Aluminium and Fluoride Levels in Soil, Water and Foods in Mwingi and Thika District

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

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DEDICATION

This thesis is dedicated to Eddy Mugambi Okoth, my son who was born in the course of My Master’s study. May he become a great scholar in his own right.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ATSDR	Agency for Toxic Substances Disease Registry.
AOAC	Association of Official Analytical Chemists
ASAL	Arid and Semi- Arid lands
EU	European Union
FAO	Food and Agriculture Organization
SPADNS	(sodium 2-(parasulphophenylazo-)-1, 8-dihydroxy-3, 6-naphthalene disulphonate)
UNEP	United Nation Environment Program
UK	United Kingdom
UV	Ultra Violet
WHO	World Health Organization

ABSTRACT

Low amount of ingested fluoride is important for prevention of dental caries. However, ingestion of high levels of fluoride may lead to disease conditions that adversely affect the skeleton. Aluminium is not known to be any nutritional value to human beings. Ingestions of high amounts of aluminium in foods and water has been reported to cause aluminium toxicity, leading to development of disease conditions such as osteomalacia and Alzheimer' disease among others. Soils, foods and water vary in their contents of aluminium and fluoride, depending on geographical location and composition of underlying rock. The aluminium content in cooked food depends on handling, processing and preservation methods. However there is little information concerning the content of aluminium and fluoride in water, soils and foods commonly eaten in Kenya. The main objective of the study was to determine the levels of aluminium and fluoride in water, food and soil in Thika and Mwingi Districts.

Aluminium was determined using the AAS with a nitrous oxide/acetylene flame. Fluoride was determined using the SPADNS calorimetric method which is based on the reaction between fluoride and zirconium- Dye Lake. The mean fluoride content in 18 soil samples analyzed was 369 ppm. The highest fluoride content in soil was that from sample in Nuu location (469 ppm) in Mwingi district, the lowest was from chain location (126 ppm) Thika district. The highest fluoride content in water samples was from Jojo borehole in Kanzanzu location, Mwingi District (2.47 ppm). The lowest fluoride content was from river Thiririka in Juja location, Thika district (0.05 ppm). The mean fluoride content in the different sources of water was as follows: boreholes 1.21 ppm; shallow wells, 0.68 ppm; rivers springs, 0.21 ppm and tap water, 0.07 ppm. fluoride content in tap water, rivers and springs was below the recommended levels, in shallow well some were within the recommended levels, while in boreholes some had higher levels than the maximum who permissible levels. The mean aluminium content in different sources of water was as follows: spring, 1.59 ppm; shallow wells, 1.29 ppm; boreholes, 0.82 ppm; rivers, 0.83 ppm and taps, 0.95 ppm; shallow aluminium content in all the water sources was above the maximum admissible levels of 0.2 ppm. The highest aluminium content in soil was from Kianguni in Chania location (1005 ppm), while the lowest was in Mwenga, Nuu where no aluminium was detected among the foods analyzed tea had the highest aluminium content (1189 ppm), while cow peas had the lowest (41 ppm) aluminium content. The aluminium content in beans from different locations ranged from 152 ppm in Chania to 40 ppm in Juja and Nuu. The greatest increase in aluminium content in foods cooked with aluminium pans as compared to stainless pans was in tomatoes where tomato cooked in aluminium pan had 266 ppm, while, in stainless it had 139 ppm. acidic de- ionized water boiled in aluminium pan had aluminium content increase from 0 ppm to 230 ppm after 30 minutes, 467 ppm after 40 minutes and 1298 ppm after one hour, while a control with stainless steel had only 3.6 ppm after one hour.

This study shows that exposure to fluoride content is varied, in different locations and populations. It is important to ensure the WHO limits are maintained to ensure the beneficial effects due to fluoride are realized, and the toxic effects are avoided, with time Kenya should set their own standards. Aluminium levels in water in this study are above the WHO set quality guidelines therefore studies need be done to relate the toxic effects of aluminium to the levels in different population in the country – Kenya.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background information and problem statement

Pollution is the introduction of contaminants into an environment that causes harm to human health, other living organisms, and the environment. Pollution can be in the form of chemical substances, or energy such as noise, heat, or light. Pollutants can be naturally occurring substances or energies, but are considered contaminants when in excess of natural levels (Adriano, 2001). Concern for environmental quality remains very much subservient to provision of food and shelter in most African communities. The exposure of African populations to increasing levels of pollutant metals in their environment represents an unrecognized health hazard. Toxicants are chemical contaminants that may harm living organisms at concentrations found in the environment. Toxic metal exposure is higher than ever before and an important cause of ill health (Nagendra Rao, 2003). Aluminium and fluoride are some of the elements identified as toxicants in the environment.

Aluminium is a serious environmental toxicant (Trond *et al.,* 1996; John *et al.,* 1985). It was previously regarded as non-toxic (Metwally and Mazhar, 2007; Day 2003). It is not known to be of any nutritional value to human beings. However, over the past 20 years more evidence has come to light to link aluminium with certain neurodegenerative diseases (Gray, 1994). Aluminium affects skeletal and bone tissue as well as the neural system (Yokel and Saiyed, 2005). Some of the diseases implicated in aluminium toxicity include osteomalacia, iron inadequate microcytic anaemia, Alzheimer’s disease and a number of respiratory allergic effects (UNEP *et al.*, 1997).

Aluminium toxicity generally leads to an accelerated cell death due to chronic disruption of cell metabolism. Among the effects, literature describes interference with the free radical-mediated cytotoxicity, lipid peroxidation, and changes in serum essential elements (Metwally and Mazhar, 2007). The fact that aluminium is a toxic element is no longer in question, although the mechanism by which this toxicity is exerted has not been fully established (Day, 2003).

With increased incidence of acid rains and the fact that aluminium deposits are highly soluble in water under acidic and strong basic conditions, the availability of aluminium to plants is expected to increase posing a serious danger to plant life. Aluminium has been shown to be toxic to aquatic life causing the death of fish. Aluminium is an extremely versatile metal with a wide variety of uses. It is used in, building and insulating materials, cosmetics, food additives, antiacids, paint pigments, and water purification. It is also used in the kitchen as cooking utensils, water heating kettles and as film for packaging. It is used in processing lines in industries and for water taps (Downs, 1993). The increased solubility of aluminium compounds with temperature poses a greater danger in use of aluminium as cooking ware. Aluminium can be leached from aluminium vessels into food during preparation and storage. Foods that are acidic such as tomatoes are more likely to absorb aluminium than neutral foods. In the presence of fluoride, aluminium leaches out of cookware at a faster rate (Baxter *et al.,* 1989).

The nutritional impact of fluoride is multifaceted. The risk of dental caries is reduced due to the uptake of fluoride by enamel crystallites which resist acid solubilization (Miller-Ihli, 2003). High fluoride content affects bones and leads to mottled teeth. Prolonged exposure to high levels of fluoride can lead to dental fluorosis. Severe fluorosis can lead to susceptibility to dental caries (Wikister *et al.*, 2002). Generally fluoride toxicity depresses thyroid activity and adversely affects the skeletal and bone tissue (Gibson, 1992). It has also been implicated in premature ageing of the human body (Stern magazine, 1978). Fluoride is found in naturally occurring rocks, air, and water in varying concentrations. It is a highly reactive element due to its existence in ionic form as a fluoride. It enters the human body through ingestion, inhalation and, in extreme cases, through the skin. Water borne fluoride is absorbed more rapidly than food borne fluoride (Wilkister *et al.*, 2002). The geology of Kenya makes it one of the countries in the world where fluoride occurs in highest concentrations, not only in rocks and soils but also in surface and ground water (Gikunju *et al.*, 2002).

Previous studies by Gikunju *et al.* (2002) on fluoride in River waters show that the highest fluoride concentration was 0.85 ppm in Laikipia District and the lowest was 0.08 ppm in Murang'a District. By region and district, the mean fluoride concentration ranged from 0.12 ppm for rivers in Laikipia to 0.24 ppm for rivers in Nairobi, with 0.32 ppm in the Upper Basin of the Athi River (Gikunju *et al*., 2002). The above study only focused on Laikipia, Nairobi, Muranga and upper basin of Athi river.

Wilkister *et al*. (2002) did a study on fluoride levels of water consumed in the Njoro division of Nakuru district, Kenya. In this study rainwater had mean fluoride levels of 0.5 ppm, dams 2.4 ppm, wells 4.1 ppm, springs 5.5 ppm, and boreholes 6.6 ppm. In a study by Kahama *et al* (1997) on fluorosis in children and sources of fluoride around lake Elementaita region of Kenya, Fluoride levels in drinking water from different boreholes were high, varying from 2.0-20.9 ppm (Kahama *et al.*, 1997). The highest water fluoride concentrations occur in certain springs, boreholes, and some lakes in the Rift Valley (Gikunju *et al.*, 2002).

There is little or no information on aluminium levels in soils foods or water consumed in Kenya. Studies on fluoride levels in water in Kenya have been done mainly in parts of Rift valley, Central, Nairobi and Nyanza Provinces of Kenya. There is no data available for eastern provinces. The Districts chosen have no data on fluoride or aluminium levels. Therefore the present study aims at providing this data. Use of aluminium pans as cookware is wide spread in Kenya. This is due to the fact that the prices of alternative cookware are far beyond the reach of the average income earning Kenyan. In both Mwingi and Thika District the common cookware in the market (supermarkets, open air market) is aluminium.

This study aims at providing data on levels of fluoride and aluminium in domestic water sources, soil and foods in the project area. It also aims at analyzing aluminium leaching during cooking with aluminium cookware. This knowledge will enable the community to make informed choices in light of the toxic effects of the two elements as well as the beneficial effects of fluoride at recommended levels.

1.2 Objectives

1.2.1 Main objective

The main objective of the study was to determine the levels of aluminium and fluoride in water, food and soil in Thika and Mwingi Districts.

1.2.2 Specific objectives

The specific objectives were to:

- Determine levels of aluminium and fluoride in water sources and soil in Thika and Mwingi District.
- Determine levels of aluminium in common foods grown in the project area.
- Determine the effect of cooking food in aluminium cookware on the content of aluminium in foods.

1.3 Hypotheses

- There are high levels of aluminium and fluoride in water, soil and commonly consumed foods, above the WHO safe limits in the project area.
- Use of aluminium cookware in food preparation increases levels of aluminium in foods.
- The aluminium content in soil is related to the aluminium content in foods grown in the same area.
- The leaching of foods cooked in aluminium pans increases with increasing acidity of the foods.

CHAPTER TWO

2.0: LITERATURE REVIEW

2.1 Introduction

Aluminium is third most abundant elements in the earth's crust, accounting for more than eight percent of all the elements (Downs, 1993). Exposure to Aluminium has increased markedly, as its production increased rapidly in the 20th century, reaching approximately 15 million tons in the early 1980s. Human exposure to aluminium has also increased substantially due to increased solubility and bioavailability to plants and aquatic life as a consequence of acid rain and industrial emissions (UNEP *et al.*, 1997). In the recent past there has been focus on aluminium as a toxic element (Day, 2003)

The fact that aluminium is a toxic element to humans and animals is no longer in question, although the mechanism by which this toxicity is exerted has not been fully established (Day, 2003). Aluminium was previously regarded as non-toxic; however over the past 20 yrs more and more evidence has come to light to link aluminium with certain neuro-degenerative diseases (Gray, 1994). In particular, Alzheimer’s disease incidence appears to be rising. Evidence strongly hints it to rising “harmful environment” (Foster, 2004). Globally soils and water are becoming more acidic and consequently aluminium more soluble. Simultaneously, commercial fertilizers have been used with increasing frequency (Foster, 2004).

There is a proposed relationship between aluminium in the brain and the occurrence of Alzheimer’s disease and other neurological disorders. Given that aluminium has no health benefits but has the potential to produce toxicity, at least in people with impaired or absent renal function, some people may wish to avoid aluminium when it is practical (Yokel and Saiyed, 2005).

The composition of surface and underground water is dependent on natural phenomena such as geological, topographical, meteorological, hydrological and biological factors in the drainage basin, and varies with seasonal differences in runoff volumes, weather conditions and water levels. Large natural variations in water quality may, therefore, be observed even where only a single watercourse is involved. Human intervention also has significant effects on water quality. Some of these effects are the result of hydrological changes, such as the building of dams, draining of wetlands and diversion of flow (WHO, 1996). More obvious, are the polluting activities, such as the discharge of domestic, industrial, urban and other wastewaters into the watercourse and the spreading of chemicals on agricultural land in the drainage basin (WHO, 1996).

Excessive fluoride intake can lead to fluorosis of both teeth and bones (Miller-Ihli, 2003). Fluoride is regarded as one of the most important environmental micro pollutant. A large number of industries emit fluoride into the atmosphere, including brick and tile products manufacturers, coal combustion and enamel factories among others. Application of phosphate fertilizers, sewage sludge and some pesticides also bring fluoride to soil (WHO, 2002). There are many parts of the world where fluorosis is an endemic disease that affects several millions of people. Fluoride is the most, biochemically active substance in the human body. It is particularly associated with diseases affecting thyroid dysfunction (Press release, 2003). Generally fluoride depresses thyroid activity which affects the skeletal and bone tissue (Gibson, 1992). It has also been implicated in premature aging of the human body (Stern magazine, 1978).

The upper limit for both fluoride and aluminium in human consumption is 0.05-0.07 mg /Kg body weight /day and 1mg /Kg body weight/day for fluoride and aluminium, respectively (WHO, 2002).

Determining the most appropriate concentrations of fluoride in drinking water is crucial for communities. It is imperative that each country calculates its own optimal level of fluoride in drinking water based on the dose-response relationship of fluoride in drinking water with the levels of caries and fluorosis (Khan *et al.,* 2004). Climatic conditions, dietary habits of the population and other possible fluoride exposures need to be considered in formulating these recommendations (Khan *et al.,* 2004). Determination of optimal concentration of fluoride for drinking water in Pakistan was performed using a modified Galagan and Vermillion equation, which applies a correction factor of 0.56 to the equation.

The optimal fluoride in drinking water in Pakistan using this modified equation was determined to be 0.39 ppm. Observation of the correlation showed that a fluoride concentration of 0.39 ppm in drinking water was associated with maximum reduction in dental caries and a 10% (lowest) prevalence of fluorosis (Khan *et al.,* 2004).

2.2 Aluminium

2.2.1 Chemistry of aluminium

Aluminium is a soft, light in weight but strong metal, with dull silver gray appearance due to thin layer of oxide that forms quickly when it is exposed to air, which prevents further corrosion (Cotton et al., 1999). The relative density of Aluminium is 2.708 g/cm^3. It has a melting point of 660^{o}C and boiling point of 2450^{o}C (Downs, 1993).

Aluminium derives its name from Alum which is a double sulphate compound, KAl (SO4)212H2O, which was used medicinally as an astringent in ancient Greece and Rome (Downs, 1993). Aluminium is a constituent of many igneous minerals including feldspar and micas. Weathering of the above minerals gives clay minerals such as kaolinite Al2 (OH)4Si2O5. Bauxite, the commercial source of aluminium metal has a composition, which varies considerably from place to place (Downs, 1993). In highly weathered tropical soil aluminium is found in the commonest form of gibbsite Al (OH)3. Aluminium also occurs in cryolite

(Na_3AlF_6) and the anhydrous oxide (Al_2O_3) found as corundum. Impure forms of corundum are found as gemstones e.g. ruby (AlO_3/Cr), sapphire (Al_2O_3/Fe) and oriental emerald (Downs, 1993; Cotton *et al.*, 1999).

Aluminium has a high chemical reactivity, therefore it is never found in nature as a metal. It always occurs in nature in its oxidized form and most commonly as aluminates and aluminosilicates in clays and shales. It is an active metal that oxidizes readily, whenever the necessary conditions for oxidation prevail. However, strong acids and alkalis usually cause rapid attack of aluminium and its alloys with exception of nitric acid and aqueous ammonia. Aluminium as an ion exists as Al^{3+}. This ion is of much concern due to the key role it plays in the environment through toxicity to terrestrial plants and aquatic life and its implications in a number of human diseases (Downs, 1993).

Chemical weathering of earth's crust minerals and resultant release of aluminium ion causes aluminium toxicity and fertility decline. Acidification and aluminium toxicity are common in high rainfall areas, which cover about 10 % of Kenya. Highly leached soil has lost its bases such as calcium, magnesium, potassium and sodium, with the result that the soil becomes acidic, leading to aluminium toxicity. The main causes of fertility decline are loss of basic cationic nutrient through leaching (Muigai, 2001).

Aluminium has a strong affinity for fluoride. In acidic water, fluoride and aluminium produce species such as AlF^{2+}, but at higher pH the predominant form of aluminium created is Al (OH4) (Foster, 2004).

2.2.2 Human exposure to aluminium

2.2.2.1 General exposure

Food is the main source of aluminium intake, some plants such as herbs and teas are known as aluminium accumulators (Soni *et al.,* 2001). Food is the single largest contributor of aluminium intake for the typical human (Yokel & Saiyed, 2005). Food additives are the major dietary source of aluminium in the USA (Soni *et al.,* 2001). These food additives are aluminium containing compounds used as preservatives, coloring agents or leavening agents. Another source of aluminium comes from cooking, packaging and handling of food in aluminium containers. (Soni *et al.*, 2001). The amount of aluminium in the air is very small ranging from 0.0005 ppm in rural areas to 0.01 ppm in urban areas (ATSDR, 1992; WHO, 2003). Pharmaceutical products also contribute to aluminium exposure to humans. It has been estimated that doses of antacids and buffered analgesics contain 840-5000 ppm and 130-730 ppm aluminium respectively. (Soni *et al.*, 2001). Aluminium is also found in many processed foods, cosmetics, toothpaste and antiperspirants **(**Zannal, 2003). Aluminium is present in foods through contact with aluminium used in preparation and storage (Yokel and Saiyed, 2005).

Aluminium content in selected food and food products containing aluminium in a study done in the USA ranged from < 1- 27,000 ppm. Considerable aluminium was found in many pan cakes and waffle mixes up to 1200 ppm and 600 ppm respectively. Daily aluminium intake in the USA was estimated to average 8-11.5 mg for adults (Yokel and Saiyed, 2005). Taking food high in aluminium content will increase this daily uptake. In a separate study the adult dietary intake of aluminium in several countries was reported as follows: Australia (1.9-2.4), Finland (6.7), Germany 8-11), Japan (4.5), Netherlands (3.1), Sweden (13), UK (3.9) and USA (7.1-8.2) (WHO, 2003). Aluminium can be toxic to bone, bone marrow, and the nervous system (Yokel and Saiyed, 2005). In a study by Mario *et al.,* (1997), the amount of aluminium in different kinds of tea and ground coffee was analyzed, the transfer of aluminium into the infusion was determined and aluminium intake via tea and coffee was calculated within the framework of their investigations (Mario *et al.,* 1997). It was shown that about 30% of the aluminium stored in black tea's dry matter was transferred into the infusion. Only black tea infusions are a significant source of aluminium intake via beverages (Mario *et al.,* 1997).

Aluminium is ubiquitous in the environment and is used in a variety of products and processes; therefore daily exposure of the general population is inevitable. During purification or treatment process, aluminium salts are frequently used as coagulants to remove color and turbidity. However aluminium levels in finished products, on average are low, ranging from 0.014-2.7 ppm. As per the estimates of World Health Organization/International Program on Chemical Safety drinking water may contribute around 0.4 mg per day (Soni *et al.,* 2001).

2.2.2.2 Aluminium toxicity and use of aluminium cookware

Aluminium can be leached from aluminium vessels into food during preparation and storage (Baxter *et al.,* 1989). This is particularly by acidic and basic foods. For example cooking tomatoes (pH=4.4) and rhubarb (pH=3.4) in an aluminium saucepan increased the aluminium content of the food from 0.16 ppm wet weight to 21.5 ppm and 42 ppm respectively. Whereas cooking them in teclon-coated saucepan raised the aluminium concentration to 0.3 ppm and 0.37 ppm respectively (Yokel & Saiyed, 2005). It is well established that cooking of acidic foods in aluminium saucepans causes leaching of the metal (Baxter *et al*., 1989). The greater leaching observed with more acidic foods arise from dissolution of the protective oxide layer on the surface of the aluminium saucepan.

In addition to pH considerations, the degree of aluminium leaching may also be influenced by the age, surface topography and alloy content of the saucepan. Aluminium content will increase during cooking due to evaporation. Presence of fluoride enhances aluminium leaching from the cooking pots (Baxter *et al*., 1989).

2.2.3 Aluminium interaction with other elements in the alimentary canal

Aluminium for example enhances fluoride absorption and may decrease the absorption of calcium and iron compounds. This will eventually lead to deficiencies of the essential minerals. This is the main way that aluminium is toxic to human health (Foster, 2004). It possibly hinders the absorption of cholesterol too by forming an aluminium-pectin complex that binds fats to non-digestible vegetable fibers (UNEP et. al., 1997). The inhibition of uptake of elements by aluminium has been used positively to treat fluorosis and to reduce phosphorous uptake in uraemic patients (UNEP *et al.*, 1997).

The developmental toxicity of aluminium by the oral route is highly dependent on the form of aluminium and the presence of organic chelators that influence bioavailability (WHO, 2003). Silica and aluminium are well known antagonists. As a consequence, water rich in silicic acid is unlikely to carry any free aluminium. This high affinity for silicon influences its absorption in the intestinal tract. It is believed that silica promotes the formation of aluminosilicates species, limiting the gastro intestinal absorption of aluminium (Foster, 2004). Hence where silicon appears with aluminium the dangers of aluminium are reduced.

Aluminium in diet interacts with a number of elements in the alimentary canal, leading to their reduced uptake. Some of these elements include calcium, iron, magnesium, and phosphorous (UNEP *et al.*, 1997). Once the absorption of essential minerals is reduced in the alimentary canal, it will eventually lead to deficiencies of the minerals. This is the main way that aluminium is toxic to human health (Foster, 2004).

2.2.4 Diseases associated with aluminium toxicity

2.2.4.1 Dementia

A number of neurological effects, including impairment of cognitive function, motor dysfunction and peripheral neuropathy have been associated with occupational exposure to aluminium, (UNEP *et al*, 1997). Aluminium can be toxic to the nervous system (Yokel and Saiyed, 2005). Dementia refers to loss of cognitive function due to changes in the brain caused by disease or trauma. Cognition is the act or process of thinking, perceiving and learning. Cognitive functions that may be affected by dementia include, decision making, memory, spatial orientation, thinking, reasoning and verbal communication. Dementia may result in behavior and personality changes, depending on area of brain affected. Dementia can be reversible. However dementia caused by incurable diseases such as Alzheimer's disease is irreversible (UNEP *et al*, 1997).

From 29,000 underground miners examined in provincial chest clinics in Ontario, Canada, between 1955 and 1979, two samples were drawn (UNEP *et al*, 1997). One sample consisted of 369 miners exposed to aluminium and 369 unexposed miners adjusted for age. The second sample consisted of 678 randomly drawn miners in equal numbers from the exposed and unexposed populations. Between 1988 and 1989, miners who could be traced were interviewed and psychometric testing was performed. Cognitive test scores and proportions impaired at least one test indicated a disadvantage for exposed miners (UNEP *et al*, 1997). A positive exposure-related trend in increased risk was described.

A group of 87 workers from an aluminium foundry in Canada, exposed to workplace aluminium concentrations ranging between 4.6 and 11.5 mg/M^3 air, with an exposure time of at least 6 years was studied. Sixty non-exposed workers matched for age, job, and seniority and social status served as control (UNEP *et al*, 1997). Psychomotor and psychometric tests were performed, except on workers who consumed alcohol or who had taken psychotropic drugs within a month prior to the test. A significant difference in complex reaction time, oculomotor coordination and the sum of manipulative tests was noted in exposed workers compared to controls. The most significant difference was found in memory subtest (UNEP *et al*, 1997). This shows that exposure to aluminium has a negative influence on memory.

2.2.4.2 Alzheimer's Disease

Alzheimer's disease is a progressive, neuro-degradative disease characterized in the brain by abnormal clumps and tangled bundles of fibers composed of misplaced proteins. Age is the most important pre-disposing factor in this disease (UNEP *et al*, 1997). Alzheimer's disease is the most common, complex and challenging form of neurodegenerative disease associated with dementia in the elderly. Neuropathological examination of the Alzheimer's disease brain shows extensive neuronal loss (Yuemang *et al.,* 2004). Three genes have also been discovered that cause early onset of Alzheimer's disease. Symptoms of Alzheimer's disease include memory loss, language deterioration, and impaired ability to mentally manipulate visual information, poor judgment, confusion, restlessness and mood swings. Eventually the disease destroys cognition, personality and ability to function. Chronic aluminium toxicity and long term accumulation of this element in humans has also been blamed as a cause of Alzheimer's disease (UNEP *et al*, 1997). Alzheimer's disease is caused by aluminium and is particularly common in those carrying the APO E4 allele(s). They are more susceptible to this toxic metal because they are less capable of removing brain beta-amyloid and tau proteins (Foster, 2004).

In particular; Alzheimer's disease incidence appears to be rising. Evidence strongly points to rising "harmful environment". Globally, soils and water are becoming more acidic due to continuous use of fertilizer and deposition of aluminium oxides in water bodies (Foster, 2004). Continuous cultivation has also depleted essential minerals from soils (Muigai, 2001). The western diet promotes Alzheimer’s disease in that diets tend to be deficient in calcium and magnesium, making those who eat it susceptible to aluminium toxicity. Moreover foods are canned, wrapped and/or cooked with aluminium (Foster, 2004).

Elevated amounts of aluminium have been shown in patients with Alzheimer’s disease. In the U.S.A. Alzheimer disease afflicts one out of thirty persons in the age group 65-74, about one out of six, in age group 75-84 and one out three of those aged above 85. Women are at a greater risk than men (WHO and FAO, 1995). This disease ranks as one of the greatest killer of the elderly in the United States. Alzheimer disease patient's brain also appears to contain slightly less than double the aluminium in those of similar aged controls. The latter have somewhere between 1.9-2.2 ppm, whereas Alzheimer victims average approximately 3.8 ppm (Foster, 1992).

There are three geographical studies that support a role for aluminium in the etiology of Alzheimer’s disease. Martyn (1989) conducted a survey of 88 districts within England and Wales to establish the rates of Alzheimer disease in people under the age of 70. These were estimated using records of computerized topographic scanning units. After certain adjustments, these data were correlated with aluminium content in water. It was concluded that the risk of Alzheimer disease was 1.5 times higher in districts where the mean water aluminium concentration exceeded 0.11 ppm, than those where levels were less than 0.01 ppm (Martyn, 1989). Epidemiologic evidence strongly suggests a causal role for local environmental conditions relating to availability of aluminum, calcium, and magnesium (Daniel, 1985). In view of the fact that a major consequence of acid rain is the liberation of large amounts of aluminum in bioavailable forms, concerns are raised about possible human health risks due to this environmental phenomenon (Daniel, 1985).

There is no question that aluminium is a potent neurotoxicant, both in experimental animals and in humans (Trond, 2001). Nine out of 13 published epidemiological studies of aluminium in drinking water and Alzheimer’s disease have shown statistically significant positive relations. Given the difficulty in producing high-quality data for the occurrence of Alzheimer’s disease and also for aluminium exposure, these studies are remarkably consistent (Trond, 2001). A major problem in their interpretation is that drinking water, even at high aluminium concentrations, only contributes a fraction of the total dietary intake of aluminium (Trond, 2001). Attempts to relate the actual levels of aluminium in drinking water to Alzheimer’s disease was reported in two parallel studies in Norway, where it was found that the mortality of dementia was higher in areas with high concentrations of aluminium in drinking water (Trond, 2001).

Foods with large amounts of aluminium-containing additives or aluminium from drinking water may increase the risk of developing Alzheimer’s disease, aluminium more likely acting as a cofactor somewhere in the cascade of events leading to the demented brain (Solfrizzi *et al.,* 2006). Healthy diets, antioxidant supplements, and the prevention of nutritional deficiencies or exposure to foods and water with high content of metals could be considered the first line of defense against the development and progression of cognitive decline (Solfrizzi *et al.,* 2006).

The role of aluminum as a toxic agent in other neurological disorders, where renal function is normal, is controversial (Michael and John, 1985). However, patients with chronic renal failure, aluminum appears to be of proven toxicological importance (Michael and John, 1985). In these patients the accumulation of aluminum in tissues causes an encephalopathy (dialysis encephalopathy or dialysis dementia), a specific form of metabolic bone disease (osteomalacic dialysis osteodystrophy), and an anaemia and also plays an etiological role in some of the other complications associated with end-stage chronic renal disease (Michael and John, 1985). Persons with Alzheimer’s disease have been found to experience increased absorption of aluminum and higher blood levels (Erik, 2001). More controversially, the majority of brain studies also show elevated aluminum levels, though there is disagreement over location of metal build up.

Clinical intervention to lower brain aluminum by chelation has slowed the progression of Alzheimer's disease (Erik, 2001).

2.2.4.3 Allergic effects of Aluminium

2.2.4.3.1 Introduction

In the Camefold legend a massive aluminium load was added to the domestic water supply of 12,000 residents and 8000 holiday visitors in the district of Lowermoor, north Cornwall-England. For 2-3 days, residents were subjected to acid tasting, milk-curdling and sometimes grossly discoloured water (Anthony and Wessely, 1995). Immediate symptoms included nausea and vomiting, skin rashes and mouth ulcers (Anthony and Wessely, 1995). Others noted that their hair, skin, or finger nails had been stained blue or brown. Widespread sickness in farm animals and disruptive behaviour in school children were experienced. For 3 days, the European Community maximum admissible concentration for aluminium (0.2 ppm) had been exceeded several hundred folds (Anthony and Wessely, 1995). This incidence points at allergic reactions due to excessive intake of aluminium.

2.2.5.3.2 Hypersensitivity

Although human exposure to aluminium is widespread, hypersensitivity has been reported following exposure to some aluminium compounds. A case of contact sensitivity to aluminium was reported in Sweden where the patient had regularly been using an aluminium chloride roll-on antiperspirant and developed an itchy dermatitis in the axillae. In another case, contact allergy to aluminium also occurred to a patient hyposensitized with aluminium precipitated grass pollen. Two cases of contact allergy to aluminium after use of topical medications containing aluminium acetate have been reported (UNEP *et al*, 1997).

2.2.4.3.3 Restrictive pulmonary disease

Occupational exposure associated with pulmonary fibrosis was experienced by "pyro powder" workers, who were exposed to very fine stamped aluminium powder (generally less than 1μm) including that used in manufacture of explosives and fireworks. In the process, oils and solvents were used to coat particles to prevent naturally occurring oxidation,in nearly all cases of fibrosis were reported in workers exposed to mineral oil-coated particles. This syndrome indicates the potential pulmonary effect of non-oxidized aluminium metal, but such exposures do not occur in nature (UNEP *et al*, 1997)

According to a UNEP *et al* 1997 report, nine cases of workers exposed to aluminium oxide for 25 years experienced abnormal chest problems. Biopsies were taken from three patients and analyzed by electron microscopy and microbe analysis. Interstitial fibrosis was the main histological finding. Metals occurred in amounts several orders of magnitude above background levels and the most frequent was aluminium oxide. The authors stated that aluminium oxide was the most likely cause for development of interstitial fibrosis in the workers and that asbestos could be ruled out (UNEP *et al*, 1997).

2.2.4.3.4 Asthma

A form of occupational asthma related to primary aluminium smelting (pot-room asthma) has been identified. It exhibits reversible symptoms of airflow limitation and increased bronchial responsiveness. The likely causes are irritant airborne particles and fumes from cryolite (sodium aluminium fluoride), gaseous hydrogen fluoride and other agents that may be adsorbed onto aluminium. A close relationship in aluminium pot room workers levels of exposure and work related asthmatic symptoms have been shown. A positive association between plasma levels of fluoride and increased bronchial responsiveness has also been reported (UNEP *et al*, 1997). A similar occupational asthma ascribed to irritant particles has also been described among workers following technical failure in plants producing aluminium fluoride and aluminium sulphate and in soldier's working with potassium aluminium tetra fluoride flux (UNEP *et al*, 1997). All this shows that exposure to aluminium and fluoride could lead to "occupational asthma".

2.2.4.3.5 Chronic bronchitis

Aluminium mining and processing may lead to high levels of work place exposure to dusts and particles. In Italy the possible association of aluminium exposure and pneumoconiosis was investigated. Chronic bronchitis symptoms were found in 39% of the 119 exposed workers and in 13 % of the 119 control subjects. The X-ray findings showed one kind of pneumoconiosis with small irregular opacities or accentuation of bronco pulmonary markings in 29% of the exposed workers and in 15% of the controls (UNEP *et al*, 1997).

A case study of 2086 people at Arkansas who were employed in the operation of a large aluminium production company was performed. The study indicated that long-term high accumulative dust exposure was associated with decreased levels of pulmonary function in active workers at a bauxite refinery and aluminium-based chemical product plant (UNEP *et al*, 1997). A follow up study of this cohort supported the conclusion regarding respiratory effect of dust in workplace related to lung function. In a cross-section study on 64 aluminium welders and 64 age matched controls (non-welding industrial workers), an increased prevalence of chronic bronchitis was observed among aluminium welders (UNEP *et al*, 1997).

2.2.4.4 Microcytic anaemia

It has been observed that a variable degree of anaemia was associated with aluminium toxicity. In a study by UNEP *et al*, 1997, 12 patients who had high plasma aluminium developed microcytic anaemia. Subsequent dialysis with aluminium-free water reduced plasma aluminium levels, reversed the red cell morphology to normal, and increased the hemoglobin concentration (UNEP *et al*, 1997). Aluminium is thought to inhibit uptake of iron in the gastrointestinal tract leading to anaemia (UNEP *et al*, 1997). In earlier studies done, it has been shown there is an anaemia associated with aluminium toxicity (UNEP *et al*, 1997). Therefore uptake of foods containing high aluminium will inhibit uptake of essential minerals. That is why it is advisable to reduce black tea intake during meals that provide the essential minerals.

2.3 Fluoride

2.3.1 Chemistry of fluoride

Fluoride is the most reactive of non-metals and the most electronegative element, and therefore almost never occurs in nature in its elemental state Fluorine (F_2) is a greenish diatomic gas. Fluorine is so highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes (WHO, 2002; Nagendra Rao, 2003). The fluoride occurs notably as Sellaite, fluorspar, CaF_2; Cryolite, Na_3AlF_6; Fluorapatite, 3Ca3 (PO4)2 Ca(F,Cl2) (Nagendra Rao, 2003). It combines with all elements, except oxygen and the noble gases, to form fluorides. Inorganic fluorides are present in all soils and water as well as in the plants and animals consumed by human for food (WHO, 2002).

Hydrogen fluoride is probably the greatest single atmospheric fluoride contaminant, due to its extensive use in industries. The contribution of volcanic activity to the content of fluoride in the earth's atmosphere is 1.7 x 10^6 tonnes per year (WHO, 2002**.** Most air borne fluoride in urban areas comes from industrial sources (WHO, 2002).

2.3.2 Human exposure to fluoride

Inorganic and organic fluorides are present in all soils and water, as well as plants and animals consumed by humans. Except for industrial emissions, the largest environmental source of fluorides is fluoridated water supplies (George, 1981). Natural fluoride in water is derived from weathering of rocks and solvent action of soils of the earth's crust. It also depends on soil-gas and rocks with which it comes into contact in the unsaturated zone, residence time and the reactions that take place within the aquifer. Therefore, considerable variation can be found, even in the same general area, especially where rocks of different compositions and solubility occur (WHO, 1996). High-fluoride-containing waters are found mostly in calcium-deficient ground waters in many basal aquifers, such as granite and gneiss, in some sedimentary basins, and in geothermal waters (Roberto and Jorge, 2004).

In some parts of the world, deposits of rocks containing a high level of fluoride cause a large increase in fluoride content in water or food and consequently the exposure to fluoride. Fluoride is found in insecticides, rodenticides and toothpaste among other products. Except under occupational exposure conditions, respiratory fluoride is almost negligible. Total fluoride intake depends on fluoride levels in foods, beverages as well as water (WHO, 2002).

Fluoride concentrations above 5.0 ppm in Ethiopian Rift Valley were found mostly in hot springs (100% of all sources), lakes (78%), shallow wells (54%) and boreholes (35%) and the lowest concentrations (below 1.5 ppm) in springs and rivers (Kloos and Haimanot , 1999). Analysis of hydrochemical, economic and demographic factors in the spatial distribution of high-fluoride domestic water sources indicates that the fluorosis problem has become more serious in the Rift Valley in recent decades (Kloos and Haimanot , 1999). Considerable spatial variation in the occurrence of fluoride, even within the same communities, and the presence of some low-fluoride water sources in the Rift Valley offer possibilities for geochemical exploration for acceptable domestic sources (Kloos and Haimanot , 1999).

In a study by Njenga *et al.,* (2005) in Nairobi- Kenya, the fluoride content in 20 different vegetable juices, ranged from 1.2 ppm to 5.4 ppm. Some of the juices contained higher fluoride levels than the limits recommended by the World Health Organization for drinking water. Consumption of vegetable juices for healing therapy has become popular, and it is therefore important to consider the fluoride intake from this source (Njenga *et al.,* 2005). High levels of fluoride in fruit juices are usually due to the fluoride in water used in their preparation. Most of the borehole water in Kenya has fluoride levels ranging from 2.5 to 5.4 ppm which is higher than the WHO recommended maximum of 1.5 ppm (Njenga *et al.,* 2005)

2.3.3 Biological effects of fluoride

Fluoride exposure disrupts the synthesis of collagen and leads to the breakdown of collagen in bone, tendon, muscle, skin, cartilage, lungs, kidney and trachea (Susheela and Mohan, 1981). Fluoride depletes the energy reserves and the ability of white blood cells to properly destroy foreign agents by the process of phagocytosis. As little as 0.2 ppm in serum levels fluorides stimulate super oxide production in resting white blood cells, virtually abolishing phagocytosis (Gibson, 1992). Even micro-molar amounts of fluoride, below 1 ppm, may seriously depress the ability of white blood cells to destroy pathogenic agents. Fluoride confuses the immune system and causes it to attack the body's own tissues, and increases the tumor growth rate in cancer prone individuals (Gibson, 1992). Fluoride also depresses thyroid activity (Hillman, 1979).

2.3.4 The role of fluoride in human health

2.3.4.1 Dental carries and dental flourosis

Intake of fluoride helps prevent tooth decay (Dental carries). The post-eruptive protective effect is attributed to the reduced acid production by plaque bacteria and an increased rate of enamel remineralization. As such, the dental community generally favors the ingestion of fluoride to promote good dental health (Miller-Ihli *et al*, 2003). Orally ingested fluoride is readily absorbed from the gastrointestinal tract. Nearly all of the fluoride in the body is found in calcified tissues and any elimination is done through the kidneys. Fluoride in drinking waters might help to prevent tooth decay, if the level of fluoride ranges between 0.7 and 1.5 ppm, as recommended by the World Health Organization (Roberto and Jorge, 2004).

A study carried out on children supplied with water containing less than 0.3 ppm fluoride had a higher incidence of dental caries compared with another group of children supplied with fluoridated water (Antwi, 2006). In a study in Riyadh Saudi Arabia, the fluoride level in the influent to the seven groundwater treatment plants and their final product water were in the range of 0.63–1.6 ppm and 0.23–1.1 ppm, respectively. In general, the fluoride level in Riyadh drinking water supplies is below the optimum recommended level of 0.7 to1.2 ppm. Saudi Arabia has set its own recommended levels for fluoride in drinking water. It is therefore recommended that fluoridation be considered in water treatment plants

(Abdulrahman, 1997). For some of the samples with low fluoride content the population consuming the water is at risk of dental carries. Fluoridation would be an important alternative for such a population. Nevertheless, the ingestion of fluoride over 1.5 ppm over long periods of time produces severe effects on human health, such as dental and skeletal fluorosis, osteoporosis, hip fracture, arthritis, mental retardation and premature aging (Roberto and Jorge, 2004). Children between the ages of 2–3 are at most risk of suffering from cosmetic fluorosis but some evidence suggests that enamel fluorosis in primary teeth may be the result of infants ingesting formula reconstituted with fluoridated water. Skeletal fluorosis is the result of ingesting elevated levels of fluoride for extended periods of time (Miller-Ihli *et al*, 2003). Experts in skeletal fluorosis agree that ingestion of 20 mg of fluoride a day for 20 years or more can cause crippling skeletal fluorosis (Chen *et al.,* 1997).

A survey was done of the prevalence of dental fluorosis among children aged 7-16 years and the occurrence of skeletal fluorosis among adults aged 40-60 years living in regions in Senegal where fluoride concentrations in the drinking water ranged from less than 0.1 to 7.4 ppm (Brouwer *et al.,* 1988). In the area where the fluoride concentration in the drinking water was 1.1 ppm, milder forms of dental fluorosis were found, the prevalence being 68.5%. In areas where fluoride concentrations exceeded 4 ppm the prevalence of dental fluorosis reached 100% (Brouwer *et al.*1988). Kyphosis was very prevalent among a community whose drinking water contained 7.4 ppm fluoride. Radiographs of the vertebral column, hand, and wrist of 3 adults with kyphosis confirmed the diagnosis of skeletal fluorosis. High sweat loss and a high intake of water because of the hot weather may account for the finding. The present World Health Organization guideline for the upper limit of fluoride concentration in drinking water may be unsuitable for countries with a hot, dry climate. (Brouwer *et al.*, 1988).

In Davangere District- India, the fluoride levels in drinking water of selected villages were found to be in the ranges of 0.22-3.41 ppm (Chandrashekar and Anuradha , 2004). A stepwise increase in the prevalence of dental fluorosis with corresponding increase in water fluoride content, 13.2 % at 0.22 ppm fluoride to 100% at 3.41 ppm fluoride, was found(Chandrashekar and Anuradha, 2004). There was a significant positive linear correlation (r=0.99) between dental fluorosis and water fluoride level. Dental fluorosis is a major dental public health problem among children in Davangere district and is related to drinking water with 0.74 ppm fluoride or above. (Chandrashekar and Anuradha, 2004).

In a study on dental fluorosis and fluoride mapping in Langtang town, Nigeria, analyses of fluoride concentrations in 136 water samples revealed, in general the highest levels in stream water (2.39-3.96 ppm), followed by wells (1.26-2.82 ppm) and the least in pipe-borne water (0.5-0.97 ppm) (Wongdem *et al*, 2001). In plotting specific fluoride readings from the different identified sources on the geographical map of the study area, a distinctive pattern emerged. High fluoride readings were generally in the highland areas from which rivers and streams originated. Approximately 50% of the town was supplied with water containing fluoride above the optimum set by WHO (Wongdem *et al*, 2001).

2.3.4.2 Fluoride intake and IQ of children

Fluoride can produce detrimental biochemical and functional changes in the developing human brain. Exposure may commence with fluoride in the maternal blood passing through the placenta to the foetus and continues during childhood from fluoride in food and drinking water (Lu *et al.,* 2000). In the a study by Lu *et al.,* (2000), a high-fluoride level in drinking water resulted in a greater intake of fluoride which was confirmed by higher urinary fluoride levels. Intelligence was, in turn, inversely related to the level of fluoride in both drinking water and urine. No confounding factors such as population size or differences in social, educational, or economic background explained the relationship (Lu *et al.,* 2000).

In a study conducted in two villages in China, the mean IQ of the children living in the area with a high-fluoride level in drinking water was significantly lower than that of the children living in the area with a low-fluoride level in drinking water (Lu *et al.,* 2000). The average IQ for children living in an area with an average fluoride content of 3.5 ppm was 92.27, while the IQ of children living in an area with an average fluoride content of 0.37 ppm was 103.05 (Lu *et al.,* 2000).

For fluoride consumption by humans 3 mg F/day is a figure that should never be exceeded, and, of course, sodium fluoride in tooth pastes should be replaced with calcium fluorides, which are much less toxic (Veressinina *et al*, 2001).

The adequate intake (AI) for adults for fluoride is 0.05 mg/kg/day while the tolerable upper intake level (UL) is 0.1 mg/kg/day (Miller-Ihli *et al.,* 2003). Because of the conflicting health impacts associated with fluoride ingestion, the issue of fluoridating water is still debated. Some people believe that, fluoridation of water is only beneficial to children and argue against fluoridation of public water supplies (Miller-Ihli *et al.,* 2003). Others lobby for fluoridation of public water supplies arguing that there is little harm to fluoridation since literature reports show that fluoride intakes of less than 10 mg/day, show no adverse effects. (Miller-Ihli *et al.,* 2003).

As drinking habits differ in various parts of the world, determination of optimal concentration of fluoride for drinking water in Pakistan was performed using a modified Galagan and Vermillion equation, which applies a correction factor of 0.56 to the equation (Khan *et al.,* 2004). The optimal fluoride in drinking water in Pakistan using this modified equation was determined to be 0.39 ppm (Khan *et al.,* 2004). Observation of the correlation showed that a fluoride concentration of 0.35 ppm in drinking water was associated with maximum reduction in dental caries and a 10% prevalence of fluorosis (Khan *et al.,* 2004). Determining the most appropriate concentrations of fluoride in drinking water is crucial for communities. It is imperative that each country calculates its own optimal level of fluoride in drinking water based on the dose-response relationship of fluoride in drinking water with the levels of caries and fluorosis (Khan *et al.,* 2004). Climatic conditions, dietary habits of the population and other possible fluoride exposures need to be considered in formulating these recommendations (Khan *et al.,* 2004).

2.3.4.3 Skeletal fluorosis

Skeletal fluorosis is a complicated illness caused by the accumulation of too much fluoride in the bones (Hileman, 1988). Excessive exposure to fluoride causes an arthritic disease called skeletal fluorosis. It has a number of stages bones (Hileman, 1988). The first two stages are preclinical in that, the patient feels no symptoms though damage to the body has taken place. In the first preclinical stage, biochemical abnormalities occur in the blood and in bone composition bones (Hileman, 1988). In the second stage, histological changes can be observed in the biopsies of the bone. Some experts call these changes harmful because they are precursors of more serious conditions. Doses as low as, 2 to 5 mg per day can cause the preclinical and earlier clinical stages of skeletal fluorosis (Hileman, 1988). In the early clinical stage of skeletal fluorosis, symptoms include pains in the bones and joints manifested as sensations of burning, pricking, and tingling in the limbs; muscle weakness; chronic fatigue; and gastrointestinal disorders and reduced appetite. During this phase, changes in the pelvis and spinal column can be detected on x-rays. The bone has both a more prominent and more blurred structure (Hileman, 1988). In the second clinical stage, pains in the bones become constant and some of the ligaments begin to calcify. Osteoporosis may occur in the long bones, and early symptoms of osteosclerosis are present. Bony spurs may also appear on the limb bones, especially around the knee, the elbow, and on the surface of tibia and ulna. In advanced skeletal fluorosis, called crippling skeletal fluorosis, the extremities become weak and moving the joints is difficult. The vertebrae partially fuse together, crippling the patient (Hilemen and Washington, 1988). Skeletal fluorosis, especially in its early stages, is a difficult disease to diagnose, and can be readily confused with various forms of arthritis including osteoathritis and rheumatoid arthritis. In one Indian village studied in detail, Bhanakpur near Delhi, water with between 0.7 and 1.6 ppm of fluoride was enough to leave 17 per cent of the population suffering from the bent bones of skeletal fluorosis (The Manchester Guardian, 1998)**.** Experts in skeletal fluorosis agree that ingestion of 20 mg of fluoride a day for 20 years or more can cause crippling skeletal fluorosis (Chen *et al.*, 1997). Extensive dental fluorosis has been observed in the population exposed to drinking water of high fluoride content (Srikanth *et al.*, 2004).

In Kenya endemic fluorosis has been chronic for over 30 years (Nair and Gitonga, 1985). A long-term study showed that the fluoride content of ground water in Kenya ranged from 0.1 ppm to > 1 ppm in the majority of samples. Surface water contained a maximum of 34 ppm (Nair and Gitonga, 1985). Over 30% of Kenya's population suffers from dental fluorosis and, in isolated regions where the people depend on ground water for domestic use; nearly 100% of the population manifests varying degrees of dental fluorosis. (Nair and Gitonga, 1985). In a study by Wilkister *et al* (2002), 48.3 % of children observed in the area had moderate to severe dental fluorosis, even though most people in the area did not know the cause of the problem (Wilkister *et al*, 2002). There is need to educate the community on the causes of fluorosis, and to lay strategies for addressing the issue, such as encouraging more rainwater harvesting (Wilkister *et al*, 2002).

Between 1977 and 1985, the fluoride content of drinking water and the incidence of endemic fluorosis were assessed and correlated in 16 large farms, villages and towns in the Ethiopian Rift Valley. The fluoride level of drinking-water collected from wells there ranged from 1.2 ppm to 36.0 ppm (mean 10.0 ppm) (Haimanot *et al.*, 1987).

2.4. Interaction of Aluminium and Fluoride Toxicity Effects on Human Health

2.4.1 Introduction

Both aluminium and fluoride affects the skeletal and bone tissue as well as the neural system (Chen *et al.,* 1997). According to a press release from National Pure Water Association Ltd., UK (Press release,2003), the US government reported that fluoride in drinking water increases the toxicity of aluminium. In 1994, the New York Times reported a scientific study, which revealed that aluminium and fluoride in water could be responsible for the alarming increase in Alzheimer's disease and pre-senile dementia (Press release, 2003). This confirmed the long held suspicion that fluoride has the ability to act synergistically with other toxic minerals in drinking water (Press release, 2003).

It is acknowledged that most drinking water contains a substantial amount of fluoro-aluminium complexes. This should be a warning to dentists who hold with simplistic notion that fluoride only affects teeth and is perfectly safe in drinking water. Fluoridation will result in aluminium fluoride complexes, which enhance neurotoxicity. Fluoride itself will enhance uptake and synergize the toxicity of aluminium (Press release, 2003).

Other studies have shown that presence of fluoride enhances aluminium leaching in cookware. For example boiling fluoridated tap water in an aluminium pan leached almost 200 ppm of Aluminium in 10 minutes. Leaching of up to 600 ppm occurred with prolonged boiling (Press release, 2003).

2.4.2 Fluoride and aluminium toxicity in skeletal changes and osteomalacia

High blood aluminium levels may halt normal bone mineralization, resulting in crippling bone disease and multiple fractures (FAO and WHO, 1995). An elevated aluminium intake is associated with rickets and osteomalacia (Chen *et al.,* 1997). The radiographic skeletal changes associated with intoxication by both fluoride and aluminium was found to be complicated with features of osteomalacia, and osteosclerosis with rickets (Chen *et al.,* 1997). Thirty-nine patients were studied from the District of Shui City in Guizhou province China, in which chronic fluoride toxicity or fluorosis was endemic (Chen *et al.,* 1997). The corn used as a major food source in Shui city is commonly contaminated by soil and coal. Many of the subjects had malformations of their limbs and joints (Chen *et al.,* 1997). Serum and urine levels of fluoride, aluminium and calcium were elevated as compared to normal controls. The changes seen at histology involved decreased ossification, a widening of the spaces between trabeculae, osteoporosis, dilatation of Haversian canal in cortical bone, a rarity of oesteoblast, and increased osteoid. The patients showed radiographic features of skeletal metabolic disease. It has been shown in animal studies that fluoride and aluminium can produce both independent and interactive effect on bone. Fluoride affected the synthesis of osteocytoplasm and resulted in increased osteoid. Aluminium affected the mineralization osteo-cytoplasm and inhibited the calcification of osteoid. Together fluoride and aluminium stimulated osteoclastic activity and the parathyroid resulting in bone reabsorption and skeletal transformation (Chen *et al.,* 1997).

It was established that in bone, calcium can be replaced by hydrogen or sodium ions as well as by cations such as strontium, radium, magnesium or lead. Aluminium ions are also known to inhibit bone formation and mineralization (Chen *et al.,* 1997). This is because oral ingested aluminium salts bind to dietary phosphate, creating reduced plasma phosphate, which is in turn linked to impaired bone mineralization (Chen *et al.,* 1997). It has been found that the systemic administration of aluminium salts during hemodialysis to patients suffering from renal failure leads to bone aluminium deposition and impaired mineralization. This may explain why an elevated intake of aluminium is associated with rickets and osteomalacia (Foster, 1992).

Osteomalacia has been observed in patients with chronic renal failure, exposed to aluminium in dialysis fluids, or in infants with renal failure treated with aluminium hydroxide to control hyperphosphataemia (UNEP *et al*, 1997). Bone pain, myopathy, pathological structures and poor response to vitamin D therapy are the characteristic symptoms of osteomalacia. This is accompanied by radiological changes, including partial and complete non-healing fractures, osteopenia, and reduction in calcified bone area (UNEP *et al*, 1997). When

Aluminium was removed from dialysis fluids, incidence of osteomalacia diminished (UNEP *et al*, 1997).

CHAPTER THREE

3.0: MATERIALS AND METHODS

3.1 Experimental design

Soil, food and water samples were obtained from project areas in a cross-sectional study. Samples were picked from different locations within the project area randomly. Aluminium and fluoride content were determined in these samples. Analysis of variance (ANOVA) of the results was done using the Genistat analytical package.

3.2 Project area

Samples were obtained from Mwingi District in Eastern Province and Thika District in Central Province. In each District, two divisions with different agro ecological zones were sampled. From each of the divisions one location was sampled. In Thika, Ruiru and Kamwangi divisions were sampled. In Ruiru, Juja location was sampled while in Kamwangi, Chania was sampled. Juja is semi-arid, with relatively lower agriculture potential than Chania. In Chania, rivers are the main source of water. In Juja boreholes, piped water and rivers are the sources of water.

In Mwingi District, Nuu and Central divisions were sampled. In Mwingi there are no permanent rivers in the area sampled. However shallow wells are dug in the semi-permanent riverbeds. In Nuu Division, Nuu location was sampled while in Central Division, Kanzanzu location was sampled. Nuu has many spring waters sources, though it is a semi arid zone. Central Division has a higher agriculture potential and diversity than Nuu. Borehole water was found across all the locations sampled.

3.3 Water analysis

3.3.1 Sampling

Different sources of water from different locations were sampled. In Juja water, samples were obtained from, four boreholes, two rivers and two sources of piped water. In Chania water samples were obtained from four boreholes and three rivers samples. In Kanzanzu water samples were obtained from four boreholes, two shallow wells, and one tap. In Nuu location the samples were obtained from three boreholes, three springs, and two shallow wells. The different sources represent the type of water available in the location for domestic use. Water samples, which were 500 ml each, were obtained in triplicate from each site. The samples were analyzed in duplicate. The samples were acidified using 1.5 ml nitric acid per liter of water to preserve them, within 24 hours of sampling.

Table 1. Water sources sampled and their locations.

Location /source of water	Boreholes	Rivers	Springs	Shallow/ wells (Seasonal rivers)	Piped
Chania	Wa mumbi Maina Mausoleum Gatukuyu	Chania Karimino Kianguni	Munyini Mola Nuu	-	-
Juja	Wa Njoki Wa Njiraini Mirimaini Wa Evans	Ndarugo Thiririka	-	-	Gachororo JKUAT
Kanzanzu	Mugo Jojo Matiti Bajaba	-	-	Tyaa Kivou	Mwingi
Nuu	Kyambua Kavingo Mwenga	-	-	Mbia Enziu	-

3.3.2 Determination of fluoride in water

Determination of fluoride was done according to the method of Greenberg *et al.,* (1998). The samples were directly analyzed for fluoride by SPADNS (sodium 2-(parasulphophenylazo-)-1,8-dihydroxy-3,6-naphthalene disulphonate) method. The SPADNS calorimetric method is based on the reaction between fluoride and zirconium- Dye Lake. This method relies on the fact that when fluoride reacts with certain zirconium dyes, a colorless complex anion and a dye are formed. The complex, which is proportional to the fluoride concentration, tends to bleach the dye which therefore becomes progressively lighter as the fluoride concentration increases. In the case of the fluoride ion reaction with Acid zirconyl-SPADNS, the resulting colored complex is measured in a spectrophotometer at 570 nm. A Spectrophotometer (Shimadzu UV mini 1240) was used. Fluoride in samples was determined from a standard curve of standard solutions made (refer to Appendix 1).

3.3.3 Determination of Aluminium in water

Aluminium in water was analyzed using the method described by Lopez (Lopez *et al.*, 2001; AOAC,1996). The AAS used a nitrous oxide/acetylene flame. A burner head of 5 cm was used and a slit width of 1.9 cm. The lamp current was 14 mA. The wavelength used was 3093 nm. This water had, however, been acidified by 1.5 ml nitric acid per liter of water for preservation and filtered. Lathanum chloride (0.1%) was added to standards and samples. Aluminium in the samples was determined from a standard curve drawn from readings of standard solutions prepared. (Refer to Appendix 2.)

3.4 Soil analysis

3.4.1 Sampling of soil

In each location soils were sampled from three sites (Table 2). From each site three samples were obtained, each weighing 500 g. soil sample was collected. Soils from 5 randomly selected parts of each sampling site were homogeneously mixed to give one composite sample. This was repeated to give a second and third sample. The soil samples were collected using a shovel, which cut vertically down picking soil from the surface to a depth of 15 cm. (Furgison. *et al.*, 2005; Crop and soil manual, 2003). The soil was then put in plastic bottles.

Table 2: Sites of soil sampling.

Location /soil sites	Chania	Juja	Kanzanzu	Nuu
Site 1	Wa Mumbi	Wa Njoki	Jojo	Kavingo
Site 2	Mausoleum	Wa Njiraini	Matiti	Mwenga
Site 3	Kianguni	JKUAT	Bajaba	Kyambua

3.4.2 Determination of fluoride in soil

SPADNS method was used for the determination of fluoride in all samples (Greenberg *et al.*, 1998). For extraction of fluoride from the soil, 20 ml of 0.2 M ammonium oxalate at pH 3 was added to a soil sample weighing 0.5 g. It was shaken for 4 hours in darkness at 300 revolutions per minute (rpm). It was then filtered using a filter paper and washed in deionised water; just enough to clean off the soil from the conical flask (Begin and Fortin, 2003). It was then topped to 25-ml with distilled water. In this method, 5-ml spadns/acid zirconyl mixture was added to the 25-ml sample and the absorbance read on the spectrophotometer, (Shimadzu UV mini 1240) at 570nm. The fluoride content was obtained from a standard curve obtained from standard fluoride solutions (refer to Appendix 3)**.**

3.4.3 Determination of aluminium in soil

A 2 g air-dried soil sample was shaken with 20 ml 1N KCl (potassium chloride), for 30 min at 300 rpm, filtered and topped with distilled water to 25 ml. It was then analyzed by the AAS, using acetylene/ nitrous oxide flame. A burner head of 5 cm was used and a slit width of 1.9cm.The lamp current was 14 mA. 0.1% Lathanum chloride was added to standards and samples. Aluminium in the samples was determined from a standard curve (refer to Appendix 2) obtained from prepared standard solutions (Lopez *et al.,* 2001; Beartsc and Bloorn, 1996).

3.5 Food analysis

3.5.1 Sampling of food

The samples were collected in triplicates and analyzed in duplicates. The food samples were from the geographical locations indicated earlier. The raw food samples were obtained from retail outlets in the geographical Locations indicated earlier in both Thika and Mwingi Districts. The food samples obtained were sweet potatoes, milk, tea, kales, tomatoes, dry maize, beans and cow peas. Maize and beans were collected in all the Locations in the project site. In Chania, tea, sweet potatoes and milk were also collected. In Juja Kales and Tomatoes were also collected. In Kanzanzu cowpeas were also collected, while in Nuu no additional sample was taken. The food samples collected reflected those commonly consumed in the location.

3.5.2 Determination of aluminium in foods

One g of each milled sample was weighed into a crucible. It was heated on a hot plate and allowed to smoke until completely charred. The samples were ashed in muffle furnace for 4 h at 550^{o} c. The ash was then dissolved in a few drops of concentrated hydrochloric acid. The hydrochloric acid was evaporated on a hot plate and the sample returned to muffle furnace for a further 4 h. The above was repeated until no more black specks were observed. The ash was then dissolved in 2 ml of 6N hydrochloric acid and diluted to 100 ml with distilled water. Lanthanum chloride (0.1%) was added to the solution. Aluminium in the samples was determined from a standard curve (Refer to Appendix 2) obtained from prepared standard solutions (Lopez *et al.*, 2001; AOAC, 1996).

3.5.3 Determination of aluminium content during cooking

Foods were cooked in both aluminium and stainless steel pots. The foods were cooked using distilled water; to be sure any additional aluminium in the food is from the pots. The changes in food due to use of aluminium pots was then determined. The aluminium content in these foods was then determined using the method described in 3.4.3, when cooked with stainless steel and aluminium pans. The foods prepared were ugali, tea, sweet potatoes, maize and beans.

3.5.3.1 Preparation of foods

3.5.3.1.1 Ugali

Water was boiled and flour added at a ratio of 5:2 and made into a smooth paste (Ugali) and cooked until ready. The whole process took 30 minutes. The ugali was dried and prepared for analysis using the AAS as for other uncooked samples, described earlier.

3.5.3.1.2 Tea

A mixture of 50 ml water and 50 ml milk was boiled and 0.5 g of tea leaves added and removed immediately. The whole process took 10 minutes. The tea sample was aimed to be representative of the type of tea most commonly consumed. It then was analyzed for aluminium as described in 3.4.3.

3.5.3.1.3 Sweet potatoes

One hundred grams of sweet potatoes were boiled in 100 ml of water for 30 minutes. When the time was over the sweet potatoes had absorbed all the water. The sweet potatoes were dried and analyzed for aluminium as described in 3.4.3.

3.5.3.1.4 Kales

One hundred grams of fresh kales were steamed for 20 minutes, without any addition of water. The kales were dried and analyzed for aluminium as described in 3.4.3.

3.5.3.1.5 Maize

One hundred grams of maize was cooked in 200 ml water. After 30 minutes, 150 ml water was added. Cooking was stopped after one hour and the residue water discarded. It then was analyzed for aluminium as described in 3.4.3.

3.5.3.1.6 Beans

One hundred grams of beans was cooked in 200 ml water. After 30 minutes, 150 ml water was added. Cooking was stopped after one hour and any residue water drained off. The beans were then analyzed for aluminium as described in 3.4.3.

3.5.4 Determination of moisture content in foods

Two grams of milled sample was weighed into a moisture dish. The dish was put in the oven at 110^{o}C for 3 h (Gomez *et al.,* 1997). It was then removed from oven and placed in a dessicator and allowed to cool. The final weight of dish and sample were determined and moisture content calculated as follows-:

% M.C. =Initial weight of sample and dish –final weight of dish and sample/Initial weight of sample and dish x 100 (Gomez *et al.,* 1997). The moisture content of foods was applied in getting all results as per dry weight matter.

CHAPTER FOUR

4.0: RESULTS AND DISCUSSIONS

4.1 Fluoride levels

4.1.1 Fluoride levels in Soil

Table 3: Fluoride content in soils

Location	*Site*	*Soil type*	*Soil pH*	*Fluoride (ppm)*
Juja	Wa Njoki	Plinthosols	7.1	406±28^{bc}
	Wa Njiraini	Plinthosols	6.8	427±37^{abc}
	JKUAT	Plinthosols	7.2	408±34^{bc}
Chania	Kianguni	Humic nitisols	4.4	126±29^{e}
	Mausoleum	Humic nitisols	5.7	211±30^{bc}
	Wa Mumbi	Humic nitisols	5.5	174±30^{d}
Kanzanzu	Jojo	Orthic acrisols	7.4	460±23^{a}
	Bajaba	Orthic acrisols	6.8	452±6^{a}
	Matiti	Orthic acrisols	7.9	447±22^{ab}
Nuu	Mwenga	Orthic ferrasols	7.7	469±14^{a}
	Kavingo	Orthic ferrasols	7.1	390±7^{c}
	Kyambua	Orthic ferrasols	7.5	463±13^{a}
Lsd				0.142

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Table 3 shows the fluoride content in soils analysed in the area of study. The highest fluoride content was from Mwenga (469 ppm) in Nuu Location, Mwingi District and the lowest recorded in this study was Kianguni (126 ppm) in Chania Location. Soils in Chania are generally acidic and with the lowest fluoride content. These soils were mainly humic nitisols. Humic nitisols are made from Olivine basalts and ashes of older volcanoes (Muchena and Gachene, 1988). The other soils from other locations are made up of orthic fererasals orthic acrisols and the plinthisols (Survey of Kenya, 2007). These soils are made up of quartz (Sio2) Kaolinite iron oxides of Fe3O2 and FeOOH as well as aluminium oxides Al(OH)3. This explains the increased levels of fluoride in these soil types as compared to the humic nitisols. The humic Nitisols also have low pH as shown above (table 3). Fluoride is found in soil, in varying concentrations (Wilkister *et al.*, 2002).The concentration of fluorides in soils is usually between 200 and 300 ppm. However, levels may be higher in areas containing fluoride-containing mineral deposit (ATSDR, 2004). Only two soil samples in this study had fluoride content less than 300 ppm (Kianguni and Wa Mumbi both in Chania location). The other ten sites had fluoride content above 300 ppm. This showed the fluoride levels in soil in this study are higher than the levels shown above.

Fluoride is ubiquitous in the environment and is always present in plants, soils and phosphatic fertilizers (Madhavan and Subramanian, 2001). Various rock types contain fluoride at different levels: basalt, 360 ppm; granites, 810 ppm; limestone, 220 ppm; sandstone and greywacke, 180 ppm; shale, 800 ppm; oceanic sediments, 730 ppm; and soils, 285 ppm (Madhavan and Subramanian, 2001). The fluoride concentration in the upper continental crust is 611 ppm. It is an essential constituent in minerals such as fluorite, apatite, cryolite, and topaz. (Madhavan and Subramanian, 2001). Approximately 20 to 400 g fluoride per hectare is annually leached from soils, about the same amount that is added to the soil from the atmosphere, but fertilizing adds another 5 to 30 kg fluoride per hectare annually. This fluoride accumulates in the soils. The main part of fluoride in rainwater may originate in sea aerosols: With increasing use of fertilizers containing fluoride, the fluoride content of surface water also increases (Madhavan and Subramanian, 2001).

Application of phosphate fertilizers, sewage sludge and some pesticides also bring fluoride to soil (ATSDR, 2004). It is common that most farmers nowadays use phosphate fertilizers in their farms. This high level may lead to fluorosis in cattle feeding from grass grown in such soils (ATSDR, 2004).

However it has been shown conclusively that the amount of fluoride which is taken up from the soil by plants is usually unrelated to the fluoride content of the soil. Soil type, calcium and phosphorus content, and soil reaction (pH) seem to be the predominant controlling factors (Raymond, 1978). Therefore it is not automatic that vegetation/plants growing in this study area will have high fluoride levels. However use of super phosphate fertilizers will add fluoride to the soil.

In a study by Kusa *et al.*, (2004) in Poland, vegetables were found to absorb fluorine, both from the soil and air, as well as from falling atmospheric dust. It was observed, both in the leaves and roots of the vegetables examined, that the concentration of fluoride was in each case higher in vegetable samples from an area 6 km from the “Katowice” Steel Works (fluorine emitters), than in the vegetable samples grown in Nowy, 200 km from the “Katowice” Steel Works (in the area of relatively low fluorine pollution) (Kusa *et al.*, 2004). The highest fluoride content was characteristic of beet leaves and root samples, the lower one was found in celery leaves and root samples and the lowest one in savoy leaf samples. The highest and lowest fluoride concentrations in the leaf samples examined in the above study on dry weight basis was 33 ppm and 11 ppm respectively (Kusa et *al.*, 2004).

4.1.2 Fluoride levels in Water

4.1.2.1 Fluoride in Borehole water

Table 4: Fluoride content of water from boreholes.

Location	Site	Fluoride (ppm)
Chania	Wa Mumbi	0.58 ± 0.08^{ab}
(Thika)	Maina	0.60 ± 0.05^{bc}
	Mauseleum	0.45 ± 0.05^{a}
	Gatukuyu	1.00 ± 0.00^{e}
Juja	Wa Njoki	0.73 ± 0.03^{cd}
(Thika)	Wa Evans	1.18 ± 0.12^{f}
	Wa Njiraini	1.27 ± 0.12^{fg}
	Mirimaini	1.16 ± 0.16^{f}
Kanzanzu	Bajaba	1.17 ± 0.06^{f}
(Mwingi)	Matiti	2.37 ± 0.10^{i}
	Jojo	2.47 ± 0.12^{i}
	Mugo	0.75 ± 0.03^{d}
Nuu	Kyambua	1.38 ± 0.12^{g}
(Mwingi)	Kavingo	2.10 ± 0.03^{h}
	Mwenga	0.55 ± 0.02^{ab}
Lsd		0.142

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Fluoride content in boreholes ranged from 0.45 ppm in a sample from Mauseleum in Thika District to 2.47 ppm in a sample from Jojo from Mwingi District (Table 3). The fluoride content of water from six samples (Wa Njiraini, Wa Njoki, Mirimaini, Gatukuyu, Kyambua and Bajaba) out of fifteen was within the WHO recommended levels of 1-1.5 ppm (WHO and FAO, 1995). All samples from Chania and Juja locations in Thika District, had fluoride levels within or below the WHO recommended levels (Table 3). Three boreholes from Mwingi District had fluoride content above the WHO recommended levels of 1-1.5 ppm (Table 3). The recommended levels prevent dental carries and do not lead to skeletal or dental flourosis. Fluoride content in water from different boreholes in the same location, as well as from different locations shows significant differences (Table 3).

Fluoride concentration of natural waters therefore depends, among other things, on the solubility of fluoride-containing mineral in the underground water and the porosity of the rocks and soil through which the water passes (Antwi, 2006). Geological basis for the high concentration of high fluoride has been established; it is presumed to be the pegmatite intrusion hosted by a granitic batholith (Srikanth *et al.,* 2002). This explains the observation that the levels of fluoride may vary in boreholes within same location. The quality of groundwater depends on the composition of the recharge water and the interactions between the water and the soil.

Soil samples from Kyambua in Nuu Location, Mwingi District and Jojo from Kanzanzu Location in Mwingi District had relatively high fluoride content, 463 ppm and 460 ppm respectively, while boreholes from the same site had equally relatively high fluoride content, 2.47 ppm and 1.38 ppm respectively. However Mwenga soil sample had the highest fluoride content (469 ppm), while water from the same site had relatively low fluoride content (0.55 ppm). Soil samples from Kianguni and Wa Mumbi sites in Chania location, Thika District had the lowest fluoride content (126 ppm and 174 ppm), while water from the same sites had relatively low fluoride content of 0.63 ppm and 0.58 ppm respectively. This shows that location had an implication on the fluoride content of the soil or water samples, although not in all cases.

The results of fluoride content observed in this study are within the range reported in other studies. The fluoride content of 97 samples of ground water collected in Douglas County ranged from 0.0 to 12 ppm. Fifteen samples, all from Pennsylvanian sandstone aquifers, contained fluoride in amounts greater than 1.5 ppm (O'Connor, 1999). In a study on fluoride variations in groundwater of an area in Buenos Aires Province, Argentina, fluoride concentration varied between 0.2 and 5 mg/l (Kruse and Ainchil, 2003). In a study on fluoride content in drinking water in Estonia the concentration of fluoride in groundwater in different regions of Estonia, was found to vary from 0 to 6 ppm, which means that the guidelines are exceeded quite frequently. Therefore, fluoride removal has to be conducted in many Estonian towns and settlements (Veressinina, et al., 2001). It is also important that fluoride analysis in boreholes for domestic use is analysed and where the levels are above the recommended level fluoride removal done. In the above study only three samples have over 1.5 ppm (table 4) and would therefore need fluoride removal.

In a study in Ghana, 50 % of the boreholes from the Accra Plains had fluoride concentrations either equal to or greater than 1.5 ppm while only 8.2 % boreholes from the Upper Regions were below this limit (Antwi, 2006). In this study fluoride content in 20 % of the borehole waters, had fluoride content above the WHO recommended levels, while 40 % were within the recommended levels and the rest were below. A study was also undertaken to estimate fluoride content in the groundwater in certain parts of rural Eritrea, North-East Africa, along the River Anseba. Results indicate elevated concentration of fluoride in groundwater. The highest concentration was found to be 3.73 ppm, well above the safety level for consumption (Srikanth *et al.*, 2002). Three of the boreholes in this study (Jojo, Matiti and Kavingo) had fluoride levels above the recommended levels. This shows that some boreholes sources of water can expose consumers to higher levels of fluoride which may eventually lead to toxicity. Generally fluoride depresses thyroid activity which affects the skeletal and bone tissue (Gibson, 1992).

4.1.2.2 Fluoride in River water

Table 5 shows fluoride content in river water samples. Samples from rivers were collected from Juja and Chania locations in Thika District. Thiririka and Ndarugo rivers from Juja had very low fluoride levels, which were not significantly different. Fluoride levels in water from within the same location were not significantly different ($p \leq 0.05$). However, fluoride levels were significantly different between locations. The highest and lowest fluoride level recorded was 0.7 ppm and 0.05 in Chania and Thiririka rivers respectively. The content of water from all the rivers was less than the WHO recommended levels of 1-1.5 ppm (WHO and FAO, 1995). Rivers from Chania location had significantly higher fluoride content than rivers in Juja location. The underlying rock at the source of the river influences the amount of fluoride in a river as well as human activity, such as use of phosphate fertilizers that add fluoride to the soil, which eventually drain to the rivers. (Gikunju *et al.,* 2002). Chania is more established in agriculture than Juja. Juja is essentially an urban centre up, with little farming activity. This means the amount of fertilizers that will go to the rivers in Juja is less compared to Chania. This partly explains the higher fluoride contents in river water from Chania as compared to Juja. The fluoride content in river water was much lower than in boreholes in this study. The results of this study are in agreement with other previous study where, surface water sources such as rivers and dams had lower fluoride levels than ground water sources such as springs and boreholes. (Wilkister *et al.,* 2002).

Table 5: Fluoride content of water obtained from rivers.

River	Location	fluoride(ppm)
Thiririka	Juja	0.05 ± 0.02^{a}
Ndarugo	Juja	0.08 ± 0.02^{a}
Karimoni	Chania	0.43 ± 0.03^{b}
Kianguni	Chania	0.63 ± 0.10^{c}
Chania	Chania	0.70 ± 0.09^{d}
		0.1315

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

In a study by Gikunju et al (2002), the highest fluoride level in river waters was found to be 0.85 ppm in Laikipia District and the lowest was 0.08 ppm in Murang'a District. The mean for all samples was 0.3 ppm. Fluoride levels tended to be higher in the drier parts of the regions. The river fluoride levels in the above study were all fairly low, and the risk of fluorosis from them is therefore minimal (Gikunju *et al.,* 2002). Thus, river waters in Central and Nairobi provinces of Kenya do not pose a potential health hazard and may be used for domestic and industrial purposes (Gikunju *et al.,* 2002).

This study also shows low levels of fluoride in river waters, the values concur with the study by Gikunju *et al.,* (2002). The levels of fluoride in rivers in this study may not cause toxic effects to human health. However dietary and other sources of fluoride must be taken into account, because water is just one of many sources of fluoride intake. Where the community is consuming only water from the rivers with very low fluoride content (Thiririka, 0.05 ppm and Ndarugo, 0.08 ppm), the beneficial effects of fluoride may be lacking, hence exposing the population to dental carries. Nevertheless, further fluoride surveys of rivers in other parts of the country should be made Gikunju *et al.,* (2002). Further studies should also be done to compare the fluoride levels with effects on health of the population at hand.

4.1.2.3. Fluoride in spring water

All the spring water samples were from Nuu location in Mwingi District. The level of fluoride in spring water samples was not significantly different (Table 6).

Table 6: Fluoride content in water obtained from springs

Sample	Location	Fluoride (ppm)
Mola	Nuu	0.18±0.08
Nuu	Nuu	0.20±0.05
Munyini	Nuu	0.25±0.05
lsd		0.1201

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Levels for fluoride were low ranging from 0.18 ppm to 0.25 ppm in Mola and Munyini respectively. The levels were lower than those *recommended by WHO in drinking water (WHO and FAO, 1995). The springs sampled in this study show exceptionally lower levels compared to other studies in the Rift Valley, which showed levels of up to 39 ppm (Wilkister* et al.*, 2002). Fluoride is found in naturally occurring rocks, air, and water in varying concentrations (Wilkister* et al.*, 2002). This explains the difference shown in fluoride content in springs in this study compared to earlier studies by Wilkister et al., (2000). In Kentucky geological survey 50% of wells had fluoride concentrations less than 0.2 ppm or less, 90% had 0.8 ppm or less. The maximum fluoride level recorded in Kentucky geological survey was 78 ppm (Conrad* et al.*, 1999).*

The population consuming the spring waters in this study could be at risk of dental carries considering that fluoride is important for prevention of dental carries. A study carried out on children supplied with water containing less than 0.3 ppm fluoride had a higher Incidence of dental caries compared with another group of children supplied with fluoridated water (Antwi, 2006). Therefore in such a community water fluoridation should be considered.

In a study on dental caries and fluorosis in a 0.25 and a 2.5 ppm fluoride area in the Sudan –Africa, 75% of the children in the low-fluoride area had decayed permanent teeth compared to 66% in the high-fluoride area (Ibrahimet *et al.*, 1997). This shows fluoride is necessary for prevention of tooth decay (Carries).

4.1.2.4. Fluoride in shallow well water

Table 7 shows fluoride content in water from shallow wells. Water from shallow wells in this study had fluoride content ranging from 0.48 ppm in Kivou, Kanzanzu location to 1.1 ppm in Tyaa in the same location. Shallow wells were sampled from Mwingi District. Generally water from shallow wells in this study has low levels of fluoride but the content was higher than spring and river water. None of the shallow well had water with fluoride levels above the WHO recommended one. The fluoride contents in the water from shallow wells in Nuu location were not significantly different ($p = 0.005$) (Table 6). Fluoride levels in well water samples from Kivou and Tyaa samples, from Kanzanzu were significantly different ($p = 0.05$).

Fluoride content in well water generally ranges from 0.02 to 1.5 ppm, but has been reported to exceed 1.5 ppm in parts of the Southwest United States (ATSDR, 2004).

Table 7: Fluoride content in water obtained from shallow wells.

Sample	Location	Fluoride (ppm)
Kivou	Kanzanzu	0.48 ± 0.03^{a}
Mbia	Nuu	0.50 ± 0.10^{ab}
Enziu	Nuu	0.62 ± 0.05^{b}
Tyaa	Kanzanzu	1.10 ± 0.00^{c}
lsd		0.1201

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

In a study in India, the surface, subsurface and thermal water sample analysis indicated fluoride concentration ranging from < 0.2 to 18 ppm in the States of Jammu and Kashmir, <0.2 to 6.5 ppm in Himachal Pradesh, > 1.5 ppm in Rajsthan, 0.2 to 0.6 ppm in Haryana, 0.35 to 15 ppm in Bihar, on an average 12 ppm in West Bengal, 15 to 20 ppm in Chattisgarh, 8.2 to 13.2 ppm in Orissa and 0.7 to 6.0 in Maharashtra. This indicates that except in Haryana, the concentration of fluoride is very high, up to 20 ppm (Sharma, 2003). Waters in nine States in India was beyond the permissible limit fixed by the WHO for human beings, the consumption of which would cause flourosis. It may also cause harm to the ecosystem and vegetation, if used for irrigation (Sharma, 2003).The fluoride content in this study compares with some studies done earlier, however it is below the levels of fluoride in most Indian states as shown above.

4.1.2.5 Fluoride in tap water

The highest fluoride content recorded in tap water was 0.09 ppm (JKUAT) and the lowest was 0.06 ppm (Mwingi) (Table 8). Tap waters were collected from Kanzanzu and Juja locations only. The source of the tap water in Mwingi is Kiambere dam, while that from JKUAT and Gachororo was Ndarugo River. All the tap water samples collected had been obtained from different treatment plants. Differences in mineral content of tap water samples could have been due to the different rivers of origin as well as different treatment procedures involved. Fluoride content in all tap water samples were not significantly different. Tap water from Mwingi had slightly more fluoride than tap water from Gachororo and JKUAT. All tap water samples in this study had very low fluoride levels. This shows their use poses no risk of fluoride toxicity. Instead it may lead to increased risk of dental caries. However there is a high possibility that the fluoride in these sources has been precipitated by aluminium salts used during water treatment (WHO, 2002).

Table 8 Fluoride content in water obtained from taps waters

Sample	Location	Fluoride (ppm)
Mwingi town	Kanzanzu	0.06±0.03
Gachororo	Juja	0.07± 0.01
JKUAT	Juja	0.09±0.02
lsd		

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Studies done elsewhere have shown that tap water may have relatively higher levels than those observed in this study. In San Luis Potosi-Mexico a biochemical and epidemiological study indicated that 61% of tap water had fluoride levels above the optimal level of 0.7–1.0 ppm, set by Mexico City (Roberto and Jorge, 2004). Fluoride levels ranged from 1.54 to 5.67 ppm in drinking water at the city of Durango (Roberto and Jorge, 2004). In addition, in the city of Durango, a water well characterization reported fluoride levels higher than 12 ppm (Roberto and Jorge, 2004). In Hermosillo, which is located in the northern part of Mexico, up to 7.36 ppm fluoride, has been reported (Roberto and Jorge, 2004). Another Mexican city with high levels of fluoride is Aguascalientes, where fluoride content of drinking water has been reported up to 11.31 ppm. Results indicated that water supply from 42% of the municipalities had a fluoride concentration over the Mexican standards of 1.5 ppm (Roberto and Jorge, 2004). In three cities, Lagos de Moreno (1.66–5.88 ppm), Teocaltiche (3.82–18.58 ppm), and Encarnación de Díaz (2.58–4.40 ppm) all water samples resulted in fluoride concentration over the maximum contaminant level (Roberto and Jorge, 2004). Water fluoridation is harmful to humans and should be used with precaution (Andreas, 2004). Therefore as much as the fluoride levels in tap water may be low fluoridation should be carried out with consideration of other sources of fluoride in the diet.

4.1.2.6 Comparison of mean fluoride content from different sources of water

Table 9 shows the fluoride content in water from different sources from the two Districts of Mwingi and Thika. The sources sampled in this project are rivers, boreholes, springs, taps and shallow wells. There were 15 boreholes, 4 shallow wells, 5 rivers, 3 springs and 3 piped sources sampled. In both Districts there were considerably wide variation of fluoride content in borehole, shallow wells and tap waters. Boreholes had the highest mean fluoride content (1.21 ppm) followed by shallow wells (0.69 ppm). Tap water had the least mean fluoride content. This study concurs with other studies that show ground water to have the highest fluoride content as compared to other sources.

Table 9: Mean fluoride content in waters from different sources.

Source	Mean Fluoride (ppm)	Min-Max. Fluoride (ppm)
Boreholes	1.21	0.45-2.47
Shallow wells	0.67	0.48-1.10
Rivers	0.38	0.05-0.70
Springs	0.21	0.18-0.25
Tap	0.07	0.06-0.09

A study by Wilkister *et al* (2002) was carried out to measure the fluoride levels of water consumed in the Njoro division, of Nakuru District, Kenya. The sources of drinking water, methods of water storage and utilization, as well as the perceptions of the local community towards dental fluorosis and the percentage of children with moderate to severe dental fluorosis were also determined. Rainwater had mean fluoride levels of 0.5 ppm, dams 2.4 ppm, wells 4.1 ppm, springs 5.5 ppm, and boreholes 6.6 ppm (Wilkister, 2002). However the springs in this study show very low levels (Mean= 0.21 ppm) of fluoride compared to those in Njoro (5.5 ppm) as shown above.

In a study carried out in parts of Asia the fluoride content ranged from 0.2 $\mu g/m^3$ in the air samples over Delhi to a very high value of over 18 ppm in a hot spring in the Western Ghats region. (Madhavan and Subramanian, 2001). Large rivers with large run-off show higher levels of fluoride and hence greater fluoride flux to the oceans. Higher fluoride exposures due to enhanced application of rock phosphates adversely affect the health of the aquatic environment (Madhavan and Subramanian, 2001). Natural fluoride in water is derived from the solvent action of water on the rocks and soils of the earth's crust. Fluoride concentration of natural waters therefore depends, among other things, on the solubility of fluoride-containing mineral in the underground water and the porosity of the rocks and soil through which the water passes (Antwi, 2006).

In a study in Ethiopia the highest fluoride levels in water sources were recorded in the Rift Valley, where 41.2% of all samples exceeded the 1.5 ppm level. (Tekle-Haimanot *et al.,* 2005). Half of the water samples from deep wells, 90 % of hot spriongs, 27.2 % of shallow wells and 12 % of cold springs exceeded the 1.5 ppm limit. The highest fluoride concentrations were recorded for Rift Valley lakes, Shala (264.0 ppm) and Abijata (202.4 ppm) and the lowest in Lake Tana, and rivers, wells and springs in the highlands (Tekle-Haimanot *et al.*, 2005).

Therefore in view of the results in this study it's important to ensure water supply to any human population has the right amount of fluoride. For health safety, the Kenya Bureau of Standards recommends a maximum of 1.5 ppm fluoride in drinking water (Gikunju *et al.*, 2002). Dietary and other sources of fluoride must be taken into account, however, because water is just one of many sources of fluoride intake.

4.2 Aluminium levels

4.2.1 Aluminium levels in soil

Table 10 shows aluminium content in all soil samples analyzed in this study. The highest aluminium content is recorded in a sample (Kianguni) from Chania location, which is 1005 ppm. This aluminium content is far much higher than all the other samples considering all the others are less than 300 ppm. In Mwenga, Nuu location, no aluminium was detected.

Table 10: Aluminium content in soils

Location	*Site*	*Soil type*	*Soil pH*	*Al (ppm)*
Juja	Wa Njoki	Plinthosols	7.1	132±21^{c}
	Wa Njiraini	Plinthosols	6.8	251±13^{d}

	JKUAT	Plinthosols	7.2	144 ± 10^{c}
Chania	Kianguni	Humic nitisols	4.4	1005 ± 22^{f}
	Mausoleum	Humic nitisols	5.7	299 ± 55^{e}
	Wa Mumbi	Humic nitisols	5.5	223 ± 30^{d}
Kanzanzu	Jojo	Orthic acrisols	7.4	72 ± 0^{b}
	Bajaba	Orthic acrisols	6.8	114 ± 28^{bc}
	Matiti	Orthic acrisols	7.9	132 ± 21^{c}
Nuu	Mwenga	Orthic ferrasols	7.7	0 ± 0^{a}
	Kavingo	Orthic ferrasols	7.1	216 ± 0^{d}
	Kyambua	Orthic ferrasols	7.5	78^{b}
Lsd				47.49

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Soils in Chania were mainly humic nitisols. Humic nitisols are made from Olivine basalts and ashes of older volcanoes. Soils in the other locations were orthic fererasals (Survey of Kenya, 2007). Orthic acrisols and the plinthisols which are made up of quartz (SiO2), Kaolinite (Al2 (OH)4SI2O5), iron oxides of Fe3O2 and FeOOH as well as aluminium oxides Al(OH)3. Soil is made from rock that has been so broken down by weathering and erosion that it will support plant life. Soil is therefore a stage in the life history of rocks. Rocks, minerals and soils are part of the Earth's crust. Natural forces, which cause great changes to the Earth’s crust, include: volcanoes, earthquakes, erosion and weathering (Downs, 1993). These changes are part of the life cycle of rocks. Igneous rocks contain feldspars and micas which on weathering yield clay minerals such as kaoliniite (Al2 (OH)4Si 2O5) and hydroxides (Downs, 1993). The clay minerals contribute to the amount of aluminium in the soil. Depending on the pH of the soil the aluminium ion may be released to the soil solution (Downs, 1993). The soils with the lowest pH have the highest aluminium content. This can be explained by the fact that at low pH the Aluminium ion is released to the soil solution. Hence at low pH the Aluminium content is highest. This is confirmed by the high correlation coefficient (85%) between the pH and Aluminium content of the soil. Therefore depending on the soil formation stage at a particular geographical location, the aluminium content can be high or low.

4.2.2 Aluminium levels in water

4.2.2.1 Aluminium in boreholes

Table 11 shows the aluminium content in borehole water. The highest aluminium concentration recorded was 2.68 ppm in Juja location, while in three (25%) boreholes aluminium was not detected (Maina, Gatukuyu, and Jojo). A five-year survey of 1 577 raw surface waters of the USA showed a 31.2% frequency of detection for aluminium, which ranged from 0.001 to 2. 76 ppm and a mean, of 0.074 ppm **(**Srinivasan *et al.,* 1999). The same survey on 380 finished waters showed a 47.8% frequency of detection for aluminium, which ranged from 0.003 to 1 .6 ppm and a mean of 0.179 ppm. **(**Srinivasan *et al.,*, 1999). This study compare well with the above study from U.S.A, however the detection frequency was higher. Aluminium levels in most of the samples were not significantly different ($p<0.05$) (Table 11). The concentration of aluminium in natural waters can vary significantly depending on various physical chemical and mineralogical factors (WHO, 2003).

Table 11: Aluminium content in, water from boreholes in Mwingi and Thika Districts.

Location	Site	Aluminium (ppm)
Juja	Wa Njoki	0.10 ± 0.17^{a}
	Wa Njiraini	0.30 ± 0.30^{a}
	Mirimaini	1.78 ± 0.60^{d}
	Wa Evans	2.68 ± 0.30^{e}
Chania	Maina	0.00 ± 0.00^{a}
	Gatukuyu	$0.00\pm.0.00^{a}$
	Mausoleum	0.60 ± 0.00^{b}
	Wa Mumbi	1.19 ± 0.00^{c}
Kanzanzu	Jojo	0.00 ± 0.00^{a}
	Bajaba	0.20 ± 0.30^{a}
	Matiti	0.20 ± 0.30^{a}
	Mugo	1.19 ± 0.00^{c}
Nuu	Mwenga	1.19 ± 0.00^{c}
	Kavingo	1.39 ± 0.34^{dc}
	Kyambua	1.78 ± 0.00^{d}
Lsd		0.384

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

For example, at the Jojo site, soil sample had low aluminium content (72 ppm) and the borehole in the same site had no aluminium detected in it. Mwenga soil sample had no aluminium detected in it; however water sample had 0.6 ppm. Kianguni soil had the highest aluminium content of 1005 ppm (Table 10), while the river water has 0.6 ppm (Table 12). Considering the fact that boreholes were at varying depths, while soil was picked at specific depth (0-15 cm), the two may not have a close correlation. The concentration of elements in the soil changes with depth and therefore the top soil collected cannot necessarily compare with water at a higher depth.

In an article by Srinivasan *et al.,* (1999), aluminium in ground water was low (0.2 to 100 ppm) and was negligible when compared to surface water concentrations. The levels found naturally in raw surface water ranged from about 10 to 2 000 ppm. Aluminium levels in areas where surface waters have become acidified (pH ~ 4.0 to 5.0) were in excess of 40 000 ppm. The maximum Aluminium level found in treated water was 1 029 ppm **(**Srinivasan, 1999). The Swedish level of 0.10 ppm was also fixed exclusively to avoid problems in the distribution systems **(**Srinivasan *et al.,*, 1999).

In Canada, the Ontario Ministry of Environment has an operational guideline of 0.1 ppm for residual aluminium. But at present there is no Canadian guideline value on the maximum acceptable concentration of aluminium in drinking water. The maximum allowable concentration of Aluminium in drinking water by the European Union is 0.2 ppm **(**Srinivasan *et al.,* 1999).In another study by Viginie *et al.,* (2000), the relative risk of dementia adjusted for age, gender, educational level, place of residence, and wine consumption was found to be 1.99 (95 %) for subjects exposed to an aluminum concentration greater than 0.1 ppm (Virginie *et al.,* 2000). These findings support the hypothesis that a high concentration of aluminum in drinking water may be a risk factor for Alzheimer's disease (Virginie *et al.,* 2000).

4.2 2.2 Aluminium in rivers

River samples were collected from Juja and Chania locations in Thika District. Thiririka had the highest aluminium content of 2.18 ppm (Table 12). Chania River had no aluminium detected in it. Ndarugo, Kianguni, and Chania were not significantly different ($p < 0.05$), while Karimino and Thiririka were significantly different ($p<0.05$). The composition of surface and underground water is dependent on natural phenomena such as geological, topographical, meteorological, hydrological and biological factors in the drainage basin, and varies with seasonal differences in runoff volumes, weather conditions and water levels (WHO, 1996). Dissolved aluminium concentration in waters with near neutral pH values usually range from 0.0001 ppm to 0.05 ppm but rise to 0.5-1 ppm in more acidic waters or water rich in organic matters. At the extreme acidity of waters affected by acid mine drainage, dissolved aluminium concentration of up to 90 ppm has been measured (WHO, 2003). Nine out of fifteen samples in this study had levels above 0.2 ppm. The maximum admissible concentration in water set by European Union is 0.2 ppm (Gray, 1994). Some samples in this study shows high aluminium levels in water in comparison to studies done elsewhere. This may have negative health implications on the populations' consuming the water.

Table 12: Aluminium content in water from rivers

River	Aluminium (ppm)
Chania	0.00 ± 0.00^{a}

Ndarugo	0.20±0.30^{a}
Kianguni	0.60±0.30^{a}
Karimino	1.19±0.00^{b}
Thiririka	2.18±0.30^{c}
Lsd	0.63

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

4.2.2.3. Aluminium in springs

Table 13 shows aluminium content in water samples from springs. The aluminium contents of water samples from all springs were significantly different. ($p<0.05$). All the springs sampled were from Nuu location. All the spring water samples had high levels of aluminium, which were higher than the EU maximum recommended levels of 0.2 ppm (Gray, 1994). The most probable reason for high levels in aluminium in this study is likely to be due to the underlying rock, which is likely to have high aluminium content. Munyini had the highest aluminium content (2.38 ppm), while Nuu had the lowest (0.79 ppm). Various investigations have suggested that Alzheimer’s disease is more common in areas where the aluminium content is highest in water supply systems, but the method and results of these studies have been questioned (Alzheimer’s Society, 2002).

Table 13: Aluminium content in water from spring’s

Sample	Location	Aluminium (ppm)
Nuu	Nuu	0.79±0.30^{a}
Mola	Nuu	1.58±0.30^{b}
Munyini	Nuu	2.38±0.00^{c}
Lsd		0.56

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

4.2.2.4. Aluminium in shallow wells

Aluminium content in water samples from shallow wells from Mbia and Enziu were not significantly different ($p<0.05$) (Table 14). The two samples from Kanzanzu location (Kivou and Tyaa) had significantly higher levels of aluminium than the other two samples from Nuu location (Mbia and Enziu). The aluminium content in shallow wells from same location (Mbia and Enziu are from Nuu, while Kivou and Tyaa from Kanzanzu) were not significantly different ($P<0.05$). This shows that the location had an influence on the aluminium content. Three out of the four shallow wells had aluminium content above the EU standard (≤0.2 ppm).

Table 14: Aluminium content in water from shallow wells

Sample	Location	Aluminium (ppm)
Mbia	Nuu	0.20 ± 0.30^a
Enziu	Nuu	0.60 ± 0.00^a
Kivou	Kanzanzu	2.18 ± 0.30^b
Tyaa	Kanzanzu	2.18 ± 0.30^b
Lsd		0.56

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

Drinking water usually contains between 0.01 and 0.15 ppm of aluminium, but some portable water may contain as much as 0.40 ppm or more (Foster, 2000). This study shows some of the shallow wells have very high aluminium levels (2.18 ppm), which may pose health problems to the consumer's. Aluminium toxicity has been implicated in neurodegradative diseases. Foster (2000), has come up with the Foster multiple antagonist hypothesis to explain the role of aluminium in Alzheimer’s disease. In this hypothesis he says aluminium shows an antagonism towards divalent metals including zinc, phosphorus, calcium and magnesium. It tends to replace them in important enzymes and proteins. This results in biological dysfunctions which eventually cause neuronal degeneration, ultimately culminating in Alzheimer’s disease (Foster, 2000),

4.2.2.5 Aluminium in tap water

Table 15 shows aluminium content in tap water samples. Only Gachororo tap water had no aluminium detected in it. Kanzanzu tap water sample had high aluminium content of 2.27 ppm, while JKUAT had 0.6 ppm. The aluminium content in tap water depends on the source as well as treatment procedures, at treatment plants. The concentration of aluminium in natural waters can vary significantly depending on various physical chemical and mineralogical factors (WHO, 2003). Some treatment plants use alum to sediment particles making the water clear. Therefore the differences can be attributed to treatment procedures as well as the source of the tap water. Aluminium in drinking water varies according to the levels found in the source water and whether aluminium coagulants were used during water treatment (WHO, 2003). In Germany, levels of aluminium in public supplies averaged 0.01 ppm in western region. In a survey of 186 community water supplies in USA, median aluminium concentration for all finished drinking water supplies ranged from 0.03 to 0.1 ppm for facilities using aluminium sulphate coagulation, the median level was 0.1 ppm with a maximum 2.7 ppm (WHO, 2003). The results in this study compares well with the above results.

Table 15: Aluminium content in water obtained from tap waters.

Sample	Location	Aluminium (ppm)
Gachororo	Juja	0.00 ± 0.00^{a}
JKUAT	Juja	0.60 ± 0.00^{ba}
Mwingi	Kanzanzu	2.27 ± 1.40^{b}
Lsd		2.08

All the values for samples within columns followed by the same letter are not significantly different ($p < 0.05$).

4.2.2.6 Comparison of aluminium levels from different sources

Table 16 shows the aluminium content in different sources of water. Borehole water had the lowest mean aluminium content of 0.82 ppm, while spring water had the highest mean aluminium content of 1.59 ppm.

The concentration of aluminium in natural waters can vary significantly depending on various physical chemical and mineralogical factors (WHO, 2003). Dissolved aluminium concentration in waters with near neutral pH values usually range from 0.0001 ppm to 0.05 ppm but rise to 0.5-1 ppm in more acidic waters or water rich organic matters. At the extreme acidity of waters affected by acid mine drainage, dissolved aluminium concentration of up to 90 ppm has been measured (WHO, 2003). Nine out of fifteen samples had levels above 0.2 ppm.

There is no safety limit for aluminium in water set by World health organization (WHO), but has voluntary quality guidelines that recommend maximum levels of 0.2 ppm (WHO and FAO, 1995). The European Union has also set a maximum admissible concentration of aluminium in water as 0.2 ppm (Gray, 1994).

Table 16: Aluminium content in water from different sources

Source	Means Aluminium (ppm)	Range Min.-Max. Aluminium (ppm)
Springs	1.59	0.79-2.38
Shallow wells	1.29	0.20-2.18
Taps	0.95	0.00-2.27
Rivers	0.83	0.00-2.18
Boreholes	0.82	0.00-2.68

4.3 Aluminium levels in foods

Beans from Chania location had the highest amount of aluminium (151.5 ppm) (Table 17), however the maize from the same location did not show significant difference ($p<0.05$) in its aluminium content from maize from other locations.

Table 17: Aluminium in foods analyzed from different locations

Food/Location	*Kanzanzu (ppm)*	*Chania (ppm)*	*Juja (ppm)*	*Nuu (ppm)*	*Average (ppm)*
Maize	116 ± 5^b	126 ± 19^a	137 ± 0^b	128 ± 10^b	127
Beans	96 ± 10^b	156 ± 10^a	65 ± 0^a	40 ± 0^a	89
C/peas	41 ± 0^a	-	-	-	41
Milk	-	107 ± 10^a	-	-	107
Tea	-	1189 ± 170^b	-	-	1189
S/potato	-	170 ± 23^a	-	-	170
Tomato	-	-	85 ± 0^{ab}	-	85
Kales	-	-	142 ± 11^c	-	142
Lsd	49	110	69	69	

All the values for samples within columns followed by the same letter show they are not significantly different from each other according to lsd test at5% probability level.

The variation in maize content across the locations is less than for beans. The aluminium content in maize ranged from 116 ppm to 137 ppm, while beans ranged from 151.5 ppm to 65 ppm. Depending on the plant varieties and soil conditions, the aluminium content of foods can vary greatly. Tea had significantly ($p<0.05$) higher aluminium content compared to other foods in Chania location. Kales from Juja location had significantly higher aluminium content compared to tomatoes from the same location. The food with the highest amount of aluminium in this study was tea followed by sweet potato, kales and cowpeas while tomatoes showed the lowest aluminium content. Some foods are naturally high in aluminium content for example potatoes, spinach, and tea (WHO, 2003). Some plants such as herbs and tea are known to be aluminium accumulators. (Soni *et al.,* 2001). This explains the high levels of aluminium in tea has compared to other foods. It has the highest aluminium content in this study (1189 ppm).

With increased incidence of acid rains and the fact that aluminium deposits are highly soluble in water, under acidic and strong basic conditions (Downs 1993), the availability of aluminium to plant will increase posing a serious danger to plant life (Downs 1993). This may in turn lead to increased levels of aluminium in foods grown in these areas. Different crops have different aluminium absorption and retention, hence the differences in aluminium levels in the different crops/foods.

In a study on aluminium content in Spanish foods the results obtained ranged from 1.362 to 6.610 ppm in seafood, 0.171 to 29.688 ppm in vegetables, 19.560 to 70.100 ppm in olive oil, 0.424 to 6.430 ppm in dairy products and 25.600 to 58.057 ppm in stimulant drinks and infusions (Lopez *et al.,* 2000). The aluminium content in the foods analyzed in this study is higher than the study done by Lopez *et al.,* 2000 above. This shows greater exposure to aluminium for the population in this study.

Aluminium has been implicated in a variety of neurological disorders that have been associated with an increase in the formation of reactive oxygen species (ROS). The exact mechanism of aluminium toxicity is not known, however accumulating evidence suggests that the metal can potentiate oxidative and inflammatory events leading to tissue damage (Arezoo, 2002). This implies high intakes of foods with high aluminium content could lead to tissue damage and hence the diseases associated with aluminium toxicity.

4.4 Comparison in aluminium contents in foods and aluminium content in soil from different locations

Table 18 shows the comparison of aluminium content in foods with average aluminium contents in soils from different locations. Beans show a positive correlation in aluminium content with the aluminium content in the soil. Maize does not show a positive correlation. This may be explained by the fact that most of the maize bought form the retail outlets in the project area was not indigenous. Maize from Kanzanzu, Nuu and Juja locations was not indigenous. Maize bought from Chania location was the only maize that was from the area. However even the maize that is not indigenous represents maize consumed by the population in the project area. This will eventually give an indication to extent of exposure to aluminium.

Table: 18 Comparison in aluminium contents in foods and aluminium content in soils

Location	*Ave. Al in soil(ppm)*	*Al in beans (ppm)*	*Al in maize (ppm)*
Juja	221	65±0	137±0
Chania	512	156±10	126±19
Kanzanzu	106	96±10	116±5
Nuu	98	40±0	128±10

The correlation coefficient between Average aluminium content in soil and the aluminium content in beans across the locations is 85%.Beans from Chania had the highest aluminium content, while the average aluminium content in Chania is the highest (512 ppm) (Table 18) as well.

In the above study geographical location influences the levels of aluminium in a food, as well as the type of food. Beans show wide variation, while maize does not show wide variation across the locations. In a separate study by Githua *et al*., (1995) kales leaves in one area had a mean aluminium content of 265±7.07 ppm, while in another area it had 177.5±3.53 ppm; Tea bottom leaves had 2067.5±60.10 ppm in the first area , while in the other area it had 1650±70.71 ppm (Githua *et al*.,1995).

In a study by Githua et al., *(1995), grains were found to contain very little aluminium and sometimes not detectable. In the first area of their study, sweet potato roots were found to contain a Mean of 490±15.15 ppm, kales leaves 265±7.07 ppm and Tea bottom leaves 2067.5 ±60.1 among other plants analyzed (Githua* et al., *1995). This concurs with this study, in that tea had the highest levels of aluminium followed by sweet potatoes, followed by the Kales and the grain in this study had the least aluminium content.*

4.5 Aluminium levels in cooked foods

4.5.1 Aluminium content in foods cooked in aluminium pots compared to foods cooked in stainless steel pots

Figure 1 shows the changes in aluminium content of different foods cooked using aluminium pots compared to stainless steel pots. The highest percentage increase in aluminium content was in tomatoes from 139 ppm to 266 ppm (91%), while in kales there was no change shown (152 ppm). Beans, maize, ugali, sweet potato all showed an increase in aluminium content when cooked with aluminium pots as compared to stainless steel. Aluminium can be mobilized from cookware, particularly by acidic and basic foods (Yokel and Saiyed, 2005).

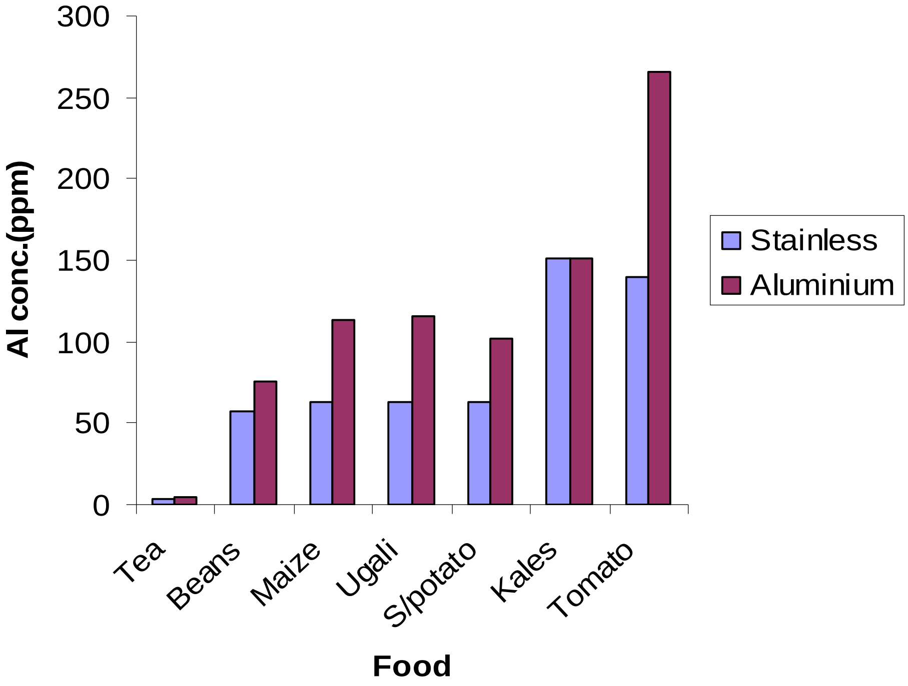

Fig 1: Aluminium content in foods cooked with aluminium pots compared to foods cooked with stainless steel pots.

Foods that are acidic such as tomatoes are more likely to absorb more aluminium than neutral foods. Aluminium can be leached from aluminium vessels into food during preparation and storage (Baxter *et al.*, 1989). In a separate study, aluminium content of tomatoes increased from 0.12 ppm to 3.1 ppm on cooking in an aluminium saucepan (Baxter *et al.*, 1989). Similarly they showed that cooking a tomato homogenate (pH 4.4) resulted in an aluminium content of 3.3 ppm compared with 0.5 ppm in uncooked sample. The increased solubility of aluminium compounds with temperature poses a greater danger in use of aluminium as cook ware.

From the results above, use of aluminium vessels in cooking adds aluminium to the diets. This increase depends on particle size and acidity or alkalinity of the food. Aluminium in diet interacts with a number of elements in the alimentary canal, leading to their reduced uptake. Some of these elements include calcium, iron, magnesium, and phosphorous (WHO and FAO, 1995). Once the absorption of essential minerals is reduced in the alimentary canal, it will eventually lead to deficiencies of the minerals. This is the main way that aluminium is toxic to human health (Foster, 2004; Foster, 2002). In earlier studies done it has been shown there is an anaemia associated with aluminium toxicity (UNEP *et al*, 1997). Therefore in view of the above considerations it is important to reduce use of aluminium vessels in cooking or storage of foods.

In a study on aluminium levels of fish fillets baked and grilled in aluminium foil, all aluminium concentrations of both baked and grilled fillets wrapped in aluminium foil increased during heating. The increase in aluminium concentration ranged from a factor of 2 (baked saithe fillets without ingredients from 0.10 up to 0.21 ppm) to a factor of 68 (grilled mackerel fillets with ingredients from 0.07 up to 5.04 ppm) (Ranau *et al.,* 2001).

Wanjau *et al.*, (2004), while investigating the effect of using abrasive agents on cleaning aluminium cookware showed that aluminium leaches from cookware, during cleaning. They also indicated that acidic and basic foods should not be cooked with aluminium cookware, so as to minimize the levels of dietary aluminium. This concurs with this study, it is important to reduce use of aluminium cookware during cooking.

4.5.2: Aluminium content in Distilled water boiled at different acidity levels and time

Table 19 shows aluminium content of distilled water boiled with aluminium pans compared with stainless steel pans under different pH condition and different exposure time. Significant leaching of aluminium takes place in acidic conditions, while; in basic and neutral conditions insignificant leaching takes place. Studies have shown that aluminium can be mobilized from cookware, particularly by acidic and basic foods (Yokel and Saiyed, 2005). Acidic distilled water boiled in aluminium pots has the aluminium content increased to over 1000 times. The acidic water after 20 minutes of boiling had 230 ppm aluminium while this increased to 467 ppm after 40 min and 1298 ppm after one hour. It is well established that cooking of acidic foods in aluminium saucepans causes leaching of the metal (Baxter *et al.*, 1989). The trace amounts of aluminium in stainless steel pot can be explained by the fact that the stainless steel used could be having impurities. Aluminium being the third most abundant element would be expected in all spheres of life. Studies done on effect of cleaning technique on aluminium leaching from aluminium cookware show that abrasive cleaning material lead to greater leaching of aluminium cookware, during cooking (Wanjau *et al.*, 2004). Cookware when exposed to air will form Aluminium oxide, which is an amphoteric oxide thus dissolving in both strong alkalis and strong acids apart from nitric acid and ammonia (Downs, 1993).

The aluminium concentration increased up to 2.6 ppm, after boiling distilled tap water for 15 min in Al pans (Judith *et al.*, 1993). Storage of Coca-Cola in coated aluminium cans resulted in aluminium levels below 0.25 ppm. In contrast, non-coated aluminium camping bottles containing lime blossom tea acidified with lemon juice released up to 7 ppm within 5 days (Judith *et al.*, 1993

Table 19: Aluminium content in distilled water boiled at different pH and time.

Time (minutes)	Basic water (pH=7.6) Al (ppm)	Neutral water (pH=7.0) Al (ppm)	Acidic water (pH =3.0) Al (ppm)
20	1.3±0.2	0±0	230±24
40	1.4±0	2.5±0.4	467±10
60	2.9±0.8	3.6±0.7	1298±113

Though the leaching of Aluminium from cooking vessels has been regarded as insignificant, the present study shows that in most foods the leaching is significant. It is therefore important to avoid or reduce cooking foods in aluminium vessels due to aluminium leaching into foods. The study also shows the longer the time the cooking takes the greater the amount of aluminium that leaches to the foods from the vessels. This means it’s important to reduce the contact time between foods and aluminium pans.

CHAPTER FIVE

5.0: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This study shows that, fluoride levels in water varies, with location. Fluoride content in water is dependent on the type of source and soil type. The variations for fluoride in water from one source to another or one site to another are wide. It is important to ensure the WHO levels in water are maintained to ensure the beneficial effects to fluoride are realized, and the toxic effects are avoided. With time Kenyan's should set their own standards, from studies that compare fluoride content in different location and incidence of dental carries as well as dental flourosis and other diseases due to toxicity or deficiency of fluoride.

Aluminium levels in water in this study are above the WHO set levels, therefore more studies need to be done to relate the toxic effects of aluminium to the levels in different populations in the country-Kenya. Soils in this study had levels above the normal, levels, this is likely to be due to increase in use of phosphate fertilizer. Aluminium content in a number of foods consumed is higher in this studies as compared to studies done else where. Though the leaching of Aluminium from cooking vessels has been regarded as insignificant, the present study shows that in most foods the leaching is significant. The fact that aluminium is a toxic element is no longer in question; however the mechanism of aluminium toxicity to human needs more investigation.

5.2 RECOMMENDATIONS

- It is important to determine the levels of aluminium and fluoride in underground sources before using the water for domestic purposes.
- It is important to carry out a comprehensive study on incidence of diseases implicated in aluminium/fluoride toxicity in Kenya. This study will improve understanding of the impact of aluminium and fluoride interaction on human health in Kenya and enable us set our own standards.
- A study on intake of aluminium/fluoride with common diets in Kenyan should be done, to help people understand how much aluminium/fluoride is ingested in the body and hence understand if the intake levels can lead to toxicity or not.
- It is important to reduce the use of aluminium pans in cooking and food storage, since this adds aluminium to foods.
- It is also important to reduce use of fertilizers that add fluoride/aluminium to the soil.
- There is need to create awareness in the community on dangers of high levels of aluminium and fluoride on human health.

CHAPTER SIX

6.0 REFERENCES

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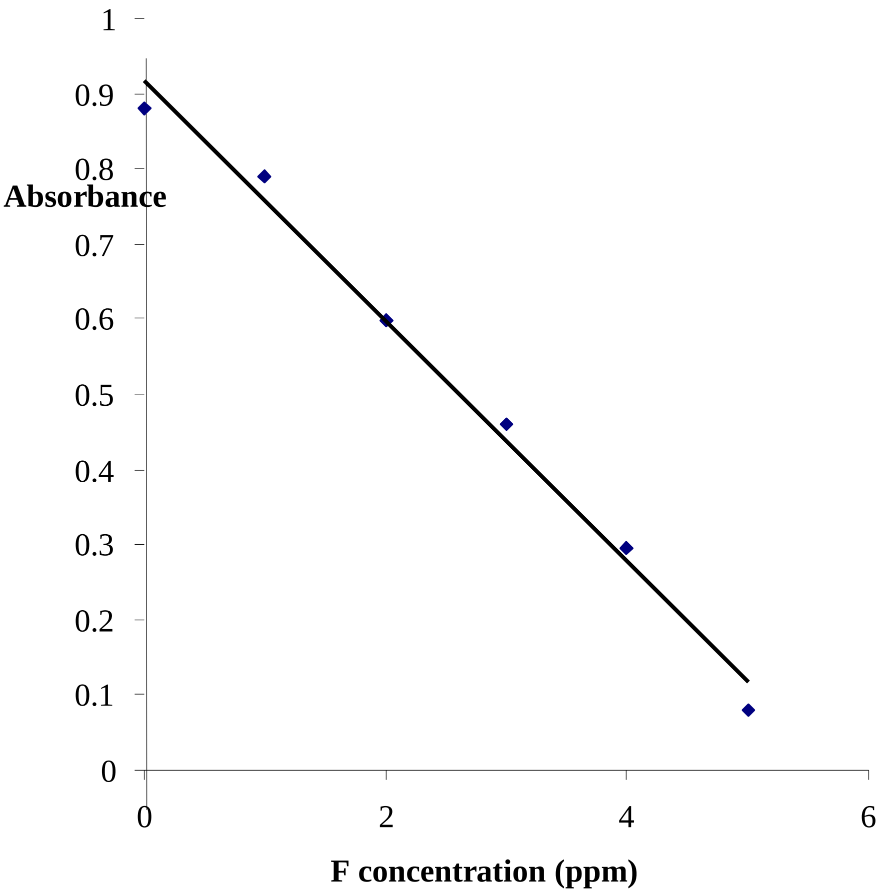
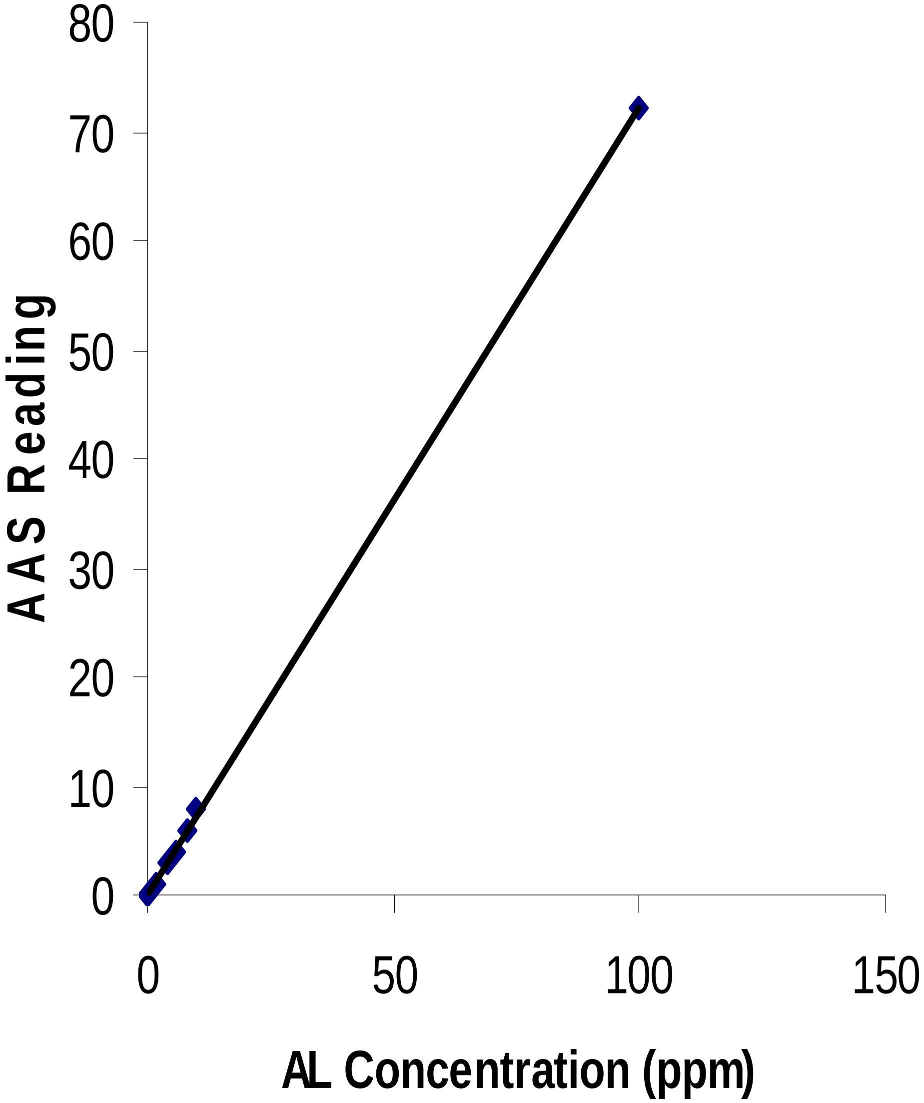
CHAPTER SEVEN

7.0 APPENDICES

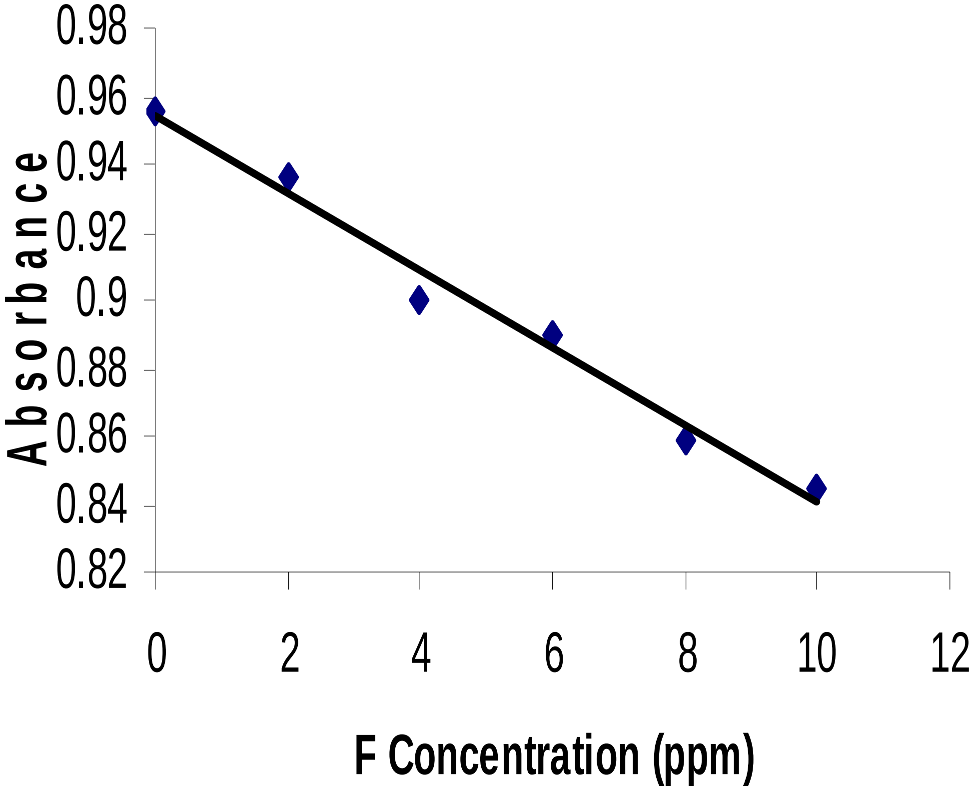
Appendix 1: Standard curve for fluoride analysis in water



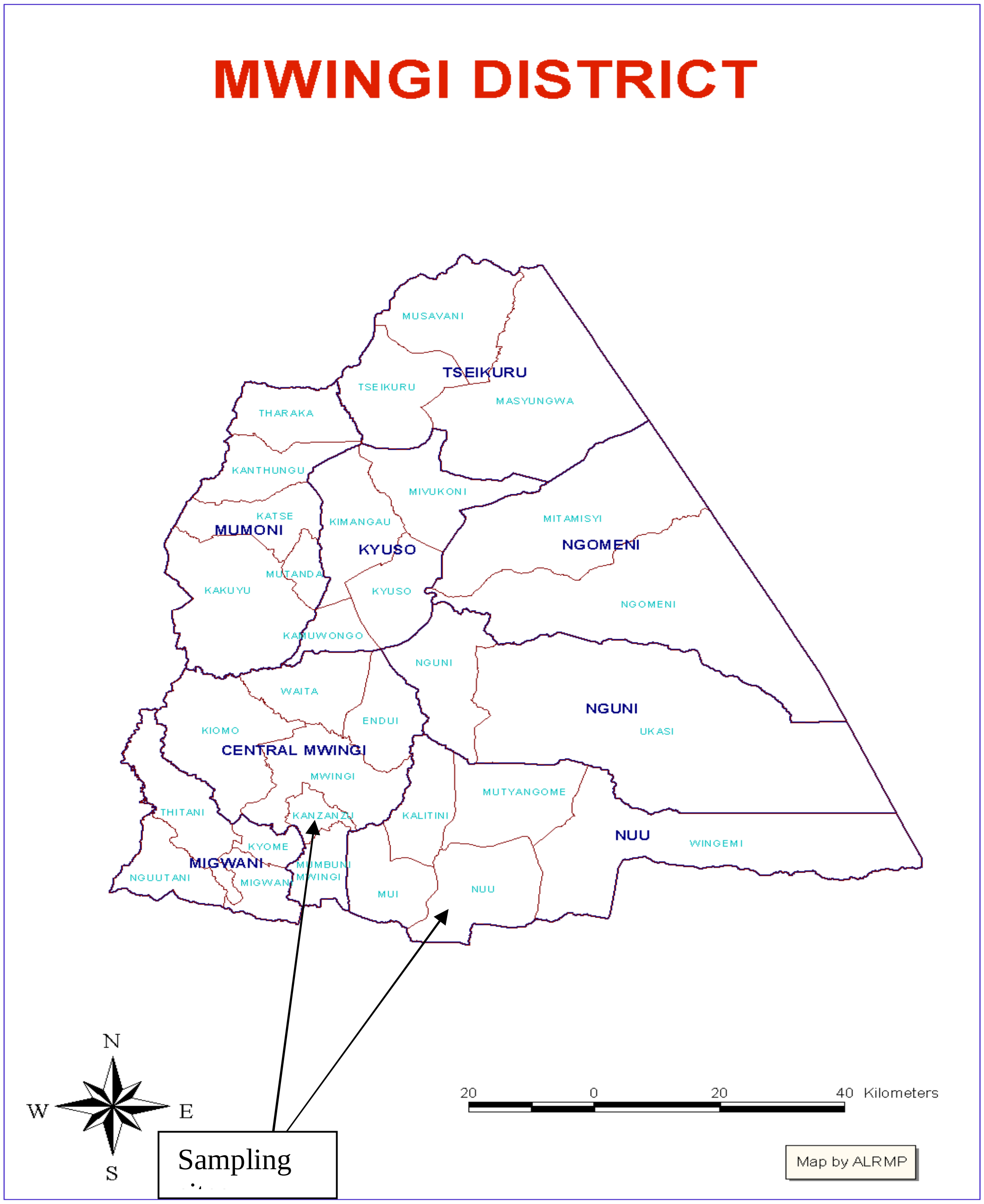
Appendix 2: Standard curve used in analysis of aluminium in all samples



Appendix 3: standard curve for fluoride analysis in soils



Appendix 4: Map of Mwingi District showing project sites



Appendix 5: Map of Thika District showing project area