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Heavy metals leaching behavior and ecological risks in water and wastewater treatment sludges

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Abstract. Single (0.005 M DTPA), sequential (six-step) and kinetic (0.05 M EDTA) extractions were performed to assess Cd, Cr, Cu, Ni, Pb, and Zn mobilization and their potential ecological risks in Abuja (Nigeria) water (WTS) and wastewater (WWTS) treatment sludges. Total metal levels (mg/kg) in WTS and WWTS, respectively were: Cd(3.67 and 5.03), Cr(5.70 and 9.03), Cu(183.59 and 231.53), Ni(1.33 and 3.23), Pb(13.43 and 17.87), Zn(243.45 and 421.29). DTPA furnished metal extraction yields (%) in WTS and WWTS, respectively as: Cd(11 and 6), Cr (15 and 7), Cu(17 and 13), Ni(23 and 3), Pb(11 and 12), and Zn(37 and 33). The metals were associated with the soluble/exchangeable, carbonate, Mn/Fe-oxide, organic matter and residual forms to varying degrees. Kinetic extractions cumulatively leached metal concentrations akin to the mobilizable fractions extracted sequentially and the leaching data fitted well into the Elovich model. Metal mobilities were concordant for the three leaching procedures and varied in the order:WTS>WWTS. Calculated ecological risk indices suggested moderate and considerable metal toxicity in WTS and WWTS, respectively with Cd as the worst culprit. The findings may be useful in predicting heavy metals bioavailability and risks in the sludges to guide their disposal and use in land applications.

Keywords: heavy metal; single extraction; sequential extraction; kinetic extraction; ecological risk; industrial sludge

1. Introduction

The production of sludges from water and wastewater treatment processes is on the increase as result of increased urbanization and industrialization (Okareh and Enesi 2015). Disposal of such sludges is problematic and is a growing challenge for treatment plants, especially in the developing parts of the world with limited resources (Bai *et al*. 2012, Topcuoğlu 2015). Currently, the methods of sludge disposal include land utilization as soil amendments or ameliorants, deposition in sanitary landfills, incineration and discharge into water bodies, of which land application is the primary method (Tao *et al*. 2012). The beneficial use of sludges through land application is based on their ability to favorably alter soil properties and increase crop yield via the recycling of valuable components including organic matter nitrogen, phosphorus and other plant nutrients

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(Huang *et al*. 2011, Liu and Sun 2013, Duan *et al*. 2015). The sludges may, however, pose environmental concerns because, aside haboring biological and physical hazards, they also inadvertently bear mixed chemical hazards such as toxic heavy metals and organic contaminants scavenged from the raw water, wastewater and residual chemicals left during treatment (Jakubus and Czekała 2001, Lewis and Gattie 2002, Clarke and Smith 2011, Usman *et al*. 2012). Crops grown on soils receiving excessive application of the sludges may accumulate the heavy metals up to toxic levels and pass them on to the next trophic levels and eventually to humans when consumed (Kidd *et al*. 2007, Sun *et al*. 2009, Oleszczuk and Hollert 2011). Information about the distribution of the chemical forms (speciation or fractionation), mobility, bioavailability and potential ecological risks of heavy metals in sludges intended for land use and other applications is necessary to strike a balance between their beneficial uses and environmental implications.

Assessment of chemical forms of heavy metals is often performed as part of an overall approach to understanding the complex chemistry and behavior of heavy metal contaminants in environmental matrices and biological systems (D'amore *et al*. 2005, Sun *et al*. 2008). This involves the determination of the associations of the metal forms among the phases viz: (i) solution, ionic or colloidal, (ii) organic or inorganic exchange complexes as readily exchangeable ions, (iii) complexes in which they are strongly bound, (iv) soluble mineral/organic phases, (v) precipitated major metal (Fe, Mn, Al) oxides and insoluble salts, and (vi) resistant secondary minerals (Gismera *et al*. 2004). The level of exposure of organisms to the metals relative to their speciation in the soil or sludge system has been referred to as bioavailability, defined as the sub-fraction of the metal (or any other substance) that can cause an effect, positive or negative, on an organism (Semple *et al*. 2007).

Methods used for assessing heavy metal forms in the solid phase of environmental matrices include chemical extractions, elutriation and filtration (D'amore *et al*. 2005). Even though variously castigated (Nirel and Morrel 1990, Zimmerman and Weindorf 2010, Cappuyns 2012**)**; owing to the good correlation between extracted amounts and uptake by biota (Tokalioğlu *et al*. 2006); chemical extractions are increasingly used as surrogate methods to provide information on the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of the heavy metals in soils, sediments and sludges (Shiowatana *et al*. 2001). It has also been hypothesized that insight into heavy metal dynamics in such matrices can be enhanced when chemical extractions are followed kinetically, possibly by monitoring the concentrations of the metal extracted by a non-selective reagent over time, and deriving kinetic parameters (for example, rate constants) from the leaching curve (Song and Greenway 2004, Labanowski *et al*. 2008, Alghanmi *et al*. 2015). Such kinetic studies would be able to predict changes over time in the fate of the heavy metal contaminants based on quantitation of the changes of the parameters that control matrix-metal interaction over time (Pueyo *et al*. 2008). Moreover, certain kinetic approaches may provide a useful tool to assess whether metal availability is under kinetic control of the soil solid phase or soil solution, and this information is critical for interpreting the results provided by different pre-described speciation approaches (Manouchehri *et al*. 2011).

To date, literature on heavy metals forms and ecological risk assessment in soils, sediments and sludges is dominated by reports on the sole use of single extractions, sequential or kinetic extractions. Reports documenting the concurrent application of two or more of these chemical extraction techniques are comparatively fewer (Tessier *et al*. 1979, Gismera *et al*. 2004, Wasay *et al*. 2007, Park *et al*. 2013, Manouchehri *et al*. 2014). In this study, single, sequential and kinetic extractions were conjointly used to assess the chemical forms and mobility of Cd, Cr, Cu, Ni, Pb, and Zn in sludges from municipal water treatment (WTS) and wastewater treatment (WWTS) plants in a rapidly expanding city (Abuja, Nigeria). Potential soil contamination and ecological risks arising from possible land utilization of the sludges were also assessed. To the best of the authors' knowledge, no such investigation has been previously reported for the sludges used in this study.

2. Materials and methods

2.1 Chemicals and apparatus

Acetic acid (99.5% w/v), hydroxylamine hydrochloride (99.0% w/w), ammonium acetate (98.0% w/w), hydrogen peroxide (30% w/v), sodium acetate (98.0% w/w), hydrochloric acid (37% w/v), nitric acid (99.5% w/v) were used to prepare extracting solutions for sequential chemical extraction. Diethylenetriaminepentaacetic acid, DTPA (*fw*=393.35 g/mol, 99.0% w/w) was used to leach the available metals. The disodium salt of ethylenediaminetetraacetatic acid ($Na_2EDTA^{\cdot}2H_2O$, *fw*=372.2 g/mol, ≥99.0% w/w) was used for kinetic extractions. All the above-mentioned chemicals were of Sigma-Aldrich patent. Apparatuses used include conductivity meter (4520-JENWAY, Bibby Scientific Ltd, United Kingdom); multipurpose flask shaker (Model TT 12F, Techmel and Techmel, USA); pH meter (HI-8424N, Hanna Instruments, UK); digitally operated high speed centrifuge (Model TGL-16G); atomic absorption spectrophotometer, AAS **(**Buck Scientific 210 VGP, USA).

2.2 Brief description of study area

The study area is Abuja, the Federal Capital Territory (FCT) of Nigeria, a rapidly growing city with land mass 7, 753.9 km^2 and total population of 776, 298 people (NPC 2006). The Lower Usman Dam Water Treatment Plant (LUDWTP) is located at $9^o11'41''$N and $7^o23'47.50''$E. Raw water for the plant is sourced from the Lower Usman Dam reservoir and the new Gurara Dam reservoir. The new and existing facilities now provide $7.2x10^8$ L of clean drinking water per day to Abuja and its environs. The water treatment technology involves aeration followed by removal of large solids implementing drum screens. The water then passes through the lamella sludge blanket clarifier/inclined-plate clarifier in place of conventional settling tanks for clarification. The technology makes use of highly compact settlers, reducing the space requirements compared with the latter by up to 90%.This clarified water is put to rapid gravity filtration by passing it through a filter medium consisting of sand filters, by gravity or under pumped pressure. The filter removes flocculated materials trapped in the sand. Then the water is disinfected in the contact tank with chlorine and goes through chemical dosing using aluminium sulphate, lime, polyelectrolyte and chlorine. Sand filters are cleaned by backwashing, which involves reversing the direction of the water and adding compressed air (Ibrahim *et al.* 2014).

The Wupa Wastewater Treatment Plant (WWTP) is located at $9^o1.406'$N and $7^o22.903'$E. The plant was designed for FCT to handle the waste generated by 700,000 population equivalent and expandable to 1,000,000 population equivalent on an average domestic water requirement of 230 cubic L/day. The plant operates on the activated sludge process that relies on microbial population in mixed suspension to achieve the wastewater treatment. The WTS generated from LUDWTP is continually collected in sludge chambers/settling tanks, thickened, dewatered and dried on concrete drying beds before conveying it to sludge lagoons. WWTS produced from WWTP is disposed in sludge lagoons which are excavated areas in which sludge is allowed to drain and dry over a period of months or even a year or more.

2.3 Collection, pre-treatment and physico-chemical characterization of sludge

Batch samples of WTS and WWTS were respectively collected monthly from the LUDWTP and WWTP (both located in Abuja, Nigeria) spanning a period of 3 months. Sludge samples were collected into five 5-L plastic containers that were previously washed with dilute HNO_3 and rinsed with distilled, followed by deionized water. The sludge samples were dewatered by gravity thickening method, air-dried on a drying bed and allowed to age for 1 month. The caked material from each batch of WTS and WWTS was pulverized, sieved (<2 mm), composited, stored at 4^oC until they were analysed for pH, organic matter, electrical conductivity, cation exchange capacity, total nitrogen, total phosphorus, and pseudototal Cd, Cr, Cu, Ni, Pb and Zn using standard operating procedures (CMSS 2006).

2.4 Single chemical extraction of heavy metals in sludge

The available metal contents of sludges were determined by extraction with a mixture of 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M triethanolamine (pH adjusted to 7.3 with 1 M HCl solution) as described by Levei *et al*. (2010). A 10-g portion of sludge sample was weighted into a 125 mL flask, and shaken for 2 h at room temperature using a magnetic shaker with 20 mL of DTPA extracting solution. The extract was filtered and diluted to 100 mL with ultrapure water followed by metal assay by AAS analysis.

2.5 Sequential extraction of heavy metals in sludge

The sequential chemical extraction protocol of Tessier *et al*. (1979) modified by Tsai *et al*. (2003) was performed on 1-g portions of sludge samples (oven-dried at 105^oC for 2 h) to partition Cd, Cr, Cu, Ni, Pb, and Zn among operationally defined pools with varying mobility and bioavailability:soluble/exchangeable (F_1), carbonate-bound (F_2), Mn oxide-bound (F_3), Fe oxide-bound (F_4), organic matter-bound (F_5), and residual form (F_6) as described hereunder.

F_1: sludge was extracted with 20 mL of 1.0 M NH_4OAc at an initial pH of 7 by shaking for 30 min at room temperature.

F_2: residue from first step was extracted with 20 mL of 1.0 M NaOAc buffered at pH 5 by shaking for 5 h at room temperature.

F_3: residue from second step was extracted with 20 mL of 0.1 M $NH_2OH \cdot HCl$ in 0.1 M HNO_3 by shaking for 30 min at room temperature.

F_4: residue from third step was extracted with 20 mL of 0.04 M $NH_2OH \cdot HCl$ in 25% (w/v) of HOAc at a pH of 2 by shaking for 6 h at 96^oC.

F_5: residue from fourth step was extracted with 5 mL of 0.1 M HNO_3 and 10 mL of 30% (w/v) H_2O_2 and shaken for 5 h at 85℃. Later 15 mL of 3.2 M NH_4OAc was added and cooled for 30 min at room temperature.

F_6: residue from fifth step was extracted with 10 mL of aqua reqia (21 mL conc. HCl + 7 mL conc. HNO_3) for 1 h. Subsequently, heavy metal amounts in solution were determined by AAS.

The efficiency of the sequential extraction procedure was checked by comparing the sum of metal concentrations obtained as $\sum_{i=1}^{6} F_i$ (i.e., F_1+F_2+F_3+F_4+F_5+F_6) with the corresponding pseudototal concentration (aqua regia-extracted). This approach furnished the recovery factor, R_f defined as

$$R_f = \left(\frac{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}{\text{Pseudototal metal concentration}} \right) \text{x}\,100 \tag{1}$$

2.6 Kinetic extraction of heavy metals in sludge

Kinetic extractions were performed according to the procedure of Song and Greenway (2006) with slight modifications. One-gram portions of the sludge were separately transferred to 250 mL flasks in duplicate. Aliquots (50 mL) of 0.05 M EDTA were added (solid/liquid ratio=1/50) and the contents shaken with the aid of an electrically operated multipurpose flask shaker. At elapse of each specified time interval: 10 min, 20 min, 30 min, 1 h, 2 h, 6 h, 10 h, 12 h, 16 h and 24 h. The slurries were filtered through an ashless filter paper (for extractions >1 h, slurries were centrifuged for 5 min before filtration) and the filtrate kept for heavy metal assay by AAS.

2.7 Quality assurance/control and statistical treatment of data

All glassware and plastics were properly washed with acid (10% v/v HNO_3) and finally with distilled water and oven-dried. Procedural blank samples were subjected to similar treatments using the same amounts of reagents. In all cases, measurements were done in triplicate. Graphical work and ecological risk calculations were performed using the Microsoft Excel® software. One-sample t-tests were used to test the significance of differences in metal concentrations sequentially extracted at the 5% probability level ($p \leq 0.05$) by means of the SPSS 17.0 (SPSS, Chicago, Ill.) statistical package. Metal concentrations from AAS measurements, C_M (mg/L) were converted to corresponding concentrations in the sludge (mg/kg dry weight) by using the mass balance relationship

$$\text{Metal concentration in sludge (mg/kg dw)} = \frac{C_M V}{m_{\text{sludge}}} \tag{2}$$

where V is total volume of digest or aliquot of extracting solution (L) and w_{sludge} is the weight of dry sludge digested or leached (kg).

3. Results and discussion

3.1 Physicochemical characteristics of sludge

Some physicochemical properties of WTS and WWTS collected for the study are recorded in Table 1. Both sludges are slightly acidic (average pH 6.67) somewhat comparable with that earlier reported by Anyakora (2013) for WTS sampled from the same locale (i.e., LUDWTP, Abuja). The organic matter contents for the two sludges are also comparable (average value=21.47%). The

Table 1 Some physico-chemical attributes[*] of sludges[†] used for the study

Attribute	WTS	WWTS
pH (H_2O)	6.64±0.03	6.69±0.05
Organic matter (%)	21.62±0.06	21.32±0.05
Nitrogen (%)	0.61±0.01	1.64±0.02
Phosphorus (%)	1.55±0.01	2.81±0.01
Conductivity (μS/cm)	1714.00±3.00	8910.33±7.01
Cation exchange capacity (cmol/kg)	3.57±0.08	33.31±0.06
Pseudototal metals (mg/kg)		
Cd	3.67±0.15	5.03±0.06
Cr	5.70±0.04	9.03±0.15
Cu	183.59±0.72	231.53±0.76
Ni	1.33±0.06	3.23±0.21
Pb	13.43±0.21	17.87±0.15
Zn	243.45±0.11	421.29±7.37

[*]Mean of triplicate measurements±standard deviation, [†]WTS=Water Treatment Sludge, WWTS=Wastewater Treatment Sludge

conductivity and cation exchange capacity of WWTS are, however, higher than those of WTS by approximately 5- and 9-folds, respectively. The moderate levels of nitrogen and phosphorus in the sludges (average N=1.13% and P=2.18%) coupled with favourable pH values and organic matter suggest that the sludges can be scrupulously utilized during land applications to enhance crop yield. Pseudototal metal concentrations (mg/kg) in WTS were: Cd(3.67), Cr(5.70), Cu(183.59), Ni(1.33), Pb(13.43), and Zn(243.45); while corresponding levels in WWTS were: Cd(5.03), Cr(9.03), Cu(231.53), Ni(3.23), Pb (17.87), and Zn (421.29). Apart from Cd and Cu, pseudototal metals in the sludges fall below their critical levels (mg/kg): Cd (3.00), Cr/Cu (100.00), Ni (70.00), Pb (164.00), and Zn (421) for healthy soil quality (NESREA 2009).

3.2 Available (DTPA extractable) heavy metals in sludge

DTPA (0.005 M) has been used to assess the solubilities of both nutrient and non-nutrient metals in soils. Evidence indicates that the DTPA-extractable metals are generally related to plant availabilities (Miles and Parker 1979). The available metal concentrations (mg/kg) in WTS were: Cd(0.40), Cr(0.83), Cu(26.12), Ni(0.30), Pb(1.47), and Zn(89.21). In WWTS these concentrations were Cd(0.30), Cr(0.63), Cu(30.67), Ni(0.47), Pb(2.13), and Zn(136.94). This means that the available Cd, Cr, Cu, Ni, Pb, and Zn accounted for: 10.90%, 14.46%, 17.01%, 22.56%, 10.95%, and 36.64% of their respective pseudototal concentrations in WTS; whereas in WWTS, 5.96%, 6.98%, 13.25%, 2.63%, 11.92%, and 32.50% of pseudototal Cd, Cr, Cu, Ni, Pb, and Zn, respectively constituted the available pools.

3.3 Heavy metals fractionation patterns in sludge

DTPA (0.005 M) has been used to assess the solubilities of both nutrient and non-nutrient metals in soils. Evidence indicates that the DTPA-extractable metals are generally related to plant availabilities (Miles and Parker 1979). Pseudototal metal levels become inadequate whenever an assessment of changes in the metal bioavailability status in the soil is intended. In this study, the procedure of Tessier *et al*. (1979) sequential extraction modified by Tsai *et al*. (2003) separated the metals into six operationally defined fractions: soluble + exchangeable (F_1), carbonate-bound (F_2), Mn oxide-bound (F_3), Fe-oxide-bound, (F_4), organic matter-bound (F_5) and residual (F_6). Metal availability decreases in the order of extracting sequence: $F_1 > F_2 > F_3 > F_4 > F_5 > F_6$.

Table 2 Heavy metal concentrations (mg/kg) in fractions[*] of sludges[†] used for the study

Metal	Fraction	WTS	WWTS
Cadmium			
	Soluble/Exchangeable	0.21±0.01	0.27±0.01
	Carbonate-bound	0.19±0.01	0.30±0.02
	Mn oxide-bound	0.46±0.01	0.53±0.03
	Fe oxide-bound	0.54±0.02	0.61±0.01
	Organic matter-bound	1.02±0.03	1.35±0.01
	Residual	1.07±0.03	1.72±0.02
	Sum (Σ)	3.50±0.05	4.78±0.04
	R_f (%)	95.37	95.03
Chromium			
	Soluble/Exchangeable	0.42±0.01	0.32±0.02
	Carbonate-bound	0.46±0.01	0.34±0.02
	Mn oxide-bound	0.59±0.01	1.28±0.02
	Fe oxide-bound	0.55±0.02	1.25±0.02
	Organic matter-bound	1.53±0.05	2.16±0.02
	Residual	1.74±0.01	2.87±0.02
	Sum (Σ)	5.29±0.02	8.22±0.10
	R_f (%)	92.81	91.03
Copper			
	Soluble/Exchangeable	15.61±0.55	16.58±0.24
	Carbonate-bound	15.79±5.20	14.41±0.26
	Mn oxide-bound	26.75±0.44	31.41±0.23
	Fe oxide-bound	27.61±0.30	36.73±0.23
	Organic matter-bound	36.97±0.56	43.47±0.36
	Residual	52.60±0.43	59.22±0.57
	Sum (Σ)	175.33±5.78	201.83±0.51
	R_f (%)	95.50	87.17
Nickel			
	Soluble/Exchangeable	0.17±0.01	0.18±0.02
	Carbonate-bound	0.14±0.01	0.28±0.01

Table 2 Continued

Metal	Fraction	WTS	WWTS
Nickel			
	Mn oxide-bound	0.15±0.01	0.37±0.01
	Fe oxide-bound	0.19±0.03	0.32±0.02
	Organic matter-bound	0.32±0.02	0.82±0.03
	Residual	0.26±0.04	0.93±0.03
	Sum (Σ)	1.23±0.04	2.91±0.09
	R_f (%)	92.48	90.09
Lead			
	Soluble/Exchangeable	0.68±0.03	1.06±0.02
	Carbonate-bound	0.75±0.01	1.18±0.02
	Mn oxide-bound	1.57±0.02	1.49±0.01
	Fe oxide-bound	1.76±0.03	1.87±0.01
	Organic matter-bound	3.65±0.01	4.31±0.03
	Residual	4.01±0.01	6.74±0.02
	Sum (Σ)	12.41±0.06	16.65±0.09
	R_f (%)	92.41	90.09
Zn			
	Soluble/Exchangeable	46.57±0.06	74.37±0.31
	Carbonate-bound	43.10±0.03	62.56±0.26
	Mn oxide-bound	11.10±0.03	36.70±0.47
	Fe oxide-bound	30.36±0.02	42.90±0.02
	Organic matter-bound	42.79±0.19	72.64±0.41
	Residual	58.17±0.02	104.56±0.43
	Sum (Σ)	232.09±0.11	393.72±0.95
	R_f (%)	95.33	93.46

[*] Mean of triplicate measurements±standard deviation extracted by modified Tessier *et al*'s (Tsai 2003) sequential method, [†]WTS=Water Treatment Sludge; WWTS=Wastewater Treatment Sludge

Metal concentrations (mg/kg) in the various fractions of the sludges (Table 2), were converted to extraction yields (%) using the relationship

$$\text{Extraction yield}\,(\%) = \frac{F_\mathrm{i}}{\sum_{i=1}^{6} F_\mathrm{i}} \text{ x } 100 \tag{3}$$

where, $\sum_{i=1}^{6}\mathrm{F}_i$: $F_1+F_2+F_3+F_4+F_5+F_6$.

3.3.1 Water soluble/exchangeable metal forms F_1

The fraction, F_1 contains the water soluble and exchangeable metal species made up of free ions and ions complexed with soluble organic matter and other constituents (Violante *et al.* 2010).

This fraction contains the water soluble and exchangeable metal species made up of free ions and ions complexed with soluble organic matter and other constituents. The water-soluble/exchangeable metal concentrations, F_1 (mg/kg) extracted in WTS were 0.21, 0.42, 15.61, 0.17, 0.68, and 46.57 for Cd, Cr, Cu, Ni, Pb and Zn, respectively. Corresponding extraction yields were 6.00, 7.94, 8.90, 13.82, 5.48, and 20.07. In WWTS, 0.27, 0.32, 16.58, 0.18, 1.06, and 74.37 mg/kg of Cd, Cr, Cu, Ni, Pb and Zn, respectively were extracted as F_1. Equivalent extraction yields (%) were 5.65, 3.89, 8.21, 6.19, 6.37 and 18.89. Metal extraction yields were higher for WTS than WWTS and appeared to rank in the order: WTS:Zn>Ni>Cu>Cr>Cd>Pb; WWTS: Zn>Cu>Pb>Ni>Cd>Cr. This fraction constitutes the most mobile and potentially bioavailable metal species and provides a measure of those heavy metals which are released most readily into the environment (Rao *et al*. 2008). The unusually high yields of the metals in this fraction suggest that they were introduced anthropogenically.

3.3.2 Carbonate-bound metal forms F_2

This phase contains loosely bound metals and may become important when the hydrous oxides and organic matter in the soil is low (Filgueiras *et al*. 2002). Approximately 5.43, 8.70, 9.01, 11.38, 6.04, 18.57% of Cd, Cr, Cu, Ni, Pb and Zn were retained in the carbonate-bound fraction in WTS. In WWTS, 6.28, 4.14, 7.14, 9.62, 7.09, 15.89 % of Cd, Cr, Cu, Ni, Pb and Zn were retained in this fraction. Order of ranking of metal extractabilities were Zn>Ni>Cu>Cr>Pb>Cd in WTS; Zn>Ni>Cu>Pb>Cd>Cr in WWTS.

3.3.3 Hydrous Fe/Mn-bound metal forms F_3/F_4

In WTS, the proportions of the metals (%) likely associated with the hydrous Mn and Fe oxides, F_3:F_4 were: Cd(13.14:15.43), Cr(11.15:10.40), Cu(15.26:15.75), Ni(12.20:15.45), Pb (12.65:14.18), and Zn (4.78:13.08). In WWTS, the ratios were: Cd(11.09:15.57), Cr (15.57:15.25), Cu(15.56:18.20), Ni(12.71:11.00), Pb(8.95:11.23), and Zn(9.32:10.90). It seemed that the metals were partitioned in F_4 to a greater extent relative to F_3. For instance, in WTS, the extraction yields of Cd, Cr, Cu, Ni, Pb and Zn in F_4 were respectively 1.17-, 0.93-, 1.03-, 1.27-, 1.12-, and 2.74-folds relative to F_3. In WWTS, Cd, Cr, Cu, Ni, Pb and Zn extraction yields, respectively occurred as 1.40-, 0.98-, 1.17-, 0.87-, 1.25-, and 1.17-folds in F_4 over F_3. Overall, the sums of metal extraction yields (%) in the two fractions (F_3+F_4) ranked as Cu(31.01)>Cd(28.57)>Ni(27.65)>Pb(26.83)>Cr(21.55)>Zn(17.86) in WTS. In the case of WWTS, these sums followed the order Cu(33.76)>Cr(30.82)>Cd(26.66)>Ni(23.71) and Zn(20.22)>Pb(20.18). Cu appeared to have the highest extraction yields as F_3+F_4. Metal sorption by hydrous oxides occurs via the formation of inner-sphere metal surface complexes and formation of metal hydroxide precipitate phases and is a major mechanism for removal of heavy metals from soil solution (Silveira *et al*. 2003).

3.3.4 Organic matter-bound metal forms F_5

In the organic matter-bound metal pool, F_5, as much as 1.02, 1.53, 36.97, 0.32, 3.65, 42.79 mg/kg of Cd, Cr, Cu, Ni, Pb and Zn were extracted in WTS furnishing equivalent extraction yields as 29.14, 28.92, 21.11, 26.62, 29.41 and 18.44%. In WWTS, 1.35, 2.16, 43.47, 0.82, 4.31 and 72.64 mg/kg of Cd, Cr, Cu, Ni, Pb and Zn, respectively were extracted as F_5, corresponding to extraction yields of 28.24, 26.28, 21.54, 28.18, 25.89 and 18.45%. On the whole, metal extractabilities in F_5 approximately followed the order Pb≈Cd>Cu>Cr>Ni>Zn, in WTS and Cd≈Ni>Cr>Pb>Cu>Zn in WWTS. Strong metal adsorption by soil organic matter by formation of metal chelates reduces metal solubility in soil.

Overall, in WTS the mobilizable metal concentrations (F_1+F_2+F_3+F_4+F_5) were 2.42, 3.55, 122.73, 0.97, 8.41, and 173.92 mg/kg representing 69.14, 67.11, 70.00, 78.86, 67.77, and 74.94% of the corresponding total metal concentrations extracted by the sequential extraction procedure. As much as 3.06, 5.35, 142.60, 4.31, 9.91, and 289.17 mg/kg of Cd, Cr, Cu, Ni, Pb, and Zn were respectively retained as the sum F_1+F_2+F_3+F_4+F_5 in WWTS indicating that 64.02, 65.09, 70.65, 67.70, 59.52, and 73.45% of the corresponding metal sums extracted by the sequential procedure were potentially mobilizable.

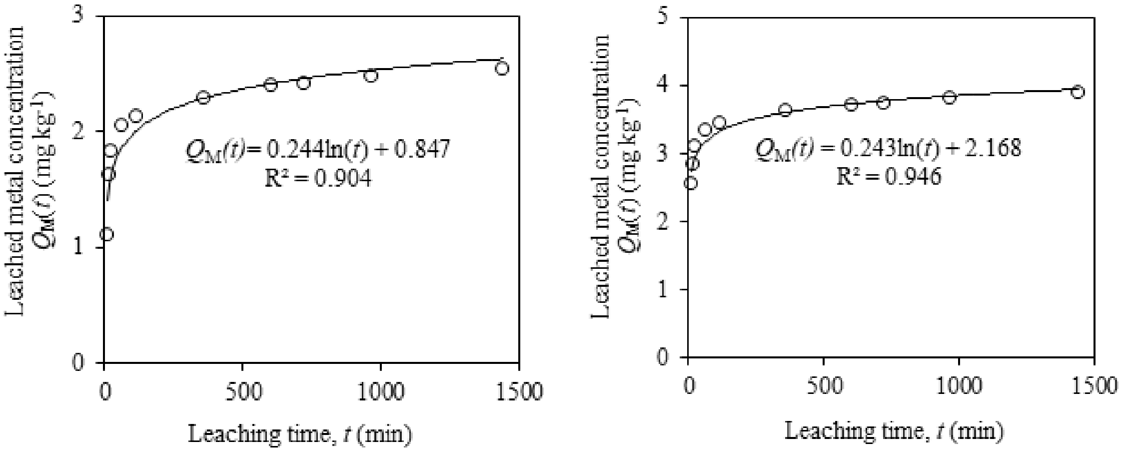
3.3.5 Residual metal forms F_6

Residual metal forms are retained in the soil silicate matrix. As much as 1.07, 1.74, 52.60, 0.26, 4.01, and 58.17 mg/kg of Cd, Cr, Cu, Ni, Pb, and Zn were associated with F_6 in WTS with equivalent extraction yields (%) ranking as Cr (32.89)>Pb (32.31)>Cd (30.57)>Cu (30.00)>Zn(25.06) Ni (21.14). Metal concentrations partitioned as F_6 in WWTS were 1.72, 2.87, 59.22, 0.93, 6.74 and 104.56 mg/kg with extraction yields (%) following the sequence Pb (40.48)>Cd (35.98)>Cr (34.91)>Ni (31.96)>Cu (29.34)>Zn (26.56). The sequences suggest that Cd, Cr and Pb were mostly associated with the residual fraction while Zn was the least. The fractionation patterns (Table 2) reveal that metal concentrations, hence extraction yields were higher in the residual fraction than in any of the other individual fractions extracted by the sequential procedure. Gawdzik *et al.* (2012) also observed that most of the metals in a sewage sludge existed in the less mobile fractions (organically bound and residual fractions). For Pb in particular, its greater retention in the residual fraction of sludges has been previously reported (Liu and Sun 2013). This is attributed to the tendency of Pb to associate with insoluble weathering products formed by the oxidation of sulphides and insoluble soil fractions (Pueyo *et al*. 2008). It has been proposed that, risk assessment involving Cd, Cr, Cu, Ni, and Zn may focus on food-chain pathways (soil-plant-human or soil-plant-animal-human), whereas pathways involving direct ingestion or dermal contact are advocated in the case of Pb (McLaughlin *et al*. 2000).

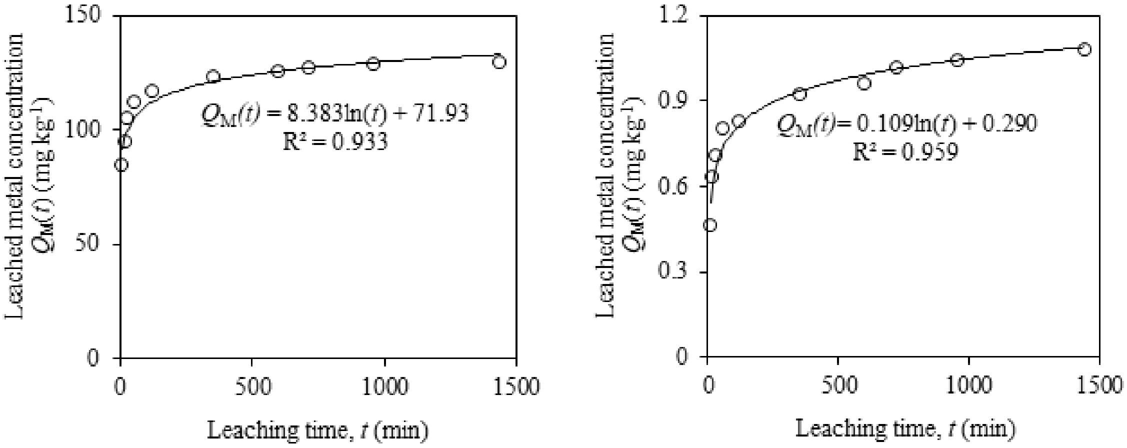
There were marked differences in the metal fractionation patterns in the two industrial sludges possibly due to different anthropogenic sources of these metals coupled with treatment processes. In both WTS and WWTS, metal recovery factors, R_f(%) in WTS ranged as Cd (95≤R_f(%)≤100), Cr (91≤R_f(%)≤100), Cu (87≤R_f(%)≤100), Ni (90≤R_f(%)≤100), Pb (93≤R_f(%)≤100), and Zn (93≤R_f(%)≤100) were mostly within ±10% indicating a good agreement between the sequential extraction and aqua regia extraction method for pseudototal metals and that the cumulative error in the sequential fractionation procedure was reasonably low.

3.3 Kinetic extractions to assess heavy metals mobilization potential in sludge

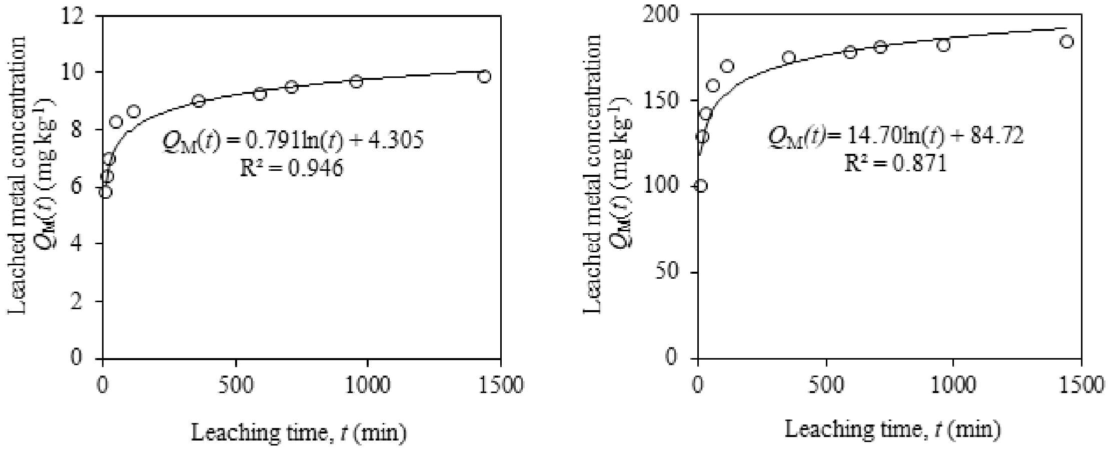
The evolution of cumulative amounts of metals (mg/kg) extracted by EDTA (0.05 M) from WTS and WWTS with time are illustrated in Figs. 1 (a)-(b). This concentration was previously established by as furnishing optimal metal removal at pH 6.6 (Morera *et al*. 2001). EDTA has been used to assess metal availability for regulating sludge application to soils. EDTA is a non-specific complexing agent capable of direct metal extraction from several soil compartments by a fast competitive complexation reaction (Gismera *et al*. 2004). The leaching curves tended towards plateaux for all the metals implying that the sludges had fixed sorption capacities providing limited sites onto which the metals were originally sorbed. The concentrations of leached metals increased rapidly within the first hour, and then slowed down by the second hour into the experiment.



(a) Cadmium (b) Chromium

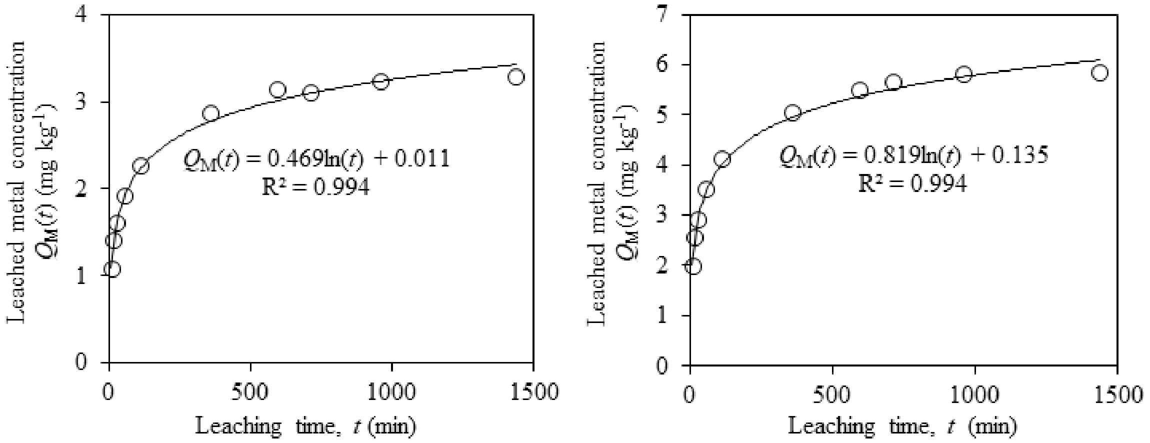


(c) Copper (d) Nickel

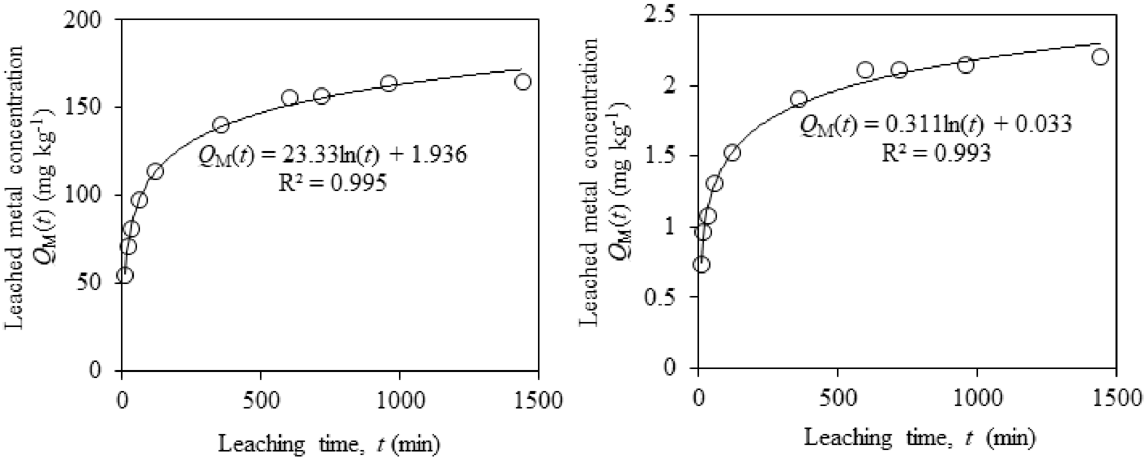


(e) Lead (f) Zinc

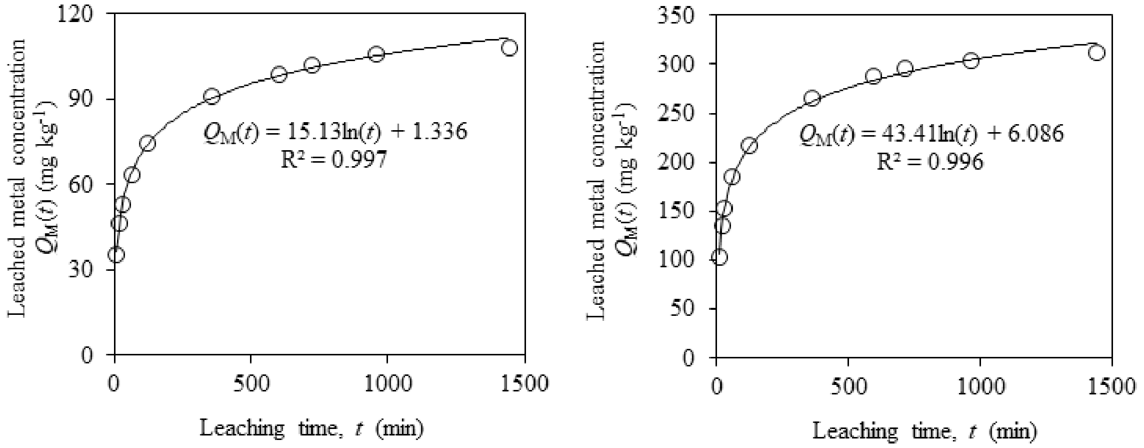
Fig. 1(a) Cumulative amounts (mg/kg) of heavy metals leached from water treatment sludge (solid/liquid ratio=1 g/50 mL) with time using 0.05 M EDTA along with curves from Elovich model



(a) Cadmium (b) Chromium



(c) Copper (d) Nickel



(e) Lead (f) Zinc

Fig. 1(b) Cumulative amounts (mg/kg) of heavy metals leached from wastewater treatment sludge (solid/liquid ratio=1 g/50 mL) with time using 0.05 M EDTA along with curves from Elovich model

Table 3 Elovich kinetic model parameters for heavy metals leaching from water treatment (WTS) and wastewater treatment (WWTS) sludges†

Sample	Parameter	Cd	Cr	Cu	Ni	Pb	Zn
WTS							
	α(mg/kg.min)	7.85	1820.95	44652.25	1.57	182.73	4680.29
	β(/mg.kg)	4.10	4.12	0.12	9.17	1.26	0.07
	R^2	0.904	0.946	0.933	0.959	0.946	0.871
WWTS							
	α(mg/kg.min)	-0.48	0.97	25.35	0.35	16.53	49.94
	β(/mg.kg)	2.13	1.22	0.04	3.32	0.07	0.02
	R^2	0.994	0.994	0.995	0.993	0.997	0.996

This implied that during the first hour (i.e. short leaching time), metal leaching rates were very fast, mobilizing high amounts of the metals (labile metal pools); whereas slow leaching rates which gradually furnished small metal amounts (less labile metal pools) were observed at long leaching times (1-24 h). The leaching curves exhibited profiles which suggested that equilibrium was almost reached after 24 h. A similar observation was reported for the kinetic extractions of Cd, Cu, Pb, and Zn in soils by EDTA and citrate (Labanowski *et al*. 2008). By the end of the 24-h leaching time, as much as 2.54, 3.86, 129.10, 1.08, 9.80, and 182.50 mg/kg of Cd, Cr, Cu, Ni, Pb, and Zn were respectively leached from WTS by EDTA. These concentrations represented 69.21, 67.72, 70.32, 81.20, 72.97, and 74.96% of their corresponding pseudototal levels. In WWTS, 3.30, 5.82, 165.20, 2.20, 10.81, and 310.62 mg/kg of Cd, Cr, Cu, Ni, Pb, and Zn were respectively leached by the 24th hour by EDTA, equivalent to 65.61, 64.45, 71.35, 68.11, 60.49, and 73.73% of their pseudototal levels. The extraction yields of EDTA were higher than those removed by any single step of the sequential extraction procedure and represented more closely the mobilizable metal pools (F_1+F_2+F_3+F_4+F_5) earlier extracted by the sequential procedure. This means that large amounts of metals such as those held in the carbonates, oxides, sulphate minerals, and organic matter are available for removal by EDTA (Beckett 1989).

Modeling the kinetic data can be helpful in characterizing the metals bound to different compartments and to study their rates of mobilization (Manouchehri *et al*. 2011). The findings from these extractions can be used for assessing the changes in heavy metal mobility and bioavailability in the sludge in the long-run. The amount of metal leached per unit mass of soil at any time, $Q_M(t)$ (mg/kg) was calculated and the experimental leaching data was analyzed using the Elovich model (Equation 4) which is frequently used for the description of heavy metal leaching behaviour soil, sediments and sludges.

$$Q_M(t) = \frac{1}{\beta}\ln(t) + \frac{1}{\beta}\ln(\alpha\beta) \quad (4)$$

where t=specific leaching time (min), α=initial desorption rate (mg/kg·min), β=desorption coefficient /mg.kg). The model parameters are reported in Table 3.

The experimental data seemed to be well modeled by the Elovich equation with values of the coefficients of determination (R^2) ranging from 0.871-0.959 in WTS and 0.993-0.997 for WWTS. The initial desorption rate, α (mg/kg.min) ranked as Zn (4680.29)>Cu (44652.25)>Cr

(1820.95)>Pb (182.73)>Cd (7.85)>Ni (1.57) in WTS; whereas in WWTS, the order was Zn (49.94)>Cu (25.35)>Pb (16.53)>Cr (0.97)>Cd (0.48)>Ni (0.35). The approximate orders of α in the two sludges are essentially the same, except that the positions for Cr and Pb are interchanged. The values of α suggest the greater leachability and availability of the metals in WTS than WWTS. The values of β showed a trend converse to that of α, but were essentially the same for WTS and WWTS.

3.4 Assessment of heavy metals contamination and ecological risks in sludge

The pseudototal metal content is an excellent criterion used to define the extent of metal build-up or degree of contamination of environmental matrices including sludges. It provides an estimate of the degree of saturation of the total cation exchange capacity of soil colloids by metals (Wuana *et al*. 2012). In this study, quantitative evaluation of the degree of potential contamination of soil by waste-dump-borne heavy metals utilized indices such as the geo-accumulation index (I_{geo}), single-metal contamination factor, (C_{f}), degree of contamination (C_{d}), composite-metal contamination index (Eqs. (5)-(8)). Single-metal ecological risk index, E_{r} and multi-metal ecological risk index (*RI*) were also calculated based on the NESREA (2009) critical soil heavy metal values using the approach of Hakanson (1980) (Eqs. (9) and (10)).

$$I_{\mathrm{geo}}^{i} = \frac{\log_{10}\left(C_{\mathrm{M}}^{\mathrm{i}} / 1.5 C_{\mathrm{M(crit)}}^{i}\right)}{0.30103} \tag{5}$$

$$C_{\mathrm{f}}^{i} = C_{\mathrm{M}}^{i} / C_{\mathrm{M(crit)}}^{i} \tag{6}$$

$$C_{d} = \sum_{i=1}^{n} C_{\mathrm{f}}^{i} \tag{7}$$

$$PI = \sqrt{\frac{1}{2}\left[\left(\frac{1}{n}\sum_{i=1}^{n} C_{\mathrm{f}}^{i}\right)^{2} + (C_{\mathrm{f\,(max)}}^{i})^{2}\right]} \tag{8}$$

$$E_{\mathrm{r}}^{i} = T_{\mathrm{r}}^{i} \text{ x } C_{\mathrm{f}}^{i} \tag{9}$$

$$RI = \sum_{i=1}^{n} E_{\mathrm{r}}^{i} \tag{10}$$

where C_{M}^{i} is the measured pseudototal concentration of a given metal; $C_{\mathrm{M(crit)}}^{i}$ is the critical or reference soil concentration of the metal; *n* is the number of metals pooled; E_r^i is the potential ecological risk of the metal; and T_r^i is the toxicity response factor of the metal given as Zn=1, Cr=2, Cu=Ni=Pb=5, and Cd=30 (Hakanson 1980). Although the foregoing risk approach was originally used as a diagnostic tool for the purpose of controlling water pollution, it has been successfully adopted for assessing the toxic heavy metal status of sediments and sludges intended for land use (Qingjie *et al.* 2008).

It is also possible to define a risk assessment code based on the mobility factor, M_{f} (%) [i.e.,

Table 4 Heavy metals contamination degrees and ecological risk in municipal water (WTS) and wastewater (WWTS) treatment sludges

Sample	Parameter	Cd	Cr	Cu	Ni	Pb	Zn
WTS							
	I_{geo}	-0.29	-4.92	0.29	-6.30	-4.20	-1.38
	C_f	1.22	0.06	1.84	0.02	0.08	0.58
	C_d	3.80					
	PI	1.37					
	M_f	11.43	16.64	17.91	25.20	11.52	38.64
	E_r	36.70	0.11	9.18	0.10	0.41	0.58
	RI	47.07					
WWTS							
	I_{geo}	0.16	-4.05	0.63	-5.02	-3.78	-0.58
	C_f	1.68	0.09	2.32	0.05	0.11	1.00
	C_d	5.25					
	PI	2.47					
	M_f	11.93	8.03	15.35	15.81	13.46	34.78
	E_r	50.30	0.18	11.58	0.23	0.54	1.00
	RI	63.83					

sum of extraction yields in the soluble/exchangeable and carbonate-bound metals] (Sundaray *et al*. 2011). The first two fractions may be considered as constituting the most weakly bound metal species and so, the mobility factor, M_f (%) was defined relative to $\sum_{i=1}^{6} F_i$ as

$$M_f = \left(\frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}\right) \text{x}\ 100 \qquad (11)$$

The I_{geo} parameter ranged from -6.30 to -0.29 for WTS and -5.02 to 0.63 for WWTS. There is no contamination when $I_{geo} \leq 0$; while $0 < I_{geo} < 1$ indicates moderate contamination. Based on the I_{geo} parameter, only Ni has the potential to moderately contaminate the soil upon WTS application. WWTS application may potentially contaminate soil due to Cd and Cu.

The C_f parameter ranged from 0.02 to 1.84 in WTS and 0.05 to 2.32 in WWTS. C_f values <2 represent non-contamination; while values ranging from 2 to 4 suggest low contamination. Based on these, none of the metals may contaminate soil when WTS is applied. WWTS application may, however, cause low soil contamination due to Cu. The degrees of contamination, Cd for WTS and WWTS were 3.80 and 5.25, respectively in low metal contamination (Abrahim and Parker 2008).

The *PI* parameter earlier suggested by Nemerow (Inengite *et al*. 2015) can be adopted to account for multi-metal pollution potential of sludge added to soil. It is considered a better approach to single-metal assessment since sludges and soils are associated with mixed metal contaminants rather than one element. Based on the *PI* parameter, heavy metals in WTS fall within the slightly contaminated domain (*PI*=1.37); whereas only moderate risk is suggested (*PI*=47.07) in the case of WWTS.

E_r values suggest that Cr (0.11), Ni (0.10), Pb (0.41) and Zn (0.58) may pose low risk; Cu (9.18) moderate risk; and Cd (36.70) high risk to soil fauna and flora and eventually humans through the food chain (soil-plant-human) when WTS is applied to agricultural land. Low risk will also occur from Cr (E_r=0.18), Ni (E_r=0.23), Pb (E_r=0.54) and Zn (E_r=1.00) in WWTS, however, Cd (E_r=50.30) and Cu (E_r=11.58) would cause very high risk and considerable risk, respectively. *RI* values of 47.07 in WTS and 63.83 in WWTS respectively suggest moderate and considerable potential biotoxicity from the metals with Cd being the worst culprit (77.96% in WTS and 78.80% in WWTS relative to *RI*).

According to Sundaray *et al*. (2011) values of M_f in the range <1, 1-10, 11-30, 31-50, and >50, would represent no risk, low risk, medium risk, high risk, and very high risk, respectively. The values of M_f (%) recorded in this study suggest that Cd ($11.43 \leq M_f \leq 11.93$), Cu ($15.35 \leq M_f \leq 17.91$), Ni ($15.81 \leq M_f \leq 25.20$), and Pb ($11.52 \leq M_f \leq 13.46$) will pose medium risks in both WTS and WWTS. Cr ($8.03 \leq M_f \leq 16.64$), however, will pose low potential risk in WTS but medium risk in WWTS. In the case of Zn ($34.78 \leq M_f \leq 38.64$), high risk would be poses in both WTS and WWTS.

4. Conclusions

The study was aimed at comparing the single (DTPA), sequential (Tsai *et al*. 2003) and kinetic (EDTA) chemical extraction schemes so as to identify a simple, rapid and cheap protocol for the routine estimation of available and mobilizable heavy metal (Cd, Cr, Cu, Ni, Pb, and Zn) fractions in sludges from municipal water (WTS) and wastewater treatment (WWTS) plants and the potential ecological risk implications for their land applications. The three approaches revealed concordant metal mobility patterns in the sludges. However, the kinetic chemical extraction procedure may be more facile since the kinetic parameters (for example, rate constants) from the leaching curve can be used to predict changes over time in the fate of the heavy metals. Moreover, certain kinetic approaches may provide a useful tool to assess whether metal mobility is under kinetic control of the soil solid phase or soil solution. The metals appeared to be more mobile in WTS than WWTS. Calculated ecological risks indices, however, suggested moderate and considerable long-term metal biotoxicity, in WTS and WWTS, respectively with Cd as the worst culprit. The findings may help in predicting heavy metal dynamics and risks in the sludges which may guide their use as soil amendments.

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