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Heavy Metal Contamination of Water, Soil and Vegetables in Urban Streams in Machakos Municipality, Kenya

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Abstract
Pollution of the environment by heavy metals emanating from rapid economic growth and improper waste and effluent disposal is a major concern. In this study, heavy metal concentrations (Cd, Cu, Pb, Zn and Cr) in vegetables, soil and water in two urban streams in Machakos municipality were analyzed. Physicochemical parameters; pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) were also measured on-site. One-way Analysis of variance (ANOVA) was used to test for the significant difference ($p \leq 0.05$) of heavy metal concentrations in the vegetables, soil, and water across the different sampling sites. The relationship between the heavy metals in the soil, water and vegetables was investigated using Pearson correlation. Temperature (21.58 – 23.05 ºC), pH (7.5 – 8.45) and TDS (577.5 – 865.83 mg/L) mean values were found to be within WHO acceptable limits for surface water while EC (864 – 1778.5 µS/cm) exceeded the set limits. Results showed that the mean concentrations (mg/kg) of Cd (BDL – 0.0011), Cu (0.0034 – 0.0055), Pb (0.0012 – 0.007), Zn (0.0232 - 0.1351), and Cr (0.0036 - 0.0292) in water and Cd (0.0058 - 0.0534), Cu (10.39 – 27.5), Pb (4.23 - 8.35), Zn (20.1 – 28.8) and Cr (8.17 – 10.03) in soil were within WHO permissible limits**.** Mean concentration values of (Zn (9.05 – 11.8), Pb (0.28 – 0.636), Cr (BDL – 1.002)) in spinach exceeded WHO permissible limits while Cd (BDL – 0.1285) and Cu (3.07 – 14.5) were within recommended levels. Cd (0.004 – 0.243), Cu (0.909 – 3.60) and Pb (BDL – 0.458) concentration levels in kale were within WHO safe limits for human consumption while Zn (12.06 – 18.8) and Cr (BDL – 1.62) exceeded WHO set limits. Presence of heavy metals (Zn, Pb, Cr) in the vegetables signifies a health risk hazard from consumption of these vegetables. Continuous monitoring of heavy metals in stream water, soil and vegetables is critical towards safeguarding public health.
Key Words: Heavy metals, urban effluent, water, soil, vegetables

1.0 INTRODUCTION

Industrial growth and urbanization coupled with high population growth have led to an increase in sewage water generation in cities and towns around the world [1]. Millions of small-scale farmers in urban and peri-urban areas in developing countries depend on urban streams, which are the recipients of urban effluent for irrigation of crops and vegetables for urban markets. This poses a direct risk as the pollutants in wastewater can affect both the environment and human health. Among the pollutants in wastewater are heavy metals and there is a global concern due to their toxicity, bioaccumulation in food chains and persistence in the aquatic ecosystems [2]. Although heavy metals in the environment could be due to natural processes, the same in urban environments of most developing countries have to a greater extent been attributed to industrial development, transportation and marketing of goods [3]. According to Feng et al., [4] atmospheric deposition can also significantly elevate the level of heavy metals in soils. Elevated levels of heavy metals have been reported in areas having long term use of treated and untreated wastewater [3,5,6].

Contamination of vegetables by heavy metals is a key aspect of food quality assurance given the importance of vegetables in the human diet. The use of polluted urban streams water for irrigation contributes significantly to the heavy metal content in soil and then the vegetables, which poses health risks to consumers of the vegetable commodities [6,7,8,9,10,11].

In Kenya, urban growth and expansion are often accompanied with the proliferation of informal settlements and general poor waste disposal. The increase in the number of processing and manufacturing plants has also increased the amount of industrial effluents. Consumption patterns on the other hand contribute to the accumulation of solid wastes. All this effluent and in some cases solid wastes find their way into the sewage treatment plants and streams. The documentary on Garbage Rivers exemplifies this sorry state [12]. Besides health risks, the heavy negative environmental load equally imposes an expensive social and economic burden on the nation and communities. This thus necessitates the need to periodically assess the quality of urban riverine systems. However, not much attempts have been done for the urban streams in Machakos municipality in this regard.

The aim of this study was thus to establish the level of heavy metal contamination in water in two urban streams flowing through Machakos town, and subsequently in soil and selected vegetables irrigated by this water. Outcomes of this study would provide key information on heavy metals, useful in contributing to sustainable domestic sewage and industrial effluent management in the interest of public and environmental health.

2. MATERIALS AND METHODS

2.1 Study Area

This study was carried out in Machakos municipality in Kenya, which lies within longitudes E 37º16’49.2829’’and E 37º21’18.78778’’ and latitudes S 1º31’507361’’ and S 1º31’27.29809’’ (Figure 1). The streams under study which flow through the municipality are Iini and Ikiwe streams. Vegetable farming through irrigation is a dominant practice in this riparian ecosystem. The market is guaranteed by the ever-increasing urban population. The two streams are surrounded by hilly terrain with a high number of family farms. The number of small-scale industries dealing in textiles, plastics, furniture and food processing is on the rise in the municipality. This inevitable landscape and societal transformation call for planning and implementing a sustainable waste management system.

2.2 Sampling sites and sample collection

Three sampling sites were selected based on land use patterns, economic activity, and suspected pollutant point sources (Figure 1). Site 1, (latitude S 1º31’507361’’ and longitude E

37º16’49.2829’’), was after Machakos town where there is much leakage of sewage into the Iini stream. Site 2 is on the upper side of Ikiwe river (latitude S 1º30̕50.26329 and longitude E 37º16̕17.40619̕̕) to which Iini stream drains its waters. The third site is on the lower side of Ikiwe River (longitude E 37º21'18.78778 and latitude S 1º31'27.29809") where there is much dilution of the water. Sampling was done during the dry season from June 2019 to October 2019. Samples were collected in triplicates from each of the sampling sites once every month for five months. The triplicates were mixed thoroughly to obtain a composite sample from each of the sampling site.
Physicochemical water parameters; pH, temperature, electrical conductivity (EC) and total dissolved solids (TDS) were measured on-site using standard meters (Hanna HI 99121 pH meter and HI 99300 EC/TDS meter). Water samples were collected using 500 mL pre-cleaned and 10% Nitric acid rinsed polyethylene bottles. The sampling bottles were rinsed twice with sample water at each site before taking the actual sample. Each sample was acidified with 2 mL of nitric acid (analytical grade) to avoid adsorption of heavy metals to the container wall [13]. 1 kilogram of each type of vegetable *Spinaciaoleracea* (spinach), and kale was randomly bought from farmers farming along the sampling sites and put in separate well-labeled bags to indicate the site and date of sampling. Soil samples (0-30 cm depth) were also collected from the same vegetable farms using a plastic scooper. Non-soil particles were removed and the soil samples stored in pre-cleaned well-labeled polyethylene containers. The water samples were put in an iced cool box and together with the soil and vegetable samples immediately transported to Kenya Plant Health Inspectorate Service (KEPHIS) Analytical Chemistry laboratory, Nairobi for heavy metal analysis.

2.3 Sample Analysis

At the laboratory water samples were then filtered through a 0.45 µm cellulose acetate membrane filter and 50 mL digested in 15 mL tri acid mixture (HNO_3, HCl and $HClO_4$) at a ratio of 5:1:2 at 150 ºC for at least 20 minutes [14]. After cooling, samples were quantitatively transferred into a 250 mL volumetric flask and filled to the mark using de-ionized water.

Vegetables were oven-dried at 100ºC then ground into powdered form. 1.5 g of vegetable powder sample was digested in 15mL tri acid mixture (HNO_3, $HClO_4$, and HCl) at 150 ºC in a microwave oven until a transparent solution appeared. The digests were then passed through a pre-washed filter and the filtrate made up to 250 mL [3].

The soil samples were dried in an oven then sieved through a 2 mm sieve and stored in labeled polyethylene sampling bags. 1.5 g of the dried soil sample was digested by 15 mL tri acid mixture i.e. HNO_3, HCl, $HClO_4$ (5:1:2 ratio) at 150 ºC until a transparent solution appeared [12,15S]. Heavy metals analysis (Cd, Pd, Cr, Zn and Cu) in the digested water, vegetable, soil samples and blanks was determined using inductively coupled plasma mass spectrophotometer (Agilent 7900 series ICP-MS).

2.4 Data Analysis

The data was analyzed using Minitab Statistical Software, version 19. The significant difference ($p \leq 0.05$) of heavy metal concentrations in vegetables, soil, and water across the different sampling sites was tested using One-way Analysis of variance (ANOVA). Separation of means was done using post-hoc Tukey's test. Pearson correlation analysis for heavy metals water, soil and in the vegetables was also done. The heavy metal concentrations in the samples were compared with the World Health Organization (WHO) set limits.

Transfer factor (TF) was used to determine the mobility of Cd, Cu, Pb, Zn and Cr from soil into the vegetable and was determined by dividing the concentration of the heavy metals in the vegetables by the concentration of the heavy metals in the soil.

$$\mathrm{TF} = \frac{Heavy\ metal\ concentration\ in\ vegetable}{heavy\ metal\ concentration\ in\ soil}$$

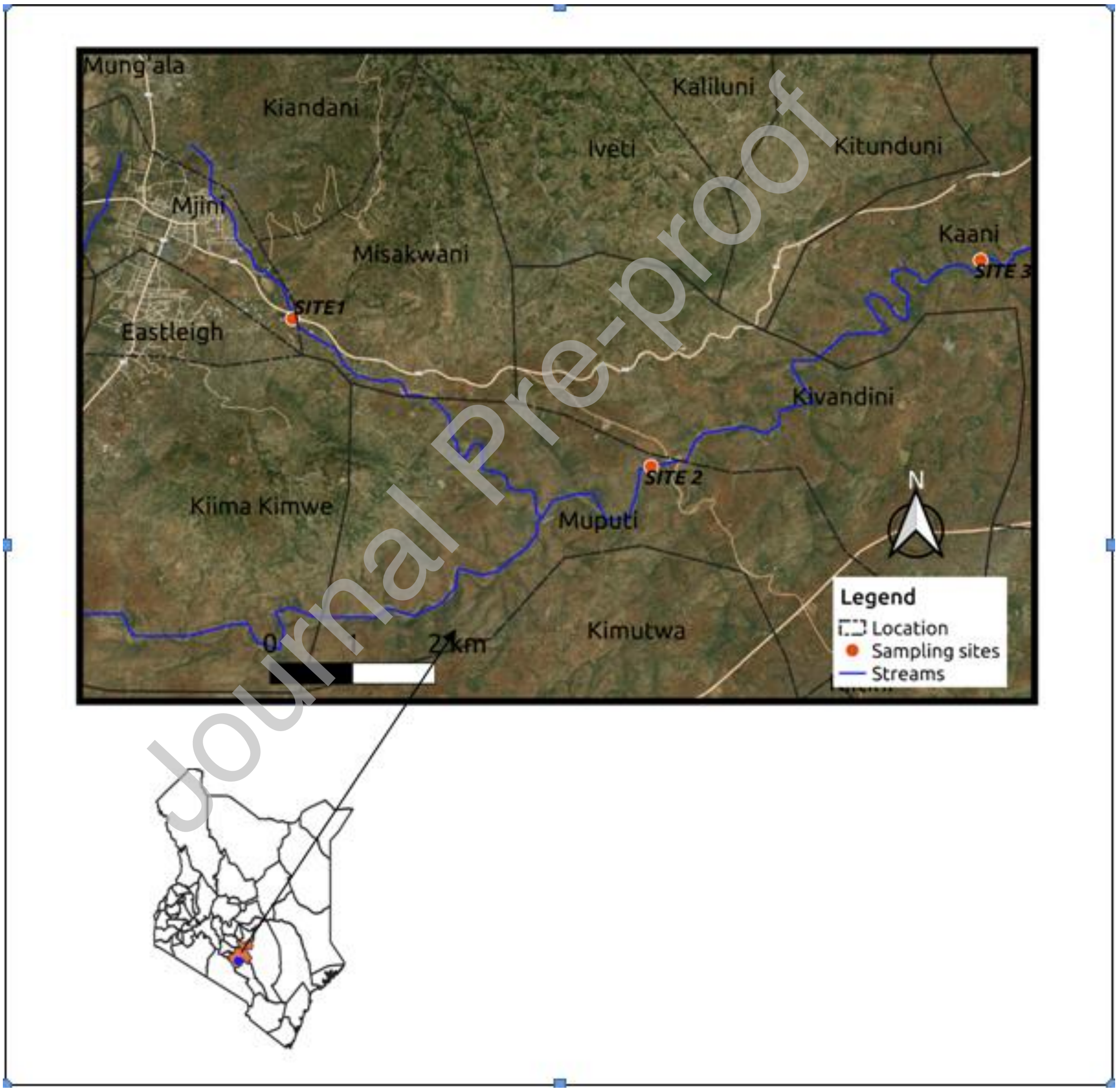

Figure 1: Location of the urban streams and sampling sites within Machakos municipality

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameters

The mean values of the physicochemical parameters of water obtained during the period of study are presented in Table 1. There were slight variations of pH values obtained from this study ranging from 7.5 to 8.45. The highest pH was recorded at site 1 and could be associated with domestic and municipal sewage effluent that flows directly into the site from surrounding residential areas. pH is a regulatory factor that ascertains the nature of ions present in surface water [15]. The pH values obtained in all the water samples were slightly alkaline hence as indicated by Badr *et al*., [6] improbable of health issues such as acidosis. The pH values were significantly different across the water sampling sites ($p \leq 0.05$). Post-hoc Tukey test showed that pH levels at each sampling site significantly varied from each other. pH values obtained in this study were lower than the pH values (5.43 - 9.34) recorded for Padma river, Bangladesh [16]. Temperature values ranged between 21.6 and 23.5 ºC. These temperature values majorly depend on the time of sampling and the season of sampling as the intensity of heat from the sun varies with time and season. There was no significant variation in temperature values in the different sampling sites ($p > 0.05$). Temperature values recorded in this study are similar to temperature values for river water in Bangladesh [16].

Table 1: Mean ±standard deviation of physicochemical parameters of water

Site/ Parameter	N	Site 1	Site 2	Site 3	WHO Limits	p-value
pH	5	8.45 ± 0.04^a	7.50 ± 0.20^b	7.91 ± 0.10^c	6.5-8.5	0.000
Temperature (^{0}C)	5	22.05 ± 1.29^a	23.05 ± 2.59^a	21.58 ± 3.47^a	-	0.988
TDS (mg/L)	5	865.83 ± 116.78^a	699.33 ± 202.60^a	577.5 ± 260.49^a	1000	0.204
EC (µS/cm)	5	1778.5 ± 102.17^a	1133.83 ± 474.22^a	864.83 ± 216.83^a	700	0.305

Means with different superscripts (a, b, c) in the same rows are significantly different at $p \leq 0.05$.

Total dissolved solids values (TDS) ranged from 577.5 to 865.8 mg/L and did not exceed the WHO acceptable limits. The highest TDS (865.83 ±116.7 mg/L) value was recorded at site 1 reflecting the effect of direct emission of untreated sewage into Iini stream at this site. Salts, engine oils, car battery acids and other solid wastes washed down into Iini stream from Machakos open-air garage and car washes around Iini stream could also contribute to the high TDS at site 1. The least value of TDS mean value was recorded at site 3 (577.5 ±260.49 mg/L). At site 3, Iini stream has joined with other streams forming larger Ikiwe River with more dilution of river water resulting in lower TDS values at this site. There was no significant difference in TDS across the sampling sites ($p > 0.05$). Electrical conductivity (EC) mean values were above WHO limits for natural water and ranged between 864.8 and 1778.5 µs/cm. This may be associated to both domestic and municipal effluents into the urban streams since the effluents contain dissolved salts. The study shows there is a correlation between conductivity and total dissolved solids; at site 1 where electrical conductivity was highest the value of total dissolved solids was also highest as the dissolved salts are responsible for the electrical conductivity of water. EC values obtained in the different sampling sites showed no significant difference ($p > 0.05$). The TDS and EC values obtained in this study were slightly higher than those recorded in Nairobi River of 176-438mg/L and 348-881µs/cm respectively [17].

3.2 Heavy metal concentration in water

The range for Cd, Cu, Pb, Zn and Cr heavy metal mean concentration in water in the different sampling sites were BDL - 0.0011, 0.0034 - 0.0055, 0.0012 - 0.007, 0.0232 - 0.1351, 0.0036 - 0.0292 mg/L respectively (Table 2). The mean heavy metal concentration in water generally varied in the order Zn> Cr> Pb > Cu>Cd. The levels of Cd in water ranged from BDL to 0.0011 mg/L with Cd having the least concentration in all the sampling sites. All were below WHO permissible limits for surface water in all the sampling sites hence the water was not contaminated with Cd and was thus safe for agricultural use. These values were lower than concentrations (0.0043 mg/L) detected in Nairobi River [2]. Additionally, Mohsin *et al.*, [18] recorded higher Cd concentration (0.02 – 0.39 mg/L) than Cd levels obtained in this study.
The average Cu concentration ranged from 0.0034 to 0.0055 mg/L with the highest value recorded at site 1. Natural weathering of rocks and discharges from industries and sewage treatment plants are some pathways through which copper is released to water [19]. The high concentration of copper at site 1 could be associated to erosion of minerals from rocks and soil and also due to fertilizers and pesticides that leached into the water from surrounding farms. The levels of Cu were lower than previous levels (1.29 - 0.727 mg/L) determined in river Chawalla, Nigeria [20]. Kacholi [21] also reported higher Cu values than those obtained in this study for wastewater in Dar es Salaam, Tanzania.

Table 2: Mean ± standard deviations of heavy metal mean concentration (mg/L) in water and WHO set limits [22]

Heavy metals in water	N	Site 1	Site2	Site 3	WHO Limit	p-value
Cd	5	0.0011±0.00	0.0005±0.00	BDL	0.003	0.395
Cu	5	0.0055±0.01	0.0037±0.01	0.0034±0.00	2.0	0.870
Pb	5	0.007±0.01	0.0012±0.00	0.0062±0.01	0.01	0.417
Zn	5	0.1351±0.12	0.0232±0.03	0.0637±0.10	3.0	0.210
Cr	5	0.0292±0.05	0.0072±0.01	0.0036±0.01	0.05	0.494

*BDL – Below Detectable Limit

The mean Pb concentrations varied between 0.0012 and 0.007 mg/L. Mean Pb levels obtained in this study were lower than WHO set limits for Pb in water indicating that the water in Iini and Ikiwe streams was not Pb contaminated. Pb in water samples could be emanating from metallic waste from Machakos open-air garage located next to Iini stream, sewage effluent released into the stream, petroleum products from the garage and airborne Pb deposition. Compared to other studies, Pb values obtained in this study were lower than those recorded in previous studies; Badr *et al*., [6] reported mean values (8.60 mg/L), 0.113mg/L of Pb was reported from Yucuambi river [23], Xiao *et al*., [24] reported 0.25 mg/L0.25 mg/L while Kacholi [21] recorded 0.46 - 0.55 mg/L from Temeke, Dar es Salaam.

Zn had the highest concentration in all the sampling sites ranging between 0.0232 and 0.1351 mg/L. Mean concentrations of Zn obtained were within WHO permissible limits. At site 1 where raw sewage drains into Iini stream, Zn had the highest concentration of 0.1351 mg/L and the raw sewage at site 1 explains the high level of zinc at that site. Higher values of Zn (2.0 – 13.7 mg/L) were detected in Bangladesh compared to Zn level values obtained in this study [13]. Comparable Zn values were reported in previous studies; (0.092 – 0.132 mg/L) were reported in study carried out in Masinga dam, Kenya [19], 0.99 – 1.26 mg/L detected in Temeke municipality in Dar es Salaam [21] and 0.34 – 1.85 mg/L recorded in Sahiwal district, Pakistan [18]. Zinc in river water could also be introduced naturally by the erosion of minerals from rocks and soil [25]. Additionally, other sources of Zinc could be burning of waste materials, steel products, leaching of fertilizers and municipal effluents released into the water.

The concentration of chromium ranged from 0.0036 to 0.0292 mg/L with the highest concentration of chromium being recorded at site 1, this could be associated with washing of motorbikes in Iini stream as some motorbikes are chrome plated and the Cr gets deposited in the water. Chromium levels obtained in this study were lower than those reported in previous studies; Njuguna *et al*., [2] detected 0.245 mg/L in Nairobi river, Xiao *et al*., [24] reported 5.13 mg/L in river water in Chinese Loess Plateau and Woldetsadik *et al*., [26] recorded 2.26 – 6.76 mg/L in Tinishu and Teleku Akaki rivers in Addis Ababa. Similar values (0 – 0.32 mg/L) to those obtained in this study were recorded in Cauvery River [27].

Generally, low concentration of heavy metals was observed at site 3 down at lower Ikiwe river. This could be associated to dilution factor of the water down at Ikiwe river as Iini stream joins with other streams forming the larger Ikiwe river. One Way ANOVA showed there was no significant variation ($p > 0.05$) in heavy metal concentrations in the different sampling sites. A comparison of mean heavy metal concentrations obtained in this study shows that the values are slightly lower compared to values obtained in a previous study carried out in Nairobi River which recorded values of Cd, Cr, Cu, Pb and Zn as 0.0043, 0.245, 0.00989, 0.158, 2.568 mg/L respectively [2]. Based on the results obtained, heavy metals are finding their way into the riverine systems raising a concern of degradation of water quality downstream the river systems.

3.3 Heavy metal concentration in soil

Table 3 shows heavy metal concentration values obtained during the period of study. For all the sampling sites, the concentrations were all below WHO set limits for heavy metals in agricultural soil. However, elevated levels of Cd, Pb, Zn, Cu and Cr were observed in soil compared to the concentration in water. This could be associated with continuous irrigation of agricultural land using polluted water. The mean values for Cd ranged from 0.0058±0.0101 to 0.0534±0.0419 mg/kg and were lower than WHO acceptable standards for Cd in soil indicating that the soil was not contaminated with Cd. Compared with the current study, a higher level of Cd (7.13 – 11.13 mg/kg) was found in the western region of Saudi Arabia in wastewater irrigated soil. Similar Cd

levels were reported in previous studies; 0.45 mg/kg in New Zealand, 0.185mg/kg in Europe and 0.11 mg/kg in Switzerland agricultural soils [28, 29,30].
The concentration of Cu in soil in this study ranged between 10.39 and 27.5 mg/kg with all the values found to be lower than the WHO permissible level of Cu in soil. This implied that the soil was not Cu polluted. Higher values for Cu in soil (40.961 mg/kg) were noted in Yangtze River Delta than the values of Cu in soil obtained in this study [31].
Concentration of Pb was between 4.23±3.71 and7.56±5.59 mg/kg all within WHO recommended standards in the different sampling sites. Similar results were obtained by Bett *et al*., [32] who recorded 5.00 ± 0.58 to 5.67 ± 0.88 mg/kg of Pb in soil in Kericho West sub-county, Kenya. Zn generally had the highest concentration in the soil samples (20.1 – 28.8 mg/kg) in the different sampling sites.
The level of Zn in soil determined in this study was lower than Zn levels (3.011 – 4.679 mg/kg) recorded in Embu, Kenya for wastewater irrigated soils [33]. Zn in soil could be associated with pesticides and fertilizers applied to the farm fields coupled with the Zn heavy metals in the wastewater used to irrigate the farms. Concentration of Cr in the study area ranged from 8.17±5.92 to 10.03±6.02mg/kg. These are values are lower compared to 30.67 - 172.75 mg/kg reported for wastewater irrigated soils in suburban areas of Varanasi India [34].

Table 3: Mean ± Standard deviations of heavy metal mean concentration in soil (mg/kg) and WHO set guidelines[26].

Heavy metals in soil	**N**	**Site 1**	**Site 2**	**Site 3**	**WHO Limit**	**p-value**
Cd	5	0.0534±0.04	0.0072±0.01	0.0058±0.01	3	0.051
Cu	5	10.39±4.72	27.4±43.0	27.5±27.7	100	0.624
Pb	5	7.56±5.59	8.35±5.91	4.23±3.71	84	0.581
Zn	5	28.0 ±31.7	28.8±23.9	20.1±19.4	300	0.894
Cr	5	10.03±6.02	9.99±4.95	8.17±5.92	30	0.319

There was no significant difference among the sampling sites for all the heavy metals studied ($p>0.05$). This may be due to the continuous uptake of heavy metals by the vegetables during their growth and development [7]. Generally, the concentration of heavy metals in soil in this area was lower than WHO safe limits implying that the soil was not contaminated with Cd, Cu, Pb, Zn or Cr and was safe for agricultural purposes. The order of magnitude of heavy metal concentration in soil (Zn>Cu>Cr>Pb>Cd) followed the same order as in irrigation water (Zn>Cr>Pb>Cu>Cd) except for Cu. Zn had the highest concentration in soil just like in water while Cd had the lowest concentration. It can thus be deduced that the contamination in the irrigation water could be contributing to the contamination in the soil.

3.4 Heavy metals in spinach and kale

The results of Cd, Cu, Pb, Zn and Cr mean concentration in the sampling sites for kale and spinach during the period of study are presented in table 4. The mean concentrations for Cd, Cu, Pb, Zn and Cr in all the sampling sites were 0.049, 7.453, 0.5127, 10.517 and 0.473 mg/kg respectively for spinach and 0.091, 1.933, 0.214, 15.337 and 0.842 mg/kg for kale respectively.

Table 4: Mean ± Standard deviations of heavy metals (mg/kg) concentrations in spinach and kale and WHO set limits [35]. BDL is below detectable limit

Heavy metals in spinach	N	Site 1	Site 2	Site 3	WHO Limit	p-value
Cd	5	BDL	0.0197±0.04	0.1285±0.12	0.20	0.154
Cu	5	4.79±6.77	14.5±11.55	3.07±3.65	10.00	0.063
Pb	5	0.622±0.88	0.28±0.625	0.636±0.93	0.30	0.547
Zn	5	11.80±16.70	9.05±9.11	10.7±18.60	5.00	0.786
Cr	5	BDL	1.002±2.19	0.416±0.50	0.30	0.432
Heavy metals in kale	**N**	**Site 1**	**Site 2**	**Site 3**	**WHO Limit**	**p-value**
Cd	5	0.243±0.33	0.0040±0.01	0.0250±0.043	0.20	0.038
Cu	5	1.29±1.820	3.60±3.74	0.909±1.57	10.00	0.336
Pb	5	BDL	0.184±0.27	0.458±0.52	0.300	0.868
Zn	5	12.06±11.90	15.15±10.08	18.8±32.60	5.00	0.835
Cr	5	BDL	0.906±1.35	1.62±2.80	0.30	0.411

The study indicated that mean concentrations of Cd in vegetables was within WHO safe limits except for Cd level in kale in site 1. This may be attributed to the raw sewage emitted directly into site 1. The results obtained in this study are comparable to those obtained for Cd (0.0017 mg/kg) in Zhejiang, China [36] but lower than those reported for Cd in spinach (0.9 – 71.7 mg/kg) in Kericho, Kenya [32].

The concentration of Cu in the vegetables ranged between 0.909 and 14.5 mg/kg in the three sampling sites. The mean concentrations were observed to be within WHO permissible limits for both kale and spinach except Cu in spinach in site 2. Fertilizers, pesticides and Cu in wastewater used to irrigate the spinach could explain the higher levels of Cu in spinach at site 2. Cu levels obtained in this study are similar to Cu levels in vegetables (4.08 – 13.9 mg/kg) presented in a study carried out in Lagos, Nigeria [37].

Pb in the three sampling sites ranged between 0.184 – 0.636 mg/kg. The mean concentration of Pb (0.214 mg/kg) was within WHO permissible limits (0.3 mg/kg) for kale but the mean concentration of Pb in spinach (0.513 mg/kg) exceeded WHO permissible limits. This was an indication that kale was safe for human consumption while Pb in spinach had health risks to the consumers. High levels of Pb have been reported to have toxic effects resulting in biochemical defects of some body organs such as the kidney, liver, lungs and the neurological system [38]. The high values were attributed to the sewage water used to irrigate the vegetables. Higher

values of Pb (5.44mg/kg) were reported in a previous study in leafy vegetables in Lagos, Nigeria [37]. Generally, Pb contaminations in vegetables can be due to contaminated soil, through sewage application or airborne deposition of Pb in highway traffic.
The highest Zn concentration recorded in sampled vegetables was 18.8 mg/kg while the lowest was 9.05 mg/kg. Zinc was abundant in all the sampling sites and was slightly exceeding WHO permissible limits. Zn is required as an essential element in the human diet to maintain the functioning of the immune system hence it's actively taken up by plants. However, high levels of zinc are associated with nausea, vomiting, diarrhea, gastrointestinal and hematological effects [39]. Similar values of Zn were recorded (12.5 – 18.55 mg/kg) in a previous study carried out in Yola and Kano for vegetables [40].
Chromium levels in sampled vegetables ranged between 0.416 and 1.62 mg/kg in the three sampling sites. Mean Cr levels in both spinach and kale exceeded WHO permissible limits (0.3 mg/kg) for human consumption implying that the spinach and kale were unsafe for human consumption with respect to Cr. Pan *et al.*, [36] recorded similar values (0.2 – 1.51 mg/kg) of Cr in leafy vegetable to the values obtained in this study.
Analysis of variance showed there were no significant differences in the level of heavy metals among the sampling sites as $p>0.05$. Similar studies have also reported that vegetables accumulate a considerable amount of heavy metals especially Pb, Zn, Cu and Cr all exceeding WHO limits in different vegetables [3,5]. The physicochemical characteristics of soil are bound to change due to the application of wastewater on the soil consequently leading to the uptake of heavy metals by vegetables grown on the soil [41]. Accumulation and transfer of Cu, Pb, Zn, Cr and Cd along the water-soil-plant food chain was evident as the wastewater contained low levels of the heavy metals while the vegetable samples showed higher values.

3.5 Transfer Factor

Transfer factor (TF) is one of the key components of human exposure to heavy metals through the food chain. The transfer factor signifies the amount of heavy metal in the soil that is transferred to the vegetable crop. Transfer factor in spinach for Cd, Cu, Pb, Zn and Cr were 2.2353, 0.3397, 0.0764, 0.4102 and 0.0503 respectively while in kale were 4.103, 0.0881, 0.0319, 0.5983 and 0.0896 respectively. The transfer factor trends in ranking order were Cd>Zn>Cu>Pb>Cr in Spinach and Cd>Zn>Cr>Cu>Pb in Kale. Cd had the highest transfer factor in spinach (2.2353) indicating a high accumulation of the metal by the vegetable while Cr had the lowest transfer factor in spinach (0.0503). Cd also had the highest TF in kale (4.103) with Pb having the least TF in kale (0.0319). From the results it's evident that vegetables are accumulating heavy metals from the soil where they are planted. Our study is in agreement with previous findings of TF reported in an industrial area in China [27].

3.6 Correlation Analysis of Heavy Metals in Water, Soil and Vegetables

Pearson correlation analysis results showing the relationship between heavy metal variables in water, soil and vegetables are presented in figure 2. A positive correlation was observed for heavy metal levels in water and those in soil ($r = 0.689$; $p = 0.188$). Concentration of heavy metals in water also showed a positive correlation with the levels in spinach ($r = 0.649$; $p = 0.236$). A significant positive correlation was observed between the levels of heavy metals in water and those in kale ($r = 0.987$; $p = 0.002$) and metals in spinach and those in the soil ($r = 0.962$; $p = 0.009$). The relationship between concentration of heavy metals in soil and that in kale indicated a positive correlation (r = 0.755; p = 0.140). A positive correlation was also observed between the level of heavy metals in spinach and that in kale (r = 0.746; p = 0.148). Positive correlation was also observed between the concentration of heavy metals in soil and concentration in vegetables in a study carried out in Varanasi, India [34].

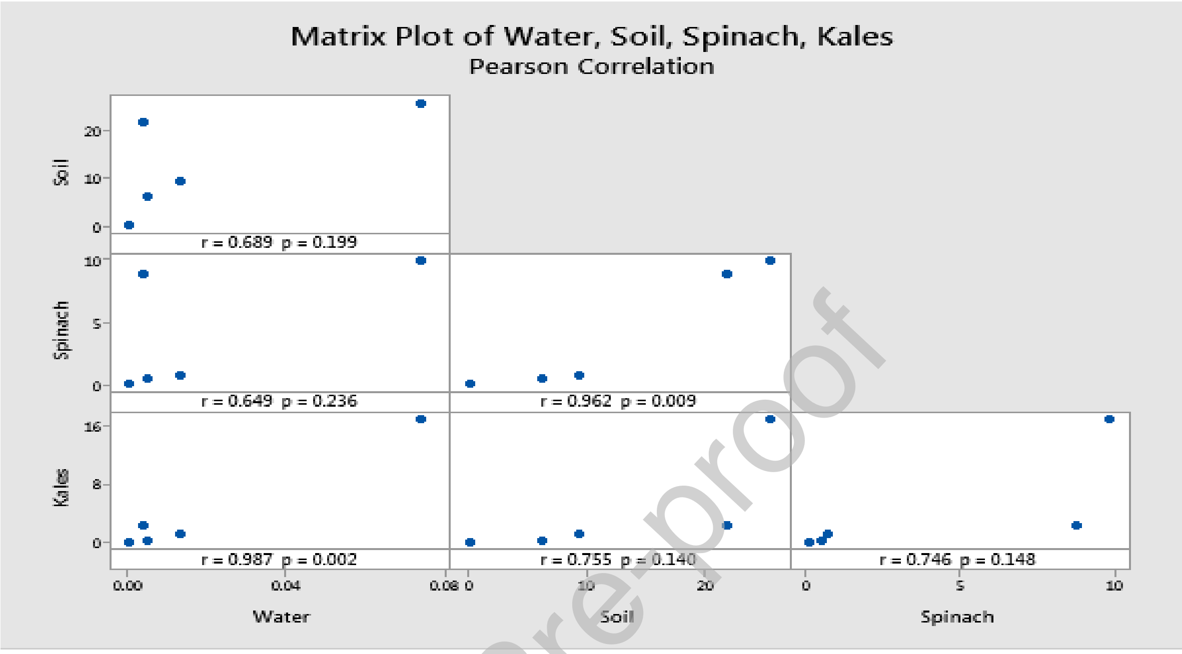

Figure 2: Pearson correlation matrix plot for heavy metals in water, soil, spinach and kale

Heavy metals that exhibited a considerable positive correlation may have originated from a similar source, have identical properties were influenced by related elements or could be mutually dependent [1,11]. Correlation between heavy metal concentration may suggest identical heavy metal accumulation properties in water, soil or vegetables [42]. In addition, physical and chemical processes occurring in the environment could also influence correlation of the heavy metals.

Conclusion and Recommendation

1) Physicochemical parameters temperature, pH and total dissolved solids were below the World Health Organization (WHO) acceptable limits for river water. Electrical conductivity was however above WHO acceptable limits indicating that the quality of water in the streams is deteriorating.
2) The concentration of heavy metals in the Iini and Ikiwe urban streams water and soil was within WHO permissible limits for surface water and agricultural soil thus safe for agricultural use. However, heavy metals showed a substantial build-up in soils than in the water.
3) Cd and Cu mean concentrations in spinach were within WHO safe limits for human consumption while Pb, Zn and Cr slightly exceeded WHO acceptable limits in spinach. On the one hand, mean values of Cd, Cu and Pb in kale were within WHO recommended limits while Zn and Cr exceeded WHO set limits. This poses a health risk to consumers of spinach and kale as they are exposed to unsafe levels of Pb, Zn and Cr.

4) Although wastewater irrigated vegetables were accumulating Cd, Cu, Pb, Zn and Cr from the wastewater and soil, the accumulation of Cd and Zn by the vegetables was higher. The mean transfer factors have indicated that wastewater irrigated vegetables were accumulating more Cd and Zn, from both the water and soil as compared to Cu, Pb and Cr.
5) Positive correlations were observed between the heavy metal concentrations in the water, soil and vegetables implying probable common sources of the heavy metals.
6) Machakos municipality requires a functional domestic and industrial effluent treatment plant, designed to engineering standards and operating based on best practices.
7) To reduce the accumulation of heavy metals in soil and vegetables calls for integrated approaches of monitoring, enforcement of compliance standards, and public education from key stakeholders including the National Environment Management Authority, Department of Public Health and Department of County Physical Planning.

Conflict of interest

The authors confirm there being no conflict of interest on this paper.

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Declaration of competing interest

The authors declare no known competing interest in this paper.

REFERENCES

[1] V. A. Makokha, Y. Qi, Y. Shen, and J. Wang, "Concentrations , Distribution , and Ecological Risk Assessment of Heavy Metals in the East Dongting and Honghu Lake , China," *Expo. Heal.*, vol. 8, no. 1, pp. 31–41, 2016.
[2] S. M. Njuguna, X. Yan, R. W. Gituru, Q. Wang, and J. Wang, "Assessment of macrophyte, heavy metal, and nutrient concentrations in the water of the Nairobi River, Kenya," *Environ. Monit. Assess.*, vol. 189, no. 9, 2017.
[3] M. H. H. Ali and K. M. Al-Qahtani, "Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets," *Egypt. J. Aquat. Res.*, vol. 38, no. 1, pp. 31–37, 2012.
[4] W. Feng, Z. Guo, C. Peng, X. Xiao, L.Shi, P. Zeng, H. Ran, "Atmospheric bulk deposition of heavy metal(loid)s in central south China: Fluxes, influencing factors and implication for paddy soils," *J. Hazard. Mater.*, vol. 371, no. August 2018, pp. 634–642, 2019.
[5] K. S. Balkhair and M. A. Ashraf, "Field accumulation risks of heavy metals in soil and vegetable crop irrigated with sewage water in western region of Saudi Arabia," *Saudi J.*

Biol. Sci., vol. 23, no. 1, pp. S32–S44, 2016.
[6] N. B. E. Badr, K. M. Al-qahtani, S. O. Alflaij, S. F. Al-qahtani, and M. A. Al-saad, "The effect of Industrial and Sewage discharges on the quality of receiving waters and human health , Riyadh City-Saudi Arabia," *Egypt. J. Aquat. Res.*, no. xxxx, 2020.
[7] N. Shaheen, N. M. Irfan, I. N. Khan, S. Islam, M. S. Islam, and M. K. Ahmed, "Presence of heavy metals in fruits and vegetables: Health risk implications in Bangladesh," *Chemosphere*, vol. 152, pp. 431–438, 2016.
[8] G. Chauhan and U. Chauhan, "Human health risk assessment of heavy metals via dietary intake of vegetables grown in wastewater," *Int. J. Sci. Res. Publ.*, vol. 4, no. 9, pp. 1–9, 2014.
[9] M. Harmanescu, L. M. Alda, D. M. Bordean, I. Gogoasa, and I. Gergen, "Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: Banat County, Romania," *Chem. Cent. J.*, vol. 5, no. 1, pp. 1–10, 2011.
[10] A. Mahmood and R. N. Malik, "Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan," *Arab. J. Chem.*, vol. 7, no. 1, pp. 91–99, 2014.
[11] F. Oghenebrorie and B. Chudy, "Natural radionuclides , heavy metals and health risk assessment in surface water of Nkalagu river dam with statistical analysis Natural radionuclides , heavy metals and health risk assessment in surface water of Nkalagu river dam with statistical analysis," *Sci. African*, vol. 8, no. June, p. e00439, 2020.
[12] Kenya Atlas, "Nairobi and its Environment," *A Burgeoning City*, vol. Chapter 5, pp. 145–160, 2007.
[13] M. Ahmed, M. Matsumoto, and K. Kurosawa, "Heavy Metal Contamination of Irrigation Water, Soil, and Vegetables in a Multi-industry District of Bangladesh," *Int. J. Environ. Res.*, vol. 12, no. 4, pp. 531–542, 2018.
[14] R. Nazir, M. Khan, M. Masab, "Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat," *J. Pharm. Sci. Res.*, vol. 7, no. 3, pp. 89–97, 2015.
[15] T. C. Ogwueleka and I. E. Christopher, "Hydrochemical interfaces and spatial assessment of Usuma River water quality in North-Central Nigeria," *Sci. African*, vol. 8, no. May, 2020.
[16] M. A. Haque, M. A. S. Jewel, and M. P. Sultana, "Assessment of physicochemical and bacteriological parameters in surface water of Padma River, Bangladesh," *Appl. Water Sci.*, vol. 9, no. 1, pp. 1–8, 2019.
[17] D. Mbui, E. Chebet, G. Kamau, and J. Kibet, "The state of water quality in Nairobi River, Kenya," *Asian J. Res. Chem.*, vol. 9, no. 11, p. 579, 2016.
[18] S. Mohsin, S. Andleeb, and A. Mahmood, "Ecological risk assessment of heavy metals in vegetables irrigated with groundwater and wastewater : The particular case of Sahiwal district in Ecological risk assessment of heavy metals in vegetables irrigated with groundwater and wastewater : The partic," *Agric. Water Manag.*, vol. 226, no. October, p. 105816, 2019.
[19] J. K. Nzeve, S. G. Njuguna, E. C. Kitur, "Assessment of Heavy Metal Contamination in surface water of Masinga Reservoir, Kenya," *J. Nat. Sci. Res.*, vol. 5, no. 2, pp. 101-108–108, 2015.
[20] M. H. Bichi and S. Dan'Azumi, "Industrial Pollution and Heavy Metals Profile of

Challawa River in Kano , Nigeria," *J. Appl. Sci. Environ. Sanit.*, vol. 5, no. 1, pp. 23–29, 2010.
[21] D. S. Kacholi, M. Sahu, "Levels and Health Risk Assessment of Heavy Metals in Soil , Water , and Vegetables of Dar es Salaam , Tanzania," vol. 2018, 2018.
[22] WHO, "Guidelines for Drinking-water Quality SECOND ADDENDUM TO THIRD EDITION WHO Library Cataloguing-in-Publication Data," pp. 17–19, 2008.
[23] M. Villa-Achupallas, D. Rosado, S. Aguilar, and M. D. Galindo-Riaño, "Water quality in the tropical Andes hotspot: The Yacuambi river (southeastern Ecuador)," *Sci. Total Environ.*, vol. 633, pp. 50–58, 2018.
[24] J. Xiao, L. Wang, L. Deng, and Z. Jin, "Characteristics, sources, water quality and health risk assessment of trace elements in river water and well water in the Chinese Loess Plateau," *Sci. Total Environ.*, vol. 650, pp. 2004–2012, 2019.
[25] G. of Saskatchewan, "Zinc (For Private Water and Health Regulated Public Water Supplies) How Does Zinc Get Into Water? How Can I Remove Zinc From My Drinking Water?," 2007.
[26] D. Woldetsadik, P. Drechsel, B. Keraita, F. Itanna, and H. Gebrekidan, "Heavy metal accumulation and health risk assessment in wastewater-irrigated urban vegetable farming sites of Addis Ababa, Ethiopia," *Int. J. Food Contam.*, vol. 4, no. 1, 2017.
[27] A. Begum, M. Ramaiah, Harikrishna, I. Khan, and K. Veena, "Heavy metal pollution and chemical profile of Cauvery river water," *E-Journal Chem.*, vol. 6, no. 1, pp. 47–52, 2009.
[28] E. Abraham, "Cadmium in New Zealand agricultural soils," *New Zeal. J. Agric. Res.*, vol. 63, no. 2, pp. 202–219, 2020.
[29] M. Birke, C. Reimann, U. Rauch, A. Ladenberger, A. Demetriades, F. Klingberg, K. Oorts, M. Gosar, E. Dineli, J. Halamic, "GEMAS: Cadmium distribution and its sources in agricultural and grazing land soil of Europe — Original data versus clr-transformed data," *J. Geochemical Explor.*, vol. 173, pp. 13–30, 2017.
[30] M. Bigalke, A. Ulrich, A. Rehmus, and A. Keller, "Accumulation of cadmium and uranium in arable soils in Switzerland," *Environ. Pollut.*, vol. 221, pp. 85–93, 2017.
[31] C. Mao, Y. Song, L. Chen, J. Ji, J. Li, X. Xuan, Z. Yang, G. Ayoko, R. Frost, F. Theiss, "Human health risks of heavy metals in paddy rice based on transfer characteristics of heavy metals from soil to rice," *Catena*, vol. 175, no. November 2017, pp. 339–348, 2019.
[32] L. Bett, O. Gilbert, W. Phanice, and S. Mule, "Determination of Some Heavy Metals in Soils and Vegetables Samples from Kericho West Sub-county, Kenya," *Chem. Sci. Int. J.*, vol. 28, no. 2, pp. 1–10, 2019.
[33] S. Sayo, J. M. Kiratu, and G. S. Nyamato, "Heavy metal concentrations in soil and vegetables irrigated with sewage effluent: A case study of Embu sewage treatment plant, Kenya," *Sci. African*, vol. 8, 2020.
[34] R. Kumar Sharma, M. Agrawal, and F. Marshall, "Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India," *Ecotoxicol. Environ. Saf.*, vol. 66, no. 2, pp. 258–266, 2007.
[35] C. Stan, "CODEX STAN 193-1995 Page 1 of 44," *Nat. Toxins*, 2009.
[36] X. Pan, P. Wu, and X. Jiang, "Levels and potential health risk of heavy metals in marketed vegetables in Zhejiang , China," *Nat. Publ. Gr.*, no. February, pp. 1–7, 2016.
[37] A. H. Adedokun, K. L. Njoku, M. O. Akinola, A. A. Adesuyi, and A. O. Jolaoso, "Potential human health risk assessment of heavy metals intake via consumption of some leafy vegetables obtained from four market in Lagos Metropolis, Nigeria," *J. Appl. Sci.*

Environ. Manag., vol. 20, no. 3, p. 530, 2016.

[38] F. Guerra, A. Ricardo Trevizam, T. Muraoka, N. Chaves Marcante, and S. Guidolin Canniatti-Brazaca, “Guerra et al. Heavy metals in food chain Heavy metals in vegetables and potential risk for human health,” *Sci. Agric.*, vol. 69, no. 1, pp. 54–60, 2012.

[39] K. Wei. Wong, C. K. Yap, R. Nulit, H. Omar, A. Z. Aris, W. H. Cheng, M. T. Latif, C. S. Leow, “Zn in vegetables: A review and some insights,” *Integr. Food, Nutr. Metab.*, vol. 6, no. 2, 2019.

[40] T. M. Chiroma and R. O. Ebewele, “Comparative Assessement Of Heavy Metal Levels In Soil, Vegetables And Urban Grey Waste Water Used For Irrigation In Yola And Kano,” *Int. Ref. J. Eng. Sci. ISSN*, vol. 3, no. 2, pp. 2319–183, 2014.

[41] R. P. Singh and M. Agrawal, “Variations in heavy metal accumulation, growth and yield of rice plants grown at different sewage sludge amendment rates,” *Ecotoxicol. Environ. Saf.*, vol. 73, no. 4, pp. 632–641, 2010.

[42] D. Xu, P. Zhou, J. Zhan, Y. Gao, C. Dou, and Q. Sun, “Assessment of trace metal bioavailability in garden soils and health risks via consumption of vegetables in the vicinity of Tongling mining area, China,” *Ecotoxicol. Environ. Saf.*, vol. 90, pp. 103–111, 2013.