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VERTICAL DISTRIBUTION AND POTENTIAL MOBILITY OF HEAVY METALS IN NEW AND OLD TAILINGS OF A LEAD/ZINC SULFIDE MINE

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Abstract

Sulfide bearing mine tailings generated through mining and processing of mineral ores is one of the serious problems around the world due to their potential environmental hazards. Current study focuses on vertical distribution and potential mobility of metals in New and Old tailings of a Lead and Zinc mining area of India. Mine tailing profiles sampled from New (0-500mm) and Old tailing (0-400mm) dams were chemically (pH, EC, Carbonate content, Cd, Pb, Zn and Mn levels) and mineralogically (using X-ray Diffraction) characterized. Both the new and old tailings are alkaline having high carbonate content. However, the pH of old tailings is less than the new tailings. The vertical profile distribution of metals in new tailings indicate a decrease in Pb levels with depth up to 200 mm and a substantial increase in Zn and Cd levels were noted below 200 mm depth. However, no differences were observed for Mn levels with depth. In case of Old Tailings, no discernible pattern for Cd, Pb, Zn and Mn levels with depth was observed. These chemical and mineralogical observations confirm that the new tailings are undergoing oxidation and weathering in the surface layers, however, the old tailings are sort of stabilized at least up to sampling depth. To estimate the potential mobility of Cd, Pb and Zn in New and Old tailings, single extraction (EDTA 0.05 mol/L) was applied to surface tailings. The correlation coefficients between total and EDTA extractable Cd and Zn (r values for Cd and Zn being 0.965 and 0.976, respectively, and P value being 0.001) indicate statistically significant relation. The results of EDTA extraction show that out of the three metals, Pb has maximum extractability in new tailings, whilst Cd has the maximum mobility in old tailings, and Zn has the least potential mobility in both types of tailings.

Key words: correlation coefficient, heavy metal, mine tailing, single extraction, vertical distribution

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1. Introduction

Mining and milling operations are the important point source of trace elements in the environment (Adriano, 1986). Mining and beneficiation processes generate four categories of large-volume waste: mine waste (overburden, barren rocks), tailings, dump heap leach, and mine water (Dudka and Adriano, 1997). Extraction and processing of base and precious metals from the sulfide ore deposits generate large volumes of sulfide tailings (Moncur et al., 2015). Sulfide minerals are thermodynamically unstable in presence of oxygen and water. When sulfidic mine tailings are exposed to water and oxygen, the resulting oxidative weathering of sulfides can generate H^+ and release sulfate and metal(oid)s to tailing pore waters (Blowes et al., 2013; Lindsay et al., 2015). Depending on the nature of ore deposits, metals such as Cu, Zn, Pb, Ni, Cd, Co, Hg, Al, Mn and U and metalloids including As, Sb and Se are released in mine drainage (Nordstrom, 2011). Sulfide-bearing mine tailings are a serious environmental problem around the world (Schuwirth et al., 2007). The extent of environmental impacts associated with sulfide tailings deposits depends upon their mineralogical and geochemical composition, and upon in situ chemical, biological, and physical processes (Lindsay et al., 2015). Mine tailings may weather and leach metals into tailing profile and ground water for several hundreds of years after mining activities have ceased. So, field studies of metals in vertical profile of tailings can be useful for predicting the pollution risk to groundwater from the sulfide tailings.

The shift in paradigm from mere determination of total elemental concentration to a more advanced fractionation-based approach points to the general recognition that information about the physiochemical forms of trace elements is required for understanding their environmental fate and behavior, including mobility, pathways and bioavailability. A variety of standardized leaching tests with variable reagents, and experimental conditions are used to mimic differing environmental conditions. Strong acids are used to determine total concentrations of potentially harmful elements, whereas weaker solutions are used to determine compounds that are relatively soluble and bioavailable (Salminen and Sipila, 1996). Various extraction schemes have been developed for discerning individual geochemical phases, ranging from simplistic methods for distinguishing the “labile” and “residual” fractions (single extractions), to more sophisticated approaches enabling the sequential removal of water soluble, exchangeable, adsorbed, carbonate bound, phosphate, Fe/Mn oxide bound, sulphide and organic bound and silicate fractions (sequential extraction procedures). In single extractions a large spectrum of extractants have been used to extract the “mobile” or “bioavailable” forms of metals (He and Singh, 1995; Karczewska et al., 1998), viz.

- Very strong acids such as aqua regia (Vidal et al., 1999), nitric acid (Sutherland et al., 2001), HCl (Filipek and Pawlowski, 1990; Rieuwerts et al., 2000; Sutherland and Tack, 2000; Sutherland et al., 2001; Taylor et al., 1993).
- Chelating agents like EDTA (Anju and Banerjee, 2011; Diaz-Barrientos et al., 1999; Filipek and Pawlowski, 1990; McGrath, 1996; Sanders et al., 1987; Sutherland et al., 2001; Tokalioglu and Kartal, 2005; Vidal et al., 1999), DTPA (Taylor et al., 1993), CH_3COOH (Filipek and Pawlowski, 1990; Vidal et al., 1999).
- Buffered salt solutions e.g. ammonium acetate (pH 7) (Ure et al., 1993).
- Unbuffered salt solutions e.g. $CaCl_2$ (Diaz-Barrientos et al., 1999; Sanders and Adams, 1987; Vidal et al., 1999), $NaNO_3$ (Gupta and Aten, 1993; Hani and Gupta, 1982), $BaCl_2$ (Juste and Solda, 1988) etc.

These extractants are hypothesized to extract exchangeable or weakly bound “available” metals in the solid matrices viz. soils, sediments etc., which are believed to be bioavailable. The content of extractable forms of heavy metals is a more precise index of their ability to migrate (Anderson, 1976; Haynes and Swift, 1986; Wiklander and Wahtras, 1977).

The present study is centered on Zawar, a historical Zn-Pb mining community in India. The relics of the historical mining can be seen as hillocks surrounding old surface and subsurface mine workings, earthen retorts and slag heaps. Modern mining, however, commenced in 1942. Zawar lies within a belt of Aravalli system. The ore is confined to the main dolomite horizon (Chakrabarti, 1967; Smith, 1964). Sphalerite (ZnS) is the predominant sulphide mineral in the ore, second most abundant being pyrite in a gangue of dolomite and quartz. Galena (PbS) is more locally concentrated. Native silver, chalcopyrite, arsenopyrite, pyrolite, and magnetite are also known to occur (Mookherjee, 1964). The conventional froth-flotation technology is adopted to produce separate lead and zinc concentrates. On an average the ore contains 5% metal (both Pb and Zn) and 95% of the total mined ore is pumped out as tailings. Fine-grained tailings generated during the beneficiation of sulphide ores are directed to the New Tailing Dam. Prior to 1980's, tailings were dumped in an area called Old Tailing Dam, which has been stabilized by plantation. The volume of tailings generated is normally in far excess of the liberated resource and the tailings often contain potentially hazardous contaminants (Kossoff et al., 2014). Thus, both tailing dams represent by far the biggest accumulations of environmentally dangerous waste materials in Zawar area.

The purpose of this study was to investigate the vertical distribution of metals (viz. Cd, Pb, Zn and Mn) in tailing profiles from New and Old Tailing Dams. Additionally, the potential mobility of Cd, Pb and Zn in New as well as Old tailings was estimated by using single extraction (EDTA 0.05 mol/L).

2. Material and methods

2.1. Sample collection and preparation

Tailing profiles were sampled as undisturbed core, by using a specially designed cylindrical stainless-steel corer from New tailing dam (n = 5, NTD1 to NTD5, 0-500mm) and Old tailing dam (n = 4, OTD1 to OTD4, 0-400mm). Soon after collection, the core samples were cut into 100mm sections and carefully transferred to clean and dry self-sealing polyethylene bags for transport to laboratory. The tailings were air-dried at room temperature, disaggregated with a wooden roller and then sieved through 2 mm sieve. The samples were homogenized by coning and quartering and stored in tightly sealed polyethylene bags for further analysis.

2.2. Analytical techniques

The pH and electrical conductivity (EC) of the tailings were measured in solid/liquid ratio of 1: 2.5 with distilled water (Okalebo et al., 1993). The carbonate content analysis involved the dissolution of carbonates in an excess of standard hydrochloric acid and back titration of excess acid with standard sodium hydroxide (Rowell, 1994). Total metal content of the tailings was determined after tri-acid digestion (using a combination of $HClO_4$, HNO_3 and HF) as described by Agemian and Chau (1975).

Only surface (0-100mm) samples from both the locations were considered for single extraction analysis. Measurement and Testing Programme (formerly BCR) of the European Commission had launched a project aiming at harmonizing measurements for extractable trace metal contents in soil. EDTA, acetic acid and ammonium acetate with DTPA were the three extractants selected for harmonization and validation of single extractions (Quevauviller et al., 1997). EDTA 0.05 mol/L (pH 7) has been used for the certification of soil reference materials by BCR.

This test is assumed to extract both carbonate bound and organically bound fractions of metals and was hence considered to be suitable for calcareous soil analysis (Quevauviller, 1998). To assess the potential mobility of Cd, Pb and Zn in tailings, a single extraction scheme using EDTA as described by Quevauviller (1998) was preferred for the present work as it has been extensively tested in previous studies also. All the vessels in contact with samples or reagents were cleaned by soaking in HNO_3 4 Mol/L (overnight) and rinsed repeatedly with distilled water. EDTA extractions were conducted in triplicate in 100 mL centrifugation tubes with tight lids by using a mechanical end-over-end shaker. All chemicals used were of analytical grade, and double distilled or Milli. Q. water was used throughout.

Cadmium, lead, zinc and manganese in digests as well as extracts were determined by flame atomic absorption spectrometry (FAAS) using a Shimadzu AA-6800 system with air/acetylene flame. Calibrants were prepared from 1000 µg/mL Spectrosol standard solutions from Merck as well as from standard solutions prepared in laboratory following APHA (1995) standard methods. Multi-level standards were prepared in the same matrix as the extracting reagent to minimize matrix effects. Blanks were run simultaneously for background correction and other sources of error. Mineralogical analysis of New and Old tailings was done by using Philips X'Pert model XRD instrument. Samples were scanned from 5^0 to 90^0 2θ. The peak analysis was done by using X'Pert data collector.

3. Results and discussion

3.1. Physicochemical and mineralogical analysis

pH, EC, Carbonate content, Cd, Pb, Zn and Mn levels in surface tailings (0-100mm) have already been discussed in previous publication (Anju and Banerjee, 2010). Briefly, the pH of both type of tailings was alkaline, which contrasts with the other studies in similar type of metal mining areas, where the pH is usually acidic (Grimalt et al., 1999; Morrell et al., 1996; Shu et al., 2001; Simon et al., 1999). In general, sulfide rich and carbonate-poor materials produce acidic conditions in areas having metal sulphide as the ores. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline conditions (Skousen et al., 2000). The pH of old tailings was less than the new, which could be because of the ability of sulphide tailings to generate acid upon weathering. The carbonate content of both the New and Old tailings was quite high, indicating calcareous nature of these tailings and hence the alkaline pH.

The color of the new tailings was gray, sometimes brownish silty material, but the colour of old tailings was always yellowish brown. The formation of efflorescent salts (ocherous and white deposition) on the surfaces of old tailings was also observed. Mineralogical analysis indicated the presence of Dolomite, Quartz, Ankerite and other sulphide minerals in New and Old tailings.

3.2. Profile distribution of metals in tailings

The flotation tailings profiles were investigated for Cd, Pb, Zn and Mn levels at two dumping sites called New tailing dam and Old tailing dam, which represent by far the biggest accumulations of environmentally dangerous waste materials in the area. The mean concentrations of Pb, Zn, Mn and Cd in New tailings (0-100mm, n=5) were 1099, 1908, 2932 and 13.96 mg kg^{-1} and in Old tailings (0-100mm, n=4) were 1903, 5098, 2271 and 22.93 mg kg^{-1}, respectively. The results indicate high levels of Cd, Pb, Zn, and Mn in both types of tailings. The levels of metals present in the tailings are comparable with the levels observed in many previous studies on tailings in similar kind of mining areas (Table 1).

The vertical profile distribution of Cd, Pb, Zn and Mn in New Tailings (0-100, 100-200, 200-300, 300-400 and 400-500 mm) and Old Tailings (0-100, 100-200, 200-300 and 300-400 mm) is shown in Fig. 1(a-d) and Fig. 2(a-d), respectively. In case of new tailings, the depth-wise distributions indicate a decrease in Pb levels with depth up to 200 mm and a substantial increase in Zn and Cd levels were noted below 200 mm depth. However, no differences were observed for Mn levels with depth.

The contrasting trend noted for Pb is explained by the formation of highly insoluble anglesite ($PbSO_4$) in the surface layer as confirmed by XRD analysis of surface samples. Shu et al. (2001) have also observed significantly lower concentrations of Zn and Cd in surface (0-10cm) and subsurface layer (10-20cm), than those of deep layers (20-50cm and 50-100cm) in their study on Pb/Zn mine tailings at Lechang, China. Morrell et al. (1996) in their study on mine tailings from New Zealand and Hofmann and Schuwirth (2008) in a study on sphelarite bearing mine waste tailings from Adolf-Helene mine, Germany have also observed increase in Zn and decrease in Pb concentration with depth.

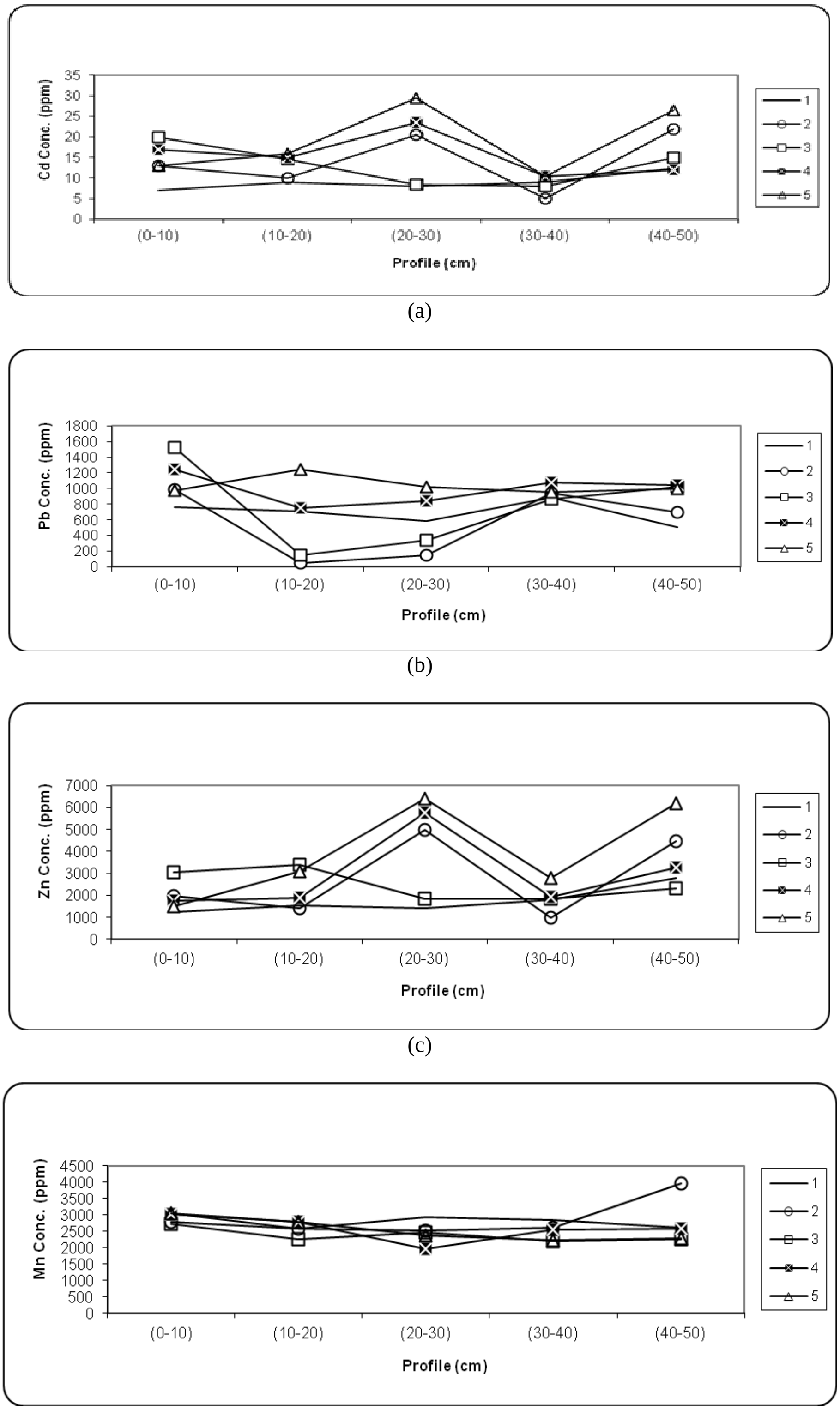
The occurrence of anglesite in surface layer and a substantial increase in concentration of Zn and Cd below 200mm depth are two chemical and mineralogical observations confirming that oxidation and weathering have been largely confined to surface tailings in new tailing dam.

Table 1. Heavy metal levels in surface tailings (µg/g) of mining areas as reported in literature

Location	***Pb***		***Zn***		***Cd***		***Cu***		***As***		***Reference***
	Range	**Mean (Median)**	**Range**	**Mean (Median)**	**Range**	**Mean (Median)**	**Range**	**Mean (Median)**	**Range**	**Mean (Median)**	
Adolf-Helena mine, Germany (former tailing pond)		27 mmol/kg		10 mmol/kg		0.035 mmol/kg		3.5 mmol/kg		0.5 mmol/kg	Schuwirth et al., 2007
Aznalcollar spill, Spain		7.05mg/g		14 mg/g		300mg/kg		2.05 mg/g		5.33 mg/g	Lacal et al., 2003
Boleslaw, Cracow, Poland	735-19555	4039	1578-36000	1.5%	9-371			1-390			Krzaklewski & Pietrzykowski, 2002
Wiesloch, Germany		0.72%		3.13%		188mg/kg		-		2.1%	Stuben et al., 2001
Lechang Pb/Zn mine, China		2784		2029		12		132			Shu et al., 2001
Aznalcollar spill, pyrite mud, Agrio river, Spain		7141		9448		31		1968			Alastuey et al., 1999
Pyrite mine Aznalcollar, Spain		(9507.3)		(7183.5)		(28.6)				(3749)	Simon et al., 1999
Baxter Springs in Cherokee County, southeast Kansas		351		17850		125					Zhu et al., 1999
Aznalcollar, Spain		7957		10707		40		2126		5321	Vidal et al., 1999
Aznalcollar, Spain		8091		8832		33		1323		4692	Lopez-Pamo et al., 1999
Guadiamar, Spain		7888		7096		25.1		1552		2878	Cabrera et al., 1999
Montevecchio(Sardinia) Coarse material (C)		17200		16400		150		700		-	Fanfani et al., 1997
Montevecchio(Sardinia) fine material (F)		20900		21300		140		570		-	Fanfani et al., 1997
Montevecchio(Sardinia) Very fine material (VF)		19000		16300		120		520		-	Fanfani et al., 1997
Tui base metal mine, Te Aroha, New Zealand		10568		486				113			Morrell et al., 1996
Southeast Kansas		1370		13700		90					Abdel-Saheb et al., 1994
Old Lead Belt, Missouri (400 mesh size)		3867		1329		33.9		88.6			Clevenger, 1990
Gold mine, Serra de Santa Cruz(Bahia, Brazil)		21		55		0.7		87		71	Andrade Lima et al., 2008
Goldmine, Zimbabwe		-		225±20		17.6±0.1		1750±100			Zaranyika and Chirinda, 2011

**Units are µg/g unless otherwise mentioned*

However, no discernible pattern for Cd, Pb, Zn and Mn levels with depth (Fig. 2a-d) was observed for Old Tailing Profile (except profile 4), indicating that these tailings are sort of stabilized for weathering at least upto a depth of 400 mm. For profile 4, an increase in Cd, Pb and Zn concentration was observed at 30-40cm depth. This indicated that acidification accelerated metal solubility, which resulted in depletion of Cd, Pb and Zn in surface tailings and relative enrichment in deep layers (30-40cm).



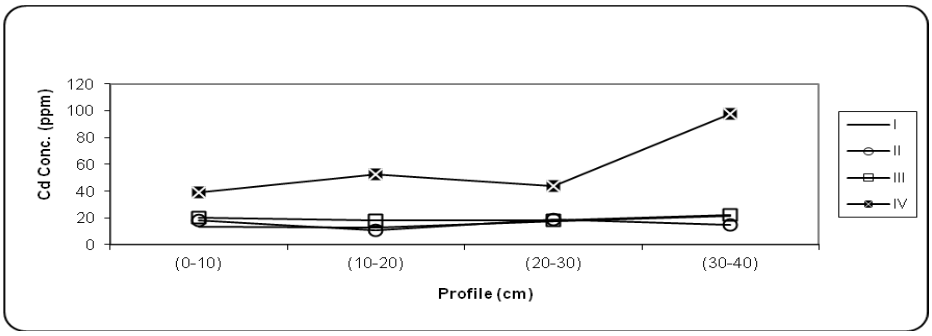
(a)

(b)

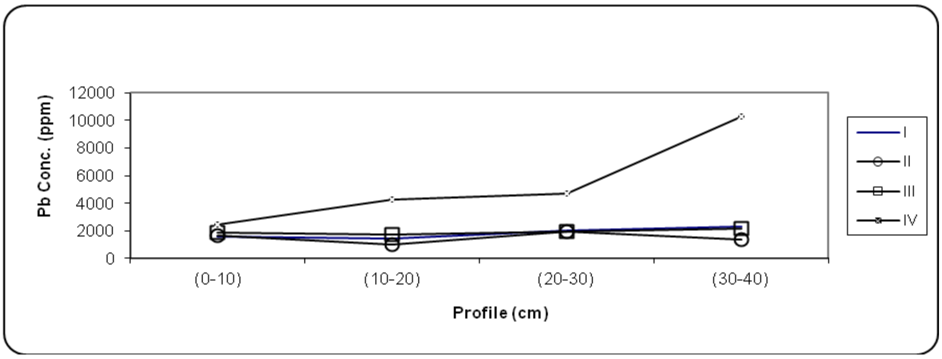
(c)

(d)

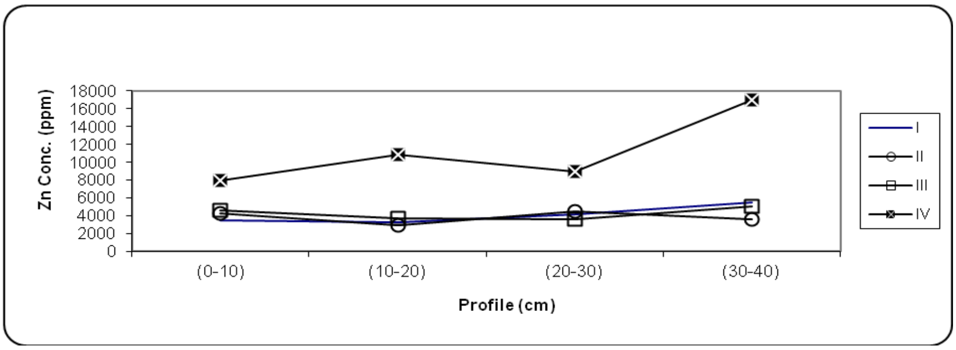
Fig. 1. (a) Depthwise distribution of Cd in New Tailings; (b) Depthwise distribution of Pb in New Tailings; (c) Depthwise distribution of Zn in New Tailings; (d) Depthwise distribution of Mn in New Tailings



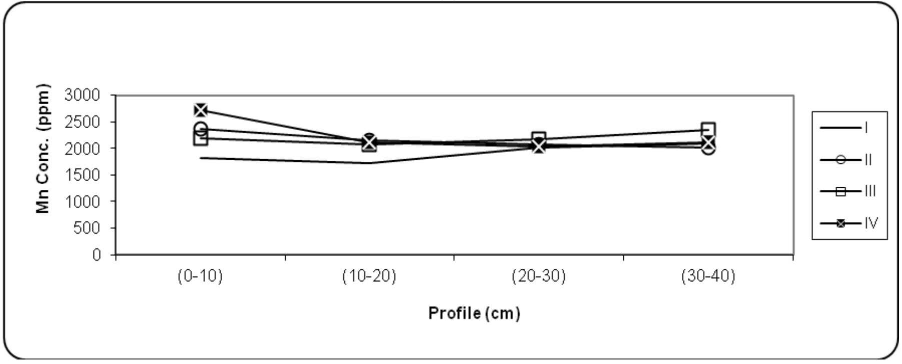
(a)



(b)



(c)



(d)

Fig. 2.(a) Depthwise distribution of Cd in Old Tailings; (b) Depthwise distribution of Pb in Old Tailings; (c) Depthwise distribution of Zn in Old Tailings; (d) Depthwise distribution of Mn in Old Tailings

3.3. Single extraction analysis

3.3.1. EDTA extraction

Single extraction tests are commonly used to study the eco-toxicity and mobility of metals in solid matrices, e.g. to assess the bioavailable metal fraction (and thus to estimate the related phyto-toxic and nutritional deficiency effects) and environmentally accessible trace metals upon disposal of sediment or wastes on a soil (thus assessing contamination of ground waters). EDTA has been extensively used for determination of extractable metal content of polluted and unpolluted soils (Anju and Banerjee, 2011; McGrath, 1996; Schramel et al., 2000; Tokalioglu and

Kartal, 2005; Viro, 1955), road sediments (Sutherland et al., 2001), municipal and industrial sludges (Lo and Chen, 1990) and is increasingly being used in the reclamation of contaminated soils and sediments (Cline and Reed, 1995; Mench et al., 1994; Sun et al., 2001). Table 2 shows the EDTA extractable concentrations and percentage of total metal extracted by EDTA in both type of tailings. Relative EDTA extractability of Cd, Pb and Zn in New tailings (Table 3) followed the order: Pb (96.53 ± 4.43) >>Cd (55.98 ± 4.81) >>Zn (33.16 ± 7.57). The EDTA extractability was maximum for Pb followed by Cd in all the profiles. Out of the three metals, Zn was least mobilizable. Vidal et al. (1999) in their study on Aznalcollar (Spain) toxic spill have also observed similar order i.e. Pb>Cd>Zn, of EDTA extractability of metals from mine sludge (tailings). Many other investigations have demonstrated the ability of EDTA to extract a large proportion of total soil Pb (Abdel-Saheb et al., 1994; McGrath and Cegarra, 1992; Pichtel et al., 2001; Sposito et al., 1982; Tsadilas et al., 1995). Clayton and Tiller (1979) observed that EDTA extracted 74-93% of total Pb from soils contaminated by smelter emissions, but only 20-60% uncontaminated soils.

Relative EDTA extractability of Cd, Pb and Zn in Old tailings (Table 3) followed the order: Cd (61.94 ± 25.09) ≥ Pb (55.42 ± 10.54) > Zn (36.23 ± 6.14). The relative extractability of these metals is consistent with the findings of the study of Anju and Banerjee (2011) on soils of a lead and zinc mining area, India and McGrath (1996)'s on Irish soils, where EDTA extractability followed the sequence Cd>Cu=Pb>Ni=Zn>Cr. EDTA extracts of soils tend to correlate well with plant contents, in particular with the plant-available fraction for Cd, Cu, Ni, Pb and Zn (Sanders et al., 1986), Cd (Lag and Elsokkary, 1978) and Cu (Sanders et al., 1987). Therefore, complexants like EDTA are frequently used to extract mobilizable (potentially bioavailable or potentially leachable) metal fraction in soil (Gupta et al., 1996).

3.3.2. Correlation

Correlation coefficients between the EDTA extractable Cd, Pb and Zn *vs* their 'total' elemental contents in Tailings are given in Table 4. The amount of Cd, Pb and Zn extracted by EDTA and their total concentrations showed a linear positive correlation, which are statistically significant (r values for Cd, Pb and Zn being 0.965, 0.638 and 0.976, respectively and P values being <0.001). The correlation coefficients indicate a strong relation between EDTA extractable and total Cd and Zn. Anju and Banerjee (2011) has also observed statistically significant linear positive correlations between EDTA extractable and total concentrations of Cd, Pb and Zn (r values for Cd, Pb and Zn being 0.901, 0.971 and 0.795, respectively, and P values being <0.001), in soils of a lead and zinc mining area, India. These findings are in agreement with other studies such as McGrath's (1996) work on Cd, Cu and Ni; Boon and Soltanpour's (1991) work on Cd, Zn and Pb and Mehra et al.'s (1999) work on Cd and Cu for contaminated soils. These results can appear to justify the use of 'total' metal contents as a useful preliminary indicator of areas where the risks of metal excess or deficiency are high.

Table 2. EDTA extractable concentrations (mg kg^{-1}) and percentages of total Cd, Pb and Zn in New and Old surface tailings

Sample ID	***Cd***			***Pb***			***Zn***		
	EDTA-Extractable	***Total***	***% Extracted***	***EDTA-Extractable***	***Total***	***% Extracted***	***EDTA-Extractable***	***Total***	***% Extracted***
NTD1	3.85	6.98	55.16	735	768	95.70	355	1227	28.93
NTD2	7.06	12.96	54.48	979	987	99.19	597	1990	30.00
NTD3	9.81	19.94	49.20	1379	1525	90.43	754	3069	24.57
NTD4	10.41	16.95	61.42	1186	1246	95.18	727	1758	41.35
NTD5	7.74	12.96	59.72	992	971	102.16	613	1498	40.92
OTD1	3.33	13.46	24.74	747	1584	47.16	956	3538	27.02
OTD2	13.81	18.44	74.89	799	1691	47.25	1686	4276	39.43
OTD3	14.19	20.44	69.42	1070	1845	57.99	1785	4588	38.91
OTD4	30.99	39.38	78.69	1727	2493	69.27	3161	7991	39.56

Table 3. Relative mobility of Cd, Pb and Zn in New and Old tailings as estimated by single extraction

Matrix Type	***Relative EDTA extractability and mobility of Cd, Pb and Zn***
New Tailings	Pb (96.53 ± 4.43) >>Cd (55.98 ± 4.81) >>Zn (33.16 ± 7.57)
Old Tailings	Cd (61.94 ± 25.09) ≥ Pb (55.42 ± 10.54) > Zn (36.23 ± 6.14)

Table 4. Correlation coefficients between amount of Cd, Pb and Zn extracted by EDTA and their "Total" content

Element	***EDTA-extractable vs 'total' (n =9)***
Cd	r =0.965 **
Pb	r = 0.638
Zn	r = 0.976**

*** All correlations are significant at the 0.01 level (2-tailed)*

4. Conclusions

From this study, it is concluded that new and old tailings are alkaline and have high carbonate content. Also, the pH of old tailings is less than the New tailings, which could be because of H^+ ions produced during mine tailing weathering.

Chemical and mineralogical observations confirm that the new tailings are undergoing oxidation and weathering in the surface layers. However, the old tailings are sort of stabilized at least up to the sampling depth. The response of the elements to single extraction (EDTA 0.5mol/L) enabled us to estimate their potential mobility in the tailings.

Based on single extraction, Zn has the least potential mobility in both types of tailings, whilst Cd in old tailings and Pb in new tailings have the highest potential mobility. Present study represents a first approach for a further environmental assessment of these environmentally hazardous tailings and possible reclamation efforts.

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