EFFECT OF LIMING ON LEVELS OF POLLUTANT HEAVY METALS IN SOILS AND THEIR UPTAKE BY MAIZE IN UASIN GISHU AND TRANS-NZOIA COUNTIES, KENYA

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DECLARATION

Declaration by the candidate

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without prior written permission of the author and/or University of Eldoret.

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To my wife Mectilda, children Daniel and Emmanuel. To my supervisors and mentors; Prof. Lusweti Kituyi and Dr. Samuel Lutta, they kept me going.

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To mum, the smile on your faces puts another one on mine.

ABSTRACT

Soil contaminated with heavy metals from agricultural and industrial sources leads to unhealthy food. The metals enter the food chain and are consumed by humans. Phosphate fertilizers too contain undetermined amounts of heavy metals and are widely applied on agricultural fields in Kenya together with lime to ameliorate effects of acidity with little regard to the chemical effects/ side effects. This research is a study involving on farm field experiments carried out in some selected fields in Uasin Gishu and Trans Nzoia counties to test the effect of liming and fertilization on heavy metal content in soils and maize grains. Samples were taken from different selected fields over four sampling periods between March 2009 to December 2009 covering both the dry and the wet seasons. The biogenic, reactive, readily available and cheap Mijingu Phosphate Rock (MPR 38.3% of CaO) was tested against agricultural grade lime (20.8% CaO), and diammonium phosphate (DAP) and monoammonium phosphate (MOP) as well as for blank (unfertilized) soils. Similar liming rates were compared for all the fields. The correlations between heavy metals concentration levels in soils with pH were determined. Seasonal variation of heavy metal concentration in soils was also determined. The soils were sampled at a depth of 15 cm using a soil auger, dried, ground, sieved and wet digested in a block digester. Freshly matured grains were also collected, dried, ground and sieved before digestion. Samples were then treated with a mixture of sulphuric acid/selenium powder and hydrogen peroxide to digest the organic material. To avoid loss of nitrogen in samples the samples were pre-treated with salicylic acid. Analysis for heavy metal contaminants was done for Zn, Cu, Pb, Cd, Mn and Cr by Atomic absorption spectroscopy. Results show insignificant correlations between the heavy metals and pH except copper metal (whose value of $r = 0.770$) which showed the strongest dependence on pH. Generally, liming of soils increased pollutant metal levels. However comparison of observed levels in the study area with threshold values set by the WHO and FAO, illustrates that the heavy metal content in soils and maize grains are within acceptable limits. Heavy metals concentrations dropped sharply from initially high soil values to low values in maize grains implying low uptake by the plants thus; Pb 380.3 ppm in soils and 137.9 ppm in grains, Cd 25.52 ppm in soils and 21.38 ppm in grains, Cu 99.98 ppm in soils and 7.71 ppm in grains, Cr 40.03 ppm in soils and 22.8 ppm in grains, Mn 1165.0 ppm in soils and 629.1 ppm in grains and Zn 243.8 ppm in soils and 150.0 ppm in grains.

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SHORT FORMS AND ACRONYMS

AAS- atomic absorption spectrometry

AEC-Anion Exchange Capacity

ATSDR -Agency for Toxic Substances and Disease Registry

ANOVA- Analysis of Variance

CEC-Cation Exchange Capacity

CP-cathodic protection

DAP- Diammonium phosphate

FAO: Food and Agriculture Organization (United Nations)

FEPA**--** Federal Environmental Protection Agency

FMANR**-** Federal Ministry of Agriculture and Natural Resources Natural Resources

FURP- Fertilizer Use Recommendation Project

ICRAF- International Center for Research in Agroforesty

KARI- Kenya Agricultural Research Institute

L- Agricultural lime

LR- Long Rains

MPR- Minjingu Phosphate Rock

NAC- Neutral Ammonium Citrate

NARL- National Agricultural Research Laboratories

OGRS- Official Gazette of the Republic of Serbia

PAR- Photosynthetic Active Radiation

ppm - parts per million or milligrams per kilogram (mg/kg)

PR- Phosphate Rock

SPR- Standard Phosphate Requirements

SR- Short Rains

SSA- sub-Saharan Africa

SSP- Single superphosphate

TSP- Triple superphosphate

USDA- United States Department of Agriculture

WHO-World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background Information

The increasing input of heavy metals in the soils from anthropogenic and natural sources needs to be monitored. In many countries of the world, industrial activities, exploitation of natural resources, agricultural practices as well as lack of environmental regulations have resulted to negative impact on the environment (Bolland and Gilkes, 1990). Efforts to restore soil fertility are numerous and have been developed in sub Saharan Africa. However, management of acid soils to restore soil fertility has been neglected. Farmers in western Kenya who can afford nutrient inputs continue to cultivate their farms with increased use of acidifying fertilizers such as diammonium phosphate (DAP) and urea. In some sugarcane growing areas of Rift valley, Nyanza and Western Provinces of Kenya, the problem of soil acidity is further worsened because production of sugarcane involves heavy fertilization with DAP and urea. Conversion of land under sugar cane cultivation to maize or legume cropping would require that liming is done, failure to which these crops would not perform optimally.

Liming is one of the methods recommended for amelioration of such soils by raising soil pH and removing deficiencies of calcium and magnesium, but little is known about the chemical effects of this practice by farmers. Globally, agricultural lime applied as calcium hydroxide ($Ca(OH)_{2,}$ calcium oxide (CaO) or calcium carbonate ($CaCO_3$) has been adopted to effectively neutralize soil acidity (Kanyanjua *et al*., 2002). Liming materials such as $CaCO_3$ and CaO (agricultural lime) are cheap and Kenya is endowed with rich deposits of these materials.

Use of agricultural lime can be compared to use of reactive indigenous phosphate rocks (PRs), which have a liming potential that has been exploited by Kenyan agriculturalists (Ndung'u *et al.*, 2006). PRs contain significant quantities of CaO; the liming component. Apart from being potential liming materials, PRs are mainly sources of P, which is lacking in the agricultural lime (Ndung'u *et al.*, 2006). Thus, sourcing P from reactive PRs reduces the cost of farm inputs (Kanyanjua *et al*., 2002). Studies on response of Minjingu Phosphate Rock (MPR) as a source of P on different crops have been carried out in western Kenya (Ndung'u *et al.*, 2006) and have been encouraged by agricultural officers for use by farmers. Being a raw ore, contaminants especially heavy metals that accompany liming of fields need be investigated.

Neither animals, plants nor micro-organisms require Pb, Cd, Cu, Cr or Zn for their metabolic processes. However, once certain concentrations are exceeded in the environment, the heavy metals have harmful effects. Effects may range from individual death with the concomitant reduction in population, stunted growth, visible leaf damage and reproductive disorders to changes in physiological processes and impairment of micro-biological metabolic processes.

Heavy metals demonstrate different mobility characteristics in soils. Decisive factors of influence are the soil pH, clay content and humus content. If a heavy metal has a high mobility then it can be leached into deeper soil levels and ground water (Jinhee *et al.*, 2010). On the other hand if a metal is lowly mobile, it is not leached and therefore can be taken up by plants and bio accumulates in the food chain. The behaviour of plants with respect to heavy metal absorption differs fundamentally according to the mode of land use, crop types, pH values and soil structure. However, there are changes in chemical ancillary conditions of the soils, for example by degradation of organic matter, pollution risks arise for example by causing organically bound heavy metals to dissolve; or through acidification which causes certain metals to mobilize (Xinde *et al*., 2002).

Motivations for the control of concentrations of heavy metals in the environment are diverse. Zn and Pb cause corrosion, Hg, Cd, Cr and Pb are dangerous to health in the environment. Hg, Cd and As affect central nervous system, Hg, Pb, Cd and Cu affect the kidneys and the liver while Ni, Cd, Cu and Cr affect the skin, bones and teeth (Sabiha *et al.*, 2008). Heavy metal pollution can arise from many sources but most commonly from purification of metals, preparation of nuclear fuels, electroplating and mining (Bolland and Gilkes., 1990). MPR used to lime soils for example is mined in the crusts of Nyanza Province of Kenya and could be a major anthropogenic source of deep seated heavy metals into the top soils of farm lands (Nekesa, 2004). Unlike organic pollutants, heavy metals do not biodegrade thus pose a serious challenge for remediation (Bolland and Gilkes., 1990).

1.2 Statement of the Problem

Contamination of soils and plant tissues have been reported which lead to poisoning of animal’s life including man. Plants and soils can accumulate trace elements such as Pb, Cd, Hg, Cr, and Cu due to exploration and exploitation of natural resources and agricultural activities of man (Sabiha *et al*., 2008). The monitoring of heavy metal pollution in the environment is therefore essential to establish patterns of pollution dispersion (Olade, 1987). The aim of this research was to determine effects of liming on concentration levels of pollutant heavy metals (Pb, Cd, Hg, Cu, and Cr) in soils.

Liming is one of the methods recommended by soil scientists for amelioration of acidic soils by raising the soil pH and removing the deficiencies of Calcium and Magnesium (Nekesa, 2007). However, little is known about the extent of heavy metal pollution caused by liming. As a consequence, large amounts of lime are applied on fields world over and Kenya in particular with little regard to its chemical side effects. Some studies have been done on cycling of heavy metals in the environment but focus largely on their pathways from industrial point sources and their biological fluxes (Olade, 1987). Very little about agricultural sources, factors influencing mobility and their redistribution is cited.

1.3 Justification of Study

Soil contaminated with heavy metals from agricultural and industrial wastes leads to unhealthy food. The metals enter the food chain and are consumed by humans. Phosphate fertilizers contain undetermined amounts of heavy metals and are widely applied in agricultural rich parts of the Rift Valley together with lime to ameliorate effects of acidity. Because of the need of improved food production, Agriculture industry tends to adopt more modern methods of farming coupled with increased fertilization of soils to make available macro and micro-nutrients in soils. Soil acidity (low pH) is therefore an issue which arises calling for liming of farm lands from time to time (Nekesa, 2007). The commonest most available lime is the MPR mined from the earth’s crust in Tanzania. This means that, being a raw ore, a number of heavy metals are introduced in farm lands from the earth’s crust during liming. Increased demand for liming of soils and fertilization is a major source of heavy metals in the soil (Rajan *et al*., 1996).

The heavy metals are toxic to humans even at relatively low concentrations. They bio-accumulate in the environment, are non bio-degradable and therefore pose major threat to plant, animal and human life (Bolland and Gilkes., 1990). Research findings indicate MPR has high heavy metal content from natural components cores of earth crust (Van Kauwenbergh and McClellan, 2004).

There is therefore need to study heavy metal contamination due to liming to ascertain availability of these elements in the environment.

1.4.0 Objectives

1.4.1 General objective

The main objective of the study was to determine the extent of heavy metal contamination in soils and maize tissues due to liming and fertilization in Uasin Gishu and Trans – Nzoia counties of Kenya.

1.4.2 Specific objectives

The specific objectives were:

1) To determine the concentration levels of heavy metals Pb, Cd, Cr, Zn Cu and Mn in soils applied with MPR, agricultural lime and inorganic fertilizers in Uasin Gishu and Trans Nzoia counties of Kenya.

2) To investigate seasonal variation of heavy metal concentration in soils and plant tissues in Uasin Gishu and Trans Nzoia counties of Kenya.

3) To establish the relationship between pH and heavy metal concentration in soils.

1.5 Scope of Study

A map of Kenya showing the districts of study is given in figures 1 and 2. The selected areas of study were from Uasin-Gishu and Trans-Nzoia counties both from the Rift Valley Province.

1.5.1 Trans-Nzoia county

Trans-Nzoia county is an administrative location in Western Kenya bearing the following coordinates in the world map; latitude (DMS) 0^{o} 49^{o} 60 N, longitude (DMS) 35^{o} 0’ 0 E.

Figure 1 below shows the map of Trans-Nzoia County as down loaded from the world map.

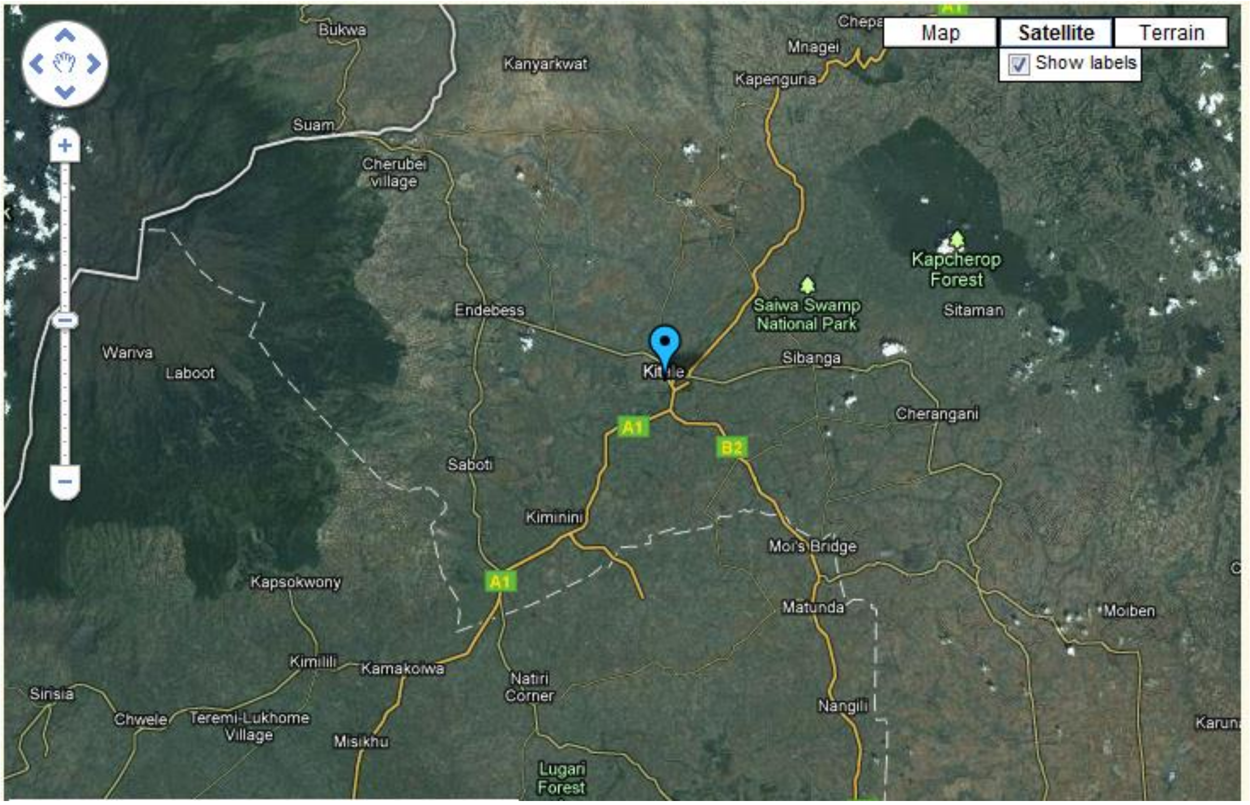


Figure 1: Map of Trans-Nzoia County (www.mapquest.com/maps)

1.5.2 Uasin Gishu County

Uasin Gishu County is in western Kenya 0030’N; 350 18E; at 2140 m above sea level. The mean temperature is 17.5 ^{o}C. The coldest month July (at 10 ^{o}C) and warmest month is February (mean maximum temperature 25 ^{o} C). Annual rainfall is moderately high (900 mm – 1300 mm from March to September.

Figure 2 below shows the map of Uasin Gishu County as down loaded from the world map.

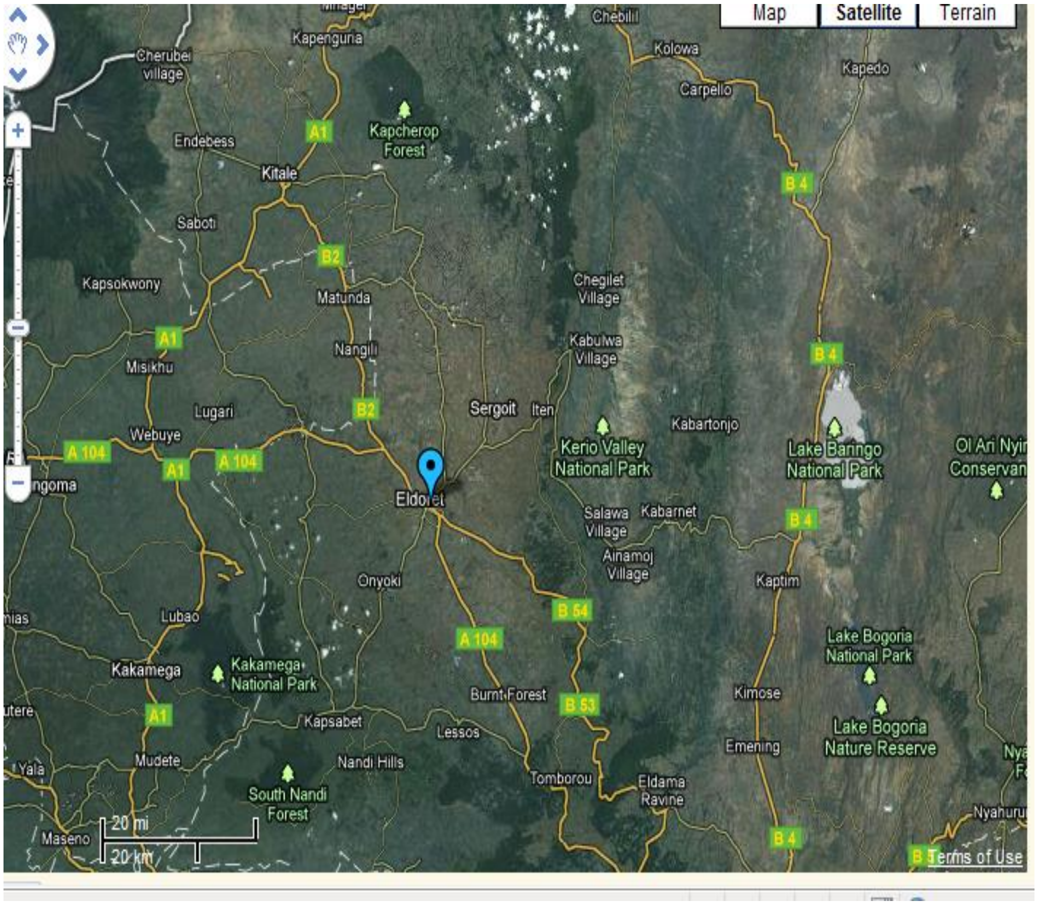


Figure 2: Map of Uasin Gishu County (www.mapquest.com/maps)

CHAPTER TWO

LITERATURE REVIEW

2.1 Soil Acidity

The term pH stands for the potential (p) of the hydrogen ion (H^+) in water. It is actually a way of reporting the concentration of H^+ in solution using an electrical "potential" to measure H^+. The pH of any solution is one of the easiest laboratory measurements to make using a pH meter and an electrode specifically designed to measure hydrogen (pH electrode). Colour indicators and litmus paper are a quick alternative for less precise measurements. By mixing a quantity of soil with demineralized or distilled water (usually a 1:1 mixture), the pH of the water solution in equilibrium with the soil can be measured (Kanyanjua *et al.*, 2002).

2.2 Acid Soil Infertility

When the pH falls below 6.0, the availability of nutrients such as P, K, Ca, and Mg decreases. The availability of the metallic micronutrients, however, like Zn, Mn, Cu, and Fe increases as the pH decreases (Kanyanjua *et al*., 2002).

Plants don't need Al to grow. It's not an essential plant nutrient. Al, however, is one of the prominent mineral components of silt and clay. Therefore, the earth's crust is naturally high in Al. Like Zn, Mn, Cu and Fe, the more acid the soil, the more Al will be dissolved into the soil solution. If the pH is allowed to drop much below 5.5, the availability of Mn and Al is increased to the point that they could become toxic to plants. Al toxicity to plants is the main concern we have with acid soils in our region (Kanyanjua *et al*., 2002).

2.3 Factors Affecting Soil pH

Soils are not homogenous and the pH can vary considerably from one spot in the field to another. It also varies with depth. Soils in different geographic regions, as already mentioned, may have different pH because of the five soil forming factors; parent material, climate, living organisms, topography, and time.Soils of an area may be very acid because of the acid nature of the rocks (granites and sandstones, respectively) which formed these soils. Limestone valley soils were formed from basic rocks (limestone) but may be acid on the surface because of time and weathering (Whitney and Lammond, 1993).

Rainfall also affects soil pH. Water passing through the soil leaches basic cations such as Ca^{2+}, Mg^{2+}, and K^+ into drainage water. These basic cations are replaced by acidic cations such as Al^{3+} and H^+. For this reason, soils formed under high rainfall conditions are more acidic than those formed under arid conditions (Whitney and Lammond, 1993).

Both chemical and organic fertilizers may eventually make the soil more acidic. Hydrogen is added in the form of ammonia-based fertilizers (NH_4^+), urea-based fertilizers [$CO\ (NH_2)_2$], and as proteins (amino acids) in organic fertilizers. Transformations of these sources of N into nitrate (NO_3^-) releases H^+ to create soil acidity. Therefore, fertilization with fertilizers containing ammonium or even adding large quantities of organic matter to a soil will ultimately increase the soil acidity and lower the pH as is shown in the equation below.

$$NH_4^+ + 2O_2 \longrightarrow \text{bacteria} \longrightarrow NO_3^- + 2H^+ + H_2O$$

Plants take up basic cations such as K^+, Ca^{++}, and Mg^{++}. When these are removed from the soil, they are replaced with H^+ in order to maintain electrical neutrality (Whitney and Lammond, 1993).

Human activity is increasing the extent of acid soils throughout the world by industrial and agricultural practices such as ammoniacal fertilizers, intensive irrigation and removal of basic cations in harvested crops (Neil, 1991).

A strongly acidic soil is one with a pH less than 5.0. Below this value, Al^{3+} progressively replaces H^+ on the colloidal complex becoming predominant at around pH 4.0. Soils also become acidic because the basic cations are replaced by hydrogen ions on the soil colloidal complexes as illustrated by the following chemical equation (Tisdale et al., 1990).

$$\left.\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix}\right\} \text{Soil} + 4H_2CO_3 \longrightarrow \left.\begin{matrix} H^{+} \\ H^{+} \end{matrix}\right\} \text{Soil} + Ca\,(HCO_3)_2 + Mg\,(HCO_3)_2$$

2.4 Soil Acidification from Nitrogenous Fertilizers

The widely used ammonium fertilizers have effects on the pH value of the soil. Nitrification of an ammonium fertilizer produces H^+ which are the major causes of soil acidity. The following equations show reaction of nitrogenous (ammonium- based) fertilizers when added to the soil (Kennedy, 1992).

1. Ammonium nitrate

$$2NH_4NO_3 + 5O_2 \longrightarrow 4NO_3^- + 2H^+ + 4H_2O$$

2. Urea

$$(NH_2)_2CO + 4O_2 \longrightarrow 2NO_3^- + 2H^+ + CO_2 + H_2O$$

3. Anhydrous ammonia

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H^+ + H_2O$$

4. Ammonium phosphate

$$NH_4PO_4^{2-} + 2O_2 \longrightarrow NO_3^- + HPO_4^{2-} + H_2O + H^+$$

5. Ammonium sulphate

$$(NH_4)_2SO_4 + 4O_2 \longrightarrow 2NO_3^- + SO_4^{2-} + 4H^+ + 2H_2O$$

2.5 Liming of Soils

Figure 3 below shows mechanized liming of a field.

Plate 1: Liming of a field in Devon (UK); the extent to which agriculturalists can go. (Source: Author: 2012)

Liming is the application of calcium- and magnesium-rich materials to soil in various forms, including marl, chalk, limestone, or hydrated lime (Sale and mukwunye, 1993). Plate 1 above shows mechanized liming of a field in UK, an illustration of the extent to which soil scientists can go in efforts to check soil acidity. This neutralizes soil acidity and increases activity of soil bacteria. However, oversupply may result in harm to plant life. When phosphate rocks dissolve in soils at low pH, they affect uptake of minerals by plants (Bolland and Gilkes, 1990).

Rock phosphates are not very effective as fertilizers even though they neutralize acid soils. Lime is a basic chemical; the effect of it makes the soil more basic thus making acidic soils neutral. The degree to which a given amount of lime per unit of soil volume will increase soil pH depends on the cation exchange capacity (CEC). Soils with low CEC will show a more marked pH increase than soils with high CEC. But the low-CEC soils will witness more rapid leaching of the added bases, and so will see a quicker return to original acidity unless additional liming is done (Huber *et al*., 2006).

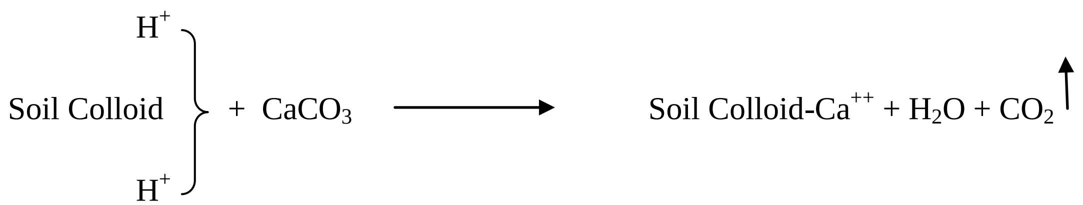
Over-liming is most likely to occur on soil which has low CEC, such as sand which is deficient in buffering agents such as organic matter and clay (Turner and Clark, 1966).

Most acid soils are saturated with Al rather than hydrogen ions. The acidity of the soil is therefore a result of hydrolysis of Al. This concept of "corrected lime potential” to define the degree of base saturation in soils became the basis for procedures now used in soil testing laboratories to determine the "lime requirement" of soils (Wild,1993). An agricultural study at the Faculty of Forestry in Freising, Germany that compared tree stocks 2 and 20 years after liming found that liming promotes nitrate leaching and decreases the phosphorus content of some leaves (Huber *et al*., 2006).

Soils are limed to reduce the harmful effects of low pH (Al or Mn toxicity) and to add Ca and Mg to the soil. The amount of lime needed to achieve a certain pH depends on the pH of the soil and the buffering capacity of the soil. The buffering capacity is related to the cation exchange capacity (CEC). The higher the CEC, the more exchangeable acidity (hydrogen and aluminum) is held by the soil colloids. As with CEC, buffering capacity increases with the amounts of clay and organic matter in the soil.

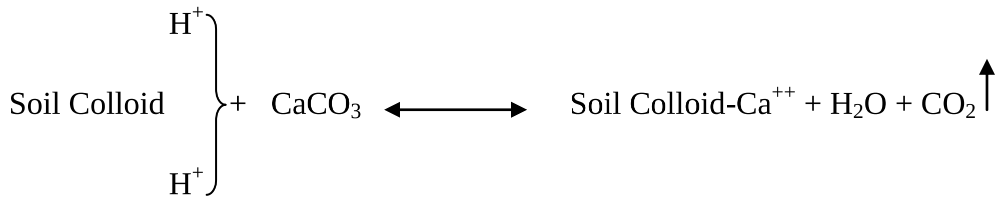
Soils with a high buffering capacity require larger amounts of lime to increase the pH than soils with a lower buffering capacity. Most soil testing laboratories use a special buffered solution to measure the exchangeable acidity. This is the form of soil acidity that must be neutralized for a change in soil pH. By calibrating pH changes in the buffered solution with known amounts of acid, the amount of lime required to bring the soil to a particular pH can be determined (Huber *et al*., 2006).

Lime reduces soil acidity (increases pH) by changing some of the hydrogen ions into water and carbon dioxide (CO_2). A Ca^{++} ion from the lime replaces two H^+ ions on the cation exchange complex. The carbonate (CO_3^-) reacts with water to form bicarbonate (HCO_3^-). These react with H^+ to form H_2O and CO_2. The pH increases because the H^+ concentration has been reduced as illustrated in the generalized chemical equation below.



$$\text{Soil Colloid}\left.\begin{matrix}H^+\\ \\ H^+\end{matrix}\right\} + CaCO_3 \longrightarrow \text{Soil Colloid-}Ca^{++} + H_2O + CO_2\uparrow$$

Similarly, the reverse of the above process can also occur. An acid soil can become more acid as basic cations such as Ca^{2+}, Mg^{2+}, and K^+ are removed, usually by crop uptake or leaching, and replaced by H^+ so the equation above can be re-written as follows;



$$\text{Soil Colloid}\left.\begin{matrix}H^+\\ \\ H^+\end{matrix}\right\} + CaCO_3 \longleftrightarrow \text{Soil Colloid-}Ca^{++} + H_2O + CO_2\uparrow$$

2.5.1 Lime requirement of an acid soil

The amount of lime required to correct soil acidity varies greatly among soils. The lime requirement of a sandy soil at pH 5.0 will be much smaller, because of the smaller base exchange capacity than that of clay at pH 5.0. Wallace *et al*., (1968) suggested that the actual physiological requirement of most plants for Ca is small, but that much larger amounts are generally needed to prevent an imbalance of Mg and to ameliorate the toxic effects of heavy metals unless these are in very low supply. It seems to be generally the case, even in acid soils, that the relative supplies of Ca, Mg and heavy metals are such that extra Ca is not required. However, some crops such as groundnuts, may require a greater supply of soil Ca, part of which is directly absorbed through the shells of the pods during their formation (Foster, 1969).

However, in practice, the acid tolerance of specific crops and other soil factors must be considered when deciding on the need for lime. Soils high in organic matter which can be expected to contain an abundance of organic chelates, which bind Al and Mg, and a high level of exchangeable Ca, which tends to alleviate the toxic effects of Al and Mg, are less likely to require liming (Foster, 1969). Also, low activity clays (kaolinites) which are variable charge soils with no permanent negative charge to accept Ca^{2+}, do not require large quantities of lime (Russell *et al.*, 1981).

At times, soil acidity occurs in patches. Although it is almost impossible to detect small patches of soils needing lime (unless a crop is suffering from acidity), it is possible to pick out large areas with the aid of a dye indicator.The most common indicator is a solution of a mixture of dyes which is blue when the pH of the solution is high and changes green, yellow and finally red as the pH becomes progressively less alkaline and finally acid.

Detection is done by adding a small amount of soil to some little volume of indicator in a white porcelain dish, gently agitating and allowing the suspension to clear and then simply comparing the colour with a standard colour chart (Dories *et al*., 1993).

Sanchez, (1976) suggested that for every milliequavalent (meq) of exchangeable Al present in the soil, 1.5 meq of Ca should be applied or 1.65 t ha^{-1} of $CaCO_3$ equivalent. The lime requirement needed to raise topsoil pH by 1.0 point is typically 5 t ha^{-1} and needs to be repeated every 5 years (Sanchez, 1976). Table 1 gives the approximate amounts of ground limestone or chalk required to correct a range of pH values in different types of soil.

Table 1: Lime requirement of ground chalk or limestone in t ha^{-1} for 150 mm depth of topsoil

pH	Sands	Loams	Clays	Peats
6.0	2.5	4	5	0
5.5	5	8	10	6
5.0	7.5	12	15	12
4.5	10	16	20	18
4.0	12.5	20	25	24

Sources: Dories et al. (1993), Mwangi et al.(1999).

2.5.2 Liming Materials

The most common liming materials are calcitic or dolomitic agricultural limestone. These are natural products made by finely grinding natural limestone. Since natural limestone is relatively insoluble in water, agricultural limestone must be very finely ground so it can be thoroughly mixed with the soil and allowed to react with the soil's acidity.

Calcitic limestone is mostly calcium carbonate ($CaCO_3$). Dolomitic limestone, according to most state laws, must have at least 6 percent magnesium, and is made from rocks containing a mixture of calcium and magnesium carbonates. Either will neutralize soil acidity. Dolomitic limestone also provides magnesium (Dories *et al*., 1993).

Because high quality, finely ground limestone is very dusty and difficult to spread, some companies market a "prilled" or "granular" limestone for home use. A small amount of clay or a polymer is added to the ground limestone so that small prills are formed instead of dust. This makes it easier to spread by hand or with a garden fertilizer spreader. Once applied, soil moisture will cause the "prills" or "granules" to dissociate and disperse the limestone particles. The limestone can then react with exchangeable acidity in the following manner.

$$\text{Soil Colloid}\left.\begin{matrix} H^{+} \\ \\ H^{+} \end{matrix}\right\} + \; CaCO_3 \longrightarrow \text{Soil Colloid-Ca}^{++} + H_2O + CO_2\uparrow$$

Table 2: Common soil liming materials

Sources: Dories et al., (1993).

Material	**Relative neutralizing value** **----------- % ------------**	**Comments**
pure $CaCO_3$	100	not generally available
Calcitic agricultural lime, (calcium carbonate, $CaCO_3$ +impurities)	90 - 100	easily available
Dolomitic agricultural lime, $CaCO_3 + MgCO_3$	95 - 108	easily available; provides Mg
Ground oyster shells	85 - 95	
Selma chalk/marl, $CaCO_3$ + clay	50 - 85	contains clay; keep dry
Burned lime, CaO	150 - 175	very caustic; don't use

2.5.3 Chemical effects of liming acid soils

Ground limestone is a salt which acts as a base when added to an acid and affects acidic soil according to the generalized equation below:

$$2\text{Soil-H} + CaCO_3 \longrightarrow \text{Soil-Ca} + H_2CO_3\ (H_2O + CO_2)$$

Consequently, lime causes the following events to occur in an acid soil:

1. Acidity is neutralized.

2. Base (Ca) saturation of the soil increases.

3. Ratios of basic cations adsorbed and in solution change.

4. Soil pH increases (as soon as the CO_2 dissipates away), which in turn affects the solubility of various compounds.

5. Toxic concentrations of Al, Mn and possibly other substances are neutralized (or otherwise inactivated).

6. Acid weathering of primary and secondary minerals is curtailed by the decreased concentration of H^+.

7. pH-dependent CEC increases, adsorbing Ca^{2+} (and Mg^{2+}) from which it is hydrolyzed (mobilized) for ready uptake or movement to lower depths in the profile.

8. pH-dependent AEC decreases, forcing previously adsorbed anions such as SO_4^{2-} into solution.

9. Nitrogen-fixation and mineralization increase at the higher pH and base saturation.

10. Electrolyte concentration increases with dissolution of lime:

    a) Where (cation exchange capacity) CEC dominates over anion exchange capacity (AEC), the electrolyte disappears from solution as CO_2 volatizes.

    b) Where AEC dominates over CEC, the increases OH ion concentration neutralizes + charges forcing SO_4^{2-} into solution.

Not all of these events following liming are beneficial to plants. Under certain conditions some may be detrimental. Most of them are highly situation dependent. If a crop depends on acid weathering for one or more of the elements it requires, liming may be quite detrimental to its growth. Also, an adequately fertilized corn crop under continuous culture may not benefit at all from increased N fixation and mineralization while one grown in a rotation under limited fertilization may benefit much from the effect of lime on these microbial-effected events. It is evident that the sequence of these occurrences as primary and secondary causes of plant response to lime will differ with individual soil situations (Dories *et al*., 1993; Mwangi *et al*., 1999).

2.5.4 Residual effects of lime

The effects of lime in soils although not permanent last longer than those of most other amendments (Bolland and Gilkes, 1990). Therefore, its effects can be felt for a long time. The residual effect of liming soils with coarse materials is greater than it is with fine materials because larger particles react slowly with acidity and remain in the soil longer (Neil, 1991).

2.5.5 Residual effectiveness of PRs

Soils that have been fertilized with PR fertilizer may contain residual fertilizer for years after application (Bolland and Gilkes.,1990) because only a portion (between about 5-40%) dissolves quickly in weeks and the remainder dissolves slowly in years (Smith, 1994; Sanchez, 1976; Hughes and Gilkes, 1986). Reasons for the more residual effect of the PR has been reported to be due to the fact that the reaction products formed from PRs are less crystalline (Kimenye, 2006).

When PRs are dissolved in soils at low pH and in moist conditions (Bollan and Hedley, 1990), the long term residual value of the PR on various plant species are retained up to ten years due to stabilization as flouropyromorphite (Xinde *et al*., 2002).

PRs immobilize lead leading to its bio accumulation to toxic levels (Jinhee et al., 2010).

2.5.6 Minjingu Phosphate Rock (MPR)

Minjingu phosphate deposit in northern Tanzania is situated about 110 km southwest of Arusha, along the Arusha- Babati road and approximately 800 km by road from western Kenya (Van Straaten, 1997). This biogenic type sedimentary deposit was formed when Lake Manyara (35^0 55' E and 3^0 43' W) was at a higher level and the current Minjingu Hill was an island. The deposit is thought to have resulted from the deaths of massive numbers of cormorants, which used to roost on the island. New Consolidated Goldfields Company discovered the deposit in 1956. However, it was not until 1983 when Minjingu Phosphate Company began production.

There are two types of ores: the ‘soft’ ore estimated to be 3.3 million tonnes and the hard ore, which lies closer to the hill, which is estimated to be 4.8 million tonnes (ICRAF, 1999).

Current and previous production has concentrated on the soft ore, which is located below the hill. The ore is processed by dry beneficiation, where the ore is crushed, screened, dried and bagged (ICRAF, 1999). This concentrated final product contains about 10-13% P, of which 3% is available as estimated by its solubility in neutral ammonium citrate. MPR is reactive and can be used as a direct source of P fertilizer on acid P-deficient and low Ca acid soils. On this basis, various workers have found variations in the effectiveness of MPR on maize yield compared to that of triple superphosphate (TSP) or single superphosphate (SSP). These include 80 to 100% effectiveness in acid soils of Western Kenya, 69% effectiveness over Eastern and Southern Africa (Okalebo and Woomer, 1994), 34% to 121% with an average of 72% effectiveness in ICRAF studies in Western Kenya (ICRAF, 1999), and 74% effectiveness in Morogoro, Tanzania (Semoka, 1996; Ngoze, 2002).

2.5.7 Dissolution of PRs in Acid Soils.

The dissolution of PR material takes place slowly and usually continues for a long time. The PR dissolution in acidic soil solution may be represented by the following equations (Rajan *et al*., 1996).

$$Ca_{10}(PO_4)_6F_2 + 12H_2O \longrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- + 12OH^-$$

$$12H^+ + 12OH^- \longrightarrow 12H_2O$$

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \longrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^-$$

From these equations it can be noted that the dissolution process of PR involves consumption of protons (H^+), and the release of Ca^{2+}, $H_2PO_4^-$ and F^- from the apatite surface. In the equation iii, the removal of Ca^{2+} gives the MPR a liming potential and in addition provides Ca^{2+} to the plants. There is also provision of orthophosphates to the plants. PR dissolution is favoured under the following conditions

(i) low soil pH

(ii) low exchangeable Ca^{2+} and

(iii) low P in soil solution according to the law of mass action.

In acid soils, the H^+ ions are furnished principally by the hydrolysis reactions of Al^{3+} in soil according to the following chemical equation (Tisdale *et al*., 1990):

$$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(OH)(H_2O)_5^{2+} + 3H^+$$

The main driving force controlling the rate of dissolution of PR in soil is therefore the supply of the H^+ ions and the removal of Ca^{2+}, $H_2PO_4^-$ and Fe^{2+} ions from the site of dissolution. Under fixed conditions these products are removed from the soil through plant uptake and leaching (for Fe, Ca) or fixation (for P). On the other hand, in strongly acidic soils where the concentration of Fe and Al ions is high, $H_2PO_4^-$ may react with Al ions to form insoluble Fe and Al phosphates (Kanabo and Gilkes,1987).

$$\underset{\text{(Soluble)}}{Al^{3+} + PO_4^{3-}} + 2H_2O \longrightarrow 2H^+ + \underset{\text{(Insoluble)}}{Al(OH)_2H_2PO_4}.$$

At high pH values > 8.0, available phosphate will react with both Ca and its carbonate (Tisdale *et al.*, 1990). This reaction is pH dependant and will take place at pH values > 8.0 regardless of exchangeable Ca levels:

$Ca(H_2PO_4)_2 + 2Ca^{2+} \longrightarrow Ca_3(PO_4)_2 + 4H^+$

$Ca(H_2PO_4)_2 + 2CaCO_3 \longrightarrow Ca_3(PO_4)_2 + 2CO_2 + 2H_2O$

(soluble) (insoluble)

Dissolution of phosphate rocks may lead to retention of heavy metals in the sub soils. For example, phosphate induced formation of flouro pyromorphite is primarily responsible for immobilizing lead in soils as $Pb[(Pb_{10}(PO_4)_6F_2)$. Other metals can be immobilized due to surface adsorption and complexation (Xinde *et al.*, 2002).

2.6 Mechanisms of heavy metal retention by phosphate rock

Experiments show that phosphate-induced formation of fluoropyromorphite is primarily responsible for Pb immobilization by phosphate rock, whereas Cu and Zn retention is mainly attributable to the surface adsorption or complexation. In a research to study the solid-liquid interface reaction between PR and metals (Pb, Cu, and Zn) by Xinde *et al* (2002), results showed PR had the highest affinity for Pb, followed by Cu and Zn, with sorption capacities of 138, 114, and 83.2 mmol/kg PR, respectively. The greatest stability of Pb retention by PR can be attributed to the formation of insoluble fluoropyromorphite $[Pb_{10}(PO_4)_6F_2]$, which was primarily responsible for Pb immobilization (up to 78.3%), with less contribution from the surface adsorption or complexation (21.7%), compared to 74.5% for Cu and 95.7% for Zn. Solution pH reduction during metal retention and flow calorimetry analysis both supported the hypothesis of retention of Pb, Cu, and Zn by surface adsorption or complexation(Xinde *et al*., 2002). This research demonstrated that PR can effectively remove Pb from solutions, even in the presence of other heavy metals (for example Cu, Zn). It appeared to be consistent with the hypothesis of Ma *et al*. (1995), who proposed that Pb retention by hydroxyapatite is controlled by hydroxyapatite dissolution, followed by hydroxypyromorphite precipitation. Similarly, PR induced reactions in the presence of a heavy metal could be simplified as follows

$Ca_{10}(PO_4)_6F_2 + 12\ H^+ \longleftrightarrow 10Ca^{2+} + 6H_2PO_4^{\ -} + 2F^-$ ………………..(8)

Dissolution

For a generalized metal ion, M^{2+},

$10M^{2+} + 6H_2PO_4^- + 2F^- \longrightarrow M_{10}(PO_4)_6F_2 + 12H^+$ ……………………..(9)

Precipitation

The exact reaction mechanism responsible for the removal of metal ions by rock phosphate/apatite is still unknown. But the sorption process, which generally involves species attachment from a solution to its co-existing solid surface by three types, namely surface adsorption, absorption or diffusion into the solid and precipitation or coprecipitation appears to be the governing mechanism for the retention of metal ions by rock phosphate. It has been shown that the primary mechanism of metal ion removal by rock phosphate is governed by its dissolution in acidic environment followed by subsequent precipitation, recent evidences support the removal to be governed by dissolution- precipitation mechanism. Hence, the process may be reduced to a generalized sorption process. In addition to the above hypothesis, where P in the form of $H_2PO_4^{\ -}$ helps in precipitating metal as a complex (Xinde *et al*., 2002).

2.7 Heavy Metal Toxicity in Cereals

Studies by Dzifa *et al.,* (2011) using maize tassels showed that, from a 2.00 ppm laboratory stimulated solution maize tissues were able to extract the solution to below 0.02 ppm in just below one hour. Soil surveys by Kurnia *et al,.* (2000) showed plants which were planted in polluted soils accumulated high levels of B, Cd, Pb, Cr and Cu in their tissues, roots and rice grains. Highest concentration was in roots. In 1999, Adiningsiih et al, studying low land rice farming in west Java (Indonesia) found that levels of Pb and Cd in cereals in such polluted soils as high as 43 ppm for Pb and 0.49 ppm for Cd where Cd content in fertilizers was up to 255 ppm.

Experiments using maize tassels on contaminated ground water with Mn toxicity 2.400 ppm and Pb toxicity 1.096 ppm, the tassels extracted the metals to below 0.002 ppm in less than one hour. The results obtained indicated that maize tassel had adsorption capabilities for As, Mn, Pb and Hg ions. The adsorption of these heavy metals by the maize tassel could be attributed to the presence of functional groups such as -H, -NH_2, -C = O and –COOH on the surface of maize tassel. These functional groups are polar and are capable of binding to heavy metals. The rate of adsorption of the heavy metals onto the tassels increased with increasing time. At the end of the 60th minutes, a significant amount of each of the metals had been removed from the solution. The values obtained after adsorption by the chosen species of maize tassels were within the permissible guideline values for As, Mn, Pb and Hg ions in drinking water by World Health Organisation (WHO), United State Environmental Protection Agency (USEPA) and Ghana Environmental Protection Agency (Alloway, 1995).

In another study to investigate whether mycorrhizal colonization influences heavy metal uptake by maize. Two experiments were carried out. In the first, 15 commercially available maize varieties cultured on industrial waste substratum and inoculated or not with *Glomus intraradices*, were treated one week before harvest with EDTA, a chelating agent known to mobilize heavy metals in soil. Estimation of mycorrhizal parameters indicated differences between varieties, but differences between treatments of the same variety generally were not statistically significant. Although EDTA treatment strongly decreased the activity of fungal alkaline phosphatase (indicator of fungal viability), the treatment did not totally eliminate arbuscular mycorrhizal fungi (AMF) from the soil (Adiningsiih *et al*., 1999).

The appearance of AMF structures within roots was modified in plants cultivated in EDTA-treated soil. Among the heavy metals studied, the highest impact of EDTA treatment on heavy metal uptake in shoots was found in the case of Pb. In most cases, EDTA treatment significantly increased the Pb level in shoots of mycorrhizal plants. Among the samples treated with EDTA, mycorrhizal plants of 6 cultivars showed higher Pb content in shoots than did nonmycorrhizal plants. Significant differences in heavy metal content in plant material were demonstrated between the varieties tested. In the second experiment, one selected cultivar was subjected to high soil Pb concentrations and to EDTA for one week, following cultivation in nonpolluted substratum. In this case, EDTA treatment more strongly influenced Pb uptake by nonmycorrhizal than by mycorrhizal plants. The results indicate the need to carefully screen cultivars as well as microorganism strains to be used in phytoextraction procedures (Adiningsiih *et al*., 1999).

In another 6-year field study performed to evaluate heavy metal accumulation in the top 20 cm of a clay-loam calcareous soil (fluventic xerochrept) amended with urban waste compost and to determine heavy metal uptake and distribution in corn plants grown in this soil. Compared with untreated soils, amended soils showed a significant increase only in Cu, Zn, Pb and, in the last 2 years, Cr concentrations. The corn plants grown on the amended soil showed a general increase in metal uptake, which was about three times greater for Pb and two times greater for the other heavy metals than in plants grown on untreated soil. At times, the diluting effect resulting from enhanced growth rates of the plants with compost application resulted in lower concentrations in the plants grown on treated plots. Cr and Pb were less mobile in the corn plant and were accumulated only in root tissues. Only in the last 3 years of the experiment were traces of Pb found also in the stalks (Giovanni *et al*., 1999).

The limited mobility of Pb was confirmed in a contemporary hydroponic greenhouse experiment. The values of the plant/soil transfer coefficients were within the lower range reported in the literature, indicating that in the soil studied (which contained 14% $CaCO_3$) there was limited transfer of heavy metal ions from the soil to the corn plants. It is concluded that the long-term application of large amounts of urban waste compost to $CaCO_3$-containing soils does not necessarily cause medium-term problems to plant, animal or human health (Giovanni *et al.,* 1999).

2.8 Concentrations of Heavy Metals Fertilizers

Adding fertilizers to soil and plants is a common agricultural practice aimed at improving soil fertility and plant production. Enlarged food production volume begins by increasing crop yields through the use of higher amounts of fertilizers. Although fertilizers are predominantly beneficial in terms of plant production, they may also be potentially harmful as substances contaminating soil and both groundwater and surface waters. Fertilizers usually get insufficiently purified in the manufacturing process and therefore often contain various levels of impurities, including heavy metals, depending on the quality of raw materials used for their production. As a result of accumulation of heavy metals in soil, groundwater and plants, toxic effects of these elements can become very harmful (Jagodin *et al*., 1991).

A high input of fertilizers in soil, particularly NPK, which in most agricultural countries totals some 300-600 kg of the main components per ha of soil cultivated, i.e. 600-800 tons annually, may cause excessive additions of heavy metals in soil through the impurities of raw materials. Imported fertilizers tend to be of poor quality and are often delivered without appropriate quality control certificates. Despite the fact that heavy metal concentrations in fertilizers have been limited in several European countries, all fertilizers used in Kenya are still not being analyzed for heavy metal contents in compliance with Standard Regulative measures (Chen and Zhu, 2004).

In an earlier research, Pb, Cd, Cu and Mn concentrations in sixteen commercial NPK fertilizers of different types and origins were determined. The results obtained provided a basis for an assessment of risks from heavy metal toxicity in representative European and one American samples. Concentrations of Pb, Cd, Cu and Mn in sixteen NPK fertilizers imported and widely used in Serbia were determined by flame atomic absorption spectrometry (AAS). The results showed that contents of heavy metals varied significantly in different fertilizers depending on N:P:K ratio and fertilizer origin. Pb and

Cd contents in water solution of fertilizers occurred at low ranges: 2.0-3.1 and 0.03-1.56 mg/kg, respectively (Jelena *et al.,* 2008).

An NPK (15:15:15) fertilizer from Romania was found to contain the highest concentration of Pb and Cd as impurities. Cu content, ranging from 7.1 to 974.7 mg/kg, was the highest in coloured fertilizers from Hungary, the Netherlands and Greece. Mn value in a Hungarian NPK product (10:10:20) exceeded the average Mn value in soil.

The data indicated variable contents of heavy metals in fertilizers, some of which were significantly higher than natural concentrations in soil, which suggests that they need to be continuously monitored (Jelena *et al.,* 2008).

Pb concentrations in sixteen fertilizer samples analyzed showed that in seven samples, two Austrian, three Dutch, one Hungarian (14:11:25) and one Russian (16:13:16), Pb was not detected. In the remaining samples, extracted in water solution, Pb was found in concentrations ranging from 2.0 to 3.1 mg/kg. The lowest contents of Pb were found in a Croatian (15:15:15) and the second Hungarian (10:10:20) NPK samples, while the highest were detected in Romanian and Russian samples. As expected, Pb contents in the investigated samples were higher in acid solutions. In acetic buffer solution at pH 4.0 the detected values were on a scale from 8.5 to 11.1 mg Pb/kg. At pH 4.5, Pb concentration was the highest in one of the NPK samples from the Netherlands (6.4 mg Pb/kg).

Cadmium was detected in almost all of the analysed fertilizers and the levels in water solutions varied from 0.03 to 1.56 mg Cd/kg. Considering the two NPK samples from Romania, Cd was found in higher concentration in the sample with higher P percentage, similar to the Pb content in the same samples. The data additionally confirmed that contaminated raw materials were used for producing these samples. The mean value of

Cd concentrations is about 1.44 mg Cd/kg fertilizer which means that about 650 mg Cd per hectare is put into neutral soil annually if this fertilizer is used. As Cd readily leaches through deeper soil layers, getting into groundwater and then to surface waters, the risk of contamination with fertilizers rich in Cd increases rapidly, especially in more acid soils.

Cu contents in the analyzed samples showed that the levels of this metal in the examined fertilizers, extracted in water and acid solutions, were highly variable depending on fertilizer type and origin. Cu values were found to vary on a large scale from 4.04 (in water solution) to 974.70 mg/kg (at pH 4.0) in one of the Hungarian samples, which was more than 240 times. Cu contents in nine NPK fertilizers was less than 30 mg/kg, which was satisfactory because the maximum allowed concentration for Cu in soil and drinking water are 100 mg/kg and 0.1 mg/L, respectively (OGRS, 1994).

Mn levels in the fertilizers investigated covered the widest range. Concentrations of this potentially toxic metal vary from 8.75 (Austrian 15:15:15 sample) to 5236.65 mg Mn/kg of fertilizer (Hungarian 10:10:20 sample) in water solution. The reason for such a high variability in concentrations was the composition of raw materials used for fertilizers products. Hence, attention should also be directed to the quality of raw materials in order to prevent highly toxic concentrations. The extremely high Mn level of 9569.71 mg Mn/kg in a Hungarian NPK (10:10:20) sample extracted in a buffer at pH 4.0 is more than ten times higher than the average Mn level that can be found in soil (about 800 mg/kg). This value must be significantly lowered by rigorously controlling the manufacturing process of fertilizers (Jelena *et al*., 2008).

Appendix 13 shows tables of concentration of selected heavy metals in commonly imported fertilizers and agricultural lime.

2.9 Heavy Metals

2.9.1 Zinc

2.9.1.1 Introduction

The most common zinc ore is sphalerite (zinc blende), a zinc sulphide mineral. The largest mineable amounts are found in Australia, Asia, and the United States. Zn production includes froth flotation of the ore, roasting, and final extraction using electricity (electro winning) (Besenhard, 1999). Corrosion-resistant zinc plating of steel (hot-dip galvanizing) is the major application for Zn. Other applications are in batteries and alloys, such as brass. A variety of Zn compounds are commonly used, such as zinc carbonate and zinc gluconate (as dietary supplements), zinc chloride (in deodorants), zinc pyrithione (anti-dandruff shampoos), zinc sulphide (in luminescent paints), and zinc methyl or zinc diethyl in the organic laboratory (Casarret *et al.*, 2007).

2.9.1.2 Applications

Major applications of zinc include; galvanizing (55%),alloys (21%),brass and bronze (16%), miscellaneous (8%) (Numbers are given for the US)(US Geological survey, 2009). The metal is most commonly used as an anti-corrosion agent galvanization, which is the coating of iron or steel to protect the metals against corrosion, is the most familiar form of using Zn in this way. Zn is more reactive than iron or steel and thus will attract almost all local oxidation until it completely corrodes away. A protective surface layer of oxide and carbonate ($Zn_5(OH)_6(CO_3)_2$) forms as the zinc corrodes.

This protection lasts even after the zinc layer is scratched but degrades through time as the zinc corrodes away. The Zn is applied electrochemically or as molten zinc by hot-dip galvanizing or spraying. Galvanization is used on chain-link fencing, guard rails, suspension bridges, light posts, metal roofs, heat exchangers, and car bodies.

The relative reactivity of zinc and its ability to attract oxidation to itself makes it an efficient sacrificial anode in cathodic protection (CP). For example, cathodic protection of a buried pipeline can be achieved by connecting anodes made from Zn to the pipe. Zn acts as the anode (negative terminus) by slowly corroding away as it passes electric current to the steel pipeline. Zinc is also used to cathodically protect metals that are exposed to sea water from corrosion (Bounoughaz et al, 2003). A zinc disc attached to a ship's iron rudder will slowly corrode while the rudder stays unattacked. Other similar uses include a plug of Zn attached to a propeller or the metal protective guard for the keel of the ship.

With a standard electrode potential (SEP) of −0.76 volts, Zn is used as an anode material for batteries. More reactive lithium (SEP −3.04 V) is used for anodes in Li batteries. Powdered Zn is used in this way in alkaline batteries and sheets of zinc metal form the cases for and act as anodes in Zn–carbon batteries (Wiaux and Waefler, 1995). Zn is used as the anode or fuel of the Zn-air battery/fuel cell. Zn is also used as a tracer to study how alloys that contain zinc wear out, or the path and the role of zinc in organisms (Apelian *et al.*, 1981).

2.9.1.3 Health Effects of Zinc

Although Zn is an essential requirement for good health, excess Zn can be harmful. Excessive absorption of Zn suppresses Cu and Fe absorption. The free Zn^{2+} ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. The free ion activity model is well-established in the literature, and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killing 93% of all *Daphnia* in water (Eisler, 1993).

The free Zn ion is a powerful Lewis acid up to the point of being corrosive. Stomach acid contains HCl, in which metallic Zn dissolves readily to give corrosive ZnCl. Swallowing a post-1982 American one cent piece (97.5% zinc) can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach (Eisler, 1993).

The U.S. Food and Drug Administration (FDA) have stated that Zn damages nerve receptors in the nose, which can cause anosmia. Reports of anosmia were also observed in the 1930s when zinc preparations were used in a failed attempt to prevent polio infections. On June 16, 2009, the FDA said that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves. The FDA said the loss of smell can be life-threatening because people with impaired smell cannot detect leaking gas or smoke and cannot tell if food has spoiled before they eat it (Muysen *et al.*, 2006).

In 1982, the United States Mint began minting pennies coated in copper but made primarily of Zn. With the new Zn pennies, there was the potential for Zn toxicosis, which can be fatal. One reported case of chronic ingestion of 425 pennies (over 1 kg of zinc) resulted in death due to gastrointestinal bacterial and fungal sepsis, while another patient, who ingested 12 grams of Zn, only showed lethargy and ataxia (gross lack of coordination of muscle movements). Several other cases have been reported of humans suffering Zn intoxication by the ingestion of Zn coins (Bennett *et al*., 1997). Pennies and other small coins are sometimes ingested by dogs, resulting in the need for medical treatment to remove the foreign body. The Zn content of some coins can cause Zn toxicity, which is commonly fatal in dogs, where it causes a severe hemolytic anemia, and also liver or kidney damage; vomiting and diarrhea are possible symptoms. (Bennett *et al*., 1997).

2.9.2 Chromium

2.9.2.1 Introduction

Chromium (Cr) is a brilliant, hard, refractory metal that melts at 1,857° C (3,375° F) and boils at 2,672° C (4,842° F). In the pure state, it is resistant to ordinary corrosion, resulting in its application as an electroplated protective coating for other metals. It dissolves in nonoxidizing mineral acids but not in aqua regia or nitric acid, which passivate the metal (Bacon and James, 2012).

Because Cr and Cr-rich alloys are brittle at room temperature, they have limited application. By far the largest consumption is as an alloying addition to iron.

In amounts varying from 10 to 26 percent, Cr imparts corrosion resistance to steel; it is also used to improve hardenability, wear-resistance, and high-temperature strength. As the mineral chromite, Cr is employed extensively as a refractory material. Other Cr chemicals are used as pigments and tanning agents (Ullman *et al*., 1985).

2.9.2.2 Applications

Cr main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Cr plating was once widely used to give steel a polished silvery mirror coating. Cr is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape (Bacon and James, 2012).

2.9.2.3 Health Effects of Chromium

People can be exposed to Cr through breathing, eating or drinking and through skin contact with Cr or its compounds. The level of Cr in air and water is generally low. In drinking water the level of Cr is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent Cr. For most people eating food that contains Cr (III) is the main route of Cr uptake, as Cr (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the Cr contents of food. When food is stores in steel tanks or cans Cr concentrations may rise (Bacon and James, 2012).

Cr (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much Cr (III) can cause health effects as well, for instance skin rashes. Cr (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to Cr (Bacon and James, 2012).

Cr (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in Cr (VI) can cause nose irritations and nose bleeds. Other health problems that are caused by Cr (VI) are; skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death (Sully and Brandes, 1967).

The health hazards associated with exposure to Cr are dependent on its oxidation state. The metal form (Cr as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent Cr compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, broncho spasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch. Carcinogenicity- Cr and most trivalent Cr compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent Cr compounds; $CaCrO_4$, CrO_3, $PbCrO_4$, $SrCrO_4$, and $ZnCrO_4$. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (Sabiha *et al*., 2008).

2.9.3 Cadmium

2.9.3.1Introduction

Cadmium (Cd) is an extremely toxic metal commonly found in industrial workplaces. Due to its low permissible exposure limit, overexposures may occur even in situations where trace quantities of cadmium are found. Cd is used extensively in electroplating, although the nature of the operation does not generally lead to overexposures. Cd is also found in some industrial paints and may represent a hazard when sprayed. Operations involving removal of Cd paints by scraping or blasting may pose a significant hazard. Cd is also present in the manufacturing of some types of batteries. Exposures to Cd are addressed in specific standards for the general industry, shipyard employment, construction industry, and the agricultural industry. Some sources of phosphate in fertilizers contain Cd in amounts of up to 100 mg/kg,(Syers *et al*, 1986),which can lead to an increase in the concentration of Cd in soil (for example in New Zealand) (Taylor, 1997).

2.9.3.2 Uses

Cd is used in a large number of industrial applications. The uses for Cd include; component of several metal alloys, component of solder (metallic cement), particularly solder for Al, electroplating, Ni-plating, engraving, Cd vapour lamps, nickel-cadmium batteries and treatment of parasites in pigs and poultry (Nordberg, 2010).

2.9.3.3 Sources of Cd Exposure

Buildup of Cd levels in the water, air, and soil has been occurring particularly in industrial areas. Environmental exposure to Cd has been particularly problematic in Japan where many people have consumed rice that was grown in Cd contaminated irrigation water.Food is another source of Cd. Plants may only contain small or moderate amounts in non-industrial areas, but high levels may be found in the liver and kidneys of adult animals.

Cigarettes are also a significant source of Cd exposure. Although there is generally less Cd in tobacco than in food, the lungs absorb Cd more efficiently than the stomach. Workers can be exposed to Cd in air from the smelting and refining of metals, or from the air in plants that make Cd products such as batteries, coatings, or plastics. Workers can also be exposed when soldering or welding metal that contains Cd. A few sources of phosphate in fertilizers contain Cd in amounts of up to 100 mg/kg which can lead to an increase in the concentration of Cd in soil (for example in New Zealand). Ni-Cd batteries are one of the most popular and most common Cd-based products, and this soil can be mined for use in them (Nordberg, 2010).

2.9.3.4 Cadmium Toxicity

Cd can be very toxic, and is dangerous if it is swallowed or inhaled. While spontaneous recovery from mild cadmium exposure is common, doses as low as 10 milligrams can cause symptoms of poisoning. There is no accepted fatal dose amount. The symptoms of ingested Cd poisoning are; increased salivation, choking, vomiting, abdominal pain, anemia and painful spasms of the anal sphincter (Jarup, 1998).

When cadmium dust or powder is inhaled, the first symptoms are a sweet or metallic taste, followed by throat irritation. Other symptoms that may appear in three to five hours include; dry throat, cough, headache, vomiting, chest pain, pulmonary edema (a congestive lung condition), bronchospasm, the abnormal tightening of airways that may be accompanied by wheezing and coughing, pneumonitis, inflammation of the lung, muscle weakness and leg pains (Baselt, 2008).

When a person has exposure to Cd in low doses over a long period of time, symptoms may include loss of sense of smell, cough, shortness of breath, weight loss, and tooth staining. Chronic Cd exposure may cause damage to the liver and kidneys (Nordberg, 2010).

2.9.3.5 Causes and symptoms of Cd poisoning

The most common cause of Cd poisoning is a lack of proper precautions in places where Cd is used. In such industries, air quality should be regularly monitored. Cd-plated containers should never be used to store acidic foods such as fruit juices or vinegar. Fossil fuels, such as coal and oil, release Cd fumes into the air. Chronic Cd poisoning is also possible through soil or water contamination. This problem may occur with improper disposal of Ni-Cd batteries used in items such as cameras. Cd concentrations in healthy persons without excessive Cd exposure are generally less than 1 μg/L in either blood or urine. The biological exposure indices for blood and urine Cd levels are 5 μg/L and 5 μg/g creatinine, respectively, in random specimens. Persons who have sustained renal damage due to chronic Cd exposure often have blood or urine Cd levels in a range of 25-50 μg/L or 25-75 μg/g creatinine, respectively. These ranges are usually 1000-3000 μg/L and 100-400 μg/L, respectively, in survivors of acute poisoning and may be substantially higher in fatal cases (Shanon, 1998).

2.9.4 Copper

2.9.4.1 Introduction

Cu is a ductile metal with very high thermal and electrical conductivity. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys.Its compounds are commonly encountered as copper (II) salts, which often impart blue or green colors to minerals such as turquoise and have been widely used historically as pigments. Copper (II) ions are water-soluble, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, they are poisonous to higher organisms; at lower concentrations it is an essential trace nutrient to all higher plant and animal life. The main areas where copper is found in animals are liver, muscle and bone (Trig and Edmund, 1992).

2.9.4.2 Properties

2.9.4.2.1 Physical Properties

Cu just above its melting point keeps its pink luster colour when enough light outshines the orange incandescence colour. The low hardness of Cu partly explains its high electrical (59.6×10^6 S/m) and thus also high thermal conductivity, which are the second highest among pure metals at room temperature (Hammond, 2004). This is because the resistivity to electron transport in metals at room temperature mostly originates from scattering of electrons on thermal vibrations of the lattice, which are relatively weak for a soft metal (Trig and Edmund, 1992). The maximum permissible current density of Cu in open air is approximately 3.1×10^6 A/m^2 of cross-sectional area, above which it begins to heat excessively. As with other metals, if Cu is placed against another metal, galvanic corrosion will occur. Together with osmium (bluish), and gold (yellow), Cu is one of only three elemental metals with a natural color other than gray or silver. Pure Cu is orange-red and acquires a reddish tarnish when exposed to air. The characteristic color of Cu results from the electronic transitions between the filled 3d and half-empty 4s atomic shells – the energy difference between these shells is such that it corresponds to orange light. The same mechanism accounts for the yellow colour of gold (Trigg and Edmund, 1992).

2.9.4.2.2 Chemical Properties

Cu forms a rich variety of compounds with oxidation states +1 and +2, which are often called *cuprous* and *cupric*, respectively (Holleman and Wiberg, 2001). It does not react with water, but it slowly reacts with atmospheric oxygen forming a layer of brown-black copper oxide. In contrast to the oxidation of iron by wet air, this oxide layer stops the further, bulk corrosion. A green layer of verdigris ($CuCO_3$) can often be seen on old Cu constructions, such as the Statue of Liberty, the largest Cu statue in the world built using repoussé and chasing. H_2S and sulfides react with Cu to form various Cu sulfides on the surface. In the latter case, the Cu corrodes, as is seen when copper is exposed to air containing sulfur compounds (Ricketts and Payer, 1995). Oxygen-containing ammonia solutions give water-soluble complexes with Cu, as do oxygen and HCl to form copper chlorides and acidified H_2O_2 to form copper (II) salts. $CuCl_2$ and Cu comproportionate to form CuCl.

2.9.4.3 Applications of Copper

The major applications of Cu are in electrical wires (60%), roofing and plumbing (20%) and industrial machinery (15%).

Cu is mostly used as a metal, but when a higher hardness is required it is combined with other elements to make an alloy (5% of total use) such as brass and bronze. A small part of Cu supply is used in production of compounds for nutritional supplements and fungicides in agriculture. Machining of Cu is possible, although it is usually necessary to use an alloy for intricate parts to get good machinability characteristics (Wiley and Hoboken, 2007). Cu compounds in liquid form are used as a wood preservative, particularly in treating original portion of structures during restoration of damage due to dry rot. Together with Zn, Cu wires may be placed over non-conductive roofing materials to discourage the growth of moss. Textile fibers use Cu to create antimicrobial protective fabrics, as do ceramic glazes, stained glass and musical instruments. Electroplating commonly uses Cu as a base for other metals such as Ni. Cu is one of three metals, along with Pb and Ag, used in a museum materials testing procedure called the Oddy test. In this procedure, Cu is used to detect chlorides, oxides, and sulphur compounds.

2.9.4.4 Copper Toxicity

Gram quantities of various Cu salts have been taken in suicide attempts and produced acute Cu toxicity in humans, possibly due to redox cycling and the generation of reactive oxygen species that damage DNA. Corresponding amounts of Cu salts (30 mg/kg) are toxic in animals. A minimum dietary value for healthy growth in rabbits has been reported to be at least 3 ppm in the diet. However, higher concentrations of Cu (100 ppm, 200 ppm, or 500 ppm) in the diet of rabbits may favourably influence feed conversion efficiency, growth rates, and carcass dressing percentages. Chronic Cu toxicity does not normally occur in humans because of transport systems that regulate absorption and excretion.

Autosomal recessive mutations in Cu transport proteins can disable these systems, leading to Wilson's disease with Cu accumulation and cirrhosis of the liver in persons who have inherited two defective genes (Li *et al., 1994).*

2.9.5 Lead

2.9.5.1 Introduction

Lead (Pb) has been known since ancient times and is relatively abundant in the earth's crust (13 g/ton, ranking 36th), where it is found in galena (PbS). The Pb crystal has a cubic structure with centered faces. Pb is a lustrous, bluish metal; it is relatively soft, extremely malleable and ductile and is a poor conductor of electricity. It is highly resistant to corrosion but oxidises and blackens when it comes into contact with air (Casarett *et al*., 2007).

2.9.5.2 Uses

Pb has a number of uses but many of these are currently being phased out because of growing awareness of its toxicity and of the damage that uncontrolled dispersion in the environment has already caused. Pb is employed in accumulators, ammunitions, piping, paints, in anti-radiation screens and tin-based welding alloys. In the past, lead was added to petrol in the form of tetra-ethyl lead (PbEt4) with an anti-knocking function; however, in developed countries this kind of petrol is currently being phased out for environmental reasons (Casarett et al., 2007). Pb may also enter the environment as a by-product of mining and of the industrial processing of other metals, such as silver, gold, bismuth, etc (Brunton *et al*., 2007).

2.9.5.3 Toxicity

Pb poisoning (also known as plumbism, colica Pictonum, saturnism, Devon colic, or painter's colic) is a medical condition caused by increased levels of the heavy metal Pb in the body. Pb interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behaviour disorders. Symptoms include abdominal pain, confusion, headache, anaemia, irritability, and in severe cases seizures, coma, and death (Dart *et al.*, 2004).

Pb ranks second in the list of prioritized hazardous substances issued by the U.S. ATSDR (Agency for Toxic Substances and Disease Registry) in 1999. The noxious effects of this metal have long been well known, especially as regards acute forms of poisoning. However, as for many other contaminants, the threshold level of safety has been drastically lowered recently. Until approximately 30 years ago, chronic Pb poisoning was defined by blood Pb levels above 80(gr/dl, while today a Pb level of 30(gr/dl in blood is considered excessive and levels at or above 10(gr/dl (0.1 ppm) are considered potentially harmful, particularly in children (Chisolom, 2004).Routes of exposure to Pb include contaminated air, water, soil, food, and consumer products. Occupational exposure is a common cause of Pb poisoning in adults. One of the largest threats to children is Pb paint that exists in many homes, especially older ones; thus children in older housing with chipping paint are at greater risk. Prevention of Pb exposure can range from individual efforts (for example removing Pb-containing items such as piping or blinds from the home) to nationwide policies (for instance laws that ban Pb in products or reduce allowable levels in water or soil (Grant, 2009).

Once absorbed by the body, mainly through breathing and feeding, Pb is not metabolized, but mostly expelled. The remaining portion (about 20%) settles into the tissues and notably; the blood, mineral tissues (including teeth and bones) and in soft tissues like kidneys, bone marrow, liver and brain.The presence of Pb in the blood stream (inside the red blood cells and mostly linked to haemoglobin) provokes anaemia. This disease cannot be considered a symptom, but rather a delayed sign of Pb poisoning. Through the blood, Pb reaches all other tissues. Because of its capacity to "mimic" Ca, Pb is stored in the bones and becomes a stable bone component, particularly in the case of insufficient Ca intake (Kosnett, 2007). This Pb deposit may be mobilized and return into the blood stream under particular states of physiological stress (pregnancy, breast-feeding, diseases), but also as a consequence of greater Ca intake in the diet. This stable presence of Pb in bones makes recovery from Pb poisoning extremely slow, even when the toxic agent has been completely eliminated (Menkes, 2006).

Pb can damage practically all tissues, particularly the kidneys and the immune system. The most deceptive and dangerous form of Pb poisoning is that affecting the nervous system. In adults, Pb damage mainly causes peripheral neuropathy, which is characterised predominantly by demyelination of the nerve fibres. Intense exposure to high Pb levels (from

100 to 200 (gr/dl) causes encephalopathy, with the following symptoms: vertigo, insomnia, migraine, irritability and even convulsions, seizures and coma. Lower levels of the metal give rise to Pb-induced neuropathy, which mainly affects the developing brain and provokes behavioral problems and cognitive impairment. Epidemiological studies have shown a strong correlation between Pb levels in blood and bones and poor performance in attitude tests (IQ or psychometric tests) (Dart et al., 2004). Treatment for lead poisoning relies on drugs that have a chelating effect on the metal; these are molecules that can bind to Pb and form a stable complex, which is then expelled. The most common drugs used are calcium-EDTA, dimercaprol (DMSA or BAL) and penicillamine, a penicillin derivative which has a chelating, rather than anti-bacterial, effect.

2.9.6 Manganese

2.9.6.1 Introduction

Manganese (Mn) has the atomic number 25. It is found as a free element in nature (often in combination with iron), and in many minerals. As a free element, Mn is a metal with important industrial metal alloy uses, particularly in stainless steels. Mn phosphating is used as a treatment for rust and corrosion prevention on steel. Depending on their oxidation state, Mn ions have various colours and are used industrially as pigments. The permanganates of alkali and alkaline earth metals are powerful oxidizers. MnO_2 is used as the cathode (electron acceptor) material in standard and alkaline disposable dry cells and batteries. In biology; Mn (II) ions function as cofactors for a large variety of enzymes with many functions. Mn enzymes are particularly essential in detoxification of superoxide free radicals in organisms that must deal with elemental oxygen. Mn also functions in the oxygen-evolving complex of photosynthetic plants. The element is a required trace mineral for all known living organisms. In larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (Rayner *et al*, 2003).

2.9.6.2 Properties

a) Chemical properties

The most common oxidation states of Mn are +2, +3, +4, +6 and +7, though oxidation states from −3 to +7 are observed. Mn^{2+} often competes with Mg^{2+} in biological systems. Mn compounds where Mn is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of the intensely purple permanganate anion MnO_4^-, are powerful oxidizing agents. Compounds with oxidation states +5 (blue) and +6 (green) are strong oxidizing agents and are vulnerable to disproportionation (Coranthers, 2008).

The most stable oxidation state for manganese is +2, which has a pale pink color, and many manganese (II) compounds are known, such as $MnSO_4$ and $MnCl_2$. This oxidation state is also seen in the mineral rhodochrosite, ($MnCO_3$). The +2 oxidation state is the state used in living organisms for essential functions; other states are toxic for the human body. The +2 oxidation of Mn results from removal of the two 4s electrons, leaving a "high spin" ion in which all five of the 3d orbitals contain a single electron. Absorption of visible light by this ion is accomplished only by a spin-forbidden transition in which one of the d electrons must pair with another, to give the atom a change in spin of two units. The unlikeliness of such a transition is seen in the uniformly pale and almost colorless nature of Mn (II) compounds relative to other oxidation states of Mn (Rayner *et al*., 2003).

The +3 oxidation state is known in compounds like Mn (III) acetate, but these are quite powerful oxidizing agents and also prone to disproportionate in solution to Mn (II) and Mn (IV). Solid compounds of Mn (III) are characterized by their preference for distorted octahedral coordination due to the Jahn-Teller effect and its strong purple-red color.

The oxidation state 5+ can be obtained if MnO_2 is dissolved in molten sodium nitrite. Manganate (VI) salts can also be produced by dissolving Mn compounds, such as MnO_2, in molten alkali while exposed to air. Permanganate (+7 oxidation state) compounds are purple, and can give glass a violet colour $KMnO_4$, $NaMnO_4$ and $Ba(KMnO_4)_2$ are all potent oxidizers. $KMnO_4$, also called Condy's crystals, is a commonly used laboratory reagent because of its oxidizing properties and finds use as a topical medicine (for example, in the treatment of fish diseases). Solutions of $KMnO_4$ were among the first stains and fixatives to be used in the preparation of biological cells and tissues for electron microscopy (Coranthers, 2008).

2.9.6.3 Applications

Mn has no satisfactory substitute in its major applications, which are related to metallurgical alloy use. In minor applications, (e.g., manganese phosphating), zinc and sometimes vanadium are viable substitutes. In disposable battery manufacture, standard and alkaline cells using manganese will be generally replaced in the future with lithium battery technology (Coranthers, 2008).

2.9.6.3 Toxicity

Mn compounds are less toxic than those of other widespread metals, such as Ni and Cu. However, exposure to Mn dusts and fumes should not exceed the ceiling value of 5 mg/m^3 even for short periods because of its toxicity level. Mn poisoning has been linked to impaired motor skills and cognitive disorders (Takeda, 2003).

The MnO_4^- permanganate exhibits a higher toxicity than the Mn (II) compounds. The fatal dose is about 10 g, and several fatal intoxications have occurred. The strong oxidative effect leads to necrosis of the mucous membrane. For example, the esophagus is affected if the MnO_4^- is swallowed. Only a limited amount is absorbed by the intestines, but this small amount shows severe effects on the kidneys and on the liver (Ong *et al.*, 1997).

2.9.6.5 Environmental health concerns

Waterborne Mn has a greater bioavailability than dietary Mn. According to results from a 2010 study, higher levels of exposure to Mn in drinking water are associated with increased intellectual impairment and reduced intelligence quotients in school-age children. It is hypothesized that long-term exposure to the naturally occurring manganese in shower water puts up to 8.7 million Americans at risk (Takeda, 2003).

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter consists of sampling procedures for soil samples, plant tissues, preparation and digestion of samples, and analysis by AAS.

3.2 Sampling procedure

Soil samples were collected using a Dutch soil auger in composite replicates of soil core samples at different depths of 0 to 15 cm (top soil) and 15 to 30 cm (sub soil). On each experimental unit, 15 to 25 soil cores per composite samples were collected and thoroughly mixed in clean plastic buckets. Samples were then taken to the laboratory, air dried, ground using mortar and pestle and sieved through 2 mm sieve. Recently matured maize grain samples were collected, dried, ground using mortar and pestle and then sieved.

Samples were taken from five selected farms from Uasin Gishu County and five other farms from Trans Nzoia County. The samples from the selected fields were taken during four sampling periods at intervals of nine (9) weeks to cover both the dry and wet seasons of the year.

Samples were taken in all five fields in the month of February 2009 coinciding with the dry season while second batch of soil samples were taken in all five fields in the month of April (late) 2009, coinciding with the wet season which was the planting season.

The third batch of soil samples were taken in all five fields in the month of October 2009 coinciding with the dry season and during harvesting period. In the fourth season, grain samples were taken in all five fields in the month of October 2009 coinciding with the dry season. The grains were freshly matured ones.

3.3 Soil Samples

Samples of soils were collected from a depth of 15cm using a soil auger, dried, ground, sieved and digested using wet and block digestion methods.

3.4 Plant Tissues

Grains were collected dried, ground and sieved before being digested. Procedures for wet digestion of soils and sediments were followed.

3.5 Sample Preparation and Digestion

Samples of plant materials and soils were treated with a mixture of sulphuric acid/selenium powder, and hydrogen peroxide to digest the organic material. To avoid loss of nitrogen in samples the samples were pre treated with salicylic acid. The digest was diluted to a definite volume (50 ml), filtered and centrifuged when necessary.

3.6 Apparatus

Mortar and pestle, soil sieve (2 mm), electrical balance, electrical oven block heater (Labonco Rapid digester), digestion tubes 25ml, and 50 ml volumetric flasks.

3.7 Reagents

The reagents used included hydrogen peroxide 30% (100 vol), selenium powder salicylic acid conc. sulphuric acid and other common laboratory reagents. All reagents were of analytical grade.

3.8 Preparation of Sulphuric Acid / Selenium Mixture:

A 1.75g of Se powder was dissolved in 500ml of concentrated sulphuric acid by heating to about 250^{o}C in a flask covered with watch glass. The originally black colour of the suspension turned via green/ blue into a clear light yellow solution after three to four hours of heating.

3.9 Preparation of Digestion Mixture

A 4.5gm of salicylic powder was dissolved in 75 ml of the sulphuric acid/ selenium mixture.

Selenium is carcinogenic must be handled with great care. Protection gloves, mask, and fume cardboards were used.

3.10 Procedure

A sample of a plant or soil material was dried in an electric oven at 105^{o}C to constant weight, ground with a mortar and pestle and sieved through 0.5 mm sieve. Before weighing, finely ground sample was heated at 70^{o}C to dryness for one hour. A 0.3gm of each was weighed out, and transferred quantitatively into a well labeled digestion tube.

A blank for each series was included.

A 3.0 ml of sulphuric acid/ selenium mixture was added and swirled gently until all the material was moistened then allowed to stand for 2 hours.

The digestion tube was placed in the block heater and heated for 2 hours at 100^{o}C. The tubes were removed from the block and allowed to cool. Aliquots of hydrogen peroxide each 1ml were added successfully three times.

The tubes were placed in a pre heated block and heated at 330^{o}C (just below boiling point) until the digest turned colorless or light yellow after approximately 4 hours and then removed from the block digester and allowed to cool to room temperature.

40ml of distilled water was carefully added, mixed well and allowed to stand for a few hours. The sample was then ready for AAS analysis.

3.11 Soil Acidity: pH of Soil Suspensions

3.11.1 Principle

The pH is a common way of expressing H^+ concentrations of aqueous solutions or soil suspensions respectively. For this purpose, the soil suspension in distilled water with a soil to water ratio of 1:1 was used.

3.11.2 Apparatus

The apparatus used included pH meter with a refillable electrode, mechanical shaker, beam balance, electrical balance measuring cylinder, (50 ml beakers and volumetric flasks) in addition to other common laboratory apparatus.

3.11.3 Reagents

Distilled water, buffer solutions of pH 4.0 and 7.0.

3.11.4 Procedure for determination of soil pH

Approximately 10g that had been air dried and passed through a 2-mm sieve was weighed and placed into a 50 ml beaker and 25 ml of distilled water added. The mixture was stirred using a mechanical shaker for 10 minutes and left to stand for 30 minutes. It was then stirred again for 2 minutes and finally, using a digital pH meter, the pH of the soil suspension was read off directly by inserting the glass electrode into the mixture.

3.12 AAS Analysis of digested samples (Atomic Analysis for Metals)

Analysis for heavy metal contaminants was done for Zn, Cu, Pb, Cd, Mn and Cr. Pb, Cd, Cu and Mn concentrations in all samples were investigated by flame atomic absorption spectrometry (SpectrAA 220 – Varian) in oxidizing air-acetylene flame, under optimal conditions. Nebulization rate was 5 mL/min in all measurements.

Elemental analysis for the different heavy metals in soils and plant tissues was carried out by atomic absorption spectrometry according to the manual prepared as a guide for elemental analysis in biochemical laboratory for the school of environmental studies, Moi University, 2004.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents, analyses, interpretation of the data and discussion of the findings. Concentrations of metals in samples are reported in figures and tables.

Correlation charts showing relationship between pH and concentration for each in the analyte were obtained using GENSTAT analysis. From the regression equations governing the scatter graphs values of R^2 were obtained and hence r values. The closer the value of r is to 1 (one) the more the perfect relationship between pH and concentration of the metal. Metals which show r closer to 1 imply pH influences their availability. Graphs and figures were also drawn to show changes in metal concentrations in soils with fertilization and liming.

4.2 Scatters for Metal Concentrations across the Four Sampling Periods

Figures 1-6 below show scatter graphs obtained for metal values showing correlation between concentration of metals under investigation and pH for the four seasons. In another study to determine mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils by Matos *et al. (2000)*, correlation studies were conducted in samples of unlimed and limed tropical soils. It was found that important soil chemical characteristics related to the retardation factors in the limed soil samples were complex formation for Cd, Ca, Cu and Pb, suggesting that precipitation may also influence the mobility and retention of the heavy metals in soil samples.

Soil pH influenced the heavy metals adsorption and movement as was shown by the significant correlation with the retardation factors when the combined data for the unlimed and limed soil samples was considered (Matosa *et al*, 2000). All these findings compare well with what was found in Uasin Gishu and Trans- Nzoia where application of liming materials caused accumulation of heavy metals Pb, Cr, Cd, Mn and Zn in soils. Generally, metals Pb, Cr, Cd, Mn and Zn showed weak correlation with pH but Cu showed very strong dependence on pH.

From the Figure 1, the regression value of r = 0.770 implies an almost perfect relationship between Cu and pH and these results corroborate earlier research findings. In a study on liming effects on availability of metals in amended soils, pH adjustment by liming reduced metal uptake by reducing their solubility except Cu (Sara *et al*., 1994). In a case study to determine availability of Cu in soils due to influence of soil pH, organic matter and extractable phosphorus, besides significant interactions between soil properties, Cu uptake was best enhanced by inclusion of pH (Dolar and Keeney, 2006). These findings are in agreement with Ross (2003) and Smith (1994) who found that availability of micro nutrient Cu in soils was pH dependent. This present research has also found that availability of Cu in soils is pH dependent.

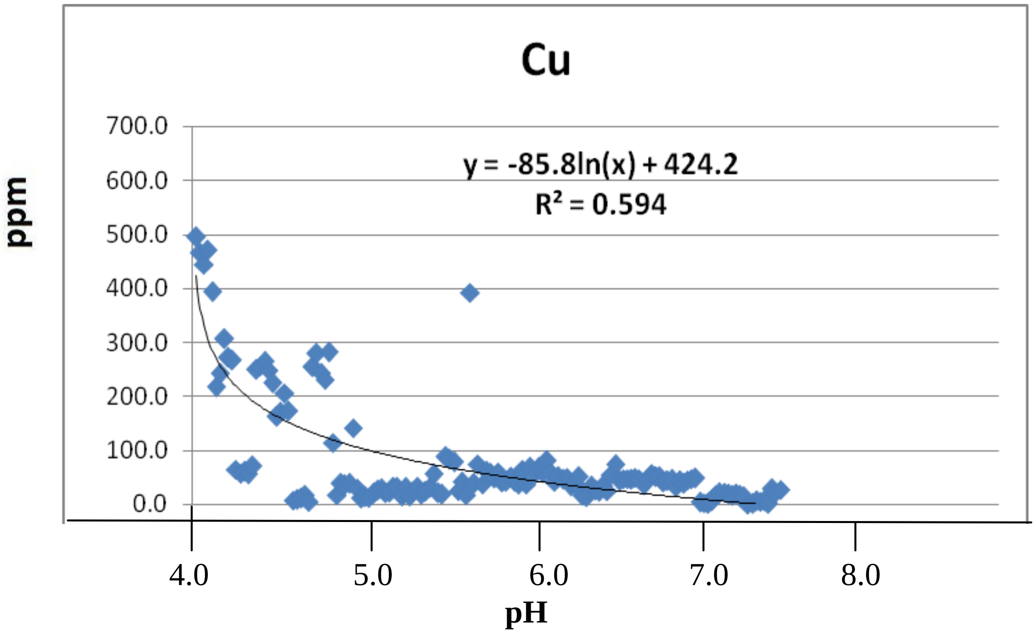


Figure 1: A scatter graph obtained for Cu values showing correlation between Cu and pH.

From the Figure 2, the regression graph gives R^2 of 0.020 (hence r = 0.1414) implying an insignificant relationship between Zn and pH implying that the soil pH did not influence the concentration levels of soil Zinc to a large extent. This is be supported by a study by Abdul *et al*. (2005) on remediation of soils contaminated with heavy metals. In a case study on the effect of liming on availability of metals in amended soils, pH adjustment by liming lowered metal uptake by reducing solubility especially for Zn (Sara *et al*., 1994). In another case study to determine availability of Zn in soils due to influence of soil pH, organic matter and extractable phosphorus, apart from significant interactions between soil properties and use of NPK, Zn uptake was not enhanced by inclusion of pH (Dolar and Keeney, 2006).

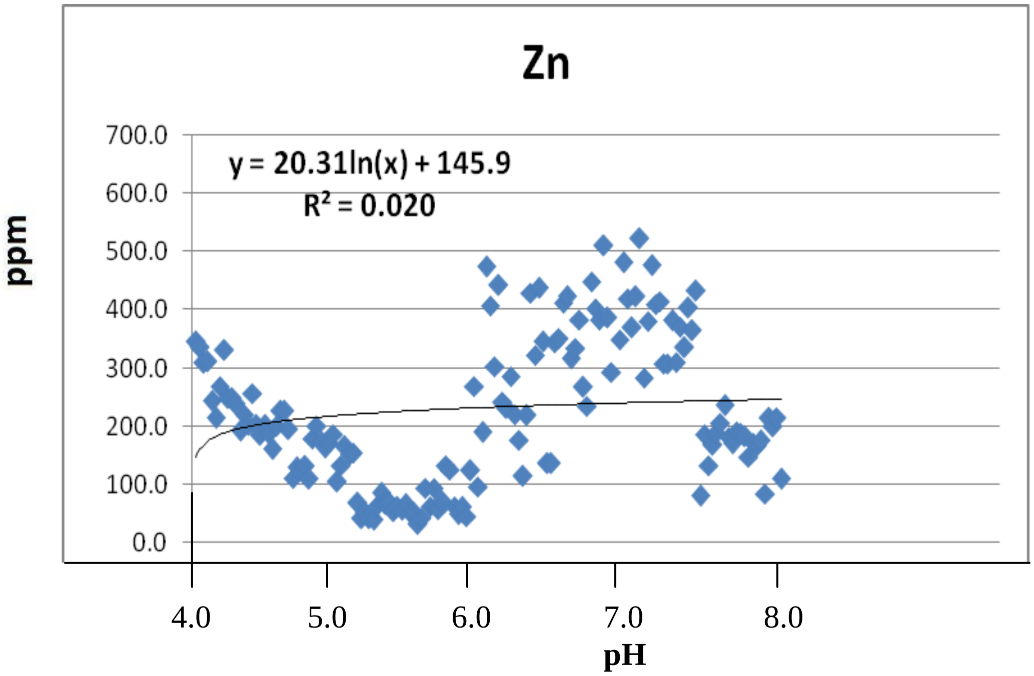


Figure 2: Scatter graph for Zn values showing correlation between Zn and pH.

From the Figure 3, the obtained value of r = 0.1183, thus implying there was no significant relationship between Pb and pH. This low corelation between soil Pb and soil pH compares very well with other research findings. Earlier research findings have shown that phosphate minerals have the potential to imobilize Pb^{2+} ions by forming stable complexes over wide pH ranges and contaminate soils. These minerals also reduce labile fractions of Pb in soils. Pb phosphates, and in particular pyromorphites, are some of the most stable forms of Pb in soils under a wide range of environmental conditions (Nriagu, 1974; Lindsay, 1979). Based on the low phosphate solubility, a number of studies involving the use of phosphates including P fertilizers for the stabilization of Pb in contaminated soils have been carried out (Ma *et al.*, 1995; Cotter-Howells and Capron, 1996; Hettiarachchi et al., 2000; Ryan et al., 2001; Tang *et al.*, 2004).

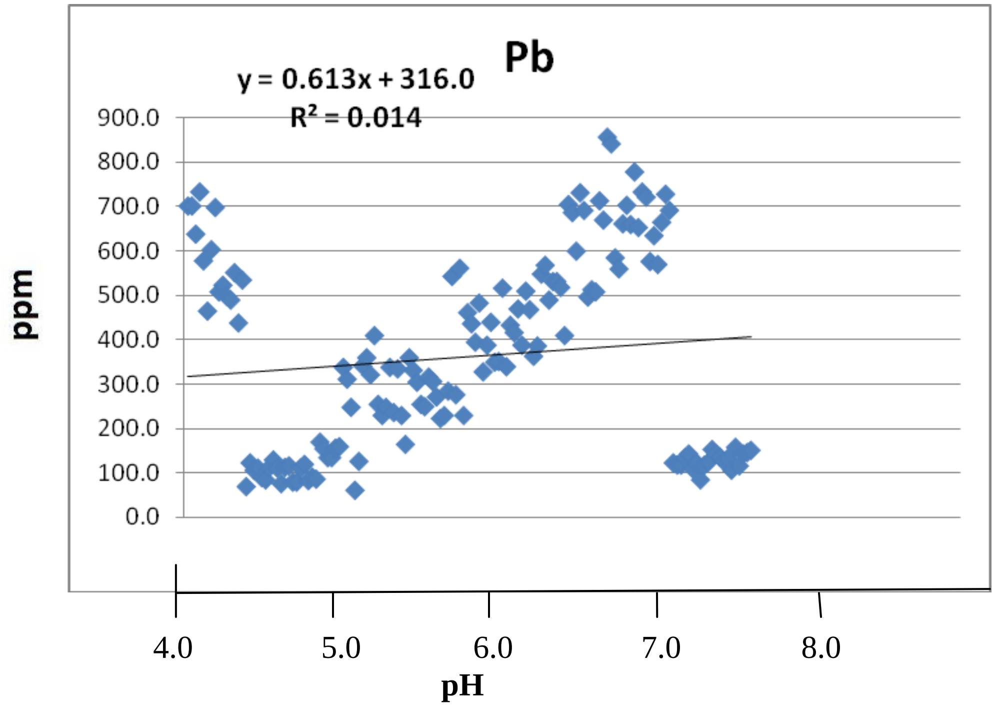


Figure 3: A scatter graph obtained for lead values showing the correlation between Pb and pH.

Formation of pyromorphites and significant reduction of Pb bioavailability in the soils upon addition of PR or single superphosphate (SSP) was observed in Pb-contaminated soils (Ma et al., 1997; Hettiarachchi *et al.*, 2001). Reduced plant uptake of Pb was also observed upon PR or SSP addition to Pb-contaminated soils (Hettiarachchi and Pierzynski, 2002; Xinde *et al.*, 2002). In a research to study the solid liquid interface reaction between PR and metals (Pb, Cu, and Zn) by Xinde et al., (2002), results showed PR has the highest affinity for Pb, followed by Cu and Zn. The greatest stability of Pb retention by PR can be attributed to the formation of insoluble fluoropyromorphite [$Pb_{10}(PO_4)_6F_2$], which was primarily responsible for Pb immobilization with less contribution from the surface adsorption or complexation. Solution pH reduction during metal retention and flow calorimetry analysis both supported the hypothesis of retention of Pb, Cu, and Zn by surface adsorption or complexation. This research demonstrated that PR can effectively remove Pb from solutions, even in the presence of other heavy metals such as Cu and Zn. It can therefore be concluded that the low significance relationship is expected.

For values of Cd, Figure 4 gives a regression equation of y = -2.11ln(x) + 36.16 with r = 0.187. This revealed that no significant relationship between soil pH and Cd content in soil existed thus concluding that Cd is not very sensitive to pH.

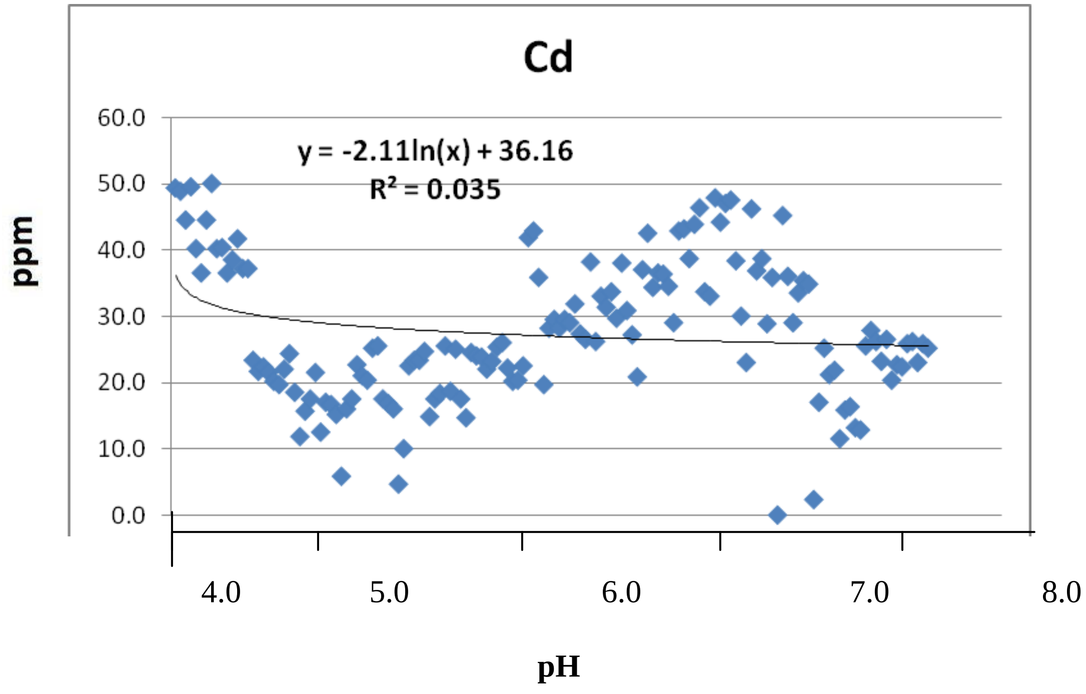


Figure 4: A scatter graph obtained for cadmium values showing correlation between Cd and pH.

Data on Cd concentrations in shoot of cabbage grown in the treated soil showed Cd content generally decreased significantly after application of phosphatic fertilizers except for SSP addition at low pH as shown in Figure 4. The lowest pH and lower P level indicate that Cd uptake was influenced by the addition of phosphorus fertilizers. The addition of P may reduce Cd phytoavailability through a combination of several mechanisms, such as sorption (including phosphate-induced Cd adsorption and surface complexation), precipitation, or co-precipitation (Laperche and Traina, 1998; Valsami-Jones *et al*., 1998). Therefore, it has been speculated that soils containing Cd have Cd in the form of Ca-Cd phosphate or Ca-Pb-Cd phosphate (Valsami-Jones et al., 1998). Chen *et al*., (1997) suggested that reduction in aqueous Cd concentrations in solutions with apatite addition occurred primarily because of sorption mechanisms, such as surface complexation, and ion exchange rather than precipitation of Cd phosphate. Liming, which adjusts the pH of soils upwards, lowers solubility of Cd and reduces its uptake by plants (Sara *et al*., 1994).

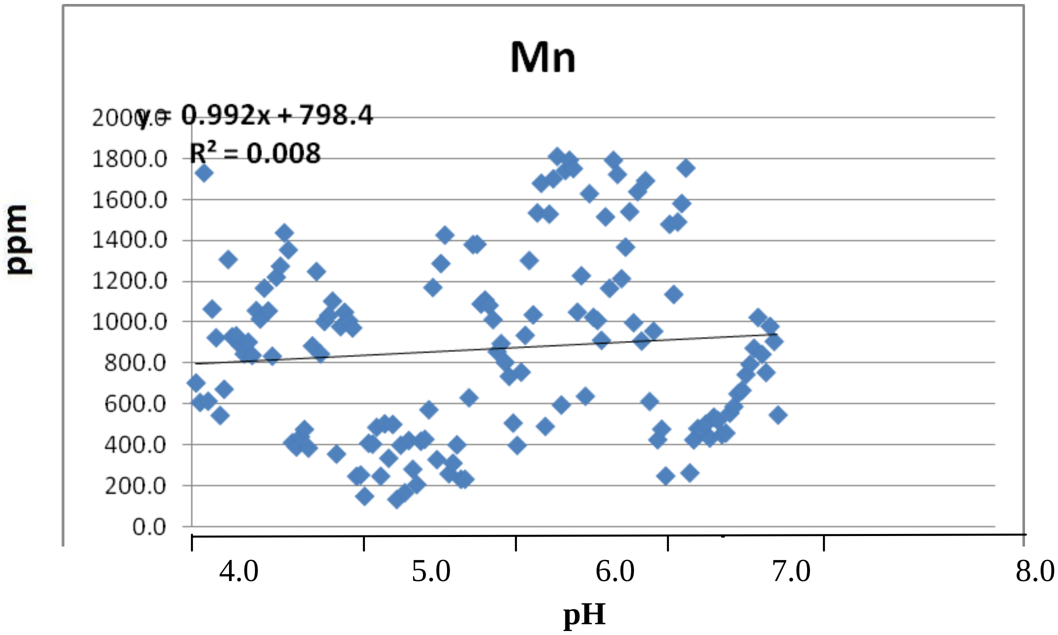


Figure 5: A scatter graph obtained for Mn values showing correlation between Mn and pH

Figure 5 for Mn, shows the value of r = 0.089. This implies there was no significant relationship between Mn concentration and pH. These findings are supported by other earlier research findings. For instance in a study on liming effects on availability of metals in amended soils, pH adjustment by liming lowered Mn uptake by reducing its solubility (Sara *et al.*, 1994). In another case study to determine availability of Mn and other nutrients in soils due to influence of soil pH, organic matter and extractable phosphorus, besides significant interactions between soil properties, Mn uptake was found to depend weakly on pH (Dolar and Keeney, 2006). These findings are in agreement with those reported by Ross (2003) on soil pH and plant nutrients and Smith (1994) using rye grass to investigate the effect of pH, who found that availability of micro nutrient Mn in soils was pH independent.

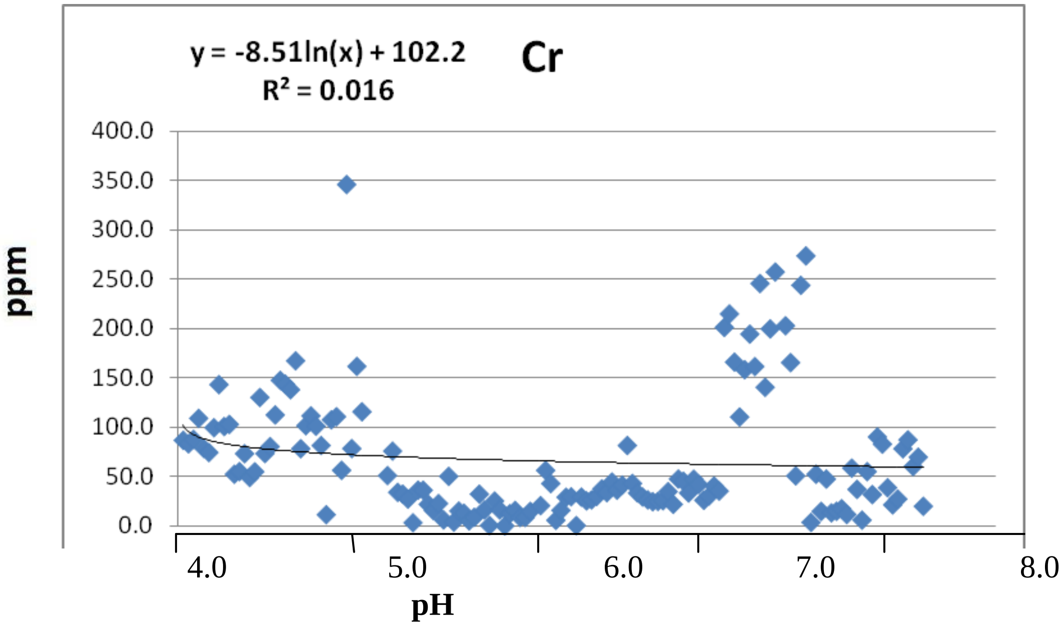


Figure 6: A scatter graph obtained for Cr values showing correlation between Cr and pH.

Figure 6, shows the regression equation obtained for Cr has value of r = 0.127 , implying no significant relationship exists between the Cr metal in soil and soil pH. These findings were largely expected, as corroborated by earlier research (Fanrong *et al*., 2011). Experiments were done to investigate the effect of soil pH and organic matter content on EDTA-extractable heavy metal contents in soils and heavy metal concentrations in rice straw and grains. EDTA-extractable Cr contents in soils and concentrations in rice tissues were weakly negatively correlated with soil pH, but positively correlated with organic matter content (Fanrong *et al*., 2011). It can be concluded from these findings of a less than significant relationship that availability of Cr in soils was mainly due to amendments including fertilizer application but little to do with pH changes.

4.3 Trends in Metal Concentrations across the Four Sampling Periods

Figures 7 - 12 show the trends in concentration of metals in soils across the three sampling periods and finally in maize grains after applying different fertilizers; (L= agricultural grade lime, DAPL = Diammonium phosphate, MPRL = Mijingu phosphate rock and MOPL = Monoammonium phosphate).

From Figure 7 it is observed that concentration of Cu in soils reduced from the first sampling period to the third and this could be most likely due to leached Cu.

Also the concentration in the maize grains was seen to be very low below acceptable levels (50µg/g), thus the maize plant did not up take Cu from soils. These results show successive reduction in concentration of Cu in soils which could be attributed to several factors, but predominantly due to leaching and complexation. In a research on Cu extraction from a sandy soil by washing the soil with aqueous solution of ethylene diamine tetra acetic acid (EDTA), results showed that decreasing the pH of the washing solution a higher Cu extraction yield was achieved (Palma and Ferrantelli, 2005).

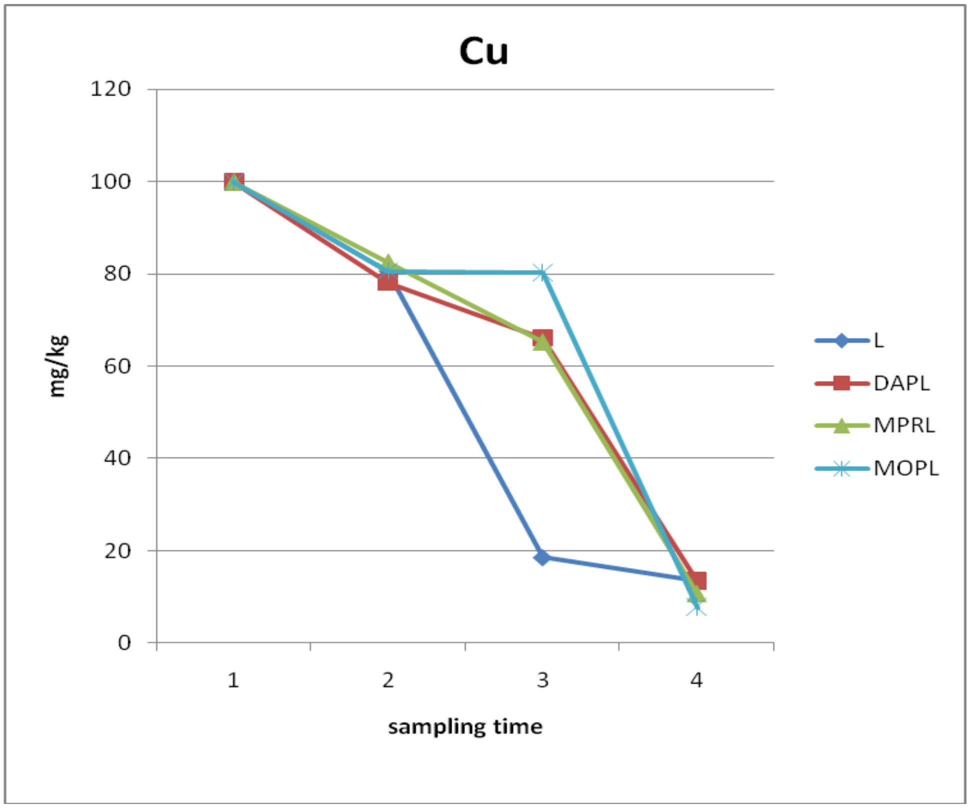


Figure 7: Trends in concentration of Cu metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

The mechanism of Cu extraction was found to involve two sequential processes: the former dissolution of metal salts, that led to an initial high concentration of both Cu and some competitive cations (essentially Ca^{2+}), and then followed EDTA exchange reaction between Ca and Cu complexes, which corresponded to an increase of pH in the washing solution (Palma and Ferrantelli, 2005). These findings would perfectly corroborate the graph given that liming and fertilizer application introduced complexing agents as well as caused pH adjustments.

From Figure 8, Zn levels increased in soils across all the sampling period from February to October, most likely as a result of complexation or surface adsorption (Xinde *et al*., 2002). The low levels of Zn in grains suggest limited uptake of this element by the plant.

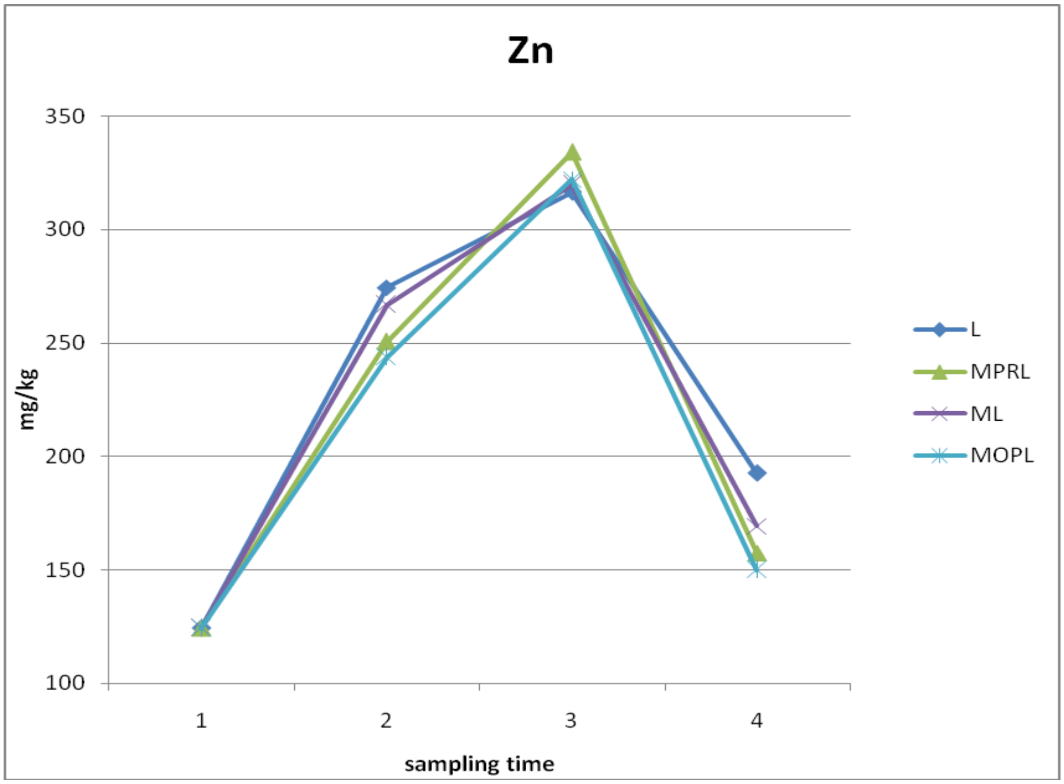


Figure 8: The trends in concentration of zinc metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

Earlier research has shown that the soil pH does not influence the concentration levels of soil Zn to a large extent (Abdul *et al*., 2005) on remediation of soils contaminated with heavy metals. In a study on liming effects on availability of metals in amended soils, pH adjustment by liming decreased metal uptake by reducing their solubility especially Zn (Sara *et al*., 1994).

In a case study to determine availability of Zn in soils due to influence of soil pH, organic matter and extractable phosphorus, apart from significant interactions between soil properties and use of NPK, Zn uptake was not enhanced by inclusion of pH (Dolar and Keeney, 2006). It can thus be concluded that accumulation of Zn in soils was due to the fact that Zn was not solubilised and therefore neither leached nor absorbed by plants. It is also noted that concentration of Zn in grains was very low. Zn levels in soils changed from 124.4 ppm to 319.9 ppm hence an increment in levels in soil. In a study to determine effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils by Xingfu and Gholamhoss, (1989), it was found that alteration of pH resulted in changes of chemical forms of the metals in the soils, and at lower pH the changes were more significant.

When soil pH values were decreased from 7.0 to 4.55, levels of Zn in exchangeable form increased (solubilized), but decreased in carbonates (precipitate forms). However, their levels in organic and residual forms were unchanged. This observation agrees with the findings of this research if it is taken that liming, which increased soil pH to above 7.0 favoured formations of Zn precipitates hence causing accumulation. The magnitude and trend of values agrees well with those by Lenart and Koładka (2012) involving the effect of heavy metal concentration and soil pH on the abundance of microbial groups within

ArcelorMittal, Poland steelworks in Cracow. In that study the levels of Zn in lime amended soils ranged from 49.0 ppm to 494.0 ppm.

Figure 9 shows that concentration of Cd increased in soils between the first and third sampling periods. In this period the soils had been limed and pH adjusted. Metal concentrations built up in soils most likely because Cd compounds were stabilized by complexing. The maize grains did not show high levels of Cd due to lack of absorption by the plant. Thus it can be concluded that Cd is not very sensitive to pH.

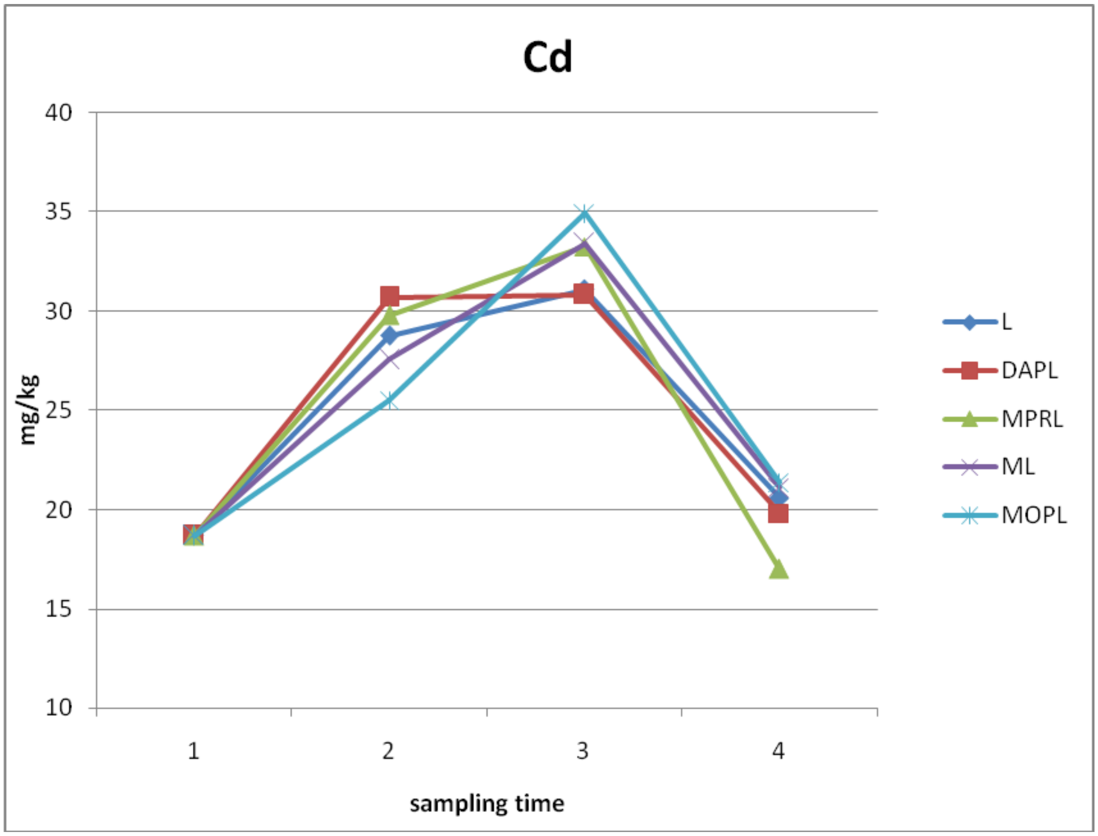


Figure 9: The trends in concentration of Cd metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

The addition of P may reduce Cd bioavailability through a combination of several mechanisms, such as sorption (including phosphate-induced Cd adsorption and surface complexation), precipitation, or co-precipitation (Laperche and Traina, 1998; Valsami-Jones *et al.*, 1998). Therefore, it has been speculated that soils containing Cd have Cd in the form of Ca-Cd phosphate or Ca-Pb-Cd phosphate (Valsami-Jones *et al.*, 1998; Chen and Wright,1997) and that reduction in aqueous Cd concentrations in solutions with appatite addition occurred primarily because of sorption mechanisms, such as surface complexation, and ion exchange rather than precipitation of Cd phosphate. Liming, has been found to lower solubility of Cd and reduces its uptake by plants (Sara *et al.,* 1994). No doubt in this research Cd values accumulated in soil but was unavailable for maize uptake. The magnitude and trend of values also agrees well with those by Lenart and Koładka (2012) involving the effect of heavy metal concentration and soil pH on the abundance of microbial groups. In that study the levels of soil Cd ranged between 1.30 ppm at low pH to 43.08 ppm at alkaline pH (~7.8).

Figure 10 shows high levels of Mn in all the soils sampled from the first to the third sampling period. The grains also showed Mn was taken in high quantities by maize most probably because it is a macronutrient. These results corroborate the findings of Dzifa *et al.* (2011) showing that maize has high adsorption capabilities for Mn ions. Being a macro nutrient the values of Mn up taken by the maize plant were exceptionally high (above 410 ppm). However, this metal concentrations being in edible portions of the plants means it is at the entry point of the human food chain and needs to be checked. However, even though it is a macronutrient, desirable in large quantities by plants, its bioaccumulation as observed from the graph is a major corncern. It is evident that all amendments caused bioaccumulation of Mn. These findings compare well with what other studies have reported. In a study on liming effects on availability of metals in amended soils, pH adjustment by liming reduced Mn uptake by decreasing its solubility (Sara *et al.*, 1994). In the present study it is observed that values of Mn increased from below 600 ppm to above 1000 ppm in all treatments of liming agreeing with earlier findings.

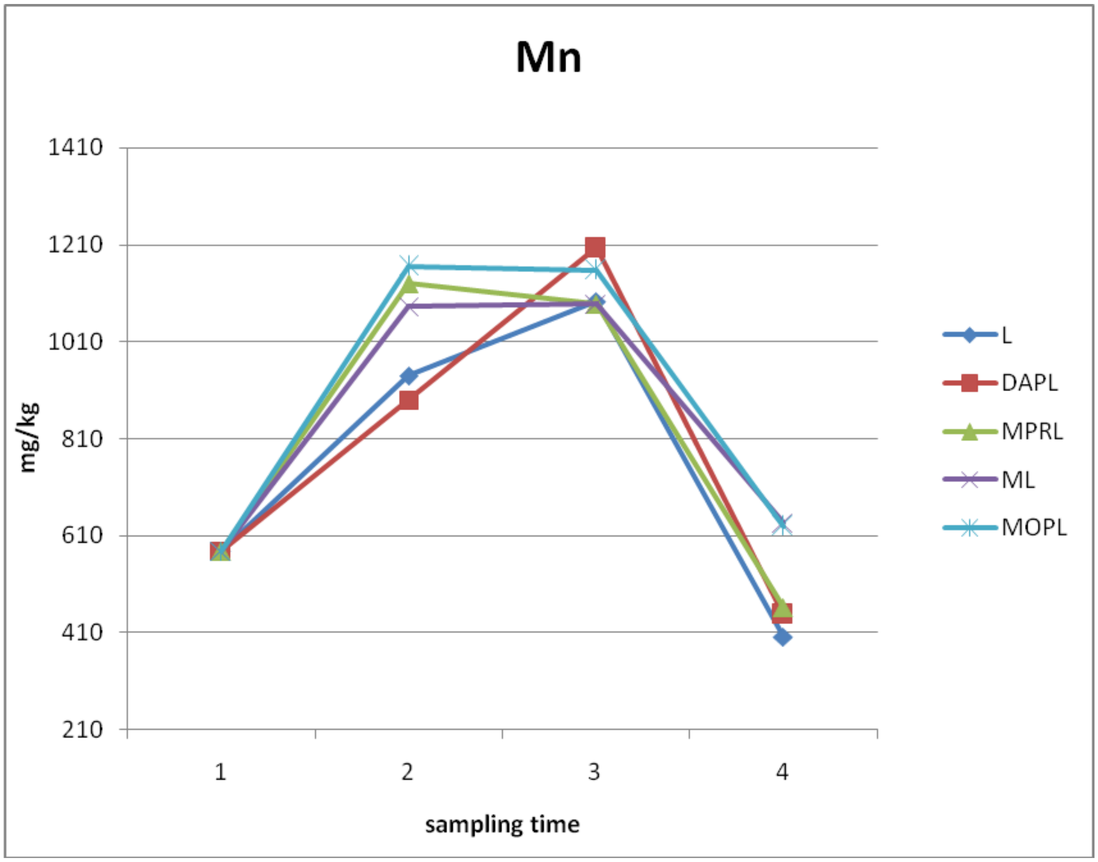


Figure 10: The trends in concentration of Mn metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

Figure 11 shows considerable accumulation of Cr in soils; however, the final quantity in the grains was low. In the graph, Cr levels in soils doubled from 40.03 ppm – 84.93 ppm by the third sampling period for MPR and from 40.03 ppm to 138.6 ppm for agricultural grade lime in the same period. Bolan and Thiagarajan (2001) in a study to determine the retention and plant availability of chromium in soils as affected by lime and organic matter amendments found that addition of the liming materials decreased the concentration of the soluble Cr(III) and bark decreased soluble Cr(VI) in soil. In that research various mechanisms were attributed to the increased Cr (III) sorption in presence of the liming materials. The major chemical components of the slaked FBA are gypsum and $Ca[(OH)_2]$ with a high pH of 12.1 (Wang *et al.* 1994), just like in MPR. Chromium is likely to precipitate above pH 5.5 as $Cr[(OH)_3]$ (Rai *et al*. 1987). Thus, the increased accumulation of Cr (III) in the presence of the MPR and lime is likely to be due to the precipitation of Cr ions to insoluble $Cr[(OH)_3]$.

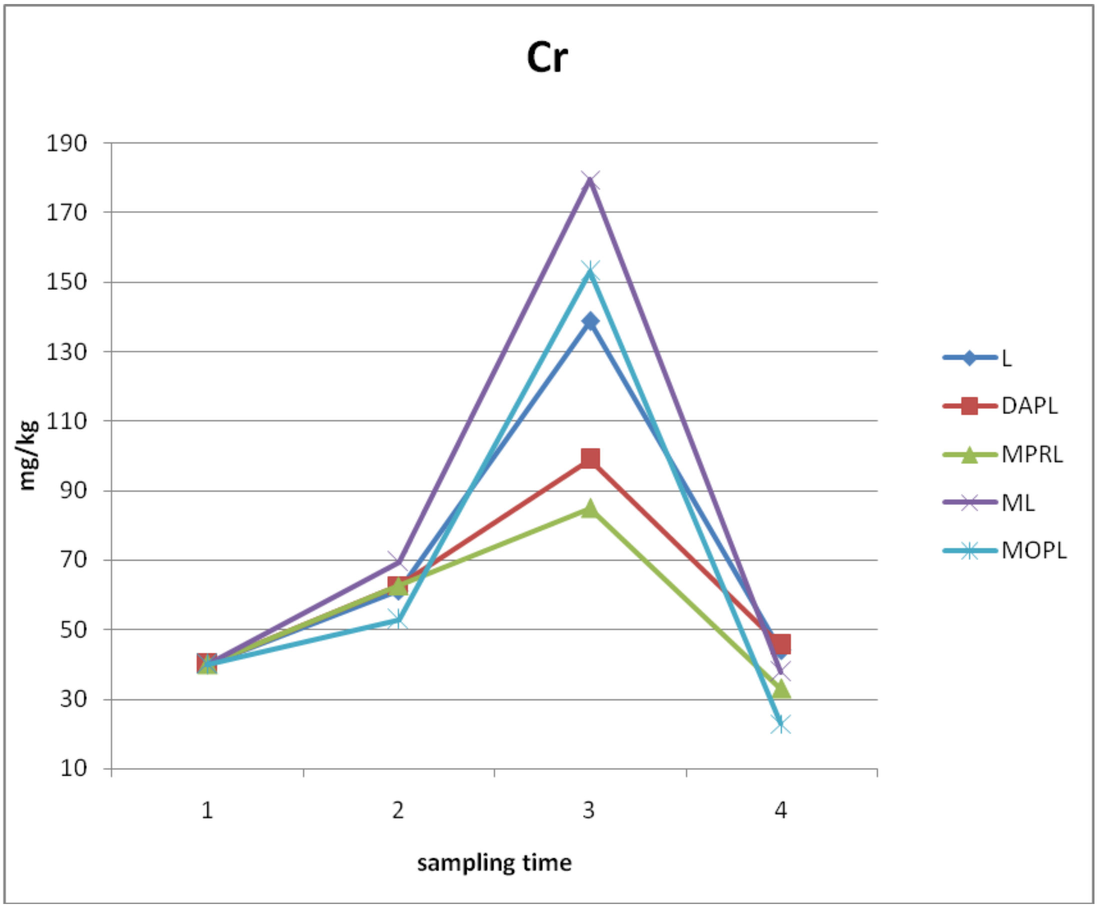


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Figure 11: Trends in concentration of Cr metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

From Figure 12, Pb content in soils was fairly high, between 300 ppm -550 ppm. Application of MPR, DAP, MOP and agricultural grade lime all caused increase in concentration levels. This is supported by the fact that Pb is immobilized using insoluble phosphate compounds. When phosphate rock was applied, phosphate solubilizing bacteria (PSB) facillitate phosphorus solubilization from the rock, immobilizing soil Pb and causing its increase (Jinhee *et al.*, 2010).

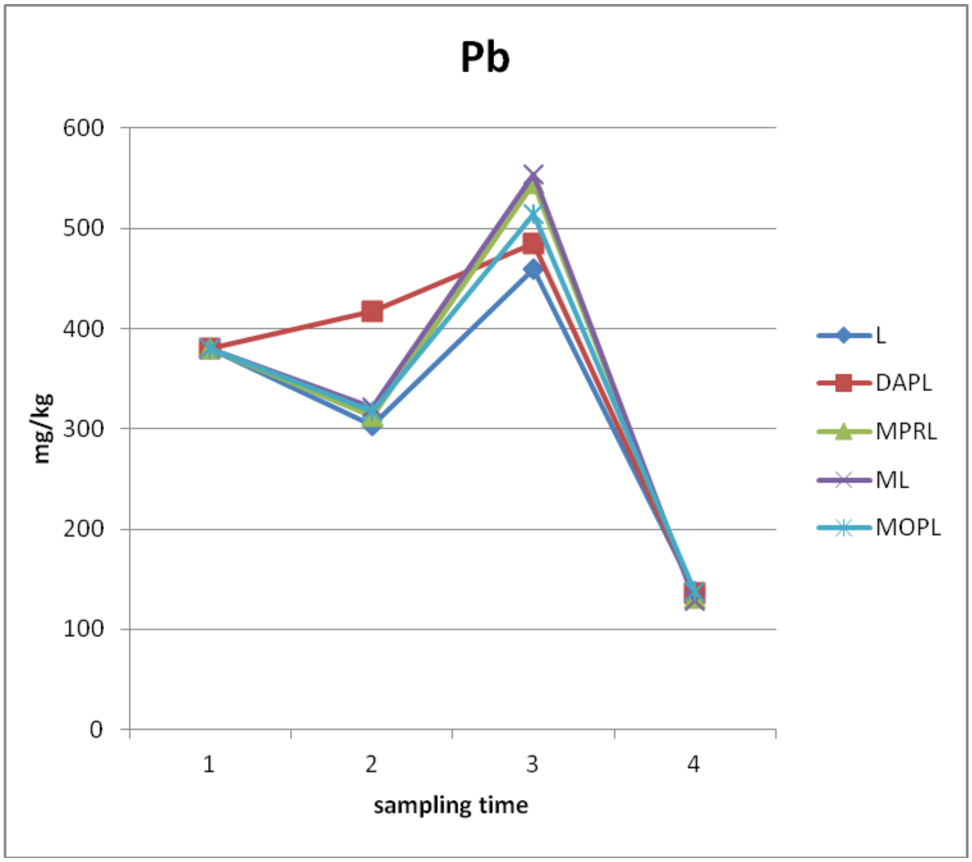

Figure 12: The trends in concentration of Pb metal in soils across the three sampling periods and finally in maize grains. (NB: 1 = Feb, 2 = April, 3 = Oct and 4 = grain samples)

Phosphate minerals have the potential to immobilize Pb^{2+} ions and contaminate soils. They also reduce labile fractions of Pb in soils. Other research findings are in tandem with these research findings. Research has also shown that Pb phosphates, and in particular pyromorphites, are some of the most stable forms of Pb in soils under a wide range of environmental conditions and pH (Nriagu, 1974; Lindsay, 1979). Based on the low phosphate solubility, a number of studies involving the use of phosphates including P fertilizers for the stabilization of Pb in contaminated soils have been carried out (Ma *et al.*, 1995; Cotter-Howells and Capron, 1996; Hettiarachchi *et al.*, 2000; Ryan *et al.*, 2001;

Tang *et al.,* 2004). From the figure, there was low concentration of Pb in maize grain samples (4th samples) implying low uptake of Pb by the maize plant. This could be due to formation of pyromorphites and significant reduction of Pb bioavailability in the soils upon addition of PR or application of phosphatic fertilisers in Pb contaminated soils (Ma *et al.,* 1997; Hettiarachchi *et al*., 2001). Reduced plant uptake of Pb was also observed upon PR or SSP addition to Pb-contaminated soils (Hettiarachchi and Pierzynski, 2002; Xinde *et al*., 2002).

In a research to study the solid- liquid interface reaction between PR and metals (Pb, Cu, and Zn) by Xinde *et al* (2002), results showed PR has the highest affinity for Pb, followed by Cu and Zn. The greatest stability of Pb retention by PR can be attributed to the formation of insoluble fluoropyromorphite [$Pb_{10}(PO_4)_6F_2$], which was primarily responsible for Pb immobilization with less contribution from the surface adsorption or complexation. Solution pH reduction during metal retention and flow calorimetry analysis both supported the hypothesis of retention of Pb, Cu, and Zn by surface adsorption or complexation. This research demonstrated that PR can effectively remove Pb from solutions, even in the presence of other heavy metals (such as Cu, Zn) (Ma *et al.*, 1995). It can therefore be concluded that as expected Pb would accumulate in soils upon application of phosphatic fertilizers and MPR but its bio availability to the maize plant would remain low. The magnitude and trend of values agree well with those reported by Lenart and Koładka (2012) involving the effect of heavy metal concentration and soil pH on the abundance of microbial groups. In that study the levels of Pb were fairly high 128.06 ppm – 686 ppm. In this current research, soil Pb values varied from lowest at

380.0 ppm to highest at 553 ppm yet remaining low in grain samples at 135.0 ppm possibly because the complexes formed were unavailable for absorption by maize.

This study has demonstrated that fertilization and liming can contaminate soils by gradual heavy metal build-up which, when absorbed are capable of making the maize grains and leaves them potentially toxic and harmful to man and livestock if consumed as food. It is worth noting that although the levels are below WHO and FAO limits, there could be a gradual build up in soils. A major inherent problem associated with this bioaccumulation of metals is that although the heavy metals are less bioavailable, as seen from the graphs having very low values in grains, the contaminant concentration in soils remains unchanged. The immobilized heavy metal may become plant-available with time through natural weathering processes.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Studies on contamination of soils by heavy metals due to liming in Uasin Gishu and Trans Nzoia counties revealed that for the concentration of metals under study Pb, Zn, Cr, Mn, Cd and Cu in soil increased when lime was applied. However, comparison of observed levels of heavy metals in the two counties with their corresponding threshold values set by the WHO and FAO (*see appendix table 3)*, illustrates that the heavy metal content of soils and maize grains does not provide grounds for concern about the health of consumers as yet.

Seasonal variation of heavy metal levels in soils did not show any dependency on water content of the soils. There seemed to be a bioaccumulation of metals in soils both during wet and dry seasons after application of fertilizer and liming materials.

The heavy metals under study showed low correlations, with r values close to zero, implying an insignificant relationship for these metals with pH except Cu which showed an almost perfect relationship with pH ($r = 0.770$).

All soil amendment inputs containing CaO (the liming component) increased soil pH at all sampling dates during crop growth across all seasons at all sites.

Metal concentrations in maize grains were very low implying low uptake of metals by the maize tassel, except for Mn. This implies that although there was accumulation of metals in soils, they were not bioavailable for uptake by maize probably because of the chemical form present then.

5.2 Recommendations

Considering the toxic effects of these metals their bio-accumulation in soils need to be checked. It is recommended that a multi metal investigation should be done to determine competition induced inhibition where the bioavailability of a metal in soils affects the presence of another. This study only investigated influence of pH on individual heavy metals only. It is possible that chemical dynamics of one metal could influence bioavailability of another metal.

It is recommended that further research on the effects of growing other food crops in acidic and contaminated tropical soils and monitoring the concentration of the heavy metal pollutants, by-products and heavy metals in the plant tissues be done. This will lead to availability of a reliable database on how such heavy metals affect food safety, grain storage and food security problems in the Rift Valley of Kenya in particular and other African countries at large.

Research on the combined application of lime, wastes and other organic amendments should also be carried out to determine how such amendments could help in the degradation of heavy metal content of lime and fertilizers.

Research should also be done to establish correlations between liming and herbicide activity. There are several herbicide families that are soil pH dependent. For example, low soil pH levels may reduce the activity or residual time of triazine (atrazine) and sulphonylurea herbicides. High soil pH levels (> 6.8) tend to increase herbicide activity that increases the risk of crop injury and/or carry over potential.

Lastly, heavy metal concentrations exceeding the average values for normal soils can be very harmful. This is important particularly in terms of a need to use greater quantities of fertilizers in crops grown on neutral and acid soils, as it is often the case in our country. These variable contents of Pb, Cd, Cu and Mn suggest that fertilizer chemical characterization should be carried out on a regular basis in order to minimize persistent contamination of soils, surface and groundwater and the biosphere in general.

Instead of liming as a remedy to soil acidity, plants which tolerate acidity for example chilies, sweet and Irish potatoes can be used. High biomass plants like maize and pine trees can also be used as a remedy to soil acidity. Animal wastes such as poultry manure is a good substitute to phosphatic rocks. Photo extraction using plants that accumulate high concentration of harmful compounds in their above the ground parts is also useful.

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APPENDICES :1

TABLE 3 a): Recommended Concentration Limits of Metals in foodstuffs.

Metal	Pb	Cd	Cr	Cu	Zn
WHO/FAO recommended values	0.010	0.003	0.050	1.000	5.000

Source: (WHO,FAO Netherlands 1998), KBS,1996

TABLE 3 b): Recommended Concentration Limits of Metals in foodstuffs and Drinking Water

		Allowed max. (ppm) as per Kenya standards		
		Mineral Water	**Drinking Water**	**Cakes as an example of food**
1.1	Manganese	0.5	0.5	-
2.2	Chromium	0.5	0.5	-
3.3	Lead	0.01	0.01	0.5
4.4	Copper (as Cu++)	0.01	1.0	2.0
5.5	Zinc (as Zn++)	5.000	5.000	-
6.6	Cadmium	0.003	0.003	-

Source :(KBS 2012)

TABLE 5: Mean values for Pb concentrations

		1st	2nd	3rd	Maize
FARMER	Trt	1	2	3	4
	L	380.3	303.4	459	137.4
	DAPL	380.3	417.2	485.1	135.6
	MPRL	380.3	312.8	544.3	131.5
	ML	380.3	321.9	553.4	128.6
	MOPL	380.3	317.8	514.7	137.9

TABLE 6: Mean values for Cd concentrations

		1st	2nd	3rd	Maize
FARMER	Trt	1	2	3	4
	L	18.7	28.76	31.1	20.6
	DAPL	18.7	30.72	30.84	19.84
	MPRL	18.7	29.8	33.26	17.02
	ML	18.7	27.56	33.41	21.12
	MOPL	18.7	25.52	34.94	21.38

TABLE 7:Mean values for Cr concentrations

		1st	2nd	3rd	maize
FARMER	Trt	1	2	3	4
	L	40.03	61.14	138.6	44.08
	DAPL	40.03	62.6	98.91	45.45
	MPRL	40.03	62.7	84.92	32.92
	ML	40.03	69.49	179.4	37.71
	MOPL	40.03	52.77	153	22.8

TABLE 8: Mean values for Mn concentrations

		1st	2nd	3rd	Maize
FARMER	Trt	1	2	3	4
	L	578.4	940.4	1094	400.7
	DAPL	578.4	-----	1203	447.7
	MPRL	578.4	1131	1087	461.4
	ML	578.4	1082	1088	636.5
	MOPL	578.4	1165	1158	629.1

TABLE 9: Mean values for Zn concentrations

		1st	2nd	3rd	Maize
FARMER	Trt	1	2	3	4
	L	124.4	274.5	316.3	192.6
	DAPL	124.4	217.7	315.3	415
	MPRL	124.4	250.7	334	157.6
	ML	124.4	266.9	319.9	169.4
	MOPL	124.4	243.8	322	150

TABLE 10: Mean values for Cu concentrations

		1st	2nd	3rd	Maize
FARMER	Trt	1	2	3	4
	L	99.98	80.63	18.58	13.5
	DAPL	99.98	78.18	66.1	13.34
	MPRL	99.98	82.54	65.26	10.63
	ML	99.98	86.54	66.16	12.64
	MOPL	99.98	80.63	80.33	7.71

Appendix II: 2a)Formula used for dilution of stock solution into standard solutions
$C_1V_1 = C_2V_2$

Where; C_1 is initial concentration of analyte

C_2 is final concentration of analyte required.

V_1 is initial volume of analyte

V_2 is final volume of analyte

Appendix 2 b): Formula used to calculate exact concentration of analyte in samples

The actual concentration in parts per million (ppm) from the tabulated results was obtained using the formula below

Concentration (ppm) = $c * v/w * f$

Where v is the final volume of extract in cm^3

W is the weight of the soil sample used in grams and f is the dilution factor

In this case v the final volume of digest was 50 cm^3 and w was 0.3g

Appendix 111: Fertilizer heavy metal analysis summary

The tables 13(a) – () below contain information concerning heavy metals in commonly imported inorganic fertilizers. The information includes sample analysis data for fertilizer samples collected by the Minnesota Department of Agriculture (MDA), heavy metals screening evaluations conducted by the Minnesota Department of Health (MDH), and specific heavy metal product information available from other states.

MAXIMUM LEVELS OF HEAVY METALS IN EACH FERTILIZER INGREDIENT AS FOLLOWS:

Table 13(a) Composition of DAP
Molecular formula: $(NH_4)_2HPO_4$
Molecular weight: 132.0
Standard executed: Q/74465717-9.1-2005(technical grade)
CAS Number: 7783-28-0
Properties:
White granular crystal, relative density at 1.619g/cm^3, melting point at 155 , easily soluble in water, insoluble in alcohol, PH value of 1% solution is 8.0.

Analysis content	**Quality standard（18-46-0）**
$N+P_2O_5$ %≥	≥64%
(NH4)2HPO4	≥98.00%
P2O5	≥53.00%
N	≥21.00%
pH(1% solution)	7.8—8.5
Fluorid (F)	≤0.005%
As	≤0.005%
Heavy metal (Pb)	≤0.005%
Water insolubles	≤0.1%
Moisture	≤0.2%

MONOAMMONIUM PHOSPHATE 12.61.0

	MAP
ARSENIC	3PPM
CADMIUM	1PPM
COBALT	0.5PPM
COPPER	ZERO
LEAD	10PPM
MERCURY	0.5PPM

MOLYBDENUM	0.5PPM
NICKEL	1PPM
SELENIUM	ZERO

DIAMMONIUM PHOSPHATE 21.53.0

	DAP
ARSENIC	3PPM
CADMIUM	1PPM
COBALT	0.5PPM
COPPER	ZERO
LEAD	10PPM
MERCURY	0.5PPM
MOLYBDENUM	0.5PPM
NICKEL	1PPM
SELENIUM	ZERO

Source: TeleChem International, Inc.(2012)