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Full Length Research Paper

Metal contamination of soils collected from four different sites along the lower Diep River, Cape Town, South Africa

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In this study, river bank and adjacent soil samples from four different sites, Milnerton Lagoon (Site 1), Lower Estuary (Site 2), Milnerton Bowling Club (Site 3) and Woodbridge Island (Site 4) from the lower Diep River, Cape Town, South Africa were evaluated for ten metals; cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn), aluminium (Al), chromium (Cr) and cobalt (Co). The highly sensitive inductively coupled plasma - mass spectrophotometry (ICP-MS) method was used to analyze the metals. Results showed that most sites were contaminated with metals evaluated. Among the metals, Al and Fe were consistently higher in all the soil samples (from both river bank and the adjacent soil) followed by Zn, Mn, Pb, Cu, Cd, Co, Cr and Ni. The concentrations of Al in river banks ranged between 1214.1 - 3176 mgkg^{-1}. In adjacent soils, the Al concentration ranged from 434.8 - 2445.4 mgkg^{-1}. The Fe concentrations from the adjacent soil samples ranged from 402.2 - 2459.8 mgkg^{-1} and the river bank values ranged from 1136.4 - 4897.2 mgkg^{-1} respectively. Generally, Zn ranged from 2.4 - 211.5 mgkg^{-1}; Mn: 5.5 - 48.05 mgkg^{-1}; Pb: 0.97 - 71.7 mgkg^{-1}; Cu: 0.3 - 45.9 mgkg^{-1}; Cd: 0.0 - 9.3 mgkg^{-1}; Co: 0.2 - 2.7 mgkg^{-1}; Cr: 0.3 - 2.1 mgkg^{-1}; and Ni 0.02 - 2.6 mgkg^{-1}. Overall, Ni had the lowest concentrations in the ecosystem.

Key words: Aluminium, cadmium, chromium, cobalt, copper, ecosystem, iron, lead, manganese, nickel, pollution, zinc.

INTRODUCTION

The increasing consumption and exploitation of the earth's raw materials (fossil fuel and minerals) coupled with the exponential population growth over the past years have resulted in environmental degradation and build up of waste products of which metals is of great concern (Kabata-Pendias and Pendias, 1992, Diagomanolin et al., 2004). Rapid industrialization and urbanization in developing countries like South Africa, has resulted in large-scale pollution of the environment, resulting in the enrichment of metals in the soil (Tong and Che Lam, 2000; Sanderson et al., 2002; Ren et al., 2006).

Soil is unconsolidated minerals and organic material found on the immediate surface of the earth that serves as a natural medium for plants growth (Brady and Weil, 2008). It is also a key component of natural ecosystems. Environmental sustainability depends largely on a sustainable soil ecosystem because when the soil is polluted the ecosystem is altered and agricultural activities are affected (Adriano et al., 1998; Heaney et al., 1999; Schiff et al., 2002; Hankard et al., 2004). In spite of the importance of soil to support different kinds of life, it has become a dumping place for several industrial and municipal wastes, most of which contain metals (Phillips, 1981; 1999; Yusuf et al., 2003). Metals are among the major contaminants found in both contaminated lands and natural soils. Their presence in excess quantities in the ecosystems threatens the life in both terrestrial and aquatic environments (Fatoki and Awofolu, 2003; Rengel,

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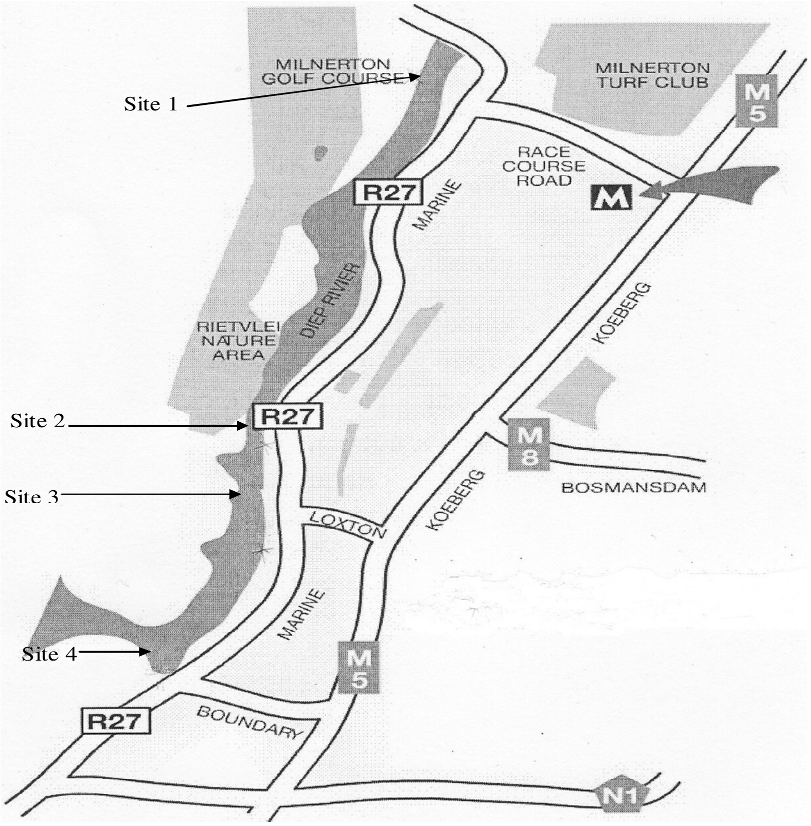

Figure 1. Map of the lower Diep River showing the study sites.

2004; Zhang et al., 2007).

Roadside soils have been shown to have considerable contamination owing to deposits of vehicle-derived metals (Adeniyi, 1996; Sutherland and Tack, 2000; Swaileh et al., 2004; Okunola et al., 2007). Crude oil and their products which are deposited on road surfaces or nearby soils, or in water bodies have been shown to have elevated levels of metals, consequently becoming toxic to plants and micro-organisms that are present in those areas (Odjegba and Sadiq, 2002; Merkl et al., 2005; Osuji et al., 2005; Nabulu et al., 2006).

Previous studies carried out by Reinecke et al. (1997; 2000) have shown that variety of metals accumulate in South Africa's urban soils. Studies conducted in Taiwan have shown that more than 800 ha of land were contaminated with industrial effluent containing metals such Cd, Cr, Cu, Pb and Zn, which were then reflected in brown rice (Chen, 2000).

Many sites around the world have been found to be polluted with metals, such as Cd, Ni, Pb, As and Zn (Reeves and Baker, 2000; Kannavou et al., 2001; Jin et al., 2002; Xendis et al., 2003; An, 2004; Cui et al., 2004). Such developments in different parts of the globe have made environmentalists and ecotoxicologists to be increasingly interested in toxicity and environmental degradation.

According to Shuping (2008) the lower Diep River has been subject to deterioration in water quality over decades due to bad farming practices and other land uses. Land use in the upper catchment is predominantly agriculture, while in the lower catchment it is largely residential (formal and informal settlements) and industrial. Jackson et al. (2009) found the lower Diep River to be polluted with a variety of metals. The concern is that industrial and household effluents could be discharging appreciable quantities of metals into the Diep River which may be detrimental to wetland plants, microorganisms, human health and ecosystem health in general.

The objective of this study was to determine the extent of metal contamination in the river banks and adjacent soil along a section of the lower Diep River.

MATERIALS AND METHODS

The study area

The study was conducted along the banks of the lower Diep River, in the following sites: 1 (Milnerton lagoon: latitude 33° 52.499'S, and longitude 18° 29.548; 2 (Lower estuary: latitude 33° 52.329'S, and longitude 18° 29.714'E; 3 (Milnerton bowling club: latitude 33° 52.183'S, and longitude 18° 29.750'E, and 4 (Woodbridge Island: latitude 33° 53.486'S, and longitude 18° 29.127'E (Figure 1). The

Diep River originates from the Kasteel Mountain, Malmesbury and flows in a south westerly direction towards Table Bay, where it flows into the Atlantic Ocean (Brown and Magoba, 2009).

Site selection

The sampling sites were selected based on their location near residential and industrial areas, which may emit a cocktail of metal pollutants to some distances in the environment. This include: Milnerton lagoon (Site 1), Lower estuary (Site 2), Milnerton bowling club (Site 3) and the lower side of the Woodbridge Island (Site 4) (Figure 1).

Collection of soil samples

For each site, four soil samples were taken from the river bank and from adjacent soil in the same vicinity (2 m apart). The soil surface was first cleared of debris using a gloved hand. Four entire plants of *Phragmites australis* including roots were dug up. The soil in close association with the roots was carefully removed and taken for analysis. The collected soil samples were put into polythene bags, sealed, appropriately labeled and transferred to the laboratory.

Preparation of soil samples

Soil samples were transferred to Petri dishes and dried at 60ºC for 48 h. The samples were removed from the oven and allowed to cool to room temperature then it was grounded with a mortar and pestle. Each sample was sieved using a nylon sieve (2 mm pore size) and then stored in plastic containers.

Digestion of soil samples

This was carried out as described by Odendaal and Reinecke (1999). For the digestion process 10 ml of 55% HNO_3 was added to each soil sample (1 g) in test tubes and stirred properly using a glass rod. Each of the mixtures was then heated on a universal block dryer (UBD) heater in a fume cupboard at 40ºC for 1 h, then at 120ºC for 3 h. The samples were then removed and allowed to cool to room temperature. Each of the cooled solution was made up to 20 ml with distilled water and filtered using cellulose nitrate filter paper (0.45 µm). Each of the filtrate obtained were further diluted to a final volume of 100 ml each with distilled water and appropriately labeled for onward analysis of metals in the laboratory.

Analysis of samples for metal contamination

The digested soil samples were analyzed for the presence of metals using the inductively coupled plasma-mass spectrophotometer (ICP - MS, Agilent 7500ce. England). To obtain the soil metal concentrations, the ICP values were converted using the formula:

$$SMC = \left(\frac{ICP_{Reading} - C_{Reading}}{WSS} \right) * DF$$

Where: SMC = soil metal concentration (mgkg^{-1}); ICP = inductively coupled plasma values; C = blank; DF = dilution factor; WSS = weight of soil sample (g). The soil metal concentration data were statistically analyzed using the STATISTICA software package 2009 (StatSoft Inc., Tulsa, OK, USA).

RESULTS

Distribution of metals in soil from the different sites

Aluminum (Al)

Table 1 shows the results of metal concentrations from both the river bank and adjacent soil from all the four sampling sites. The concentrations of Al in river banks ranged between 1214.1 - 3176 mgkg^{-1}. In adjacent soils Al concentration ranged from 434.8 - 2445.4 mgkg^{-1}. Generally, the river bank, samples had significantly highest concentrations of Al compared with adjacent sites (Table 1).

Chromium (Cr)

In this study, Cr concentrations were significantly higher in samples collected from the river bank compared with those from the adjacent sites (Table 1). The concentrations of Cr in river banks ranged between 0.4 - 2.1 mgkg^{-1}. In adjacent soils Cr concentration ranged from 0.3 - 1.7 mgkg^{-1}. The highest Cr concentration was found at Site 3 (Table 1).

Cobalt (Co)

Table 1 shows significant differences in Co concentration when comparing river bank and adjacent soil samples in Sites 2, 3 and 4. Cobalt levels from adjacent soils ranged from 0.2 - 1.9 mgkg^{-1}. The highest (1.9 mgkg^{-1}) Co values from adjacent soil were found in Site 4. The concentrations of Co in river banks ranged between 0.8 - 2.7 mgkg^{-1}, with Site 4 having the highest value.

Nickel (Ni)

For the river bank samples, Ni concentrations ranged between 0.02 - 2.6 mgkg^{-1}, and for the adjacent soil, it ranged from 0.02 - 0.1 mgkg^{-1}. There was a slight variation in the concentration of Ni in all the sites, except in Site 1. The highest concentration in the river bank soil was found at Site 3 (2.6 mgkg^{-1}). There were statistically significant differences between Sites 2, 3 and 4, while Site 1 had no statistically significant difference. Ni had the lowest concentration of 0.02 mgkg^{-1} for the adjacent soil and 0.03 mgkg^{-1} for river bank soil samples (Table 1).

Cadmium (Cd)

Generally, the river bank soil samples in all sites had

Table 1. Concentrations of metals in soil samples from different sites along the Diep River, Cape Town, South Africa.

Site	Status	Concentrations of metals (mgkg^{-1})					
		Al	Cr	Co	Ni	Cd	Pb
1	Adjacent soil	434.8 ± 19.1b	0.3 ± 0.01b	0.7 ± 0.07a	0.02 ± 0.002a	3.5 ± 0.10b	0.97±0.14b
	River bank	1214.1 ± 31.2a	0.4 ± 0.01a	0.8 ± 0.09a	0.02 ± 0.003a	7.12 ± 0.25a	2.6±0.3a
	F Statistics	455***	81.55***	0.03NS	0.67NS	192.12***	27.2***
2	Adjacent soil	527.2 ± 21.9b	0.3 ± 0.01b	0.2 ± 0.13b	0.02 ± 0.002b	6.19 ± 0.17b	1.5 ± 0.11a
	River bank	1532.8 ± 60.9a	0.5 ± 0.02a	0.9 ± 0.10a	0.03 ± 0.001a	9.3 ± 0.47a	1.5 ± 0.2a
	F Statistics	241.55***	73.58***	21.61***	6.08***	40.19***	0.02N
	Adjacent soil	2445.4 ± 182.9b	1.7 ± 1.53b	1.4 ± 0.22b	0.05 ± 0.05b	0.11 ± 0.01b	49.6 ± 3.2b
	River bank	2988.6 ± 513.6a	2.1 ± 0.74a	1.9 ± 0.07a	2.6 ± 0.7a	0.3 ± 0.05a	71.7±19.2a
3	F Statistics	2.69*	323.85***	179.54**	1743.52***	333949.5*	1.06*
	Adjacent soil	2279.2 ± 179.5b	0.3 ± 181.4b	1.9 ± 0.5b	0.1 ± 0.01b	0.00 ± 0.00b	4.6 ± 0.4b
4	River bank	3176.0 ± 244.3a	0.7 ± 244.3a	2.7 ± 0.2a	0.4 ± 0.03a	7.2 ± 19.2a	49.6 ± 3.2a
	F Statistics	11.52***	81.35***	3663.96*	1308914*	34.06*	7110.61*

Mean ± SE followed by dissimilar letter in the same column are significant at $P \leq 0.05$ according to Fischer LSD. (*: $P \leq 0.05$; **: $P \leq 0.01$, ***: $P \leq 0.001$; NS = not significant).

significantly highest concentrations of Cd in river bank soils compared with adjacent sites (Table 1). Cd concentrations in the river banks ranged from 0.3 - 9.3 mgkg^{-1}. The highest concentration (9.3 mgkg^{-1}) of Cd in the river bank soil was recorded at Site 2 and the lowest concentration (0.3 mgkg^{-1}) was found at Site 3. No Cd was detected in the adjacent soil samples at Site 4.

Lead (Pb)

Table 1 show that significant differences in Pb concentration were found only in Sites 1, 3 and 4 when comparing river bank and adjacent soil samples. Pb had the highest concentrations of 71.7 mgkg^{-1} in the river bank at Site 3, followed by 49.6 mgkg^{-1} at site 4. Similarly, the highest concentration in the adjacent soil was also recorded at Site 3 (49.6 mgkg^{-1}). This implies that Site 3 had the highest Pb metal load.

Manganese (Mn)

The comparison of Mn between the adjacent soil and the river bank soil samples was significantly different at each site. Mn in the river bank soil samples ranged from 6.7 - 48.05 mgkg^{-1}, whereas for the adjacent soil sites it ranged from 5.4 mgkg^{-1} (Site 1) to 27.02 mg.kg^{-1} (Site 4) (Table 2).

Iron (Fe)

Table 2 indicated that Fe had the highest concentration in all the 4 sites investigated. The river bank soil samples had significantly highest concentrations of Fe compared with adjacent sites. For instance, in Site 1, the concentration of Fe was 402.2 mgkg^{-1} (adjacent soil) and 1136.4 mgkg^{-1} (river bank).

Copper (Cu)

Table 2 showed that across the 4 sites, the river bank soil samples had significantly highest concentrations of Cu compared with adjacent sites. Site 4 of the river bank had the highest concentration of Cu (45.9 mgkg^{-1}), followed by Site 3 (34.7 mgkg^{-1}) and Site 1 (5.6 mgkg^{-1}), while the lowest value was at Site 2 (2.56 mgkg^{-1}). With the adjacent soil, the concentrations were recorded in a decreasing order of 12.56 mgkg^{-1} (Site 3), 5.40 mgkg^{-1} (Site 4), 0.5 mgkg^{-1} (Site 1) and 0.3 mgkg^{-1} (Site 2) respectively.

Zinc (Zn)

The concentrations of Zn are given in Table 2. Overall, the river bank soil samples in Sites 2, 3 and 4 had significantly highest concentrations of Zn compared with adjacent sites. Highest Zn value in river bank (211.5mgkg^{-1}) and adjacent soil (53.9 mgkg^{-1}) were found at Site 4; followed by Site 3; river bank (164.5 mgkg^{-1}), adjacent soil (52.3 mgkg^{-1}) and Site 2 river bank (11.6 mgkg^{-1}) and adjacent soil (2.6 mgkg^{-1}), respectively.

Table 2. Concentrations of essential micronutrients in the soil samples from different sites along the Diep River, Cape Town, South Africa.

Site	Status	Concentrations of essential micronutrients (mgkg^{-1})			
		Mn	**Fe**	**Cu**	**Zn**
	Adjacent soil	5.4 ± 0.1b	402.2 ± 13.3b	0.5 ± 0.03b	2.4 ± 0.2a
1	River bank	6.7 ± 0.2a	1136.4 ± 23.7a	5.6 ± 2.3a	2.9 ± 1.4a
	F Statistics	33.5***	730***	5.13***	0.12NS
	Adjacent soil	6.6 ± 0.2b	659.7 ± 28.0b	0.3 ± 0.3b	2.6 ± 1.2b
2	River bank	11.5 ± 0.4a	4596.9 ± 418.8a	2.56 ± 0.16a	11.6 ± 2.3a
	F Statistics	132.54***	87.97***	50.43***	11.51***
	Adjacent soil	25.6 ± 3.3b	1444.8 ± 185.1b	12.56 ± 0.9b	52.3 ± 5.5b
	River bank	39.2 ± 6.9a	2685.4 ± 221.9a	34.7 ± 6.1a	164.5 ± 24.9a
3	F Statistics	9.33**	13.61**	21.49***	9.72***
	Adjacent soil	27.02 ± 4.5b	2459.8 ± 199.1b	5.40 ± 0.6b	53.9 ± 3.8b
	River bank	48.05 ± 3.5a	4897.2 ± 411.1a	45.9 ± 3.2a	211.5 ± 14.8a
4	F Statistics	18.44***	20.08***	127.73***	53.81***

Mean ± SE followed by dissimilar letter in the same column are significant at P≤0.05 according to Fischer LSD. (**:P≤ 0.01, ***; P≤0.001; NS = not significant).

DISCUSSION

Al and Fe had the highest concentration followed by Zn,Mn, Pb, Cu while Cr and Ni had the lowest concentrations. The concentrations of Al from all sites in the river bank and adjacent soils were above the level recommended by Peverill et al. (1999). The recommended and acceptable concentration for Al is 4.1 - 5.5 mgkg^{-1} for soil (Peverill et al., 1999). In this study, the concentrations obtained were 434.8, 527.2, 2445.4 and 2279.2 mgkg^{-1} (adjacent soil) and 1214.1, 1532.8, 2988.6 and 3176.0 mgkg^{-1} (river bank) for Sites 1, 2, 3 and 4 respectively. These concentrations all exceeded the established guidelines recommended by Peverill et al. (1999). Such high levels are undesirable as they may cause poor root growth and proliferation in the soil and hinder other forms of life (Sammut et al., 1995; Vuori, 1996). Research evidence elsewhere suggests that toxic levels of Al in the soil resulted into shallow rooting due to Al toxicity (Kochian, 1995; Foy et al., 1999; Kinraide, 2003), a condition which could also be present in the study area. Other forms of life may also be impeded by high Al concentrations in the ecosystem. Similar to our results, Jackson et al. (2009) also reported higher levels of Al in selected areas along the Diep River.

The concentrations of Cr in the river bank soil ranged from 0.4 - 2.1 mgkg^{-1} whereas in the adjacent soil, it ranged from 0.3 - 1.7 mgkg^{-1}. These values are far below the recommended value of 64 mgkg^{-1} in Canada (CCME, 1999), implying that they were within the accepted limits for the growth and development of different organisms such as plants and micro-organisms (Kimbrough et al., 1999; Segura-Muñoz et al., 2004). This justifies that the industrial discharges close to study sites into the ecosystem does not contain significant concentration of Cr and the reported values could sustain life of different organisms in the study area.

With regard to Co, research reports suggest that cobalt is not considered a harmful metal in soil (Shuhaimi-Othman, 2008). In this study, Co levels ranged from 0.2 - 2.7 mgkg^{-1}. These levels are below the proposed toxic levels of between 4.1 and 14.0 mgkg^{-1} in different ecosystems (Choueri et al., 2009). Therefore, Co levels in the study sites cannot be linked to causing adverse biological effects to different organisms growing in these habitants.

The comparison of Ni concentrations from all the 4 sites provided evidence that this metal was not a threat in the environment. Nickel concentration ranged from 0.02 - 2.6 mgkg^{-1}, values far below the Canadian soil quality guideline of 50 mgkg^{-1} (CCME, 1999).

Considering the established guideline, toxic levels were observed for Cd at Site 1 (3.5 mgkg^{-1} in the adjacent site and 7.1mgkg^{-1} in the river bank) and Site 2 (6.19 mgkg^{-1} in the adjacent site and 9.3 mgkg^{-1} in the river bank). Results for Cd in Site 3 (0.11 mgkg^{-1} in the adjacent site and 0.3 mgkg^{-1} in the river bank) however, were lower than 1.4 mgkg^{-1} as recommended in the Canadian soil quality guidelines (CCME 1999), while at Site 4, no Cd was detected in the adjacent site, whereas in the river bank high value (7.2 m.kg^{-1}) was recorded. Considering the established guidelines, it can be suggested that Cd could jeopardize the life and health of certain plants and other forms of life at Sites 1, 2 and 4.

The concentrations of Pb ranged from 0.97 - 49.6 mgkg^{-1} in adjacent soil and from 1.5 - 71.7 mgkg^{-1} in the river bank soil. The proposed interim soil quality guideline for Pb in Canada is 70 mgkg^{-1} for agricultural soil (CCME, 1999). Out of the 4 sites, elevated levels were observed in Site 3 (river bank and adjacent soil) and 4 (river bank soils) suggesting a probable Pb contamination which could be associated with adverse biological effects on organisms living in the ecosystem and possible negative effect on the ecosystem health.

Studies on the concentrations of Mn, Fe and Zn showed that these metals exceeded the recommended concentrations in the soil (Viets and Lindsay, 1973; Lindsay and Norvell, 1978; Silanpää, 1982; Temmerman et al., 1984; Lindsay and Cox, 1985). Concentrations of Mn ranged between 6.71 and 48.05 mgkg^{-1} for the river bank samples and 5.3 - 27.0 mgkg^{-1} for the adjacent soil samples in all the sites. Values recorded from both sites exceeded the recommended standard of 2.0 - 5.0 mg kg^{-1} (Silanpää, 1982).

The high concentration of Fe in the soil (402.2 - 2459.8 mgkg^{-1}) for adjacent soil and (1136.4 - 4859.1 mgkg^{-1}) for the river bank samples gives a clear indication that the sites are heavily polluted with this metal and may cause hazardous effects to plants and other organisms. The recommended concentration of Fe in the soil for the cultivation of plants range from 0.30 - 10 mgkg^{-1} (Lindsay and Cox, 1985).

Zinc, an essential micronutrient of many enzymes systems, such as respiration enzymes activators and the biosynthesis of plant growth hormones, is required in concentration not exceeding 200 mgkg^{-1} for agricultural soil according to Kabata-Pendias (2001) and the Canadian soil quality guideline (CCME, 1999). The concentration beyond this may becomes toxic to plants and other organisms. However, results from this study revealed that concentration of Zn in the soil samples ranged between 2.4 - 53.9 mgkg^{-1} for the adjacent soil and 2.9 - 211.5 mgkg^{-1} for river bank soil samples (Table 2). The results of this study suggest that the contamination would likely be in Site 4 as their values are higher than what can be tolerated by most plants.

Cu levels in the adjacent soils ranged from 0.3 - 12.5 mgkg^{-1} and in the river bank from 2.56 - 49.9 mgkg^{-1}. These results showed that all 4 sites had values which are less than the Canadian soil quality guideline of 63 mgkg^{-1} for agricultural soil (CCME, 1999). Hence, Cu is not a threat in this ecosystem.

Results of this study revealed that most sites investigated were generally contaminated with the metals studied. This was due to the fact that the study sites were located in an area with industrial manufacturing activities as well as residential areas. Some of the effluents from these industries are emitted directly into the river. Furthermore, other types of runoff from the streets drain in the river. It is therefore logical to assume that contaminants in these effluents find its way into the river and get deposited into the river bank soil. The study sites were also close to a major road characterized by heavy traffic, which could also be contaminated directly from pollutants from the vehicles.

Conclusion

Results of this study showed some degree of high metal contamination in soil collected from river bank compared with lowest concentration in the adjacent soil in all sites investigated. The concentrations of some of these metals exceeded the established guidelines in the soil. Site 3 and 4 were more polluted than Site 1 and 2, respectively. The high level of industrial activities and the close proximity of the study area to a highway may be largely responsible for the high level of pollution observed. This data may act as an important guideline for future studies in this area.

An integrated approach between both the industrial and environmental scientist for the control of pollution in this area is required (Ayeni et al., 2010). Future studies should focus on the impact of these metals on different organisms found in this ecosystem as some may find their way into food chain and cause harmful effects to plants, animals and ecosystems at large. Recommended for further studies are quality standard guidelines for sediment in this wetland.

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