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ORIGINAL ARTICLE

Determination of heavy metals in the fruit of date palm growing at different locations of Riyadh

Ibrahim M. Aldjain [a], Mohamed H. Al-Whaibi [b,*], Salim S. Al-Showiman [c], Manzer H. Siddiqui [b]

[a] *General Directorate of Gardens and Landscaping, Riyadh Municipality, P.O. Box 16444, Riyadh 11778, Saudi Arabia*
[b] *Department of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*
[c] *Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*

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Abstract Exposure of heavy metals to human beings has risen dramatically in the last 50 years. In today's urban and industrial society, there is no escaping from exposure to toxic chemicals and heavy metals. Humans are more likely to be exposed to heavy metal contamination from the dust that adheres to edible plants than from bioaccumulation. This is because it is very difficult to wash off all the dust particles from the plant material before ingesting them. The objectives of this experiment were to determine the concentrations of lead (Pb) and cadmium (Cd) in washing residues and in the tissues of fruits of date palm growing in 14 sites of Riyadh and also to assess whether the fruits were safe for human consumption. The washing residues and tissue of date palm fruits collected from different sites showed the presence of significant amounts of the Pb and Cd. The concentration of Pb in the dust and fruit tissue increased with increasing anthropogenic sources. Therefore, fruits of date palm might be used as a pollution indicator; it might be recommend that fruits of date palm could be safe for human consumption after washing. The mean concentration of Pb and Cd in all the samples collected from different sites is within the safe limits recommended by FAO/WHO.

* Corresponding author.
E-mail address: mwhaibi@ksu.edu.sa (M.H. Al-Whaibi).

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1. Introduction

The date palm (*Phoenix dactylifera* L., family Arecaceae) is one of the oldest cultivated trees in arid and semi-arid regions. Saudi Arabia is one of the major date producing countries in the world and estimated production of dates in 2006 was 986,000 MT (Arab Agricultural Statistics Yearbook, 2009). The tree is valued mainly for its fruits (date) as well as for its ornamental value almost in every garden, square and avenue in Saudi Arabia. Dates are very rich in nutritive

components, viz., carbohydrates, fats, minerals, protein, vitamins and dietary fibres (Fayadh and Al-Showiman, 1990; Al-Shahib and Marshall, 2003). It is preferable to consume dates at the Rutab (semi-ripe) and Tamr (fully-ripe) stages; however, the consumption of processed dates is rapidly and steadily growing (Al-Hooti et al., 1997).

The rapid increasing population in urban areas led to anthropogenic activities and fossil fuel combustion. Emissions from road traffic that uses fossil fuel, industry, agriculture, sewage sludge, and waste incineration are the chief sources of air pollution (Vouk and Piver, 1983; Celik et al., 2005). Air pollution due to the heavy metals arises from these sources as well as from the dust storms (NRDC, 2005) in Saudi Arabia. Most of the pollutants deposit on ground and on other objects such as exposed plant parts (Khairiah et al., 2004; Chojnacka et al., 2005; Hashmi et al., 2006). Air pollutants especially lead (Pb) and cadmium (Cd) are hazardous and toxic to human beings depending on their concentrations in the food stuff (Senesi et al., 1999; Järup, 2003). Presence of these pollutants (Pb and Cd) in date fruits above the permissible limit may lead to severe health hazards to the people consuming it. So the estimation of their levels in contaminated food is very important for the safety of human health (Gilbert, 1984; Zakrzewski, 1991; Kennish, 1992).

Metal pollutants exist as superficial contaminants on leaflets of date palm thereby, resulting it a suitable biomonitoring indicator for metal pollution in Riyadh and in arid and semi-arid environments (Al-Shayeb et al., 1995). In early 1999s, the highest level of environmental lead pollution was found in central area of Riyadh (Bounessah et al., 2001). Studies regarding the contamination of heavy metals in the fruit of date palm are scanty. Therefore, it is important to study the heavy metals contamination in the fruit of date palm that could presumably be used as a biological indicator of heavy metal pollution so as to decide if it is safe or not for human consumption. During the past few decades, there has been an increase in the use of levels of higher plant as biomonitors of heavy metal pollution in the terrestrial environment (Al-Shayeb et al., 1995; Aksoy and Öztürk, 1997; Due and Kreeb, 1993; Aksoy et al., 2000). The fruit of date palm is highly prone to heavy metals contamination. It would be the first in this regard and a dual approach assessing the environmental pollution using date fruit as an indicator of pollution and evaluating the quality of the fruit on the basis of heavy metal content.

The aim of this study was to determine the concentrations of Pb and Cd in the dust precipitated on the surface of fruits of date palm as well as in the fruit tissue after washing. Further, this experiment was aimed at evaluating the date fruit as a biomonitor of heavy metals (Pb and Cd) pollution in Riyadh, Saudi Arabia in order to assess whether the fruits were safe for human consumption.

2. Materials and methods

Riyadh is the capital of Kingdom of Saudi Arabia and located in the central province (Latitude: 24.7°, Longitude 46.71° and Altitude 635 m), it has an estimated human population of more than four million in 2006 (Riyadh Chamber of Commerce and Industry, 2010)

2.1. Sampling

Fruits were collected from different sites of Riyadh during July to October 2008. Samples were collected at three stages viz. Bisr (about 15 weeks after pollination), Rutab (Semi ripe, about 20 weeks after pollination) and Tamr (fully ripe, about 25 weeks after pollination) from 14 sites: (1) Dammam Freeway-bridge-4, (2) Dammam Freeway-bridge-6, (3) Manakh Garden-1, (4) Manakh Garden-2, (5) Naseriah Road (near gas station), (6) Naseriah Road, (7) Bat-ha-manfooha Road, (8) University Road (Malaz), (9) King Fahad Freeway (Faisalliah), (10) King Fahad Freeway (Near Toyota), (11) King Fahad Freeway, (12) Al-Shafa Highway, (13) Mashtal (Palm Groove) and (14) King Abdulaziz highway and stored in the freezer.

2.2. Washing the dust

To determine the concentration of Cd and Pb in the adhered dust on fruits, the dust was collected from each fruit sample collected from each site. Samples were weighted (80 g at Bisr, 60 g at Rutab and 40 g at Tamr stage) and washed thrice with deionized distilled water (DDW) and the washing residues were collected in a beaker maintaining the final volume up to 150 mL using DDW. All beakers were kept on hot plate for complete dryness. The residue was kept for Cd and Pb estimation. After washing, all fruit samples were again kept for the estimation of Cd and Pb concentrations in the tissue of the fruit.

2.3. Sample preparation

Preparation of the samples (washing residue and the tissue of dates after removal of seeds) was done by adopting the wet washing method of Al-Whaibi (2008) for the estimation of Cd and Pb. All the chemical reagents, used in this procedure, were of analytical grade. The digestion approach was partly modified by Hseu (2004) from that of Zheljazkov and Nielson (1996). One gram of the sample was placed in a 250 mL digestion tube and 10 mL of concentrated nitric acid and perchloric acid in the ratio 2:1 was added. The samples were heated for 45 min at 90 °C; later, the temperature was increased to 150 °C at which the samples were boiled for at least 2–3 h until a clear solution was obtained. Concentrated nitric acid and perchloric acid were added with hydrogen peroxide to the sample (5 mL was added at least three times) and digestion continued until the volume was reduced to about 1 mL. The interior walls of the tube were washed down with a little DDW and the tubes were swirled throughout the digestion to keep the wall clean and prevent the loss of the samples. After cooling, 5 mL of 1% HNO_3 was added to the sample. Thereafter, the solution was filtered using Whatman No. 42 filter paper and < 0.45 μm Millipore filter paper. The filtrate was then transferred to a 25 mL volumetric flask and volume was made up using distilled water. The content of heavy metals (Cd and Pb) was determined by anatomic absorption spectrometer (Perkin-Elmer Model 300).

2.4. Statistical analysis

There were three replicates for each sample. The data were analyzed statistically with SPSS-17 statistical software (SPSS

Inc., Chicago, IL, USA). Mean was statistically compared by Duncan's multiple range test at $P < 0.05\%$ level.

3. Results

A considerable variation was observed with regard to Pb and Cd concentrations in washing residues and fruit tissues of date palm, the differences were significant for different stages of fruit development in the date palm trees growing on different sites of Riyadh, KSA (Tables 1–3).

At Bisr, the levels of metals found in washing residues and the fruit tissues at different sites are presented in Table 1. Mostly, the level of Pb was found to be highest in fruit tissues as compared to washing residues collected from the date palm trees growing in different sites. However, the Cd concentrations were found mostly higher in washing residues than in fruit tissues. The date palm trees grown in Al-Manakh Garden 1 and 2 showed the highest concentration of Pb in washing residues at Bisr stage. However, the lowest concentration of Pb was recorded in plants growing in King Fahad Freeway (near Toyota), followed by that of Naseriah Road (near gas station) and Dammam Freeway-bridge-4. The date palm growing in Naseriah Road and Bat-ha-manfooha Road exhibited the highest concentration of Cd (0.64 and 0.62 $\mu g\, g^{-1}$ dry wt., respectively) in washing residues as compared to plants growing in other sites. However, the content of Cd in washing residues of fruits of date palm growing in King Fahad Road, Naseriah Road (near gas station), Dammam Freeway-bridge-6

Table 1 Concentration of lead and cadmium ($\mu g\, g^{-1}$ dry wt.) in date palm fruit growing in different locations of Riyadh.

Sites name	Fruit stage – Bisr			
	Washing		Flesh	
	Lead	Cadmium	Lead	Cadmium
Dammam Freeway-bridge-4	0.22 ± 0.01 gh	0.38 ± 0.06 bc	1.07 ± 0.51 f	0.10 ± 0.02 bcd
Dammam Freeway-bridge-6	1.46 ± 0.08 d	0.47 ± 0.02 ab	1.87 ± 0.03 abcd	0.12 ± 0.02 bcd
Manakh Garden-1	6.57 ± 0.37 a	0.39 ± 0.07 bc	2.06 ± 0.07 abc	0.13 ± 0.02 bcd
Manakh Garden-2	3.37 ± 0.01 b	0.35 ± 0.06 bcd	2.14 ± 0.03 ab	0.10 ± 0.01 cd
Naseriah Road (near gas station)	0.17 ± 0.01 gh	0.49 ± 0.13 ab	2.29 ± 0.01 a	0.09 ± 0.03 cd
Naseriah Road	2.27 ± 0.07 c	0.64 ± 0.04 a	1.85 ± 0.04 abcd	0.12 ± 0.01 bcd
Bat-ha-manfooha Road	0.78 ± 0.01 e	0.62 ± 0.08 a	1.57 ± 0.10 de	0.08 ± 0.01 d
University Road (Malaz)	0.43 ± 0.04 fg	0.50 ± 0.07 ab	1.40 ± 0.03 def	0.14 ± 0.01 bc
King Fahad Freeway (Faisalliah)	0.72 ± 0.01 ef	0.28 ± 0.04 cd	1.28 ± 0.04 ef	0.14 ± 0.01 bc
King Fahad Freeway (Near Toyota)	0.16 ± 0.01 gh	0.20 ± 0.03 d	1.68 ± 0.06 bcde	0.15 ± 0.01 ab
King Fahad Freeway	0.73 ± 0.01 ef	0.51 ± 0.03 ab	1.35 ± 0.07 ef	0.16 ± 0.01 ab
Al-Shafa Highway	1.51 ± 0.01 d	0.39 ± 0.03 bc	1.63 ± 0.04 cde	0.19 ± 0.01 a
Mashtal (Palm Groove)	ND	ND	1.36 ± 0.08 ef	0.08 ± 0.02 d
King Abdulaziz Highway	0.35 ± 0.01 g	0.19 ± 0.03 d	1.58 ± 0.04 de	0.16 ± 0.02 ab

Each value is a mean of three replicates ($n = 3$) ± SE. Data with the same letter within a column are not significantly different at $P < 0.05$ level as determined by Duncan's multiple range test.
ND, not detected.

Table 2 Concentration of lead and cadmium ($\mu g\, g^{-1}$ dry wt.) in date palm fruit growing in different locations of Riyadh.

Sites name	Fruit stage – Rutab			
	Washing		Flesh	
	Lead	Cadmium	Lead	Cadmium
Dammam Freeway-bridge-4	0.56 ± 0.12 fg	0.78 ± 0.04 d	2.13 ± 0.02 abc	0.17 ± 0.003 ab
Dammam Freeway-bridge-6	1.62 ± 0.36 de	1.03 ± 0.03 b	2.14 ± 0.02 ab	0.17 ± 0.020 b
Manakh Garden-1	8.38 ± 0.59 a	0.32 ± 0.03 g	2.07 ± 0.02 abc	0.19 ± 0.005 ab
Manakh Garden-2	5.10 ± 0.15 b	0.89 ± 0.02 cd	2.20 ± 0.06 a	0.18 ± 0.003 ab
Naseriah road (near gas station)	0.33 ± 0.08 fg	0.99 ± 0.06 bc	1.98 ± 0.05 bcd	0.19 ± 0.002 ab
Naseriah road	3.15 ± 0.50 c	1.19 ± 0.12 a	1.79 ± 0.01 efg	0.19 ± 0.010 ab
Bat-ha-manfooha road	0.79 ± 0.08 fg	0.64 ± 0.03 e	1.69 ± 0.12 fg	0.19 ± 0.015 ab
University road (Malaz)	0.69 ± 0.03 fg	0.56 ± 0.01 ef	1.74 ± 0.05 fg	0.20 ± 0.008 a
King Fahad Freeway (Faisalliah)	0.94 ± 0.03 ef	0.49 ± 0.05 f	2.13 ± 0.12 abc	0.19 ± 0.007 ab
King Fahad Freeway (Near Toyota)	0.24 ± 0.02 fg	0.26 ± 0.00 g	1.63 ± 0.04 g	0.20 ± 0.006a
King Fahad Freeway	0.90 ± 0.04 ef	0.80 ± 0.04 d	1.85 ± 0.02 def	0.19 ± 0.005 ab
Al-Shafa highway	1.84 ± 0.08 d	0.65 ± 0.01 e	2.07 ± 0.06 abc	0.18 ± 0.013 ab
Mashtal (Palm Groove)	0.03 ± 0.02 g	0.05 ± 0.00 h	1.81 ± 0.06 defg	0.11 ± 0.003 c
King Abdulaziz highway	0.50 ± 0.02 fg	0.23 ± 0.01 g	1.95 ± 0.01 cde	0.17 ± 0.008 ab

Each value is a mean of three replicates ($n = 3$) ± SE. Data with the same letter within a column are not significantly different at $P < 0.05$ level as determined by Duncan's multiple range test.

Table 3 Concentration of lead and cadmium (μg g^{-1} dry wt.) in date palm fruit growing in different locations of Riyadh.

Sites name	Fruit stage – Tamr			
	Washing		Flesh	
	Lead	Cadmium	Lead	Cadmium
Dammam Freeway-bridge-4	1.04 ± 0.08 g	0.80 ± 0.05 bcd	1.56 ± 0.01 ab	0.20 ± 0.010 bc
Dammam Freeway-bridge-6	1.43 ± 0.09 f	1.14 ± 0.08 a	1.32 ± 0.65 ab	0.21 ± 0.004 ab
Manakh Garden-1	8.87 ± 0.18 a	0.51 ± 0.02 def	1.30 ± 0.65 ab	0.22 ± 0.002 ab
Manakh Garden-2	4.87 ± 0.12 b	0.74 ± 0.32 cd	0.84 ± 0.76 b	0.21 ± 0.001 ab
Naseriah road (near gas station)	0.34 ± 0.04 h	1.14 ± 0.03 a	2.26 ± 0.02 a	0.21 ± 0.009 bc
Naseriah road	2.03 ± 0.16 e	1.10 ± 0.12 ab	1.82 ± 0.25 ab	0.21 ± 0.004 ab
Bat-ha-manfooha road	0.93 ± 0.09 g	0.90 ± 0.08 abc	2.12 ± 0.03 a	0.21 ± 0.002 ab
University road (Malaz)	0.94 ± 0.05 g	0.66 ± 0.01 cde	2.12 ± 0.03 a	0.23 ± 0.002 a
King Fahad Freeway (Faisalliah)	1.26 ± 0.09 fg	0.49 ± 0.03 def	2.11 ± 0.02 a	0.21 ± 0.013 bc
King Fahad Freeway (Near Toyota)	3.43 ± 0.20 c	0.38 ± 0.02 ef	1.88 ± 0.23 ab	0.21 ± 0.003 ab
King Fahad Freeway	0.96 ± 0.04 g	0.76 ± 0.01 cd	1.97 ± 0.21 ab	0.19 ± 0.003 c
Al-Shafa highway	2.52 ± 0.22 d	0.78 ± 0.03 cd	2.05 ± 0.24 a	0.22 ± 0.003 ab
Mashtal (Palm Groove)	ND	0.07 ± 0.00 g	2.11 ± 0.02 a	0.12 ± 0.003 d
King Abdulaziz highway	0.56 ± 0.04 h	0.24 ± 0.01 fg	1.93 ± 0.22 ab	0.20 ± 0.006 bc

Each value is a mean of three replicates ($n = 3$) ± SE. Data with the same letter within a column are not significantly different at $P < 0.05$ level as determined by Duncan's multiple range test.
ND, not detected.

and University road (Malaz) showed parity with each other. When the level of Pb in fruit tissues of date palm growing in different sites was compared, the maximum Pb content was found in fruit flesh of date palm growing in Naseriah Road (near gas station) as compared to other sites. Moreover, concentration of Pb in the samples collected from Naseriah Road (near gas station) was at par with that of the samples from Manakh-Garden-1 and 2. The highest concentration of Cd (0.19 μg g^{-1} dry wt.) was recorded in fruit tissues of date palm trees growing in Al-Shafa Highway as compared to the other locations. Whereas the lowest concentration of Cd (0.08 μg g^{-1} dry wt.) was recorded in samples collected from Bat-ha-manfooha Road and Mashtal (Palm Groove).

At Rutab stage of fruit, significantly ($P < 0.05$) elevated Pb concentration (8.38 μg g^{-1} dry wt.) was recorded in the washing residues of date palms growing in Manakh Garden-1, whereas the value form Mashtal (Palm Groove) was minimum (0.03 μg g^{-1} dry wt.), as compared to other sites (Table 2). However, the maximum Cd concentration (1.19 μg g^{-1} dry wt.) was recorded in the sample collected from Naseriah Road and the lowest value (0.05 μg g^{-1} dry wt.) was found in Mashtal (Palm Groove) (Table 2). When Pb concentration in tissues of fruits of date palm trees from different sites was compared, it appeared that sample from Manakh Garden-2 had the highest content, while the King Fahad Freeway (Near Toyata) sample had the lowest content. Moreover, the highest levels of Cd (0.20 μg g^{-1} dry wt.) were analysed in samples collected from the University Road (Malaz) and King Fahad Freeway and the lowest level was found in the sample from Mashtal (Palm Groove) (Table 2).

At Tamr stage of fruit, the maximum Pb concentration (8.87 μg g^{-1} dry wt.) was observed in washing residues of sample collected from Manakh Garden-1, whereas minimum (0.34 μg g^{-1} dry wt.) value was recorded in sample collected from Naseriah Rroad (near gas station) as compared to the other sites samples (Table 3). However, the samples collected from Naseriah Road (near gas station) and Dammam Freeway-bridge-6, being at par with that of Naseriah Road and Bat-ha-manfooha Road, exhibited the highest Cd concentration in washing residues, whereas samples from Mashtal (Palm Groove) showed the lowest Cd content (0.07 μg g^{-1} dry wt.) (Table 3). The samples from Naseriah Road (near gas station), Bat-ha-manfooha Road, University Road (Malaz), King Fahad Freeway (Faisalliah), Al-Shafa Highway and Mashtal (Palm Groove) showed similar concentration of Pb in flesh, whereas samples from University road (Malaz), being at par with Dammam freeway-bridge-6, Manakh Garden-1, Manakh Garden-2, Naseriah road, Bat-ha-manfooha road, King Fahad Freeway (Near Toyota) and Al-Shafa highway, exhibited maximum values for Cd concentration in fruit tissues (Table 3).

4. Discussion

In the present study, elevated levels of Pb indicate the increasing industrialization and uncontrolled development of urban areas. The increasing concentration of Pb in date palm samples collected from Manakh Garden might be due to the presence of many industries (cement, porcelain, plastic and wood) as well as heavy traffic emissions within the vicinity of the area. This finding is supported by the work of Al-Shayeb et al. (1995), who reported high level of Pb released in the environment due to the large consumption of leaded fuel by road vehicles. Lead is generally added to the environment by aerial deposition on available surfaces including soil and plants parts. It might be a reason behind the higher Pb content in washing residues than in the tissues of fruit of date palm trees growing in Manakh Garden 1 and 2 (Tables 1–3). At all the stages of fruit development, Pb content in the fruit tissue was found to be higher than in the washing residues in almost all the samples collected from different sites of Riyadh (Tables 1–3). This might be due to the presence of heavy metals in soil and genetic make-up of plants growing in different locations of the city. Delibacak et al. (2002) reported elevated levels of trace elements and heavy metals in the fruits of apple, plum, pomegranate, walnut, watermelon, peach, cherry and grape collected from 12 different sites. However, more detailed

investigation is needed to assess the environmental pollution on the basis of soil contamination and genetic make-up of plants that might perhaps be used as a biomonitoring agent regarding heavy metals pollution. Little (1973) mentioned that metal accumulation could occur either through retention of heavy metals on foliage or through deposition of heavy metals on foliage and uptake from the soil. Metal uptake by plant is one of the main pathways through which metals enter the food chain. The accumulation of heavy metals varies with plant species (Antonious and Snyder, 2007; Melo et al., 2007; Antonious and Kochher, 2009). Motto et al. (1970) have shown that the uptake of lead by plants in the greenhouse is through the root system but in the field it is mostly through the leaves. They suggested that the uptake of Pb by plants from the soil was related to the soluble part of Pb in the soil and not to the total Pb in the soil. The results indicate that the amount of Pb removed by washing the fruits in water was higher than that percent in the fruit tissue, indicating that atmospheric deposition of Pb and other metals differs greatly in these areas. Ahmed and Al-Swaidan (1993) exhibited that the mean Pb and Cd levels in industrial areas of the city were 208 and 2.8 μg/g, whereas in rural areas these levels were 106 and 1.6 μg/g, respectively.

The concentration of Cd was recorded to be higher in washing residues than in the fruit tissues at all the stages of fruit development in the samples collected from different sites of Riyadh and its level is statistically not greatly different among the samples of the different sites (Tables 1–3). According to Ahmed and Al-Swaidan (1993), Cd level in industrial areas was 78 times lower than the Pb levels in Riyadh. The present study also revealed that level of Cd was very low as compared to that of the Pb. The variation in Cd level occurring among the samples collected from different sites might be due to the uptake capacity of plant that depend on the genetic make-up of plant and on the heavy metals content in the soil.

5. Conclusion

As per the results obtained, it is concluded that washing residues and fruit tissue of date palm contained considerable amounts of Pb and Cd. The concentration of Pb in dust and the tissue of date palm fruits increased with increasing anthropogenic sources and activities. There is probability that fruits of date palm may be used as bioindicator for pollution and may be recommended for its consumption after washing as human health safety measure. The results, however, indicate that the fruits of date palm contained the concentration of heavy metals within the safe limits (FAO/WHO, 2001) (Banerjee et al., 2010).

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