

Sequential Leaches of Trace Elements from Top Soil and Lacustrine Sediments in Sebkhath Séjoumi Basin near Municipal Solid Waste Landfill of Henchir El Yahoudia, South of Tunis City

Extraction des éléments traces par lessivage séquentiel d'échantillons de sol et de sédiments lacustres de Sebkhath Séjoumi à proximité de la décharge d'ordures ménagères

Mitsuo YOSHIDA, Hamadi KALLALI, Fethia AYARI, and Mahar CHEBERLI

Laboratoire Eau & Environnement, Institut National de Recherche Scientifique et Technique, B.P.95, 2050 Hammam-Lif, Tunisia. E-mail: myoshida@planet.tn Hamadi.Kallali@inrst.nrnt.tn

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Abstract: Sequential leaches (sequential extractions) of 59 trace elements were carried out for assessing environmental pollution of top soil and lacustrine sediment. Applied extractants in the sequential leaches are: (A) distilled water for extracting water soluble components, (B) 1M sodium-acetate for extracting exchangeable cations and co-precipitations of carbonates, (C) 0.1M sodium-pyrophosphate for extracting the elements sorbed/bound with organic matter, (D) 0.1M hydroxylamine for extracting the elements sorbed/bound with amorphous Mn hydroxides, and (E) 0.25M hydroxylamine for extracting the elements sorbed/bound with amorphous Fe hydroxides and more crystallized Mn hydroxides. Although the total leaching of trace elements from the top soil sample is often greater than that from the lacustrine sediment sample, similar trend could be observed in the result of sequential leaches for each trace element. According to the results of Leach A (extraction by distilled water), the mobility of seven potentially toxic elements (PTEs), Ni, Cu, As, Se, Mo, Sb, and Hg, show hazardous level in comparing with the Environmental Quality Standard (EQS). Environmental pollution of these PTEs is probably caused by the migration and inputs from the solid waste landfill through runoff and atmospheric transports.

Keywords: Environmental pollution, Soil contamination, Sequential leaches, Extractants, Trace elements, Heavy metals, Mobility

Résumé: Des extractions par lessivages séquentiels de 59 éléments traces ont été réalisées pour évaluer la pollution de sols de surface et de sédiments lacustres.

Les différents extractants utilisés dans les lessivages séquentiels sont : (A) Eau distillée pour extraire les composants solubles dans l'eau, (B) 1M d'acétate de sodium pour extraire les cations échangeables et les précipitations de carbonates reliées, (C) 0,1M de pyrophosphate de sodium pour extraire les éléments adsorbés à la matière organique, (D) 0,1M d'hydroxylamine pour extraire les éléments liés aux hydroxydes de Mn amorphe et (E) 0,25 M d'hydroxylamine pour extraire les éléments liés aux hydroxydes de Fe amorphe et aux hydroxydes de Mn plus cristallisés. La quantité totale d'éléments traces lessivée à partir des échantillons du sol de surface est souvent plus grande que celle extraite à partir des échantillons de sédiments, une constatation similaire peut être faite sur le résultat des lessivages séquentiels pour chaque élément.

Selon les résultats du lessivage A (extraction avec l'eau distillée), la mobilité de sept éléments potentiellement toxiques (EPTs), Ni, Cu, As, Se, Mo, Sb et Hg atteint un niveau dangereux par comparaison aux normes de qualité environnementale (NQE). La pollution environnementale de ces EPTs serait vraisemblablement causée par migration avec les eaux drainant à partir de la décharge d'ordures ménagères et des transports atmosphériques.

Mots clés: pollution environnementale, contamination des sols, lessivage séquentiel, extractants, élément trace, métaux lourds, mobilité.

1. Introduction

Soil acts as a 'sink for trace elements' (Alloway, 1995; Madrid, 1999). The environmental behaviour of trace elements such as potentially toxic heavy metals, their reactivity, mobility, and availability in ecosystems, and possible effects (in terms of biological harm or benefit), strongly depend on their particular chemical form. Trace elements exist in the soil as either water soluble species, as structural elements in solids, as sorbed onto the surface of mineral particles, and/or as bound with organic matters. While many of these trace elements are present naturally in the environment, their indigenous levels are usually non-threatening. The growth of these elements, *contamination*, is generally a result of industrial activities or disposal practices. The following are a few examples of common sources of contamination (Strawn and Sparks, 1999): disposal of batteries that contain Pb, Cd, and Hg; exhaust from automobiles that burn gasoline with Pb additives; use of pesticides that contain Pb and As; the use of Pb in paint; various trace elements in industrial wastes and bi-products; agricultural runoff water in ponds which results in Se and As concentration; disposal of sewage; and mine drainage that contains heavy metals. The contamination tends to rise to the greater amount of concern with regard to the human health, it has been named as *pollution*.

Actually, trace elements have concentrated numerous times in geologic history, which are described by geologists as ore-bodies. All ore-forming processes have in common the *mobilization* of the metal elements within a large reservoir by some agent such as hydrothermal liquid and the *redeposition* in relatively small, high-grade ore-bodies. Weathering and erosion of such bodies at some later stage cause some dispersion of metal elements again. Rivers transport large amounts of dissolved substances to the sea. However most trace elements had been incorporated by isomorphic substitution in the lattice of compounds of major elements (=mineralization) and immobilized. Thus, immobilization mechanisms like these keep the concentrations of many elements in the oceans at very low levels. Nature thus provides us with many environmentally sound examples of how wastes can be treated (Schuiling, 1996).

Soil contaminations should be similarly considered by the aspect of the equilibrium of material balance in natural soil. Most soils are heterogeneous media that contain a host of different materials, solids, and organic materials. Some of contaminated elements are, thus, bonding with such materials but some are easily soluble with water. The former case shows natural '*environmental protection*' which immobilize toxic contaminants in the soil, or allows them to enter the biosphere only at such low concentration and rates that no harmful effects result. While the later case permits the contaminants to mobilize and often they merge into a food chain of biosphere through water, which provoke environmental pollution problems for human beings (Figure 1). Ecologically unacceptable forms of trace elements may include the following criteria (Reuther, 1996): (i) high geochemical mobility, (ii) easy biological uptake, (iii) high

chemical stability, and (iv) long ecological half-life.

In this paper we report the results of *sequential leaches* (*sequential extractions*; Tessier et al., 1979) of contaminated soil and lacustrine (salt lake) sediment collected from near the open-dumping type municipal solid waste (MSW) landfill that had been operated since 1960s and closed in 1998. Differentiated leaching agents clarify the characteristics of mobilization of trace elements in the soil, which provides us information on environmental protection and pollution control in soil contamination site.

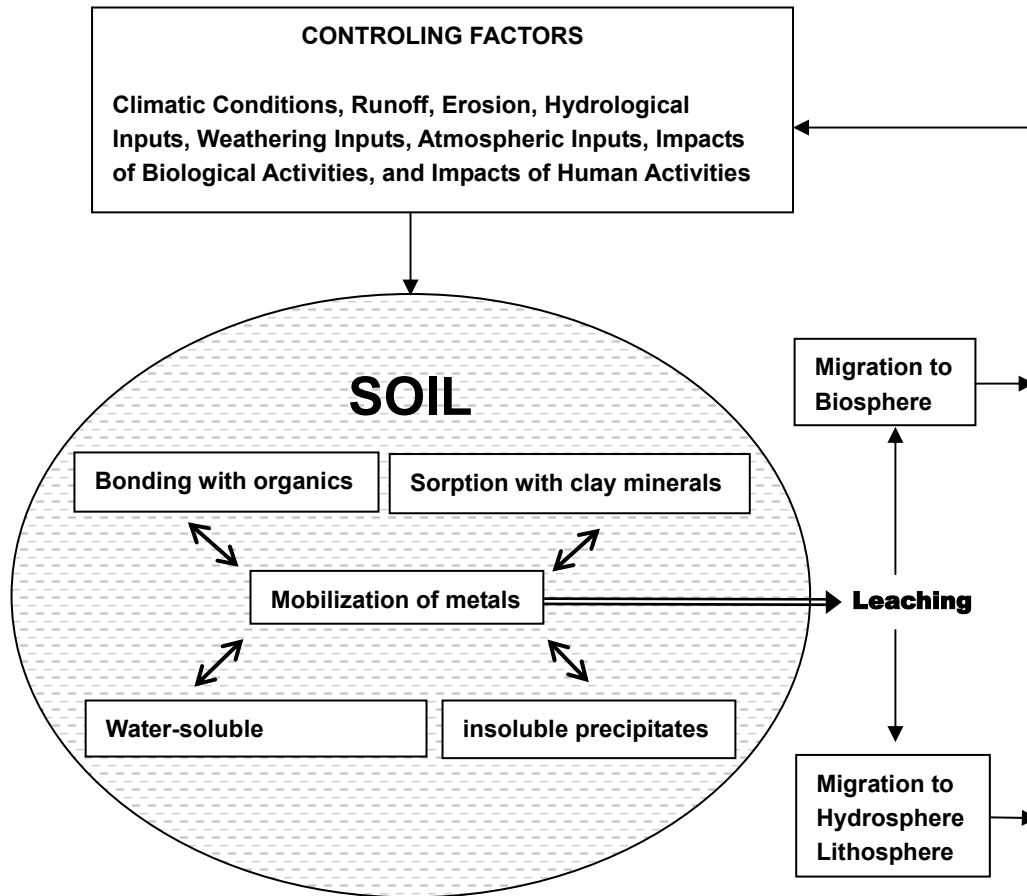


Figure 1: Equilibrium of metal mobility in soil and migration to hydrosphere, lithosphere, and biosphere..

2. Sequential Leaches

It is useful to apply sequential leaches or sequential extractions for characterizing the trace element in soil and the state of soil contamination. The laboratory technique we applied is as follows:

2.1 Extractants

Sequential leaches make possible to differentiate metal mobility (=‘leachability’) in soil, which has been discussed by various researchers in environmental analytical chemistry. More than ten sequential leaches (extraction procedures) using different extractants and defining from three to nine extraction steps to identify ‘forms’ of metal binding, have been elaborated (Tessier et al., 1979; Ure, 1995; Ure and Davidson, 1995; Hirner, 1996; Karczewska, 1996; Pérez-Sirvent et al., 1999; Peter, 1999; Ponizovsky et al., 1999; Twardowska et al., 1999; Zehetner and Wenzel, 1999; Yu et al., 2000; etc). In present study we used five extractants summarized in Table 1.

Table 1: Extractants in the Sequential Leaches procedure

Leach	Leaching Agent (Extractant)	Target
A	Distilled water (H ₂ O)	water-soluble components such as salts and weakly adsorbed ions
B	1M sodium-acetate (CH ₃ COONa)	Exchangeable cations by clay and elements co-precipitated with carbonates
C	0.1M sodium pyrophosphate (Na ₄ P ₂ O ₇)	Elements adsorbed by organic matter (humic and fulvic compounds)
D	0.1M hydroxylamine (NH ₂ OH)	Elements adsorbed by amorphous Mn hydroxides
E	0.25M hydroxylamine (NH ₂ OH)	Elements adsorbed by amorphous Fe hydroxides and more crystalline Mn hydroxides

2.2 Experimental Procedure

Soil sample were dried at room temperature, disintegrated by a porcelain mortar, and sieved through a 1.0 mm screen. Chemical analysis involved: total content of organic matter (TOC) and sequential leaches.

The sequential leaches were performed in following five steps:

(A) At the first step, 1.0 gm sample was prepared from given dried soil. Then the sample was mixed with 20mL distilled neutral water and extracted one hour (Leaching Process A). The mixture was centrifuged and the solution was analyzed. In this process mainly water-soluble component can be extracted.

(B) The residue of above-mentioned ‘Leaching Process A’ was retained for next leach, Leaching Process B, where the sample was mixed with 20mL of 1M sodium-acetate (CH₃COONa) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. In this process adsorbed and/or exchangeable cations by clay minerals and elements co-precipitated with carbonates are mainly extracted.

(C) The residue of above-mentioned ‘Leaching Process B’ was retained for next leach, Leaching Process C, where the sample was mixed with 20mL of 0.1M sodium pyrophosphate (Na₄P₂O₇) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. In this process elements adsorbed by organic matter (humic and fulvic compounds) can be extracted.

(D) The residue of above-mentioned ‘Leaching Process C’ was retained for next leach, Leaching Process D, where the sample was mixed with 20mL of 0.1M hydroxylamine (NH₂OH) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. This extractant is a reducing reagent, which extracts easily amorphous form of Mn oxides and hydroxides and the metals

associated with them (Ure and Davidson, 1995; Pérez-Sirvent et al., 1999).

(E) The residue of above-mentioned ‘Leaching Process D’ was retained for next leach, Leaching Process E, where the sample was mixed with 20mL of 0.25M hydroxylamine (NH₂OH) solution and the leaching was made for one hour. The mixture was filtered and the solution was analyzed. In this higher concentration (0.25M hydroxylamine) treatment elements adsorbed by more crystalline Mn oxides/hydroxides and amorphous Fe hydroxides can be extracted.

In present sequential leaches, leaching components in earlier sequences are more mobile (unstable) than those in later sequences.

The analysis of trace element was made using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS).

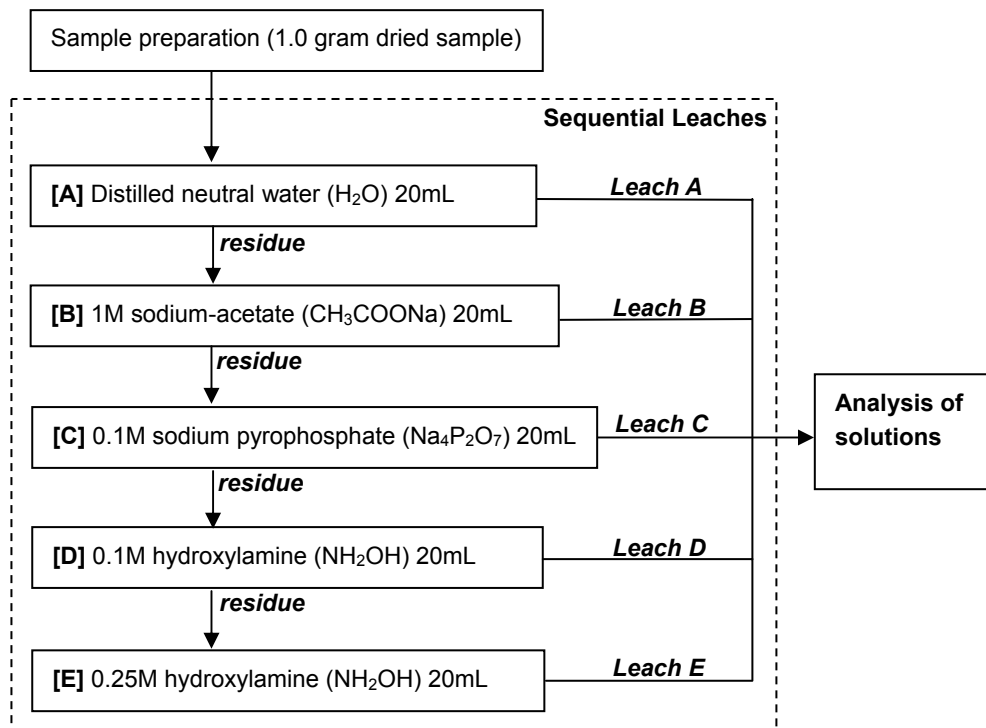


Figure 2: Experimental procedure for the Sequential Leaches. Leaching time is one hour for each.

3 Samples

Total six samples were collected in and around the ANPE/SC5 borehole site penetrated nearby the Henchir El Yahoudia landfill, where 0.20m unconsolidated surface soil and underlying 2.60m semi-consolidated brown clayey silt bed are distributed. The later can be correlated with recent (Quaternary) lacustrine sediments of Sebkhata Séjoui. The latitude and longitude of the SC5 site is N 36° 43' 43", E 10° 10' 53" (Figure 3).

In the ANPE/SC5 site, one sample, SC5(-0.10m), was collected from the surface soil of 0.10m in depth, while another one, SC5(-0.30m), was collected from the 0.30m in depth, the uppermost part of the brown

clayey silt bed (lacustrine sediments). Other four samples, A,B, C, and D were collected from the recent lake sediments (0-0.15m in depth) distributed around the drilling site. The contents of total organic carbon (TOC) are differ from each other; the SC(-0.10m) indicates high TOC 1.005%, but the SC(-0.30m) does 0.231% only (Sothom, 2000).

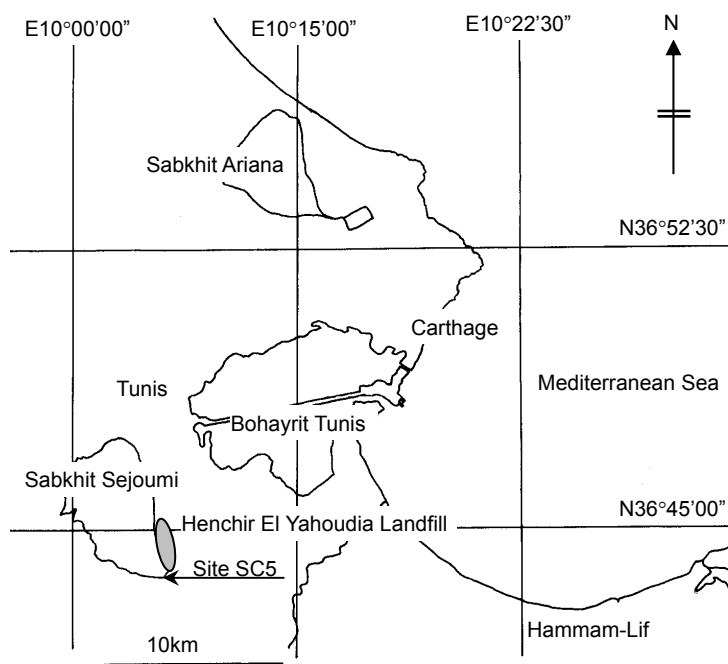


Figure 3: Locality map for sampling site

4. Results of Sequential Leaches

A total of 59 trace elements were analysed for each solution obtained from the sequential leaches of two samples. According to the interference of leaching agents, Na and P could be analysed in limited sequences only. In the case of sample SC5(-0.30m), we used average values of two measurements for interpretation. To determine the contribution of each leaching effect in the overall leaches, leaching ratios, L_A , L_B , L_C , L_D , and L_E , was calculated for each element. It was defined as following equation:

$$L_X = [\text{Concentration in Leaching X}] / [\text{Sum of concentrations from the Leachings A to E}]$$

where X = A, B, C, D, or E.

The leaching concentration of In and Ta could not be detected (less than detection limit) in any sequence. Ten elements, Ti, Ge, Nb, Ag, Sn, Te, Cs, Hf, W, and Re, also show very trace leaching concentration around their detection limits, which are rejected from the database for further interpretation.

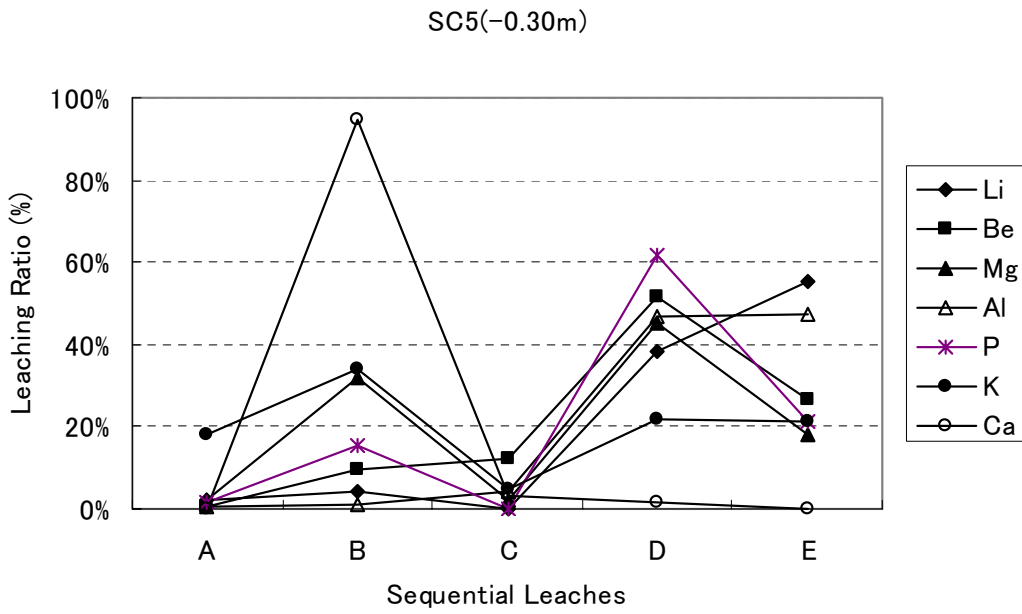
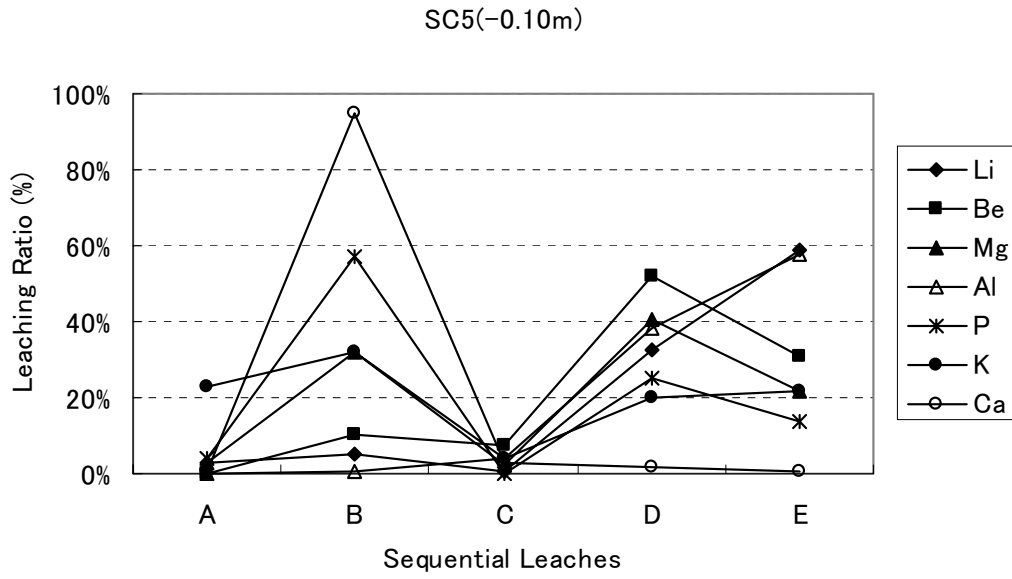


Figure 4(1): Variation of leaching ratio of seven elements in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

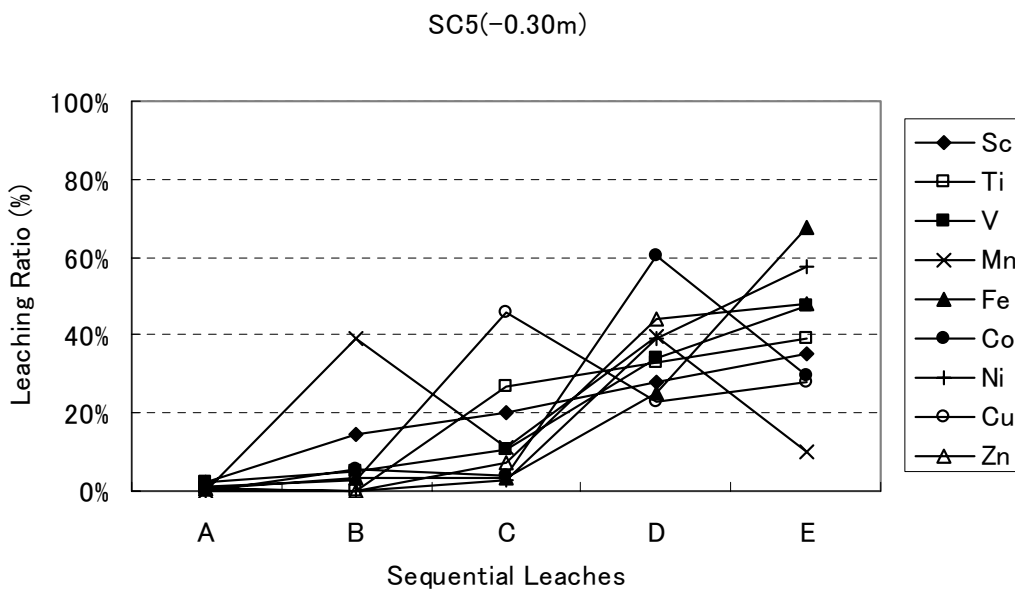
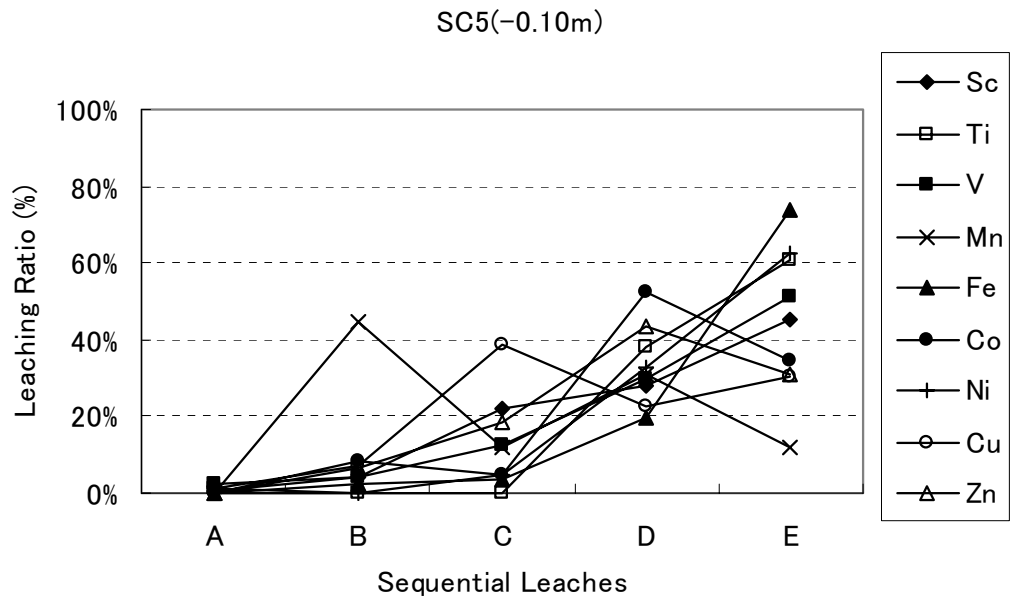


Figure 4(2): Variation of leaching ratio of nine elements in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

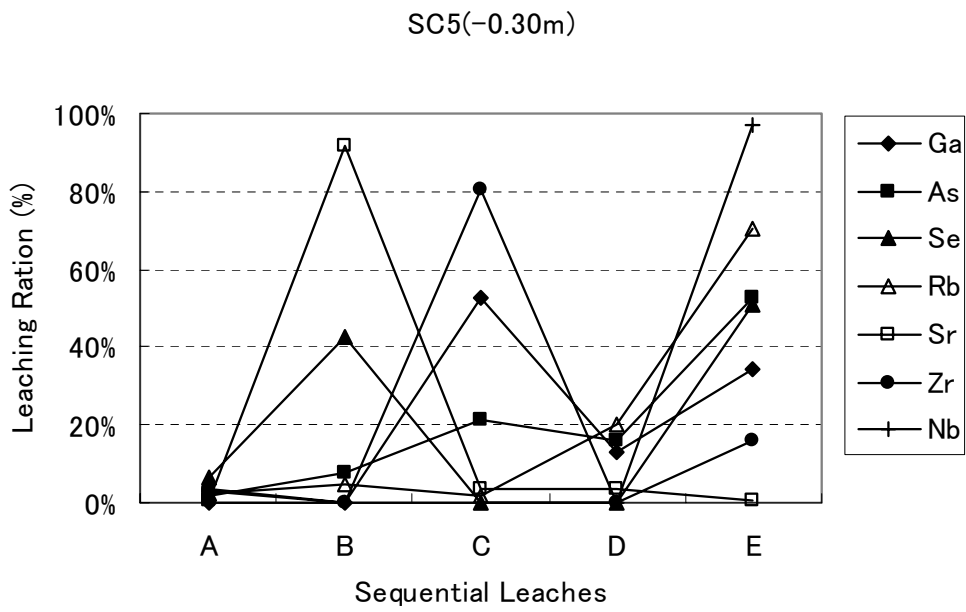
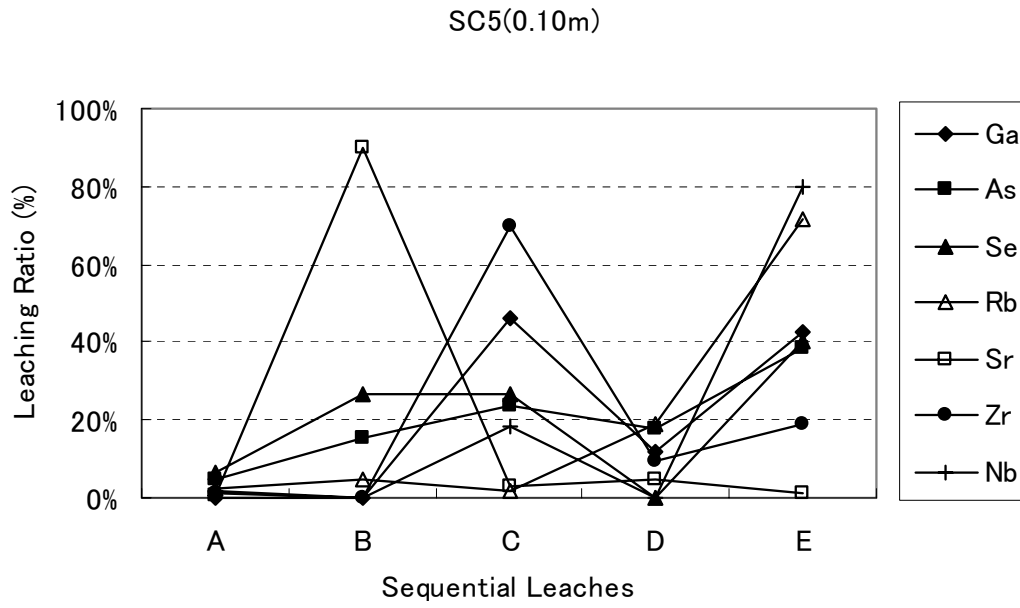


Figure 4(3): Variation of leaching ratio of seven elements in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

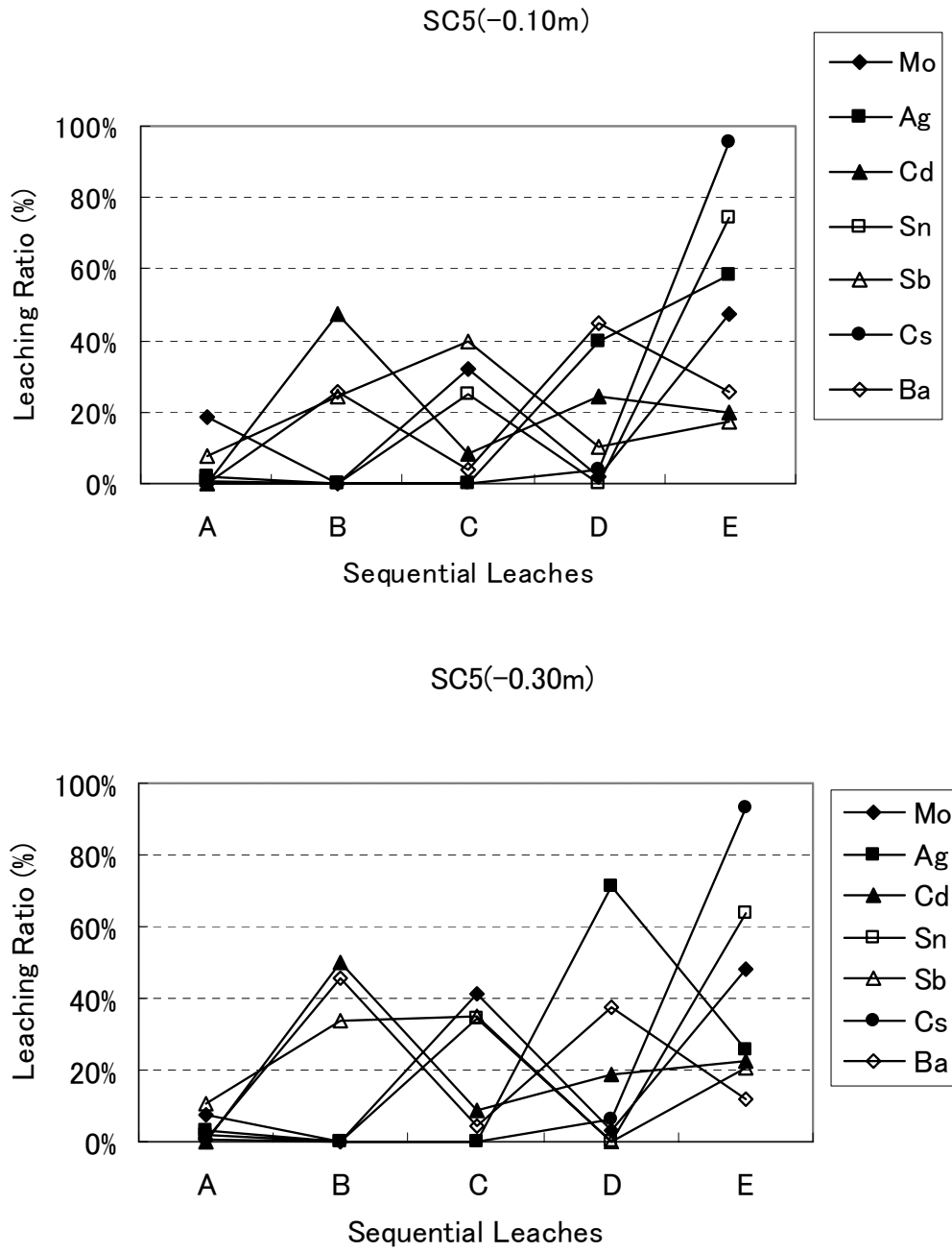


Figure 4(4): Variation of leaching ratio of seven elements in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

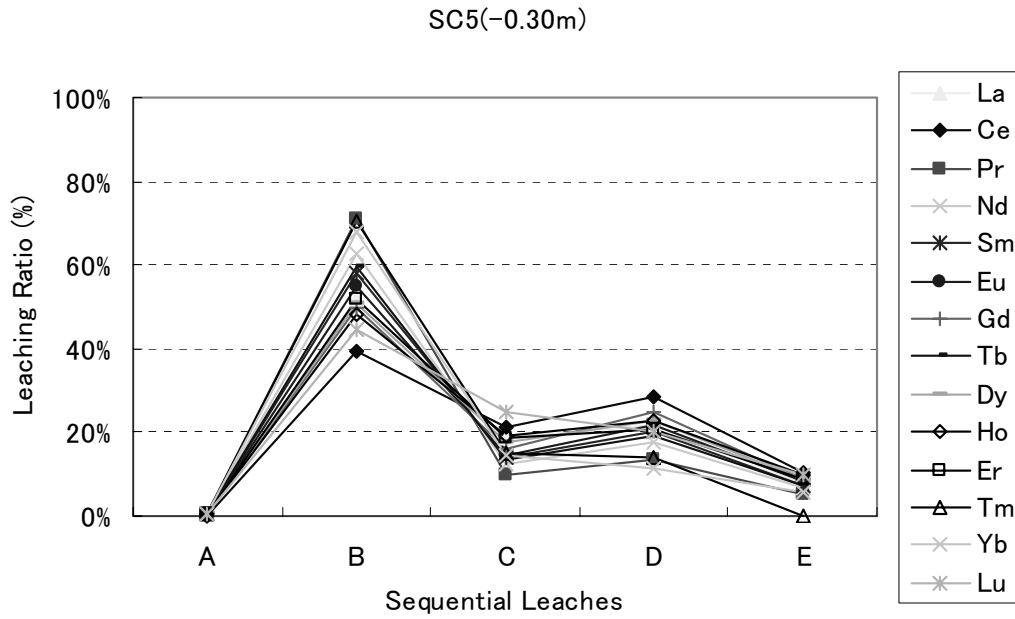
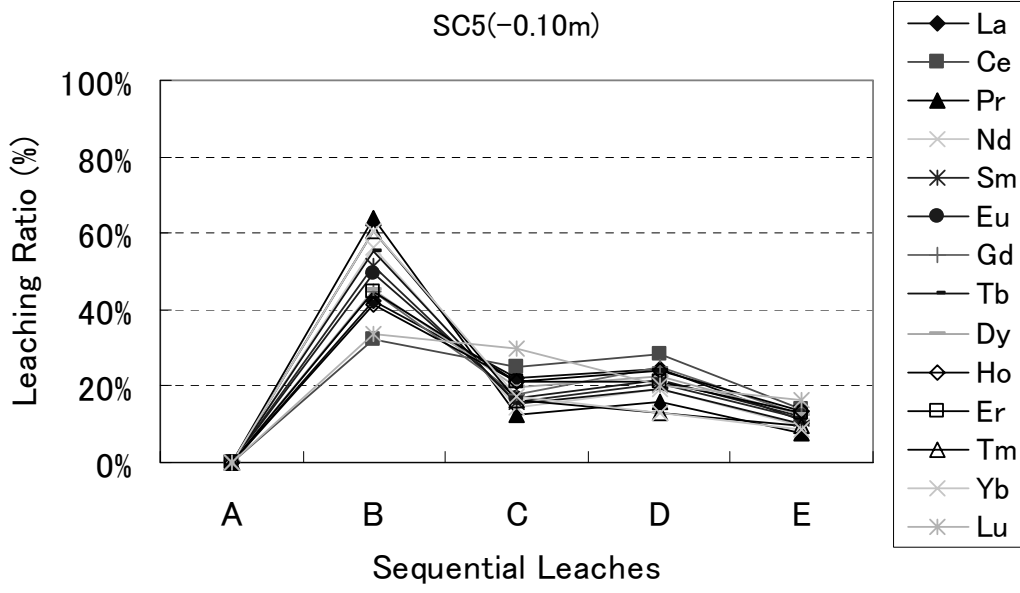


Figure 4(5): Variation of leaching ratio of fourteen rare earth elements (Lanthanide) in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

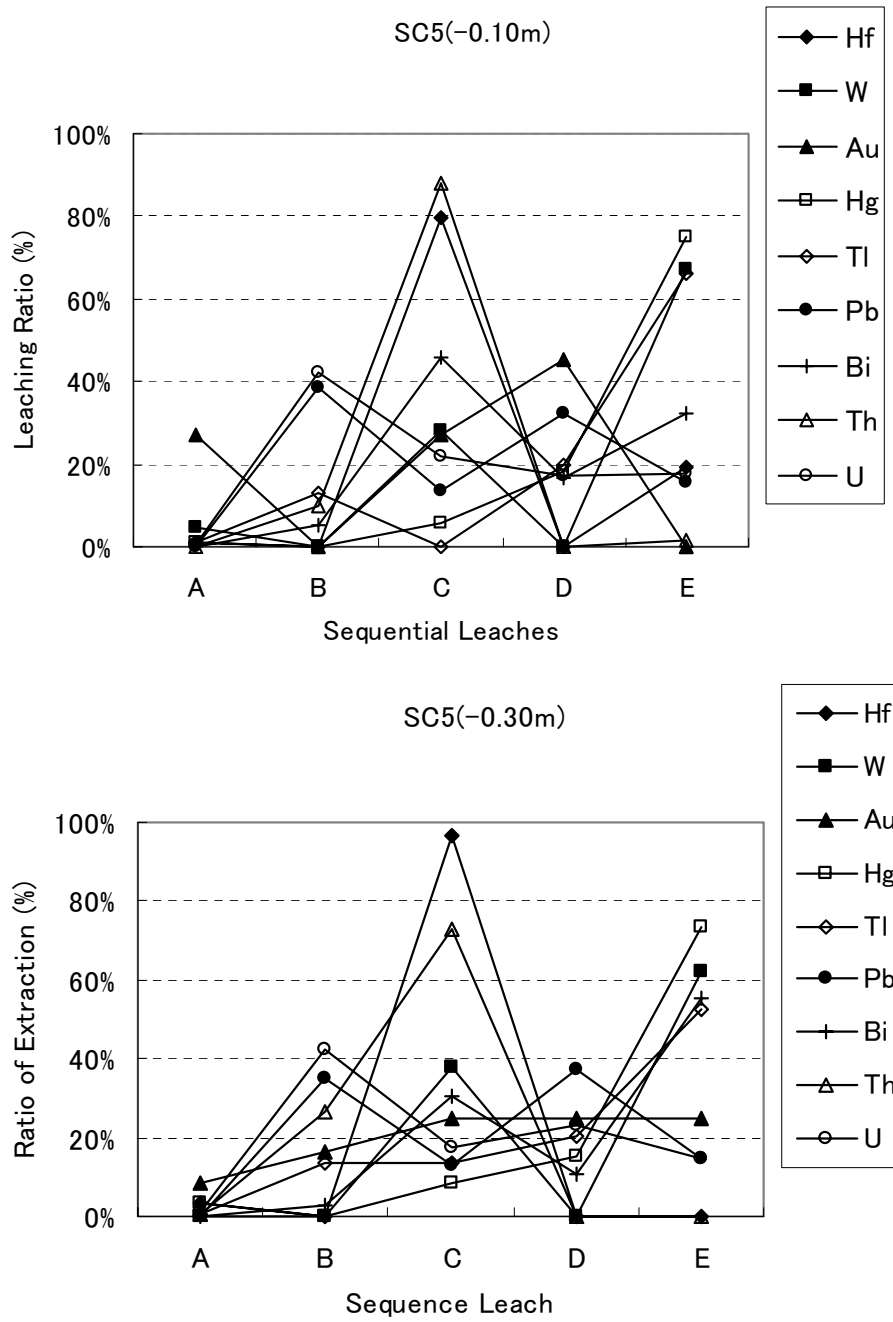


Figure 4(6): Variation of leaching ratio of nine elements in the sequential leaches. See Table 1 and Figure 2 for the condition of sequential leaches, A to E.

5. General Trends in Sequential Leaches

The leaching concentration value of trace elements from the top soil sample (SC5(-0.10m)) is often greater than that from the lacustrine sediment sample (SC5(-0.30m)). While general tendency of the result in sequential leaches is quite similar among them. Diagrams of the variation of leaching ratio (%) of each element in the sequential leaches are shown in Figures 4(1) - (6). Variations of mobility ("leachability") of trace elements in each leaching sequence are summarized in Tables 2(1) and 2(2).

5.1 Water soluble components

Two elements, K and Au, show larger contribution of water-soluble component (the Leaching A) in total leaches. where their leaching ratio are more than 20%. Mo and Sb also show relatively larger ratios. These elements probably form water-soluble salts or very weak bonding with soil particles. However, the others are showing rather smaller leaching ratios.

5.2 Exchangable components

In the Leaching B, Ca, and Sr show very high extraction owing to co-precipitation with carbonates, which indicates more than 90% of total leaches. Other three elements, Pr, Tm, and Yb, also show high leaching ratio (>60%) but the concentration is very small. Other elements such as K, P, Mg, Zn, Se, As, Cd, Sb, Ba, Hg, Pb, U, and rare earth elements (Lanthanide) also show relatively high leaching ratios (>20%). These elements were immobilized by the co-precipitation with carbonates or cationic adsorption/ion-exchange by clay minerals or other exchangeable minerals. It is noticeable that this group includes well-known potentially toxic elements (PTEs) such as Zn, Se, As, Cd, Sb, Hg, and Pb.

5.3 Organics-bonding components

In the Leaching C, four elements, Zr, Hf, and Th, show very high leaching ratio (>60%). Other elements such as Ga, Sc, Cu, As, Se, Nb, Mo, Sn, Sn, W, Au, and Bi show relatively high leaching ratio (>20%), while the rare earth elements (Lanthanide) give moderately high leaching ratio of around 20%. These elements easily tend to bond with organic matters (humic and fluvic). Fluvic acids probably play more important role in the transport of heavy metals in water, due to their lower molecular mass and much greater solubility as compared humic acids (Madrid, 1999).

5.4 Mn hydroxides complex

In the Leaching D, many elements, Li, Be, Mg, Al, P, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Rb, As, Ag, Cd, Ba, Au, Pb, Tl, Bi, and U, show relatively high leaching ratio (>20%). P and Co indicate very high leaching ratio in sediment sample (SC(-0.30m)). Leaching ratio of rare earth elements (Lanthanide) are around 20%. These elements are easily bonding with amorphous Mn hydroxides. In contrast, Se, Sr, Nb, Mo, Sn, Cs, Sb, Hf, W, and Th show very low leaching ratio.

5.5 Fe hydroxides complex

In the Leaching E, that is the most extractive treatment, Fe, Ti, Ni, Rb, Nb, Cs, Sn, W, Tl, and Hg are showing very high leaching ratio (>60%). Li, Al, Be, Mg, K, V, Sc, Co, Cu, Zn, As, Se, Ga, Sr, Mo, Ag, Ba, Cd and Bi are also moderately leached (>20%). These elements are probably immobilised with amorphous Fe hydroxides or more crystallised Mn hydroxides, which are probably the most resistant trace elements.

Table 2(1): Mobility of trace elements in the soil sample SC(-0.10m)

Components	Leaching ratio>60%	60%>Leaching ratio>20%	Leaching ratio<20%
(A) Water soluble components		K, Au,	Li, Be, Mg, Al, P, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Hg, Tl, Pb, Bi, Th, U,
(B) Exchangable components	Ca, Sr, Pr, Tm, Yb,	Mg, P, K, Mn, Se, Cd, Sb, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Lu, Pb, U,	Li, Be, Al, Sc, Ti, V, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Zr, Nb, Mo, Ag, Sn, Cs, Hf, W, Au, Hg, Tl, Bi, Th,
(C) Organics bonding components	Zr, Hf, Th,	Sc, Cu, Ga, As, Se, Mo, Sn, Sb, La, Ce, Ho, Er, Lu, W, Au, Bi, U,	Li, Be, Mg, Al, P, K, Ca, Ti, V, Mn, Fe, Co, Ni, Zn, Rb, Sr, Nb, Ag, Cd, Cs, Ba, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Hg, Tl, Pb,
(D) Mn hydroxides bonding components		Li, Be, Mg, Al, P, K, Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ag, Cd, Ba, La, Ce, Sm, Eu, Gd, Dy, Ho, Er, Lu, Au, Pb,	Ca, Fe, Ga, As, Se, Rb, Sr, Zr, Nb, Mo, Sn, Sb, Cs, Pr, Nd, Tb, Tm, Yb, Hf, W, Hg, Tl, Bi, Th, U,
(E) Fe hydroxides bonding components	Ti, Fe, Ni, Rb, Nb, Sn, Cs, W, Hg, Tl,	Li, Be, Mg, Al, K, Sc, V, Co, Cu, Zn, Ga, As, Se, Mo, Ag, Cd, Ba, Bi,	P, Ca, Mn, Sr, Zr, Sb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Au, Pb, Th, U,

Table 2(2): Mobility of trace elements in the sediment sample SC(-0.30m)

Components	Leaching ratio>60%	60%>Leaching ratio>20%	Leaching ratio<20%
(A) Water soluble components		Au,	Li, Be, Mg, Al, P, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Hg, Tl, Pb, Bi, Th, U,
(B) Exchangable components	Ca, Sr, Pr, Nd, Tm, Yb,	Mg, K, Mn, Se, Cd, Sb, Ba, La, Ce, Sm, Eu, Gd, Tb, Dy, Ho, Er, Lu, Pb, Th, U,	Li, Be, Al, P, Sc, Ti, V, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Zr, Nb, Mo, Ag, Sn, Cs, Hf, W, Au, Hg, Tl, Bi,
(C) Organics bonding components	Zr, Hf, Th,	Sc, Ti, Cu, Ga, As, Mo, Sn, Sb, Ce, Lu, W, Au, Bi, U,	Li, Be, Mg, Al, P, K, Ca, V, Mn, Fe, Co, Ni, Zn, Se, Rb, Sr, Nb, Ag, Cd, Cs, Ba, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Hg, Tl, Pb,
(D) Mn hydroxides bonding components	P, Co,	Li, Be, Mg, Al, K, Sc, Ti, V, Mn, Fe, Ni, Cu, Zn, Ag, Ba, La, Ce, Sm, Eu, Gd, Dy, Ho, Er, Lu, Au, Tl, Pb, U,	Ca, Ga, As, Se, Rb, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Pr, Nd, Tb, Tm, Yb, Hf, W, Hg, Bi, Th,
(E) Fe hydroxides bonding components	Ti, Fe, Rb, Nb, Sn, Cs, W, Hg,	Li, Be, Al, K, Sc, V, Co, Ni, Cu, Zn, Ga, As, Se, Mo, Ag, Cd, Tl, Bi, Au,	P, Mg, Ca, Mn, Sr, Zr, Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th, U,

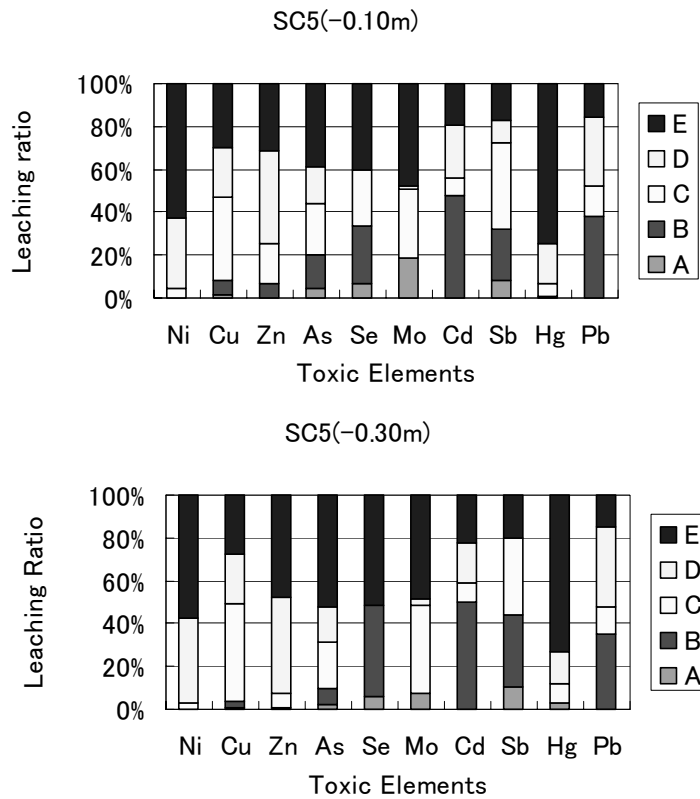


Figure 5: Variation of the leaching ratios in toxic elements.

6. Trace Elements in Soil/Sediment

In order to determine the composition of trace elements in given six samples, a 15.0 gm sample split was digested in 90 mL aqua regia (HCl-HNO₃-H₂O) at 95°C for one hour. The solution is diluted to 300 mL with water. Analysis was also made by ICP-AES and ICP-MS. Total 37 elements were measured: B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Mo, Ag, Cd, Sb, Te, Ba, La, W, Au, Hg, Tl, Pb, Bi, Th, and U. The aqua regia digestion of sediments extracts only a fraction of the major elements because silicates are not completely dissolved with this method. Owing to this limitation, results are total to near total for trace and base metals and possibly partial for rock-forming elements such as Na, Mg, Al, K, Ca, Mn, and Fe. However, environmentally concerned components like heavy metals or PTEs not bound to silicates are efficiently dissolved (Ure, 1995; Giusti, 2001). The results of total content analysis are shown in Table 3.

The composition of trace elements are not very different between SC5(-0.10m), SC5(-0.30m), and other lake sediment samples, while heavy metals and metalloids are generally enriched in the uppermost soil sample SC5(-0.10m). In particular the concentration of Cu, Zn, Ag, Cd, Sb, Hg, and Pb in the sample SC5(-0.10m) is significantly higher than that in SC5(-0.30m). The concentration of Co, Cu, Zn, Cd, and Ba

are above the reference value based on concentration in nature reserve where only the contamination is from atmospheric deposition (Environmental Quality Standards of Netherlands).

Table 3: Heavy metal composition of soil and lake sediments in and around SC5 site, Henchir El Yahoudia

ELEMENT	Cr	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sb	Ba	Hg	Tl	Pb
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm	ppm
Detection Limit	0.5	0.1	0.1	0.01	0.1	0.1	0.1	0.01	0.01	0.02	0.5	5	0.02	0.01
Sediment A	65.1	10.1	24.5	26.79	169.6	9.2	0.6	0.46	0.45	0.69	150.4	61	0.20	101.52
Sediment B	56.7	9.5	22.6	23.91	155.6	9.4	0.3	0.40	0.30	0.55	142.0	53	0.18	70.91
Sediment C	57.0	9.0	23.2	26.29	145.9	8.6	0.3	0.36	0.34	0.62	153.1	65	0.18	70.69
Sediment D	57.1	8.4	21.0	27.57	126.2	8.1	0.5	0.69	0.45	0.65	124.0	62	0.18	68.78
SC5(0.1)	62.8	10.6	23.9	36.68	333.5	7.4	0.3	0.85	1.95	0.71	210.7	94	0.18	52.52
SC5(0.3)	54.3	10.1	24.1	16.91	79.7	5.9	0.5	0.55	0.32	0.20	192.8	43	0.16	30.54

7. Assessment of Potentially Toxic Elements (PTEs)

'Heavy metals' is the term applied to a group of trace metals with a density greater than 6 gm/cm³ which are both industrially and biologically important. They are essential in small but critical concentrations for the normal healthy growth of plants and/or animals, although they are toxic at high concentrations. This group of elements was, therefore, previously called 'toxic metals'. Such trace elements, not only exact 'heavy metals' but also the other trace elements that are toxic to living organisms when present in excess, are now collectively called as a holistic term '*potentially toxic elements* (PTEs)' (Alloway, 1995). The toxic level of presence of PTEs has been often defined by a law or a regulation in soil pollution. However, definition of the regulation value in soil pollution, or classification of 'soil pollution grade', is not very simple issue in practice.

Government institutes usually give strict guidelines (regulation values) for each PTE in order to make prompt decisions or remedial actions in soil pollution site. In general, there are two different criteria adopted by the classification: *total content* and *mobility and/or bioavailability* (Hirner, 1996). The former criteria are based on the total PTE content in given soil sample extracted by strong acid solution. To establish mobility and/or bioavailability of PTE pollutants, the regulation values based on total content are too high (Hirner, 1996). In the second criteria, given soil sample is eluted by neutral water and determines the concentration of each PTE as leaching. It is better to assess toxicity but the concentration is often very low (= difficulty in analysis) and the leaching method is strictly defined. No regulation on soil pollution has been legally defined so far in Tunisia.

The data obtained from the Leach A (1:20 water leach) are almost comparable to 1:10 water leach test in the regulation, the Environmental Quality Standard for Soil Contamination in Japan (EQS(soil)). According to the results of Leach A, leaching concentrations of three PTEs, As, Se, and Hg, from both samples SC5(-0.10m) and SC5(-0.30m) show higher values than the EQS(soil) critical values (Table 4). The leaching concentrations of other four PTEs, Ni, Cu, Mo, and Sb, also indicate noticeable values comparing with the Environmental Quality Standard for Groundwater, Japan (EQS(groundwater)); that generally extrapolates for the critical value of EQS(soil)). Only two PTEs, Cd and Pb, are lower than the EQS.

Although it has not been legally defined the regulation value for soil/groundwater contamination in Tunisia, when we applied the regulation values wastewater drained to public water body (Table 4), seven PTEs, As, Se, Hg, Ni, Cu, Mo, and Sb, are again in anxious levels of contamination. Soil pollution of these

trace elements is probably caused by the migration from the solid waste landfill through runoff and atmospheric transports.

Thus, natural leaching of these seven PTEs (As, Se, Hg, Ni, Cu, Mo, and Sb) by meteoric water should be concerned in present area. Further monitoring of groundwater is recommended.

Figure 5 shows bar diagrams about the variation of leaching ratio in the sequential leaches for above-mentioned seven PTEs. The total of Leaches A, B, and C shows significant values in six PTEs, Cu, Zn, As, Se, Mo, and Sb. It means that natural clay, carbonates (lime), and organic matter play very important roles for immobilization of these PTEs. However, in the cases of Ni and Hg, such agents are less effective, and sorptions by amorphous Mn/Mn hydroxides is much more essential for immobilization. Ni concentrations in soil solutions may be controlled by either adsorption/desorption or by precipitation/dissolution processes (Zehetner and Wenzel, 1999). Chemical speciation for each PTE is desirable for planning appropriate counter measure.

Table 4: Leaching concentration of selected toxic elements. The leaching concentrations of six elements, Ni, Cu, As, Se, Mo, Sb, and Hg, from present samples exceed the Environmental Quality Standards (EQS).

ELEMENT	Ni	Cu	As	Se	Mo	Cd	Sb	Hg	Pb
Unit	ppm	ppm	ppb	ppm	ppb	ppb	ppb	ppb	ppb
SC5(-0.10m)	0.031	0.364	157	0.050	95.0	1.4	17.0	1	< 3
SC5(-0.30m)	0.028	0.098	64	0.037	27.5	< .5	6.5	2	< 3
EQS (soil)*	0.01	0.04	10	0.01	70	10	2	0.5	10
Tunisian regulation**	0.2	0.5	50	0.05	500	5	100	1	100

* Environmental Quality Standards for Soil, Japan. where, leaching condition is 1(soil):10(water).

The values of Ni, Cu, Mo, and Sb are adopted from EQS (groundwater).

** Regulation for the wastewater drained to public water body, Tunisia

6. Conclusions and Recommendations

- (1) In order to characterize the state of soil contamination related to MSW landfill, sequential leaches were attempted for two soil/sediment samples.
- (2) General tendency of the result in sequential leaches is quite similar between these two samples.
- (3) According to the leaching concentration of water soluble components, seven PTEs, As, Se, Hg, Ni, Cu, Mo, and Sb, are in the level of soil pollution based on the EQS regulation values. Environmental pollution of these trace elements is probably caused by the migration from the solid waste landfill through runoff and atmospheric transports.
- (4) Natural clay, carbonates (lime), and organic matter play very important roles for immobilization of Cu, Zn, As, Se, Mo, and Sb. On the other hand, such agents are less effective in the case of Ni and Hg, where sorptions by amorphous Mn/Mn hydroxides is much more essential for immobilization
- (5) Chemical speciation of each PTE such as heavy metals and detailed grid survey around the area is recommended. Groundwater monitoring is also recommended for observing PTEs migration into hydrosphere.

(6) Legal regulation and criteria for defining soil contamination/pollution is desirable in Tunisia.

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