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ASSESMENT, BIODISTRIBUTION AND ENVIRONMENTAL HEALTH IMPACT OF CHROMIUM (VI) IN TANNERY EFFLUENTS

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INTRODUCTION

Heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities, and humans are exposed to them through various pathways[1]. These metals are extremely toxic and it is readily mobilized by human activities such as mining and dumping industrial waste in natural habitats such as forests, rivers, lakes, and ocean[2]. These discharge of toxic trace metals in water bodies cause metal assimilation in aquatic animals[3]. The untreated industrial waste is widely used in agriculture either as manure in the production of vegetables or as liquid sewage as a source of water for irrigation, and again as a feed for fish bred in the wetland areas and ponds[4]. Some environmental risks are always asssociated with these industrial effluent fed farming and aquaculture.

The heavy metal like Cr^{VI}, an essential component of the tanning process, is coming out with the effluent of tannery industry. This effluent is an important source of nutrient to vegetables and fish. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern. Though chromium exists in nine valency states ranging from -2 to +6, Cr^{III} and Cr^{VI} are of major environmental significance. Cr^{VI} is more mobie and toxic than Cr^{III}[5]. In the present study concentration of Cr^{VI} in the tannery effluent and sludge was estimated. Bioaccumulatioin of Cr on vegetables grown in tannery effluent irrigated soil and waste water fed fish as determined and the associated health risks due to the consumption of these foods were assessed.

RESULTS

Estimation of Cr^{VI} in tannery effluent and sludge

The contamination of total Cr, Cr^{VI} and Cr^{III} in tannery effluent and sludge at four stations is presented in Table 1 while the same for soil of affected agricultural land and water or wetland is presented in the Table 2.

Bioaccumulation study of Cr in vegetables and fish

The pollution load index (PLI) of the water samples collected from the wetland areas was 1.87. The concentration of Cr in two different types of vegetables such as cauluflower (*Brassica bortrytis*) and spinach (*Spinacia oleracae*) are presented in the Table 3.

Table 1. Level of Cr in effluent and sludge

Station	Concentration of Cr in effluent (mg/L) (n=4)			Concentration of Cr in sludge (mg/L) (n=4)		
	Total Cr	Cr^{VI}	Cr^{III}	Total Cr	Cr^{VI}	Cr^{III}
I	188.82 ± 2.261	26.11 ± 3.293	162.71 ± 1.504	2976.55 ± 71.436	2530.08 ± 62.575	446.47 ± 58.442
II	113.67 ±4.3417	17.00 ± 2.173	96.67 ± 4.712	3149.14 ± 84.538	2676.96 ± 82.690	472.18 ± 38.395
III	67.78 ± 1.884	10.08 ± 2.092	57.70 ± 2.0366	3237.48 ± 58.963	2800.00 ± 50.483	437.48 ± 60.888
IV	53.86 ± 3.929363	8.07 ± 0.650	45.78 ± 3.790	3328.47 ± 35.633	2829.20 ± 30.288	499.27 ± 5.345

Table 2. Level of Cr in soil and water

Type of sample	Concentration of Cr in contaminated sample (mg/L) (test sample)			Concentration of Cr in non-contaminated sample (mg/L) (controlled)			PLI
	Total Cr	Cr^{VI}	Cr^{III}	Total Cr	Cr^{VI}	Cr^{III}	
Concentration of Cr in soil at 15 cm depth (n=8)	123.30 ± 4.757	106.74 ± 4.137	16.02 ± 0.620	34.66 ± 3.036	30.14 ± 2.640	4.52 ± 0.396	3.54
Concentration of Cr in soil at 30 cm depth (n=8)	85.33 ± 4.448	74.20 ± 3.867	11.13 ± 0.580	28.44 ± 2.815	24.74 ± 2.448	3.71 ± 0.367	2.99
Concentration of Cr in water (n=4)	0.056 ± 0.009	0.030 ± 0.005	0.025 ± 0.004	0.029 ± 0.003	0.016 ± 0.002	0.013 ± 0.001	1.87

Table 3 The concentration of Cr in the edible portions of vegetables and fish of wetland area and the pollution load index (PLI)

Type of vegetables	Type of samples	Concentration of Cr (mg/L)			PLI
Cauliflower (*Brassica bortrytis*) (n=8)	Non-contaminated (Control)	Leaf	Range	0.18-0.28	3.83
			Mean ± S.D	0.24 ± 0.032	
		Flower	Range	BDL	
			Mean ± S.D		
	Contaminated (test sample)	Leaf	Range	0.85-0.98	
			Mean ± S.D	0.92 ± 0.043	
		Flower	Range	0.19-0.25	
			Mean ± S.D	0.24 ± 0.041	

Spinach (*Spinacia oleracae*) (n=8)	Non-contaminated (Controlled)	Range Mean ± S.D	1.81-2.42 2.14 ± 0.235	4.45
	Contaminated (test sample)	Range Mean ± S.D	8.81-9.82 9.36 ± 0.289	
Tilapia (*Tilapia mossambica*) (n=4)	Non-contaminated (Controlled)	Range Mean ± S.D	0.041-0.053 0.048 ± 0.005	2.08
	Contaminated (test sample)	Range Mean ± S.D	0.08-0.12 0.1 ± 0.018	
Bata (*Labio bata*) (n=8)	Non-contaminated (Controlled)	Range Mean ± S.D	0.045-0.05 0.048 ± 0.002	2.08
	Contaminated (test sample)	Range Mean ± S.D	0.07-0.13 0.1 ± 0.027	

Note: BDL = Below Detection Level

The Biological concentration factor (BCF) values of Cr in both vegetables and fish samples are presented in the Table 4. The estimated Daily intake of metal (DIM) through the food chain and the corresponding Health risk index (HRI) of adults and children are presented in Table 5.

DISCUSSION

These results indicate that there occurs a decline in chromium concentration in effluent as a function of distance while reverse trend is observed in case of sludge.

In the tannery effluent-irrigated soils and in the wetland where tannery effluent and sludge used as the food for fish, Cr concentration were significantly higher compared to their respective controlled samples. PLI of Cr in soil and water from wetland which repersents the number of times by which the heavy metal concentration in soils and fish at particular horizon exceeds the background concentration[6]. In this study area, soil contamination with metal is mainly due to the irrigation by the tannery effluent, application of sludge in the farmlands, and possible atmospheric deposition. The PLI of soil samples indicates that rate of accumulation of Cr at surface of the soil is greater as compared to the deep soil and therefore, hazardous to plant biomass[7]. The wetland are contaminated by tannery effluent and sludge as there are used as feed for the fish. The PLI values of vegetables and fish samples indicate high degree of contamination in the samples.

Table 4. Biological concentration factor (BCF) of Cr in vegetables and fishes

Types of samples (vegetables/fishes)	BCF of non-contaminated (control) sample		BCF of contaminated (test) sample	
	Leaf	Flower	Leaf	Flower
Cauliflower (*Brassica bortrytis*)	0.0079 ± 0.0015	-	0.0086 ± 0.0002	0.0024 ± 0.0002
Spinach (*Spinacia oleracae*)	0.069 ± 0.011	-	0.0087 ± 0.0005	-
Tilapia (*Tilapia mossambica*)	2.8 ± 0.490	-	3.35 ± 0.788	-
Bata (*Labio bata*)	3.0 ± 0.381	-	3.44 ± 1.037	-

Table 5. The estimated DIM through the food chain and the corresponding HRI of adults and children

Samples	DIM (mg/kg/person day)		HRI	
	Adults	Children	Adults	Children
Leaf of cauliflower (*Brassica bortrytis*)	4.82×10^{-4}	5.54×10^{-4}	0.16	0.18
Flower of cauliflower (*Brassica bortrytis*)	1.25×10^{-4}	1.44×10^{-4}	0.041	0.048
Spinach (*Spinacia oleracae*)	4.91×10^{-3}	5.64×10^{-3}	1.63	1.88
Tilapia (*Tilapia mossambica*)	4.29×10^{-3}	7.33×10^{-5}	0.014	0.024
Bata (*Labio bata*)	4.29×10^{-3}	7.33×10^{-5}	0.014	0.024

The bioaccumulation of environmental pollutants in aquatic and terrestrial biota is quantified with the assumption that organisms achieve a chemical equilibrium with respect to a particular media or route of exposure[8] and expressed with the help of 'Biological concentration factor'. Typically, the soil-to-plant and water to fish transfer factors are one of the key components of human exposure to metals through the food chain.

The high transfer values for Cr from soil to vegetables indicate a strong accumulation of the respective metals by food crops, particularly by leafy vegetables[9]. The above mentioned analysis indicates that the accumulation of metal is higher in the water containing body part. The rate of transfer of Cr in both types of fish samples are the same.

The above discussion indicates that some toxic heavy metal like Cr become concentrated instead of dispersed in the food chain. The accumulation of heavy metal like Cr in the food chain depends to a great extent on the environmental condition.

In order to assess the health risk of any chemical pollutant, it is essential to estimate the level of exposure by quantifying the routes of exposure of a pollutant to the target organisms. There are various possible exposure pathways of pollutants to humans but the food chain is one of the most important pathways. As the tannery induced Cr contaimnated vagetables and fish produced in the study area are mostly sold in the local urban market, therefore, the average metal concentrations of vegetables and fish were used for calcultion of the HRI. The determination of DIM is aldo required to calculate the HRI.

The data of HRI values were < 1 except in spinach. Therefore, the health risks due to chromium (VI), exposure through the food chain is not very significant except in case of spinach. Although the findings of this study regarding DIM and HRI suggest that the consumption of plants, except spincah, grown in wastewater-contaminated soils and the fish cultured in wetland contaminated by tannery effluent and sludge could be considered to be less hazardous, but there are also other soures of metal exposures such as dust inhalation, dermal contact and ingestion (for children) of metal contaminated soils, which were not included in this study. The HRI value of consumption of spinach for both adults and children was > 1. So, the frequent consumption of spinach, collected from the affected agricultural land could cause severe problems as Cr^{VI} poses a health risk. Hexavalent chromium is considered extremely toxic (causing liver damage, dermatitis and gastrointestinal ulcers), mutagenic and carcunogenic[10].

EXPERIMENTAL

Study area

Effluent and sludge samples were collected from Tannery Complex of Raebareli (India). The vegetables and waste water irrigated soil were collected from adjoining agricultural fields. Fish and water samples were collected from local wetland areas which were again fed by the above mentioned wastes.

Sampling and treatment of different samples

Tannery effluent samples were collected from four different sampling stations, which are located 0.05 km (station I), 0.25 km (station II), 0.5 km (station III) and 0.75 km (station IV), away respectively from the last discharge point of tannery complex. In case of sludge, around 3 kg of wet sludge was collected from four previously described sampling stations. 0.5 g of wet sludge was taken from the estimation and suspended in triple distilled water.

Samples of soil were collected from two different depths (15 cm and 30 cm) of the agricultural field which is irrigated by tannery effluent while the water samples were collected from the four different adjoining wetlands.

Two types of vegetables cauliflower (*Brassica bortrytis*) and spinach (*Spinacia oleracae*) were collected from the same sites where soils. In case of cauliflower, the leaves as well as flowers were considered while only the leaf part of spinach was taken for the experiment. Two types of fish (*Labio bata and Tilapia mossambica*) were sampled from same wetland area from where water samples were collected.

Analysis of the sample

The Cr^{VI} concentrations in the effluent, sludge, soil and water samples were determined spectrophotometrically at 540 nm after complexation with 1, 5- diphenylcarbazide[11] using a UV-V is spectrophotometer (Hitachi U-3410) and compared it with the standard curves. The concentration of total Cr in other samples including effluent and sludge were determined by atomic absorption spectrophotometer.

Quality control of the samples

The quality control of the samples was performed by comparing with the determined value of Cr in the respective non contaminated samples.

Biological concentration factor (BCF)

The biomagnification of pollutants in aquatic and terrestrial biota may be expressed with the help of BCF. BCF was calculated as follows :

$$BCF = \frac{\text{Concentration of metal in organism}}{\text{Concentration of metal in environment}}$$

Pollution load index (PLI)

The degree of pollution by metal was measured using the PLI technique. The following modified equation was used to assess the PLI level in different segment of environment.

$$PLI = \frac{\text{Concentration of metal in samples}}{\text{Concentration of metal in controlled samples}}$$

Daily intake of metals (DIM)

The DIM was determined by the following eqution.

$$DIM = \frac{C_{metal} \text{ X } C_{factor} \text{ X } C_{food\ intake}}{B_{averageweight}}$$

where, C_{metal} = heavy metals concentrations in vegetables and fish (mg kg^{-1}), C_{factor} = conversion factor = 0.085 and 0.16 was used to convert fresh weight to dry for vegetables and fish respectively, as described by Rattan *et al.*[12] , $D_{food\ intake}$ = daily intake of vegetables or fish = 0.345 and 0.232 kg $person^{-1}$ day^{-1} (average intake of vegetables for adult and children) = 0.150 kg $person^{-1}$ day^{-1} (average intake of vegetables for adult and children)[13] and $B_{average\ weight}$ = average body weight, respectively = 55.9 and 32.7 kg (adult and children respectively)[14].

Health risk index (HRI)

The HRI for the locals through the consumption of contaminated vegetables was assessed based on the DIM and the reference oral dose (ROD). The RFD for chromium(VI) as previously reported is 0.003 mg/kg/day[15], HRI = DIM/RFD[9].

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