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Trace element levels in some kinds of dates

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Abstract

Trace elements, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Na Ni, Pb and Zn were determined in 18 date samples purchased from different localities of Saudi Arabia (Madinah, Al-Laith, Yanbu, Al-Ahsaa Najran, Besha, Riyadh and Al-Kasseem). The dried powdered samples were digested in HNO_3–$HClO_4$ acid mixture, and element concentrations were determined with a recording atomic absorption spectrophotometer. The results were in the ppm range 1413–4340 (Ca), 0.05–0.74 (Cd), 0.06–0.11 (Co), 0.02–1.45 (Cr), 0.11–0.65 (Cu), 0.44–7.94 (Fe), 8872–19000 (K), 925–2800 (Mg), 0.10–0.51 (Mn), 5–184 (Na), and 0.22–2.02 (Zn). However, Ni reached 0.21, 0.19 pp for Succari and Safawi only, and Pb was not detected. Ni and Pb may not be present in the date samples or may need a more sensitive method for measurement.

1. Introduction

Trace elements play a vital and important role in chemical, biochemical, physiological, metabolic, synthetic and enzymatic reactions in living cells (plants, animals, and human beings). A number of papers have dealt with trace elemants in Egyptian crops fruit vegetables and dates (Sherif, 1978; 1979; Sherif Awadallah & Amrallah, 1980) [the concentration of these metals in some Egyptian dates called Abrimi (Estimated by neutron activation analysis) were: Ca: 0.14%, Cd: 0.13, Co: 0.40, Cr: 0.41, Cu: 1.9, Fe: 38.85 ppm K: 0.77%, Mg: 0.07%, Mn: 3.89 ppm, Na: 0.005%, Ni: 0.39, and Zn: 3.9 ppm]. Egyptian cane sugar and molasses (Awadallah, Sherif, Mohamed & Grass, 1984, 1985, 1986; Mohamed, 1986; 1999; Mohamed, Awadallah & Hassan, 1989), Fish, Awadallah, Ismail and Mohamed (1995), Nile water and Nile mud sediments (Awadallah, Mohamed & Gabr, 1985; Awadallah, Ismail, Abd El-Aal, Soltan, 1993; Awadallah, Ismail, Arifen, Moalla & Grass, 1994).

The present work is targeted to assay trace element levels in different types of dates, to find ecological and environmental relationships between trace elements in different types of Saudi Arabian dates, and to collect information on the safety and hazardous baseline levels of trace elements, applying atomic absorption spectrophotometric techniques.

2. Materials and methods

All chemicals used were of A.R. grade (99.99%) and purchased from BDH, Aldrich Sigma and E. Merck. Eighteen date samples of different types and different origins were collected from different localities. These include various provinces in the Kingdom of Saudi Arabia: Western Provence [Madinah (local names of dates, Hadrami, Succari, Lubana, Shalabi, Mabroom, Burhi, Rabeah, Safawi and Beed); Al-Laith (local name: Qassab); Yanbu (local name: Barni Al-Issa)] Eastern province [Al-Ahsaa (local name: Balah and Sufferi)], Southern province [Najran (local name: Helwa); Besha (local name: Sufferi and Surrey)] and Central province [Riyadh (local name: Naboot Al-Saif), Al-Kasseem (local name: Al-Sagei)].

Certified atomic absorption spectroscopic standard solutions (1 mg/ml) for Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn were purchased from BDH (UK). Working standard solutions were prepared by appropriate dilution of the the stock solutions and biological standards (Backer, Veglia & Scmidt, 1974) [Bown's kale (BK), Orchard Leaves (OL), and Tomato Leaves (TOML)], as well as the certified atomic absorption spectroscopic standards, were used to check the accuracy of the results.

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2.1. Samples preparation

The different date samples, after removing seeds (interior pulp), were washed several times with tap water, then with deionized water, and finally with thrice-distilled water. The samples were dried on filter papers then in an electrical furnace at 105°C for 12–24 h to remove water. After dryning and cooling, the dried samples were crushed, powdered using a mechanical agate mortar, and kept in polyethylene bottles.

Two portions of 5g each of dried date samples were wet ashed in a 250 ml Teflon beaker using 50 g of 1:1 concentrated HNO_3–$HC1O_4$ acid mixture, followed by the addition of few drops of hydrofluoric acid. The beaker was placed on a sand bath and heated until the acid fumes ceased to evolve. Near dryness, the beaker was removed from the sand bath and left to cool; then a 10 ml portion of the acid mixture was added to the beaker containing the sample, and heated again until complete digestion. After cooling, the clear solution was transferred into 50 ml volumetric flask and completed to the mark using thrice-distilled water.

2.2. Analytical determinations

A recording flame atomic absorption spectrophotometer, Perkin–Elmer, Model 603, digital, direct readout of the concentration, was utilized for Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, measurements using element hollow cathode lamps. An atomic absorption spectrophotometer, Perkin–Elmer HGA-600 carbon furnace was utilized for K and Na measurments.

3. Results

The results obtained from analysis of the date samples are recorded in Tables 1–6. The results show the relationships between metal (Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb and Zn) concentrations in different date samples and localities. Table 1 shows the metal concentrations in nine date samples cultivated in Madinah district (Western Saudi Arabia); low water content appears in date type succari, and high in type Beed. High concentrations of Ca, Cd, Co, K and Mg appear in type

Table 1
Trace element concentrations in Saudi Arabian dates cultivated in Madinah district (by AAS)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Hardrami	1413	0.20	0.0	0.09	0.16	4.72	11 865	1375	0.21	15	0.0	0.0	0.34	33.70
Succari	2648	0.49	0.52	1.45	0.41	1.94	14 025	1800	0.35	184	0.21	0.0	0.78	22.10
Lubana	4340	0.74	0.63	0.09	0.28	0.0	19 000	2550	0.24	87	0.0	0.0	0.22	29.50
Shalabi	1545	0.30	0.27	0.24	0.48	3.60	8872	925	0.21	5	0.0	0.0	0.36	27.30
Mabroom	2175	0.25	0.18	0.09	0.24	0.0	17 050	1375	0.51	72	0.0	0.0	0.30	37.70
Burhi	1760	0.15	0.19	0.02	0.20	0.0	10 937	1300	0.50	22	0.0	0.0	0.57	30.10
Rabeah	2693	0.22	0.42	0.16	0.24	0.0	15 072	1850	0.49	173	0.0	0.0	0.42	58.50
Safawi	1840	0.66	0.35	1.45	0.44	1.00	17 977	2100	0.10	20	0.19	0.0	0.29	28.40
Beed	3020	0.05	0.48	0.09	0.52	0.0	12 235	1275	0.49	159	0.0	0.0	0.48	57.20

Table 2
Trace element concentrations in Saudi Arabian dates cultivated in Western district (Al-Laith and Yanbu) (by AAS)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Qassab	2261	0.27	0.37	0.16	0.65	0.0	15 090	2350	0.23	127	0.0	0.0	0.02	21.20
Barni-Al Issa	3070	0.16	0.55	0.09	0.31	0.0	7852	2125	0.32	103	0.0	0.0	0.34	22.30

Table 3
Trace element concentrations in Saudi Arabian dates cultivated in Eastern district (Al-Ahsaa) (by AAS)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Balah	1870	0.47	0.54	0.52	0.37	7.94	7340	2275	0.28	135	0.0	0.0	0.52	27.40
Suffuri	3553	0.39	0.48	0.02	0.18	0.0	16 545	2050	0.28	47	0.0	0.0	0.17	33.70

Table 4
Trace element concentrations in Saudi Arabian dates cultivated in Southern district (Najran and Besha) (by AAS)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Helwa	5353	0.57	0.84	0.09	0.22	0.0	9570	2600	0.23	19	0.0	0.0	0.39	28.50
Suffuri	2728	0.25	0.25	0.09	0.37	0.0	17 965	1750	0.35	24	0.0	0.0	0.42	22.80
Surry	1863	0.0	0.0	0.16	0.33	0.0	16 982	1072	0.41	27	0.0	0.0	0.31	38.40

Table 5
Trace element concentrations in Saudi Arabian dates cultivated in Central district (Riyadh and Al-Kasseem) (by AAS)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Naboot Al-Saif	3138	0.05	0.41	0.02	0.11	0.0	17 700	2800	0.21	71	0.0	0.0	0.28	34.40
Al-Sagei	2815	0.0	0.11	0.09	0.22	0.0	9465	2675	0.35	0.0	0.0	0.0	0.25	25.90

Table 6
Comparison between metal concentration in two date samples cultivated in two different district (Al-Ahsaa) and Southern (Besha)

Date type	Metal concentrations (ppm)													H_2o
	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	(%)
Al-Ahsaa	3553	0.39	0.48	0.02	0.18	0.0	16 545	2050	0.28	47	0.0	0.0	0.17	22.80
Besha	2728	0.25	0.25	0.09	0.37	0.0	17 965	1750	0.35	24	0.0	0.0	0.42	33.70

Lubana, but Cr, Na, Ni and Zn are concentrated in Succari. Cu is concentrated in type Shalabi and Fe more concentrated in Hadrami (4.72 ppm); this variation may be related to the ability of the date trees to absorb metals from the soil and concentrate them in the dates.

Table 2 shows the metal concentrations in two date samples cultivated in south-western district of Saudi Arabia (Qassab in the Al-Laith district, and Barni Al-Issa in Yanbu district). Water content seems to be nearly the same in the two samples, but Cd, Cr, Cu, K, Mg, Na and Zn are concentrated in Qassab, and Ca, Co and Mn are concentrated in Barni Al-Issa. Fe, Ni and Pb are not detected. These metals may be absent in the dates, or may need another analytical method to determine whether their concentrations exist at a level less than the detectable limit.

Table 3 shows the metal concentrations in two date samples (Balah and Suffuri) cultivated in the eastern district (Al-Ahsaa). It is noticeable that all metals are concentrated in type balah, except Ca, K and water content is high in type Suffuri; this may be due to the ability of type Balah to absorb the metals and concentrate them more than type Suffuri.

Table 4 shows the metals concentrations in three dat sample cultivated in the Southern district (Najran and Besha). The higher water content (38.4%), and higher concentrations of Cr, Mn, and Na appear in type Surrey, while Ca, Cd, Co and Mg are higher in type Helwa, and Cu, K and Zn are higher in type Suffuri. However, Fe, Ni and Pb disappear in all samples.

Table 5 shows the data obtained for the metal concentrations in two date samples cultivated in the central district (Riyadh and Al-Kasseem). From the data it is clear that, most of the estimated elements are concentrated in type Naboot Al-Saif (Riyadh district) and also the water content, but Cu and Mn are concentrated in type Al-Sagai (Al-Kasseem district).

Table 6 shows a comparison between metal concentrartions in two Suffuri date samples cultivated in two districts, one from the Eastern (Al-Ahsaa) and one from the Southern (Besha). Water contents of dates from Al-Ahsaa are lower than in those of Besha. Ca, Cd, CO are Mn and Na are more concentrated in Al-Ahsaa samples, and Cr, Cu, K, Mn and Zn are more concentrated in Besha samples. Fe, Ni and Pb disappear. This variation of metal concentrations in the same date type may be related to variations in texture, structure, chemical and mineral composition of soil in these districts.

4. Discussion

The existence of trace elements, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn in the investigated date samples indicates their valuable, important and essential vital roles for plant growth as well as, animals and humans (Russel, 1973). Different water contents may be largely related to the degree of ripeness and different environments. Dates of high water contents possess hydrophobic properties (storing of water). The results show that metal concentrations are within the safety baseline levels (according to the international standards limits). Most of these elements are essential activators for enzyme-catalyzing reactions. For example, Mn plays a structural role in the chloroplast membrane system and may be responsible for colour, taste and smell, and a cofactor for fatty acids, DNA and RNA synthesis (Gibbs, 1978). Cobalt causes substantial catalytic activity, and is essential for nitrogen fixation in addition to its usefulness as vitamin B_{12} (Russel, 1973). Fe and Cu may exist as Fe and Cu proteins. Iron is an essential activator for enzyme-catalysing reactions involving chlorophyl synthesis and for ferrodoxin nitrate reductase (Bowling, 1976). Chromium is essential for hair growth, for increasing glucose tolerance, and has a vital function for mammalian sugar metabolism in preganacy (Gibbs, 1978). Potassium is an essential nutrient and has an important role in the synthesis of amino acids and proteins (Malik, 1982). Ca and Mg play a significant role in photosynthesis, carbohydrate metabolism, nucleic acids, and binding agents of cell walls (Russel, 1973). Zn is an esstial micronutrient and is associated with a number of enzymes, especially those for synthesis of ribonucleic acids (Oser, 1979). From the above, the existence of these trace elements in dates underlines the usefulness of dates for human beings, especially in Arabic countries.

4.1. Statistical analysis of data

Statistical analysis shows significant correlation coefficient values ($r = 0.757$–0.999). The results give a new picture of significant (due to proportionality, i.e. as one element increases the other increase), and negative (ion antagonism) correlation coefficients in dates, arising from ion absorption and uptake of essential trace elements by the date tree from the surrounding soil solution.

Negative correlation coefficient values ($r = -0.99$ to -0.053) in dates give new information about the ion antagonism (anticorrelations) and the deficiency or excess of some element in the soil solution. Negative correlations may be ascribed to a result of counteraction, blocking, stunting, interlocking or due to the effect of some elements on the mobility and on the absorption (uptake) of the other elements remaining in the surrounding soil solution (Bowling, 1976). Significant correlations may also be ascribed to proportional relationships between trace elements (as one element increases, the others increase together), leading to increase the mobility of these elements which facilitate their uptake into the plants. Statistical analysis clarifies the relationship between these elements; for example, if Ca increases, Mg increases.

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