HEAVY METAL CONCENTRATIONS IN SEDIMENTS, SOILS, WATERS AND MOSSES AROUND PAN AFRICAN PAPER MILLS, WEBUYE

BY

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ABSTRACT

Atomic absorption spectroscopic analysis of soils, sediments, water and mosses in the vicinity of Pan African Paper Mills, Webuye, Kenya has revealed the prevalence of the heavy metals Cu, Zn, Cr, Cd, Fe and Pb in the environment. Mean concentrations of Zn ranged between 30.0 and 91.0µg/g in soils and 569.2 and 976.9µg/l in water. Mean Fe concentrations ranged between 2116.6 and 2444.2µg/g in soils, and between 1107.7 and 3170.7µg/l in water. The mean concentrations of Pb and Cd were the lowest, ranging between 0.3 and 93.9µg/g of dry soil. The concentrations of Fe and Zn in the soil samples were higher than the rest of the metals analyzed. The concentrations of these metals varied seasonally with the mean season concentrations of the heavy metals ranging between 2.8 and 2636.3µg/l in the water samples and between 6.89 and 2202.4µg/g of dry weight in the sediment samples. The soils and mosses recorded slightly higher levels of the heavy metals during the dry season. The concentrations of these heavy metals in water samples downstream of River Nzoia are significantly higher than the international water quality guidelines as outlined by USEPA, except for Zn. The data obtained in this work shows that the Pan-African Paper Mill contributes to the impairment of the environment through atmospheric deposition of heavy metal particulates in the vicinity of the factory and effluent discharged into the nearby River Nzoia. This pollution load may play a significant role in the impairment of plant and animal (human) health in vicinity of the factory.

CHAPTER ONE

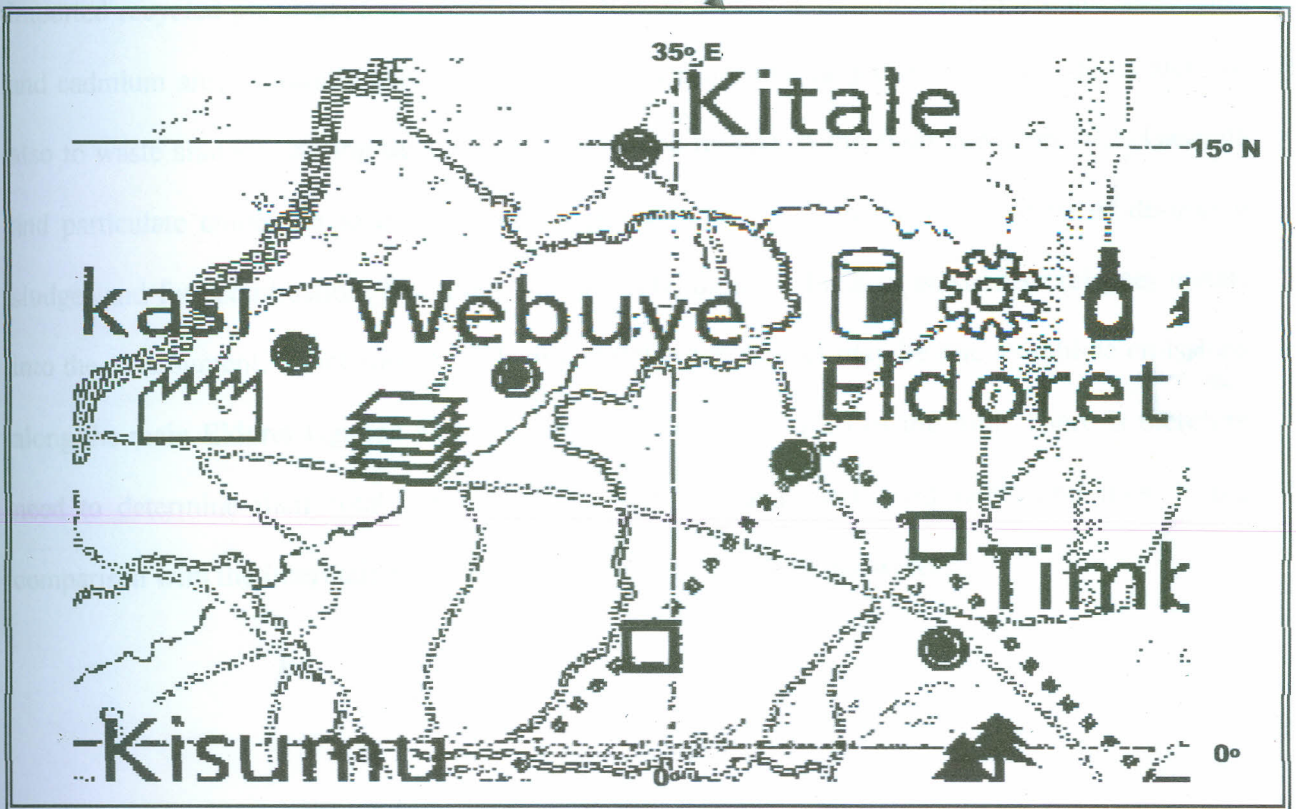# INTRODUCTION

1.1 AREA OF STUDY

Webuye is an industrial town in Bungoma district, in the western province of Kenya. It is located at $0.62°$ N latitude and $34.77°$ E longitude (Fig 2), on the main road to Uganda. The division covers approximately $269.1 km^2$; with a population density of 533 persons per km^2. It has a population of about 143,489 people, which is steadily growing. This population growth is a major challenge especially when viewed against limited resources, like agriculture, in the district. Therefore, industrial development is of necessity, in order to eradicate poverty, which at present stands at 56%. The Webuye division hosts the Pan African Paper Mills, the largest paper industry in the East African region, which offers employment to approximately 1,931 people. The region has a tropical climate, and the heavily populated land around it is used for subsistence agriculture and sugarcane farming.

The Pan African Paper Mill is situated in an environmentally sensitive area on the banks of River Nzoia, which flows into Lake Victoria. The factory belches out smoke and sludge, polluting air, soils and water, in the nearby rivers. According to a survey performed by Oduor *et al.* in 1994, pollution caused by this mill is believed to be responsible for a number of health problems. More than 60% of the children born after 1974, when the plant begun to operate, have had breathing problems from the age of one to five years (Oduor, 1994). Other health problems verified in Webuye region include chronic coughing, flue, nervous disorders, diarrhoea, typhoid and

1

nigraine, which health officials attribute largely to the air and water pollution of the immediate environment of the Paper Mill.

Heavy metals in the Paper industry's recycling mill effluents, direct landfill, incinerator ash disposal and compositing are of great concern. Metals like Cu, Cr, Pb, Zn and Cd are commonly used in printing inks and are discharged not only to waste water, but also to waste sludges and some remain in the paper product (Harland, 1995).

Fig 1: Location of the study area.
(Source: Longman Secondary Atlas)

Pan African Paper mill

1.2   STATEMENT OF THE PROBLEM.

Heavy metals pose a significant problem when the levels exceed the threshold levels. Industrial activities of the Pan African Paper Mill (PAPM) contribute to the high levels of heavy metals deposited in the Webuye region of Western Kenya. The Pan African Paper Mill evidently belches smoke into the air and releases waste sludge into the nearby rivers at the same time. The airborne pollutants eventually get deposited onto soils in the vicinity of these industries and during the rainy season, the runoff washes into River Nzoia, which ends up in Lake Victoria. Water from the nearby rivers is used for drinking by both humans and animals. The gaseous pollutants emitted from the mill are the causes of rusting and other forms of corrosion, which result in metal depositions (Fig 1). Some heavy metals find their way into the vicinity of PAPM through local and imported recycled paper used in the recycling mill. Metals such as copper, chromium, lead, zinc, and cadmium are commonly used in printing inks and are discharged not only to wastewater but also to waste sludges, ending up in the soils as some remain in the final paper product. Gaseous and particulate emissions to the atmosphere primarily come from the incineration of de-inking sludges and fuel combustion. Burning of fossil fuels, biomass fuels or waste also releases metals into the environment. Other sources of heavy metals such as lead may be due to vehicle emissions along the main Eldoret-Uganda highway and at the transport yard of the mill. There is therefore need to determine their total concentration levels in water, soils, sediments and mosses and comparison with the internationally recommended levels in drinking water.

4

Fig 2: Semi aerial view of Pan African Paper Mill and the motor yard from the northern direction (photo taken on 16th February 2007).

1.3 JUSTIFICATION OF THE RESEARCH

Prevalence of heavy metals in the ecosystem often leads to complications in the environmental quality as well as human health. Activities of industries such as the Pan African Paper Mill result in variable quantities of these metals being released into the environment leading to pollution. Information on the status of these heavy metals (lead, cadmium, copper, chromium, iron and zinc) in the regions surrounding PAPM is lacking and the data generated from this study will form a baseline study. Depending on their quantities, the heavy metals could adversely affect the life forms in the region through their toxicity. The research was therefore necessary to assess the levels of these heavy metals in the soils, water, sediments and moss plants in the region in order to ascertain the status of heavy metal pollution in the region. This was to also help identify the pollution load that is dispatched into River Nzoia which pours its water into the great Lake Victoria. Assessment of the contribution of aerial deposition of heavy metal pollution by use of mosses was of great importance. There was also need for heavy metal studies to be carried out on the part of River Nzoia adjacent to the paper mill in order to evaluate the direct effects of the paper mill wastes on the river's resources.

1.4 RESEARCH OBJECTIVES

The objectives of the research were to:

1. Determine the heavy metals (Cu, Zn, Cr, Cd, Fe, Pb) content in the soil, water, sediments and mosses around Pan African Paper Mills, Webuye.

2. Determine concentration profile of heavy metals around Pan African Paper Mills during the wet and dry seasons.

3. Establish the extent of distribution of the heavy metals in the region with reference to the distance and direction from the factory.

4. Evaluate the pollution status of the region using the data obtained and asses the possible impact of the industry on this status.

1.5 HYPOTHESES

This work hypothesizes that:

i. The levels of the heavy metals (Cu, Zn, Cr, Cd, Fe, and Pb) in the part of River Nzoia water adjacent to PAPM are above the internationally recommended levels.

ii. The southern side of Pan African Paper Mills is the most polluted by heavy metals due to runoffs as a result of the terrain.

iii. Zinc and Iron metals are present in higher concentrations in comparison to the other metals.

iv. The extent of the heavy metal distribution depends on proximity to the industry.

v. The Pan African Paper Mill contributes greatly to the heavy metal pollution in the region.

LITERATURE REVIEW

In this chapter we review the literature on sources, uses, effects and distribution of heavy metals (Pb, Cd, Cu, Cr, Zn and Fe) in soils, sediments and water, as well as the use of mosses in monitoring environmental pollution by these metals.

2.1 HEAVY METALS

Heavy metals move to and from a variety of natural and anthropogenic sources. In fluvial environments, however, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products (Dawson and Macklin, 1998). Coal combustion is one of the most important anthropogenic emission sources of trace elements and an important natural source of a number of metals (Wagner and Boman, 2003). Industrial effluents comprise several pollutants, including heavy metals, some of which are extremely toxic (Stumn and Morgan, 1970). Wrong disposal methods of industrial wastes have lead to increased and differential mortality of populations, impairment of reproduction and disruption of species composition and balance (UNESCO, 1972). Pollutants introduced into the environment are distributed in water, sediment and biota. Survey of water, sediment, soil and biota is required in order to determine the concentration of the heavy metal contaminants (Phillips, 1977). Due to non-biodegradability of heavy metals and their long biological half lives for elimination, their accumulation in the food chain have a significant effect on human health in the long term (Alloway, 1990).

Heavy metal contamination of the biosphere has increased sharply since 1900 (Nriagu, 1979). If heavy metals are deposited constantly even in small rates, over long periods of time, they accumulate in the environment and will eventually pose a major environmental and human health hazard in future (Walkenhorst *et al.*, 1993). Thus it seems very important to develop a sequential assessment plan to determine the type and level of heavy metal pollution in our industrialized regions such as Webuye, Kenya. Heavy metal contaminated soils can be a long-term environmental concern and a potential health hazard to land users. This explains why assessment of heavy metal contamination of soils has received much attention in the last few decades. Heavy metal contamination of sediment is also of environmental concern, since heavy metals can be toxic to marine organisms and can bio-accumulate and move up the food chain. Lead, for example, was identified as a major contaminant at about 30% of 546 evaluated Superfund (common name for the United States environmental policy, officially known as CERCLA) sites, while arsenic, cadmium, chromium and zinc were each of concern at about 15% of the sites (Watson *et al.*, 1989).

In aquatic systems, heavy metals are serious pollutants because of their environmental persistence, toxicity and ability to be incorporated into food-chains (Mwamburi and Oloo, 1997). Heavy metals such as cadmium, lead, copper and zinc are pollutants of great concern in aquatic ecosystems because of their toxicity (El Nabawi *et al.*, 1987). Heavy metal salts are readily soluble in water and their ions are stable in solution and therefore tend to exist for extended lengths of time. These metal ions become available to aquatic organisms that accumulate them in their tissues. Subsequently, these heavy metals move up in the food chain when the aquatic organisms are consumed by higher organisms.

Past studies have revealed that human exposure to high concentrations of heavy metals will lead to their accumulation in the fatty tissues of the human body and thus affect the central nervous

system, or the heavy metals may be deposited in the circulatory system and disrupt the normal functioning of the internal organs (Nriagu, 1988). A number of studies have indicated that children exposed to contaminated soils, dust and air particulates may ingest a significant amount of toxic elements through the hand- mouth pathway and through other routes of exposure (Davies *et al.*, 1990)

2.2 ATMOSPHERIC PARTICULATES

A major pathway of soil contamination is through atmospheric deposition of heavy metals from point sources such as industrial activities. Other non point sources of contamination affecting predominantly agricultural soils include inputs such as fertilizers, pesticides, sewage sludge, organic manures and composts (Singh, 2001). Atmospheric deposition of heavy metals in soils and / or vegetables growing in the vicinity of industrial areas has also been investigated (Gzyl, 1995, Voutsa *et al.*, 1996). Soil plays an important role in biogeochemical balance of the biosphere. Degradation of soil leads to a reduction or complete loss of its ecological and productive values. Such degradation is caused primarily by chemical pollution, especially with excessive, unnatural amounts of trace metal elements such as cadmium, lead, zinc, aluminum, chromium and copper, which may disturb the function of the complex system of processes occurring in the soil and cause imbalances and malfunctions in the biological and physical properties of the soil.

Interest in the effects of atmospheric particulates on health has increased in the last ten years on the basis of the evidence that this type of pollution is linked to respiratory illness and death (Dockery and Pope, 1994). Metals adsorbed on ambient particles were recently found to produce tissue damage in the lungs (Dreher *et al.*, 1997).

10

2.3 MOSSES AND ATMOSPHERIC DEPOSITS

In recent times, increasing attention is being paid to plants as passive bioindicators of pollution (Bargagli, 1998) due to elevated costs and technical difficulties associated with common pollution monitoring programs. The use of mosses as bioindicators is one such reliable, versatile and inexpensive method which can assist decision makers on the subject of health and environmental protection against potentially hazardous trace elements. The idea of using mosses to measure atmospheric heavy metal deposition had been developed in the late 1960's by Ruhling and Tyler (Ruhling and Tyler, 1968; Tyler, 1970). Thereafter, heavy metal in mosses survey was established in 1980 as a joint Danish Swedish initiative under the leadership of Aka Ruhling. The idea of using mosses is based on the fact that mosses, especially the carpet forming species, obtain most of their nutrients directly from precipitation and dry-deposition. There's little uptake of metal from the substrate since they lack a root system. Heavy metal deposited from the atmosphere tend to be retained by the mosses at concentrations higher than originally deposited, thereby making sampling and chemical analysis more robust. By 1995 studies had included 29 European countries and 8,000 samples of mosses had been analyzed (Ruhling 1998). The technique of moss analysis provides a surrogate, time-integrated measure of the spatial patterns of heavy metals deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis for metal concentration in mosses. The capacity of the mosses to be used as bio indicators primarily depends on their ability to absorb and fix metallic pollutants as well as their interdependence (Brown and Brumelis, 1996). These plant group species are amenable to bio monitoring because they are widespread, easy to handle and they lack cuticle, vascular and root system, thus reflecting directly on the aerial heavy metal deposition. Their high cation exchange capacity and high surface to volume ratio

favours the accumulation of the large concentrations of heavy metals across the moss cell wall for long periods (Brown, 1982; Tyler, 1990; Sarvidis *et al.*, 1993; Thoni *et al.*, 1996; Markert *et al.*, 1999; Gerdol *et al.*, 2000; Fernandez *et al.*, 2002). Mosses can therefore indicate the presence of elements and their concentration gradients. Their use constitutes an effective method in air pollution monitoring because many species are widely distributed, grow in a range of habitats and are small and easy to handle. Most of them are evergreen and can be surveyed all year round. Since they lack a cuticle and a root system they obtain nutrients as particulates and in solution directly from atmospheric precipitation. Mosses have a good bio accumulating ability, particularly for heavy metals, where metal concentration reflects deposition, without the complication of additional uptake via the root system (Kansanen and Venetraara, 1991). The ability of mosses to accumulate elements in very high concentration aids chemical analysis of the tissues and may facilitate the detection of elements present in very low concentration in the environment. Mosses were therefore found to be the best bioindicators for heavy metals, particularly Zinc (Zn) in a study of biological indicators around the Rautavuukki steel work in northern Finland (Mukherjee and Nuorteva, 1994). The use of the epigeic mosses (mosses growing naturally on the ground) has been recommended in Scandinavia for assessment of heavy metal deposition on a regional scale (Steiness *et al.*, 1994).

2.4 HEAVY METALS IN WATER AND SEDIMENTS

There are many possible sources that contribute to trace metals' presence in the aquatic environment. These include industrial, domestic wastewaters and runoffs from agricultural soils (Nriagu, 1988). Sediments represent an important sink for trace metals in aquatic systems, and metal concentrations in sediment can be several orders of magnitude greater than in overlying water (Luoma *et al.*, 1989). Sediment associated metals pose a direct risk to detrital and deposit

feeding benthic organisms, and may also represent a long term source of contamination to higher trophic levels (Luoma, 1983; Smock, 1983). However, heavy metals appear in riverine sediments in low concentrations, ranging from microgram/kg to milligram/kg (Szefer, 2002).

Many of the dissolved metals that enter rivers are adsorbed onto colloidal particulates. At high alkalinity, the metals, particularly lead and cadmium, precipitate by forming complexation products, resulting in an array of chemical speciation of metals that dramatically influence the metal toxicity (Van Aardt and Booysen, 2004; Van Aardt and Venter, 2004).Therefore, precipitation and sedimentation of cadmium and lead and to a lesser extent copper and zinc in alkaline water bodies could be greater at the inlet where sedimentation processes act as a sink for the metals (Harding and Whitton, 1978). Heavy metals such as lead, copper and zinc are usually deposited in sediments not deeper than 15cm (Santos Bermejo et al., 2003). Remobilization of bound metals due to the acidic environment also leads to leaching of heavy metals into the canals and rivers (Demirak and Balci, 2001).

2.5   LEAD

2.5.1   Sources of Lead

Lead is a useful and widely used material. Therefore most humans are exposed to lead from sources such as old paint, industrial emissions and petrol and lower level sources such as fertilizers and building materials. Lead remains in dusts, soils and sediments for very long periods and accumulates as more lead is released into the environment.

2.5.2   Uses of Lead

English word *plumbing*, referring to the water piping, is derived from the Latin word for lead, *Plumbum*. Lead has been used in water piping in many cultures since ancient times. Examples include pieces recovered from 4th millennium remains in Mesopotamia (Aitchison, 1960; Nriagu,

1983). Lead has also been widely used for joining masonry, by pouring molten lead into the joints themselves, or around iron or bronze clamps for extra strength (Nriagu, 1983). Many compounds of lead are strongly coloured and durable. Red and yellow oxides of lead were used for purposes of decoration. Galena (lead sulphide) has been widely used as black eye paint in many ancient Middle Eastern cultures, which was believed to treat eye diseases. (Nriagu, 1983). In medicine lead found application in dentistry and was used in fillings in Europe up to the 17th century. Organic lead additives, tetraethyl and tetra methyl lead were added into petrol to enhance octane rating, prevent knocking and lubricate engine valves. This was to provide the grade of petrol needed for the efficient operation of internal combustion engines of high compression ratio. Due to international pressure, lead additives in petrol have been phased out. Use of leaded fuel in cars has been on its declining trend, especially in the developed countries particularly in the northern hemisphere and this marked a drop in the overall atmospheric lead levels as was witnessed from measurement of marine aerosols (Stokinger, 1981; Kersten et al., 1994).In Kenya, this phasing out of lead in petrol started in December, 1995.

2.5.3   Effects of lead

Lead can cross the placenta, accumulate in the foetus and has disadvantageous effects on ionic transmission, alter the functional amniotic membrane and compete with Magnesium and Zinc ions, which are essential elements in living organisms (Semczuk and Semczuk-Sikora, 2001). Zinc levels of the organism determine lead absorption and toxicity (Miller, et al., 1989; Boscolo et al., 1992). Lead causes changes that may be more serious in the foetus as they affect young structures, intensively developing, with no well-formed defense mechanisms. In humans, the gastrointestinal absorption of lead after chronic exposure also exerts a wide number of adverse biological effects during lactation and more so in adult life (Bogden, et al., 1992), since neonates absorb 40-50 times more lead than adults. Lead interferes with heme synthesis as well as altering Zn-dependent

14

enzyme function (Gupta, *et al.*, 1997). The effects of lead on adult rat testis have been widely studied and observations demonstrate that Pb in particular alters the functions of those organs (McGivern, *et al.*, 1991), as evidenced by testicular necrosis and atrophy in rodents. In men, especially in professional workers, lead exposure results in infertility and sterility (Cullen, *et al.*, 1984), testicular atrophy, cellular degeneration, and reductions in seminiferous tubule diameter (STD) and sperm count, depending on the dose and time of exposure (Chowdhury, *et al.*, 1986; Rodamilans, *et al.*, 1988; Foster, *et al.*, 1993; Singh, *et al.*, 1993). . Lead affects almost every organ and system in the body, particularly the central nervous system. It can enter the body through uptake of food (65 %), water (20 %) and air (15 %). Lead can cause several unwanted effects such as; disruption of the biosynthesis of haemoglobin, a rise in blood pressure, kidney damage, miscarriages and abortions, disruption of the nervous system, brain damage and decline in fertility in men through sperm damage (Joachim and Felistas, 2000).

The Kenya Bureau of Standards (KEBS) (1996) requires that lead content in drinking water should not exceed 0.05 ppm. In the United States of America, the national primary drinking water standard for maximum content of lead is put at 0.05 ppm (USEPA, 1979). A safe guideline value of 0.01 ppm of lead in drinking water has been given by WHO (1998). Allowable maximum limits for lead in drinking water in the UK, EU and USA are 0.05 ppm, 0.01 ppm and 0.015 ppm respectively (Neubauer and Wolf, 2004).

2.6   CADMIUM

2.6.1   Sources and exposure

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). All soils and rocks, including coal and mineral fertilizers, contain some

15

cadmium. The general population is exposed to cadmium from breathing cigarette smoke or eating cadmium contaminated foods, air or water. It is known to accumulate in kidneys and its concentration increases with the age of an animal (Frape, 2004). Cadmium is a heavy metal widely spread in the biosphere. It most often occurs in small quantities associated with zinc ores, such as sphalerite (ZnS). Almost all cadmium is obtained as a by- product in the treatment of zinc, copper, and lead ores. Soil acidification increases the absorption of cadmium in the crops (Anderson, 1992). In the general population, the main exposure routes are food and cigarette smoking (Friberg et al., 1986; Vahter et al., 1991). One cigarette contains about 1-2µg of cadmium and an average of about 10% is inhaled during smoking (Elinder et al., 1983). After inhalation, 10- 40% of cadmium may be absorbed, in contrast to less than 10% from ingestion (WHO, 1992). In Sweden, the blood cadmium concentrations in smokers are four to five times higher than in non smokers, while kidney cadmium concentrations are about two- three times higher than in non smokers (Vahter, 1992).

2.6.2   Uses of cadmium

Cadmium is a component of some of the lowest melting alloys and is therefore used in bearing alloys with low coefficients of friction and great resistance to fatigue. It is extensively used in electroplating, which accounts for about 60% of its use. It is used in many types of solder, for standard EMF cells, for Ni- Cd batteries and as a barrier to control nuclear fission. Cd compounds are used in black and white TV phosphors and in blue and green phosphors for colour TV tubes. Cadmium forms a number of salts, of which the sulphate is most common and the sulphide is used as a yellow pigment.

2.6.3 Effects of Cadmium

Cadmium (Cd) is ubiquitous in the human environment and has been recognized as one of the most deleterious heavy metal pollutants (Robards et al., 1991; Christine, 1997). It has no biochemical or nutritional function, but is highly toxic to both plants and animals (USPHS, 1997; WHO, 1992; Alloway, 1990). In humans and animals there is strong evidence that the kidney is the main target organ of cadmium toxicity, following extended exposure (USPHS, 1997; Elinder and Jarup, 1996; Goyer, 1996; WHO, 1992). After exposure, Cd is distributed mainly to the liver and kidneys and it accumulates with metallothionein (MT). MT is a small metal-binding protein that is characterized by its high thiol content, one of its 61 amino acids being cysteine. In addition to these toxic effects it has also been suggested that Cd may play a role in the development of hypertension (high blood pressure) and heart disease (USPHS, 1997; Goyer, 1996; Elinder and Jarup, 1996). Cadmium in urine is known to give a good estimation of the body burden, whereas Cd in blood mainly reflects more recent exposure (Jarup et al., 1998). Regarding plant toxicity, adverse effects on plant growth and yield have been reported. Alloway (1990) reported stunted growth and toxic signs on leaves of lettuce, cabbage, carrot and radish plants (which resulted from a Cd content of around 20mg/kg in the upper parts of the plants). Cadmium easily moves from soil to food plants through root absorption and accumulates in their tissues (Oliver, 1997). In this way, Cd may enter the food chain and affect the human health (Adriano, 1986). Other studies have shown reduction in the rate of photosynthesis and transpiration (WHO, 1992). In the aquatic life, some species of phytoplankton are very sensitive to cadmium, with inhibition of growth, observed at concentrations as low as 1µg/l (Bryan and Langston, 1992). Reductions in reproductive rates and population numbers in copepods and isopods have been shown at concentrations as low as 5 µg/l, and exposure to similar levels has resulted in changes in the immune function in some fish, and depressed growth in juvenile fish and invertebrates (Thuvander, 1989). Fish exposed to high

concentration of Cd^{2+} quickly develop lack of Calcium and low blood haemoglobin. Cd^{2+} has multiple cytotoxic and metabolic effects such as interfering with normal actions of essential metals (Chmielnicka, et al., 1996) including oxidative stress (Casalino, et al., 1997) and altering the activities of various enzymes (Bagchi, et al., 2000; Patra, et al., 1999). Among many heavy metals polluting the soils, Cd is of great concern because of its potentially harmful effects not only on humans and animals, but also has the most adverse effects on microbial biomass. It also plays an important role in the biological cycles of almost all the major plant nutrients cycling, soil nutrient cycling and in maintaining soil fertility (Smith, 1996; Jose et al., 2002; Yao et al., 2000). Microorganisms may suffer growth inhibition at Cadmium concentrations of 0.25 mg/l (Roberts, 2003). Other long-term effects are lung damage and fragile bones. When exposed to Cd^{2+} in food or water, animals develop high blood pressure, iron-deficient blood, liver disease, and nerve or brain damage. Studies on animals also have indicated that more cadmium is absorbed into the body if the diet is low in calcium, protein, or iron, or is high in fat. A few studies show that younger animals absorb more cadmium and are more likely to lose bone and bone strength than adults. Cadmium can be analyzed by AA flame spectroscopy (detection limits 5 µg / l) or with graphite furnace procedures (detection limits 0.1 µg / l).

2.7   COPPER

2.7.1   Sources of Copper

Copper is a naturally occurring metal that exists by itself as an element or in combination with other elements in various minerals and compounds. It is commercially available in the form of sheets, wires, tubings and powder (merck index, 1983). Copper is introduced into the environment from natural sources (about $4.0x10^8$ kg per year) and as a result of human activity (about $4.5x10^9$

kg per year). It is accumulated in the soil, especially in the soil's surface layers, and can be washed into water bodies.

2.7.2 Uses of Copper

Copper is one of the essential elements for humans; the adult human requires about 2.0mg per day. It is both vital and toxic in many biological systems depending on its concentration (Greenwood *et al.*, 1984). Thus the determination of trace amounts of copper is becoming increasingly important because of the increased interest in environmental pollution (Yamin *et al.,* 1999). Most copper that is refined in the United States is used in copper wires and rods. Other uses of copper and its compounds are highly varied as shown in these examples compiled from the Copper Development Association and International Copper Association (CDA, 2002; CDA. 2003; ICA, 2004).

- Plumbing pipes
- Heat exchangers and radiators
- Industrial catalysts and electrodes
- Jewellery and other decorations
- Utensils such as pots and pans
- Coins
- Fertilizer
- Coating in cathode ray tubes
- Animal feed additives and dietary supplements
- Roofs, gutters and other architectural works
- Motor vehicle components like bearings, bushes, gears and wires.
- Pesticides (algaecides, fungicides, bactericides and wood preservatives)
- Batteries (as an electrolyte or contaminant; an ingredient in alkaline batteries)

Copper is one of the relatively small groups of metallic elements that are essential to human health. It influences life support functions like production of red blood cells and carbohydrate synthesis (Malmstron, 1979) and is involved in the absorption, storage and metabolism of iron.

2.7.3 Copper Deficiency

Copper deficiency in humans results in a number of complications, which include:

- Iron deficiency anaemia
- Bone and joint problems
- Frequent infections
- Fatigue and weakness
- Difficulty in breathing and irregular heart beat
- Skin sores
- Loss of hair and skin colour, among others.

Menkes' disease, a copper deficiency disease, is a disorder in the metabolism whereby there exists an inability to absorb copper (USEPA, 1980).

In plants, copper deficiency results in dieback of stems and twigs, yellowing of leaves, stunted growth and pale green leaves that wither easily. Copper uptake by plants decreases as soil pH increases and also due to increased availability of iron and phosphorus.

2.7.4 Copper Toxicity

Copper toxicity is a problem of both agricultural and environmental significance. Sources of copper contamination include mining and smelting, industrial and agricultural wastes as well as the use of agrochemicals. Copper is present in many forms in soils, with free Cu^{2+} activity considered to be the best indicator of bio availability (Sauve *et al.*, 1996). Adsorption of Copper to organic matter is highly pH dependent and bioavailability of Cu increases with decreasing pH. Due to its

20

high affinity for organic matter, copper is not readily leached from the soil profile and tends to accumulate in the surface soil (McBride *et al.*, 1997). While Copper is an essential micronutrient, exposure to excess Cu has a detrimental effect on both animal and plant growth. In plants the effect of Cu^{2+} toxicity is largely on root growth and morphology. Copper tends to accumulate in the root tissue with little being translocated to the shoots (Marschner, 1995). The effect of Copper toxicity on root morphology is similar to that of Aluminum toxicity (Hecht-Buchholz *et al.*, 1990; Marschner, 1995). In humans, the toxic effects of high tissue levels of copper are seen in patients with Wilson's disease, a genetic disorder characterized by copper accumulation in various organs due to the inadequate synthesis of ceruloplasmin (a protein that transports copper through the blood) by the liver (Strausak *et al.*, 2001). Wilson's disease primarily affects the liver, kidneys and brain causing degenerative physiological changes (including cirrhosis of the liver) that are fatal if untreated.

2.8   CHROMIUM

2.8.1   Sources of Chromium

Chromium (III) occurs naturally as a trace compound of most crude oils and the concentration of chromium found on residual and distillate oils have been measured. Available information suggests that the chromium is emitted in the trivalent state from oil combustion, sewer sludge incineration, cement production or works, municipal waste incinerators and refractories (ARB, 1986). Chromium (III) has also been detected, but not quantified in motor vehicle exhaust by the Air Resources Board (ARB, 1995). Chromium emissions can occur for chromium (VI) firebrick lining of glass furnaces (ARB, 1986). Lead chromate, CrO_4Pb, is the pigment in the yellow paint used to mark traffic lanes. In addition, hexavalent chromium in water solution is converted through electroplating to the bright metallic chromium coating seen on plastic or metal products such as

showerheads or car bumpers. The primary stationary sources that have reported emissions of chromium (III) compounds in California are lumber and wood products manufactures, stone, clay production and petroleum refining. Reported sources also include electrical services, aircraft and parts manufacturing and steam and air conditioning supply services (ARB, 1997). Cigarettes also contain a certain amount of chromium (III) although the intake of chromium from smoking is not known (ARB, 1986). Chromium (III) is found in most fresh foods and drinking water. Dietary sources rich in chromium (III) include whole meal bread, cereals, spices, fresh vegetables, meats and fish. Other significant sources of chromium (III) are mineral supplements, brewer's yeast and beer.

2.8.2 Uses of Chromium

Chromium is used for corrosion resistance, steel production and as a protective coating for automobile and equipment accessories. It is a permanent and stable inorganic pigment used for paints, rubber and plastic products as well as wood treatment in the chemical industry (Howard, 1990). Smaller amounts are used in water treatment catalysts and corrosion inhibitors. Chromium (III) is an essential trace element and a daily intake of 50 to 200µg per day is recommended for normal glucose, protein and fat metabolism. It potentates insulin for normal glucose metabolism. The body can reduce Cr (VI) to Cr (III) and this process leads to increased levels of chromium (III) (US EPA, 1994).

2.8.3 Effects of Chromium

Chromium and its compounds were the major contributors to the overall cancer risk in one of the approximated 550 risk assessments done (OEHHA, 1996). The principal acute effects of Chromium (VI) exposure are renal toxicity, gastrointestinal haemorrhage and intravascular haemolysis. In occupational settings, the most commonly reported chronic effects of chromium exposure include contact dermatitis, skin ulcers, irritation and ulceration of the nasal mucosa and

perforation of the nasal septum (NIOSH, 1975). The toxicological targets considered for chronic toxicity are the respiratory tract, kidney, gastrointestinal system and the liver (CAPCOA, 1993).

Scanty human studies suggest that occupational chromium exposure may be associated with complications during pregnancy and childbirth. Chromium (VI) has been reported to cause adverse development effects in orally exposed mice including decreased litter size, decreased foetal weight and decreased foetal ossification. In males, testicular pathology has been reported with oral or injection exposure and dominant lethal effects have been reported with injection exposure (U. S. EPA, 1994; ATSDR, 1993). There is epidemiological evidence that exposure to inhaled chromium may result in lung cancer. The US EPA has classified Chromium (VI) as a human carcinogen with an estimated potency value of $1.2 \times 10^{-2} \mu g/m^3$.

2.9   IRON

2.9.1   Sources of Iron

Iron is found in virtually every food, with higher concentrations in animal tissues than in plant tissues (Hammond and Beliles, 1980). Some drinking waters are high in iron, for instance, about 140μg of iron comes from average United States drinking waters per day (Snyder et $al.$, 1975). All forms of steel are composed mainly of iron with less than 2% carbon and other elements such as manganese, nickel, chromium, tungsten and vanadium. Rusting of iron (Evans and Leigh, 1979) occurs due to the formation of a hydrated oxide of iron [Fe (OH)$_3$] or FeO (OH). In moist and acidic air, iron rusts rapidly. The hydrous oxide gives no protection as it flakes off exposing fresh metal surfaces leading to extensive corrosion and therefore iron deposition in the environment.

2.9.2   Uses of Iron

Iron is a trace element which is needed by the body for the formation of blood. The human body normally contains between 4.2g- 4.5g of iron (Stokinger, 1981; Snyder et $al.$, 1975), more than

half of which is in the form of haemoglobin, the red pigment in blood responsible for oxygen transport from lungs to tissues. Iron has the tendency to take up oxygen readily changing its colour to red (Kapoor, 2003). This is the basis for its function in the blood, where it is the carrier of oxygen to the tissues of the body. Although many other substances besides iron are necessary to synthesize red blood cells, iron deficiency is one of the most common causes of anemia. Iron contributes significantly to the development of the brain (Agarwal, 1990).

Symptoms associated with abnormalities in mental behavior and reduced intellectual performance has been observed in iron deficient animals and children (Pollit, 1989; Prasad and Oberleas, 1976). They include apathy, irritability, and lack of concentration, low scores in school and reduced assimilation and learning capacity (Lozoff et al, 1991). Significant correlations have been found between iron levels and IQ. Although these abnormalities may have multifactor causes, iron plays an important role in changes in some neurotransmitters in the brain and brain development (Lattunde, 2000). Iron is definitely established as an essential micronutrient, required by all plants and animals. Most enzymes, the liver, as well as the muscle protein myoglobin contains iron. Iron exists in different ionic states and can therefore serve as a co-factor to enzymes involved in oxidation-reduction reactions (Da Silver and Williams, 1991).

2.9.3   Effects of Iron

Iron overload is an insidious toxicity which turns into chronic toxicity that may progressively damage patients' vital organs, causing significant morbidity, and ultimately threatening their survival (Olivieri and Brittenham, 1997; Porter, 2001). Excessive iron may induce the formation of insoluble iron-phosphates, which interfere with the normal absorption of phosphorus and lead to rickets in the animal. Controlling excess iron has been shown to reduce injury to vital organs, improve quality of life and extend lives of patients (Brittenham et al., 1994).

The Kenya Bureau of Standards requires that the concentration of Fe in safe drinking water should not exceed 0.3ppm (KEBS, 1996). In drinking water, these levels stain laundry and sanitary ware (WHO, 1998). The recommended daily allowance is 10mg for men and 18mg for women (Stokinger, 1981).

2.10 ZINC

2.10.1 Sources of Zinc

Ores containing Zn are widespread geologically and geographically. Abundance of zinc in the earth crust is approximately 132ppm. Zinc may also be made available in the atmosphere from galvanized surfaces, in which case there is a likelihood of galvanized iron corroding and flakes of zinc oxide peeling off and being deposited on the ground surface and finally into water bodies. Dietary sources include meat, whole grain bread, peas and beans as well as sea foods (URL, 1999).

2.10.2 Uses of Zinc

The largest use of zinc is as a protective coating for iron, a process known as galvanizing. This is carried out by dipping carefully cleaned iron or steel in molten zinc, which gives the rather thick, robust coating required. It gives excellent protection against weather and moisture. In human health, zinc is vital for many biological functions such as disease resistance, wound healing, digestion, reproduction, physical growth, diabetes control, taste and smell (Eastwood, 2003). It is a cofactor in DNA and protein synthesis and cell division- every cell in the human body requires zinc to multiply and more than 300 enzymes need zinc for proper functioning. Zinc supplements are recommended as adjunct therapy during the treatment of diarrhoea in children (Bahl *et al.,* 2001). These supplements, given during acute or persistence diarrhoea reduce the severity and duration of diarrhoea (Bhutta *et al.,* 1999).

2.10.3 Zinc Deficiency

The World Health Organization's report (2002) estimated that one-third (33%) of the world's population is at risk of inadequate zinc intakes. The effects of zinc deficiency may be severe, ranging from impaired neuropsychological functions, growth retardation and stunting, impaired reproduction, immune disorders, dermatitis, impaired wound healing, lethargy, loss of appetite and loss of hair, among others (Diaz-Gomez *et al.*, 2003).

2.10.4 Effects of excess Zinc

Zinc appears to be rather non-poisonous, though in large quantities it is carcinogenic. It is considered to be an inorganic element of potential risk to animals mainly the bovine species (Marcal *et al.*, 1999). Zinc toxicity is dependant on the form of Zinc; greater than 0.1% dietary Zn as lactate or carbonate is toxic and greater than 0.5% Zinc as ZnO is toxic. Zinc Sulphate is a gastrointestinal irritant and the fatal dose has been estimated as 10-30g (Murphy, 1970). Ingestion of excess $ZnSO_4$ may induce reversible anaemia and leucopoenia, transient irritability, tremor and seizures. These neurological features occurred in a premature infant inadvertently given excess Zinc Sulphate supplements (Tasic *et al.*, 1982). Ruminants are more susceptible to Zinc intoxication than monogastic animals (Venugopal *et al.*, 1979). Zn induced hemolytic anaemia and internal hemorrhage has been reported in dogs that consumed pennies containing high levels of Zinc alloys since 1983 (Ogden *et al.*, 1988; Latimer *et al.*, 1989).

CHAPTER THREE

METHODOLOGY

3.1 SAMPLING

Moss, soil, water and sediment samples were collected from twelve sites, three sites radiant in every direction from the PAPM as the epicenter. Sampling was conducted in two seasons- wet (October, 2006) and dry (February, 2007). For mosses, each sampling point was situated 3m away from the nearest trees, without pronounced influence from canopy drip from trees, preferably on the ground or on the level surface of decaying stumps (Ruhling, 1994). Water and sediment samples were collected at the upstream, factory discharge point and downstream part of River Nzoia. A composite sample of the moss, sediment, soil and water was made from each sampling point, collected within a distance of 100 m, 500 m and 1000 m from the industrial plant. Samples were collected in triplicates at every sampling point. Plastic gloves or a plastic bag over hand was used when picking up the moss, surface soil and surface sediment samples (Ruhling, 1989). The triplicate samples were placed in plastic or polythene bags and carefully closed to prevent contamination during transportation. The bags were labeled with information on monitoring areas, sampling site and date of collection and transported to the laboratory for pretreatment and analysis. Randomized complete block sampling design was used. The initial moss data set was a matrix with rows and columns, where the rows corresponded to the sampling site and the columns to the six

27

heavy metal concentrations recorded in the moss samples. In this case, S_1, S_2 and S_3 represented the three different radii, 100 m, 500 m and 1 km from the Pan Paper Plant and triplicates were taken from every sampling point. $S_{1,1}$, $S_{1,2}$, $S_{1,3}$, are the triplicates sampled at 100m distance, and so on.
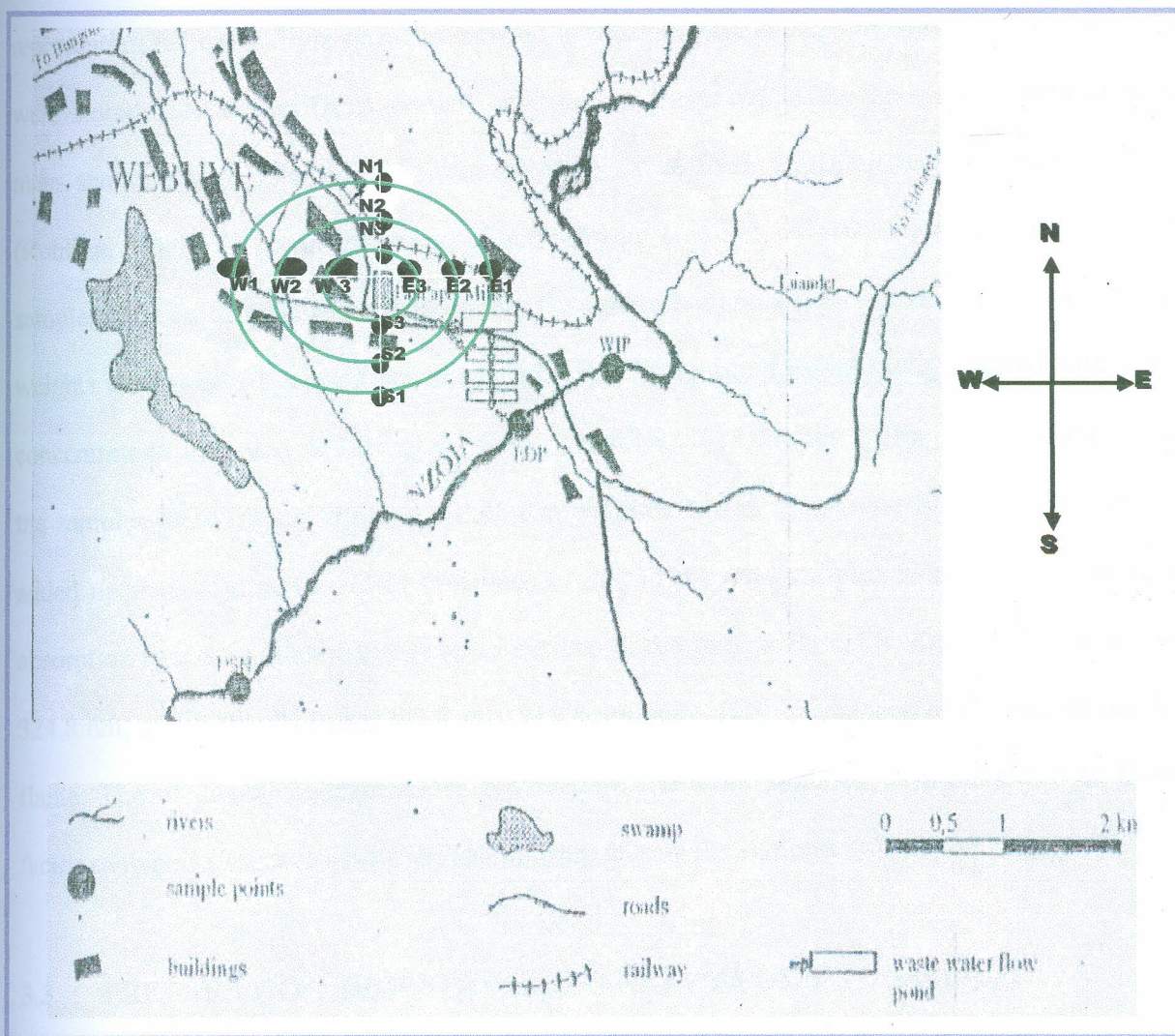

Fig 3: Sampling sites. (Source: Bungoma District DDP 1989- 1993).

28

Foreign materials adhering to the surface of the moss samples such as tree bark, lichens, soil, dust and detritus were removed carefully in dry condition. The Greenish-brown part of the moss plant representing the last 2-3 yrs growth was used in this analysis. If cleaning was delayed, the samples were stored deep frozen (refrigerated) until further treatment. After the cleaning procedure, the moss samples were dried at 40^0 C for 48 hours in an oven until constant weight was attained (Ruhling, 1989). In some instances, if such drying was not possible soon after collection, the samples were air dried at room temperature for a period of about four weeks. Samples of 1.0 g (dry weight) were crushed using a pestle and a mortar. The ground sample was digested with 6 ml of concentrated nitric acid at 120^0 C for 6 hours (Miller, 1998). After cooling at room temperature, the samples were filtered through a 0.45 μm polyethersulfon membrane filter and distilled water added up to a volume of 50 ml (Steinnes *et al.*, 1994). The samples were analyzed by atomic absorption spectrophotometry for concentrations of the trace metals, Cu, Zn, Pb, Cr, Cd and Fe at 324.8 nm, 213.9 nm, 217 nm, 357.9 nm, 228.8 nm and 248.3 nm respectively, using an air- C_2H_2 flame. The elemental concentrations recorded in the moss samples were subjected to Q-mode factor analysis in order to assess the relationship among the samples (Norusis, 1990).

3.3 PREPARATION, DIGESTION AND ANALYSIS OF SOIL SAMPLES.

Soil samples were air-dried, mechanically ground and sieved through a filter with a mesh to obtain < 2 mm fraction. A 20-30 g-sub sample was drawn for the bulk soil (< 2 mm fraction), and reground to obtain < 200 μm fraction using a mortar and a pestle. This fine material was then sieved through a 45 μm sieve and exactly 1.0 g weighed and transferred into a digestion tube. 20

ml of concentrated nitric acid was then added to each sample and placed in a digester heated to a temperature ranging from 130^0 C to 140^0 C, for 3 hrs until all the brown fumes of nitrogen dioxide gas were completely expelled, according to the US EPA method 3050B (US EPA, 1996). The solutions were cooled to room temperature. The digests were sieved using Whatman no. 1 filter paper into 50 ml volumetric flasks and made up to volume using deionized water (Loring et al., 1990; McCarthy et al., 1991). Heavy metals (copper, zinc, chromium, cadmium iron and lead) in the digests were then determined using Atomic Absorption Spectrophotometer (AAS), with appropriate standards prepared in a similar matrix.

3.4   PREPARATION, DIGESTION AND ANALYSIS OF SEDIMENT SAMPLES

The sediment samples were placed in separate and clean polyethylene containers carefully labelled and pre-weighed. The label contained the sample identification number, date and location of sampling. Tools and containers for sediment sample handling prior to the sampling were washed by soaking for 2-3 days in diluted (10%) HNO_3, then rinsed with high purity water and stored dust-free. The sediment samples (1 g) were wet sieved through a 63 µm nylon sieve (Smedes et al., 2000). This was followed by drying the wet sediment at 100 ^{0}C for 24 hrs. The dried samples were protected from cross-contamination (particles and vapours) by covering with a lid with a small hole covered with a filter paper over the sample container. Method of digestion was similar to the one used for the soils as outlined in section 3.3. Instrumental determination was also carried out as in the soils, and standard stock solutions were used for calibration purposes. All standard solutions were stored in polyethylene volumetric flasks.

3.5   PREPARATION, DIGESTION AND ANALYSIS OF WATER SAMPLES

The procedure adopted by Mzimela *et al* (2003) for total metal extraction was followed. A water sample measuring 50 ml was filtered through a 1 μm cellulose acetate filter (Millipore) into an acid-washed 100 ml beaker and placed on a hot plate (60 °C) for 1 hr to concentrate it to 20 ml. The water sample was placed in a Pyrex digester tube and digested using concentrated nitric acid (10 ml) at 120 °C for 2 hrs. The digested sample was transferred to a 50 ml volumetric flask and made up to volume with double-distilled water. The concentrations of Cu, Zn, Cr, Cd, Fe, Pb and Zn were then determined using an Atomic Absorption Spectrophotometer at the specified wavelengths.

3.6   AAS ANALYSIS

A Shimadzu AA-6300 model of an Atomic absorption spectrophotometer was used to determine the levels of the listed heavy metals in water, soils, sediments and mosses (Table 1). For each metal, analytical grade reagents, i.e., $Pb(NO_3)_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $Zn(NO_3)_2$ $K_2Cr_4O_7$ and $Fe(NO_3)_2 \cdot 4H_2O$ were used to prepare 1000 ppm stock solutions. Working standard solutions of concentrations 1, 2, 3, 4, 5 and 6 ppm were prepared by diluting respective stock solutions of the metals using the equation: $C_oV_o = C_1V_1$ Where V_o is the initial volume (ml) required in order to make C_1, C_o is the concentration of the metal (ppm) in the stock solution, C_1 is the metal concentration (ppm) required in V_1 and V_1 is the volume (ml) as determined by the volumetric flask. The corresponding absorbance for each concentration were read from the AAS instrument and used to draw standard curve for each metal. The concentrations of the metals in the

unknown samples were then read from these curves, and calculations made to obtain the metal

concentrations in the samples.

The elements were determined at the wavelengths and spectrophotometer set-ups shown below:

Table 1: AAS set up

Element	Wavelength(nm)	Slit(nm)	Flame type
Copper	324.8	0.7	Air- C_2H_2
Zinc	213.9	0.7	Air- C_2H_2
Chromium	357.9	0.7	Air- C_2H_2
Cadmium	228.8	0.7	Air- C_2H_2
Iron	248.3	0.7	Air- C_2H_2
Lead	217.0	0.7	Air- C_2H_2

3.7 STATISTICAL ANALYSIS OF RESULTS

The initial data was arranged in a matrix of rows and columns, where the rows corresponded to the

sampling site and the columns to the six heavy metal concentrations recorded in the

moss, soil water and sediment samples. Samples were analyzed in triplicates and means presented.

The results were subjected to MSTAT- C package of statistical analysis. Results for water and

sediments were analyzed using a Two Factorial design with sections as the main treatments and

seasons as the sub-treatments, while those of soils and sediments were subjected to a Three

Factorial design. ANOVA tables extracted to evaluate significance differences as well as

interactions and relevant bar graphs drawn using MS- Excel.

32

RESULTS AND DISCUSSION

4.1 HEAVY METAL CONCENTRATIONS AROUND PAN AFRICAN PAPER MILLS

4.1.1 Soils

Table 2 summarises the total measured mean metal levels in soil samples at the different sites in $\mu g/g$. The results indicate that there was a significance difference in the concentrations of all the metals in the different directions of the industry ($P \leq 0.05$), with LSD values ranging between 1.7 (Cd) and 82.8 (Fe).

It is evident from table 2 that copper and cadmium are evenly concentrated on all sides of the industry, with the southern side and the eastern side having slightly higher concentrations. Zinc is more concentrated on the western, southern and the eastern side and is slightly in higher amounts compared to the rest of the metals except Iron. This is may be due to remobilization of Zinc and high rate of corrosion of galvanized iron as a result of the acidic environment around the industry (Oduor, 1994). Cadmium and Lead have relatively very low concentrations in comparison with all the other metals especially in the eastern and northern directions (fig 4a&4b) because of lesser activity on the northern side and limited use of leaded fuel at the motor yard. Iron (Fe) had the highest concentration of the heavy metals (Table 2). The abundance trend of these heavy metals in the soils was thus Fe>Zn>Cr>Cu>Pb>Cd which shows that rusting due to the high acidity in the environment surrounding Pan African Paper Mills probably plays a very major role in the bioaccumulation of Fe and Zn in the soils.

Item	Seasons	Direction South	West	East	North	Mean seasons
Cu (µg/g)	Wet	31.6	27.8	28.8	29.9	29.5
	Dry	33.0	30.4	36.2	29.5	32.3
	Mean Direction	32.3	29.1	32.5	29.7	
	CV%			6.4		
	LSD,P≤0.05			2.1		5.9
	Interaction			2.9		
Zn (µg/g)	Wet	56.3	74.9	90.6	45.6	66.9
	Dry	65.8	37.4	67.2	36.1	51.6
	Mean Direction	61.1	56.1	78.9	40.8	
	CV%			7.3		
	LSD,P≤0.05			4.6		12.9
	Interaction			6.5		
Cr (µg/g)	Wet	37.3	35.1	35.5	31.3	34.8
	Dry	45.2	31.1	46.4	36.5	39.8
	Mean Direction	41.2	33.1	41.00	33.9	
	CV%			8.9		
	LSD,P≤0.05			3.5		10
	Interaction			5.0		
Cd (µg/g)	Wet	14.4	13.5	15.1	13.3	14.1
	Dry	14.6	15.0	13.1	15.0	14.4
	Mean Direction	14.5	14.3	14.1	14.1	
	CV%			11.1		
	LSD,P≤0.05			1.7		4.8
	Interaction			2.4		
Fe (µg/g)	Wet	2256.4	2269.5	2270.4	2143.2	2234.9
	Dry	2275.7	2281.1	2264.1	2252.7	2268.4
	Mean Direction	2266.0	2273.3	2267.3	2198.0	
	CV%			3.5		
	LSD,P≤0.05			82.8		234
	Interaction			117.1		
Pb (µg/g)	Wet	0.2	19.7	13.7	5.1	9.7
	Dry	62.6	39.8	1.4	1.4	26.3
	Mean Direction	31.4	29.8	7.5	3.3	
	CV%			24.8		
	LSD,P≤0.05			4.7		13.4
	Interaction			6.7		

However comparison using bar graphs (Fig 4b) shows higher concentrations of Pb on the western side, and higher concentrations of Zn on the eastern side. However, Cu, Cr and Cd had varied

34

concentrations on either side of the industry. Wind carries along with it dust particles, vehicular emissions, incineration and industrial particulates, which continuously add to the pool of heavy metal contaminants in the environment (Harrison *et al.*, 1981).
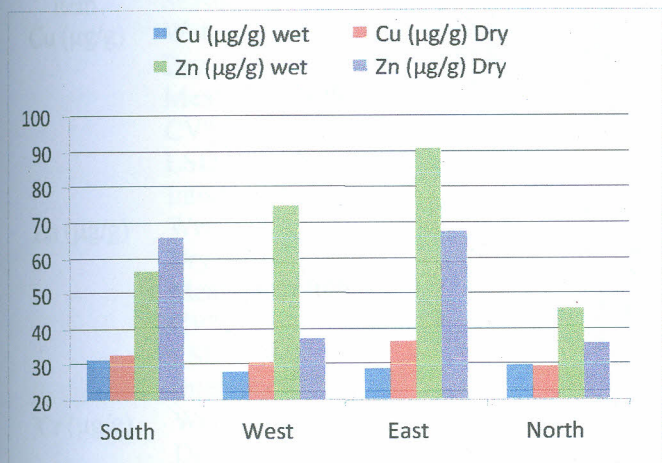

Fig 4 (a): Concentration of Cu& Zn (μg/g) in soil around PAPM in two seasons due to direction.
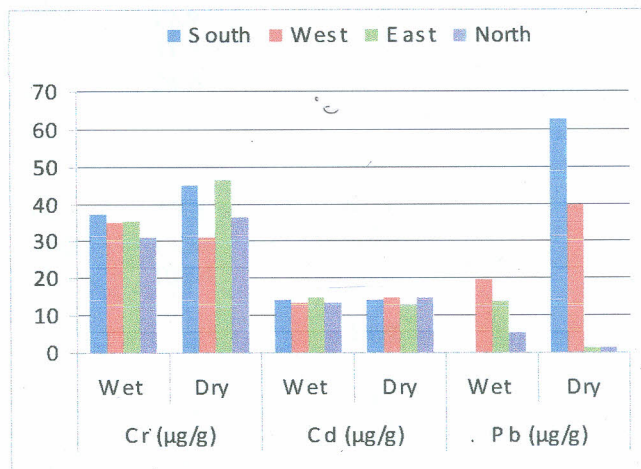
Fig 4 (b): Concentration of heavy Cr, Cd&Pb (μg/g) in soil around PAPM in two seasons due to direction.

Sources of these metals include, and are not limited to, old paints which are washed off by rain and find their way to soils around the industry. Most of these metals have a very high affinity for organic matter and tend to accumulate in surface soils (McBride *et al.*, 1997). Anthropogenic activities of the industry, through aerial and effluent discharge, therefore contribute to the high concentration of these metals in the soils in the study area.

4.1.2 Mosses

Table 3 gives a summary of the metal loads in the moss plants on the four directions of the industry. The concentration of each metal varied significantly in the different compass directions of the industry.

Table 3: Concentration of heavy metals (µg/g) in moss samples around PAPM in two seasons due to direction.

Item	Seasons	South	West	East	North	Mean seasons
Cu (µg/g)	Wet	38.4	22.7	26.5	17.9	26.3
	Dry	30.8	38.4	30.3	31.7	32.8
	Mean Direction	34.6	30.5	28.4	24.8	
	CV%		5.8			
	LSD,P≤0.05		2.1			5.1
	Interaction		3.0			
Zn (µg/g)	Wet	101.3	64.4	46.0	57.5	67.3
	Dry	152.0	175.2	97.0	153.2	144.4
	Mean Direction	126.7	119.8	71.5	105.4	
	CV%		3.9			
	LSD,P≤0.05		5.1			14.9
	Interaction		7.2			
Cr (µg/g)	Wet	20.2	19.2	27.3	13.5	20.1
	Dry	43.2	32.7	49.9	49.8	43.9
	Mean Direction	31.7	25.9	38.6	31.6	
	CV%		6.6			
	LSD,P≤0.05		6.1			6.3
	Interaction		3.7			
Cd (µg/g)	Wet	15.7	15.4	13.7	13.3	14.5
	Dry	15.1	14.7	14.8	16.2	15.2
	Mean Direction	15.4	15.1	14.2	14.8	
	CV%		8.6			
	LSD,P≤0.05		NS			3.8
	Interaction		2.2			
Fe (µg/g)	Wet	2111.6	2084.9	2164.3	1831.0	2047.8
	Dry	2046.3	2178.6	2072.2	1985.1	2070.5
	Mean Direction	2079.0	2131.7	2118.2	1908.0	
	CV%		2.7			
	LSD,P≤0.05		69.6			NS
	Interaction		98.4			
Pb (µg/g)	Wet	1.0	15.0	14.0	3.0	8.2
	Dry	21.3	42.7	0.0	0.0	16.0
	Mean Direction	11.1	28.9	7.0	1.5	
	CV%		11.3			
	LSD,P≤0.05		1.7			4.1
	Interaction		2.4			

Concentrations of all the investigated metals except Cd varied significantly at the different compass directions of the industry. LSD values were 2.1, 5.1, 6.1, 69.6, and 1.7 for Cu, Zn, Cr, Fe and Pb respectively ($P \leq 0.05$). There were also significant interractions between the sites in all the metals, which indicates that the contamination due to the metals is not similar.

The presence of heavy metals in mosses around Pan African Paper Mills is mainly attributed to

atmospheric deposition which indicates that the environment surrounding the paper mill has significantly very high concentrations of the investigated heavy metals. Industrial activities (anthropogenic) at the Pan Paper mill, which include welding, incineration of the de-inking sludge that scatter metallic particulates or dust into the atmosphere add to the concentration of heavy metals in the air.

Burning of fossil fuels, biomass fuels or waste also releases metals oxides which then enter the atmosphere (Ruhling, A., 1998). At the Pan African Paper Mill, fuel oil is used on a very large scale to run the boilers, whereas diesel and petrol are used to run the engines. Studies have shown that residual fuel oils, since they are composed of the less volatile matter of the crude oil, are richer in metals (Reid, 1973).
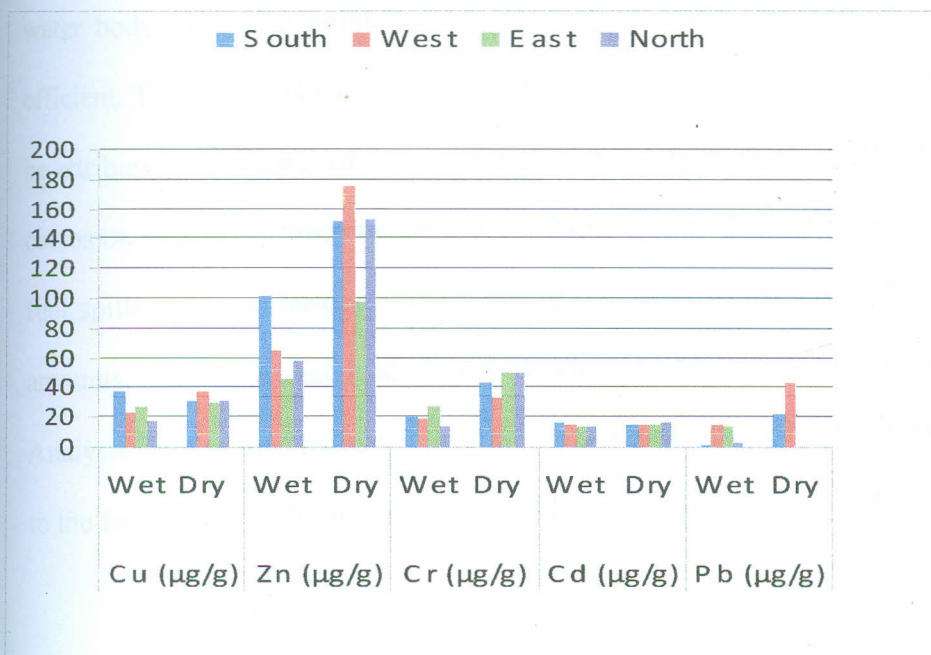

Fig 5: Concentration of heavy metals (µg/g) in moss samples around PAPM in the different directions.

Data representation through bar graphs (Fig 5) clearly shows Zn is in very high concentrations, followed by Cu and Cr, which may result from existence of these metals in gaseous forms that are

easily absorbed by the mosses. The south and western parts of the industry exhibited higher loads of Cu, Zn and Cd. Some of these particulates are adsorbed on the substrates where the mosses grow and may be absorbed directly. Some of the metal loads, such as Cu, Pb, Zn and Cd are commonly used in printing inks and are usually discharged through gaseous and particulate emissions as a result of the incineration of de-inking sludges and fuel combustion.

4.1.3 Water

Mean concentrations of the total heavy metals in the part of River Nzoia adjacent to the Paper Mill were determined and have been presented in Table 8. Clearly, the discharge point samples of the river exhibits high amounts of the metals than the upstream and the downstream samples, an indication that the effluents from the industry have a role to play in the heavy metal load in the water body. It is also points to the fact that the waste treatment in the treatment ponds is not efficient. The high concentrations of Fe in the water samples at the discharge point of the river can be attributed to presence of large amounts of scrap metal at the factory grounds, as well as the high corrosion rate of the machine parts in the Mill. The other metals may be resulting from old paints, fuel spills, fuel combustion and de-inking processes at the Mill. However Pb is in very limited amounts, indicating that lead contamination may be due to sources other than the Paper Mill. Analysis Of Variance indicated that there was significant difference between the different sites due to the fact that the pollution factors around the industry influenced the chosen sites differently.

	Cu	Zn	Cr	Cd	Fe	Pb
This study (mean)[a]	300.2	779.1	373.1	303.3	2230.6	4.35
Min – max	138.8-425.8	569.2-976.9	255.5-467.5	151.2-408.2	1107.7-3170.7	0.0 -13.4
Water quality criteria[b]						
CMC	13	120	16	4.3		65
CCC	9	120	11	2.2		2.5

[a] Number of examined samples = 36, min- max =minimum – maximum levels, Nd – not determined.

[b] US EPA (1999).

The metal pollution status of the part of River Nzoia adjacent to the industry is presented in Table 4. The table is generated by comparing measured concentrations of the heavy metals with water quality standards as outlined by US EPA, 1999. In this comparison, the mean concentrations of Cu, Zn, Cr, Cd and Fe (except Pb) are much higher than the criteria maximum concentration (CMC) and the criteria continuous concentration (CCC) values of the US EPA water quality criteria. However, the concentrations of Pb are within the limits of water quality standards as set by US EPA (1999).

4.1.4 Sediments

Table 5: Concentration of heavy metals (µg/g) in sediments along river Nzoia in two seasons due to the course of the river.

Item	Seasons	Upstream	Section Discharge	Downstream	Mean seasons
Cu (µg/g)	Wet	17.7	49.2	35.7	34.2
	Dry	14.8	32.8	28.35	25.3
	Mean section	16.2	40.9	32.1	
	CV%		10.2		
	LSD,P≤0.05		7.6		18.24
	Interaction		10.7		
Zn (µg/g)	Wet	39.8	79.7	66.2	61.9
	Dry	16.2	46.9	27.7	30.27
	Mean section	27.9	63.3	47.0	
	CV%		8.5		
	LSD,P≤0.05		9.8		23.5
	Interaction		13.8		
Cr (µg/g)	Wet	17.5	48.3	39.7	38.2
	Dry	15.6	38.9	31.6	28.7
	Mean section	16.6	43.6	35.7	
	CV%		7.2		
	LSD,P≤0.05		5.7		13.7
	Interaction		NS		
Cd (µg/g)	Wet	12.3	24.8	22.0	17.7
	Dry	10.2	22.0	17.3	17.4
	Mean section	11.3	23.4	19.7	
	CV%		6.5		
	LSD,P≤0.05		2.9		6.9
	Interaction		NS		
Fe (µg/g)	Wet	1990.5	2415.3	2201.4	2202.4
	Dry	1801.3	2230.1	1947.9	1993.1
	Mean section	1895.9	2322.7	2074.7	
	CV%		2.2		
	LSD,P≤0.05		114.9		399.4
	Interaction		NS		
Pb (µg/g)	Wet	0.4	89.4	1.8	30.6
	Dry	19.9	103.0	89.2	70.7
	Mean section	10.15	96.2	45.5	
	CV%		14.2		
	LSD,P≤0.05		17.9		43.1
	Interaction		25.3		

Table 5 shows the levels of metals in the sediments along River Nzoia (which feeds the Paper Mill with water) at different sampling sites. The concentration of all the metals is highest at the discharge point. Compared to the concentration of the metals in the sediments taken upstream, all the samples downstream showed elevated concentration of the metals; the concentration of lead downstream increased nearly five-fold, chromium and copper increased two-fold, Fe, Zn and Cd by 10, 68 and 74% respectively.

These results indicate outright that the PAPM feeds into river Nzoia effluent carrying these metals. The concentration of these metals are highest at the discharge point and decrease with distance, showing that some of the waste water from the industry carries along these metals from the activities at the plant. Heavy metal pollution in the sediments is mainly influenced by discharge from the industry, as shown by the concentrations at the discharge point. The metallic wastes in the water body apparently gets adsorbed onto particulates while some are deposited on the river bed and may constantly be in equilibrium with the river water thereby steadily polluting the river water. This confirms that the water treatment procedure used at the treatment ponds does not fully eliminate the adsorbed metals. The metallic wastes therefore end up in the water body. Humans and other aquatic life are then exposed to these toxic metals through drinking and fish consumption (fish obtain their food from sediments thereby ingesting the heavy metals). There is clear indication from statistical analysis that the metal loads at the different sediment sites are significantly different.
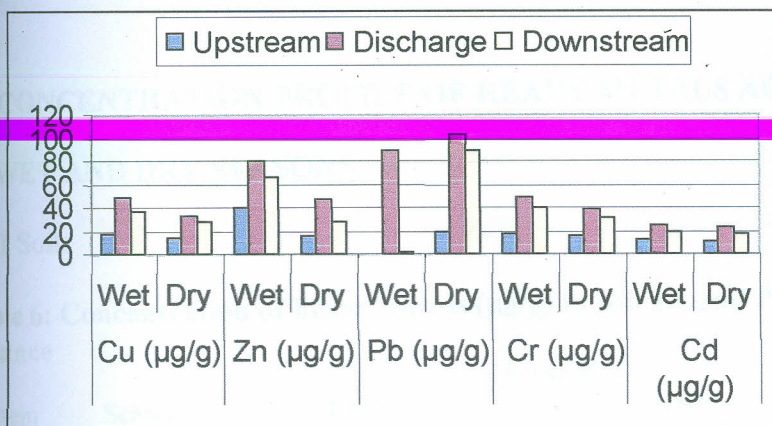
Fig 6: **Metal concentrations in sediments along part of R. Nzoia (adjacent to the industry)**

A representation of the concentrations of the heavy metals in the sediments is shown by the bar graphs in Fig 6 above. The concentration trend is such that Pb>Zn>Cu>Cr>Cd. Earlier discussion on water indicated that the Pb concentrations were relatively very low in the water and therefore their higher loads in sediments shows that Pb settles to the bottom sediments and very little is left suspended in water.

4.2.1 Soils

Table 6: Concentration of heavy metals (µg/g) in soil around PAPM in two seasons due to distance

Item	Seasons	Distance(m) 100m	500m	1Km	Mean seasons
	Wet	25.5	27.4	35.7	29.5
	Dry	27.7	32.5	36.6	32.3
	Mean Distance	26.6	30.0	36.1	
Cu (µg/g)	CV%		6.4		
	LSD,P≤0.05		2.4		5.9
	Interaction		3.5		
	Wet	66.8	61.7	72.1	66.9
	Dry	44.7	46.9	63.2	51.6
	Mean Distance	55.8	54.3	67.6	
Zn (µg/g)	CV%		7.3		
	LSD,P≤0.05		5.4		12.9
	Interaction		7.6		
	Wet	24.0	34.0	46.4	34.8
	Dry	34.6	36.9	48.0	39.8
	Mean Distance	29.3	35.5	47.2	
Cr (µg/g)	CV%		9.0		
	LSD,P≤0.05		4.1		10
	Interaction		5.9		
	Wet	14.1	14.1	14.0	14.1
	Dry	14.3	13.8	15.1	14.4
	Mean Distance	14.2	14.0	14.5	
Cd (µg/g)	CV%		11.0		
	LSD,P≤0.05		2.0		4.8
	Interaction		2.8		
	Wet	2131.0	2211.7	2361.9	2234.9
	Dry	2165.7	2234.1	2405.3	2268.4
	Mean Distance	2148.4	2222.9	2267.3	
Fe (µg/g)	CV%		3.0		
	LSD,P≤0.05		97		234
	Interaction		137		
	Wet	15.7	6.1	7.3	9.7
	Dry	75.0	2.5	1.4	26.3
	Mean Distance	45.4	4.3	4.3	
Pb (µg/g)	CV%		25		
	LSD,P≤0.05		5.5		13.4
	Interaction		7.8		

Table 6 shows the mean concentrations of the heavy metals in soils in different seasons in μg/g of dry weight. Generally, the metal concentrations were higher during the dry season as compared to the wet season except for Zn (Fig 7a&7b). Table 5 also shows that the concentrations of all the metals in the soils increase, except Pb, as one move away from the factory.
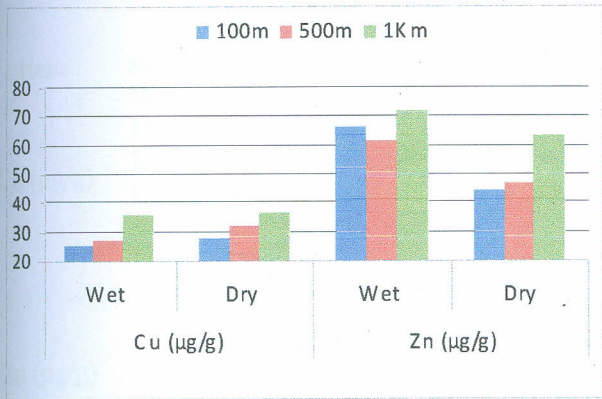

Fig 7 (a): Concentration of Cu&Zn (μg/g) in soil around PAPM in two seasons due to distance.

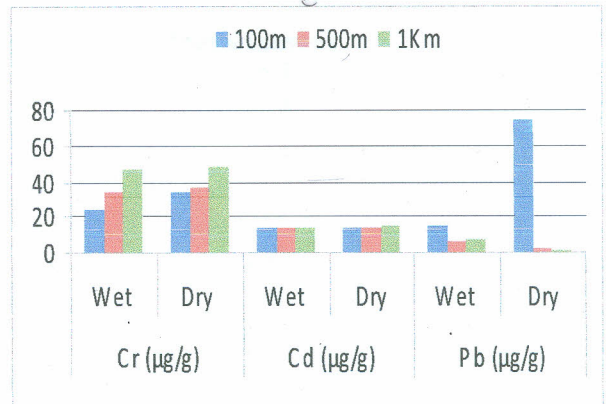Fig 7 (b): Concentration of Cr,Cd,Pb (μg/g) in soil around PAPM in two seasons due to distance.

This could be attributed to leaching of the metals deeper into the ground and run offs that may have washed them down to the water bodies. Analysis Of Variance (appendix 1) shows that the concentrations of all the metals were significantly difference between the seasons ($p < 0.05$), with LSD values ranging between 2.0 (for Cd) and 97.0 (for Fe).

During the wet season more of the heavy metals in surface soils were washed away in runoffs into water bodies and some seeped deeper into the ground. It is evident that the top soils collected at 0-15cm had little of these metals due to the runoffs, deeper seepage and due to the dilution effect of the rainy season. Webuye area consists of a gently sloping erosional surface falling from 2100m elevation in the north east to 1200m elevation in the south west (DDP, 1989-1993). The dry season did not experience runoffs or seepage. This explains the high concentrations of Fe, Cu, Cr and Pb in soils during the dry season and the wet season being marked by lower concentrations.

4.2.2 Mosses

Table 7: Concentration of heavy metals (µg/g) in moss samples around PAPM in two seasons due to distance.

Item	Seasons	100m	500m	1Km	Mean seasons
Cu (µg/g)	Wet	20.6	26.4	32.0	26.3
	Dry	41.0	29.1	28.3	32.8
	Mean Distance	30.8	27.7	30.2	
	CV%		5.8		
	LSD,P≤0.05		2.1		5.1
	Interaction		3.0		
Zn (µg/g)	Wet	44.9	68.8	88.2	67.3
	Dry	176.3	127.1	129.7	144.4
	Mean Distance	110.6	98.0	108.9	
	CV%		3.9		
	LSD,P≤0.05		5.1		14.9
	Interaction		7.2		
Cr (µg/g)	Wet	9.6	20.9	29.6	20.1
	Dry	48.8	42.9	39.9	43.9
	Mean Distance	29.2	31.9	34.8	
	CV%		6.6		
	LSD,P≤0.05		6.1		6.3
	Interaction		3.7		
Cd (µg/g)	Wet	14.0	14.4	15.1	14.5
	Dry	16.2	15.2	14.2	15.2
	Mean Distance	15.1	14.8	14.7	
	CV%		8.6		
	LSD,P≤0.05		NS		3.8
	Interaction		2.2		
Fe (µg/g)	Wet	1813.6	2124.8	2205.5	2047.8
	Dry	2193.7	2052.3	1965.6	2070.5
	Mean Distance	2003.6	2088.5	2085.5	
	CV%		2.7		
	LSD,P≤0.05		69.6		NS
	Interaction		98.4		
Pb (µg/g)	Wet	6.1.	9.2	9.4	8.2
	Dry	23.4	14.1	10.5	16.0
	Mean Distance	14.7	11.7	9.9	
	CV%		11.3		
	LSD,P≤0.05		1.7		4.1
	Interaction		2.4		

Table 7 compares the mean concentrations of the heavy metals in mosses in different seasons and

results presented in µg/g of dry weight. All metal concentrations were higher in the wet season

than the dry season, which shows that they were absorbed by the mosses mainly from deposition from the atmosphere.
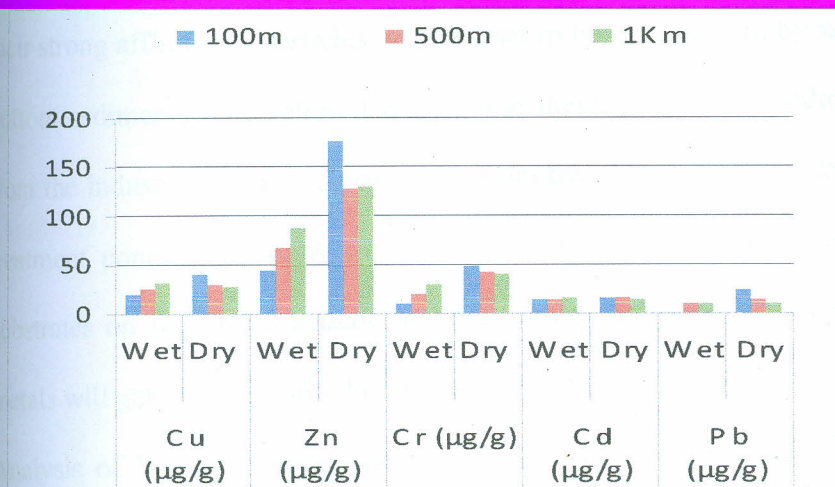

Fig 8: Concentration of heavy metals (μg/g) in moss samples around PAPM in two seasons due to distance.

Higher concentrations of Zn Cr and Pb were clearly recorded for mosses during the dry season but less clearly for Cu. These results confirm the hypothesis that the concentrations of these metals are higher in mosses during the dry season. This indicates that these metal ions are more available in the atmospheric environment during the dry season. Mosses obtain their nutrients directly from precipitation and dry deposition as they lack a root system and this is the likely reason for the higher concentrations during the dry period. The high loads of the metals in the mosses in this season shows that the contamination levels of the metals in the atmospheric environment increase during this season.

4.2.3 Sediments

Mean concentrations of heavy metals in river sediments in the different seasons are presented in Table 5. It is clear that the dry season showed lower amounts of the metals confirming the hypothesis that the metal loads in sediments are higher during the wet season.

Sediments along River Nzoia recorded higher metal concentrations during the wet season. Due to their strong affinity for particles, metals tend to be accumulated by suspended matter or trapped by bottom sediments (Dauvalter, 1998). These metals may be in sediment through direct discharge from the industrial activity or run- offs from the sludge disposal sites, which get their way to the treatment ponds and finally to the river at the discharge point. Since sediments are the main substrates on which the aquatic animals obtain their food, it is likely that most of these heavy metals will get their way into humans through the food chain.

Analysis of Variance (appendix 3), showed that there was significance difference between the seasons for Cu (LSD=7.6; $P \leq 0.05$), Zn (LSD=9.8; $P \leq 0.05$), Cr (LSD=5.7; $P \leq 0.05$), Cd (LSD=2.9; $P \leq 0.05$), Fe (LSD=114.9; $P \leq 0.05$) and Pb (LSD=17.9; $P \leq 0.05$). However, this shows that the region around the Paper mill is more polluted with heavy metal load during the wet season.

4.2.4   Water

Table 8 compares the mean concentrations of the heavy metals in water samples in the wet and dry seasons. Except for Cu, the concentrations of the heavy metals- Zn, Cr, Cd, Pb and Fe are higher during the wet season compared to the dry season. During the wet season most of the heavy metals are easily dissolved and are washed to the water bodies through run offs.

Table 8: Concentration of heavy metals (µg/g) in water along river Nzoia in two seasons due to the course of the river.

Item	Seasons	Upstream	Discharge	Downstream	Mean seasons
Cu (µg/g)	Wet	138.8	289.9	253.8	227.5
	Dry	293.7	425.8	399.2	372.9
	Mean section	216.3	357.9	326.5	
	CV%		1.46		
	LSD,P≤0.05		10.9		32.2
	Interaction		15.4		
Zn (µg/g)	Wet	569.2	976.9	923.6	823.2
	Dry	599.1	852.2	753.5	734.9
	Mean section	584.1	914.5	838.6	
	CV%		2.8		
	LSD,P≤0.05		54.4		131.1
	Interaction		76.9		
Cr (µg/g)	Wet	255.5	467.5	402.8	375.3
	Dry	290.2	440.6	381.5	370.8
	Mean section	272.9	454.1	392.2	
	CV%		3.3		
	LSD,P≤0.05		30.9		NS
	Interaction		43.7		
Cd (µg/g)	Wet	313.9	408.2	325.8	349.3
	Dry	151.2	315.2	305.5	257.3
	Mean section	232.6	361.7	315.6	
	CV%		7.7		
	LSD,P≤0.05		57.8		139.4
	Interaction		81.8		
Fe (µg/g)	Wet	1932.0	3170.7	2806.3	2636.3
	Dry	1107.7	2403.4	1963.4	1824.8
	Mean section	1519.9	2787.1	2384.8	
	CV%		3.8		
	LSD,P≤0.05		210.1		1482.7
	Interaction		NS		
Pb (µg/g)	Wet	0.0	13.4	4.2	5.9
	Dry	8.5	0.02	0.0	2.8
	Mean section	4.2	6.7	2.1	
	CV%		137.3		
	LSD,P≤0.05		NS		NS
	Interaction		NS		

Copper's concentration varied significantly between the seasons and between the different sites of the river course (LSD = 10.9, P≤ 0.05).
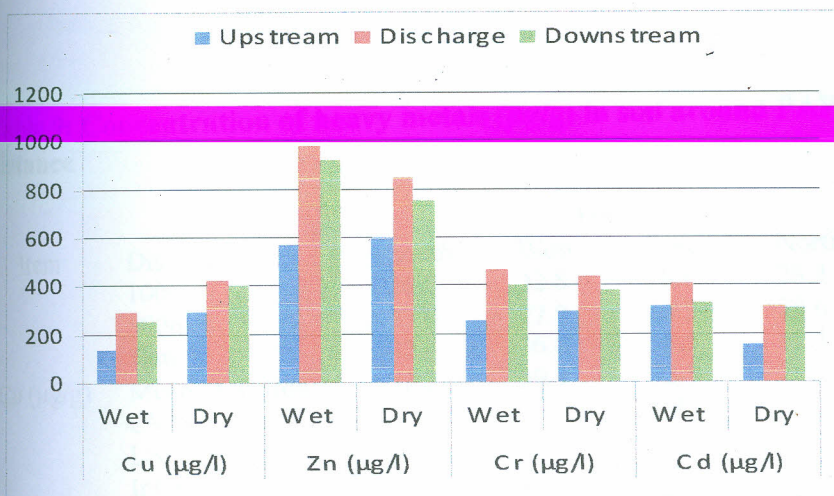
Fig 9: Concentration of heavy metals (µg/g) in water along river Nzoia.

The bar graph (Fig 9) shows that the concentrations of heavy metals in waters along the river were different in the two seasons. Similarly, statistical analysis denotes significant differences in all the metal concentrations in the seasons (Table 8).

4.3 DISTRIBUTION OF HEAVY METALS BY PROXIMITY TO PAN AFRICAN PAPER MILL.

The concentrations of the metals by proximity to the industry in the soil and moss samples were determined and statistical analysis done.

4.3.1 SOILS

The concentrations of all the metals in the soils varied significantly at various distances from the industry (Table 9). This indicates that their distribution is highly dependent on the proximity to the industry.

Table 9: Concentration of heavy metals (µg/g) in soil around PAPM due to direction and distance

Item	Distance	Direction				Mean Distance
		South	West	East	North	
	100m	26.5	22.8	28.6	28.4	26.6
	500m	33.0	27.9	30.5	28.6	30.0
	1km	37.4	36.6	38.3	32.1	36.1
Cu (µg/g)	Mean Direction	32.3	29.1	32.5	29.7	
	CV%			6.4		
	LSD,P≤0.05			2.1		2.4
	Interaction			2.8		
	100m	49.2	75.4	68.4	30.0	55.8
	500m	53.8	46.8	77.3	39.4	54.3
	1km	80.2	46.3	91.0	53.0	67.6
Zn (µg/g)	Mean Direction	61.1	56.1	79.0	40.8	
	CV%			7.3		
	LSD,P≤0.05			4.6		5.4
	Interaction			6.1		
	100m	33.6	26.0	30.6	27.0	29.3
	500m	37.1	37.5	37.3	30.1	35.5
	1km	53.1	35.8	55.1	44.7	47.2
Cr (µg/g)	Mean Direction	41.3	33.1	41.0	34.0	
	CV%			9.0		
	LSD,P≤0.05			3.5		4.1
	Interaction			4.7		
	100m	13.8	15.4	13.1	14.4	14.2
	500m	14.7	13.3	14.1	13.9	14.0
	1km	14.9	14.1	15.1	14.1	14.5
Cd (µg/g)	Mean Direction	14.5	14.3	14.1	14.1	
	CV%			11.1		
	LSD,P≤0.05			1.7		2.0
	Interaction			2.2		
	100m	2167.6	2133.6	2175.8	2116.6	2148.4
	500m	2233.8	2248.2	2258.6	2151.9	2222.9
	1km	2396.7	2444.2	2367.4	2326.2	2383.6
Fe (µg/g)	Mean Direction	2266.0	2275.3	2267.3	2197.9	
	CV%			3.5		
	LSD,P≤0.05			97		83
	Interaction			110		
	100m	93.9	70.0	15.9	1.6	45.4
	500m	0.3	11.8	0.7	4.3	4.3
	1km	0.0	7.4	5.9	3.9	4.3
Pb (µg/g)	Mean Direction	31.4	29.8	7.5	3.3	
	CV%			25		
	LSD,P≤0.05			4.7		5.5
	Interaction			6.3		

Except for Pb and Cd the concentration of Cu, Zn, Cr and Fe increase as one move away from the epicenter. The concentration of cadmium remained almost constant.
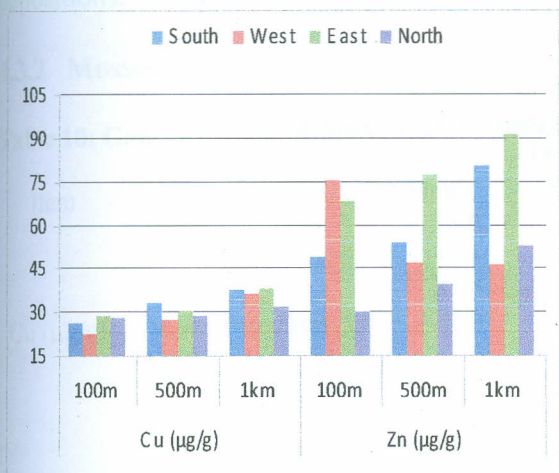

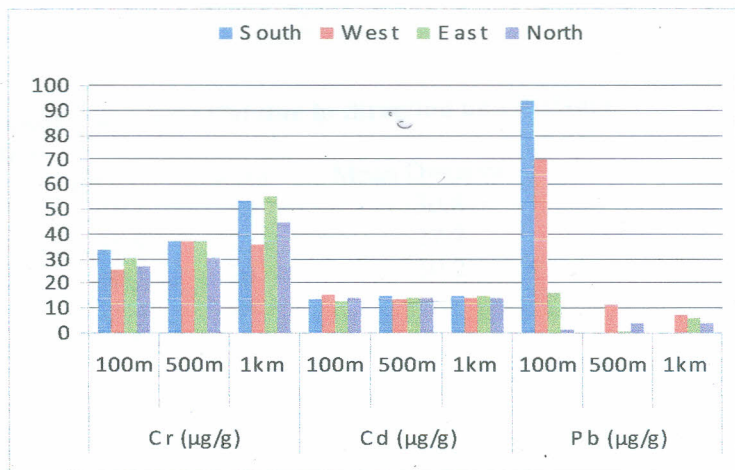**Fig 10 (a): Concentration of Cu&Zn (µg/g) in soil around PAPM due to direction and distance**

Fig 10 (b): Concentration of Cr, Cd&Zn (µg/g) in soil around PAPM due to direction and distance

Comparison using bar graphs shows slightly higher concentrations of most metals at 1km away from the industry. A different trend was observed for Pb possibly because other sources not attributable to the PAPM may be responsible. The tall chimneys in the factory may be instrumental in throwing away the acidic gaseous emissions released by the paper plant that start depositing at a distant and thus slightly increase the concentrations of these metals 1km away due to atmospheric depositions and remobilization of the metals.

Synergic effects or reactions by acidic gases released by the Paper Mill may increase the rate of corrosion at a considerable distance from the industry. This trend was observed for Cu, Zn, and Cr (Fig 10a&10b), metals contained in gaseous emissions of activities like incineration of de-inking of sludges and fuel combustion. The concentration of Cd remained almost constant. Runoffs also contribute to the heavy metals being washed to distances further away from the Paper Mill. A different trend is observed for Zn and Pb possibly due to the fact that vehicle emissions on the Eldoret–Uganda highway could be the major sources of the large concentrations of these metals

51

Cu, Zn and ... metals with ... concentrations ... the ... ... industry. Para contributes ... around the Mill. The slightly higher concentrations 1km away could be due to atmospheric ... depositions.

4.3.2 Mosses

Table 10: Concentration of heavy metals (µg/g) in moss around PAPM due to direction and distance

Item	Distance	Direction South	West	East	North	Mean Distance
	100m	35.8	34.1	28.1	25.2	30.8
	500m	34.1	27.3	26.9	22.8	27.7
	1km	33.8	30.2	30.2	26.4	30.2
Cu (µg/g)	Mean Direction	34.6	30.5	28.4	24.8	
	CV%			5.8		
	LSD,P≤0.05			1.8		
	Interaction			2.4		
	100m	76.4	136.4	94.1	135.6	110.6
	500m	121.9	109.7	70.8	89.6	98.0
	1km	181.7	113.5	49.7	90.9	108.9
Zn (µg/g)	Mean Direction	126.7	119.8	71.5	105.4	
	CV%			3.9		5.1
	LSD,P≤0.05			4.3		
	Interaction			5.8		
	100m	20.8	23.4	36.7	35.9	29.2
	500m	34.1	24.4	39.0	30.1	31.9
	1km	40.1	30.0	40.1	28.9	34.8
Cr (µg/g)	Mean Direction	31.7	25.9	38.6	31.6	
	CV%			6.6		2.6
	LSD,P≤0.05			2.2		
	Interaction			3.0		
	100m	15.7	15.5	14.3	14.7	15.4
	500m	14.9	15.1	14.5	14.9	14.8
	1km	15.7	14.5	13.9	14.6	14.7
Cd (µg/g)	Mean Direction	15.4	15.1	14.2	14.8	
	CV%			8.6		1.6
	LSD,P≤0.05			1.4		
	Interaction			1.8		
	100m	1947.3	2085.1	2046.7	1935.5	2003.6
	500m	2114.1	2169.4	2153.6	1917.1	2088.6
	1km	2175.5	2140.7	2154.4	1871.5	2085.5
Fe (µg/g)	Mean Direction	2078.9	2131.7	2118.2	1908.0	
	CV%			2.7		
	LSD,P≤0.05			59.4		69.5
	Interaction			79.1		
	100m	13.1	40.6	5.1	0.1	14.8
	500m	12.3	25.1	9.0	0.3	11.7
	1km	8.0	20.8	6.9	4.1	9.9
Pb (µg/g)	Mean Direction	11.1	28.8	7.0	1.5	
	CV%			11.3		
	LSD,P≤0.05			1.5		1.7
	Interaction			1.9		

Cu, Zn and Cd metals were more concentrated on the southern side of the industry. This contributes to run offs resulting in distribution of these metals to the southern side. There were significant differences in all the metals with relation to distance from the industry (Table 10), LSD values ranging between 1.4 (Cd) and 59.4 (Fe).
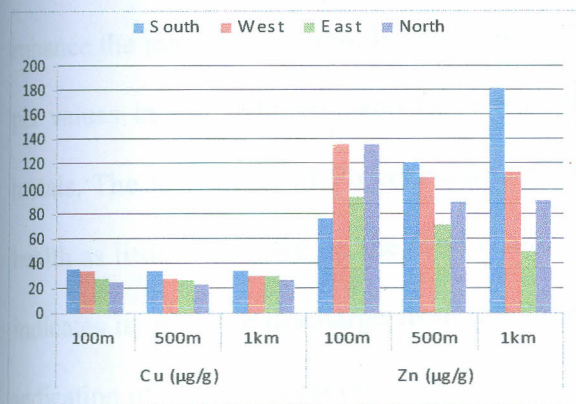

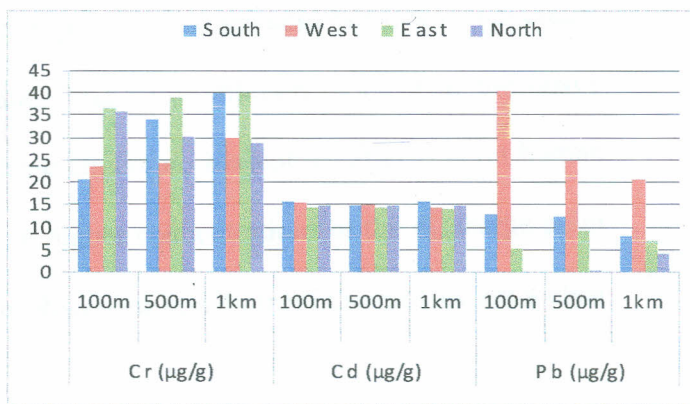Fig 11(a): Concentration of Cu&Zn (µg/g) in moss around PAPM due to direction and distance

Fig 11(b): Concentration of Cr,Cd&Pb (µg/g) in moss around PAPM due to direction and distance

The pattern exhibited by metal concentrations in mosses (Figs 11a&11b) is a clear indication of environmental depositions. ANOVA analysis showed significant difference between distances, for every metal investigated, which confirms that these metals are aerially distributed differently with proximity to the industry.

The foregoing results indicate that heavy metals are distributed differently in the soils, mosses, sediments and the waters as they have different bioabsorption properties. However the concentrations in the soils are alarming and of great concern. This is likely due to dominant influence of the anthropogenic activities and other natural sources. The metal particulates then get their way to the soils either through atmospheric deposition or by precipitation

Generally higher levels of Fe recorded in all the sample types may be due to influx of Fe wastes as a result of the high rates of corrosion of the roof tops and stationary metal parts in the factory and from the activities of the paper and the surrounding industries. This is linked to the high acidity in the environment surrounding the industries which may remobilise some of the metals and also enhance the rate of corrosion. In this region, the Pan Paper plant causes acid rains, which decrease pH values in the sediment, and these low pH values lead to dissolution of most of the heavy metals. The low levels of Pb concentrations may have almost no toxicological effects on human health as little will move up the food chain, although higher concentrations at the discharge point indicates its possible discharge from the Paper Mill. Recorded results from the mosses are a clear indication of aerial deposition.

CHAPTER FIVE

CONCLUSIONS, RECOMMENDATIONS AND SUGGESTIONS FOR FURTHER STUDY

5.1 CONCLUSION

1. This study has generated pioneer data on the concentrations of heavy metals in sediments, soils, waters and mosses around Pan African Paper mill, Webuye. The concentrations of all the heavy metals in the water samples exceeded the US EPA water quality guidelines, except for lead. The levels of Cu, Zn, Cr, Cd, Fe, and Pb ranged between $27.8 - 36.2$ µg/g, $36.1 - 90.6$ µg/g, $31.1 - 46.4$ µg/g, $13.3 - 15.1$ µg/g, $2143.2 - 2281.1$ µg/g and $0.2 - 62.6$ µg/g respectively in soils, between $17.9 - 38.4$ µg/g, $46.0 - 175.2$ µg/g, $13.5 - 49.9$ µg/g, $13.3 - 16.2$ µg/g, $1831.0 - 2178.6$ µg/g and $0.0 - 42.7$ µg/g respectively in mosses, between $14.8 - 49.2$ µg/g, $16.2 - 79.7$ µg/g, $15.6 - 48.3$ µg/g, $10.2 - 24.8$ µg/g, $1801.3 - 2415.3$ µg/g and $0.4 - 103.0$ µg/g respectively in sediments and between $138.8 - 425.8$ µg/l, $569.2 - 976.9$ µg/l, $255.5 - 467.5$ µg/l, $151.2 - 408.2$ µg/l, $1107.7 - 3170.7$ µg/l and $0.0 - 13.4$ µg/l respectively in water. Generally higher levels of Fe were recorded in all the sample types.

2. Metal concentrations in sediments and water were generally higher during the wet season. Percentage increase in the concentration of the metals downstream ranged between 10% (Fe) and 348% (Pb). This was attributed to the run offs experienced during this season. The

mosses and soils experienced slightly higher concentrations during the dry season as a result of atmospheric deposition. ANOVA analysis showed significant differences in the soils, mosses, water and sediments between the different seasons. This shows that the different seasons have an impact on the distribution of these metal contaminants. This result therefore approves the hypothesis that there are higher loads during the wet season.

3. Generally, metal concentrations increased as distance from the epicentre (industry) increased as shown by ANOVA, except for Pb and Cd.

4. The results of the heavy metal concentrations in the water and sediments of the part of River Nzoia adjacent to Pan African Paper Mill show that the Mill releases effluents to the regions around it through direct discharge of its wastes. Wastes containing ions are discharged through tall chimney stacks as atmospheric deposition. Other secondary contributions of heavy metal load in the region are caused by exhaust acidic gases (SO_2 & SO_3) from the operations of the Mill.

5.2 RECOMMENDATIONS

1. Studies should be carried out to establish methods of phytoextraction of the investigated heavy metals in soils, sediments, plants and water.

2. More phytochemical studies should be done on the moss plant to ascertain at what time of its life cycle it most readily absorbs the metals, and therefore could be useful in the phytoextraction of these metals.

5.3 SUGGESTIONS FOR FURTHER WORK

- This is a pioneer work in this area and therefore future Impact Assessment of heavy metals in this region would be recommended.

- There is need to use other digestion procedures of the samples in order to compare results and set quality guidelines for heavy metals in the soils, plants, sediments and water around this industry in particular. These procedures would provide for the bioavailable and total metal contents. Similarly the AAS results should also be compared with results of other heavy metal analytical instruments like ICP – AES, XRF, etc.

- The study did not investigate the concentrations of the heavy metals that ascend to the food chain into the plants and animals and therefore bioavailability, in order to asses the health risk factor. Hence there is need for comprehensive studies covering this region and a wider circumference of its environs as well as intensive sampling for quantification of results, after which routine monitoring will be of necessity.

- Further investigation on the extent of the heavy metal distribution in relation to a larger distance and radius from the Paper Mill to establish any remarkable difference is also recommended.

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