Distribution Characteristics of Potentially Toxic Elements (PTEs) in and around Closed Solid Waste Landfill near Tunis, Tunisia

Abdoul Nasser IBRAHIM*, Jamila TARHOUNI**, and Mitsuo YOSHIDA***
* Laboratoire Eau & Environnement, INRST, Tunisia
** Institut National Agronomique de Tunisie (INAT), Tunisia
*** Institute for International Cooperation, JICA, Tokyo, Japan

I. Introduction
The Henchir El Yahoudia landfill was constructed along the lakeside of Sebkhat Sejoumi (Lake Sejoumi) for discarding various kind of solid wastes, mostly municipal solid wastes (MSW), generated from the greater Tunis region. The waste dumping operations started in 1960s and stopped in 1999. Landfill capping and closure operations have been made since 1999 by the Tunisian government as a rehabilitation project of the landfill site. An environmental monitoring that is indispensable after a closure of solid waste landfill was led in the scoop of this project to assess the impact of the landfill on the surrounding environment. Present study is a part of the environmental monitoring, where the main concern is the migration of potentially toxic elements (PTEs) contamination off the landfill site, land, groundwater, and lake.

II. Location, Geology, and Samples
Sebkha Sejoumi represents the end point of a nearly 230 km² catchment area known as the Manouba-Sejoumi watershed. This watershed is characterized by a deltaic sedimentation that has setup a variety of deposits. In order to precise the subsurface geology of the landfill basement, we have setup a borehole HY1 at the lakeside. According to the borehole core observation, the subsurface strata can broadly be divided into two geologic units; Neogene-Quaternary Upper Unit and Paleogene Lower Unit. Based on the results of the drilling survey, three potential aquifers were detected within the Upper Unit. These aquifers are potentially a migration path of pollutants from the landfill. The samples are collected from the following five media:

(1) Buried Solid Waste: Thirteen waste sludge samples were collected from the exposures of buried waste deposits in the landfill and were analyzed for determining PTEs concentrations. The landfill solid wastes show a greatly variable occurrence, but generally it can be distinguished macro-scale solid waste such as plastic, glass, metal, wood, leather, brick fragments, hospital wastes, and sludge-like matrix of fine-grained materials probably generated by decomposition of buried wastes.

(2) Lake Sediments: A total of 33 sediment samples were collected at the surface of the lake bottom sediment along the lake shoreline bordering the landfill, at a distance of approximately 10 to 20m far from the landfill. All the samples were clayey; their preparation included drying at room temperature, grounding and sieving at 1mm mesh.

(3) Landfill Leachate: Ten landfill leachate samples were collected from the open standpipe piezometers and leachate spills and leachate pools in the landfill, where landfill leachate continuously pollute the Sebkha Sejoumi that is an isolated salt lake basin without major inlet and outlet.

(4) Groundwater: The groundwater samples analyzed were collected from the three aquifers, at 10th May 2002, two days after the rainfall. Groundwater samples are collected using hand pumping method directly from the well. In order to obtain fresh groundwater sample representing each aquifer, the sampling was made after the complete discharge of groundwater filled in each hole.

Abdoul Nasser IBRAHIM: Laboratoire Eau & Environnement, INRST, B.P.95, 2050 Hammam-Lif, Tunisia
Tel/Fax: (+216)-71-410740, E-mail: abdoul_nasser@yahoo.com
Keywords: Groundwater pollution, Sediment contamination, Aquifer, Landfill leachate, PTEs
(5) Subsurface Sediments: A total of 33 sediment samples were also collected from the borehole cores of HY1 for examining subsurface sediments contamination.

III. Analytical Methods

(1) Solid Sample Analysis: A 15.0 gm waste sample split was digested in 90 mL aqua regia (HCl-HNO$_3$-H$_2$O) at 95°C for one hour. The solution is diluted to 300 mL with distilled water. Analysis was made by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (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, Ti, Pb, Bi, Th, and U. The aqua regia digestion extracts only a fraction of the major elements (pseudo-total analysis) 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, which is indicative for the assessment of toxicity. However aqua regia extraction results should be regarded as referenced values since that extraction method is stronger than leaching method that is best indicative of PTEs mobility. For that reason, apart from the aqua regia extraction, weak extraction using sodium acetate leach was also attempted on 50g size waste and lake bed sediment samples to 10 times dilution, which is expected to dissolve cations that are weakly bounded to clay and organics. For that extraction method, five PTEs, Cu, Ni, Zn, Cd, and Pb, were measured by Atomic Absorption Spectrometry (AAS).

(2) Leachate and Water Analysis: Liquid samples were at first treated by H$_2$O$_2$ 30% solution for completely dissolving their organic matter content. Then the samples were prepared for pH<2.0 using HNO$_3$. Analysis was performed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Total 74 elements were measured: Li, Be, B, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Ti, Pb, Bi, Th, and U.

IV. Results and Discussion

(1) Waste Sludge: The results of aqua regia extraction suggest that the concentration of ten regulated PTEs, V, Cr, Ni, Zn, As, Cd, Sb, Ba, Hg, and Pb, indicate abnormally higher values in comparing with the natural background concentration. According to the results of sodium weak extraction using sodium acetate leach, 100% (US EPA standard) of samples in Ni, 17% (US EPA standard) of samples in Zn, 67% (Standard of Japan) or 58% (US EPA standard) of samples in Cd, and 58% (Standard of Japan) of samples in Pb appeared to be hazardous in leaching. In particular five non-metal trace elements, B, S, As, Se and Br, are showing abnormally higher concentrations in comparing with each regulation value. Other five toxic heavy metals: Ti, Cr (total), Co, Ni, and Hg, also indicate higher concentrations in comparing with the regulation values. The analytical result of waste sludge is similar to that of leachate samples at abnormally higher concentrations in comparing with the regulation values, particularly in the case for Cr, Ni, As and Hg. However leaching test concentrations for PTEs obtained from weak sodium acetate extraction seem not to exhibit a clear correlation with leachate PTEs concentrations except for Ni. This may be due to some natural mechanisms like ion adsorption on clay minerals and precipitation during leachate flow.

(2) Landfill Leachate: The concentration of dissolved elements in the leachate samples that were collected from leachate pools is much higher than that from landfill’s interior, which may be caused by a condensation effect of natural evaporation affecting leachate pools. According to the Tunisian regulation, NT 106.002 (1989), for waste water quality, ten elements: Be (not detected from all the samples), Mn, Zn, Mo, Ag, Cd, Sn, Sb, and Pb, are showing lower concentrations than the respective regulated concentration levels. But the concentrations of thirteen elements, B, P, S, Ti, Cr, Fe, Co, Ni, As, Se, Br, Ba, and Hg fully or partly exceed each regulation value. In particular five non-metal trace elements, B, S, As, Se and Br, are showing abnormally higher concentrations in comparing with each regulation value. Other five toxic heavy metals: Ti, Cr (total), Co, Ni, and Hg, also indicate higher concentrations in comparing with the regulation values. The analytical result of waste sludge is similar to that of leachate samples at abnormally higher concentrations in comparing with the regulation values, particularly in the case for Cr, Ni, As and Hg. However leaching test concentrations for PTEs obtained from weak sodium acetate extraction seem not to exhibit a clear correlation with leachate PTEs concentrations except for Ni. This may be due to some natural mechanisms like ion adsorption on clay minerals and precipitation during leachate flow.

(3) Lake Water: The elements composition in lake water samples (L1 and L2) of Sebkha Sejoumi at Henchir El Yahoudia area indicates a brine characteristics of salt lake, where Na, Mg, Ca, and Cl are relatively concentrated.
According to the results, the concentration of five non-metal elements B, S, As, Se, and Br is higher than each regulation value. The concentration of Ti is also showing abnormally high values, while that of other heavy metals such as Cr, Co, Ni, and Hg is below the regulation level. The trace elements composition shows similarity with the PTEs composition of landfill leachate as for B, S, As, Se, and Br. However the toxic heavy metals composition of lake water is not correlated with that of leachate since their concentration in lake water is very low in comparing with that of leachate, except for Ti and Cu. The relative depletion of PTEs within lake water samples is probably due to some natural attenuation processes such as cation adsorption, cation exchange, and precipitation during transportation and standing in lake basin.

(4) Groundwater: The result of groundwater analysis indicates that the Aquifer-1 and Aquifer-3 show similar chemical compositions with abundant Na, Mg, K, Ca, Mn, and Cl, while the composition of the Aquifer-2 is relatively poor in most elements except Cd, Ba and Lanthanoids. The groundwater collected from the Auifer-1 and Aquifer-3 contains approximately 3% of salt (NaCl) showing a linkage with salt lake water. Potentially toxic elements (PTEs) such as V, Cr, Co, Cu, Zn, As, and Pb are relatively enriched. The concentration of bromine (Br) in Aquifer-1 and 3 is also abnormally high. The groundwater quality is examined using the water quality criteria (US EPA, 1999) and wastewater regulation standards in Tunisia (N.T106.002). The concentration of Al, Cu, Zn, Se, and Pb in the groundwater samples is above the CCC, and that of Cu, Zn, Se, and Pb is above the CMC. The concentration of Se and Pb is much higher than CCC and CMC, which is above the wastewater regulation. The high concentrations of Cu, Zn, Se, and Pb are possibly due to a pollution caused by the landfill. Se is the common pollutant between landfill leachate and groundwater, while other elements, Cu, Zn, and Pb (heavy metals), do not exhibit a clear correlation.

(5) Lake Sediments: The results show that all the samples examined present a significant contamination by Ni, Zn, Cu, Cd and Pb in comparing with the leaching test from US EPA regulation. Lake sediments are even more contaminated than leachate probably due to the fact that heavy metals preferably adsorb to fine-grained sediments. The composition of lake bed sediments for Ni, Zn, Cu, Cd, Pb appears similar to the compositions of leachate and waste for the same PTEs; this suggests that PTEs from the landfill wastes are possibly impacting the chemical composition of lake sediments through the leachate spills that flow almost year round along the lake shoreline.

IV. Conclusions

On the basis of distribution characteristics and migration of PTEs around the closed landfill at Henchir El Yahoudia, five different media of the landfill environment were investigated for determining their PTEs composition: the buried waste sludges, landfill leachate, lake water, groundwater, and lake sediments. The PTEs concentration of waste sludge samples was rather heterogeneous while the concentration of V, Cr, Ni, Zn, As, Cd, Sb, Ba, Hg, and Pb, are abnormally higher than surrounding natural soil/sediment. Five heavy metal elements, Ti, Cr, Co, Ni, and Hg, were detected in leachate at high concentration exceeding the regulation values. Lake water analysis showed similar composition as leachate for B, S, As, Se, and Br while its heavy metal content did not correlate with that of leachate. Trace element composition of groundwater respectively showed that Cu, Zn, Pb, and Se are above the quality standard. The concentration of five toxic heavy metals, Ni, Zn, Cu, Cd and Pb, that were probably derived from the landfill was high in lake bed sediment samples. Thus, the Henchir El Yahoudia landfill is significant as PTEs contamination source to surrounding environment.

Acknowledgements: We thank Ahmed Ghrabi and all the members of Laboratoire Eau et Environnement, INRST, for their supports during the lab analysis. This collaborative work was partly supported by the technical cooperation project (expert dispatching programme) between Institut National de Recherche Scientifique et Technique (INRST), Tunisia and Japan International Cooperation Agency (JICA), 2000-2002.