Indian Journal of Pure & Applied Physics
Vol. 61, June 2023, pp. 484-488
DOI: 10.56042/ijpap.v61i6.2426

Analysis of Heavy Metals using ICP-MS in Soils around some Tannery Industries

Arti & Rohit Mehra*

Department of Physics, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144 011, India.

Received 20 February 2023; accepted 23 May 2023

Heavy metals are naturally present in the soil. But increased industrial activities have led to an increased level in the soils. Industries discharge their wastes into the environment immediate to them. The effluent mainly carries many heavy metals. Most of the effluents from industry carrying many heavy metals are being disposed into drains, affecting the soil underneath and around it. Soil serves as one of the most important sources of heavy metal exposure to humans and animals. Soil samples were collected from different sites in the industrial area of Jalandhar, Punjab and analyzed using ICP-MS (Inductively coupled plasma mass spectrometer) for potential contamination of heavy metals (Cr, Cd, As, Zn, Cu & Pb). The order of the average concentrations of tested heavy metals is Cr > Zn >Cu > Pb > Cd >As. The average concentrations of Cr, Cd, As, Zn, Cu and Pb in the soil samples are 36.7µg/g, 0.15µg/g, 0.10µg/g, 24.8µg/g, 4.47µg/g and 2.44µg/g respectively. The corresponding contamination factors for these heavy metals are found to be 0.52, 0.76, 0.01, 0.19, 0.13 and 0.15 for Cr, Cd, As, Zn, Cu and Pb respectively. The contamination factors for all the heavy metals are found to be below 1, which suggests that the soil in the area has mild contamination of heavy metals. Pollution load index of the area has been found to be 0.166, which again suggests a Low level of deterioration of the study area due to heavy metals.

Keywords: Soil Pollution; Tannery Industry; ICP-MS; Contamination factor; Heavy Metals

Introduction

Heavy metals have found many applications in the industrial world today. Most of them are so indispensable that dependency on them cannot be discarded. But, employing such heavy metals in enormous amounts in the process of manufacturing or processing of goods is leading to their increased levels in the environment[1]. The effluent carrying enormous number of heavy metals are being discharged into the water bodies and soil directly without being treated which leads to their contamination and rise in the level of toxic heavy metals[2]. Along with the pollution of water by the direct involvement in processing and manufacturing units, soil on which the effluent is discharged is also being affected by the industrial discharge[3]. Tanning is the process of converting skin hides into leather. A large amount of water is being used in the process and most of it is usually being discharged into the water bodies and into drains without proper treatment. This process involves several chemicals being added to the skin hides for increasing the strength and durability of the processed leather. The effluent that is being discharged from these industries, when assessed for heavy metals have been found to contain many heavy metals[4,5].

Chromium being one of the majorly used chemicals for tanning has been found to be in increased levels in discharge from the industries[6]. Along with the assessment of tannery effluent directly, the environs in direct contact with the discharge have also been assessed and show higher levels of heavy metals in water as well as soil[7]. The discharge has been found to affect not only the surface waters but also the groundwater[8]. Water used for drinking is also found to be contaminated by heavy metals[9]. This water containing heavy metals above the prescribed limits when consumed by the human population can lead to varied levels of toxicity[10]. Along with it when this discharge is disposed of directly onto soil without proper treatment, it leads to higher levels in the soil too[11]. Soil forms the main source of nutrition to plants and thus leading to a transfer of these heavy metals from the soil to the food chain[12]. The increased levels of chromium in the consumed water or soil may lead to many other metabolic deformities too[13]. Heavy metals are also found to cause induced toxicity, fatality and gut microbial dysbiosis in aquatic animals[14]. Varied levels of heavy metals and the induced toxicity as a result of Tannery industrial wastes and effluents has been reported [15].

The aim of this study was to study the effect of industrial effluent from the tannery industry being directly disposed into the soil on the net heavy metal

*Corresponding author: (E-mail: mehrar@nitj.ac.in)

concentration in soil. As has been indicated in various studies that the levels have been found to be higher in certain regions[16,17]. This study was conducted in the leather complex area of Jalandhar, Punjab, India for the potential contamination of heavy metals in soil. The contamination factor for area and pollution load index have also been studied for a better understanding.

2.1 Materials and Methods

2.1 Area of study and sample collection

Jalandhar, Punjab is one of the major leather producers in India. Most of the leather industries are in the Leather complex area of Jalandhar. These industries discharge their effluents directly into the Kala Sanghian drain in the city and thus leading to a direct contact between the tannery effluent and soil of the area. Samples were collected from the leather complex area of Jalandhar, which is in proximity to the Leather industries as shown Fig. 1. For the analysis the area was divided into 24 grids. Within each grid cell, one random sampling site was chosen, taking into account the availability of soil. The samples were collected in air tight polythene bags and labelled properly.

2.2 Pre-processing of soil samples

he collected soil samples were dried in the oven properly to remove any moisture content and then sieved through a 150 µm sieve to remove any stones and organic matter (Fig. 2). After the pre-processing, the samples are taken for digestion, so that all the heavy metals in the soil can be brought to liquid matrix for analysis. For this, a prepared soil sample weighing 0.25 g was precisely weighed into a vessel. The digestion of samples is done by aqua regia [18]. The vessels were taken for digestion by microwave digestor and kept inside the digestor for a heating time of 20 minutes and a cooling time of 5 minutes (Fig. 3). The resultant solution was filtered and diluted in a volumetric flask to the 25.0 mL mark.

2.3 Analysis of soil samples

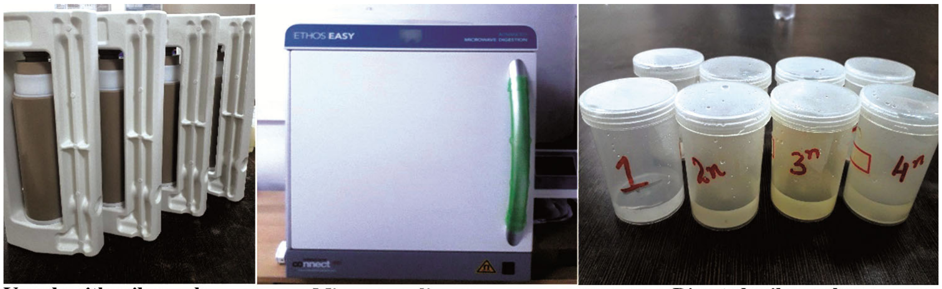
The heavy metal analysis was performed using AgilentTriple Quad Inductively Coupled Plasma Mass Spectrometer (ICP-MS QQQ- 8900). The pre-processed digested and diluted samples were taken for the analysis of Heavy metals *i.e.*, Cr, Cd, As, Zn, Cu & Pb. For the calibration of the instrument Agilent's IMS-102 standard was used. The samples were made by proper dilution using standard micropipettes Millipore water.

3 Results and Discussion

After the pre-processingof samples and proper microwave digestion, the samples have been analyzed for the targeted heavy metals i.e., Cr, Cd, As, Hg, Cu, Pb, Fe, Ni. The results obtained by the He collision method in ICP-MS have been tabulated in Table 1.

Fig. 1 — Representation of Sample collection locations.

Fig. 2 — Pre-processing of soil samples.



Vessels with soil samples **Microwave digestor** **Digested soil samples**

Fig. 3 — Microwave of digestion of processed soil samples.

Table 1 — Concentration of heavy metals(µg/g)

Sample number	Chromium	Cadmium	Arsenic	Zinc	copper	Lead
1	30.23	0.01	0.23	33.21	1.23	2.11
2	31.23	0.11	0.14	17.23	2.34	1.21
3	43.24	0.22	0.03	12.34	0.54	1.54
4	44.37	0.13	0.01	40.23	10.34	4.34
5	28.15	0.25	0.04	23.34	2.45	2.23
6	11.23	0.26	0.22	34.45	13.23	8.34
7	71.22	0.17	0.02	12.34	0.56	2.44
8	29.13	0.07	0.12	35.44	0.32	1.32
9	19.41	0.12	0.11	24.82	2.44	2.44
10	37.43	0.13	0.22	25.23	8.43	1.34
11	52.14	0.15	0.21	15.62	0.25	2.23
12	43.92	0.11	0.12	17.87	1.25	3.21
13	22.84	0.13	0.13	21.76	0.67	0.32
14	21.25	0.25	0.01	23.11	9.24	2.32
15	23.28	0.23	0.23	11.12	3.22	0.81
16	41.27	0.24	0.01	18.21	5.32	3.21
17	30.48	0.17	0.05	21.21	6.11	2.24
18	32.17	0.11	0.20	28.31	4.22	3.43
19	61.21	0.01	0.11	31.21	3.42	3.11
20	32.24	0.05	0.02	41.22	9.32	0.62
21	41.13	0.21	0.14	21.22	9.37	1.25
22	55.27	0.23	0.02	18.32	3.20	3.23
23	62.33	0.15	0.01	34.94	4.32	3.01
24	17.32	0.13	0.06	33.84	5.43	2.32
Max	71.22	0.26	0.23	41.22	13.23	8.34
Min	11.23	0.01	0.01	11.12	0.25	0.32
Average	36.77	0.15	0.10	24.85	4.47	2.44

Average concentration of Heavy metals

The average concentrations of Cr, Cd, As, Zn, Cu and Pb in the soil samples are 36.7µg/g, 0.15µg/g, 0.10µg/g, 24.8µg/g, 4.47µg/g and 2.44µg/g respectively. The concentration of chromium in the soil samples varied in the range 11.23-71.22 µg/g. which suggests that the concentration of chromium is higher in certain samples than the background soil concentration. Similarly, the concentration range of cadmium is 0.01-0.26 µg/g, for Arsenic it is 0.01-0.23 µg/g, for copper 0.25-13.23, for zinc 11.12- 41.22 µg/g and 0.32-8.34 µg/g for Lead. Most of the samples have heavy metal concentrations below the world average background values suggested by Martin and Meybeck (1979)[19].

3.2 Order of heavy metals in the soil

The order of mean concentrations of heavy metals in the soil so obtained is Cr > Zn >Cu > Pb > Cd >As. Chromium has been found to have the maximum average value and some of the samples show higher values of chromium content.

This may be attributed to the leather industries in the area. Further, as the samples have been collected in the month of August- September, which marks the post monsoon season chances of higher concentrations of chromium in the soil can be predicted.

3.3 Contamination factor

The amount of a given metal present in a soil sample is expressed as Contamination factor calculated using equation 1. Here C_{Hm} (sample) is the concentration of the metal present in the soil sample and C_{Hm} (background) is the metal's value equal to the world surface rock average presented in Table 2[19].

$$C_n = \frac{C_{Hm}\,(sample)}{C_{Hm}\,(Background)} \quad \ldots(1)$$

The contamination factor is referred to using the words below: C values less than 1 indicates mild contamination, C values less than 3 indicates moderate contamination, C values between 3 and 6 indicates significant contamination, and C values greater than 6 indicates extremely high contamination.

Table 2 — Background Heavy metal Concentration

Heavy Metal	Background concentration (μg/g)[19]
Cr	71
Cd	0.2
As	7.9
Zn	127
Cu	32
Pb	16

Using the equation 1, contamination factors for all the samples have been calculated and tabulated in Table 3. For each sample, the contamination factors for chromium, cadmium, copper, Arsenic, Zinc, and lead have been calculated. The values for chromium range in between 0.2 to 1, for cadmium 0.05 to 1.3, for Arsenic 0.001 to 0.03, for copper 0.41 to 0.007, for zinc 0.08 to 0.32 and for lead 0.02 to 0.52.

The average values of contamination factors are 0.52, 0.76, 0.01, 0.19, 0.13 and 0.15 for Chromium, cadmium, arsenic, zinc, copper, and lead respectively. For a proper analysis of the values obtained for contamination factors a graph has been plotted in Fig. 4, between average concentration of heavy metals and the respective heavy metals.

3.4 pollution load index

To assess the net heavy metal pollution in the area of study, Pollution load index for all the samples have

Table 3 — Contamination factors for different samples

Sample number	C_1 (Cr)	C_2 (Cd)	C_3 (As)	C_4 (Zn)	C_5 (Cu)	C_6 (Pb)
1	0.43	0.05	0.030	0.26	0.03	0.13
2	0.44	0.55	0.020	0.14	0.07	0.07
3	0.61	1.10	0.003	0.09	0.01	0.09
4	0.62	0.65	0.001	0.32	0.32	0.27
5	0.39	1.25	0.005	0.18	0.07	0.13
6	0.15	1.30	0.027	0.27	0.41	0.52
7	1.01	0.85	0.002	0.09	0.01	0.15
8	0.41	0.35	0.015	0.28	0.01	0.08
9	0.27	0.60	0.010	0.19	0.07	0.15
10	0.52	0.65	0.020	0.19	0.26	0.08
11	0.73	0.75	0.030	0.12	0.01	0.13
12	0.61	0.55	0.010	0.14	0.04	0.20
13	0.32	0.65	0.020	0.17	0.02	0.02
14	0.29	1.25	0.001	0.18	0.29	0.15
15	0.32	1.15	0.030	0.08	0.10	0.05
16	0.58	1.20	0.001	0.14	0.17	0.20
17	0.43	0.85	0.006	0.16	0.19	0.14
18	0.45	0.55	0.030	0.22	0.13	0.21
19	0.86	0.05	0.010	0.24	0.11	0.19
20	0.45	0.25	0.002	0.32	0.29	0.04
21	0.58	1.05	0.020	0.17	0.29	0.07
22	0.78	1.15	0.002	0.14	0.10	0.20
23	0.87	0.75	0.001	0.27	0.13	0.18
24	0.24	0.65	0.010	0.27	0.17	0.15
Average	0.52	0.76	0.010	0.19	0.13	0.15
Max	1.01	1.30	0.029	0.32	0.41	0.13
Min	0.15	0.05	0.001	0.087	0.038	0.07

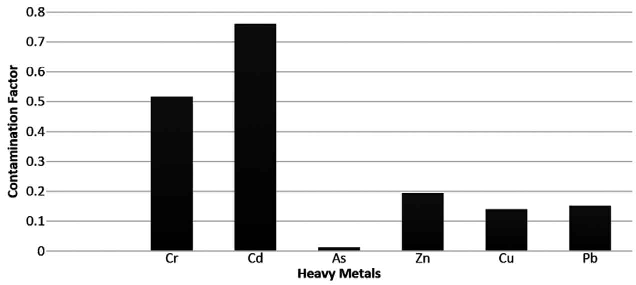


Fig. 4 — Graph showing the variation of contamination factors in the study area.

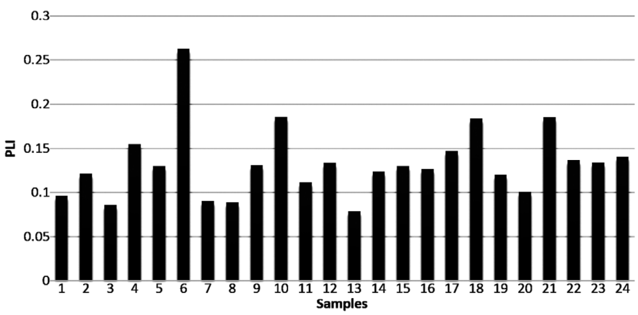


Fig. 5 — Graph showing Variation of Pollution Load Index with samples.

been plotted in Fig. 5. PLI is used to assess the level of heavy metal pollution, and it has been done in accordance with the methodology suggested by Tomlinson et al. (1980)[20]. It gives sufficient details on the importance of the metal concentrations that have been detected in relation to the inherent soil properties. The expression for this parameter is:

$$PL = C_1 \times C_2 \times C_3 \ldots\ldots \times C_n \qquad \ldots(2)$$

PL is a comparative tool for evaluating a site's quality; a value of PL less than 1 indicates that the site is perfect or pollution-free, while PLI = 1 indicates that only baseline conditions exist. PL greater than 1 would signify a decline in the quality of the site[20].

Conclusions

Soil samples in the area have been assessed for heavy metal contamination *i.e.*, Cr, Zn, As, Cu, Pb and Cd for the sample collection period August-September. The order of the mean concentrations of tested heavy metals is Cr > Zn >Cu > Pb > Cd >As. The average concentration of Cr, Zn, As, Cu, Pb and Cd in the study area are 36.74µg/g, 24.82µg/g, 0.10µg/g, 4.47µg/g, 2.44µg/g and 0.15 µg/g. It is found that the contamination factor for all the heavy metals is less than 1, which suggests that the soil in the area has mild contamination of heavy metals.

The Pollution load index of the area is found to be 0.22, which is again less than one suggesting a mild contamination of the study site with heavy metals. Concentration of chromium in some of the samples is found to be little higher, suggesting to a need of further assessment of heavy metals in the area.

Acknowledgement

The authors are thankful to Director, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar for providing Lab facilities to carry out research activities.

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