



Investigation of Essential Metals in Branch, Pericarp and Seed of three Date Varieties at Different Maturity Stages

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Abstract

Date fruit contains a wide range of metals, including essential and toxic elements. The aim of present study was to explore the amount of essential metals in branch, pericarp and seed of the date fruit in order to examine correlation of these metals at various maturity stages. The studied parts are generally considered as waste. Therefore, levels of essential elements such as Na, Mg, Ca, Fe, Mn and Zn were determined in the branch, pericarp and seed of three date varieties (Dallay wari, Noori and Khaki wari) at four ripening stages (kimri, khalal, rutab and tamar) using atomic absorption spectrophotometry. Oven dried samples were digested separately in HNO_3 and H_2O_2 following wet acid digestion method. Analytical results shows that Na, Mg, Fe, Zn, and Mn were not detected in branch, pericarp and seed in Dallay wari variety at tamar stage, while Na and Mn were also absent in branch of Noori at tamar stage, whereas Mn was present in pericarp and seed at tamar stage of Noori variety. However, Mg was not detected in branch and pericarp at rutab and tamar, while Fe was not detected in pericarp at rutab and tamar stage in Khaki wari variety.

Keyword: Date palm (*Phoenix dactylifera* L.), Elemental analysis, Micronutrients, Atomic Absorption Spectroscopy.

Introduction

Date palm (*Phoenix dactylifera* L.) is considered as one of the oldest fruit trees, which were cultivated in hot arid regions of Middle East and North Africa from 5000 years [1-3]. Date fruit is a major source of staple food in these areas and is being marketed worldwide due to high nutritional value and storage capacity [4-5]. Dates are a concentrated source of energy for humans, as they are rich in carbohydrates, fats, proteins, minerals, salts, fibers and vitamins [6, 7]. Along with its direct consumption, it is processed to many nutritious products as, date paste, syrup, depis, jams, ice creams and chutneys [8] as well as used in folk medicines [9]. The production of date increases day by day and the world production estimate of

dates in 2004 were 6.8 million tons [10].

Seed of the date palm plays an important role to supply the nutrients to the pulp of date fruit during its development. It is covered with pulp, sealed by pericarp that is connected with branch of the fruit bunch. Each bunch contains 50-100 branches, each branch contain 15-30 dates and each date contain only one seed as middle part of the fruit. Seed is very soft and white in color in beginning stages (kimiri to khalal) then slowly and gradually change their color become hard in latter stages (rutab to khalal). However, seed exist in pollinated date while non-pollinated date fruit doesn't contain seed, so that the growth of the fruit

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in non-pollinated is lesser as compared to pollinated. Dates contain 5.5-14.4 % of the seed and 85.6-94.5% weight of the flesh. Generally, dates are known as complete diet and superior than most of other fruits due to higher caloric value, more essential elements and vitamins. It accumulates high percentage of carbohydrates (44-88 %), dietary fiber (6.4-11.5 %), protein (2.3-5.6 %) and low level of oils (0.2-0.5 %), while the seed possesses high level 7.7-9.7 % of oil as compared to flesh and act as good source of energy [11, 12]. More than 15 elements were found in dates, level of each element in different stages of fruit varies, depending on environmental conditions, date palm variety, location and age of the palm. Among which the most important elements includes Mg, K, Na, Ca, Cu, Fe, Zn, Mn, B, Co, F, P and Se. Different elements play different role in the biological system, fluorine is useful for protecting teeth against decay and selenium to prevent cancer and increase immune system of the tissues. Dates contains 23 types of amino acids, a number of which are not found in most popular fruits e.g., apple, banana and orange. The polysaccharides obtained from dates are used as efficient food and energetic constituent in the development of drugs, in addition to that it contain at least six vitamins such as vitamin C, vitamin B1 (thiamine), B2 (riboflavin), nicotinic acid (niacin) and vitamin A [13].

The physicochemical properties of the date fruit has been studied on dry matter basis of two date varieties (Deglet-Nour and Allig) of Degach region, Tunis. The analytical results of these cultivars showed that high total DF contents (between 88% and 92.4% DM), low protein and ash contents (8.98–9.12% and 2.0–2.1% DM), respectively [14]. In another study, it was noted that the pulp and seed of date contain at least 17 elements include B, Ca, Co, Cu, F, Fe, Mg, Mn, K, P, Na, Zn, Al, Cd, Cl, Pb and S in various proportions depending on the variety of date [15]. Two years comparative study on seasonal dates was carried out to find the variation uptake of nutrients i.e. macro and micro-nutrients/elements [16]. Uptake of minerals in the various parts of date fruit continued from kimri to khalal then slowdown or stopped at rutab and terminated at tamar due to osmosis [17]. Market date samples of Saudi Arabia belong to different genotypes were

analysed to observe the exact concentration of variable minerals [18].

Date is eaten at all stages of fruit development, these stages are named as Kimri, green in colour, which is immature 1st stage, Khalal full-coloured mature, the 2nd stage of fruit, Rutab, the soft, brown 3rd stage of fruit and Tamar is the last 4th stage and hard raisin-like [19]. Different date palm cultivars have different physical and chemical characteristics due to variable morphology and physical structure of the fibers of plant, hence the chemical composition and structure of the fruit and its parts are not same as well as ripening period is also variable.

The present research is targeted to assay the concentration of essential elements flowing from branch to seed via pericarp and their deposition at these three parts during flow in different genotypes at four maturing stages of dates, and to gather information of essential metals on the safety and hazardous baseline at periods by applying atomic absorption spectrophotometric techniques.

Materials and Methods

Material

The date palm cultivars; Dallay wari, Noori and Khaki wari were selected for determining the level of six essential elements (Na, Mg, Ca, Fe, Zn and Mn) at four ripening stages, kimiri, khalal, rutab and tamar. Experimental date palm garden was selected for sampling purpose, situated at union Baberloi, taluka and district Khairpur, Sindh, Pakistan, that is considered as thick and saturated area of date palm in the region. The age of date palm was between 16 to 18 years, each date palm containing 12 to 18 bunches and each bunch comprises 35 to 50 branches, each branches holds 18 to 26 dates. However, this number varies variety to variety and year to year on the basis of age of date palm and environmental conditions.

Sample collection

A total of thirty six samples of branch, pericarp and seed at four ripening stages of three date varieties were freshly cut from bunches of

date palm, packed in air tight polyethylene bags without chemical treatment. Samples were collected from 15th April to 10th of August 2010 at four ripening stages. i.e. The distance between sampling stations and laboratory was round about 10 to 30 km, so samples were brought on the same day to the laboratory, Department of Chemistry, Shah Abdul Latif University, Khairpur for the analysis of minerals.

Pre-treatment

Wet digestion method

Wet acid digestion method as reported in the literature [20, 21] was used to destroy organic matrix present in sampling material and made transparent solution that contain elements only which were analyzed on AA 100 atomic absorption spectrophotometer.

Procedure of wet digestion method

The sample (2 grams each) of branch, pericarp and seed in triplicate were weighed separately on digital balance to made three replicate of each and placed in 100 ml conical flask parallel to that one blank was run. 5 ml of HNO₃ were added to each flask covered with watch glass placed on temperature controlled hot plate at 70-75 °C round about 60 to 90 minutes till semi dried content obtained. Removed the flask from hot plate added more 5ml HNO₃ and repeated heating similarly to obtain semi dried content. Again removed sample flasks from hot plate and left to cool down for 10 minutes. In the next step 3 ml of H₂O₂ was added and kept on hot plate for further heating until semi dried content obtained. In the end 50 ml of deionized water added and continued

heating without covering watch glasses until half of the water evaporated from flasks. Removed the flasks from hot plate, left them to cool down and filtered the content on whatman # 42 papers in to 25ml volumetric flask. The color of the digestion mixture was light yellow and very low viscous. The content of the flask were brought to volume with water and added 2ml of 2N HNO₃ and brought to flame atomic absorption spectrophotometer.

Chemicals and Standards

All those chemicals were purchased from BDH, Sigma Aldrich and E. Merck and were of A.R. grade (99.99%). Certified standard solutions (1mg/ml) of Na, Mg, Ca, Fe, Zn and Mn for atomic absorption spectroscopy were purchased from BDH (UK) and working standard solutions made by appropriate dilution of stock solutions. The accuracy of results was checked by using certified atomic absorption spectroscopic standards and biological standards [22] [Bown's kale (BK), Orchard Leaves (OL), and Tomato Leaves (TOML)].

Instrumentation

The flame atomic absorption spectrophotometer coupled with computer, made up of Perkin-Elmer Company, Model AA100 was used for determining the concentration of Na, Mg, Ca, Fe, Zn and Mn. The hollow-cathode lamps (made by Perkin-Elmer) of all above elements were operated at lamps current 9.5, 9.5, 7.3, 7.0, 9.5, and 9.5 mA, respectively. All instrumental parameters are given in (Table 1 and 2).

Table 1. Instrumental conditions for the FAAS measurement of Na, Ca, Mg, Fe, Mn and Zn.

Elements	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Fuel flow (acetylene) (l/min)	Flow rate (Air) (l/min)	Burner height (mm)	Oxidant (Air) kg/cm ²	Fuel (Acetylene) kg/cm ²	Signal out put
Na	590	0.4	9.5	2.21	9.4	7.5	1.60	0.25	100%
Ca	422.2	2.6	7.3	2.6	9.4	12.5	1.60	0.4	100%
Mg	285.5	2.6	7.0	2.0	9.4	7.5	1.60	0.2	100%
Fe	248.3	0.2	9.5	2.30	9.4	7.5	1.60	0.3	100%
Zn	214.0	1.3	9.5	2.0	9.4	7.5	1.60	0.2	100%
Mn	279.8	0.4	9.5	2.0	9.4	7.5	1.60	0.2	100%

Table 2. Statistical data for standards of elements.

Elements	Concentration range ppm (x)	Absorbance	Statistical calculation $y = m x + c$		
			m	c	r^2
Na	0 - 1	0 - 0.395	0.3952	-0.0013	0.9990
Ca	0 - 1	0 - 0.1850	0.1852	0.0001	0.9998
Mg	0 - 0.2	0 - 0.352	1.743	0.0036	0.9993
Fe	0 - 1	0 - 0.300	0.3011	0.0004	0.9997
Zn	0 - 1	0 - 0.235	0.2349	0.0027	0.9989
Mn	0-1	0-0.196	0.1962	0.0005	0.999

Results and Discussion

Three date palm cultivars, Dallay wari, Noori, Khaki wari were selected for the determination of the level of six essential elements (Na, Mg, Ca, Fe, Zn and Mn) at four ripening stages, kimiri, khalal, rutab and tamar. The branches of fresh fruit was cut from bunches of above date cultivars during April to August 2010 without chemical treatment for the analysis of minerals from branch, pericarp and seed of fruit to estimate the concentration of essential elements during their migration from bunch to seed via pericarp at four ripening stages.

Sodium (Na)

The analytical results of sodium showed that its value increased from branch, pericarp to seed in all three cultivars at kimiri and khalal, as well as in rutab stage of Noori and khaki wari cultivar, whereas it decreased in Dallay wari at rutab stage. However, sodium is not detected in the branch, pericarp and seed of Dallay wari and branch of Noori. The results of sodium in branch, pericarp and seed shows that seed of fruit had accumulated maximum concentration of sodium, which was its last station and minimum in branch from which it transported and is known as transporting channel.

Magnesium (Mg)

Magnesium level in Dallay wari jumps from kimiri to khalal, down at rutab and absent at tamar stage in branch, smoothly raised in pericarp at all stages except tamar whereas in case of seed highest concentration of magnesium was found in kimiri, lowest in khalal then jumps at rutab but not observed in its last stage. The value of magnesium

increased continuously from kimiri to rutab and slightly falls at tamar stage in branch of Noori, decreased in pericarp at khalal and tamar stage.

Calcium (Ca)

The Dallay wari, Noori and Khaki wari date cultivars show same pattern of calcium concentration with variable values; calcium level decreased in groups at kimiri, khalal, and rutab from branch to seed but in tamar, it increased in pericarp then decreased in seed. However, calcium level in period's decreased from kimiri to khalal whereas increased from khalal to tamar except branch in tamar stage.

Iron (Fe)

Iron level rose with precise values in kimiri but lot of difference in the value of iron was detected in rutab stage in groups while its value lowered nearly half in branch then raised ten times in seed at khalal stage, iron was not found in tamar stage of Dallay wari. It may be possible that iron migrated to date pulp because its colour changes to brownish at tamar. Generally, iron falls in branch and pericarp in periods but its value in seed obtained highest level at khalal stage. As far as Noori variety is concerned it possesses identical value in branch and seed that is higher than pericarp at kimiri. Moreover, iron level decreased at kimiri after that continuously up to post maturing (tamar) stage in branch, pericarp and seed. Among all these, seed accumulates highest level of metal, so far it looks grey-brownish colour at final stage, may be due to high level of iron deposition.

Iron concentration decreased in Khaki wari cultivar from branch to seed in kimiri, khalal, and

rutab but maximized in seed at tamar, however it is not detected in branch at rutab and tamar stage. High value of iron in seed at tamar is evidenced that iron passes from branch to seed where it is stored and made it hard. The periodic study of table 5 of Khaki wari highlights that iron value decreased from kimiri to khalal in branch, pericarp and seed then increased at rutab to tamar in branch and seed only.

Zinc (Zn)

Analytical results of Dally wari (Table 3) revealed that high value of zinc was determined in seed, moderate in branch and lowest in pericarp at all stages except tamar in groups where as in periods it lowered at khalal, raised at rutab in branch and pericarp but reverse trend was observed in seed. Meanwhile zinc was not detected at all in tamar.

The absorption rate of zinc is high in beginning part (branch), which continuously flow to seed and least trapped at pericarp, so that the

concentration of zinc was lower at middle portion (pericarp) and highest at seed in groups to almost all stages in Noori (Table 4). The case of periods is different; it continuously increased from kimiri to tamar with no significant difference in last two stages to the branch of mentioned variety where as zinc continuously decreased up to rutab then raised at tamar. As far as seed is concerned, its value gradually increased from kimiri to tamar, which is one of the recorded values compared to branch and pericarp.

The concentration of zinc in the branch of Khaki wari (Table 5) was found highest that decreased at pericarp and increased at seed. There was no significant difference of zinc in the value of branch and seed, which indicated that it passed from pericarp to seed in kimiri. Comparative study of zinc in all stages showed that maximum value of zinc was deposited in seed as compared to branch and pericarp, it means pericarp act as a controlling role to pass zinc to seed, when concentration of zinc in seed is in excess then pericarp deposit it.

Table 3. Analysis of six elements in three parts (branch, pericarp and seed) at four stages in Dally Wari variety (mg/Kg).

Varieties	Various parts	Elements	Stages							
			Kimiri		Khalal		Rutab		Tamar	
			Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.
Dallay wari	Branch	Na	360.07±3.78	1.05	307.92±0.38	0.1	253.30±9.92	2.81	ND	ND
		Mg	148.8±2.41	1.62	854.5±4.82	0.6	463.2±1.37	0.3	ND	ND
		Ca	818.98±3.24	0.18	824.98±3.81	0.5	969.83±1.83	0.19	848.91±11.14	1.312
		Fe	21.03±0.261	1.24	17.69±0.261	1.5	7.44±0.261	3.51	ND	ND
		Zn	5.95±0.06	0.93	5.39±0.303	5.6	10.42±0.303	2.91	ND	ND
		Mn	2.526±0.043	1.71	2.509±0.164	6.5	4.688±0.284	6.06	ND	ND
	Pericarp	Na	425.17±3.43	0.81	321.64±2.26	1	148.50±6.79	4.57	ND	ND
		Mg	450.7±3.68	0.28	487.6±3.679	0.8	558.6±2.365	0.42	ND	ND
		Ca	764.81±1.846	0.24	443.49±1.90	0.4	702.95±1.83	0.26	1059.34±4.21	0.397
		Fe	22.54±0.26	1.16	8.484±0.261	3.1	11.972±0.69	5.78	ND	ND
		Zn	1.747±0.147	8.41	0.788±0.091	12	2.924±0.061	2.07	ND	ND
		Mn	3.714±0.163	4.4	2.941±0.164	8.4	15.047±0.09	0.58	ND	ND
	Seed	Na	497.10±3.068	0.62	334.70±3.77	3	91.62±2.98	3.25	ND	ND
		Mg	1618.0±4.82	0.3	786.3±1.39	0.2	1041.0±2.37	0.23	ND	ND
		Ca	479.38±1.87	0.39	252.2±8.3	3.3	333.76±1.83	0.55	338.8±1.822	0.538
		Fe	24.74±0.052	1.1	84.722±0.52	0.6	25.408±0.05	0.18	ND	ND
		Zn	6.3±0.028	0.49	61.94±0.802	1.3	38.953±0.80	2.06	ND	ND
		Mn	17.854±1.071	6	8.286±0.328	4	15.346±0.04	0.28	ND	ND

Table 4. Analysis of six elements in three parts (branch, pericarp and seed) at four stages in Noori Wari variety (mg/kg).

Varieties	Various parts	Elements	Stages							
			Kimiri		Khalal		Rutab		Tamar	
			Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.
Noori	Branch	Na	422.60±3.130	0.6	380.94±3.01	1.2	253.30±9.92	2.81	ND	ND
		Mg	189.0±1.391	0.74	240.4±2.408	1	296.1±2.365	0.8	277.9±1.912	0.688
		Ca	552.8±19.43	0.97	528.14±3.808	0.7	714.56±9.49	1.33	711.42±4.860	0.683
		Fe	43.222±0.261	0.61	17.693±0.261	1.5	25.710±0.69	2.69	62.832±7.596	12.09
		Zn	5.032±0.073	1.46	7.493±0.303	4	9.891±0.303	3.07	9.891±0.606	6.131
		Mn	2.300±0.163	7.1	2.794±0.164	5.9	1.657±0.164	9.9	ND	ND
	Pericarp	Na	476.45±0.359	0.1	399.23±0.996	0.3	261.30±0.66	0.25	250.19±1.992	0.721
		Mg	501.6±6.961	1.39	148.0±11.124	7.5	794.2±4.923	0.62	449.9±1.107	0.246
		Ca	703.01±3.197	0.46	409.41±1.904	0.5	709.28±1.83	0.26	1093.01±8.42	0.77
		Fe	31.446±0.943	3	20.26±0.261	1.3	50.015±7.17	14.3	67.059±0.052	0.78
		Zn	4.151±0.278	6.69	3.116±0.303	9.7	0.280±0.030	10.8	9.366±0.303	3.237
		Mn	2.394±0.163	6.82	3.150±0.33	1.5	16.241±0.16	1.01	ND	ND
	Seed	Na	515.96±1.44	0.28	425.53±0.376	0.1	275.11±0.57	0.47	48.56±3.591	0.879
		Mg	1328.2±3.68	0.28	383.3±5.014	1.3	975.5±1.365	0.14	677.6±1.912	0.282
		Ca	683.40±4.947	0.72	221.42±1.904	0.9	284.18±9.49	3.34	700.76±3.157	0.45
		Fe	43.222±0.261	0.61	6.371±0.261	4.1	22.298±0.26	1.17	95.441±0.943	0.988
		Zn	4.744±0.073	1.55	5.342±0.303	7	34.05±0.303	0.89	40.179±0.525	1.307
		Mn	16.44±0.163	0.99	4.167±0.043	1	16.624±0.16	0.99	ND	ND

Table 5. Analysis of six elements in three parts (branch, pericarp and seed) at four stages in Khaki Wari variety (mg/kg).

Varieties	Various parts	Elements	Stages							
			Kimiri		Khalal		Rutab		Tamar	
			Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.	Mean±Stdv.	%Rsdv.
Khaki wari	Branch	Na	352.95±506	2.75	175.12±0.376	0.2	266.64±0.33	0.12	323.14±7.779	2.407
		Mg	225.1±2.781	1.24	137.6±8.684	0.8	ND	ND	104.7±4.417	0.40
		Ca	998.49±3.739	0.63	782.10±1.904	0.2	801.06±1.83	0.23	715.63±2.430	0.34
		Fe	43.675±0.261	0.6	7.1260.261	3.7	29.786±0.26	0.88	44.263±0.261	0.591
		Zn	5.923±0.010	0.16	7.318±0.303	4.1	9.891±0.303	3.07	9.366±0.080	0.857
		Mn	3.149±0.163	5.19	3.362±0.134	4	4.422±0.033	0.74	3.324±0.028	0.855
	Pericarp	Na	374.27±3.783	1.18	216.20±0.753	0.3	267.22±0.66	0.25	368.78±0.753	0.204
		Mg	478.9±1.062	0.22	421.8±6.061	1.4	ND	ND	ND	ND
		Ca	985.40±1.846	0.19	561.13±40.97	7.3	1076.37±1.8	0.17	1386.22±6.43	0.464
		Fe	28.28±0.26	0.93	21.467±0.784	3.7	ND	ND	ND	ND
		Zn	3.173±0.292	9.22	4.342±0.303	7	0.280±0.030	10.8	10.417±0.303	2.911
		Mn	4.223±0.043	1.02	1.278±0.232	18	4.508±0.091	2.03	2.604±0.164	6.298
	Seed	Na	457.30±3.130	0.68	287.51±0.753	0.4	275.03±0.66	0.38	260.76±1.725	0.662
		Mg	1345.9±8.684	0.65	810.4±2.781	0.3	947.2±2.731	0.29	1104.7±4.417	0.4
		Ca	696.35±8.150	1.17	218.12±1.904	0.9	384.39±1.83	0.48	567.13±7.944	1.401
		Fe	21.181±3.852	18.2	3.955±0.261	6.6	21.845±0.26	1.2	76.419±0.523	0.684
		Zn	5.817±0.048	0.83	3.48±0.504	14	45.781±0.80	1.75	56.04±0.105	0.187
		Mn	12.575±0.163	1.3	2.509±0.134	5.3	18.518±0.16	0.89	17.850±0.164	0.919

Manganese (Mn)

The level of manganese gradually increased in ascending order; branch, pericarp and seed at kimiri, khalal and rutab but not detected in tamar at all in Dallay wari and Noori cultivar. However, their rutab stages had accumulated highest level of manganese in pericarp and seed, and do not have any significant difference in both values to each cultivar within itself.

Khaki wari cultivar got same pattern of manganese absorption only in kimiri but rest of stages deviate from above two cultivars. Manganese lowered at pericarp when flow from branch and in seed, it means pericarp allows it to pass whereas its maximum concentration is deposited at seed. Moreover, one of the most important characteristic of this cultivar is that flow of manganese was continued till last stage (tamar) but it slow down as compared to rutab, may be due to hardness of seed.

Results illustrated in tables (3-5) showed that mineral contents vary from stage to stage, part to part of fruit as well as date variety on the basis of genetic character of date palm. Moreover, environmental factors also have effect on the value of minerals deposited in different parts of fruit and the movement of minerals from one part to another part of the fruit.

Mineral content in initial two stages (kimiri and khalal) of branch, pericarp and seed is new study that cannot be compared with reported work, while mineral content in last two ripening stages (rutab and tamar) are similar to those reported earlier [23,24]. However, in our previous research work only pulp of above four stages of date palm reported [18].

Most of date growing countries, particularly developing such as Pakistan do not use branch, pericarp and seed of the date fruit for isolation and extraction of different components such as carbohydrate, phenolic compounds, oils and minerals, which have wide biological scope and can also be used for pharmaceutical purpose as they are rich in nutrients. However, they are discarded, used for burning or feed for domestic animals due to the lack of technology and expertise

that may cause loss of economy of our country. Therefore, positive measurements are needed to utilize the each part of date to boost up the economy of Pakistan.

Statistical Analysis

For statistical analysis, SPSS Version 19 was used. The statistical results are summarized in table 6 to table 14. The branch, pericarp and seeds were analyzed for six elements at four ripening stages of date fruit. In some cases, there was a strong positive correlation between metals whereas, in other cases a negative correlation was observed (Table 6). Depending upon p values, there was not a uniform pattern of significance among three varieties at various stages of maturity and in most of the cases the correlation coefficient was highly significantly different from zero ($p > 0.001$). Some values show significance where others do not exhibit any considerable correlation between metal content as well among different stages studied (Table 7 –13). Strong negative correlation between Zn and Mg was observed at significance of 0.034 (Table 6). Strong correlation was also shown by Fe and Ca. Pearson correlation as given in table 7 indicated that Mg and Na showed strong negative correlation with significance level 0.04. Fe and Na also correlated but their p-value was greater than 0.05. Strong negative correlation between Zn and Ca was found with p-value of 0.003 (Table 8) where as Ca and Mg displayed strong positive correlation with a significance level of 0.004. Zn and Mg exhibited strong negative correlation means these were independent of each other. Table 9 shows strong positive correlation between Zn and Mg with $p = 0.013$, whereas Na and Zn displayed strong negative correlation and same was observed between Ca and Na. The Zn and Fe showed strong positive correlation (table 10, 11) and a similar trend were observed in Fe and Ca. The strong positive correlation of Mg and Zn was observed with $p = 0.015$, same trend was observed between Fe and Na (Table 12). Furthermore strong positive correlation was seen between Fe and Mg, Mn and Na, Mg and Na, Mn and Mg with $p < 0.05$ (Table 13, 14).

Table 6. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of branch of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.914				
P-Value	0.086				
Ca	-0.437	-0.580			
P-Value	0.563	0.420			
Fe	0.640	0.692	-0.961		
P-Value	0.360	0.308	0.039		
Zn	-0.829	-0.961	0.780	-0.842	
P-Value	0.171	0.039	0.220	0.158	
Mn	-0.732	-0.861	0.914	-0.947	0.966
P-Value	0.268	0.139	0.086	0.053	0.034

Table 7. Pearson's Correlation among Na, Mg, Ca, Fe, Zn, Mn at various ripening stages of pericarp of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	-0.989				
P-Value	0.011				
Ca	-0.510	0.614			
P-Value	0.490	0.386			
Fe	0.932	-0.869	-0.229		
P-Value	0.068	0.131	0.771		
Zn	-0.791	0.815	0.818	-0.683	
P-Value	0.209	0.185	0.182	0.317	
Mn	-0.848	0.799	0.431	-0.909	0.870
P-Value	0.152	0.201	0.569	0.091	0.130

Table 8. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of seed of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.534				
P-Value	0.466				
Ca	0.493	0.998			
P-Value	0.507	0.002			
Fe	0.304	-0.644	-0.679		
P-Value	0.696	0.356	0.321		
Zn	-0.475	-0.992	-0.997	0.689	
P-Value	0.525	0.008	0.003	0.311	
Mn	0.210	0.882	0.907	-0.809	-0.934
P-Value	0.790	0.118	0.093	0.191	0.066

Table 9. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of branch of Noori variety.

	Na	Mg	Ca	Fe	Zn
Mg	-0.891				
P-Value	0.109				
Ca	-0.941	0.835			
P-Value	0.059	0.165			
Fe	-0.455	0.002	0.438		
P-Value	0.545	0.998	0.562		
Zn	-0.941	0.987	0.854	0.134	
P-Value	0.059	0.013	0.146	0.866	
Mn	0.898	-0.638	-0.934	-0.730	-0.705
P-Value	0.102	0.362	0.066	0.270	0.295

Table 10. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of pericarp of Noori variety.

	Na	Mg	Ca	Fe	Zn
Mg	-0.442				
P-Value	0.558				
Ca	-0.580	0.397			
P-Value	0.420	0.603			
Fe	-0.826	0.535	0.933		
P-Value	0.174	0.465	0.067		
Zn	-0.904	0.634	0.836	0.976	
P-Value	0.096	0.366	0.164	0.024	
Mn	-0.888	0.771	0.435	0.716	0.851
P-Value	0.112	0.229	0.565	0.284	0.149

Table 11. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of seed of Noori variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.347				
P-Value	0.653				
Ca	0.024	0.501			
P-Value	0.976	0.499			
Fe	-0.995	-0.322	0.070		
P-Value	0.005	0.678	0.930		
Zn	-0.964	0.094	-0.170	0.972	
P-Value	0.036	0.906	0.830	0.028	
Mn	0.049	0.929	0.317	-0.047	0.186
P-Value	0.951	0.071	0.683	0.953	0.814

Table 12. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of branch of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.414				
P-Value	0.586				
Ca	0.446	0.985			
P-Value	0.554	0.015			
Fe	0.984	0.245	0.284		
P-Value	0.016	0.755	0.716		
Zn	-0.107	-0.874	-0.782	0.059	
P-Value	0.893	0.126	0.218	0.941	
Mn	-0.227	-0.428	-0.272	-0.154	0.717
P-Value	0.773	0.572	0.728	0.846	0.283

Table 13. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of pericarp of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.212				
P-Value	0.788				
Ca	0.751	-0.474			
P-Value	0.249	0.526			
Fe	0.410	0.978	-0.280		
P-Value	0.590	0.022	0.720		
Zn	0.443	-0.423	0.586	-0.322	
P-Value	0.557	0.577	0.414	0.678	
Mn	0.439	0.073	0.454	0.188	-0.445
P-Value	0.561	0.927	0.546	0.812	0.555

Table 14. Pearson's Correlation among Na, Mg, Ca, Fe, Zn and Mn at various ripening stages of seed of Khaki Wari variety.

	Na	Mg	Ca	Fe	Zn
Mg	0.980				
P-Value	0.020				
Ca	0.322	0.495			
P-Value	0.678	0.505			
Fe	-0.053	0.139	0.779		
P-Value	0.947	0.861	0.221		
Zn	0.409	0.548	0.655	0.834	
P-Value	0.591	0.452	0.345	0.166	
Mn	1.000	0.980	0.322	-0.053	0.409
P-Value	*	0.020	0.678	0.947	0.591

Conclusion

Metals have some important physiological functions and their deficiency and/or excess may result severe health related problems. Our study was focused to check if these essential elements were entirely transferred to date fruit during its ripening or some of their amount was retained by the branch, pericarp and seed of the fruit, during migration from bunch of the date palm. It has been found that Na, Mg, Fe, Mn and Zn were not observed in tamar stage to various parts of date fruit but Na, Mg, Fe, and Mn increased and Ca decreased in kimiri stage; Na and Mn increased and Ca decreased in khalal stage; Mg, Fe, Zn and Mn increased and Na and Ca decreased in rutab stage of Dally wari. However, Na, Mg and Mn increased in groups; Mg and Zn increased in periods while Ca and Zn decreased in groups and Na and Ca decreased in periods in all maturing phases except Mn that was not detected in tamar of Noori. Na, Mg and Mn increased in groups at kimri level and Mg was not detected at rutab and

tamar level while rest of metals have shown variable behavior at different stages and parts of fruit in khaki wari variety.

Keeping in view the results of the study, it can be said that different metals show different behavior of transference and accumulation in various parts of the date fruit at different maturity stages of the fruit.

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