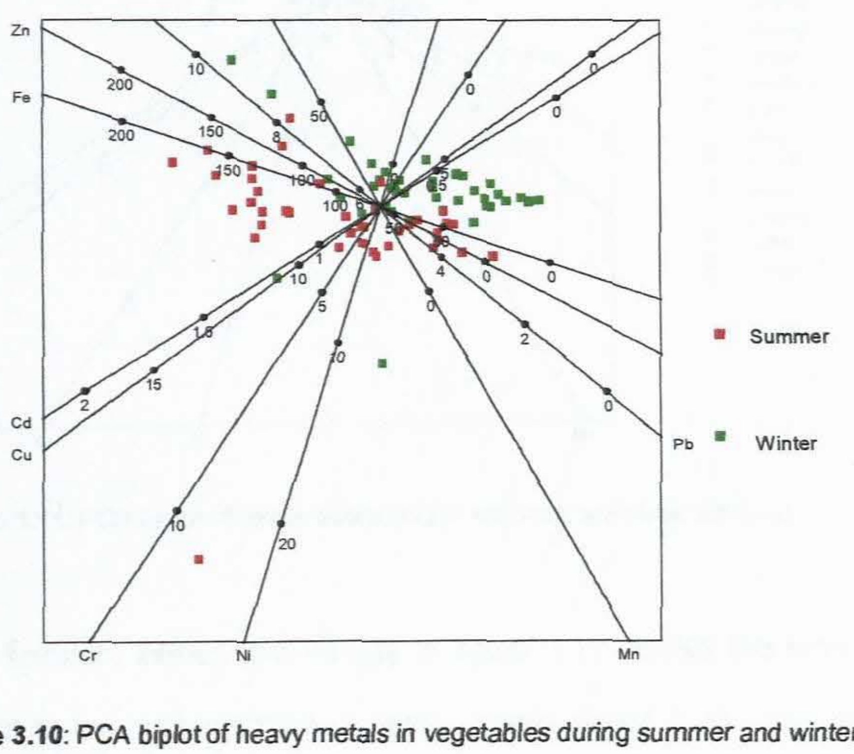

Figure 3.10: *PCA biplot of heavy metals in vegetables during summer and winter*

The winter data, which is more closely grouped, indicates that the results obtained from the various sampling sites are more comparable. There are however a few outliers. Once again, seasonal variation of heavy metal concentration in the vegetables can be observed.

3.5.4 Inter-relationship between the heavy metal concentration in various vegetable species sampled

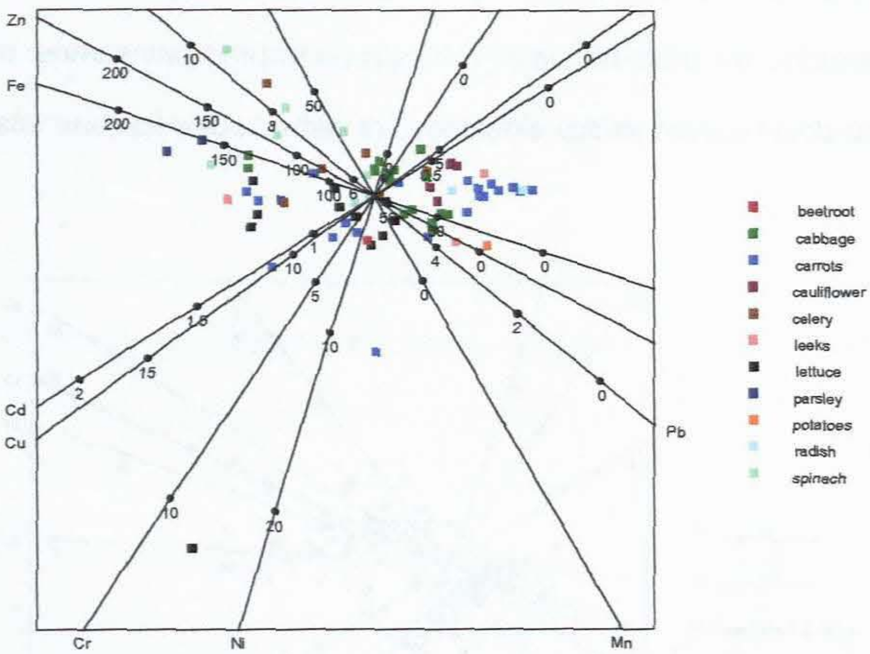

Figure 3.11: *PCA biplot of heavy metals in the various vegetables sampled*

The spinach, lettuce and carrots in figure 3.11 display the most variation with regard to the concentration of heavy metals during both seasons. The spinach data seem to be significantly different from the rest of the data. This phenomenon is represented by the data points, which appear farther away from the group. The cabbage and the cauliflower display the smallest degree of scattering, therefore there is not much variation in the heavy metal concentration during summer and winter. This biplot indicates that the vegetables differ in heavy metal uptake.

3.5.5 Inter-relationship between the heavy metal concentration in vegetables, soil and water during summer and winter

In the following PCA biplot the heavy metal values for soil, water and vegetables are represented simultaneously. It is clear that there are differences between the water and soil values, while the vegetable values have a much smaller spread.

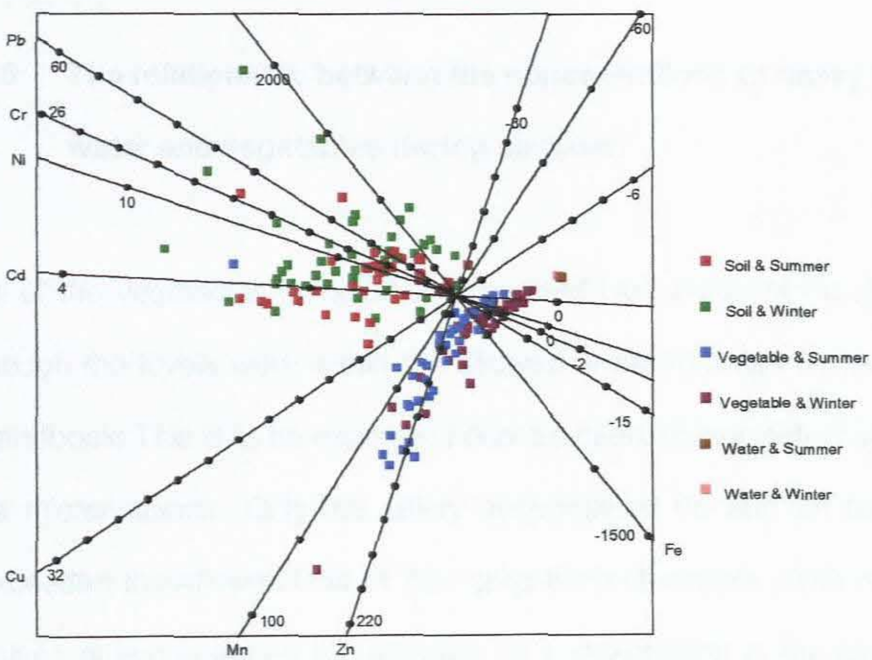

Figure 3.12: PCA biplot of heavy metals in vegetables, soil and water during summer and winter

Figure 3.12 illustrates the differences and similarities between all the variables, namely soil, water and vegetables. The vegetables sampled during summer and winter are very similar, with the summer vegetable results exhibiting more scattering toward the higher concentrations of Zn and Mn. The soil sampled during summer and winter also seems to be similar. This is represented by the overlap of data points. The soil sampled during winter exhibited more scattering toward the higher concentrations of Fe, Pb, Cr, Ni and Cd. Summer and winter water samples can be regarded as the same because of the direct overlap illustrated in the biplot. The three variables (vegetables, soil and water) are very clearly separated.

3.6 The relationship between the concentrations of heavy metals in soil, water and vegetables during summer.

All of the vegetables sampled accumulated high levels of Fe, Zn and Mn even though the levels were within the allowed limits specified by the Plant Analysis Handbook. This is to be expected because these heavy metals are also regarded as micronutrients. Only the celery accumulated Fe and Zn to the extent that exceeded the allowed limit of 70 mg/kg for both metals. With regard to the soil values during summer, the average Fe concentration is the highest in the soil, followed by Zn and then Mn. The Fe concentration was the highest in all of the vegetables and this could be due to the fact that the average concentration of this metal in both the soil and the water was relatively high.

When studying the relationship between the soil, water and vegetables with regard to heavy metal concentration, some of the heavy metal concentrations in the vegetables coincide with the high bioavailability of the same metals present in the soil. Some of the high metal concentrations in the vegetables cannot be explained by their concentrations in the corresponding soils. This could probably be ascribed to accumulation patterns influenced by the soil factors. Ni, Cu and Cd concentrations in the carrots, spinach, leeks and lettuce, in some cases also exceeded the concentration present in the soils in which these vegetables were grown. Mn concentrations were greater in the cabbage, spinach and lettuce than in the soil at some of the sampling sites.

Table 3.3 shows that lettuce accumulated Ni to the extent that it exceeded the allowed limit. Carrots, spinach, celery and lettuce were amongst those vegetables whose Pb concentration had exceeded the allowed limit. Celery accumulated the highest level of Pb when compared to the other values. Carrots, leeks, spinach, celery and lettuce contained high levels of Cu, although still below the allowed limit. Cd and Cr concentrations were also below the allowed limit in all of the vegetables. On average, the lettuce and the spinach exhibited a high accumulation tendency because both vegetables accumulated most of the heavy metals in much larger quantities than the rest of the vegetables.

All the vegetables that were sampled during summer contained concentrations of Pb and Cd that exceeded the allowed limit. Ni and Cr concentrations exceeding the allowed limit were found in only 2 out of 37 vegetable samples. 1 out of 37 vegetable samples contained concentrations of Fe and Zn that exceeded the allowed limit and 3 out of 37 vegetable samples contained Cu concentrations that exceeded the allowed limit.

Table 3.6: Summary of the Farming areas that exhibited elevated heavy metal concentrations during summer

PLOTS	*FARMING AREA*	*FARMS WITH THE HIGHEST METAL CONTENT DURING SUMMER*							
		Fe	**Ni**	**Pb**	**Mn**	**Cu**	**Cd**	**Cr**	**Zn**
1-5	**1**						√		
6-10	**2**					√			
11-14	**3**								
15-23	**4**		√	√				√	
24-31	**5**								
32-36	**6**								√
37-38	**7**				√				
39-40	**8**	√							

Table 3.6 indicates the farming areas with the highest average heavy metal concentration found in their vegetables during summer. Plots 1 to 5 represents farming area 1 for which the highest concentration of Cd in the vegetables during summer, were found. Farming area 4 had the highest Ni, Pb and Cr.

The plots were grouped as indicated in table 3.6, according to the actual farming area. Each farming area was sub-divided into smaller plots, each having its own dam. Therefore farming area 4, for example, had 9 dams and nine plots.

3.7 The relationship between the concentrations of heavy metals in soil, water and vegetables during winter.

Rainfall during the winter months could influence the distribution of heavy metals in the soil in two ways. It could either cause a degree of enrichment of the soil, or it could cause the depletion of certain metals. The concentration of heavy metals in vegetables during winter was generally lower than that of summer. This concentration of heavy metals in the dams also followed a similar pattern. The fact that the concentration of heavy metals was lower in the vegetables during winter suggested that the rainfall over this region had contributed to the depletion of the metals in the soil, therefore making them less available for uptake. However, it was observed that the concentration of heavy metals in the soil was generally higher during winter. This could be attributed to the soil being more neutral to slightly basic, making the heavy metals less available for uptake.

Fe, Mn and Zn concentrations increased in the cauliflower during winter compared to the results obtained in summer. Pb, Mn and Zn concentrations have also increased in the cabbage during winter, while the Mn concentration has almost tripled in the celery. Mn also increased in the lettuce.

Cu concentrations in all of the vegetables, except lettuce, also exceeded the concentration present in the corresponding soils. There is generally not a strong relationship between the concentrations in the soil and vegetables, because it depends on various factors such as soil metal bioavailability, plant growth and metal distribution to plant parts (Voutsa et al., 1996). Stalikas (1997: 22) also found that certain high metal concentrations recorded in the crops cannot be explained by their concentrations in the corresponding soils. The cauliflower, celery, leeks, spinach and lettuce Mn concentration also exceeded the soil concentration at some of the plots. The remaining heavy metals were much lower in the vegetables than in the soil. The contribution of the water to the heavy metal concentration in the soil and the vegetables during both seasons seems to be insignificant.

All the vegetables that were sampled during winter had levels of Pb and Cd exceeding the allowed limit. The average Ni, Cr, Mn and Cu concentrations in the vegetables were below the allowed limit. Fe, Zn and Cu concentrations exceeding the allowed limits were found in 3 out of 37 vegetables and 1 out of 37 vegetables and 3 out of 37 vegetables respectively.

Table 3.7: Summary of the Farming areas that exhibited elevated heavy metal *concentrations during winter*

PLOTS	*FARMING AREA*	*FARMS WITH THE HIGHEST METAL CONTENT DURING WINTER*							
		Fe	**Ni**	**Pb**	**Mn**	**Cu**	**Cd**	**Cr**	**Zn**
1-5	**1**								
6-10	**2**					√	√	√	
11-14	**3**								
15- 23	**4**								
24-31	**5**	√			√				√
32-36	**6**								
37-38	**7**			√					
39-40	**8**								

Table 3.7 indicates the farming areas with the highest average heavy metal concentration found in the vegetables that were grown in that area during winter. Plots 6 to 10 represents farming area 2 for which we have found the highest concentration of Cu, Cd and Cr in the vegetables sampled during winter, while farming area 5 has a the highest concentration of Fe, Mn and Zn.

3.8 The effect of Pb deposition on roadside plots

Seven of the selected plots were situated along frequently used roads. It was therefore decided that it would be of interest to investigate lead deposition in the soil and the vegetables at these plots to determine whether there were any patterns that could be observed. The vegetables selected for this investigation were based on availability.

The Pb concentration of the soil and vegetables was plotted against the distance away from the road starting from 5 m at 10 m intervals. Even though 7 different plots were sampled, the same vegetables were grouped together onto one graph to determine whether there were similarities within a specific vegetable species.

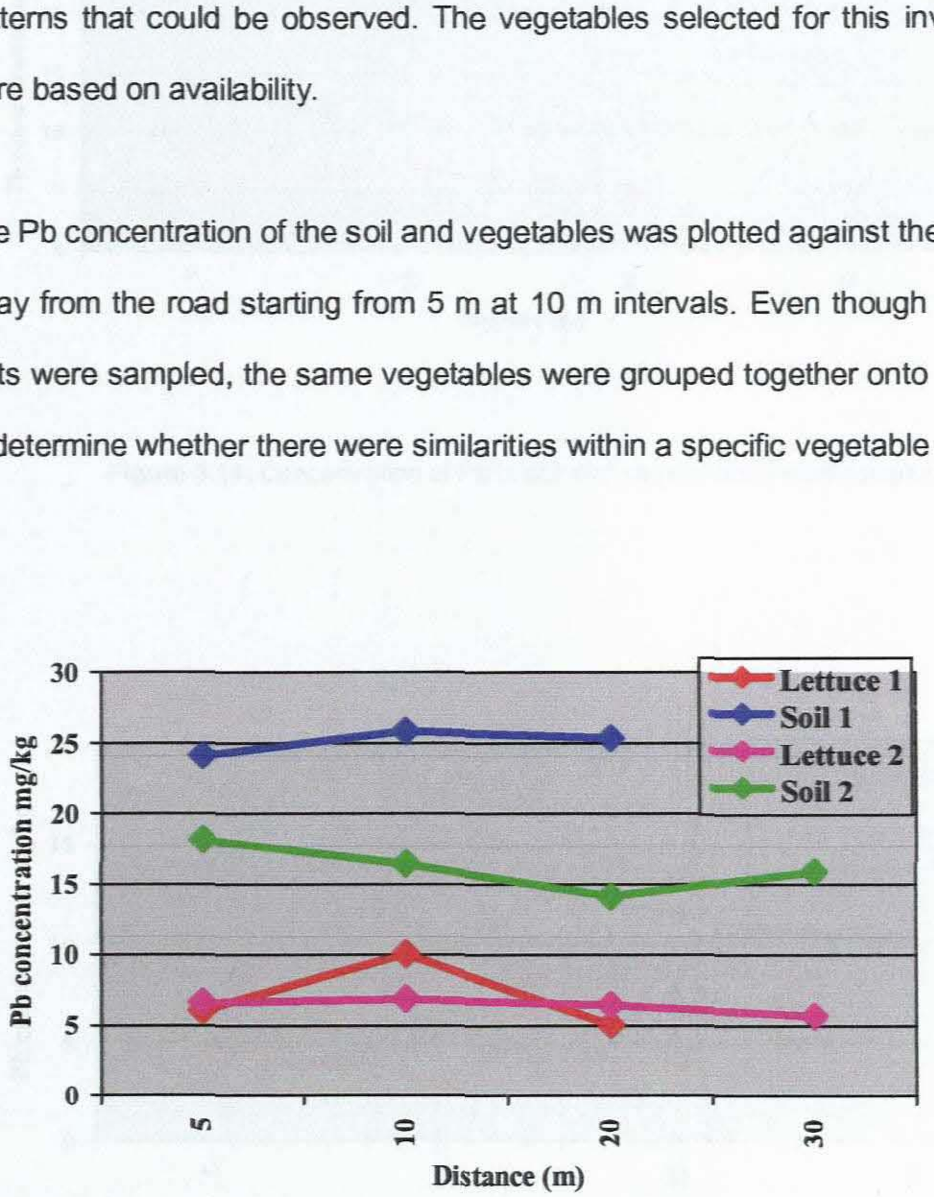

Figure 3.13: Concentration of Pb in soil and vegetables at roadside plots

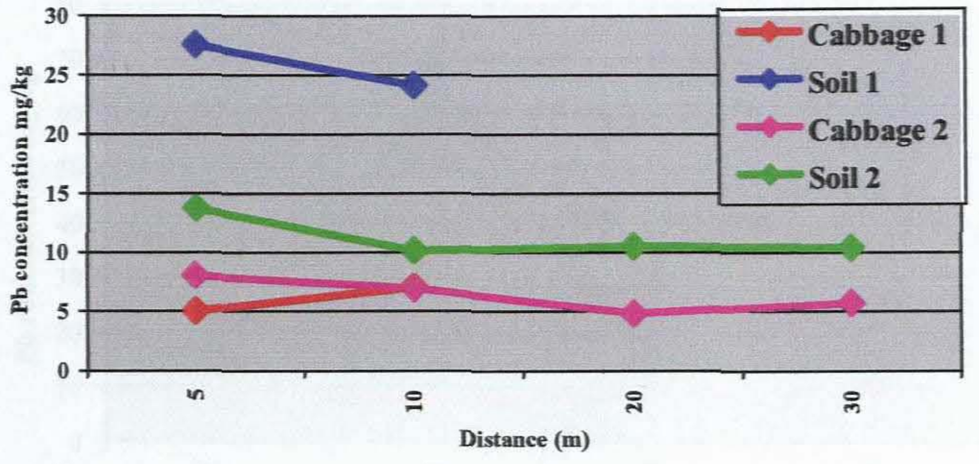

Figure 3.14: Concentration of Pb in soil and vegetables at roadside plot

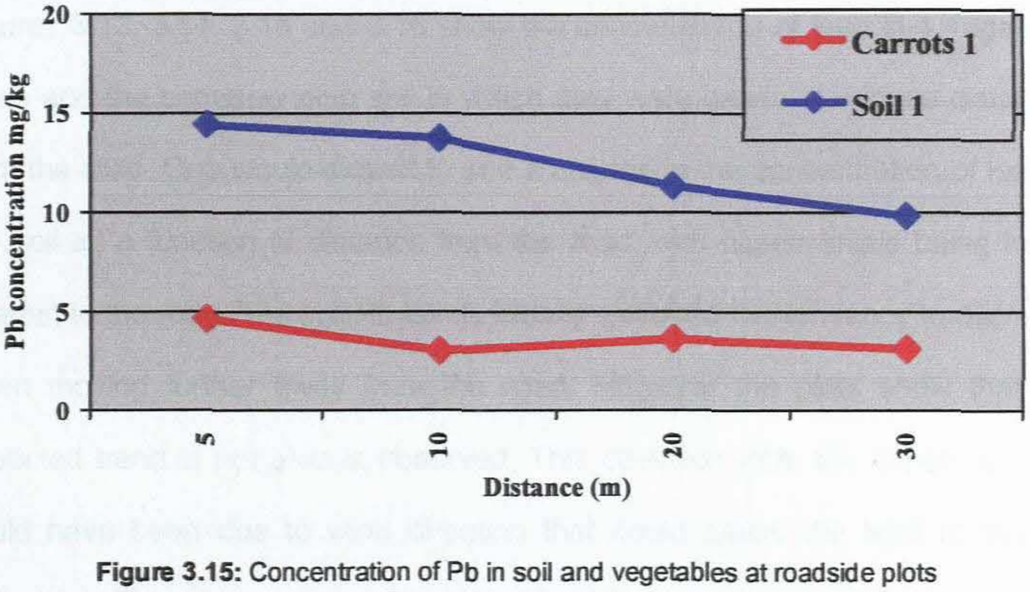

Figure 3.15: Concentration of Pb in soil and vegetables at roadside plots

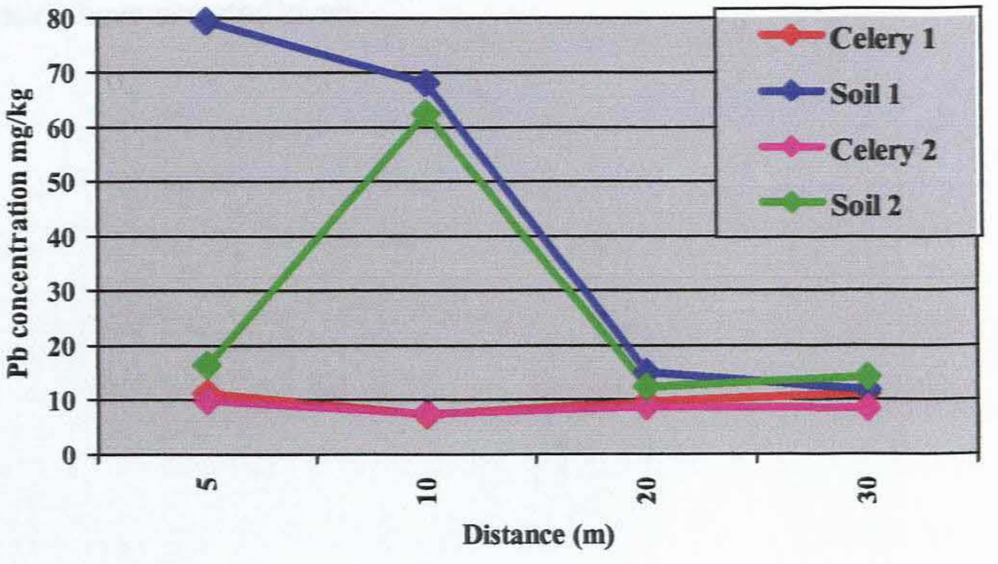

Figure 3.16: Concentration of Pb in soil and vegetables at roadside plots

Figures 3.13, 3.14, 3.15 and 3.16 show the concentration of lead in 4 vegetable types and the corresponding soil in which they were grown at various distances from the road. One would expect to see a change in the concentration of lead in the soil as a function of distance from the road, with higher levels being found nearest to the road. The soil Pb levels initially exhibited the tendency to decrease when moving further away from the road. However the plots show that the expected trend is not always observed. This deviation from the expected trend could have been due to wind direction that could cause the lead to deposit elsewhere. The concentration of lead in the various vegetables behaved similarly.

This does not clearly illustrate the effect of traffic through the release of Pb from the exhaust fumes, as a major source of pollution. The deposition mechanism is somewhat more complex, but there is indication that vegetables grown near the roadside have elevated levels.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusion

The results of this study indicate that the concentration of the heavy metals in the soil and water resources were within the allowed limits, with the exception of one sampling site. Even though the soil and water resources were not contaminated, certain vegetable species contained heavy metals in concentrations that exceeded the allowed limits. This demonstrates the ability of plants to concentrate metals in their tissues to levels exceeding those present in the soil or water.

In this study, statistical differences were found between summer and winter results with respect to heavy metal concentration in the soil, water and the vegetables. The results indicate that seasonal change can have an effect on the availability of heavy metals. During winter, the heavy metal concentration in the soil was higher due to possible enrichment of these metals in the soil, while the water and vegetables had lower concentrations of heavy metals.

There is evidence to suggest that vegetable species vary in their uptake of heavy metals. This study showed that spinach exhibited an accumulation pattern that differed significantly from the rest of the vegetables. Spinach, celery and lettuce can be regarded as good accumulators because they accumulated high concentrations of most of the heavy metals tested. The cauliflower exhibited the lowest accumulation tendency during summer, while the carrots and leeks had the lowest accumulation tendency during winter.

pH and organic matter were identified in a number of studies as important factors that contribute to relative metal uptake. The findings of this study indicates that, statistically, uptake relationships only existed for Fe, Mn and Cd.

It was difficult to determine whether there were accumulation tendencies unique to the above ground and below ground vegetables. The results of this study indicates that this difference cannot be clearly defined. Although there is evidence that below ground vegetables such as carrots and leeks exhibit lower accumulation tendencies. Even though there is a translocation of heavy metals from the soil and water to the vegetable, those vegetables exceeding the allowed limit is small relative to the total sample size.

Addressing the potential hazards is essential first and foremost in order to protect farmers, their families and ultimately the consumers from contaminated vegetables.

4.2 Recommendations

Attempting to discontinue cultivation of vegetables on the various plots is not an option for these farmers as this is their main source of income. One solution would be for these farmers to consider some treatment methods. Researchers have therefore sought ways to avoid harm without compromising the economic stability of households that depend on agriculture.

It would be useful to establish the source of heavy metal contamination in order to minimize levels in soils and water, therefore decreasing availability to the vegetable crops. One of the ways to effectively manage the bioavailability of metals in the soil is to manipulate the soil pH (Jackson & Alloway, 1991: 180). Liming of soils has been shown to reduce availability of metals to a number of plant species. Another means of soil remediation is to make use of metal scavenging plants to cleanse the soil. These types of plants will take up toxic metals through their roots and transport them to stems or leaves where they could be easily removed by harvesting. Other cost effective techniques involve removal of contaminated soil and replacing it with clean soil, or mixing the contaminated soil with clean soil to dilute the concentration of heavy metals. These are just some of the ways in which the farmers can reduce the bioavailability of heavy metals.

In terms of future research in this field, variation in heavy metal uptake between vegetable crops should be studied more closely in order to determine which vegetable crops would be 'high risk' in terms of accumulation tendencies. Future studies should also investigate the contribution of heavy metals through atmospheric deposition. Procedures should be put in place so that future monitoring of heavy metals in vegetables are carried out by environmental health officials on a regular basis. This type of monitoring would in ensure that no contaminated vegetables ever reach the public.

4.3 REFERENCES:

1. ALLOWAY, B.J. and BRIAN, J. 1993: Chemical Principles of Environmental Pollution. Glasgow: Chapman and Hall.

2. ALLOWAY, B.J. 1995: Heavy Metals in Soils. London: Blackie Academic and Professional, p. 141.

3. ALLOWAY, B.J.; TILLS A.R. and MORGAN H. 1984: The speciation and Availability of Cadmium and Lead in Polluted Soils. Columbia: University of Missouri, pp. 187-201.

4. BAHEMUKA, T.E. and MUBOFU, E.B. 1999: Heavy metals in edible green vegetables grown along the sites of the Sinza and Msimbazi rivers in Dar es Salaam, Tanzania. Food Chemistry, Vol. 66, pp. 63-66.

5. BEATON, J.D. and WALSH, L.M. 1973: Soil Testing and Plant Analysis. Washington, D.C: Soil Science Society of America, Inc.

6. BOSNIR, J. and PUNTARIC, D. 1997: Lead Concentration in Brassicas from Zagreb Home Gardens. Public Health Institute, pp. 95-112.

7. BUCHET, J.P.; LAUWERYS, R.; ROELS, H.; BERNARD, A.; BRUAUX, P. 1990: Renal effects of cadmium body burden of the general population. Lancet 336, pp. 699 – 702.

8. BURROWS, D. 1993. Chromium: metabolism and toxicity. Boca Raton (FL): CRC Press, Inc.

9. CARLOSENA, A.; ANDRADE, J.M.; TOMAS, X.; FERNANDEZ, E. and PRADA, D. 1999: Classification of edible vegetables affected by different traffic intensities using potential curves. Talanta, Vol.48, pp. 795-802.

10. CASDORPH, H. and WALKER, M. 1995: Toxic Metal Syndrome. New York: Avery Publishing, p. 95.

11. CARTER M.R. 1993: Soil Sampling and Methods of Analysis. Lewis Publishers.

12. Codex Alimentarius Commission, 1994: Contaminants, Joint FAO/WHO Food Standards Program, Vol.XVII.

13. COETZEE, C.B.; CASEY, N.H. and MEYER, J.A. 2000: Quality of groundwater used for poultry production in the Western Cape. Water SA, Vol.26, p. 565.

14. COOKE, B.J. 1999: Heavy Metal Accumulation in Vegetables in the Scaga and Quacker Community Gardens. B-Tech Project.

15. DAVIS, R.D. and CARLTON-SMITH, C. 1980: Crops as indicators of the significance of contamination of soil by heavy metals. Technical Report TR140, Stevenage: UK, p. 44.

16. DUBE, F. 2001: personal communication.

17. EPA – Method 200.7, 1991: Determination of metals and trace elements in water and wastes by Inductively Coupled Plasma – Atomic Emission Spectrometry.

18. FRIEDMAN, K. 1994: Reporting on the Environment: A handbook for Journalists, p. 8.

19. GABRIEL, K.R. 1971: The biplot graphical display of matrices with application to principal component analysis. Biometrika, Vol 58, pp. 453-467.

20. Global Report 1990/91. Unido, Industry and Development: The need for Ecologically Sustainable Industrial Development, pp. 132-133.

21. GORDAN, E. 1999: Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. National Academy of Sciences. Vol.96, pp. 3388-3395.

22. GOLUEKE, C. 1998: Heavy Metal mobility and soil pH levels. BioCycle, Vol.39, p. 28.

23. GOLUEKE, C. 1995: Effect of lead and cadmium on vegetables. BioCycle., Vol. 36, p. 29.

24. GOWER, J.C and HAND, D.J. 1996: Biplots. London, Chapman and Hall.

25. GOYER, R.A. 1997: Toxic and Essential metal interactions. Annual Review of nutrition. Vol. 17, pp. 37-50.

26. GUTTORMENSEN, G., SINGH, B.R. and JENG, A.S. 1995: Cadmium concentration in vegetable crops grown in sandy soil as affected by Cd levels in fertilizer and soil pH. Fertilizer Research. Vol.41, pp. 27-32.

27. HARDMAN, J.G. and LIMBIRD, L.E. 1995: The Pharmacological Basis of Toxicity. McGraw-Hill, New York, p. 1324.

28. HARTE, J. 1991: Toxics A to Z: A guide to everyday pollution hazards. University of California press, Berkeley, p. 103.

29. HOGUE, E.J. and NEILSEN, G.H. 1996: Effect of soil cadmium application and pH on growth and cadmium accumulation in roots, leaves and fruit of strawberry plants. Journal of Plant and Soil, Vol. 180, pp. 267-276.

30. International Atomic Energy Agency. 1979. Lab/243.

31. ITANNA, F. 2002: Metals in leafy vegetables grown in Addis Ababa and toxicological implications. Ethiopian Journal of Health Development, Vol.16, pp. 295 – 302.

32. JACKSON, A. and ALLOWAY, B. 1991: Plant and Soil, Vol 132, pp. 179 – 186.

33. JONES, J.B; WOLF, B and MILLS, H.A. 1991: Plant Analysis Handbook. MicroMacro Publishing.

34. KABATA-PENDIAS, A. and PENDIAS, H. 1992: Trace Elements in Soils and Plants. Boca Raton: CRC Press, p. 365.

35. KELLAS, B. and DWORKIN, A. 1996: Surviving the Toxic Crisis. Olivenhain: Professional Reference Publishing, pp. 187-230.

36. LIU, H.; PROBST, A. and LIAO, B. 2004: Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill. The Science of the Total Environment.

37. LOZET, J. and MATHIEU, C. 1991: Dictionary of Soil Science, 2nd ed. Balkema, Rotterdam.

38. MATHEE, A.; von SCHIRNDING, Y.E.R.; LEVIN, J.; ISMAIL, A.; HUNTLEY, R. AND CANTRELL, A. 2002: A survey of blood lead levels among young Johannesburg school children. Environmental Research, Vol.90, pp 181 – 184.

39. McGILL, R.; TUKEY, J.W. and LARSEN, W.A. 1978: Variations of Box Plots. The American Statistician, Vol.32(1), pp. 12 – 16.

40. Metro South East plan – The future of the Philippi Horticultural Area. 1997. Chittenden Nicks Partnership, pp. 4- 9.

41. MORRIS, R. 1997: *Protecting Scarce Groundwater resources*. Cape Times

42. NOVAK, M.; EMMANUEL, S.; VILE, M.; EREL, Y.; VERON, A.; PACES, T. 2003: Origin of lead in eight central European peat bogs determined from isotope ratios, strengths and operations times of regional pollution sources. Environmental Science and Technology. Vol.37, p. 437.

43. QUEIROLO, F.; STEGEN, S.; RESTOVIC, M.; PAZ, M.; OSTAPCZUK, P.; SCHWUGER, M.J. and MUNOZ, L. 2000: Total arsenic, lead and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. The Science of the Total Environment . Vol.255, pp. 75-84.

44. RAHLENBECK, S.I.; BURBERG, A. and ZIMMERMANN, R.D. 1999: Lead and Cadmium in Ethiopian Vegetables. Bulletin of Environmental Contamination and Toxicology, Vol. 62, pp. 30-33.

45. RÖLLIN, H.; MATHEE, A.; LEVIN, J.; THEODOROU, P. and WEWERS, F. 2005: Blood manganese concentrations among first-grade schoolchildren in two South African cities. Environmental Research. Vol.97, pp. 93-99.

46. South African Bureau of Standards 241:1999 – Specification for ground water.

47. South African Bureau of Standards 241:1984 – Maximum metal and inorganic content in soil and permissible application rate of metal and inorganic content to soil.

48. SALIM, R.; ISA, M.; AL-SUBU, M.; SAYRAFI, S.A.; and SAYRAFI, O. 1995: Effect of irrigation with lead and cadmium on the growth and on the metal uptake of cauliflower, spinach and parsley. Journal of Environmental Science and Health, Vol. 4, pp. 831-849.

49. Senate Administration for Town development and environmental protection Berlin, 1991: – Results of the heavy metal analyser for allotments, paper IV E, pp. 224-226.

50. STALIKAS, C.D.; CH.MANTALOVAS, A. and PILIDIS, G.A. 1997: Multielement concentrations in vegetables species grown in two typical agricultural areas of Greece. The Science of the Total Environment, Vol.206, pp.17-24.

51. STORER, DONALD A.: 1984. A Simple High Sample Volume Ashing Procedure for Determination of Soil Organic Matter. Soil Science and. Plant Analysis, Vol 15(7), pp. 759 – 772.

52. SAUERBECK, D.R. 1991: Plant, Element and Soil properties governing uptake and availability of Heavy Metals derived from sewage sludge. Water, Air and Soil Pollution 57-58, pp. 227-237.

53. SECER, M.; BODUR, A.; ELMACI, O.L.; DELIBACAK, S. and IQBAL, N. 2002: Trace element and heavy metal concentrations in fruits and vegetables of the Gediz River region. International Journal of Water, Vol.2, pp. 196 – 211.

54. TRIPATHI, R.M.; RAGHUNATH, R. and KRISHNAMOORTHY, T.M. 1997: Dietary intake of heavy metals in Bombay city, India. The Science of the Total Environment, Vol.208, pp. 149-159.

55. U.S. EPA. EPA's Terms of Enviroment. 2000.

56. U.S Food and Drug Administration FDA Consumer, January – February 1998.

57. VOUTSA, D.; GRIMANIS, A. and SAMARA, C. 1996: Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. Environmental Pollution, Vol.94, pp. 325-335.

58. WHO, 1993: Evaluation of certain food additives and contaminants. Technical report, Series 751, pp. 35 – 53.

59. WRC Report No 166/1/89 Studies on Irrigating Management Based on PAWC and Soil Water Monitoring. FMG Vanassche and MC Laker.

60. WRC Report No 572/1/99 Investigation of Contaminant Attenuation Characteristics of the soil aquifer system with special emphasis on the Vadose Zone. Sililo, O.N.T.; Conrad, J.; Murphy, K.O.H.; Tredoux, G.; Eigenhuis, B.; Ferguson, M.C.D.; Moolman, J.H.

61. XUE, Q. and HARRISON, C. 1991: Effect of soil zinc, pH, and cultivar on cadmium uptake in leaf lettuce. Soil science and plant analysis, Vol.22, pp. 975 – 991.

APPENDIX

WATER DATA COLLECTED DURING SUMMER (mg/L)

Dams	Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
D1	0.43	0.02	0.08	0.02	0.02	0.01	0.17	0.00
D2	6.65	0.04	0.13	0.10	0.04	0.02	0.05	0.00
D3	11.85	0.04	0.15	0.13	0.04	0.02	0.06	0.01
D4	0.69	0.03	0.17	0.04	0.05	0.02	0.01	0.00
D5	0.19	0.03	0.14	0.03	0.04	0.02	0.01	0.00
D6	2.41	0.03	0.16	0.05	0.09	0.02	0.04	0.01
D7	0.07	0.03	0.12	0.02	0.05	0.02	0.00	0.01
D8	0.47	0.04	0.16	0.27	0.04	0.02	0.06	0.01
D9	1.15	0.03	0.15	0.07	0.05	0.02	0.02	0.01
D10	0.08	0.04	0.20	0.02	0.03	0.02	0.01	0.01
D11	0.34	0.04	0.15	0.03	0.05	0.02	0.02	0.00
D12	0.13	0.03	0.14	0.02	0.05	0.02	0.01	0.00
D13	0.88	0.03	0.12	0.03	0.05	0.02	0.01	0.00
D14	0.06	0.02	0.13	0.02	0.05	0.03	0.01	0.00
D15	0.05	0.03	0.11	0.02	0.06	0.03	0.01	0.00
D16	0.05	0.03	0.14	0.02	0.05	0.03	0.00	0.00
D17	0.06	0.03	0.12	0.02	0.06	0.03	0.01	0.00
D18	0.14	0.03	0.14	0.04	0.06	0.02	0.07	0.00
D19	0.09	0.03	0.12	0.03	0.05	0.03	0.01	0.00
D20	0.33	0.04	0.17	0.07	0.05	0.03	0.02	0.03
D21	0.46	0.04	0.14	0.07	0.06	0.03	0.04	0.01
D22	0.07	0.03	0.12	0.02	0.07	0.03	0.01	0.00
D23	0.87	0.05	0.23	0.08	0.04	0.02	0.05	0.02
D24	3.31	0.05	0.16	0.46	0.07	0.03	0.05	0.04
D25	0.99	0.04	0.16	0.08	0.07	0.03	0.01	0.00
D26	2.57	0.05	0.16	0.11	0.07	0.03	0.04	0.00
D27	1.54	0.10	0.46	0.13	0.07	0.03	0.04	0.00
D29	0.37	0.10	0.41	0.05	0.08	0.03	0.00	0.00
D30	0.57	0.11	0.46	0.12	0.08	0.03	0.09	0.01
D31	0.74	0.10	0.45	0.05	0.08	0.03	0.03	0.00
D32	1.46	0.10	0.45	0.06	0.08	0.03	0.09	0.03
D33	1.45	0.11	0.49	0.04	0.08	0.03	0.03	0.01
D34	0.21	0.11	0.43	0.03	0.08	0.03	0.01	0.17
D36	0.66	0.11	0.47	0.08	0.07	0.03	0.02	0.02
D37	0.38	0.11	0.47	0.05	0.06	0.03	0.03	0.01
D38	0.46	0.10	0.44	0.04	0.08	0.04	0.02	0.01
D39	0.69	0.11	0.44	0.05	0.08	0.03	0.02	0.01
D40	0.17	0.11	0.48	0.03	0.07	0.04	0.03	0.01
Average	1.13	0.06	0.24	0.07	0.06	0.03	0.03	0.01
Max	11.85	0.11	0.49	0.46	0.09	0.04	0.17	0.17
Min	0.05	0.02	0.08	0.02	0.02	0.01	0.00	0.00
Median	0.46	0.04	0.16	0.04	0.06	0.03	0.02	0.01
Std Dev	2.16	0.03	0.15	0.08	0.02	0.01	0.03	0.03

WATER DATA COLLECTED DURING WINTER (mg/L)

Dams	Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
D1	0.38	0.01	0.07	0.02	0.02	0.01	0.11	0.02
D2	0.21	0.01	0.15	0.01	0.01	0.01	0.01	0.00
D4	1.13	0.02	0.08	0.08	0.02	0.12	0.02	0.01
D5	0.14	0.01	0.15	0.05	0.02	0.01	0.01	0.00
D6	0.40	0.01	0.60	0.03	0.02	0.10	0.01	0.03
D7	0.06	0.01	0.05	0.01	0.02	0.01	0.26	0.00
D8	0.70	0.01	2.23	0.12	0.05	0.01	0.05	0.01
D9	0.14	0.01	1.87	0.04	0.05	0.01	0.05	0.01
D10	0.06	0.01	1.19	0.01	0.04	0.01	0.06	0.00
D11	0.09	0.01	0.08	0.02	0.02	0.01	0.04	0.00
D12	0.07	0.01	0.02	0.02	0.01	0.01	0.01	0.00
D13	0.97	0.01	0.03	0.04	0.02	0.01	0.08	0.00
D14	0.92	0.01	0.05	0.02	0.01	0.01	0.06	0.00
D15	0.06	0.01	0.02	0.01	0.01	0.01	0.08	0.00
D16	0.13	0.01	0.03	0.01	0.01	0.01	0.02	0.00
D17	0.07	0.01	0.06	0.01	0.01	0.01	0.21	0.01
D18	0.08	0.01	0.05	0.01	0.01	0.01	0.12	0.01
D19	0.08	0.00	0.03	0.01	0.00	0.01	0.00	0.00
D20	0.34	0.01	0.05	0.09	0.01	0.01	0.05	0.02
D21	0.08	0.01	0.03	0.01	0.01	0.01	0.02	0.01
D22	0.09	0.01	0.07	0.01	0.01	0.01	0.01	0.01
D23	0.17	0.01	0.09	0.02	0.01	0.01	0.10	0.02
D24	0.28	0.02	0.08	0.03	0.01	0.01	0.01	0.02
D25	0.67	0.02	0.08	0.11	0.01	0.01	0.04	0.02
D26	0.49	0.03	0.11	0.04	0.01	0.01	0.01	0.02
D27	0.24	0.02	0.11	0.04	0.01	0.01	0.06	0.02
D28	1.57	0.03	0.11	0.05	0.01	0.01	0.06	0.02
D29	0.87	0.02	0.11	0.06	0.06	0.01	0.08	0.02
D30	0.13	0.03	0.12	0.04	0.04	0.01	0.04	0.02
D31	2.14	0.03	0.11	0.05	0.01	0.01	0.06	0.02
D32	0.23	0.02	0.11	0.04	0.01	0.01	0.01	0.02
D33	0.13	0.03	0.13	0.03	0.01	0.01	0.01	0.02
D34	0.28	0.03	0.11	0.02	0.00	0.01	0.02	0.02
D35	0.35	0.04	0.15	0.03	0.01	0.01	0.02	0.03
D36	0.21	0.03	0.15	0.03	0.01	0.01	0.03	0.03
D37	0.44	0.03	0.17	0.14	0.01	0.01	0.01	0.03
D38	0.58	0.03	0.43	0.04	0.01	0.01	0.01	0.03
D39	0.23	0.03	0.23	0.02	0.01	0.01	0.02	0.03
D40	0.12	0.04	0.95	0.04	0.02	0.01	0.02	0.03
Average	0.39	0.02	0.26	0.04	0.02	0.01	0.05	0.01
Max	2.14	0.04	2.23	0.14	0.06	0.12	0.26	0.03
Min	0.06	0.00	0.02	0.01	0.00	0.01	0.00	0.00
Median	0.23	0.01	0.11	0.03	0.01	0.01	0.03	0.02
Std Dev	0.45	0.01	0.49	0.03	0.01	0.02	0.05	0.01

COMPARISON OF SUMMER AND WINTER DATA FOR WATER (mg/L)

		Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
D1	summer	0.43	0.02	0.08	0.02	0.02	0.01	0.17	0.00
	winter	0.38	0.01	0.07	0.02	0.02	0.01	0.11	0.02
D2	summer	6.65	0.04	0.13	0.10	0.04	0.02	0.05	0.00
	winter	0.21	0.01	0.15	0.01	0.01	0.01	0.01	0.00
D3	summer	11.85	0.04	0.15	0.13	0.04	0.02	0.06	0.01
	winter								
D4	summer	0.69	0.03	0.17	0.04	0.05	0.02	0.01	0.00
	winter	1.13	0.02	0.08	0.08	0.02	0.12	0.02	0.01
D5	summer	0.19	0.03	0.14	0.03	0.04	0.02	0.01	0.00
	winter	0.14	0.01	0.15	0.05	0.02	0.01	0.01	0.00
D6	summer	2.41	0.03	0.16	0.05	0.09	0.02	0.04	0.01
	winter	0.40	0.01	0.60	0.03	0.02	0.10	0.01	0.03
D7	summer	0.07	0.03	0.12	0.02	0.05	0.02	0.00	0.01
	winter	0.06	0.01	0.05	0.01	0.02	0.01	0.26	0.00
D8	summer	0.47	0.04	0.16	0.27	0.04	0.02	0.06	0.01
	winter	0.70	0.01	2.23	0.12	0.05	0.01	0.05	0.01
D9	summer	1.15	0.03	0.15	0.07	0.05	0.02	0.02	0.01
	winter	0.14	0.01	1.87	0.04	0.05	0.01	0.05	0.01
D10	summer	0.08	0.04	0.20	0.02	0.03	0.02	0.01	0.01
	winter	0.06	0.01	1.19	0.01	0.04	0.01	0.06	0.00
D11	summer	0.34	0.04	0.15	0.03	0.05	0.02	0.02	0.00
	winter	0.09	0.01	0.08	0.02	0.02	0.01	0.04	0.00
D12	summer	0.13	0.03	0.14	0.02	0.05	0.02	0.01	0.00
	winter	0.07	0.01	0.02	0.02	0.01	0.01	0.01	0.00
D13	summer	0.88	0.03	0.12	0.03	0.05	0.02	0.01	0.00
	winter	0.97	0.01	0.03	0.04	0.02	0.01	0.08	0.00
D14	summer	0.06	0.02	0.13	0.02	0.05	0.03	0.01	0.00
	winter	0.92	0.01	0.05	0.02	0.01	0.01	0.06	0.00
D15	summer	0.05	0.03	0.11	0.02	0.06	0.03	0.01	0.00
	winter	0.06	0.01	0.02	0.01	0.01	0.01	0.08	0.00
D16	summer	0.05	0.03	0.14	0.02	0.05	0.03	0.00	0.00
	winter	0.13	0.01	0.03	0.01	0.01	0.01	0.02	0.00
D17	summer	0.06	0.03	0.12	0.02	0.06	0.03	0.01	0.00
	winter	0.07	0.01	0.06	0.01	0.01	0.01	0.21	0.01
D18	summer	0.14	0.03	0.14	0.04	0.06	0.02	0.07	0.00
	winter	0.08	0.01	0.05	0.01	0.01	0.01	0.12	0.01
D19	summer	0.09	0.03	0.12	0.03	0.05	0.03	0.01	0.00
	winter	0.08	0.00	0.03	0.01	0.00	0.01	0.00	0.00
D20	summer	0.33	0.04	0.17	0.07	0.05	0.03	0.02	0.03
	winter	0.34	0.01	0.05	0.09	0.01	0.01	0.05	0.02
D21	summer	0.46	0.04	0.14	0.07	0.06	0.03	0.04	0.01
	winter	0.08	0.01	0.03	0.01	0.01	0.01	0.02	0.01
D22	summer	0.07	0.03	0.12	0.02	0.07	0.03	0.01	0.00
	winter	0.09	0.01	0.07	0.01	0.01	0.01	0.01	0.01
D23	summer	0.87	0.05	0.23	0.08	0.04	0.02	0.05	0.02
	winter	0.17	0.01	0.09	0.02	0.01	0.01	0.10	0.02
D24	summer	3.31	0.05	0.16	0.46	0.07	0.03	0.05	0.04
	winter	0.28	0.02	0.08	0.03	0.01	0.01	0.01	0.02
D25	summer	0.99	0.04	0.16	0.08	0.07	0.03	0.01	0.00

	winter	0.67	0.02	0.08	0.11	0.01	0.01	0.04	0.02
D26	summer	2.57	0.05	0.16	0.11	0.07	0.03	0.04	0.00
	winter	0.49	0.03	0.11	0.04	0.01	0.01	0.01	0.02
D27	summer	1.54	0.10	0.46	0.13	0.07	0.03	0.04	0.00
	winter	0.24	0.02	0.11	0.04	0.01	0.01	0.06	0.02
D28	summer								
	winter	1.57	0.03	0.11	0.05	0.01	0.01	0.06	0.02
D29	summer	0.37	0.10	0.41	0.05	0.08	0.03	0.00	0.00
	winter	0.87	0.02	0.11	0.06	0.06	0.01	0.08	0.02
D30	summer	0.57	0.11	0.46	0.12	0.08	0.03	0.09	0.01
	winter	0.13	0.03	0.12	0.04	0.04	0.01	0.04	0.02
D31	summer	0.74	0.10	0.45	0.05	0.08	0.03	0.03	0.00
	winter	2.14	0.03	0.11	0.05	0.01	0.01	0.06	0.02
D32	summer	1.46	0.10	0.45	0.06	0.08	0.03	0.09	0.03
	winter	0.23	0.02	0.11	0.04	0.01	0.01	0.01	0.02
D33	summer	1.45	0.11	0.49	0.04	0.08	0.03	0.03	0.01
	winter	0.13	0.03	0.13	0.03	0.01	0.01	0.01	0.02
D34	summer	0.21	0.11	0.43	0.03	0.08	0.03	0.01	0.17
	winter	0.28	0.03	0.11	0.02	0.00	0.01	0.02	0.02
D35	summer								
	winter	0.35	0.04	0.15	0.03	0.01	0.01	0.02	0.03
D36	summer	0.66	0.11	0.47	0.08	0.07	0.03	0.02	0.02
	winter	0.21	0.03	0.15	0.03	0.01	0.01	0.03	0.03
D37	summer	0.38	0.11	0.47	0.05	0.06	0.03	0.03	0.01
	winter	0.44	0.03	0.17	0.14	0.01	0.01	0.01	0.03
D38	summer	0.46	0.10	0.44	0.04	0.08	0.04	0.02	0.01
	winter	0.58	0.03	0.43	0.04	0.01	0.01	0.01	0.03
D39	summer	0.69	0.11	0.44	0.05	0.08	0.03	0.02	0.01
	winter	0.23	0.03	0.23	0.02	0.01	0.01	0.02	0.03
D40	summer	0.17	0.11	0.48	0.03	0.07	0.04	0.03	0.01
	winter	0.12	0.04	0.95	0.04	0.02	0.01	0.02	0.03

SOIL DATA COLLECTED DURING SUMMER (mg/kg)

	soil pH	Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
S1	**7.22**	1241.98	3.74	17.73	28.71	10.22	2.28	32.25	9.69
S2	**7.59**	746.19	3.58	17.15	30.07	11.44	1.81	31.39	9.31
S3	**7.48**	762.76	3.54	18.15	24.12	8.69	2.11	24.34	8.42
S4	**7.9**	759.79	3.61	17.57	24.19	9.30	2.03	21.99	8.16
S5	**7.81**	772.12	3.45	15.38	33.44	10.38	1.80	30.80	7.91
S6	**7.84**	821.21	4.32	23.83	43.63	18.47	2.34	43.13	14.66
S7	**7.89**	747.71	3.92	22.04	34.42	17.41	2.14	35.10	13.72
S8	**7.62**	905.14	4.51	24.18	39.56	20.82	2.57	47.76	17.90
S9	**7.4**	672.58	3.80	20.73	35.67	17.41	2.17	37.00	13.53
S10	**7.52**	731.82	4.61	24.53	39.10	19.27	2.67	42.83	15.14
S11	**7.49**	560.91	3.40	15.75	17.84	7.79	2.03	20.58	9.55
S12	**7.75**	753.27	3.72	19.10	36.70	10.84	2.18	43.37	13.98
S13	**7.79**	557.02	3.12	16.20	11.73	6.60	2.32	13.11	8.15
S14a	**7.66**	550.60	3.19	17.14	19.07	7.60	1.93	20.91	9.59
S14b	**7.66**	1997.86	3.02	17.79	15.61	6.74	2.40	13.28	7.99
S15	**7.49**	535.22	3.91	19.21	13.63	7.89	2.38	16.14	9.23
S16	**7.45**	458.39	3.40	4.84	14.03	7.88	2.41	10.74	6.42
S17	**7.6**	401.83	3.16	15.11	10.72	7.33	2.41	11.32	7.58
S18	**7.46**	564.46	3.50	14.90	21.16	8.50	2.18	22.10	8.89
S20	**7.46**	546.29	3.02	14.10	34.51	16.47	2.74	35.47	10.94
S21	**7.24**	482.14	3.05	14.15	14.33	4.47	0.54	20.44	10.64
S22 a	**7.28**	567.52	2.82	15.25	21.47	3.01	0.09	21.90	11.07
S22 b	**7.28**	480.35	2.93	13.58	16.54	4.26	0.40	21.00	11.60
S23	**7.02**	427.83	2.18	10.57	17.08	5.73	1.02	22.45	10.35
S24	**7.25**	765.09	3.47	18.29	26.84	5.61	0.56	35.49	12.77
S25	**7.39**								
S26	**6.92**	769.43	2.47	14.68	22.95	7.04	1.48	30.57	11.12
S27	**6.8**	513.93	2.13	11.45	23.84	8.08	1.34	34.42	8.14
S28	**6.63**	345.77	1.75	7.70	14.23	6.30	1.35	23.73	5.27
S29	**6.51**	416.75	1.79	7.06	17.40	7.01	1.36	22.34	10.76
S30	**6.7**	721.79	2.10	10.02	16.35	11.08	1.79	33.33	11.40
S31	**6.62**	502.75	2.33	12.14	26.54	14.37	1.74	48.67	11.70
S32	**6.75**	588.84	1.77	16.15	12.04	9.44	1.56	26.20	9.80
S33	**7.37**	1950.61	4.67	26.68	15.80	14.37	2.40	27.99	19.36
S34	**6.08**	171.42	1.53	4.65	8.67	7.50	1.90	10.58	7.01
S35	**6.17**	227.96	1.76	6.82	3.78	4.68	1.73	4.08	4.82
S36	**6.95**	857.47	2.19	11.51	10.74	9.00	2.03	19.30	9.26
S37	**6.6**	696.18	2.51	11.34	24.64	9.21	2.02	38.24	5.18
S38	**6.52**	342.26	1.61	7.74	13.30	8.14	1.67	16.26	4.40
S39	**5.96**	498.08	2.74	8.07	36.07	16.48	2.10	45.33	5.84
S40	**6.16**	400.43	2.07	9.04	27.47	14.71	2.07	40.06	9.68
Average	**7.2**	609.40	2.74	13.46	20.41	9.13	1.68	24.91	9.11
Max		1997.86	4.67	26.68	43.63	20.82	2.74	48.67	19.36
Min		171.42	1.53	4.65	3.78	3.01	0.09	4.08	4.40
Median		565.99	3.08	15.18	21.32	8.59	2.03	25.27	9.63
Std Dev		362.97	0.88	5.51	9.89	4.56	0.62	11.39	3.33

SOIL DATA COLLECTED DURING WINTER (mg/kg)

	soil pH	Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
S1	7.1	743.06	4.91	26.33	24.87	21.15	1.49	26.36	9.48
S2	7.2	2168.48	5.49	26.76	30.21	13.74	1.59	33.80	8.81
S3	7.3	797.47	4.79	26.43	29.60	15.06	1.30	34.02	8.09
S4	7.3	837.61	5.72	30.58	33.37	8.15	1.56	34.36	10.05
S5	7.6	837.79	5.41	29.96	25.40	8.06	1.37	26.92	6.09
S6	7.2	885.41	6.52	35.31	40.62	24.98	1.57	46.91	13.14
S7	7.4	640.06	5.86	31.18	22.82	21.77	1.63	37.42	12.76
S8	7.4	797.83	5.09	28.70	35.80	14.52	1.48	43.01	13.53
S9 a	7.3	737.93	5.32	31.11	34.89	15.04	1.44	43.95	15.81
S9 b		959.54	5.33	29.62	55.41	16.51	1.53	47.44	10.08
S10	7.3	661.54	5.71	33.70	28.88	14.78	1.62	40.91	14.33
S11	7.4	535.85	4.63	23.22	14.79	5.38	1.27	22.57	8.12
S12 a	7.4	471.13	4.22	22.44	16.86	5.13	1.30	21.57	7.23
S12 b		522.73	4.82	27.37	20.52	13.77	1.46	26.77	10.13
S13	7.5	550.16	4.79	23.08	22.25	12.07	1.29	49.65	6.81
S14	7.5	489.30	4.59	22.42	16.75	5.81	1.24	28.54	8.90
S15	7.3	495.22	5.31	26.03	14.75	5.81	1.49	23.56	8.18
S16	7.2	385.91	4.38	23.37	14.92	3.89	1.32	14.87	5.09
S17	7.3	616.64	5.80	29.42	17.80	8.11	1.54	29.00	13.35
S18	7.1	581.37	4.57	24.21	27.39	8.71	1.29	37.37	10.09
S19		582.80	3.81	19.89	10.33	2.93	1.14	9.26	4.70
S20	7.1	391.55	3.72	21.51	11.32	3.25	0.96	10.04	4.17
S21 a	7.2	602.74	5.62	29.80	25.91	7.62	13.25	33.94	11.88
S21 b		658.57	5.20	32.71	0.98	2.76	1.04	38.14	14.15
S22	6.8	630.47	5.58	27.35	1.00	2.60	0.99	20.92	7.30
S23 a	7.0	438.99	4.21	22.01	1.95	4.60	0.84	21.13	6.07
S23 b		301.13	1.53	9.42	20.13	4.41	0.19	20.67	7.68
S24	6.9	863.59	5.82	30.68	43.26	8.12	1.22	39.20	10.21
S25	7.2	924.52	5.89	38.47	40.87	9.76	1.35	43.51	11.33
S26	6.5	842.02	3.10	20.43	21.95	4.49	0.67	31.47	8.11
S27	6.0	460.68	3.60	18.57	29.21	7.36	0.71	36.85	9.66
S28	6.4	631.42	2.94	18.46	9.06	2.00	0.70	23.55	1.67
S29	6.6	370.35	3.01	16.97	27.52	5.89	0.61	31.46	4.54
S30	6.2	350.57	3.46	23.34	18.31	6.61	0.77	35.10	11.15
S31	7.1	498.40	5.04	23.42	19.59	9.37	0.81	36.91	12.38
S32	6.9	4625.52	6.91	25.30	11.04	5.22	1.18	17.70	9.54
S33	7.5	743.83	6.50	15.48	3.42	1.50	0.67	4.67	10.95
S34	6.1	160.52	3.43	12.05	8.58	3.21	0.49	9.19	4.97
S35	7.5	2609.98	4.87	26.64	10.31	2.69	1.05	11.64	11.11
S36	5.7	1325.75	4.39	23.68	15.85	6.67	0.71	26.22	11.11
S37	6.4	471.59	5.97	21.29	12.39	2.73	0.63	20.63	11.84
S38	6.8	2047.85	7.70	63.02	26.66	7.61	1.19	50.02	12.73
S39	5.3	396.61	3.43	15.68	35.86	5.30	0.68	38.94	4.18
S40	6.1	443.37	4.54	19.87	38.60	9.29	0.72	48.02	6.70
Average		820.18	4.85	25.62	22.09	8.37	1.39	30.19	9.28
Max		4625.52	7.70	63.02	55.41	24.98	13.25	50.02	15.81
Min		160.52	1.53	9.42	0.98	1.50	0.19	4.67	1.67
Median		623.55	4.89	24.76	21.23	7.01	1.23	31.47	9.60
Std Dev		756.05	1.18	8.34	12.23	5.62	1.87	11.92	3.23

COMPARISON OF SUMMER AND WINTER DATA FOR SOIL (mg/kg)

		Fe	Ni	Pb	Mn	Cu	Cd	Zn	Cr
S1	summer	1241.98	3.74	17.73	28.71	10.22	2.28	32.25	9.69
	winter	743.06	4.91	26.33	24.87	21.15	1.49	26.36	9.48
S2	summer	746.19	3.58	17.15	30.07	11.44	1.81	31.39	9.31
	winter	2168.48	5.49	26.76	30.21	13.74	1.59	33.80	8.81
S3	summer	762.76	3.54	18.15	24.12	8.69	2.11	24.34	8.42
	winter	797.47	4.79	26.43	29.60	15.06	1.30	34.02	8.09
S4	summer	759.79	3.61	17.57	24.19	9.30	2.03	21.99	8.16
	winter	837.61	5.72	30.58	33.37	8.15	1.56	34.36	10.05
S5	summer	772.12	3.45	15.38	33.44	10.38	1.80	30.80	7.91
	winter	837.79	5.41	29.96	25.40	8.06	1.37	26.92	6.09
S6	summer	821.21	4.32	23.83	43.63	18.47	2.34	43.13	14.66
	winter	885.41	6.52	35.31	40.62	24.98	1.57	46.91	13.14
S7	summer	747.71	3.92	22.04	34.42	17.41	2.14	35.10	13.72
	winter	640.06	5.86	31.18	22.82	21.77	1.63	37.42	12.76
S8	summer	905.14	4.51	24.18	39.56	20.82	2.57	47.76	17.90
	winter	797.83	5.09	28.70	35.80	14.52	1.48	43.01	13.53
S9	summer	672.58	3.80	20.73	35.67	17.41	2.17	37.00	13.53
	winter	737.93	5.32	31.11	34.89	15.04	1.44	43.95	15.81
S10	summer	731.82	4.61	24.53	39.10	19.27	2.67	42.83	15.14
	winter	661.54	5.71	33.70	28.88	14.78	1.62	40.91	14.33
S11	summer	560.91	3.40	15.75	17.84	7.79	2.03	20.58	9.55
	winter	535.85	4.63	23.22	14.79	5.38	1.27	22.57	8.12
S12	summer	753.27	3.72	19.10	36.70	10.84	2.18	43.37	13.98
	winter	471.13	4.22	22.44	16.86	5.13	1.30	21.57	7.23
S13	summer	557.02	3.12	16.20	11.73	6.60	2.32	13.11	8.15
	winter	550.16	4.79	23.08	22.25	12.07	1.29	49.65	6.81
S14a	summer	550.60	3.19	17.14	19.07	7.60	1.93	20.91	9.59
	winter	489.30	4.59	22.42	16.75	5.81	1.24	28.54	8.90
S14b	summer	1997.86	3.02	17.79	15.61	6.74	2.40	13.28	7.99
	winter								
S15	summer	535.22	3.91	19.21	13.63	7.89	2.38	16.14	9.23
	winter	495.22	5.31	26.03	14.75	5.81	1.49	23.56	8.18
S16	summer	458.39	3.40	4.84	14.03	7.88	2.41	10.74	6.42
	winter	385.91	4.38	23.37	14.92	3.89	1.32	14.87	5.09
S17	summer	401.83	3.16	15.11	10.72	7.33	2.41	11.32	7.58
	winter	616.64	5.80	29.42	17.80	8.11	1.54	29.00	13.35
S18	summer	564.46	3.50	14.90	21.16	8.50	2.18	22.10	8.89
	winter	581.37	4.57	24.21	27.39	8.71	1.29	37.37	10.09
S19	summer								
	winter	582.80	3.81	19.89	10.33	2.93	1.14	9.26	4.70
S20	summer	546.29	3.02	14.10	34.51	16.47	2.74	35.47	10.94
	winter	391.55	3.72	21.51	11.32	3.25	0.96	10.04	4.17
S21	summer	482.14	3.05	14.15	14.33	4.47	0.54	20.44	10.64
	winter	602.74	5.62	29.80	25.91	7.62	13.25	33.94	11.88
S22a	summer	567.52	2.82	15.25	21.47	3.01	0.09	21.90	11.07
	winter	630.47	5.58	27.35	1.00	2.60	0.99	20.92	7.30
S22b	summer	480.35	2.93	13.58	16.54	4.26	0.40	21.00	11.60
	winter								

S23	summer	427.83	2.18	10.57	17.08	5.73	1.02	22.45	10.35
	winter	438.99	4.21	22.01	1.95	4.60	0.84	21.13	6.07
S24	summer	765.09	3.47	18.29	26.84	5.61	0.56	35.49	12.77
	winter	863.59	5.82	30.68	43.26	8.12	1.22	39.20	10.21
S25	summer								
	winter	924.52	5.89	38.47	40.87	9.76	1.35	43.51	11.33
S26	summer	769.43	2.47	14.68	22.95	7.04	1.48	30.57	11.12
	winter	842.02	3.10	20.43	21.95	4.49	0.67	31.47	8.11
S27	summer	513.93	2.13	11.45	23.84	8.08	1.34	34.42	8.14
	winter	460.68	3.60	18.57	29.21	7.36	0.71	36.85	9.66
S28	summer	345.77	1.75	7.70	14.23	6.30	1.35	23.73	5.27
	winter	631.42	2.94	18.46	9.06	2.00	0.70	23.55	1.67
S29	summer	416.75	1.79	7.06	17.40	7.01	1.36	22.34	10.76
	winter	370.35	3.01	16.97	27.52	5.89	0.61	31.46	4.54
S30	summer	721.79	2.10	10.02	16.35	11.08	1.79	33.33	11.40
	winter	350.57	3.46	23.34	18.31	6.61	0.77	35.10	11.15
S31	summer	502.75	2.33	12.14	26.54	14.37	1.74	48.67	11.70
	winter	498.40	5.04	23.42	19.59	9.37	0.81	36.91	12.38
S32	summer	588.84	1.77	16.15	12.04	9.44	1.56	26.20	9.80
	winter	4625.52	6.91	25.30	11.04	5.22	1.18	17.70	9.54
S33	summer	1950.61	4.67	26.68	15.80	14.37	2.40	27.99	19.36
	winter	743.83	6.50	15.48	3.42	1.50	0.67	4.67	10.95
S34	summer	171.42	1.53	4.65	8.67	7.50	1.90	10.58	7.01
	winter	160.52	3.43	12.05	8.58	3.21	0.49	9.19	4.97
S35	summer	227.96	1.76	6.82	3.78	4.68	1.73	4.08	4.82
	winter	2609.98	4.87	26.64	10.31	2.69	1.05	11.64	11.11
S36	summer	857.47	2.19	11.51	10.74	9.00	2.03	19.30	9.26
	winter	1325.75	4.39	23.68	15.85	6.67	0.71	26.22	11.11
S37	summer	696.18	2.51	11.34	24.64	9.21	2.02	38.24	5.18
	winter	471.59	5.97	21.29	12.39	2.73	0.63	20.63	11.84
S38	summer	342.26	1.61	7.74	13.30	8.14	1.67	16.26	4.40
	winter	2047.85	7.70	63.02	26.66	7.61	1.19	50.02	12.73
S39	summer	498.08	2.74	8.07	36.07	16.48	2.10	45.33	5.84
	winter	396.61	3.43	15.68	35.86	5.30	0.68	38.94	4.18
S40	summer	400.43	2.07	9.04	27.47	14.71	2.07	40.06	9.68
	winter	443.37	4.54	19.87	38.60	9.29	0.72	48.02	6.70

SOIL ORGANIC MATTER DURING WINTER

Sample	Mass of Crucible (g)	Mass of soil (g)	S+C after heat (g)	Soil after heat (g)	Organic matter (g)	% Organic matter
S1	17.588	1.2912	18.8452	1.2572	0.034	2.6
S2	15.9242	1.2648	16.5458	0.6216	0.6432	50.9
S3	18.3274	2.8765	15.4509	1.1348	1.7417	60.5
S4	16.6913	1.6843	17.1477	0.4564	1.2279	72.9
S5	15.828	1.3232	17.0436	1.2156	0.1076	8.1
S6	16.453	1.0572	17.4734	1.0204	0.0368	3.5
S7	15.134	1.2402	16.3453	1.2113	0.0289	2.3
S8	17.812	1.407	19.1464	1.3344	0.0726	5.2
S9	16.0192	1.22	17.2042	1.185	0.035	2.9
S10	16.6738	1.5838	18.2053	1.5315	0.0523	3.3
S11	16.5917	1.3045	17.8681	1.2764	0.0281	2.2
S12	16.6825	1.3068	17.9596	1.2771	0.0297	2.3
S13	16.2847	1.5743	17.7913	1.5066	0.0677	4.3
S14	17.3279	1.5351	18.7864	1.4585	0.0766	5.0
S15	15.533	1.7391	17.2326	1.6996	0.0395	2.3
S16	15.9256	1.2899	17.1855	1.2599	0.03	2.3
S17	15.3641	1.5737	16.9025	1.5384	0.0353	2.2
S18	15.6863	1.6762	17.3228	1.6365	0.0397	2.4
S20	16.3103	1.5438	17.8321	1.5218	0.022	1.4
S21	18.1516	1.3816	19.4939	1.3423	0.0393	2.8
S22	16.989	1.489	18.4219	1.4329	0.0561	3.8
S23	15.1669	1.4522	16.5573	1.3904	0.0618	4.3
S24	16.0636	1.1642	17.1963	1.1327	0.0315	2.7
S25	15.8303	1.0873	16.874	1.0437	0.0436	4.0
S26	16.227	1.9628	18.1377	1.9107	0.0521	2.7
S27	15.3105	1.4428	16.7124	1.4019	0.0409	2.8
S28	16.6949	1.9997	18.6755	1.9806	0.0191	1.0
S29	14.9963	1.2126	16.1815	1.1852	0.0274	2.3
S30	17.2624	1.3277	18.5682	1.3058	0.0219	1.6
S31	15.9007	1.7727	17.6294	1.7287	0.044	2.5
S32	16.7068	1.6713	18.335	1.6282	0.0431	2.6
S33	15.747	1.2187	16.9057	1.1587	0.06	4.9
S34	16.8426	1.3795	18.199	1.3564	0.0231	1.7
S35	17.7345	1.6952	19.3118	1.5773	0.1179	7.0
S36	15.5397	1.3032	16.8147	1.275	0.0282	2.2
S37	16.1899	1.3921	17.5598	1.3699	0.0222	1.6
S38	16.9309	1.4243	18.3081	1.3772	0.0471	3.3
S39	15.8986	1.3722	17.232	1.3334	0.0388	2.8
S40	15.6686	1.1275	16.7517	1.0831	0.0444	3.9

SOIL ORGANIC MATTER DURING SUMMER

	Mass of Crucible (g)	Mass of soil (g)	S+C after heat (g)	Soil after heat (g)	Organic matter (g)	% Organic matter
S1	18.9983	1.1581	20.0732	1.0749	0.0832	7.2
S2	15.5415	1.4469	16.9068	1.3653	0.0816	5.6
S3	15.9082	1.2008	17.0667	1.1585	0.0423	3.5
S4	17.1673	1.0834	18.1241	0.9568	0.1266	11.7
S5	18.4019	1.2463	19.5876	1.1857	0.0606	4.9
S6	16.0012	1.0566	16.9331	0.9319	0.1247	11.8
S7	16.0222	1.2607	17.2178	1.1956	0.0651	5.2
S8	17.3978	1.1886	18.4578	1.06	0.1286	10.8
S9	16.2495	1.3878	17.5807	1.3312	0.0566	4.1
S10	15.7089	1.3226	16.9751	1.2662	0.0564	4.3
S11	16.2755	1.4739	17.6835	1.408	0.0659	4.5
S12	16.2393	1.3366	17.4332	1.1939	0.1427	10.7
S13	18.1588	1.4908	19.6209	1.4621	0.0287	1.9
S14	18.4747	1.0944	19.5406	1.0659	0.0285	2.6
S15	17.5088	1.5436	19.0184	1.5096	0.034	2.2
S16	17.5991	1.2603	18.8385	1.2394	0.0209	1.7
S17	15.179	1.1045	16.2648	1.0858	0.0187	1.7
S18	18.1199	1.4024	19.4878	1.3679	0.0345	2.5
S20	18.029	1.1222	19.1089	1.0799	0.0423	3.8
S21	15.8086	1.1463	16.9215	1.1129	0.0334	2.9
S22	17.2854	1.1056	18.3462	1.0608	0.0448	4.1
S23	18.6464	1.1216	19.7292	1.0828	0.0388	3.5
S24	16.266	1.9708	18.1085	1.8425	0.1283	6.5
S25	18.0734	1.0879	19.0943	1.0209	0.067	6.2
S26	15.7561	1.4232	17.1582	1.4021	0.0211	1.5
S27	15.1053	1.0693	16.1443	1.039	0.0303	2.8
S28	15.5747	1.3373	16.8802	1.3055	0.0318	2.4
S29	16.4092	1.5645	17.9409	1.5317	0.0328	2.1
S30	15.3385	1.1413	16.4452	1.1067	0.0346	3.0
S31	16.7138	1.7584	18.3508	1.637	0.1214	6.9
S32	16.0173	1.0665	17.0293	1.012	0.0545	5.1
S33	16.9187	1.1363	17.9297	1.011	0.1253	11.0
S34	16.3123	1.2875	17.5839	1.2716	0.0159	1.2
S35	15.9476	1.3532	17.2539	1.3063	0.0469	3.5
S36	18.5023	1.188	19.6599	1.1576	0.0304	2.6
S37	17.8856	1.3627	19.1558	1.2702	0.0925	6.8
S38	17.4902	1.2274	18.6958	1.2056	0.0218	1.8
S39	16.3986	1.2014	17.559	1.1604	0.041	3.4
S40	15.903	1.1393	17.0105	1.1075	0.0318	2.8

VEGETABLE DATA COLLECTED DURING SUMMER (mg/kg)

	Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
carrots	138.33	2.48	6.53	26.97	11.03	1.55	2.86	51.60
carrots	41.03	2.07	3.70	10.56	9.72	0.91	2.10	33.88
carrots	114.62	2.92	6.68	17.97	10.40	0.60	2.60	53.02
carrots	79.65	2.65	4.48	17.10	10.72	1.08	3.06	47.37
carrots	71.84	2.65	5.78	12.53	11.24	1.21	3.71	39.12
carrots	56.73	2.13	5.57	8.26	10.00	1.26	2.82	45.48
carrots	89.77	2.33	6.42	4.86	11.21	1.42	3.13	48.54
Average	84.57	2.46	5.60	14.04	10.62	1.15	2.90	45.57
Max	138.33	2.92	6.68	26.97	11.24	1.55	3.71	53.02
Min	41.03	2.07	3.70	4.86	9.72	0.60	2.10	33.88
Median	79.65	2.48	5.78	12.53	10.72	1.21	2.86	47.37
Stdev	33.36	0.31	1.12	7.35	0.60	0.32	0.50	6.86
cabbage	43.82	1.96	4.07	15.24	5.19	0.78	2.10	28.27
cabbage	90.81	2.78	6.17	36.43	3.53	0.72	2.98	44.74
cabbage	73.36	3.07	4.61	25.81	4.65	0.85	3.22	38.57
cabbage	46.04	1.78	3.14	18.77	4.31	0.85	3.38	5.06
cabbage	51.22	2.15	3.95	10.79	3.87	0.74	2.57	18.64
cabbage	37.26	2.06	4.20	11.69	4.96	1.08	2.56	24.59
cabbage	153.17	2.81	8.75	10.42	5.22	1.01	3.95	52.47
cabbage	46.99	1.96	5.63	10.43	3.97	1.05	2.69	18.43
cabbage	143.70	2.87	5.91	11.72	4.94	1.19	3.68	31.56
Average	76.26	2.38	5.16	16.81	4.52	0.92	3.01	29.15
Max	153.17	3.07	8.75	36.43	5.22	1.19	3.95	52.47
Min	37.26	1.78	3.14	10.42	3.53	0.72	2.10	5.06
Median	51.22	2.15	4.61	11.72	4.65	0.85	2.98	28.27
Stdev	44.23	0.49	1.68	8.96	0.62	0.17	0.60	14.62
parsely	104.76	2.80	7.27	32.65	13.78	1.22	2.87	81.11
parsely	195.60	2.36	8.38	32.73	11.29	1.32	3.97	84.56
Average	150.18	2.58	7.82	32.69	12.54	1.27	3.42	82.83
Max	195.60	2.80	8.38	32.73	13.78	1.32	3.97	84.56
Min	104.76	2.36	7.27	32.65	11.29	1.22	2.87	81.11
Median	150.18	2.58	7.82	32.69	12.54	1.27	3.42	82.83
Stdev	64.24	0.31	0.78	0.06	1.76	0.07	0.78	2.44

	Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
spinach	83.65	2.22	5.75	31.50	10.98	0.79	2.45	23.33
spinach	170.69	2.97	9.44	15.90	8.14	0.81	5.78	61.73
spinach	120.19	1.92	6.41	101.40	6.67	0.88	2.86	91.34
spinach	117.35	2.47	6.98	89.22	7.99	1.02	3.44	88.27
Average	122.97	2.40	7.14	59.50	8.44	0.87	3.63	66.17
Max	170.69	2.97	9.44	101.40	10.98	1.02	5.78	91.34
Min	83.65	1.92	5.75	15.90	6.67	0.79	2.45	23.33
Median	118.77	2.35	6.69	60.36	8.06	0.84	3.15	75.00
Stdev	35.88	0.44	1.61	42.12	1.82	0.11	1.49	31.50
cauliflour	43.93	2.28	5.27	16.95	2.80	0.75	2.67	21.75
leeks	30.83	2.21	3.04	4.66	5.80	0.95	2.19	47.35
leeks	58.80	2.53	5.83	4.17	6.15	1.07	3.62	32.02
leeks	184.48	2.68	5.75	11.49	8.27	1.51	3.95	41.58
Average	91.37	2.47	4.88	6.77	6.74	1.18	3.25	40.31
Max	184.48	2.68	5.83	11.49	8.27	1.51	3.95	47.35
Min	30.83	2.21	3.04	4.17	5.80	0.95	2.19	32.02
Median	58.80	2.53	5.75	4.66	6.15	1.07	3.62	41.58
Stdev	81.84	0.24	1.59	4.09	1.34	0.30	0.93	7.74
potatoes	8.51	1.36	2.06	4.65	5.34	1.01	1.74	14.78
celery	123.41	3.24	7.46	11.52	10.97	0.88	4.04	72.39
beetroot	51.83	2.64	5.12	10.73	9.21	1.30	3.09	33.69
lettuce	59.06	3.07	5.57	8.24	9.92	0.67	2.53	45.85
lettuce	85.74	3.26	7.15	19.63	11.91	0.75	2.99	67.79
lettuce	82.38	3.29	4.44	14.51	9.88	1.16	2.90	79.17
lettuce	62.96	2.30	4.64	9.30	8.15	1.19	2.90	41.06
lettuce	120.62	36.74	5.45	30.41	9.42	1.26	9.94	56.95
lettuce	170.52	3.43	7.48	14.25	7.73	0.96	4.10	52.53
lettuce	134.94	6.91	7.07	29.96	9.30	1.53	3.34	76.74
lettuce	93.14	1.87	5.08	14.97	9.25	1.27	2.30	56.89
lettuce	160.33	2.50	5.99	21.35	11.50	1.53	3.45	68.59
Average	107.75	7.04	5.88	18.07	9.67	1.15	3.83	60.62
Max	170.52	36.74	7.48	30.41	11.91	1.53	9.94	79.17
Min	59.06	1.87	4.44	8.24	7.73	0.67	2.30	41.06
Median	93.14	3.26	5.57	14.97	9.42	1.19	2.99	56.95
Stdev	40.82	11.23	1.12	8.04	1.37	0.30	2.35	13.29

VEGETABLE DATA COLLECTED DURING WINTER (mg/kg)

	Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
carrots	34.13	0.71	2.11	7.12	3.70	0.20	0.78	15.04
carrots	23.39	0.82	2.55	6.24	2.40	0.19	0.83	10.44
carrots	28.19	0.68	3.02	7.60	4.36	0.23	0.66	13.85
carrots	40.29	0.79	2.87	12.89	6.42	0.31	1.30	29.31
carrots	36.67	1.08	3.72	8.30	4.97	0.40	1.51	20.23
carrots	32.78	0.91	3.06	7.38	4.36	0.30	0.97	19.53
carrots	34.21	0.84	3.39	7.03	9.85	0.26	14.66	16.72
carrots	77.70	0.96	4.26	16.85	26.50	1.54	2.29	33.68
carrots	48.09	0.97	4.34	9.18	5.23	0.29	1.34	23.08
carrots	34.54	1.48	4.31	5.02	3.66	0.36	1.45	15.27
carrots	30.61	1.03	4.38	4.39	3.91	0.30	1.06	17.15
carrots	74.84	1.11	3.94	7.14	6.01	0.33	3.10	20.88
carrots	36.91	0.93	3.38	9.37	4.61	0.39	3.27	32.82
Average	40.95	0.95	3.49	8.35	6.61	0.39	2.56	20.62
Max	77.70	1.48	4.38	16.85	26.50	1.54	14.66	33.68
Min	23.39	0.68	2.11	4.39	2.40	0.19	0.66	10.44
Median	34.54	0.93	3.39	7.38	4.61	0.30	1.34	19.53
Std Dev	16.74	0.21	0.74	3.32	6.24	0.35	3.73	7.30
cabbage	67.49	1.64	6.64	30.61	4.83	0.43	1.26	24.79
cabbage	68.55	1.78	8.58	25.83	3.73	0.57	3.57	21.13
cabbage	75.20	2.14	7.63	28.35	5.60	0.60	3.15	32.19
cabbage	57.06	1.23	6.49	11.95	4.17	0.41	2.87	29.36
cabbage	99.27	1.29	6.06	23.59	5.18	0.46	2.99	56.20
cabbage	84.64	1.45	6.27	32.86	5.48	0.50	3.51	67.27
cabbage	74.16	1.51	6.40	28.41	5.69	0.52	3.72	66.52
Average	75.20	1.58	6.87	25.94	4.95	0.50	3.01	42.49
Max	99.27	2.14	8.58	32.86	5.69	0.60	3.72	67.27
Min	57.06	1.23	6.06	11.95	3.73	0.41	1.26	21.13
Median	74.16	1.51	6.49	28.35	5.18	0.50	3.15	32.19
Std Dev	13.55	0.31	0.91	6.87	0.75	0.07	0.83	20.11
cauliflour	78.20	0.90	4.50	26.71	5.25	0.34	1.20	49.69
cauliflour	53.63	1.18	4.86	25.75	4.77	0.36	1.20	39.88
cauliflour	73.55	1.14	4.36	23.85	4.88	0.36	0.86	49.36
cauliflour	64.16	1.09	5.04	23.38	4.59	0.39	3.45	39.59
Average	67.39	1.08	4.69	24.92	4.87	0.36	1.68	44.63
Max	78.20	1.18	5.04	26.71	5.25	0.39	3.45	49.69
Min	53.63	0.90	4.36	23.38	4.59	0.34	0.86	39.59
Median	68.86	1.12	4.68	24.80	4.83	0.36	1.20	44.62
Std Dev	10.87	0.12	0.31	1.57	0.28	0.02	1.19	5.66

celery	56.18	1.65	6.34	17.63	5.55	0.49	1.63	45.26
celery	69.67	1.68	8.99	21.90	4.83	0.44	3.59	32.20
celery	72.33	1.54	6.16	14.53	8.58	0.55	3.43	56.08
celery	90.84	1.58	11.80	71.49	5.21	0.65	3.81	47.55
celery	77.69	1.47	7.88	51.64	12.43	0.61	3.88	61.64
Average	73.34	1.58	8.23	35.44	7.32	0.55	3.27	48.55
Max	90.84	1.68	11.80	71.49	12.43	0.65	3.88	61.64
Min	56.18	1.47	6.16	14.53	4.83	0.44	1.63	32.20
Median	72.33	1.58	7.88	21.90	5.55	0.55	3.59	47.55
Std Dev	12.59	0.08	2.31	25.00	3.22	0.09	0.93	11.26
Leeks	39.87	0.97	4.59	5.26	2.70	0.28	1.15	14.31
Leeks	52.18	1.29	4.06	8.64	5.00	0.35	3.31	22.85
Average	46.03	1.13	4.33	6.95	3.85	0.32	2.23	18.58
Max	52.18	1.29	4.59	8.64	5.00	0.35	3.31	22.85
Min	39.87	0.97	4.06	5.26	2.70	0.28	1.15	14.31
Median	46.03	1.13	4.33	6.95	3.85	0.32	2.23	18.58
Std Dev	8.70	0.23	0.37	2.39	1.63	0.05	1.53	6.04
Radish	25.81	0.66	2.81	6.06	3.49	0.24	0.76	23.51
Radish	47.72	0.84	4.18	12.05	4.63	0.33	2.79	71.11
Average	36.77	0.75	3.50	9.06	4.06	0.29	1.78	47.31
Max	47.72	0.84	4.18	12.05	4.63	0.33	2.79	71.11
Min	25.81	0.66	2.81	6.06	3.49	0.24	0.76	23.51
Median	36.77	0.75	3.50	9.06	4.06	0.29	1.78	47.31
Std Dev	15.49	0.13	0.97	4.24	0.81	0.06	1.44	33.66
Spinach	67.62	4.07	5.25	17.22	11.07	0.45	1.52	52.14
Spinach	83.44	1.42	6.05	23.70	14.11	0.43	3.69	76.00
Spinach	92.87	1.18	5.87	12.29	7.35	0.35	3.61	38.18
Spinach	131.09	1.51	6.79	180.61	11.03	0.67	3.44	383.15
Spinach	100.09	1.24	5.85	76.60	5.95	0.48	3.65	54.50
Average	95.02	1.88	5.96	62.08	9.90	0.48	3.18	120.79
Max	131.09	4.07	6.79	180.61	14.11	0.67	3.69	383.15
Min	67.62	1.18	5.25	12.29	5.95	0.35	1.52	38.18
Median	92.87	1.42	5.87	23.70	11.03	0.45	3.61	54.50
Std Dev	23.54	1.23	0.55	71.11	3.26	0.12	0.93	147.28
Lettuce	78.44	1.48	5.43	21.01	6.47	0.53	4.44	36.80
Lettuce	87.19	1.03	5.14	33.73	7.23	0.54	3.14	60.56
Lettuce	116.51	1.44	5.71	22.58	8.80	0.74	3.61	62.90
Average	94.05	1.32	5.43	25.77	7.50	0.60	3.73	53.42
Max	116.51	1.48	5.71	33.73	8.80	0.74	4.44	62.90
Min	78.44	1.03	5.14	21.01	6.47	0.53	3.14	36.80
Median	87.19	1.44	5.43	22.58	7.23	0.54	3.61	60.56
Std Dev	19.94	0.25	0.29	6.94	1.19	0.12	0.66	14.44

COMPARISON OF SUMMER AND WINTER DATA FOR VEGETABLES (mg/kg)

		Fe	Ni	Pb	Mn	Cu	Cd	Cr	Zn
carrots	summer	84.57	2.46	5.60	14.04	10.62	1.15	2.90	45.57
	winter	40.95	0.95	3.49	8.35	6.61	0.39	2.56	20.62
cabbage	summer	76.26	2.38	5.16	16.81	4.52	0.92	3.01	29.15
	winter	75.20	1.58	6.87	25.94	4.95	0.50	3.01	42.49
parsley	summer	150.18	2.58	7.82	32.69	12.54	1.27	3.42	82.83
	winter								
spinach	summer	122.97	2.40	7.14	59.50	8.44	0.87	3.63	66.17
	winter	95.02	1.88	5.96	62.08	9.90	0.48	3.18	120.79
cauliflower	summer	43.93	2.28	5.27	16.95	2.80	0.75	2.67	21.75
	winter	67.39	1.08	4.69	24.92	4.87	0.36	1.68	44.63
leeks	summer	91.37	2.47	4.88	6.77	6.74	1.18	3.25	40.31
	winter	46.03	1.13	4.33	6.95	3.85	0.32	2.23	18.58
potatoes	summer	8.51	1.36	2.06	4.65	5.34	1.01	1.74	14.78
	winter								
celery	summer	123.41	3.24	7.46	11.52	10.97	0.88	4.04	72.39
	winter	73.34	1.58	8.23	35.44	7.32	0.55	3.27	48.55
beet	summer	51.83	2.64	5.12	10.73	9.21	1.30	3.09	33.69
	winter								
lettuce	summer	107.75	7.04	5.88	18.07	9.67	1.15	3.83	60.62
	winter	94.05	1.32	5.43	25.77	7.50	0.60	3.73	53.42
radish	summer								
	winter	36.77	0.75	3.50	9.06	4.06	0.29	1.78	47.31

VEGETABLE DATA COLLECTED FOR THE Pb STUDY (mg/kg)

sample	mass/kg	Vol/L	Pb conc		mg/kg
Lv1	0.001053	0.05	0.1294		6.15
Lv2	0.00101	0.05	0.2076		10.28
Lv3	0.00101	0.05	0.0935		4.63
Lv4	0.001032	0.05	0.0997		4.83
Lv5	0.001074	0.05	0.1477		6.88
Lv6	0.001109	0.05	0.1462		6.59
Lv7	0.001006	0.05	0.136		6.76
Lv8	0.001032	0.05	0.1326		6.43
Lv9	0.001028	0.05	0.1144		5.56
Lv10	0.00101	0.05	0.1621		8.03
Lv11	0.001035	0.05	0.1436		6.94
Lv12	0.001078	0.05	0.1041		4.83
Lv13	0.001052	0.05	0.1189		5.65
Lv14	0.001023	0.05	0.0943		4.61
Lv15	0.001094	0.05	0.0655		2.99
Lv16	0.001058	0.05	0.0754		3.56
Lv17	0.001078	0.05	0.0658		3.05
Lv18	0.001006	0.05	0.22		10.94
Lv19	0.001066	0.05	0.1528		7.17
Lv20	0.001096	0.05	0.2106		9.61
Lv21	0.001045	0.05	0.231		11.05
Lv22	0.001044	0.05	0.2051		9.82
Lv23	0.001076	0.05	0.1582		7.35
Lv24	0.001015	0.05	0.1767		8.70
Lv25	0.001051	0.05	0.176		8.37
				Average	6.83
				Max	6.59
				Min	6.45
				Median	6.53
				Std Dev	6.59

SOIL DATA COLLECTED FOR THE Pb STUDY (mg/kg)

sample	mass/kg	Vol/L	Pb conc		mg/kg
Ls1	0.001074	0.1	0.2588		24.10132
Ls2	0.001036	0.1	0.2669		25.75758
Ls3	0.001025	0.1	0.2594		25.30485
Ls4	0.001027	0.1	0.282		27.46932
Ls5	0.001036	0.1	0.2497		24.11163
Ls6	0.001085	0.1	0.1972		18.18349
Ls7	0.001005	0.1	0.1647		16.39132
Ls8	0.001057	0.1	0.1485		14.04787
Ls9	0.001125	0.1	0.1774		15.76889
Ls10	0.00132	0.1	0.1811		13.7249
Ls11	0.00138	0.1	0.1392		10.09061
Ls12	0.001141	0.1	0.1193		10.46032
Ls13	0.001294	0.1	0.1341		10.36642
Ls14	0.001026	0.1	0.1475		14.37342
Ls15	0.001075	0.1	0.1468		13.652
Ls16	0.001203	0.1	0.1356		11.27463
Ls17	0.001101	0.1	0.1077		9.782016
Ls18	0.001087	0.1	0.862		79.32272
Ls19	0.001128	0.1	0.767		68.00248
Ls20	0.001012	0.1	0.1512		14.94366
Ls21	0.001056	0.1	0.1232		11.66225
Ls22	0.001029	0.1	0.1672		16.24721
Ls23	0.001046	0.1	0.653		62.41636
Ls24	0.001117	0.1	0.1377		12.32325
Ls25	0.001064	0.1	0.1498		14.0763
				Average	22.55419
				Max	79.32272
				Min	9.782016
				Median	14.94366
				Std Dev	18.77166

VEGETABLE DATA COLLECTED FOR THE Pb STUDY (mg/kg)

sample	mass/kg	Vol/L	Pb conc	mg/kg
Lv1	0.001098	0.05	0.1275	5.81
Lv2	0.001041	0.05	0.2123	10.19
Lv3	0.001036	0.05	0.1352	6.52
Lv4	0.001015	0.05	0.1521	7.49
Lv5	0.001083	0.05	0.1438	6.64
Lv6	0.001049	0.05	0.1494	7.12
Lv7	0.001069	0.05	0.166	7.76
Lv8	0.001145	0.05	0.1012	4.42
Lv9	0.001071	0.05	0.1023	4.78

SOIL DATA COLLECTED FOR THE Pb STUDY (mg/kg)

Ls1	0.001074	0.1	0.2588	24.101322
Ls2	0.001036	0.1	0.2669	25.757576
Ls3	0.001025	0.1	0.2594	25.304848
Ls4	0.001027	0.1	0.282	27.469316
Ls5	0.001036	0.1	0.2497	24.111626
Ls6	0.001085	0.1	0.1972	18.183495
Ls7	0.001005	0.1	0.1647	16.391322
Ls8	0.001057	0.1	0.1485	14.047867
Ls9	0.001125	0.1	0.1774	15.768889
Ls10	0.00132	0.1	0.1811	13.724896
Ls11	0.00138	0.1	0.1392	10.090613
Ls12	0.001141	0.1	0.1193	10.460324
Ls13	0.001294	0.1	0.1341	10.366419
Ls14	0.001026	0.1	0.1475	14.373416
Ls15	0.001075	0.1	0.1468	13.652004
Ls16	0.001203	0.1	0.1356	11.274632
Ls17	0.001101	0.1	0.1077	9.7820163
Ls18	0.001087	0.1	0.862	79.32272
Ls19	0.001128	0.1	0.767	68.002482
Ls20	0.001012	0.1	0.1512	14.943665
Ls21	0.001056	0.1	0.1232	11.662249
Ls22	0.001029	0.1	0.1672	16.247206
Ls23	0.001046	0.1	0.653	62.416364
Ls24	0.001117	0.1	0.1377	12.32325
Ls25	0.001064	0.1	0.1498	14.076301
			Average	22.554193
			Max	79.32272
			Min	9.7820163
			Median	14.943665
			Std Dev	18.771659