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Physico-Chemical Characteristics of Pollinated and Non Pollinated Date Fruit of District Khairpur, Sindh, Pakistan

Ghulam Qadir Shar[1], Abdul Hafeez Memon[1], Pirbho Mal J. Makhija[2], Shamroz Bano Sahito[1] and Wahid Bux Jatoi[1]

[1]*Department of Chemistry, Shah Abdul Latif University, Khairpur, Pakistan*
[2]*Ghulam Mohammad Mahar Medical College, Sukkur, Sindh, Pakistan*

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Abstract

Elemental patterns are often used for the classification or identification of date fruit varieties. Five ripening stages of six date varieties were collected and studied from the pre ripening to the post ripening stage. Pollinated and non-pollinated date fruit of the same varieties were compared for their physical and chemical parameters. Physical parameters such as size, mass, colour, moisture, and pH were measured. In case of chemical characteristics the mineral composition of six different varieties of district Khairpur dates palm (*Phoenix dactylifera* L.) fruit (Gorho, Asul Khurmo, Nur Aseel, Ghuray Wari, Toto, and Allah Wari) were analysed using Atomic Absorption Spectroscopy (AAS). Generally, size, moisture and mineral content of the pollinated fruit increased up to 3rd and 4th stage then declined.

Keywords: Date palm fruit; Essential metals; *Phoenix dactylifera*

Introduction

Date palm belongs to family Arecaceae, sub-family Coryphoideae, tribus Phoeniceae, genus Phoenix and species Phoenix dactylifera. It is commonly known as *Phoenix dactylifera* L.

There are 202 genera and 2600 species of the date palm, most of which are grown in tropical, subtropical and warm temperate climates. All of these palms are distinguished by their physical appearance such as bark, stem and leaves.

The importance of date fruit is based on their utility and ingredients, which are essential for the human being health. On the basis of these ingredients, it has high religious impact and is extensively cultivated. Most of the religious people use date fruit in their religious traditions and it is a part of cultural food that is used with breads. It is used for the preparation of different type of sweets along with other fruit to form delicious cakes. Besides this, extracts of date fruit is used in place of honey and high concentrated sucrose. It is also used for medical purpose as Hakims (local practioners) are forming herbal formulae from various parts of date plant.

Essential elements play a vital and important role in chemical, biochemical, physiological, metabolic, synthetic and enzymatic reactions in living cells (plants, animals and human beings). There are many papers in Pakistan which are concerned with the study of minerals in various crops including fruits, vegetables and dates. In this connection, physico-chemical characteristics of five date fruit cultivars grown in the United Arab Emirates are reported [1]. Comparative study was reported on composition of commercial indigenous and imported date varieties [2]. Mineral ion content of the seeds of six cultivars of Bahraini

*Corresponding Author Email: drgq_khp@yahoo.com

date palm was also investigated [3]. Besides this, trace element levels in some kinds of dates were determined [4, 5]. Polysaccharides of the date fruit containing glucan act as an anti-cancer agent in human beings [6-12]. Date fruit is a potential anti-oxidant for the treatment of cerebral ischemia [13]. Date fruit is commonly used all over the world due to its biological importance for human being for its anti-oxidant and anti-mutagenic properties [14]. The analytical study of date palm seed shows that it has also similar nutrient value to that of date flesh [15-16]. The chemical study of date fruit was carried out by various researchers [17-20]. The concentration of metals in some Egyptian dates called Abrimi (Estimated by neutron activation analysis) was: 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.

Twenty different Fruits and twenty vegetables were analyzed for determination the content of essential elements that are necessary for maintaining health [21].

Essential nutrient elements are needed in bulk quantity to regulate number of biochemical processes and trace and toxic nutrient elements required in minute level because they have dietary benefits but some of heavy metals like Cd, Cr, Ni, As, Hg are highly toxic in nature for human if their quantity exceeds than that of permissible limit [22-24]. Various studies have shown that deficiency or excess of certain heavy nutrient elements may be linked with permanent or interminable illness such as diabetes, hepatitis and cancer etc [25]. The study of heavy metals such as Pb, Cd and Cr in diabetes and cancer patients was carried out as compared to normal persons [26]. Analytical work was also carried out on polluted and non-polluted *Marsilea minuta* plants for the biological activity of Cd and Cr [27].

The aim of the present work was to check the physico-chemical characteristics of pollinated and non pollinated date fruit at different stages of district Khairpur, Sindh, Pakistan, and to collect information on the safety and hazardous baseline levels of trace elements, applying atomic absorption spectrophotometric technique.

Materials and Methods

All chemicals used were of A.R. grade (99.99%) and purchased from BDH, Aldrich Sigma and E. Merck. Six date samples of different types and different origins were collected from different localities. These include various gardens in the District Khairpur, Sindh, Pakistan. The local names of dates include Ghuray Wari, Toto, Allah Wari, Gorho, Asul Khurmo and Nur Aseel. Certified atomic absorption spectroscopic standard solutions (1 mg/ml) for K, Mg, Ca, Na, Fe, and Zn were purchased from BDH (UK). Working standard solutions were prepared by appropriate dilution of the stock solutions and biological standards [21]. [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.

Samples preparation

The different date samples, after removing pericarps and seeds (out side and interior pulp respectively), were washed several times with tap water, then with deionized water, and finally with triply de-ionised water. The samples were dried on filter papers then in an electrical furnace at 105 ^{0}C for 12-24 h to remove water. After drying and cooling, the dried samples were crushed and powdered using a mechanical agate mortar, and kept in polyethylene bottles. Triplicate flasks were prepared for the same sample by adding 2g in each of the conical flask along with blank. Dried date samples of different varieties were wet ashed in a 100 ml conical flasks of Pyrex manufactured, by adding 5-8 ml concentrated HNO_3 acid followed by the addition of 3-5 ml of hydrogen peroxide. Depending upon the stage of the date fruit, finally was covered with watch glasses. The conical flasks were placed on a hot plate and heated until the acid fumes ceased to evolve. When it was near to get dried, the conical flasks were removed from the hot plate and left to cool; then a same portion of acids were added to the conical flasks containing the sample, and heated again until complete digestion. After cooling, deionized water was added and filtered on Whatman # 42 filter paper, the clear solution was transferred into 25 ml

volumetric flask and made to the mark using deionized water.

Analytical determinations

Prior to analysis, all instruments were calibrated according to manufacturer's recommendations. pH was measured by using Mettler Toledo MP 220 digital pH meter with combined glass electrode. Samples were weighed by balance AB 204-S made up by Mettler Toledo. A Perkin-Elmer Analyst 100 model atomic absorption spectrometer equipped with deuterium background correction and connected with computer and printer was used for the essential metal determinations such as K, Mg, Ca, Na, Fe, and Zn. Hollow cathode lamps (made by Perkin Elmer Company) of K, Mg, Ca, Na, Fe, and Zn, were used as radiation source. Air- acetylene gas was used as a fuel during atomization step of K, Mg, Ca, Na, Fe, and Zn.

Statistical analysis of data

Statistical analysis shows significance 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 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 (anti-correlations) and the deficiency or excess of some element in the soil solution. Negative correlations may be ascribed to a result of counter- action, 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.

Results and Discussion

Physical Characteristics

Size of date fruit at various ripening stages

Table 1 shows the size of the six date varieties cultivated in district Khairpur; low size (i.e., length and width) appears in the 1st stage of all date types. Large size appears in the 4th stage of Ghuray Wari, Allah Wari, Gorho, and Nur Aseel and then declined at 5th stage in case of pollinated except the length of Allah Wari. All varieties in case of non-pollinated possess the maximum size at 5th stage. The size of the pollinated Toto, Allah Wari and Asul Khurmo increases up to the final stage (post ripening stage), because these are late ripening varieties, they continuously absorb water and minerals and increase in size. Overall, the length of six varieties in five stages was found to be higher than their size as compared to other stages.

The comparative study of the size in case of pollinated and non pollinated (Table 1) shows that Ghuray Wari variety increased in length from1st to 3rd stage and decreased from 4th to 5th stage in pollinated, where as in non-pollinated, it is going to be increased up to the 5th stage. However length of non-pollinated is higher in 4th and 5th stage as compared to the pollinated. Nur Aseel size in pollinated increases, which is terminated at 4th stage and it is continuously increasing in non-pollinated up to the 5th stage, where as size of 5th stage of non-pollinated is higher than pollinated. Length of Toto cultivar is maximum at 1st to 2nd stage in pollinated and then minimum at 3rd to 5th stage as compared to non-pollinated where as the width of the pollinated gradually increases up to the last stage compared to non-pollinated date fruit. Allah Wari, Gorho and Asul Khurmo possess higher size (i.e., length and width) in pollinated than that of non-pollinated fruit from pre-mature to post maturing stage.

Water content at various ripening stages

Table 1 shows the percentage of water content of the six cultivars at five sampling stages. The percentage of water content decreases in pollinated and non-pollinated but higher percentage of water decline was observed in pollinated than non-pollinated as fruit reaches to

post ripening stage. This may be due to conversion of water into sucrose by the action of CO_2 in the presence of sun light. This photochemical reaction utilized more water content in pollinated rather than non-pollinated. High percentage of water decline was found in decreasing order; Ghuray Wari > Gorho > Allah Wari > Nur Aseel > Toto > Asul Khurmo as the fruit proceeded towards the maturing stage.

Table 1. **Physical Parameters (Length and Width in cm) of six date cultivars grown in district Khairpur (Mirs), Sindh, Pakistan**

Varieties		1st Stage		2nd Stage		3rd Stage		4th Stage		5th Stage	
		P	NP	P	NP	P	NP	P	NP	P	NP
Ghuray wari	Length	3.05	2.58	3.13	3.02	3.23	3.4	3.25	3.47	3.15	3.3
	Width	1.72	1.23	1.75	1.47	1.82	1.58	1.83	1.68	1.8	1.82
	A.Wt. FF	5.867	2.37	5.917	2.903	6.327	3.543	6.527	3.75	6.05	3.993
	% W	75.51	79.04	69.58	77.61	45.94	76.86	37.18	74.22	29.59	73.71
Toto	Length	3.2	3.1	3.78	3.37	3.9	4.12	4.02	4.2	4.33	4.42
	Width	2.17	1.88	2.3	1.93	2.35	2.03	2.38	2.07	2.5	2.3
	A.Wt. FF	7.103	5.79	10.77	6.927	11.31	8.07	12.18	8.447	14.65	10.33
	% W	83.67	85.03	78.14	84.55	64.41	82.36	57.09	76.56	42.32	74.89
Allah wari	Length	2.77	1.63	3.23	1.87	3.93	2.17	3.95	2.32	3.98	2.83
	Width	1.73	1.23	1.92	1.4	2.33	1.52	2.4	1.57	2.33	1.8
	A.Wt. FF	4.767	1.653	6.813	1.743	11.07	2.307	12.21	3.3	12.01	3.783
	% W	83.36	84.88	79.26	80.5	61.92	78.32	53.81	67.07	38.88	65.2
Gorho	Length	2.3	2.08	2.88	2.32	3.5	2.53	3.58	2.73	3.07	3
	Width	1.87	1.43	2.08	1.6	2.37	1.77	2.4	1.88	2.25	2.08
	A.Wt. FF	4.413	2.097	6.757	2.627	10.45	3.073	10.69	3.877	8.54	5.337
	% W	77.19	77.58	73.31	75.76	68.69	75.27	55.04	73.43	36.85	70.08
Asul Khurmo	Length	3.05	1.85	3.75	2.02	3.95	2.18	3.98	2.33	4.02	2.87
	Width	1.85	1.05	2.23	1.12	2.4	1.23	2.42	1.3	2.48	1.55
	A.Wt. FF	5.19	1.093	9.693	1.27	11.09	1.34	11.4	1.71	12.85	3.253
	% W	84.91	86.59	81.95	85.3	76.1	82.84	63.49	80.31	54.94	76.54
Nur Aseel	Length	3.18	2.98	4.23	3.48	4.57	3.67	4.6	4.2	3.95	4.27
	Width	2.33	1.82	2.78	2.05	2.88	2.28	3.12	2.65	2.4	2.73
	A.Wt. FF	9.1	5.127	17.21	6.987	20.02	9.153	23.62	12.51	13.36	13.52
	% W	82.82	82.38	80.69	80.73	63.56	72.8	58.89	72.19	40.45	68.86

P= Pollinated
NP= Non Pollinated
A.Wt. FF= Average weight of fresh fruit
% W= percentage of water

Colour at various ripening stages

The colour of Ghuray Wari changes from green to slightly red, Allah Wari green to yellowish, Toto and Gorho green to redish yellow, Asul Khurmo and Nur Aseel green to yellow during initial to ripening stage.

pH at various ripening stages

pH of pollinated fruit was found to be greater than non-pollinated and it increases in all five stages and six cultivars from 1st to 5th stage of sampling. High level of pH (6.01) was found in 5th stage of pollinated Asul Khurmo and low level (4.24) in 1st stage of non-pollinated Toto cultivar.

Chemical characteristics

The results obtained from analysis of the date fruit samples are recorded in Tables 2a and 2b. The results show the relationship between metal (K, Mg, Ca, Na, Fe, and Zn) concentrations in different date samples at different stages. Table 2a & 2b shows the metal concentrations in six date samples cultivated in Khairpur district (Sindh, Pakistan). High concentration of K appeared in Asul Khurmo (P) in 1st & 3rd stage and its high concentration appeared in 4th & 5th stage of Allah Wari (NP), low concentration detected in Ghuray Wari (NP). Maximum values of K in Asul Khurmo (P) and Ghuray Wari (P) indicates that their values were close to each other whereas minimum values were observed in Ghuray Wari (NP) and Gorho (NP) and their values were also close to each other. The level of K in different ripening stages of date fruit was found in decreasing order:

Table 2a. **Concentration (mg/kg) of Essential Macro Elements in Date Fruit Varieties**

		Name of the Date Fruit Variety																	
		Ghuray Wari						Toto						Allah Wari					
		Pollinated			Non Pollinated			Pollinated			Non Pollinated			Pollinated			Non Pollinated		
Stages	Element	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD
1st	K	12235	182	1.49	6319.3	38.6	0.61	11533	85.1	0.74	7272.9	91.4	1.26	8917.3	84.6	0.95	9325.7	38.1	0.41
	Mg	1229.3	21.7	1.77	857.7	4.45	0.52	1787.5	30.2	1.69	1290.3	14.6	1.14	1465.2	27.2	1.86	1114.0	8.63	0.78
	Ca	828.7	8.97	1.08	521.6	5.06	0.97	881.8	5.15	0.58	580.0	8.13	1.40	1165.1	5.63	0.48	804.6	5.53	0.69
	Na	128.6	3.29	2.56	128.2	3.73	2.91	162.7	2.16	1.33	208.7	2.71	1.30	121.8	1.87	1.53	165.6	0.62	0.78
	Fe	30.9	1.14	3.70	27.1	1.18	4.37	37.7	1.31	3.48	54.2	1.83	3.37	30.3	0.87	2.86	26.7	0.98	3.69
	Zn	34.3	0.17	0.60	24.0	0.43	1.80	23.2	0.33	1.42	17.9	0.16	0.91	18.1	0.30	1.63	13.5	0.37	2.73
2nd	K	11406	173	1.52	7587.4	45.3	0.60	9196.0	127	1.38	7459.5	72.2	0.97	9687.2	116	1.20	10727	59.0	0.55
	Mg	1507.9	17.5	1.16	1211.9	26.4	2.18	1349.8	12.5	0.93	1004.2	6.06	0.60	1026.6	7.97	0.78	1303.6	18.3	1.41
	Ca	767.1	9.11	1.19	720.8	4.17	0.58	854.0	8.51	1.00	846.2	4.96	0.59	977.2	8.36	0.86	1138.3	2.25	0.20
	Na	167.7	1.24	0.74	139.0	3.23	2.33	173.9	3.46	1.99	202.9	3.46	1.71	125.4	2.71	2.16	171.0	2.24	1.31
	Fe	54.9	1.64	2.97	34.7	0.98	2.84	54.0	1.50	2.79	52.5	0.87	1.65	41.5	1.14	2.74	51.9	2.56	4.94
	Zn	21.5	0.21	0.95	16.9	0.66	3.89	19.4	0.26	1.35	16.3	0.42	2.57	16.2	0.13	0.77	12.8	0.30	2.30
3rd	K	12251	218	1.78	8005.3	76.2	0.95	7682.5	39.4	0.51	7791.7	128	1.64	6803.4	28.5	0.42	12591	36.7	0.29
	Mg	1319.3	5.20	0.39	1023.8	7.71	0.75	1297.3	8.76	0.68	872.2	6.73	0.77	833.2	14.8	1.77	1208.2	10.7	0.89
	Ca	734.1	5.40	0.74	692.3	10.6	1.53	645.6	10.1	1.57	717.1	4.47	0.62	783.1	6.11	0.78	1019.0	9.58	0.94
	Na	123.2	3.46	2.81	134.0	2.71	2.02	114.9	1.65	1.43	196.8	1.24	0.63	97.7	2.24	2.30	141.9	2.24	1.58
	Fe	28.4	0.98	3.46	41.7	1.18	2.84	29.0	0.57	1.96	34.1	1.14	3.33	57.4	2.05	3.57	31.4	0.33	1.04
	Zn	18.7	0.36	1.90	16.2	0.14	0.88	20.7	0.19	0.91	13.3	0.26	1.98	10.4	0.13	1.28	9.15	0.08	0.89
4th	K	6308.1	56.4	0.89	8982.4	146	1.63	5143.8	70.1	1.36	9622.7	49.8	0.52	6196.0	74.0	1.19	10895	86.4	0.79
	Mg	1040.4	8.16	0.79	928.8	24.0	2.59	873.3	46.8	5.36	827.9	26.9	3.25	649.9	36.1	5.55	816.7	8.64	1.06
	Ca	557.5	3.28	0.59	502.6	4.96	0.99	501.4	7.49	1.49	629.4	5.51	0.88	515.5	6.04	1.17	1147.8	8.13	0.71
	Na	103.1	2.71	2.63	155.2	3.89	2.50	185.3	1.08	0.58	215.9	4.98	2.31	133.6	2.16	1.61	160.9	2.49	1.55
	Fe	26.3	0.66	2.49	53.0	1.43	2.70	27.8	1.14	4.08	33.5	0.57	1.70	43.6	1.43	3.28	36.7	0.33	0.89
	Zn	10.2	0.17	1.67	13.5	0.33	2.44	11.9	0.17	1.43	13.2	0.22	1.64	7.46	0.17	2.28	9.64	0.22	2.24
5th	K	6296.9	45.3	0.72	6938.4	128	1.85	5014.1	12.2	0.24	6790.5	128	1.88	4348.0	35.7	0.82	8909.6	76.4	0.86
	Mg	652.1	16.6	2.54	638.7	9.83	1.54	703.4	13.9	1.97	788.7	31.2	3.96	507.2	5.15	1.02	557.2	3.11	0.56
	Ca	426.2	2.60	0.61	441.7	4.65	1.05	385.1	6.55	1.70	391.7	3.15	0.80	357.7	3.15	0.88	656.6	2.73	0.42
	Na	113.5	1.65	1.45	163.1	3.29	2.02	206.9	3.41	1.05	201.9	0.75	0.37	112.1	2.85	2.54	127.2	2.85	2.24
	Fe	18.4	0.33	1.77	19.1	0.87	4.54	25.2	0.87	3.45	25.4	0.33	1.29	13.3	0.87	6.55	28.2	0.86	3.07
	Zn	6.1	0.21	3.37	12.2	0.28	2.31	9.56	0.08	0.86	11.8	0.26	2.23	4.96	0.13	2.52	6.0	0.33	4.08

1st Sampling = 01-06-2005 2nd Sampling = 15-06-2005 3rd Sampling = 01-07-2005 4th Sampling = 16-07-2005
5th Sampling = 02-08-2005

Table 2b. **Concentration (mg/kg) of Essential Macro Elements in Date Fruit Varieties**

Stages	Element	Name of the Date Fruit Variety																	
		Gorho						Asul Khurmo						Nur Aseel					
		Pollinated			Non Pollinated			Pollinated			Non Pollinated			Pollinated			Non Pollinated		
		Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD
1st	K	9099.2	107	1.18	6488.3	61.5	0.95	12638	20.9	0.17	8092.7	63.3	0.78	10182	23.2	0.23	6628.5	60.0	0.91
	Mg	1801.8	29.6	1.64	930.1	23.7	2.54	1615.7	26.9	1.67	949.8	3.80	0.40	1336.9	34.9	2.61	1052.4	4.23	0.40
	Ca	507.3	9.09	1.79	392.3	4.49	1.15	877.9	8.97	1.02	640.1	2.41	0.38	951.8	6.49	0.68	606.2	4.39	0.72
	Na	194.1	2.18	1.12	130.7	1.65	1.26	190.7	3.23	1.70	115.7	4.36	3.77	164.5	4.36	2.65	113.5	1.65	1.45
	Fe	59.7	0.57	0.95	45.8	1.18	2.58	34.7	0.98	2.84	28.8	1.18	4.11	26.9	1.18	4.40	30.5	0.66	2.15
	Zn	15.9	0.08	0.51	14.7	0.37	2.51	14.4	0.13	0.87	14.9	0.24	1.58	20.3	0.29	1.45	16.1	0.33	2.04
2nd	K	9329.8	44.9	0.48	6879.7	65.9	0.96	9666.7	156	1.61	9891.4	38.4	0.39	12044	196	1.63	8894.9	120	1.34
	Mg	1417.9	30.0	2.11	1225.8	27.6	2.25	1115.7	31.4	2.81	1134.8	5.38	0.47	1490.4	25.7	1.73	1167.8	3.88	0.33
	Ca	810.3	6.11	0.75	557.7	4.12	0.74	1062.9	11.7	1.10	921.8	5.06	0.55	1078.8	10.7	0.99	951.0	7.27	0.77
	Na	149.4	2.49	1.67	164.2	4.49	2.73	150.9	1.08	0.71	165.6	3.29	1.99	122.1	2.24	1.84	109.9	2.16	1.96
	Fe	36.2	0.87	2.40	47.5	2.00	4.20	37.9	1.18	3.12	41.3	0.87	2.10	35.8	0.57	1.59	45.1	0.87	1.93
	Zn	12.2	0.21	1.68	13.9	0.31	2.22	13.1	0.46	3.48	16.5	0.30	1.79	15.5	0.37	2.41	15.22	0.25	1.64
3rd	K	8703.1	114	0.42	7107.4	30.5	0.43	13776	57.4	0.42	9243.0	97.0	1.05	8947.8	139	1.55	8439.6	136	1.61
	Mg	1337.1	50.4	3.77	1024.9	9.45	0.92	1043.8	13.3	1.27	998.5	3.04	0.30	900.0	14.8	1.65	1021.3	18.3	1.79
	Ca	632.5	7.15	1.13	634.3	8.81	1.39	886.5	8.04	0.91	813.3	10.7	1.32	759.1	3.96	0.52	732.1	5.16	0.70
	Na	120.7	2.85	2.36	143.3	3.23	2.26	128.6	3.46	2.69	97.0	1.87	1.93	98.8	1.65	1.67	138.3	2.49	1.80
	Fe	25.2	0.66	2.61	43.0	0.33	0.76	39.8	1.14	2.86	52.5	1.74	3.31	48.1	2.30	4.77	46.8	1.43	3.06
	Zn	11.8	0.08	0.69	10.0	0.28	2.82	10.8	0.46	4.22	13.9	0.25	1.79	14.7	0.39	2.62	15.0	0.22	1.44
4th	K	6208.9	75.9	1.22	7541.1	122	1.62	9625.0	67.7	0.70	8944.3	23.4	0.26	4786.4	90.9	1.90	6847.4	36.1	0.53
	Mg	910.0	24.0	2.64	1095.3	6.80	0.62	714.7	22.0	3.08	948.9	7.29	0.79	646.5	4.59	0.71	993.3	8.24	0.83
	Ca	411.7	3.39	0.82	406.6	6.04	1.49	550.4	7.18	1.30	615.3	1.82	0.30	417.8	5.10	1.22	673.2	7.02	1.04
	Na	86.6	2.24	2.59	137.2	3.29	2.40	137.9	1.87	1.35	148.7	2.85	1.92	84.8	1.65	1.94	140.4	1.24	0.89
	Fe	33.9	1.43	4.22	42.2	1.64	3.88	54.5	1.50	2.76	60.2	2.05	3.40	38.8	1.31	3.38	42.0	2.48	5.89
	Zn	9.29	0.25	2.69	9.45	0.17	1.80	8.42	0.14	1.68	13.4	0.25	1.86	8.14	0.13	1.53	12.4	0.33	2.67
5th	K	4217.7	20.6	0.49	5930.2	72.9	1.23	6183.1	81.9	1.32	8436.0	91.6	1.09	4501.2	63.2	1.41	6748.8	108	1.60
	Mg	653.5	17.8	2.73	870.8	8.64	0.99	557.0	15.8	2.84	881.8	22.3	2.53	501.8	8.43	1.68	952.7	17.3	1.82
	Ca	275.6	4.49	1.63	412.7	7.68	1.86	303.4	3.83	1.26	432.3	2.41	0.56	364.3	2.06	0.57	521.0	3.96	0.76
	Na	98.1	2.85	2.91	111.0	2.85	2.57	115.3	1.87	1.62	146.2	2.24	1.53	88.4	2.15	2.44	84.1	2.85	3.39
	Fe	32.6	1.64	5.04	22.2	0.98	4.44	27.1	0.33	1.21	28.7	0.86	3.01	20.1	0.33	1.63	19.5	0.65	3.36
	Zn	4.44	0.17	3.83	8.41	0.28	3.36	5.09	0.21	4.03	11.7	0.12	1.06	6.51	0.13	1.92	11.0	0.19	1.72

1st Sampling = 01-06-2005 2nd Sampling = 15-06-2005 3rd Sampling = 01-07-2005 4th Sampling = 16-07-2005
5th Sampling = 02-08-2005

First pre-mature ripening stage of date fruit specifies the level of K in decreasing order; Asul Khurmo (P)> Ghuray Wari (P) > Toto (P) > Nur Aseel > Allah Wari (NP) > Gorho (P) > Allah Wari (P) > Asul Khurmo (NP) > Toto (NP) > Nur Aseel (NP) > Gorho (NP) > Ghuray Wari (NP). Results of K in P and NP date fruit reveals that higher concentration were found in pollinated fruit to all cultivars except Allah Wari (NP), which had lesser value of K than that of four pollinated cultivars i.e. Asul Khurmo, Ghuray Wari, Toto, Nur Aseel and greater than two pollinated cultivars i.e. Gorho (P), Allah Wari respectively.

Second pre-mature ripening stage illustrates that the highest concentration of potassium was in pollinated Nur Aseel and lowest in non-pollinated Gorho. Decreasing order of potassium was observed in such a way; Nur Aseel (P) > Ghuray Wari (P) > Allah Wari (NP) > Asul

Khurmo (NP) > Allah Wari (P) > Asul Khurmo (P) > Gorho (P) > Toto (P) > Nur Aseel (NP)> Ghuray Wari (NP) > Toto (NP) > Gorho (NP). Here non-pollinated Asul Khurmo got third position in accumulating the potassium in its pulp where as all other non-pollinated varieties of date fruit possesses lesser value of potassium as compared to pollinated fruit. Comparative study of 1st and 2nd sampling stages demonstrate that the potassium decreases in three varieties at 2nd stage to Ghuray Wari (P), Toto (P) and Asul Khurmo (P) while as increases in other three varieties Allah Wari (P), Gorho (P), and Nur Aseel. In case of non-pollinated fruit, potassium level increases in all six cultivars when fruit passes from 1st to 2nd stage.

Third stage of sampling shows variable behavior and order in absorbing the potassium as compared to 1st and 2nd stages of sampling because in this initial maturing stage the colour of fruit changes almost from green to light yellow and the concentration of potassium is not higher in majority of the pollinated fruit as found in first two stages but mixed to pollinated and non-pollinated as indicated here by symbols; Asul Khurmo (P) > Allah Wari (NP) > Ghuray Wari (P) > Asul Khurmo (NP) > Nur Aseel (P) > Gorho (P) > Nur Aseel (NP)> Ghuray Wari (NP) > Toto (NP) > Toto (P) > Gorho (NP) > Allah Wari (P). The potassium concentration was increased in two varieties i.e. Ghuray Wari and Asul Khurmo pollinated while decreased in rest four pollinated varieties at 3rd stage level. Potassium metal deposition increased in all non-pollinated fruit varieties at 3rd stage with exceptions that it slightly decreases in Asul Khurmo (NP) and Nur Aseel (NP) when fruit enter from 2nd to 3rd stage.

Fourth stage of sampling shows that the maximum concentration was found in Allah Wari (NP) and minimum in Nur Aseel (NP) where as rest of date varieties indicate its concentration; Asul Khurmo (P) > Toto (NP) > Ghuray Wari (NP) > Asul Khurmo (NP) > Gorho (NP) > Nur Aseel (NP) > Ghuray Wari (P) > Gorho (P) > Allah Wari (P) > Toto (P) > Nur Aseel (NP). The value of potassium declined at 4th repining stag to all pollinated and inclined to all non-pollinated except Nur Aseel date fruit variety. The results of 5th and last post ripening stage were very surprising and almost inverse to 1st and 2nd stage of sampling in which the concentration of non-pollinated is higher than pollinated fruit of various varieties as mentioned here in decreasing order; Allah Wari (NP) > Asul Khurmo (NP) > Ghuray Wari (NP) > Toto (NP) > Nur Aseel (NP) > Ghuray Wari (P) > Asul Khurmo (P) > Gorho (NP) > Toto (P) > Nur Aseel (P) > Allah Wari (P) >Gorho (P).

Mg was concentrated in 1st, 3rd, and 4th stage of Gorho (P), 2nd & 5th stage of Ghuray Wari (P) and Nur Aseel (NP) date fruit varieties respectively. The uptake of Mg in Gorho (P) and Toto (P) are found to be more or less same at initial stages. There is negligible difference in the concentration of Mg in Gorho and Toto pollinated cultivars at 1st stage. Up take of Mg at various ripening stages of the date fruit was observed as in decreasing order; Gorho (P) > Toto (P) > Asul Khurmo (P) > Allah Wari (P) > Nur Aseel (P) > Toto (NP) > Ghuray Wari (P) > Allah Wari (NP) > Nur Aseel (NP) > Asul Khurmo (NP) > Gorho (NP) > Ghuray Wari (NP) in 1st stage sampling. First and pre-mature stage of fruit discloses that the Mg concentration is higher in pollinated than that of non-pollinated fruit with the exception of Toto variety.

The second phase of sampling explain that the absorption of Mg was in order of decreasing intensity in six date fruit varieties; Ghuray Wari (P) > Nur Aseel (P) > Gorho (P) > Toto (P) > Allah Wari (NP) > Gorho (NP) > Ghuray Wari (NP) > Nur Aseel (NP)> Asul Khurmo (NP) > Asul Khurmo (P) > Allah Wari (P) > Asul Khurmo (P) >Toto (NP). Out of six varieties, four pollinated fruit have better level of Mg than non-pollinated as mentioned above. Third period of sampling specifies that the concentration of Mg was found in order of; Gorho (P) > Ghuray Wari (P) > Toto (P) > Allah Wari (NP) > Asul Khurmo (P) > Gorho (NP) > Ghuray Wari (NP) > Nur Aseel (NP)> Asul Khurmo (NP) > Nur Aseel (P) >Toto (NP) > Allah Wari (P) in dates.

Fourth stage of fruit shows different activities than above three stages in the capacity of uptake of the Mg nutrient and is noted was; Gorho (NP) > Ghuray Wari (P) > Nur Aseel (NP)> Asul Khurmo (NP) > Ghuray Wari (NP) > Gorho (P) > Toto (P) > Toto (NP) > Allah Wari (NP) > Asul Khurmo (P) > Allah Wari (P) > Nur Aseel (P) in

sequence. Fifth and last ripening stage of fruit that is also known as post ripening stage of fruit shows entirely different behavior than that of initial ripening stages in which pollinated fruit contain higher concentration of Mg as compared to non-pollinated: Nur Aseel (NP)> Asul Khurmo (NP) > Gorho (NP) > Toto (NP) > Toto (P) > Gorho (P) > Ghuray Wari (P) > Ghuray Wari (NP) > Allah Wari (NP) > Asul Khurmo (P) > Allah Wari (P) > Nur Aseel (P).

It is important to note that high level of Ca and Na was obtained in all stages of Allah Wari and Toto varieties respectively. The stage wise variations of Ca and Na in date pulp in decreasing order are given as under:

The first stage of date fruit indicate that the Ca concentration decreases from variety to variety in order; Allah Wari (P) > Nur Aseel (P) > Asul Khurmo (NP) > Toto (P) > Asul Khurmo (P) > Ghuray Wari (P) > Allah Wari (NP) > Nur Aseel (NP) > Toto (NP) > Ghuray Wari (NP) > Gorho (P) > Gorho (NP) whereas Na concentration in order; Toto (NP) > Gorho (P) > Asul Khurmo (P) > Allah Wari (NP) > Nur Aseel (P) > Toto (P) > Gorho (NP) > Ghuray Wari (P) > Ghuray Wari (NP) > Allah Wari (P) > Asul Khurmo (NP) > Nur Aseel (NP). In second phase of sampling, Ca and Na absorption decreases stage by stage and variety to variety. The maximum and minimum up take of Ca was observed in non-pollinated Allah Wari and Gorho cultivars respectively where as rest of cultivars are lying between both of these in decreasing content of calcium; Allah Wari (NP) > Nur Aseel (P) > Asul Khurmo (P) > Allah Wari (P) > Nur Aseel (NP)> Asul Khurmo (NP) > Toto (P) > Toto (NP) > Gorho (P) > Ghuray Wari (P) > Ghuray Wari (NP) > Gorho (NP). Non-pollinated Gorho variety is one of small sized fruit, therefore, the content of calcium is also lesser as compared to other date fruit varieties.

Observing table No. 2a and 2b, we find that the Ca concentration usually increases in period while decreases in group in five stages to all cultivars. However, Ca concentration rises in 2nd stage of Gorho (P), Asul Khurmo (P) and Nur Aseel (P) then fall down up to late ripening stage. The analysis of six metals (K, Mg, Ca, Na, Fe and Zn) indicates that the value of Ca was on third number after K and Mg at all stages in all date varieties.

Similarly, the second stage of sampling for the analysis of Na indicates that the Na concentration is in order of; Toto (NP) > Toto (P) > Allah Wari (NP) > Ghuray Wari (P) > Asul Khurmo (NP) > Gorho (NP) > Asul Khurmo (P) > Gorho (P) > Ghuray Wari (NP) > Allah Wari (P) > Nur Aseel (P) > Nur Aseel (NP). Symbolized representation shows that the highest content of Na was found in non-pollinated Toto and lowest in non-pollinated Nur Aseel.

The Ca concentration was calculated on the third stage of sampling in which Allah Wari (P) secured highest and Khurmo (NP) the lowest level of Ca and the decreasing level of Na was observed in different varieties in such a way; Allah Wari (NP) > Asul Khurmo (P) > Asul Khurmo (NP) > Allah Wari (P) > Nur Aseel (P) > Ghuray Wari (P) > Nur Aseel (NP)> Toto (NP) > Ghuray Wari (NP) > Toto (P) > Gorho (NP) > Gorho (P). In the same stage the value of Na changes in different cultivars at various stages of fruit; Toto (NP) > Gorho (NP) > Allah Wari (NP) > Nur Aseel (NP) > Ghuray Wari (NP) > Asul Khurmo (P) > Ghuray Wari (P) > Gorho (P) >Toto (P) > Nur Aseel (P) > Allah Wari (P) > Asul Khurmo (NP). There is trivial distinction in the concentration of Na when compared pollinated Ghuray Wari, Gorho and Asul Khurmo. In the same way insignificant variation in the value of Na was found in non-pollinated Asul Khurmo, pollinated Nur Aseel and Allah Wari in 3rd stage.

The concentration of Ca and Na decreases in fourth stage of sampling as compared to previous three stages of sampling that means either both metals may be deposited in seed or due to back pressure, they are deposited in pericarp and branch of the fruit bunch. It has been observed that most of the non-pollinated fruit acquire high level of Ca and Na as compared to the pollinated at fourth and fifth stage than initial stages of sampling, it may be that the non-pollinated fruit takes lot of time to be mature and its delay period of maturing holds these metals longer. Second possibility is that that the non-pollinated fruit does not contain seed where these metals are transferred. Results of Ca and Na are compiled in

nut shell and shown their concentration by decreasing order; Allah Wari (NP) > Nur Aseel (NP)> Toto (NP) > Asul Khurmo (NP) > Ghuray Wari (P) > Asul Khurmo (P) > Allah Wari (P) > Ghuray Wari (NP) > Toto (P) > Nur Aseel (P) > Gorho (P) > Gorho (NP). Similarly, the Na absorption in different date fruit cultivars are given as under; Toto (NP) > Toto (P) >> Allah Wari (NP) > Gorho (NP) > Asul Khurmo (NP) > Nur Aseel (NP) > Asul Khurmo (P) > Gorho (NP) > Allah Wari (P) > Ghuray Wari (P) > Gorho (P) > Nur Aseel (P).

Fifth and last ripening stage of fruit indicates that the Ca was more in Allah Wari (NP) and lesser in Gorho (P) as are given according to the decreasing concentration in date fruit varieties; Nur Aseel (NP) > Ghuray Wari (NP) > Asul Khurmo (NP) > Ghuray Wari (P) > Gorho (NP) > Toto (NP) > Toto (P) > Nur Aseel (P) > Allah Wari (P) > Asul Khurmo (P) > Gorho (P). Same pattern was also adopted for Na nutrient in which higher level was detected in Toto (P) > Toto (NP) > Ghuray Wari (NP) > Asul Khurmo (NP) > Allah Wari (NP) > Asul Khurmo (P) > Ghuray Wari (P) > Allah Wari (P) > Gorho (NP) > Gorho (P) > Nur Aseel (P) > Nur Aseel (NP). One of the interested thing has been recorded in post ripening stage of the non-pollinated Nur Aseel that it has deposited the highest amount of Ca and least amount of the Na as compared to remaining pollinate and non-pollinated date fruit cultivars.

Iron was rich in 1st and 5th stage of pollinated Gorho whereas 2nd, 3rd, and 4th stages possessed high level of Fe in Ghuray Wari (P), Allah Wari (P) and Asul Khurmo (NP) respectively, but Zn was concentrated in 1st to 5th stage of Ghuray Wari except 3rdstage, which was concentrated in Toto variety. These variations may be related to the ability of the date trees to absorb metals from the soil and concentrate them in the date's fruit. It is noticeable that all metals are concentrated in non-pollinated type rather than the pollinated fruit; this may be due to the absence of seed in non-pollinated type date to absorb the metals and concentrate them in seed. The variable levels of Fe and Zn in different stages are as:

The concentration of iron was found in decreasing order in various pollinated and non-pollinated varieties as indicated in table 2; Gorho (P) > Toto (NP) > Gorho (NP) > Toto (P) > Asul Khurmo (P) > Ghuray Wari (P) > Nur Aseel (NP) > Allah Wari (P) > Asul Khurmo (NP) > Ghuray Wari (NP) > Nur Aseel (P) > Allah Wari (NP). Over view of the mentioned tables shows that iron level increases at middle stages of fruit then decreases at last stage of the fruit. However highest level of iron was detected in 1st stage of the pollinated Gorho, which is very close to the 3rd stage of pollinated Allah Wari.

Zinc values were found in such a way; Ghuray Wari (P) > Ghuray Wari (NP) > Toto (P) > Nur Aseel (P) > Allah Wari (P) > Toto (NP) > Nur Aseel (NP) > Gorho (P) > Asul Khurmo (NP) > Gorho (NP) > Asul Khurmo (P) > Allah Wari (NP). These varieties show their concentration in pollinated and non-pollinated date fruits.

At second stage of sampling in which maximum level of Fe was detected in Ghuray Wari (P) and minimum level in Gorho (NP) with the order; Ghuray Wari (P) > Toto (P) > Toto (NP) > Allah Wari (NP) > Gorho (NP) > Nur Aseel (NP) > Allah Wari (P) > Asul Khurmo (NP) > Asul Khurmo (P) > Gorho (P) > Nur Aseel (P) > Ghuray Wari (NP). When you look to the table 2a and 2b you will find that values of zinc is in decreasing order as given in symbolized form; Ghuray Wari (P) > Toto (P) > Ghuray Wari (NP) > Asul Khurmo (NP) > Toto (NP) > Allah Wari (P) > Nur Aseel (NP) > Nur Aseel (P) > Gorho (P) > Asul Khurmo (P) > Allah Wari (NP) > Gorho (NP).

In third stage of date fruit sampling of iron in which top level of Fe were analysed in Allah Wari (P) and rest of varieties are given Allah Wari (P) > Asul Khurmo (NP) > Nur Aseel (P) > Nur Aseel (NP) > Gorho (NP) > Ghuray Wari (NP) > Asul Khurmo (P) > Toto (NP) > Allah Wari (NP) > Toto (P) > Ghuray Wari (P) > Gorho (P). Similar pattern was found in Zn; Toto (P) >Ghuray Wari (P) > Ghuray Wari (NP) > Nur Aseel (NP) > Nur Aseel (P) >Asul Khurmo (NP) > Toto (NP) > Gorho (P) > Asul Khurmo (P) > Allah Wari (P) > Gorho (NP) > Allah Wari (NP).

At fourth, Fe was detected higher in Asul Khurmo (NP) > Asul Khurmo (P) > Ghuray Wari (NP) > Allah Wari (P) > Gorho (NP) > Nur Aseel

(NP) > Nur Aseel (P) > Allah Wari (NP) > Gorho (P) > Toto (NP) > Toto (P) > Ghuray Wari (P). The concentration of Zn in the same stage was observed as; Ghuray Wari (NP) > Asul Khurmo (NP) > Toto (NP) > Nur Aseel (NP) > Toto (P) > Ghuray Wari (P) > Allah Wari (NP) > Gorho (NP) > Gorho (P) > Asul Khurmo (P) > Nur Aseel (P) > Allah Wari (P).

Fifth phase of sampling illustrate the Fe concentration in decreasing order; Gorho (P) > Asul Khurmo (NP) > Allah Wari (NP) > Asul Khurmo (P) > Toto (NP) > Toto (P) > Gorho (NP) > Nur Aseel (P) > Nur Aseel (NP) > Ghuray Wari (P) > Allah Wari (P). Zn concentration is somewhat different than that of Fe in which non-pollinated Ghuray Wari super seated in their concentration and the order of cultivars are in increasing order is ; Ghuray Wari (NP) > Toto (NP) > Asul Khurmo (NP) > Nur Aseel (NP) > Toto (P) > Gorho (NP) > Nur Aseel (P) > Ghuray Wari (P) > Allah Wari (NP) > Asul Khurmo (P) > Allah Wari (P) > Gorho (P). This variation of metal concentrations in the same date type at different stages and different date cultivars may be related to variations in texture, structure, chemical and mineral composition of soil and date varieties in this district.

The existence of essential elements, K, Mg, Ca, Na, Fe and Zn in the investigated date samples indicates their valuable, important and essential vital roles for plant growth as well as for animals and humans [28]. 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, Fe and Cu may exist as Fe and Cu proteins. Iron is an essential activator for enzyme-catalysing reactions involving chlorophyll synthesis and for ferrodoxin nitrate reductase [29]. Potassium is an essential nutrient and has an important role in the synthesis of amino acids and proteins [30]. Ca and Mg play a significant role in photosynthesis, carbohydrate metabolism, nucleic acids, and binding agents of cell walls [31]. Zn is an essential micronutrient and is associated with a number of enzymes, especially those with synthesis of ribonucleic acids [32]. From the above discussion, the existences of these essential elements in dates underline the usefulness of dates for human beings, especially in Indo-Pak sub-continent.

Conclusion

Date palm fruit of Khairpur district was studied using AAS to analyze the mineral content and trace elements. Two types of date fruit i.e. pollinated and non-pollinated of the same varieties were compared for their physical and chemical parameters. Physical parameters such as size, mass, color, moisture, and pH were measured. The size increased in all varieties as ripening stage achieved in pollinated and non pollinated fruit, however, the size of the pollinated increased more rapidly than non-pollinated and seed was not detected in latter date fruit. Water content and pH were found in the range of 75.51-86.59 %, and 4.24 - 6.01 respectively in all five stages of collected varieties. Color changes were seen during initial to final ripening stage; green to slightly reddish yellow, and yellowish red of Ghuray Wari and Allah Wari respectively, green to reddish yellow of the Toto and Gorho, green to yellow of the Asul Khurmo and Nur Aseel. In case of chemical characteristics, the mineral composition of six different varieties of district Khairpur dates palm (*Phoenix dactylifera* L.) fruit (Gorho, Asul Khurmo, Nur Aseel, Ghuray Wari, Toto, and Allah Wari) were analyzed using AAS. Wet acid digestion method was used for sample preparation. The decreasing order of essential metal concentrations is K> Mg >Ca >Na >Fe >Zn. Generally, metal concentration of pollinated fruit increased up to 3rd stage and then declined from 4th to 5th stage of the ripening fruit, where as the concentration of metals in non pollinated dates smoothly increased up to 5th stage except Na and Fe in Toto and Gorho variety respectively at last stage.

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