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Distribution and Mobility of Vanadium in Cultivated Calcareous Soils and Some Food Chain Crops

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RECENTLY, vanadium levels have been increased in soil crust particularly in industrial areas. Vanadium content in food directly depends upon total initial content in soil. The distribution and mobility of vanadium in some calcareous soils along northwestern coastal region of Egypt were studied. The relationship between soil physical and chemical properties and vanadium fractions was studied. The results indicate that the less dominant chemical speciation of vanadium in calcareous soils was soluble and exchangeable vanadium followed by vanadium bound to carbonate < vanadium bound to organic matter < vanadium bound to Fe-Mn oxyhydroxides < vanadium bound to soil matrix (residual). The major species of vanadium was the residual form that accounted for 81.6 % to 90.1% of total vanadium. The mobility index of vanadium was found to be in the following sequence according to the studied cities Burg El Arab > Al Alameen > Marsa Matrouh > El Hammam > Ras Alhekma > Al Dabaa > Sidi Abdl Rahman. The mobility index ranged among 0.8 % and 4.2 %. The high concentrations of vanadium in the studied plants were found in those around industrial areas of Burg El Arab City.

Keywords: Vanadium levels, Vanadium fractions, Calcareous soils, Food chain , Coastal region

Introduction

Vanadium content in food is directly affected by the total concentrations presented in soil. The concentration of vanadium in soils and sediments also depends on parent material, and vanadium containing ore minerals in subsoil and may be influenced by anthropogenic activities. The average content of vanadium in soil over the world is 90 mg kg^{-1}, and the average value in earth's crust is 97 mg kg^{-1}. Vanadium is an essential element when exists in low concentration because it is useful for cell growth at µg l^{-1}. It plays an important role in physiological systems including normalization of sugar levels and participation in various enzyme systems as an inhibitor and cofactor of oxidation of amines. Apparently, vanadium is essential for chlorophyll and porphyrin biosynthesis during plant growth of some plants. Vanadium acts as a growth promoting factor and participates in fixation and accumulation of nitrogen in plants, however high concentrations of vanadium reduces plants productivity (Kabata-Pendias & Pendias, 1993, Edwards et al., 1995, Reimann & Caritat, 1998, Rudnick & Gao , 2005 and Chowdary & Basha, 2015).

Vanadium exists in different oxidation forms 2^+, 3^+, 4^+ and 5^+. The oxidation state of vanadium is primarily controlled by redox potential (Eh) and pH of the media. Under oxidizing and more alkaline conditions vanadium is found in anionic form, as vanadate (HVO_4^{2-} or $H_2VO_4^-$, oxidation state 5^+), whereas vanadyl (VO^{2+}, oxidation state V^{4+}) has cationic properties and occurs under more acid conditions. V^{5+} is more mobile and more toxic for both plants and animals compared to V^{4+}. Vanadium is transported mainly as V^{4+} or V^{5+} and precipitate in V^{3+} form. Vanadium is mainly associated with Fe hydroxides, clay minerals, and organic matter and it can also found as discrete mineral phases such as carnotite ($K(UO)_2(VO_4)_2.3H_2O$) and vanadinite ($Pb_5(VO_4)_3Cl$). Adding fertilizers such as ($(NH_4)_2PO_4$, Na_3PO_4) increases the solubility, mobility, and uptake of vanadium by plants (Edwards et al.,1995, Meunier,1994, Panichev et al., 2006 and Cappuyns & Slabbinck, 2012)].

Although the total content of vanadium is still useful in many areas, but the knowledge of speciation is important because toxicity, mobility, bioavailability, and bioaccumulation highly

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depend on chemical species (Teng et al., 2011). The aim of this study is to evaluate vanadium levels in calcareous soils and food chain crops along northwestern coastal region of Egypt. As a rare element, there are few studies in literature focused on vanadium pollution and content in plant. These areas contain new industrials cities that may increase the emission of vanadium in soils and consequently plants. Vanadium fractions and mobility index were investigated in soil and plant samples.

Materials and Methods

Soil sampling

Soil samples were collected from different locations between latitude 27° 2` E - 29° 55` E and 30° 40` N - 31° 22` N. Those areas include Burg El Arab, El Hammam, Al Alameen, Sidi Abdl Rahman, Al Dabaa, Ras Alhekma, and Marsa Matrouh cities. Forty three surface and subsurface soil samples were collected from 22 sites to represent calcareous soils zone along northwestern coastal plain as depicted in Fig. 1. Twenty two olive samples of plant representing *Olea europea sativa* and *Ficus carica* were randomly collected from 14 locations in the studied area to represent the tendency of vanadium uptake in plant.

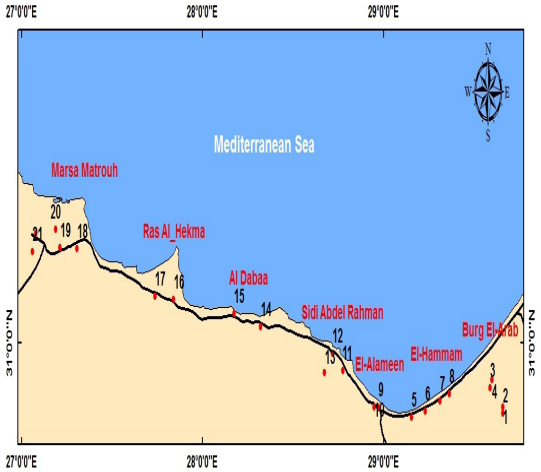


Fig. 1. A map showing the distribution of the studied .areas along northwestern coastal of Egypt

Mechanical analysis of soil texture was carried out by using international pipette method, for coarse textured samples. The dry sieving method was followed. Organic matter content was determined according to Walkley and Black. Soil pH was determined in the soil extract 1:2.5. Total soluble salts were determined in soil extracted (1:2.5). Total carbonate content was determined using Collin's calcimeter.

Vanadium content was determined using Inductivity Coupled Argon Plasma (ICAP), in which 1g dry soil well grounded, moistened with distilled water and heated in 100 ml Teflon beaker with 10 ml concentrated HNO_3 and evaporated to small volume. Then, 5 ml concentrated HNO_3, 5 ml 70% $HClO_4$, and 10 ml concentrated were added. HF is added and heated until elevating perchlorate fumes. After 30 min of fuming, 10 ml of HCl (1/1, v/v) was added and the mixture was boiled for 10 min. Finally, mixture cooled and diluted to 100 ml with distilled water. V^{5+} contents were determined by T 60 UV-VIS Spectrophotometer. Vanadium fractionates of soil were carried out using sequential extraction (Kilmer and Alexander, 1949, Piper, 1950, Jackson, 1973, Tessier et al., 1979), Ahmed & Banoo, 1999, Ure, 1995, Yang et al., 2012), and Jena et al., 2013).

Plant analysis

Plant samples (aerial parts and roots) were thoroughly washed and dried at 70° C. Afterwards, plant samples were digested using H_2O_2 and H_2SO_4 according to Nicholson (1984). Vanadium content was determined using Inductivity Coupled Argon Plasma (ICAP).

Results and Discussion

The present study dealt with distribution and mobility of vanadium in some Egyptian calcareous soils in different cities including Burg El Arab, El Hammam, Al Alameen, Sidi Abdl Rahman, Al Dabaa, Ras Alhekma, and Marsa Matrouh. The main physical and chemical properties of the investigated soils are summarized in Table 1. Soil texture varies from sandy to sandy clay loam. Soil pH ranged from 7.0 to 8.92 indicating neutral to alkaline soil reaction. Soil salinity varied from non-saline to saline except for location (1) in Burg El-Arab City that was extremely saline. Organic matter content was less than 1% except for few samples. $CaCO_3$ content ranged from 13.08 % to 41.79%.

Vanadium levels in soil

Chemical fractions are very important to distinguish between vanadium derived from lithogenic origins and those anthropogenic origins. Vanadium released from anthropogenic sources is mainly contained in earlier extractions, while those derived from lithogenic sources exist

TABLE 1. Soil physical and chemical properties of the studied areas

Site No.	Depth cm	pH	EC dSm^{-1}	OM %	$CaCO_3$ %	Sand %	Silt %	Clay %	Tex.	CEC $meq/100g^{-1}$
Burg El Arab										
1	0-25	8.4	70.1	0.6	26.9	84.3	10.0	5.6	LS	3.2
	25-50	8.5	52	0.2	22.1	91.5	2.5	5.9	S	3.4
2	0-25	7.9	1.0	1.2	24.2	68.3	16.4	15.2	SL	10.1
	25-50	8.1	8.0	0.7	20.6	61.4	16.8	21.8	SCL	10.7
3	0-25	8.1	3.5	1.6	35.4	46.8	22.4	30.8	SCL	14.1
	25-50	8.2	2.9	1.6	34.6	46.2	21.0	32.8	SCL	18.9
4	0-25	8.2	0.6	0.1	37.6	91.5	2.6	5.85	S	2.8
El –Hammam										
5	0-25	8.2	4.6	0.1	39.6	87.4	4.0	8.5	S	5.1
	25-50	8.0	5.7	0.1	42.8	85.5	5.9	8.4	LS	5.3
6	0-25	7.8	0.6	0.1	41.3	93.5	1.9	4.4	S	2.7
	25-50	7.2	0.6	-	41.7	94.6	1.8	3.5	S	2.1
7	0-25	8.6	0.6	0.1	37.9	83.6	5.9	10.4	LS	6.8
	25-50	8.1	3.1	-	40.1	71.5	11.9	16.4	SL	12.2
8	0-25	8.1	2.8	0.1	38.2	82.7	10.4	6.8	LS	4.9
	25-50	8.2	2.2	0.1	33.4	72.7	17.3	9.9	SL	9.6
Al Alameen										
9	0-25	8.9	0.2	0.8	13.0	92.1	2.9	4,9	S	3.3
	25-50	8.6	0.8	0.0	15.2	94.1	1.9	3.8	S	2.4
10	0-25	8.7	0.2	0.4	17.4	71.4	11.5	16.9	SL	13.1
	25-50	8.7	0.3	0.4	16.1	78.1	11.0	10.7	LS	2.2
Sidi Abdl Rahman										
11	0-25	8.4	0.8	0.3	40.5	94.8	2.1	3.0	S	1.9
	25-50	8.1	0.5	0.2	41.4	95.6	1.7	2.6	LS	1.7
12	0-25	7.7	6.9	0.3	39.2	78.6	4.5	16.7	SL	10.6
	25-50	7.8	11.2	0.3	40.4	61.1	16.6	22.2	SCL	14.8
13	0-25	8.2	0.9	-	38.1	90.0	5.9	3.9	S	2.5
	25-50	8.0	1.2	-	41.5	77.4	11.	10.8	S	6.3
Al Dabaa										
14	0-25	7.1	2.5	0.4	18.3	68.2	10.1	21.6	SL	14.7
	25-50	7.2	4.4	0.4	14.3	75.2	12.6	12.1	SL	8.9
15	0-25	7.0	1.4	0.4	22.6	77.0	17.6	5.3	LS	4.2
	25-50	7.0	3.7	0.2	22.6	74.3	16.5	9.1	SL	6.7
Ras Alhekma										
16	0-25	7.8	0.8	0.8	13.0	92.8	3.1	4.0	S	2.9
	25-50	7.7	0.8	0.1	15.2	92.6	3.7	3.6	S	2.6
17	0-25	7.7	0.9	0.3	12.9	76.3	15.5	8.1	SL	7.0
	25-50	7.7	0.8	0.3	13.9	79.1	16.6	4.2	LS	3.2
Marsa Matrouh										
18	0-25	7.2	1.7	0.7	25.0	73.1	19.3	7.5	SL	5.9
	25-50	7.1	3.1	0.6	41.0	79.5	9.4	11.0	SL	7.8
19	0-25	7.3	1.7	0.3	26.4	86.1	9.6	4.2	LS	2.7
	25-50	7.2	3.2	0.1	29.7	86.2	10.3	3.4	LS	2.4
20	0-25	7.2	0.9	1.0	12.3	87.2	7.7	5.0	LS	3.3
	25-50	7.2	1.6	1.0	15.2	83.9	11.0	5.1	LS	3.8
21	0-25	7.2	12.2	1.1	32.6	85.0	9.2	5.7	LS	4.0
	25-50	7.3	5.6	0.6	29.5	71.7	18.1	10.1	SL	7.6
22	0-25	7.3	3.5	0.5	20.8	85.2	8.5	6.2	LS	4.9
	25-50	7.6	2.7	0.3	22.3	83.6	10.1	6.2	SL	5.1

in residual fraction (Rubio et al., 2000). Vanadium concentrations in individual fractions depend relatively on locations and total concentration of vanadium. Total vanadium content ranged between 8 mg kg-1 and 178 mg kg^{-1} (Table 2). The highest values of vanadium were detected in soil samples located in Burg El Arab City. This is because of the widespread of industrial emissions in this area. Generally, the accumulation of heavy metals in the coastal beach has considerably increased in recent times owing to anthropogenic activities (Yang et al., 2012).

Vanadium contents were determined in all fractions using sequential extraction procedure as listed in Table 2. Vanadium distribution in the studied soils compared to Chinese and Canadian standard in shown in Fig. 2. In general, the total contents of vanadium in soil were lower than reference levels of vanadium in Chinese standard of 86 mg kg^{-1} (China National Environmental Monitoring Center, 1990), and maximum permissible value (MPV) of 130 mg kg-1 according to Canadian standard (Canadian soil quality for V ,1999). As clearly seen from Fig. 2, soil samples number 3 and 4 collected from Burg El Arab City showed the higher levels of vanadium due to anthropogenic activities in this area. The more soluble vanadium compounds are more mobile and toxic. As reported by Jayawardana et al. (2015), the high concentrations of vanadium > 200 mg kg-1 in non-agricultural soils cause chronic kidney disease (Jayawardana et al., 2015).

The exchangeable and bond to carbonates species are generally called bio-available. The mobility index (MF) of vanadium was calculated according to Kabala and Singh (2001) as follows:

$$MF= (F1+F2) / (F1+F2+F3+F4+F5) \times 100$$

Vanadium in bio-available forms ranged between 1.40% and 7.59%. The average percentage of vanadium is arranged in the following order Burg El Arab > Sidi Abdl Rahman > Al Dabaa > Ras Alhekma > El Hammam > Al Alameen > Marsa Matrouh. This may be due to the difference of active calcium carbonates content in these areas.

Vanadium bound to Fe-Mn oxides ranged between 7% and 10.3% of total vanadium content. Low amounts of vanadium bound to organic matter and ranged between 1% and 5% of total vanadium content. This is owing to organic matter content in studied profiles was generally less than 1%. The average percentage of vanadium fractions took the following sequence F_1-exchangeable (Ex-) < F_2- bound to carbonate (Car-) < F_4-bound to organic matter (OM) < F_3-bound to Fe-Mn oxyhydroxides (Fe-Mn) and < F_5-residual (Res-). The major species of vanadium were found in the residual form that account for 81.6 % to 90.1% of total vanadium content. The obtained results were not in harmony with other data reported by Teng et al. (2006). The chemical speciation of vanadium was in the following order: insoluble residue > organically bound > Fe (amorphous) oxide-bound > Mn oxide-bound > soluble component. The results reported by Teng et al. (2011) showed that the mobile fractions of vanadium in natural soils were as low as 14 % from total vanadium content in soil compared to the residual fraction that was as high as 86%.

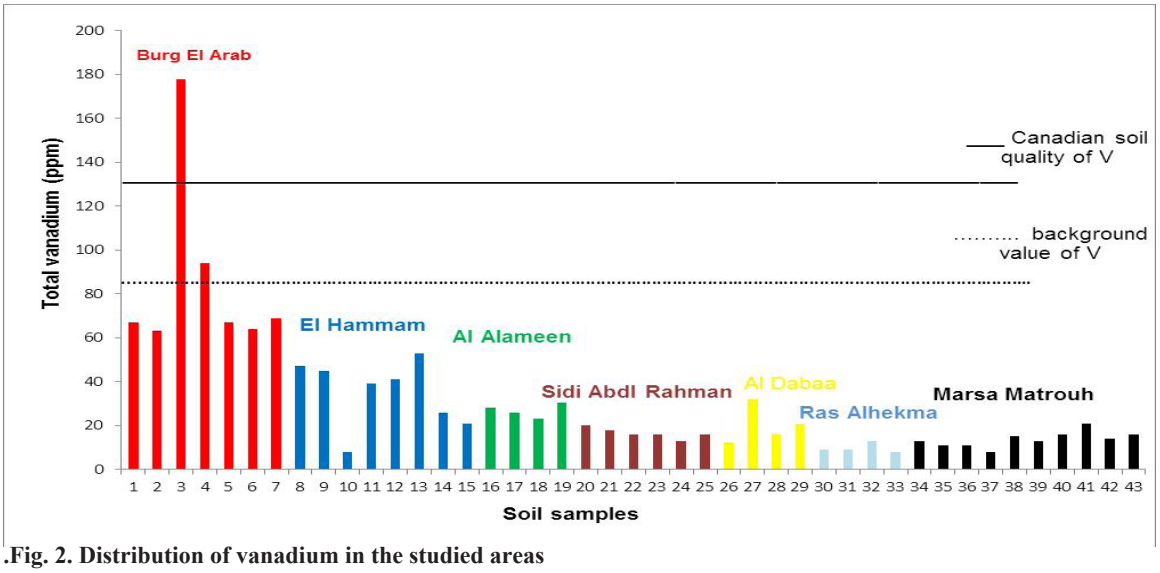
The relationship between total vanadium content and some soil variables was evaluated using SPSS and listed in Table 3. The statistical analysis revealed that total vanadium content in soils is correlated positively with pH, organic matter and CEC. On the other hand, it is being correlated negatively with sand content (%). Other relations between total vanadium content and rest of soil variables were insignificant. Vanadium content in F1-exchangeable fraction and F2-carbonate fraction are correlated positively with organic matter. Vanadium content in F2-carbonate fraction correlated positively with EC. Vanadium content in F1 and F2 are negatively correlated with sand (%). Exchangeable fraction (F1) is correlated positively with texture and CEC. According to vanadium content in F3-bound to Fe-Mn oxyhydroxides (Fe-Mn-), F4-bound to organic matter (OM-), and F5-residual (Res-) it is clear seen that they are significant positively correlated with organic matter while being correlated negatively with sand (%). Vanadium contents in F3-bound to Fe-Mn oxyhydroxides (Fe-Mn-), and F5-residual (Res-) they are correlated positively with pH.

Vanadium levels in plants

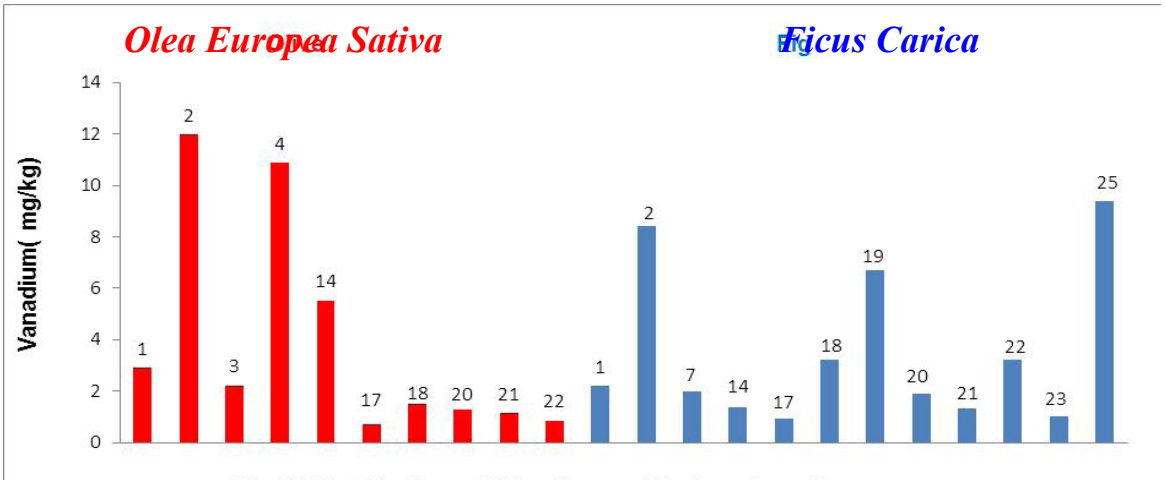
Vanadium concentrations in plants were as high as around the industry area of Burg El Arab compared to other areas as it shown in Figure 3. In General, vanadium in plants is one-tenth the concentration of vanadium in soil, thus plants in general have a soil bioaccumulation factor (BCF) of 0.1 (WHO, 1988). Kaplan et al. (1990)] reported that if vanadium reaches

TABLE. 2 Total content and fractions of vanadium and fractions mg kg^{-1} in the studied soils

Site No.	Depth cm	Sample No.	F1	F2	F3	F4	F5	Total V	*Total V	Recovery %
Burg El Arab										
1	0-25	1	1.19	2.67	4.58	1.97	53.23	63.65	67	95
	25-50	2	1.14	2.46	6.55	2.33	52.39	64.89	63	103
2	0-25	3	4.76	6.40	17.44	8.90	140.49	178.00	178	100
	25-50	4	2.37	2.91	7.24	3.76	77.80	94.10	94	100
3	0-25	5	2.46	2.73	6.08	2.52	54.54	68.34	67	102
	25-50	6	2.41	2.37	6.32	2.90	51.91	65.92	64	103
4	0-25	7	1.22	2.02	5.54	3.38	55.45	67.62	69	98
El –Hammam										
5	0-25	8	0.37	0.43	4.26	1.48	41.39	47.94	47	102
	25-50	9	1.16	1.42	3.84	1.29	35.47	43.20	45	96
6	0-25	10	0.11	0.26	0.64	0.16	6.98	8.16	8	102
	25-50	11	0.66	0.74	2.91	1.57	33.49	39.39	39	101
7	0-25	12	0.50	0.38	3.88	0.80	36.66	42.23	41	103
	25-50	13	0.47	0.45	5.40	0.89	45.25	52.47	53	99
8	0-25	14	0.40	0.42	2.67	0.53	22.74	26.78	26	103
	25-50	15	0.29	0.25	1.79	0.85	18.22	21.42	21	102
Al Alameen										
9	0-25	16	0.43	0.47	1.96	0.97	23.88	27.72	28	99
	25-50	17	0.39	0.53	2.54	0.79	22.26	26.52	26	102
10	0-25	18	0.19	0.27	2.11	0.46	20.18	23.23	23	101
	25-50	19	0.86	0.93	2.54	0.93	25.75	31.01	31	100
Sidi Abdl Rahman										
11	0-25	20	0.27	0.35	1.46	0.41	18.11	20.61	20	103
	25-50	21	0.32	0.34	1.63	0.73	15.32	18.36	18	102
12	0-25	22	0.44	0.48	1.61	0.80	12.81	16.16	16	101
	25-50	23	0.11	0.13	1.24	0.15	13.87	15.52	16	97
13	0-25	24	0.09	0.11	1.05	0.38	11.10	12.74	13	98
	25-50	25	0.10	0.12	1.27	0.30	13.41	15.21	16	95
Al Dabaa										
14	0-25	26	0.13	0.13	1.06	0.47	10.07	11.88	12	99
	25-50	27	0.44	0.51	2.75	1.60	26.70	32.01	32	100
15	0-25	28	0.23	0.29	1.27	0.16	14.36	16.32	16	102
	25-50	29	0.39	0.42	1.73	0.85	18.18	21.42	21	102
Ras Alhekma										
16	0-25	30	0.06	0.07	0.76	0.18	8.18	9.27	9	103
	25-50	31	0.06	0.08	0.67	0.18	8.17	9.18	9	102
17	0-25	32	0.31	0.28	1.05	0.40	11.34	13.39	13	103
	25-50	33	0.16	0.24	0.67	0.32	6.61	8.01	8	100
Marsa Matrouh										
18	0-25	34	0.29	0.11	1.12	0.66	11.06	13.26	13	102
	25-50	35	0.17	0.20	1.02	0.21	9.27	10.89	11	99
19	0-25	36	0.16	0.19	1.00	0.32	9.10	10.78	11	98
	25-50	37	0.09	0.16	0.80	0.15	6.87	8.08	8	101
20	0-25	38	0.13	0.13	1.28	0.23	13.67	15.45	15	103
	25-50	39	0.36	0.40	0.93	0.30	11.38	13.39	13	103
21	0-25	40	0.31	0.41	1.31	0.48	14.12	16.64	16	104
	25-50	41	0.50	0.54	1.85	0.82	18.11	21.84	21	104



.Fig. 2. Distribution of vanadium in the studied areas



.Fig. 3. Vanadium content in Olea europea sativa and Ficus carica in different locations

TABLE 3. Pearson correlation coefficients of the total and different fractions of vanadium compared to some physical and chemical properties of the investigated soils

	Total V	F1	F2	F3	F4	F5	MF
pH	0.330*	0.242	0.267	0.317*	0.219	0.342*	1.00
EC	0.237	0.146	0.334*	0.201	0.150	0.243	0.302*
OM	0.346*	0.538**	0.455**	0.340*	0.383*	0.329*	0.514**
$CaCO_3$	0.077	0.038	0.014	0.085	0.020	0.083	0.00
Sand %	-0.342*	-0.483**	-0.354*	-0.347*	-0.324*	-0.334*	-0.348*
Silt %	0.196	0.341	0.239	0.198	0.208	0.186	0.293
Clay %	0.019	0.014	-0.007	-0.003	0.020	0.023	-0.016
Texture	0.229	0.358*	0.246	0.231	0.229	0.221	-0.158
CEC	0.303*	0.378*	0.265	0.325*	0.278	0.299	0.317*

*Significant at α = 0.05 (two- tailed)

** Significant at α =0.01 (two-tailed)

concentrations higher than 80 mg kg-1, it may cause significant reduction in Brassica biomass in sandy soil. However, as reported by WHO (2001) if the concentrations of vanadium up to 100 mg kg-1 represented no effect in loamy sand [(WHO, 2001)]. Hopkins et al. (1977)] found that the concentrations of vanadium may cause toxic effects in plants if it varies between 10 mg kg-1 and 1300 mg kg-1 depending on plant species, and vanadium forms. [Poledniok and Buhl (2003)] found that low concentrations of vanadium lower than 2 mg kg-1 will positively influence chlorophyll synthesis, potassium consumption, and nitrogen assimilation.

Conclusions

Vanadium fractions in calcareous soils as associated with existing plants were studied. It was found that total vanadium content ranged between 8 mg kg-1 to 178 mg kg-1. High vanadium values were detected in soil samples that collected from Burg El Arab city because of industrial emissions in this area.

The major species of vanadium were in residual forms that accounted for 81.6% to 90.1% of total vanadium content. The mobility index of vanadium in the studied soils was arranged with the following order Burg El Arab > Al Alameen > Marsa Matrouh > El Hammam > Ras Alhekma > Al Dabaa > Sidi Abdl Rahman, respectively.

The high concentrations of vanadium in plant samples were found in Burg El Arab. pH Soil reaction and organic matter were the most significant variables that may affected vanadium mobility.

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