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Chapter

Distribution of Potentially toxic elements in Water, Sediment and Soils in the Riparian Zones around a Kraft Pulp and Paper Mill in Western Kenya

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Abstract

This chapter discusses the impact of effluent discharge on the distribution of potentially toxic elements (Pb, Cd, Cu and Zn) in water, sediments and soils near a Kraft mill in Western Kenya. Potentially Toxic Elements (PTEs) concentrations were determined at three sites: Water Intake Point, Effluent Discharge Point and Downstream Point. The mill liquid effluent parameters and gaseous emissions were also characterized. One-way ANOVA was used to analyze the spatial differences in PTEs concentrations. Principal component analysis determined the correlations between the proximity to the Kraft mill and the PTEs in soils, water and sediments. In riverine soils, Cd was 0.78 ± 0.01 mg/kg, while Pb was 94.38 ± 9.65 mg/kg. In sediments, the concentration was 16.81 ± 2.46 mg/kg for Zn, 6.16 ± 0.72 mg/kg for Cd and 75.28 ± 5.97 mg/kg for Pb. In water, Zn was 0.26 ± 0.038 mg/L, Cu was 0.75 ± 0.11 mg/L, Cd was 0.05 ± 0.004 mg/L and Pb was 1.26 ± 9.65 mg/L. The spatial distributions of PTEs in soils near the factory and across the river may have resulted from the factory's effluent discharge and gaseous emissions. These findings should help formulate more stringent industrial effluent management programs in Western Kenya.

Keywords: potentially toxic elements, gaseous emissions, industrial effluent, Kenya, pollution, pulp and paper

1. Introduction

Potentially toxic elements (PTEs) pollution is one of the most important environmental problems in many developed and developing countries [1–8]. PTEs are naturally occurring elements throughout the earth's crust and they exert key

biochemical and physiological functions in plants and animals. At low concentrations as trace elements, they are important constituents of several enzymatic and biological functions and play important roles in various oxidation-reduction reactions in the human body.

At higher concentrations, however, PTEs become environmental contaminants, causing many ailments in humans through exposure to anthropogenic activities such as agriculture, mining and smelting operations [9–12]. Significant contribution to PTEs contamination may also come from natural phenomena i.e. metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of potentially toxic elements. Other natural phenomena include sediment re-suspension and metal evaporation from water resources to soil and groundwater volcanic eruptions and weathering [4, 13–15]. Industrial sources of PTEs include: metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation, leather tanning and paper manufacture plants [4, 14, 16–19].

Metal occurrence in the environment can increase significantly from industrial effluent leachates and accumulate near the surface layer of soil and at water column. Metal chemistry, biotic species or specific differences in water resource can affect patterns of metal exposure, uptake and metabolism. Analyzing sediments best assesses metal pollution in river, as they are less susceptible to flow conditions than water column and act as sink for metal pollutants. The metals attach to any of these phases (water, soil and sediments) in proportions that depend on the physico-chemical conditions such as conductance, pH and temperature prevailing in these phases.

The pulp and paper industry, in particular, has historically been a major contributor of pollutants into the environment, including PTEs [18, 20, 21]. There are five steps in the production of pulp and paper, namely, 1) preparation of raw materials, 2) pulping, 3) bleaching, 4) pulp handling and/or paper production, and 5) recovery of chemicals through the combustion of spent or black liquor [22, 23]. The paper manufacturing process consumes large volumes of fresh water, most of which becomes contaminated with recalcitrant compounds before effluent discharge.

The composition of each mill's effluent depends on the pulping process used; the grade of paper manufactured; the volume of fresh water consumed; the wastewater cleaning technique; and wastewater reuse programs. Paper mills effluents are complex mixtures with more than 200–300 different organic chemicals [24, 25] and approximately 400–500 inorganic compounds [26, 27]. Raw effluent from paper mills has characteristics of high BOD, COD, high levels of chlorinated ligno-sulphonic acids, total dissolved and suspended solids, chlorinated resin acids, chlorinated phenols and hydrocarbon. In addition, the effluent may contain PTEs such as Fe, Zn, Cu, Cd, Mn, Ni, Cr and Pb, that can be present in high concentrations well above permissible limits [20].

1.1 Source of PTEs in a Kraft pulp mill

The main chemical ingredients in a Kraft pulp mill are sodium hydroxide (NaOH) and sodium sulphide (Na_2S). The primary PTEs found in wood and wood products are Ca, Mg, K, Mn, Ba, Al, Ni, Cu, Zn, Cd, Pb. In addition, PTEs are generated through other make-up chemicals, such as sodium sulfate (Na_2SO_4); bleaching agents; water; the chemical recovery system where the cooking liquor is regenerated; Green Liquor Dregs (GLD); Lime Mud (LM); Slaker Grits (SG); Boiler Fly Ash (BFA) and waste

	GLD			SG		LM		BFA		
Element	[*]	[**]	[**]	[#]	[**]	[##]	[*#]	[**]	[*##]	[**##]
Pb	6.12	46.8	13	<3	34.1	6.79	<3	44.3	28.7	31
Cd	3.81	5.19	9.4	0.3	4.75	0.91	<0.3	4.7	2.9	3.3
Cu	229	80.9	102	<10	4.6	0.73	4.1	25.8	63.6	72
Cr	295	56.0	118	12.6	12.4	16.7	7.0	24.1	66.9	74
Ni	233	189	84	23.9	25.2	ni	4.0	97.4	32.4	33
Zn	3197	160	1000	9.9	15.0	ni	36	68.9	295.3	320
Hg	<0.05	ni	ni	<0.03	ni	<0.04	<0.03	ni	0.03	0.1
V	ni	ni	1.9	39.0	ni	ni	ni	ni	92.7	ni
Mo	0.29	ni	1.7	<1	ni	ni	2	ni	3.8	ni
As	<0.1	ni	0.3	<3	ni	0.38	2.7	ni	13.0	14

*[31]; #[32]; **[33]; ##[34]; *#[35]; *## [36]; **## [37].

Table 1.
Content of potential toxic element [23].

paper recycling [28–30]. **Table 1** shows the chemicals composition of GLD, LM, SG, BFA determined in a few mills throughout the pulp and paper industry. These elements leave the mill system through wastewater, fugitive uncontrolled air emissions or flue gases from the recovery boiler [38, 39]. Apart from the fugitive emissions, the mill effluents (liquid and gaseous) undergo treatment in the wastewater purification plant or the air pollution control system depending on the local effluent discharge standards before final disposal into the environment.

There is increasing awareness of potentially toxic elements pollution from industrial discharges, especially their potential effects in a rural setting such as Western Kenya. The area houses several agro-industrial factories; including a Kraft pulp and paper mill, several sugar milling plants, tea factories and fish processing plants. Because of the various amounts of chemicals used in the manufacturing processes, the roles of these industrial discharges could be significant in metal concentration, fate and transport in the adjacent water bodies and soils. An extensive assessment of PTEs contamination in such a setting is therefore required. The objective of this study was to estimate PTEs (Pb, Cd, Zn and Cu) distribution in water, sediments and soils collected near a Kraft pulp and paper mill in Western Kenya.

2. Materials and methods

2.1 Study area

This study was carried out on a Kraft pulp and paper mill in Webuye (34–36° E, 0° 03′-1°15' N) in the upper catchment of the Nzoia River (**Figure 1**). The Nzoia River basin is approximately 12,696 km^2 [40] and lies within the Lake Victoria basin in Kenya, East Africa. The river flows between 2700 and 1134 m above sea level. The region receives an average annual rainfall of 1350 mm. The average annual air temperature varies between 8°C and 28°C, with minimum temperatures between 8°C and 12°C and maximum temperatures of 24 and 28°C [41]. Food crops such as maize,
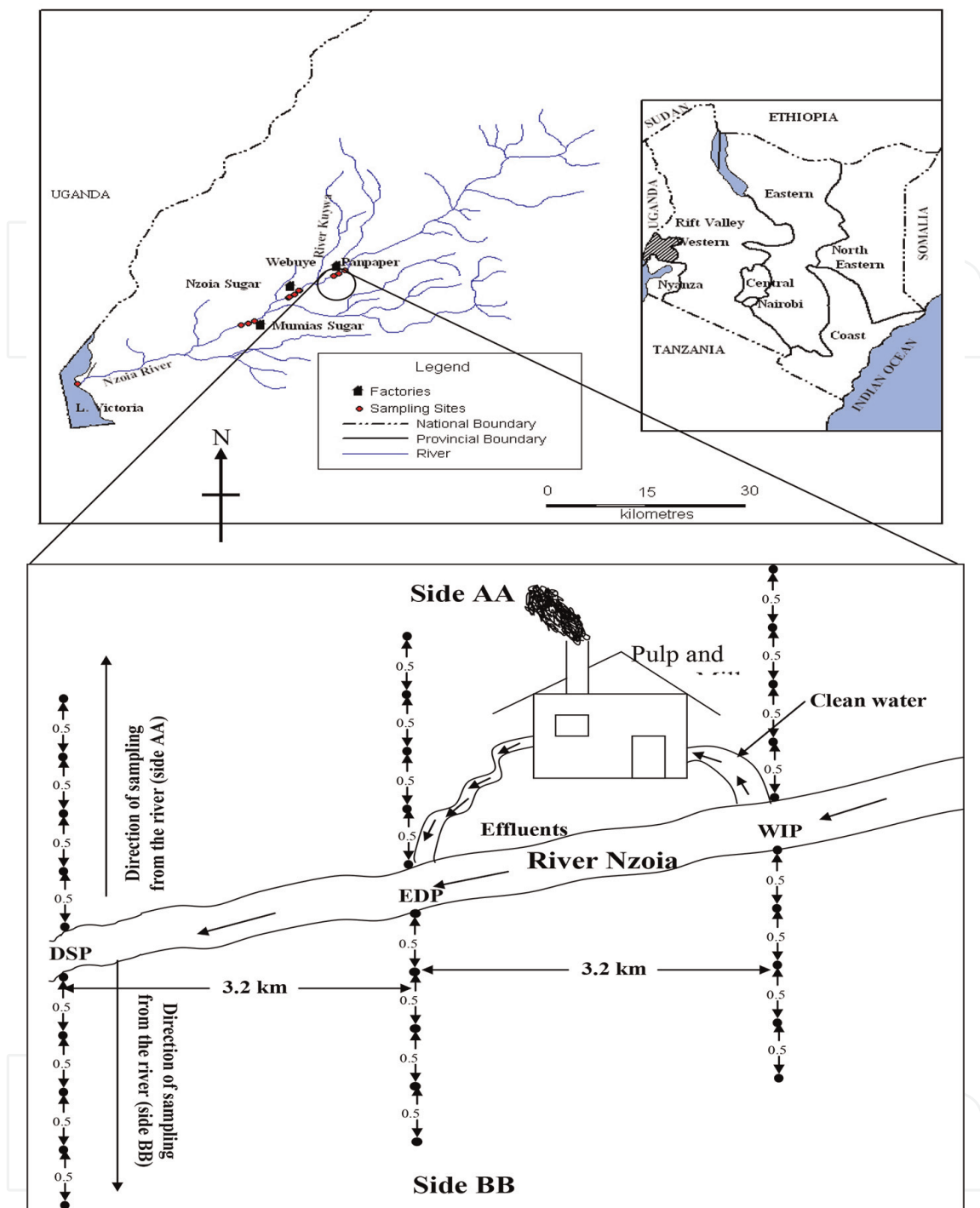
Figure 1.
Study area and study sites.

sweet potatoes and cassava, sorghum, millet and vegetables are grown on small-scale farms, usually extending up to the river banks. Livestock farming is practiced and River Nzoia provides water for both domestic and industrial use. The mill consumes about 40,000 m³ of fresh water and discharges between 35,000 to 40,000 m³ daily into the river at a dilution rate between 0.3 to 3.2%, depending on the seasonality of the river discharge. The mill's effluent takes 6 weeks to flow through a set of settling tanks (one primary and one secondary), two aerated lagoons, and two stabilization ponds before discharge into River Nzoia. Recent expansion programs within the mill have led to an overloaded wastewater treatment system, initially designed to treat only 25,000 m³ of mill effluent per day.

2.2 Study sites

There were three sampling sites, namely, the 'Water intake point' (WIP), the 'Effluent deposition/discharge point' (EDP) and the 'Downstream point' (DSP). These sites were located along the profile of River Nzoia (**Figure 1**). The WIP was situated upstream of the factory discharge point and the river width at this location was 6.53 m. The EDP was approximately 3.2 km from the WIP and the river width was 5.92 m. The downstream point was 3.2 km from the EDP with a river width of 6.44 m. All the sampling sites located on the factory side were designated Side AA (**Figure 2**), while those on the opposite side were designated as Side BB.
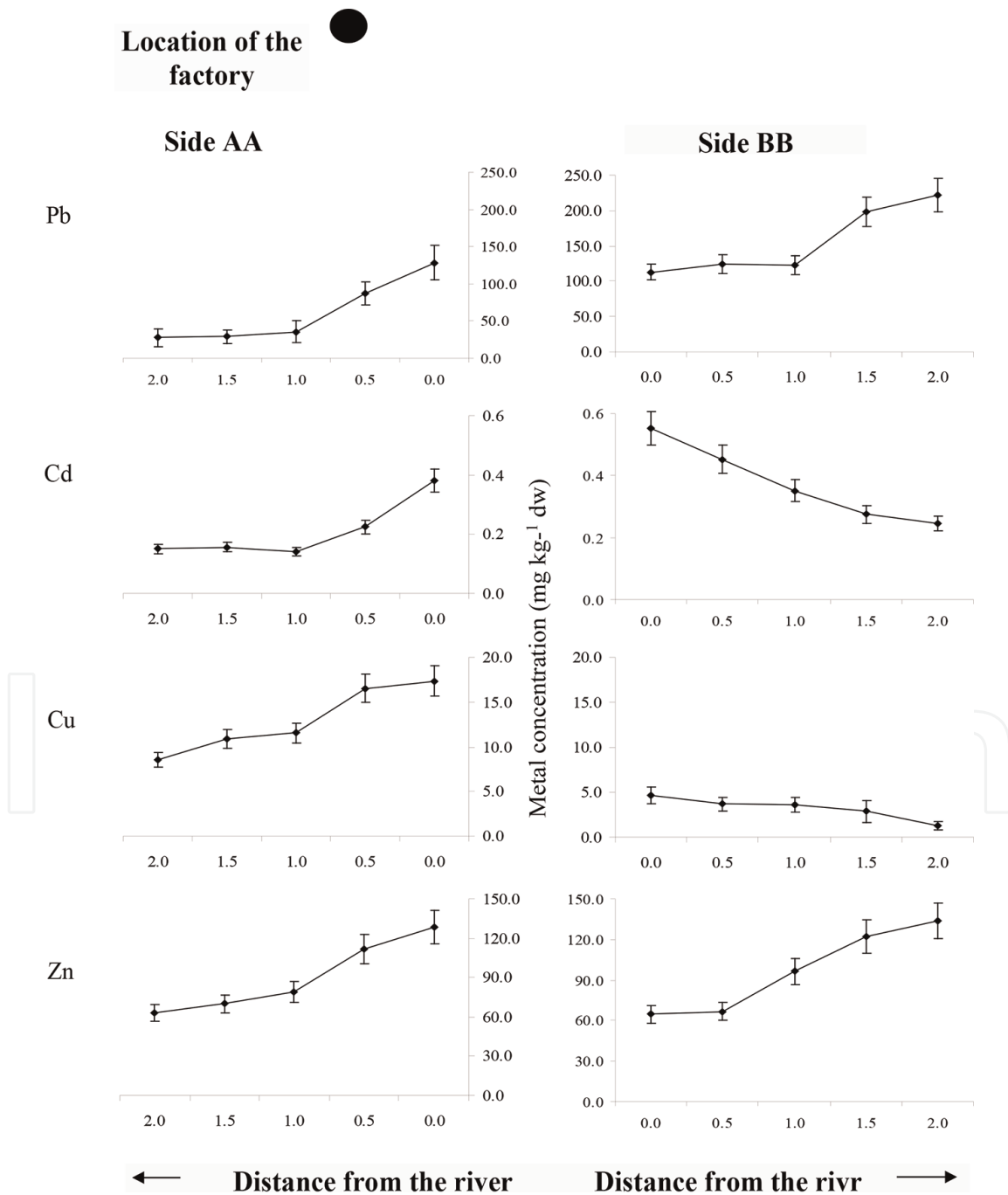

Figure 2.
Trends of heavy metal concentration mg/g in wetland soil at WIP in PanPaper.

2.3 Sampling and analysis of pulp and paper industrial wastes

Grab samples of 3 kg each of lime mud and boiler ash were collected from the recovery area of the pulp and paper mill in Webuye. These samples were spread on trays; air dried overnight, sieved using a No. 9 mesh sieve (2.00 mm) and stored in plastic bags. The pH of these samples was determined using the ASTM D 4972–01 Standard Test Method for soil pH (Electrometric method). The ASTM D 2216–98 Standard Test Method for Laboratory Determination of moisture was used to measure the moisture content. The concentration of PTEs was determined using an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The mill liquid effluent was tested for various parameters at different treatment stages and compared with national effluent discharge standards.

2.4 Sampling and analysis of river water

Grab river water samples were collected using half liter metal free *Van Dorn* bottle. These samples were collected at about 0.5 m below the water surface. Before collecting the samples, the *Van Dorn* bottle were washed in 2 L tap water, and rinsed three times in distilled water. The collected samples were then transferred to half liter polythene bottles pre-soaked in nitric and sulfuric acids solution at 1:1 volume ratio. The water samples were acidified to a pH 2 using concentrated nitric acid [42], and stored in an ice box before transportation to the laboratory for chemical analysis.

Temperature, pH and electrical conductivity (EC) were measured *in situ* using a calibrated JENWAY 3405 electrochemical analyzer (Barloword Scientific Ltd., Essex, UK), with a specific probe for each variable. The equipment was calibrated using de-ionized water before measurements. The measurements were conducted in triplicate for each site included in the study.

2.5 Sediments and soil sampling

Thirty-six sediment samples were collected from each sampling site. The sediments were collected at the bottom of the river using an *Ekmans* Grab Sampler. A polypropylene spatula was used to transfer the sediment sub-samples to acid rinsed polypropylene bottles and placed in an icebox for transportation to the laboratory for chemical analyses. Soil samples were collected using a soil auger along the river banks within the organo-mineral layer of 0–25 cm of the soil. The samples were then kept in black polythene bags, labeled and stored in an icebox before transportation to the laboratory for chemical analyses.

To determine PTEs concentration, soil samples were scooped at five equidistant points from the river bank, i.e. 0.0, 0.5, 1.0, 1.5 and 2.0 kilometers respectively away from the River Nzoia bank on both sides AA and BB. The 0.5 km distance was deemed sufficient to reflect lateral variations of potentially toxic elements concentrations in the soil.

2.6 Determination of leaching capability of PTEs in sediment and soils

A leachability tests were used to evaluate the possible elution of Pb, Cu and Zn from the sediment under selected treatment conditions. These tests took place because

the paper mill periodically discharges the recovery boiler ash and lime mud into the river. The sediment and soil samples were filtered through a Ø 9.0 mm filter paper, air dried, crushed and then sieved through of 9.5 mm pore size. Distilled water was used as the leaching solution, adjusted to a pH 5 using a mixture of sulfuric and nitric acids (80, 20 by weight). Initially, 50 grams of sediments were added to the leaching solution followed by soil at a solid to liquid ratio of 1:20 (proportional to 1000 mL leaching solution). The mixture was agitated in a rotary agitator for 18 hours at 30 rpm and a constant temperature of 25°C. After agitation, the soil slurry was filtered through a 0.8 mm glass fiber filter. The liquid extract was digested using concentrated HNO_3 and analyzed for Cr, Cu, Pb and Zn using an ICP-OES. All the analyses were run in triplicate.

2.7 Analytical determination of PTEs in water

Water samples were digested using sulfuric and nitric acids before spectro-photometric analysis was conducted to minimize the interference of complex organic matter [43]. The samples were digested and concentrated on a hot plate from 100 mL to 25 mL for 3 hours. After digestion, the samples were allowed to cool to room temperature and then 2 mL of 30% hydrogen peroxide (H_2O_2) were added to oxidize any residual organic matter. Further cooling followed before the digested samples were filtered through a 0.45 μm nucleopore membrane filter over a vacuum pump. The filtrates were stored in 125 mL polyethylene sample bottles, at 4°C before analysis for Zn, Cu, Pb, and Cd in an Atomic Absorption Spectrophotometer (Model AA 10/20). In this study, at least two calibration standards were prepared for each metal before recording the measurements. The PTEs were determined at various spectrophotometric wavelengths and slit width (Pb = 17.0 nm; Zn = 13.9 nm; Cu = 324.8 nm; Cd = 228.8 nm and slit width for Pb and Zn = 1.0 nm and Cd and Cu = 0.5). The concentrations of PTEs in water were calculated and reported in mg L^{-1}.

2.8 Determination of PTEs in soil, sediment and industrial wastes

The study used analytical grade reagents and the stock solutions met the Merck certificate AA standards. In addition, all experiments used milli-Q water. Plastic and glassware were cleaned by soaking them in 14% (v/v) HNO_3 for 24 hours and rinsed with nano pure water. The sediments, soils samples and industrial wastes were crushed and homogenized using a Fritsch, Pulverisette 5, planetary mill (Fritsch GmbH Laborgerate, Idar-Oberstein, Germany) for 5 minutes at 400 rpm. About 0.20 g of soil and sediment samples and about 25 mL of water were weighed in Teflon (© poly-tetra-fluoretheen (PTFE), DuPont™) high pressure vessels. Then 4.0 mL concentrated nitric acid (65%), 1.0 mL concentrated hydrochloric acid (37%) and 1.0 mL ultrapure water were added to the samples. Six samples of each item were placed in the carousel of a *Paar* Microwave oven (Anton Paar GmbH – Graz –Austria). The samples were digested in a microwave oven (Anton Paarâ GmbH Kärntner Straße 322 A-8054 Graz/Austria) at a maximum temperature of 220°C and pressure of 75 bars for 15 minutes.

After cooling, the resultant clear solutions were poured into 50 mL volumetric flasks and diluted to the mark with ultra-pure demineralized water (Barnstead NanoPure, Thermo Fisher Scientific Inc., Barnstead International,

Iowa USA). Finally, the diluted solutions of the respective samples were transferred into acid cleaned polyethylene bottles. All elements were determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (Perkin Elmer Optima 3000 XL, ICP-OES) with the PE calibration standards. The concentrations of PTEs in soil and sediments were calculated and reported in mg kg^{-1} dry weight. The quality of the analytical process was controlled by the analysis of IAEA MA-A-3/TM certified standard reference material of river sediment. Care was taken to ensure analytical results varied from certified values by less than 10%.

2.9 Estimation of atmospheric discharge of gaseous pollutants from the Kraft paper mill

Previous studies have indicated that atmospheric deposition is a major source of most PTEs entering agricultural land [44, 45]. Thus, emission (E) estimates of selected gases, particulates, ash and chemical elements were calculated using emission factors (E$_f$) from literature [31, 39]. The equation used was E = AixEf, where A$_i$ = Activity or industrial production of the paper mill. The maximum production was 300 metric tonnes per day or 105,000 metric tonnes per year air-dried unbleached pulp. The study assumed that Kraft pulping was the only system at the mill and that the emissions came solely from the recovery boiler at the factory. In addition, we assumed that only an electrostatic precipitator was used to treat flue gases from the mill.

2.10 Data analysis

Statistical analyses were performed using STATISTICA 6.0 [47]. Data collected were first tested for homoscedasticity [48] before subjecting them to statistical analysis. Data on PTEs in water, soils and sediments were calculated as means ($\pm$ S.D) for each site. Spatial differences in metal concentrations were analyzed using One-way ANOVA. Duncan's Multiple Range Tests (DMRT) were used for Post-hoc discrimination between the means that differed significantly. The data for all the sites were subjected to Principal Component Analysis (PCA) to determine the correlation between the PTEs concentration in soil, water and sediments and their proximity to the Kraft mill [49].

3. Results

A summary of the liquid effluent from the paper mill at various stages of the treatment process are presented in **Table 2**. Most effluent parameters decreased or reduced as we moved from the primary clarifier to the final stabilization pond prior to discharge into the river and the difference was statistically significant (p < 0.05). Only turbidity and color of the treated effluent increased markedly. For example, the effluent color increased on average by almost 250% from 133 ^{O}H to 331 ^{O}H, while its turbidity rose by 155%, from 1574 NTU to 2431 NTU.

Table 3 summarizes emission estimates from the Kraft Paper mill in Western Kenya. The volume of total reduced sulfur (TRS) was still high during the study, and

Parameters	Primary clarifier overflow	Treated after last stabilization lagoon	Effluent discharge standards*
pH	8.5–9.3	6.9–7.5	6.5–8.5 (non-marine)
Alkalinity (mg/L)	330.0–346.4	70.0–88.15	—
Temp (OC)	39.0–39.6	19.0–21.2	± 3
TS (mg/L)	872.4–980.7	440.0–474.5	30
TDS (mg/L)	670.0–699.6	300.0–348.5	1200.00
TSS (mg/L)	212.5–291.5	94.6–133.0	30
Color (OH)	1280.5–1867.7	1600.0–3263.3	15
BOD5 (mg/L)	182.5–234.7	62.8–117.6	30
COD (mg/L)	536.0–591.54	296.7–401.5	50
Turbidity (NTU)	130.0–136.1	311.0–351.3	—
Conductivity (mScm-1)	1339.2–2109.3	790.0–891.3	—
Dissolved oxygen (mg/L)	0	0.40–0.30	—
Phosphorus (mg/L)	0.056–0.067	0.0050.0015	—
Nitrites (mg/L)	0.004–003	0.008–0.01	—
Nitrate (mg/L)	0.020.01	0.036–0.05	—
Cd (mg/L)	0.193–0.182	—	—
Co (mg/L)	0.041–0.035	—	—
Cr (mg/L)	0.568–0.63	—	—
Cu (mg/L)	0.105–0.146	—	—
Fe (mg/L)	0.211–0.235	—	
K (mg/L)	0.24–0.34	—	—
Mg (mg/L)	0.65–0.71	—	—
Mn (mg/L)	1.325–1.41	—	—
Na (mg/L)	0.083–0.92	—	—
P (mg/L)	0	—	—
Pb (mg/L)	0.08–0.09	—	—
Zn (mg/L)	0.04–0.46	—	—

Table 2.
*Raw and treated Kraft pulp and paper mill effluent by current treatment system (*source: Kenya effluent discharge standard. 3rd schedule).*

confirmed the characteristic strong foul smell in and around the mill. The concentration of Cu, Pb and Cr remained relatively high, while Zn, Ni and Cd were low over the course of the study period.

The river Nzoia's water physico-chemical parameters results within the three sampling sites (WIP, EDP and DSP) are presented in **Table 4**. Temperature, pH and electrical conductivity (E.C) in the three sites exhibited significant variations ($p < 0.05$) (Type III, One-Way ANOVA). Temperature, pH and EC were significantly higher at EDP as compared to other sites but there was not enough evidence of significant difference in pH between WIP and DSP sites.

Air Pollutants	Emission factor (kg/metric tonne)	Energy (MJ/ metric tonne)	Paper Production at PanPaper (tonne/year)	Emission (kg/year)
Particulates	1	33763.2	105,000	105,000
SO$_2$[a]	3.5	33763.2	105,000	367,500
CO[a]	5.5	33763.2	105,000	577,500
TRS[ab]	7.5	33763.2	105,000	787,500
NOX[ac]	1	33763.2	105,000	105,000
Hg[d]	1.0E-05	33763.2	105,000	1.06
Cd[d]	1.6E-04	33763.2	105,000	16.31
Cr[d]	6.7E-04	33763.2	105,000	70.19
Cu[d]	1.0E-03	33763.2	105,000	108.13
Ni[d]	4.0E-04	33763.2	105,000	42.19
Pb[d]	1.3E-03	33763.2	105,000	132.23
Zn[d]	4.0E-04	33763.2	105,000	42.19
Sn[d]	2.7E-04	33763.2	105,000	28.36
Co[d]	8.1E-05	33763.2	105,000	8.51
Ash[d]	1.1E-04	33763.2	105,000	11.70

[a]*Emission Factors expressed in unit weight of air –dried unbleached pulp (ADP) from Recovery boiler and direct evaporators –Controlled by Electrostatic Precipitators from US EPA, 1990.*
[b]*TRS (Total Reduced Sulfur) includes methyl mercaptan, dimethyl disulphide, and hydrogen sulphide.*
[d]*Emission factors from [42].*

Table 3.
Estimated Kraft pulp mill emissions.

	Sampling sites			One-Way ANOVA	
Parameters	WIP	EDP	DSP	F	P
Temperature °C	20.78 ± 0.14[a]	23.83 ± 0.53[b]	21.54 ± 0.25[a]	20.735	<0.0005
pH	8.13 ± 0.11[a]	8.43 ± 0.57[b]	8.13 ± 0.07[a]	4.871	0.014
Electrical conductivity (µS/cm)	109.6 ± 0.6[a]	2720.5 ± 219.3[b]	333.3 ± 21.5[a]	129.403	<0.0005

*Mean values ± SEM followed by different superscripts 'a' or 'b' across the rows are significantly different at α = 0.05. Mean values across the rows with the same superscripts 'a' are not statistically different at α = 0.05. For example, the pH at DSP is not statistically different from the pH value at WIP because it carries the same superscript 'a'.

Table 4.
*mean values ± SEM of the physico-chemical parameters along the sampling sites at PanPaper Mills, Webuye, Kenya during the study period.

The results for lime mud and recovery boiler ash in **Table 5** showed their pH level, Cd and Zn concentrations were not significantly different, but the moisture content, Pb and Cu concentrations were significantly higher in lime mud compared to recovery boiler ash (p < 0.05). In terms of chemical compositions, calcite (calcium carbonate and calcium oxide) was probably the major component of lime mud, while recovery boiler ash was mainly composed of burkeite (sodium carbonate sulfate), aphthitalite (potassium sodium sulfate), and halite (sodium chloride).

Parameter	Pulp and paper industrial wastes	
	Lime mud	Recovery boiler ash
pH	11.9	11.5
Moisture content (% w/w)	1.11	0.25
Potentially Toxic Elements		
Pb (mg/kg)	32.11	20.66
Cd (mg/kg)	1.69	1.42
Cu (mg/kg)	8.73	3.36
Zn (mg/kg)	109.22	122.22
Chemical composition[1]	CaCO3	Na4SO4CO3
		K3Na(SO)2
		NaCl

[1]*Determined by X-ray diffraction analysis (XRD).*

Table 5.
Chemical characteristics and metal concentration in the Kraft pulp and paper mill solid waste.

Metal	Soil	Sediments	P-value
Pb (mg/g)	0.250	0.451	0.002
Cd (mg/g)	0.008	0.009	0.432
Cu (mg/g)	0.036	0.037	0.124
Zn (mg/g)	0.060	0.192	0.019

Table 6.
Amount of leachable metals in soils and sediments near the pulp and paper industry.

	Solubility product constant (Kp)			
	Theoretical values		Experimental value	
Metal	LM 80 g/L	LM 110 g/L	RB 80 g/L	RB 110 g/L
As hydroxide				
Pb	2.5×10^{-16a}	1.95×10^{-12}	7.23×10^{-17}	3.11×10^{-16}
Cd	8.0×10^{-31a}	1.53×10^{-13}	6.44×10^{-21}	1.54×10^{-19}
Cu	2.0×10^{-19a}	8.45×10^{-12}	4.12×10^{-15}	1.77×10^{-14}
Zn	6.0×10^{-18a}	5.93×10^{-12}	3.24×10^{-16}	2.22×10^{-15}
As carbonate				
Pb	7.4×10^{-14a}	2.43×10^{-8}	6.50×10^{-8}	1.21×10^{-7}
Cd	—	—	—	—
Cu	2.3×10^{-10a}	1.22×10^{-7}	3.97×10^{-6}	5.93×10^{-6}
Zn	3.0×10^{-08b}	7.55×10^{-8}	2.96×10^{-7}	7.81×10^{-7}

No data reported for the precipitation of Cd as carbonate.
[a]*Values from [50].*
[b]*Values from [51].*

Table 7.
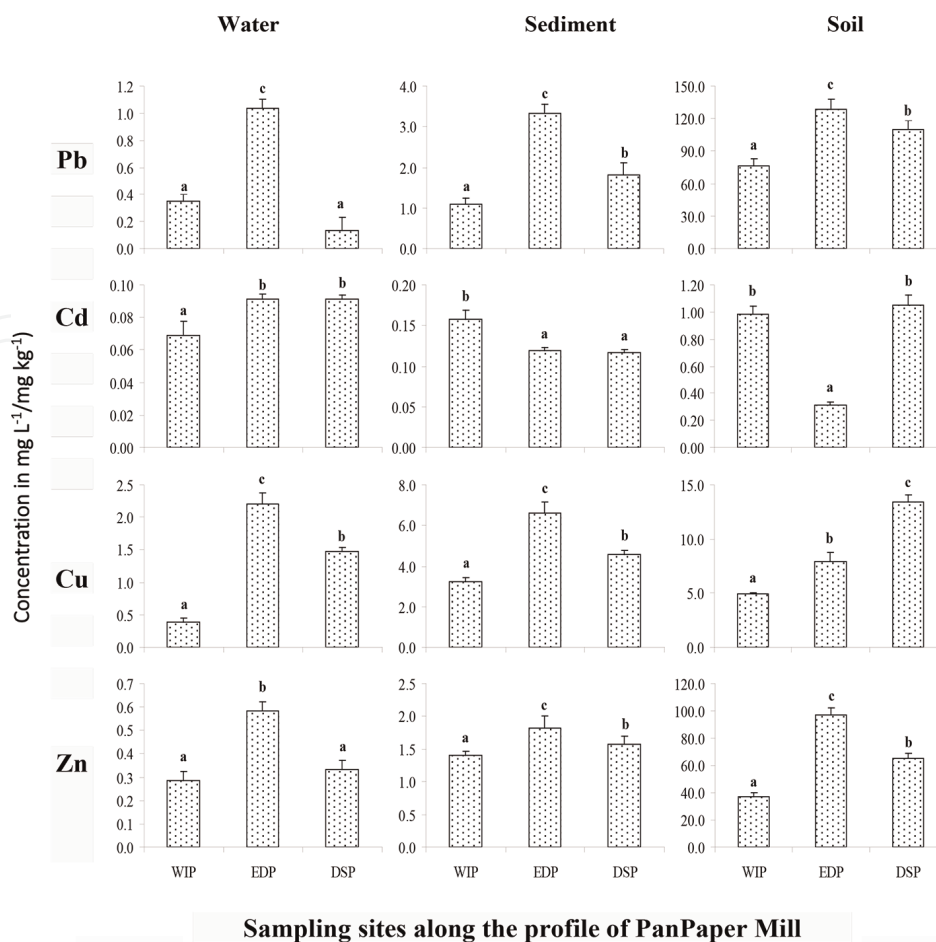*Solubility product constants between the theoretical values and experimental values.*

Figure 3.
Variations in concentration of heavy metals in water, sediment and soils along the three sampling sites in PanPaper, Webuye during the study period. One way-ANOVA test for heavy metals concentrations at WIP, EDP and DSP showed significant differences denoted by different letters 'a', 'b' and 'c'. For each sets where columns had the same letter 'b' or 'a', the difference was not statistically significant.

The leaching tests yielded only small amounts of Pb, Cd, Cu and Zn (**Table 6**). Statistical analysis confirmed that treatment with the different types and dosages of pulp and paper industrial wastes had an effect on the leaching behavior of these PTEs. However, treatments with 80 and 110 g L^{-1} of lime mud did not yield any statistical difference for Cu concentration (p = 0.124) and Cd (p = 0.432) (**Table 7**). Compared to the local standards, only the leaching of chromium and lead was within the regulatory limits.

The results of PTEs concentration in water at the WIP, EDP and DSP are presented in **Figure 3**. In this graph, the concentrations of PTEs in the soil were consolidated (8 values for each sampling point) and a mean concentration was calculated at WIP, EDP and DSP. In water, all the PTEs exhibited highest concentration at EDP but the difference in Cu concentration between ESP and DSP was not statistically significant. For soil samples, Pb, Cu and Zn remained higher at EDP, while Cd and Cu exhibited higher concentration at DSP, although the difference of Cd level between WIP and DSP was not statistically significant (p > 0.05).

PTEs distributions from the river, with respect to the paper mill are represented in **Figures 2, 4**, and **5**. In **Figure 4**, at WIP, concentrations of Zn, Cu and Cd significantly (p < 0.05) reduced away from the river as one approached the factory (AA side), while Pb increased. On the BB side at WIP, Pb, Cd and Cu concentrations also decreased significantly (p < 0.05) away from the river, while Zn reduced (**Figure 4**).
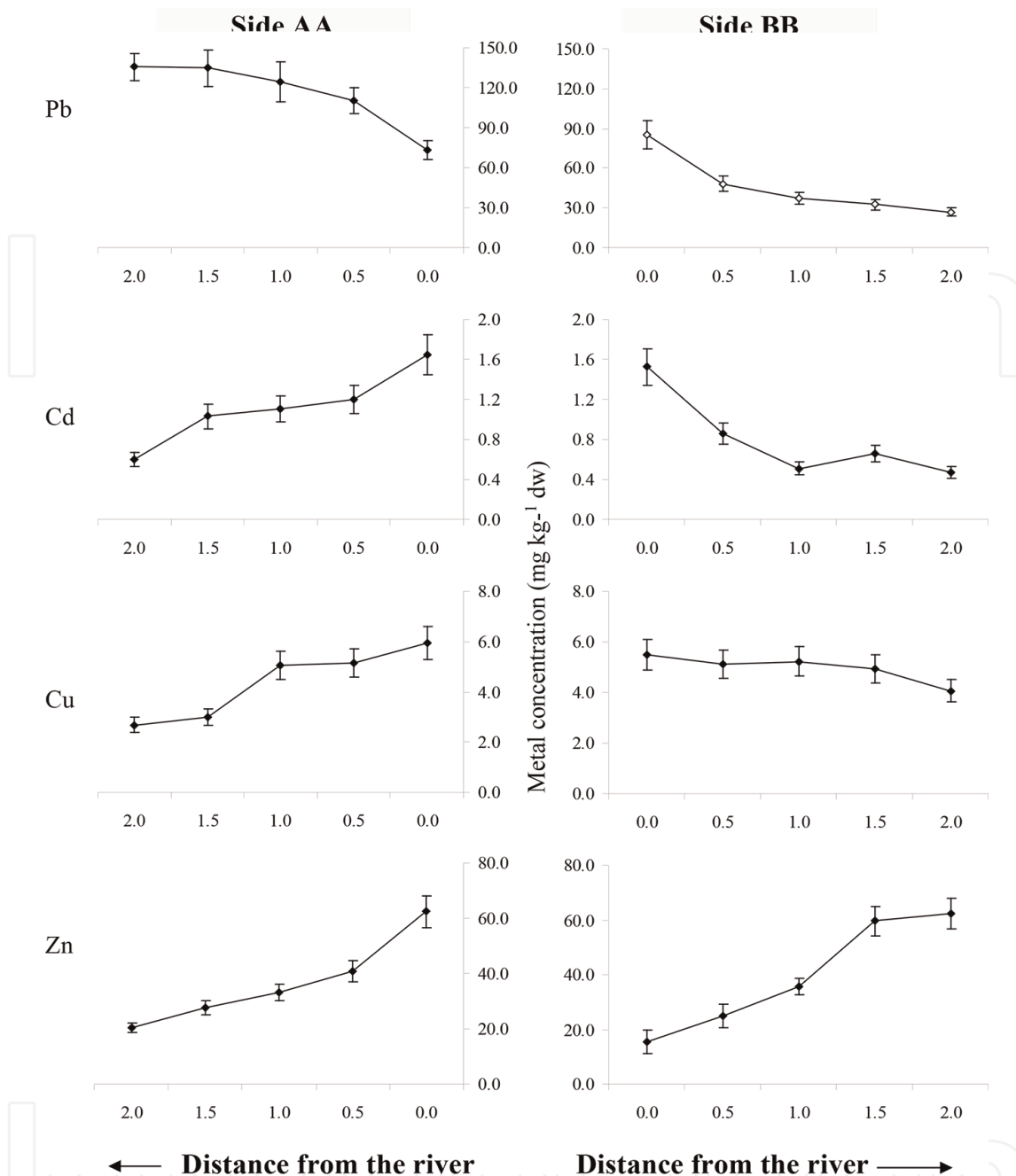
Figure 4.
Trends of heavy metal concentration mg/g in wetland soil at WIP in PanPaper.

In **Figure 2**, at EDP, all metals concentrations decreased ($p < 0.05$) away from the river as one moved closer to the factory (AA), while on the side opposite the factory away from the river, concentrations of Zn and Pb increased significantly as there was a marked reduction in Cu and Cd levels (BB side). Finally, at DSP (**Figure 5**), only Zn and Cu reduced away from the river bank to the factory, on the AA side, with an increase in Pb ($p < 0.05$). On the side BB, Pb, Cu, and Zn concentrations reduced away from the river ($p < 0.05$). Cd exhibited the same trend on both side of the river, with an initial increase followed by a slight and steady decrease as you moved away from the river.

The results of principal component analysis (PCA) on PTEs at 0 km, 0.5 km, 1 km, 1.5 km and 2.0 km on both sides (AA and BB) in the sediments, soil and water are
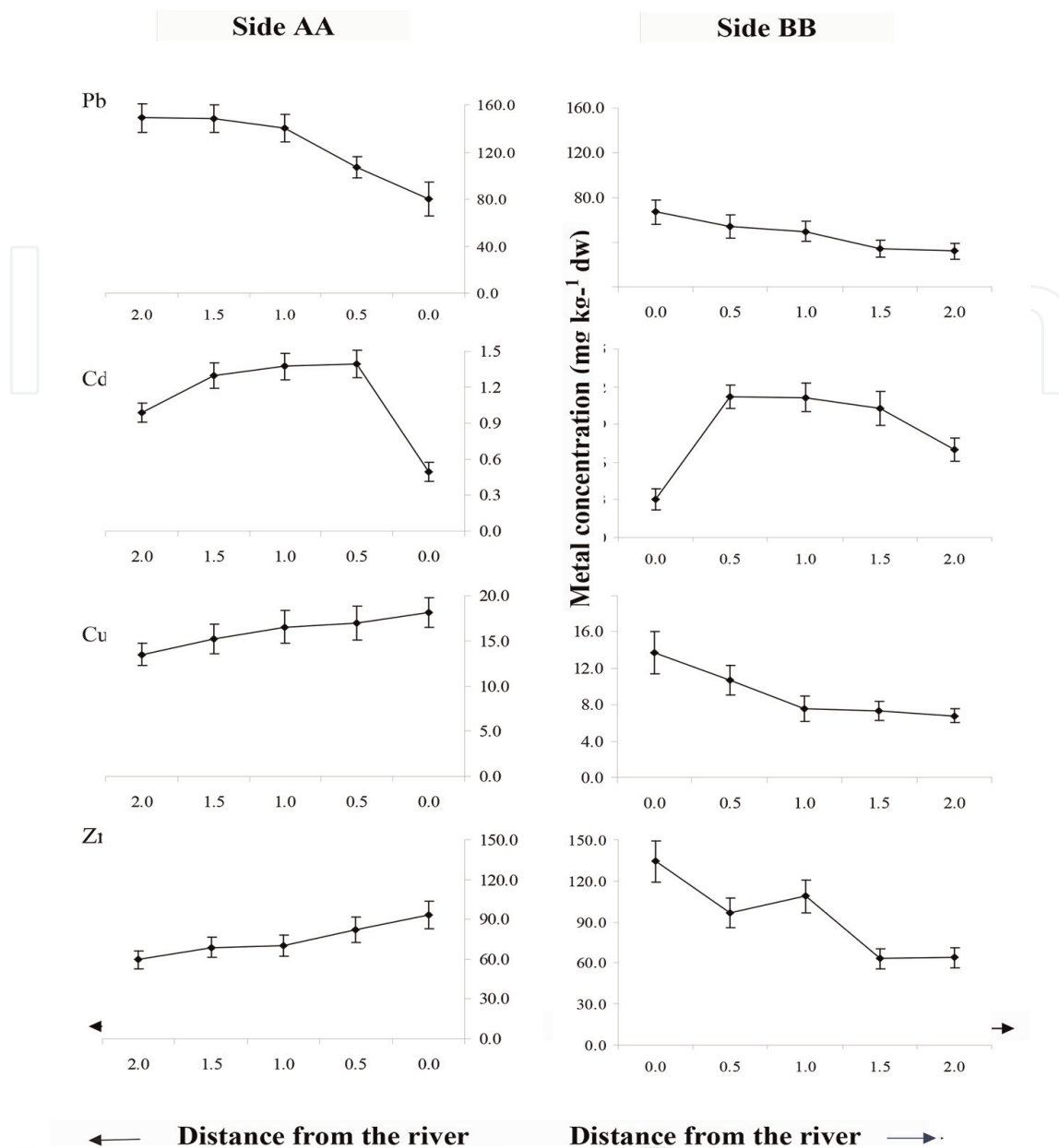
Figure 5.
Trends of heavy metal concentration mg/g in wetland soil at DSP in PanPaper.

presented in **Figures 6–10**. At 0 km from the river, two Principal Components (PC) could explain 96% of the variation in the data. There was a high positive score of Cd and Pb at EDP on AA side and high positive score of Zn and Cu at the DSP on both AA and BB sides. Generally, high score values were associated with the AA side at the EDP on the first PC (73.34%) but no clear association between PTEs concentration in soil, sediment and water. On the second PC (23.25%), there was a high positive score of Cd and Pb at the EDP but a high negative score of Zn and Cu at DSP at both AA and BB side (**Figure 8**).

In **Figure 7**, at 0.5 km from the river, two Principal Components could explain 93.26% of the variations in the data. There was a high positive score of Pb at the WIP on AA side and high positive score of Cd at EDP on BB side on PC1. A high positive score of Zn and Cu was recorded at DSP on BB side. Generally, high values were associated with the AA side at both EDP and DSP on the first PC (75.50%) but with no
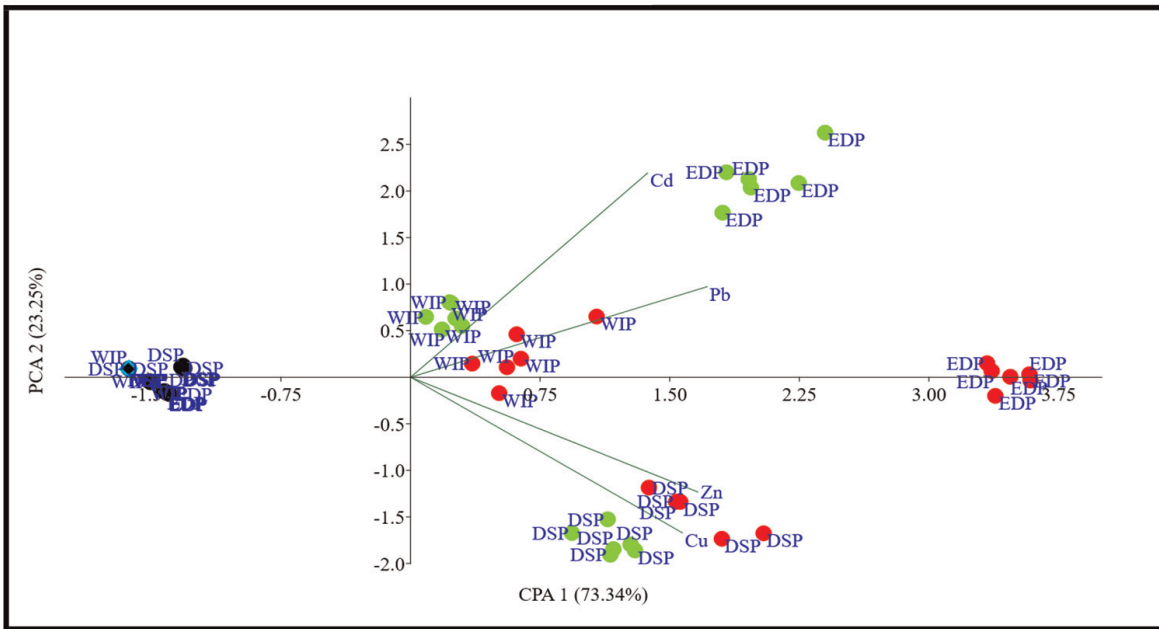
Figure 6.
Principal component analysis of heavy metals (Cd, Pb, Zn and Cu) sampled in sediments, water and at 0 km (both sides 0 km of the buffer zone at Webuye, PanPaper mill. sample location at WIP, EDP, DSP.
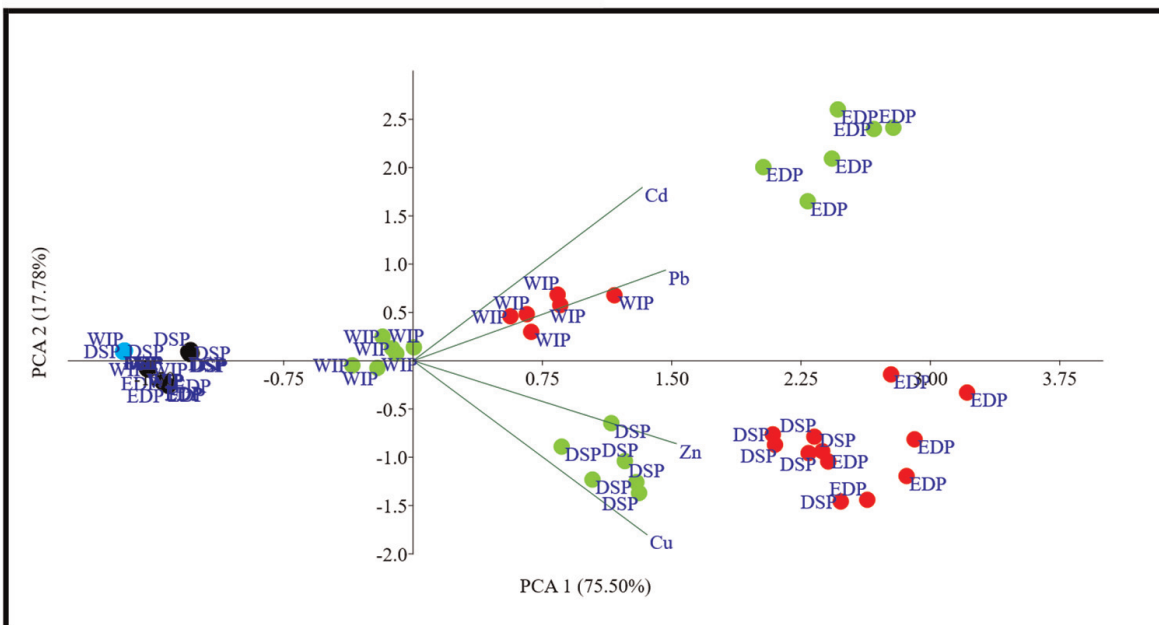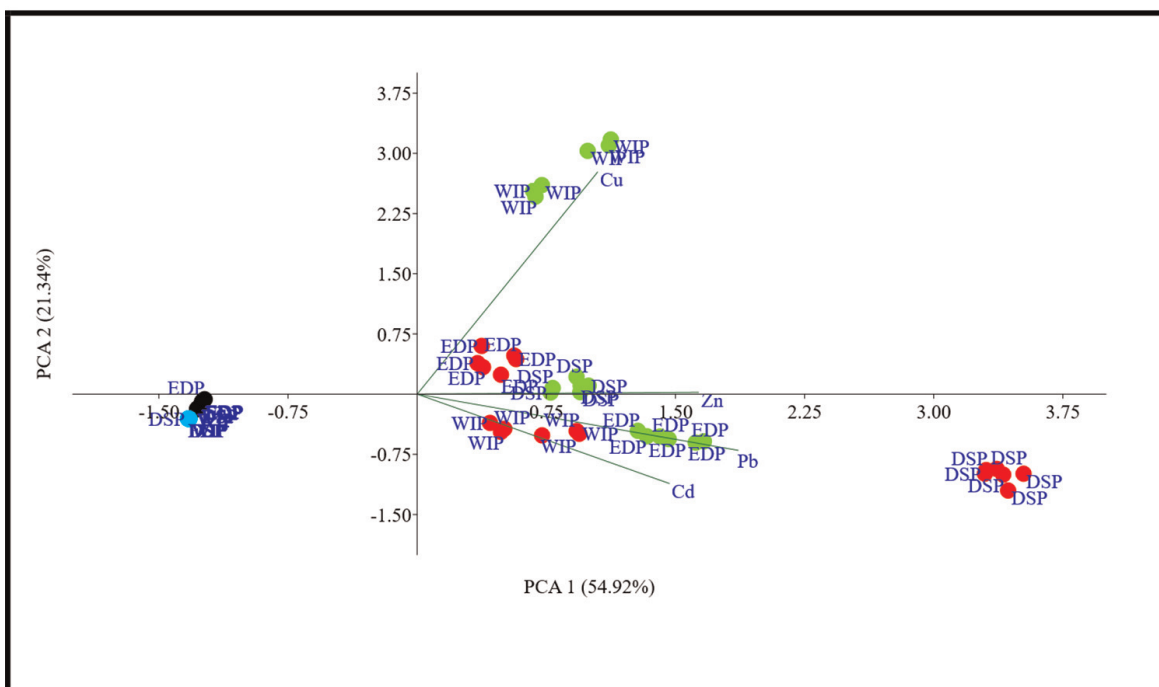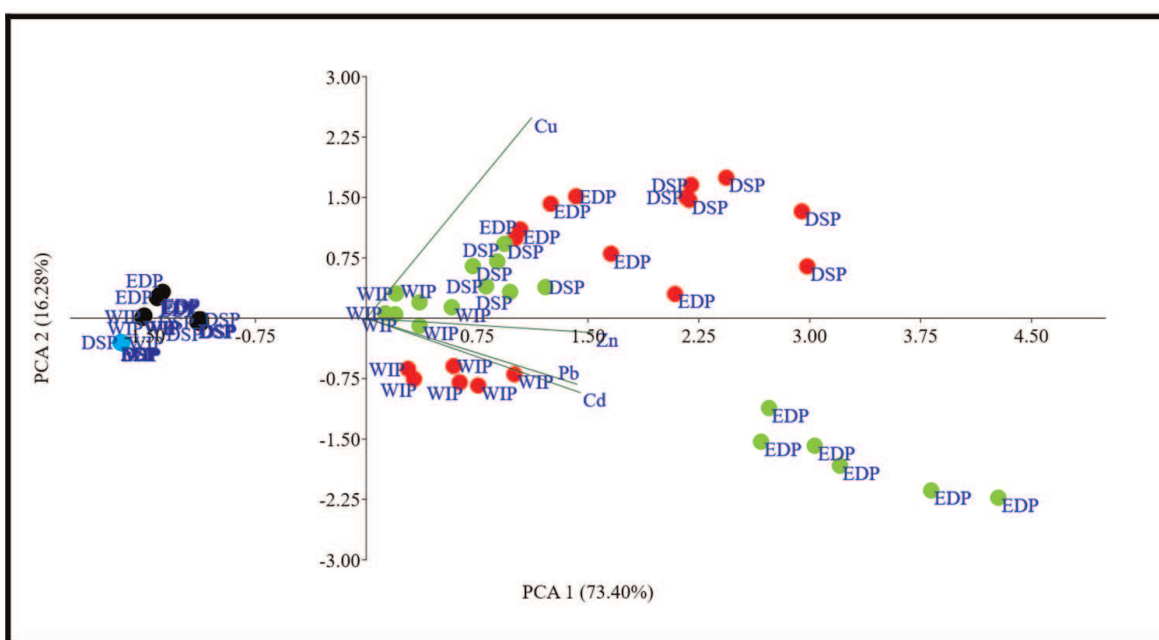

Figure 7.
Principal component analysis of heavy metals (cadmium, Lead, zinc and copper) sampled in sediments, water and at 0.5 km (both sides of the buffer zone at Webuye, PanPaper mill. sample location at WIP, EDP, and DSP.

clear association between PTEs concentration in the soil sediments and water. PC2 explained 17.78% of the total variability, and there was a high positive score of Cd at EDP and Pb at WIP on BB and AA sides respectively. There was a high negative score of Zn and Cu at DSP on BB side (**Figure 7**).

Figure 8.
Principal component analysis of heavy metals (cadmium, Lead, zinc and copper) sampled in sediments, water and at 1 km (both sides of the buffer zone at Webuye pan-paper industry. Sample location at WIP, EDP and DSP.

Figure 9.
Principal component analysis of heavy metals (cadmium, Lead, zinc and copper) sampled in sediments, water and at 2 km (both sides of the buffer zone at Webuye pan-paper industry. Sample location at WIP, EDP, DSP.

In **Figure 8**, at 1 km from the river bank, there was a high loading of Cu on PC1 at WIP, Zn at DSP and Pb at EDP, all on the BB side, and high positive score of Cd at WIP on AA side. Generally, high scores were associated with AA side on PC1 (54.92%). On PC2 (21.34%), there was high positive loading of Cu at WIP on BB side and negative but weak loading of Cd at WIP on AA side. PC1 and PC2 explained up to 76% of the variability in the data.

In **Figures 9** and **11**, at 1.5 km and 2.0 km from the river bank, the concentrations of Pb and Cd had a high positive loading at WIP on the AA side. There was equally high positive score of both Cu and Zn, but they were not associated with any particular sampling points nor sides. At both distances (1.5 km and 2.0 km), there was a general strong influence of DSP and EDP on side AA and BB respectively on the PTEs loading from the river bank. The concentrations of PTEs followed a pattern similar to the one in **Figure 8** where Cu > Zn > Pb > Cd. However the concentration of Cu was higher on the side (AA) of the factory at DSP and EDP. While Zn and Cd levels were higher on the opposite side of the factory. The concentration of PTEs in sediment and water remain lower. The PCA1 and PCA2 could explain 73.4% of the observed variation in these measurements. WIP recorded the lowest concentrations of the PTEs at all the sampling points and on both sides (AA and BB) of the paper mill.

Figure 10. described the Principle Component Analysis of variation of HMs between PTEs concentrations at EDP with pH, Temperature and electrical conductivity as secondary variables. The results show that Zn had relatively high positive score at EDP in relation to the pH, temperature and electrical conductivity on the first axis (56.75%). Pb had a high negative loading at WIP. Cu had a high negative score at DSP but was not associated with any environmental variable. On the second axis, Cd had a high positive score at WIP but was also not associated with any environmental variable. The second axis could only explain 26.53% of the total variability.
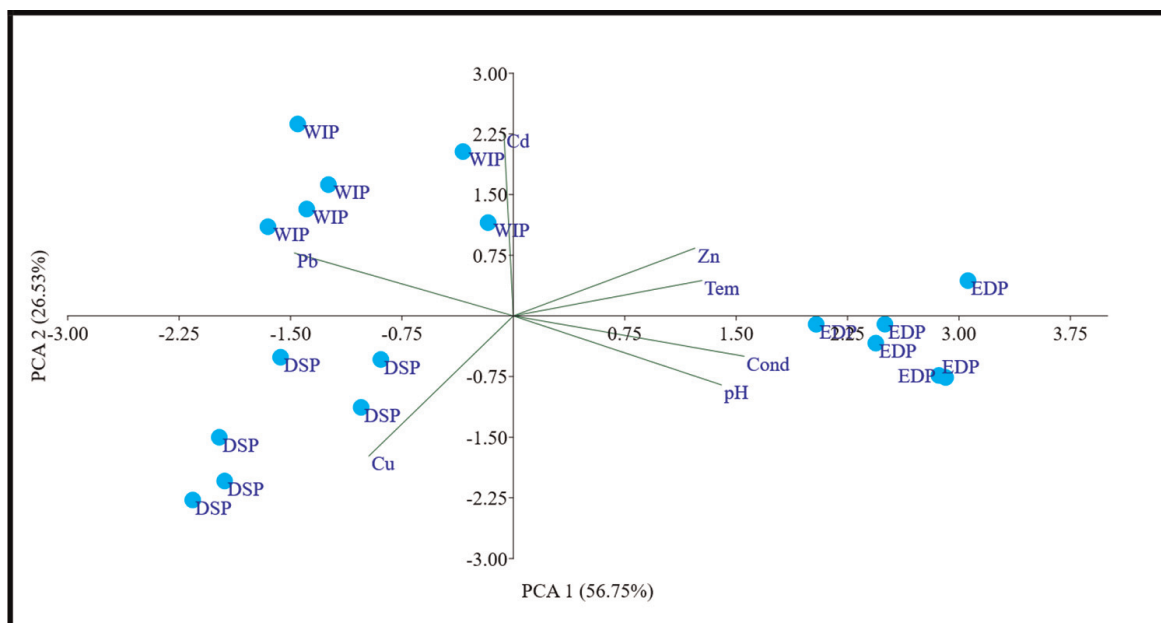

Figure 10.
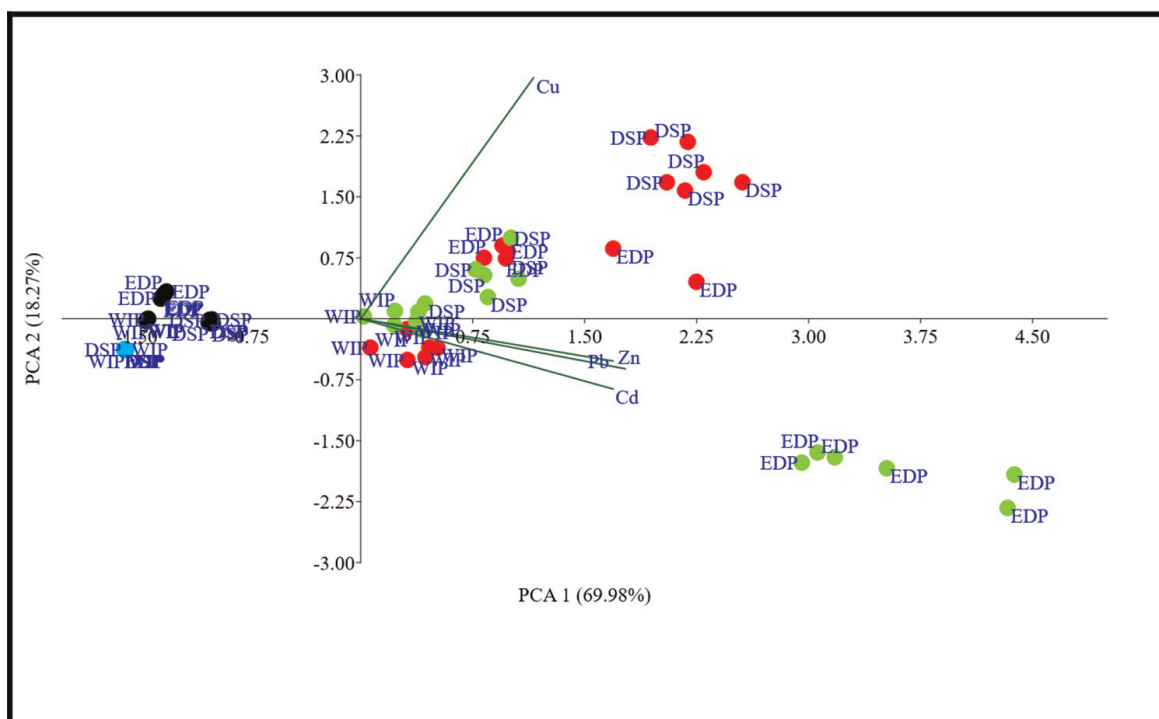*Relationship between pH, EC and Temperature and Zn concentration at the EDP.*

Figure 11.
Principal Component Analysis of heavy metals (Cadmium, Lead, Zinc and Copper) sampled in sediments, water and at 2 km (both sides of the buffer zone at Webuye pan-paper industry. Sample location at WIP, EDP and DSP.

4. Discussion

The results of this study indicate that the factory had an impact on the river's physico-chemical parameters. For example, at EDP, pH, Temperature and EC were much higher than at WIP upstream and DSP downstream, with a slight distortion at 1 km from the river bank. Since there was no other point source between WIP and EDP, the effluent discharged from the pulp and paper mill at EDP probably accounted for much of the observed increased levels in the physico-chemical parameters. Higher pH at EDP sites was likely the result of alkaline industrial effluent discharges. In the factory, sodium hydroxide and sodium sulphide (Kraft process) used during the cooking process of wood pulps, [22, 23, 26], might have resulted in an increase in alkaline condition of the water body at the EDP. In addition, after Kraft cooking process at the mill, the wood pulp underwent bleaching through CEHP or CEHH bleaching sequences. It is likely that the strong caustic extraction in the bleaching sequence was not completely neutralized by the final hypochlorite stage, thereby leading to additional alkalinity into the river water.

In addition to pH, high conductivity at EDP was probably the result of the paper mill discharge into the river. Wastewater from pulp and paper mills is known to contain substantial amounts of dissolved ions and electrolytes. The discharge of such electrolytes ultimately increased the electrical conductivity of the liquid effluent and by extension the EC of the receiving river water. For instance, alkaline sulfates dissociate under high temperature to liberate the positively charged alkali metals (X^+, X^{2+} or X^{3+}) and the sulfate ions (SO_4^{2-}), which all increase the electrical conductivity of the water body [52].

The major components of lime mud and recovery boiler ash in the paper mill contain carbonate compounds [53]. Since the mill sometime releases lime mud and recovery ash into its effluent, this practice more likely exacerbated the alkaline conditions of its wastewater and the increase in pH and EC at the EDP when compared with WIP.

The leaching test results (**Table 6**) showed only marginal leachable concentrations of Cd and Cu. This can be explained by the fact the soils around the paper mill are of *Planesol* type, which are of fine texture intensely weathered and negatively charged. *Planesols* tend to attract positively charged ions such as Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}, which will be strongly bound to the soils around the paper mill.

There were significant spatial variations in the potentially toxic elements concentrations in water, sediment and soils near the pulp and paper mill. Reports by Jumbe and Nandini, 2009 [54] had shown that average abundance of Pb in the Earth's crust is 13 ppm, but in natural soils the background level for Pb ranges from 2.6 to 25 ppm. In the same report, Cd in the Earth's crust is 0.16 ppm but in soils, it ranges from 0.1 to 0.5 ppm. The average abundance of Cu in the Earth's crust is 68 ppm while, in soils, it is between 9 and 33 ppm. The average abundance of Zn in Earth's crust is 76 ppm and in soils it ranges between 25 to 68 ppm. Our results show that Pb, Cd, Cu and Zn concentrations in the soils near the paper mill were approximately 5, 2, 0.5 and 2 times higher than the respective natural background levels of these metals in the earth's crust suggesting anthropogenic input of these metals. The high concentrations of Pb and Zn at EDP, suggest possible enrichment from the paper mill effluent as the source of the metals [18, 20, 29, 55–60]. The levels of the PTEs were not consistently high on the (AA) side of the mill, suggesting that the river bank was not an accurate reference point for the factory (AA) and opposite (BB) factory sides. In addition, high PTEs levels away from the river bank on the opposite (BB) side of mill indicate that river water was not the only source of the metals after effluent discharge.

Some of these PTEs may been deposited on soils through air emission from the paper factory, as suggested by Adoli *et al*, 2011 [61] while analyzing moss and topsoil to monitor metal emission from the same mill. Paper mills have been reported as potential hazardous substances emitters of metals. The presence of high Zn concentrations can be related to the use zinc dithionite as a bleaching agent of stone-ground wood pulps produced within the mill. Zn concentrations at EDP was probably influenced by pH, electrical conductivity, and temperature at the same sampling point. The reduced concentration of Cd as we moved from the EDP to DSP is due to absence of Cd compounds during pulp and paper processing. We can postulate that the factory effluents probably neutralized any geochemical Cd and higher Cd levels obtained at the soils at the downstream sites probably came from the recovery boiler system through the mill's gaseous emissions.

Most of the sulfates from industries are often associated with metal complexation causing insoluble inorganic substances [62], which have higher chances of removing Cd from the water. It is possible that the lack of such complexation agents from the paper mill probably resulted in increased Cd at DSP. Because the study area has higher rate of fertilizer use by farmers for sugarcane production, the net impact of fertilizer use on PTEs in the vicinity probably surpassed Cd concentration from the industrial effluents. However, it seems that it was efficiently reducing Cd, and therefore Cd enrichment of water was low. While it has generally been assumed that most of the metals are immobile in soils or sediments [63], there are factors that enhance their mobility resulting in differential metal distribution. These factors include the properties of the metals, soil texture, pH and competing cations in the soil and sediments

solution [52]. Cd retention is reported to be greater in fine-textured soils with high CEC than in coarse-textured soils with lower CEC, while McBride, 1995 [63] noted that potentially toxic elements mobility was most closely associated with metal-organic complexation and soil pH, all these were likely to affect the distribution of Cd and Pb in water, soils and sediments. *Ultisol* soils around the paper mill are generally known to be poor in organic matter and therefore retained little of the Cd which was transported away from the EDP.

5. Conclusion

The concentration of Pb and Zn were consistently high near the effluent discharge points indicating enrichment through the Pulp and paper liquid effluents or gaseous emissions. Cu was consistently high from 1 km onward away from the river bank, while Cd was the lowest. Zn was highly influenced by pH, temperature and EC. The levels of PTEs in soils around the paper mill confirm anthropogenic enrichment and should therefore influence policy makers for industrial management in Western Kenya.

Acknowledgements

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