

**MODELLING CADMIUM AND LEAD UPTAKE FROM IRRIGATION
WATER BY SOME VEGETABLES THROUGH TRANSPIRATION IN THE
SEMI-DECIDUOUS FOREST ZONE OF GHANA**

By

KNUST

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**A Thesis submitted to the Department of Civil Engineering,
Kwame Nkrumah University of Science and Technology
in partial fulfilment of the requirements for the degree of**

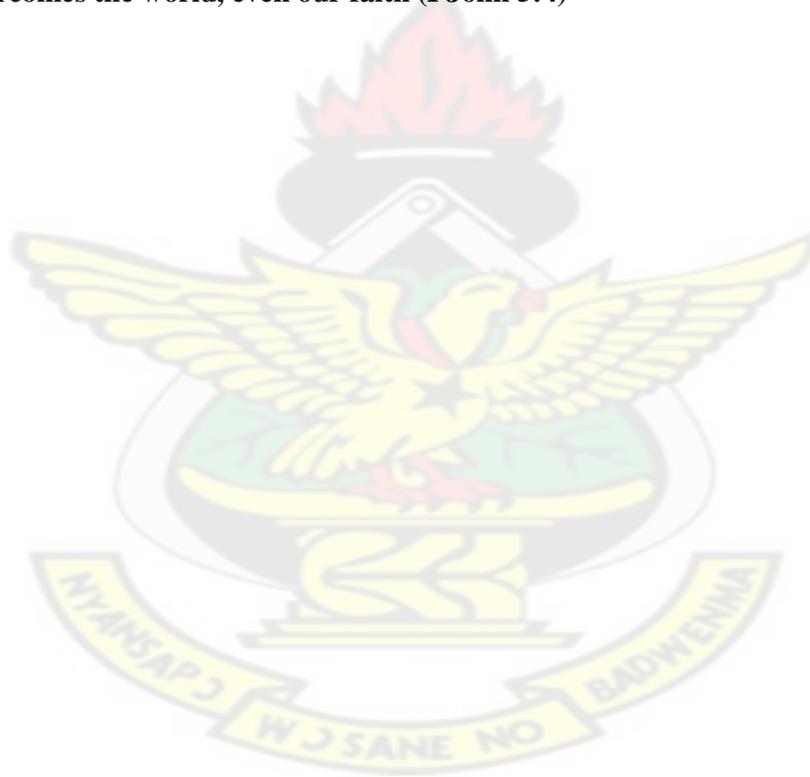
DOCTOR OF PHILOSOPHY

2007

To God Be the Glory

.....Ebenezer, thus far has the Lord helped us (I Samuel 7:12)

For whoever is born of God overcomes the world and this is the victory that overcomes the world, even our faith (I John 5:4)



ABSTRACT

Heavy metal contamination of agricultural soils is a major concern to food production all over the world. Agricultural soil heavy metal contamination is from wastewater irrigation, application of sewage and air deposition from the atmosphere and is of great importance because of its implications for human health. Systemic health problems can develop as a result of excessive accumulation of dietary heavy metals such as Cd, Pb, Ni, Cu and Cr in the human body. A study was carried out at the Kwame Nkrumah University of Science and Technology (KNUST) in Ghana using water to which Cd and Pb had been added to irrigate cabbage, carrots and lettuce. Cadmium solutions of concentrations 0, 0.05 and 0.1 mg L⁻¹ and Pb solutions of concentrations of 0, 30 and 50 mg L⁻¹ were prepared and used to irrigate the crops. Kinetics of Cd and Pb concentrations in irrigation water were studied by preparing a 1:1 ratio of the sandy loam soil from the experimental site and irrigation water and shaken for 8 hours. The results showed that Cd concentration stabilized within the first 1 hour and the partition coefficients (K_d) for the 0.05 and 0.1mg L⁻¹ irrigation water concentrations were 4 and 11.5, respectively. For Pb solutions the partition coefficients (K_d) were not constant but varied with time with values ranging between 0 and 6.94 after 6 hours of shaking. Moisture content of soil is known to influence the release of metals in soil solutions, however agricultural soils are generally of low moisture content. It was found from the study that the release of metals in soils was non-linear resulting in variation in the metal distribution coefficient. Soil Ca and dissolved organic carbon (DOC) concentrations gave a better prediction of soil Cd concentration than soil solution pH. Plant and soil samples from the experimental fields were collected for laboratory analysis. The results showed a reduction in the yields of lettuce by 11 and 16% for the treatments with Cd concentrations of 0.05

and 0.1 mg Cd L⁻¹ in irrigation water respectively, compared with yields from the control treatment (0 mg Cd L⁻¹ in irrigation water). On the other hand, there were increases of 61 and 53%, respectively in yields of carrots irrigated with water containing 0.05 and 0.1 mg Cd L⁻¹. Yields of crops irrigated with water containing Pb concentrations of 30 and 50 mg L⁻¹ were reduced compared with yields from the control plots suggesting that lead has the potential to suppress yields of crops. Plant Cd and Pb concentrations increased significantly with irrigation water concentrations of Cd and Pb with p-values of <0.0001 for Cd and <0.05 for Pb. Cadmium concentrations for cabbage were between 0.09 and 1.11 mg kg⁻¹ while carrots and lettuce had values between 0.04 and 1.0 mg kg⁻¹ and 0.12 and 1.02 mg kg⁻¹, respectively. Lead concentrations in cabbage were between 0.18 and 15.2 mg kg⁻¹ while for carrots and lettuce the concentrations were between 0.43 and 6.24 mg kg⁻¹, and 1.41 and 187 mg kg⁻¹, respectively. The percentage of the total Cd in the soil that is considered available, based on extraction with 0.01 M CaCl₂, ranged between 18.7 and 96.8% for the top 5 cm depth and between 8.5 and 89.6% for the 5-10 cm depth. The percentage of soil total Pb considered available was in the range 0.058-7.86% for the top 5 cm depth; and 0.077 - 2.78% for the 5-10 cm depth. Both soil total and available Cd and Pb decreased with depth. Free ion activities of cadmium constituting the ions absorbed by the plants were determined by prediction using Windemere Humic Aqueous Model (WHAM) VI and measurement by cadmium electrode. Inputs for WHAM VI included soil properties like organic matter content in humic and fulvic forms, Na, Mg, K, balanced cations and anions. However, lead free ion activities were determined by prediction using WHAM VI only due to lack of lead electrode. Mathematical modelling of heavy metals uptake by plants is useful for predicting the quality of crops produced for human and other animals. The

models also help to predict yields of crops produced using soil or irrigation water that is contaminated by heavy metals. In plant science, modelling of solute uptake is achieved by empirical models fitted with an equation or a set of equations to data. A modified transpiration model was therefore developed based on climatic variables such as temperature, saturation vapour-pressure deficit and relative humidity that govern transpiration and used to estimate crop dry matter content and irrigation water metal concentration, Cd and Pb concentrations in the test vegetables. The estimated and measured values were compared to determine the efficiency (EF) of the developed model. For Cd, EF values ranged between 0.911 and 0.953, while for Pb, the range was 0.514-0.995. The overall results showed that the model output using transpiration pull driven by environmental factors was reliable to predict the uptake of the heavy metals.



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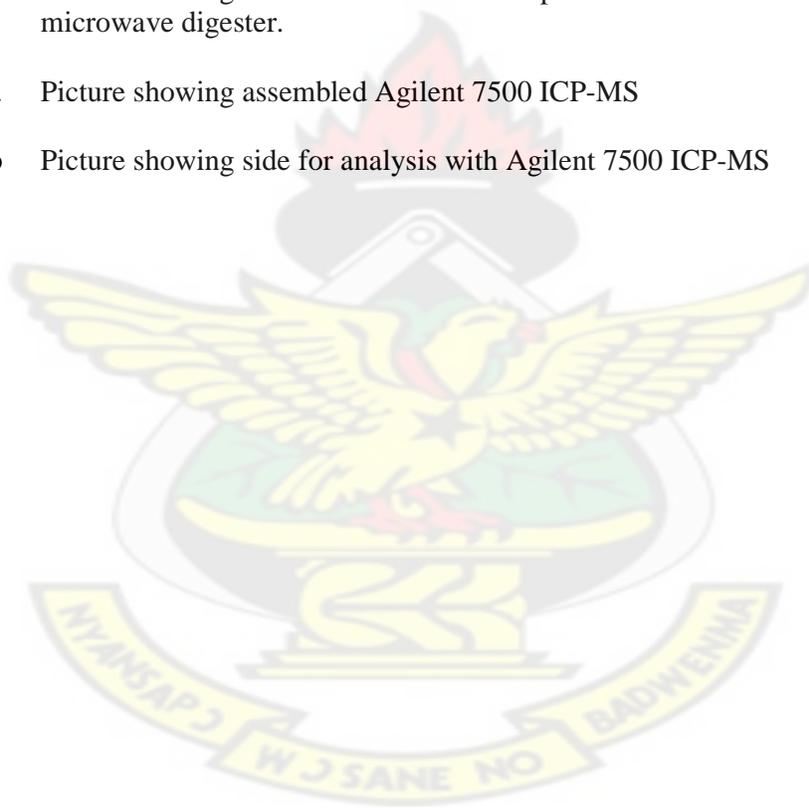


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ACKNOWLEDGEMENT

Many people have contributed in one form or the other to the successful execution of this study and they have to be acknowledged for their contribution. However, time and space will not permit me to mention all their names. Therefore a few are mentioned here.

I am very much thankful, first and foremost, to the Almighty God, the Creator of all things, for the thoughts, strength, wisdom and provision in all kinds that made it possible for this study to be made.

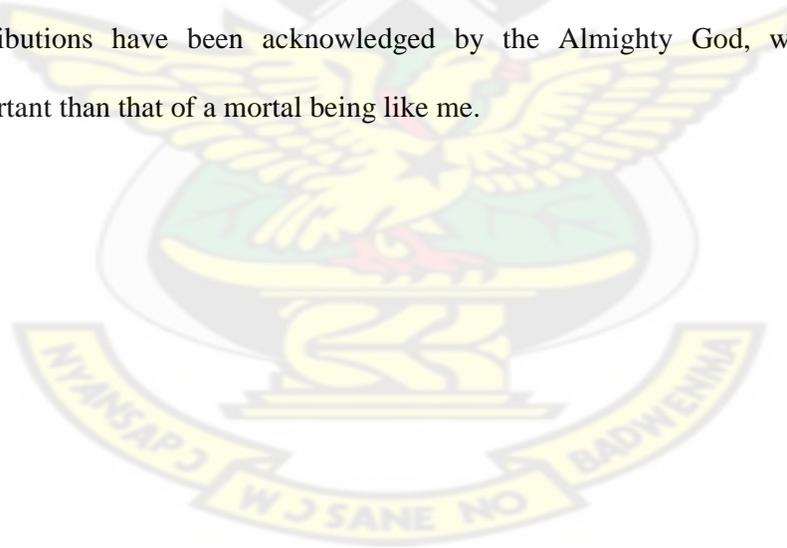
I am thankful to the following people: Professor Herbert Allen, Director of the Centre of the Study of Heavy Metals in the Environment (CSME), Department of Civil and Environmental Engineering, University of Delaware, Newark, USA, Reverend Father Professor Mensah Bonsu of the Faculty of Agriculture, Kwame Nkrumah University of Science and Technology (KNUST), Ghana, Professor S.K Agodzo and Dr S.N. Odai of the College of Engineering, KNUST for their supervisory role: I am also indebted to the following organisations: Ministry of Food and Agriculture through AgSSIP and the Water Supply and Environmental Sanitation Project (WSESP) of Department of Civil Engineering, KNUST, whose invaluable contribution in a form of provision of access to laboratory facilities for analysis, supervision, guidance, advice, encouragement and financial support made it possible to complete the study.

I would like to express my gratitude to my wife Dorothy and my two sons, Nana Kwame Oppong Mensah and Kofi Adu Mensah for their tolerance, endurance and sacrifices they had to make at some point in time so that I could have the peace of mind to concentrate on my studies.

My special appreciation and gratitude go to Mr Godwin Ofori Amoah and the family, Dr N.Kyei-Baffour, Dr Emmanuel Ofori and Mr Joseph Boamah, Director of the Agricultural Engineering Services Directorate, Ministry of Food and Agriculture (MOFA) for their support and contributions in one form or the other towards the execution of this study.

Finally, last but not least, I would like to thank the members of my cell (prayer) group, the Oduros, Agyeman-Yeboahs, Gambrahs, Odais, Asenso-Gyambibis, Yeboah-Awudzis, Pupilampus, Ellis' and Sackeys for their prayer and moral support, encouragement and other forms of assistance offered me and the rest of my family especially during periods that I had to be in the United States of America for laboratory analysis of the samples.

To those whose names could not be mentioned, I know that all your contributions have been acknowledged by the Almighty God, which is more important than that of a mortal being like me.



CHAPTER ONE

1.0 INTRODUCTION

Urban and peri-urban agriculture is a dynamic sector that is characterized by the proximity of production to consumption sites. Its performance, however, is limited by unavailability of water (Gueye and Moussa, 2001). One of the strategies adopted to offset the water deficit is irrigation with wastewater. The use of wastewater in crop production enhances the availability of fresh water for other purposes. Dakar, for example, has a daily drinking water deficit of 100,000 to 162,000 m³. Dakar, meanwhile, generates 100,000 m³ of wastewater a day (Niang, 1999 in Sonou, 2001). In Ghana, a study carried out in Kumasi showed that between 1997 and 2003 water demand deficit increased from 78.54 to 80.51% (Ofosu, 2005). Water consumption within the period increased by 39.71% but production levels could only increase by 26.85%. The use of potable water for urban/peri-urban crop production in Ghana is constrained by high tariffs, making it uneconomical and non-viable (Sonou, 2001). There is also a lack of accessibility of potable water typically in the peri-urban communities. Peri-urban is the urban hinterland - a zone influenced by the presence of the urban centre, but often rural or semi-rural in characteristics. Production is carried out on a larger scale, with most produce being sold to generate a cash income (Cornish and Lawrence, 2001). Numerous studies carried out worldwide show that wastewater contains high organic matter and fertilizing potential that can enrich and recondition agricultural soils to increase crop production (Birley and Kock, 1999; Kock *et al.*, 2001). This is confirmed by analyses carried out on some wastewater bodies in Dakar and Ghana that showed high values of biological oxygen demand (BOD) (Cornish *et al.*, 1999). This indicates the presence of organic matter and high concentrations of nitrogen and phosphorus that constitute

essential nutrients for proper plant development (Gueye, 2001; Sonou, 2001). The benefits of application of wastewater are constrained by the presence of pathogens, heavy metals and other pollutants that can be a health hazard to the consumers of agricultural produce.

A build up of heavy metals in soils results from the application of soil-fertility improving sources like inorganic phosphorus fertilizers, sewage sludge, wastewater, etc. (He *et al.*, 1993; Smith, 1993). There are also contributions from anthropogenic sources, including mining, incineration, production of plastics, nuclear radiation, fossil fuel burning from vehicles and power generating plants (Maisto *et al.*, 2003; Nicola *et al.*, 2003). Some of these heavy metals are picked up by the roots of plants growing in such soils as named above and are stored in different parts of the plants in different concentrations based on the type of plant (Chang *et al.*, 1997; Kulli *et al.*, 1999; van Lune and Zwart, 1997).

The movements and levels of accumulation of heavy metals in a plant depend on soil type, plant and environmental factors (Alloway, 1995). The soil factors include properties like pH, texture, organic matter, cation exchange capacity (CEC) and complexation of soil constituents. The availability of heavy metals to plants, for example, is controlled by the pH of the soil. Adsorption of heavy metals to clay minerals and organic matter increases by increasing soil pH (Kiekens, 1984 in Smith, 1993). The plant factors include the rooting system, type of leaves etc. Transpiration of water through the stomata of leaves is the driving force for heavy metal uptake through the soil. Plants, while losing water by this process, will draw more water from the soil into the xylem and, as this takes place, the heavy metal is drawn into the root by diffusion. Environmental factors include temperature, relative humidity and wind. Low relative humidity promotes metal uptake through the cuticle, since

the environment is dry with high evaporative demand. Under low relative humidity condition the cuticle shrinks and the deposits of epicuticular lipids (waxes) become compressed, impairing the passage of water-soluble metals (Martin and Juniper, 1970). Increase in temperature also leads to increase in uptake of metals. For example Macek *et al.*, (1994) showed that Cd uptake in *Solanum nigrum* increased with high temperature. An increase in temperature leads to a high release of metals like Cd that makes it more accessible to plant for uptake.

A study in the United Kingdom on accumulation of cadmium in potato established that the cadmium intake of an average consumer, taking potatoes and other vegetable plant foods only from sludge treated soil at the maximum permissible concentration of 3mg Cd/kg (CEC, 1986), will be approximately 34µg/day for sandy loam at pH of 6.5 (Smith, 1993).

Information on health risk effects from consumption of vegetables produced in Ghana, particularly those irrigated with wastewater has been speculative and subjective. The few studies conducted so far concentrated on the pathogenic aspect by examination of the exterior parts of the edible plants (Owusu, 1998). These studies assessed the bacteriological implications of consumption of such produce, if not properly washed in a fresh state. Information from studies on the uptake of heavy metals from soil by vegetables, the mode of picking, the soil and weather conditions influencing uptake, is lacking in Ghana and almost all the tropical African countries. Virtually no studies have been conducted in this area. Studies on soils and plants are not targeted toward investigating the perceived problems associated with the consumption of vegetables in Ghana.

Modelling heavy metals uptake by crops through irrigation is also a subject matter that has not been extensively carried out in the agricultural sector of Ghana.

There is, therefore, a gap of knowledge and information on application of models to the uptake of heavy metals by vegetables in the Ghanaian agricultural sector. There is also the need to carry out detailed research into urban/peri-urban vegetable production where wastewater is the main source of irrigation and poultry manure and sludge are intensively applied all year round to improve the fertility of the soil.

1.1 Statement of problem

In Ghana, the urban/peri-urban vegetable production sector is growing at an appreciable rate and is of particular concern due to the rate of the application of wastewater for irrigation, and poultry manure and sewage sludge to improve the soil fertility. Lately, there is the promotion of sludge and poultry manure to improve the quality of agricultural soils. This is said to be more economical and environmentally friendly (Mensah *et al.*, 2001). A survey in September, 2005 of vegetables on some local markets in Kumasi showed from laboratory analysis that vegetables on markets had higher heavy metal concentrations than the permissible values set by FAO/WHO (Mensah *et al.*, 2007). For example, cabbage samples showed the presence of the following metals in the corresponding ranges: Cd-0.5-4.01 mg kg⁻¹, Ni-21.98-76.35 mg kg⁻¹, Pb-6.1-45.21 mg kg⁻¹, Fe-990.36-8163 mg kg⁻¹ and Cu-40.17-65.08 mg kg⁻¹. However, the problem is that no scientific research has been conducted to quantify the amount of heavy metals from irrigation water, poultry manure and sewage sludge into soil solution for uptake by vegetables.

The amount of Cd and Pb being ingested into the body of consumers when consuming these vegetables is therefore not known. For proper management of urban/peri-urban wastewater irrigated vegetables, there is the need to develop a tool for predicting plant concentration levels of Cd and Pb as they change with irrigation

water concentrations and with organic and inorganic fertilizers applied (Oliver and Naidu, 2003; Maisto *et al.*, 2004; Nicholson *et al.*, 2003). This tool is lacking and hence the study seeks to provide a valuable contribution towards its development.

The population of Africa is estimated to triple by 2050 and this will be primarily in the urban and peri-urban areas or communities (UN-Habitat, 2001). As at 2004 about 44% of the population in the West African sub-region live in urban areas (UN Population Division, 2004), compared to 4% in 1920. In Ghana the urban population is also estimated to be 44% which is expected to increase rapidly as a result of 6 to 9% growth rates of her (peri)urban areas (Ghana Statistical Service, 2002).

The urbanization phenomena influence both the quantitative and qualitative changes in urban food demand. These changes challenge food production, rural-urban linkages, transport and traditional market chains (Obuobie, 2006).

In Ghana, urban crop farming comprises two forms: (i) open-space production for the urban market and (ii) backyard gardens cultivated mostly for home consumption.

Basically, 85% of wastewater generated from urban centres worldwide ends up in the environment in its untreated form. In Ghana only a minor share of the wastewater is treated and less than 5% of the population has sewerage connections (Obuobie *et al.*, 2006). Most domestic grey water passes through storm water drains into streams. In Accra about 3,300 ha are under wastewater irrigation mainly during the dry season. This is equivalent to about 60% of the total area currently under formal irrigation (schemes) in Ghana. In Accra, there are about 800-1000 vegetable farmers of whom 60% produce exotic vegetables (lettuce, cabbage, spring onions and cauliflower) and 40% indigenous local or traditional vegetables (tomatoes, okro,

garden eggs (aubergine and hot pepper). Plot sizes under cultivation range between 0.01-0.02 ha per farmer and a maximum of 2.0 ha in peri-urban areas of Ghana.

In Kumasi, there are about 41 ha in the urban area under vegetable irrigation while the peri-urban area has more than 12,000 ha under irrigated vegetable farming during the dry season (Cornish and Lawrence, 2001).

Water pollution from heavy metals does not, in most cases, exceed common irrigation standards (Cornish *et al.*, 1999; Keraita and Drechsel, 2004). Possible exceptions may be streams passing through gold mining areas.

Urban and peri-urban farmers involved in open space agriculture have little alternatives to using polluted water from streams, drains and wells. Only in a few cases do they have access to pipe-borne water and can afford its use. In Kumasi, urban farmers mostly use watering cans while peri-urban farmers often use pumps to convey water from rivers and streams to their farms which are often farther away from water sources than the plots in urban areas.

Urban wastewater vegetable production in Ghana has been found to be generating the highest net revenues per hectare. Even with plot sizes that are significantly smaller than those in the rural areas, urban farmers earn at least twice as much as rural farmers (Obuobie, 2006).

1.2 Research hypotheses

This study was carried out on the basis of the following hypotheses:

- i) Heavy metals in irrigation water are absorbed by roots of irrigated vegetables and accumulate in the edible parts.
- ii) Plant uptake of heavy metals from irrigation water depends on the exposure rate of the root to irrigation water applied.

- iii) Concentration of heavy metals in vegetables will increase as the metal concentration in irrigation water increases.
- iv) Different vegetables at different development stages respond differently to cadmium and lead concentrations in irrigation water.

1.3 Study objectives

The general research objective was to develop a predictive model that can be used to estimate heavy metal concentration in plants, given the concentration in irrigation water and its application rate, certain soil properties and climatic factors.

The specific objectives of the study were to:

- i) Establish the levels of cadmium and lead concentrations in irrigation water made accessible to plant roots in soil after irrigation.
- ii) Establish, if any, a correlation between plant cadmium and lead concentrations corresponding to predetermined concentrations of cadmium and lead, respectively in irrigation water.
- iii) Find out an appropriate method in predicting Cd concentration in soil solution to establish a relationship between soil Cd concentration and moisture content.
- iv) Develop a predictive mathematical model that can be used to estimate the concentrations of cadmium and lead in vegetables grown on land irrigated with wastewater.

CHAPTER TWO

2.0 LITERATURE REVIEW

In this chapter an extensive literature was reviewed in areas of sources of heavy metals in agricultural soils through to different types of modelling heavy metal concentration in crops without having physical measurement. Literature reviewed included those on Cd and Pb uptake by vegetables, factors affecting metal uptake, effects of heavy metal concentration in irrigation water, nutritional status and trace element contamination, heavy metal distribution between solid and liquid phases (partition coefficient) based on soil and water properties and health effects of heavy metals on both human and crop and also their effects on biological activity of soil. This chapter also outlines the processes and factors that influenced the translocation of irrigation water metal content into the crops and how the crop metal concentration could be determined without physical field or laboratory analysis.

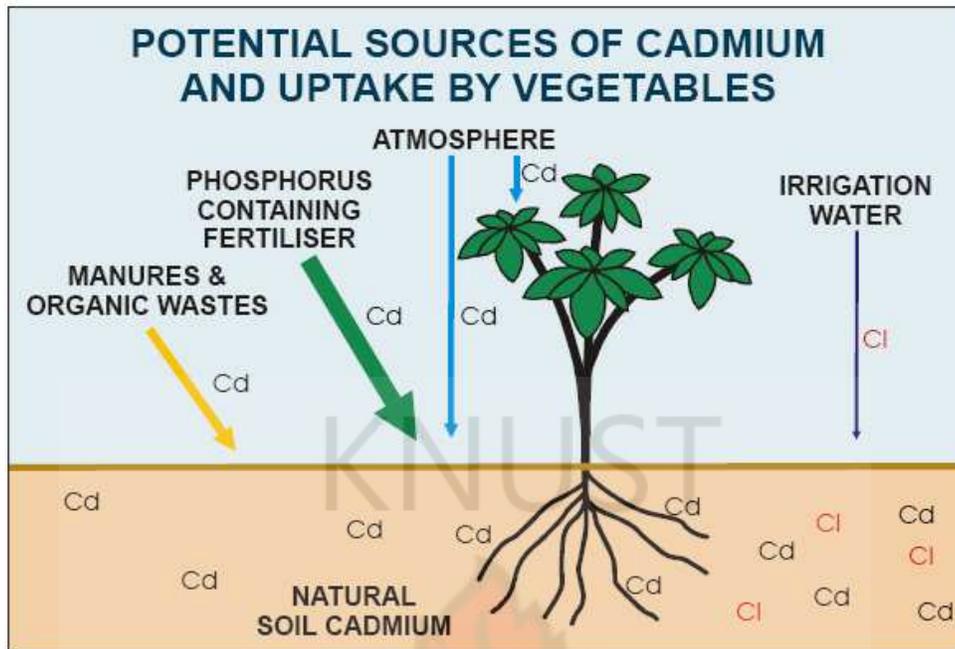
2.1 Sources of heavy metals in agricultural soils

This section outlines the major sources of heavy metals that could be accessed by crops in media used for crop production. The major media for crop production are soil and water and the presence of heavy metal in either of these media is accessible to plant roots. While cadmium is naturally present in low concentrations in soil (< 10 ppb), its concentration can reach the 100 ppm range in areas immediately adjacent to mines, smelters, and Ni-Cd battery plants. While these industries may affect a limited amount of agricultural land, Cd is actually deposited in a wide area as a result of the agricultural practice of using untreated sewage sludges as fertilizer.

Nicholson *et al.*, (2003), studying the inventory of heavy metals inputs on agricultural soils in England and Wales, concluded that the major sources of soil heavy metals include atmospheric deposition, sewage sludge, livestock manures, inorganic fertilizers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts. Of these sources, atmospheric deposition was found to be the main source of most heavy metals entering agricultural land, with livestock manures and sewage sludge also being locally important sources. Joshi and Luthra (2000) carried out a study in India and found that the main sources of soil heavy metal pollution are geogenic, mining and smelting, disposal of municipal industrial wastes, use of fertilizers, pesticides and fumes from automobiles.

2.2 Cadmium and Pb uptake by vegetables

The main sources of heavy metals in agricultural soils are atmospheric deposition (Plate 1.1), fertilization, sewage, compost and wastewater application (Alloway and Ayres, 1993; Ingwersen and Streck, 2005; Ross, 1994). While some of these heavy metals may be nutrients for plants at low concentrations, some are harmful to plants as well as soil organisms. Lead, one of the hazardous heavy metals found in agricultural soils, originates from a number of sources including paints, gasoline additives, smelting and refining of Pb, pesticide production and Pb acid battery disposal (Eick *et al.*, 1999; Paf and Bosilovich, 1995). Cadmium in agricultural soils may be from phosphate fertilizers, sewage sludge, wastewater for irrigation, waste from smelting sites, and others. Cadmium is one of the most mobile and bioavailable heavy metals in soil and may cause human and ecotoxicological impacts even at low concentrations.



Source: Horticulture Australia, 2003

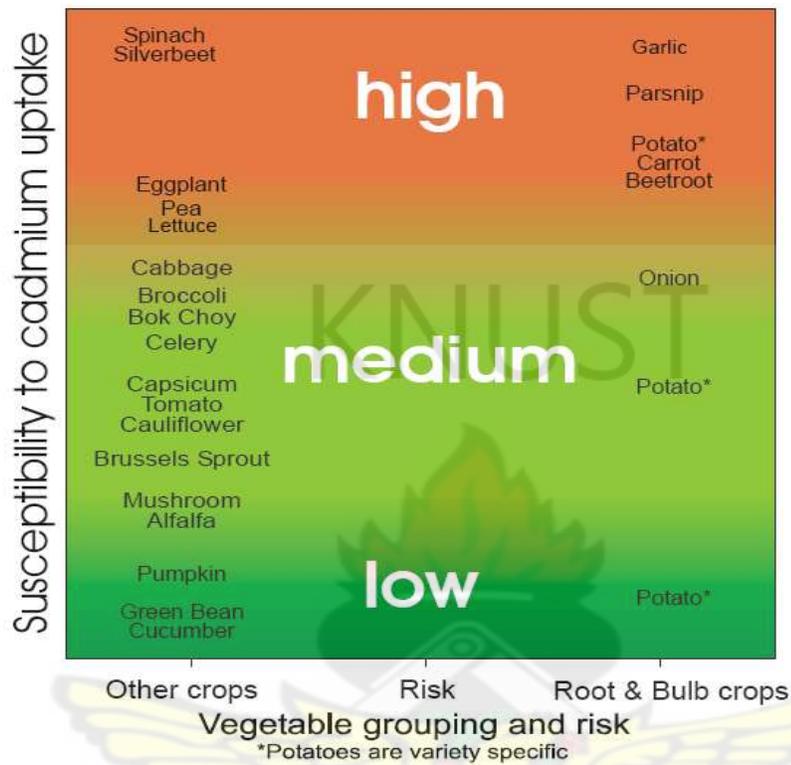
Plate 2.1: Potential sources of cadmium for plant uptake

Deposition of metals to soil may be deleterious to crop growth and soil productivity and may also produce crops containing unacceptably high metal levels that may impact negatively on animal and human health (Nouri, 1980). The available metal concentration in soil is reduced by sorption and the extent of partitioning is determined by soil properties that may include organic matter, pH, clay and iron oxides/hydroxides (Bergkvist and Jarvis, 2004; Krishnamurti and Naidu, 2003; Streck and Richter, 1997).

Metal uptake by vegetables is often characterized by a soil-plant transfer factor, TF, (e.g. Baes III *et al.*, 1984). However, the 'Free-Ion Activity Model' (FIAM) suggests that uptake may be controlled by metal ion activity in the soil pore water (Parker and Pedler, 1997).

The uptake of heavy metals and their distribution in crops differ among crop species and even among cultivars within a species (Plate 1.2). Variation of Cd uptake by cultivars of potato has been reported by McLaughlin *et al.*, (1994b); wheat by

Chaudri *et al.*, (2001) and Oliver *et al.*, (1995); maize by Florijn and van Beusichem, (1993); and spinach and carrots by He and Singh (1994).



Source: Horticulture Australia, 2003

Plate 2.2: Crop susceptibility levels to cadmium

The yield of a crop and its development are functions of the quality and the quantity of water supplied to the root zone of the crop (Rao and Mathur, 1994). Yield is also a function of soil texture and of nutrient availability. The presence of heavy metals in soil solution adversely affects the enzymatic activities of photosynthesis minimising dry matter production.

Heavy metal contamination of agricultural soils from wastewater irrigation is of serious concern because of its negative impact on human health. Serious systemic health problems can develop as a result of excessive accumulation of dietary heavy metals such as Cd, Pb and Cr in the human body (Oliver, 1997). Heavy metals are not degradable; hence, they can accumulate to toxic levels in soils due to long-term

application and in the body of consumers of produce from such soils (Bohn *et al.*, 1985). Produce from such places has higher probability of having heavy metal concentrations beyond the permissible level for human consumption.

Metals, in ionic form in soil solution, get to the roots of plants by mass flow (transpiration flux) or diffusion (Marschner, 1995) and possibly both. Root solute uptake is coupled with the root water uptake (Ingwersen, 2001). Accordingly, the root metal uptake may depend on the water uptake rate even when active uptake is dominant. The use of industrial and municipal wastewater is a common practice in many parts of the world (Feigin *et al.*, 1991; Urie, 1986), particularly in developing countries including Ghana (Cornish *et al.*, 1999). Access to adequate quantity and quality of water for irrigation in the urban/peri-urban communities of Ghana has been a major concern (Cornish, 1999). About 80 – 90 % of vegetables consumed by people in urban communities are produced in urban/peri-urban areas where high quality water may not be accessible. Where accessible, the high cost of irrigation water makes its use prohibitive. Growers of vegetables therefore use wastewater from drains that receive effluents from various sources and other urban polluted water bodies. A few of them use hand-dug wells if the water table is high. Irrigation of crops is by the use of watering cans and the method is either broadcasting or plant specific (localised) with an application rate that could be about 25 – 30 L/m² for a single application. The urban/peri-urban vegetable production in Ghana has wider land coverage than the state-owned irrigation schemes in Ghana. For example, the irrigation coverage of urban/peri-urban vegetable production in the Kumasi cosmopolitan area covers 164,000 ha as compared to 11,000 ha of state-owned irrigation schemes countrywide (Cornish and Aidoo, 2000).

Since the 1980s there has been systematic increase of vegetables in the diets of the urban population as a result of changes in the eating habits due to factors including socio-economic improvement, population growth, job creation for the army of the urban unemployed and “westernization” of culture. This has brought pressure on government acquired lands for development in the urban areas as well as resources like water.

A number of previous studies from developing countries have reported heavy metal contamination in wastewater (Cao and Hu, 2000; Ingwersen and Streck, 2005; Mapanda *et al.*, 2005; Nyamangara and Mzezewa, 1999; Singh *et al.*, 2004). This has consequently led to soil contamination. Cornish (1999) assessed the water quality of a few water bodies in Ghana concentrating on heavy metals levels for drinking purposes. Plant metal concentrations of produce from urban/peri-urban areas have not been studied in Ghana so there is lack of data on vegetable metal concentrations from areas that practice wastewater irrigation.

Most studies carried out on metal uptake have been concerned with metal uptake from soil by crops other than vegetables. Uptake from applied irrigation water has virtually not been considered. Where vegetables are concerned, most studies have been at the greenhouse level. Data on studies on direct metal uptake from irrigation water are limited. In Ghana, there has not been any study of metal uptake by crops particularly vegetables from irrigation water through transpiration.

2.3 Effects of heavy metal concentrations in irrigation water

Heavy metal concentration in irrigation water is an important source for crop uptake. Soil solution is may be formed from irrigation water and become heterogeneous in the soil after irrigation. Wastewater, whether treated or not, is used

in crop production globally. Wastewater may contain various pollutants, notably pathogens and heavy metals which have detrimental effects on soil organisms and irrigated crops. Huy *et al.*, (1996) carried out research on metal contamination of soils near Ho Chi Minh City in Vietnam and a river in the city. The studied metals (Mn, Cu, Pb, Zn, Fe and Cd) were found to occur in different concentrations in river water, water in canals and 'soil-contained' water. The metals were found to accumulate in earthworm in very high concentrations and in correlation with the concentration of these metals in the soil. It was observed that the influence of Cd^{2+} on the growth of rice was stronger than the influence of Pb^{2+} . Spinach or morning glory was able to adapt itself in an environment where water was polluted by lead. However, when the concentration of Pb exceeded 5 ppm, the roots of the morning glory turned black and the plant got rotten after one week. At lower concentrations, spinach could grow but when concentrations were increased, growth was stalled. Cadmium in soil caused the death of spinach plants at a concentration of 2.5 ppm.

2.3.1 Kinetics of irrigation water Cd and Pb in sandy loam soil

Soil solutions are formed from rain and irrigation water entering the soil. Soil solutions are found to be heterogeneous, containing different substances such as trace metals, organic and inorganic ligands, oxides and hydroxides and other cations. There is therefore, an interaction between some of these components of the soil solution that is influenced by the prevailing conditions affecting availability and mobility of metals in solution. Due to the mobility of soil solution, the retention and release reactions of soluble contaminants with soil like metals are time-dependent rather than instantaneous equilibrium processes (Yin, 1997).

Soil solutions in agricultural soils, sludge-amended soils, and industrially polluted soils often contain heavy metals such as Cd and Pb. The mobility of these metals in terms of bioavailability to plants may depend not only on the total concentration in solution but also on the speciation of the metals (Bingham *et al.*, 1984). Soil solution may contain Cd and Pb as different chemical species – free divalent cations, inorganic complexes, and organic complexes.

The speciation, adsorption and distribution of Cd in soils are governed by factors such as pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (Holm *et al.*, 1995; Bingham *et al.*, 1984). Soil pH affects the speciation and adsorption of heavy metals in soil, determining the mobility, bioavailability and toxicity of the metal.

Heavy metal uptake by plants occurs via the soil solution. Free metal ion activities are usually better indices of metal bioavailability and toxicity than are total soluble metal concentrations. As the mass of the water transpired by the plant increases the Cu concentration in both the root and shoot increase as reported by Cheng and Allen (2001). The results indicated that Cu concentration in lettuce is dependent on the growing period of the plants.

The time required to reach equilibrium depends on soil properties, the higher the soil organic matter content, the longer the time needed for a reaction to reach equilibrium. For example, the adsorption of Hg (II) on the freehold sandy loam, which contained a very small amount of organic C, did not increase significantly after 60 min, while adsorption on the Dunellen sandy loam kept increasing until equilibrium was achieved at about 5h (Yin *et al.*, 2002).

The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution. Proton concentration is the principal factor affecting the partitioning process. The ratio of the metal concentration in the soil, $[M]_s$ to the concentration of metal in the solution phase, $[M]_w$ may be described by a partition coefficient (K_d , mL g⁻¹), which is a function of pH, metal concentration, and other properties of the solution and the solid matrix (Lee *et al.*, 1996):

$$K_d = \frac{[M]_s}{[M]_w} \quad (1)$$

Metal adsorption is highly pH dependent. The different soils have different adsorption abilities. Among all soil properties, the organic matter plays the most important role in controlling Cd(II) and Pb(II) sorption by soils. The adsorption coefficient (K_d) increases with increasing pH values (Yin *et al.*, 1997).

Indiscriminate disposal of city wastes, sewage and industrial effluents and solid waste aggravates the heavy metal (eg. cadmium (Cd) and lead (Pb)) pollution. Cadmium and lead sorption isotherms vary among soil types and depend on various factors such as the chemical and mineralogical characteristics of the soils (Miner *et al.*, 1997).

Urban/peri-urban vegetable production has been mainly by wastewater irrigation. The water bodies being used have been serving as receptacles of effluents from garages, industries, residential areas and non-point sources. The effluents pick heavy metals as pollutants that end up in these water bodies being used for irrigation of urban/peri-urban vegetables. The kinetics of dissolved heavy metals in irrigation water when they end up in the soil through irrigation determines the bioavailability and mobility of metals to vegetables for uptake.

2.3.2 Cadmium release in low moisture content soils

Bioavailability of trace metals in soils has been related to the concentration or activity of metal ions in soil solutions rather than to total metal content (Holm, 1995; Allen, 1993; Van Gestel and Koolhaas, 2004). Partitioning of the metals between soil solid and solution phases has been studied extensively in soil suspensions but usually not in soil solutions at low moisture content as commonly observed in field conditions. Thus, development of approaches to extrapolate the data obtained in soil suspensions to the soil solutions remains a challenging problem.

Several options have been proposed in the literature to predict Cd partitioning in soil. The partition coefficient (K_d) was found to fit the distribution of the metal in the suspensions of contaminated soils at relatively low Cd content (Anderson and Christensen, 1988; Lee *et al.*, 1996). However, over a wider range of Cd concentrations, the relationships between sorbed Cd and dissolved Cd were non-linear (Street *et al.*, 1977; Tiller *et al.*, 1979). Cadmium sorption by soils followed the Freundlich equation (Buchter *et al.*, 1989; Elzinga *et al.*, 1999), but application of this approach is limited, as the relationship between the parameters of this equation and soil properties still remains unclear. Tipping *et al.*, (2003) applied the Windermere Humic Aqueous Model (WHAM VI) to fit the concentration of Cd in soil solutions of field-contaminated soil samples. The average predicted dissolved Cd concentration was 2.8-fold larger than the average observed value. Weng *et al.*, (2002) used WHAM VI and the NICA –Donnan model to fit the Cd activity determined with a Donnan membrane technique in the solutions obtained by extraction of field-contaminated soil samples with 0.002 M $\text{Ca}(\text{NO}_3)_2$ (soil: water ratio 1 : 2). The Root-Mean-Square Errors (RMSE) of the predicted values of the logarithm of Cd activity was 0.26 to 0.35. Windermere Humic Aqueous Model VI

(WHAM VI) and NICA-Donnan models were applied to calculate free Cd^{2+} activity in salt extracts (soil : solution = 1:2), where it was measured with differential pulse anodic stripping voltammetry, and the values of RMSE of $\log(\text{Cd})$ were reported to be 0.54 and 0.57, respectively (Ge *et al.*, 2005).

However, the models available in the literature were developed and tested mainly based on the data obtained for soil suspensions and were not validated for the metal partitioning in soil at low moisture content required for the prediction of metal toxicity in soils.

2.3.3 Soil water movement to plant root

Soil metal is accessed by plant in dissolved form, that is, in solution. McCoy *et al.*, (1984) examined plant water uptake from a uniformly rooted soil volume by numerically solving the nonlinear diffusion equation. The equation they gave was for a soil cylinder bounded externally by an insulating surface, located at the half-distance between adjacent roots and internally by the root surface. A sinusoidally varying uptake rate was employed to simulate the diurnal evaporative demand, while the actual water flux across the inner surface was controlled by the root surface matric potential through a stomatal adjustment function. The analysis was conducted for Chino clay, Pachappa sand, and Indio silt loam, using hydraulic parameters. The analysis also used root radii of 0.003, 0.005, 0.010 and 0.020 cm and root densities of 0.080, 0.142, 0.318, and 0.650 cm root length per cubic centimeter of soil. The study concluded that the parameter for determining potential gradients for soil water uptake by roots is the diffusive resistance, i.e., radial distance divided by soil water diffusivity, since it provides information on the potential loss required to transport water from the soil to the root and not just the potential loss from transmitting water through the soil.

Wilderotter (2002), using the Richards equation came out with an efficient numerical method to simulate soil water flow and plant root growth. The method allowed the calculation of the water uptake of an entire root system while preserving the local impact of single roots. Through this she was successful in combining a model for water flow based on Richard's equation with a root growth model. Also she was able to show that the adaptive finite-element method was an important contribution for computationally upscaling from the individual root level to the level of a complete root system.

2.3.4 Trace metals in soil and plant leaves

Trace metals of plant leaves may come about either through atmospheric deposition or absorption from soil solution by plant roots or through leaves stomates. Maisto *et al.*, (2004) in a study measured the concentrations of Cd, Cr, Cu and Pb in *Quercus ilex L.* leaves and soils collected from 15 sites of the Campania Region of Italy, to evaluate the effect of translocation and/or direct deposition from air on leaf element concentrations. Using the concentration factor (leaf/soil) they investigated the translocation of the element from soil to leaves. Their findings suggested that leaf concentrations of trace metals were affected significantly by air concentrations. The translocation of the studied elements from roots to leaves appeared significant only for Cu. Thus, Cd, Cr and Pb leaf accumulation appeared due essentially to deposition and direct uptake from the air by foliar absorption.

2.4 Nutritional status and trace element contamination

In this section mode of heavy metal transportation to roots and supply mechanism for ions in soil has been reviewed. This explains the uptake by root of

crops according to the root morphology as metal distribution in the soil profile decreases with depth. Nicola *et al.*, (2003) assessed the nutritional status and trace element contamination of holm oak tree woodlands in Vesuvius National Park by analyzing *Quercus ilex* leaves and surrounding soils. The concentrations of Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn were measured in 1-year-old leaves and in the soils at 0-5 and 15-20 cm depths. The potentially available concentrations were also measured for the soils. Cadmium and Pb showed higher soil concentrations at surface layers than at deep layers. Cadmium, Pb and Zn percentages of available soil concentrations with respect to the total soil concentrations of each element was high and considerable translocation of Zn from soils to leaves was noted.

2.4.1 Nutrient transport in the rhizosphere

Metals, e.g. Cd and Pb, are transported from soil to plant roots by mass flow, diffusion, and root interception (Ingwersen and Streck, 2005). Mass flow and diffusion are considered to be the most important supply mechanism for ions in soil (Marschner, 1995). Where the uptake by roots is greater than the supply by mass flow, the ion concentration will decrease at the root surface and diffusion will become increasingly important.

Cushman (1982) examined the differences in nutrient availability and transport between the rhizosphere and bulk soil matrix by reviewing absorption mechanism of root surface through discussion of absorption models. The differences were found to manifest themselves in the diffusion coefficients, buffering powers, soil mechanical structure, and nutrient solubility and production. Cushman (1982) found that transport and availability of nutrient between the inside and outside of the rhizosphere could be different as a result of different coefficients of transport and the

varying nutrient productivity rates. Evaluating the analytical concentration equation at root surface and substituting into an equation representing total nutrient uptake for a root growing at an exponential rate, he was able to give a closed form exact description of the cumulative nutrient uptake.

2.5 Factors affecting metal uptake

Heavy metal availability to plant roots for uptake depends on the properties of the medium in which the heavy metal is present. This section discusses major factors and properties of soil and water influencing metal availability through speciation and sorption. The uptake of Cd by plants depends on both soil and plant factors as well as by management practices. It has been shown that the Cd content of plants increases with the amount of superphosphate applied (Williams and David, 1973) and with a decrease in soil pH (Williams and David, 1977; Tiller, 1988; Whitten and Ritchie, 1991). The pH is one of the most important factors affecting the lability of heavy metals in soils both directly and indirectly. Aqueous metal speciation changes with pH which affects metal sorption and desorption on solid surfaces. For example, hydrolysis of metal ions at higher pH tends to increase sorption because hydrolyzed species have lower solvation energies for surface binding than do aquo metal ions (James and Healy, 1972). Increases in pH decrease surface potential and proton competition and thus favour metal binding (Yin *et al.*, 2002).

Plants take up metals from the soil solution so any factor that affects their concentrations in solution and the rate of replenishment of the solution concentration (after it has been depleted) will affect the extent of the metal uptake.

When Cd enters the soil it may remain in solution as a free cation or complex with inorganic or organic ligands (Tills and Alloway, 1983). The reactions of Cd with each soil component will depend upon a number of factors, e.g. soil type, pH, rainfall, temperature, time, management practices, species of plant, the ability of the soil to bind cations and source of applied Cd. For example, specific adsorption of Cd onto the edges of clay minerals is pH dependent (Forbes *et al.*, 1976; Tiller *et al.*, 1984; Brummer *et al.*, 1988).

The optimal pH for a contaminated home-garden is suggested to be greater than 6.5 because this would ensure strong binding of most metal contaminants (Tiller, 1988). However, problems may be encountered with raising the pH above this level such as decreased availability of micronutrients and the onset of deficiency symptoms. Soil pH is an important factor controlling availability only for polar species that may become charged with changes in soil pH and then become sorbed to charged clay particles within the soil (Oliver and Naidu, 2003).

Soluble and exchangeable forms of Cd are considered to be the most labile and available pools for leaching and uptake by plants (Harrison *et al.*, 1981; Hickey and Kittrick, 1984). Hence, the amount of Cd in these forms will be indicative of the potential for Cd accumulation in plants or for Cd contamination of ground waters via leaching. At lower pH values, soils with appreciable organic matter would retain more Cd in forms that are unavailable or unleachable in comparison to soils with low organic matter. However, at higher pH values, soils with oxides would contribute more to Cd retention. When the number of sites on oxides is appreciable, Cd could be preferentially adsorbed by hydrous oxides at the expense of adsorption onto organic matter. A study by Mann and Ritchie (1993) showed that a decrease in pH or the amount of adsorption components in the soil favoured Cd occurring in forms that

are more soluble or absorbable by plants. The forms of Cd were also influenced by the rate of Cd application. At lower rates, Cd was present as less soluble forms in soils dominated by oxides and the clays, whereas in siliceous and peaty sands, the Cd rate had no significant effect on the forms of Cd. Thus, Cd would be more available to plants when it was applied at higher rates to soils dominated by oxides or clays and equally available in sandy soils and soils with organic matter at all the application rates.

Sipos *et al.*, (2005) studied adsorption characteristics of lead on each genetic horizon of a natural brown forest soil profile to recognize the possible immobilizing effect of a mineralogical diverse soil profile in the case of a possible lead contamination. The experiment was carried out on whole soil samples, soil clay fractions as well as on their carbonate and organic matter free variant and analyzed with Transmission Electron Microscopy-Elemental Determination X-ray Spectroscopy (TEM-EDS). The study showed that organic matter greatly influenced lead adsorption and its natural distribution. Consequently, soils characterized by high amount of organic matter, swelling clay mineral accumulation horizon and calcareous subsoil are able to immobilize a significant lead pollution.

Van Lune and Zwart (1997), investigating the uptake of cadmium by crops like spinach, carrots, celery, maize and potatoes from the subsoil of different soil texture found that cadmium uptake by some of the crops increased linearly with increasing depth of cadmium addition to the soils. To the rest of the crops (spinach and potato), the increase was exponential. They also found out that cadmium uptake by crops on sand was higher than on sandy loam. They concluded that acceptable cadmium concentration levels in soils should be based on both concentrations of cadmium in the topsoil and the rooted subsoil. Thus, crop cadmium uptake was affected by both cadmium concentrations in the topsoil and subsoil, soil type and plant species.

Smith (1993) examined the effect of soil pH on concentrations of Ni, Cu and Zn in ryegrass grown on two sludge-treated soils under field conditions and the maximum permissible soil limit values for these elements were determined. Concentrations of all the elements in ryegrass were found decreasing as simple linear functions of increasing soil pH and this was consistent across the range of pH values measured (pH 4.2-7.0). Individual elements responded differently with Cu being less sensitive to changing pH conditions compared with Zn and Ni.

Climatic factors such as humidity, wind speed and temperature have impact on plant metal uptake. These factors influence vapour pressure deficit that is temperature dependent, and governs transpiration which is the driving force for ion uptake by plants. Ehlers (1989) conducting a study on transpiration efficiency of oat established that dry matter production and the quantity of water used by the crop via transpiration are linearly related. Also he showed that normalizing water use by either the rate of potential evapotranspiration or saturation deficit of the air improves the relation to biomass production. Ingwersen and Streck (2005) concluded from their study on crop uptake of Cd from sandy soils that Cd uptake by crops was related to the saturation vapour deficit of the atmosphere. This indicates that apart from several other plant and soil factors, climate also plays a role in controlling metal uptake.

2.5.1 Cadmium uptake by potato

McLaughlin *et al.*, (1994b) sampled fifty commercial potato crops and associated soils for a study. Soil solutions were extracted from rewetted soils by centrifugation and solution composition related to Cd concentrations in tubers. Soils were extracted with 0.01 M Ca(NO₃)₂ and 0.01 M CaCl₂ solutions. Relating tuber Cd concentrations to chloro-complexation in soil solution suggested that Cd species

other than the free Cd^{2+} ion were involved in the transport through soil and uptake of Cd by plants.

2.5.2 Kinetics of metals in soil solution

The dynamic equilibrium between metals in solution and soil-solid phase is determined by the properties of the soil and composition of the soil solution. The equilibrium in turn controls the availability of contaminants to plants for uptake. The major soil factors controlling the equilibrium are soil pH, ionic strength and presence of cations in soil solution that may compete for sorption, presence of ligands in soil solution that may affect sorption, soil organic matter and dissolved organic material (Oliver and Naidu, 2003).

The mobility of metals in terms of bioavailability to plants and leachability to groundwater may depend not only on the total concentration in solution but also on the speciation of the metals (Holm *et al.*, 1995). Soil solutions may contain metals as different chemical species -free divalent cations, inorganic complexes, and organic complexes. Holm *et al.*, (1995) showed that Cd and Zn concentrations in different solutions decreased within the first hour of the experimental period of 30 h and remained constant until the end of the experiment. The study also showed that increasing Ca concentration decreased the K_d and increased the total metal concentration in solution at equilibrium.

The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution (Lee *et al.*, 1996). The most important factor controlling the partitioning of a metal to soil is the solution pH. Generally, the percentage of a cationic metal adsorbed increases as pH increases with a transition range of 2 to 3 pH units. The high dependence of Cd adsorption on pH is

explained by the fact that hydrogen ions affect the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate (Elliot and Huang, 1981 in Lee *et al.*, 1996). A study has shown that the proton concentration is the principal factor affecting the partitioning process. Schulte and Beese (1994) showed that over specified pH intervals, the sorption of Cd onto different soils could be related to their specific surface areas. At low concentrations of soil organic matter, the contribution of other binding sites such as metal oxides and ion exchange sites on clay minerals are expected to become more important in the partitioning of Cd. The results of a study by Lee *et al.*, (1996) showed that the partition coefficients were highly correlated with the organic matter content at a fixed pH and diffusion of Cd.

2.5.3 Phosphorus and heavy metal attachment and release in sandy soil

Zhang *et al.*, (2003) separated five aggregate-size fractions ranging from 0.50 to 1.00 mm from seven Florida sandy soils by dry sieving. Each aggregate fraction was characterized by phosphate sorption, sequential fractionation of P, total water- and Mehlich III-extractable concentrations of P and heavy metals. Size differences in sand, silt and clay aggregates influenced the amount and strength of element binding. Elemental attachment (particularly heavy metals) increased with decreasing aggregate sizes. Elements that are attached to particle surfaces will be more readily accessible to the soil solution. Consequently, the elements may be leached more rapidly, especially if they are present in water-soluble forms than those that are not water-soluble. Their findings were that sandy soils were often clay- and organic matter- deficient and weakly aggregated. Attachment of P and heavy metals in various fractions to sandy soils tended to increase with decreasing aggregate size, suggesting that surface attachment mechanisms control the distribution of these

elements among the different aggregate-size fractions. Heavy metals are readily transported to surface waters through suspended fine particles. The percentages of water-extractable and Mehlich III-extractable P and heavy metals were higher in both the 0.50 to 0.25 and 0.25 to 0.125-mm aggregate fractions, suggesting that P and heavy metals in these two fractions would be more readily released to surface runoff or leached to ground water.

2.5.4 Sorption characteristics of Cd and Pb

Adhikari and Singh (2003) carried out an experiment on soils of five ecological zones of India to evaluate the sorption mechanism of cadmium and lead. The thermodynamic parameters (thermodynamic equilibrium constant (K^0), the standard free energy (ΔG^0), the standard enthalpy (ΔH^0) and the standard entropy (ΔS^0)) were determined using sorption data and concentrations of Cd and Pb in equilibrium solution at two different temperatures (25 and 45 °C) of soil suspension. The results showed that the soil CEC, pH, organic matter, clay and CaCO_3 content could be considered as most important factors responsible for the sorptive capacity of soils for Cd and Pb. Thermodynamic studies revealed that Cd sorption reaction in all the soils were spontaneous and exothermic, while for Pb it was also spontaneous but the reaction was endothermic. This suggests that the soils of tropical countries would be more vulnerable to Cd toxicity due to higher release of the metal with increase in temperature compared to that of Pb, although it also showed higher sorption capacity.

2.5.5 Influence of soil properties on solubility of metals

Plants absorb metals through the roots in solution form. However, the solubility of metal in soil solution is strongly influenced by some soil properties such as organic matter content, pH and clay content. Rieuwerts *et al.*, (1998) attempted to use empirical model to predict bioavailable metal concentrations from existing data on total metal concentrations and those soil factors thought to influence the partitioning of metals between the solid and solution phases of soils. They used statistical analysis to quantify the influence of soil factors on partition. Regression analyses performed on secondary data showed pH to be a consistent predictor of the extractability of soil metals by reagents accepted as surrogates for bioavailability. They concluded that because metals formed complexes with soluble as well as solid phase organic matter it might be the reason for low incidence of organic matter as a predictor variable.

2.5.6 Solute travel times

The traveling time of a solute determines its availability to plant roots for uptake. In a sandy soil, a plant with shallow roots may have a shorter time of contact with the frontline of the solute as it travels in the soil. Gish and Jury (1982) conducted experiments in two soil columns with wheat grown at constant leaching fractions of 0.2 and 0.3. Chloride breakthrough experiments were conducted during the constant leaching fraction phase to determine the effect of water uptake distribution on solute movement through a root zone. A piston- flow model for calculating breakthrough times based on analogy with work on bare soils was used to predict the time when the chloride pulse would reach the outlet end of the column. They concluded that the presence of plant roots in a porous medium lowers the fraction of wetted pore space available for solute and water flow as compared with

flow through the same soil without plants. Thus, models that use pore water velocities calculated as the ratio of local water flux to local water content will under-predict the velocity and hence over-predict the time required to traverse a given distance within the root zone.

2.5.7 Transport of reacting solutes through unsaturated zone

Kuechler and Noack (2002) used rainwater of annual precipitation on two different soil classes for numerical computation of flow of water, the chemical reaction at the water- mineral interface and the transport of chemical species caused by such flows. The water movement led to corresponding variations in the concentrations resulting in different load of the ground water in the time period.

2.6 Cadmium distribution coefficient (K) and soil characteristics

Heavy metal concentration in soil varies between the soil medium and the solution as conditions like temperature and acidity. The distribution of heavy metal between soil and water media (distribution coefficient) determines the concentration of metal ions accessible to plant roots. This section reviews literature on cadmium distribution coefficient as affected by soil properties. Holm *et al.*, (2003) conducted a study on the components important for Cd binding in soil. Cadmium distribution coefficients at two fixed pH values and at low Cd loadings for 49 soil samples from Denmark were measured. Correlating parameters were grouped and step-wise regression analysis revealed that the organic carbon content was a significant variable at both pH values. Cation Exchange Capacity and gibbsite were important at the low pH (5.3), while iron oxides were important at the high pH (6.7). They concluded that among the different soil parameters and soil components present only the carbon content and CEC were significant and that the Cd soil coefficient could be

described reasonably at the fixed pH value by the percentage of carbon in the soil, CEC of the soil, and the content of pyrophosphate-extractable iron. The study did indicate that equilibrium pH was the dominant parameter describing Cd soil sorption.

2.6.1 Metal availability to vegetables

Intake of trace metals from dietary sources may represent a significant exposure pathway for human populations (Baes III *et al.*, 1984; Reilly, 1991). However, dietary exposure to trace metals is highly variable. For example, the major source of Pb in human diets is from postharvest processing of food (Bolger *et al.*, 1996). For Cd, however, the principal exposure route for the general population is through uptake by food plants (López-Artíguez *et al.*, 1993). Where metal concentrations in crops exceed the limits, it may be possible to use this produce in animal feeds in order to minimize the effect upon the human diet. However, animals fed on a metal-enriched diet may have elevated concentrations of these metals in their tissues and milk (Baars *et al.*, 1992; Crews *et al.*, 1992). The greatest degree of metal accumulation occurs in offal, such as livers and kidneys (Beresford *et al.*, 1999). Regular consumption of metal-enriched animal products may also lead to adverse health effects in humans (Reilly, 1991).

Contaminants as well as micronutrients generally accumulate in the outer skin layer (peel) of vegetables. Helgesen and Larsen (1998) found, for example, total As and Cu in carrot peel was approximately 2 times and 2.5 times respectively greater than in the core of the carrot. Higher Cd concentrations were found in potato peel than in the potato tuber (McLaughlin *et al.*, 1994b).

Initial findings in India show that Cd, Pb and Zn levels in important vegetables like spinach, beet, cauliflower and radish regularly exceed acceptable

limits set by the Government of India posing food safety threat to urban consumers using products for home consumption.

Bunzl *et al.*, (2001) studied the soil to plant transfer of some heavy metals (arsenic, copper, lead, thallium and zinc) by vegetables bean (*Phaseolus vulgaris* L. and dwarf bean), kohlrabi (*Brassica oleracea* var. *gongylodes* L.), mangold (*Beta vulgaris* var. *macrorhiza*), lettuce (*Lactuca sativa* L. 'American gathering brown'), carrot (*Daucus carota* L. 'Rotin', Sperlings's), and celery [*Apium graveiolum* var. *dulce* (Mill.) Pers.] from a control soil (Ap horizon of an Entisol) and from a contaminated soil (1:1 soil-slag mixtures). The transfer coefficients for plant uptake of As, Cu, Pb, and Zn from soils contaminated by two slags were considerably smaller compared with an uncontaminated soil. The data revealed that for a given type of slag and a given metal not only the concentration ratios, but also the relative availability of a metal in the slag for plant uptake with respect to its uptake from a control soil depended strongly on the plant species. Thallium from both types of slags was more available for plant uptake by kohlrabi, carrots, and celery than soil-borne Tl. For several vegetables, however, the availability for root uptake from slag with respect to the control soil was reduced by the same factor. The results thus demonstrate that the factor by which the metal uptake of a plant from slag is decreased (or increased) with respect to an uncontaminated soil could be plant specific, suggesting that some plants are able to mobilize the metals in the slag to a higher extent. Thus, plant-specific effects for metal mobilization might therefore be a cause for a moderate success of estimation in the laboratory for the availability of a metal for plant uptake from solid contaminant by leaching tests with extractants.

2.6.2 Crop uptake of Cd from P-fertilisers

Phosphorus based fertilisers have been found to contain cadmium. The applications of such fertilisers tend to affect crops on soil to which the fertilizer has been applied. He *et al.*, (1994) investigated the effects of different P fertilisers on the yields and Cd contents of oats (*Avena sativa L.*), ryegrass (*Lolium multiflorum L.*), carrot (*Daucus carota L.*) and spinach (*Spinacia oleracea L.*) grown in greenhouse using soils treated with lime to achieve three levels of pH ranging from 4.77 to 5.94 for sandy soil and 4.97 to 6.80 for a loam soil. Crop yields were generally not affected by liming or application of different kinds of P fertilizers, with a few exceptions. Application of Cd-containing nitrogen, phosphorus, potassium (NPK) fertilizers in all cases tended to increase the Cd concentrations in crops, the highest concentrations in crops being obtained when the high-Cd NPK fertilizer was applied (adding $12.5\mu\text{g Cd kg}^{-1}$ soil). Cadmium concentrations in crops in most cases decreased with increasing soil pH. Cadmium concentrations in plant species increased with increasing Cd contents in the fertilizers except phosphate from rock in which Cd was not easily available to plants, and these effects were more pronounced in the sandy soil than in the loam soil. Inorganic Cd-salt, applied at the same level, tended to give higher Cd concentrations in plants than Cd in a fertilizer. Liming decreased Cd concentration in plants. Application of different P fertilizers affected the P/Cd ratios in plant tissues mainly through their effects on the Cd concentrations in plants. In conclusion, application of Cd-containing fertilizers might increase Cd concentrations in plants, especially when high Cd fertilizer is used. The availability of Cd in phosphate rock was relatively low and the low recovery of the added Cd seemed to suggest that Cd-containing NPK fertilizer, even at the normal rate of application, will result in net accumulation of Cd in soils. Also the low availability of Cd in rock phosphate could be associated with the low solubility of rock phosphate-P in soil solutions.

2.7 Health effects of metals

Crop heavy metal bioaccumulates in consumers of such crops. Bioaccumulation of heavy metals in consumers has been identified to have major adverse health effects and also the crops that absorb them. This section reviews health effects of high Cd and Pb vegetable concentrations on consumers and crops.

2.7.1 Health effects of cadmium (Cd)

Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel and zinc can cause deleterious health effects in humans (Reilly, 1991) as well as plants and micro-organisms (Wong *et al.*, 2001). Metal contamination of garden soils may be widespread in urban areas due to past industrial activity and the use of fossil fuels (Chronopoulos *et al.*, 1997; Sanchez-Camazano *et al.*, 1994; Sterrett *et al.*, 1996; van Lune, 1987; Wong, 1996). Heavy metals may be accumulated by plants irrigated with water containing high concentrations of heavy metal or metal-contaminated soil (Cambra *et al.*, 1999; Dudka and Miller, 1999; Hawley, 1985). Potentially toxic metals are also present in commercially produced foodstuffs [Department of Environment, Food and Rural Affairs (DEFRA), 1999].

Risk assessment strategies are often aimed at population subgroups. It is common practice to identify vulnerable people in society such as young children or the elderly, and assess potential risks to the health of these population subgroups [Dudka and Miller, 1999; Government/Research Councils Initiative on Risk Assessment and Toxicology (GRCIRAT), 1999]. Ryan and Chaney (1995) considered young children to be highly exposed individuals (HEIs). Thus risk assessment can usefully focus on highly exposed subpopulations on the basis that if the risk to the HEI is acceptable then most of the population is protected.

Cadmium is toxic to most forms of life. It has a tendency to accumulate in both plants and animals. Mushrooms in particular can be very rich in cadmium. Cadmium is moderately toxic to aquatic invertebrates, reducing their growth and decreasing the survival of larvae. In fish, cadmium poisoning can lead to an ion imbalance and interfere with calcium metabolism. In higher animals, cadmium accumulates in the kidneys and liver, where most of it binds to a special protein that makes the metal harmless to the animal. If the uptake is greater than this natural defense, cadmium can damage the kidneys and upset metabolism of vitamin D and calcium. Kidney damage and a decalcification of the skeleton are the serious chronic effects of high cadmium exposure. Based on human toxicology, cadmium concentrations of 100 to 200 $\mu\text{g/g}$ (wet weight) in the kidneys represent a risk for mammals.

One of the threats to food quality and safety are heavy metals in industrial effluents and from sewage plants. Dietary intake of heavy metals is a substantial risk to the health of those who depend upon the use of contaminated irrigation water to grow crops to meet their food requirements. Heavy metal contamination also can affect plant health and the nutritional value of crops. The extent of contamination in food crops is likely to increase with intensification of production systems, urbanization and industrialization but levels of food contamination are not regularly monitored.

Cadmium is a byproduct in the production of zinc and lead, and the pyrometallurgical production of zinc is the most important anthropogenic source to the environment. Other major sources are fossil fuel combustion and waste incineration. Cadmium is used in a wide spectrum of applications, including alloys,

pigments, metal coatings, batteries, and in the electronics industry. It is also a contaminant in chemical fertilizer, manure, compost and sewage sludge.

2.7.2 Health effects of lead (Pb)

Lead in the environment is strongly adsorbed by sediments and soil particles, and is therefore largely unavailable to plants and animals. Many of the inorganic salts of lead (lead oxides and sulphides) are not readily soluble in water and are sequestered in sediments. In aquatic systems, uptake is influenced by various environmental factors such as temperature, salinity, pH, and presence of organic matter. Lead accumulates in the liver, kidney, spleen and skeleton. Damage to the nervous system and gastrointestinal symptoms are the main signs of lead poisoning. Lead also interferes with the formation of red blood cells, leading to anaemia. It is especially toxic to the growing brain and can affect the behavioral development of young children, even at low concentrations. Lead can pass through the placenta and thus affect a growing fetus. Organic lead compounds are fat-soluble and are more toxic than other forms.

In fish lead accumulates primarily in the gill, liver, kidney and bone. In juvenile fish, lead causes a blackening of the tail followed by damage to the spine. It also reduces larvae survival.

Leaded gasoline is the major source of increased environmental levels on a global scale. Other anthropogenic sources include mining and metallurgic industries, ammunition, and trash incineration.

Hough *et al.*, (2004) in a study on risk assessment categorised the study group in three; i) average person, ii) highly exposed person and iii) highly exposed infant population subgroups and determined the proportion of the hazard index (HI),

a relative index that indicates the relative severity of risks. Hazard index was used to identify population subgroups that potentially were at higher risk and could be attributable to the different metals used in the study which did not vary among population subgroups. The largest contribution to HI was from Pb (about 40% of HI) and Cd (about 30% of HI). Nickel and Cu provided the lowest contribution to HI at about 10 and 14%, respectively. The proportion of the HI attributable to different exposure pathways varied between population subgroups. In all cases most HI was attributable to dietary exposure (average person 94%, highly exposed person 86%, highly exposed infant 73% of the HI).

Metallothionein (Cd-MT) is considered the more nephrotoxic form of cadmium for the reason that while the kidney can tolerate accumulation of Cd-MT to an extent, it is thought that once a threshold has been exceeded (approximately 200 $\mu\text{g/g}$), Cd may distribute to other cellular proteins, and compromise the function of the renal tubules. Also, Cd^{2+} could be considered as a hepatotoxic form that produces considerable damage at the site of absorption, leading to lung inflammation and cancer when inhaled, or enteropathy and nutrient malabsorption syndromes when ingested. Also, experimental poisoning by Cd have been shown to have cardiovascular effects such as increased blood pressure, anaemia, and cardiomyopathy as well as effects on the reproductive system in both sexes and skeletal effects. For most agricultural animals it is the organ component of meat which accumulates Cd to the greatest extent (about 5-200 ppm depending on the amount of exposure) and presents the greatest hazard to humans; contamination of muscle meats is a fraction of that in organ meats (usually 1-50 ppb). Cadmium exposure in laying poultry results in very little transfer to the eggs. Human exposure to Cd also result in bone deformities (osteomalacia), resulting in pain upon walking,

particularly in the joints, chronic renal disease resulting in hypercalciuria, proteinuria, and glycosuria (Casarett and Doull file:///AI/ntH.htm).

The most relevant form of cadmium, from the point of view of nutritional exposure, is the form of cadmium that is bound to the protein metallothionein, a family of proteins of low molecular weight (8500-10000 daltons), rich in cysteine residues (25-33% cysteine), highly conserved across a broad spectrum of eukaryotic organisms.

2.7.3 Cadmium uptake by crops and human dietary implications

Smith (1993) assessed the implications of potential human dietary intake of cadmium from pH-related permissible soil-limit concentrations for cadmium in sewage sludge-treated agricultural soils estimated from the proportional changes in concentrations of cadmium in potatoes, oats and ryegrass grown on two sludge-amended soils at different pH values. Crop yields increased with increasing soil pH, probably in response to decreasing uptake of zinc as soil pH value was raised. Generally cadmium concentrations in peeled potato tubers, potato peelings, oats straw and ryegrass decreased as simple linear functions of increasing soil pH over the range measured (pH 3.9- 7.6). Appropriate permissible concentrations of cadmium in sludge-treated agricultural soil which protect the human food chain were determined as 2.0 and 2.5 mg Cd kg⁻¹ for banded pH ranges of 5.0-5.5 and 5.5-6.0, respectively.

2.8 Effects of heavy metal concentrations on biological activity of soil

Soil heavy metal concentration does not only influence high crop metal concentration but also affect enzymatic activities of soil microorganisms. Dehydrogenase activity, for example, seems to be a sensitive indicator of soil

pollution by heavy metals. Under this section literature on effects of Cd and Pb concentrations on biological activity of soil has been reviewed.

2.8.1 Activity of soil microorganisms

Smejkalova *et al.*, (2003) investigated the distribution of cadmium, lead and zinc in exchangeable, organic, and 2M HNO₃ extractable fractions and the effect of heavy metal concentrations on soil microflora. The concentrations of Cd and Zn in exchangeable fraction were higher than in organically bound fraction, while a reverse trend was found in Pb speciation. Different microbial parameters were found as good indicators of the level of soil contamination by heavy metals. Increasing amounts of heavy metals were found to inhibit enzymatic activities especially dehydrogenase activity seemed to be a sensitive indicator of soil pollution by heavy metals.

2.8.2 Heavy metal phytotoxicity in soils

Naidu *et al.*, (2003) presented an overview of knowledge on heavy metal phytotoxicity to plants in Australian environment. From the overview, it became evident that metal concentrations at which plants showed phytotoxicity were dependent on a number of factors that included soil type, plant type, soil properties and the bioavailable metal concentrations. Different soils may have the same total metal concentrations but remarkably different effect on plant metal uptake and potential for metal phytotoxicity. This suggests that total metal concentration may not be appropriate and sensitive indicator for phytotoxicity.

2.8.3 Growth stage heavy metal tolerance by plants

Peralta *et al.*, (2004) investigated alfalfa plants grown in soil at different growth stages using separate batches of Cr (VI) at 100 mg/L, and Cd(II), Cu(II),

Ni(II), or Zn(II) at 500mg/L. Four days after germination, all metals, except Zn (II), had lethal effects on the seedlings. When applied 16 days after germination, Cr(VI) and Ni(II) still had lethal effects on the seedlings and Cd(II) and Cu(II) destroyed more than 50% of the plant population. While approximately 90% of the plants exposed to Cd(II), Cu(II) and Zn(II) were able to grow without apparent negative effects 20 days after germination, Cr(VI) and Ni(II) still showed lethal effects. These results demonstrated that the tolerance of alfalfa plants to Cd, Cu and Zn was positively correlated with the age of the plants. Thus, alfalfa seedlings tolerated Zn(II) at 500 mg/l at the growth stage of 4 days after germination. Alfalfa plant could be considered potentially feasible to be transplanted in uncontaminated soils where the concentrations of Cd, Cu or Zn are high enough to interfere with alfalfa seed germination.

Heavy metals are largely transported apoplastically in plant tissue. To be able to reach the xylem vessels of the roots, the metals have to cross the endodermis and the suberized casparian strips. Consequently, most of the metal uptake is performed by the younger parts of the roots where the casparian strips are not yet fully developed (Hardiman *et al.*, 1984; Marschner, 1995).

Translocation of metals to the shoot is performed in the xylem and this translocation is promoted by transpiration of water via leaves. A young plant, however, has a small ratio of shoot-to-root mass and in such plants the root pressure determines the translocation of xylem sap to the shoot. Translocation is also promoted for some metal ions by cation exchange at the negative charges of the xylem vessel walls (Van de Geijn and Petit, 1979; Wolterbeek, 1987).

2.8.4 Effect of evaporation/transpiration on metal uptake by plants

Plants absorb metals by either active mechanism that is by diffusion through the cells of roots or by passive mechanism which is through the xylem initiated by a transpiration pull. Kashem and Singh (2002) and Lorenz *et al.*, (1994) observed that the uptake of Cd into plants (such as radish, oats and water spinach) is affected by transpiration and positively correlated with mass flow (Ingwersen and Streck, 2005). The observed trend of relatively increased Cd uptake in the year with the higher saturation deficit of the atmosphere suggests that transpiration affects the uptake.

Evaporation takes place at the surface of the soil and lowers the soil moisture in the top layer. This affects the concentration of solute dissolved in the soil solution as well as its distribution in the soil. Ozturk and Ozkan (2004) carried out a study on water evaporation and solute transport processes in large columns filled with sandy clay loam (SCL) and clay loam (CL) soils. Different water flow velocity through the soil column was created by using 3 cm and 6 cm depths of ponded water at the soil surface during leaching. After leaching, the soils were left to evaporate for 10 days. The study showed that when sufficient water had been applied for leaching, there was a net downward movement of salt. As the soil surface dried, the direction of salt movement was reversed towards the soil surface. It was also observed that the magnitude of transport was mainly determined by the soil texture. The electrical conductivity (EC) at the soil surface after evaporation increased, to 41- 46% of the pre-drying level for the SCL and 28- 31% for the CL, suggesting an accumulation of solutes on the soil surface during evaporation.

2.9 Model for root solute uptake

A mathematical model usually describes a system by means of variables. Tsutsumi *et al.*, (2003) developed a two-dimensional model that combined root-

system and water extraction by roots to simulate the dynamic interaction between root growth and soil-water flow, considering hydrotropism and gravitropism as the controlling factors of root growth. In employing the finite-element method to compute the soil-water flow caused by water extraction, evaporation and irrigation, they succeeded in simulating the plagiogravitropic elongations of lateral roots under a plane condition and the asymmetric architecture of root system under a sloped condition. The developed model was found to be potentially useful for investigating how the various conditions of soil water affect root-system development and soil-water extraction. The model could simulate root-system development and soil-water extraction under moist or drought conditions which is an important information on the efficiency of irrigation methods.

A widely used functional model approach for simulating the root solute uptake assumes that solute uptake is linearly proportional to the product of soil solution concentration and water uptake (Christensen and Tjell, 1984; Behrendt *et al.*, 1995; Trapp, 2000; Schoups and Hopmans, 2002).

Wang *et al.*, (2003) studied two methods of extraction of soil heavy metals; single low-molecular-weight-organic-acids (LMWOAs) and a sequential extraction procedure recommended by the European Community Bureau of Reference (BCR). Extracted soil solutions were further fractionated as colloidal and truly dissolved fractions. Comparing the correlation coefficients between extractable metals from soil taken up by plant (maize) roots and shoots between the two extraction methods, a good correlation was obtained under the LMWOAs method. In contrast, the correlation coefficients were poor when the BCR method was used. They concluded by proposing that wet rhizosphere soil and LMWOAs be used for bioavailability test purpose for good correlation coefficients. Also heavy metals in soil solution can be

partitioned between different colloidal fractions and metals in dissolved fraction are easily available to plants. Heavy metals adsorbed by plant root cell wall are taken up by cross-membrane and become responsible for plant availability.

Reginato *et al.*, (2000) in determining whether a moving boundary model that accounts for increasing root competition could improve predictions of nutrient uptake developed a model that predicts nutrient uptake by coupling nutrient flux to roots and nutrient absorption on a variable domain in time. The model output was compared with measured uptake of Mg, K, P, and S by various crops and soils using experimental data obtained from literature. Predicted Mg, K, and P uptake by pine seedlings was close to that observed for K and P, although for Mg the predicted uptake showed deviations similar to those of the Barber-Cushman model. Sulphur uptake by wheat in different soils was better predicted by the moving boundary model in at least 10 out of 18 measured cases. The model prediction was also compared with measured K uptake by three maize hybrids grown on Typic Hapludult of Rio Cuarto, Argentina, in a growth chamber. The moving boundary model appeared to provide a better description of coupling between transportation, absorption of nutrient, and root growth than the Barber-Cushman model, and it improved the prediction for nutrient uptake in some tests.

Fyrillas and Kontoghiorghes (2004) used the boundary element method to address the three-dimensional problem of advection-dispersion associated with an elliptical non-aqueous-phase liquid (NAPL) pool. They verified the numerical results by asymptotic analytical solutions obtained in the limits of diffusion-dominated and convection-dominated mass transport. They were able to derive a Fredholm integral equation of the first kind for the concentration gradient that is de-singularized and solved numerically using a collocation boundary-element method which gave a

satisfactory agreement between the numerical results and the asymptotic results. Comparison with experimental results suggests that the corresponding numerical results predict a higher overall mass transfer coefficient.

Keller *et al.*, (2001) used an empirical stochastic balance model, PROTERRA-S, that estimates heavy metal and phosphorus accumulation in agricultural soils on regional level. The basic units of the balances were land use systems defined by livestock production and cultivated crops. It was shown that metal balances varied largely between the land use systems (LUS) resulting from differences in the agricultural farming systems and their fertilization management. The estimated cadmium and zinc balances of the LUS were in good agreement with reported metal balance studies on experimental farms. Therefore they concluded that stratification of heavy metal balances according to agricultural management systems and linking the metal inputs through fertilizers with the P balances of the strata seemed to be useful approaches to account for agricultural characteristics in modeling metal accumulation in soil.

2.9.1 Modelling the role of active biomass on heavy metal transport

Nedunuri *et al.*, (1998) investigating the influence of active biomass in immobilizing heavy metals in the soil rhizosphere through mechanistic models, modelled the movement of water in the soil using Richards equation. An advection-dispersion equation, with a sink term for metal uptake by biomass was used for modelling the fate and transport of lead. A hypothetical one-dimensional vertical soil column containing metal biomass and carbon substrate was used for analyzing lead movement. The extent of immobilization of lead in soil was found to be dependent on the growth of biomass, which in turn depended on the availability of root exudates

in the rhizosphere. The investigation showed that adsorption processes retard heavy metal transport in unsaturated soils. Soluble organic acids present in the rhizosphere also serve as good sources of substrates for the growth of microorganisms but their availability at deeper locations in soils is dictated by processes of advection and diffusion. It was found that the partition coefficient of biomass to the soil depended on the soil characteristics and the type of the biomass. For example, clay yielded higher partition coefficients for the biomass compared to silty loam soils. Also the factors that enhance biomass growth and adsorption of biomass to soil generally contributed positively to metal immobilization and retardation.

2.9.2 Prediction of uptake of metal from solution by lettuce

Cheng and Allen (2001) studied the effects of free copper ion activity and total copper concentration on copper uptake by lettuce from nutrient solution and developed a model to substantiate the studies. It was found that in EDTA and dissolved organic matter treatments, when pH and free copper ion activity were the same, root copper concentration did not change with the total copper concentration. However, at fixed pH and total copper concentration, root copper concentration increased with, and was log-log linearly related to free copper ion activity. Copper uptake by plant roots was affected by free copper ion activity, pH, and the concentration of other competing ions such as Ca^{2+} . The study revealed that the mass of solution transpired by the plant, the composition of the growth medium, and copper speciation in solution were the factors that affected copper uptake from nutrient solution. Copper concentration in plant root and shoot reached a stable level after the plant had transpired a certain amount of solution. Copper uptake was found to be linearly related to free copper ion activity and was independent of total copper

concentration in solution. The developed model revealed that free copper ion partitioning between plant root and solution was linearly related to proton and calcium concentrations in the solution and independent of the different types of soluble ligands present.

2.9.3 Modelling nutrient uptake by plants

Modelling nutrient uptake by plants helps to predict or estimate the amount of nutrient that may be required by a crop to be established under similar conditions and on soil of similar properties for planning purposes. The modelling could be done using different approaches such as computer software, mathematical equation developed from a generated data from field work and mechanistic model developed using mathematical principles. For example Barber (1984) used personal computer version of Barber-Cushman model, a mechanistic nutrient uptake model, to predict magnesium, phosphorus and potassium uptake by loblolly pine seedlings. The input parameters included initial soil solution concentration of ions $[C_s]$ $\mu\text{mol/L}$ that equilibrate with ions in solution $[C_k]$ $\mu\text{mol/L}$, water content at field capacity, volumetric water content $[\Theta]$, the effective diffusion coefficient in water D_1 and the impedance factor which accounts for the tortuosity of the diffusion path, f_i . Diffusion was found to be the primary mechanism delivering nutrient ions to the root surface, a factor that is controlled by concentration gradient.

Alloway *et al.*, (1990) used an empirical model to predict Cd uptake and accumulation by vegetables (cabbage, lettuce and raddish) from soil contaminated with Cd. The prediction was done using eighteen physico-chemical parameters. Also Browne *et al.*, (1984) in Alloway *et al.*, (1990) developed a model based upon soil parameters to predict Cd uptake by a number of species using model equation:

$$\text{Log } P = \delta + \beta \log \text{Cd}_{\text{DTPA}}$$

Where:

P – plant Cd concentration, ($\mu\text{g/g}$)

Cd_{DTPA} – extractable Cd, ($\mu\text{g/g}$)

δ and β – linear regression coefficients (β – a function of soil pH and CEC and δ - a function of the plant species).

Hutton (1980) proposed a model to describe the transfer of Cd from soils to plants using the equation:

$$P_{sp} = \frac{(\beta S \Omega \phi)}{(\phi + \Omega \infty)}$$

Where:

β – water flow associated with plant production, m/s

S – plant selectivity coefficient

Ω – soil adsorption coefficient

ϕ – soil bulk density, kg m^{-3}

∞ – soil moisture content, m^3 / m^3

P_{sp} – soil- plant transfer coefficient, ms^{-1}

Christensen and Tjell (1984) presented a conceptual model to determine Cd uptake from sewage sludge amended soils. The model divided plant Cd concentration into three fractions based upon their source: topsoil, subsoil and atmosphere. Plant uptake from the topsoil was described by the equation:

$$B = P.T_t.C_t = P.T_t.(S_t, K_t)$$

Where:

b – root uptake from topsoil

P – plant factor (constant for a specific plant)

T – transpired amount of water

C_t – solute Cd concentration

S_t – soil Cd concentration

K_t – Cd distribution coefficient.

Plant uptake from subsoil was described by the equation:

$$C = P.T_s \frac{S_s}{K_d}$$

where:

C – root uptake of Cd from the subsoil

S_s – index for subsoil.

Caasen and Barber (1976), using equation from Nye and Marriott (1969)

described the flux of nutrients to the root by mass flow and diffusion:

$$\frac{\partial c_l}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial c_l}{\partial r} + \frac{v\theta_r c_l}{b} \right)$$

where:

r – radial distance from the root axis

r_o – root radius

c_l – ion concentration in soil solution

v_o – inward flux of water at the root surface

D – differential diffusion coefficient in the soil

b – differential buffer power

t – time of uptake (age of the root segment)

Initial conditions describing the condition before flux occurred were

t = 0; r > r_o, C_l = C_{ij} where C_{ij} – initial ion concentration in soil solution.

2.9.4 Simple mathematical consideration under steady state conditions

Ions reach the surface of roots by mass (or convective or bulk) flow in the stream of water that finally enters the root, and by diffusion of particular ions in the direction of decreasing concentration in the soil solution.

The transfer of ions carried by convective flow of the water is given by

$$\Gamma_s = q_w c \quad (1)$$

Where Γ_s is the flux density of the solute, q_w is the flux density of water (in the horizontal direction) and c is the concentration of the ions concerned.

The flux density of the ion transferred by ionic diffusion in a solution is given by Fick's law:

$$q_s = D_o (dc/dx) \quad (2)$$

where q_s is the quantity of the diffusing substance per time transferred in unit cross-sectional area normal to the horizontal (x) direction, c is the concentration (quantity of the ion in unit volume of the solution) and D_o is the diffusion coefficient in bulk water.

Diffusion of ions through soil is restricted to the fraction θ of the cross-sectional area that is water-filled and it has to follow a tortuous path.

In that case the flux across unit cross-section of the soil is then represented by

$$J_s = -D_p (dc/dx) \quad (3)$$

where $D_p = b\theta D_o$ and b is a tortuosity factor which probably varies with θ . (D_p varies between 2×10^{-12} and $5.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$)

When both diffusion and convective flow contribute to the ionic transfer equations (1) and (3) are combined to give

$$J_s = -D_p (dc/dx) - q_w C \quad (4)$$

The second term on the right hand side of equation (4) dominates when the plant is transpiring actively.

Assuming with irrigation, water is not limiting, the volume of water extracted per volume of soil due to transpiration (T_p) is

$$T_p = \int_0^t C q_r dt \quad (5)$$

Assuming negligible diffusion, then the combined ionic flow in transpiration stream is given by equation (5) where q_r is the flow equal to the convective flow and C is the concentration of solute.



CHAPTER THREE

3.0 MATERIALS AND METHODS

The study comprised two phases, field and laboratory experiments. The first phase, a field experiment, was to study the behaviour of Cd and Pb in soil under irrigation water of different concentrations. This was to ascertain the proportion of these elements available for plant uptake. Emphasis was laid on Cd release at different soil moisture contents.

The second phase involved field studies on Cd and Pb uptake from irrigation water using cabbage, carrots and lettuce as test crops. The details of the experiments are described in the following sections.

3.1 Laboratory experiments

3.1.1 The temporal variation in the concentration of irrigation water Cd and Pb in soil

Sandy loam soil samples (classified as *Nta* series by local classification or Stagnic Cambisol (Dystric) in the WRB (2006) or Typic Dystrustept in the USDA system (2003)) were collected from an experimental plot established on KNUST campus, Kumasi, Ghana. The samples were air-dried for 6 days. Twenty litres (20 L) of pre-determined Cd (0.1 and 0.5 mg L⁻¹) and Pb (5 mg L⁻¹) solution concentrations prepared from Cd(NO₃)₂ and Pb(NO₃)₂ salts were added to 20 g of air-dried composite soil in 50 ml centrifuge tubes. The filled centrifuge tubes were shaken on a LTE Scientific shaker for 8 h. Samples were collected from the shaker at an hourly interval, centrifuged and filtered through filter paper No 45. The filtrates were

analysed for Cd and Pb concentrations using Buck Scientific Atomic Absorption Spectrophotometer (Model 210 VGP).

3.1.2 Moisture: soil ratio effect on Cadmium release in soil

The work described in this section was carried out at the Centre for the Study of Metals in the Environment (CSME), Department of Civil and Environmental Engineering, University of Delaware in the USA.

The study was carried out on 4 soil samples collected from the upper 0-20 cm layer in different geographic and climatic zones (USA, North America; UK, Europe; and Ghana, Africa). The soil samples were air-dried and sieved to pass through a 2-mm screen.

Appropriate volumes of a 2.5 g L^{-1} or a 25 g L^{-1} stock solution of $\text{Cd}(\text{NO}_3)_2$ were added to 60-g soil samples placed in 200 ml plastic bottles to obtain Cd loading of 0, 5, 10, 20, 50, 100, 200, 400, and 800 mg kg^{-1} soil, in duplicate. The samples were mixed with a spatula for 2 min and incubated for one day. Then, the samples were moistened with deionized water of 0, 4000, 8000 and 12000 g/kg and incubated at $20 \pm 1 \text{ }^\circ\text{C}$ for eight days. After incubation, soil solutions were separated by centrifugation and analysed.

3.1.3 Effect of variable soil: extractant ratios on Cd concentration in soil solutions

The effect of moisture content on Cd concentration in soil solutions was studied on four soils, Typic Dystrochrep, Avery Hill (AH) Farm, England Typic Hapludult, North Carolina (NC), USA, Typic Hapludult, New Jersey (NJ), USA and Typic Dystrustept, Kumasi (GK), Ghana. Soil samples were spiked with the $\text{Cd}(\text{NO}_3)_2$ stock solution up to 400 mg Cd kg^{-1} , mixed with a spatula for 2 min,

incubated in closed plastic bottles for one day, and air-dried. Then, sub-samples of the spiked soils were placed in 200-mL plastic bottles and in 50-mL plastic centrifuge tubes. The 0.01 M CaCl₂ was added to the samples to attain moisture content corresponding to 1.2 FMC (in the bottles) and to obtain soil: solution ratios 1:1, 1:5, and 1:10 (in the centrifuge tubes). The bottles and the centrifuge tubes were placed on an orbital shaker and shaken at 20 ± 1 °C for 8 days before the solutions were separated using the centrifugation double chamber equipment described in section 3.2.2 and analysed.

3.1.4 Separation and analyses of soil solutions

Soil solutions were separated from the samples after incubation using the centrifugation ‘double chamber’ method. The design of the ‘double chamber’ (Merckx *et al.*, 2001) was similar to the one suggested by Davies and Davies (1963) but the inner chamber was made of a cut 50-mL disposable syringe with a piece of quartz wool placed on the bottom. The solutions were filtered through a 0.45 µm nitrocellulose membrane filter and analysed to determine dissolved organic carbon (DOC), Cd, Ca, Mg, and Na concentrations, and pH. The DOC concentration was determined with a Tekmar-Dohrmann Apollo 9000 TOC-analyser and Cd, Mg, Ca, and Na were analysed with an Agilent 7500c Induced Couple Plasma –Mass Spectrometer (ICP-MS). Cadmium distribution coefficient (K) was calculated as the ratio between sorbed Cd content and concentration of dissolved Cd.

3.1.5 Modelling of Cd partitioning in soil solutions using WHAM VI

The partitioning of Cd in soil solution was modelled with the Windermere Humic Aqueous Model VI (WHAM VI) using the assumptions suggested for modelling speciation of Cu and Ni in aquatic systems (Lofts and Tipping, 1998) and

in soils (Vulkan *et al.*, 2000; Nolan *et al.*, 2003; Ponizovsky *et al.*, 2006). Windermere Humic Aqueous Model VI is a discrete-site model considering equilibrium interaction of dissolved metal cations and protons with solid and colloidal soil components. Windermere Humic Aqueous Model VI model for prediction uses two approaches, the solution and whole soil. The type of approach to use depends on the set of input parameters available. It was assumed that soil organic matter (SOM) is the main soil component sorbing Cd. As suggested by Tipping *et al.*, (2003), 69% of SOM was taken to be “active” in sorption of the metal. This amount of “active” organic matter was assumed to be composed of 84% humic acid (HA) and 16% fulvic acid (FA). Dissolved organic matter was assumed to contain 69% “active” FA in conformity with Tipping *et al.*, (2003). The input variables also included pH, as well as dissolved Ca, Mg, Na, Cl⁻, and SO₄²⁻ concentrations. The ratio between Cl⁻ and SO₄²⁻ was taken to be 3:1 (moles of charge : moles of charge) and total charge of these anions was equal to the charge of the cations as recommended by Tipping (1998) and Vulkan *et al.*, (2000) to maintain electroneutrality of the soil system. Iron (Fe³⁺) competes with Cd²⁺ for binding sites of the solid phases. So, Fe³⁺ activity was also used as an input variable. It was calculated by assuming that soil solutions were in equilibrium with Fe(OH)₃ and that equilibrium constant for the reaction is given below:



for which $\text{p}K_{\text{Fe}(\text{OH})_3}$ is 3.0 (Tipping *et al.*, 2003; Ponizovsky *et al.*, 2006).

3.2 Field experiments

3.2.1 Cadmium and Pb uptake by vegetables from irrigation water

Experimental mini plots of 1.8 m × 1.8 m were set up on Typic Dystrustept (USDA 2003) or Stagnic Cambisol (Dystric) (FAO-WRB, 2006) at KNUST

agricultural experimental field from May to September, 2005. The soil is moderately well drained, developed over granites and drift materials. The textures vary from sandy loam to sandy clay loam. Average daytime temperature during the period of the experiment at the experimental site was about 32°C and relative humidity in the day was around 40-60 % although the period was supposed to be the major rainy season. Land preparation was by hand clearing, followed by burning and stumping using cutlass and mattock. This was followed by the preparation of beds with the hoe and leveling with rake and manually-operated wooden plank. The experimental design used was factorial experiment arranged in Randomised Complete Block Design (RCBD (Figs. 3.1a and 3.1b). The factorial experiment was used because it allows the imposition of some treatments on existing ones later. Also, it gives more information about one factor than on the other and factors being considered can be put into strips which give a higher degree of precision to the interacting factors.

Cabbage, carrots and lettuce seeds were purchased from the Grains Development Board of the Ministry of Food and Agriculture (MOFA), Ghana. Cabbage and lettuce seeds were nursed in wooden boxes about 1m² size, each filled with sterilized black soil provided by the Department of Horticulture and kept in the greenhouse of the Department of Horticulture, Faculty of Agriculture, KNUST. The vegetables were watered with water from the main supply by Ghana Water Company Limited. Three weeks after sowing, cabbage seedlings were pricked on to the field for another three weeks before transplanting them on the moistened beds. Lettuce seedlings were transplanted three weeks after emergence. Treatment with Cd and Pb solutions started on the same day of transplanting cabbage and lettuce. Carrot seeds were sown directly into the moistened beds to an average depth of about 2 cm in lines on the beds and covered with palm branches to reduce evaporation and thereby conserve moisture. The beds were irrigated each other day with 5L of pipe-borne

water per bed. The palm branches were removed two weeks after emergence followed by the initiation of the Cd and Pb solution treatments.

Cabbage, carrots and lettuce were planted on the plots in three replicates. Cadmium solutions of 0, 0.05 and, 0.1 mg L⁻¹; and Pb solutions of 0, 30 and 50 mg L⁻¹ were prepared and used to irrigate the crops. Cadmium (10 and 20 mg) and lead (6 and 10 g) nitrate salts were added to 200 L capacity containers and filled to the 200 L mark with water from the main pipe supply and stirred to obtain the predetermined Cd and Pb solution concentrations.



Plate 3.1: Picture of lettuce and cabbage for transpiration determination setup



Plate 3.2: Pictures showing soil sampling from a bed and root structure of cabbage

The crops were irrigated each day using 11 liters per plot on each occasion. A plastic watering can was used to avoid introduction of additional metal that would have been the case if a galvanized watering can had been used.

Weeding was by hoe and cutlass. There was no fertilization of any form and dithane was used to spray the cabbage against pest infestation on one occasion before the formation of the heads.

3.2.2 Determination of transpiration

Transpiration of samples of the test crops was measured by the phytometer or gravimetric method by potting the crops in polysacs filled with surface soil with the surface of soil in the plastic pots covered with plastic sheet to prevent evaporation and kept at the edge or border of the experimental field (Plate 3.1). Water loss through transpiration was determined by weighing the pot at predetermined time intervals.

Table 3.1: Average measured transpiration rates of cabbage, carrots and lettuce on controlled plots during the growing period

CROP	Average Transpiration rates (kg/m ²)
CABBAGE	4.94
CARROTS	3.69
LETTUCE	11.59

Average measured transpiration rates of the test crops, cabbage, carrots and lettuce, are presented in Table 3.1. The values were higher compared to Cd and Pb treated crops.

Table 3.2: Determined transpiration rates of Cadmium and Lead treated cabbage, carrots and lettuce

CROP TREATMENT	Transpiration rates (kg/m ²)
CADMIUM	
Cabbage _{0.05}	2.18
Cabbage _{0.1}	1.93
Carrots _{0.05}	9.89
Carrots _{0.1}	6.89
Lettuce _{0.05}	10.35
Lettuce _{0.1}	9.67
LEAD	
Cabbage ₃₀	2.14
Cabbage ₅₀	1.34
Carrots ₃₀	2.36
Carrots ₅₀	2.78
Lettuce ₃₀	10.30
Lettuce ₅₀	6.76

In Table 3.2 are the results of determined transpiration rates of Cd and Pb treated cabbage, carrots and lettuce. The values were found to decrease with increase of irrigation water metal concentration.

FACTORIAL EXPERIMENT

REPLICATION	IRRIGATION WATER mg/L)	CROPS			
		CABBAGE	CARROTS	LETTUCE	
I	0 (Control)	CdCb ₀	CdCr ₀	CdLT ₀	
	0.05	CdCb _{0.05}	CdCr _{0.05}	CdLT _{0.05}	
	0.1	CdCb _{0.1}	CdCr _{0.1}	CdLT _{0.1}	
II		CROPS			
		CARROTS	LETTUCE	CABBAGE	
		0	CdCr ₀	CdLT ₀	CdCb ₀
		0.05	CdCr _{0.05}	CdLT _{0.05}	CdCb _{0.05}
0.1	CdCr _{0.1}	CdLT _{0.1}	CdCb _{0.1}		
III		CROPS			
		LETTUCE	CABBAGE	CARROTS	
		0	CdLT ₀	CdCb ₀	CdCr ₀
		0.05	CdLT _{0.05}	CdCb _{0.05}	CdCr _{0.05}
0.1	CdLT _{0.1}	CdCb _{0.1}	CdCr _{0.1}		

Fig. 3.1a: Experimental design of cadmium (Cd) treated plots

REPLICATION	IRRIGATION WATER (mg/L)	CROPS		
		LETTUCE	CARROTS	CABBAGE
I	0	PbLT ₀	PbCr ₀	PbCb ₀
	30	PbLT ₃₀	PbCr ₃₀	PbCb ₃₀
	50	PbLT ₅₀	PbCr ₅₀	PbCb ₅₀
II	0	PbCr ₀	PbCb ₀	PbLT ₀
	30	PbCr ₃₀	PbCb ₃₀	PbLT ₃₀
	50	PbCr ₅₀	PbCb ₅₀	PbLT ₅₀
III	0	PbCb ₀	PbLT ₀	PbCr ₀
	30	PbCb ₃₀	PbLT ₃₀	PbCr ₃₀
	50	PbCb ₅₀	PbLT ₅₀	PbLT ₅₀

Fig. 3.1b: Experimental design of lead (Pb) treated plots

3.2.3 Sample collection

Samples of irrigation water were collected every two weeks from their storage tanks for analysis of Cd and Pb content (Table 3.1). This was to determine the actual concentrations in irrigation water applied instead of the formulated nominal concentrations.

Table 3.1: Cd and Pb concentrations of irrigation water prepared and used

IW [Cd solution (mg/L)]	Av. concentration (mg/L)	Std. deviation
0.05	0.045	0.002
0.1	0.098	0.045
IW [Pb solution (mg/L)]		
30	31.3	5.38
50	49.44	1.75
TANK (0 mg/L)		
Cd content	0.0067	0.003
Pb content	13.36	3.8
TAP (mains supply)		
Cd content	Below detection limit	nil
Pb content	1.36	0.13

Plant and soil samples were collected at three different stages during the plants' growth that was divided almost into three equal segments. Lettuce samples were collected after 20, 40 and 55 days after transplanting (DAT) while cabbage and carrot samples were collected at 40, 70 and 100 days after sowing (DAS). The plant samples were washed thoroughly with distilled water. They were chopped into approximately 2 cm pieces on a kitchen chopping board which had been washed and rinsed with distilled water. The pieces were then sun-dried for about 6 h before oven-drying at 80 °C for about 20 h. The dried samples were milled to <1 mm.

Soils samples were collected from 0 to 20 cm depth using a core sampler and a cone of 9.5 cm diameter and 5 cm height. This was done four times for each location and the soil in the cone was trimmed with a knife at the base. The samples were air dried for 6 – 8 days, depending on the moisture content at the time of sampling by spreading them on polyethylene sheets. Each sample was thoroughly mixed and passed through a 2 mm sieve before packaging. Sampling of soil and plants were done on the same day.

3.3 Analysis of samples

3.3.1 Determination of Cd and Pb concentrations in test crops

The plant samples were digested using EPA Method 3052 (USEPA, 1996) to determine the Cd and Pb concentrations of the test crops. Nine milliliters of HNO_3 and 2 ml of HCl were added to 0.25 g of plant sample in a Teflon tube. The content of the Teflon tube was weighed and assembled in a rotor (tightened with a torque wrench) and placed in a MRS-200 microwave digester. The microwave, which had been temperature programmed, was then switched on. The samples were left in the microwave after digestion until the temperature decreased to about 30 °C. Teflon heads were unscrewed and removed from the rotor. Each Teflon tube was reweighed to check for any loss of the content of the tube. The digested sample in a solution form was poured into a 15-ml centrifuge tube. One milliliters of the digest was diluted in a ratio of 1:4 using deionized water in a 15-ml centrifuge tube before Cd and Pb analysis with an Agilent 7500 ICP-MS. A standard reference material 1573a of tomato leaves certified by National Institute of Standards and Technology (NIST) was also digested and analyzed for Cd as a quality assurance control.



Plate 3.3: Picture showing the exterior and interior parts of MRS-200 microwave digester

Data generated were analyzed statistically using the Statistical Analysis Software (SAS) package to establish the significance of relationships between the various parameters considered (Appendix 2).

3.3.2 Determination of Cd and Pb in soil samples

The soil samples were analyzed for available and total Cd and Pb. The model WHAM VI (Tipping *et al.*, 2003) was used to predict the free ion activity of the soil samples by the whole soil approach using solution dissolved organic carbon (DOC), pH, total Cd and Pb, soil organic matter (SOM), dissolved metals (Na, Ca and Mg) and NO_3^- as input data (Ponizovsky *et al.*, 2006). Eighty-four percent of the SOM determined by loss-on- ignition (LOI) was assumed to be humic acid (HA) and the remaining 16% as fulvic acid (FA) (Tipping *et al.*, 2003). The DOC value was determined using a TEKMAR DOHRMANN Apollo 9000 TOC analyzer. The TOC was multiplied by 2 and 65% of this value was considered to be colloidal FA for the input data (Tipping *et al.*, 2003).



Plate 3.4a: Picture showing assembled Agilent 7500 ICP-MS



Plate 3.4b: Picture showing side for analysis with Agilent 7500 ICP-MS.

A solution of 0.01 *M* CaCl₂ was used for the extraction of available Cd and Pb. Twenty grams of CaCl₂ solution was added to 2 g of soil sample in a 50-ml centrifuge tube and placed on a shaker for 24 hours. The tube was then centrifuged using a Beckman J2 MC for 10 minutes at 4000 rpm. The supernatant was filtered into a 15 ml centrifuge tube using 0.45 μm membrane filter. The extracted solution was analyzed for Cd and Pb using the Agilent ICP-MS.

The EPA 3051 microwave digestion method was used to extract Cd and Pb for determination of total Cd and Pb. Ten milliliters of concentrated HNO₃ was added to 0.5 g of a soil sample in a Teflon tube and the same procedure as for plant microwave digestion was followed. One milliliter of the digested solution was placed in a 15-ml centrifuge tube and diluted with 4 ml of deionized water for analysis with the Agilent ICP-MS.

3.4 MODELLING

An empirical model was used in modelling the uptake of Cd and Pb. An empirical model is essentially a description of observational data. It is used to fit an equation or a set of equations to data. For example, empirical models of root uptake seek to relate bulk soil parameters to plant parameters by ignoring any contribution from other sources.

3.4.1 Model equation of Cd and Pb uptake based on transpiration

Ingwersen and Streck (2005) developed a mathematical model for plant metal uptake of sugar beet, potato and winter wheat grown on wastewater irrigation area of Braunschweig, Germany. The SEFAH programme for modelling the environmental fate of heavy metals was used. The uptake of heavy metals by plants was modelled using a transpiration-based approach by mass-flow and dry matter production represented by equation (1):

$$C_p = \eta \frac{\Delta e}{\rho_w k_p} \frac{1 + Q_y}{1 + Q_y Q_{HM}} [\exp(\omega \Delta z) - 1] \sum_{i=1}^n \exp(-\omega i \Delta z) C_i \quad (1)$$

Where:

C_p –plant metal concentration (mg kg^{-1})

η – transpiration stream concentration factor

Δe –average saturation vapour deficit of the atmosphere

ρ_w – density of water (kg m^{-3})

k_p – crop specific constant

Q_{HM} –metal ratio

Q_y –dry matter yield ratio between processed (edible) and unprocessed (non-edible) plant parts

ω – distribution of root length density with depth

Δz – change in soil depth

C_i – solution phase metal concentration (mg L^{-1}).

Equation (2) is a modified form of equation (1) for the processing (edible) parts of the test vegetables (cabbage, carrots and lettuce). The modification was done by considering stabilised irrigation water Cd and Pb concentrations in place of soil solution phase metal concentration. The plant and soil factors of root length, density and depth, soil depth, the rooting system, crop characteristics influencing metal ion uptake in addition to climatic factors in the original equation were represented by a constant factor K. The modified equation is represented by:

$$C_p = \eta \frac{1}{Y} TC \quad (2)$$

Where:

C_p – heavy metal content of plant parts (mg kg^{-1})

η – empirical transpiration stream concentration factor,

Y – dry matter content/ unit area of production of crop (kg m^{-2}),

T – cumulative transpiration (L m^{-2}),

C – available metal concentration in soil solution (stabilised irrigation water, mg L^{-1})

Equation (2) is an empirical one formulated on the principles of dimensional analysis. The original equation presented by Ingwersen and Streck (2005) had root density, rooting depth and other factors. It is more suitable for the uptake through the root system but the present model assumes that the uptake is controlled by transpiration stream through the xylem into the leaves and other edible parts. It is also assumed that these metals have an element of bioaccumulation in the edible parts. This is true because studies have shown that metal concentrations are usually higher in the edible parts of vegetables.

As a first step, crop specific constant, K_p (P_a) is defined by the equation (3):

$$K_p = \frac{Y}{T} \Delta e \quad (3)$$

Where:

Δe – average saturation vapour deficit of air for vegetation period (P_a),

T- average measured transpiration of crop growth ($L m^{-1}$)

The calculated K_p value for the controlled sample is then used to calculate K_p of the Cd and Pb treated samples.

Crop Δe values are calculated using equation (4) as presented by Maidment (1993)

$$\Delta e_{ji} = 6.108(100 - rH_{ji}) \exp\left(\frac{17.27T_{ji}}{237.7 + T_{ji}}\right) \quad (4)$$

Where:

rH_{ji} - relative humidity of air

T_{ji} – air temperature.

The Δe values of the three crops are given below from computation using equation (4).

$$\Delta e_{\text{lettuce}} = 693.899$$

$$\Delta e_{\text{cabbage}} = 719.33$$

$$\Delta e_{\text{carrots}} = 719.33$$

The transpiration (T) values of other treatments are calculated using the calculated or determined K_p values of various treatments using equation (5) below derived from equation (3):

$$T = \Delta e \frac{Y}{K_p} \quad (5)$$

The next step is to calculate the transpiration stream factor, η using calculated/determined transpiration values for various treatments. The transpiration stream factor, η , was determined using the equation,

$$\eta = \frac{C_{xy}}{C_w} = \frac{\frac{Q}{K_{rw}}}{\frac{Q}{K_{RW}} + KM} \quad (5)$$

Where:

C_{xy} - metal concentration in the xylem (mg L^{-1})

C_w - metal concentration in soil water (mg L^{-1})

Q - transpiration stream (L d^{-1})

K_{rw} - equilibrium between concentrations in root (C_r) and water (C_w)

M - plant mass (kg)

K - 1st order growth rate (d^{-1})

Average values of η for various treatments of the crops are then determined by adding the calculated values of a treatment for all the replications of a particular crop and dividing the sum by the number of replications.

“Available” metal concentration in soil solution, C , was replaced with $IW k^{-1}$, where IW is irrigation water concentration and k is a constant of proportionality between irrigation water concentration and soil solution concentration by the equation (6):

$$IW = kC \quad (6)$$

The values of k differ for different treatments of different crops.

The model parameters were determined using the above equations (2) to (5). Dry matter yield for each crop was determined by first washing the crop components, sun-drying, oven-drying at 80°C for 24h weighing. This was determined for each replicate of crop. Soil solution concentration (C) in equation (2) was determined by

dividing irrigation water concentration by a constant (k) which is crop dependent. Using equation (4) the average saturation vapour deficit (Δe) of air for each crop was determined by substituting average temperature and relative humidity collected from the Mechanical Engineering Department, KNUST weather station. The value obtained for Δe for each crop was substituted in equation (6) to determine transpiration rate. The average values of transpiration stream factor (η) for various treatments of the crops for all the replications for a crop were then determined using equation (5).

3.4.2 Assumptions for model development

The following assumptions were made for the development of the model used to predict crop metal uptake by the test vegetables:

- i) Soil moisture was not limited to ensure continuous uptake through transpiration.
- ii) The driving force for the uptake was atmospheric evaporativity, E_o ; that is, the pertinent atmospheric factors that control evaporation was not limiting.
- iii) Direct leaf absorption and diffusion from the atmosphere were not considered.
- iv) Initial soil metal concentration was negligible and that metal uptake was from irrigation water.
- v) Soil solution available Cd and Pb to the crop for uptake was equal to the stabilised irrigation water metal concentration applied.

Root mean square error (RMSE) was used for sensitivity analysis of free ion activity of soil solution predicted using WHAM VI. Analysis of variance (ANOVA) was used to establish the significance of the factors related to Cd and Pb concentrations in crops. To throw more light on the reliability of the predicted model values of vegetable Cd and Pb concentrations were compared to the measured values using the model efficiency.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

In this chapter the data of the various aspects of the study, both field and laboratory, have been analysed and the results discussed and presented.

4.1 The temporal variation in the concentration of irrigation water Cd and Pb in soil

The temporal variations in the concentration of irrigation water Cd and Pb in soil are presented in Fig. 4.1 below:

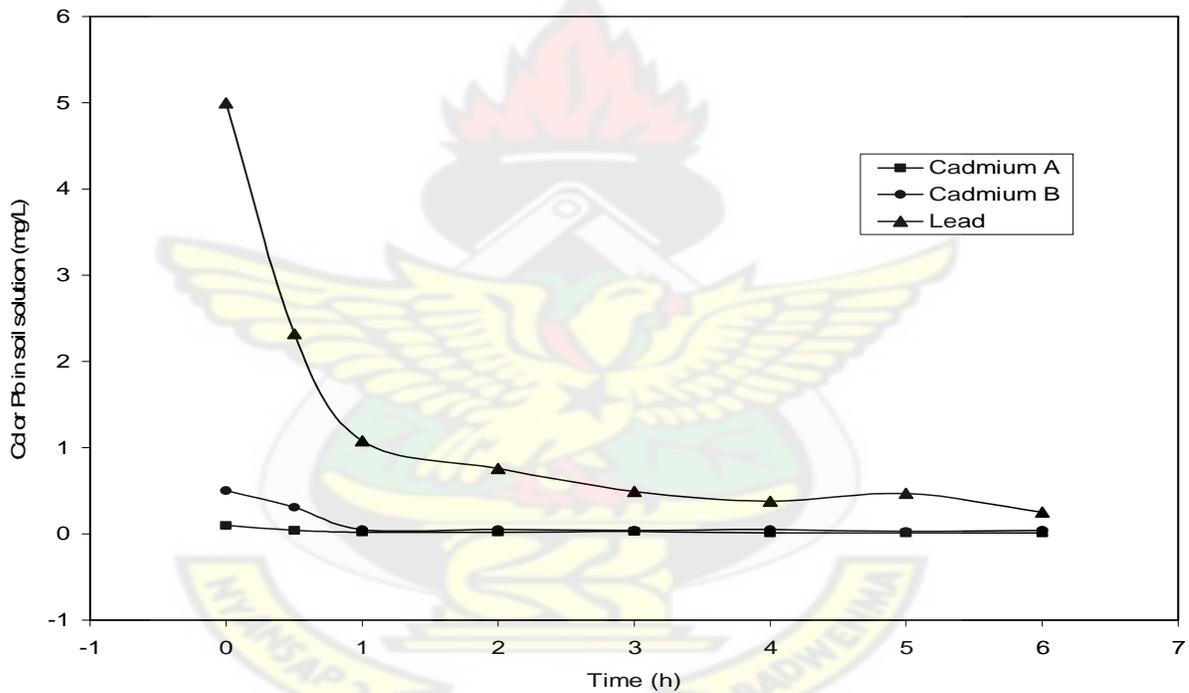


Fig. 4.1: Variation of soil solution Cd and Pb concentrations with time

Cadmium concentration under 0.1 mg L^{-1} stabilized after 1h at a value of 0.01 while Cd concentration under 0.5 mg L^{-1} stabilized within 1h at a value of 0.05. The partition coefficients (K_d) of 0.1 and 0.5 mg L^{-1} concentrations were 4 and 11.5 respectively.

The solution Cd concentration of 0.1 mg L⁻¹ reduced to 0.01 mg L⁻¹, a percentage reduction of 90% of the initial solution concentration. The 0.5 mg L⁻¹ cadmium concentration reduced to 0.04 mg L⁻¹ at the equilibrium or stability point, a percentage reduction of 92%. The equilibrium point was indicated where the concentration of the heavy metal started to become almost constant with time. The time required to reach stability depends on soil properties. Higher soil organic matter content increases the time needed for a reaction to reach equilibrium (Yin *et al.*, 2002). Yin *et al.*, (2002) showed that an influent concentration of 8 mg L⁻¹ had 257 µg g⁻¹ adsorbed at equilibrium for Freehold Sandy Loam with organic matter content of 1.2 g kg⁻¹, Sassafras sandy loam with

Table 4.1: Selected properties of the soils for sorption study

Location of the sampling site	Soil type	Soil ID	Texture	pH ^a	Soil organic matter ^b (%)	Fe ^c , (mg kg ⁻¹)
Ghana, Kumasi, KNUST ^d	Typic Dystrustept	GK	sandy loam	6.1	1.45	378
U.S.A., New Jersey	Typic Hapludult	NJ	sandy loam	5.4	1.90	23700
U.S.A., North Carolina	Typic Hapludult	NC	silty clay	4.8	1.51	20550
England, Avery Hill Farm	Typic Dystrochrept	AH	sandy clay loam	6.1	1.82	25700

^a H₂O, 1:1;

^b Walkley-Black method;

^c Mehlich 1 method.

^d KNUST is the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana; the soil sample was taken at the Research Farm of Department of Horticulture, KNUST.

organic matter content of 3.5 g kg⁻¹ had 1216 µg g⁻¹ adsorbed at equilibrium and Dunellen sandy loam having organic matter content of 11.0 g kg⁻¹ had 3610 µg g⁻¹ adsorbed from 8 mg L⁻¹ mercury solution. The organic matter content of the experimental soil was 1.16%, which was comparatively low. Also at low metal concentrations the principal factor affecting partitioning process is the proton concentration while at higher concentration sorption could be related to specific

surface areas of soil particles (Schulte and Beese, 1994). While that of 0.1 mg L⁻¹ Cd solution may have been due to proton concentration in the solution, that of 0.5 mg L⁻¹ Cd solution may have been as a result of specific surface areas of the soil particles.

Partition coefficient (K_d) of Pb varied with time. The K_d values ranged between 0 and 6.94 between the time 0 to 6 hours. Table 4.2 describes the partition coefficient values of Pb (partitioning between soil and water) of samples collected at different time intervals. The most important factor controlling the partitioning of a metal to soil is the solution pH (Sposito, 1984). Above pH 6, the relative adsorption of Pb is nearly 100% while below this pH level its adsorption decreases quickly. Also at pH values above 6, Pb is either adsorbed on clay surfaces or forms Pb carbonate. With pH value of 6.10 of experimental soil, Pb concentration in irrigation water was adsorbed faster and this explains the fast reduction of Pb concentration in irrigation water, adsorbed on clay surfaces.

Table 4.2: Partition coefficient values of Cd and Pb with time

Time (h)	Partition Coefficient Values (K_d)		
	0.1 Cd mg/L conc.	0.5 Cd mg/L conc.	5.0 Pb mg/L conc.
0	0	0	0
1	4.0	9.57	0.85
2	4.9	10.01	1.63
3	2.6	10.79	3.07
4	6.9	9.87	4.21
5	12.9	13.71	3.29
6	7.3	13.29	6.94

The soil pH value was 6.10 and the soil organic matter 1.16%.

4.1.1 Cadmium release in soil solutions

The cadmium release isotherms for three temperate and one tropical soils are presented in Fig 4.2a while their partition coefficients in relation to sorbed cadmium content are illustrated in Fig. 4.2b. The strongest sorption was observed in Dystrochrept soil at Avery Hill farm (AH) (sandy clay loam), in England (Fig.4.2a), having the highest pH, soil organic matter, and iron contents. However, difference in

sorption can be related to sorption by clay. Typic Dystrustept soil (sandy loam) from Kumasi, Ghana (GK) was the weakest sorbed meaning higher uptake of Cd by vegetables irrigated with contaminated water although the pH was one of the highest.

This could have been as a result of the lowest organic matter and iron contents of the soil (Table 4.1). Cadmium release isotherms of typic Hapludult soils of New Jersey (NJ) and North Carolina (NC) showed that iron content had a significant influence on Cd adsorption of soils of the same type with soil of higher iron content having the higher adsorption Fig. 4.2a). The partition distribution coefficient decreased with the increase in metal loading in NC, NJ, and GK soils

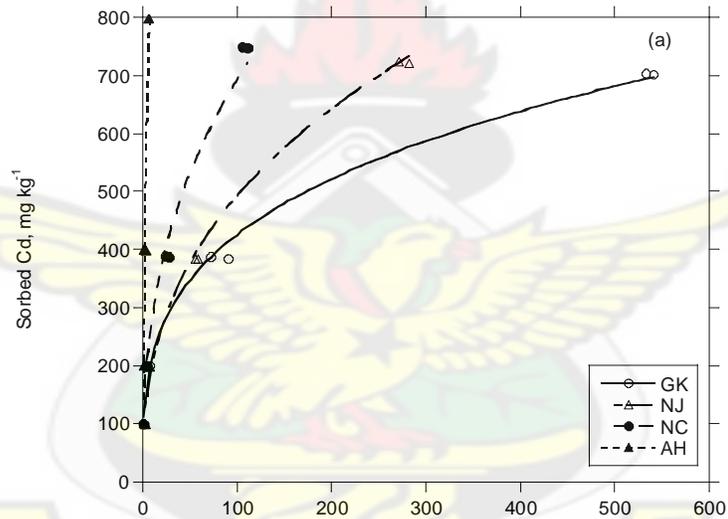


Fig. 4.2a: Cadmium release isotherms

(Fig. 4.2a). The AH soil isotherm was the highest with that of GK being the least amongst the experimental soils.

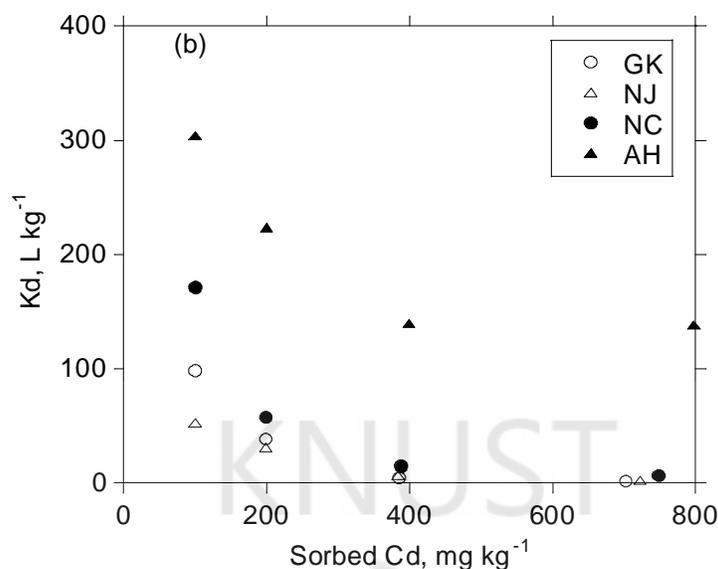


Fig. 4.2b: Cd partition coefficient as function of the sorbed Cd content

In AH soil with the lowest Cd concentration in the solution phase K_d values were larger than in NC, NJ, and GK soils. However, the general trend for K_d in AH soil was similar to that observed in the other soils for Cd loadings below 400 mgkg⁻¹.

4.1.2 Variation of dissolved Cd concentration with moisture:soil ratio: measured and WHAM VI predicted values

The influence of water content on dissolved Cd concentration as measured and predicted using WHAM VI model for AH soil and NJ soil is shown in Figs 4.3a and 4.3b, respectively. The increase in moisture:soil ratio resulted in an exponential decrease in Cd concentration in the solutions (Figs. 4.3a and 4.3b). For AH soil (Fig. 4.3a) as an example, the magnitude of the decrease of Cd concentration was almost 1 mg L⁻¹ for 9500 g kg⁻¹ moisture:soil ratio: while in the case of NJ soil (Fig. 4.3b) there was a decrease of 60 mg Cd L⁻¹ for 9500 g kg⁻¹ moisture:soil ratio. Whereas there was a convergence of the predicted and measured curves at 10000 g kg⁻¹ moisture:soil ratio for AH soil with the predicted being higher than the measured at

moisture:soil ratio $< 8000 \text{ g kg}^{-1}$ (Fig 4.3a), the situation was the reverse for NJ soil (Fig. 3b). There was an asymptotic convergence of the predicted and measured curves with the measured values being higher than the predicted values at all levels of moisture:soil ratio content (Fig 4.3b).

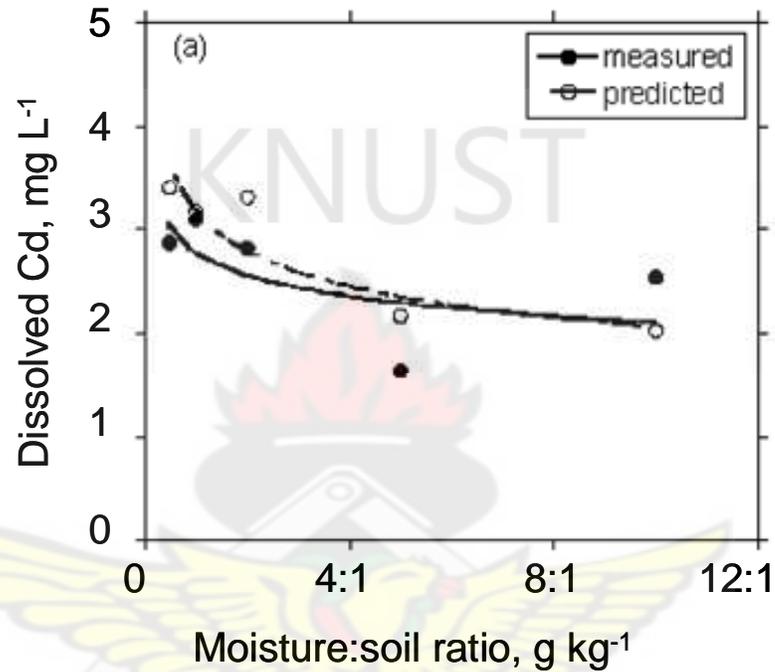


Fig. 4.3a: Effect of moisture: soil ratio on Cd concentration in AH soil solution

Reduction of Cd concentration with increase in moisture:soil ratio may lead to less Cd availability to crops for uptake, resulting in minimum uptake of Cd by crops.

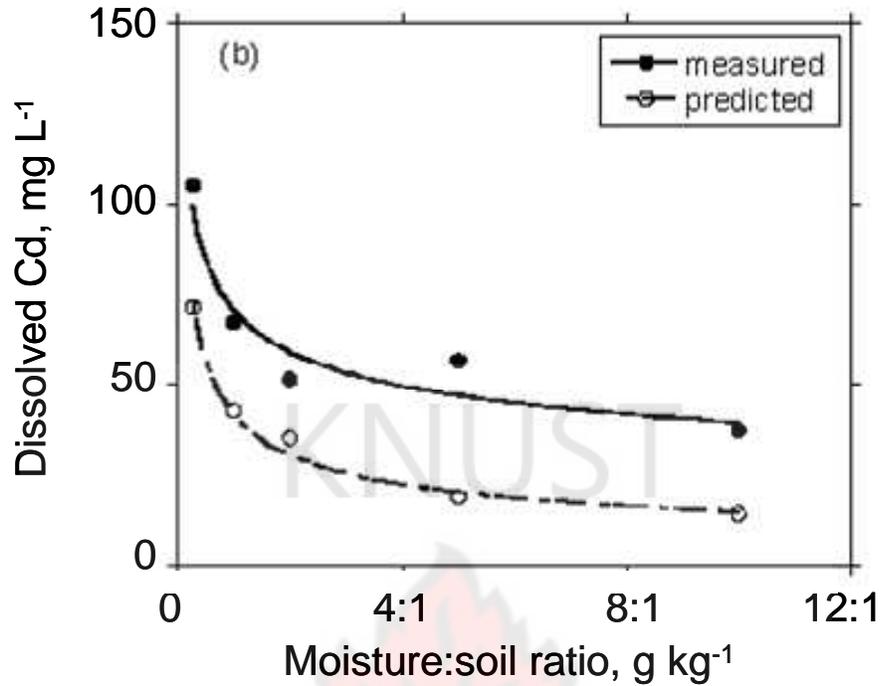


Fig.4.3b: Effect of moisture: soil ratio on Cd concentration in NJ soil solution

In AH soil, 20.8-fold increase in moisture:soil ratio (from 48 to 100 g/100g) gave 1.1-fold decrease in Cd concentration (from 2.9 to 2.5 mg L⁻¹). For NJ soil, 20.8-fold increase in moisture:soil ratio (from 48 to 100 g/100 g) resulted in 2.8-fold decrease in Cd concentration (from 106 to 37 mg L⁻¹).

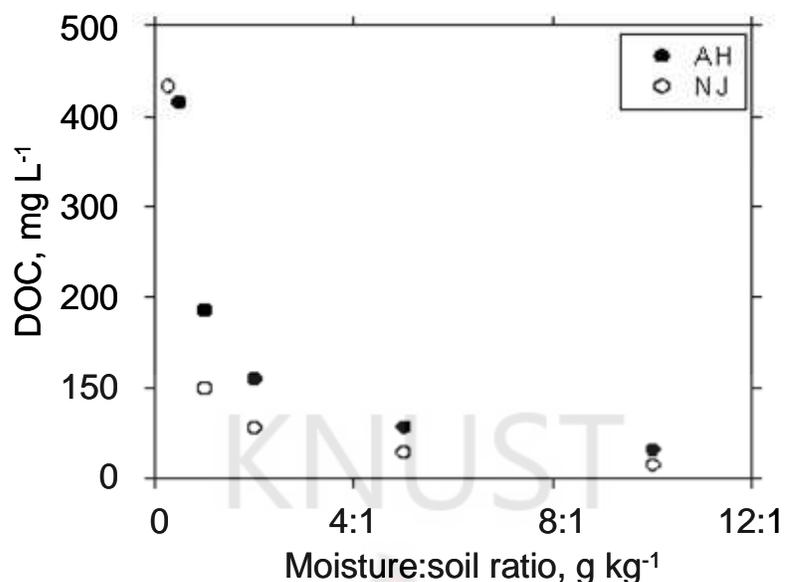


Fig. 4.4: The effect of moisture: soil ratio on DOC concentration

4.1.3 The effect of soil moisture:soil ratio on dissolved organic carbon (DOC) concentration

The concentration of dissolved organic carbon (DOC) as a function of moisture content is depicted for Ah and NJ soils in Fig. 4.4. The concentration of DOC decreased with increasing moisture:soil ratio (Fig. 4.3). Dissolved organic carbon concentration in soil solutions has been found to vary and may depend not only on the soil type (Herbert and Bartsch, 1995) and the moisture:soil (Hagedorn *et al.*, 2000) but also on wetting-drying cycles, microbial activity and metal loadoistuing (Merckx *et al.*, 2001). Reduction of DOC with increasing soil moisture:soil ratio may lead to high metal accessibility to plants for uptake.

4.1.4 Model (WHAM VI) predicted and measured soil Cd concentration relationship

The relationship between dissolved cadmium concentration predicted with WHAM VI and measured values of total Cd concentration in soil solution at 1.2 field moisture capacity (FMC) is presented in Fig. 4.5a.

Root mean square error (RMSE) is the distance, on average, of a data point from the fitted line, measured along a vertical line. It is used for forecasting the accuracy of a model. The smaller the RMSE value of data the better the performance of the model.

Ninety-three percent of the predicted values of Cd concentration in soil solution at 1.2 field moisture content (FMC) were within 1 order of magnitude of the measured ones and the root mean square error (RMSE) of the calculated logarithm of Cd concentration ($RMSE_{\log[Cd]}$) was 0.54 (n=37). The $RMSE_{\log[Cd]}$ for GK and NJ soils valued 0.24 and 0.16, respectively were lower than those for AH ($RMSE_{\log[Cd]}=0.51$) and NC ($RMSE_{\log[Cd]}=0.89$). The logarithmic values establishing the linear relations of predicted and measured values of GK and NJ soils were low indicating the closeness of the predicted Cd values to the measured. However, general relationships between dissolved and sorbed Cd, and between predicted and measured concentrations were similar for the soils of different geographic origin with similar organic matter content and pH (Fig. 4.5a). Calculation of Cd concentration as a function of moisture/soil ratio resulted in values reasonably close to the measured ones (Figs. 4.3a, 4.3b and Fig. 4.5b) with the $RMSE_{\log[Cd]}=0.25$ for the set of data for both AH and NJ soils (n=20).

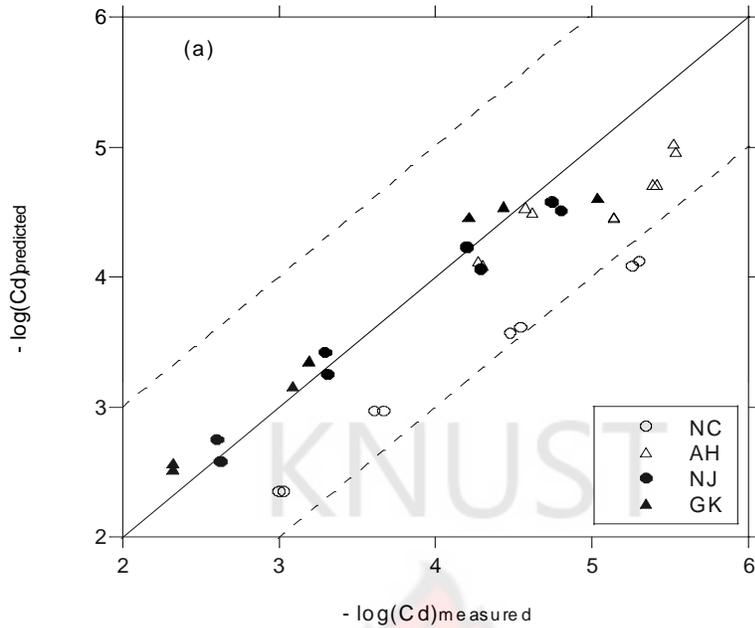


Fig.4.5a: The relationship between Cd concentrations predicted with WHAM VI and measured Cd concentration in soil solutions at moisture content corresponding to the ‘field moisture capacity’. Solid lines represent 1:1 ratio and dashed lines show ± 1 unit deviation from the 1:1 line.

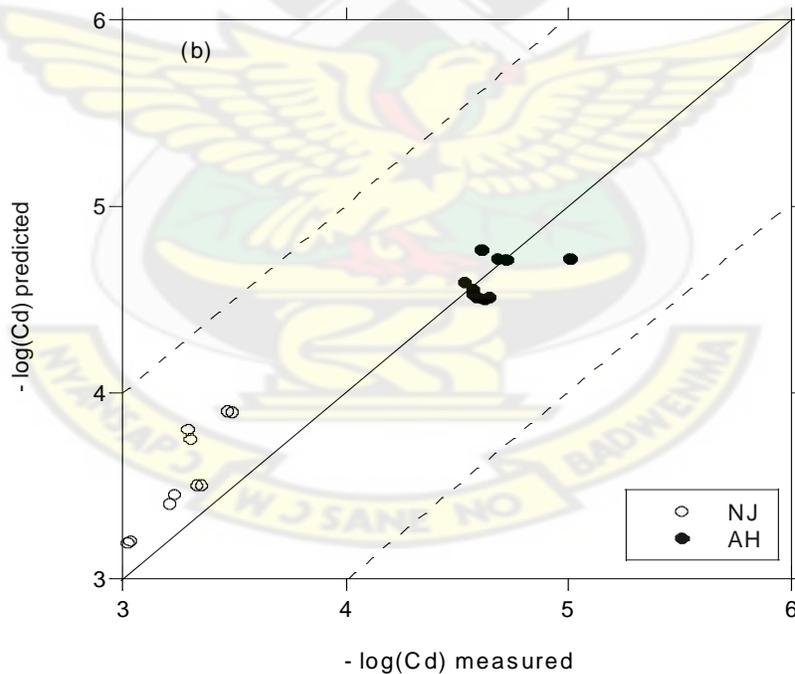


Fig. 4.5b: The relationship between Cd concentrations predicted with WHAM VI and measured Cd concentration in soil solutions at varying soil moisture content.

The composition of soil solution is usually unknown and, in this case, concentrations of dissolved cations, DOC, and soil solution pH cannot be used as the input variables for prediction of Cd concentration, e.g., in toxicological studies. Usage of generic concentrations of the constituents of soil solutions may be helpful for practical applications of WHAM VI if the errors related with this approach are acceptable.

Sensitivity of the model predictions to the uncertainty in the input variables was evaluated by calculating the $RMSE_{\log[Cd]}$ as a function of the variability of the input for NC and NJ soils. In the ranges of SOM and Fe contents, and of DOC and Ca concentrations from -50% to +200%, and pH from -0.5 pH to +0.5 pH of their actual values; calculated $\log[Cd]$ was most sensitive to the variation of SOM content. For the soils with lower $RMSE_{\log[Cd]}$, calculated $\log[Cd]$ was less influenced by the

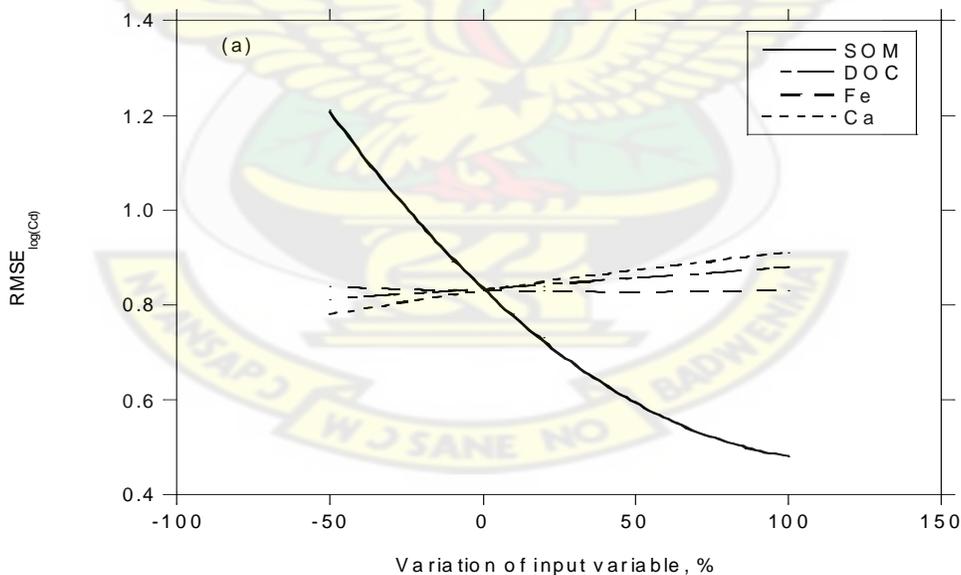


Fig. 4.6a: Root Mean Square Error of calculated logarithm of Cd concentration in soil solutions as a function of the variation of the WHAM VI input concentrations for NC.

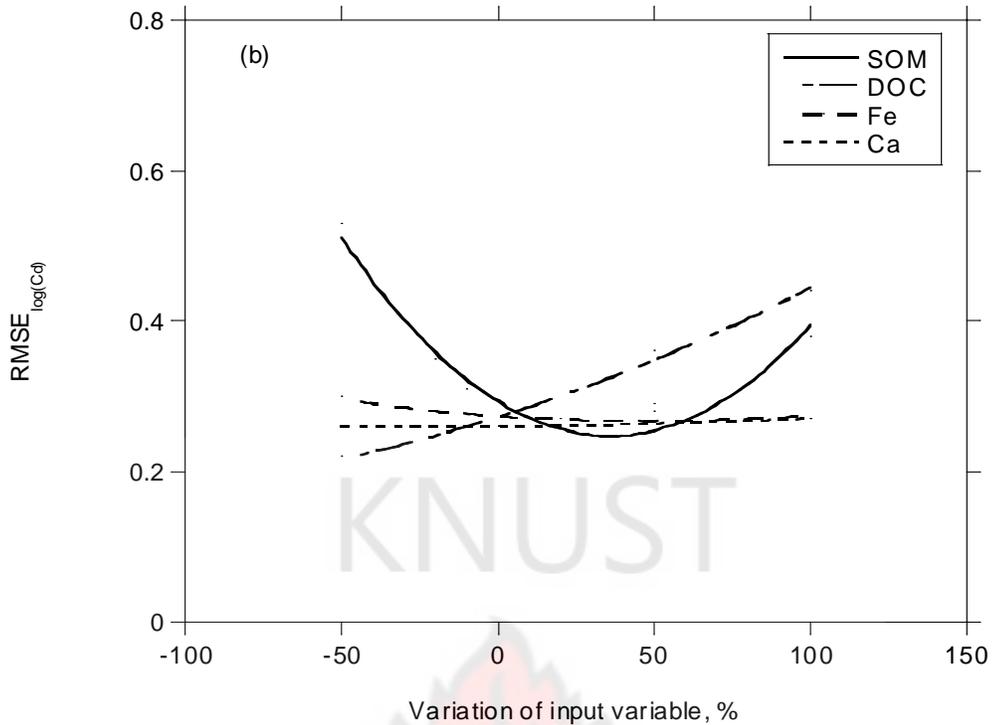


Fig. 4.6b: Root Mean Square Error of calculated logarithm of Cd concentration in soil solutions as a function of the variation of the WHAM VI input concentrations for NJ soils.

variability in pH and slightly more influenced by the variability in DOC, than for the soils with higher RMSE_{log[Cd]} (Figs. 4.5a and 4.5b).

Variation in soil Fe content and dissolved Ca concentration only slightly influenced predicted log [Cd] (Figs 4.5a and 4.5b). Variation in solution pH from -0.5 pH to +0.5 pH of their actual values resulted in the variation of RMSE_{log[Cd]} from 0.22 to 0.18 for NC and from 0.09 to 0.01 for NJ soils. Thus, usage of generic values of some of the input variables may result in prediction errors that are acceptable for some purposes, such as computing critical loading on a regional basis.

Better prediction may be expected using the values of soil properties specific to each kind of soil. Using values of Ca and DOC concentrations measured with no addition of Cd for each of the soils and soil pH as input variables to calculate Cd concentration in soil solutions after spiking the soils resulted in RMSE_{log[Cd]} 0.66, 0.52, 0.33, and 0.52 for NC, AH, NJ, and GK, respectively; and for all 4 soils

$RMSE_{\log[Cd]} = 0.49$ giving better prediction of $\log[Cd]$ than when the values were taken as the average for all soils studied.

General relationships between dissolved and sorbed Cd and predicted and measured concentrations were similar for the soils of different geographic origin with similar organic matter content and pH.

4.1.5 Statistical analysis of Cd and Pb concentrations in crops and soil

Crops absorb Cd and Pb from sources like the soil on which they are grown and the irrigation water used if they are contaminated with these metals. The presence of these metals in the soil affects the nutrient uptake by crops to give optimum yield per unit area of land under cultivation.

Statistical analysis of crop Cd and Pb concentrations (ANOVA) of samples was done using General Linear Model (GLM) procedure in Statistical Analysis System (SAS) package. The results showed the factors considered to affect (time, metal concentration and crop) Cd metal concentration in water was significant (p-value $0.0001 < 0.05$) (Appendix 4). For Pb, type of crop was found to be significant (p-value, $0.0137 < 0.05$) (Appendix 4).

4.1.6 Influence of Cd and Pb concentrations on crop yields

The effects of Cd and Pb on the yields of lettuce and carrot are presented in Tables 4.3a and 4.3b. Crop yields were negatively influenced by Cd and Pb concentrations generally. The yields of lettuce from the Cd treated plots were 17,232, 15,408 and 14,400 kg ha^{-1} for 0, 0.05 and 0.1 mg Cd L^{-1} irrigation water concentrations, respectively. The yields for the plots treated with 0.05 and 0.1 mg L^{-1} of Cd were reduced by 11 and 16 %, respectively, compared to the yield of the

control treatment (0 mg L⁻¹). In the case of Pb treatments of lettuce the yields were 23,424, 20,208 and 13,296 kg ha⁻¹ for 0, 30 and 50 mg L⁻¹ irrigation water treatments, respectively. Comparing the yields from 30 and 50 mg L⁻¹ irrigation water treatments to that of 0 mg L⁻¹ treatment, there were reductions of 14 and 43 %, respectively (Table 4.3a).

Table 4.3a: The effect of Cd and Pb concentrations on lettuce yields

Cd conc. (mg L ⁻¹)	Crop yield (kg ha ⁻¹)	Percent # reduction in yield	Pb conc. (mg L ⁻¹)	Crop yield (kg ha ⁻¹)	Percent # reduction in yield
0	17,232	-	0	23,424	-
0.05	15,408	11	30	20,208	14
0.1	14,400	16	50	13,296	43

Carrots responded differently to Cd and Pb in the irrigation water (Table 4.3b). Plots of carrots irrigated with Cd solutions yielded 21,000, 53,760 and 45,120 kg ha⁻¹ for 0, 0.05 and 0.1 mg L⁻¹ treated plots, respectively. A comparison of the yields from the 0.05 and 0.1 mg L⁻¹ treatment plots with those from 0 mg L⁻¹ plots showed increases of 61 and 53 %, respectively. Yields from Pb irrigated carrot plots were 36,240, 25,680 and 31,920 kg ha⁻¹ for 0, 30 and 50 mg L⁻¹ irrigation water treatments, respectively. There were reductions of 29 and 12%, respectively, when yields from 30 and 50 mg L⁻¹ irrigation water treatments were compared with yields from 0 mg L⁻¹ irrigation water treatment. A study of the effect of heavy metals on alfalfa plants by Peralta *et al.*, (2004) showed that a Cd dose of 5 mg L⁻¹ reduced the shoot size by about 16% compared with the control. At a dose of 20 mg L⁻¹ there was 63% reduction in the size of alfalfa shoot and a lethal effect on the plant at a dose of

40 mg L⁻¹. Öncel *et al.*, (2000) found that Cd reduces the level of chlorophyll a and b, implying that photosynthetic activity may be reduced by the presence of Cd.

Table 4.3b: The effect of Cd and Pb concentrations on yield of carrot

Cd conc. (mg L ⁻¹)	Crop yield (kg ha ⁻¹)	Percent # reduction in yield	Pb conc. (mg L ⁻¹)	Crop yield (kg ha ⁻¹)	Percent # reduction in yield
0	21,000	-	0	36,240	-
0.05	53,760	61	30	25,680	29
0.1	45,120	53	50	31,920	12

In this work the yield of Cd treated carrots showed a different trend compared with that of lettuce. Yields of carrot from 0.05 and 0.1 mg Cd L⁻¹ treated plots increased by 60.9 and 53.3%, respectively, compared with yields from 0 mg Cd L⁻¹ treated plots. This may be ascribed to Cd forming soluble complexes with some soil constituents that were taken up by carrots as nutrients on those plots (Oliver and Naidu, 2003). However, this anomaly may require further studies by plant scientists interested in the role of heavy metals in plant nutrition.

4.1.7 Effect of Cd and Pb concentrations in irrigation water on crop Cd and Pb content

Table 4.3 presents the concentrations of Cd and Pb in test crops in relation to the rates of the metal treatments in irrigation water at different stages of growth. Cadmium and Pb concentrations in the test crops increased significantly ($p < 0.05$) as concentrations of the metals in the irrigation water increased. However, the increases were non-linear as illustrated in Fig.4.7a.

Table 4.4: Mean cadmium (Cd) and lead (Pb) concentrations in cabbage, carrots and lettuce crops under different irrigation water (IW) Cd and Pb contents

Crop	Days	IW conc (mg/L) Cd	Av Crop Cd conc (mg/kg dry wt)	IW conc (mg/L) Pb	Av Crop Pb conc (mg/kg dry wt)
Cabbage	40	0	0.249 (0.125)	0	0.601 (0.095)
		0.05	0.542 (0.284)	30	11.76 (3.98)
		0.1	0.961 (0.215)	50	15.22 (5.82)
	70	0	0.093 (0.024)	0	0.183 (0.015)
		0.05	0.389 (0.067)	30	0.367 (0.093)
		0.1	0.592 (0.142)	50	0.499 (0.082)
	100	0	0.344 (0.185)	0	0.216 (0.125)
		0.05	0.85 (0.219)	30	0.874 (0.185)
		0.1	1.11 (0.328)	50	0.945 (0.426)
Carrots	40	0	0.062 (0.021)	0	0.557 (0.298)
		0.05	1.04 (0.334)	30	3.22 (0.912)
		0.1	0.732 (0.295)	50	6.07 (1.09)
	70	0	0.432 (0.041)	0	0.73 (0.262)
		0.05	0.701 (0.168)	30	2.61 (0.656)
		0.1	0.898 (0.688)	50	4.32 (1.17)
	100	0	0.181 (0.029)	0	0.427 (0.18)
		0.05	0.997 (0.208)	30	4.54 (1.23)
		0.1	0.799 (0.298)	50	6.24 (2.64)
Lettuce	20	0	0.263 (0.082)	0	1.41 (0.563)
		0.05	0.602 (0.238)	30	21.80 (4.45)
		0.1	0.549 (0.181)	50	21.9 (3.62)
	40	0	0.241 (0.092)	0	1.62 (0.827)
		0.05	1.0 (0.843)	30	79.20 (24.9)
		0.1	0.534 (0.101)	50	82.4 (22.90)
	55	0	0.121 (0.053)	0	2.25 (0.812)
		0.05	0.968 (0.392)	30	133.6 (44.6)
		0.1	1.022 (0.311)	50	187.4 (39.9)

* Values in brackets represent standard deviation

Cadmium concentrations for cabbage were between 0.09 for zero concentration at 70 days and 1.11 mg kg⁻¹ for 0.1 mg L⁻¹ concentration at 100 days, while carrots and lettuce had values of 0.062 for zero concentration at 40 days to 1.0 mg kg⁻¹ and 0.12 to 1.02 mg kg⁻¹, respectively. Lead concentrations in cabbage ranged between 0.18 for zero concentration at 70 days and 15.2 mg kg⁻¹ for 50 mg L⁻¹ concentration at 40 days while for carrots and lettuce the concentrations were 0.43 for zero concentration at 100 days to 6.24 mg kg⁻¹ for 50 mg L⁻¹ concentration at 100 days and 1.41 to 187.4 mg kg⁻¹, respectively. Cadmium and Pb concentrations in lettuce were the highest among the three crops. The Cd and Pb concentrations in

the test crops (cabbage, carrots and lettuce) for zero irrigation water treatment might have been absorbed from soil during the nursery stage. The soil for the nursery was collected from an abandoned waste-dump site. The soil was sterilized but the soil sterilization could not influence the effect of heavy metals present since heavy metals are not thermophilic.

Table 4.5 shows the time effect on crop Cd and Pb concentration levels.

Table 4.5: Average Cd and Pb concentrations in cabbage, carrots and lettuce for each irrigation water concentration after 20, 40 and 55 days for lettuce and 40, 70 and 100 days for cabbage and carrots after transplanting.

Element	Crop	Days after transplanting	IW conc (mg L ⁻¹)			
			0	0.05	0.1	
Cd	Cabbage	40	Plant conc (mg kg ⁻¹)			
			0.25	0.54	0.96	
			0.09	0.39	0.59	
		70	0.34	0.85	1.11	
			100	0.06	1.04	0.73
				0.43	0.70	0.90
		0.18		1.0	0.80	
		Lettuce	20	0.26	0.60	0.55
			40	0.24	1.01	0.53
	55		0.12	0.97	1.02	
	Pb	Cabbage	40	0	30	50
				0.60	11.76	15.22
0.18				0.37	0.50	
70			0.22	0.87	0.95	
			100	0.56	3.22	6.07
				0.73	2.61	4.32
Carrots		40		0.43	4.54	6.24
			1.41	21.78	21.87	
			1.62	79.16	82.41	
		55	2.25	133.60	187.4	

Metal concentrations (Cd and Pb) of the first set (40 days) of harvested cabbage samples were very high compared with concentrations after 70 days (Table 4.5). This might be for the fact that the initial samples were taken from the leaves and not “heads” which is the edible part, because at the time of the first sampling the

“heads” had not formed. The concentration appeared to be higher in the leaves than in the heads”.

From Table 4.5 there were no systematic increases of Cd concentration with time for any of the crops. However, Pb concentrations in lettuce increased consistently with time during the period of growth and irrigation water concentration.

Plant Cd and Pb uptake rates of the three crops, in mg day^{-1} , increased with irrigation water concentrations and the trend was similar to those of plant and irrigation water concentrations relationships (Figs. 4.6a and 4.6b).

Crop yield was affected by irrigation water concentration of Cd and Pb. For lettuce there was a reduction in yield for both Cd and Pb treatments with increase in concentrations of Cd and Pb in irrigation water. Yields from treatments with 0.05 mg L^{-1} Cd concentration reduced the yield by 10.7% of the control (0 mg L^{-1}) while treatment with 0.1 mg L^{-1} Cd concentration reduced the yield by 16.4%. For Pb the yield was reduced compared to the control by 13.7 and 43.2% for 30 and 50 mg L^{-1} , respectively (Tables 4.3a and 4.3b). Reduction in yield with Cd and Pb treatments shows that the presence of the metals possibly had repressive effects on the physiological functions of the plants. The Cd and Pb in the irrigation water compete with essential macronutrients like Ca and Mg required by plants for healthy growth, thus creating nutritional imbalance (Nouri *et al.*, 2001).

Cadmium and Pb concentrations in cabbage, carrots and lettuce increased as their content in irrigation water increased. Root solute uptake has been found to increase with root water uptake (Ingwersen and Streck, 2005). The root solute uptake may depend on the water uptake rate even when active uptake is dominant. During periods of high temperature the decomposition rate of organic matter is likely to be high leading to the release of heavy metals in soil solution to make them mobile or

available for uptake by plants (McGrath *et al.*, 1994). Also, there is a tendency for an increase of vapour saturation deficit at high temperatures. The increase in saturation deficit will in turn increase the atmospheric evaporativity and transpiration rate. The climatic conditions during the period of field experimentation were expected to result in high transpiration rates of plants. The crops' Cd and Pb concentrations were found to be high and the values are comparable with results obtained from a study on wastewater irrigation of crops in India by Singh *et al.*, (2004). Higher Cd and Pb concentrations in the crops found in this study may therefore be ascribed to climatic-induced high transpiration rates (Tables 3.1 and 3.2). Marschner (1995) reported from a study of Cd uptake by crops that crop Cd uptake was by mass flow with the transpiration flux. This is in line with observations made in other studies by Lorenz *et al.*, (1994) and Kashem and Singh (2002) on Cd and Zn uptake by radish, oats and water spinach. Hardiman and Jacoby (1984) made similar observation on Cd uptake by bean plants.

The World Health Organisation (WHO, 1989) recommended that daily intake of Cd per unit (kg) body weight of an adult should not exceed 1 μg . Therefore the maximum daily Cd intake by a vegetarian of 50 kg weight will be 50 μg . This value is higher than the Cd intake of 4.32 μg from composite meal of a vegetarian feeding on produce irrigated with 0.05 mg L^{-1} Cd concentration in irrigation water. Considering individual crops, carrots provided the highest value of 3.2 μg for a daily intake of 113 g. A meal of cabbage, carrots and lettuce from crops irrigated with 0.1 mg Cd L^{-1} in irrigation water would contain 4.44 μg Cd. For an adult of 50 kg weight this falls below the WHO recommended maximum value of 50 $\mu\text{g day}^{-1}$.

Lead content for the same composite daily meal of an adult vegetarian of produce irrigated with 30 mg Pb L^{-1} of irrigation water is 33.9 μg while that of crops

irrigated with 50 mg Pb L⁻¹ Pb of irrigation water is 37.9 µg. The WHO (1987) recommended maximum Pb daily intake per kg body weight is 3.57 µg. So an adult vegetarian of 50 kg body weight, for example, has a recommended maximum daily Pb intake of 180 µg. The recommended maximum value is 4.75- and 5.31-fold the intake values of vegetables irrigated with 50 mg Pb L⁻¹ and 30 mg Pb L⁻¹ Pb in irrigation water, respectively. The recommended maximum Pb daily intake of 14 µg from carrots (ANZFA, 2001) was, however, exceeded by crops irrigated with 30 and 50 mg L⁻¹ Pb concentrations by 2.14- and 2.4-fold respectively.

Langmuir equation was fitted to the data points to show the trend of plant Cd and Pb concentrations as the irrigation water concentration varied (Figs. 4.7a and 4.6b). Langmuir equation is expressed in equation 4.1 as:

$$C_{plant} = \frac{K \times C_w}{(1 + n \times K \times C_w)} \quad (4.1)$$

Where:

C_{plant} -plant metal concentration (mg kg⁻¹),

C_w – Irrigation water metal concentration (mg L⁻¹) and

K and n are constants.

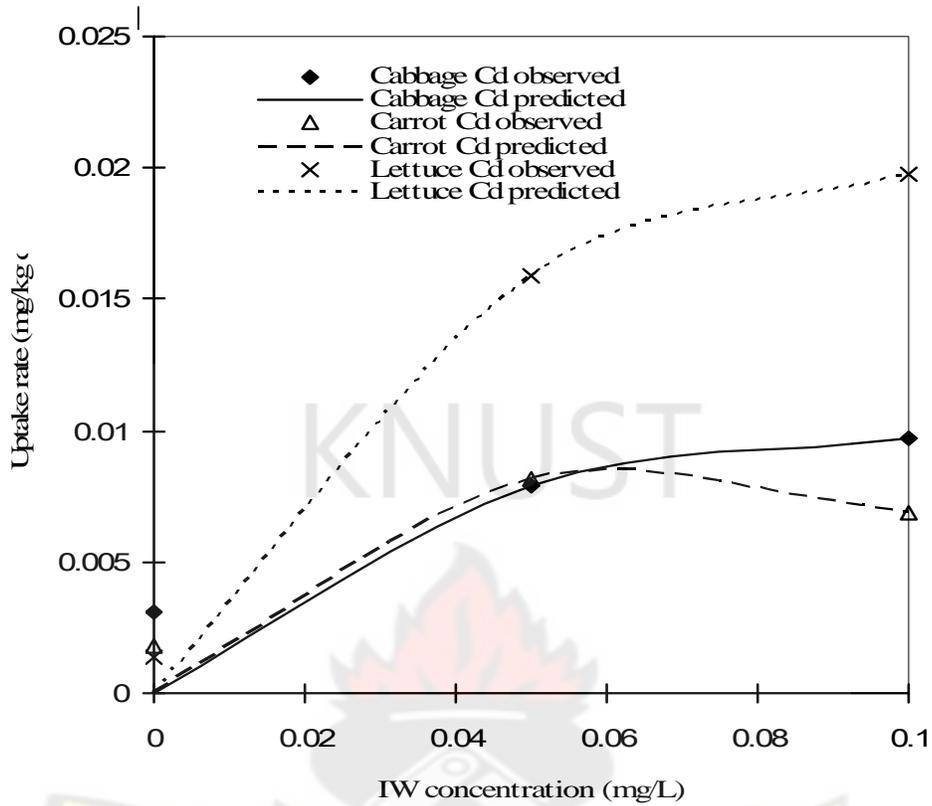


Fig. 4.7a: Plant Cd uptake rate (mg/kg/day) and irrigation water concentration (mg/L) relationship for measured and predicted (Langmuir) values

Lettuce Cd and Pb concentrations were found to be highest. Figure 4.7a showed that Cd and Pb concentrations of the vegetables increased with concentration and time, those of lettuce being significant at $p\text{-value} < 0.05$. This might be due to the difference in transpiration rates of the different crops that have different physiology that influences transpiration.

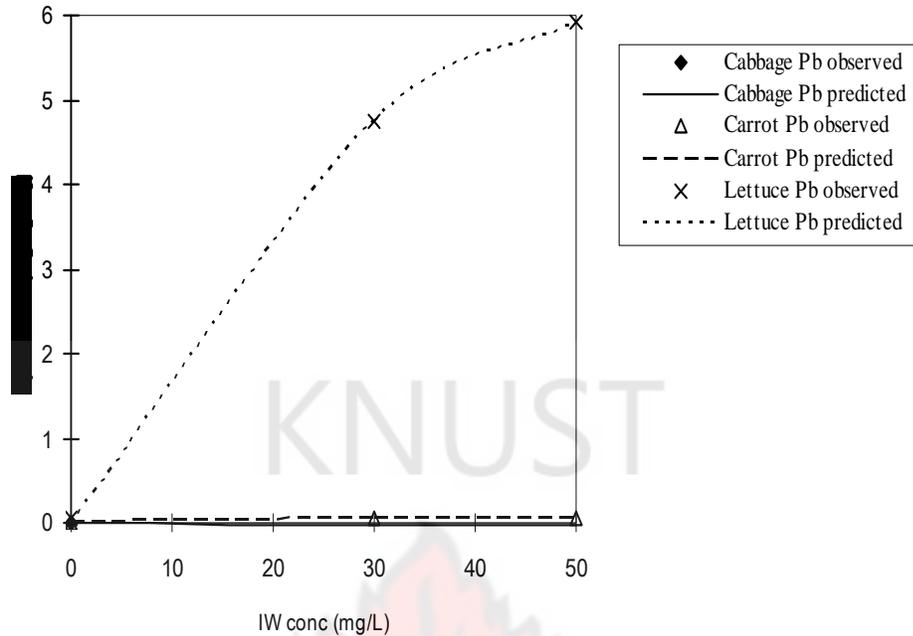


Fig. 4.7b: Plant Pb uptake rate (mg/kg/day) and irrigation water concentration (mg/L) relationship for measured and predicted (Langmuir) values.

The intake rate of Pb was negligible and insignificant and could hardly be seen on the graph (Fig 4.7b). For both Cd and Pb, lettuce had the highest concentration values. Also Cd and Pb concentrations in all plants increased with concentration as well as time. Those of lettuce were significant (p -value < 0.05) (Figs. 4.7a and 4.7b).

Cadmium and Pb concentrations of the cabbage, carrots and lettuce increased as the plants grew. Plant metal content varies with time of harvesting and stage of maturity (Sauerbeck, 1991). This confirmed the results of a study on barley plants by Nouri *et al.*, (2001) and on maize by Chrysaopoulou *et al.*, (2005). However the magnitude of time dependence of plant Cd and Pb concentration variations differed among crops and metals. The uptake and distribution of metals in crops differ among species and cultivars within a species (Ingwersen and Streck, 2005). Lettuce had the highest Cd and Pb concentrations among the three crops tested in this study, confirming Cd concentration in lettuce as reported by other researchers (Pettersen,

1997) and from studies on crops like carrots and spinach (He and Singh, 1994). Sauerbeck (1991) indicated that when plants are young mineral absorption is relatively rapid and dry matter production is rather slow. But later when large and active photosynthetic areas are being formed, dry matter production may outstrip absorption of mineral elements, leading to a reduction in their level. During this time there is also a redistribution of elements within the plant and variation between and within different organs may be quite large (Moreno, 1996). Lead is usually accumulated in the roots and only a very small amount is accumulated in the shoots. However some plants translocate Pb effectively to shoots without chelators that aid Pb translocation from roots (Chrysaopoulou *et al.*, 2005). High Pb concentrations in lettuce showed the probability of lettuce being one of such plants that effectively translocate Pb from roots to shoots. High Pb concentrations in plants may be an indication of metal uptake from irrigation water by transpiration since Pb concentrations in plants do not exceed 10 mg/kg with the exception of leafy plants such as lettuce (Kabata-Pendias and Pendias, 1986).

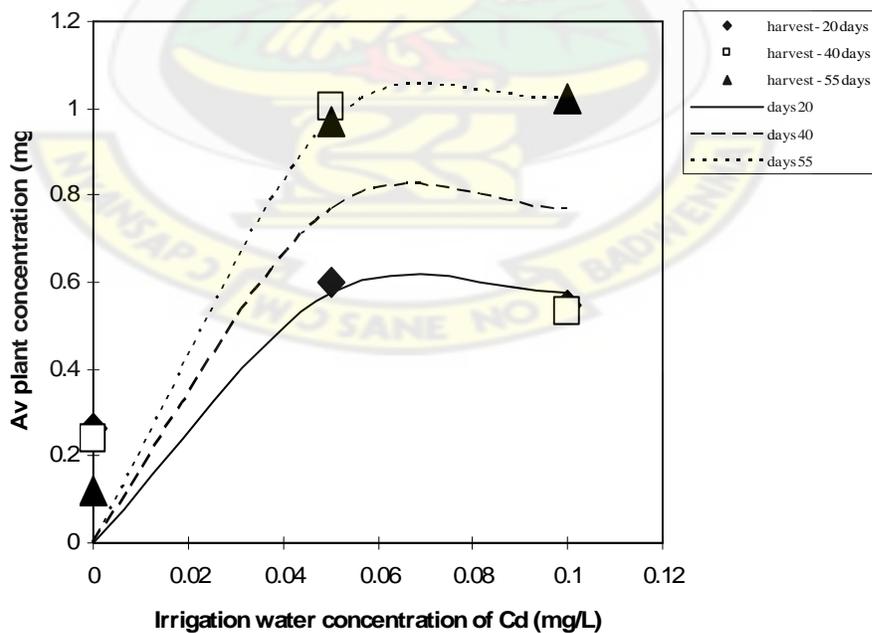


Fig 4.8: Average plant Cd and irrigation water concentration relationships for measured and predicted (Langmuir) values.

Plant Cd and Pb concentrations of the three crops using the Langmuir equation gave a correlation coefficient of 0.999 when related to measured values (Fig 4.8) and a RMSE range of 0.054 – 0.25 for Cd; and 0.11 – 1.30 for Pb (Table 4.6).

Table 4.6: RMSE of the relationship of measured and predicted Cd and Pb concentrations (mg/kg) of cabbage, carrots and lettuce using the Langmuir equation.

Element	Crop	Days after transplanting	RMSE values
Cd	Cabbage	40	0.144
		70	0.054
		100	0.199
	Carrots	40	0.13
		70	0.249
		100	0.132
	Lettuce	20	0.153
		40	0.237
		55	0.07
Pb	Cabbage	40	0.347
		70	0.106
		100	0.125
	Carrots	40	0.387
		70	0.422
		100	0.246
	Lettuce	20	0.813
		40	0.938
		55	1.298

The Langmuir equation applied to Cd uptake by Swiss chard grown on composted sewage treated fields gave a linear plot at lower soil Cd and Pb concentrations while a non-linear (curvilinear) relation was obtained at higher concentrations (Chang *et al.*, 1997). The crops' Cd and Pb concentrations determined in this study were comparable to those in similar studies carried out in Ethiopia (Rahlenbeck *et al.*, 1999) and in India (Singh *et al.*, 2004).

Root uptake of solute is assumed to be linearly proportional to the product of soil solution concentration and water uptake (Christensen and Tjell, 1984; Behrendt *et al.*, 1995; Trapp, 2000; Schoups and Hopmans, 2002; Grant *et al.*, 1998). This may be a reason for the crops (cabbage, carrots and lettuce) Cd and Pb concentrations

increasing with the concentrations of the irrigation water as shown in Figs. 4.6a and 4.6b. Considering an adult vegetarian in Ghana whose vegetable intake is the same as a vegetarian in India, who by recommendation takes 113 g each of carrots and cabbage and 21g of lettuce (USEPA, 2002), his Cd intake from produce irrigated with 0.05 mg L^{-1} Cd in irrigation water will be $4.32 \mu\text{g}$ and from a produce irrigated with water containing 0.1 mg L^{-1} Cd, it will be $4.44 \mu\text{g}$. Heavy metal intake also depends on body weight and the age of the consumer (Oliver and Naidu, 2003).

4.2 Total and available soil Cd and Pb concentrations

Soil total Cd concentrations had a minimum value of 0.36 mg kg^{-1} and a maximum value of 14.7 mg kg^{-1} (Table 4.7). Total Cd of 20 mg kg^{-1} applied that was recovered in the 0 – 5 cm depth ranged between 39.1 and 77 %; and for the 5 – 10 cm depth the range was 11 to 39%. The distribution of the total that constituted available Cd ranged between 18.7 and 96.8 % for the top 5 cm depth and 8.5 and 89.6 % for the 5 – 10cm depth. With respect to soil samples from plots of specific crops (cabbage, carrots and lettuce), the percentage of available Cd of the soil ranged between 25.3 and 70.5 for the 0 – 5 cm depth; and from 20.7 to 89.6 for the 5 – 10 cm depth. The available soil Cd relative to soil total Cd from carrots and lettuce plots ranged from 18.7 to 55.3 % for the 0 –5 cm depth; and 8.46 to 55.6 % for the 5 –10 cm depth. For lettuce, Cd ranged from 24.9 to 96.8 % for the 0 – 5 cm; and 11.9 to 96.8 % for the 5 –10 cm depths. The minimum available soil Cd concentration was 0.02 mg kg^{-1} and the maximum value was 7.48 mg kg^{-1} .

Table 4.7: Soil Total and available Cd and Pb concentrations at the top 10 cm depth of experimental plots

Element	Crop	Irrigation water conc (mg L ⁻¹)	Soil sample depth (cm)	Soil metal concentration (mg kg ⁻¹)	
				Total	Available
Cd	Cabbage	0.05	0 - 5	9.8	3.8
			5 - 10	4.97	1.8
		0.1	0 - 5	13.24	4.34
			5 - 10	7.22	2.98
	Carrots	0.05	0 - 5	12.11	5.09
			5 - 10	7.91	3.61
		0.1	0 - 5	14.7	7.48
			5 - 10	8.96	3.75
	Lettuce	0.05	0 - 5	8.78	3.18
			5 - 10	0.36	2.08
		0.1	0 - 5	9.7	2.65
			5 - 10	6.33	0.02
Pb	Cabbage	30	0 - 5	394.9	1.73
			5 - 10	202.0	0.09
		50	0 - 5	991.8	4.23
			5 - 10	345.29	1.12
	Carrots	30	0 - 5	419.2	1.58
			5 - 10	32.6	0.18
		50	0 - 5	499.0	8.45
			5 - 10	82.22	0.88
	Lettuce	30	0 - 5	284.4	7.86
			5 - 10	95.25	1.67
		50	0 - 5	661.2	13.31
			5 - 10	187.56	1.75

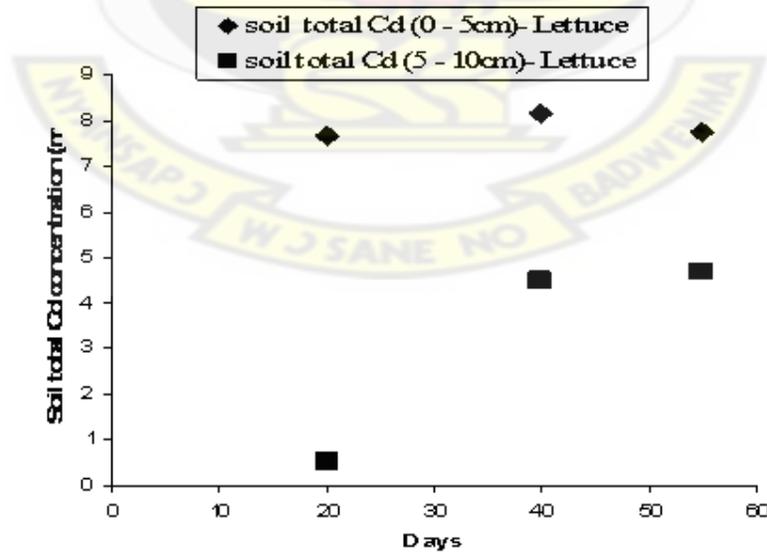


Fig 4.9: Total Soil Cd concentration variation with time at varying depths for lettuce plots.

The available Cd ranged between 18.7 and 96.8 % for the top 5 cm depth and between 8.46 and 89.6 % for the 5 – 10 cm depth. With respect to soil samples from plots of particular crops, the percentage of available Cd to the soil total soil Cd ranged between 25.3 and 70.48 for the 0 – 5 cm depth and from 20.7 to 89.6 for the 5 – 10 cm depth. Carrots and lettuce had percentage ranges of total soil Cd of 18.7 to 55.3 for the 0 – 5 cm depth and 8.46 to 55.6 for the 5 – 10 cm depth. For lettuce the range was 24.9 to 96.8 for the 0 – 5 cm and 11.9 to 96.8 for the 5 – 10 cm depths.

The total Pb concentrations of soil samples ranged between 32.6 and 991.8 mg kg⁻¹ (Table 4.7). The minimum available concentration was 0.09 mg kg⁻¹ and the maximum value was 8.45 mg/kg. The percentage of the total Pb that is available was very low in comparison to that for Cd. The percentage values for available Pb ranged from 0.058 to 7.9 for the 0 – 5 cm depth and 0.077 to 2.8 for the 5 – 10 cm depth. Available Pb concentrations were highest in soils from lettuce plots, the top 5 cm having 0.058 to 7.9 mg kg⁻¹. The 5 – 10 cm depth had 0.15 to 2.52 mg kg⁻¹ (Fig 4.9.1a). High soil metal concentrations retrieved from the soil suggest that the metals could have residual effects on any succeeding crops.

Total soil Cd concentrations ranged between 0.36 and 14.7 mg kg⁻¹ while that of Pb was between 32.6 and 991.8 mg kg⁻¹ dry soil (Table 4.7). Available soil Cd and Pb concentrations were 0.022 – 7.49 mg Cd kg⁻¹ and 0.092 – 8.45 mg Pb kg⁻¹, respectively (Table 4.7). Although these values compare favourably with results of other studies for a few wastewater irrigation sites (Mitsios *et al.*, 2005; Ingwersen and Streck, 2005), their values were rather too high. This might be due to the low soil pH which favours uptake of heavy metals and which frequent irrigation in the high temperature environment promotes it.

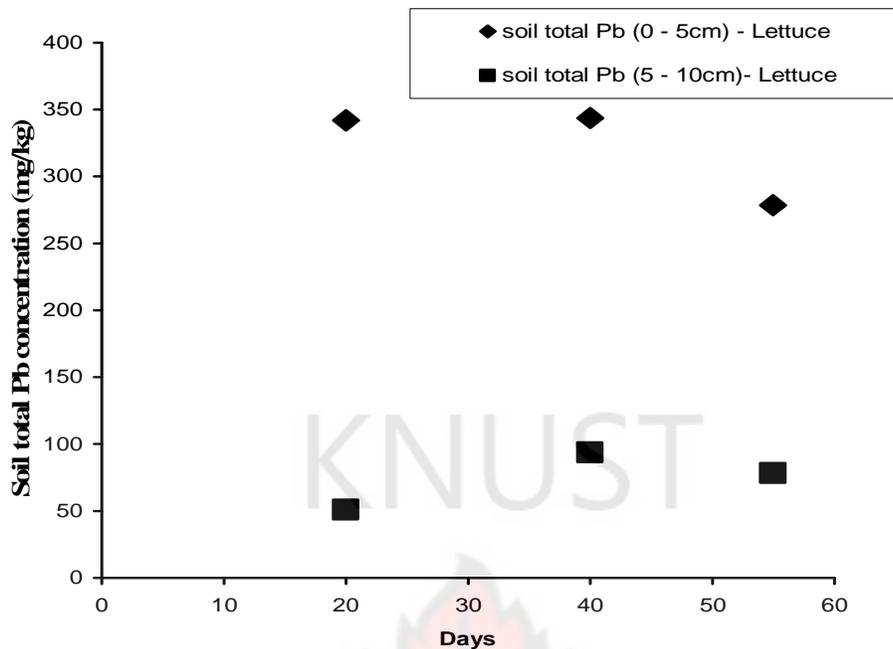


Fig 4.10a: Total soil Pb variation with time at two depths of the lettuce plots

Soil Cd and Pb concentrations decreased with depth. The total Cd values were 51.3 % at 0-5 cm depth and 24.4 % at 5-10 cm depth. The values for Pb were 7.64% at 0-5 cm and 1.73% at 5-10 cm depth. The applied and the available values of Cd of 0-5 cm were 19.5% and 8.37% respectively. At 5-10 cm depth Cd decreased by 0.12% at 0-5 cm and 0.01% at 5-10 cm for Pb. These may be ascribed to the fact that water movement may be lower with depth due to increasing clay content with depth thus causing the soil heavy metals to be concentrated at the soil surface.

The percentage of total Cd that was available was between 18.7 and 96.8 for the top 5 cm soil depth and between 8.46 and 89.6 for the 5-10 cm depth. These values were higher than those for Pb that were 0.058-7.86 and 0.077-2.78 for the 0-5 and the 5-10 cm depths, respectively. In a study carried out in Greece, the range of available soil Cd was between 0.1 and 1.37 mg/kg (Mitsios *et al.*, 2005).

4.2.1 Predicted Cd and Pb ion activities in soil

WHAM VI predicted Pb activity gave a coefficient of determination (R^2) of 0.99 when related to soil total Pb, while the predicted Cd free ion activity gave a coefficient of determination (R^2) of 0.55 when related to total soil Cd (Fig 4.9.1b).

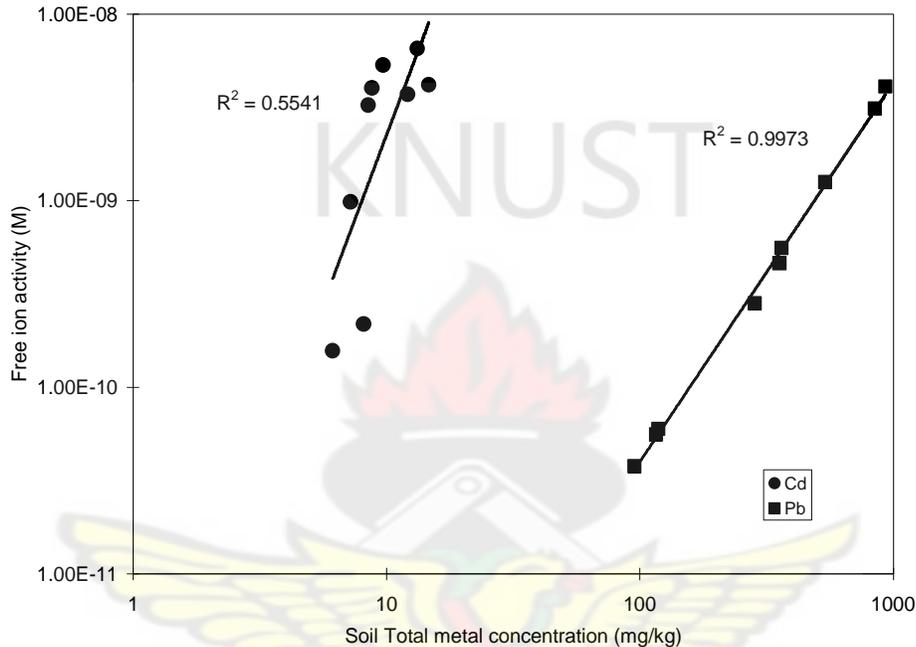


Fig 4.10b: Soil Cd and Pb free ions activities and total concentrations relationships

Lead free ion activity ranged between 5.5×10^{-10} and 4.62×10^{-9} mol/kg. This represents 4×10^{-6} % of the total Pb. Cadmium free ion activity was between 1.57×10^{-10} and 6.54×10^{-9} mol/kg. This represents 2×10^{-6} % of soil total Cd.

The trend of greater available concentration of Cd than that of Pb is reflected in the WHAM VI predicted results of ion activities where free ion activity of Cd was insignificant or negligible compared with soil total Cd and free ion activity of Pb. This may be due to the fact that Pb is more strongly sorbed to soil than Cd. Relatively high uptake of the metals by the plants from irrigation water could be as a

result of transpiration. However this could not significantly affect Cd and Pb levels ending up in the soil with part being sorbed to reduce the available metals.

Dissolved organic carbon concentration in soil solutions is usually very variable and may depend not only on the soil type (Herbert and Bertsch, 1995) and on the moisture content (Hagedorn *et al.*, 2001) (Fig. 4.5a), but also on wetting-drying cycles, microbial activity, metal loading (Merckx *et al.*, 2001), and other factors. Complexation of Cd by DOC in some systems, e.g., solution phase of leaf compost was reported to be minimal showing that in these systems Cd exists mostly in the free ionic form or as weak (labile) organic complexes (Martinez and McBride, 1999). However, the portion of complexed Cd depends on the ratio between DOC and Cd concentrations. Based on WHAM VI calculations, for the soils studied at the lowest Cd loading up to 78%, Cd was complexed by dissolved organic matter but with the increase in total Cd content in soils this fraction decreased to 1.3%. Taking DOC concentration for all the soils to be 320 mg C L^{-1} and Ca concentration to be 0.007 M (both equal to the average values for the studied data set), soil solution pH equal to soil pH, and assuming that Ca^{2+} is the main cation in soil solution and the concentrations of other cations are negligible, resulted in a $\text{RMSE}_{\log[\text{Cd}]}$ for all 4 soils of 0.56.

Plant Cd concentration was poorly related to either free ion activity or total Cd concentration of soil (Figs. 4.11a and 4.11b). The values were more scattered in the case of carrots and lettuce with cabbage showing a better linear correlation between plant Cd concentration and either free ion activity or total soil Cd (Figs. 4.11a and 4.11b).

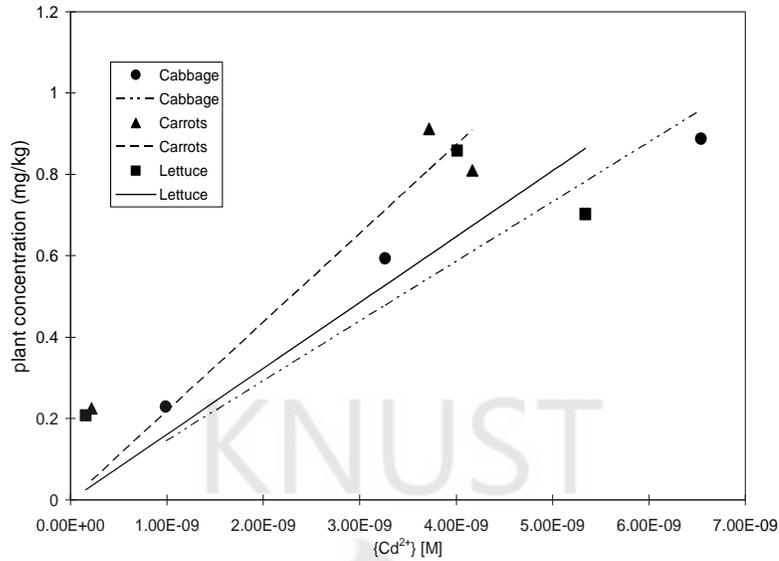


Fig 4.11a: Plant Cd concentration and Cd free ion activity relationship

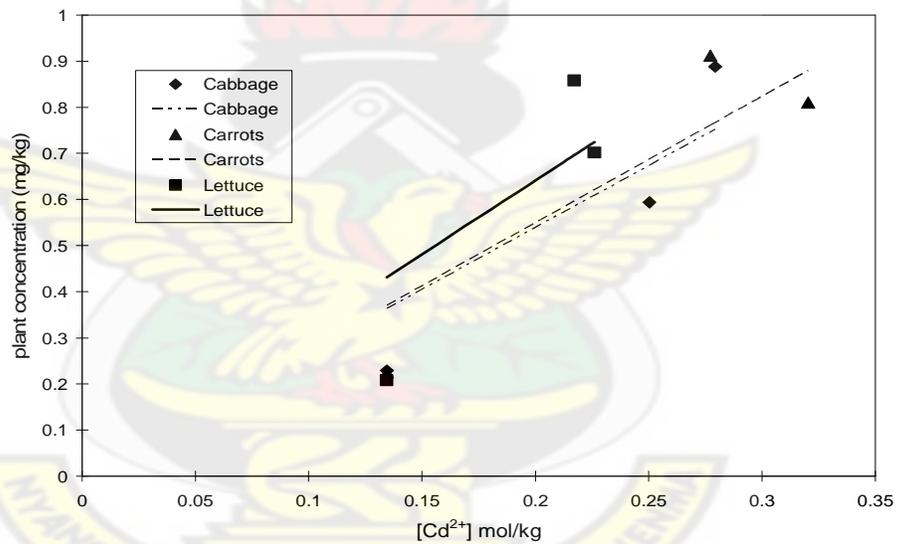


Fig.4.11b: Plant Cd concentration and total soil Cd concentration relationship

In contrast, plant Pb concentration had a better relationship with either free ion activity or total soil Pb. The trend was similar in both cases and Pb concentration in lettuce increased with free ion activity as well as total soil Pb concentration (Figs 4.12a and 4.12b).

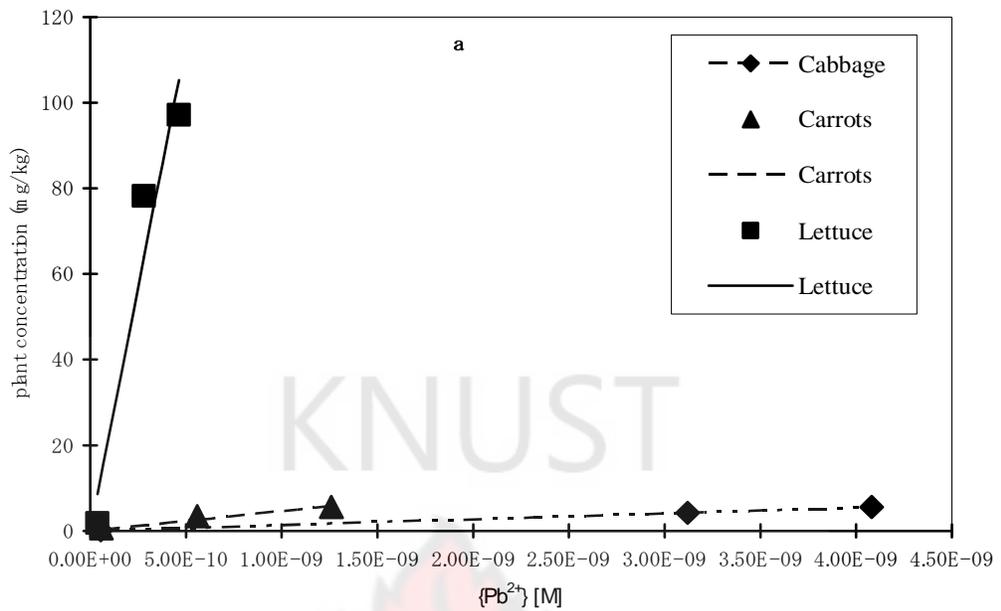


Fig. 4.12a: Plant Pb concentration and Pb free ion activity relationship

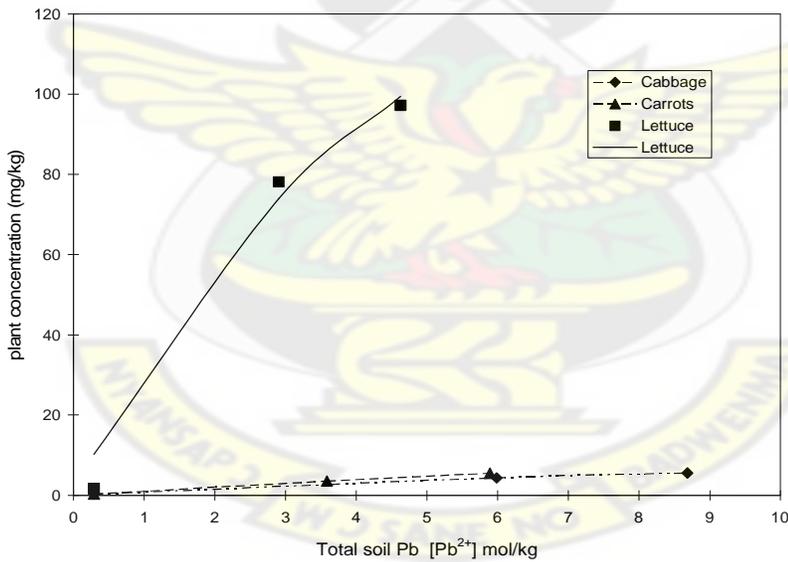


Fig. 4.12b: Plant Pb concentration and total soil Pb concentration relationship

The crop Pb concentrations showed a good relationship with both free ion activity and total soil Pb. However, the crop Cd concentrations did not show any correlation with either the free ion activity or total soil Cd except in the case of cabbage. There was a linear correlation between cabbage Cd and free ion activity

while in the case of lettuce and carrots there was greater scatter of points. This may be ascribed to cabbage having greater number of stomates to increase transpiration pull that draws free ions in soil solution.

Soil properties like pH and organic matter are influenced by frequency of irrigation at high temperature and low soil moisture availability. A higher soil pH at high temperature may lead to higher concentrations of heavy metals being maintained in the topsoil as a result of higher evaporation. The experimental soil was medium acid (pH = 5.9 – 6.0). Cadmium and Pb concentrations in the top 0 – 5 cm depth were higher than values at lower depth, which may be due to the fact that the movement of the metal to deeper depths was restricted. A higher decomposition rate of organic matter to release heavy metals to soil solutions resulting from high surface temperatures (McGrath *et al.*, 1994) could also be a possible factor.

4.3.1 Modelling of plant Cd and Pb concentrations by using transpiration rate

Modelling based on transpiration rate of modified Ingwersen and Streck (2005) equation was used to predict vegetable Cd and Pb concentrations (see equation (2), p.62 under materials and methods section).

4.3.2 Modelling efficiency (EF)

Values of modelling efficiency (EF) of cabbage, carrots and lettuce were calculated using equation (7) (Loague and Green, 1991):

$$EF = 1 - \frac{\sum_{i=1}^n (P_i - O_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (7)$$

Where:

P_i – is the predicted (calculated) plant heavy metal concentration (mg kg^{-1})

O_i – is the observed (measured) plant heavy metal concentration (mg kg^{-1}),

\bar{O} – is the mean of observed plant heavy metal concentration (mg kg^{-1}).

Modelling efficiency (EF) is a measure of the extent to which predicted values approach a corresponding set of measured observations. Modelling efficiency is thus more appropriate than regressing modelled values on observed ones because a good modelling performance requires that observed and predicted data are identical rather than simply linearly related. However, the meaning of EF is similar to that of the coefficient of determination, R^2 . The EF can be seen as the R^2 for a regression line with a slope of unity and an intercept of zero.

Relative errors were calculated without considering the different treatments. Lead treated cabbage had the highest relative error (Table 4.8). This is as a result of a wide range of difference between the measured and predicted values of the control treatment. The relative error was calculated using the equation (8) below:

$$\text{Rel Error} = \left| \frac{\text{measured} - \text{predicted}}{\text{measured}} \right| \times 100\% \quad (8)$$

Table 4.8: Model efficiency average relative error (EF) and average relative error of treatments of test crops

Element	Crop	EF Value	Av Rel. Error(%)	Av Rel. Error (treatments) %
Cd	Cabbage	0.953	7.729	3.641
	Carrots	0.911	10.272	3.295
	Lettuce	0.934	10.272	5.767
Pb	Cabbage	0.514	33.047	25.259
	Carrots	0.982	8.209	4.768
	Lettuce	0.995	0.742	4.602

The values in column 5 of Table 4.8 ranged between 32 and 56% of the values in column 4 (Table 4.8) for Cd treated vegetables. For Pb the values average relative error ranged between 58 and 62%. The values for Pb treated plots were higher than those for Cd treated. In terms of crops the values were in the following order: lettuce > cabbage > carrots. Carrot values of relative error for Cd were 32%

and that of Pb were 58% which were least for both elements. The highest values were recorded for lettuce.

Results of Pb treated samples showed that the model does not favour Pb treated cabbage as compared to carrots and lettuce because cabbage had the least model efficiency.

Table 4.9: Relationship between treatments of various crops and their respective relative errors

Element	Crop	Sample Identification	Rel. Error, %
Cd	Cabbage	CdCb ₀ (0 mg/L)	31.02
		CdCb ₁ (0.05 mg/L)	2.795
		CdCb ₂ (0.1 mg/L)	4.289
	Carrots	CdCr ₀ (0 mg/L)	79.498
		CdCr ₁ (0.05 mg/L)	10.036
		CdCr ₂ (0.1 mg/L)	5.116
	Lettuce	CdLT ₀ (0 mg/L)	86.882
		CdLT ₁ (0.05 mg/L)	15.195
		CdLT ₂ (0.1 mg/L)	3.163
Pb	Cabbage	PbCb ₀ (0 mg/L)	98.635
		PbCb ₁ (30 mg/L)	32.591
		PbCb ₂ (50 mg/L)	18.477
	Carrots	PbCr ₀ (0 mg/L)	95.247
		PbCr ₁ (30 mg/L)	8.333
		PbCr ₂ (50 mg/L)	2.164
	Lettuce	PbLT ₀ (0 mg/L)	69.853
		PbLT ₁ (30 mg/L)	0.101
		PbLT ₂ (50 mg/L)	0.306

Ninety-five percent of cadmium extracted by cabbage can be ascribed to the model. Similarly, 91 and 93% of Cd extracted by carrots and lettuce respectively can be attributed to the model. Since the relative errors for the three vegetable crops ranged between 8 and 10%, it can be said that the model has performed creditably well with respect to Cd.

Analysis with Pb using carrots and lettuce yielded similar results as Cd with the exception of cabbage that showed a remarkable variation with Pb. It was observed that the relative error was quite substantial with Pb extraction by cabbage.

In the early part of the experiment, the edible part of the cabbage had not formed. So the analysis was done on the leaves. Since the model estimation is based on the edible part, it is not surprising to notice such large disparity in the performance for Pb and cabbage relationship. It is likely that Pb behaves differently with cabbage from Cd. Such anomaly is not easily explicable as the reasons given are based on conjecture.

Table 4.9 contains the relative error of individual treatments of the experimental crops. Relative error values of all the controls of the crops were the highest, ranging between 31 and 98.6%. These high values of the controls could be attributed to the fact that the initial concentration of the metals in soil was not zero. The data also showed that apart from Pb treated lettuce, as the metal concentration increased, the predicted value approached the observed value.

The model was not tested under different soil and environmental conditions. However, since the model's performance was good under the soil and environmental conditions used, it may be possible that it would work under different soil and environmental conditions as well. Nevertheless, depending on the clay type and the level of organic matter content, the sorption of the heavy metals may show variation. This may influence the uptake of heavy metals by crops.

Since the model is not based on systems approach like Decision Support System for Agrotechnology Transfer (DSSAT) (CERES MAIZE, CERES RICE, etc.) used to estimate yield of cereals, this model is based on deterministic equation and therefore there is no need for calibration and validation.

T-test analysis was performed for the model predicted values of the test crops treated with Cd and Pb. The obtained values of t-test for the various crops of different treatments are presented in Table 4.10.

Table 4.10: T-test values of model predicted vegetable Cd and Pb concentrations

Element	Crop	t-test ($t_{\text{calculated}}$)	$t_{\text{tabulated}}$
Cd	Cabbage	1.58	12.706
	Carrots	0.829	
	Lettuce	0.565	
Pb	Cabbage	0.553	
	Carrots	1.015	
	Lettuce	4.89	

The t-test showed that there was no significant difference between the measured and predicted vegetables Cd and Pb concentrations in the vegetables as the calculated t-values were all less than the tabulated value of 12.706.

The rate of uptake of ions by crops depends on the concentration of ions in the extracellular solution as well as on the carriers and energy available for transport. In plants with a vascular system, the ions are dumped into the root xylem where they are carried along in the transpiration stream at rates that depend on that of water entry into the xylem. When water enters rapidly, ion concentration in the xylem can become quite low due to dilution effect. However, the rate of delivery of ions to the shoot is determined strictly by the rate of delivery from the roots and thus the ability of the roots to unload ions to the root xylem.

The ions are carried to the root surface by mass, bulk or convective flow, diffusion and hydrodynamic dispersion. The mass flow occurs along with water that is absorbed by roots. Diffusion occurs because absorption during periods of low transpiration lowers the concentration at the root surface and creates a concentration gradient extending from the soil to the root surfaces, and the ions diffuse down the gradient to the roots. The supply of nutrients can be calculated from the concentration in the soil solution multiplied by the flow of the solution to the root. Hydrodynamic dispersion occurs because of (i) non-uniformity of soil pores, (ii)

flow in the centre of pores being faster than the edges and (iii) tortuosity of flow path.

If the ions are absorbed at a relatively greater rate than can be provided by the bulk flow to the root, the concentration of the ions in the soil solution will decrease in the vicinity of the root. As a result, ions are released from the soil particles in an attempt to buffer the concentration. Since in this circumstance there is a lowering of ionic concentration at the root surface, ions will tend to move into the depletion zone by diffusion in addition to mass flow. On the other hand, if the ion is absorbed at a relatively slow rate compared to the bulk flow to the root, the concentration in the soil solution may build up in the vicinity of the root. Thus, depending on how rapidly transpiration occurs, there will be an accumulation of ions around the roots. When transpiration is slow, it is likely that there could be an accumulation zone in vicinity of the root zone because of back diffusion. Evidence suggests that over long times transpiration has little effect on ion uptake by roots when the external solution concentrations are low, but has a significant effect when the external concentrations are high. It is being proposed that ion uptake may tend to proceed independently of transpiration probably because ion uptake depends on energy requiring processes quite different from the physical factors driving transpiration.

In reality, when transpiration is rapid, xylem concentrations of the ions are low because the incoming water dilutes the xylem solution. In such a case, root uptake is rapid because opposing concentration gradients are small inside the root. When transpiration is slow, the ionic concentrations build up to high levels in the xylem because metabolically driven ion uptake proceeds even though water flow is slow. However, if xylem concentrations build up, root uptake can be inhibited.

In this study the model efficiency (EF) values for all the crops were high, except Pb in cabbage (Table 4.8). This suggests that the model based on transpiration with the environmental factors as the driving force is acceptable. The model outcome suggests that the external concentrations of the heavy metals were high during the experiment, since this scenario could favour uptake of ions.

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CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 SUMMARY

5.1.1 Kinetics of Cd and Pb in irrigation water

The study showed that Cd and Pb concentrations in irrigation water become reduced in soil. The level of reduction depends on the type of metal and is also influenced by soil properties such as pH, organic matter content and texture. The reduction in Cd and Pb concentrations results from adsorption or partitioning of the metals between the solid and liquid phases of the soil. While it takes about an hour for Cd to reach an equilibrium stage, Pb in solution takes a longer time ($\approx 3-4$ h) to reach equilibrium in soil.

Partition coefficient (K_d) for Cd was found to increase with its concentration in irrigation water. The study has shown that the Cd and Pb concentrations of irrigation water accessible to roots of irrigated crops are far less than initial concentrations of the irrigation water. Therefore to find a relationship between irrigation water and irrigated vegetable metal uptake, one may have to use the reduced irrigation water concentration at equilibrium in soil for Cd which takes a shorter time to equilibrate. Since Pb concentration takes a longer time to equilibrate, it may be appropriate to use the mean between the initial and the equilibrium values to establish a relationship between Pb concentration of irrigation water and its concentration in irrigated plants.

5.1.2 Cadmium release in soil solutions

Cadmium release isotherms in all the studied soils were non-linear resulting in variation in the metal distribution coefficient. Thus, the partition coefficient (K_d) approach is not applicable for the prediction of Cd concentration in soil solutions.

The use of WHAM VI provided reasonable fits of the data on Cd concentration in soil solutions of the studied soils and variation of Cd concentration with soil moisture content. Based on total Cd content, concentrations of DOC, Ca, Mg, and Na, and soil solution pH as the input variables, WHAM VI was used to predict Cd concentration in soil solutions with the Root Mean Square Error (RMSE) of the $\log[\text{Cd}]$ equal to 0.47 (n=51). Using average values of Ca and DOC concentrations for each of the soils, and soil pH at soil: water ratio of 1:1 instead of soil solution pH, enabled prediction of $\log[\text{Cd}]$ with RMSE from 0.33 to 0.66.

5.1.3 Cadmium and Pb uptake by vegetables from irrigation water

Irrigation water quality is essential to ensure good quality produce. The use of irrigation water containing high metal concentration leads to increase of plant metal concentration and as the concentration of the metal in the water increases, there is also an increase in plant concentration although not linear. The results of the study have shown that for example, a daily Cd of a composite meal of vegetables irrigated with 0.05 and 0.1 mg Cd/L concentrations of irrigation water of an adult vegetarian weighing 50 kg would constitute 9 and 9.4% respectively of the WHO recommended maximum value of 50 μg of Cd. Lead daily intake of the same person based on meals of cabbage, carrots and lettuce irrigated with 30 mg Pb/L in the irrigation water will constitute 18.8% of the WHO recommended maximum value of 180 μg while that from produce irrigated with 50 mg/L Pb in the irrigation water would be 20.8%. It is therefore safe to consume crops irrigated with Cd concentration of irrigation water up to 0.1 mg/L and Pb concentration of up to 50 mg/L. Lead content of carrots, however, exceeds the recommended daily intake from carrots of 13.8 μg by 2.14-fold and 2.4-fold for crops irrigated with 30 and 50mg/L Pb concentrations of irrigation water, respectively. It is therefore not safe to process such carrots irrigated with Pb concentration 30 mg/L and above into baby food as they are toxic to humans.

Plant Cd and Pb contents increased with time. Cadmium concentrations in lettuce, carrots and cabbage increased by 66, 42 and 118%, respectively, for a period of 20 days for lettuce and 40 days for carrots and cabbage. Lead concentrations in lettuce, carrots and cabbage increased by 130, 44 and 89%, respectively, for the same number of days as with Cd. However the amount of metal increment depends on the stage of plant maturity.

Irrigation water containing elevated metal concentration generally reduced the yield of crops. Crop yield reduction by Cd ranged between 10.2 and 16.4% while reduction by Pb was between 13.7 and 43.2%, depending on the concentration. Thus, the Cd and Pb concentrations of irrigation water negatively affect food security.

Irrigation water of high metal concentration leads to a build-up of the soil metal concentration. As the concentration of metal in the soil builds up there is a corresponding increase of metal concentration of soil solution. Therefore, the concentration in the crops will increase.

5.1.4 Measured versus predicted vegetable Cd and Pb concentrations

Predicted Cd values for the tested crops gave a high model efficiency values close to unity (0.911-0.953). This means the predicted values using the model were almost the same as the measured. For Pb, predicted cabbage Pb concentration was about half the measured value. However for carrots and lettuce the model predicted Pb concentrations were closer to unity than Cd treated samples (0.982 and 0.995 respectively).

5.2 CONCLUSIONS

From the study the following conclusions may be drawn:

1. Heavy metals in irrigation water behave differently and their sorption in soil depends on soil properties like pH, organic matter content and soil texture. Therefore, their concentrations in applied irrigation water in the soil accessible to plant roots are less than their concentrations in the irrigation water.
2. The partition coefficient approach (K_d) is not appropriate for predicting Cd concentration in soil solution, but using WHAM VI model it is possible to establish a relationship between Cd concentration and soil moisture content.
3. As the concentrations of Cd and Pb in irrigation water increase, their concentrations in vegetables also cumulatively increase with time but the relationship is not linear based on the concentration of Cd and Pb used. Only the concentration of Pb in carrots exceeds WHO recommendation for safe food accumulations, implying carrot has affinity for lead accumulation.
4. It is possible to predict the uptake of Cd and Pb in vegetable crops using the concept of transpiration pool in reference with environmental factors that serve as driving force for the process of transpiration.

5.3 RECOMMENDATIONS

For this study to have positive impact on the safety of wastewater irrigated vegetables (cabbage, carrots, lettuce and other exotic ones) in Ghana the following recommendations are made:

1. An inventory of all wastewater producing sites of farmers, inputs, crops produced, land size and tenure system and sources of irrigated water has to be taken and documented.

2. A study should be carried out to generate data on the volumes of wastewater contributed by the industrial, domestic and stormwater sources from major garages and waste dump sites to urban water bodies being used for vegetable irrigation.
3. There is the need to repeat the study on heavy metal contaminated soil where the vegetables will be irrigated with polluted water so that soil heavy metal contribution to plant metal uptake apart from contribution from irrigation water may be determined.
4. There is a need to replicate field experiments in different ecological zones where activities carried out generate effluents with heavy metals as pollutants. This will help to determine the effects of climatic factors on heavy metals uptake by vegetables and the percentage contribution of transpiration and irrigation water concentrations to heavy metal content of vegetables.
5. Research should be carried out to develop cost-effective and low level technology for small-scale treatment of effluents to reduce metal concentrations to safe levels for vegetable irrigation.
6. There should be periodic measurement of heavy metal content of vegetables sold in the markets in the urban and the peri-urban centres.
7. A policy enforcement if it exists or formulation of one where none exists to ensure that industries whose activities produce effluents containing heavy metals initiate treatment of the effluents to reduce metal concentrations before releasing such effluents into the environment.

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APPENDICES

Appendix 1: Some selected properties of experimental soil

Table 1: Selected soil properties

Sample No	pH	Organic C, %	OM, %	% SAND	%CLAY	% SILT
1	6.5	0.76	1.31	90.4	5.6	4.0
2	6.13	0.59	1.02	90.4	2.0	7.6
3	6.39	0.79	1.36	96.4	2.0	1.6
4	6.02	0.92	1.59	90.4	2.0	7.6
5	5.8	0.89	1.53	90.4	5.6	4.0
6	5.7	1.26	2.17	96.4	2.0	1.6

Table 2: Data generated from infiltration test

Time, min	Depth of water infiltrated, mm	
	Replicate 1	Replicate 2
2	100	100
4	158	160
6	209	250
8	265	323
10	317	385
12	361	446
14	409	506
16	457	571
18	507	624
20	556	689
22	602	748
24	647	799
26	691	859
28	733	909
30	775	974
32	818	1019
34	859	1066
36	899	1120
38	938	
40	977	1226
42	1015	1284
44	1051	1330
46	1084	1385
48	1121	1427
50	1153	
52	1186	1523
54	1216	1576
56	1247	1621
58	1279	1673
60	1309	1733
62	1338	1823
64	1366	1853

68	1426	1896
72	1484	1949
76	1539	2003
80	1592	2048
84	1642	2096
88	1690	2143
92	1735	2188
96	1778	2231
100	1820	2275
104	1860	2319
108	1899	2361
112	1937	2401
116	1975	2442
120	2013	2472

The average terminal infiltration rate is $(570.0 + 547.5)/(2\text{mm/h}) = 558.75\text{mm/hr}$.



Appendix 2: Summary of statistical analysis using MINITAB software package.

CABBAGE Cd CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

$$\text{Measured Cp} = 0.120 + 0.915 \text{ Predicted Cp}$$

Predictor	Coef	SE Coef	T	P
Constant	0.11953	0.04242	2.82	0.217
Predicted	0.91510	0.05377	17.02	0.037

S = 0.03231 R-Sq = 99.7% R-Sq(adj) = 99.3%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.30242	0.30242	289.67	0.037
Residual Error	1	0.00104	0.00104		
Total	2	0.30346			

The regression equation is:

$$C_{pm} = 0.120 + 0.915 C_{pp}$$

where

C_{pm}	measured plant Cd concentration (mg/kg)
C_{pp}	predicted plant Cd concentration (mg/kg)
T_{calc}	calculated T value
T_{tab}	tabulated T value from student's t distribution table
P	probability
S	standard error of the predicted draught force
R-Sq	coefficient of determination
R-Sq(adj)	adjusted value of coefficient of determination
Coef	constant terms in regression equation
SE Coef	standard error

The regression equation relating measured plant Cd concentration (mg/kg) and predicted plant Cd concentration (mg/kg) is a straight line. In order to investigate if the measured plant Cd concentration is significantly different from the predicted plant Cd concentration, it is necessary to assume initially that there is no difference between the two variables. Thus the coefficient of the predicted plant Cd concentration is assumed to be equal to 1.

Let

H_0	null hypothesis
H_1	alternative hypothesis
β	coefficient (0.915) of the predicted plant Cd concentration
s_β	standard error of the β

Hypotheses:

H_0 : $\beta = 1$ The coefficient of the predicted plant Cd concentration is equal to 1

H_1 : $\beta \neq 1$ The coefficient of the predicted plant Cd concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_{\beta}}$$

$$t_{calc} = \frac{0.915 - 1}{0.05377}$$

$$t_{calc} = -1.58$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = -1.58$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|1.58| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Cd concentration and the predicted plant Cd concentration.

In order to investigate if the intercept of the regression equation (0.120) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (0.120) of the plant Cd concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

coefficient (0.120) of the predicted plant Cd concentration

standard error of the α

Hypotheses:

H_0 : $\alpha = 0$ The coefficient of the predicted plant Cd concentration is equal to 0

H_1 : $\alpha \neq 0$ The coefficient of the predicted plant Cd concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\alpha - 0}{s_{\alpha}}$$

$$t_{calc} = \frac{0.120 - 0}{0.04242}$$

$$t_{\text{calc}} = 2.83$$

Rejection Criteria:

Reject H_0 if $|t_{\text{calc}}| > t_{\text{tab}}$

Fail to reject H_0 if $|t_{\text{calc}}| \leq t_{\text{tab}}$

The Test

From the calculation $t_{\text{calc}} = 2.83$ and from t-distribution tables, $t_{\text{tab}} = 12.706$

i.e. $|t_{\text{calc}}| < t_{\text{tab}}$ or $|2.83| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the intercept of the regression equation (0.120) relating measured and predicted plant Cd concentration and 0. This means that the regression line passes through the origin.

CARROT Cd CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

$$\text{Measured Cp} = 0.144 + 0.872 \text{ Predicted Cp}$$

Predictor	Coef	SE Coef	T	P
Constant	0.1436	0.1096	1.31	0.415
Predicted	0.8717	0.1544	5.64	0.112
S = 0.1050		R-Sq = 97.0%		R-Sq(adj) = 93.9%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.35130	0.35130	31.86	0.112
Residual Error	1	0.01103	0.01103		
Total	2	0.36233			

The regression equation is:

$$C_{\text{pm}} = 0.144 + 0.872 C_{\text{pp}}$$

where

C_{pm}	measured plant Cd concentration (mg/kg)
C_{pp}	predicted plant Cd concentration (mg/kg)
T_{calc}	calculated T value
T_{tab}	tabulated T value from student's t distribution table
P	probability
S	standard error of the predicted draught force
R-Sq	coefficient of determination
R-Sq(adj)	adjusted value of coefficient of determination
Coef	constant terms in regression equation
SE Coef	standard error

The regression equation relating measured plant Cd concentration (mg/kg) and predicted plant Cd concentration (mg/kg) is a straight line. In order to investigate if the measured plant Cd concentration is significantly different from the predicted plant Cd concentration, it is necessary to assume initially that there is no difference

between the two variables. Thus the coefficient of the predicted plant Cd concentration is assumed to be equal to 1.

Let

H_0 null hypothesis

H_1 alternative hypothesis

β coefficient (0.872) of the predicted plant Cd concentration

s_β standard error of the β

Hypotheses:

$H_0: \beta = 1$ The coefficient of the predicted plant Cd concentration is equal to 1

$H_1: \beta \neq 1$ The coefficient of the predicted plant Cd concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_\beta}$$

$$t_{calc} = \frac{0.872 - 1}{0.1544}$$

$$t_{calc} = -0.829$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = -0.829$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|0.829| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Cd concentration and the predicted plant Cd concentration.

In order to investigate if the intercept of the regression equation (0.144) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (0.144) of the plant Cd concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

α coefficient (0.144) of the predicted plant Cd concentration

s_α standard error of the α

Hypotheses:

H₀: $\alpha = 0$ The coefficient of the predicted plant Cd concentration is equal to 0

H₁: $\alpha \neq 0$ The coefficient of the predicted plant Cd concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\alpha - 0}{s_{\alpha}}$$

$$t_{calc} = \frac{0.144 - 0}{0.1096}$$

$$t_{calc} = 1.314$$

Rejection Criteria:

Reject H₀ if $|t_{calc}| > t_{tab}$

Fail to reject H₀ if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = 1.314$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|1.314| < 12.706$

Therefore, do not reject H₀

Conclusion

There is no significant difference between the intercept of the regression equation (0.144) relating measured and predicted plant Cd concentration and 0. This means that the regression line passes through the origin.

LETTUCE Cd CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

$$\text{Measured Cp} = 0.127 + 0.915 \text{ Predicted Cp}$$

Predictor	Coef	SE Coef	T	P
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Constant	0.1267	0.1157	1.09	0.471
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Predicted	0.9153	0.1500	6.10	0.103
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S = 0.1156 R-Sq = 97.4% R-Sq(adj) = 94.8%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.49735	0.49735	37.24	0.103
Residual Error	1	0.01336	0.01336		
Total	2	0.51071			

The regression equation is:

$$C_{pm} = 0.127 + 0.915 C_{pp}$$

where

C_{pm} measured plant Cd concentration (mg/kg)

C_{pp} predicted plant Cd concentration (mg/kg)

T_{calc} calculated T value

T_{tab} tabulated T value from student's t distribution table

P	probability
S	standard error of the predicted draught force
R-Sq	coefficient of determination
R-Sq(adj)	adjusted value of coefficient of determination
Coef	constant terms in regression equation
SE Coef	standard error

The regression equation relating measured plant Cd concentration (mg/kg) and predicted plant Cd concentration (mg/kg) is a straight line. In order to investigate if the measured plant Cd concentration is significantly different from the predicted plant Cd concentration, it is necessary to assume initially that there is no difference between the two variables. Thus the coefficient of the predicted plant Cd concentration is assumed to be equal to 1.

Let

H_0	null hypothesis
H_1	alternative hypothesis
β	coefficient (0.915) of the predicted plant Cd concentration
s_β	standard error of the β

Hypotheses:

H_0 :	$\beta = 1$	The coefficient of the predicted plant Cd concentration is equal to 1
H_1 :	$\beta \neq 1$	The coefficient of the predicted plant Cd concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_\beta}$$

$$t_{calc} = \frac{0.9153 - 1}{0.15}$$

$$t_{calc} = -0.5647$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = -0.5647$ and from t-distribution tables, $t_{tab} = 12.706$
 i.e. $|t_{calc}| < t_{tab}$ or $|0.5647| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Cd concentration and the predicted plant Cd concentration.

In order to investigate if the intercept of the regression equation (0.120) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (0.120) of the plant Cd concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

α coefficient (0.120) of the predicted plant Cd concentration

s_α standard error of the α

Hypotheses:

$H_0: \alpha = 0$ The coefficient of the predicted plant Cd concentration is equal to 0

$H_1: \alpha \neq 0$ The coefficient of the predicted plant Cd concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\alpha - 0}{s_\alpha}$$

$$t_{calc} = \frac{0.1267 - 0}{0.1157}$$

$$t_{calc} = 1.095$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = 1.095$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|1.095| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the intercept of the regression equation (0.127) relating measured and predicted plant Cd concentration and 0. This means that the regression line passes through the origin.

CABBAGE Pb CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

$$\text{Measured Cp} = 0.228 + 0.992 \text{ Predicted Cp}$$

Predictor	Coef	SE Coef	T	P
Constant	0.22765	0.07799	2.92	0.210
Predicted	0.9923	0.1393	7.12	0.089
S = 0.07901		R-Sq = 98.1%		R-Sq(adj) = 96.1%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.31691	0.31691	50.76	0.089
Residual Error	1	0.00624	0.00624		
Total	2	0.32315			

The regression equation is:

$$C_{pm} = 0.228 + 0.992C_{pp}$$

where

C_{pm}	measured plant Pb concentration (mg/kg)
C_{pp}	predicted plant Pb concentration (mg/kg)
T_{calc}	calculated T value
T_{tab}	tabulated T value from student's t distribution table
P	probability
S	standard error of the predicted draught force
R-Sq	coefficient of determination
R-Sq(adj)	adjusted value of coefficient of determination
Coef	constant terms in regression equation
SE Coef	standard error

The regression equation relating measured plant Pb concentration (mg/kg) and predicted plant Pb concentration (mg/kg) is a straight line. In order to investigate if the measured plant Pb concentration is significantly different from the predicted plant Pb concentration, it is necessary to assume initially that there is no difference between the two variables. Thus the coefficient of the predicted plant Pb concentration is assumed to be equal to 1.

Let

H_0	null hypothesis
H_1	alternative hypothesis
β	coefficient (0.915) of the predicted plant Pb concentration
s_β	standard error of the β

Hypotheses:

$H_0:$	$\beta = 1$	The coefficient of the predicted plant Pb concentration is equal to 1
$H_1:$	$\beta \neq 1$	The coefficient of the predicted plant Pb concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_\beta}$$

$$t_{calc} = \frac{0.9923 - 1}{0.1393}$$

$$t_{calc} = -0.0553$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{\text{calc}} = -0.158$ and from t-distribution tables, $t_{\text{tab}} = 12.706$

i.e. $|t_{\text{calc}}| < t_{\text{tab}}$ or $|0.0553| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Pb concentration and the predicted plant Pb concentration.

In order to investigate if the intercept of the regression equation (0.228) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (0.120) of the plant Pb concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

α coefficient (0.120) of the predicted plant Pb concentration

s_α standard error of the α

Hypotheses:

$H_0: \alpha = 0$ The coefficient of the predicted plant Pb concentration is equal to 0

$H_1: \alpha \neq 0$ The coefficient of the predicted plant Pb concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{\text{calc}} = \frac{\alpha - 0}{s_\alpha}$$

$$t_{\text{calc}} = \frac{0.22765 - 0}{0.07799}$$

$$t_{\text{calc}} = 2.919$$

Rejection Criteria:

Reject H_0 if $|t_{\text{calc}}| > t_{\text{tab}}$

Fail to reject H_0 if $|t_{\text{calc}}| \leq t_{\text{tab}}$

The Test

From the calculation $t_{\text{calc}} = 2.919$ and from t-distribution tables, $t_{\text{tab}} = 12.706$

i.e. $|t_{\text{calc}}| < t_{\text{tab}}$ or $|2.919| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the intercept of the regression equation (0.228) relating measured and predicted plant Pb concentration and 0. This means that the regression line passes through the origin.

CARROT Pb CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

$$\text{Measured Cp} = 0.642 + 1.13 \text{ Predicted Cp}$$

Predictor	Coef	SE Coef	T	P
Constant	0.6425	0.6330	1.02	0.495
Predicted	1.1338	0.1830	6.19	0.102

S = 0.6736 R-Sq = 97.5% R-Sq(adj) = 94.9%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	17.412	17.412	38.37	0.102
Residual Error	1	0.454	0.454		
Total	2	17.866			

The regression equation is:

$$C_{pm} = 0.642 + 1.1338C_{pp}$$

where

C_{pm}	measured plant Pb concentration (mg/kg)
C_{pp}	predicted plant Pb concentration (mg/kg)
T_{calc}	calculated T value
T_{tab}	tabulated T value from student's t distribution table
P	probability
S	standard error of the predicted draught force
R-Sq	coefficient of determination
R-Sq(adj)	adjusted value of coefficient of determination
Coef	constant terms in regression equation
SE Coef	standard error

The regression equation relating measured plant Pb concentration (mg/kg) and predicted plant Pb concentration (mg/kg) is a straight line. In order to investigate if the measured plant Pb concentration is significantly different from the predicted plant Pb concentration, it is necessary to assume initially that there is no difference between the two variables. Thus the coefficient of the predicted plant Pb concentration is assumed to be equal to 1.

Let

H_0	null hypothesis
H_1	alternative hypothesis
β	coefficient (0.915) of the predicted plant Pb concentration
s_β	standard error of the β

Hypotheses:

H_0 :	$\beta = 1$	The coefficient of the predicted plant Pb concentration is equal to 1
H_1 :	$\beta \neq 1$	The coefficient of the predicted plant Pb concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_{\beta}}$$

$$t_{calc} = \frac{1.1338 - 1}{0.1830}$$

$$t_{calc} = 0.731$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = 0.731$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|0.731| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Pb concentration and the predicted plant Pb concentration.

In order to investigate if the intercept of the regression equation (0.642) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (0.642) of the plant Pb concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

\square coefficient (0.120) of the predicted plant Pb concentration

s_{\square} standard error of the α

Hypotheses:

H_0 : $\alpha = 0$ The coefficient of the predicted plant Pb concentration is equal to 0

H_1 : $\alpha \neq 0$ The coefficient of the predicted plant Pb concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\alpha - 0}{s_{\alpha}}$$

$$t_{calc} = \frac{0.6425 - 0}{0.6330}$$

$$t_{calc} = 1.015$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = 1.015$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|1.015| < 12.706$

Therefore, do not reject H_0

Conclusions

There is no significant difference between the intercept of the regression equation (0.642) relating measured and predicted plant Pb concentration and 0. This means that the regression line passes through the origin.

LETTUCE Pb CONCENTRATION

Regression Analysis: Measured Cp versus Predicted Cp

The regression equation is

Measured Cp = 2.14 + 0.993 Predicted Cp

Predictor	Coef	SE Coef	T	P
Constant	2.1367	0.4760	4.49	0.140
Predicted	0.993341	0.006791	146.28	0.004

S = 0.4800 R-Sq = 100.0% R-Sq(adj) = 100.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	4929.3	4929.3	21398.33	0.004
Residual Error	1	0.2	0.2		
Total	2	4929.5			

The regression equation is:

$C_{pm} = 2.1367 + 0.99334C_{pp}$

where

C_{pm} measured plant Pb concentration (mg/kg)

C_{pp} predicted plant Pb concentration (mg/kg)

T_{calc} calculated T value

T_{tab} tabulated T value from student's t distribution table

P probability

S standard error of the predicted draught force

R-Sq coefficient of determination

R-Sq(adj) adjusted value of coefficient of determination

Coef constant terms in regression equation

SE Coef standard error

The regression equation relating measured plant Pb concentration (mg/kg) and predicted plant Pb concentration (mg/kg) is a straight line. In order to investigate if the measured plant Pb concentration is significantly different from the predicted

plant Pb concentration, it is necessary to assume initially that there is no difference between the two variables. Thus the coefficient of the predicted plant Pb concentration is assumed to be equal to 1.

Let

H_0 null hypothesis

H_1 alternative hypothesis

β coefficient (0.915) of the predicted plant Pb concentration

s_β standard error of the β

Hypotheses:

$H_0: \beta = 1$ The coefficient of the predicted plant Pb concentration is equal to 1

$H_1: \beta \neq 1$ The coefficient of the predicted plant Pb concentration is equal not to 1

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\beta - 1}{s_\beta}$$

$$t_{calc} = \frac{0.99334 - 1}{0.006791}$$

$$t_{calc} = -0.9810553$$

Rejection Criteria:

Reject H_0 if $|t_{calc}| > t_{tab}$

Fail to reject H_0 if $|t_{calc}| \leq t_{tab}$

The Test

From the calculation $t_{calc} = -0.981$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|0.981| < 12.706$

Therefore, do not reject H_0

Conclusion

There is no significant difference between the measured plant Pb concentration and the predicted plant Pb concentration.

In order to investigate if the intercept of the regression equation (2.1367) is significantly different from 0 (i.e. if the regression line passes through the origin) it is necessary to assume initially that there is no difference between the intercept (2.1367) of the plant Pb concentration regression equation and the origin. Thus the intercept can be assumed to be 0.

Let

H_0 null hypothesis

H_1 alternative hypothesis

α coefficient (2.1367) of the predicted plant Pb concentration

s_α standard error of the α

Hypotheses:

H₀: $\alpha = 0$ The coefficient of the predicted plant Pb concentration is equal to 0

H₁: $\alpha \neq 0$ The coefficient of the predicted plant Pb concentration is not equal 0

Test Statistic (Student's t-test):

$$t_{calc} = \frac{\alpha - 0}{s_{\alpha}}$$

$$t_{calc} = \frac{2.1367 - 0}{0.4760}$$

$$t_{calc} = 4.89$$

Rejection Criteria:

Reject H₀ if $|t_{calc}| > t_{tab}$

Fail to reject H₀ if $|t_{calc}| \leq t_{tab}$

The Test

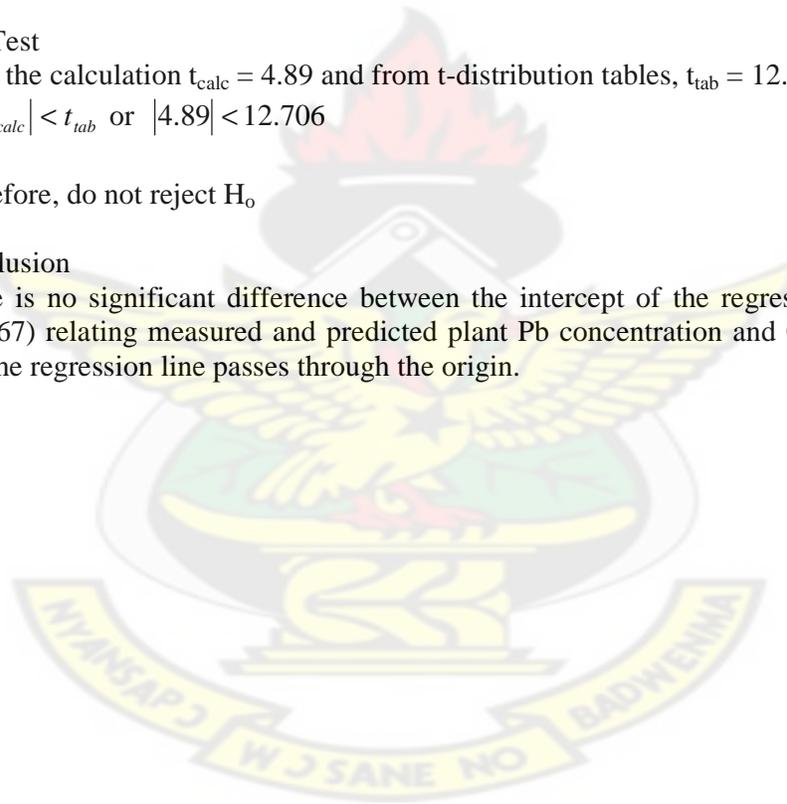
From the calculation $t_{calc} = 4.89$ and from t-distribution tables, $t_{tab} = 12.706$

i.e. $|t_{calc}| < t_{tab}$ or $|4.89| < 12.706$

Therefore, do not reject H₀

Conclusion

There is no significant difference between the intercept of the regression equation (2.1367) relating measured and predicted plant Pb concentration and 0. This means that the regression line passes through the origin.



Appendix 3: Statistical analysis of plant samples data using SAS statistical software package.

Two metals (cadmium (Cd) and lead (Pb)), and three plant species (cabbage, carrot, and lettuce), were investigated to find the metal uptake by plants. There are three treatments: metal concentration 1, metal concentration 2, and control (water). The samples were collected at three different times.

For different metal, the ability of plant uptake is different. So a linear model is built for each of metal

$$Y = \alpha + a_1x_1 + a_2x_2 + a_3x_3 + \sigma$$

where, Y is the metal concentration in plant, α is the intercept, X_1 is the effect of plant, X_2 is the effect of time, X_3 is the effect of metal is the error, with normal concentration in the irrigation water, and σ distribution $N(0, \sigma^2)$.

For metal cadmium (Cd):

The results show that only the effect of metal concentration in water is significant at $\alpha=0.05$ level ($p\text{-value} < 0.0001 < 0.05$).

The results from GLM (general linear model) procedure in SAS

Source	DF	Squares	Mean square	F Value	Pr > F
Model	6	2.16	0.36	9.69	< .0001
Error	20	0.74	0.04		
Corrected	26	2.9			
Total					

R-Square	Coeff Var	Root MSE	Plant Mean
0.74	31.96	0.19	0.60

Summary of statistics for Cd treatment

Source	DF	Type III	Mean square	F Value	Pr > F
Plant	2	0.03	0.015	0.41	0.67
Time	2	0.16	0.078	2.11	0.15
Metal water	2	1.97	0.99	26.56	< 0.0001

For lead (Pb):

The results show that only the effect of plant in $\alpha=0.05$ level ($p\text{-value} = 0.0137 < 0.05$) water is significant at < 0.05).

The results from GLM (general linear model) procedure in SAS

Source	DF	Squares	Mean square	F Value	Pr > F
Model	6	60463.5	10077.3	2.96	0.031
Error	20	68024.3	3401.2		
Corrected Total	26	128487.8			

R-Square	Coeff Var	Root MSE	Plant Mean
0.47	199.125	58.32	29.29

Table 6: Summary of statistics for Pb treatment

Source	DF	Type ISS	Mean square	F Value	Pr > F
Plant	2	36476.60	18238.30	5.36	0.014
Time	2	12848.51	6424.26	1.89	0.18
Metal water	2	11138.39	5569.20	1.64	0.22

From the above results, the effect of plant and metal concentration are not the same for two metals.

Table 7: Application rates of Cd and Pb through irrigation water

Crop	Days	Irrigation Water			
		Cd		Pb	
		0.05 mg/L	0.1 mg/L	30 mg/L	50 mg/L
Application Rates (mg/kg)					
Lettuce	20	3.3	6.6	1964	3274
	40	5.9	11.8	3536	5893
	55	7.5	15.1	4518	7530
Cabbage	40	5.8	11.8	3536	5893
	70	8.8	17.7	5304	8839
	100	10.8	21.6	6482	10827
Carrots	40	6.2	12.4	3732	6220
	70	8.2	16.4	4911	8185
	100	9.5	19.0	5696	9494

Appendix 4: Regression analysis of model data or results

Regression

Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	CBAVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: CBCP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.990 ^a	.981	.962	*****

^a. Predictors: (Constant), CBAVCP

^b. Dependent Variable: CBCP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.414	1	.414	51.750	.088 ^a
	Residual	.008	1	.008		
	Total	.422	2			

^a. Predictors: (Constant), CBAVCP

^b. Dependent Variable: CBCP

Coefficients^a

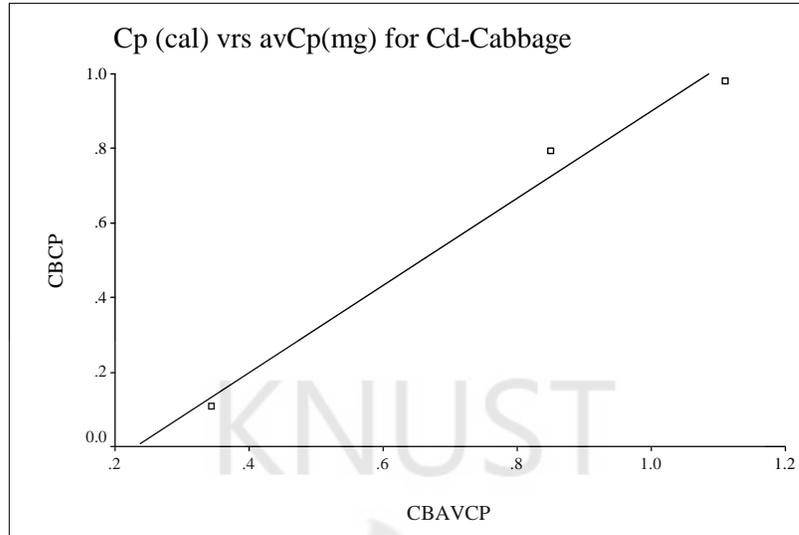
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-.270	.135		-1.997	.296
	CBAVCP	1.169	.162	.990	7.194	.088

^a. Dependent Variable: CBCP

Residuals Statistics^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.088	.878	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.530	.803	.000	.707	3
Stud. Residual	-1.000	1.000	-.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.044	1.185	.667	.577	3
Cook's Distance	.276	6.234	2.596	3.190	3
Centered Leverage Value	.022	.592	.333	.289	3

^a. Dependent Variable: CBCP



Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	CAAVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: CACP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.941 ^a	.885	.770	*****

^a. Predictors: (Constant), CAAVCP

^b. Dependent Variable: CACP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.340	1	.340	7.714	.220 ^a
	Residual	.044	1	.044		
	Total	.384	2			

^a. Predictors: (Constant), CAAVCP

^b. Dependent Variable: CACP

Coefficients ^a

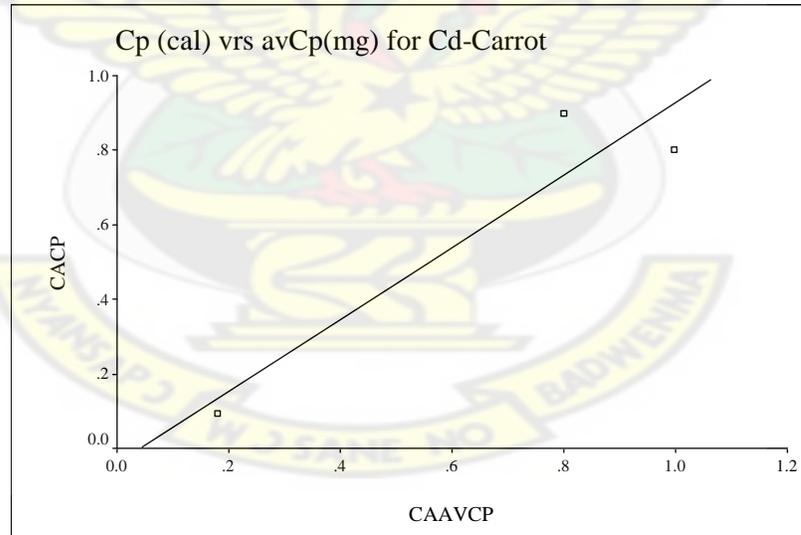
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-4.093E-02	.260		-.158	.901
	CAAVCP	.968	.349	.941	2.777	.220

^a. Dependent Variable: CACP

Residuals Statistics ^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.123	.794	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.593	.783	.000	.707	3
Stud. Residual	-1.000	1.000	-.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.108	1.261	.667	.577	3
Cook's Distance	.316	13.363	4.867	7.364	3
Centered Leverage Value	.054	.631	.333	.289	3

^a. Dependent Variable: CACP



Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	LEAVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: LECP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.976 ^a	.953	.907	*****

^a. Predictors: (Constant), LEAVCP

^b. Dependent Variable: LECP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.408	1	.408	20.492	.138 ^a
	Residual	.020	1	.020		
	Total	.428	2			

^a. Predictors: (Constant), LEAVCP

^b. Dependent Variable: LECP

Coefficients^a

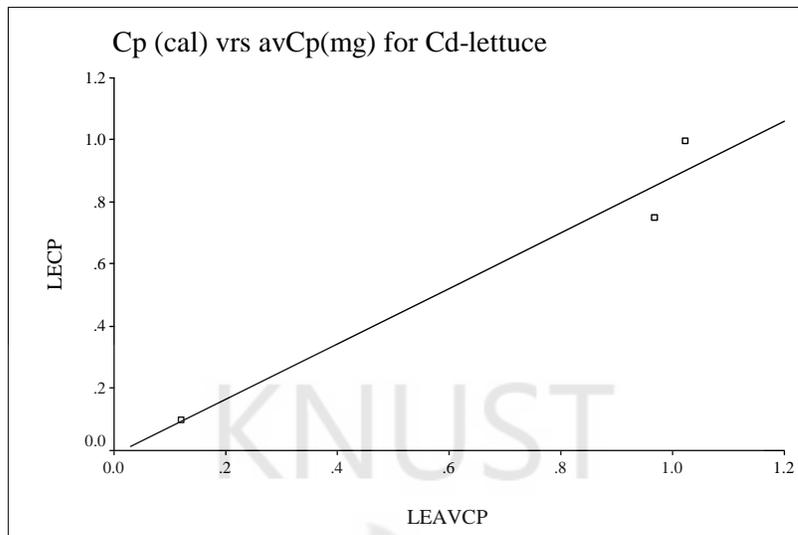
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-1.412E-02	.161		-.088	.944
	LEAVCP	.894	.198	.976	4.527	.138

^a. Dependent Variable: LECP

Residuals Statistics^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.153	.630	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.728	.684	.000	.707	3
Stud. Residual	-1.000	1.000	.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.274	1.330	.667	.577	3
Cook's Distance	.444	262.210	87.741	151.095	3
Centered Leverage Value	.137	.665	.333	.289	3

^a. Dependent Variable: LECP



Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	PBCBVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: PBCBCP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.980 ^a	.960	.919	*****

^a. Predictors: (Constant), PBCBVCP

^b. Dependent Variable: PBCBCP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.192	1	.192	23.832	.129 ^a
	Residual	.008	1	.008		
	Total	.200	2			

^a. Predictors: (Constant), PBCBVCP

^b. Dependent Variable: PBCBCP

Coefficients ^a

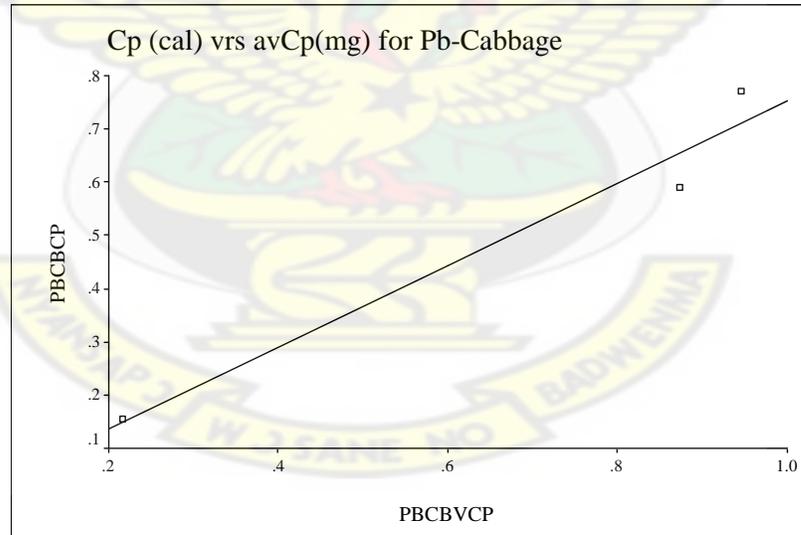
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-1.834E-02	.119		-.154	.903
	PBCBVCP	.771	.158	.980	4.882	.129

^a. Dependent Variable: PBCBCP

Residuals Statistics ^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.150	.663	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.740	.668	.000	.707	3
Stud. Residual	-1.000	1.000	.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.237	1.323	.667	.577	3
Cook's Distance	.412	95.656	32.229	54.929	3
Centered Leverage Value	.118	.661	.333	.289	3

^a. Dependent Variable: PBCBCP



Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	PBCAVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: PBCACP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.984 ^a	.967	.935	*****

^a. Predictors: (Constant), PBCAVCP

^b. Dependent Variable: PBCACP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	11.995	1	11.995	29.561	.116 ^a
	Residual	.406	1	.406		
	Total	12.400	2			

^a. Predictors: (Constant), PBCAVCP

^b. Dependent Variable: PBCACP

Coefficients^a

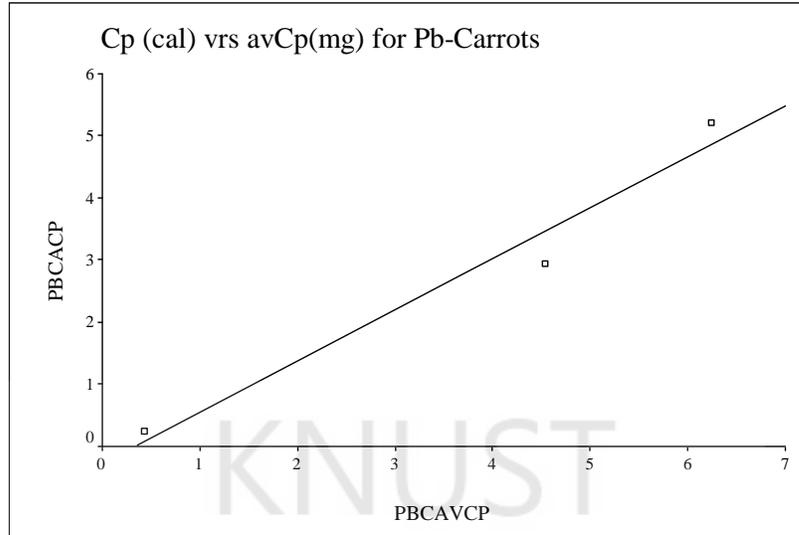
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-.260	.672		-.387	.765
	PBCAVCP	.819	.151	.984	5.437	.116

^a. Dependent Variable: PBCACP

Residuals Statistics^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.107	.838	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.794	.562	.000	.707	3
Stud. Residual	-1.000	1.000	.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.072	1.225	.667	.577	3
Cook's Distance	.293	8.773	3.383	4.684	3
Centered Leverage Value	.036	.613	.333	.289	3

^a. Dependent Variable: PBCACP



Warnings

The chart: *sdresid by *zpred is not produced because it is empty.

Variables Entered/Removed^b

Model	Variables Entered	Variables Removed	Method
1	PBLEAVCP ^a	.	Enter

^a. All requested variables entered.

^b. Dependent Variable: PBLECP

Model Summary^b

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.994 ^a	.988	.976	*****

^a. Predictors: (Constant), PBLEAVCP

^b. Dependent Variable: PBLECP

ANOVA^b

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	15723.975	1	15723.975	83.746	.069 ^a
	Residual	187.759	1	187.759		
	Total	15911.734	2			

^a. Predictors: (Constant), PBLEAVCP

^b. Dependent Variable: PBLECP

Coefficients^a

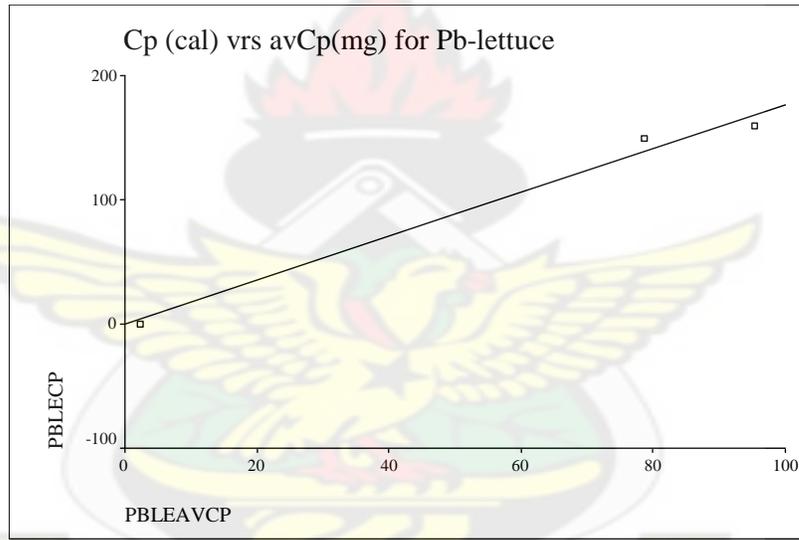
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-1.777	13.930		-.128	.919
	PBLEAVCP	1.786	.195	.994	9.151	.069

^a. Dependent Variable: PBLECP

Residuals Statistics ^a

	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	*****	*****	*****	*****	3
Std. Predicted Value	-1.138	.738	.000	1.000	3
Standard Error of Predicted Value	*****	*****	*****	*****	3
Adjusted Predicted Value	*****	*****	*****	*****	3
Residual	*****	*****	*****	*****	3
Std. Residual	-.628	.766	.000	.707	3
Stud. Residual	-1.000	1.000	-.333	1.155	3
Deleted Residual	*****	*****	*****	*****	3
Stud. Deleted Residual	0
Mahal. Distance	.160	1.295	.667	.577	3
Cook's Distance	.352	25.698	8.940	14.515	3
Centered Leverage Value	.080	.648	.333	.289	3

a. Dependent Variable: PBLECP



Appendix 5: Anova analysis of model data using Genstat

Genstat 5 Release 3.2 (PC/Windows NT) 7 September 2006 17:10:27
 Copyright 1995, Lawes Agricultural Trust (Rothamsted Experimental Station)

Genstat 5 Second Edition (for Windows)
 Genstat 5 Procedure Library Release 3[3] (PL9)

Identifier	Minimum	Mean	Maximum	Values	Missing
reps	1.000	2.000	3.000	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
fact_A_	1.000	2.000	3.000	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Fact_B_	1.000	2.000	3.000	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Cd_Cabba	0.0165	0.5702	1.9250	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Cd_carro	0.0066	0.6490	1.3508	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Cd_Lettu	0.0132	0.5892	2.1956	27	0
Identifier	Values	Missing	Levels		
reps	27	0	3		
Identifier	Values	Missing	Levels		
fact_A_	27	0	3		
Identifier	Values	Missing	Levels		
Fact_B_	27	0	3		
Identifier	Minimum	Mean	Maximum	Values	Missing
Cd_carro	0.0066	0.6490	1.3508	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Cd_Cabba	0.0165	0.5702	1.9250	27	0

64.....

***** Analysis of variance *****

Variate: Cd_Cabba

Source of variation d.f. s.s. m.s. v.r. F pr.

reps stratum	2	1.72935	0.86467	3.33	
reps.fact_A_ stratum					
fact_A_	2	0.76144	0.38072	1.47	0.333
Residual	4	1.03761	0.25940	3.07	
reps.fact_A_.Fact_B_ stratum					
Fact_B_	2	1.96073	0.98037	11.59	0.002
fact_A_.Fact_B_	4	0.09449	0.02362	0.28	0.886
Residual	12	1.01507	0.08459		
Total	26	6.59869			

* MESSAGE: the following units have large residuals.
 reps 2.00 fact__A_ 1.00 Fact__B_ 1.00 -0.463 s.e. 0.194
 reps 2.00 fact__A_ 1.00 Fact__B_ 3.00 0.504 s.e. 0.194
 ***** Tables of means *****

Variate: Cd_Cabba
 Grand mean 0.570
 fact__A_ 1.00 2.00 3.00
 0.585 0.358 0.768
 Fact__B_ 1.00 2.00 3.00
 0.229 0.594 0.888
 fact__A_ Fact__B_ 1.00 2.00 3.00
 1.00 0.250 0.543 0.961
 2.00 0.093 0.389 0.592
 3.00 0.344 0.850 1.111
 *** Standard errors of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
e.s.e.	0.1698	0.0969	0.2182
d.f.	4	12	9.56

Except when comparing means with the same level(s) of
 fact__A_ 0.1679
 d.f. 12

*** Standard errors of differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
s.e.d.	0.2401	0.1371	0.3086
d.f.	4	12	9.56

Except when comparing means with the same level(s) of
 fact__A_ 0.2375
 d.f. 12

*** Least significant differences of means ***

able	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
l.s.d.	0.6666	0.2987	0.6919
d.f.	4	12	9.56

Except when comparing means with the same level(s) of
 fact__A_ 0.5174
 d.f. 12

***** Stratum standard errors and coefficients of variation *****

Variate: Cd_Cabba

Stratum	d.f.	s.e.	cv%
reps	2	0.3100	54.4
reps.fact_A_	4	0.2941	51.6
reps.fact_A_.Fact_B_	12	0.2908	51.0
70.....			

***** Analysis of variance *****

Variate: Cd_Lettu

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
reps stratum	2	1.1003	0.5501	14.99	
reps.fact_A_ stratum					
fact_A_	2	0.2439	0.1220	3.32	0.141
Residual	4	0.1468	0.0367	0.15	
reps.fact_A_.Fact_B_ stratum					
Fact_B_	2	2.0692	1.0346	4.31	0.039
fact_A_.Fact_B_	4	0.5516	0.1379	0.58	0.686
Residual	12	2.8778	0.2398		
Total	26	6.9897			

* MESSAGE: the following units have large residuals.

reps 2.00 fact_A_ 2.00 Fact_B_ 2.00 0.856 s.e. 0.326

***** Tables of means *****

Variate: Cd_Lettu

Grand mean	0.589		
fact_A_	1.00	2.00	3.00
	0.471	0.593	0.704
Fact_B_	1.00	2.00	3.00
	0.208	0.858	0.701
fact_A_ Fact_B_	1.00	2.00	3.00
1.00	0.263	0.602	0.548
2.00	0.241	1.004	0.534
3.00	0.121	0.968	1.022

** Standard errors of means **

Table	fact_A_	Fact_B_	fact_A_
		Fact_B_	
rep.	9	9	3
e.s.e.	0.0639	0.1632	0.2395
d.f.	4	12	13.67

Except when comparing means with the same level(s) of

fact_A_	0.2827
d.f.	12

*** Standard errors of differences of means ***

Table	fact_A_	Fact_B_	fact_A_
		Fact_B_	
rep.	9	9	3
s.e.d.	0.0903	0.2309	0.3387
d.f.	4	12	13.67

Except when comparing means with the same level(s) of

fact__A_ 0.3999
 d.f. 12

*** Least significant differences of means ***

Table	fact__A_	Fact__B_	fact__A_	Fact__B_
rep.	9	9	3	
l.s.d.	0.2508	0.5030	0.7282	
d.f.	4	12	13.67	

Except when comparing means with the same level(s) of

fact__A_ 0.8712
 d.f. 12

***** Stratum standard errors and coefficients of variation *****

Variate: Cd_Lettu

Stratum	d.f.	s.e.	cv%
reps	2	0.2472	42.0
reps.fact__A_	4	0.1106	18.8
reps.fact__A_.Fact__B_	12	0.4897	83.1

***** Analysis of variance *****

Variate: Cd_carro

Source of variation	d.f.	s.s.	m.s.	v.r.	F	pr.
reps stratum	2	0.6829	0.3415	2.08		
reps.fact__A_ stratum						
fact__A_	2	0.0210	0.0105	0.06	0.939	
Residual	4	0.6568	0.1642	1.15		
reps.fact__A_.Fact__B_ stratum						
Fact__B_	2	2.4725	1.2363	8.68	0.005	
fact__A_.Fact__B_	4	0.4375	0.1094	0.77	0.566	
Residual	12	1.7083	0.1424			
Total	26	5.9790				

***** Tables of means *****

Variate: Cd_carro

Grand mean	0.649		
fact__A_ 1.00	2.00	3.00	
	0.611	0.677	0.659
Fact__B_ 1.00	2.00	3.00	
	0.225	0.912	0.810
fact__A_ Fact__B_ 1.00	2.00	3.00	
	1.00	0.062	1.038
	2.00	0.432	0.701
	3.00	0.181	0.997

*** Standard errors of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
e.s.e.	0.1351	0.1258	0.2233
d.f.	4	12	14.93

Except when comparing means with the same level(s) of

fact__A_	0.2178
d.f.	12

*** Standard errors of differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
s.e.d.	0.1910	0.1779	0.3158
d.f.	4	12	14.93

Except when comparing means with the same level(s) of

fact__A_	0.3081
d.f.	12

*** Least significant differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
l.s.d.	0.5303	0.3875	0.6735
d.f.	4	12	14.93

Except when comparing means with the same level(s) of

fact__A_	0.6712
d.f.	12

***** Stratum standard errors and coefficients of variation *****

Variate: Cd_carro

Stratum	d.f.	s.e.	cv%
reps	2	0.1948	30.0
reps.fact__A_	4	0.2339	36.0
reps.fact__A_.Fact__B_	12	0.3773	58.1

Identifier	Minimum	Mean	Maximum	Values	Missing
reps	1.000	2.000	3.000	27	0

Identifier	Minimum	Mean	Maximum	Values	Missing
fact__A_	1.000	2.000	3.000	27	0

Identifier	Minimum	Mean	Maximum	Values	Missing
Fact__B_	1.000	2.000	3.000	27	0

Identifier	Minimum	Mean	Maximum	Values	Missing
Pb_Cabba	0.013	3.406	20.464	27	0

Identifier	Minimum	Mean	Maximum	Values	Missing
Pb_carro	0.224	3.190	11.387	27	0

Identifier	Minimum	Mean	Maximum	Values	Missing
Pb_Lettu	0.93	81.27	738.76	27	0

Identifier	Values	Missing	Levels		
reps	27	0	3		
Identifier	Values	Missing	Levels		
fact_A_	27	0	3		
Identifier	Values	Missing	Levels		
Fact_B_	27	0	3		
Identifier	Minimum	Mean	Maximum	Values	Missing
Pb_Cabba	0.013	3.406	20.464	27	0
Identifier	Minimum	Mean	Maximum	Values	Missing
Pb_carro	0.224	3.190	11.387	27	0

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***** Analysis of variance *****

Variate: Pb_Cabba

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
reps stratum	2	32.343	16.172	0.94	
reps.fact_A_ stratum					
fact_A_	2	452.258	226.129	13.10	0.018
Residual	4	69.026	17.256	3.18	
reps.fact_A_.Fact_B_ stratum					
Fact_B_	2	134.172	67.086	12.37	0.001
fact_A_.Fact_B_	4	216.919	54.230	10.00	<.001
Residual	12	65.054	5.421		
Total	26	969.771			

* MESSAGE: the following units have large residuals.

reps 1.00	fact_A_ 1.00	Fact_B_ 1.00	3.61	s.e. 1.55
reps 2.00	fact_A_ 1.00	Fact_B_ 1.00	-4.54	s.e. 1.55
reps 2.00	fact_A_ 1.00	Fact_B_ 2.00	3.64	s.e. 1.55

***** Tables of means *****

Variate: Pb_Cabba

Grand mean	3.41		
fact_A_ 1.00	2.00	3.00	
	9.19	0.35	0.68
Fact_B_ 1.00	2.00	3.00	
	0.33	4.33	5.55
fact_A_ Fact_B_ 1.00	2.00	3.00	
	1.00	0.60	11.76
	2.00	0.18	0.37
	3.00	0.22	0.87
			0.94

*** Standard errors of means ***

Table	fact_A_	Fact_B_	fact_A_
		Fact_B_	
rep.	9	9	3
e.s.e.	1.385	0.776	1.767
d.f.	4	12	9.37

Except when comparing means with the same level(s) of

fact_A_	1.344
d.f.	12

*** Standard errors of differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
s.e.d.	1.958	1.098	2.499
d.f.	4	12	9.37

Except when comparing means with the same level(s) of

fact__A_	1.901
d.f.	12

*** Least significant differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
l.s.d.	5.437	2.391	5.619
d.f.	4	12	9.37

Except when comparing means with the same level(s) of

fact__A_	4.142
d.f.	12

***** Stratum standard errors and coefficients of variation *****

Variate: Pb_Cabba

Stratum	d.f.	s.e.	cv%
reps	2	1.340	39.4
reps.fact__A_	4	2.398	70.4
reps.fact__A_.Fact__B_	12	2.328	68.4

***** Analysis of variance *****

Variate: Pb_Lettu

Source of variation	d.f.	s.s.	m.s.	v.r.	F	pr.
reps stratum	2	68625.	34313.	1.03		
reps.fact__A_ stratum						
fact__A_	2	124037.	62019.	1.86	0.269	
Residual	4	133636.	33409.	2.28		
reps.fact__A_.Fact__B_ stratum						
Fact__B_	2	86975.	43487.	2.96	0.090	
fact__A_.Fact__B_	4	64094.	16024.	1.09	0.404	
Residual	12	176155.	14680.			
Total	26	653522.				

* MESSAGE: the following units have large residuals.

reps 2.00	fact__A_ 3.00	Fact__B_ 1.00	-208.	s.e. 81.
reps 2.00	fact__A_ 3.00	Fact__B_ 3.00	244.	s.e. 81.

***** Tables of means *****

Variate: Pb_Lettu

Grand mean 81.

fact__A_ 1.00	2.00	3.00
15.	54.	174.
Fact__B_ 1.00	2.00	3.00
2.	111.	131.

fact__A_ Fact__B_	1.00	2.00	3.00
1.00	1.	22.	22.
2.00	2.	79.	82.
3.00	2.	234.	287.

*** Standard errors of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
e.s.e.	60.9	40.4	83.5
d.f.	4	12	11.23

Except when comparing means with the same level(s) of

fact__A_	70.0
d.f.	12

*** Standard errors of differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
s.e.d.	86.2	57.1	118.1
d.f.	4	12	11.23

Except when comparing means with the same level(s) of

fact__A_	98.9
d.f.	12

*** Least significant differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
l.s.d.	239.2	124.4	259.3
d.f.	4	12	11.23

Except when comparing means with the same level(s) of

fact__A_	215.5
d.f.	12

***** Stratum standard errors and coefficients of variation *****

Variate: Pb_Lettu

Stratum	d.f.	s.e.	cv%
reps	2	61.7	76.0
reps.fact__A_	4	105.5	129.9
reps.fact__A_.Fact__B_	12	121.2	149.1
145.....			

***** Analysis of variance *****

Variate: Pb_carro

Source of variation	d.f.	s.s.	m.s.	v.r.	F	pr.
reps stratum	2	22.286	11.143	0.93		
reps.fact__A_ stratum						
fact__A_	2	6.415	3.208	0.27	0.777	
Residual	4	47.824	11.956	3.35		
reps.fact__A_.Fact__B_ stratum						
Fact__B_	2	112.168	56.084	15.70	<.001	

fact__A__Fact__B_	4	6.370	1.592	0.45	0.774
Residual	12	42.863	3.572		
Total	26	237.926			

* MESSAGE: the following units have large residuals.
 reps 1.00 fact__A_ 3.00 Fact__B_ 1.00 -3.24 s.e. 1.26
 ***** Tables of means *****

Variate: Pb_carro
 Grand mean 3.19

fact__A_ 1.00	2.00	3.00		
	3.28	2.55	3.74	
Fact__B_ 1.00	2.00	3.00		
	0.57	3.45	5.54	
fact__A_ Fact__B_ 1.00	2.00	3.00		
1.00	0.56	3.21	6.07	
2.00	0.73	2.61	4.32	
3.00	0.43	4.54	6.24	

*** Standard errors of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
e.s.e.	1.153	0.630	1.457
d.f.	4	12	9.12

Except when comparing means with the same level(s) of

fact__A_	1.091
d.f.	12

*** Standard errors of differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
s.e.d.	1.630	0.891	2.060
d.f.	4	12	9.12

Except when comparing means with the same level(s) of

fact__A_	1.543
d.f.	12

*** Least significant differences of means ***

Table	fact__A_	Fact__B_	fact__A_
		Fact__B_	
rep.	9	9	3
l.s.d.	4.525	1.941	4.651
d.f.	4	12	9.12

Except when comparing means with the same level(s) of

fact__A_	3.362
d.f.	12

***** Stratum standard errors and coefficients of variation *****

Variate: Pb_carro			
Stratum	d.f.	s.e.	cv%
reps	2	1.113	34.9
reps.fact_A_	4	1.996	62.6
reps.fact_A_.Fact_B_	12	1.890	59.3

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