TOXICITY AND ENVIRONMENTAL IMPACT ASSESSMENT OF HEAVY METALS CONTAMINATED SOIL OF HAZARIBAGH TANNERY AREA

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ABSTRACT

Present study investigated the soil pollution at Hazaribagh tannery area in terms of heavy metals contamination and their impact on ecosystem and human health. The soil was slightly alkaline (pH 7.6). Concentrations of six heavy metals (Cr, Pb, Ni, Zn, Cd and Cu) were determined and they ranged over the following rounded intervals: Pb: 16-130 mg/kg; Cr: 35- 23149 mg/kg; Cu: 33- 301 mg/kg; Zn: 54-1034 mg/kg; Ni: 3-20 mg/kg and Cd was below detection level. The average concentrations of all heavy metals in the soil samples were lower compared to EU and others guidelines except chromium which was found to be about 29 times higher than the guideline value (EU). Toxicity Characteristics Leaching Procedure (TCLP) test indicated that Pb and Zn are the potential threat of ground water pollution. In addition, heavy metal uptake beyond standard limit by Basella alba (Vine spinach) also posed a potential threat to human and herbivorous animals. To quantitatively assess the environmental burden of the heavy metals associated with soil, the IMPACT 2002+ methodology was used under the SimaPro software environment. Impact results indicated that studied metals have impact on Aquatic ecotoxicity, Terrestrial ecotoxicity and Non-carcinogens midpoint impact category which led to impact on Ecosystem Quality and Human Health damage category.

Keywords: Soil pollution; heavy metals; TCLP; IMPACT 2002+

INTRODUCTION

Leather industry in Bangladesh is considered as considerable growth and investment potential, located in the southwestern part of the Dhaka city on the area of 25 ha in the Hazaribagh area, within one and half kilometer northeast of the River Buriganga (Shams et al., 2009). Tannery industries have been vitally important to the economy of Bangladesh, yet they been proved to be detrimental to the environment mainly due to the discharge of huge quantities of untreated wastewater containing heavy metal chromium (Ahmed and Chowdhury, 2016). About 220 metric tons of raw hides and skins are processed every day. Most of the tanneries follow chrome tanning process. After leather processing all the liquid waste and solid waste are discharged as green (without treatment) through drain in the low-lying areas and finally fall into the river Buriganga. As a consequence, heavy metals used in tanneries for tanning and or subsequent leather processing operations are accumulated in low-laying area or in river sediment. The tanneries discharge more than 22000 m^3 of highly toxic effluents and 1.6 tons chromium per day. About 1.25 t/days of chromium are disposed into Buriganga river and 0.35 t/day of chromium are settled into a lagoon of 25 ha which are suspected to be the source of chromium contamination of the groundwater (Karim et al., 2012). Previous studies showed that the subsoil of Hazaribagh tannery area is seriously contaminated with Cr, Zn, Cu, Pb, phenols and hydrocarbons (Karim et al., 2012; Shams et al., 2009). These heavy metals are very harmful, because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in biological systems (Wilson and Pyatt, 2007; Singh et al., 2004). Soil contamination by chromium is often irreversible and may repress or even kill parts of the microbial community (Viti and Giovannetti, 2008). Cr^{3+} is readily being converted into Cr^{6+} under natural conditions through various oxidation processes. $Cr^{6+}$is much more toxic than Cr^{3+} and mutagenic to most organism and humans (Ajmal et al., 1984).

Vegetables are often cultivated in some part of these contaminated area, as a result these metals may be taken up by the vegetable roots and incorporated into the plant tissue. Ultimately, these toxic metals can get entrance into the human body and lead to bio-accumulation and bio-magnification (Muchuweti et al., 2006). Hazaribagh has drawn a significant attention in the recent years due to high concern of soil, air, surface water pollution and also for potential risk of ground water pollution of Dhaka city. According to a directive of Bangladesh high court, the shifting process of tannery industry from Hazaribagh to new location at Savar is in progress. This area will be redeveloped after the relocation of the tanneries as a residential area having open space, health, and education facilities. However, the area should be cleaned up and remediated before starting the residential area. The present condition of heavy metals pollution and environmental risk assessment of this site is important for formulating a reclamation and clean up strategy. In this study, the extent of soil pollution was determined in terms of heavy metals contamination and their bioavailability in the soil. The purpose is also to determine the uptake of heavy metals by different parts of vegetables grown in contaminated area. In addition, an impact analysis of these heavy metals was conducted using IMPACT 2002+ in SimaPro software.

METHODOLOGY

Soil samples were collected from 11 sites of Hazaribagh, Dhaka. Among 11 sampling locations, location no. L1 to L9 are located in between western part of tannery industry and inner side of flood protection embankment whereas location no. L10 – L11 are in main tannery industries. Soil samples were collected from a depth of 5 to 25 cm. For heavy metal analysis of soil samples, 5 gm. lightly ground oven dried soil sample was digested with acid (HNO_3: HCl =1:3 volume ratio) for 24 hours, then added 350-400 ml distilled water and boiled for 2.5 hour and prepared a 500 ml solution. Finally, solution was filtered through 0.45 µm pore size filter paper and filtrate was collected for the determination of heavy metals (Cr, Pb, Cd, Ni, Cu, and Zn) by using Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA 6800) (Juel et al., 2016; Choudhury et al., 2015). The Toxicity Characteristics Leaching Procedure (TCLP) in accordance with USEPA 1311 (USEPA, 1992) was used to evaluate the risk of heavy metals leaching and reaching to natural ground water.

Among the 11 sample sites, Basella alba (Vine spinach), a locally popular vegetable, was found to cultivate in two sites (L1 and L3). Vine spinach was then collected from these two sites. After collection, the plant samples were washed with distilled water and divided into two parts: i) leaf and ii) shoot. The sample was oven dried for 48 hours in aluminum bowl. For the digestion of plant sample, Approximately 2 gm. of oven-dried sample was taken in a volumetric flask and a few milliliters of distilled water was added, then 25 mL of nitric acid was added to the sample and kept overnight. The flask was heated to boil for 2 h, then after cooling 10 mL of perchloric acid was added to the flask and heated again for 1 h to boiling. If the color of the sample turns yellow, the digestion process is assumed to be completed; if color of the sample turns dark, 2 to 3 mL of nitric acid is added to the flask and heat is applied; the process is repeated until the sample color turns yellow. Finally distilled water was added up to the 200 mL graduation mark of the volumetric flask and filtered using a filter paper (0.45 lm) followed by analysis using an AAS (Shimadzu, AA6800) (Choudhury et al., 2015). The environmental impact assessment conducted based on impact 2002+ methodology using SimaPro. This software is integrated with various databases and impact assessment methods (PRé, 2013).

RESULTS AND DISCUSSIONS

Physical Properties of Soil

The average pH of the soil samples was found to be 7.6 which indicates slightly alkaline conditions. The high pH of the topsoil is caused by the disposal of tannery effluents containing a large amount of $Ca(OH)_2$ used in the liming process (Karim et al., 2012). Similar pH value of Hazaribagh soil was reported in other studies (Karim et al., 2012; Shams et al., 2009). The high organic content ranging from 3 to12%, was observed due to accumulation of organic substance of solid waste and tannery effluent.

Heavy Metal Content in Soil

The concentrations of heavy metals in the samples were compared with the European standards because there is no standard regulation for soil contamination in Bangladesh. The concentration of selected heavy metals (Pd, Cr, Zn, Cu, Ni and Cd) for each soil sample found in this study was shown in Table 1.

High amount of chromium ranging 34.85 to 23148 mg/kg was found to be distributed in the study area. It revealed that the concentration of Cr of all samples markedly exceeded the maximum permissible limit of 150 mg/kg (EU standard) except sample no. L7. Comparatively higher concentration of Cr was distributed in waste lagoon or inner side of embankment (L1 to L9), because tannery effluent often flooded this area due to blockage of cannel during passing to Buriganga river. Previous studies (Karim et al., 2012; Shams et al., 2009; Zahid et al., 2006) also reported high chromium concentration ranging 1000 to 30000 mg/kg in the topsoil of the Hazaribagh area. Most of the Cr accumulated in the soil was present as Cr(III) (Saha and Ali, 2001) and insignificant amount (maximum 1 mg/kg) of Cr was present as Cr(VI) (Shams et al., 2009).

Table 1: Heavy metal concentration in soil of Hazaribagh tannery area

Sample ID	Pb (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Cd (mg/kg)
L1	61.25±1.2	1834.8 ± 3.67	304 ± 1.2	58.25 ± 7.4	8.45 ± 0.49	n.d
L2	59.6 ± 1.1	2438.9 ± 10.8	193.7 ± 1.13	271.8 ± 0.28	19.9 ± 0.42	n.d
L3	70.6 ± 1.1	1458 ± 3.67	250.9 ± 1.34	115 ± 0.28	8.65 ± 0.21	n.d
L4	52.4 ± 1.1	23148 ± 48.6	558.9 ± 2.75	66.3 ± 0.2	4.05 ± 0.07	n.d
L5	130 ± 0.77	2492.6 ± 10.8	1034 ± 14.56	301 ± 0.07	12.25 ± 0.21	n.d
L6	15.7 ± 1.5	294.6 ± 10.88	20 ± 1.2	30 ± 0.12	5.55 ± 0.07	n.d
L7	61.5 ± 0.1	34.85 ± 2.19	327.1 ± 2.67	323.2 ± 0.56	9 ± 0.56	n.d
L8	16.75 ± 0.77	115.8 ± 5.25	77.8 ± 2.26	32.5 ± 0.28	6.6 ± 0.14	n.d
L9	23.95 ± 0.77	12682 ± 51.56	53.75 ± 1.76	35.9 ± 0.14	3 ± 0.42	n.d
L10	41.9 ± 0.42	145.45 ± 7.28	127.5 ± 32.4	133.05 ± 2.1	9.25 ± 0.92	n.d
L11	62.9 ± 0.42	2888.9 ± 0.2	210.35 ± 0.77	75.5 ± 0.42	9.85 ± 0.35	n.d
China limit [a]	350	200	300	100	60	0.6
EU limit [b]	300	150	300	140	NA	3.0

[a] SEPA, (1995); [b] European Union, (2002); n.d: not detected; detection limit of Cd is > 0.001 mg/l

The analytical result revealed that the concentration of cadmium was below the detection limit in all soil samples. Pb contamination in soils has been seriously emphasized in recent years since this metal is very toxic for humans and animals (Rahman et al., 2012). The concentration of Pb and Ni in all soil sample, ranged from 15.7 to 130 mg/kg and 3 to 19.9 mg/kg, respectively, were below the EU and China limit (Table 1). The Zn concentration varied from 20 to 1034 mg/kg where Zn level in 4 sites (L1, L4, L5 and L7) was higher than the maximum allowable concentration of 300 mg/kg (both for China and EU limit). Similar pattern of Cu distribution was observed in the study area ranging from 30 to 301 mg/kg. The Cu concentration of 5 sampling sites exceeded the China limit of 100 mg/kg whereas this number reduced to 4 sites when compared with EU limit of 140 mg/kg.

Mobility of Heavy Metals

The mobilization of targeted heavy metals were measured in the leachates and compared with the total amount of metal present (HNO_3/HCl extraction) (Karim et al., 2012). The mean leaching concentration of Cr, Pb, Zn, Cu and Ni were 1.875 mg/kg, 3.365 mg/kg, 14.52 mg/kg, 2.205 mg/kg and 0.516 mg/kg, respectively. From the leaching test results shown in Table 2, a leaching of only 0.03% of the total chromium content was found. This indicated that only a small fraction of the chromium present in the topsoil of the Hazaribagh area is mobilized by rainwater. Similar leaching result was found by Karim et al., (2012). On the other hand, the concentration of Zn in the leachate was 14.52 mg/kg corresponding to 4.98% of the total zinc content, indicating most mobile metal in this study. High mobility of Zn was reported in the previous study (Rahman et al., 2012). The leaching concentration of Pb was found to be 3.365 mg/kg which is corresponding to about 6.13% of the total lead content. This indicates that Pb and Zn are the potential threat of ground water pollution though total content of these metals are much lower compared to total chromium content.

Table 2. Leaching of Cr, Pb, Zn, Cu and Ni under standard TCLP leaching test

Heavy metals	Average (mg/kg)	S.D	Leaching (%) (relative to HNO_3/HCl extraction)
Cr	1.875	0.860	0.03
Pb	3.365	1.418	6.13
Zn	14.52	12.210	4.98
Cu	2.205	1.540	1.64
Ni	0.516	0.436	4.41

Heavy metals in vegetables

Concentrations of heavy metals accumulated in leaf and shoot portions of the vegetables (Vine spinach) are presented in Table 3 and compared with the safe limit regulated by FAO/WHO, India and China for these elements in fresh vegetables. It is apparent for lead that concentration in both leaf and shoot greatly exceeded all the standards. In case of chromium, high concentration was found to accumulate in shoot compared to leaf and also exceeded both FAO/WHO standards and Chinese national food standards whereas high level of Zn accumulated in leaf compared to shoot that exceeded all the standards (Table 3). The higher concentration of Zn is found in vegetables compared to other metals analyzed in this study that support the bioavailability or mobility of zinc described in earlier part of this article. Though Cu and Ni concentration were below the FAO/WHO standards but exceeded the China national standards. Therefore consuming these vegetables grown the study area have harmful impacts on the human's health.

Table 3: Accumulation of targeted heavy metals (mg/kg dry wt.) in Vine spinach grown in study area

Metals (mg/kg)	Soil sample code L1		Soil sample code L3		Safe limit [a]	Safe limit [b]	Safe limit [c]
	Leaf	Shoot	Leaf	Shoot			
Cr	3	6.1	4.9	10.1	5	20	0.5
Pb	14	18.6	6.6	8.8	5	2.5	0.02
Zn	66.9	35.2	72.6	45.5	60	50	20
Cu	14	12.4	10.3	9.1	40	30	10
Ni	1.9	1.6	1.7	1.5	20	1.5	-

[a] FAO/WHO, (1999); [b] India limit (Awasthi, 2000); [c] Chinese national food standards, (2012)

Impact Assessment

Impact assessment is a technical quantitative, and/or qualitative process to characterize and assess the effects of the environmental burdens. The impact assessment of soil contaminated with heavy metals was conducted based on IMPACT 2002+ methodology. This method links all types of results via several midpoint categories like carcinogens, non-carcinogens, aquatic ecotoxicity, terrestrial ecotoxicity, aquatic acidification, aquatic eutrophication, terrestrial acidification/nitrification, land occupation, global warming, non-renewable energy consumption and mineral extraction to four damage categories (human health, ecosystem quality, climate change and resources). Linking to midpoint is associated with certain conversion factors for each pollutant and conversion to damage categories is also associated with damage factors (Juel et al., 2016). SimaPro was used to analyze the impact of heavy metals measured from total extraction. It has been found that chromium, zinc and copper has impact in terms of aquatic and terrestrial ecotoxicity (contributing to the damage category of ecosystem quality) and non-carcinogens (contributing to the damage category of human health). The extent of impact with respect to the USEPA standard for all impacts and damage categories is shown in Fig. 1. Assessment has been done based on heavy metals (avg.) per kg of soil in the industrial area of Hazaribagh against corresponding EU standard. It can be seen that all emissions are below standard except chromium which is the one of the major chemicals used in leather production. Considering overall impact, the non-carcinogenic impact of Zn is much higher which is estimated to be about 9 times higher than Cr in the soil but the Aquatic ecotoxicity effect of Cu is much higher followed by Cr and Zn. In addition, in case of Terrestrial ecotoxicity, greatest contribution comes from Cr followed by Zn and

Cu. The damage category Ecosystem Quality is dominated by Cr followed by Zn and Cu and Human Health mainly controlled by Zn followed by Cr. This is mainly due to the toxic effect of heavy metals on the ecosystem (both aquatic and terrestrial) and human health. In Fig. 1, Kg equivalent of a reference substance expresses the amount of a reference substance that equals the impact of the considered pollutant (e.g. TEG-Triethylene glycol) in the midpoint categories. PDF·m^2·y (Potentially Disappeared Fraction of species disappeared on 1 m^2 of earth surface during one year) is the unit to measure the impacts on ecosystems. DALY (Disability-Adjusted Life Years) characterizes the disease severity, accounting for both mortality (years of life lost due to premature death) and morbidity (the time of life with lower

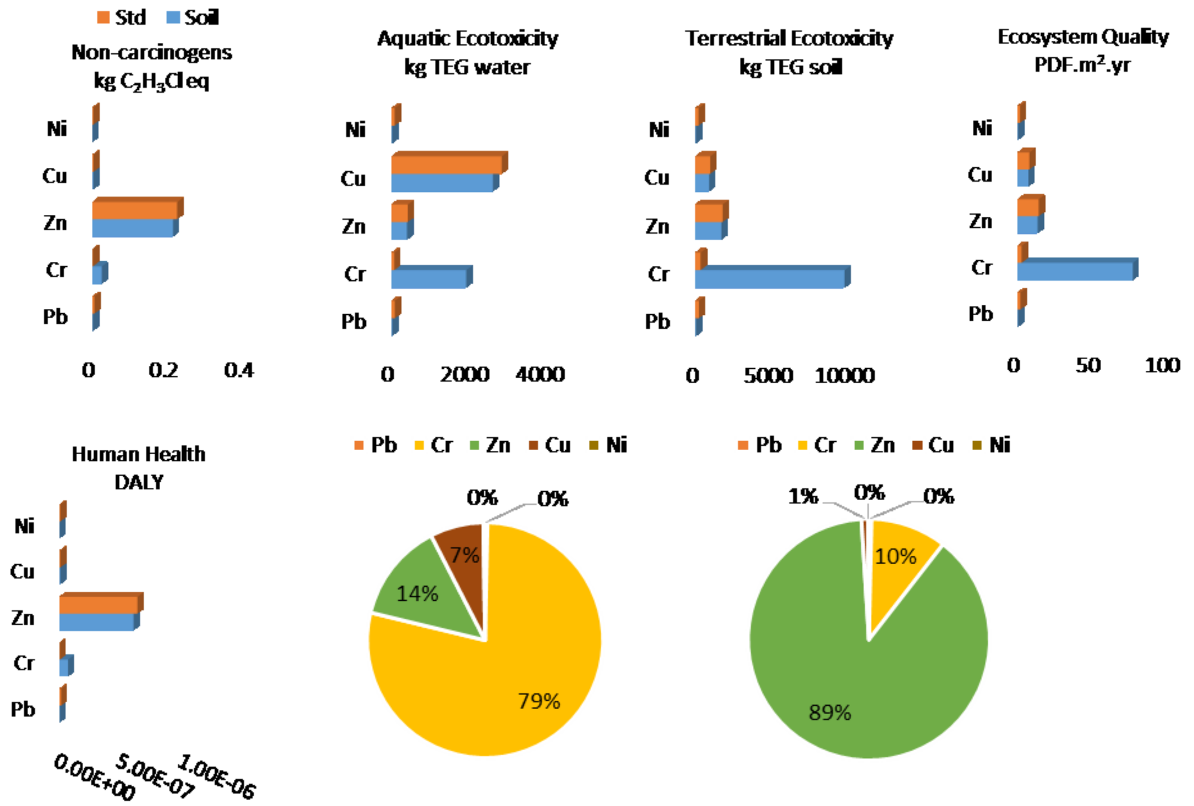

Fig. 1: The environmental impact (Non-carcinogens, aquatic ecotoxicity and terrestrial ecotoxicity) and damage assessment (ecosystem quality and human health) of heavy metals obtained from total extraction. Pie charts indicate the relative contribution of heavy metals over damage categories Ecosystem Quality and Human Health

quality due to an illness, e.g., at hospital)(Juel et al., 2016). The relative contribution of heavy metals over these damage categories has also been assessed. It has been estimated that Cr has higher order of toxicity (79%) in the Ecosystem Quality damage category followed by Zn (14%). On the other hand, Zn contributes the maximum (89%) to Human Health followed by Cr (10%). This assessment has only been done based on the total heavy metal content of the soil samples.

CONCLUSIONS

The uncontrolled release of heavy metals led to soil and groundwater pollution in the study area. In addition, heavy metal uptake by vegetables is another concern. Though total extraction showed that the average emissions into soil is under standard limit except Cr but all of them have impact on ecosystem and human health which has been confirmed by the impact assessment using SimaPro. It also showed that Cr has about 6 times higher impact on Ecosystem quality compared to Zn whereas Zn has about 9 times higher impact on Human Health compared to Cr. Results presented in this study show that Cr is the principal heavy metal contaminant in soil which is usually used as a basic chromium sulfate for the tanning of animal skins. Other sources of heavy metals weren't traced.

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