ASSESSMENT OF HEAVY METALS, pH AND EC IN EFFLUENT RUN-OFF, RIVER AND ADJACENT SOIL AROUND A FLORICULTURE INDUSTRY IN HOLETA, WELMERA DISTRICT, ETHIOPIA

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Abstract

Heavy metal contents from effluent run-off, neighboring Holeta River, and adjacent soils around floriculture greenhouses in Holeta town, Ethiopia were determined using Atomic Absorption Spectrophotometer (AAS) to assess their potentialities as pollutants. Samples were taken from four sites for the effluent, two river bank locations and two soil locations about 10 meters apart. The evaluated metals were Cu, Fe, Ni, Mn, Cr, Zn, Cd, Co, and Aq. The pH, EC, TDS, DO were determined in the effluent, river and soil samples while particle size and total carbon contents were determined in the soil sample. Results showed that levels of heavy metals were higher in the soil sample than in the effluent and river samples. The metal concentrations ranged from 5.6-1309 mg/kg in soil, 0.31-3.43 mg/L in the river sample and 0.09-0.93 mg/L in the effluent. Highest concentration of Fe (1309 mg/kg), Ni (132 mg/kg), Mn (129 mg/kg), Cu (78 mg/kg), Cd (28.5 mg/kg), Co (5.6 mg/kg) and Zn (0.52 mg/kg) were recorded for the soil samples. These values were above permissible levels for agricultural soils. The findings reveal that the effluent and river samples contained low levels of heavy metals, but the high heavy metal concentrations in the soil could seriously influence soil characteristics by contaminating the soil. Since scanty information is available on the impact of floriculture effluent on agricultural soil in this region, the result of this work could provide baseline data for future monitoring of pollution from the floriculture enterprises **Key words:** Heavy metals, AAS, contamination, floriculture and effluents.

Introduction

Metals and in particular trace metals are a major class of contaminant in our present world principally arising from natural and anthropogenic sources. The anthropogenic sources are primarily from industrialization and mining activities which are of paramount importance ecosystem sustainability to (Adriano, 2001). Contamination of heavy metals in the environment has become a major concern because of their toxicity and threat to human life and the environment (Ma and Rao, 1997). Trace metals can be regarded as common pollutants and the level of these metals in the environment has increased tremendously in the last decades as a result of human inputs and activities (Merian, 1991; O'Neil, 1993).

The cut-flower industry is a short-cycle production process that requires the extensive use of agrochemicals (fertilizers and pesticides), which have a negative effect on the soil and water supply. These agrochemicals leave residues such as heavy metals and organic compounds which pose health risks to humans and hazardous ecological risks to plants, animals and microorganisms. Studies on heavy metals contents in rivers, soils and discharges from the industry have been a primary environmental focus especially in the last decades, due to their health implications (Klavins *et al.*, 2000; Grosheva *et al.*, 2000).

The presence of these metals in aquatic far-reaching ecosystem has implications directly to the biota and indirectly to man. Cadmium has been reported to have carcinogenic effects in humans leading to chronic kidney dysfunction (Goering et al., 1994), and its main source includes wastes from Cd-based batteries incinerators and phosphate fertilizers (Stoeppler, 1991). Heavy metals such as Fe, Mn, Cr, Ag etc of which many are known as essential elements for growth, but almost all become phytotoxic at higher concentration and cause considerable amount of

 ¹Dept of Chemical Sciences, Cross River University of Technology, Calabar, Nigeria
²Wollega University, Department of Chemistry, P. O. Box 416, Nekemte, Ethiopia.
*Corresponding autor: louattah@yahoo.com environmental degradation and ecological damage to water, air and soil (Nesa and Azad, 2008).

In Ethiopia, floriculture as an industry is only a decade old but has expanded from two in 2000 to 85 industries in 2011 (Hortiflora Magazine, 2011). This level of production has promoted Ethiopia as the second-largest producer of roses in Africa next to Kenya and sixth in the world after Holland, Colombia, Ecuador, Kenya and Israel (Getu, 2009). The industry is blamed for using too much chemicals which damage the environment through its discharge (Sisay, 2007). The production uses more than 300 chemicals as pesticides and growth regulators, which kills useful organisms in the soil and disturbs the biodiversity. Getu (2009) confirmed that intensive chemical fertilizers and pesticides that are frequently applied to produce a quality rose resulted in the negative impact on the environment.

Although detailed research on floriculture effluent is scant, studies have shown the impact of industrial effluents and municipal wastes on soil quality. Osibaizo and Addie (2007) have reported on the impact of effluent from Bodija abattoir on the physico-chemical parameters of stream in Ibadan, Nigeria. The influence of pharmaceutical effluent on some soil properties and early growth of maize have been reported by Osiago et al. (2006). Cobalt is regarded as an essential element but there is a wide margin of safety between toxic levels and nutritional requirement levels (Awofolu et al., 2005). Recently, Kebede et al. (2012) have studied the influence of floriculture effluent on the soil quality and dry matter yield of wheat versitols at Debrezeit, Ethiopia and found that it affected the performance of wheat and soil quality parameters,. Fayad et al. (2013) have reported the content level of heavy metal pollution in samples taken from Ishaqi river bank and adjacent agricultural soil.

Holeta town is one of the industrial zones in Welmera district, Ethiopia, which has seen an upsurge in floriculture activities in recent years with extensive use of fertilizers and pesticides in the industry. The effluent from the flower industry is discharged into a channel that flows through agricultural farmland into the river Holeta.

The purpose of this study was to determine the levels of heavy metals (Cd, Zn, Co, Cu, Ni, Fe, Mn, Cr, and Ag) in the effluent run-off, river and the adjacent soil around the floriculture industry in Holeta Town, Welmera district in Ethiopia and assess their potentials as pollutants.

Methodology

Study Area

The two floriculture greenhouses used in this study are located at Holeta Town in Welmera district, west of Addis Ababa, the capital city of Ethiopia. This study was conducted in Holeta Town, Welmere district, West Shoa Zone (Figure 1). The district is characterized by its proximity (35 km) to Addis Ababa, latitude of 09°02 North, longitude of 38°34 East and altitudes which ranges from 2060 to 3380 m.a.s.l. Topographically, it is characterized by dissected plateaus, mountains, plains and valleys. The agroclimatic zone of the district are high land (Dega) 41%, middle land (Woyna Dega) 59% with average highest temperature 21°C and average lowest temperature 1.7°C and annual rain fall of 900-1100 mm having a bimodal rain fall pattern. Welmera receives highest rainfall which is observed in July and August (EMA, 2006).

The geology of the study area is younger volcanic of trachy-basalt, trachytes, ignimbrites and tuff belonging to the Wechecha Mountain ranges (Tadesse, 2004). The dominant soil groups of the study district are Chromic and Orthic Luvisols (90.3%), and chormic and pellic Vertisols (9.7%). The Vertisol is heavy and sticky when wet and hard when dry. The major land use and land cover types of the watershed are agriculture land, forest. pastureland, settlement, water bodies and barren land.

Sampling sites

The floriculture greenhouses labeled F1 and F2, sampling sites for effluents labeled E1, E2, E3 and E4, river bank water (R1 and R2) and soil (S1and S2).

Sample Collection and Preparation

Effluent and river bank water samples were collected in sealed plastic bottles which have been thoroughly washed with detergent, rinsed with distilled water, soaked in 5% HNO₃ for about 24 hours and finally rinsed with doubly distilled water. Effluents E1 and E2 were collected from the outlet drain of the floriculture enterprise while E3 and E4 were collected just before the outflow of the drain into River Holeta. River bank water (R1 and R2) were collected a few meters away from the

points where the effluent drainage empties into the river.

Soil samples labeled S1 and S2 were collected from 15 m away from the floriculture enterprises using a stainless steel plated auger soil probe at depth ranging from top soil up to 20 cm. For each soil sample, twelve composite soil samples were randomly collected from approximately two hectares for each sample (S1 and S2)., manually mixed, air dried, ground in a mortar and pestle and sieved through a 75 μ m pore sieve.



Figure1 The location map of study area

Chemical Analysis

The pH, temperature, TDS, DO and EC were determined in the effluent, river and soil samples, while texture and total carbon content were determined in the soil sample using standard methods (APHA, 2005). Soil texture was determined by hydrometer method (Gee and Or, 2002). The soil pH was potentiometrically measured in the supernatant suspension of a 1:2.5 soil to water ratio using the glass electrode in VWR Scientific Model

2000 pH meter (Rayment and Higginson, 1992) while the electrical conductivity (EC) was measured in 1:5 soil to water ratio using a Model 4310 Conductivity meter. Organic carbon was determined using Walkley-Black oxidation method (Allison, 1965).

The samples were prepared for metal analysis following the standard procedures described by Pinta (1975) using Atomic Absorption Spectrophotometer (PerkinElmer Double Beam AAS model SL-194, USA).

Statistical Analysis

Mean values are reported from five sample $(n=5) \pm SD$.

Results and Discussion *Effluent, River and Soil Properties*

The main effluents and river properties are shown in Table 1 while the soil properties are presented in Table 2. The results indicated that both the effluent and the river were mildly acidic to neutral. The mean concentrations of total dissolved solid (TDS), dissolved oxygen (DO) and electrical conductivity (EC) were 193.75 mgl⁻¹, 3.32 mgl⁻¹ and 298 μ Scm⁻¹ in the effluent while that of the river were 173 mgl⁻¹, 5.0 mgl⁻¹ and 265 μ Scm⁻¹ respectively. The depletion of oxygen in the water system is due to high content of nutrients and low dissolved oxygen shows the decomposition of the aquatic body (Wang *et al.*, 2007).

The soils were generally silt- clay with fine textures. The pH was neutral and the organic carbon (OC) and EC were generally low. The mean value for the carbon content was 2.01% while that for EC was 440 µScm⁻¹. According to Patterson (1999), any effluent having pH and higher than 7.0 and 1000 μ Scm⁻¹ EC respectively could affect the physico-chemical properties of soil. In this work, the pH was neutral and the EC was lower in the effluents and therefore will not affect the soil properties. The chemical compositions of the effluent in this work are similar to that reported by Getu, (2009) and Babyshakilla (2009) using effluents from different industries.

Table 1 Characteristics of effluent and river samples

Sample	pН	Temp (⁰ C)	TDS (mgl ⁻¹)	DO (mgl ⁻¹)	$EC(\mu Scm^{-1})$
E2	7.0	18.8	211	3.37	325
E3	6.9	18.9	178	4.15	274
E4	7.3	19.4	205	3.25	315
R1	6.9	19.4	176	4.22	270
R2	7.0	19.5	171	5.79	263

Table 2 Characteristics of the soil samples

Sample	% Texture			pН	OC	EC	
-	Sand	Silt	Clay	_	%	(μScm^{-1})	
S1	12.98	22.3	64.72	6.7	1.83	423	
S2	27.28	18.0	54.72	7.1	2.18	458	

Heavy Metals Content in Effluent, River and Soil

The result of heavy metal contents of effluent run-off (E1 E2, E3 and E4), river (R1 and R2) and soil (S1 and S2) are shown in 2-4 respectively. Heavy Figures metal concentrations in E1 ranged from 0.02-1.04 mgl⁻¹ with the highest concentration found in Zn and the lowest concentration found in Ag. Metal concentrations in E2 ranged from 0.19-0.89 mgl⁻¹ with the highest concentration recorded in Zn and the lowest concentration found in Cd. In effluent E3, metal concentration ranged from 0.14-0.77 mgl⁻¹ with the highest concentration recorded by Ni and the lowest

concentration found in Cd. In E4, metal concentration ranged from 0.13-0.70 mgl⁻¹ with the highest concentration found in Zn and the lowest in Cd. The concentration of all metals decreased from effluent E1 to E4 except for Fe which was highest in E3. The mean values of the elements followed the sequence: Zn > Fe>Ni>Cr>Mn>Cu>Cd>Co>Ag.

In the river sample, R1, metal concentration ranged from $0.18-0.91 \text{ mgl}^{-1}$ with the highest concentration found in Zn and the lowest concentration found in Cd. For the river water (R2), the concentration of the metals ranged from $0.37-0.3.4 \text{ mgl}^{-1}$. The highest concentration was found in Ni while the lowest

concentration was found in Cu. Concentrations of Cu, Fe, Ni, Cr and Mn were found to increase in R2 while Zn concentration was similar in both river samples was found to increase in R2. The mean values in R2 followed the sequence:

Ni>Co>Fe>Zn=Cd.>Mn>.Cr>Ag>Cu.

In soils, the concentration of the metals ranged from 6.38-156 mg/kg in S1 with the highest concentration recorded for Mn and Cr and the lowest concentration recorded for Co. In S2, the metal concentration ranged from 4.82- 228 mg/kg with the highest concentration recorded for Mn and the lowest recorded for Co. Concentrations of Cu, Ni, and Mn increased in S2 while Zn, Cd and Co concentrations were decreased. The mean values of the elements followed the sequence: Fe>Mn=Cr>Ni>Zn>Cu>Cd>Co. Ag was not detected in both soil samples.



Figure 2 Heavy metal contents in effluent samples



Figure 3 Heavy metal contents in Holeta River bank samples



Figure 4 Heavy metal contents in soil samples

Metal	Soil	River	Effluent	*Permissible level in
	(mg/kg)	(mgl^{-1})	(mgl^{-1})	agricultural soil
				(mg/kg)
Cu	78±0.004	0.31±0/002	0.37±0.002	5-60
Fe	1309±0.011	0.75 ± 0.005	0.93±0.006	0.3-10
Ni	132±0.009	3.43 ± 0.007	0.69 ± 0.006	100
Mn	142±0.009	0.42 ± 0.006	0.35±0.003	64
Cr	129±0.010	0.37 ± 0.003	0.47±0.001	100
Zn	52±0.012	0.42±0.010	0.87 ± 0.007	<50
Cd	28.5±0.008	0.56 ± 0.007	0.13±0.005	1.4
Co	5.6±0.015	1.69 ± 0.003	0.02±0.001	4.1-140
Ag	ND	0.41±0.003	0.005 ± 0.001	
• (CCME (1999)			

Table 3 Means and standard deviations of heavy metal concentration in effluent, river and soil

Comparison of mean concentrations of heavy metal contents in effluent, river and soil samples

The mean concentrations of heavy metals in effluent, river and soil are presented in Table 3. *Copper (Cu)*

The Cu content in the soil sample was higher than that of the river sample and the effluent. Cu content in the adjacent soil ranged from 69 to 93 mg/kg with mean concentration of 78 mg/kg, 0.25 to 0.37mgl⁻¹ in the river, with mean concentration of 0.31mgl⁻¹ and 0.28 to 0.47mgl⁻¹ in the effluent with mean concentration of 0.37mgl⁻¹. The increase in level of Cu in soil and its decrease in effluent

may be due to the retention of metal ions in soil. Cu content of agricultural soil is 5-50mg/kg. In this study, the mean Cu content (78mg/kg) was higher than the permissible level (CCME, 2007).

Iron (Fe) and Manganese (Mn)

Fe content was higher in the adjacent soil than in both river and effluent. Fe content in the soil ranged from 1185 to 1419 mg/kg with the mean value of 1309 mg/kg, 0.47 to 1.04mgl⁻¹ in the river sample with a mean value of 0.75mgl⁻¹ and 0.75 to 1.11mgl⁻¹ in the effluent with a mean value of 0.93mgl⁻¹. The high Fe content in the soil could be attributed to adsorption of the metal while dilution may be responsible for the

lowest value in the river sample. The soil sample recorded the highest Mn content than both effluent and river samples. The Mn concentration ranged from 0.07-0.62 mgl⁻¹ in the effluent, with a mean value of 0.35 mgl⁻¹, in the river sample it ranged from 0.31 to 0.55mgl⁻¹ with a mean value of 0.42 mgl⁻¹ and 128 to 156 mg/kg in the adjacent soil sample with a mean value of 142 mg/kg.

general, the soil Fe In and Mn concentrations are not reported in studies focusing on soil heavy metal content because they are not contaminant elements. Both metals are important in plant nutrition as they are essential crop nutrients. These elements can be in insoluble forms on calcareous soils causing deficiencies (e.g. ferric chlorosis). In spite of elevated soil content in this work, total Fe and Mn concentrations are not good indicators of their plant availability.

Nickel (Ni)

Ni content was highest in soil sample than river and effluent. In the soil samples, Ni content ranged from 81 to 183 mg/kg with a mean concentration of 132 mg/kg, while in the effluent it ranged from 0.61 to 0.77mgl⁻¹ with a mean concentration of 0.69 mgl⁻¹ and for the river sample it ranged from ND to 3.43 mgl⁻¹, with a mean concentration of 1.71mgl⁻¹. The mean Ni content reported in this study was higher than those reported by Mico et al (2006), Lopez and Grau (2004) and Campos (1997) in agricultural soils and also exceeded the reference value (100mg/kg) of Kabata-Pendias and Pendias (2001).

Chromium (Cr)

In this study, Cr concentration was highest in the soil sample when compared to the effluent and river samples. Cr content in the effluent ranged from 0.28 to 0.66 mgl⁻¹, with a mean value of 0.47 mgl⁻¹, 0.31 to 0.42 mgl⁻¹ in the river sample, with a mean value of 0.37 mgl⁻¹ and 102 to 156 mg/kg with a mean value of 129 mg/kg in the soil. The highest Cr content recorded in the soil sample which was above the permissible level (64 mg/kg) in agricultural soil may be attributable to constant discharge of effluent from the floriculture enterprise. The Cr mean value reported in this study was higher than those reported by Mico *et al.* (2006), Lopez and Grau (2004) and Kabata-Pendias and Pendias (2001). Both soils have high clay contents (65% and 55% respectively), which seems to suggest high Cr adsorption by this soil component. The presence of high clay content and human activities from the floriculture enterprise can increase the normal content of Cr in the soils.

Zinc (Zn)

The soil sample recorded the highest concentration of Zn when compared to the effluent and river sample. The Zn content in river sample ranged from 0.91 to 0.94 mgl⁻¹, with a mean value of 0.46 mgl⁻¹ while in the effluent it ranged from 0.70 to 1.04 mgl⁻¹, with a mean value of 0.87 mgl⁻¹ and in soil ranged from 48 to 57 mg/kg, with a mean value of 52.5 mg/kg. The mean Zn value in this work the reference value (51mg/kg) of Perez *et al.* (2002), for agricultural soils and contained less than the maximum permissible concentration of 300 mg/kg by Kabata-Pendias and Pendias (2001).

Cadmium (Cd)

Cd content in the soil was highest when compared to the effluent and river sample. The concentration ranged from 24 to 33 mg/kg in the soil, with a mean value of 28.5 mg/kg, while a range of 0.18 to 0.94 mgl⁻¹ with a mean value of 0.56 mgl⁻¹ was recorded for the river sample, and a range of 0.09 to 0.17 mgl^{-1} with a mean value of 0.13 mgl⁻¹ was recorded for the effluent sample. Different international authors fix a normal Cd range of 0.07 and 1.1 mg/kg in agricultural soil (Alloway, 1990; Kabata-Pendias and Pendias, 2001). Concentrations above 0.5mg/kg could reflect the influence of human activity. In this work Cd level was higher than those reported by Mico et al. (2006), Kabata-Pendias and Pendias (2001).and Perez et al., 2002. The increased Cd levels which have exceeded toxic level could be as a result of floriculture activity and agricultural practices in this area.

Cobalt (Co)

The amount of Co in the soil was higher than that found in the river sample. The concentration ranged from 4.82 to 6.38 mg/kg, with a mean value of 5.6 mg/kg, while the concentration in river sample ranged from ND to 1.69 mgl⁻¹ with a mean concentration of 0.422mgl⁻¹ and in the effluent it ranged from ND to 0.09mgl⁻¹ with a mean concentration of 0.02mgl⁻¹. The mean Co content in this work was lower than those reported by Mico *et al*, (2006) in Mediterranian agricultural soil but was within the normal range, the influence of human activities has not occurred.

Silver (Ag)

The Ag concentration in the river sample was was higher than those of the effluent and soil samples. Ag content ranged from ND to $0.02mgl^{-1}$ in the effluent while it ranged from ND to $0.41mgl^{-1}$ in the river and ND in the soil sample.

The concentrations of all the metals studied in this work were highest in the soil sample when compared to effluent and river samples (Table 3). Fe, Cu, Ni, Mn, Cr, Zn, Co and Cd contents were above the permissible levels in the soil as recommended by CCME (1999). The heavy metal concentrations found in the soil were significantly higher than those reported for agricultural soils in Spain (Mico et al., 2006), horticultural soil in the region of Mucia (Perez et al., 2002), and agricultural soil in Iraq (Fayad et al., 2013). Such high levels are undesirable as they may cause poor root growth and proliferation in the soil, resulting in poor soil quality (Cheng, 2000). The low metal contents obtained for the effluent agreed with those obtained by Kebede et al. (2012), which reported similar low heavy metal contents in floriculture effluent from Debri Zeit, Ethiopia. However with increasing volume of effluent discharge and application, the soil acidity could change from non-saline to saline which has the potential for degradation of the soil quality.

The findings reveal that the effluent and river samples contained low levels of heavy metals, but the high heavy metal concentrations in the soil could seriously influence soil characteristics by contaminating the soil. Prolonged use of the effluent and river water for irrigation of the agricultural farmland could result in further degradation of the soil around the horticulture greenhouse.

Conclusions

Heavy metal contents (Fe, Cu, Ni, Mn, Zn, Cr, Co and Cd) were higher in soil than in both floriculture effluent and river samples the studied. Higher than permissible levels of the metals found in the soil adjacent to the floriculture greenhouses suggest that the soil has been contaminated with these metals which could result in soil degradation, thereby affecting the soil quality. Since scanty information is available on the impact of floriculture effluent on agricultural soil in this region, the result of this work could provide baseline data for future monitoring of pollution from the floriculture enterprises

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