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INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

International Journal of Current Research
Vol. 5, Issue, 06, pp.1571-1576, June, 2013

ISSN: 0975-833X

RESEARCH ARTICLE

HEAVY METAL CONCENTRATION IN WASTEWATER FROM CAR WASHING BAYS USED FOR AGRICULTURE IN THE TAMALE METROPOLIS, GHANA

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ARTICLE INFO

Article History:
Received 10th March, 2013
Received in revised form
14th April, 2013
Accepted 25th May, 2013
Published online 15th June, 2013

Key words:
Wastewater,
Heavy Metals,
Concentration,
Car Washing Bay.

ABSTRACT

Car washing generates a lot of wastewater into our environment which flows into our water bodies or drains into soils. Water from these water bodies or drains is mostly used for vegetable crop irrigation purposes in urban areas. The study assessed heavy metal concentration in wastewater from car washing bays in the Tamale Metropolis of Ghana. Wastewater samples from three (3) different washing bays were analyzed for presence and concentration of Zinc (Zn), Copper (Cu), Cadmium (Cd), Chromium (Cr), Lead (Pb), Iron (Fe) and Manganese (Mn). Results indicate that concentration levels of Cr (0.42 mg/l), Fe (4.97 mg/l), Pb (0.28 mg/l) and Mn (2.36 mg/l) in the samples were in high levels. Zn (0.18 mg/l), Cd (< 0.002 mg/l) and Cu (0.06 mg/l) however recorded lower limits of concentration. ANOVA of the heavy metals indicates a significant difference with F-probability value of 0.027. It was also observed that the concentration and occurrence of Fe and Mn are inter- related whilst Mn was also inter-related with Zn, Cu, Cd, Cr and Pb. The bio-accumulation of these heavy metals in the soil and also downstream effect of them need to be checked. The use of wastewater from car washing bays for crop irrigation should therefore be with extreme caution as a result of contamination.

INTRODUCTION

According to Tchobanoglous and Frank (1995), wastewater is said to be water which has been fouled by a variety of uses. As freshwater sources become scarcer, wastewater use has become an attractive option for conserving and expanding available water supplies. Wastewater use can have many types of applications, including irrigation of agricultural land, aquaculture, landscape irrigation, urban and industrial uses, recreational and environmental uses, and artificial groundwater recharge (Asano *et al*., 2007). Estimates on wastewater use worldwide indicate that about 20 million hectares or agricultural land is irrigated with (treated and untreated) wastewater (Jiménez and Asano, 2008). This study assessed the presence and concentration of heavy metals in wastewater from car washing bays in the Tamale Metropolis of Ghana.

MATERIALS AND METHODS

Study Area

The Tamale Metropolitan area is located at the centre of the Northern Region of Ghana. It occupies 750 km^2 which is 13% of the total area of the Northern Region. The population of Tamale Metropolis is said to be 371,351. In the Metropolis are several car washing bays and the wastewater from them are mostly used for irrigation of vegetable crops such as pepper, *amaranthus, chochorus*, etc.

Materials and Data Collection

Sample Collection Materials

- 1.5 litre sampling bottles were used to collect water for laboratory analysis.
- Permanent marker was used to label the bottles.
- Ice Chest,
- Ice
- Field notebook

Laboratory Materials

- Pipette,
- Measuring cylinder,
- Conical flasks and,
- Atomic Absorption Spectrophotometer (AAS),

Sample Collection Design

Samples were collected from three (3) different car washing bays in the Tamale Metropolis in December 2011 as in Table 1.

Sampling Procedure

- Samples of wastewater from car washing bay were collected directly into sample bottles.
- Bottles were filled to within two inches of the top to allow for thermal expansion.
- The samples were placed immediately into an ice chest with ice to maintain a 4°C environment until delivery to the laboratory.
- Samples were delivered within the shortest holding time of the water parameters needed to be analyzed.

Digestion of Wastewater Samples for Heavy Metals Determination

Wastewater samples were digested as follows.

- Wastewater sample of 100 cm^3 was transferred into a beaker and 5 ml concentrated HNO_3 added.

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Table 1. Locations of Sample Sources (Washing Bays)

Washing Bay	Sample	Location		
	Label	Latitude	Longitude	Elevation
Savanna Washing Bay	1	$09^{0}41^{1}892^{11}$ N	$08^{0}56^{1}431^{11}$ W	193 m
Under Way Washing Bay	2	$09^{0}44^{1}765^{11}$ N	$08^{0}45^{1}371^{11}$ W	153 m
Back to Life Washing Bay	3	$09^{0}41^{1}776^{11}$ N	$08^{0}29^{1}010^{11}$ W	173 m

- The beaker with the content was placed on a hot plate and evaporated down to about 20 ml.
- The beaker was allowed to cool and another 5 ml concentrated HNO_3 was added.
- The beaker was covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solution appeared light coloured and clear.
- The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove any insoluble materials that could clog the atomizer.
- The volume was adjusted to 100 cm^3 with distilled water as described by Ademoroti (1996).
- Determination of heavy metals in the wastewater samples was done using Atomic Absorption Spectrophotometer (AAS) AA6300 as described in the manufacturer's instruction manual.

METHODS

The levels of concentration of the various parameters were determined using the following methods.

Cadmium (Absorption Spectrophotometer Method)

1. 100 ml of acidified wastewater sample was mixed with 5 ml each of concentrated HNO_3 and concentrated H_2SO_4.
2. The mixture was heated until it was reduced to about 20 ml on hot plate.
3. The digested samples were cooled to room temperature, filtered through a 0.45 µm Whatman filter paper and the final volume adjusted to 100 ml with double distilled water and stored (APHA, 1998).
4. The concentration of cadmium was determined using flame Atomic Absorption Spectrophotometer (AAS) Shimadzu model AA 6300.

Lead (Atomic Absorption Spectrophotometer Method)

1. 10 – 3 mol/L Alizarin yellow GG was added to the samples and its pH was adjusted to 6 by the addition of 3 ml of the buffer solution.
2. 1 ml NaCl (0.1 M) and 7 ml CTAB solution (0.5 gm/L) were also added and the volume reached to 100 ml with freshwater.
3. The solution was maintained for 12 minutes to form complex and then transferred to a 100 ml separating funnel.
4. 12 ml of n-hexane was added to it. The funnel was stopped and vigorously shaken for 90 seconds, and then left to rest for 5 minutes to give a perfect floated layer in the aqueous/organic interface.
5. The floated layer was adsorbed on the inner walls of the funnel. By slowly opening the stopcock of the funnel, the aqueous phase was released in 5 minutes.
6. 2 ml pure methanol was added to the funnel and vigorously shaken again for few minutes to extract the lead.
7. The organic phase containing only the lead–alizarin complex was separated and its absorbance was measured at 364 nm against a reagent blank prepared in the same manner.

Iron (Ferrover Method)

1. A 25 ml cell was filled with the wastewater sample.
2. One Ferrover Iron Reagent Powder Pillow is added to the sample in the 25 ml cell and swirl to mix.
3. A 5 minutes reaction period of the mixture is allowed.
4. Another sample cell (the blank) of 25 ml is filled of the wastewater sample as a blank.
5. The blank is placed into the cell holder of the spectrophotometer for zeroing (0.00 mg/l).
6. After the zeroing the spectrophotometer, the 25 ml mixture in the cell is placed into the cell holder of the spectrophotometer and the iron reading is taken.

Copper (Bicinchoninate Method)

1. A 25 ml cell is filled with the wastewater sample.
2. One CuVer 1 Copper Reagent Powder pillow is added to the wastewater sample in the cell and swirl to mix.
3. The mixture is left for a period of 2 minutes for reaction to take place.
4. Another cell with 25 ml of the wastewater sample is filled and used as a blank.
5. The blank is placed into the cell holder of the spectrophotometer for zeroing (0.00mg/l).
6. After the zeroing the spectrophotometer, the 25 ml mixture in the cell is placed into the cell holder of the spectrophotometer and the copper reading is taken.

Manganese (Pan Method)

1. A 25 ml of demineralized water is poured into a cell as a blank.
2. Also, another 25 ml of sample is poured into another cell and one Ascorbic Acid powder pillow added to each cell and swirled to mix.
3. 1.0 ml of Alkaline Cyanide Reagent solution is added to the mixture in the cell and swirl to mix.
4. 1.0 ml of 0.01% PAN indicator solution is added to the mixture and swirl to mix; an orange colour develops in the sample if Manganese is present.
5. A 2 minute reaction period is allowed for the mixtures.
6. The blank is placed on the spectrophotometer for zeroing.
7. After the reaction period of the mixture, it is placed on the spectrophotometer and the readings of manganese taken.

Zinc (Zincon Method)

1. A 50 ml graduated mixing cylinder is filled with the wastewater sample.
2. The content of one Zincover 5 reagent powder pillow stopper is added. Invert several times to completely dissolve powder.
3. Measure 25 ml of the wastewater sample into cell (blank).
4. 1.0 ml of cyclohexanone is added to the remaining 25 ml solution in the cylinder.
5. Stopper the cylinder and shake for 30 seconds.
6. A reaction period of 3 minutes is observed.
7. Pour the solution from the cylinder into the sample cell.
8. After the 3 minutes, the blank is placed onto spectrophotometer for zeroing.
9. After the zeroing, the solution is placed on the spectrophotometer and the zinc reading.

Chromium (Absorption Spectrophotometer Method)

1. 5 ml of concentrated H_2SO_4 and 2.5 ml of concentrated HNO_3 are added to 100 ml of water sample and thoroughly shaken to get a homogeneous mixture.

2. 15 ml of 5 % (w/w) of $KMnO_4$ and 8 ml of 5 % (w/w) potassium per sulphate were added to the mixture and heated at 95 °C for 2 hours.
3. The mixture was then allowed to cool to room temperature and 6 ml of 12% (w/w) hydroxylamine hydrochloride were added to the resulting solution to reduce the excess permanganate.
4. The digested solution was stored for analysis (APHA, 1998).
5. Chromium was determined using a carrier solution containing 3% (v/v) HCl and a reducing agent 1.1% (m/v) $SnCl_2$ in 3% (v/v) HCl was added to digested sample to generate chromium vapour using flame Atomic Absorption Spectrophotometer (AAS) Shimadzu model AA 6300.

RESULTS AND DISCUSSIONS

Contamination of soils, groundwater, surface water and air with hazardous and toxic chemicals poses significant problems for both human health and the environment (Ansari and Malik, 2007). The study results indicate concentrations of Zn, Cd, Cu and Pb as being below the recommended maximum concentrations (RMC) as in Table 2.

Table 2. Heavy Metals Concentration in Water Samples and RMC

Sample ID	Zn mg/l	Cd mg/l	Cu mg/l	Pb mg/l	Cr mg/l	Fe mg/l	Mn mg/l
1	0.158	<0.002	0.018	0.209	0.511	8.933	4.204
2	0.132	<	0.027	0.214	0.343	4.930	1.816
3	0.249	<	0.127	0.423	0.406	1.073	1.073
RMC (FAO, 1992; WHO, 2006).	2.00	0.01	0.20	5.00	0.10	5.00	0.20

RMC= Recommended Maximum Concentration

The concentrations of Cr, Fe and Mn were however observed to be above the recommended maximum concentration (RMC). Also, Zn, Cd, and Cu concentrations fell below the Ghana EPA and WHO permissible limits (Table 3) of their release into the environment whereas Pb, Cr, Fe and Mn concentrations exceeded the Ghana EPA and WHO permissible limits.

Table 3. Ghana EPA and WHO Permissible Heavy Metals Concentrations in the Environment

Parameter (mg/l)	Recommended Limits	
	Ghana EPA (mg/l)	WHO (mg/l)
Manganese	-	0.4
Lead	0.1	0.01
Copper	-	2.0
Zinc	10	3.0
Iron	-	0.3
Cadmium	-	0.003
Chromium	0.1	0.2

Variation of Heavy Metals in Wastewater Samples

The analysis of the data of the concentration of the various heavy metals to determine variance among the parameters indicated a significant difference with F-probability value of 0.027. Fe recorded the highest mean level of 4.98 Mg/l whiles Cu on the other hand recorded the lowest, with a mean level of 0.06 Mg/l. Fe was significantly different from all the other heavy metals with the exception of Mn. However, concentration differences occurred among the remaining parameters (Cu, Zn, Pb, Cr, Mn,) but were not statistically significant. The occurrence of Fe was directly related to the occurrence of Mn and therefore not significantly different. Also, Mn did not vary significantly from the other heavy metals – Cr, Pb, Zn and Cu. Table 4 presents the ANOVA of the various heavy metal concentrations.

Table 4. ANOVA of Heavy Metal Concentration

Parameter (mg/l)	Means
Fe	4.98^{a}
Mn	2.36^{ab}
Cr	0.42^{b}
Pb	0.28^{b}
Zn	0.18^{b}
Cu	0.06^{b}
LSD	3.094
FP <0.05	0.027

Values with different superscripts ^{a} or ^{b} imply significant difference whiles common superscripts have no significant difference.

Concentration of Lead (Pb) in the Wastewater Samples

Lead concentrations recorded in the samples 1, 2 and 3 were 0.209 mg/l, 0.214 mg/l and 0.423 mg/l respectively. None of the samples recorded concentrations exceeding the recommended maximum concentration (RMC), (Table 2) for crop irrigation (FAO, 1992; WHO, 2006). However, samples recorded concentrations exceeding the Ghana EPA and WHO permissible limit (Table 3) of release of lead contaminated water into the environment. Sources of lead in the wastewater of car washes could be attributed to lead paints and car batteries (Divya *et al.*, 2012). From Figure 1, it is observed that sample 3 recorded the highest concentration as compared to samples 1 and 2 and this can be attributed to car engine washing at the site of sample 3. According to Pescod (1992), lead in irrigation water can inhibit plant cell growth at very high concentrations. Also in humans, lead accumulates in bones and teeth, where it has a biological half-life of 20 years. Although bones and teeth are not harmed, they function as reservoirs for releasing lead into the bloodstream where it then travels to target organs such as the brain. People with a calcium-deficient diet will accumulate more lead in their bones; this results in greater lead toxicity (Bradl, 2005). In aquatic ecosystems, lead bioconcentrates in the skin, bones, kidneys, and liver of fish rather than in muscle and does not biomagnify up the food chain. This makes lead less problematic via this route of exposure. When lead concentrations in algae exceed 500 ppb, enzymes needed for photosynthesis are inhibited (Taub, 2004).

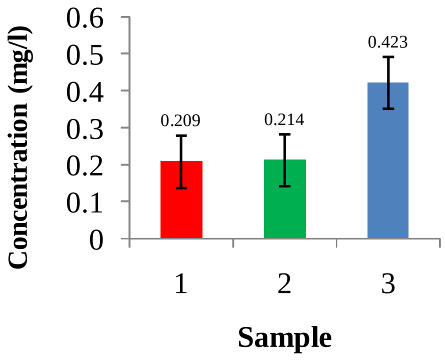

Figure 1. Concentration of Lead (Pb) in Wastewater samples

Concentration of Chromium (Cr) in Wastewater Samples

From the results, the concentrations of chromium in samples 1, 2 and 3 were 0.511 mg/l, 0.343 mg/l and 0.406 mg/l. Chromium concentrations in wastewater from all the samples exceeded the recommended maximum concentration (Table 2) for crop irrigation (FAO, 1992; WHO, 2006) and also the Ghana EPA's permissible limit (Table 3) of release of chromium into the environment. According to Gietka *et al.* (1994), chromium is a common metal surface coating. Therefore chromium was detected in the samples through the washing of chromium coated parts of cars like the car wheels and bumper at the various sample sources. Figure 2 is a graphical presentation of the chromium concentrations from the various samples. Chromium is one such toxic pollutant due to its harmful effects on human health, especially in its hexavalent form (Ting *et al*., 2010).

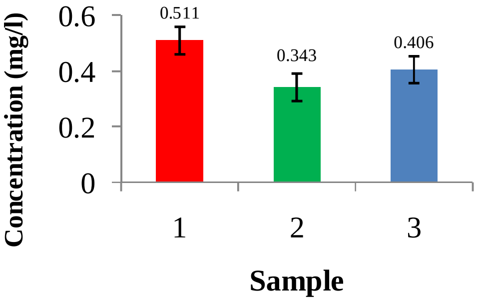

Figure 2. Concentration of Chromium (Cr) in Wastewater Samples

Concentration of Manganese (Mn) in Wastewater Samples

The results showed the concentrations of manganese in samples 1, 2 and 3 to be 4.204 mg/l, 1.816 mg/l and 1.073 mg/l respectively. These concentrations in the samples exceeded the recommended maximum concentration (RMC) (Table 2) for irrigation (WHO, 2006) as well as the Ghana EPA and WHO permissible limits (Table 3) of release into the environment. Metallic manganese (ferromanganese) is used principally in steel production along with cast iron and super-alloys to improve hardness, stiffness, and strength (HSDB, 1998). This makes manganese a component in iron alloys since it is used to improve iron stiffness, hardness and strength. Manganese concentrations in the wastewater samples will therefore increase with increase in iron concentration since manganese contained iron parts of cars were washed. Thorough washing of car engine block had the potential of releasing higher levels of manganese into the environment. It was also observed from the ANOVA that there were no significant difference between Fe and Mn indicating their co-usage in manufacturing of car parts. Figure 3 shows the concentrations of manganese in the observed samples. Toxic manganese concentrations in crop plant tissues vary widely, with critical values ranging from 100 to 5000 mg/kg (Hannam and Ohki, 1988). Also, in aquatic environments, manganese can induce iron deficiency in some algae, notably blue-green algae, and this can lead to inhibition of chlorophyll synthesis (Csatorday *et al*., 1984).

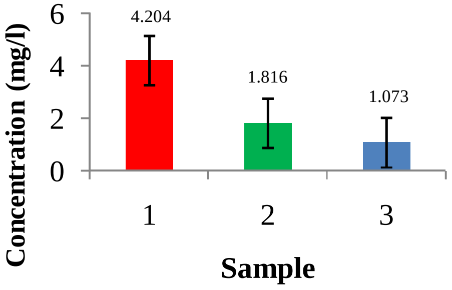

Figure 3. Concentration of Manganese in Wastewater Samples

Concentration of Iron (Fe) in Wastewater Samples

Concentrations of iron in the samples 1, 2 and 3 were 8.933 mg/l, 4.930 mg/l and 6.898 mg/l respectively. Iron concentrations in samples 1 and 3 exceeded the recommended maximum concentration (RMC) (Table 2) for irrigation (FAO, 1996; WHO, 2006) whereas sample 2, it fell slightly below the recommended maximum concentration but was observed to be very high. The sample concentration of iron can therefore be said to be high for crop irrigation purposes in the area. Also, iron concentrations in the samples exceeded the Ghana EPA and WHO permissible limits (Table 3) of release into the environment. Parts of cars commonly made of iron included engine block, intake manifold, brake drums and rotors, etc. Iron was therefore detected in the wastewater samples through the washing of car engines at the various sample sources. Comparing the concentration of iron in the samples, the highest concentration was recorded in sample 1 as shown in Figure 4. According to Ayers and Westcot (1985), high concentration of iron in wastewater contributes to soil acidification and loss of availability of phosphorus and molybdenum when applied to the soil. Wastewater from samples will therefore increase soil acidity and diminish phosphorous in soil when applied.

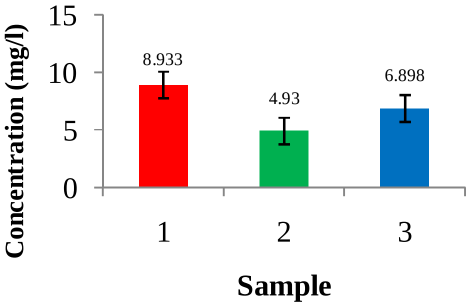

Figure 4. Concentration iron (Fe) in Wastewater Samples

Concentration of Copper (Cu) in Wastewater Samples

The results showed the concentration of the copper metal in samples 1, 2 and 3 to be 0.018 mg/l, 0.027 mg/l and 0.127 mg/l respectively. Concentrations of copper in the samples were below the Ghana EPA and WHO permissible limits (Table 3) of release into the environment. Copper concentration levels in the wastewater are therefore not toxic to the environment. Also, comparing the concentrations of copper in the various samples to the recommended maximum concentration (RMC) (Table 2) for irrigation (FAO, 1996; WHO, 2006), the concentrations in all the samples fell below the RMC, rendering the wastewater from the sample sources low in copper toxicity. However, when copper, cadmium, zinc, lead, mercury, arsenic, chromium, nickel and manganese accumulate in the soil over long times, they reduce food quality and quantity. A high heavy metals load in the soil reduces the functioning of soil biota resulting in reduced microbial activity (Kandeler *et al.*, 1999). At concentrations slightly above those required as a micronutrient, copper becomes toxic, especially to the larval stages of marine invertebrates. A single copper fitting in a seawater system may destroy most invertebrate embryos (Strathman, 1987). Copper does not break down in the environment and therefore can accumulate in plants and animals when it is found in soils. According to Metcalf and Eddy (2003), Copper may be present in wastewaters from a variety of chemical manufacturing processes employing copper salts or a copper catalyst in different range from 0.12 mg/l to 183 mg/l such as mining acid, mine drainage, paint and pigment manufacturing and motor vehicles.

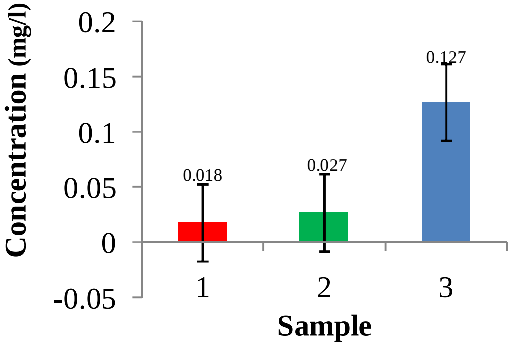

Figure 5. Concentration of Copper in Wastewater Samples

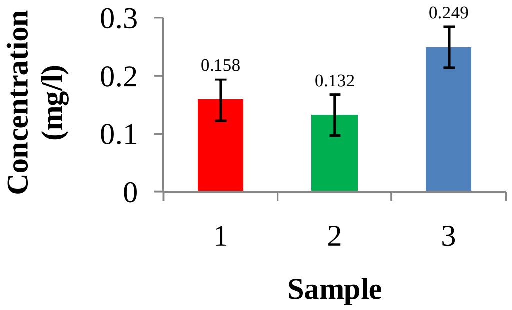

Figure 6. Concentration of Zinc (Zn) in Wastewater Samples

Concentration of Zinc (Zn) in the Wastewater Samples

The results show that the Zn concentrations in the samples 1, 2 and 3 are 0.158 mg/l, 0.132 mg/l and 0.249 mg/l respectively. Though sample 3 recorded the highest concentration than that of samples 1 and 2 (Figure 6), it was below the recommended maximum concentration (RMC) (Table 2) for irrigation (FAO, 1992; WHO, 2006) and also below the Ghana EPA and WHO permissible limits (Table 3) of release into the environment. Zinc contained in wastewater of car wash may have their source as from metal working, surface treatments, paint and varnish manufacturing, transport (brakes, wheels, and asphalt) and galvanized surfaces (Annon, 2011). Zinc toxicity in wastewater from the sample sources is therefore very low. Although zinc is an essential element to plants, animals and man, very high concentrations of zinc is very toxic, hence harmful to the body. The toxicity of zinc is due to having cadmium as an impurity. It causes phytotoxicity (Essumang *et al*., 2008). This indicates that increased cadmium concentration increases zinc concentration and toxicity. It is also evident in the results that very little cadmium was detected in the samples hence zinc toxicity is low. However, the high concentration of zinc recorded in sample 3 can be attributed to washing of more car wheels at the sample source. Risk analyses that have been conducted on aquatic and soil environments conclude that present-day zinc levels do not pose a risk to the environment (van Assche *et al*., 1996).

Concentration of Cadmium (Cd) in Wastewater Samples

Cadmium was not detected in samples 2 and 3 with a negligible concentration of < 0.002 mg/l being recorded in sample 1. Concentration recorded in sample 1 fell below the recommended maximum concentration (RMC) (Table 2) for irrigation (FAO, 1992; WHO, 2006) and thus below the Ghana EPA and WHO permissible limits (Table 3) of release into the environment. According to Townshend (1995), cadmium is a rare element and is derived exclusively from zinc ores. The non-detection of cadmium in samples 2 and 3 could be attributed to the scarcity of the cadmium metal hence the lower probability of using it in the manufacturing of vehicle parts. Cadmium recycling has been practical only for Ni-Cd batteries, some alloys, and dust from electric arc furnaces (Kuck and Plachy, 1996). The presence of cadmium in sample 1 could be attributed to the washing of Ni-Cd batteries. Also, zinc containing materials can contain cadmium. Cadmium substances from the road dust are attached to the surface of the car and transferred to the car wash centers. Cadmium can also be present in the petroleum fuel used in cars (Annon, 2011). Once in the soil, cadmium is relatively immobile and as a surface derived contaminant, it accumulates in the surface layer. Here it poses a great risk to the ecosystem, as plant cadmium concentrations have been found to increase with increase in soil cadmium concentrations, this accumulation of cadmium may overtime increase the flow of cadmium through the food chain (Zanders, 1996). Cadmium effects on aquatic organisms are analogous to those in humans, and include skeletal deformities and impaired functioning of kidneys in fish. Cadmium is more toxic in freshwater than in saltwater because cadmium combines with chlorides in saltwater to form a molecule that is less available from solution (Bradl, 2005).

Conclusion

Average zinc and copper concentrations of the samples were observed to be below the RMC and EPA Ghana and WHO limits. Lead was however below the RMC but above the EPA Ghana and the WHO levels of wastewater released into the environment. Chromium and manganese recorded average levels above the RMC, EPA Ghana and WHO levels. Average iron concentration was above the WHO recommended environmental release level but slightly below the RMC level. An inter-occurrence relationship was observed for iron and manganese and also manganese, chromium, lead, zinc and copper. Bio-accumulation of these heavy metals is likely to lead to very high toxicity levels especially in the immediate environment of the car washes. Irrigation of crops as its being currently practiced also poses a health risk as a result of bio-accumulation as well as a direct effect on the growth performance of the crops themselves.

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