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## Full Length Research Paper

# Seasonal Variation of Heavy Metals Pollution in Soil and Date Palm *Phoenix dactylifera* L. Leaves at Basra Governorate /Iraq

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**Abstract.** Heavy metals pollution has become a worldwide problem, and its toxicity affects crop yield, environment, human and animal health, as well as, soil fertility. In this study, the quantities of different heavy metals including Pb, Cd, Cr and Co have been assessed in Basra governorate. Soil and date palm *Phoenix dactylifera* L. leaves have been collected from different sites (Zubair highway, Najibya electric power station, Faw, Qurna, Shat Al-Arab and Abo Al-Kaseeb districts) during the rainy and dry seasons. The analysis of heavy metals revealed that the total, available and leaf content of Pb was found to be high at all investigated sites during both season, followed by Cr, while the lowest averages of heavy metals were reported with Cd. Results indicate that the total level of heavy metals pollution during the dry season was higher than what was observed during rainy season in all analysed heavy metals. It is noteworthy, that the levels of Pb and Cd in Basra's soils have exceeded the permissible limits according to European standards, thus, an urgent interaction is required to decrease these levels by introducing a suitable remediation procedure.

**Keywords:** Anthropogenic, deposition, Environment, Heavy metals, Pollution

## 1. INTRODUCTION

Heavy metals pollution becomes one of the most serious environmental problems recently (Kumar et al., 2009) The term of heavy metals refers to any metallic elements that have a relatively high density and are toxic or poisonous even at low concentration (Singh, 2008), included metalloids such as arsenic, which are able to induce toxicity at low level of exposure (Duffus, 2002). Although they occur naturally, heavy metals also enter into environment throughout anthropogenic activities (You et al., 2015). The increasing of anthropogenic activities leads to intensifying emission of various pollutants including heavy metals, such increase in these activities may cause a genuine health hazard to both people and plant (Onder and Dursun, 2006). Thus, the evaluation and monitoring of heavy metals levels in soil, air, dust, water and food are so important, and biological indicators have been used for many years to detect the deposition, accumulation and distribution of heavy metal pollution (Zurayk et al., 2001).

The leaves of higher plants have been used for heavy metals biomonitoring including date palm *Phoenix dactylifera* L. (Al-Shayeb et al., 1995; Divrkli et al., 2006; Al-Khalifat et al., 2007; Al-

Khashman et al., 2011). Abass et al. (2015) reported that, the date palm leaves can be used as a biomonitor of heavy metals in Basra governorate, also other parts of date palm have been used such as fiber (Al-Shayeb and Seaward, 2000), bark (Bu-Olayan and Thomas, 2002) fruits (Aldjain et al., 2011). Noteworthy, this tree is a typical urban tree in Basra governorate and cultivated over large areas, usually growing by roadsides in industrial, rural, residential and agricultural areas. Soils are the major sink for pollutants released to the environment, and the contamination of soils, particularly agriculture soil by toxic elements such as heavy metals attracts the interest of scientists not only because metals build up of soil, but also because metals can be accumulated in crops, causing a significant potential risk to human health (Haung et al., 2007). It is widely accepted that determining the total content of heavy metals in a soil is neither sufficient to understand their relative mobility and ecological availability as pollutants nor particularly useful as a tool to estimate potential risks (Adriano, 2001). The toxicity of metals to the plants and animals, including humans does not depend on their total concentrations only, but also depends on their mobility and reactivity with other components of the ecosystem (Adriano, 2001; Albolino et al., 2002).

The risk of heavy metal transfer to the food chain is dependent on the mobility of heavy metals species and their availability in the soil (Richards et al., 2000). Mobility and availability of heavy metals are mainly influenced by soil properties such as pH, organic matter, ionic strength, cation exchange capacity (CEC), soil texture, salinity and other soil properties (Sherene, 2010), additionally environmental factors, such as soil temperature and humidity, significantly influence the availability of heavy metals (Karmaker et al., 2016).

The aim of this study was to evaluate heavy metals pollution in Basra governorate by assessment both total and available heavy metals in soil and the level of pollution in date palm leaves at different areas of Basra governorate during the rainy and the dry season.

## 2. MATERIAL AND METHODS

### 2.1. Description of sampling sites

Basra governorate is located in the southern of Iraq and borders Iran, Kuwait and Saudi Arabia, it is situated at 30.53° North latitude, 47.79° East longitude and 3 meters elevation above the sea level. Six different sites have been selected to investigate their heavy metals pollution in the soil and date palm leaves during the rainy and the dry seasons, which were as follows:

1-Zubair highway (two way street along 15 km) (ZHW); 2-Najibya electric power station (NS); 3-Faw district (F); 4-Qurna district (QR); 5-Shat Al-Arab district (SA); 6-Abo Al-Khaseeb district (AK).

### 2.2. Samples collection

Samples of soil and date palm leaves from selected sites were collected during the rainy season in December 2014 and during the dry season in July 2015. Compound samples of soil (six samples from each area) were collected from upper. Approximately 200 g of leaf samples were collected from young date palm trees, each of a maximum 3 m trunk height in order to reduce age variation among leaves samples (Al-Shayeb et al., 1995). Samples were collected from the distal portion of the middle age leaves which are not covered by higher leaves, and from all directions as a mixed sample (Al-Shayeb & Seaward, 2000).

### 2.3. Samples preparation

Soil samples were air dried, homogenized and sieved through 2 mm plastic sieve, physical and chemical properties of soil were carried out. pH was tested according to McLean (1982), electrical conductivity ( $\text{ds m}^{-1}$ ) according to Richards (1954) which

determined in a mixture of soil and distilled water at a ratio (1:1), organic matter was measured according to Walkely and Black method described by Schulte (1995), Cation Exchange Capacity (CEC) ( $\text{Cmole /Kg soil}$ ) according to Polemio and Rhoades (1977) and soil texture was determined with the pipette method described by Miller & Miller (1987).

### 2.4. Heavy metals analysis

Total and available concentrations of Pb, Cd, Cr and Co in soil and date palm leaves samples were analysed using Flame Atomic Spectrophotometer (Perkin Elmer AAS Analysis 300, USA). Acid digestion method was used to evaluate total heavy metals content in the soil according to Davidson (2013). Briefly: 1 g of dry soil finely ground, moistened with distilled water heated in 100 ml Teflon beaker with 10 ml conc.  $\text{HNO}_3$  and evaporated to a small volume, 5 ml conc.  $\text{HNO}_3$ , 5 ml 70%  $\text{HClO}_4$  and 10 ml conc. HF (Hydrofluoric acid) were added and then all were heated to perchlorate fume, after 30 min. Fuming, 10 ml HCl (1/1, v/v) was added. The mixture was boiled for 10 min, cooled and diluted to 100 ml with distilled water. The available metal content of soils was extracted by DTPA extractable solution as described by Lindsay & Norvell (1978). Extractable solution (a mixture of  $0.005 \text{ mol L}^{-1}$  DTPA (Diethylenetriaminepentaacetic acid),  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  and  $0.1 \text{ mol L}^{-1}$  TEA (Triethanolamine)). An amount of 15 g of dry soil sample was weighted into a 100 ml flask, and shaken for 2 h at room temperature using a mechanical shaker with 30 ml of extractable solution, the extracts were filtered and diluted to 100 ml with distilled water.

Wet acid digestion of the date palm leaflets was performed using  $\text{HNO}_3/\text{HClO}_4$  digestion (Jones, 1984), briefly, 5 ml of  $\text{HNO}_3$  (70%) and 1.5 ml  $\text{HClO}_4$  (60%) were added to 0.5 g of sample, and the solution was heated until the disappearance of the brown fume, then cooled, subsequently a 5 ml of diluted (1:1) HCl was added, finally the mixture was diluted with distilled water to 25 ml.

### 2.5. Statistical analysis

The obtained data were analysed statistically with SPSS-21 statistical software (SPSS Inc., Chicago, IL., USA). Mean was statistically compared by LSD test at  $P < 0.05$  level with triplicates for each samples.

## 3. Result

### 3.1. Soil properties

The analysis of soil properties presented in Table (1) showed that the soil texture at QR, SA and AK sites

was silty clay, while other sites varied from clay for F site, clay loam for NS site and sandy loam for HW site. Other soil properties were estimated during the rainy and the dry seasons, pH values for all investigated sites during both seasons were within 7 and 8 with an exception for HW during the rainy season which was 6.91. Regarding soil Ec the lowest levels were found at NS site 5.1 and 5.46 ds during the rainy and the dry seasons respectively, while the highest value during the rainy season was found at F site 17.53 ds and 16.93 ds during the dry season at HW site. Soil organic matter (OM) content showed that the collected samples from NS site had the highest content of OM which was 5.63 % during the rainy season and 5.34 % during the dry season, while the lowest OM contents were reported at SA site with the averages of 0.84 and 0.74 % during the rainy and dry season, respectively.

In terms of soil Cation Exchange Capacity (CEC) results showed that the highest values were found at NS site which was 22.15 Cmole during the rainy season and 20.88 Cmole during the dry season, while the lowest values were found at HW found which were 10.28 Cmole and 9.29 Cmole during the rainy and dry seasons, respectively.

## 3.2. Soil heavy metals

### 3.2.1. Total heavy metals in soil

Total heavy metals Pb, Cd, Cr and Co concentrations in soils were determined during the rainy and the dry seasons at six sites of Basra governorate/ Iraq. The results presented in Table (2) proved that there were seasonal variations between total heavy metals levels in the soil, which were higher during the dry season compared with the rainy season. As grand mean in both seasons, Pb has the highest concentrations of 157.85 and 196.73 mg/kg, while, Cd has the lowest of 5.55 and 6.27 mg/kg, during the rainy and dry seasons, respectively. The order of investigated total heavy metals levels in the soil in both seasons was:

Pb > Cr > Co > Cd

During the rainy season, the Pb levels were the highest at QR site 229.64 mg/kg, and the lowest level was observed at F site 100.78 mg/kg. The levels of Cr, Co and Cd were found higher at NS site, which were 138.91, 42.31 and 8.84 mg/kg, respectively, while the lowest total level of Cr in soil was at F site

(46.26 mg/kg), Co at SA site (23.58 mg/kg) and Cd at F site (3.16 mg/kg) without significant difference of AK site.

During the dry season, the Pb levels, as well as, during the rainy season were the highest at QR site 276.47 mg/kg, and the lowest was seen at HW site 164.3 mg/kg. The highest Cr, Co and Cd levels were reported at NS site 145.85, 44.74 and 9.65 mg/kg, respectively, while the lowest level of Cr was observed at F site 63.08 mg/kg, Cd at SA site 4.78 mg/kg without any significant difference than QR, HW and AK sites and Co at SA site which was 28.09 mg/kg.

### 3.2.2. Available heavy metals in soil

The results of available concentrations of heavy metals in soil are presented in Table (3), it could be concluded that the collected samples during the rainy season had highest available concentrations than dry season. The orders of available heavy metals concentrations as grand means were found to be similar to the order of total concentrations. Collected samples from NS site during the rainy season had the highest concentrations of all investigated heavy metals, which were Pb 32.43 mg/kg, Cr 24.9 mg/kg, Co 14.17 mg/kg and Cd 1.84 mg/kg, while the lowest level of the Pb was found at HW site 17.22 mg/kg without significant difference than F site, Co at HW site 6.85 mg/kg, Cr at HW site 10.63 mg/kg. Regarding the dry season, the highest levels of available heavy metals were found at NS site, with an exception of Co at AK site, the available concentration of Pb, Cr and Co were 30.79, 1.61 and 26.86 mg/kg, respectively, and Co was 11.35 mg/kg. All available heavy metals were found to be low in collected samples from HW site, which were Pb 13.95 mg/kg, Cd 0.59 mg/kg, Cr 5.94 mg/kg and Co 4.12 mg/kg without significant difference of SA site.

## 3.3. Heavy metals content in date palm leaves

The analysis of heavy metals in date palm leaves (Table 4) showed that the collected samples during the dry season had the higher levels of heavy metals compared with the rainy season, our results proved the following order according to grand means of heavy metals during both investigated seasons:

Pb > Co > Cr > Cd

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**Table 1:** Soil properties of investigated sites during the rainy and the dry seasons

| Property     | Unit | HW         |       | NS        |       | F     |       | QR         |       | SA         |       | AK         |       |
|--------------|------|------------|-------|-----------|-------|-------|-------|------------|-------|------------|-------|------------|-------|
|              |      | Rainy      | Dry   | Rainy     | Dry   | Rainy | Dry   | Rainy      | Dry   | Rainy      | Dry   | Rainy      | Dry   |
| pH           | 1:1  | 6.91       | 7.49  | 7.5       | 7.59  | 7.22  | 7.8   | 7.45       | 7.68  | 7.1        | 7.5   | 7.25       | 7.3   |
| Ec           | ds   | 10.36      | 16.93 | 5.1       | 5.46  | 17.53 | 14.46 | 7.83       | 9.3   | 8.16       | 7.26  | 9.3        | 10.8  |
| OM           | %    | 1.55       | 1.57  | 5.63      | 5.34  | 1.23  | 1.14  | 0.89       | 0.85  | 0.84       | 0.74  | 2.75       | 2.5   |
| CEC          | cmol | 10.28      | 9.29  | 22.15     | 20.88 | 14.68 | 14.65 | 14.1       | 13.35 | 12.75      | 13.71 | 19.97      | 16.53 |
| Sand         | %    | 75.8       |       | 41.1      |       | 8.89  |       | 11.82      |       | 8.12       |       | 4.89       |       |
| Clay         | %    | 16         |       | 30.5      |       | 57.84 |       | 44.46      |       | 51.32      |       | 47.12      |       |
| Silt         | %    | 8.2        |       | 28.4      |       | 36.27 |       | 43.72      |       | 40.56      |       | 48.01      |       |
| Soil texture |      | Sandy loam |       | Clay loam |       | Clay  |       | Silty clay |       | Silty clay |       | Silty clay |       |

**Table 2:** Total heavy metals concentrations in different soil sites at Basra governorate (mg/kg)

| Site       | Pb                 |                    | Cd               |                  | Cr                 |                    | Co                |                   |
|------------|--------------------|--------------------|------------------|------------------|--------------------|--------------------|-------------------|-------------------|
|            | Dry                | Rainy              | Dry              | Rainy            | Dry                | Rainy              | Dry               | Rainy             |
| HW         | 164.3<br>±2.26 e   | 113.48 ±<br>2.88 e | 5.5 ± 0.82<br>c  | 5.86 ±<br>0.56 b | 111.61 ±<br>1.98 c | 97.75 ±<br>1.95 c  | 32.95 ±<br>1.58 d | 32.25 ±<br>2.08 c |
| NS         | 208.95 ±<br>1.66 b | 198.77 ±<br>2.26 b | 9.65 ±<br>0.68 a | 8.84 ±<br>0.86 a | 145.85 ±<br>2.34 a | 138.91 ±<br>2.62 a | 44.74 ±<br>2.08 a | 42.31 ±<br>1.58 a |
| F          | 165.39 ±<br>1.25 f | 100.78 ±<br>1.66 f | 7.49 ±<br>1.27 b | 6.05 ±<br>0.68 b | 63.08 ±<br>5.04 e  | 46.26 ±<br>2.62 f  | 31.91 ±<br>1.58 d | 30.52 ±<br>1.58 c |
| QR         | 276.47 ±<br>3.82 a | 229.64 ±<br>2.26 a | 5.14 ±<br>1.23 c | 4.78 ±<br>1.09 b | 131.55 ±<br>1.95 b | 118.98 ±<br>2.08 b | 40.58 ±<br>1.04 b | 37.46 ±<br>2.08 b |
| SA         | 174.46 ±<br>2.88 d | 146.15 ±<br>2.88 d | 4.87 ±<br>1.08 c | 3.16 ±<br>0.82 c | 80.63 ±<br>2.08 d  | 70.88 ±<br>5.52 e  | 28.09 ±<br>2.08 e | 23.58 ±<br>2.16 d |
| AK         | 190.8 ±<br>4.99 c  | 156.68 ±<br>2.74 c | 4.96 ±<br>1.38 c | 4.6 ± 1.23<br>bc | 114.86 ±<br>2.28 c | 82.8 ±<br>4.05 d   | 37.11 ±<br>1.58 c | 33.64 ±<br>2.61 c |
| Grand mean | 196.73 ±<br>40.09  | 157.85 ±<br>46.43  | 6.27 ±<br>2.03   | 5.55 ±<br>1.95   | 107.93 ±<br>29.24  | 92.76 ±<br>31.25   | 35.9 ± 592        | 33.29 ±<br>6.21   |
| LSD        | 4.49               | 3.59               | 1.61             | 1.51             | 4.12               | 4.92               | 2.46              | 2.98              |

\*Mean follows by standard deviation; \*Means within each column followed by the same letter are not significantly different at  $p < 0.05$ ;

\*Each number in the table is an average of triplicate

Regarding the rainy season, Pb levels were the highest in the date palm leaves samples at NS site 39.27 mg/kg without significant difference than the levels of HW, QR and AK sites, while, the lowest levels were observed at F site 23.56 mg/kg, Cd had the highest level at NS site 5.38 mg/kg, while the lowest level was reported at SA site 1.48 mg/kg. Regarding Cr level, the highest level was found at NS site 11.7 mg/kg without significant difference of HW, QR and SA sites, while the lowest was observed at AK site 3.47 mg/kg, without significant difference than F site. Highest levels of Co were reported at AK site 18.76 mg/kg, no significant difference was noted between the rest of sites for Co concentration in date palm leaves.

The analysis of dry season results showed that the high levels of Pb and Cd were found in samples which collected from NS site, which were 43.34 and 5.67 mg/kg, respectively. The lowest level of Pb was found in F site 28.34 mg/kg, without any significant difference than what was observed at SA and AK sites, while the lowest level of Cd was found at SA site 1.92 mg/kg. Regarding Cr the highest level was observed at QR site 17.73 mg/kg without significant difference than NS site, while the lowest level was found in F site 9.07 mg/kg without significant

difference of HW and AK site, the highest level of Co was found in AK site 24.87 mg/kg and the lowest level was found at F site 8 mg/kg.

### 3.4. Correlation Coefficient analysis

Table (5) summarizes the analysis of correlation coefficient between total heavy metals in soil and soil properties during the rainy and dry seasons. Statistical analysis of correlation coefficient revealed that, most of the results were identical at both investigated seasons, thus, was evident with soil pH criteria, no correlation was detected between pH values and any considered heavy metals. Regarding Ec correlation coefficient, our results showed there were a positive correlation ( $> 60$ ) with Cr at both seasons, while for Pb, a positive correlation was observed just during the rainy season. No significant correlation was observed with Cd and Co during both seasons. OM results proved the positive correlation with Cd, Cr and Co ( $> 60$ ) at ( $P < 0.01$ ) at the rainy and dry seasons, while, no significant correlation between OM and Pb was seen during both seasons. In terms of CEC, no correlation was reported for all investigated heavy metals during the rainy and dry seasons, with an exception of Cd and Co during the dry season.

Regarding available of heavy metals; Table (6) explained the correlation coefficient analysis, no correlations were observed for soil pH and Ec with all investigated heavy metals during both seasons, with an exception of Ec and Pb during the rainy season (>

60). The opposite was observed for OM and CEC criteria with all investigated heavy metals during the rainy and dry seasons, which positive correlations were reported.

**Table 3:** Available heavy metals concentrations in different soil sites at Basra governorate (mg/kg)

| Site  | Pb      |         | Cd      |            | Cr         |            | Co         |            |
|-------|---------|---------|---------|------------|------------|------------|------------|------------|
|       | Dry     | Rainy   | Dry     | Rainy      | Dry        | Rainy      | Dry        | Rainy      |
| HW    | 13.95 ± | 17.22 ± | 0.59 ±  | 0.89 ±     | 5.94 ± 0.3 | 10.63 ±    | 4.12 ± 0.1 | 6.85 ±     |
|       | 2.83 d  | 0.92 c  | 0.02 e  | 0.04 c     | e          | 0.5 c      | e          | 0.08 f     |
| NS    | 30.79 ± | 32.43 ± | 1.61 ±  | 1.84 ±     | 26.86 ±    | 24.9 ± 0.9 | 10.46 ±    | 14.17 ±    |
|       | 1.8 a   | 1.46 a  | 0.07 a  | 0.05 a     | 0.81 a     | a          | 0.17 b     | 0.16 a     |
| F     | 18.98 ± | 19.1 ±  | 1.19 ±  | 1.15 ±     | 12.71 ±    | 13.99 ±    | 6.6 ± 0.16 | 9.14 ± 0.2 |
|       | 1.4 c   | 1.12 c  | 0.12 b  | 0.26 b     | 0.8 c      | 0.81 b     | d          | d          |
| QR    | 24.12 ± | 23.54 ± | 0.94 ±  | 1.1 ± 0.09 | 14.19 ±    | 13.52 ±    | 8.53 ± 0.9 | 11.63 ±    |
|       | 2.63 b  | 1.05 b  | 0.02 c  | b          | 0.5 b      | 0.6 b      | c          | 0.46 c     |
| SA    | 19.8 ±  | 22.95 ± | 0.78 ±  | 0.84 ±     | 10.9 ± 0.8 | 11.37 ±    | 4.68 ±     | 7.31 ± 0.2 |
|       | 2.11c   | 1.23 b  | 0.05 d  | 0.05 c     | d          | 0.3 c      | 0.18 e     | e          |
| AK    | 21.32 ± | 25.53 ± | 0.83 ±  | 0.96 ±     | 12.31 ±    | 14.19 ±    | 11.35 ±    | 13.66 ±    |
|       | 2.48 bc | 2.75 b  | 0.06 cd | 0.02 bc    | 0.72 c     | 0.7 b      | 0.35 a     | 0.14 b     |
| Grand | 21.49 ± | 23.46 ± | 0.99 ±  | 1.13 ±     | 13.82 ±    | 14.76 ±    | 7.62 ±     | 10.46 ±    |
| mean  | 5.63    | 5.18    | 0.34    | 0.36       | 6.59       | 4.87       | 2.83       | 2.98       |
| LSD   | 4.49    | 3.59    | 0.13    | 0.17       | 0.99       | 0.97       | 0.69       | 0.35       |

\*Mean follows by standard deviation; \*Means within each column followed by the same letter are not significantly different at  $p < 0.05$ ;

\*Each number in the table is an average of triplicate

### 3.5. The permissible limit of heavy metals in soil

The comparisons of the permissible limits of investigated heavy metals in soil (based on total concentration) were performed according to the European Union's (EU) standard (2006), our results revealed that the levels of Pb and Cd have exceeded the EU permissible limits at all sites during both seasons (above 100 mg/kg and 3 mg/kg for Pb and Cd, respectively). Hence, the level of Co in the soil was found to be less than the permissible limit which was 50 mg/kg according to EU standard at all investigated sites during both seasons. The Cr levels at NS and QR sites have exceeded the permissible limits (100 mg/kg) during the rainy season and at HW, NS, QR and AK sites during the dry season.

## 4. Discussion

### 4.1. Total heavy metals

The results of this study showed that the soil content of total heavy metals were varied according to the season, all investigated heavy metals were found to be higher during the dry season compared with the rainy

season, thus could be attributed to the effect of rainfall during the rainy season which facilitates the leaching of the soil and dilute soil solution (Yahaya et al., 2010), additionally, the dominant high temperature during the dry season lead to more intense evaporation, thus, soil solution become more concentrated (Oluyemi et al., 2008). Heavy metals analysis proved high level of pollution in Basra governorate (at all investigated sites), thus, could be explained by the several reasons such as emissions from the rapidly expanding industrial areas, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, spillage of petrochemicals and atmospheric deposition (Khan et al., 2008; Zhang et al., 2010), conventional oil production activities (Khoo and Tan, 2006), power generation plants (Nriagu, 1989), the traffic activities and fossil fuel burning (Al-Khashman et al., 2011), particularly the use of leaded gasoline (Chen et al., 2005). With special emphasizing on the usage of leaded gasoline in Iraq which still going on according to United Nations Environment Program.

In Basra governorate, different anthropogenic sources of heavy metals emission can be identified such as power generation plants, factories of

petrochemical, fertilizer, longitudinal pipe (iron and steel), liquid gas, conventional oil production activities, in the area surrounding this governorate has substantial petroleum resources and many oil wells, all of these activities are considered as potential

sources of heavy metals pollution, in addition to the local sources, there is a possibility of heavy metals move from sources outside parts of the governorate and deposit on the inside parts (WHO, 2000).

**Table 4:** Heavy metals concentrations in date palm leaves *Phoenix dactylifera* L. (mg/kg)

| Site       | Pb               |                    | Cd                |                   | Cr                 |                    | Co                 |                   |
|------------|------------------|--------------------|-------------------|-------------------|--------------------|--------------------|--------------------|-------------------|
|            | Dry              | Rainy              | Dry               | Rainy             | Dry                | Rainy              | Dry                | Rainy             |
| HW         | 34.38<br>±1.66 b | 37.85<br>±3.27 a   | 3.65<br>0.37 c    | ± 3.5 ± 0.12<br>b | 11.67<br>1.29 bce  | ± 9.53<br>1.98 a   | 14.75<br>3.43 d    | ± 12.8<br>2.81 b  |
| NS         | 43.34<br>3.27 a  | ± 39.27<br>1.23 a  | ± 5.67<br>0.12 a  | ± 5.38<br>0.21 a  | ± 15.13<br>2.7 ab  | ± 11.7<br>1.29 a   | ± 20.37<br>1.71 b  | ± 15.03<br>1.7 b  |
| F          | 28.34<br>2.47 c  | ± 23.56<br>2.14 c  | ± 2.85<br>0.33 d  | ± 2.35<br>0.21 d  | ± 9.07<br>1.29 e   | ± 6.07 ± 2.7<br>bc | 8 ±<br>1.71 e      | ± 11.68<br>2.81 b |
| QR         | 39.05<br>4.45 ab | ± 35.7<br>4.45 ab  | ± 4.22<br>0.33 b  | ± 3.57<br>0.12 b  | ± 17.73<br>3.9 a   | ± 11.26<br>1.49 a  | ± 18.87<br>2.34 bc | ± 13.92<br>2.81 b |
| SA         | 33.34<br>5.39 bc | ± 30.7<br>2.47 b   | ± 1.92<br>0.21 e  | ± 1.48<br>0.21 e  | ± 13.83<br>1.98 bc | ± 8.67<br>3.29 ab  | ± 15.87<br>1.71 cd | ± 12.43<br>2.23 b |
| AK         | 34.05<br>3.71 bc | ± 33.56<br>4.45 ab | ± 3.29<br>0.12 cd | ± 3.07<br>0.12 c  | ± 10.37<br>2.24 ce | ± 3.47 ± 2.7<br>c  | ± 24.87<br>2.34 a  | ± 18.76<br>2.32 a |
| Grand mean | 35.42<br>5.76    | ± 33.44<br>6.02    | ± 3.6 ± 1.22      | 3.23<br>1.24      | ± 12.97<br>±3.64   | 8.45<br>3.57       | ± 17.12<br>5.71    | ± 14.1<br>3.19    |
| LSD        | 5.91             | 6.23               | 0.51              | 0.25              | 3.52               | 3.41               | 3.33               | 3.61              |

\*Mean follows by standard deviation; \*Means within each column followed by the same letter are not significantly different at  $p < 0.05$ ;

\*Each number in the table is an average of triplicate

**Table 5:** Correlation coefficient analysis between total heavy metals and soil properties during the dry and the rainy seasons

| Dry season   |        |         |         |         |
|--------------|--------|---------|---------|---------|
|              | pH     | Ec      | OM      | CEC     |
| Pb           | -0.109 | -0.44   | 0.039   | 0.189   |
| Cd           | 0.347  | -0.121  | 0.675** | 0.618** |
| Cr           | -0.244 | 0.726** | 0.633** | 0.372   |
| Co           | -0.129 | 0.492*  | 0.708** | 0.615** |
| Rainy season |        |         |         |         |
|              | pH     | Ec      | OM      | CEC     |
| Pb           | 0.527* | 0.740** | 0.316   | 0.427   |
| Cd           | 0.114  | -0.112  | 0.748** | 0.507*  |
| Cr           | 0.366  | 0.816** | 0.627** | 0.354   |
| Co           | 0.518* | 0.414   | 0.696** | 0.526*  |

\*\* Correlation is significant at 0.01 level (2-tailed)

Our results showed that the concentrations of Pb and Cd were above the permissible limits at all investigated sites during both seasons. Regarding to sites, the high level of Pb was found at QR site during both seasons, this could be due to conventional oil production activities which taking place at this site and emission of heavy metals, particularly Pb come from combustion of natural gas used in crude oil separators, venting and flaring operations (Efe, 2010), in addition to fossil fuel burning of equipment's and automobiles, while the highest level of Cd was found at NS site, which at this site exist power generation station (Najibiya Station), in which the process and production of power require a substantial amount of energy supplied by fossil fuel burning, as well as

traffic activities in the station (Carreras and Pignata, 2002; Banatet et al., 2005). The Cr level during the rainy season was exceeded permissible limits only at NS and QR sites, during the dry season at NS, QR, AK and HW. Since the oil combustion considered a second source of chromium emission to the atmosphere (Cheng et al., 2014), thus, activities that used oil combustion such as oil production activities at QR site and power generation at NS site could be the reason behind the high level of Cr at these sites.

#### 4.2. Available heavy metals

The analysis of available concentrations results of heavy metals in soil showed that the highest levels of

all heavy metals were found at the NS site during the rainy and the dry season, with an exception of Co level at AK site during rainy season, while the lowest

levels of all heavy metals were found at the HW site during both season.

**Table 6:** Correlation coefficient analysis between available heavy metals and soil properties during the dry and the rainy seasons

|    | seasons      |         |         |         |
|----|--------------|---------|---------|---------|
|    | Dry season   |         |         |         |
|    | pH           | Ec      | OM      | CEC     |
| Pb | -0.205       | 0.566   | 0.652** | 0.838** |
| Cd | 0.095        | -0.186  | 0.718** | 0.835** |
| Cr | -0.07        | 0.515   | 0.812** | 0.914** |
| Co | -0.356       | -0.336  | 0.611** | 0.781** |
|    | Rainy season |         |         |         |
|    | pH           | Ec      | OM      | CEC     |
| Pb | 0.522        | 0.656** | 0.768** | 0.894** |
| Cd | 0.507        | -0.32   | 0.807** | 0.771** |
| Cr | 0.476        | -0.422  | 0.907** | 0.894** |
| Co | 0.533        | -0.419  | 0.690** | 0.815** |

\*\* Correlation is significant at 0.01 level (2-tailed)

The variation in soil properties such as pH, organic matter content and its quality, texture, quality and quantity of sorption sites may significantly influence the distribution as well as availability of heavy metals to plant (Barancikova and Makovnikova, 2003), thus, heavy metals in soil directly or indirectly depends on the soil organic matter, any variation of organic matter may be the predominant cause of variation in heavy metals in soil (Van der perk and Van Gaans, 1997), also from particles fractions (sand, silt and clay), the finer particles show higher concentrations of heavy metals due to increased surface area (Forstner, 1980), as well as, Cation Exchange Capacity (CEC) of a soil depend upon its organic matter and clay content. Generally, the higher CEC increase the soil's ability to retain heavy metals. Mitsios et al. (2005) reported that the total concentrations of heavy metals correlated significantly with their available concentrations. Therefore, the highest available concentrations of heavy metals were found at NS site, which soil at this site contain the higher organic matter and CEC than other sites, this could be interpreted by the lowest levels of available heavy metals were found at HW site, which the CEC and clay fractions are low compared with other sites, in spite the organic matter was not the least among the sites. Korte et al. (1976) reported that the soil's ability to retain heavy metals is more closely tied to the specific surface than to the soil CEC, which the specific surface is closely related to clay content and type.

The analysis of correlation coefficient presented in Table (3) during the rainy season and Table (4) during the dry season, confirmed that the positive correlation

between soil organic matter and CEC with available heavy metals concentrations. Results also showed that the seasonal variation of available heavy metals concentration, the available concentrations of most heavy metals during the rainy season were higher than those during the dry season, thus, the variation may be due to change in organic matter and CEC between the rainy and dry season, which some environmental factors such as temperature and rainfall can change the organic matter content as well as heavy metals concentration in soil (Ashworth and Alloway, 2004).

#### 4.3. Heavy metals content in date palm leaves

Results showed that there was a variation in the content of heavy metals between the rainy and the dry seasons, which could be explained by the washing process by rain during the rainy season, this results are in a good agreement with the results of Al-Shayeb et al.(1995), who reported a considerable amount of metal particulates is removed from leaflets surface by washing process, a natural washing process by rainfall during the rainy season led to the removal of heavy metals that deposited on leaves. Its noteworthy that, at all investigated sites, the levels of heavy metals in date palm leaves exceeded the available concentrations of heavy metals in soil, which indicates another source of pollution comes from foliar uptake, which both essential and non-essential metal can be taken up by the leaves (Marschner, 1995) or to dust deposition on the date palm leaves, subsequently heavy metal release into the atmosphere can be either deposited in the vicinity of the emission source or

subjected to long-range transport via air masses, this could be an explanation for the high levels of Pb, Cd and Cr in date palm leaves samples collected from NS and Qr sites.

## 5. CONCLUSION

Our results showed that there was a seasonal variation of heavy metals pollution in Basra governorate in soil as total and available concentrations, as well as, in date palm leaves. The heavy metals as total concentrations in soil and in date palm leaves were found to be higher during the dry season, while available concentrations in soil were higher during the rainy season, and positively correlated with soil properties, particularly organic matter and CEC. Results proved that the soil of this governorate considered polluted by Pb and Cd metals and their concentrations found to be higher than the permissible limits at all sites, and Cr at some sites, while Co levels within permissible limits at all sites. In the future work, further studies are required to assess the levels of more heavy metals at different sites in order to get a general evaluation of heavy metals in Basra governorate.

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