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Levels of Vanadium in Tern Eggs and Sediments of Shidvar and Bani Farour Islands, Persian Gulf

Fahimeh Goudarzi Avazpour[1, 2*], Alireza Riyahi Bakhtiari [3] & Mir Masoud Sajjadi [4]

1) *Marine Biology Department, Faculty of Basic Science, Hormozgan University, Bandar Abbas, Iran*
2) *Hormozgan Provincial Office of the Department of the Environment (DOE), Bandar Abbas, Iran*
3) *Department of Environmental Science, Tarbiat Modares University, Noor, Iran*
4) *Department of Fisheries, Faculty of Natural Resources, Gilan University, Sowmea-Sara, Iran*

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Abstract
Oil contains several heavy metals such as vanadium, which in high concentrations have adverse effects on animal breeding, physiology and their behaviour. Marine birds and sediments which are known as sentinel species and metal reservoir respectively are appropriate indicators of pollutions in marine ecosystems. This survey was conducted in July 2012. Objectives of the study were to examine the concentrations of Vanadium in randomly collected eggs of three breeding tern species and sediments on Shidvar and Bani Farour Islands, in the Persian Gulf; to survey the suitability of terns eggs as a biomonitoring agent. The highest mean of Vanadium level of egg contents and eggshells were found in Bridled Tern from Shidvar Island. The comparison between the same species from these islands indicated that the mean Vanadium level in the White-cheeked Tern and Bridled Tern on Bani Farour Island were more than Shidvar Island while the average was, in contrast, more for the Lesser Crested Tern nesting on Shidvar Island. There was significant difference between concentrations of Vanadium in sediments of these two islands (p<0.01). Although most Vanadium levels in eggs were lower than FSNZ and WHO standards, and the rates in sediments were lower than RSA standard, the relative coordination between concentrations of Vanadium in eggs and sediments in the present study shows that tern eggs represent the pollution status of studying areas as a proper biomonitoring agent.

1. Introduction

Since public concern about environmental health is increasing, it is necessary to assess the status and trend of pollutions (Burger & Gochfeld 2004). Oil contains several heavy metals, such as Vanadium, which, high concentrations of them have harmful effects on physiology, behaviour and reproduction of animals (Irwin *et al.* 1997; Moreno *et al.* 2011). Toxic heavy metals, which belong to the group of inorganic pollutants, are durable in the environment and accumulate in tissues because pollutant levels increase during the lifetime of the organism (bioaccumulation) and each succeeding step in the food-chain (biomagnification) (Gochfeld & Burger 1998; Stankovic & Stankovic 2013).

Due to human interventions and the dominant natural conditions, the Persian Gulf is an extremely stressed marine environment (Khan 2007). The undesirable nature of the Persian Gulf has introduced various anthropogenic stressors which influence its ecological integrity and sustainability.

* *Corresponding: fg1360@gmail.com*

However, growing economic development brought wide achievements for the region. The most important activities include oil exploration and production, petrochemical industries and marine transportation (UNEP 2004, Khan 2007). The southern coasts and islands of Iran are constantly exposed to numerous pollutants resulting from human activities and oil spills. Shidvar Island is close to Lavan Island, which is one of the four major terminals for exporting crude oil in Iran. Hence, Shidvar Island is exposed to organic and inorganic contaminants in crude oil. Bani Farour Island is situated through international waterways in the Persian Gulf and small cargo ships and tankers pass its nearby daily.

Birds, especially raptors, waterbirds, waders and seabirds have frequently been used as bioindicators of environmental pollutions such as heavy metal contaminations (Burger & Gochfeld 2004). Seabirds are top level carnivores. Thus they accumulate pollutants, mainly by consuming contaminated foods (Lam *et al.* 2004; Shahbaz *et al.* 2013). Thousands of migratory terns travel to both of these islands annually, for feeding, nesting and breeding. Whenever seabirds are exposed to pollutants, they can respond relatively fast to contamination events. Thus they are useful as sentinel species of ecosystem health (Lewis & Furness 1991; Thyen *et al.* 2000; Burger and Gochfeld 2004; Pereira *et al.* 2009). Bird eggs partly reflect pollutant concentrations through foraging by females around the breeding colony during the daytime before nesting and laying the eggs (Furness & Camphuysen 1997; Becker *et al.* 2001; Goutner *et al.* 2001; Ross *et al.* 2008; Pereira *et al.* 2009).

Soil is also one of the main sources of heavy metals in sediments, but surface contamination with trace metals is witnessed a history of pollution. In addition, due to high physico-chemical consistency and their characteristics that usually indicate the average condition of the system, sediments illustrate the average water quality (Boncompagni *et al.* 2003; Santos *et al.* 2005; Kazemi *et al.* 2012).

However, determination of Vanadium concentration using bird eggs, especially utilizing bird eggs and sediments simultaneously, has been rarely done (Mora 2003; Ikemoto 2005; Lam 2005). The objectives of this study were to examine the concentrations of Vanadium in eggs of three tern species (the White-cheeked Tern *Sterna repressa*, Bridled Tern *Sterna anaethetus* and Lesser Crested Tern *Thalasseus bengalensis*), nesting on Shidvar and Bani Farour Islands, and in sediments of the mentioned islands in the Persian Gulf. It also aimed to survey the suitability of tern eggs as a biomonitoring agent.

2. Materials and Methods

2.1. Study area

Study areas were Shidvar and Bani Farour Islands in the Persian Gulf (Fig. 1). Shidvar Island (26º47’37’’–26º47’44’’N; 53º25’15’’–53º24’08’’E) is situated about 1.5 km east to Lavan Island. This Ramsar site covers an area of 98 ha as a Wildlife Refuge and 870 ha as an International Wetland. Bani Farour Island (26º07’04’’–26º47’06’’N; 54º26’54’’–54º26’09’’E) is located about 16 km southwest to Farour Island. This protected area covers an area of 86 ha. Both Shidvar and Banifarur Islands, which are designated as Important Bird Areas (IBAs) in the Middle East, are suitable habitats for breeding colonies of four species of terns consisted of the White-cheeked Tern *Sterna repressa*, Bridled Tern *Sterna anaethetus*, Lesser Crested Tern *Thalasseus bengalensis* and Swift Tern *Sterna bergii*. Nesting locations of three tern species on Shidvar and Bani Farour Islands are shown in Figs. 2-3.

2.2. Methods

In July 2012, Simple random sampling method was carried out under the license of Hormozgan Provincial Office of the Department of the Environment (DOE). In total, 11, 11 and 15 fresh eggs of White-cheeked Tern, Bridled Tern and Lesser Crested Tern were collected, respectively on

Shidvar Island and 8, 5 and 7 eggs of White-cheeked Tern, Bridled Tern and Lesser Crested Tern were taken, respectively on Bani Farour Island.

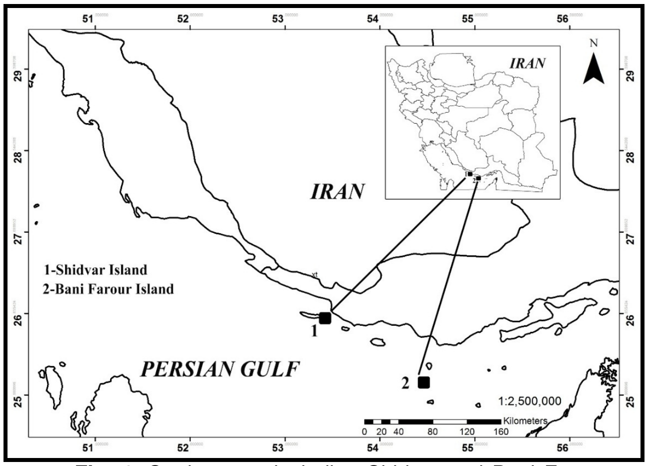

Fig. 1. Study areas including Shidvar and Bani Farour Islands in the Persian Gulf.

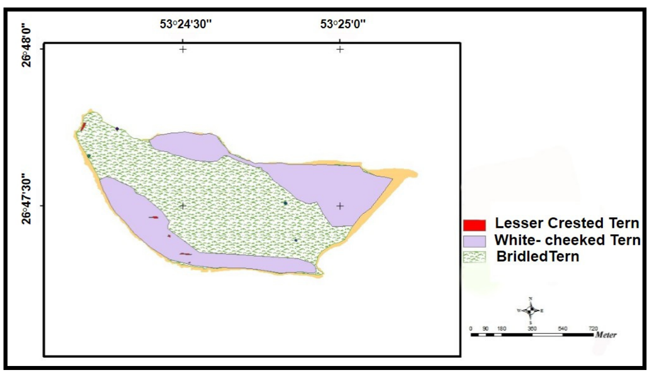

Fig. 2. Nesting locations of three tern species on Shidvar Island in the Persian Gulf.

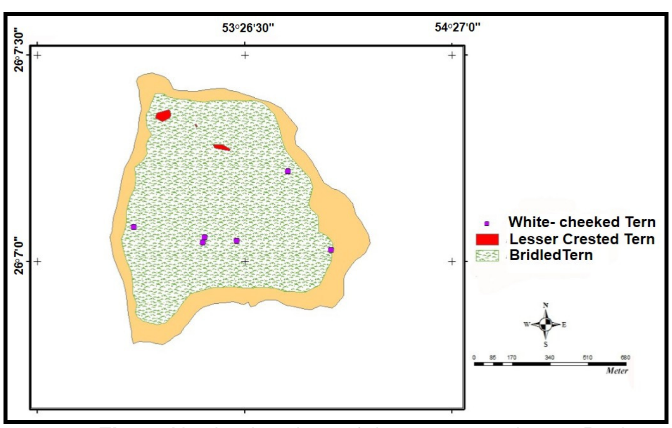

Fig. 3. Nesting locations of three tern species on Bani Farour Island in the Persian Gulf.

Fig. 4. Nest of White cheeked Tern *Sterna repressa*, Shidvar Island, July 2012. © F. Goudarzi.

Fig. 5. Nest of Bridled Tern *Sterna anaethetus*, Bani Farour Island, July 2012. © F. Goudarzi.

Fig. 6. Nest of Lesser Crested Tern *Thalasseus bengalensis*, Shidvar Island, July 2012. © M. Ghasemi.

Table 1. Sediment sampling stations coordinates in Shidvar and Bani Farour Islands, the Persian Gulf, July 2012.

Island	Station Number	Coordinates	
		Latitudes	Longitudes
Shidvar	1	26°47'36.70" N	53°25'13.23" E
	2	26°47'23.00" N	53°24'60.00" E
	3	26°47'26.18" N	53°24'19.82" E
	4	26°47'43.63" N	53°24'26.02" E
	5	26°47'38.16" N	53°24'52.04" E
Bani Farour	1	26°07'06.68" N	54°26'45.84" E
	2	26°06'48.44" N	54°26'13.47" E
	3	26°07'25.10" N	54°26'15.71" E

Eggs were collected during laying or the early incubation period from separate nests of each colony. Sampling of the surface sediment (0-5cm) was done on Shidvar and Banifarur Islands in five and three stations respectively, each with 3 times replications, from the intertidal zone. The longitudes and latitudes of sampling stations were recorded by the GPS (Table 1). The packed eggs and sediments were labeled in polyethylene plastic bags and transferred to the laboratory within an ice box. The samples were frozen at –20°C until they were prepared and analyzed.

The surface of eggs was cleaned carefully with deionized water and eggs were thawed at room temperature. The biometry of eggs consisted of the length (0.01 mm), width (0.01 mm) and weight (0.001 mm). Eggs were cracked and separated in two parts: egg contents and eggshells, both parts were weighed. Egg contents were homogenized. Both egg contents and eggshells were dried for 48 h at 60°C in an oven to stable weight. Sediment samples were also weighed and dried for at least 16 h at 70°C in an oven to constant weight. Then, all the dried samples were ground in a stone mortar to a powder, separately (Yap *et al.* 2002; Lam *et al.* 2004).

Samples were prepared for the analysis in accordance with MOOPAM 1999 method (ROPME 1999). A sample of 0.2 g – for both egg contents and eggshells- were weighed in Teflon bombs and 5 ml of concentrated nitric acid were added. Samples were predigested at room temperature for 1 h, and were totally digested at high temperature (90° C) for 3 h on a hot-plate and were filtered through Whatman 42 filter paper and the residues were diluted with double-deionized water to 50 ml volume. For determining the Vanadium concentration in sediment samples, samples of 0.2 g were mixed with a combination of nitric acid and hydrochloride acid in the ratio of 1:3 and 6 ml of concentrated hydrofluoric acid at room temperature for 1 h, and were fully digested at high temperature (120° C) for 2.5 h on a hot-plate. Then 2.7 g boric acids were placed in polyethylene dishes and about 20 ml of double-deionized water was added. Digested samples were filtered through Whatman 42 filter paper and the residues were diluted with double-deionized water to 50 ml volume. All filtrates were stored. After preparation and digestion steps, the Vanadium levels in prepared samples were determined, using an Atomic Absorption Spectrometer (AAS) GBC935 Model. To avoid probable contaminations, all used dishes and equipments were washed with nitric acid. Detection limit of AAS for Vanadium (0.01 µg/g, dry wt) was determined. To ensure that the samples were devoid of contaminations, blank samples were utilized using the same procedure. The accuracy of the analysis was checked and the percentage of recoveries was above 95%.

2.3. Statistical analysis

For statistical purposes, non-detected concentrations were instated a value of half the limit of detection. Statistical analysis was done with SPSS 17.0 software, applying descriptive statistics (mean and standard deviation) and analytical test (Independent t-test). Independent t-test was used to determine whether significant differences exist between the concentrations of Vanadium in sediments of these two islands. To conduct the statistical analyses, non-detectable values were replaced by half of the detection level (LOD/2) (0.005 µg/g) (Croghan & Egeghy 2003; Helsel 2005; Gochfeld & Burger 2005).

3. Results

3.1. Vanadium level in egg contents and eggshell samples

The concentration of Vanadium (mean ± SD and range in µg/g dry wt.) in the egg components of the three tern species and sediments is summarized in Tables 2-3. The concentration of Vanadium in the egg contents and eggshells were below the Limit of Detection (0.01 µg/g), except for one sample of the egg content of Bridled Tern from Shidvar Island and six samples of eggshells of all the three species from both islands.

The mean concentration of Vanadium in the egg contents, eggshells and eggs (altogether) were respectively 0.01±0.00, 0.05±0.2 and 0.06±0.2 (µg/g dry wt) for the White-cheeked Tern, 0.129±0.49, 0.448 ±1.26, 0.733±1.75 (µg/g dry wt) for the Bridled Tern and 0.03±0.12, 0.12±0.3, 0.18±0.41 (µg/g dry wt) for the Lesser Crested Tern.

The highest concentration of Vanadium in egg content and eggshell samples (1.983 and 5.005 µg/g dry wt, respectively) and the highest mean of Vanadium level in egg contents and eggshells (0.185 and 0.546 µg/g dry wt, respectively), were in Bridled Tern from Shidvar Island.

The statistical analysis between species was not possible because more than half of the data of egg samples were below the limit of detection, but comparison between the same species from two islands indicated that the mean Vanadium level in the White-cheeked Tern and Bridled Tern from Bani Farour Island were more than Shidvar Island while the average was more for the Lesser Crested Tern nesting on Shidvar Island.

3.2. Vanadium level in sediment samples

The mean concentration of vanadium for sediments in Shidvar and Banifarur Islands were 1.014±0.132 and 3.029±1.807 µg/g dry wt, respectively. The highest and the lowest Vanadium level in sediment samples were from Bani Farour and Shidvar Islands (5.727 and 0.767 µg/g dry wt, respectively). Independent *t*-test showed that there was a significant difference between the concentration of Vanadium in sediments of these two islands ($p<0.01$).

Table 2. Concentrations of Vanadium (mean ± S.D. and range in µg/g dry wt.) in the egg components of Lesser Crested Tern (LCTE), Bridled Tern (BTE), White-cheeked Tern (WCTE) three tern species from Shidvar and Bani Farour Islands, Persian Gulf, July 2012.

Study Area	Sample Unit	WCTE (Num: SHI 11, BI 8, Total 19)		BTE (Num: SHI 11, BI 5, Total 16)		LCTE (Num: SHI 15, BI 7, Total 22)	
		Means±SD	Range	Means±SD	Range	Means±SD	Range
Shidvar Island	Egg Content	0.005±0.000	<0.01-<0.01	0.005±0.000	<0.01-<0.01	0.045±0.153	<0.01-0.60
	Eggshell	0.005±0.000	<0.01-<0.01	0.091±0.285	<0.01-0.95	0.129±0.339	<0.01-1.17
	Egg (total)	0.010±0.000	<0.01-<0.01	0.300±0.600	<0.01-1.86	0.210±0.470	<0.01-1.77
Bani Farour Island	Egg Content	0.005±0.000	<0.01-<0.01	0.400±0.880	<0.01-<1.98	0.005±0.000	<0.01-<0.01
	Eggshell	0.117±0.310	<0.01-0.89	1.230±2.160	<0.01-5.00	0.097±0.243	<0.01-0.66
	Egg (total)	0.120±0.310	<0.01-0.90	1.630±3.030	<0.01-6.98	0.100±0.240	<0.01-0.65
Shidvar & Bani Farour Islands (Persian Gulf)	Egg Content	0.010±0.000	<0.01-<0.01	0.129±0.490	<0.01-1.98	0.030±0.120	<0.01-0.60
	Eggshell	0.050±0.200	<0.01-0.89	0.450±1.260	<0.01-5.57	0.120±0.300	<0.01-0.65
	Egg(total)	0.060±0.200	<0.01-0.90	0.733±1.750	<0.01-6.98	0.180±0.410	<0.01-1.77

Table 3. Concentrations of Vanadium (mean ± S.D. and range in µg/g dry wt.) in sediments from Shidvar and Bani Farour Islands, Persian Gulf, July 2012.

Island	Station	Number of Samples	Means±SD	Range
Shidvar	1	3	1.04±0.11	0.95-1.16
	2	3	0.93±0.15	0.82-1.1
	3	3	0.88±0.11	0.77-0.99
	4	3	1.07±0.04	1.03-1.11
	5	3	1.14±0.08	1.05-1.19
	Total Stations of Shidvar Island	15	1.01±0.13	0.76-1.19
Bani Farour	1	3	1.98±0.63	1.32-2.58
	2	3	5.39±0.32	5.08-5.73
	3	3	1.73±0.05	1.67-1.78
	Total Stations of Bani Farour Island	9	3.02±1.80	1.32-5.72

4. Discussion

Symptoms of toxicity of Vanadium have been observed in many organisms. The most repetitious signs were in the liver, kidneys, gonads and the nervous, haematological and cardiovascular systems (WHO 2000). In the present study, Vanadium level in all egg components of terns were lower than the Food Standards Australia New Zealand (FSNZ) (2 µg/g). Except for the mean concentration of Vanadium in eggshell and egg (total) of Bridled Tern from Bani Farour Island (1.23±2.16 and 1.63±3.03 µg/g dry wt, respectively) and mean concentration of Vanadium in the whole egg of Bridled Terns from these two islands (0.733±1.75 µg/g dry wt), the other results were lower than the WHO standard (0.5 µg/g) (WHO 2000).

Antagonistic interaction between Vanadium (V) and Chromium (Cr) seems to be one of the possible reasons of low Vanadium levels. It means that the presence of one of them leads to inactiveness of the other one (Davies 1974). This was found in some previous researches on Vanadium and Chromium levels in bird eggs at the same time. However, in the present study, the concentration of Cr was not determined. Therefore, the ratio of Cr and V levels was calculated. In 2005, the concentration of Cr to V ratio in the egg contents of Short-tailed Albatross and Black-footed Albatross were calculated 32.3 and 14.7, respectively (Ikemoto *et al.* 2005). In another study, the ratio in the egg content of Black-crowned Night Heron *Nycticorax nycticorax*, Little Egret *Egretta garzetta* and Bridled Tern was reported 39.7, 12.6 and 20.3, respectively during the same year. This ratio in eggshell of Black-crowned Night Heron and Little Egret was calculated 7.72 and 1.89, respectively while the concentration of Cr in eggshell of Bridled Tern was 0.241 µg/g and Vanadium level was below the limit of detection (Lam *et al.* 2005).

The concentration of 18 trace elements were determined in eggs of Short-tailed Albatrosses *Phoebastria albatrus* and Black-footed Albatrosses *Phoebastria nigripes* from Torishima Island in Japan, 0.023 and 0.013 µg/g dry wt, respectively (Ikemoto *et al.* 2005). In the present study, mean concentration of Vanadium in the egg content of Bridled Tern and Lesser Crested Tern were 0.13 and 0.03 µg/g, respectively, more than the forenamed study. However,, the concentration of Vanadium in the egg content of the White-cheeked Tern was 0.01 µg/g and less than that of Torishima Island.

Lam *et al.* (2005) reported Vanadium level in egg contents of Little Egret, 0.008 µg/g dry wt, Black-crowned Night Heron 0.03 µg/g dry wt and Bridled Tern 0.096 µg/g dry wt, from Hong Kong, China. Compared with the present study, Vanadium level in egg content of Bridled Tern (0.129 µg/g dry wt) from the Persian Gulf was more than all the three studied species in Hong Kong; which implies more probable contamination in the Persian Gulf. Vanadium level in egg content of the Lesser Crested Tern in this study (0.03 µg/g dry wt) was equal to the Little Egret, more than the Black-crowned Night Heron and less than the Bridled Tern studied by Lam *et al.* (2005). Determined concentration of Vanadium in the eggshells of Little Egret, Black-crowned Night Heron and Bridled Tern were 0.107 µg/g dry wt, 0.011 µg/g dry wt and below the limit of detection, respectively while in the present study, the Vanadium level in the eggshells of Bridle Tern (0.45 µg/g dry wt) and Lesser Crested Tern (0.12 µg/g dry wt) were more than all the three mentioned species by Lam *et al.* (2005). The concentration in the White-cheeked Tern (0.05 µg/g dry wt) was more than the Black-crowned Night Heron and Bridled Tern and less than the Little Egret.

Mora *et al.* (2003) determined concentration of Vanadium in eggshell and egg contents of Yellow-breasted Chat *Icteria virens* and in egg (total) of Willow Flycatcher *Empidonax traillii extimus* 5.2, 4.8 and 0.5 µg/g, respectively and more than the Vanadium level in eggshells of all the three terns in this study. Besides, the Vanadium level in egg (total) of Yellow-breasted Chat was 0.5 µg/g and less than V level of the Bridled Tern in the Persian Gulf. Generally, the different rates of metals, such as Vanadium, in eggs of various species of birds depend on the diversity in feeding habits, including type of food and foraging region, physiology and bioavailability as some species like Black-crowned Night Heron and Reef Heron feed along the shorelines while terns and other seabirds are offshore feeders (Burger 2002).

The bioaccumulation of the metals depends on the size and age of female birds. It increases with the age and size of females and the amount of metal excretion (Gochfeld *et al.* 1996; Ikemoto *et al.* 2005). The number of eggs laid by female birds is also effective in increasing the bioaccumulation. The range of Vanadium levels on Shidvar and Bani Farour Islands were 0.76-1.19 and 1.32-5.72 µg/g dry wt, respectively; less than the RSA (ROPME Sea Area) Guideline (allowed range: 20–30 µg/g). The high Vanadium level in sediment samples of Bani Farour Island (5.73, 5.08 and 5.35 µg/g) made a significant difference between the concentrations of Vanadium in sediments of these two islands. Regardless of this station, there were no significant differences in the mean concentration of Vanadium in the sediments. One of the possible reasons is oil spills from sinking ships in station 2 in Bani Farour Island, which have been collided due to the rocky coasts at high tide. Shidvar Island is nearby the Lavan Island, one of the most important islands for exporting crude oil in Iran, and we expect higher Vanadium levels in sediment samples of the Shidvar Island than Bani Farour Island. However, not only there were not any significant differences in the mean concentration of Vanadium in the sediments (irrespective of the station 2 in Bani Farour Island) but also the Vanadium levels in sediment samples of Bani Farour Island was higher. Since Bani Farour Island is located through international waterways in the Persian Gulf, this island is exposed to oil spills of military and cargo ships, tankers and several vessels passing near the island. Comparing the concentration of Vanadium in sediments of Shidvar and Bani Farour Islands and earlier studies in the Persian Gulf (Table 4), results of Vanadium levels in the present study are less, but a large increase is obvious in Vanadium levels of sediments from Shidvar Island compared with a study in this area in 2009 (Taghizadeh 2009). Since the existence of Vanadium is an indicator of oil pollution in an ecosystem, it may be as a result of increase in oil contamination level in recent years. In general, the lower Vanadium levels of the present study than standards in eggs (FSNZ and WHO standard) and sediments (RSA standard) represent a relative coordination between the concentration of Vanadium in eggs and sediments. Therefore, tern eggs can be used as a proper biomonitoring agent for the pollution status of the study areas.

5. Recommendation

Monitoring of heavy metal is necessary for aquatic environments. Some suggestions are provided to reduce environmental impacts in the study areas.

- Annual monitoring of Vanadium level and other heavy metals in the coastal waters around the Shidvar and Bani Farour Islands to assess trend of pollutions using tern egg as a monitoring agent.
- Using different monitoring agents such as bivalves to survey oil pollutions.
- The ministry of petroleum of Iran is required to monitor the sensitive marine areas to determine oil and heavy metal contaminations.
- Studying resident population in Lavan Island to measure heavy metals in their body tissues such as blood and hair, in different genders and ages.

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