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Distribution and pollution level of nickel and vanadium in sediments from south part of the Caspian Sea, Iran

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Distribution and pollution level of nickel and vanadium in sediment from south part of the Caspian Sea, north of Iran, were studied. Sediment samples obtained by Van Veen Grab from four stations, including, Turkaman, Amirabad, Fereydunkenar and Noushahr along the south part of the Caspian Sea, during fall of 2015 and april, summer and winter of 2016. The concentrations of metal were ranged from 21.63 µg/g to 55.45 µg/g for nickel and from 58.23 µg/g to 146.27 µg/g for vanadium in sediments samples collected from all stations. There was significant difference in metals concentration between different stations along the Caspian Sea ($P < 0.05$), and the highest mean concentration of metals was absorbed in Fereydunkenar estuary, followed by Amirabad, Turkaman and Noushahr, respectively. The results showed that there were significant differences between metals pollution during four seasons ($P < 0.05$), and the highest concentration of metals were absorbed in dry season (summer) and the lowest concentration in wet season (winter). There was a positive correlation between nickel and vanadium concentration in sediment samples, and the Pearson correlation was ($r = 0.67$) between nickel and vanadium in sediment samples. The positive correlation between heavy metals can be related to same source of both metals in the environment. Based on our results, anthropogenic activities such as oil industry and agriculture activities are the main sources of pollution in the coasts along south part of Caspian Sea.

[**Keywords***:* Pollution; Nickel; Vanadium; Sediment; Caspian Sea]

Introduction

Heavy metals are important source of hazardous pollutants in the aquatic ecosystems[1]. They cause serious problems in the aquatic organisms, intertidal organisms and humans. There is worldwide concern about heavy metal contamination because of the environmental persistence of these elements, biogeochemical recycling and the ecological risks that the metals present. A large number of anthropogenically generated heavy metals from urban areas, agricultural areas and industrial sites are discharged into aquatic environment where they are transported in the water column, accumulated in sediment, and biomagnified through the food chain, resulting in significant ecological risk to benthic organisms, fish and humans[2].

The contamination of aquatic systems by heavy metals, especially in sediments, has become one of the most challenging pollution issues owing to the toxicity, abundance, persistence, and subsequent bio-accumulation of these materials[3,4]. When discharged into aquatic ecosystems, heavy metals can be absorbed by suspended solids, then strongly accumulated in sediments and biomagnified along aquatic food chains. Moreover, these sediments act as sinks, and may in turn act as sources of heavy metals[5]. Thus, heavy metal pollution in the sediments of aquatic ecosystems has recently been extensively investigated to effectively manage these ecosystems. Therefore, sediments are the main sink for heavy metals in aquatic environment, and sediment quality has been recognized as an important indicator of water pollution[6,7].

The Caspian Sea is the largest inland water body on the earth and debate still exists whether this water body should be referred to as a sea or as a lake. The biodiversity of the Caspian Sea and its coastal zone makes the region one of the most valuable ecosystems in the world. There are many countries around the Caspian Sea[8]. Recently, anthropogenic activities for economic development, especially by industry have intensified continuously and rapidly, particularly in south part of the Caspian Sea[9]. Therefore, Caspian Sea receives a lot of anthropogenic and industrial wastewater through rivers flowing from the surrounding countries, Azerbaijan, Iran, Kazakhstan, Russia and Turkmenistan. Study on heavy metals in aquatic ecosystems can give valuable information about the environmental condition of that ecosystem[10]. The main aim of this study was to evaluate distribution and pollution level of Ni and V in sediment from different stations along the south part of the Caspian Sea. Also, we investigated the correlation between metals in sediments.

Materials and Methods

Sediment samples were obtained from four station including, Turkaman, Amirabad, Fereydunkenar and Noushahr along the south part of the Caspian Sea (Fig. 1).

Surface sediments were collected by Van Veen Grab in fall of 2015 and April, summer and winter of 2016. Sub samples were taken from the uppermost layer of the sediments to minimize contamination. Surface sediments (5 cm) were sectioned and stored in pre-combusted glass jars in a freezer (−20 °C) until analysis. Before analysis, sediments were freeze-dried and ground to achieve homogeneity. For determining the relationship between grain size and metal contents, the grain size of surface sediments was measured using a Beckman-Coulter laser particle size analyzer (Model LS 13 320). Briefly, 20 mL deionized water was added to 1 g of freeze-dried sediment in a beaker. After soaking for 24 h, the sediment was subjected to vortex mixing for 5 min to disaggregate loosely-attached aggregates[11, 12].

For each sample, a known quantity (1 g) of sediment was digested with a solution of concentrated $HClO_4$ (2 ml) and HF (10 ml) to near dryness. Subsequently, a second addition of $HClO_4$ (1 ml) and HF (10 ml) was made and the mixture was evaporated to near dryness. Finally, $HClO_4$ (1 ml) alone was added and the sample was evaporated until white fumes appeared. The residue was dissolved in concentrated HCl and diluted to 25 ml. Recovery varied between 97.8% and 103%. Metal concentrations were determined by a cold vapor Atomic Absorption Spectrometer Leco AMA-254. The accuracy of the analytical procedures was assessed using the certified reference material BCR-1 and yielded results were within the reference value range[13,14].

All data were tested for normal distribution with Shapiro-wilk normality test. One-way analysis of variance (ANOVA) fallowed by Duncan post hoc test was used to compare the data by station. The metal concentration of each sample was expressed in micrograms of metal per gram dry of sediment (µg/g) and a probability of $p = 0.05$ was set to indicate statistical significance.

Results and Discussion

The Ni and V concentration (mean ± SD) in different stations during four seasons from south part of the Caspian Sea are presented in Table 1. The concentrations of Ni ranged from 21.63 µg/g to 55.45 µg/g in sediments samples collected from all stations. The mean concentration of Ni was 28.06 µg/g in

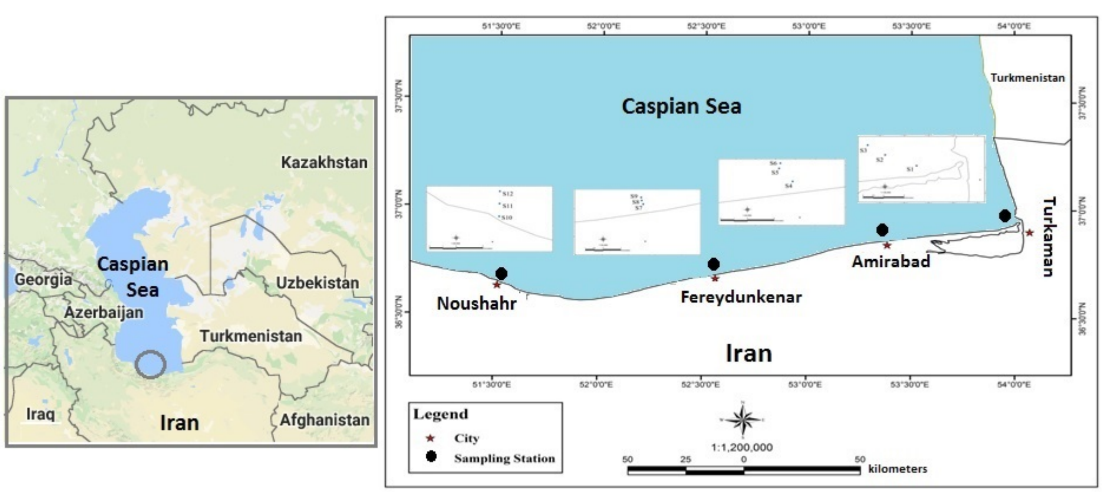

Fig. 1 — Map showing sampling sites and area

Table 1— Ni and V concentration in different stations during four seasons from Caspian Sea

Metal	Season	Station			
		Turkaman	Amirabad	Fereydunkenar	Noushahr
Ni	Spring	28.54 ± 2.22	31.25 ± 3.73	45.37 ± 2.03	25.53 ± 2.13
	Summer	40.26 ± 1.13	49.28 ± 1.38	65.45 ± 5.13	34.47 ± 6.53
	Fall	31.63 ± 4.45	27.34 ± 6.47	41.25 ± 0.53	33.24 ± 3.27
	Winter	18.81 ± 0.28	19.46 ± 3.03	34.57± 2.46	24.12 ± 4.21
	Average	30.02 ± 2.08	31.59 ± 2.31	46.65 ± 1.35	29.34 ± 0.282
V	Spring	49.73 ± 2.26	79.23 ± 1.48	101.18 ± 0.23	93.25 ± 0.28
	Summer	82.38 ± 1.13	112.28 ± 3.53	146.27 ± 0.23	123.68 ± 2.55
	Fall	67.91 ± 5.56	85.74 ± 6.28	112.55 ± 0.23	83.65 ± 1.63
	Winter	58.23 ± 3.38	65.58 ± 2.24	95.82 ± 0.23	79.57 ± 5.26
	Average	64.56 ± 2.15	85.71 ± 4.53	113.95 ± 1.65	95.04 ± 2.46

Turkaman, 28.83 µg/g in Amirabad, 38.66 µg/g in Fereydunkenar and 29.34 µg/g in Noushahr. The concentration of V ranged from 58.23 µg/g to 146.27 µg/g in sediments sample collected from all stations. The mean concentration of Ni was 64.56 µg/g in Turkaman, 85.71 µg/g in Amirabad, 113.95 µg/g in Fereydunkenar and 95.04 µg/g in Noushahr.

The comparison of heavy metals concentration between different seasons from sampling area along the Caspian Sea is shown in Figure 2. The results show that there were significant differences between heavy metals pollution during four seasons ($P < 0.05$). The highest concentrations of metals were absorbed in dry season (summer) and the lowest concentration in wet season (winter). This may be due to slow movement of water in the sediment and the possible high absorption ability of heavy metals by the sediment. Therefore, in summer season, movement of water in the sediment is slower as compared to other seasons and the ability of sediments is higher for absorption of metals from water. Dan et al., (2014) reported that metal pollution in sediments in summer season was higher than the other seasons, because movement of water is slow and sediments can absorb high concentration of metals. Hosseini et al., (2014) showed sediments have high ability to absorb and accumulate metals in the summer than the other seasons[25].

Seasonal variations in concentration of the heavy metals could be due to the industrial activities and level of industrial wastewater in environment. In the dry season (summer) industrial activities and discharge of wastewater in to environment increased as compare to other seasons. Therefore, this result is in agreement with high enrichment factors of Ni and V during the summer season indicating anthropogenic inputs. Pakzadtoochaei and Einollahipeer, (2013) and

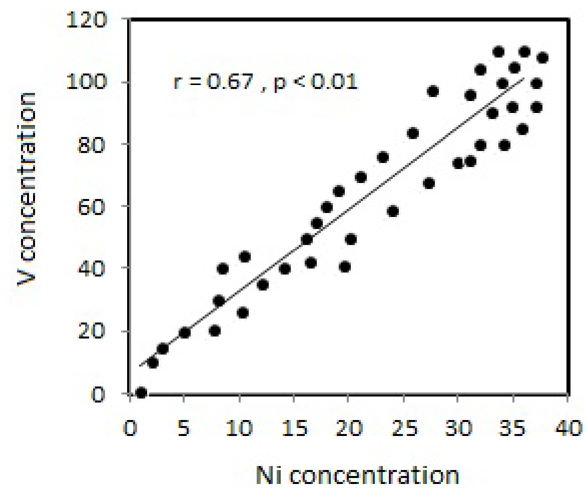

Fig. 2 — The correlation between Ni and V concentration in sediment from Caspian Sea

Ebah et al., (2016) showed that in the summer season anthropogenic activities and wastewater discharge in to aquatic environment such as sediment and water were higher than other seasons[26].

The concentration of the heavy metals in sediments could be due to the environmental parameters such as temperature and salinity and there are positive correlation between pollution levels and temperature and salinity levels. Therefore, concentration of heavy metals increased with increase in temperature and salinity and its levels in summer season are higher than the other seasons. Che et al., (2003), Chen et al., (2004) and Bastamim et al., (2015) reported that metal pollution in the sediments during summer season was higher than the other seasons, because with increase in temperature and salinity causes increase in metal concentration in sediments[27-30]. Also, the low values of heavy metals during the wet season (winter) may be due to dilution of the surface water due to rain and high input of fresh water from river into the sea. Increase in rain and high level water input into estuary can reduce concentration heavy metals, because increase in levels and movement of water causes removal of pollutants from environment. Raeisi Sarasiab et al., (2014) showed that metal concentrations in winter is lower that other seasons, because with increase in rainfall and water currents dilution of metals reduces pollution level[31]. Also, El-Sayeda et al., (2015) and Qingzhen et al., (2015) are in agreement with our results. Therefore, it can be concluded that the reasons such as slow movement in water, high temperature and salinity, high wastewater discharge in to environment and low rainfall in summer season, heavy metal concentration is higher in summer as compared to the other seasons[32, 33].

There was a positive correlation between nickel and vanadium concentration in sediment samples collected from different stations, and increase in nickel concentration causes increase in vanadium concentration (Fig. 3). Pearson correlation was ($r = 0.67$) between nickel and vanadium in sediment samples. The positive correlation between heavy metals can be related to same source of both metals, bioavailability of metal in sampling area, the same accumulation mechanism for metal, similar ionic charge, the reaction of metal with the soil particles and tendency of sediment compounds such as organic matter, organic carbon and carbonate to combine with metal.

Anirudh et al. (2009) reported that there is positive correlation between metals related to oil pollution such as Ni, V, Cd and Hg in sediments from aquatic environment[32]. Tabari et al., (2010) showed that oil industry is main source of Ni, Hg and V accumulation in sediments, therefore, there is high positive correlation between this metal in environment. Abdolahpour Monikh et al., (2012) reported that Khor-Ghazale located in north part of the Persian Gulf was relatively rich in Ni and V concentration[34]. It is likely that this high concentration of Ni was related to the oil tankers traffic in this creek. Saghali et al., (2014) showed that the high concentration of Ni and V in the sediments was related to oil tankers traffic and activities of oil industry in the Caspian Sea. Therefore, high positive correlation between Ni and V concentration in sediments is related to sources of both metals, bioavailability, and the reaction of metals with sediment compounds such as organic matter, organic carbon and carbonate.

Comparison with other studies

The comparison of Ni and V concentration with some standards is shown in Table 2. The mean concentration of Ni in three stations including Turkaman, Noushahr and Amirabad estuaries was lower than all studied in Table 2, but its concentration was higher than studies by Lak et al., 2015, Parizanganeh, 2008 in Caspian Sea. But, the mean concentration of Ni in Fereydunkenar station was higher than all last studied, but Ni concentration in this estuary was lower than studies by Jahangiri, 2001, Karbassi et al., 2004 and Saghali et al., 2014 in Caspian Sea and by Hosseini et al., 2014 in Persian Gulf.

The mean concentration of V in the sediments from Turkaman estuary was higher than all last studies in Caspian Sea and Persian Gulf, except in Caspian Sea by Karbassi et al,. (2004), Pirsaheb et al., (2015) and Bastami et al., (2015). The V concentration in Amirabad station was higher than all studies, except

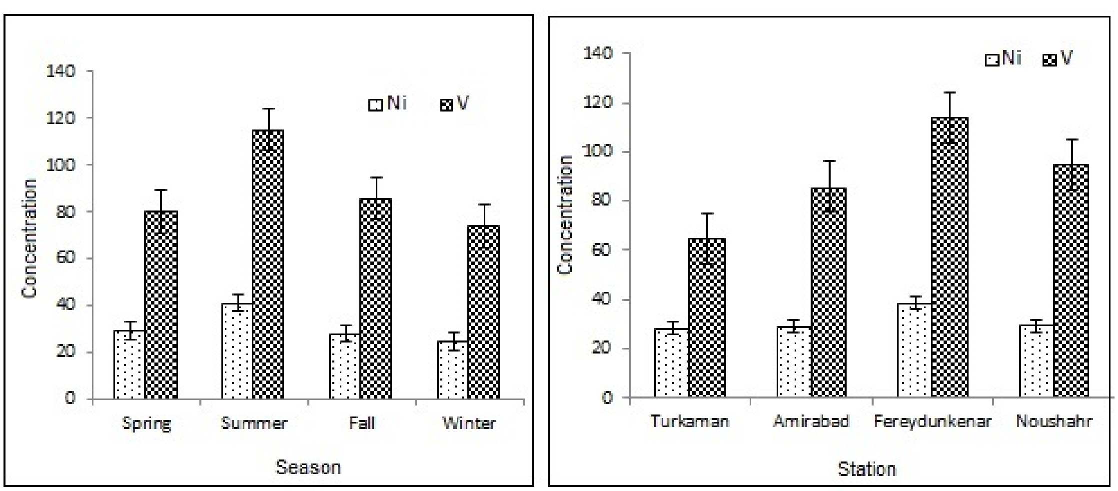

Fig. 3 — The comparison of metals concentration between different seasons and stations from Caspian Sea

Table 2— The comparison of Ni and V concentration in different coasts of word

Ni	V	Location	Reference
34.76	45.32	Caspian Sea	Hasanzadeh, 2000
55.14	55.12	Caspian Sea	Jahangiri, 2001
56.00	76.32	Caspian Sea	Karbassi et al., 2004
39.51	24.54	Caspian Sea	De Mora et al., 2004
38.65	45.32	Caspian Sea	Parizanganeh et al., 2007
9.65	57.43	Caspian Sea	Parizanganeh, 2008
35.54	43.12	Caspian Sea	Lahijani et al., 2010
31.54	34.76	Caspian Sea	Tabari et al., 2010
25.76	63.45	Caspian Sea	Hassanpour et al., 2012
51.16	-	Persian Gulf	Abdolahpour Monikh et al., 2012
45.14	-	Persian Gulf	Hosseini et al., 2014
64.55	-	Persian Gulf	Hosseini et al., 2014
55.43	68.45	Caspian Sea	Saghali et al., 2014
33.65	103.61	Caspian Sea	Pirsaheb et al., 2015
12.45	69.54	Caspian Sea	Lak et al., 2015
43.27	117.84	Caspian Sea	Bastami et al., 2015
44.56	-	Caspian Sea	Pakzad et al., 2016
11.5-16.8	84.54	Caspian Sea	Ghorbanzadeh Zaferani et al., 2016
30.02	64.56	This study	Turkaman
31.59	85.71	This study	Amirabad
46.65	113.95	This study	Fereydunkenar
29.34	95.04	This study	Noushahr

in Caspian Sea by Pirsaheb et al., (2015) and Bastami et al., (2015). The V concentration in Fereydunkenar and noushahr stations were higher than all studies as shown in Table 3, except in Caspian Sea by Bastami et al., (2015). Therefore, Ni concentration in Fereydunkenar station was very high and this station was polluted for Ni. Also, V concentration in the sediments collected from all stations was high and all estuaries were polluted for V.

The comparison of Ni and V concentration with some standards is shown in Table 3. The mean concentration of Ni in surface sediment in Turkman estuary was lower than ROPME and NOAA (ERM) standards, but was higher than NOAA (ERL), USEPA, ISQG and USFDA standards. The V concentration in this station was higher than the ROPME standard. Also, Ni concentration in Amirabad, Fereydunkenar and Noushahr estuaries was higher than all standards, expect ROPME standard. The mean concentrations of V in all stations in four seasons was higher than all standards. Based on our results, the mean concentrations of V in all station in four seasons was higher than all standards, also the mean concentration of Ni in all stations was higher than all standards, expect ROPME and NOAA.

Table 3 — The comparison of Ni and V concentration with some standards

Ni	V	Standard	Reference
70-80	20-30	ROPME	ROPME, 1999
20/9	-	NOAA (ERL)	de Astudillo et al., 2005
51/6	-	NOAA (ERM)	de Astudillo et al., 2005
15/9	-	USEPA	USEPA,1999
35/9	-	ISQG	Maret and Skinner, 2000
9.79	-	USFDA, 1993	USFDA, 1993
8.42	-	CCME, 1999	CCME, 1999

Conclusion

Distribution and pollution level of Ni and V in sediments from south part of the Caspian Sea, were studied. The concentration of metal ranged from 21.63 µg/g to 55.45 µg/g for Ni and from 58.23 µg/g to 146.27 µg/g for V in sediment samples collected from all stations. There was significant difference in metal concentration between different stations along the Caspian Sea ($P < 0.05$). The highest mean concentration of metals was absorbed in Fereydunkenar estuary, followed by Amirabad, Turkaman and Noushahr, respectively. The results showed there were significant differences between heavy metal pollution during four seasons ($P < 0.05$). The highest concentration of metals was absorbed in dry season (summer) and the lowest in wet season (winter). This may be due to slow movement of water in the sediments and the possible high absorption ability of the heavy metals by the sediment. Therefore, in summer season movement of water in the sediments is slower as, compared to other seasons and the ability of sediments is higher for absorption of metals from water. There was a positive correlation between metal concentration in sediment samples collected from different stations, and increase in Ni concentration caused increase in V concentration. Pearson correlation was ($r = 0.67$) between Ni and V in sediment samples. The positive correlation between heavy metals can be related to same source of both metals, bioavailability of metal in sampling area, the same accumulation mechanism for metal, similar ionic charge, the reaction of metal with the soil particles and tendency of sediment compounds such as organic matter, organic carbon and carbonate to combine with metal. The sources of pollution are oil and petroleum industry, oil pipelines, oil spills from the tankers oil storage tanks and petroleum compounds.

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