KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KNUST.

KUMASI

HEAVY METAL CONTENTS OF SOIL AND CITRUS GROWN IN SELECTED DISTRICTS OF ASHANTI REGION, GHANA.

A THESIS SUBMITTED TO THE DEPARTMENT OF CROPS AND SOIL SCIENCES, FACULTY OF AGRICULTURE, COLLEGE OF AGRICULTURE AND NATURAL RESOURCES MANAGEMENT, KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY. KUMASI.

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BY

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DECLARATION

The report presented in this thesis is the result of the research carried out by the Author.

This thesis has not been submitted in whatever form to any other institution, organization or body for the award of any degree.

All inclusions from the work of others have been duly acknowledged.

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ABSTRACT

Soil and edible citrus fruit samples from two mining districts (Obuasi and Asante Akim North) and two non-mining districts (Ejisu-Juaben and Sekyere West) of Ashanti Region, Ghana were assessed for their relative Zn, Cu, Fe, Cd, Pb and Mn contents and to ascertain whether citrus fruit heavy metal contents are within permissible limits. Representative areas were selected from these sites with sampling depending on the variability of the terrain. From each sampling unit, ten (10) soil cores/slice were taken from 0-15, 15-30 and 30-45 cm soil depths separately, each depth thoroughly mixed by hand in plastic bucket and sub-samples taken for laboratory analyses. Twenty-four edible citrus fruit samples were also taken from four trees at each sampling unit for laboratory analyses. A 0.1 M EDTA solution was used to extract the metals in soil. The citrus fruit pulp was digested in H_2SO_4/HCl mixture after evaporation to dryness. Mining activities, use of agrochemicals in agriculture production and vehicle exhaust fumes were proposed as the main sources of heavy metals. The accumulation of these metals in these municipalities were in the order Obuasi > Sekyere West > Asante Akim North > Ejisu-Juaben. There were significant differences of the selected metals levels in citrus fruits and soils from the four districts. Soils of low pH had higher citrus fruit uptake of heavy metals than those of moderate to high pH while soils of high organic matter content also had high metal content but low citrus uptake. There were either strong negative or positive correlations between soil and citrus fruit heavy metal contents.

Though the heavy metal load of soils from all the four municipalities were below the permissible limit set by the Dutch standards for soil contamination assessment, the levels of citrus fruit Zn and Pb of all the four districts were above the permissible limits set by FAO/WHO while Cd in citrus fruit of Obuasi, Asante Akim North and Sekyere West were above the permissible limit.

Therefore, consumption of citrus fruit from the selected districts could pose health hazards to humans as at the time of the study.

Further research is required to determine the heavy metal content of soil and citrus fruit grown in other citrus-growing regions of the country as well as socio-economic and health status of neighbouring communities for sustainable citrus production in Ghana.

CHAPTER ONE

1.0 INTRODUCTION

The mining sector accounts for about 38 % of gross foreign exchange earnings, which is about 6% of Gross Domestic Product (GDP) of Ghana and employs about 36,000 workforce (Bonney, 2009). Exploitation of gold puts immense stress on air, water, soil and vegetation and also poses potential and real hazards to human health. This is due to the usage and production of wastes which are deposited in landfills adjacent to farmlands. Mine wastes contain heavy metals which have permissible levels in crops for safe consumption by man and animals. The term heavy metals refer to any chemical element with a specific gravity that is at least five times the specific gravity of water and is toxic or poisonous. Often it refers to metals discharged by industry of which the metalloid arsenic, cadmium, copper, lead, mercury, nickel and zinc are listed by a European commission directive as representing the greatest hazard to plants and animals. Interestingly, small amounts of these elements are common in the environment and their minute quantities in diet are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metals are natural components of the earth's crust. They cannot be degraded. To a small extent they enter the human body via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations, they can lead to poisoning. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment (Bernard, 1995). Compounds accumulate in living things anytime they are taken up and stored faster than metabolized or excreted. Since the Industrial Revolution, the production of heavy metals such as lead, copper and Zinc has increased exponentially. Between 1850 and 1990, production of these three metals increased nearly 10-fold, with emissions rising in tandem (Nriagu, 1996). Pollution in plants is of concern for two major reasons. Firstly, pollutants may have direct phytotoxic impact on the plants themselves, leading to a decline in crop yield and threatening food supplies.

Secondly, the plants may act as a vehicle for transferring pollutants into the food chain. For example, Cd is readily accumulated by plants and may get to levels which are adverse to the plants themselves, consequently posing a significant threat to humans and animals that consume these plants. Heavy metals and pesticides are major pollutants in this respect (Radojevic and Bashkin, 1999).

Since crops take up nutrients from the soil, the presence of heavy metals in high concentrations is expected to correspond to high concentrations in agricultural produce from these affected soils. Agricultural produce have their permissible levels for heavy metals upon which consumption will be harmless, especially for edible fruits. Extensive long term studies on the uptake of soil metals by plants illustrate that metals can accumulate in edible tissues of plants. However, because metals are toxic to both plants and animals, there are definite limits on the amounts that can be present in plants consumed by them

(http://www.pirg.org/toxics/reports/wastelands/index.html).

In Ghana, pollutants emanating from the mining sector have been of concern recently. Several concerns have been expressed about the quality of air we breathe, the water we drink and the soils that produce us food [Nyinah, (2002), Gobah (2005) and Anthony (2005)]. There are three primary areas affected by heavy metals in humans. These are the nervous system, the cardiovascular system and blood cells. Metals such as mercury and lead can disrupt nerve cells.

Lead, cadmium, nickel and mercury can affect blood cells. The build-up of heavy metals can cause damage to the liver, kidneys and the circulatory system. Lead can substitute for calcium, particularly in bone. In children, when bones are developing and inadequate quantity of calcium is taken, lead can accumulate in the bones. This can cause damage to nerve cells and the brain (http://www.gtrnew.com/greater-tulsa-reporter 1363). Majority of mining in Ghana occurs in the forest and transitional zones where citrus is also cultivated in large acreages. There is even a perception held by some citrus consumers that citrus from Obuasi (a prominent mining community in Ghana) is the sweetest in the country. There is a greater possibility for citrus from these mining sites to be concentrated with heavy metals from the mines. Hazardous industrial wastes introduce several dozen toxic substances and chemicals into farms, lawns and garden soils, including such well known toxic substances as lead and mercury. Many plants and crops extract these toxic metals from the soil, increasing the chance of their dangerous impact on human health as crops and plants enter the food chain

(http://www.pirg.org/toxics/reports/wastelands/index.html.). In Ghana citrus is produced in the forest and transitional zones of the country and production has been increasing over the years in terms of acreage. Currently, there is a Citrus Growers Association in the Ashanti Region of Ghana which is championing the welfare of the producers in the region in terms of marketing, credit acquisition and training. Central, Eastern, Volta and Ashanti regions are suitable areas of production in Ghana (MOFA, 2004). Heavy metal concentrations in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods (Eja et al., 2003; Zawyah et al., 2004). Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. The main sources of heavy metals to crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokoshwad and Chandrappa, 2006).

Studies reveal that the presence of toxic heavy metals like Fe, Pb and Hg reduces soil fertility and agricultural output (Lokhando and Kelkar, 1999). Recently concerns have been raised over the levels of heavy metals in the environment (soil, water, etc) where some scientists suggest that foodstuff from mining communities contain toxic amounts of heavy metals. Thus the urgent need to characterize the heavy metal contents of mining and non-mining sites and correlate these with the heavy metal content of fruits grown in these sites and make the necessary recommendations for sustainable citrus production in Ghana.

1.1 Main objectives

This research work was undertaken to characterize mining sites as against non –mining sites in terms of heavy metal content.

1.2 **Specific objectives**

1. To establish the heavy metal content of citrus fruit from mining and non-mining sites
2. To establish the heavy metal content of soil from mining and non-mining sites
3. To assess the relationship between soil heavy metal contents and citrus fruit heavy metal content from these mining and non-mining sites of Ghana.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Citrus

Citrus trees are aromatic, broad-leaved, evergreen trees native to the subtropical regions of Eastern Asia. Trees vary in size from 3-5 m tall for lime and up to 10 m tall for grapefruit cultivars. The primary species of cultivated citrus are the sweet orange (*Citrus sinensis*), the lemon (*Citrus limon*), the grapefruit (*Citrus paradise)*, the lime (Citrus *aurantifolia*) and the mandarin, also known as tangerine (*Citrus reticulata*). Various hybrids include the tangor (tangerine and sweet orange) and the tangelo (tangerine and grape fruit).

2.1.1 Economic Importance and Distribution of Citrus

Citrus are now the major fruits of subtropical regions. The main centres of production in the world are the Southern Africa, Israel, the US, Brazil, Spain, Japan, Italy and Mexico with US being the largest producer. Citrus can be produced economically in the tropics although fruit quality is sometimes inferior in colour to that produced in sub-tropical regions (Rice, 1987).

2.1.2 Citrus Production in Africa

Within Africa, large scale production of citrus occurs on the Mediterranean coast and in Southern Africa, Zimbabwe, Mozambique and Swaziland. Minor producers include Zambia, Kenya and Ivory Coast. In most of the remaining regions of Africa, production is on a small scale and is primarily for local consumption.

2.1.3 Citrus Production in Ghana

In Ghana citrus is produced in the forest and transitional zones of the country and production has been increasing over the years in terms of acreage. Currently, there is a Citrus Growers Association in the Ashanti Region of Ghana which is championing the welfare of the producers in the region in terms of marketing, credit acquisition and training.

Important commercial varieties of citrus in Ghana are the sweet orange (*Citrus sinensis*) which are classified based on the maturity group as in Table 1.

Table 1: Citrus varieties in Ghana and their maturity periods.

Maturity	**Varieties**
Early maturing (Aug.-October)	Ovaletto, sekkan
Mid-season (oct.-january)	Obuasi, Mediterranean sweet, Red blood
Late maturity (march-April)	Late Valencia, olinda and frost Valencia

Tangerine (Citrus reticulate) is another commercial variety which has Satsuma (May-June) and purcan (Sept.-Oct.). Other important commercial varieties are grapefruit, lemons, lime, tangors, tangelos and ortanique.

Central, Eastern, Volta and Ashanti regions are suitable areas of production in Ghana (MOFA, 2004).

2.2 Mining

Mining is the process of taking minerals or coal from the earth. Most substances obtained from the earth are obtained by mining. Mines supply salt for food, gold, silver and diamonds for jewelry and coal for fuel. Mining itself, not only of heavy metals but also of coal and other minerals, is another major route of exposure. Despite some noted improvements in worker safety and cleaner production, mining remains one of the most hazardous and environmentally damaging industries.

In Bolivia, toxic sludge from a Zinc mine in the Andic had killed aquatic life along a 300-kilometer stretch of river systems as of 1996. It also threatened the livelihood and health of 50,000 of the region's subsistence farmers. (www.sciencedirect.com).

2.2.1 History of Mining in the World

People have mined the earth for thousands of years, perhaps first in Africa. Prehistoric people in Europe dug pits and tunnels to get flint, a hard stone used to make tools and weapons. Sometimes after 3500 BC, people were mining tin and copper. They combined these metals to make bronze, a hard alloy that made better tools and weapons.

The ancient Romans probably were the first people to realize mining could make a nation rich and powerful. Merchants traded valuable stones and metals and brought riches to them. The Romans took over the mines in every country they conquered.

The Roman Empire ended in AD 400's. For about a thousand years, little advancements were made in mining. During the 1400's, coal, iron and other materials were mined in Europe, especially in Sweden, Germany and France. Mining also developed in South America. The Inca Indians and other people of South America used metals to make tools, jewelry and weapons. Mining began in US in the 1700's. French explorers mined lead and zinc in the valley of the Mississippi River. In the mid 1800's, miners began to dig up large amounts of coal in Pennsylvania. At about the same time, thousands of people rushed to California hoping to find gold. In the west, the gold rush led to the discovery of copper, lead, silver and other useful minerals (Encyclopaedia, 2001)

2.2.2 History of Mining in Ghana with Special Reference to Obuasi

Anglogold Ashanti, formerly Ashanti Goldfields Corporation (AGC), has been mining Gold in Obuasi area since 1897. At that time Obuasi was a village of 12 houses (Anon, 1992). In a likelihood, the metal was being panned or dug-out of placer deposits well before the 14th century. Although there is written evidence indicating that mine shafts were being dug by about 1700 AD, mining by this method may go back far earlier.

Written accounts by Europeans describe “slaves” being employed in mining, while other accounts imply miners worked for themselves or on behalf of chiefs or kings. In the 19th centrury some mining seemed to have been carried out by groups of men and women who were obliged to work on particular days for their chiefs.

Domestic slaves may also have been allocated to mining duties by their owners. It is also known that a tribal group called the Nzemas from the South-west edge Western region had begun to be more or less professional miners, giving up farming and moving into other areas to develop new goldmines. Whenever the local labour supply could not meet the mines requirements, Muslims were recruited from neighbouring Northern countries (Ayensu,1997).

The mines produced both gold and minor silver in the form of dore’ bars, which were refined in Switzerland. The underground workings have been developed along a strike length of 8 km

(5 miles) and to a depth of 1500 m. The mine complex has more than 10 functional shafts, which among them hoist some 2 million tons of ore and 700,000 tonnes of waste every year (Ayensu, 1997).

2.3 Soil Quality

The capacity of a specific kind of soil to function within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation. Public interest in soil quality is increasing throughout the world as humankind recognizes the fragility of earth's soil, water, and air resources and the need to protect them to sustain human civilization (www.sci.agr.ca/london/faq/soil_sols_e.htm). Soil quality in its broadest sense is enhanced by land-use decisions that weigh the multiple functions, and is impaired by land-use decisions that focus on single functions. Soil quality can be degraded by using inappropriate tillage and cropping practices; through excessive livestock grazing or poor timber harvesting practices; or by misapplication of animal manures, irrigation water, fertilizers, pesticides, and municipal or industrial by-products.

2.4 Heavy Metals

The term heavy metal refers to any chemical element with a specific gravity that is at least five times the specific gravity of water and is toxic or poisonous at higher amounts (Wild, 1993). Often it refers to metals discharged by industry of which the metalloid arsenic, cadmium, copper, lead, mercury, nickel and zinc are listed by a European commission directive as representing the greatest hazard to plants and animals. Interestingly, small amounts of these elements are common in our environment and their minute amount in diet is actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning).

Heavy metals are natural components of the Earth crust. They cannot be degraded or destroyed. To a small extent, they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical’s concentration in the environment. Compounds accumulate in living things anytime they are taken up and stored faster than metabolized or excreted.

Since the Industrial Revolution, the production of heavy metals such as lead, copper and Zinc has increased exponentially. All foods and water contain metals and non-metals that at high concentrations, whether from natural or industrial sources can become harmful (Wild, 1993).

In several areas of the world exposure of the general population to heavy metals has reached levels that are significantly high to cause some effects among sensitive groups of the general population. The major critical organs for environmentally exposed populations are the central nervous system of the developing foetus or child (lead and mercury) and the kidney (cadmium) (Bernard, 1995).

Many metals and metalloids are present in minute (trace) amounts in the soil water. These trace elements occur naturally as a result of rock weathering. They can be leached into surface water or ground water, taken up by plants, released as gases into the atmosphere or bound semi-permanently by soil components such as clay or organic matter.

In small amounts, many of these trace elements (e.g. boron, zinc, copper and nickel) are essential for plant growth. However in higher amounts they may decrease plant growth. Other trace elements (e.g. arsenic, cadmium, lead and mercury) are of concern primarily because of their potential harm to soil organisms, animals and man.

The impact of heavy metals on soils depends upon many factors, such as pH, organic matter, CEC and speciation of metals (Dai et al., 2004). The possible hazards arising from pollution of the environment by heavy metals have surfaced more recently and the toxicity of some of these metals towards humans especially children when exposed to them from the atmosphere, water or food has been well documented.

Most of the gold in the mining communities is locked in mineralized dyke and schist (pyrite and arsenophyte) associated with arsenic and sulphur. The extraction of the gold involves roasting which releases airborne particles and large quantities of arsenic (14-19 tons) daily in Obuasi. The Arsenic content of samples analysed from Obuasi was generally higher than those from Kumasi (Amonoo-Neizer et al., 1993).

Obuasi and its surrounding areas have high levels of heavy metals such as iron, arsenic and manganese in most streams. Also, waters in the area are acidic, falling outside Ghana's Environmental Protection Agency and World Health Organization range of standards for portable water. Arsenic values are between 10-38 times higher than levels permitted by EPA general guidelines and over 1,800 times higher than the WHO maximum allowable values. Also concentration of heavy metals in fruit (oranges) was higher than in the corresponding concentration of metals in water. Mercury values are up to five times more than the EPA limits and 26 times more than WHO limits. Analysis of disease prevalence patterns showed that malaria, acute respiratory infections, diarrhoea, skin diseases, acute eye infections constituted the top six causes of Out Patients Department attendance (www.modernghana.com).

Past and present large scale and illegal small-scale mining activities have affected water resources in Obuasi and its satellite communities. Stream water is significantly polluted by As, Hg, Fe, and, to some extent, Cu, Ni and Zn (www.sciencedirect.com). The three most pollutant heavy metals are lead, cadmium and mercury. Cadmium, As, Cr and Hg are extremely toxic, Pb, Ni, Mo and F are moderately toxic whereas B, Cu, Mn, Zn and Fe are low in toxicity (Brady, 1990).

Pollution of plants is of concern for two major reasons. Firstly, pollutants may have direct phytotoxic impacts on the plants themselves, leading to a decline in crop yields and threatening food supplies. Secondly, the plants may act as a vehicle for transferring pollutants into the food chain. For example, Cd is readily accumulated by plants and may get to levels which are adverse to the plants themselves, consequently posing a significant threat to humans and animals that consume plants.

Food chain contamination by heavy metals has become a burning issue in recent year because of their potential accumulation in biosystems through contaminated water, soil and air. The main sources of heavy metals to crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokoshwad and Chandrappa, 2006).

2.4.1 Beneficial Heavy Metals

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as trace elements (e.g. copper, iron, manganese and zinc). Some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products.

Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in parental nutrition mixtures, and the use of lead radiation shield around x-ray equipment. Heavy metals are also common in industrial applications in the manufacture of pesticides, batteries, alloys, and electroplated metal parts, textile dyes, steel and so forth. Many of these products are in homes and actually enhance quality of life when properly used (www.lef.org/protocols/prtcl-156. html.).

2.4.2 Harmful Effects of Heavy Metals on Humans

Heavy metal toxicity represents a common medical condition. If unrecognized or inappropriately treated, it can result in significant morbidity and even death. Occupational exposure to heavy metals has accounted for the vast majority of poisonings throughout human history. Hippocrates described abdominal colic in a man who extracted metals, and the pernicious effects of arsenic and mercury among smelters were known even to Theophrastus of Erebus (370-287 BC).

Heavy metals are stable elements- they cannot be metabolized by the body and are bioaccumulative, that is, they are passed up the food chain to humans. In general, they have no function in the body and can be highly toxic.

There are 35 metals that concern humans because of occupational or residential exposure; 23 of these are the heavy metals-antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium and zinc.

Humans have been exposed to lead, mercury and other toxic heavy metals over the entire course of our history and this exposure has had some marked effects on the health of human species. We are exquisitely sensitive to accumulation and concentration of heavy metals in our bodies; apparently humans can manage low levels of exposure but the present global levels of heavy metals are simply too high to process (www.agnet.org).

Some historians claim that lead created the conditions leading to the fall of the Roman Empire. After stone water reticulation systems were replaced with lead piping, the Romans went orgiastically nutty and were overrun by clear-headed barbarians. The presence of extremely high levels of lead is borne out by proof of peaks in atmospheric lead pollution-the result of increased human lead production-around 0 AD, again from 1300 to 1500 AD during the age of alchemy, and most recently from the industrial revolution to the present.

Children are particularly sensitive to even extremely low levels of mercury and lead. Negative effects on neurological development have been well established.

Generally, heavy metals disrupt enzymatic and protein synthesis, thereby altering biological molecular structures. A wide range of diseases can be caused, triggered or exacerbated by heavy metal toxicity. Included are not only lead and mercury but also arsenic, cadmium, copper, iron and manganese. An excess of these elements and compounds in the environment leads to increased levels in human bodies, thus decreasing their ability to remain healthy.

2.4.2.1 Arsenic

Arsenic is the most common cause of acute heavy metal poisoning in adults and is the number one on The Agency for Toxic Substances and Disease Registry of The US list. Arsenic is released into the environment by the smelting process of copper, zinc and lead, as well as by the manufacturing of chemicals and glasses. Arsine gas is a common by -product produced by the manufacturing of chemicals that contain arsenic. Arsenic may also be found in water supplies worldwide, leading to the exposure of shellfish, cod and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. Target organs in the body are the blood, kidneys, and central nervous, digestive and skin systems.

Large amounts of arsenic in soils, water, plants, some food items, and human hair in Obuasi samples have been established (Amasa, 1975; Amonoo-Neizer et al., 1980).The arsenic content of food crops in Kumasi where arsenic is not directly released into the atmosphere as a result of industrial activity, ranged from 0.07 (in oranges) to 0.97 (in pepper) mg/kg wet mass. The total arsenic in Obuasi food crops ranged from 0.14 9 (in cocoyam leaves) to 1.86 (in plantains) mg/kg wet mass (Amonoo-Neizer et al., 1993). The Arsenic concentrations in some food crops from farms in Kumasi and Obuasi are presented in Tables 2 and 3 respectively.

Table 2: Total Arsenic Concentrations in Some Food Crops from Kumasi Farms (Amonoo-Neizer et al., 1993)

Sample	Mean Concentrations (mg/kg) Wet (Dry) Mass
Cassava	0.28 (1.03)
plantain	0.36 (1.10)
Cocoyam	0.42 (0.97)
Pepper	0.28 (0.58)
Orange	0.13(0.05)
Beans	0.26 (0.52)
Pear	0.15 (0.76)

Table 3: Total Arsenic Concentrations in Food Crops from Obuasi Farms (Amonoo-Neizer et al., 1993)

Sample	Mean Concentrations (mg/kg) Wet (Dry) Mass
Plantain	1.33 (3.43)
Cocoyam	0.98 (2.26)
Pepper	0.28 (0.910
Orange	0.55 (3.46)
Cassava	0.98 (2.59)
Beans	0.49 (0.99)
pear	0.31(1.59)

2.4.2.2 Lead

Lead is number 2 on The Agency for Toxic Substances and Disease Registry (ATSDR) of The US ‘Top 20 list’ of toxic heavy metals. It accounts for most of the cases of pediatric heavy metal poisoning. It is a very soft metal and was used in pipes, drains and soldering materials for many years. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of these are used for batteries. The remainder is used for cable coverings, plumbing, ammunition, and fuel additives. It is also found in PVC plastics; x-ray shielding, crystal glass production, pencils and pesticides. Target organs are the bones, brain, blood, kidneys and thyroid gland.

Some studies suggest that there may be a loss of 2 IQ points for a rise in blood lead levels from 10-20 micro gram/dl in young children. Average daily lead intake for adults in the UK is estimated at 1.6 micro gram from air, 20 micro gram from drinking water and 28 micro gram from food.

Leaded gasoline accounts for 80 to 90% of airborne lead pollution in some large cities, elevating the blood levels of people living in the area (Gavaghan, 2002).

Tetraethyl lead was previously used as a fuel additive to increase its octane rating or to act as an anti-knock agent. However, the use of this additive has contributed immensely to lead pollution of the environment. As a result, the addition of lead anti-knocking agents to fuels has been phased out in many developed countries. They have been replaced by the Mn compound Methylcyclopentadienyl Manganese Tricarbonyl (MMT). The Government of Ghana on January 1^{st}, 2004 approved a legislative instrument (L.I. 1732) banning the production, importation, storage, sale and use of leaded fuel due to the environmental health effects on humans and subscribed to the use of MMT (TOR Unpublished report, 2005).

2.4.2.3 Manganese

In a healthy individual excess Mn that enters the body through diet is eliminated by the liver and intestine, expelling the metal primarily in solid waste. Individuals with liver problems or other health issues, however, may not be able to eliminate Mn, causing the metal to reach toxic concentrations in certain tissues (www.sciencedirect.com). Tissues in the mid-region of the brain are particularly prone to accumulating Mn. High concentrations of Mn in the mid-region tissue can produce a condition called Manganism. This condition has symptoms similar to (but not identical with) Parkinson's disease. Weakness of muscles, dullness, headache, insomnia, and mood changes are also associated with elevated levels of Mn in the body (Barbeau, 1984; Beuter et al., 1994). Food is a major source of Mn exposure. Certain foods, such as tea leaves, pecans, and grape nuts, have especially high levels of Mn (Schroeder et al., 1966). Manganese emissions from tailpipes contaminate soil and dust near roadways, such as lead did when it was used as a gasoline additive (Lytle et al., 1995). This material could be taken up by children when they play on contaminated surfaces, and ingested following hand-mouth contact. Crops on the roadsides that take up Mn might become very Mn-rich foods (Brault et al., 1994).

2.4.2.4 Mercury

Number 3 on the ATSDR's 'Top 20 list" is mercury. Mercury is generated naturally in the environment from the depth of the earth crust, from volcanic emissions. It exists in three forms: elemental mercury and organic and inorganic mercury. Mining operations, chloralkali plants, and paper industries are significant producers of mercury. Mercury is used in thermometers, thermostats, and dental amalgam (Many researchers suspect dental amalgam as possible source of mercury toxicity). The organic form is readily absorbed in the gastrointestinal tract (90-100%) but significant amounts of inorganic mercury are absorbed in gastrointestinal tract (7-15%). Target organs are the brain and kidneys (www.lef.org/protocols/prtcl--156.html.).

2.4.2.5 Cadmium

Cadmium is a by product of the mining and smelting of lead and zinc and is number 7 on the ATSDR's "Top 20 list". It is found in Nickel-cadmium batteries, cigarettes, PVC plastics and paint pigments. Cadmium can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Lesser known sources of cadmium are dental alloys, electroplating, motor oil and exhaust. Targets in the body are the liver, placenta, kidneys, lungs, brain and bones. Symptoms of acute cadmium exposure are nausea and vomiting. Chronic exposure causes hair loss, anaemia, arthritis, learning disorders, migraines, growth impairment, osteoporosis, loss of taste and smell, chronic obstructive lung disease and cardiovascular disease (jamaicaobserver.com/lifestyle/html).The average daily intake for humans is estimated at 0.15 micro gram from air and 1.0 micro gram from water.

2.4.2.6 Iron

Iron does not appear on the Agency for Toxic Substances and Diseases Registry's (ATSDR) "Top 20 list", but is a heavy metal of concern, particularly because ingesting dietary iron supplements may acutely affect young children. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. Drinking water and iron pipes are sources of iron. Target organs are the liver, cardiovascular systems and kidneys.

2.5 Soil pH

Soil pH affects the availability and absorption of nutrients by plants particularly micronutrients. Metal solution chemistry and soil surface chemistry are mutually affected by p^H to such an extent that soil p^H is basically the most important factor in determining metal retention by soil. The number of p^H dependent, surface sites that are negatively charged increase with p^H. Thus, increase in p^H can lead to significant increases in the Cation Exchange Capacity (CEC), if a soil contains large number pH dependent charges (Reed et al., 1994). Generally, at low p^H, there is little metal retention. At intermediate, relative to the hydrolysis p^H of the metal ion being adsorbed, adsorption increases from near zero to near complete adsorption over a relatively low small p^H range. At high p^H, the metal ion is completely adsorbed by the soil with exceptions relative to amphoteric metals which form soluble hydroxides and polynuclear anionic hydroxo-complexes at elevated p^H (Crawford et al., 1999).

2.6 Bioavailability of Heavy Metals

Heavy metals (Cu, Fe, Mn and Zn) are elements which are essential for plant growth, but are required in much smaller amounts than the major nutrients.

With the exception of Fe and Mn, which are among the 12 most abundant elements, the other elements occur at concentrations of less than 0.1 % in the lithosphere, another reason for their being named minor or trace elements. Deficiencies of micronutrients have been increasing in some crops. Some reasons are higher crop yields which increase plant nutrient demand, use of high analysis NPK fertilizers containing lower quantities of micronutrient contaminants, and decreased use of farmyard manure on many agricultural soils.

2.6.1 Forms of Iron, Manganese, Copper and Zinc in the Soil

These four metallic micronutrient cations occur mainly in the divalent form in soils; differences in the ionic character of their chemical bonding are great enough so that only Fe^{2+} and Mn^{2+} can substitute extensively for each other. Chemical forms of micronutrients have been defined by pools determined by various chemical extractions.

Pickering (1981) termed these pools as ion exchangeable, absorbed, organically bound, hydrous oxide segment and lattice component micronutrients. Iron is the fourth most abundant element in soils, ranging from 7,000 to 500,000 mg/kg, with a mean concentration of 38,000 mg/kg (3.8%) in soils (Lindsay, 1979). Iron occurs mainly in the Fe^{2+} and Fe^{3+} forms as iron oxides, silicates, sulphates and carbonates in the earth's crust.

The most abundant form is Fe_2O_3, which is very stable and insoluble in water. Manganese is similar to Fe in both its chemistry and geology. Concentrations of Mn in the Earth crust, igneous and sedimentary rocks, and soil are second only to those of Fe. Concentrations of total Mn in soils range from 20 to 6,000 mg/kg, with a mean concentration of 600 mg/kg in soils. Neither total nor exchangeable Mn in soil is correlated with the composition of the bedrock, which indicates the mobility of Mn in the earth crust.

Manganese has three common valences ($Mn^{2+,}$ $Mn^{3+,}$ and Mn^{4+}) of which the divalent form is the most common, especially with reference to plant nutrition. The trivalent ion is unstable in solution, while the divalent ion forms stable compounds in reducing environments. The most stable compound is MnO_2 in oxidizing environments.

Copper occurs in the earth's crust mainly as sulphide minerals. Less stable forms include oxides, silicates, sulphates and carbonates. Copper occurs as Cu^+ and Cu^{2+} forms, but can also occur in metallic form in some ores. The concentrations of total Cu in soils range from 2 to 100 mg/kg, with a mean concentration of 30 mg/kg. Copper is present mainly in the adsorbed form and as organic complexes in soils in the Cu^{2+} form, which is also of primary interest in plant nutrition.

The principal Zn ore is spharelite (ZnS) but Zn also occurs as silicates and carbonates in the earth's crust. Total Zn concentrations in soils range from 10 to 300 mg/kg, with a mean concentration of 50 mg/kg. Zinc occurs as the divalent cation ($Zn^{2+)}$ in soils and does not undergo reduction in nature, due to its electropositive nature (Krauskopf, 1972). In comparison with Cu, Zn migrates further in soil and is known as the most mobile of the heavy metals. Divalent Zn is sorbed less strongly than Cu, probably because the covalent bonds holding Cu^{2+} is stronger than those of $Zn^{2+.}$

2.6.2 Factors Affecting Bioavailability of Heavy Metals

2.6.2.1 Soil pH

Bioavailability of all four of the metallic micronutrients is significantly affected by soil pH, decreasing with increasing pH. Solubility of Fe decreases a thousand fold for each unit increase in soil pH in the range of 4 to 9 (Lindsay, 1979), and consequently, most Fe deficiencies occur on calcareous soils. This decrease in solubility is much greater for Fe than for Mn, Cu or Zn. The activity (and consequently bioavailability) of Mn, Cu and Zn decreases 100- fold for each unit increase in soil pH.

Complex ions of Mn, such as $MnHCO_3^-$ and $MnOH^-$, in addition to Mn^{2+}, exist in soil solution and their relative concentrations are affected by pH (Lindsay, 1979). Ion species of Cu in soil solution are Cu^{2+} at pH values 7.3, while CuOH- is most common above that pH. The most common form of Zn in solution is Zn^{2+} below pH7.7, while $Zn(OH)_2$ is most common above that level. Both Ca and Mg can replace Zn from solution complexes and from adsorption sites on soil solids (Barak and Helmke, 1993). The amounts of exchangeable metals in soils are related to their concentrations in soil solution, so soil pH affects exchangeable Fe, Mn, Cu and Zn similarly.

2.6.2.2 Soil Organic Matter

Reactions with soil organic matter (SOM) significantly affect bioavailability of these metallic micronutrients (Stevenson, 1991). Copper reacts with soil organic matter to form very stable complexes, especially with carboxyl and phenolic groups. Some of these complexes are so stable that most Cu deficiencies have been associated with organic soils.

Reactions of Zn with SOM are also important in providing bioavailable Zn, but the strength of these bonds is not as great as with Cu.

Manganese also forms stable complexes with organic ligands, and Mn deficiencies also occur in organic soils. The stability of these complexes is such that the incidence of Mn deficiency above pH 6.5 is much lower in soils with appreciable levels of SOM than in low organic matter soils. While Fe also complexes with SOM, its bioavailability are more affected by soil pH than by SOM content.

2.6.2.3 Redox Reactions

Redox reactions are very common in soils, and these relationships affect micronutrient availability. The redox potential of a soil is dependent upon soil pH, soil aeration and soil microbial activity. Iron is significantly affected by redox potential. The reduced form (Fe^{2+}) is found under waterlogged conditions in soil.

Mn can occur in three oxidation states, so it is significantly affected by soil redox status. Trivalent Mn is unstable in aqueous solutions because it reduces to Mn^{2+} or disproportionate to Mn^{2+} and MnO_2 (Hamsen and Vlek, 1985).

The reduction of Mn^{4+} to Mn^{2+} is greater at lower soil pH levels, and very acid soil conditions can lead to Mn toxicities in some sensitive plant species. Although Cu^{2+} can be reduced to Cu^{+} ions, neither Cu nor Zn is affected by oxidation-reduction reactions which occur under most soil conditions.

2.7 Relationship between Bioavailability of Trace Elements in the Soil, and Uptake by Crops

Three patterns of the relationship between the bioavailability of nutrients and uptake in crops have been proposed (www.agnet.org). In Type 1, uptake increases as the crop grows, then falls when the crop reaches maturity. This pattern is seen in the uptake of major nutrients such as nitrogen, potassium and phosphorus. Type 2 has a similar but steeper peak, and is seen with the uptake of micro nutrients such as copper or zinc. In Type 3, uptake is highest at the early growing stages, and falls during the later stages of growth. This pattern is seen for heavy metals such as arsenic, cadmium, chromium, lead, nickel and mercury. Cadmium is soluble in soil under oxidized conditions. Under reducing conditions, it is precipitated as cadmium sulphate.

2.8 Management Factors Affecting the Concentration of Heavy Metals in Contaminated Soils

Many field and pot experiments on remediation techniques for contaminated soils have been carried out in Taiwan (www.agnet.org). These include;

1. Chemical stabilization, to reduce the solubility of heavy metals by adding non-toxic materials to the soil;
2. Removal of polluted surface soil, and replacing it with clean soil;
3. Covering the original polluted soil with clean soil;
4. On-site chemical leaching, using some acid agent;

5. The dilution method, mixing polluted soil with clean soil to dilute the concentration of heavy metals;
6. Remediation by plants, using suitable tree species.

Chemical stabilization seems to be the most cost-effective remediation technique for contaminated sites. However, methods involving the removal of polluted soil, and the addition of clean soil to the surface, or remediation by plants were also effective in some cases.

2.9 How Soil Chemical Amendments Affect Heavy Metals in Soils

Some chemical techniques are available which help immobilize heavy metals in soil, so that they cannot be taken up by plants. These include the application of dolomite, phosphate or organic matter into polluted soil. Such materials can reduce the concentration of heavy metals by precipitation, adsorption, or complexation (www.agnet.org). The application of calcium carbonate (limestone) materials significantly reduces the solubility of heavy metals in contaminated soils. Many reports also indicate that the application of iron hydroxide or manganese oxides significantly reduces the concentration of soluble cadmium or lead in contaminated soil.

2.10 Regulation of Heavy Metals in Soils in Developed Countries

Various approaches are used in different countries to assess the level of heavy metals in contaminated soils. Most governments who have not developed their own formal guidelines governing the maximum permitted levels follow the ¨Dutch Standard¨ to support their decisions in assessing and monitoring sites. Other governments have developed their own regulations, based on the soil qualities they require (www.agnet.org).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sampling Sites and Methods

Two mining municipalities (Obuasi and Asante Akim North) where large quantities of citrus are grown were selected together with two (2) non-mining municipalities (Sekyere West and Ejisu-Juaben). Obuasi is about 64 km south of Kumasi and is home to the largest gold mine in Ghana-Anglogold Ashanti. It is located between latitudes $5^{o}35'$N and $5^{o}65'$N, and longitudes $6^{o}35'$W and $6^{o}90'$W. Konongo-Odumasi – the district capital of Asante Akim North -is about 45 km east of Kumasi and is noted for its small scale mining activities. Ejisu is about 20 km east of Kumasi and there is no mining activity. It lies within latitude $1^{o}15'$N and $1^{o}45'$N and longitude $0^{o}15'$W and $7^{o}00'$W. Asante Mampong –the district capital of Sekyere West- is about 57 km north of Kumasi and there was no mining activity. The farms selected in Obuasi were Wioso (20 km from the mine site), Sasu (5 km from the mine site) and Apitikooko (8 km from the mine site). The soil in the Wioso farm was Mim series (Orthi-Ferric Acrisol), Sasu's farm was Kokofu series (Dystric Nitisol) and Apitikooko was Nzima series (Orthi-Ferric Acrisol) (Adu, 1992). The farms selected in Asante Akim North were Acquah (10 km from the mine), Barfi (6 km from the mine) and Gye Nyame (7.5 km from the mine). The soil in these farms was Juaso series (Orthi-Ferric Acrisol) (Adu and Mensah Ansah, 1995).The farms selected in Ejisu-Juaben were Achiaa, Agyenim and Janet. The soil of Achiaa was Nzima series (Orthi-Ferric Acrisol), Agyenim's soil was Kokofu series (Dystric Nitisol) and the soil of Janet was Bomso series (Orthi-Ferric Acrisol) (Adu, 1992).

The farms selected in Sekyere West were Gyasi. Acheampong and Rockson. The soil in these farms was Bediesi series (Ferric Lixisol) (Adu and Mensah Ansah, 1995). The climate of the selected districts is hot and humid, influenced by monsoon air masses, and the hot, dry harmattan wind from the Sahara. The mean annual temperature is 27.9^{o}C with a small variation of less than 30%. The recorded temperature range is from 23.3 ^{o}C (August) to 35 ^{o}C (November). The mean annual rainfall is 1588 mm with a considerable variation in distribution. November to February is the driest months (January, 13 mm). The annual average relative humidity is 85% at 0900 hrs and 84% at 1500 hrs. In summary, the climate is characterized by consistent warmth, high humidity and generally light winds. Mining is the main industrial activity in Obuasi. In addition to the mining process, associated operations such as the maintenance of heavy duty machinery and equipment are also performed. These activities involve the use of lubricants, acids, cooling waters and other components. The type of mining practices in Obuasi is predominantly the deep mining where a vertical shaft is dug to intercept the mineral reserves. Mining and its associated activities are generally the main industrial activities prevailing. The main industrial activities in Konongo-Odumasi are agro processing, small scale mining and maintenance of equipment. Ejisu-Juaben and Asante Mampong are characterised by agro processing, wood processing and maintenance of equipment.

Three citrus farms were selected based on the availability of edible fruits. The selected farms in Obuasi were Nicholas Agyei's farm at Apitikooko, Sasu's farm at Obuasi and Wioso farm at Wioso (about 20 km from Obuasi). Apitikooko is about 5 km from the centre of Obuasi and the farm was about 0.5 ha with a gently sloping topography into a stream. There was no industrial activity nearby. Sasu's farm is at the outskirts of Obuasi on the Cape Coast road. It was about 0.1 ha and is near a poultry farm. It is also near mechanical shops. Wioso farm is about 0.4 ha and is at the outskirts of Wioso village. There is no industrial activity nearby. All these farms were by the road. Representative areas were selected from these sites with sampling depending on the variability of the terrain. From each sampling unit, ten (10) soil cores/slice were taken to make a composite sample from 0-15, 15-30 and 30-45 cm soil depths respectively, each depth thoroughly mixed and sub-samples taken for laboratory analysis. Twenty-four edible citrus fruit samples were also taken from four (4) trees at the sites for analysis. The citrus from the Apitikooko and Wioso were of the Late Valencia variety whereas Sasu was of the local variety.

Three citrus farms were selected in Konongo-Odumasi. These were Gye Nyame farms at Agyareago, Acquah's and Barfi's farms all at Odumasi. Gye Nyame farm was about 12 ha with a deeply sloping topography. It is about 5 km from Konongo-Odumasi where there were small scale mining activities but there were no industrial activities nearby. Acquah's farm is near Ghana Water Company Ltd. and is about 0.5 ha. The land had a flat topography with a gravelly soil. Barfi's farm was about 1.2 ha and grown to the local variety. The land had a flat topography and a clayey soil. Barfi and Gye Nyame farms were nearer the highway than Acquah's farm. Soil and citrus fruit samples were taken using the same procedure as in Obuasi. The citrus from the Acquah and Gye Nyame farms were of the Late Valencia variety whereas the citrus from Barfi's farm was of the local variety. The three citrus farms selected in Ejisu-Juaben were Achiaa and Agyenim's farm at New Koforidua and Janet's at Duampompo. Achiaa's farm was about 4 ha and the land was of flat topography. It is by the Kumasi-Konongo road and is about 20 km from Ejisu. The soil was very gravelly. Agyenim's farm is about 2 ha and is also by the Kumasi-Konongo road. The topography of the land is gently sloping and the caretaker resides in the farm. It also lies close to a valley bottom where rice is cultivated annually.

There is no industrial activity in the New Koforidua township. Janet's farm is about 0.8 ha and is at the CEPS barrier at Duampompo about 15 km from Ejisu. The topography of the land is flat and there is a vulcanizing shop nearby. Soil and citrus fruit samples were taken for laboratory analysis. The citrus from all three farms were of the Late Valencia variety. Three citrus farms selected in Asante Mampong were Rockson's farm at Bobeng, Acheampong's farm at Kyirimfaso and Gyasi's farm at Ninting. Rockson's farm is about 15 ha with a flat topography. It is about 15 km from Mampong and the caretaker resides in the farm. Animals are also reared in the farm. There was gari processing in the farm about two (2) years ago. There is no industrial activity in the Bobeng village. Acheampong's farm is at Kyirimfaso about 10 km from Mampong.

The topography of the land is flat and the farm is about 2 ha. There is no industrial activity in Kyirimfaso. Gyasi's farm is at Ninting about 12 km from Mampong on the Mampong -Kumasi road. The farm is about 6 ha and the topography is rolling. It lies near the main road and there is no industrial activity in Ninting. Soil and edible citrus fruit samples were taken for laboratory analysis. The citrus from all the three farms were of the Late Valencia variety.

Within each citrus farm, a plot of size 1.0 ha was demarcated for sampling. From each sampling plot, ten (10) soil cores were taken with an auger from points that were uniformly distributed across the plot in a zigzag manner. From each point, three soil layers (0-15, 15-30 and 30-45 cm) were sampled separately into three plastic buckets. Composites were obtained from each layer (depth). The soil cores in each bucket were thoroughly mixed by hand to form one composite sample and about 1.0 kg taken for laboratory analysis.

Six edible citrus fruits per tree were also taken from the middle part of the crown of the citrus trees within the plots where soil samples were taken for analysis. Four (4) trees were sampled within each sampling plot.

3.2 Laboratory Procedures

The thirty-six (36) soil samples were air-dried at room temperature and ground in a wooden mortar to pass through a 2 mm mesh sieve and stored in labelled soil bags. Sub-samples were taken from each soil sample and analysed for soil pH, organic matter, zinc, lead, manganese, copper, cadmium and iron. The citrus fruit pulp was also ashed and analysed for zinc, lead, manganese, copper, cadmium and iron.

3.2.1 Soil Analysis

The composite soil samples were air-dried at room temperature, sieved through a 2-mm mesh sieve and stored in labelled bags. Organic carbon, pH, zinc, lead, arsenic, manganese, copper, cadmium and iron were determined on each soil sample. Soil pH was determined in a 1:1 suspension of soil and distilled water using a HI 9017 microprocessor pH meter.

Organic carbon was determined by a modified Walkley and Black procedure as described by Nelson and Sommers (1982). The soil heavy metals were extracted using 0.1M EDTA solution (Cottenie *et al*., 1979). In the extract, Cu, Zn, Mn, Pb, Cd and Fe were determined using atomic absorption spectrophotometer (Buck Scientific, model VGP) using air-acetylene mixture.

3.2.2 Analysis of Citrus Fruit Samples

The citrus fruit was washed and peeled. With the aid of a knife and fingers, the mesocarp was separated from the pulp (carpel + juice sac). The pulp was chopped into pieces with a stainless steel knife, put in a food blender with stainless steel cutters and homogenized and put in an oven for 72 h at 70^{o}C to dry. The samples were weighed and ground in a stainless steel mill to pass through a 1.0 mm sieve. A 0.5 g sample of the dry pulp was placed in a Kjedahl flask and 5 ml $HNO_3/HClO_3$ (1/1) mixture and 5 ml of conc. H_2SO_4 were added and digested at 360 ^{o}C until sample was clear. The sample was allowed to cool, 20 ml distilled water added and filtered into a 100 ml flask. The Kjeldahl flask was rinsed twice with 20 ml portion of distilled water which was passed through the filter into the 100 ml volumetric flask. Distilled water was added to the mark.

3.3 Statistical Analysis of Results

The results were analysed using the GenStat statistical package. ANOVA was used to determine differences between treatment means. Correlations between soil and citrus fruit heavy metal contents were also determined.

CHAPTER FOUR

4.0 RESULTS

4.1 Data of soil and citrus fruit analyses for Ejisu-Juaben municipality

The results of soil analysis for pH, organic carbon as well as extractable zinc, copper, iron, cadmium, lead and manganese for Ejisu-Juaben are presented in Table 4. Data on total heavy metal content of citrus fruit are given in Table 5.

Table 4: Properties of soil samples from Ejisu-Juaben municipality

Farm	Soil depth (cm)	pH 1:1 H_2O	Org. C (%)	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Janet	**0-**15	5.55	1.57	14.0	5.96	1.20	0.24	3.20	108.00
	15-30	5.14	0.53	7.20	4.52	0.80	0.16	2.80	100.40
	30-45	5.65	0.48	7.20	1.40	1.20	0.08	2.00	75.60
Achiaa	0-15	5.45	1.68	15.60	7.08	2.00	0.28	2.00	106.40
	15-30	4.70	0.65	24.80	5.04	1.20	0.20	0.80	88.80
	30-45	4.67	0.50	12.00	4.10	0.80	0.20	2.40	50.80
Agyenim	0-15	4.93	1.42	24.00	4.64	2.00	0.20	1.20	82.80
	15-30	4.61	0.39	10.80	3.20	0.80	0.16	2.00	20.80
	30-45	4.51	0.35	15.60	4.16	0.80	0.12	1.60	4.40

Table 5: Heavy metal content of citrus fruit from Ejisu-Juaben municipality.

Farm	Zn	Cu	Fe	Cd	Pb	Mn
			(mg/kg)			
Achiaa	56	12	180	Nd	Nd	20
Agyenim	72	24	192	Nd	Nd	20
Janet	96	32	152	Nd	4	16

Nd= not detectable (Cd < 0.005 and Pb < 0.01)

4.1.1 Soil and Citrus Fruit Zinc

The highest mean value for zinc =17.47 mg/kg (Table 4) was recorded in the soil from Achiaa's farm and was closely followed by soil from Agyenim's farm (16.80 mg/kg). The lowest value was recorded in the soil from Janet's farm (9.47 mg/kg). For the citrus fruit, the highest Zn concentration was obtained from Janet's farm (96.00 mg/kg) (Table 5) next was the Agyenim's farm (72.00 mg/kg) and the lowest was Achiaa's farm (56.00 mg/kg). This shows that zinc accumulation in citrus fruit was highest in Janet's farm followed by Agyenim and then Achiaa's farm.

4.1.2 Soil and Citrus Fruit Copper

For Cu, the highest mean value was observed in Achiaa's farm (5.41 mg/kg), followed by Agyenim's farm (4.00 mg/kg) and Janet's farm had the least value (3.96 mg/kg). For the citrus fruit, on the other hand, the highest value was recorded in Janet's farm (32.00 mg/kg), followed by Agyenim's farm (24.00 mg/kg) and the least was in Achiaa's farm (12.00 mg/kg).

4.1.3 Soil and Citrus Fruit Iron

Soil iron content was highest in Agyenim's and Achiaa's farms (1.20 mg/kg) (Table 4) and least in Janet's farm (1.06 mg/kg). The citrus fruit also had the highest Fe concentration in Agyenim's farm (192.00 mg/kg) (Table 5), followed by Achiaa's farm (180.00 mg/kg) and the least was Janet's farm (152.00 mg/kg).

4.1.4 Soil and Citrus Fruit Cadmium

Soil cadmium content was higher in Achiaa's farm (0.23 mg/kg) than in Agyenim and Janet's farms with the same value (0.16 mg/kg). The levels of Cd in the citrus fruit from all the three farms could not be detected by the AAS.

4.1.5 Soil and Citrus Fruit Lead

The highest citrus fruit Pb content was in Janet's farm (2.67 mg/kg), followed by Achiaa's farm (1.73 mg/kg) which was closely followed by Agyenim's farm (1.60 mg/kg). The citrus fruit Pb content was highest in Janet's farm (4.00 mg/kg) with no detectable levels in Achiaa and Agyenim's farms.

4.1.6 Soil and Citrus Fruit Manganese

Janet's farm had the highest concentration of soil Mn (94.70 mg/kg), followed by Achiaa's farm (82.00 mg/kg) and the least value was recorded in Agyenim's farm (36.00 mg/kg).

The citrus fruit Mn content was higher in Achiaa and Agyenim's farms (20.00 mg/kg) than Janet's farm (16.00 mg/kg)

4.2 Data of Soil and Citrus fruit Analysis for Sekyere West municipality.

The results of soil analysis for pH, organic carbon as well as extractable zinc, copper, iron, cadmium, lead and manganese from Sekyere West are presented in Table 6. Total citrus fruit heavy metal content is given in Table 7.

Table 6: Properties of soil samples for Sekyere West municipality

Farm	Soil depth (cm)	pH 1:1 H_2O	Org. C (%)	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Rockson	0-15	5.41	0.98	4.80	5.51	1.20	0.24	2.40	106.80
	15-30	5.27	0.39	13.60	4.44	1.20	0.24	1.20	103.20
	30-45	5.25	0.31	24.80	4.24	1.80	0.20	1.20	188.80
Gyasi	0-15	5.47	1.57	11.20	3.28	1.60	0.20	1.60	98.00
	25-30	4.56	0.80	23.60	2.76	1.20	0.16	1.60	49.20
	30-45	4.30	0.80	21.60	3.20	1.20	0.16	2.00	38.40
Acheampong	0-15	5.42	1.35	8.40	3.84	1.20	0.16	2.80	106.80
	15-30	3.98	0.72	23.20	2.60	1.20	0.20	3.20	101.60
	30-45	4.02	0.39	8.80	2.68	1.80	0.20	2.00	35.20

Table 7: Total heavy metal content of citrus fruit from Sekyere West.

Farm	Zn	Cu	Fe	Cd	Pb	Mn
			(mg/kg)			
Rockson	116	28	168	2	6	20
Gyasi	124	72	352	2	8	16
Acheampong	112	8	240	2	10	24

4.2.1 Soil and Citrus Fruit Zinc

Gyasi's farm recorded the highest soil Zn concentration (18.80 mg/kg), followed by Rockson's farm (14.40 mg/kg) and Acheampong's farm (13.47 mg/kg) (Table 6). The citrus fruit from Gyasi's farm had the highest concentration of Zn content (124.00 mg/kg), followed by Rockson's farm (116.00 mg/kg) and Acheampong's farm (112.00 mg/kg) (Table 7). These show the high mobility of Zn in these soils and its accumulation in the orange from the soil.

4.2.2 Soil and Citrus Fruit Copper

Soil Cu content was highest in Rockson's farm (4.73 mg/kg), followed by Gyasi's farm (3.08 mg/kg) with Acheampong's farm recording the least (2.04 mg/kg). Gyasi's farm had the highest citrus fruit Cu content, (72.00 mg/kg) next was Rockson's farm (28.00 mg/kg) and Acheampong's farm was the least (8.00 mg/kg).

4.2.3 Soil and Citrus Fruit Iron

Iron content was higher for soils of Acheampong's (1.40 mg/kg) and Rockson's farm (1.40 mg/kg) than Gyasi's farm (1.33 mg/kg). The highest concentration of Fe in citrus fruit was in Gyasi's farm (352.00 mg/kg), followed by fruits from Acheampong's farm (240.00 mg/kg) and Rockson's farm (168.00 mg/kg). This shows the high accumulation of Fe in the citrus fruits of these farms, particularly for Gyasi.

4.2.4 Soil and Citrus Fruit Cadmium

Rockson's farmhad the highest soil Cd content (0.23 mg/kg), followed by Gyasi's farm (0.17 mg/kg) and Acheampong's farm (0.15 mg/kg). The citrus fruits from the three had the same Cd concentration of 2.00 mg/kg. This indicates the low accumulation of Cd in the soils but high accumulation in the citrus fruit.

4.2.5 Soil and Citrus Fruit Lead

Acheampong's farm (2.67 mg/kg) had the highest soil lead content, next was Gyasi's farm (1.73 mg/kg) which is closely followed by Rockson's farm (1.60 mg/kg). Acheampong's farm (10.00 mg/kg) had the highest citrus fruit lead content, with Gyasi's farm (8.00 mg/kg) and Rockson's farm (6.00 mg/kg) following in that order. Again lead is accumulated in the citrus fruit.

4.2.6 Soil and Citrus Fruit Manganese

Manganese soil content was highest in Rockson's farm (132.93 mg/kg) with Acheampong's farm (81.2 0mg/kg) and Gyasi's farm (61.87 mg/kg) following in that order (Table 6).

The citrus fruit Mn content was highest in Acheampong's farm (24.00 mg/kg), followed by Rockson's farm (20.00 mg/kg) and Gyasi's farm (16.00 mg/kg) (Table 7).

4.3 Data of Soil and Citrus Fruit Analyses for Asante Akim North

The results of soil analysis for pH, organic carbon as well as extractable zinc, copper, iron, cadmium, lead and manganese for soils from Asante Akim North are presented in Table 8. Data on total citrus fruit analysis are presented in Table 9.

Table 8: Properties of soil samples for Asante Akim North municipality

Farm	Soli depth (cm)	pH 1:1 H_20	Org. C (%)	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Acquah	0-15	4.21	1.72	16.00	6.28	1.60	0.16	3.20	106.40
	15-30	4.39	0.65	16.00	5.84	1.20	0.12	2.80	105.60
	30-45	3.75	0.41	16.00	4.56	0.80	0.24	3.20	76.80
Barfi	0-15	4.39	0.50	15.20	2.60	1.20	0.24	2.00	93.60
	15-30	5.34	0.17	13.60	1.56	0.80	0.16	1.60	75.20
	30-45	4.32	0.09	20.40	1.80	0.80	0.12	2.00	46.00
Gye Nyame	0-15	5.72	1.72	26.00	8.36	8.36	0.32	2.40	106.80
	15-30	5.67	0.53	28.40	5.48	5.48	0.12	3.60	63.60
	30-45	4.60	0.35	16.80	6.40	6.40	0.12	3.20	94.80

Table 9: Total heavy metal content of citrus fruit from Asante Akim North.

Farm	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Acquah	108	20	304	1	12	20
Gye Nyame	116	8	284	2	8	24
Barfi	120	52	372	2	8	8

4.3.1 Soil and Citrus Fruit Zinc

Soil zinc content was higher in Gye Nyame's farm (23.33 mg/kg) than both Barfi and Acquah's farms with similar value (16.00 mg/kg). The citrus fruit zinc content was highest in Barfi's farm (120.00 mg/kg), followed by Gye Nyame's farm (116.00 mg/kg) and Acquah's farm (108 mg/kg).

4.3.2 Soil and Citrus Fruit Copper

Gye Nyame's farm had the highest copper content (6.75 mg/kg), followed by Acquah's farm (5.56 mg/kg) and Barfi's farm (1.98 mg/kg) (Table 8).

The citrus fruit from Barfi's farm had the highest Cu content (52.00 mg/kg). Acquah's farm (20.00 mg/kg) followed with the lowest being Gye nyame's farm (8.00 mg/kg) (Table 9). These values again show the high bioavailability and concentration of Cu in the citrus fruits of Asante Akim North municipality with Barfi as the best illustration due to the low concentration in the soil and high concentration in the fruit.

4.3.3 Soil and Citrus Fruit Iron

Soil iron content was highest in Gye Nyame's farm (1.33 mg/kg), followed by Acquah's farm (1.20 mg/kg) and Barfi's farm (0.93 mg/kg). The citrus fruits from Barfi's farm had the highest Fe content (372.00 mg/kg), followed by Acquah's farm (304.00 mg/kg) and Gye nyame's farm (284.00 mg/kg). These values again depict the high bioavailability and concentration of Fe in the citrus fruits of these farms.

4.3.4 Soil and Citrus Fruit Cadmium

Soil cadmium content was 0.17 mg/kg in both Acquah and Barfi's farms, and was 0.13 mg/kg in Gye Nyame's farm. The citrus fruits cadmium content was higher in Gye Nyame and Barfi's farms (2.00 mg/kg) than in Acquah's farm (1.00 mg/kg). These values indicate the low concentration of Cd in the soils of these farms.

4.3.5 Soil and Citrus Fruit Lead

Soil lead contents of Acquah and Gye Nyame's farms (3.06 mg/kg) were higher than Barfi's farm (1.87 mg/kg). The citrus fruit lead content was higher in Acquah's farm (12.00 mg/kg) than both Gye Nyame and Barfi's farms (8.00 mg/kg).

4.3.6 Soil and Citrus Fruit Manganese

Highest soil concentration of Mn was observed in Acquah's farm (96.27 mg/kg), followed by Gye nyame's farm (88.40 mg/kg) and Barfi's farm (71.60 mg/kg). The citrus fruit Mn content was highest in Gye nyame's farm (24.00 mg/kg), followed by Acquah's farm (20.00 mg/kg) and least in Barfi's farm (8.00 mg/kg).

4.4 Data of Soil and Citrus Fruit Analyses for Obuasi.

The results of soil analysis for pH, organic carbon as well as extractable zinc, copper, iron, cadmium, lead and manganese for Obuasi are presented in Table 10. Data on total citrus fruit heavy metal content is given in Table 11.

Table 10: Properties of soil samples from Obuasi municipality

Farm	Soil depth (cm)	pH 1:1 H_2O	Org. C(%)	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Sasu	0-15	4.93	1.98	26.80	4.24	13.20	0.20	2.00	31.20
	15-30	6.62	1.04	24.80	5.04	3.60	0.16	2.40	2.40
	30-45	6.70	0.72	28.00	5.32	1.60	0.20	2.40	78.40
Apitikooko	0-15	4.16	1.98	18.00	3.00	3.60	0.20	1.60	36.01
	15-30	4.08	1.13	28.00	3.76	3.20	0.20	1.60	4.00
	30-45	4.07	0.80	29.20	3.60	2.40	0.20	2.40	7.60
Wioso	0-15	3.84	1.24	28.40	5.96	1.60	0.20	2.80	75.60
	15-30	5.84	0.52	24.00	3.72	0.80	0.16	9.60	14.40
	30-45	6.68	0.52	21.60	5.60	0.80	0.12	2.00	14.40

Table 11: Total heavy metal content of citrus fruit for Obuasi municipality.

Farm	Zn	Cu	Fe	Cd	Pb	Mn
			(mg/kg)			
Sasu	144	20	208	Nd	4	12
Apitikooko	172	24	300	2	12	28
Wioso	96	40	260	2	10	12

Nd= not detectable (< 0.005 mg/kg)

4.4.1 Soil and Citrus Fruit Zinc

The highest soil Zn content was in Sasu's farm (26.53 mg/kg); next was Apitikooko's farm (25.06 mg/kg) which was followed closely by Wioso's farm (24.67 mg/kg) (Table 10).

The citrus fruits from Apitikooko's farm had the highest Zn content (172.00 mg/kg), followed by Sasu's farm (144.00 mg/kg) and Wioso's farm (96.00 mg/kg) (Table 11).

The high mobility of Zn in the soil and accumulation in the citrus fruit was observed.

4.4.2 Soil and Citrus Fruit Copper

For soil Cu, the highest level was observed in Wioso's farm (5.07 mg/kg), followed by Sasu's farm (4.87 mg/kg) and Apitikooko's farm (3.45 mg/kg). The highest Cu concentration in fruits was obtained in Wioso's farm (40.00 mg/kg), followed by Apitikooko's farm (24.00 mg/kg) and Sasu's farm (20 .00 mg/kg).

4.4.3 Soil and Citrus Fruit Iron

The highest soil Fe was in Sasu's farm (6.13 mg/kg), with Apitikooko's farm (3.07 mg/kg) and Wioso's farm (1.07 mg/kg) following in that order. The highest citrus fruit Fe content was in Apitikooko's farm (300.00 mg/kg), followed by Wioso (260.00 mg/kg) and Sasu's farm (208.00 mg/kg). High accumulation of Fe in the citrus fruit was observed.

4.4.4 Soil and Citrus Fruit Cadmium

Cadmium level was highest in Apitikooko's farm (0.20 mg/kg), followed by Sasu's farm (0.19 mg/kg) and Wioso's farm (0.16 mg/kg). The citrus fruit Cd content was highest at Wioso (2.00 mg/kg), followed by Apitikooko's farm (2.00 mg/kg) and Sasu's farm (not detectable).

4.4.5 Soil and Citrus Fruit Lead

Wioso's farm (4.80 mg/kg) had the highest soil lead concentration (0.23 mg/kg), next was Sasu's farm (2.27 mg/kg) and Apitikooko's farm (1.87 mg/kg). The citrus fruit analysis had the highest lead content in Apitikooko's farm (12.00 mg/kg), followed by Wioso's farm (10.00 mg/kg) and Sasu's farm (4.00 mg/kg) had the lowest.

4.4.6 Soil and Citrus Fruit Manganese

For soil Mn, Sasu's farm had the highest level (62.53 mg/kg), followed by Wioso's farm (34.80 mg/kg) and Apitikooko's farm (15.87 mg/kg) (Table 10). Citrus fruit Mn was highest in

Apitikooko's farm (28.00 mg/kg), followed by both Wioso's farm (12 mg/kg) and Sasu's farm (12 mg/kg) (Table 11). The results show accumulation of Mn in soils of the study site.

4.5 COMPARISON OF HEAVY METAL LEVELS IN THE SELECTED MUNICIPALITIES OF GHANA

4.5.1 Soil and Citrus Fruit Zinc Content

The highest mean soil Zn content (Table 12) was in Obuasi (25.43 mg/kg) next was Asante Akim North (18.70 mg/kg) while Ejisu-Juaben (16.20 mg/kg) and Sekyere West (15.10 mg/kg) followed in that order (Fig. 2). There was no significant difference between values obtained in Ejisu-Juaben and Sekyere West as well as Ejisu-Juaben and Asante Akim North. Significant differences were however obtained for all other comparisons (Table 15). The highest mean citrus fruit Zn content (Table 13) was in Obuasi (140.67 mg/kg) followed by Sekyere West (117.30 mg/kg). Asante Akim North (114.70 mg/kg) was the next and Ejisu-Juaben (74.70 mg/kg) had the lowest (Fig. 3). The least significant differences of means (2.49) were significant for all possible comparison except for Asante Akim North and Sekyere West.

Table 12: Comparison of mean soil metal levels in the selected municipalities

District	Zn	Cu	Fe (mg/kg)	Cd	Pb	Mn
Obuasi	25.43 a	4.50 a	3.47 a	0.18 a	3.00 a	32.20 a
Asante Akim North	18.70 b	4.80 a	1.07 b	0.17 a	2.70 a,b	85.43 b
Ejisu-Juaben	16.20 b,c	4.43 a	1.30 b	0.18 a	2.00 b	70.90 c
Sekyere West	15.10 c	3.63 a	1.37 b	0.19 a	2.03 b	90.90 d
LSD	3.23	1.24	0.61	0.03	0.85	4.04

LSD= Least significant difference

Values with similar alphabet are not significantly different

Table 13: Comparison of mean citrus fruit metal levels in the selected municipalities

District	Zn	Cu	Fe	Cd	Pb	Mn
			(mg/kg)			
Obuasi	140.67 a	28.00 a	256.00 a	1.33 a,b	8.70 a	17.33 a
Asante Akim North	114.70 b	26.67 a,b	320.00 b	1.67 a	9.30 a	16.00 a
Ejisu-Juaben	74.70 c	22.67 b	174.70 c	0.00 b	1.30 b	18.67 a
Sekyere West	117.30 b	36.00 c	253.30 a	2.00 a	8.00 a	20.00 a
LSD	6.10	4.48	11.40	1.37	3.94	6.39

LSD= Least significant difference

Values with similar alphabet are not significantly different

Table 14: Correlation Analysis between soil and citrus fruit metals in the Municipalities

HEAVY METAL	CORRELATION COEFFICIENT (r)/MUNICIPALITY			
	Ejisu-Juaben	Asante Akim North	Obuasi	Sekyere West
Cadmium	0.00	0.50	-0.28	-0.87
Lead	0.99	0.50	0.15	0.90
Manganese	-0.67	0.85	-0.99	0.27
Iron	0.00	-0.85	-0.66	-0.92
Zinc	-0.83	0.23	0.35	0.98
Copper	0.28	-0.99	0.43	-0.22

Strong correlations are shown in figures 4,5,9,10,14,15,16,20,21,22,26 and 27.

These results confirm the high requirement of citrus for Zn. Sekyere west had a lower mean soil pH (4.85) and soil organic matter content (1.40%) than Ejisu-Juaben (5.02 and 2.18% respectively). Thus even though soil Zn level in Sekyere west was lower than Ejisu-Juaben, the fruit Zn in Sekyere west was higher than Ejisu-Juaben. There was a positive correlation ($r=0.35$, $p<0.05$) (Table 14) between soil and fruit Zn at Obuasi. Soil and fruit Zn at Sekyere West were also positively correlated ($r=0.98$, $p<0.05$) (Fig. 4). Soil and citrus fruit Zn were positively correlated ($r=0.23$, $p< 0.05$) (Table 14) at Asante Akim North. Soil and citrus fruit Zn content, however, were negatively correlated ($r=-0.83$, $p<0.05$) (Fig. 5) at Ejisu-Juaben.

The highest top soil Zn content was observed at Obuasi (29.20 mg/kg), followed by Asante Akim North (26.00 mg/kg) and both Ejisu-Juaben and Sekyere West (24.80 mg/kg) (Fig. 1).

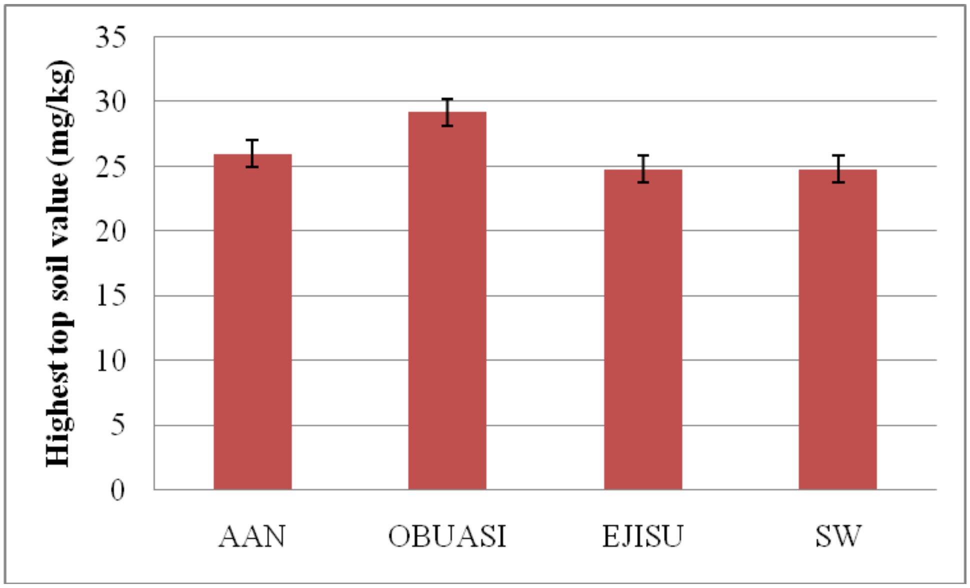

Fig. 1: Comparison of top soil zinc in the selected municipalities.

Table 15: Soil and fruit heavy metal contents (mg/kg) and least significant differences at 5% level

Source of metal	Ejisu-Juaben	Sekyere west	Obuasi	Asante Akim North	Least significant difference (5% level)
Fruit cadmium	0.00	2.00	1.33	1.67	1.37
Soil cadmium	0.18	0.19	0.18	0.18	0.03
Fruit copper	22.67	36.00	28.00	26.67	4.48
Soil copper	4.43	3.63	4.50	4.80	1.24
Fruit iron	174.70	253.30	256.00	320.00	11.40
Soil iron	1.30	1.37	3.47	1.07	0.61
Fruit manganese	18.67	20.00	17.33	16.00	6.39
Soil manganese	70.90	90.90	32.20	85.43	4.04
Fruit lead	1.33	8.00	8.67	9.33	3.94
Soil lead	2.00	2.03	3.00	2.70	0.85
Fruit zinc	74.67	117.33	140.67	114.67	6.10
Soil zinc	16.17	15.10	25.43	18.70	3.23

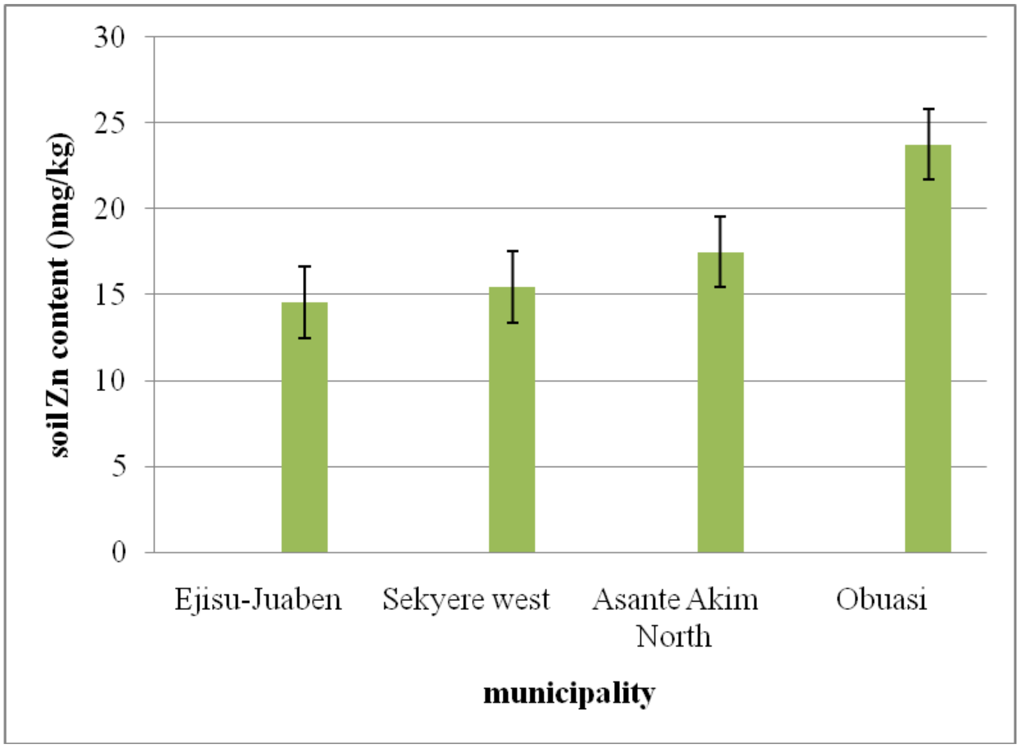

Fig. 2: Soil Zn content in selected municipalities.

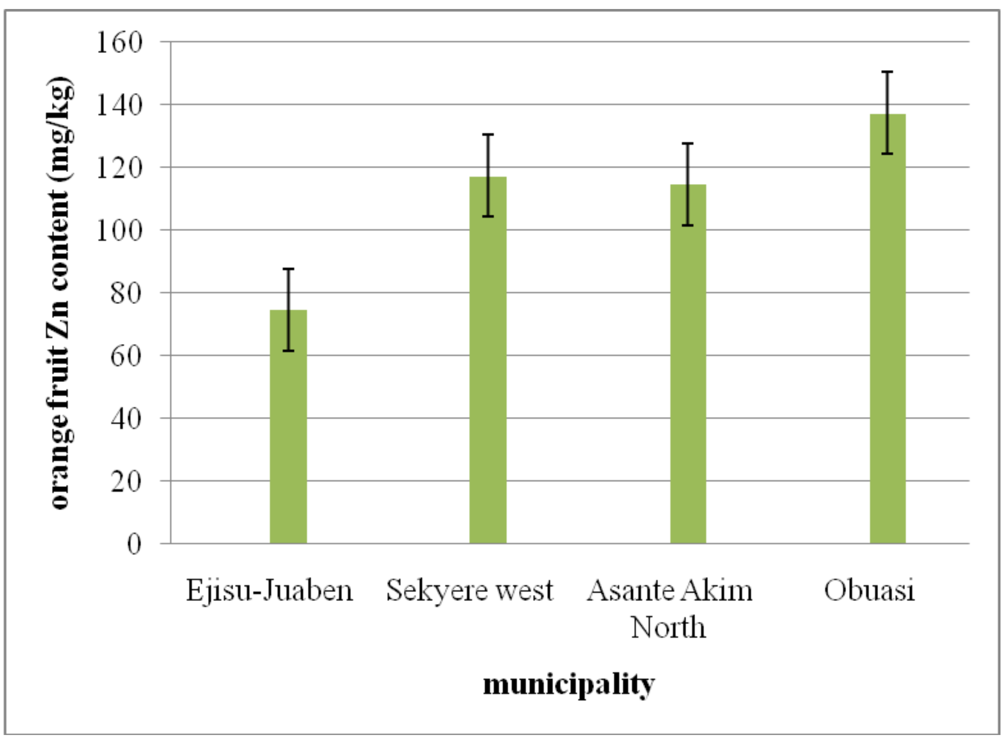

Fig. 3: Citrus fruit Zn content in selected municipalities.

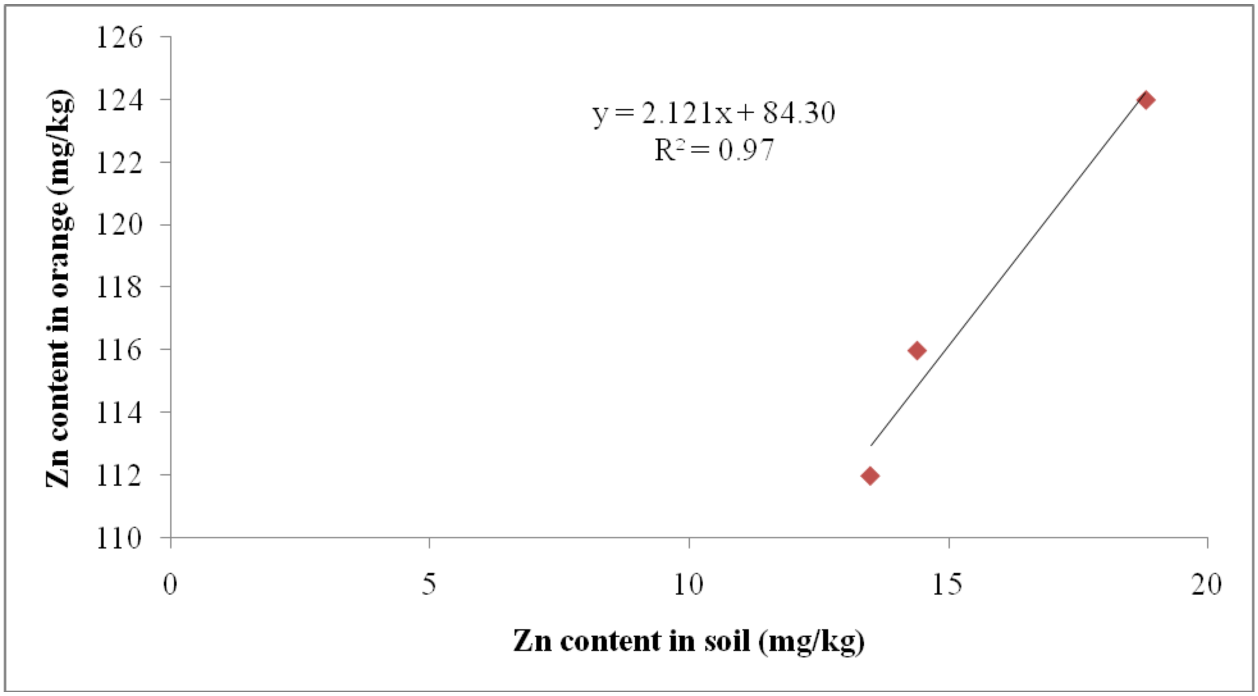

Fig. 4: Relationship between Zn content in soil and citrus fruit of Sekyere West.

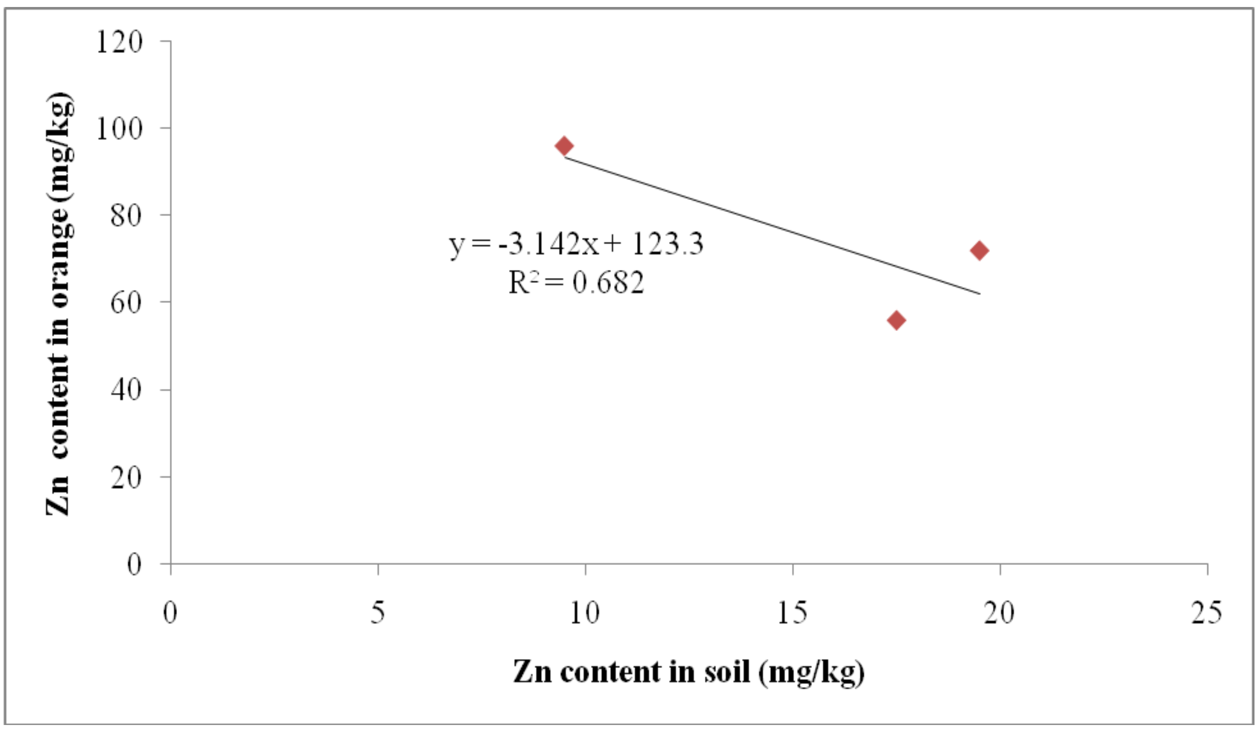

Fig. 5: Relationship between Zn content in soil and citrus fruit of Ejisu-Juaben.

4.5.2 Soil and Citrus Fruit Copper

The highest soil Cu content (Table 12) was in Asante Akim North (4.80 mg/kg) followed by Obuasi (4.50 mg/kg), Ejisu-Juaben (4.43 mg/kg) and Sekyere west (3.63 mg/kg) (Fig. 7). There were no significant differences between all possible comparisons.

Nearness to mines and use of agrochemicals were the main sources of Cu. The highest citrus fruit Cu content was in Sekyere west (36 mg/kg) followed by Obuasi (28 mg/kg), Asante Akim North (26.67 mg/kg) and Ejisu-Juaben (22.67 mg/kg) (Fig. 8). The least significant differences of means (4.48) were significant between all possible comparisons except for Obuasi and Asante Akim North as well as Asante Akim North and Ejisu-Juaben (Table 15). For the selected municipalities, Sekyere west and Asante Akim North had the lowest soil pH and accounts for the highest uptake of Cu in fruits of these municipalities. There was a positive correlation ($r=0.43$, $p<0.05$) between soil and fruit Cu content at Obuasi. Soil and fruit Cu content at Sekyere West were negatively correlated ($r=-0.22$, $p<0.05$) (Table 14). Similarly, there was a negative correlation between soil and fruit Cu content ($r=-0.99$, $p<0.05$) (Fig. 9) at Asante Akim North. Soil and fruit Cu contents at Ejisu-Juaben were, however, positively correlated ($r=0.28$, $p<0.05$) (Table 14).

The highest top soil Cu content was observed at Asante Akim North (8.36 mg/kg), followed by Ejisu-Juaben (7.08 mg/kg), Obuasi (5.96 mg/kg) and Sekyere West (5.51 mg/kg) (Fig. 6).

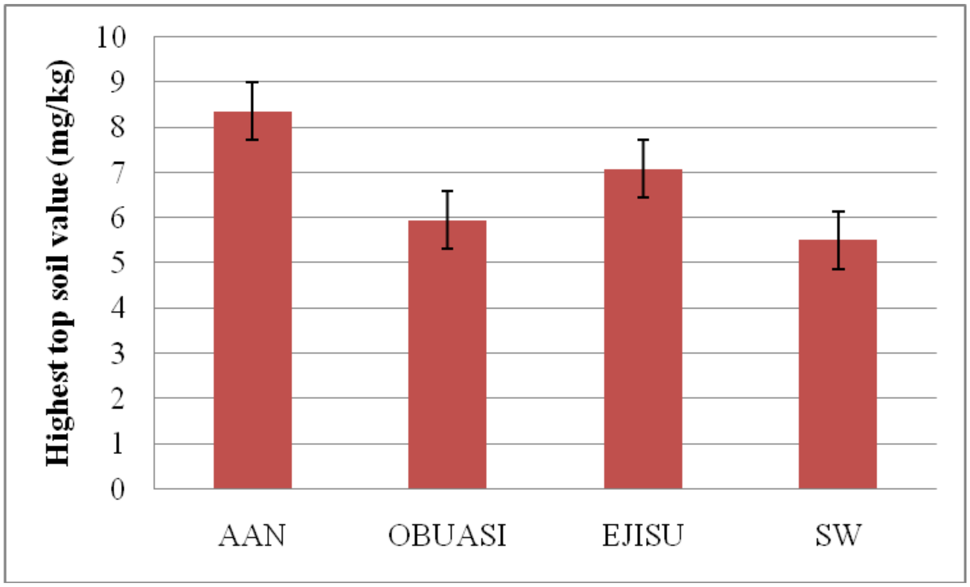

Fig. 6: Comparison of top soil Cu levels in the municipalities.

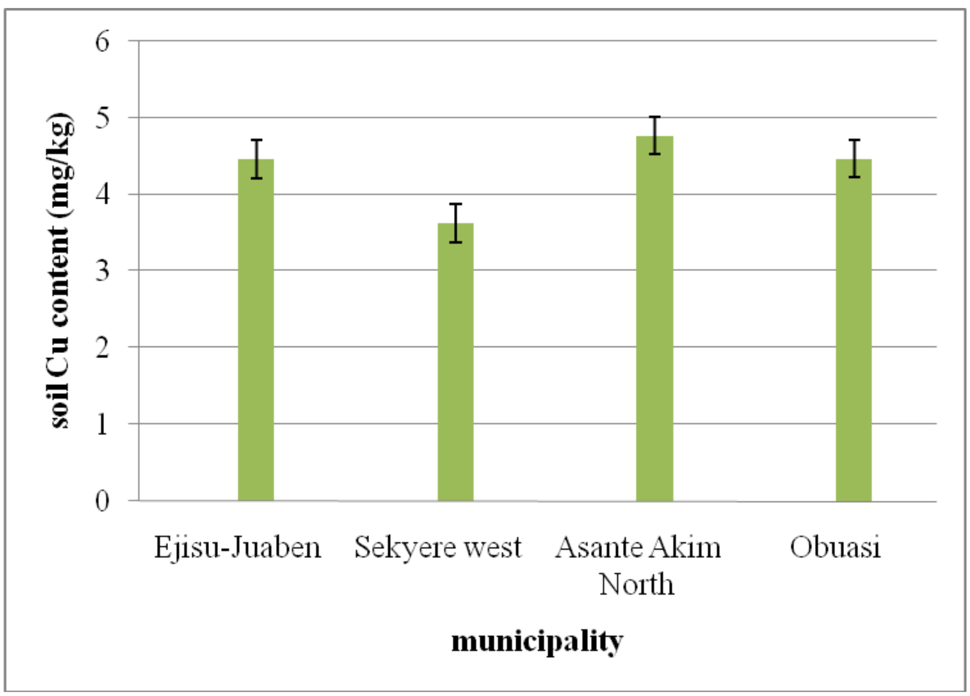

Fig. 7: Soil copper content in selected municipalities.

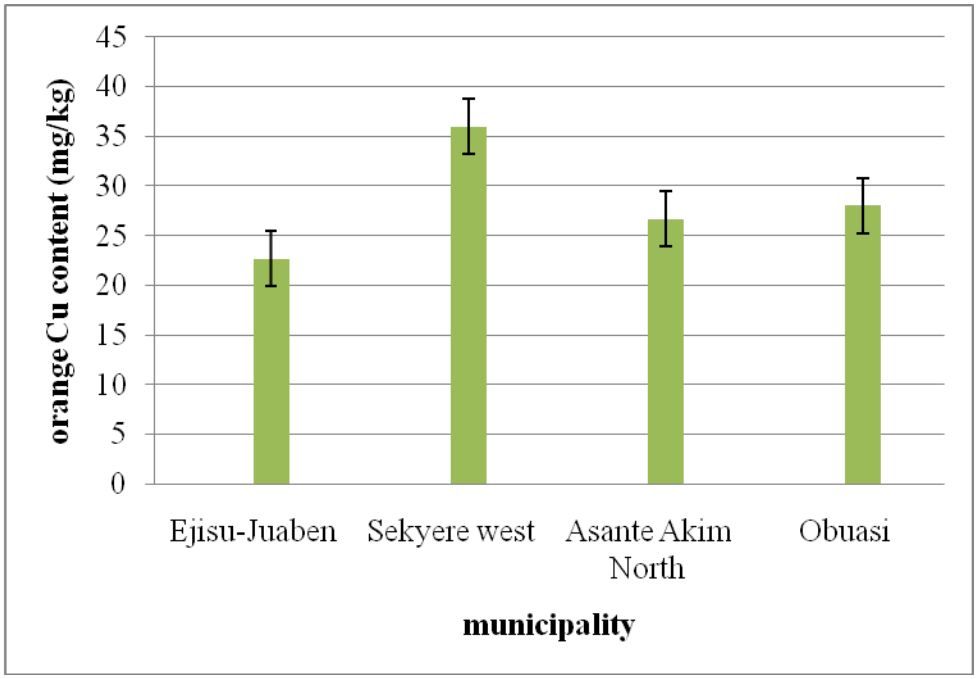

Fig. 8: Citrus fruit Cu content in selected municipalities.

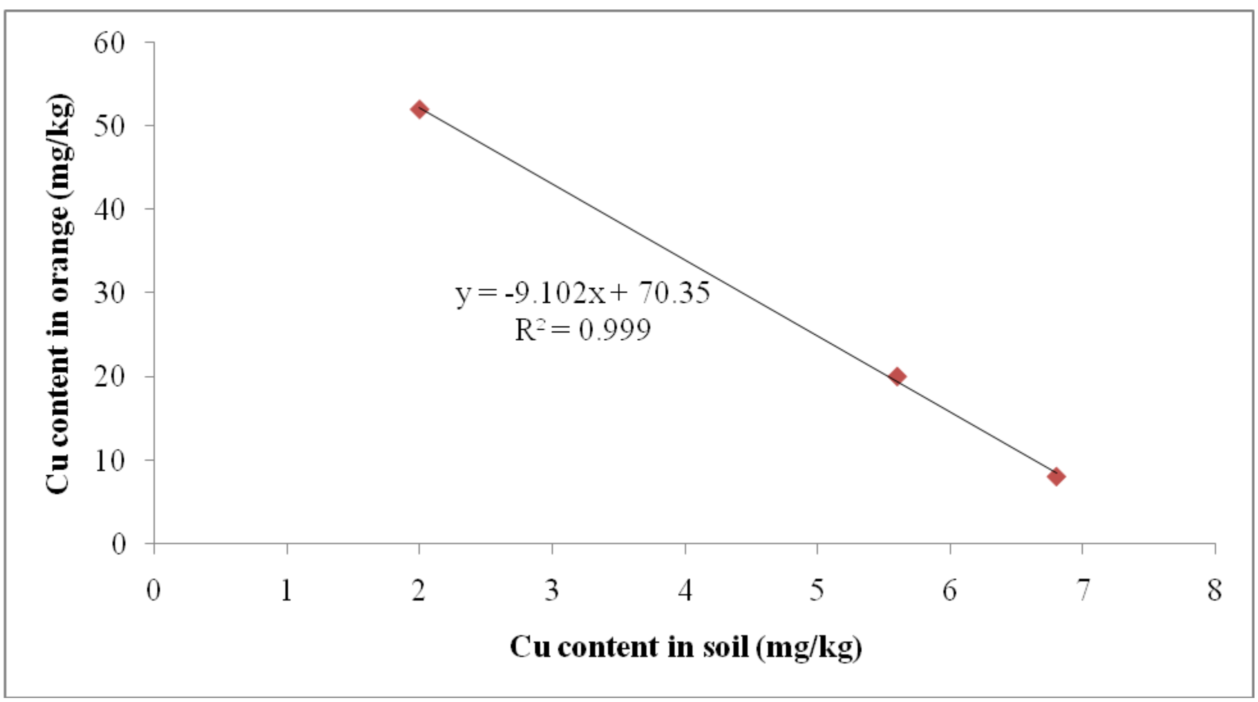

Fig. 9: Relationship between Cu content in soil and citrus fruit of Asante Akim North.

4.5.3 Soil and Citrus Fruit Cadmium

The highest soil Cd content was in Sekyere west (0.19 mg/kg) (Table 12) followed closely by Ejisu-Juaben (0.18 mg/kg) and Obuasi (0.18 mg/kg) with Asante Akim North (0.17 mg/kg) having the lowest content. The least significant differences of means (0.03) were not significantly different between all possible comparisons.

The farms in Sekyere West and Ejisu-Juaben had the highest agrochemical inputs. The highest mean citrus fruit Cd was also in Sekyere West (2.00 mg/kg), followed by Asante Akim North (1.67 mg/kg) (Table 13). The next was Obuasi (1.33 mg/kg) with Ejisu-Juaben having trace of Cd. The least significant differences of means (1.37) were significantly different between Ejisu-Juaben (0.00) and Sekyere West (2.00) farms, Asante Akim North (1.67) and Obuasi (1.33) farms. However, no significant differences were observed between all other comparisons. There was a negative correlation between soil and fruit cadmium contents ($r=-0.28$, $p<0.05$) at Obuasi (Table 14). Asante Akim North's soil and fruit Cd content were positively correlated ($r=0.50$, $p<0.05$) (Fig.10). No correlations were obtained in Sekyere West and Ejisu-Juaben municipalities.

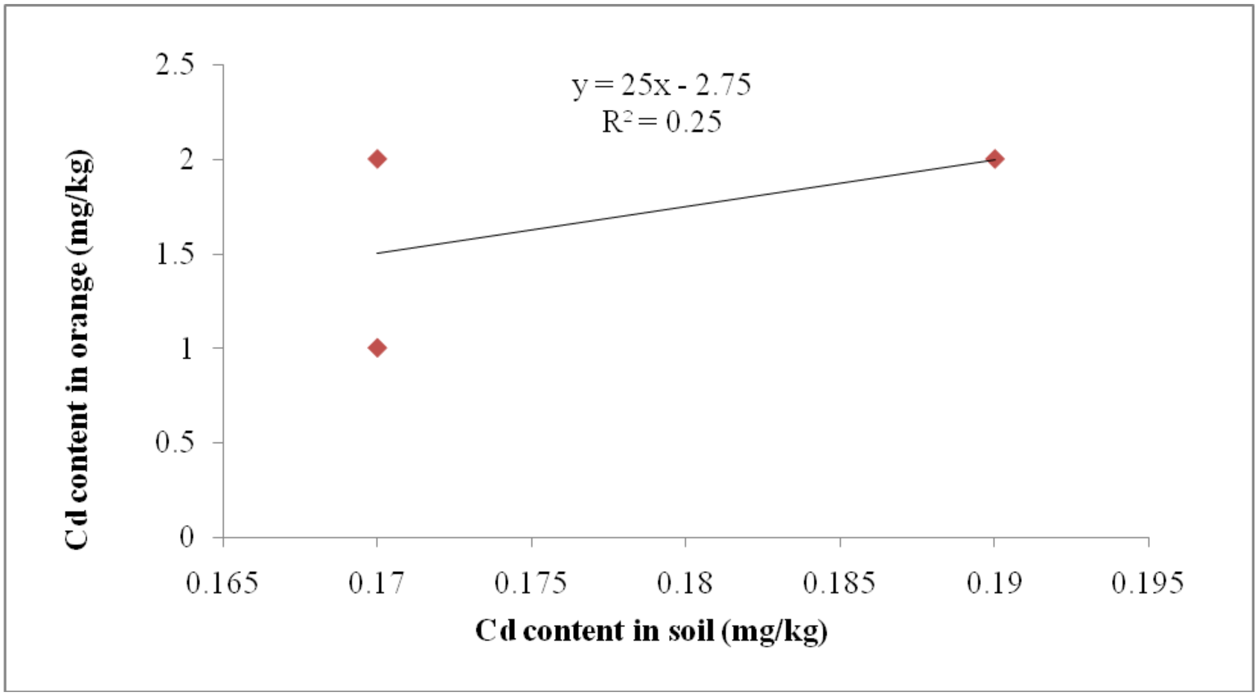

Fig. 10: Relationship between Cd content in soil and citrus fruit of Asante Akim North.

4.5.4 Soil and Citrus Fruit Iron

The highest soil Fe content was in Obuasi (3.47 mg/kg) followed by Sekyere west (1.37 mg/kg), Ejisu-Juaben (1.30 mg/kg) and Asante Akim North (1.07 mg/kg) had the lowest (Fig. 12). The least significant differences of means (0.61) were significantly different between Ejisu-Juaben (1.30) and Obuasi farms (3.47), Sekyere West (1.37) and Obuasi as well as Obuasi and Asante Akim North (1.07) farms (Table 12). However, there were no significant differences between Ejisu-Juaben and Sekyere west farms, Ejisu-Juaben and Asante Akim North farms as well as Obuasi and Asante Akim North farms. The highest fruit Fe content was in Asante Akim North (320.00 mg/kg) followed by Obuasi (256.00 mg/kg), Sekyere west (253.3 mg/kg) and Ejisu-Juaben (174.7 mg/kg) (Fig.13).

The least significant differences of means (11.40) were significant between Ejisu-Juaben (174.7) and Sekyere West (253.3) farms, Obuasi (256) and Asante Akim North (320) farms (Table 15). Also, differences between Sekyere west and Asante Akim North as well as Obuasi and Asante Akim North farms were significant. However, there was no significant difference between Sekyere west and Obuasi farms. Asante Akim North had the lowest soil Fe content but the highest citrus fruit content. This could be attributed to the low soil pH and organic matter recorded compared to the other three municipalities. Citrus fruit of Asante Akim North had the highest Fe content. There was a negative correlation (r=-0.66, p<0.05) between soil and fruit Fe contents at Obuasi (Fig.15). No correlation existed between soil and citrus fruit Fe in Ejisu-Juaben.

Soil and fruit Fe at Sekyere West were also negatively correlated (r=-0.92, p<0.05) (Fig.14). There was also a negative correlation (r=-0.85, p<0.05) at Asante Akim North (Fig.16).

The highest top soil Fe content was observed at Obuasi (3.60 mg/kg), followed by Ejisu-Juaben (2.00 mg/kg) and both Asante Akim North and Sekyere West (1.60 mg/kg) (Fig. 11).

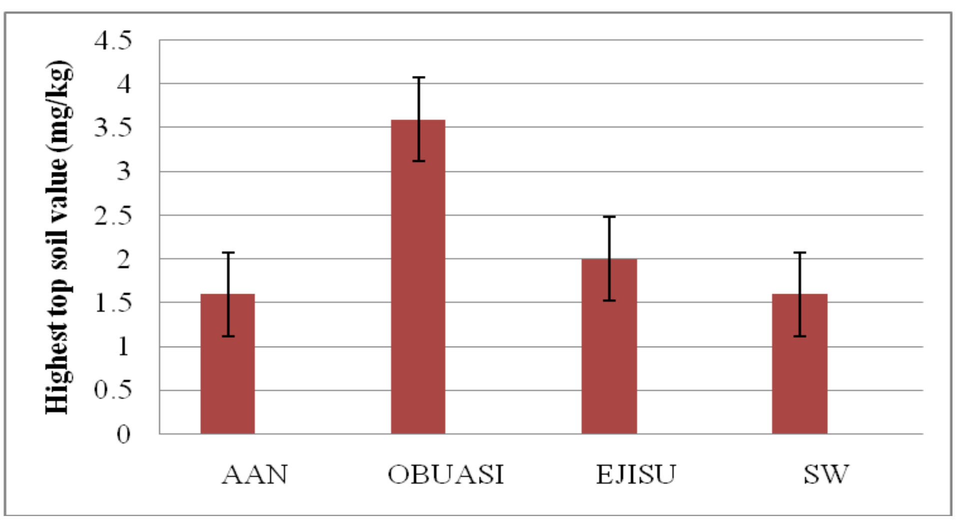

Fig. 11: Comparison of top soil Fe levels in the municipalities

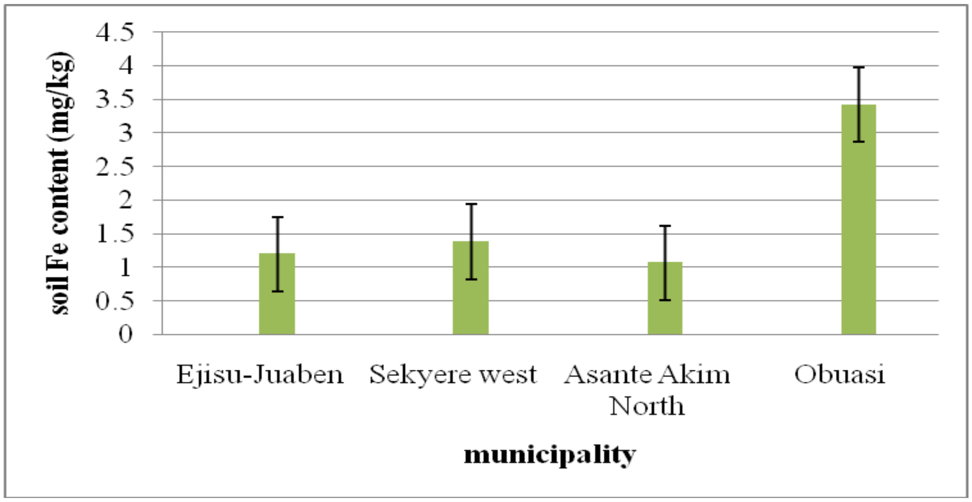

Fig. 12: Soil Fe content in selected municipalities.

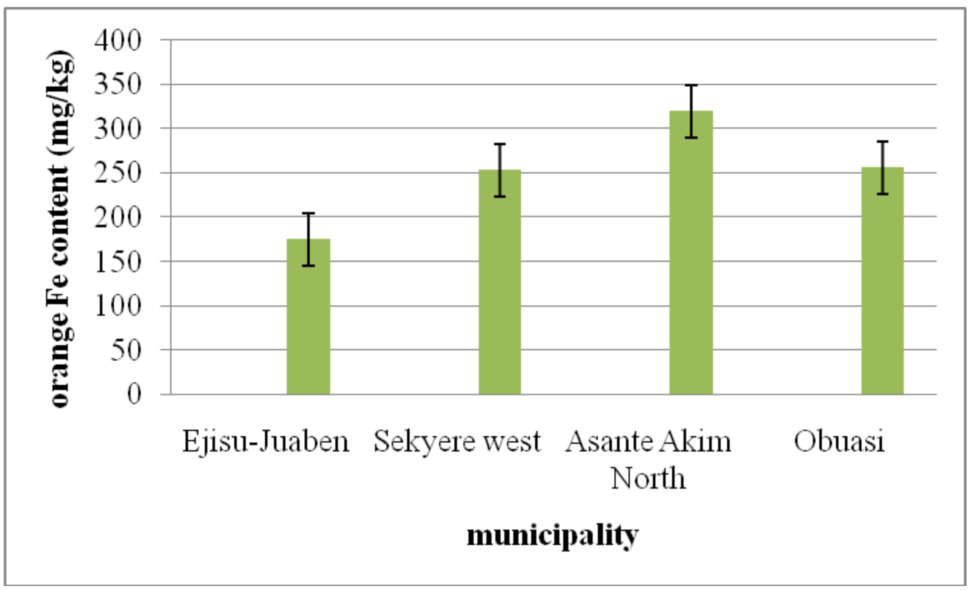

Fig. 13: Citrus fruit Fe content in selected municipalities.

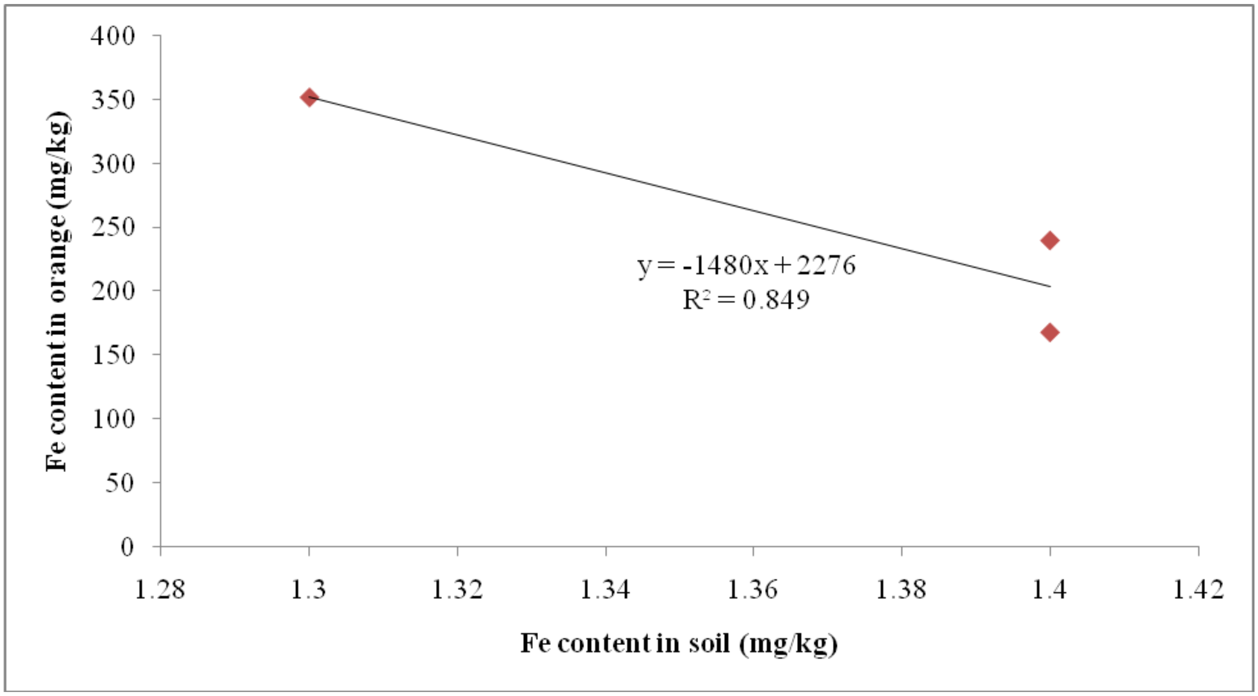

Fig. 14: Relationship between Fe content in soil and citrus fruit of Sekyere West.

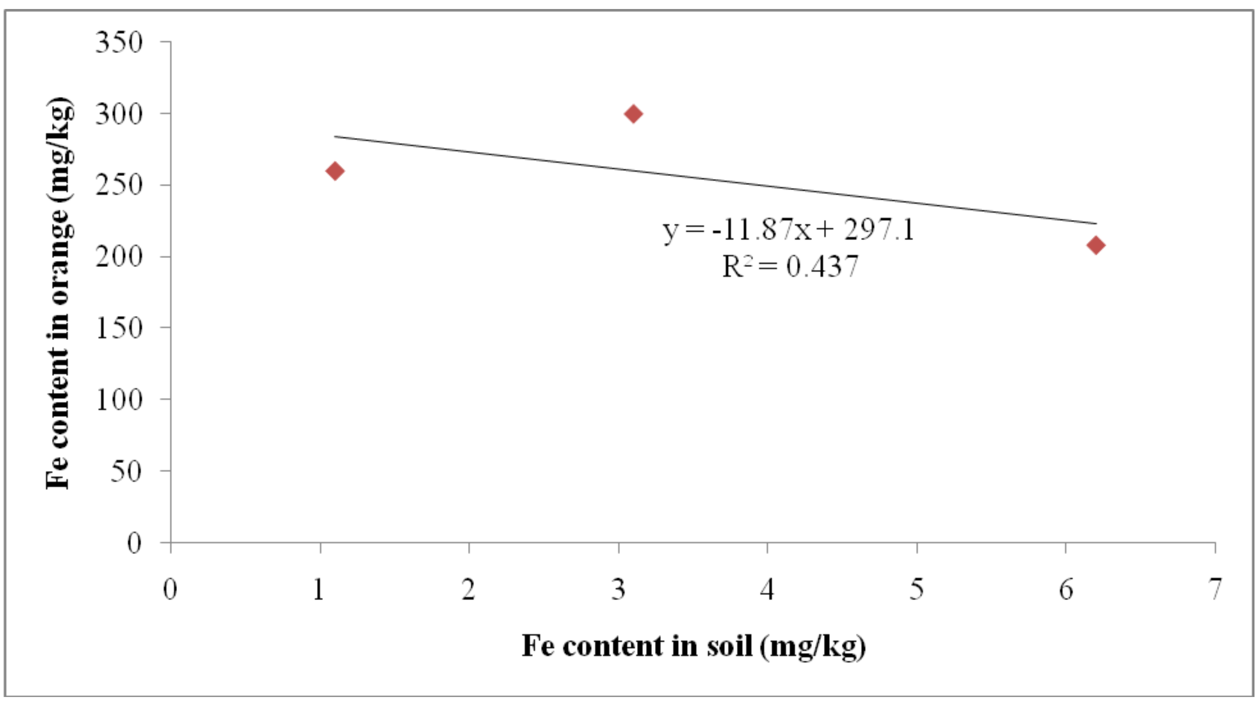

Fig. 15: Relationship between Fe content in soil and citrus fruit of Obuasi.

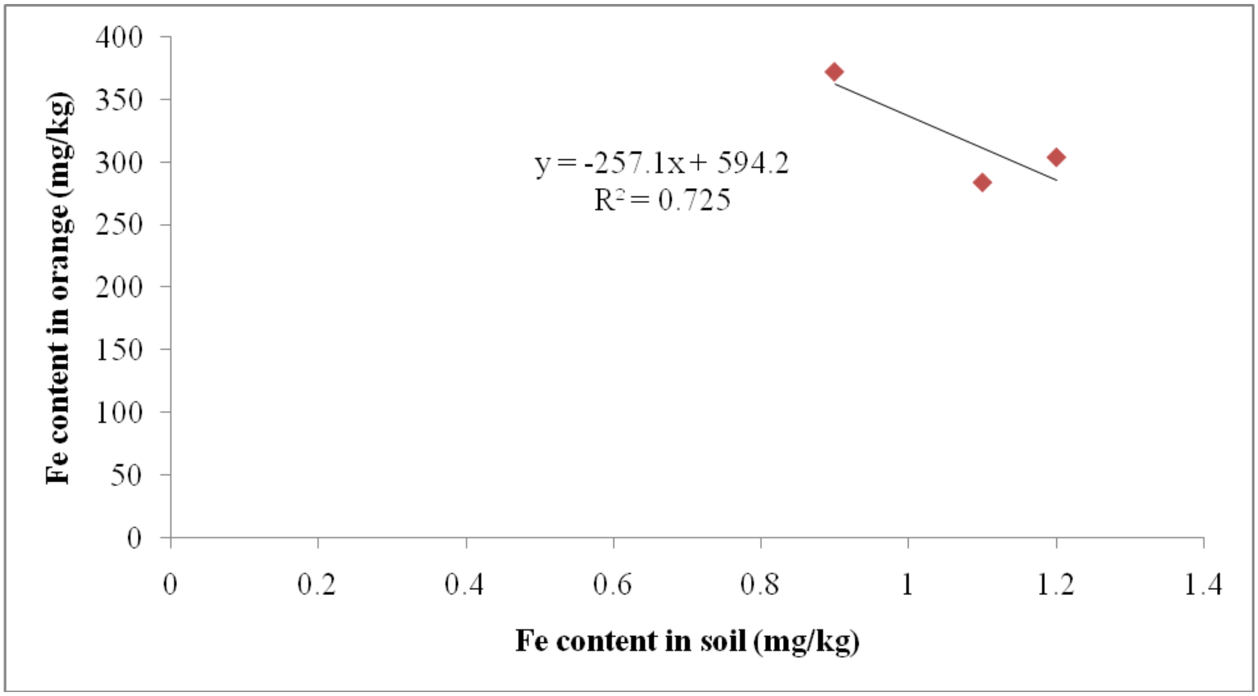

Fig. 16: Relationship between Fe content in soil and citrus fruit of Asante Akim North.

4.5.5 Soil and Citrus Fruit Lead

The highest soil Pb content was in Obuasi (3.00 mg/kg). Asante Akim North (2.70 mg/kg) had the next highest, followed by Sekyere West (2.03 mg/kg) and Ejisu-Juaben (2.00 mg/kg) (Fig. 18). There were significant differences between Pb contents in the Ejisu-Juaben (2.00) and Obuasi farms (3.00) as well as Sekyere West (2.03) and obuasi farms (3.00). (Table 15). However, there were no significant differences in soil Pb contents between all other comparisons. The highest citrus fruit Pb (Table 13) was in Asante Akim North (9.30 mg/kg) followed by Obuasi (8.70 mg/kg), Sekyere West (8.00 mg/kg) and Ejisu-Juaben (1.30 mg/kg) (Fig. 19).

There were significant differences between Ejisu-Juaben (1.33 mg/kg) and Sekyere West (8.00 mg/kg), Ejisu –Juaben and Obuasi (8.67 mg/kg) as well as Ejisu-Juaben and Asante Akim North (9.33 mg/kg). However, there were no significant differences between all other comparisons. Asante Akim North had the lowest soil pH (4.71) compared to Obuasi (5.21) which had the highest.

The highest concentration of Pb in citrus fruit was in Asante Akim North. Soil and fruit lead contents at Obuasi had a positive correlation ($r=0.15$, $p<0.05$) (Table 14). As the Pb content in the soil increased, the fruit content also increased at Sekyere West district ($r=0.90$, $p<0.05$) (Fig.20). The soil and citrus fruit Pb content at Asante Akim North had a positive correlation ($r=0.50$, $p<0.05$) (Fig. 22). Soil and fruit Pb contents at Ejisu-Juaben (Fig. 21) were also positively correlated ($r=0.99$, $p<0.05$).

The highest top soil Pb content was observed at Asante Akim North and Ejisu-Juaben (3.20 mg/kg), followed by both Obuasi and Sekyere West (2.80 mg/kg) (Fig. 17).

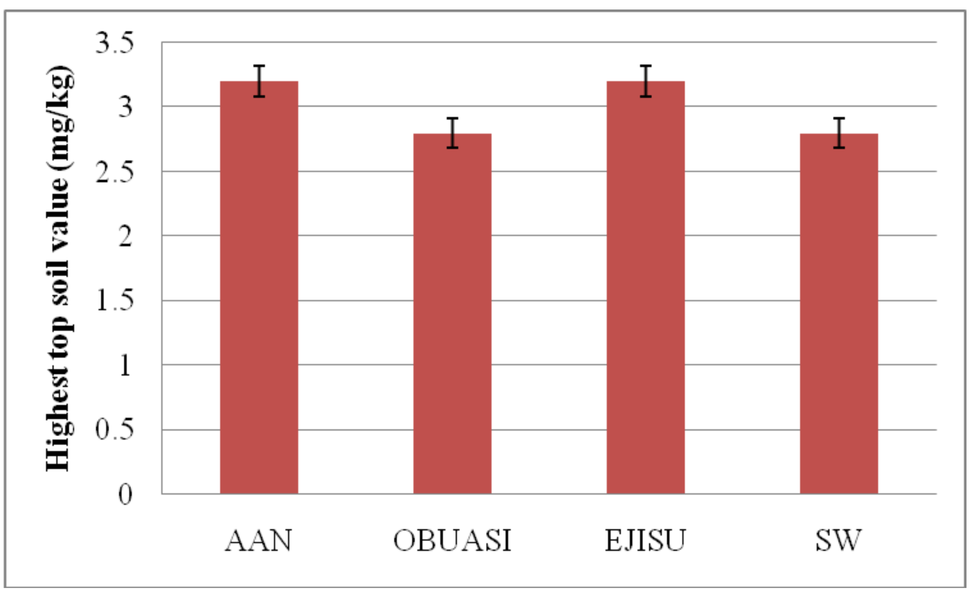

Fig. 17: Comparison of top soil Pb levels in the municipalities.

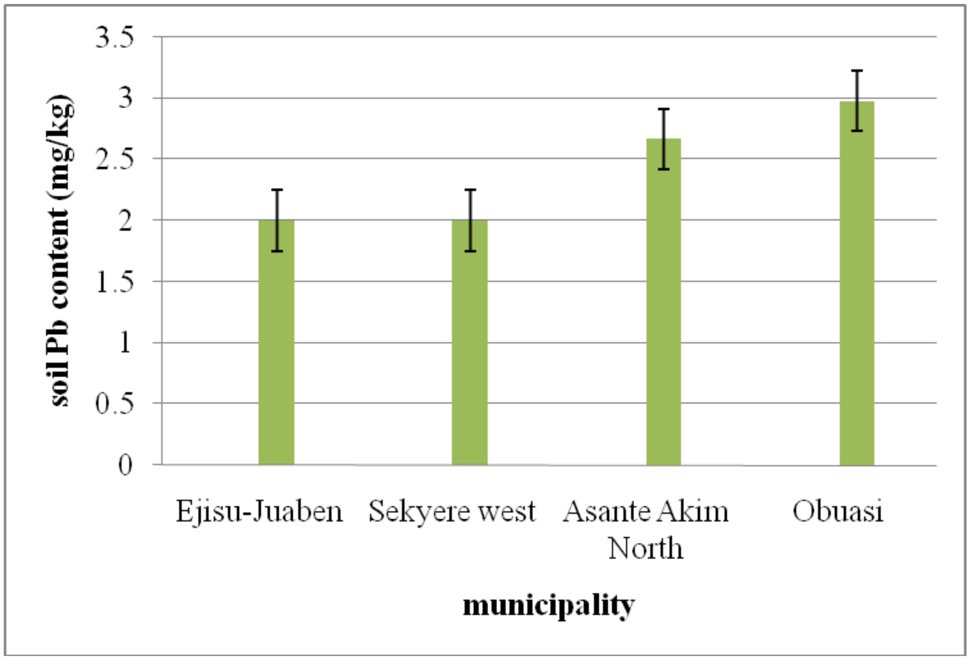

Fig. 18: Soil Pb content in selected municipality.

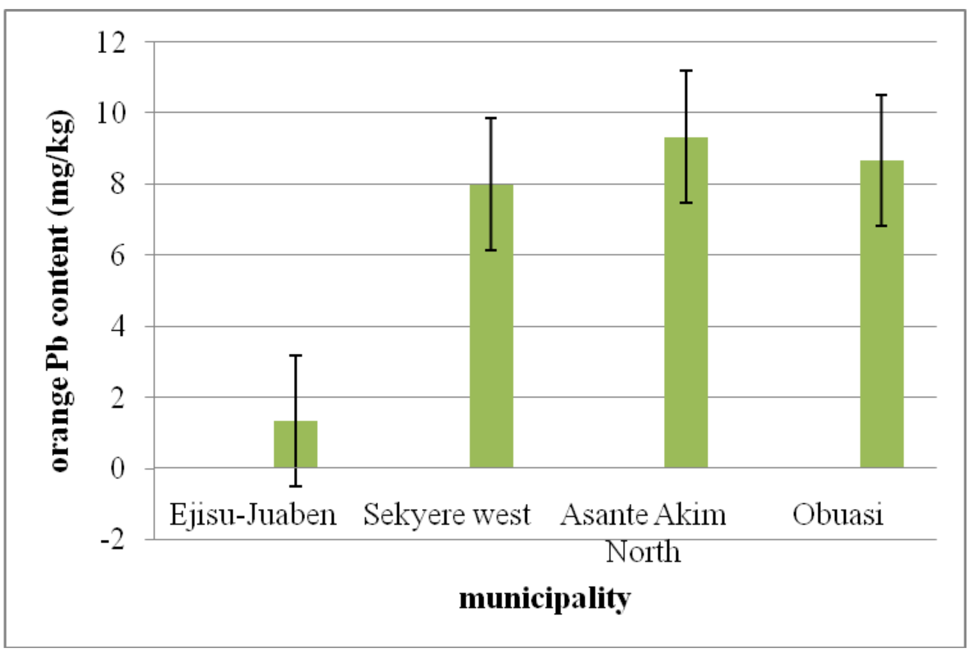

Fig. 19: Citrus fruit Pb content in selected municipalities.

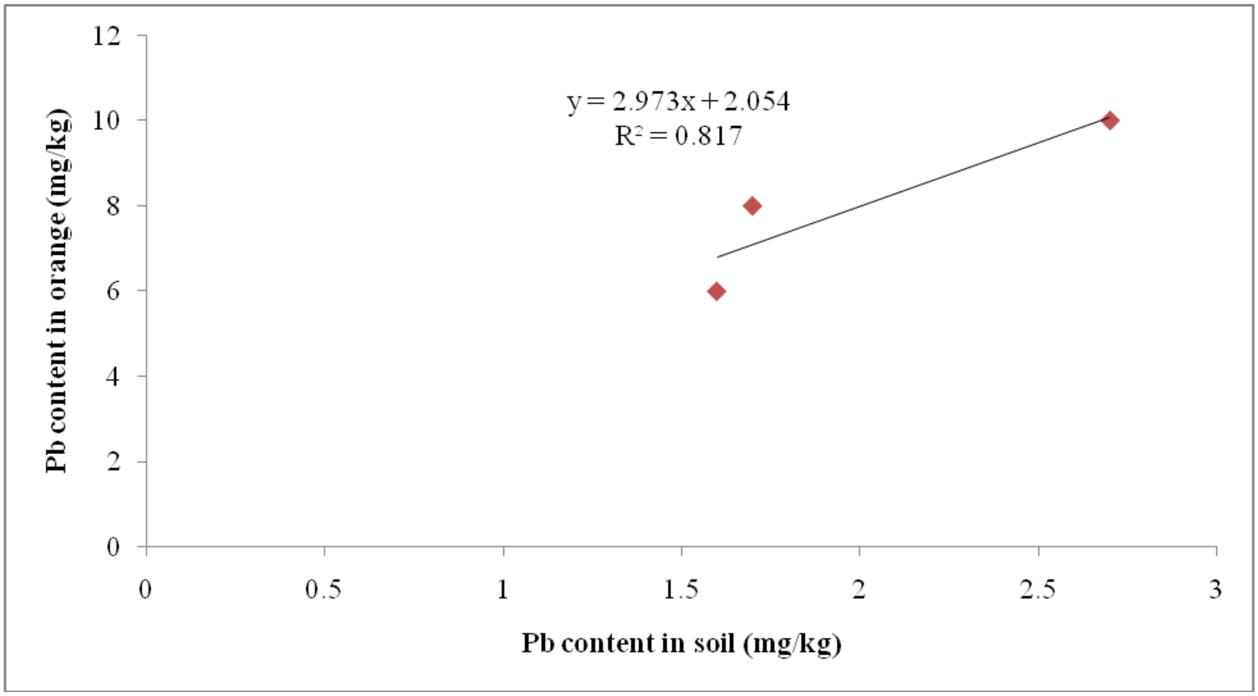

Fig. 20: Relationship between Pb content in soil and citrus fruit of Sekyere West.

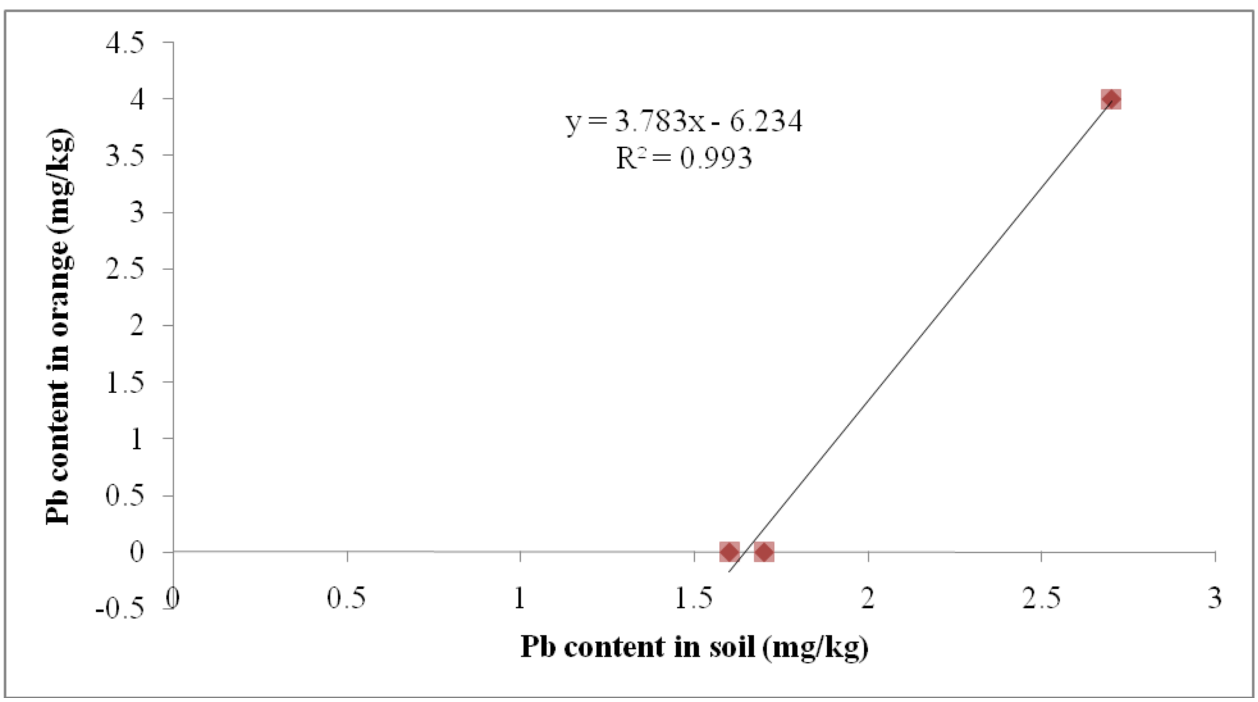

Fig. 21: Relationship between Pb content in soil and citrus fruit of Ejisu-Juaben.

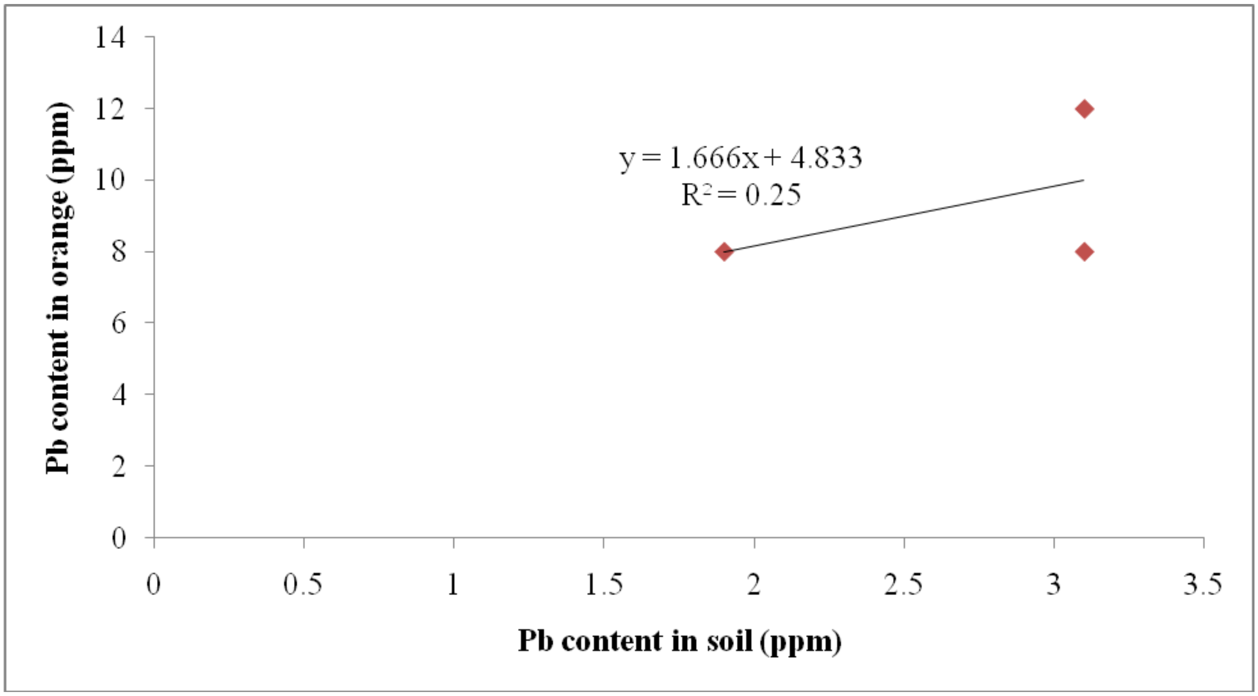

Fig. 22: Relationship between Pb content in soil and citrus fruit of Asante Akim North.

4.5.6 Soil and Citrus Fruit Manganese

The highest mean soil Mn was in Sekyere west (90.90 mg/kg) followed by Asante Akim North (85.43 mg/kg), Ejisu-Juaben (70.90 mg/kg) and Obuasi (32.20) (Fig. 24). There were significant differences between Ejisu-Juaben (70.90) and Obuasi (32.20), Ejisu and Sekyere West farms (90.90), Ejisu and Konongo farms (85.43), Sekyere West and Obuasi farms, Sekyere West and Asante Akim North farms as well as Obuasi and Asante Akim North farms. The highest mean citrus fruit Mn level was in Sekyere west (20.00 mg/kg), followed by Ejisu-Juaben (18.67 mg/kg), Obuasi (17.33 mg/kg) and Asante Akim North (16.00 mg/kg) (Fig. 25). Sekyere West had the highest soil Mn content as well as the highest citrus fruit content. Thus, the higher the soil Mn content, the higher the citrus fruit content. No significant differences were observed between all selected farms. Asante Akim North had the second highest soil Mn content but the lowest citrus fruit Mn content. Soil and fruit Mn contents had a negative correlation ($r=-0.99$, $p<0.05$) at Obuasi (Fig. 27). Soil and citrus fruit Mn had a positive correlation ($r=0.27$, $p<0.05$) at Sekyere West district (Table 14). Soil and fruit Mn contents were also positively correlated ($r=0.85$, $p<0.05$) at Asante Akim North (Fig. 26). However, soil and citrus fruit Mn contents were negatively correlated ($r=-0.67$, $p<0.05$) at Ejisu-Juaben (Table 14).

The highest top soil Mn content was observed at Ejisu-Juaben (108 mg/kg), followed by both Asante Akim North and Sekyere West (106.8 mg/kg) and Obuasi (75.6 mg/kg) (Fig. 23).

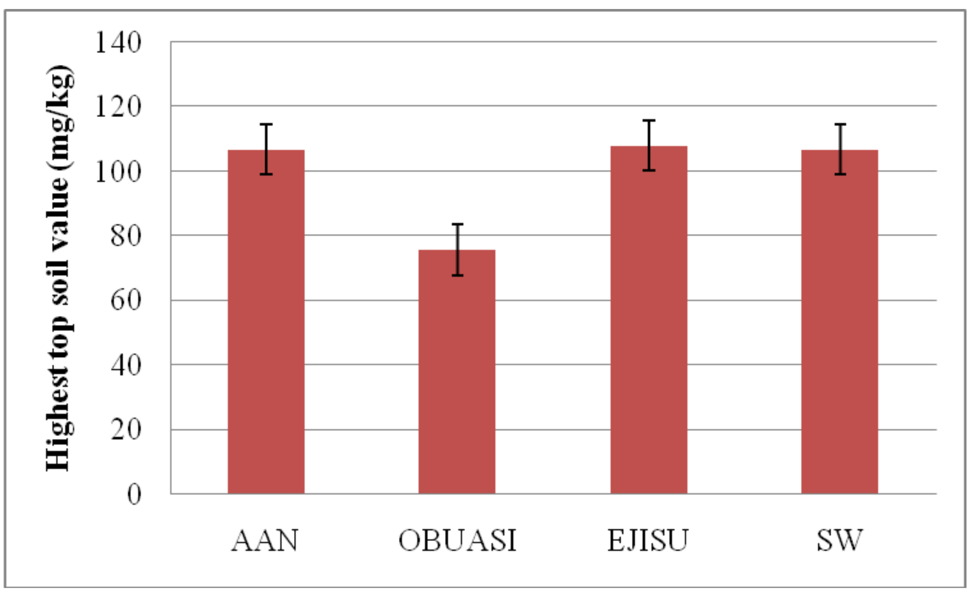

Fig. 23: Comparison of top soil Mn levels in the municipalities

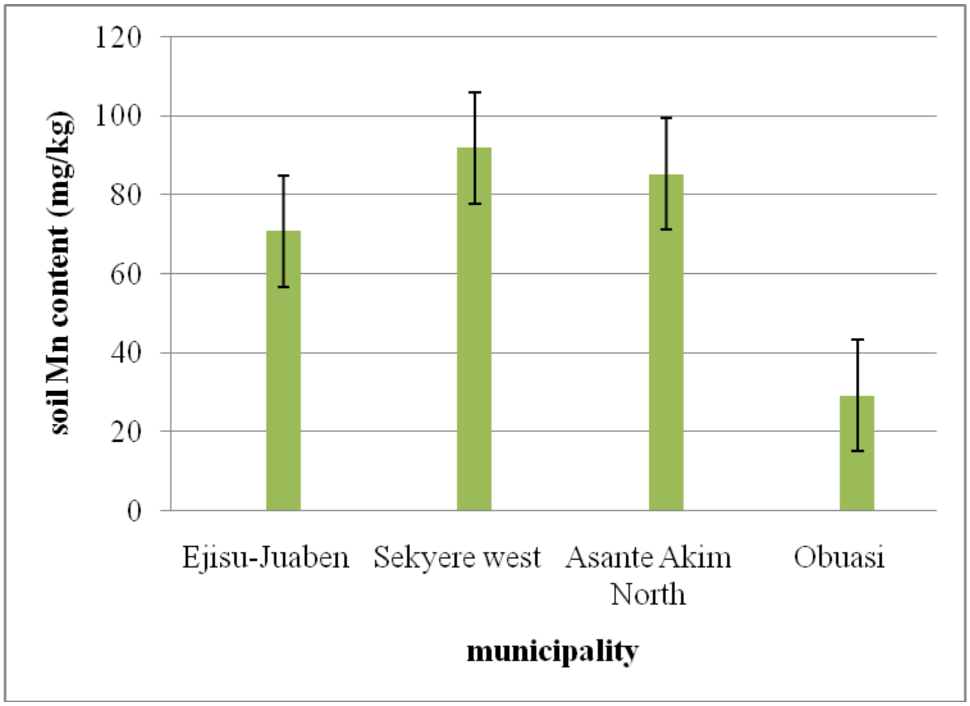

Fig. 24: Soil Mn content in selected municipalities.

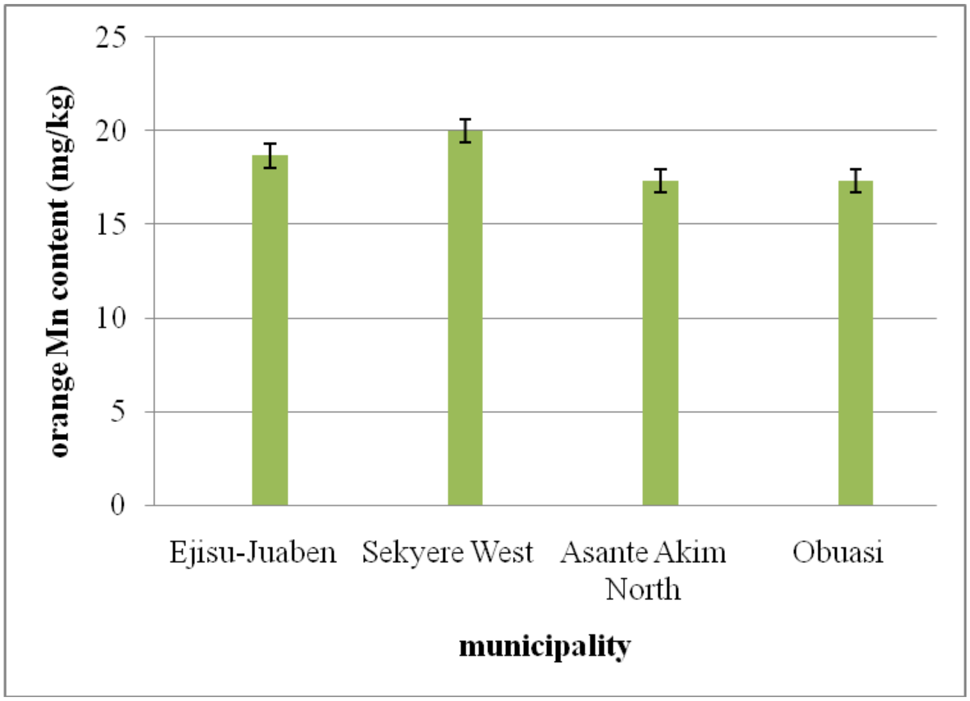

Fig. 25: Citrus fruit Mn content in selected municipalities

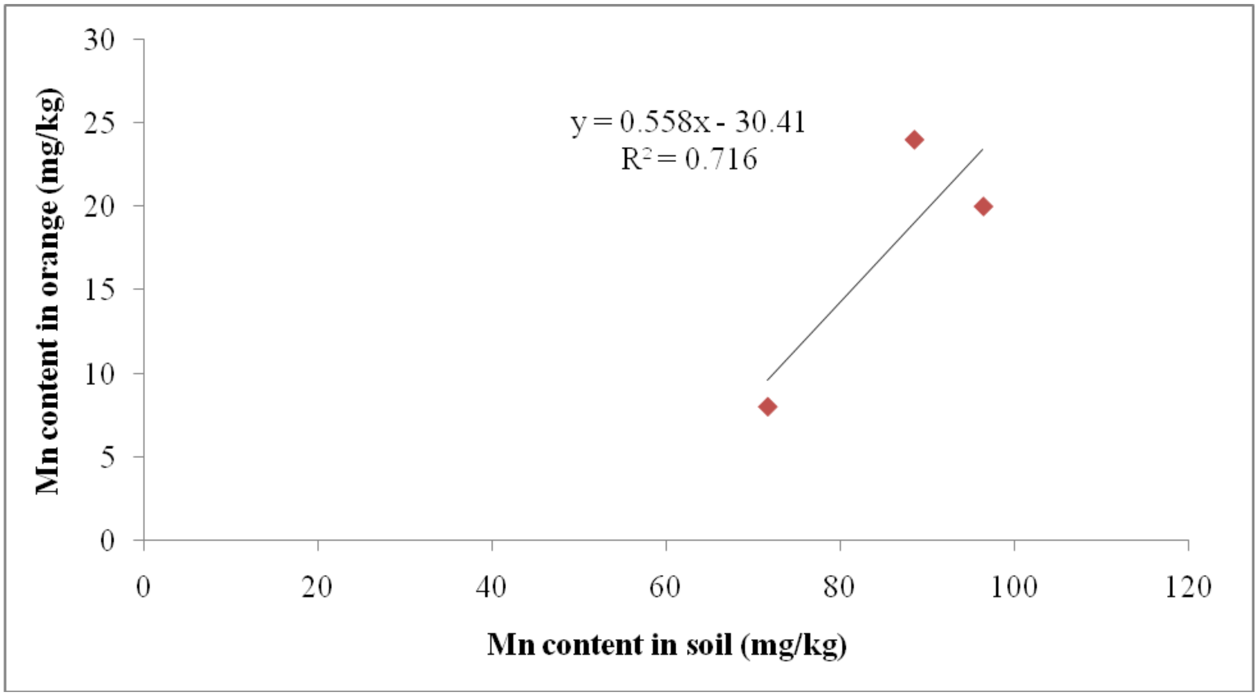

Fig. 26: Relationship between Mn content in soil and citrus fruit of Asante Akim North

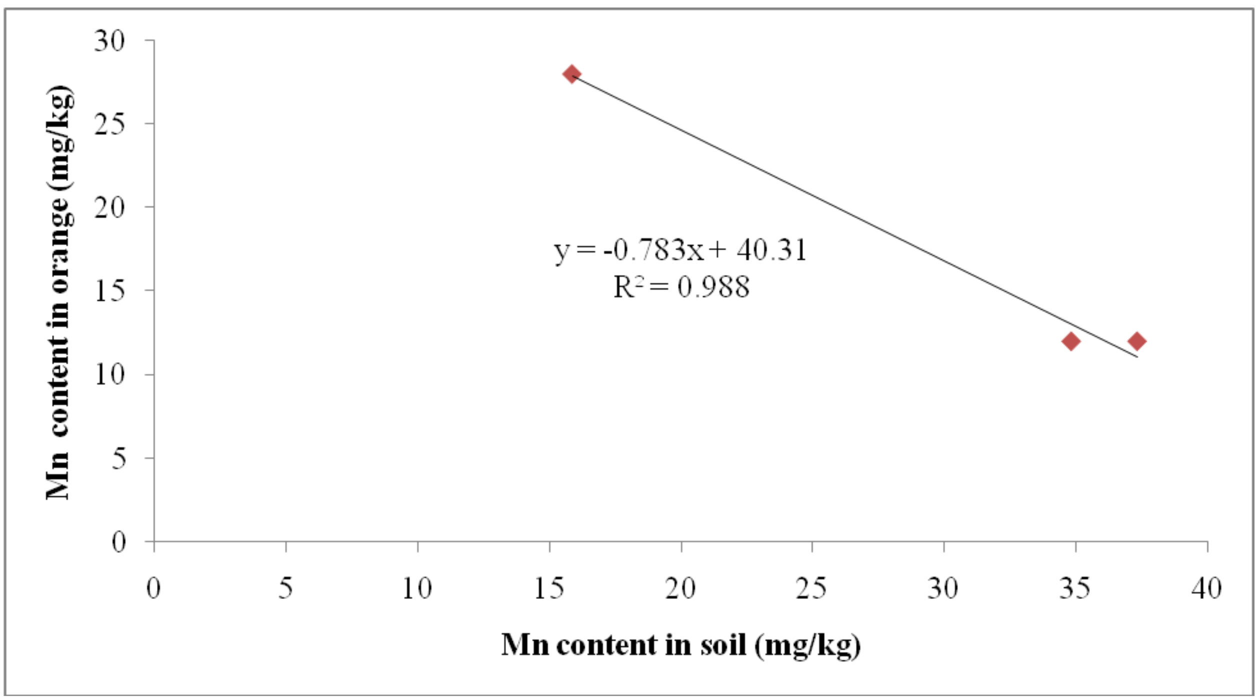

Fig. 27: Relationship between Mn content in soil and citrus fruit of Obuasi.

CHAPTER FIVE

5.0 DISCUSSION

5.1 Soil and Citrus Fruit Zinc

The highest values in Obuasi and Asante Akim North farms indicate that mining was the major source of Zn in these selected districts. The mean soil Zn (16.17 mg/kg) level in Ejisu-Juaben was within permissible limit. Three hundred (300) mg/kg is the standard for soil contamination assessment for Zn (www.agnet.org). The recommended maximum permissible limit set by FAO/WHO for Zn in fruit vegetables is 50 mg/kg (www.scialert.net). However, the mean citrus fruit Zn (74.67 mg/kg) level was about 2 times higher than recommended. Muchuweti et al., (2006) analyzed Zn content in maize and Tsunga leaves in Zimbabwe and had 221 mg/kg, over 4 times the EU standards (50 mg/kg).This trend is similar to those reported in Nigeria (Akan et al., 2009), Tanzania (Bahemuka and Mubofu, 1999) and Ethiopia (Rahlenbek et al., 1999).

The mean soil zinc content (18.70 mg/kg) in Asante Akim North is within standards of maximum permissible level. Soil Zn level of 300 mg/kg is the Dutch standard for soil contamination assessment (www.agnet.org). The mean citrus fruit zinc content (114.67 mg/kg), however, was 2 times higher than recommended standards. The maximum limit set by FAO/WHO is 50 mg/kg (www.scialert.net). Akan et al., 2009 also had Zn levels higher than the FAO/WHO guideline values when they analyzed some samples of leafy vegetables in Nigeria. The mean soil Zn (15.10 mg/kg) content in Sekyere West was within standard. The mean citrus fruit Zn content (117.33 mg/kg) was higher than the recommended 50 as set by FAO/WHO (www.scialert.net and www.tm.mahidol.ac.th/seameo/2008). The soil mean Zn content (25.43 mg/kg) in Obuasi was within permissible limit set at 300 mg/kg by the Dutch standards for soil contamination assessment. The fruit mean Zn content (140.67) was about 3 times higher than recommended. The recommended maximum value is 50 mg/kg (www.scialert.net). The term heavy metals refers to any chemical element with a specific gravity that is at least five times the specific gravity of water and is toxic or poisonous (Wild, 1994). Often it refers to metals discharged by industry of which the metalloid arsenic, cadmium, copper, lead, mercury, nickel and zinc are listed by a European commission directive as representing the greatest hazard to plants and animals. Interestingly, small amounts of these elements are common in our environment and their inclusion in diets is actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning).

5.2 Soil and Citrus Fruit Copper

Citrus has a high requirement for Cu, Mn and Zn (Brady, 1990). For the selected municipalities, Sekyere west and Asante Akim North had the lowest soil pH and accounts for the highest uptake of Cu in citrus fruit of these municipalities. Solubility and plant availability of most heavy metals in any given soil are known to be inversely related to pH (Sinha et al., 1978).

The standard for soil contamination assessment for Cu is 150 mg/kg. Thus, soil Cu (4.43 mg/kg) level in Ejisu-Juaben was within permissible limit. Citrus fruit Cu content was also within standard. Mean soil Cu content (4.80 mg/kg) was within standard for farms in the Asante Akim North municipality. The Dutch standard for soil contamination assessment is 150 mg/kg. However, citrus fruit Cu content of Barfi’s farm (52 mg/kg) was higher than the EPA permissible level. The recommended maximum limit of Cu set by FAO/WHO for fruit vegetables is 40 mg/kg (www.tm.mahidol.ac.th/seameo/2008). Maize and Tsunga leaves Cu content of 111 mg/kg, 5 times the EU standard (20 mg/kg), was obtained by Muchuweti et al., 2006 in Zimbabwe. The mean soil Cu (3.63 mg/kg) content in Sekyere West was within permissible limits. Gyasi's fruit Cu (72.00 mg/kg) was higher than the recommended 40 mg/kg as set by FAO/WHO (www.scialert.net and www.tm.mahidol.ac.th/seameo/2008). The soil Cu content in Obuasi (4.50 mg/kg) was within permissible limit. The citrus fruit mean Cu content (28.00 mg/kg) was also within a standard set at 40 mg/kg by FAO/WHO (www.tm.mahidol.ac.th/seameo/2008). Maize and Tsunga leaves Cu content of 111 mg/kg, 5 times the EU standard (20 mg/kg) were obtained by Muchuweti et al., 2006 in Zimbabwe.

5.3 Soil and Citrus Fruit Cadmium

The major sources of Cd in the selected municipalities were agrochemical inputs and vehicle exhaust fumes, especially for Ejisu-Juaben. The presence of Cd, Ni, Zn and Pb in grasses and roadside soil has been reported to be presumably derived from motor vehicles exhaust fumes, tyre wear and motor oils (Lagerweff and Specht, 1970). The farms in Sekyere West and Ejisu-Juaben had the highest agrochemical inputs. The highest mean value of citrus fruit Cd was also in Sekyere West (2.00 mg/kg), followed by Asante Akim North (1.67 mg/kg) (Table 13). The next was Obuasi (1.33 mg/kg) with Ejisu-Juaben having trace of Cd. Significant differences were also observed between Sekyere West and both Konongo-Odumasi and Obuasi farms. However, there was no significant difference between treatment means of Obuasi and Konongo-Odumasi farms. Cadmium occurs mainly in the free ion form and therefore very bioavailable to plants (Page et al., 1986). Ejisu-Juaben had the highest soil organic matter content (2.18%) but had trace of Cd in the citrus fruit whereas Asante Akim North had the lowest soil organic matter content but highest citrus fruit Cd content. Positive correlation has been reported to exist between some heavy metals and organic matter content for same soils (Fergusson, 1991). There was a negative correlation between soil and fruit cadmium contents ($r=-0.87$, $p<0.05$) (Fig.11) at Obuasi. Asante Akim North's soil and fruit Cd were positively correlated ($r=0.50$, $p<0.05$) (Fig.1). No correlations were obtained in Sekyere West and Ejisu-Juaben municipalities.

For Cd in Ejisu-Juaben, the concentrations are within tolerable limits for soils. The tolerable limit of soil for Cd is 2 mg/kg (Zhenli et al., 2005). There were traces of Cd in the citrus fruit. The mean soil Cd (0.17 mg/kg) in Asante Akim North was within EPA permissible standards. The set standard by The Dutch for soil contamination assessment is 2 mg/kg (www.agnet.org).

The mean fruit Cd (1.67 mg/kg) was about 8 times higher than the FAO/WHO recommended maximum limit (0.2 mg/kg) (www.tm.mahidol.ac.th/seameo/2008). Cadmium levels of 3.68 mg/kg, over 18 times the permissible level were obtained for maize and Tsunga leaves analysis (Muchuweti et al., 2006). The trend is similar to those reported in Tanzania (Bahemuka and Mubofu, 1999) and in Nigeria (Akan et al., 2009) for some leafy vegetables.

The soils mean Cd content (0.19 mg/kg) in Sekyere West was within standards which is 2 mg/kg (www.agnet.org). The fruit mean Cd content (2.00 mg/kg) was 10 times higher than the recommended (0.2 mg/kg) (www.tm.mahidol.ac.th/seameo/2008). Some trace metals such as Cd and Pb enter the soil as impurities of fertilizers (Zhenli et al., 2005).

The mean soil Cd (0.18 mg/kg) in Obuasi was within permissible limit of 2 mg/kg by the Dutch standards (www.agnet.org). However, the fruit Cd in Apitikooko (2 mg/kg) and Wioso (2 mg/kg) were about 10 times higher than recommended. Cadmium targets in the body are the liver, placenta, kidneys, lungs, brain and bones. Symptoms of acute cadmium exposure are nausea and vomiting. Chronic exposure causes hair loss, anaemia, arthritis, learning disorders, migraines, growth impairment, osteoporosis, loss of taste and smell, chronic obstructive lung disease and cardiovascular disease (jamaicaobserver.com/lifestyle/html).

5.4 Soil and Citrus Fruit Iron

Asante Akim North had the lowest soil Fe content but the highest citrus fruit content. This could be attributed to the lowest soil pH and organic matter recorded compared to the other three municipalities. Citrus fruit of Asante Akim North had the highest content of Fe and could be recommended as a good source of haemoglobin for malnourished children and pregnant women.

The levels of soil Fe in all four districts were within standards of maximum permissible levels whilst citrus fruit content was also safe for consumption. Iron is required in the largest amount by plants and an average soil contains about 50,000 mg/kg Fe (Stevenson, 1986).

5.5 Soil and Citrus Fruit Lead

There were no significant differences in soil Pb contents between Ejisu and Sekyere West, and Obuasi and Konongo farms. Nearness to mines was the main source of soil Pb in Obuasi and Asante Akim North whereas agrochemical usage and vehicle exhaust fumes could probably be responsible for soil Pb levels in Sekyere West and Ejisu-Juaben. Some trace metals such as Cd and Pb enter the soil as impurities in fertilizers (Zhenli et al., 2005). The highest citrus fruit Pb content was in Asante Akim North (9.30 mg/kg) followed by Obuasi (8.70 mg/kg), Sekyere West (8.00 mg/kg) and Ejisu-Juaben (1.30 mg/kg) (Table 13).

There were significant differences between Ejisu-Juaben and Sekyere West, Ejisu –Juaben and Obuasi as well as Ejisu-Juaben and Konongo. However, there were no significant differences between Sekyere west and Obuasi, Sekyere west and Konongo and Obuasi and Konongo. Asante Akim North had the lowest soil pH (4.71) compared to Obuasi (5.21) which had the highest. Thus, the highest accumulation of Pb in citrus fruit was at Asante Akim North. Solubility and plant availability of most heavy metals in any given soil are known to be inversely related to pH (Sinha et al., 1978). Soil and fruit lead contents at Obuasi had a positive correlation ($r=0.15$, $p<0.05$) (Fig.15). As the Pb content in the soil increased, the fruit content also increased at Sekyere West district ($r=0.90$, $p<0.05$) (Fig.20). The soil and citrus fruit Pb content at Asante Akim North had a positive correlation ($r=0.50$, $p<0.05$) (Fig.5). Soil and fruit Pb contents at Ejisu-Juaben were also positively correlated ($r=0.99$, $p<0.05$) (Fig.9).

The mean soil Pb (2.00 mg/kg) in Ejisu-Juaben was within tolerable limit. The maximum limit set as the Dutch standards for soil Pb is 200 mg/kg (www.agnet.org). The fruit Pb level in Janet's farm (4 mg/kg) was 13 times higher than recommended. The recommended limit set by FAO/WHO is 0.3 mg/kg for fruit vegetables (www.tm.mahidol.ac.th/seameo/2008). Muchuweti et al., 2006 analyzed Pb content in maize and Tsunga leaves and had 6.77 mg/kg, over 22 times the permissible levels allowed by EU standards and UK guidelines (0.3 mg/kg). This trend is similar to other works on leafy vegetables in Nigeria (Akan et al., 2009).

The mean soil Pb content (2.70 mg/kg) in Asante Akim North was within standards. The standard set by the Dutch for soil contamination assessment is 200 mg/kg. The mean fruit Pb (9.33 mg/kg) was about 31 times higher than recommended. The recommended maximum limit as set by FAO/WHO is 0.3 mg/kg (www.tm.mahidol.ac.th/seameo/2008). The soil mean Pb content (2.03 mg/kg) for Sekyere West was within standards. The Dutch standard is 200 mg/kg.

However, the fruit mean lead (8.00 mg/kg) was about 26 times higher than the recommended maximum permissible level which is set at 0.3 mg/kg by FAO/WHO (www.tm.mahidol.ac.th/seameo/2008). The mean level of soil Pb in Obuasi municipality (3.00 mg/kg) was within a standard (200 mg/kg) (www.agnet.org). The fruit mean Pb level (8.67 mg/kg) was about 28 times higher than recommended. The fall-out of residual lead, aerosol with lead contaminated particles and dust near roadways within a densely populated area, may also pose much environmental health problems to livestock and humans that feed directly on plants and vegetables grown in soils along the roadway (Diouf, 2001). Even small amounts of Pb can be dangerous, especially for the development of the brain: studies have shown that intelligent quotient falls by up to six points for every 10 micrograms of lead per decilitre of blood (Yasmin et al., 1996). Lead exposure can also cause anaemia, kidney disease, hearing damage, and impaired fertility; at high levels, it can result in coma or death (Yasmin et al., 1996).

5.6 Soil and Citrus Fruit Manganese

Apart from parent material, agrochemical usage and fuel combustion as exhaust fumes could be the main factors that accounted for the high level of Mn encountered in Sekyere West. The highest citrus fruit Mn level was in Sekyere West (20.00 mg/kg), followed by Ejisu-Juaben (18.67 mg/kg), Obuasi (17.33 mg/kg) and Asante Akim North (16.00 mg/kg) (Table 13). Sekyere west had the highest soil Mn content as well as the highest citrus fruit content. Thus, the higher the soil Mn content, the higher the citrus fruit content. There were significant differences between soil and fruit Mn content of Ejisu-Juaben (18.67) and Sekyere west (20.00), Ejisu-Juaben and Konongo (16.00), Sekyere west and Obuasi (17.33) as well as Sekyere West and

Konongo. No significant differences were observed between Ejisu and Obuasi as well as Obuasi and Konongo. Asante Akim North had the second highest soil Mn content but the lowest citrus fruit Mn content. This was due to the higher clay content of soils encountered in this municipality. Positive correlation has been reported to exist between some heavy metals and clay content for a soil type (Fergusson, 1991). Soil and fruit Mn had a negative correlation ($r=-0.99$, $p<0.05$) at Obuasi (Fig.14). Soil and citrus fruit Mn had a positive correlation ($r=0.86$, $p<0.05$) at Sekyere West district (Fig.19). Soil and fruit Mn contents were also positively correlated ($r=0.85$, $p<0.05$) at Asante Akim North (Fig.4). However, soil and citrus fruit Mn contents were negatively correlated ($r=-0.67$, $p<0.05$) at Ejisu-Juaben (Fig.8). Manganese is not classified as a human carcinogen (www.epa.gov). In a healthy individual excess Mn that enters the body through diet is eliminated by the liver and intestine, expelling the metal primarily in solid waste. Individuals with liver problems or other health issues, however, may not be able to eliminate Mn, causing the metal to reach toxic concentrations in certain tissues (www.sciencedirect.com). Tissues in the mid-region of the brain are particularly prone to accumulating Mn. High concentrations of Mn in the mid-region tissue can produce a condition called Manganism. This condition has symptoms similar to (but not identical with) Parkinson’s disease. Weakness of muscles, dullness, headache, insomnia, and mood changes are also associated with elevated levels of Mn in the body (Barbeau, 1984; Beuter et al., 1994).

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The study was undertaken to:

1. Establish the extractable soil Cu, Zn, Cd, Pb, Fe and Mn contents from mining and non-mining sites.
2. Establish the concentrations of these metals in edible citrus fruit from study sites;
3. Assess the relationship between soil and citrus fruit metal contents.

The results obtained from soils and citrus fruit analysis for Zn, Cu, Pb, Fe, Cd and Mn indicate appreciable levels of these metals in these samples. Highest accumulation of these analyzed heavy metals were recorded in samples from Obuasi municipality, next was soil and citrus fruit samples from Sekyere West which was closely followed by samples from Asante Akim North and the lowest was samples from Ejisu-Juaben municipality. Highest mining activity occurs in Obuasi municipality, light mining activity in Asante Akim North but there is no mining in Sekyere West and Ejisu-Juaben. Thus the accumulation of heavy metals in both Obuasi and Asante Akim North municipality could be attributed to the mining activities and agrochemical inputs. Sekyere West's accumulation of heavy metals could be attributed to high agrochemical inputs whilst Ejisu-Juaben's accumulation could be attributed to agrochemical inputs and vehicle exhausts fumes due to the nearness of the farms to the main Kumai-Accra highway. Soils with high organic matter content had high contents of the selected heavy metals but low uptake by citrus. Furthermore, soils of moderate to high pH had higher concentrations of the selected heavy metals than those of low pH. However, uptake by citrus was higher at low soil pH than moderate to high. For Zn, Pb and Cu there was a positive correlation between soil and citrus fruit whereas a negative correlation was obtained for Mn, Fe and Cd of Obuasi farms. Positive correlations were also obtained for Zn, Pb and Mn soil and fruit contents whereas negative correlations were obtained for Fe and Cu of Sekyere West. Asante Akim North farms had positive correlations between soil and fruit Zn, Pb, Mn, Cu and Cd contents while Fe produced a negative correlation. Positive correlations were also obtained for Pb and Cu soil and fruit contents while negative correlations were obtained for Zn and Mn from Ejisu-Juaben.

The maximum Zn, Cu, Cd and Pb levels of 300, 150, 2 and 200 mg/kg respectively which are the metals of greatest potential hazard are set as the Dutch standards for soil contamination assessment and these are used by countries yet to develop their own standards. Iron and Mn are metals of low toxicity with maximum value of 400 mg/kg plant dry matter reported for Mn. Thus, the levels obtained in this research are within permissible limits for soil contamination assessment.

Recommended maximum permissible limits of 50, 40, 0.2 and 0.3 mg/kg have been set respectively for Zn, Cu, Cd and Pb in fruit vegetables by FAO/WHO. Thus citrus fruit Zn and Pb levels are above the recommended maximum limits in all farms of the four (4) municipalities while Cd is above the recommended maximum limit in Obuasi, Asante Akim North and Sekyere west municipalities. Therefore, consumption of these citrus fruits may constitute health hazards to humans at the time of this research.

The concentration of the heavy metals in the citrus fruit and soil samples could serve as a baseline data for the assessment of these mining, agricultural and vehicular exhaust pollutants in soils and citrus fruit obtained in the Ashanti region of Ghana.

6.2 Recommendations

There is bioaccumulation of Zn and Pb in citrus fruit of the four selected municipalities as well as Cd in Obuasi, Sekyere West and Asante Akim North so citrus farms should not be sited too close to mines and highways and recommended dosage of agrochemicals must be used. Lime materials, manure or compost could be applied to affected soils to reduce the solubility of Cd and Pb while heavy application of phosphate will cause soluble Zn to precipitate for sustainable citrus production in affected farms.

Government of Ghana should task and resource scientists to establish the maximum permissible limits for heavy metal levels in soils and crops while regularly monitoring metals level for food safety.

Further research is required to determine the heavy metal content of soil and citrus fruit grown in other citrus- growing regions of the country as well as socioeconomic and health status of the neighbouring communities for sustainable citrus production.

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APPENDICES

Appendix 1

Maximum metal concentrations in soils permitted under EU regulations (Wild, 1993).

Metal	**Maximum soil concentration (mg/kg)**
Zinc	300
Copper	140
Nickel	75
Cadmium	3
Lead	300
Mercury	1.5

Appendix 2

Potential Effects of Mining Activity on the Environment (Adapted from UNEP, 1991)

	Surface water pollution	**Underground water pollution**	**Air pollution**	**Solid waste**	**Excavation**	**Noise and vibration**	**Remarks**
Human health and activity	Soluble contaminants in domestic and/or agricultural use waters Depositio	Soluble contaminants in wells, springs, etc Natural	Dust blown on inhabited, agricultural lands (2)	Hazards related to lack of stability of waste deposits		Effects of noise on human health Damage in	(1) Occurrence of such impacts on underground waters is a general case; it depends

	n of solids on agricultural lands; in sea shallow zones Withdrawal of water for industrial purposes.	water sources drying up as a consequence of water table lowering				buildings due to blasting vibration	essentially on the hydrology of the area (2) Plant and especially underground mine atmosphere
Fauna	Alteration of aquatic fauna including destruction of fish species, accumulation of toxic elements by fish				Loss of habitat	Disturbance of habitat feature (3)	(3) Issues regarding unique habitat features (migration a corridors, watering areas, etc) for threatened or endangered species should especially be addressed
Flora	Alteration of aquatic flora		Accumulation in plants of toxic elements carried by dust		Loss if habitat		Spatial requirements of mining operations are normally quite restricted; within that area the disturbance

							can be significant. Effects on species with limited geographic extent are essentially to be considered
Land use	Sand deposition in river channels; sea shallow zones			Land disturbance Withdrawal of agricultural land	Land disturbance Land subsidence due to underground mining.		