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DISTRIBUTION OF VANADIUM IN BOTTOM SEDIMENTS FROM THE MARINE COASTAL AREA OF THE EGYPTIAN SEAS

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ABSTRACT

The present study aims to measure the concentration of vanadium in 73 sediment samples collected along the coastal area of the Egyptian seas (Mediterranean and Red Seas). The results indicated that the mean value of vanadium in Red Sea sediments (52.61 µg/g) was higher than the mean value of the Mediterranean (40.58 µg/g) and the variation between the two means was insignificant ($p = 0.241$). This result could be attributed to the high petroleum activities of the Red Sea. Along the Mediterranean coast, the sector in front of Port Said area exhibited the highest mean value of vanadium (103.9 µg/g) than other sectors, which suffers from many sources of pollution. While the highest mean value along the Red Sea coast (73.20 µg/g) was found at the sector of Red Sea proper. ANOVA analysis showed that the differences in vanadium levels at the Mediterranean sectors were mostly significant at $p < 0.05$. While for Red Sea sectors, the differences were insignificant except that between Red Sea proper and Aqaba Gulf. Station M10 (at Mediterranean – Port Said sector) and station S2 (at Red Sea – Suez Bay) recorded values of vanadium higher than the typical concentration in sediments (20 – 150 µg/g). These two stations receive huge amount of wastes as industrial and agricultural effluents, sewage discharge, in addition to shipping activities, fishing ports and ship waiting areas; in particular, station S2 (Suez Bay) is characterized by petroleum activities.

1. INTRODUCTION

Vanadium is a ubiquitous element in the earth's crust, ranking 22nd in abundance with a mean concentration 150 mg/kg. Although igneous rock, carbonatite complexes, titaniferous magnetite complexes, and deposits of iron, uranium, chromium, and manganese all contain vanadium, high-content ores include vanadinite, descloizite, partonite, rescoelite, and carnotite. Higher concentrations can also be found in many coals and other fossil fuel. Vanadium is a hard acid, so it prefers to complex with oxides and nitrogen. It has a number of possible oxidation states (V^0, V^+, V^{2+}, V^{3+}, V^{4+} and V^{5+}). The pentavalent form is the most soluble, and is the primary agent of transport in surface water (Moore, 1991). The main source of vanadium to the environment is the atmospheric fallout, principally due to the combustion of fossil fuels and, to a lesser degree, windblown dusts. Other significant sources include the dumping of sewage sludge, discharge of domestic wastewater and the industrial effluents specially fertilizers containing materials with high vanadium content. Vanadium is also solublized from stabilized oil ash waste in seawater (Breslin and Duedall, 1988).

Studies on the levels of vanadium in sediments as well as in all marine ecosystem of the Egyptian seas are very rare (Abd El-Azim, 2002; El-Moselhy and Abd El-Azim, 2005). So, the present work aims to determine the level of vanadium in the sediment samples among the coastal area of the Mediterranean and Red Seas (Egypt).

2. MATERIALS AND METHODS

Seventy-three sediment samples were collected from the coastal area along the Egyptian seas, among of which, 37 samples were collected along the Mediterranean and 36 samples along the Red Sea (Fig. 1). Samples were collected from the selected stations using Van-veen grab sampler (Amini Ranjbar, 1998). The samples were taken from the central part of the grab to avoid contamination, kept in pre-cleaned plastic bags, dried in the lab and stored until metal analysis. The samples were prepared to determine the concentration of vanadium according to Tessier *et al*. (1979) and Perin *et al*. (1997). The fine fraction (< 63 µm) of sediments was digested with 5 : 1 mixture of HF and $HClO_4$ acids. 1g (dry weight) sample was digested by 2 ml $HClO_4$ and 10 ml HF to near dryness, subsequently a second addition of 1 ml of $HClO_4$ and 10 ml of HF and evaporated to near dryness. Finally, 1ml of $HClO_4$ was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12N HCl and diluted to 10 ml with deionized water. The vanadium was determined by using nitrous oxide - acetylene flame Atomic Absorption Spectrophotometer, Perkin Elmer model Aanalyst 100. The results obtained were expressed in µg/g. Each sample was measured in triplicate; mean, standard deviation and CV % were calculated.

All chemicals used were pure analytical grade and reagent blanks were processed throughout all the determinations. The precision and accuracy for the method of vanadium determination in sediments were checked by replicate measurements of the vanadium in sediment sample. Precision was found satisfactory which was 12.7 %.

3. RESULTS AND DISCUSSION

Concentration of vanadium in sediments of Mediterranean coast, Egypt, is presented in Table 1. The absolute highest concentration of vanadium (168.0 µg/g) was recorded at station M10 (sector II). This station receives huge amount of wastewater effluents from Lake Manzala, as well as the effect of waiting area for ships passing through the Suez Canal to the Red Sea. While the lowest one (3.76 µg/g) was observed at station M2 (sector I) in front of El-Arish City, representing a relatively clean surrounding area. Along the different sectors of the Mediterranean coast, it can be noticed that the lowest mean value of vanadium (5.73 µg/g) was found at sector V which is faraway from the pollution sources. In contrast, sector II (Port Said area) showed the highest mean value of vanadium which was 103.9 µg/g (Fig. 2). Port Said area suffers from pollution through different sources such as many industrial effluents, shipping activities, fishing port, ship waiting area, and effluents from Lake Manzala which contains agricultural wastes, sewage discharge in addition to the industrial wastes. Hamed (1996), El-Moselhy *et al*. (1998); Abd El-Azim (2002) and Abd El-Azim and El-Moselhy (2005) recorded high levels of metals at Port Said area which attributed to effect of the different pollution sources contain high concentrations of metals. Applying ANOVA analysis on the different results, most of the vanadium levels in the sediment at different sectors of the

Mediterranean were significantly different (at $p < 0.05$), except for sector I: sector IV and sector II: sector III.

Distribution of vanadium in sediments along the coastal area of Red Sea showed a wide range of variation (Table 2). Where, the lowest value (8.50 µg/g) was observed at station A8 (Aqaba Gulf sector) representing clean surrounding area, and the highest one (214.4 µg/g) was recorded at station S2 (Gulf of Suez sector). Station S2 is located in the Suez Bay (northern part of the Gulf of Suez) which is characterized by petroleum activities in addition to many industrial structures and sewage effluent of the Suez City. Breslin and Duedall, (1988) and FAO (1992) stated that the main source of vanadium is the petroleum activities and fuel burn. In respect to the mean values of vanadium throughout the different sectors of Red Sea, it can be stated that, Aqaba Gulf sector exhibited the lowest mean value (25.48 µg/g) while the highest mean value (73.20 µg/g) was recorded for the Red Sea proper (Fig. 2). Statistically, only mean values of vanadium in Red Sea proper and Aqaba Gulf showed significant difference ($p < 0.05$).

In spite of that the mean value of vanadium in sediments of Red Sea (52.61 µg/g) was higher than those of the Mediterranean (40.58 µg/g) as shown in Fig. 2; but this difference was insignificant at confidence limit 95 % ($p = 0.241$). The high level of vanadium in sediments of Red Sea may be attributed to the most of the important petroleum activities of Egypt that are condensed in the Red Sea. Al-Abdali *et al.* (1996) studied the bottom sediments of the Arabian Gulf (hydrocarbon and metal relationship) and recorded high concentration of vanadium in samples collected at locations affected by chronic oil pollutants; they stated that vanadium might be direct indication of oil pollutant inputs.

Comparing the level of vanadium in sediments of the Egyptian waters (present study) with other data elsewhere (Table 3) showed that the concentration of vanadium in the present investigated areas was in the range of other recorded data. Moreover, most of the present concentrations of vanadium were below/within the range of typical and background values (20 - 150 µg/g) recorded by Moore (1991), except stations M10 and S2 which had the extreme values of vanadium in the sediments of Mediterranean and Red Seas, respectively.

By using the background and measured concentrations of vanadium in sediments, an index of metal pollution in the investigated regions has been attempted to evaluate the extent of pollution. For this purpose, the technique of Muller (1979) was utilized which is defined as:

$$I_{geo} = \log C_n / (1.5 \times B_n)$$

where C_n is the measured concentration of vanadium; B_n is the background value; 1.5 is used to compensate for the possible variations of the background due to the lithogenic effect (Table 4). Data of the index of geoaccumulation values for sediment samples from the present investigation regions showed that the quality of the sediment samples varied between unpolluted to moderately polluted which belonged to class I ($I_{geo} = 0 - < 1$), especially, the stations had high concentration of vanadium, which may be attributed to the land-based activities.

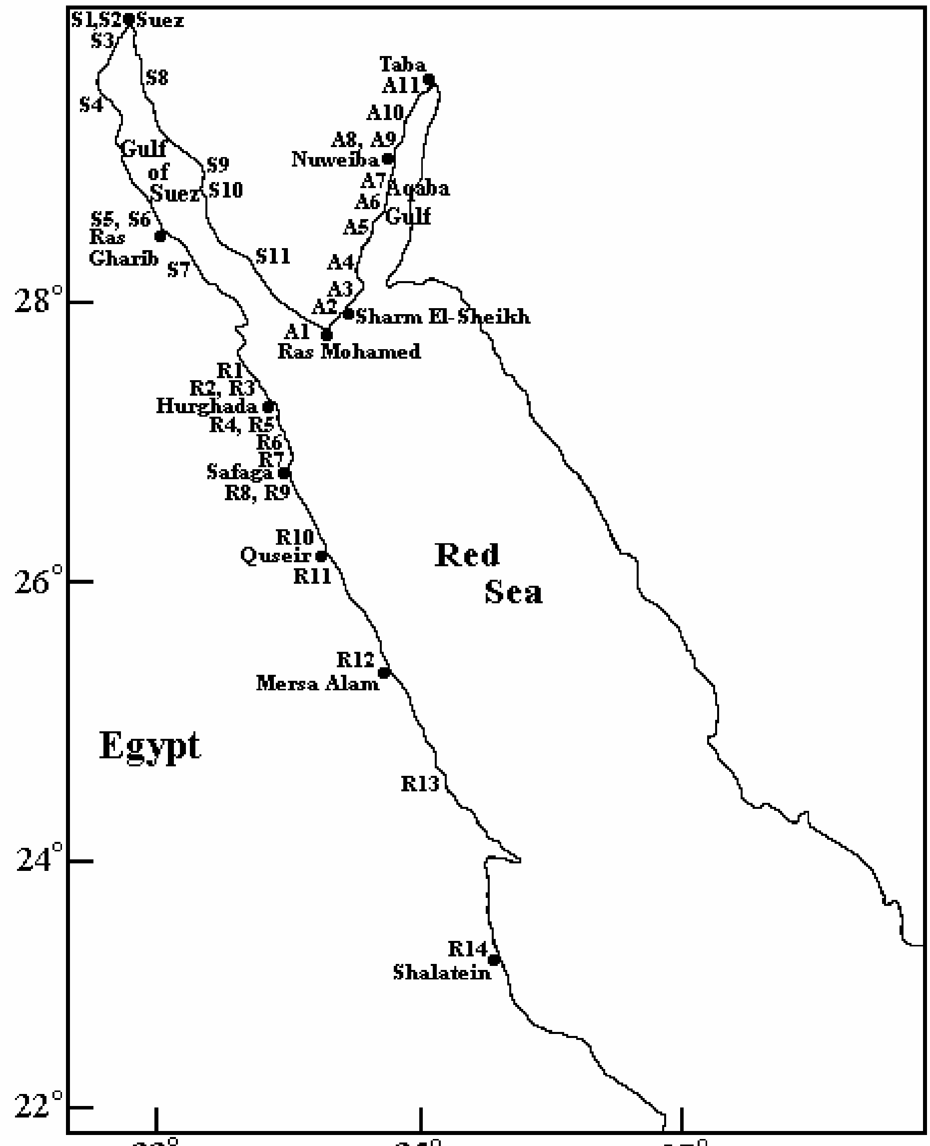


Fig. (1): Map of the Mediterranean and Red Seas showing the selected sectors and sampling stations.

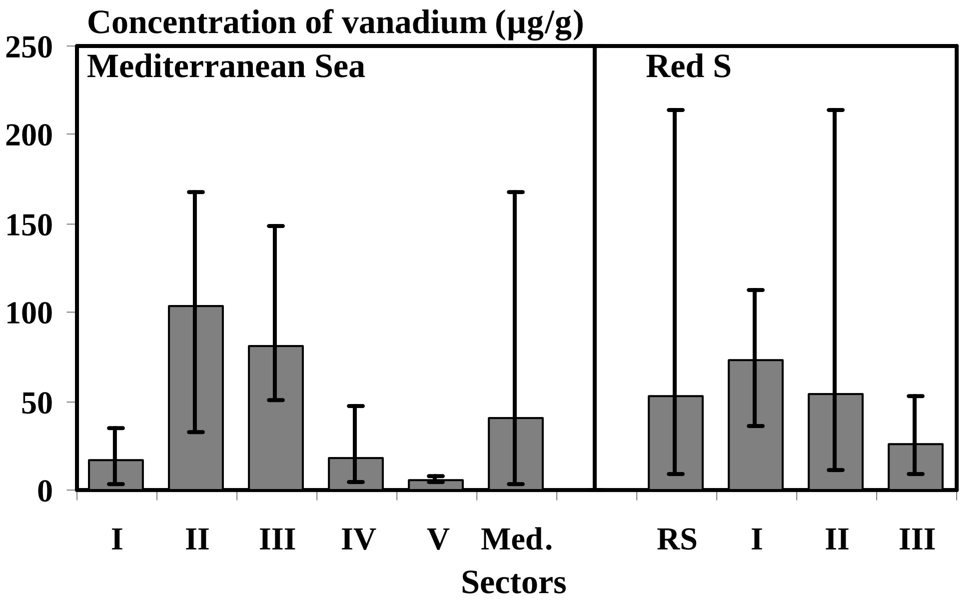
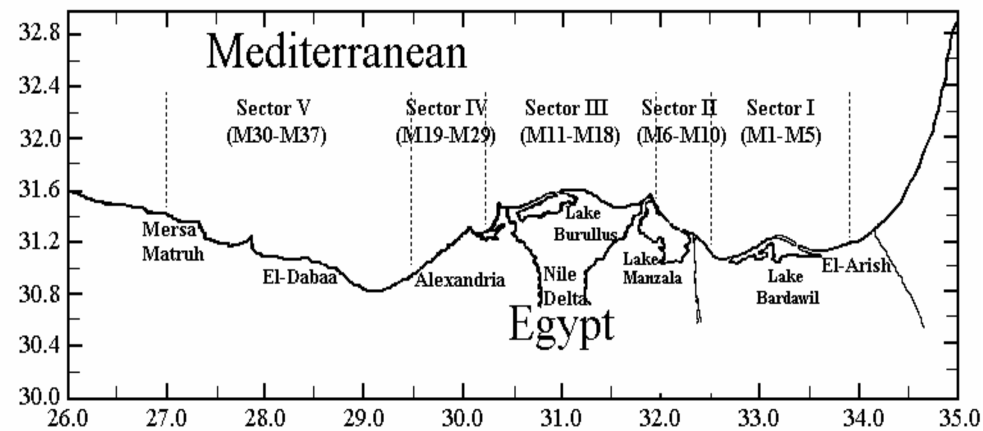


Fig. (2): Mean concentrations of vanadium in sediments at different sectors of the Mediterranean and Red Seas.
(Error bar represents the lowest and highest value for each sector)



Sector I: Sinai coast, Sector II: Port Said coast, Sector III: Nile Delta coast, Sector IV: Alexandria coast, and Sector V: North coast

Table (1): Range, mean, standard deviation and CV % of vanadium in sediments collected from Mediterranean, Egypt (μg/g dry wt.)

Sector	Station	Range	Mean ± SD	CV %
I	M1	15.93 – 16.61	16.29 ± 0.34	2.10
	M2	2.91 – 4.27	3.76 ± 0.74	19.72
	M3	3.89 – 5.80	4.78 ± 0.96	20.15
	M4	26.70 – 27.00	26.88 ± 0.16	0.60
	M5	34.06 – 35.76	35.10 ± 0.91	2.59
II	M6	94.53 – 96.41	95.61 ± 0.97	1.01
	M7	71.04 ± 73.34	72.16 ± 1.15	1.59
	M8	149.7 – 152.6	151.4 ± 1.52	1.01
	M9	32.02 – 32.23	32.15 ± 0.11	0.35
	M10	166.0 – 169.2	168.0 ± 1.86	1.11
III	M11	74.28 – 77.38	75.71 ± 1.57	2.07
	M12	69.09 – 69.47	69.28 ± 0.19	0.28
	M13	68.75 – 71.98	70.35 ± 1.62	2.30
	M14	90.02 – 93.09	91.70 ± 1.55	1.69
	M15	147.7 – 149.4	148.8 ± 0.95	0.64
	M16	56.06 – 56.40	56.22 ± 0.17	0.31
	M17	82.02 – 82.96	82.41 ± 0.49	0.60
	M18	50.45 – 51.98	50.99 ± 0.86	1.69
IV	M19	46.87 – 47.21	46.99 ± 0.20	0.42
	M20	14.22 – 14.60	4.41 ± 0.19	1.32
	M21	14.82 – 16.12	15.51 ± 0.66	4.24
	M22	19.25 – 20.26	19.71 ± 0.51	2.60
	M23	17.51 – 18.19	17.85 ± 0.34	1.89
	M24	18.53 – 19.67	19.16 ± 0.58	3.03
	M25	22.75 – 23.38	23.13 ± 0.34	1.45
	M26	16.08 – 17.43	16.95 ± 0.76	4.46
	M27	15.39 - 16.32	15.99 ± 0.52	3.24
	M28	16.34 – 16.88	16.69 ± 0.31	1.83
	M29	7.30 – 7.89	7.70 ± 0.34	4.43
V	M30	4.52 – 5.07	4.83 ± 0.28	5.82
	M31	4.35 – 4.60	4.49 ± 0.13	2.90
	M32	4.94 – 5.32	5.18 ± 0.21	4.02
	M33	5.49 – 6.71	6.29 ± 0.69	11.05
	M34	8.27 – 8.57	8.41 ± 0.15	1.76
	M35	4.85 – 6.87	5.63 ± 0.69	12.19
	M36	4.94 – 5.44	5.22 ± 0.26	4.94
	M37	5.11 – 6.25	5.84 ± 0.64	10.88

Table (2): Range, mean, standard deviation and CV % of vanadium in sediments collected from Red Sea, Egypt (µg/g dry wt.)

Sector	Station	Range	Mean ± SD	CV %
I	R1	72.50 – 76.75	74.96 ± 2.20	2.93
	R2	33.97 – 38.01	36.19 ± 2.05	5.67
	R3	42.77 – 44.41	43.68 ± 0.84	1.92
	R4	83.18 – 90.53	86.94 ± 3.68	4.23
	R5	47.99 – 51.76	49.63 ± 1.93	3.89
	R6	107.7 – 116.7	112.4 ± 4.56	4.05
	R7	39.44 – 41.67	40.87 ± 1.24	3.04
	R8	63.48 – 65.46	64.45 ± 0.99	1.54
	R9	71.81 – 73.46	72.77 ± 0.86	1.18
	R10	108.2 – 110.8	109.9 ± 1.48	1.35
	R11	91.19 – 91.43	91.32 ± 0.13	0.14
	R12	74.45 – 76.10	75.52 ± 0.93	1.23
	R13	101.9 – 104.2	103.0 ± 1.14	1.10
	R14	62.66 – 64.31	63.21 ± 0.95	1.51
II	S1	109.6 – 112.8	110.8 ± 1.74	1.57
	S2	203.4 – 222.5	214.4 ± 9.86	4.60
	S3	54.09 – 55.38	54.85 ±0.68	1.23
	S4	24.86 – 25.37	25.16 ± 0.26	1.05
	S5	12.73 – 13.90	13.16 ± 0.64	4.89
	S6	14.15 – 14.86	14.54 ± 0.36	2.48
	S7	10.93 – 12.39	11.57 ± 0.75	6.48
	S8	18.34 – 19.51	18.78 ± 0.63	3.38
	S9	11.64 – 12.18	11.83 ± 0.30	2.56
	S10	43.33 – 46.38	44.81 ± 1.53	3.42
	S11	64.96 – 74.03	68.88 ± 4.66	6.76
III	A1	38.83 – 39.49	39.21 ± 0.34	0.88
	A2	23.04 – 26.09	24.43 ± 1.54	6.32
	A3	27.08 – 28.08	27.72 ± 0.55	1.98
	A4	52.85 – 54.33	53.41 ± 0.80	1.51
	A5	14.80 – 16.02	15.57 ± 0.67	4.31
	A6	26.59 – 27.67	27.16 ± 0.54	2.00
	A7	29.97 – 30.63	30.32 ± 0.33	1.10
	A8	8.35 – 8.70	8.50 ± 0.18	2.11
	A9	11.63 – 12.35	11.91 ± 0.38	3.22
	A10	11.05 – 11.35	11.15 ± 0.17	1.52
	A11	29.93 ± 32.15	30.91 ± 1.13	3.66

Table (3): Comparison of the present levels of vanadium in sediments from the Egyptian waters with reported levels of different regions.

Region	Level of vanadium in sediments (µg/g)	References
New Mexico	< 5 – 13.4	O'Brien, 1990
Western United	18 – 270	O'Brien, 1990
States	130	Leoni and Sartori, 1996
Italy	76	Leivuori, 1998
Finland	51 – 269	Abd El-Azim, 2002
Suez Canal	20.5 – 32.8	Pehaim, 2004
California	37 – 380	El-Moselhy and Abd El-Azim, 2005
Suez Bay	3.76 – 168	Present study
Mediterranean	8.5 – 214.4	Present study
Red Sea		
Typical sediments	20 - 150	Moore, 1991

Table (4): I_{geo} classes with respect to sediment quality (Muller, 1979).

I_{geo}	I_{geo} classes	Sediment quality
< 0	0	Unpolluted
0 - < 1	1	Unpolluted and moderately polluted
1	2	Moderately polluted
2 – 3	3	Moderately to highly polluted
3 – 4	4	Highly polluted
4 – 5	5	Highly to very highly polluted
> 5	6	Very highly polluted

4. SUMMARY AND CONCLUSION

The present study deals with the distribution of vanadium in sediments of the Egyptian marine coasts. The obtained data showed that the Red Sea sediments had a mean concentration of vanadium higher than those of the Mediterranean, but it was insignificant. The highest extreme value of vanadium (214.4 µg/g) was recorded at station S2 located at the Suez Bay (northern part of the Gulf of Suez – Red Sea), which is characterized by the petroleum activities. These results indicated that the vanadium is very closed to the petroleum activities, and therefore it can be used as indicator for petroleum pollution. In general, the high concentrations of vanadium – as most metals – were recorded at the stations and sectors affected directly by the different pollution sources as industrial and agricultural effluents, sewage discharge, harbours, shipping activities as well as the inland water drains.

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