Studies on Environmental Pollution in Bangladesh using Reactor based Neutron Activation Analysis Technique

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Abstract

To assess the environmental degradation, the concentration of heavy metal such as chromium (Cr) in soil samples at various depths of existing tannery area of Hazaribagh, Dhaka, Bangladesh and the proposed tannery industrial area at Tatuljhora, Savar Dhaka, Bangladesh were analyzed by reactor based Neutron Activation Analysis (NAA) method. Arsenic levels in water, soil and herbal at different locations of Sonargaon Upzilla in Narayanganj district, Bangladesh were determined by the same method. The Cr-content at different depths of Hazaribagh area was found in the range of 38 to 33,500 ppm. Higher accumulations were observed in top soil that is above the US permissible level (20 to 85 ppm) except only one sample. The Cr-concentration in soils of Tatuljhora was in the range of 50.9 to 93.6 ppm, which is within the range of chromium background levels reported in worldwide (7 to 221 ppm). Arsenic detected in soil was in the range of 2.06-11.35 ppm. Few water samples contain arsenic above permissible level (0.05 ppm). Surprisingly, arsenic was also found considerably high in some herbals. The arsenic was not found in some herbal corresponding to the water samples where arsenic was not detected. Therefore, some Ayurvedic herbal medicine may be contaminated when they will be prepared with arsenic rich herbs.

1. Introduction

Environmental and health related problems have become a major global concern in the recent years. Bangladesh is now facing a serious problem about arsenic (As) and chromium (Cr) toxicity, which contaminate our environment. Arsenic exposure is a potential health risk to local population in most of the parts of Bangladesh.

Chromium is a naturally occurring element found in soil, rocks, and plants. Another source of Cr is chemical emissions in the manufacturing industry. Chromium normally exists in oxidation states ranging from chromium (II) to chromium (VI). The trivalent is the most common form found in nature. All forms of chromium can be toxic at high levels, but hexavalent compounds are more toxic than its trivalent form. Chromium is extensively used in industries. Generally, the hexavalent form of chromate compounds is of greater industrial importance, particularly in leather tanning. One of the largest sources of chromium emission in the environment comes from the waste of leather tanning industries.

Hazaribagh is a densely populated area of Dhaka city in Bangladesh, where about 149 leather processing industries are in operation and discharge a lot of solid and liquid wastes directly to the low-lying areas, river and natural canals without proper treatment. These tanneries follow the practice of chrome tanning. In this practice the leather takes only 50-60% of the applied chromium and the remaining is discharged as waste [1]. The pollution load emanating from tanneries is directly affecting surface water, ground water, soil and air. A number of people have been affected directly and indirectly with chromium of wastes from tannery industries.

In Bangladesh, as over 97% of its population are dependent on the ground water for drinking and cooking purposes [2], where soil is second most or equally used substance. Moreover, now a day, the villagers frequently consume Basil leaves as Ayurvedic Herbal Medicine for the treatment of various diseases such as cold headache. The present research has involved in analyzing tube well water, soil and herbal for assessing arsenic contamination in the villages of Sonargaon Upzilla in Narayanganj district.

Environmental research using instrumental neutron activation analysis (INAA) for the determination of trace and ultra-trace element pollutants has a great potential in relation to human health. The total element concentration has been traditionally used to assess environmental impact and health risk of the element. We have a 3MW TRIGA Mark-II research reactor at Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh. Our interest is to study environmental pollution due to As and Cr through distribution in environment over Bangladesh. Particularly, this work was undertaken for determining As-content in water, soil and herbal plants, and Cr-content in soil of tannery industrial areas as a part of our systematic studies.

2. Experimental techniques

2.1 Sample collection and preparation

For Cr-determination, thirty soil samples were collected at several depths of different locations (L-1, L-2 ......) from both of Hazaribagh tannery area and the Tatuljhura proposed tannery area. The samples were dried in an oven at a temperature of about 70° C until they attained constant weight followed by ground. About 55 mg of each dried soils and IAEA certified reference materials Soil-7, SL-1 and NIST standard reference material Coal Fly Ash

(1633b) were placed into a clean small polyethylene bags, respectively. The packs were heat sealed and then encapsulated in polyethylene papers, which were also heat-sealed.

The water, soil and herbal samples were collected from the five villages of Sonargaon, Narayangong district. Data were collected through house-to-house survey by interviewing a certain number of tube-well owners. The surface soil and herbal samples were collected around the tube-wells from where the water samples were collected. The tube-well water samples were collected in a polypropylene bottle, which was cleaned by HNO_3 and dried to avoid contamination and absorption of As within the bottle. About 500 μl of water from each water sample, standard reference material of arsenic (Chinese As standard) and trace metal element in water (1643d) from NIST were pipetted using micropipette on eight folds of whatman filter papers.

For As-determination, soil samples were collected in polyethylene bags from rooting zone of the herbals grown around the tube-wells from where the water samples were collected. The soil samples were dried in an oven at temperature of about 70^{o}C until they attained a constant weight and followed by ground.

Collected Herbal samples (Basil leaves) were washed with distilled water and then dried at 70^{o}C for thirty-five hours in oven and grounded to make powder. The herbal sample is also prepared in the same way as soil.

2.2 Irradiation

Two sets of samples for Hazaribagh and Tatuljhura were prepared for separate irradiations. The Cr-containing samples and standards [IAEA Soil-7 & SL-1 and NIST Coal Fly Ash (CFA) 1633b] were irradiated with thermal neutrons of ~ 2×10^{12} n cm^{-2} sec^{-1} for 3 hours at 250 kW in Lazy Susan of the 3 MW TRIGA Mark-II research reactor.

The three individual sets for water, soil and herbal samples together with standard and blank were irradiated with thermal neutrons of flux about 7.6×10^{12} n/cm^2/s for 80 minutes at 250 kW in DCT at the same reactor with the aim to determine As.

Three Fe foils were also irradiated simultaneously at bottom, middle and top of stack of samples to correct the variation of beam flux along the stacked samples.

2.3 Data analysis

The activities of the irradiated samples were measured nondestructively by HPGe gamma spectrometry system with associated electronics and S-100 MCA computer acquisition software. The activity measurement was started two days after end of bombardment (EOB) because of high activity. Before counting, the outer envelopes of irradiated samples were replaced with a new polyethylene bags to avoid radioactive contamination. Gamma spectra of both samples and standards were collected in same geometry. During counting, the dead time was kept below 10% and the counting statistics of peak area was less than 5%. Each sample was recounted 3 times by giving sufficient cooling time interval to avoid the disturbance of overlapping γ-lines from undesired sources.

The concentrations of the investigated elements in samples were determined in comparison of standard material with known concentration. The relative method is the most simple and accurate way of quantifying the concentration of an element. In this method sample and standard are irradiated together, and both are counted under exactly the same conditions by the same detector. This procedure eliminates any uncertainty in the parameters e.g., cross sections, neutron flux, decay scheme and detector efficiency. Therefore, the formula for the determination of element using the comparative method is as follows;

$$m_{unk} = \frac{R_{unk}(e^{\lambda T})_{unk}}{R_{std}(e^{\lambda T})_{std}} \times m_{std} \qquad \text{....................(1)}$$

where , m_{unk} = mass of element in the unknown sample

m_{std} = mass of element in the standard

R_{unk}= count rate of the unknown sample

R_{std} = count rate of the standard

T = decay time.

3. Results and discussion

3.1 Chromium in soil

Quality control (QC) test is performed to investigate the reliability of the analysis by measuring chromium concentration in standard reference materials CFA, SL-1 and Soil-7 relative to primary standard. The experimental results are varied with the certified values within 6%. The deviation was achieved within the uncertainties quoted with the certified values. Therefore, INAA is an efficient method to determine chromium in soil samples. It should have to mention that the concentration of chromium in soil of Hagaribagh tannery area, Bangladesh was also determined using prompt gamma-ray analysis (PGA) technique at the JRR-3M reactor, Japan Atomic Energy Agency [3]. In PGA method, Cr-content was found 1.45 %, where 1.53 % was obtained in same sample by INAA.

The Cr-element was identified via the $^{50}Cr(n,\gamma)^{51}Cr$ reaction. The gamma ray emitted from ^{51}Cr at 320.1 keV was not interfered from other short-lived radioactive nuclides since the samples were measured after long cooling time. But ^{51}Cr can also be produced *via* the ^{54}Fe (n, $\alpha)^{51}Cr$ reaction in the sample. To observe this interference effect, a simultaneous experiment with pure iron foil (99.9%) was performed. In the present study the peak at 320.1 keV was not observed due to the $^{54}Fe(n,\alpha)^{51}Cr$ reaction. Therefore, in the analyzed samples the chromium peak at 320.1 keV is not interfered due to the $^{54}Fe(n,\alpha)^{51}Cr$ reaction. As shown in Fig. 1, in Hagaribagh, the Cr-content in the range of 880 to 33550 ppm was found in surface soils and it was 71-90 ppm for Tatuljhura as shown in Fig. 2. For Hagaribagh, the Cr-concentration decreases with the increasing of depth upto 180 cm, then scattered results were found as shown in Fig.1. The Cr-concentrations of soils in Hagaribagh are rather high and in the most cases these are above permissible level. The Cr-concentration of Tatuljhora was in the range of 50.87 to 93.63 ppm, which is below the permissible level reported in worldwide (Sandia Corporation, 2000) [4].

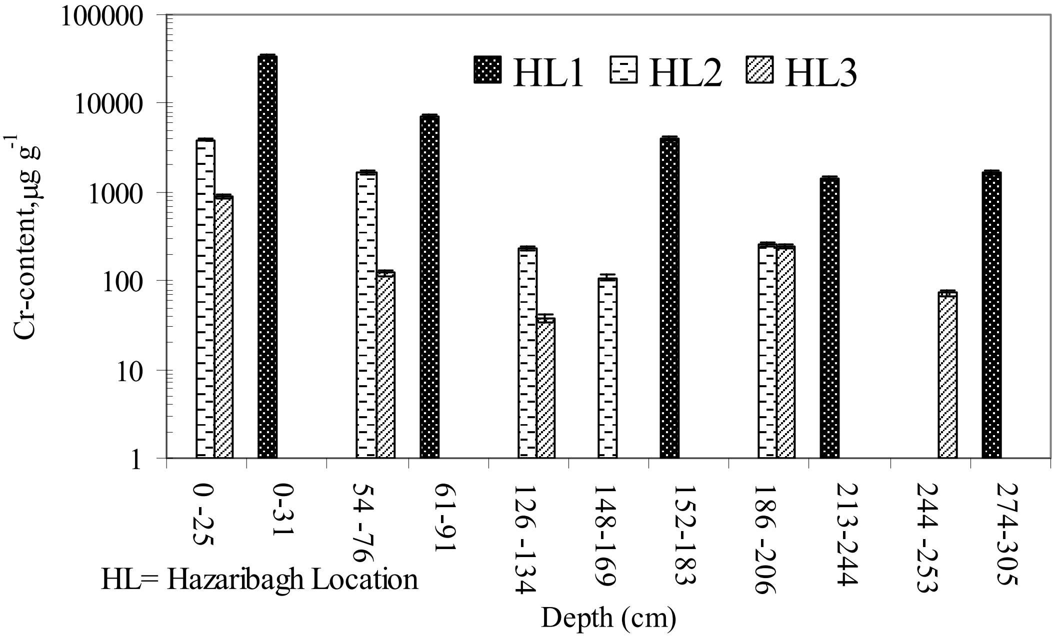

Fig. 1 Chromium content in soils at different locations of tannery area in Hazaribagh.

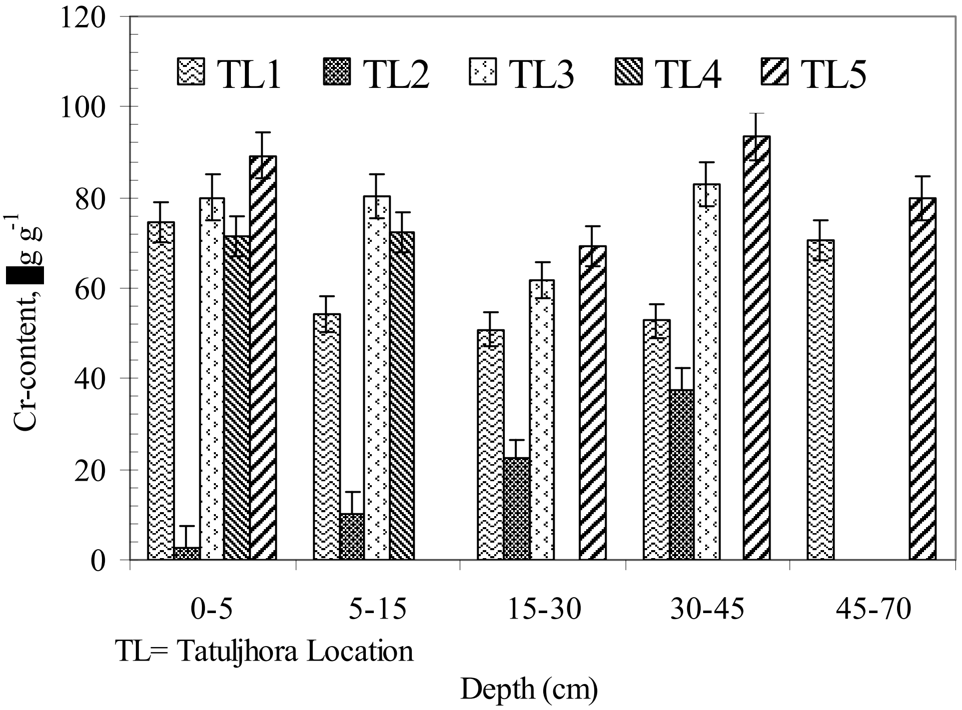

Fig. 2 Chromium content in soils at different locations of the proposed tannery area in Tatuljhora, Savar.

Background levels for chromium in soils have not been compiled for Bangladesh. However, chromium soil background data collected by scientists in the United States provide enough information to discuss the toxicity of Bangladesh soils from the tannery area. The Sandia Corporation (2000) [4] reported that chromium background levels in soils of the world range from 7 to 221 ppm and in soils of the United States range from 20 to 85 ppm. The Cr-concentrations of soils in Hagaribagh are rather high and in the most cases these are above permissible level. Chromium levels in Tatuljhora soil are found to be within the range of chromium background levels reported in worldwide (Sandia Corporation, 2000).

3.2 Arsenic in water, soil and herbal

The concentrations of As in water, soil and herbal were determined using the instrumental neutron activation analysis technique. The obtained results are quoted in table 1. The uncertainties are also given. The details are given in the following subquent sections.

i) Arsenic in tube-well water

Tube-well water of Sonargaon region is highly contaminated by arsenic. Six out of ten samples were contaminated by arsenic varied from 0.064 to 0.244 ppm. The maximum permissible level of arsenic in water is 0.050 ppm for Bangladesh (World health organization

Report). The detection limit of As in water is 0.036 ppm. The concentration of As in water of around 50% investigated tube-wells of Sonargaon exceeds the permissible level. In the most cases, the water sources of the investigated area are not suitable for drinking, cooking and agriculture purposes.

Table 1 Measured concentration in water, soil and herbal.

Sample No.	Arsenic concentration (ppm)		
	Water	Soil	Herbal
1	0.084±0.016	4.35±0.41	0.41±0.11
2	0.067±0.013	4.02±0.43	0.79±0.22
3	0.244±0.033	6.28±0.66	1.18±0.27
4	0.065±0.011	3.63±0.48	BDL
5	BDL	3.61±0.46	BDL
6	0.064±0.012	2.06±0.38	0.42±0.11
7	BDL	8.27±0.87	BDL
8	BDL	11.35±1.10	BDL
9	BDL	10.86±0.97	BDL
10	BDL	3.69±0.41	BDL

Note: BDL = Below detection limit
Error: Due to counting statistics only (1σ)

ii) Arsenic in soil

The arsenic concentration in soil of Sonargaon varied from 2.06 to 11.35 ppm. The detection limit of As in soil is 0.91 ppm. The normal level of arsenic in soil for Bangladesh is less than 3 ppm, where as 5 ppm arsenic containing soil can be considered toxic to sensitive crops. Therefore, the soil of Sonargaon is highly contaminated by arsenic. So the region is at risk to grow crops on the fields.

iii) Arsenic in herbal

Arsenic also contaminates herbal plants, which were collected from basil plants grown with tube-well water. From these tube-wells water samples were also collected. In the four out of ten herbal samples arsenic was found. The arsenic contents in herbal samples varied from 0.41 to 1.18 ppm. The detection limit of As in herbal sample is 0.33 ppm under the present experimental conditions. The Basil leaves are frequently used as Ayurvedic especially for children to recover from cold headache and many other diseases. Since herbals are being used in preparing of Ayurvedic medicine, manufacturer should consider the arsenic contamination.

4. Conclusion

In the present study, chromium contamination was assessed in the surrounding soils of Hazaribagh tannery industries and in the proposed Tatuljhora (Savar) tannery complex (under development). From the results of the present experiments it appears that Hazaribagh area is seriously contaminated with chromium. Almost all the soil samples were found to contain chromium at elevated level. The maximum chromium concentration recorded in soils at Hazaribagh in this study is 33,500 ppm. The high level of Cr found in surrounding soils of existing tannery industries at Hazaribagh, Dhaka due to discharging of tannery effluents to the environment without treatment. The chromium concentrations in Tatuljhora soil ranging between 50.9 to 93.6 ppm from the surface to a depth of 70 cm, the maximum depth of sampling. These values are within the background range of chromium values in soils over the world. These results will be useful as baseline data that will help to assess the level of contamination when the tannery industries will discharge their waste in the environment.

Arsenic was detected in each of ten soil samples in the concentration range of 2.06-11.35 ppm, where only one was around the permissible level (2 ppm). Five water samples out of ten contain arsenic above permissible level (0.05 ppm). Surprisingly, arsenic was also found considerably high in some herbal samples. The arsenic was not found in some herbal samples corresponding to the water samples where arsenic was not detected. Therefore, the presence of arsenic in ayurvedic herbal medicine may be done through the contamination of herbal plants with arsenic contaminated water and soil.

The obtained results will play important role to create public awareness on contamination with As and Cr. This study reports baseline data for the proposed tannery industry in Tatuljhura that will help to assess the level of contamination when the tannery industries will discharge their waste in the environment. It is suggested that in the proposed tannery industries, the effluents should be released to the environment by passing through the proper effluent treatment plant (ETP) to reduce the chromium level.

Acknowledgements

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