Analysis of the accumulation of chromium in vegetables in effluent affected and non-affected soil: A Case Study

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Abstract: Leather and Leather products rank the 4th in earning foreign exchange for Bangladesh. Statistics prepared by Export Promotion Bureau of Bangladesh for the Financial Year 2011-12, the leather sector grew by 17.5 percent and earned $765 million in revenue. The department of environment (DOE) has categorized the industry as 'red' meaning it is one of the worst polluting industries in Bangladesh.Of the 220 registered tanneries in Bangladesh 90% are located on 25 hectors of land in Hazaribag in south-west corner of the Dhaka city. Most of the tannery factories are non –mechanized and semi mechanized and uses old and polluting leather processing methods. High percentage of chromium discharge through the waste liquor. Which is affected the soil of surroundings of hazaribag. Moreover it also affected the low land near river Buriganga.For this reason we try to find out the accumulation of chromium in vegetables in effluent affected and non-affected soil.

Index Terms— Vegetables, Chromium, Soil, Effluent, Accumulation, Tannery, wasteliquor,

1 Introduction

From 1800 to the mid-1960s South Asia used the vegetable tanned crust, a non-polluting tanning process which worked well as an environment friendly process. The Indian tannery industry was able to produce unfinished leather for export to W. Pakistan, Iran and Turkey among others for many years. The process was introduced in Bangladesh in the late 1940s, m 1965 the manufacture of "wet blue" leather generated a new chrome-tanned semi-processed leather industry that developed rapidly. The "wet blue" leather is made by an environmentally destructive process because of the use of chromium and other toxicants for tanning hides and skins. Never the less, chrome-tanned leather, became a major industry in just one decade. In 1977, the Government imposed an export duty on wet blue leather which forced the industry to convert crust and finished leather into value added leather products. Many joint ventures took advantage of the Promotion and Protection Act of 1980 which brought a large amount of foreign investment to Bangladesh. German, Italian and other European countries as well as American companies, among others, constructed joint venture leather processing plants in Hazaribag. From 1980 onwards the leather industry in Bangladesh flourished. The export value of this commodity was US$ 250 million by the end of the twentieth century, up from US$ 60 million in the late-1980s (Rashid, 1991).

According to world banks survey world bank (1993:128),of the 220 tanneries of Bangladesh ,4.07% are big size units (with annual production capacity of more than five million square feet each) 9.620% are medium size (with annual capacity of 1 to 3 million square feet each)8.5 % are light medium size (with annual production capacity of .5 to 1 million square feet each) and 40.7% are small size (with annual capacity of .5 million square feet or less each), the rest 30.03% are cottage based (with annual capacity of .5 million square feet each)

TANNERY INDUSTRIAL UNITS IN BANGLADESH

Total tannery units -	220
Dhaka -	90%
Chittagong -	6%
Others places -	4%

1.1 Ecological Impact

Ecosystem is the interacting system of a biological community and its nonliving surroundings. Ecosystem consists of media of environment (air, water and land), living organisms and compartments (for example; atmosphere, surface water, biota, soil, etc.). The mains ecosystems are atmoshreric ecosystem, aquatic ecosystem and terrestrial ecosystem.

- **Ecological impact** is the total effect of an environmental change, natural or man-made, on the community of living things. In any study of ecological impact, fate and transport

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routes, the key variables and processes need to be identified. Then they can be mathematically described and implemented into models assessing the ecological impact. This is important for development of remedial strategies.

- For Chromium that is produced from many industries for example; leather tanning, electroplating etc. into the environment. In aquatic system, there are many pathways, and it can cause ecological effects into the ecosystem; can effect on fishes and wildlife, etc. High concentrations of chromium (Cr 6+) in these systems (fish, sediment, plant, etc.) can due to the problems of bioaccumulation of toxic metals.

1.2 Impact of Chromium (Cr) in Human health

The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure.

1.3 Toxic effects of chromium in plants

Chromium compounds are highly toxic to plants and are detrimental to their growth and development. Although some crops are not affected by low Cr concentration. Cr is toxic to higher plants. In the following sections, we review several of the metabolic and physiological processes affected by Cr in plants. [1], [2], [3], [4], [5].

Effect of chromium on plant development

Process	Crop/plant	Effects
Germination	E. colona, bush bean, lucerne,mung bean,sugarcane	Reduced germination percentage and reduced bud sporouting
Root growth	Salix viminalis, caesalpinia pulcheeima, mung bean,rice, sorghum	Decrease in root length and dry weight, increase in root diameter and root hairs, proportional variations in cortical and pith tissue layers.
Shoot growth	Oats, curcumasativa, Lactuca sativa	Reduction in plant height
Leaf growth	Albizia lebbek, Acacia holocerica, Leucaena luecocephala, rice bush bean	Reduction in leaf number leaf area biomass. Trifoliate leaves more affected than primary leaf tip, negative effect on leaf mesostructure
Yield and dry matter production	Portaluca oleracea, cauliflower, cabbage, radish, bush bean, maize, finger millet, faba beans	Up to 50% reduction in yield ,reduced number of flowers per plant, reduced grain weight, increased seed deformity, reduced pod weight;

Effect of Chromium on Plant (Lal shak):

Fig: Non effected soil by effluent   Fig: Effluent effected soil

Process	Crop/plant	Effects
photosynthesis	Wheat, peas, nice, maize, beans, sunflower	Electron transport inhibition, Calvin cycle enzyme inactivation, reduced co_2 fixation, chloroplast disorganization
Water relations	Bush beans, sunflower, mung bean	Decreased water potential, increased transpiration rate, reduced diffusive resistance, wilting, reduction in tracheary vessel diameter.
Mineral nutrition	Soybean, tomato, bush bean, sunflower, maize	Uptake of N, P, K, Fe, Mg, Mn, Mo, Zn, Cu, Ca, B, affected inhibition of assimilatory enzymes, increase activity of ROS scavenging enzymes, changes in glutathione pool, no production of phytochelatins

Fig. 1. Effect of Chromium on Plant (Red amaranth)

Effect of chromium on plant physiology:

2 RESEARCH METHODOLOGIES

Materials and Method:

Soil pollution by heavy metals is great concern to public health. The source of heavy metal in plant is the environment in which they grow and their growth medium (soil) from which heavy metals are taken up by roots or foliage of plants. Plants grown in polluted environment can accumulate heavy metal (Chromium) at high concentration causing serious risk to human health when consumed. Moreover, heavy metal (Chromium) is toxic because they tend to bioaccumulate in plants and animals, bioconcentrate in the food chain and attack specific organs in the body. [6]

Vegetables constitute an important part of the human diet since there contain Carbohydrates, proteins, as well as vitamins, minerals and heavy metals. Heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of fresh vegetables. A number of elements, such as lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), chromium (Cr), Copper (Cu) and Selenium (Se) (IV) can be harmful to plants

And humans even at quite low concentrations (Bowen, 1979). Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of Industrial and urban wastes, etc. Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality, crop growth and environmental health.

Plant species have a variety of capacities in removing and accumulating heavy metals. So there are reports indicating that some plant species may accumulate specific heavy metals. The uptake of metals from the soil depends on different factors, such as their soluble content in it, soil pH, plant species, fertilizers, and soil type. Vegetables, especially leafy vegetables, accumulate higher amounts of heavy metals (Sharma and Kansal, 1986). Roots and leaves of herbaceous plants retain higher concentration of heavy metal than stems and fruits. There are limited studies on heavy metal content at different growth stages of vegetables, the most studies focused on the status of metal content in edible parts of vegetables. And an investigation of the literature also shows a scarcity of data on comparison of metal content at different leafy vegetable species in Bangladesh. Therefore, the present study was undertaken-

To quantity the concentrations of heavy metal content by different vegetable species.

3 COLLECTING THE SOIL FROM:

1. Beside the road of Hazaribag beri badh
2. Soil which are using in nursery

Soils from 0-15 cm depth were collected from two areas. Composite soil sampling was done from each sampling spot with the help of an auger as suggested by the Soil Survey Stuff of the [9] **USDA (1951)**. The collected soil samples were dried in air, ground, sieved and preserved for physical, chemical and physico-chemical analysis.

- **Preparation of soil:**

There are two source of soil which I collected. Crushing the soil to produce fine granules. Then clear all the unnecessary materials and add equal amount of cow dung as fertilizer with sample soil to nutrition the soil. After that, fill both two experimental bowls with prepared soil. Then wait for few days.

- **Chosen of seeds:**

There are two reason I chosen the seeds.

1. Most of the people used to feed themselves.
2. The quick growth rate.

With consideration above two reasons I chose –

a. Lal shak (*Red amaranth*)
b. Pat shak (*Corchorus olitorius*)
c. Pui shak (*Basella alba*)

for my experiment.

- **Plantation of vegetables:**

After collection of the seeds and show them to the prepared soil and wait for a month.

- **Plant sample collection:**

For successful analysis after a month I collected the sample from two bowls. Then take the sample to BCSIR.

Methods for plant analysis:

Distilled water was used throughout the study. All glassware and plastic containers used were washed with detergent solution followed by 20% (v/v) nitric acid and then rinsed with tap water and finally with distilled water. In the present study analyzed vegetables are lal shakh, pui shakh, pat shakh.

Sampling:

300 g of edible portion of different vegetables get collected and washed with distilled water to remove dust particles. They were separated in three parts (100g each). Then these three parts were chopped into small pieces using a knife and kept in air-dried condition for approximately 70 hours. Dried samples of different parts of vegetables were grind into a fine powder and powders were used for heavy metal analysis. Heavy metals in vegetable samples were extracted by acid digestion.

Powdered samples (15 g each) were accurately weighed and placed in a silica crucible and few drops of concentrated nitric acid were added. Dry ashing process was carried out in a muffle furnace by stepwise increase of the temperature up to 550°C and then left to ash at this temperature for 6h. The ash was kept in desiccators and then rinsed with 3N hydrochloric acid. Filtered the ash suspension in a 50 ml volumetric flask with the help of Whatman paper No 1 and made a volume by adding 3N hydrochloric acid up to the mark.

Analysis:

Concentrations of heavy metals in the acidic solution were estimated using Atomic Absorption spectrophotometer (Thermo Scientific Pvt. Ltd., India, and Model No.AA-303).

Methods for Soil analysis:

Sample Preparation:

[7]Homogenize the diet samples in a Waring Blendor or other suitable device. Place samples in a platinum or glazed porcelain dish and dry at90 °C. Transfer to a muffle furnace and ash at 400 °C for four hours. Cool. Weigh 0.5 g of ash into a 150-mL beaker and wet with 3 to 5 mL of deionized water, and dissolve with 2 mL of concentrated HNO_3.

Evaporate to dryness on a hot plate and add 2 mL of concentrated HNO_3. Evaporate again to dryness and dissolve the residue in HNO_3 with warming. Transfer to a 35-mL graduated conical-bottom glass stoppered centrifuge tube using in

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HNO_3 and dilute to volume. Mix well and centrifuge at 825 rpm to remove any silica particles.

Analysis:

Determine the concentration of the element of interest (in the supernatant) using the conditions listed in the "Standard Conditions" section. Standards are prepared by diluting the stock standard solution, described in the "Standard Conditions" for Cr with deionized water. Deionized water should be used as a blank.

4 RESULT & DISCUSSION

Naturally occurring amounts of heavy metals do not disturb the biochemical balance of soil. Slightly higher quantities of heavy metals might stimulate the activity of soil enzymes, whereas in larger dosages they will have an inhibitory effect. Heavy metals, however, are regarded as inhibitors of enzymatic and microbiological activity of soil. This is because if added to soil (whether on purpose or by accident) they cause quantitative and qualitative changes in the composition of micro flora and in enzymatic activity. The range of impact heavy metals have on microorganisms, soil enzymes and crops depends on the physicochemical properties of metals and soil. Chromium had an inhibitory influence of dehydrogenases, urease and acid and alkaline phosphatases. The inhibitory effect of chromium was correlated with the amendment of soil with nitragine. It was stronger in nitragine inoculated soil and weaker in the soil without symbiotic bacteria. In both series of experiments a negative correlation was observed between the degrees of soil contamination with chromium. Even the lowest rate of chromium (10 mg Cr ′ kg-1 of soil) was enough to depress the activity of dehydrogenases by nearly 20% in non-inoculated and 7% in inoculated soil. The highest concentration of chromium (150 mg Cr ′ kg-1 of soil) in both non-inoculated and inoculated soil caused a nearly complete inhibition of the activity of dehydrogenases. Chromium applied at 10 to 40 mg Cr ′kg-1 of soil stimulated, while higher rates of the pollutant inhibited the activity of urease.

Table 1 shows that mean chromium concentration of sample soil. Table 2 shows that mean chromium concentration of Leafy vegetables. table 3 shows that typical contents of some elements in soil and plants.

TABLE 1:
Mean Chromium (Cr) Concentration in Sample Soil

Sl No.	Sample	Mean(g/kg)
1.	Affected	42.523
2.	Non Affected	.0571

The Chromium (Cr) content in initial soil was quite high. The source of soil contamination by heavy metal may be as a result of top dressd-soil, which was collected from Hazaribag beribadh, near the bank of river Buriganga a highly industrial effluents polluted area. There is no doubt that heavy metals are also present in soil naturally and non-degradable. For these reason plants take more chromium than tolerance level. In table 2 we can see the chrome uptake of some leafy vegetables.

TABLE 2
Mean Chromium (Cr) Concentration in Leafy Vegetables

Sl No.	Sample	Uptake from effected soil (mg/kg)	Uptake from Non-effected soil (mg/kg)
1.	Pui Shak	4.52	1.16
2.	Lal Shak	11.3	
3.	Pat Shak	3.13	

if we consider table 3 as below as a standard value of some element in soil and plant we can compare the standard value and the resultant value. when the amount of chromium in leafy vegetable is cross the tolerance level of environment, then it is harmful for both plant and human body. it causes different types of diseases.

Sl No.	ESSENTIAL ELEMENTS	TYPICAL CONTENT			
		MEAN (mg/kg)		RANGE (mg/kg)	
		SOIL	**PLANT**	**SOIL**	**PLANT**
1	**B**	38	8	0.9-500	6-120
2	**C**	2%	45%	0.7-5%	
3	**Ca**	2%	0.5%	0.01-32%	
4	**Cl**	485	100	18-806	10-5500
5	**Co**	12		0.3-200	4-80
6	**Cu**	26	6	2.5-60	1-20
7	**Fe**	3.2%	100	0.01-21%	18-3580
8	**K**	1.8%	1%	0.005-7.9%	
9	**Mg**	0.83%	0.2%	0.005-16%	
10	**Mn**	437	25	7-8423	17-334
11	**Mo**	1.8	0.1	0.013-17	0.07-1.75
12	**N**	0.20%	1.5%	0.002-2.5%	2-6%
13	**Na**	1.1%		0.005-10%	
14	**P**	0.04%	0.2%	0.002-0.6%	0.18-0.41%
15	**S**	433	0.1%	3-8200	0.1-1%
16	**SiO_2**	60%	0.1%	50-70%	0.04-1.2%
17	**Zn**	64	20	3-762	6-75
TRACE ELEMENTS AND HEAVY METALS					
18	**Ag**	0.1	0.25	0.01-5	0.07-2.0
19	**As**	8.0	1.0	0.1-40	0.009-1.5
20	**Be**	1.6	0.02	0.7-3.52	0.001-0.4
21	**Cd**	<1	0.7	0.06-1.10	0.013-21
22	**Co**	10	1.0	<1-65	0.1-100
23	**Cr**	**65**	**0.11**	**5-1500**	**0.014-2.9**
24	**Hg**	0	0.003	0.04-0.4	0.002-0.09
25	**Li**	30	0.10	1.3-56	0.01-31
26	**Pb**	32	2.0	2-200	0.1-10
27	**Se**	0.33	0.10	0.01-2.32	0.003-0.98

TABLE 3
Typical contents of some elements in soil and plants: [8]

8 CONCLUSION

Industrialization in Bangladesh that had started in the early fifties is slowly growing. The contribution of the industrial sector to the GDP has still not exceeded 10%. Although Bangladesh is comparatively a late comer in industrialization and its size is still small, the pollution problems caused from the sector are quite remarkable. The tannery industry is in the forefront among the industries that pollute. In fact, the pollution from the tannery factories which are concentrated mainly in Dhaka, is phenomenal. On the one hand, the technologies used in the tannery industry are considerably old and inferior, on the other, almost all the solid and liquid wastes generated in the tannery units are dumped untreated in violation of the environmental laws. The unavoidable consequences are serious damages to the land, soil, air, water, habitat and human health.

Chromium content in different leafy vegetables varies significantly. The Cr contents in leafy vegetables in this study were detected higher than the permissible limits as per the WHO standard. The magnitude of time dependence of plant metal concentration variations differed among crop species and metals. Further research is needed to obtain more specific information about the effect of age of the plants on accumulation and distribution of the Chromium in the different plant parts, variations in uptake between different plant species, cropping history and fertilization.

Suggestions to minimize the problems:

Despite of its adverse effects, its contribution to the GDP (Gross Domestic Product) in a poor country like Bangladesh is not negligible. Rather a sustainable approach should be taken to minimize the adverse effects of tanneries.

Following steps may be taken for minimize the effect of chromium:

1. Vegetation should be avoided in chrome affected land.
2. Establishment of Central Effluent Treatment Plant (CETP) for treating the waste water.
3. Less amount of chromium should be used in tanning process.
4. Assess the effects of tannery wastes on soil quality with respect to physical biological studies.
5. Using of chemicals within acceptable limits according to the regulation provided by the Department of Environment (DoE).
6. Proper disposal of solid wastes containing harmful chemicals should be ensured, no wastes should be burnt in open place under any circumstances.
7. Considering the socioeconomic aspect of Bangladesh low cost coagulant such as alum, lime and ferric chloride can be chosen for the treatment of tannery effluents.
8. Effective Environmental Management Plan (EMP) should be introduced for minimize the pollution.
9. Several researches should be continued to replace the chrome tanned leather.
10. Recovery, recycle and reuse the chromium

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