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Single modified fractionation technique of lead in sediments of Shatt Al-Hilla-Iraq

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ABSTRACT

Lead is one of the most abundant heavy metals and its toxic effects cause environmental and health problems. Sediments samples were collected from three depths of five stations at the right bank of Shatt Al-Hilla in Babylon province, starting from Saad bridge (station 1) to the north of Al-Hashimia city (station 5). A five-step single modified sequential extraction procedure was used to determine chemical phases of lead element in the sediments samples. The results of sediments properties which is related to the speciation of studied heavy metal Pb showed that the sediments were weakly alkaline, calcareous nature and poor organic content. The fractionation of lead ions showed that the large amount is associated with available and carbonates fractions which are considered as weakly bound and easily available in the aqueous phase for organisms in aquatic environment, indicates the dominance of anthropogenic sources,. On other hand the residual fraction which constitutes a percentage of 26.3% of the total content of the element is considered relatively safe because, the element is not easily released under normal conditions.

Key words : *Lead, Fractionation, Sediments, Available, Carbonates.*

Intoduction

Sediments are habitat for many aquatic organisms and a major reservoir for many of the toxic metals that can move back into the water column under favorable environmental conditions. The mobility of metals between the aqueous, particulate, and sediment phases are mainly controlled by pH, redox potential, cation exchange capacity, texture, carbonate, and organic carbon contents (Soares *et al*., 1999; Grosheva *et al*., 2000; Feng *et al*., 2004; Du *et al*., 2007). Therefore, sediments have been extensively used to ascertain sources of pollution and to assess the quality of aquatic environments. It is therefore very important to recognize the distribution of heavy metals in sediments in order to develop plans and approaches for pollution control (Javed *et al.,* 2018). Heavy metals are pollutants whose harmfulness is related to their persistence and toxicity, some of them are known as essential elements (zinc, iron and copper) that play a crucial role in the biological processes. Other metals like lead, cadmium, arsenic are not necessary to the metabolic activities thus, considered as non-essential metals (no role in the biological processes) able to induce toxic effects when their concentration exceeds certain threshold of acceptability (Glasby *et al*., 2004; Lafabrie *et al.,* 2007; Chen *et al.,* 2016). They enter into aquatic systems mainly through natural inputs such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal (Barakat *et al.,* 2012). The increasing load of heavy metals cause imbalance in aquatic ecosystems and the biota growing under such habitats accumulate high amounts of heavy metals which in turn, are being assimilated and transferred within food chains by the process of magnification(Kuntal *et al.*, 2014).

Materials and Methods

Study Area and Sampling

This study was conducted on Shatt Al-Hilla which located in Babylon Governorate in the southern part of Baghdad city. The river is 102 km in length, which starts flowing from a Euphrates river at front of Al-Hindia dam in the north of Al-Hilla city. Sediments samples were collected from five main sampling stations (depth:0-10,10-20 and 20-30 cm) at the right bank of Shatt Al-Hilla, starting from Saad bridge (station 1) to the north of Al-Hashimia city (station 5).

To reduce possible contamination, the sampler was decontaminated by washing with detergent and was rinsed with tap water and followed by rinsing distilled water before each use. Sediments were placed in a clean polyethylene bags. The sediments samples were air-dried. The large stones and other coarse debris were manually removed from the sediments samples and were homogenized and ground using a pestle and mortar. The samples were then sieved to pass through 2 mL sieve to obtain fine-powdered particles. Powdered sediments samples were placed in a clean polyethylene bags and were kept refrigerated until next analysis.

Properties of Sediments

pH and EC were measured in 1:2 sediment water suspension (Richards, 1954). Organic matter content was determined following Walkley and Black (1934) .Total Carbonates in sediments samples was measured by method as described by Black(1965). The proportions of sand, silt and clay-sized particles (texture) were determined according to (Day, 1965).

Modified single sequential extraction technique:

A five-step sequential extraction procedure was used to determine heavy metal-Pb fractions (chemical phases) in the sediments (Badri and Aston, 1983; Ismail and Ramli, 1997).The method is modified and designed to separate the heavy metal-Pb into five fractions.

(1) Fraction 1: *Easily, freely or leachable and exchangeable (EFLE)*. About 5 g of sample was continuously shaken for 3 h with 25 mL 1.0M ammonium acetate (NH_4CH_3COO), pH 7.0 at room temperature.
(2) Fraction 2*: Metal bound to carbonate*. 5 g of sample was continuously shaken for 5 h with 25 mL 1.0M ammonium acetate (NH_4CH_3COO), pH 5.0 at room temperature.
(3) Fraction 3 : *Metal bound to Oxides and-organic*. 5 g of sample was first oxidized with 7.5 mL H_2O_2 (R&M Chemicals 35%) in a water bath at 90^o C. After cooling, the metal complexes was continuously shaken for 3 h with 25 mL of 1.0M ammonium acetate (NH_4CH_3COO) acidified to pH 2.0 with HCl, at room temperature.
(4) Fraction 4: *Total*.. 5 g of sample was digested in a 5 mL combination (ratio of 4:1) of concentrated HNO_3 (AnalaR grade, R&M Chemicals 65%) and $HClO_4$ (AnalaR grade, R&M Chemicals 70%).
(5) Fraction 5*: Residual* (metal fixed with primary and secondary minerals).This fraction calculated according the following expression:
F5(*Residual*) = F4 - (F1+F2+F3)

Results and Discussion

Sediment

The results of the present study (Table 1) showed the properties of the sediments of studies stations, which related to lead fractionation. The pH values varies from 7.22 to 7.83 indicating that the sediments were natural to weakly alkaline. The EC values varies from 0.91 to 6.61 dS.m$^-$ indicating the anthropogenic influences on the sediment quality (Zhan *et al.*, 2010; Al-Robai, 2013). Heavy metals are easy to combine with organic matter and carbonates (Wang *et al*., 2010). The sediments content of organic matter and carbonates are within the range of 20.70% to 36.93% and 0.17 to 1.03%, respectively, indicating the calcareous nature and poor organic content of sediments.

Fractionation of Lead

Lead is one of the most abundant heavy metals and its toxic effects cause environmental and health problems because of its stability in contaminated site and complexity of mechanism in biological toxicity (Tiwar *et al*., 2013)

It is clear from the results of Figure 1-6 and Table 1 that the concentration of the lead metal (mg.kg$^-$) in available phase ranged from 0.26at S5, 20-30cm to

2.70 at S3, 20-30 cm with a mean value of 1.6 and percentage of 2.5% of the total content of the metal. The concentrations of lead that bound with: 1.carbonates ranged from 8.5 at S5, 20-30 cm to 38.16 at S3,20-30 cm with a mean value of 1.6 and percentage of 37.22%. 2. oxides and organic matter ranged from 8.13 at S2,10-20 cm to 35.64 at S3,20-30 cm with a mean value of 1.6 and percentage of 20.86%. 3. residual phase (mainly clay and silt) ranged from 4.26 at S1,10-20cm to 25.75 at S4,20-30 cm with a mean value of 17.0 and percentage of 26.63%.The total concentration ranged from 27.7 at S2,10-20 cm to100.3 at S3,20-30 cm with a mean value of 63.08. The statistical analysis showed that there was presence of a positive correlation between the total concentration of metal with clay (r=0.81), carbonates (r=(0.73 and organic matter (r=0.99).

The fractionation of lead ions showed that the large amount is associated with available and carbonates fractions (39.85%) which are considered as weakly bound and easily available in the aqueous phase (Gibbs, 1997) for organisms in aquatic environment, indicates the dominance of anthropogenic sources, followed by oxides and organic fraction (33.17%) which provide a sink and reservoir for heavy metal (Tessier *et al*., 1979).

The high lead ions concentration which is found to be high in this fraction inferring less risk to the

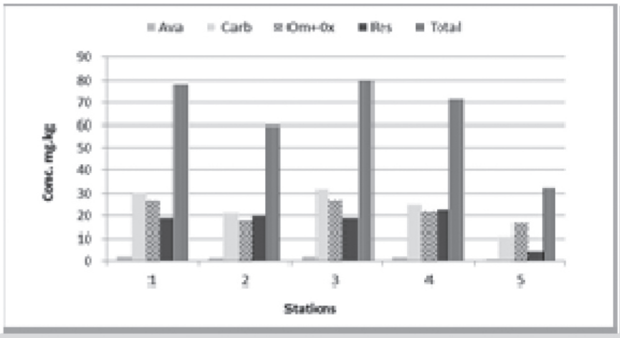

Fig. 1. Concentrations of Pb: depth (0-10 cm)

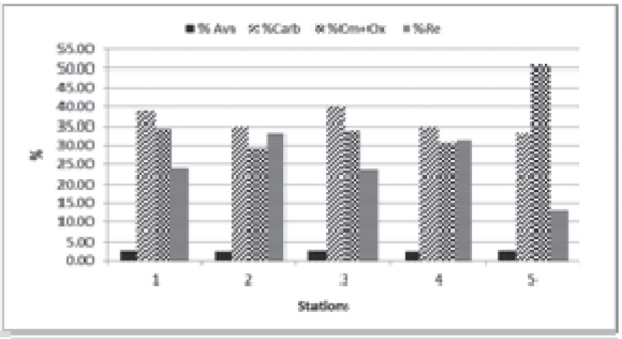

Fig. 2. Percentage of Pb: depth (0-10 cm)

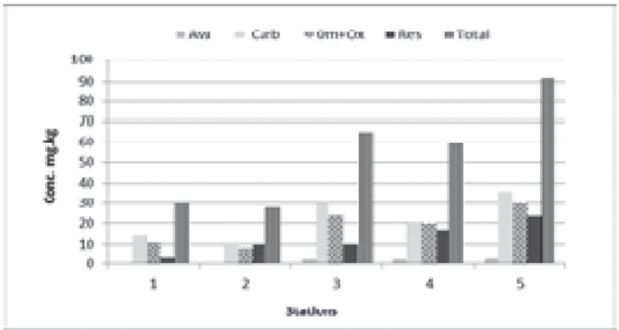

Fig. 3. Concentrations of Pb: depth (10-20 cm)

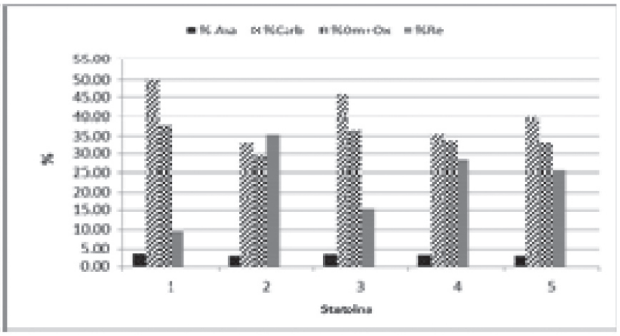

Fig. 4. Percentage of Pb: depth (10–20 cm)

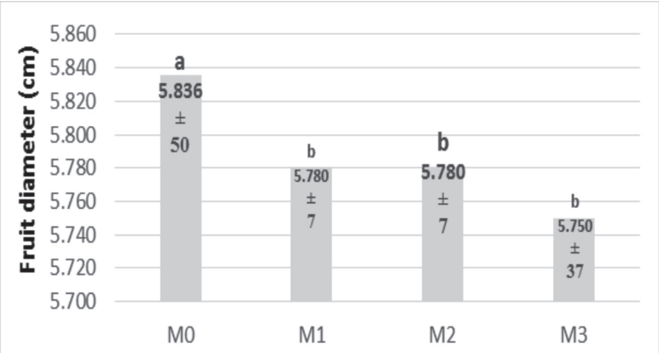

Fig. 5. Concentrations of Pb: depth (20–30 cm)

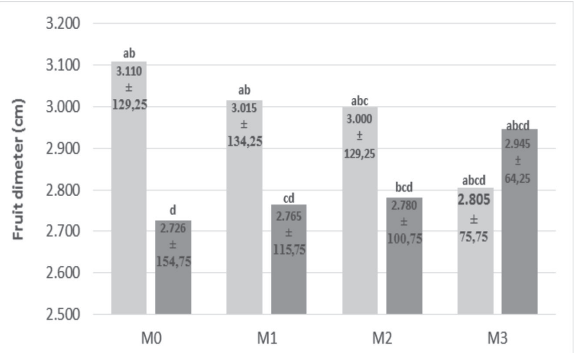

Fig. 6. Percentage of Pb: depth (20–30 cm)

Table 1. Sampling stations and some properties of sediments

Stations	Depth cm	pH	EC dS.m-	$CaCO_3$ %	O.M	Clay + Silt%
1	0-10	7.74	1.66	35.28	1.03	54.0
	10-20	7.33	1.16	25.58	0.34	56.8
	20-30	7.45	0.91	34.11	0.45	56.8
2	0-10	7.33	0.96	30.13	0.17	54.0
	10-20	7.27	6.61	23.88	0.28	58.2
	20-30	7.42	1.99	29.56	0.28	59.6
3	0-10	7.83	0.98	36.38	0.21	58.2
	10-20	7.55	0.93	30.70	0.69	56.8
	20-30	7.5	1.12	36.93	0.86	56.0
4	0-10	7.42	2.57	30.70	0.34	70.8
	10-20	7.35	2.86	27.86	0.34	66.0
	20-30	7.35	2.72	34.86	0.86	64.8
5	0-10	7.22	1.41	30.13	0.47	77.4
	10-20	7.67	1.50	20.70	0.69	58.8
	20-30	7.31	2.43	24.45	0.35	58.2

environment (Pradhanang, 2014). On other hand the residual fraction which constitutes a percentage of 26.3% of the total content of the metal is considered relatively safe because, the metal ions are not easily released under normal conditions. But when the environment becomes increasingly reducing or oxidizing, metal ions can be mobilized (Yobouet *et al*., 2010; Yin *et al.*, 2002). Generally, the results showed that the distribution nature of lead ions did not take a specific patterns in the chemical fractions for all studied stations.

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