Journal of Hazardous Materials 172 (2009) 1145–1149

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Quantification and distribution of heavy metals from small-scale industrial areas of Kanpur city, India

Manju Rawat*, AL. Ramanathan, V. Subramanian

School of Environmental Sciences, Jawaharlal Nehru University, Lab No. 216, New Delhi 110067, India

ARTICLE INFO

Article history:
Received 13 October 2008
Received in revised form 28 July 2009
Accepted 28 July 2009
Available online 4 August 2009

Keywords:
Small-scale industries
Tanneries
Kanpur city
Heavy metals
Fractionation

ABSTRACT

Kanpur city has large number of small-scale industries (SSIs), primarily comprising of textile and leather industries. This study inventorises the presence of heavy metals in the samples collected from Panki and Jajmau Industrial Areas of Kanpur city. The bulk concentration of heavy metals found in solid waste samples was Fe as 1885 and 2340 mg/kg, Mn 173 and 445 mg/kg, Zn 233 and 132 mg/kg, Cu 20 and 28 mg/kg, Cd 1.4 and 1.1 mg/kg, Ni 26 and 397 mg/kg, Pb 107 and 19 mg/kg, Cr 1323 and 734 mg/kg, respectively. Heavy metal concentration was also found to be high in soil and road dust samples viz. Ni and Pb were in higher concentration in few samples, whereas Cr was found in higher concentration in all samples than the recommended values of USEPA and specifications for compost quality contained in the Indian Municipal Solid Wastes (Management and Handling) Rules, 2000. The heavy metal pollution so detected is indicative of contamination in ground and surface water and food chain. This raises concerns pertaining to adverse consequences to environment and human health.

1. Introduction

India has over 4.5 millions small and medium scale industries (SMI's) accounting for 40% of the total industrial production that causes an estimated 70% of the total industrial pollution load [1]. Among them there are 3 million small-scale industries (SSIs) accounting for approximately 30–35% of industrial production and 50% of pollution. Mostly, industries like textile, dyeing, tanneries, food processing, distilleries, chemical manufacturing, electroplating, printing, foundries etc. are in the small-scale sector [2]. Primarily, two reasons are ascribed for excessive pollution caused by the SSIs, one, use of obsolete technologies, and two, SSIs generally are outside regulatory measures.

Situated on the banks of river Ganges, Kanpur city, the commercial capital of the state of Uttar Pradesh (UP) in India, has a population of 2.5 million living in an area of 267 km^2 [3]. The untreated industrial effluent generated by the industries is generally discharged in Ganges. Even the Supreme Court of India in the *Kanpur Tanneries Case*, had noted that the discharge of trade effluents from these tanneries into the Ganges had been causing considerable damage to the life of the people and also to the aquatic life in the river [M.C. Mehta v. Union of India AIR 1988 SC 1037]. The apex court had directed for the establishment of primary treatment plants by the industries operating from Jajmau [4]. The city's Municipal Solid Waste (MSW) is estimated at 1100 tons per day [5], of which industrial solid waste accounts for 250–350 tons per day. Kanpur is a large and growing production centre for leather goods, produced by tanneries classified as SSIs, with most of them located in Panki and Jajmau Industrial Areas.

Wastewater management is problematic in tanneries and represents major inputs of suspended and dissolved metals, most importantly chromium sulphate and other inorganic salts and sulphur [6]. In the process of leather tanning, fresh sludge has only trivalent chromium which is not toxic but undergoes oxidation (with MnO_2) and there is formation of hexavalent chromium, which is highly toxic and mutagenic [7,8]. A large quantity of wastewater is released by various processes such as paddle operation (washing, liming and unhairing the skin), fleshing and drum operation (washing, deliming, bating, pickling and chrome plating) and discharged without treatment in the open drains [6].

This paper presents an inventory of quality and quantity of heavy metals in industrial solid waste, soils, road dust around industrial area, landfill areas and bed sediments from river Ganges. The distribution and environmental mobility of the heavy metals has also been addressed. Sequential extraction [9,10] are utilised, although these methods have some limitation, such as sensitivity to procedural variables, post extraction, re-adsorption and selectivity and sample preservation [11,12], but those do not apply when first assessment of the degree of contamination is conducted. The

* Corresponding author at: School of Environmental Sciences, Jawaharlal Nehru University, Lab No. 216, New Delhi 110067, India. Tel.: +91 11 26741998.
E-mail addresses: mrawat@yahoo.com (M. Rawat), alrjnu@gmail.com (AL. Ramanathan), subra42@gmail.com (V. Subramanian).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.07.115

Table 1
Description of sampling sites.

Sample number (Panki and Jajmau Industrial Area)[a]	Distance
1	At the beginning of industrial area around 15–30 m distance from industries.
2, 3 and 4	In between the industrial area around 10–35 m distance from industries.
5–6	At the end of industrial area. Industries were at 15–20 m away from these sites.

[a] From same sites with some distance soil samples from road sides, road dust from roads and industrial solid waste from dumps were collected.

sequential extraction was recognised as an appropriate method for gaining information on origin, bioavailability, mobilisation and transport of heavy metals [13–15].

2. Experimental

2.1. Study area and sampling sites

Samples were collected from Panki and Jajmau Industrial Areas of Kanpur city. Sampling sites were at 10–35 m distance from industries and within the industrial areas (Table 1).

2.2. Sample collection and materials

The samples of industrial solid waste and soil were collected from road sides from Panki and Jajmau Industrial Areas. Solid waste and soil samples were collected by stainless steel auger after removing top layer from the depth of 1–5 cm depth after removing grass, waste paper and polythene [16]. Road dust is mainly airborne soil or mixed of soil and waste from industries. The road dust samples were collected after sweeping the roads with broom. These samples were collected twice within a gap of 5 months before and almost at the end of rainy season (March and August) in the year 2005. Six samples were collected for soil, road dust and solid waste in each sampling time. Besides the two bed sediments sample from the Ganges River and similarly, three sample of MSW disposal area at G.T. Road were collected once from Kanpur city in August.

These samples were collected in air-tight polythene bags after proper mixing and then labeled carefully. The samples were carried to laboratory and stored in a cold room at a temperature of 4 °C for further analysis. Then the samples were dried at room temperature, homogenised and sub-sampled by quartering and ground to pass through 2 mm sieve. These processed samples were sub-sampled for further analysis.

Table 2
Methodologies used for sample analyses.

S.No.	Parameters and methodologies used
1	pH, EC by Cyberscan, pH and EC meter, Eutech Instrumentation, Singapore using Okalebo et al. [17]
2	Kjeldhal's nitrogen by Okalebo et al. [17]
3	Phosphorus by Okalebo et al. [17]
4	Carbon and sulphur by infrared radiation (IR) based ELTRA, CS (1000) Analyser
5	Metals (Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni) by Loring and Rantala [18]
6	Fractionation of metals by Ma and Rao [15]

2.3. Methodology

The pH, EC, Kjeldhal's nitrogen and phosphorus in samples were measured according to the standard methodologies [17]. The pH and EC were measured immediately after collecting samples in field by mixing 10 g of sample in 25 ml (1:2.5) of deionised water using Cyberscan, pH and EC meter. The 50–100 mg of the sample was used for analysis of total carbon and sulphur using ELTRA CS (1000) analyser (Table 2). Inorganic carbon and sulphur were measured after digesting with H_2O_2. The organic carbon and sulphur contents were computed as the difference between the total and inorganic fractions.

For bulk analysis of heavy metals, 0.1 g of finely grounded solid waste, road dust and soil samples were digested using triple acid using standard Loring and Rantala method [18] and metals were analysed by Atomic Absorption Spectrophotometer (AAS), Shimadzu AA 1600.

The Canadian soil standards SO1, SO2, SO3 and SO4 were digested in same manner and used for calibration. Replicated samples were analysed against standards for precision and accuracy. Data for the standards had reproducible error as ~5–10% of there published values. The detection limits of instrument for heavy metals were as Fe 0.05, Mn 0.02, Zn 0.01, Cu 0.03, Cd 0.01, Cr 0.05, Pb 0.02 and Ni 0.04 mg/kg. All chemicals used for this analysis were from MERCK of high purity. The deionised mille Q distilled water was used for all preparation.

Sequential extraction of heavy metals was carried out according to procedure given by Ma and Rao [15]. Six operationally defined phases were separated viz. mobile fractions F1–F5 (water-soluble F1, exchangeable F2, carbonate-bound F3, Fe–Mn oxides F4, organic-bound F5) and residual fractions F6 [15]. Mass and material balance was taken care of while following this procedure.

Table 3
Chemicals characterisation of samples collected from small-scale industrial areas of Kanpur city.

	pH	EC (mS/cm)	TC (%)	OC (%)	TS (%)	OS (%)	TN (%)	TP (%)
PIA[a] (no. of samples)								
SW (12)	7.20	3.49	1.44	0.78	1.90	1.34	0.15	0.75
S (12)	6.99	3.30	3.13	2.50	1.94	0.51	0.15	0.52
RD (12)	7.77	2.00	1.03	0.54	1.58	1.25	0.27	0.94
JIA[b]								
SW (12)	8.07	3.73	1.98	1.29	1.12	0.71	0.09	1.06
S (12)	7.94	0.78	1.31	0.76	1.44	0.60	0.22	0.59
RD (12)	8.05	0.57	1.12	0.62	0.59	0.44	0.29	0.52
Landfill (3)	8.35	0.59	0.87	0.45	1.50	0.85	0.22	0.55
Ganga bed sediment (2)	7.48	0.20	0.97	0.37	0.76	0.23	0.07	0.97

SW, solid waste samples; S, soil samples; RD, road dust samples.
[a] Panki Industrial Area.
[b] Jajmau Industrial Area.

Table 4
Heavy metals (mg/kg) studied in samples collected small-scale industrial areas of Kanpur city.

	Fe	Mn	Zn	Cu	Cd	Ni	Pb	Cr
USEPA Std. (MSW)	–	–	–	281	3.3	7.5	34	76
Compost Std. (MSW, India)	–	–	–	300	5	50	100	50
PIA[a] (no. of samples)								
SW (12)	1884.57	173.14	232.93	20.10	1.42	26.11	107.11	1323.45
S (12)	871.64	40.86	346.04	8.19	1.03	10.98	55.49	859.24
RD (12)	1083.99	75.09	144.49	15.23	1.17	18.00	85.53	939.71
JIA[b]								
SW (12)	2340.32	444.81	131.82	28.38	1.12	396.68	19.20	733.61
S (12)	1689.48	266.34	77.21	13.39	1.66	11.85	8.21	393.30
RD (12)	838.22	188.59	43.00	12.19	1.07	22.90	3.50	406.92
Landfill (3)	953.43	176.13	32.93	6.47	1.50	1.61	4.10	23.50
Ganga bed sediment (2)	245.87	46.00	134.00	23.00	0.60	0.68	1.70	66.00

SW, solid waste samples; S, soil samples; RD, road dust samples.
[a] Panki Industrial Area.
[b] Jajmau Industrial Area.

3. Results and discussion

Analytical data drawn from this study is given in Tables 3 and 4 and in Figs. 1 and 2.

3.1. pH and EC in industrial solid waste

The average value of pH in solid waste samples of Panki and Jajmau were 7.2 and 8.0, respectively. The slightly alkaline nature was expected in these samples as tanneries use basic salts. Similarly, soil and also road dust samples had neutral to alkaline pH. Landfill sample showed pH as 8.35 and Ganges bed sediments as 7.48 indicative of the fact that tannery waste had some environmental impact (Table 3). Due to alkaline nature of waste, it would further promote adsorption to soil and in the ground. The average values of EC in samples of Panki and Jajmau were 2.00–3.49 and 0.57–3.75 mS/cm, respectively. The high EC contents in these samples might be due to higher concentration of dissociated ions like HCO^{3-}, $SO_2{}^{4-}$, Cl^-, NO^{3-}, Ca^{2+}, Mg^{2+}, Na^+ in tannery waste [6,19]. Similar high concentration of EC > 5.00 mS/cm was reported in the tannery waste collected from Tamil Nadu, India [6].

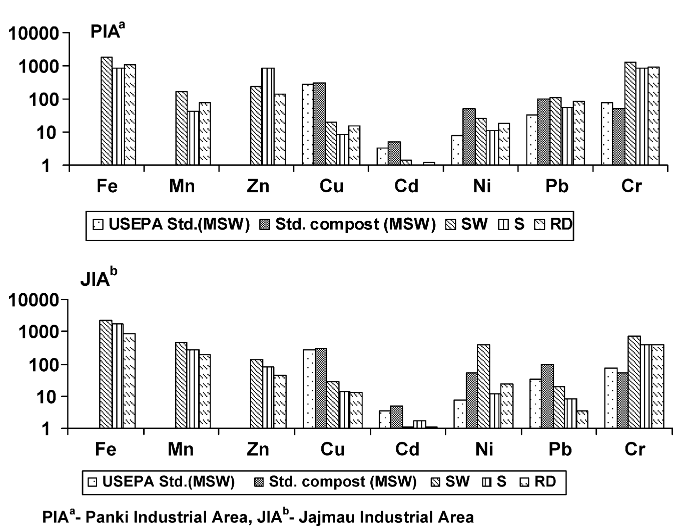

Fig. 1. Heavy metals concentration (mg/kg) in samples collected from small-scale industrial areas of Kanpur city.

3.2. Total carbon (C), sulphur (S), nitrogen (N) and phosphorus (P)

Carbon, sulphur, nitrogen and phosphorus were estimated in the collected samples to assess their fertility for the soil conditioning. The average value for total C was 0.87–3.13%, for total S 0.59–1.94%, for total N 0.07–0.29% and for total phosphorus was 0.52–1.06% in Panki and Jajmau Industrial Areas soil, solid waste and road dust samples (Table 3). The sulphur content in the samples might be due to basic chrome sulphate, ammonium sulphate, sodium bi-sulphite, sulphric acid etc. used for processing raw skins of animals [6]. Total carbon too was high in some samples probably because of presence of fats, hairs and skins of animals in the waste discharged from tannery industries [20].

3.3. Bulk estimation of heavy metal

The bulk concentration was studied for eight metals (Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni) in the collected samples. Average concentration of heavy metals in soil, solid waste and road dust samples are given in Fig. 1. Heavy metals like Ni, Pb and Cr were found in higher concentration then recommended by USEPA standards and MSW standards in India for composting (Table 4). Beside solid waste samples, the soil and road dust were also reported with high concentration of heavy metals, this might be due to dust from industries deposited there. Chromium concentration was found quite high 1323 mg/kg at Panki as this area had large number of tanneries. Similarly, Chromium was reported as 12,960 mg/kg in soil due to dust from tanneries and other factories in Guanajuato, Mexico [21] and 3940 mg/kg in spent chrome tar liquid from a tannery processing 500 hides in a day [22].

The high concentration of Fe, Mn, Ni and Pb in samples might be due to presence of other ferrous and non-ferrous industries like printing, electroplating, dyeing etc. in the industrial areas (Table 4). Similar results were obtained by authors from the solid waste and wastewater samples analysed from the SSIs in Delhi, India [23,24]. They also reported that the untreated industrial waste from SSIs goes for dumping in landfill areas with municipal solid waste thereby raising the possibility of causing soil, surface water and ground water pollution in and around dumping areas [19,25].

A good correlation (0.9–0.5) was observed between almost all the metals studied in Panki and Jajmau Industrial Areas, which indicated that source could be same type of industrial activities. Whereas, in Panki Zn had showed a significant negative correlation (−0.9 to −0.5) with almost all metals. This has indicated that

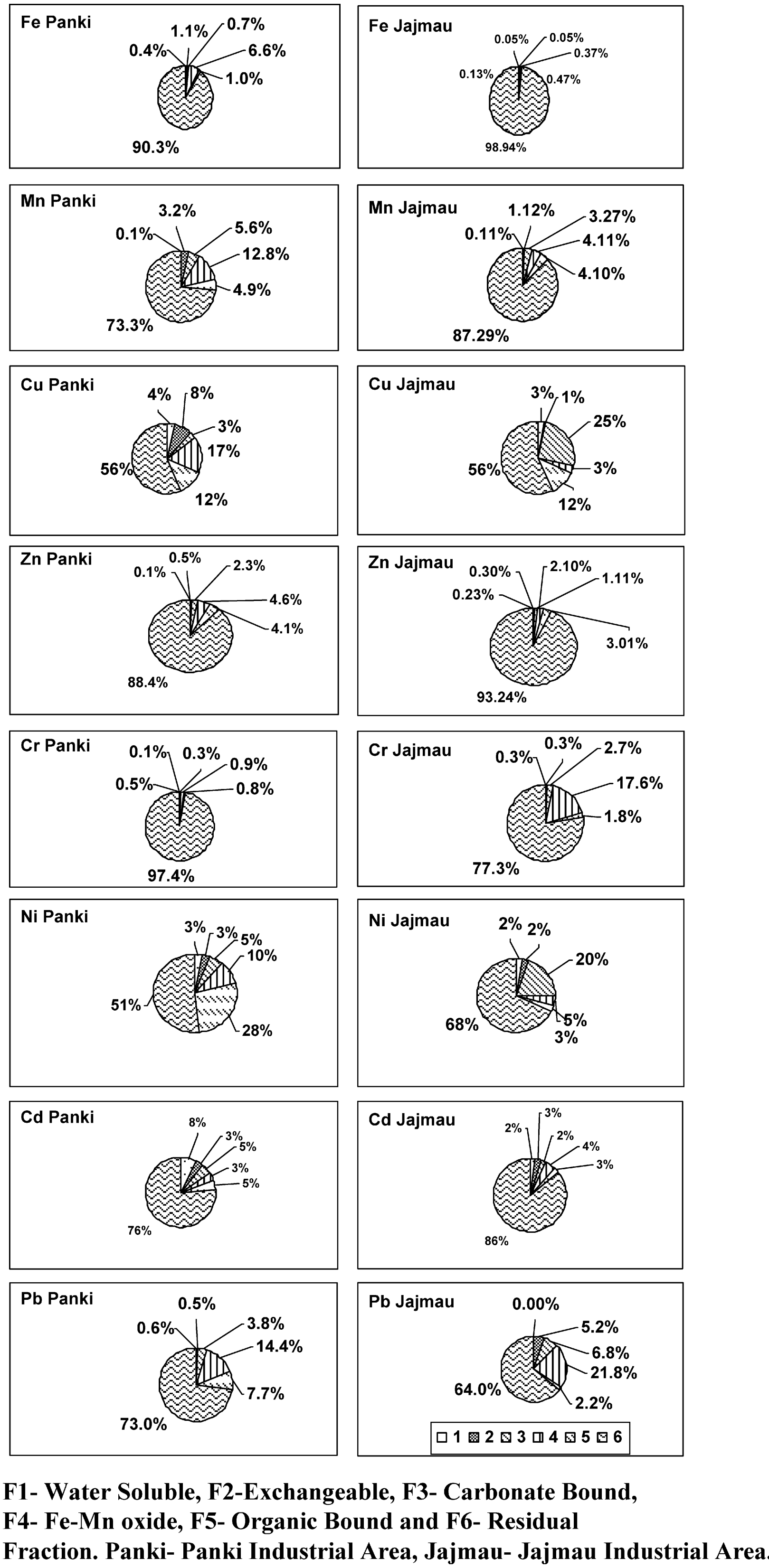

Fig. 2. Percentage of heavy metals in different fractions of bulk sample. F1, water soluble; F2, exchangeable; F3, carbonate bound, F4, Fe–Mn oxide, F5, organic bound; F6, residual fraction. Panki, Panki Industrial Area; Jajmau, Jajmau Industrial Area.

there might be some Zn based industry activities there. Similarly, in Jajmau, heavy metals seem to be well correlated with each other except Cd, which showed negative correlation with Mn, Zn and Cu, but not a significant correlation.

The data from these two industrial areas shows that the soil and road dust is equally polluted in these industrial areas. Collective pollutant release from these industrial areas is liable to cause long-term environmental impact [25].

3.4. Fractionation of heavy metals

Chemical fractionation was studied to analyse heavy metal distribution from industrial areas (Fig. 2), which constitute the major reservoir for potential subsequent release of contaminants into the environment [9–12].

Fig. 2 shows the percentage of metals in mobile fractions F1–F5 and residual fractions F6 in the solid waste samples of Panki and Jajmau Industrial Areas. The high percentage i.e., 7% of Fe was reported in Fe–Mn oxide fraction in Panki, whereas, highest 0.48% in organic-bound fraction of Jajmau area, though residual fraction had 90% and 99% of Fe fractions, respectively. Similar results were reported by many other authors [13,24] in past. The 4% and 8% of Mn fraction were reported in exchangeable and carbonate-bound fraction of Panki, whereas, Jajmau had higher concentration of mobile fraction in Fe–Mn oxide and organic-bound fraction. The higher metal concentration in exchangeable fraction indicates the higher possibility of leaching of metals.

Among the toxic metals studied for fractionation, i.e., Cr, Ni, Cd and Pb. Panki had, 97% of Cr in residual fraction, whereas Jajmau, had 77%, in which carbonate and Fe–Mn oxide bound fraction showed higher fraction. This indicated that Cr contamination could be more from Jajmau waste. The Ni fraction in Panki, 49% in mobile fraction, among the mobile fraction, organic bound > Fe–Mn oxide > carbonate > exchangeable > water-soluble fraction, whereas, in Jajmau, carbonate bound > Fe–Mn oxide > organic bound > exchangeable > water-soluble fraction. Similarly, Cd fraction in mobile fraction was 24% and 14%, Pb as 27% and 36%, respectively, in Panki and Jajmau Industrial areas. The heavy metals like Ni, Pb and Cr found in higher amounts in mobile or environmentally bio-available fraction would lead to higher possibilities to pollute ground, surface water in and around disposal sites [23–25].

4. Conclusions

The high concentration of heavy metals viz. Cr 1323 mg/kg in solid waste, 859 mg/kg in soil and 940 mg/kg in road dust at Panki Industrial area and 734 mg/kg in solid waste, 393 mg/kg in soil and 407 mg/kg in road dust at Jajmau Industrial area of Kanpur city, in view of its toxicity are liable to pose adverse effect on environment and human health. Therefore, it is imperative to prescribe regulatory norms/standards for SSIs for waste disposal by treating them collectively not individually in an Industrial Area. Further, the possibility of resource recovery from these waste materials also needs to be inquired. Such a step can lead to conservation of non-renewable natural resource thereby contributing to sustainable development.

Acknowledgements

Authors are thankful to Council of Scientific and Industrial Research (CSIR) and Department of Science and Technology (DST), Government of India, for the financial assistance granted for carrying out research work.

References

[1] World Bank Report, Strengthening Institution for sustainable Growth: Country Environmental Analysis for India, http://www.worldbank.org.in/WBSITE/EXTERNAL/COUNTRIES/SOUTHASIAEXT/INDIA, 2007.
[2] Annual Report on Environment, Submitted to World Bank. Published by Ministry of Environment and Forests, Government of India, 1996, p. 135.
[3] The Uttar Pradesh Government Website. http://www.upgov.nic.in/.
[4] S. Diwan, A. Rosencranz, Environmental Law and Policy in India—Cases Material and Statutes, second ed., Oxford University Press, New Delhi, India, 2001.
[5] CPCB (Central Pollution Control Board), Municipal Solid Waste—Waste generation and Composition. http://www.cpcb.nic.in/Municipal%20Solid%20Waste/Waste_generation_and_Composition.html, 2004–2005.
[6] D. Mazumder, K. Rahul, A. Chaudhary, Waste water management practices for a chrome tanning industry—Part I, Indian J. Environ. Health 40 (1) (1998) 79–92.
[7] A.D. Apte, S. Verma, V. Tare, P. Bose, Oxidation of Cr (III) in tannery sludge to Cr (VI): Field observations and theoretical assessment, J. Hazard. Mater. 121 (1–3) (2005) 215–222.
[8] M.M. Hassanien, I.M. Kenawy, A.M. El-Menshawy, A.A. El-Asmy, A novel method for speciation of Cr (III) and Cr (VI) and individual determination using Duolite C20 modified with active hydrazones, J. Hazard. Mater. 158 (2008) 170–176.
[9] D.L. Lake, P. Kirk, J. Lester, Fractionation, characterization and speciation of heavy metals in sewage sludge and sludge-amended soils: a review, J. Environ. Qual. 13 (1984) 175–183.
[10] A. Tessier, P.G.C. Campbell, Partitioning of trace metals in sediments, in: J.R. Kramer, H.E. Allen (Eds.), Metal Speciation: Theory Analysis and Application, Lewis Publ., Chelsea, MI, 1988, pp. 183–199.
[11] P.M.V. Nirel, F.M.M. Morel, Pitfalls of sequential extractions, Water Resour. 24 (8) (1990) 1055–1056.
[12] F.M.G. Tack, H.A.H. Vossius, M.G. Verloo, A comparison between sediment metal fractions obtained from sequential extraction and estimated from single extractants, J. Environ. Anal. Chem. 63 (1996) 61–66.
[13] G.J. Chakrapani, V. Subramanian, Fractionation of heavy metals and phosphorus in suspended sediments of the Yamuna River, India, Environ. Monit. Assess. 43 (11) (1996) 7–124.
[14] M.J. Belcunze-Segarra, J.R. Bacon, R. Prego, M.J. Wilson, Chemical forms of heavy metals in surface sediments of the San Simon Inlet, Ria de Vigo, Galicia, Environ. Sci. Health A32 (5) (1997) 1271–1297.
[15] L.Q. Ma, G.N. Rao, Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils, Environ. Qual. 26 (1997) 259–264.
[16] S. Ray, P.S. Khillare, T. Agarwal, V. Shridhar, Assessment of PAHs in soil around the International Airport in Delhi, India, J. Hazard. Mater. 156 (2008) 9–16.
[17] J.R. Okalebo, K.W. Gathua, P.L. Woomer, Laboratory Methods of Soil and Plant Analysis: A Working Manual, Marvel EPZ (Kenya) LDT, Nairobi, Kenya, 1993.
[18] D.H. Loring, R.T.T. Rantala, Manual for the geochemical analyses of marine sediments and suspended particulate matter, Earth Sci. Rev. 32 (1992) 235–283.
[19] N.C. Mondal, V.K. Saxena, V.S. Singh, Impact of pollution due to tanneries on groundwater regime, Curr. Sci. 88 (12) (2005) 25–29.
[20] R. Barrena, E. Pagans, A. Artola, F. Vázquez, A. Sánchez, Co-composting of hair waste from the tanning industries with de-inking and municipal wastewater sludge, Biodegradation 18 (3) (2007) 257–268.
[21] M.A. Armienta, R. Rodrlguez, N. Ceniceros, F. Jufirez, O. Cruz, Distribution, origin and fate of chromium in soils in Guanajuato, Mexico, Environ. Pollut. 91 (3) (1996) 391–397.
[22] A.A. Siddiqui, A. Khursheed, I.H. Farooqi, R.H. Siddiqui, Economics of chromium recovery from spent chrome tan liquor, Indian J. Environ. Health 40 (2) (1998) 142–152.
[23] M. Rawat, M.C.Z. Moturi, V. Subramanian, Inventory compilation and distribution of heavy metals in wastewater from small-scale industrial areas of Delhi, India, Environ. Monit. Assess. 5 (2003) 1–7.
[24] M.C.Z. Moturi, M. Rawat, V. Subramanian, Distribution and sequential extraction of heavy metals in solid waste from the industrial belt of Delhi, India, Environ. Monit. Assess. 95 (1–3) (2004) 185–199.
[25] A.F. Al Yaqout, Assessment and analysis of industrial liquid waste and sludge disposal at unlined landfill sites in arid climate, Waste Manag. 23 (2003) 817–824.