Int. J. Environ. Sci. Technol.
DOI 10.1007/s13762-017-1584-8

ORIGINAL PAPER

Trace metals level in sediments and bivalve *Trachycardium lacunosum* shell in the Persian Gulf

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Received: 14 October 2016 / Revised: 20 September 2017 / Accepted: 26 September 2017

Abstract The current investigation has monitored the concentration of Cd and Pb in bivalve *Trachycardium lacunosum* shells and the sediment samples in Asaluyeh Bay (north of the Persian Gulf). The samples were taken from 40 stations located in two sites in Asaluyeh region, Nayband Bay as a "contaminated" site and Lavar-e Saheli as a "control" site. The results showed that the mean concentration of Pb and Cd in the sediments were 3.56–5.25 and 1.16–1.44 µg/gdrw, respectively, and in the shell ranged from 11.30 to 13.71 and 2.38 to 2.75 µg/gdrw, respectively. Data indicated that contaminated site contained significantly higher concentration compared with the control site. There were significant positive correlations between the level of Pb and Cd in the shell as well as sediment samples. A biota-sediment accumulation factor of more than one indicated the occurrence of biomagnification of the studied metals in Nayband Bay. Therefore, the elevated amount of the sediments trace metals has led to bioaccumulation in the bivalve shell.

Keywords Bioaccumulation · Biomagnification · Cd · Pb · Sediment

Introduction

Marine environment contaminated by heavy metal is one of the main challenges around the world (Irabien and Velasco 1999; Bai et al. 2011; Qu et al. 2016). Due to high toxicity and bioaccumulation of heavy metals in living organisms, they are ecologically important and can damage the diversity of marine species and ecosystems (Usero et al. 2005; Gao et al. 2013; Rogowska et al. 2015). Since trace metals are persistent and mostly not biodegradable, there is a high tendency to concentrate in the sediments and ultimately metal toxicity endangers human health (de Astudillol et al. 2005; Berkowitz et al. 2008; Hu et al. 2016; Islam et al. 2015).

High levels of heavy metals have an adverse effect on marine organisms. The use of polluted bivalves with heavy metal threatens the health of consumers. Because of very high toxicity of heavy metals and extensive lifetime in food chains, it is very important to monitor their levels in marine environment. Cd and Pb are among the most toxic trace elements that have long been the subject of environmental toxicological studies (Gold-Bouchon et al. 1995; Ma et al. 2003). The toxicity of these metals includes tissue damage, inhibition of growth, and reproduction in some species of bivalve, as well as reduced metallobiotin synthesis in the shells (Gold-Bouchon et al. 1995; Lim et al. 1995). When these compounds enter aquatic environments, they are absorbed by organic and inorganic substances and

Editorial responsibility: X. Han.

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Published online: 05 October 2017

ultimately enter sediments (Farzadkia et al. 2014; Dehghani et al. 2014a, b). Therefore, the sediments of coastal regions have been accumulated with the considerable amounts of metals. Therefore, high amounts of these metals have been detected in the sediments of coastal regions. The coastal sediment can be used as a sensitive indicator for monitoring the contamination in these regions (Ochieng et al. 2007; Dias et al. 2009).

Human activities have also increased the level of heavy metal in the coastal sediments. Highly polluted sediments can be observed in urban and industrial areas (Birch 1996; Merian et al. 2004; Dias et al. 2009). Living organisms, especially bivalves, have a capability to uptake the metals from sediments and bioaccumulate them in their bodies (Zorita et al. 2006). The variation of trace metal concentrations in the bivalve shell is significantly associated with metal concentrations in the sediments. In addition, there are also many different physicochemical characteristics of sediments which affect the metal concentration in *Trachycardium lacunosum* shells. Therefore, determination of the metals concentration in the bivalve shell, sediments, and the correlations between them can improve our knowledge in the studied area (Cranston 1990; Burger and Gochfeld 2006).

Nowadays, the contaminations of soil and water sources and their impact on ecosystems are important issues (Dehghani et al. 2010, 2013; 2014a, b). There are many reports on heavy metals contents in water, sediments, and aquatic animals around the world such as the Gulf of Mexico Sanadrey (Silva et al. 2003), the Southeast of India (Priya et al. 2011), the coast of Moyan (Kanakaraju et al. 2008a, b), Persian Gulf, Hendurabi Island, Bandar Abbas in Iran (Pourang et al. 2005; Riahi Bakhtiari and Shah Mortazavi 2007), and Piodelaplate coast in Argentina (Bilos et al. 1998).

The accumulation of metals in the soft tissue of the marine organism is more than the shells. Therefore, there are many studies focusing on soft tissue, but only limited studies were conducted on the shell material in monitoring metal rather than the soft tissue (Zuykov et al. 2013).

Previous studies indicated that there were lower fluctuations of metal concentration in shell compared to the soft tissue. They also offer a better evidence of metal exposure during the life of the organism. This information is even maintained after the death of the organisms (Huanxin et al. 2000a; Richardson et al. 2001).

Asaluyeh is an industrial region located on the coast of the Persian Gulf. In this region, Pars special economic energy zone is significantly well known for producing gas and is shared between Iran and Qatar. Trace metals, especially Cd and Pb, have been extensively applied in the industrial processes. Therefore, it is highly expected to observe large amounts of these contaminants in different environmental media and their adverse effect on human well-being. The bivalve *T. lacunosum* shell is indigenous in this studied region. Because of large distribution and abundance of the shell in two parts of the Persian Gulf (Nayband Bay and Lavar-e Saheli), *T. lacunosum* shell is used in this study for metal bioaccumulation. In addition, very few studies have been done on the sediments and bivalve *T. lacunosum* shells in this part of the Persian Gulf region. The aims of the present research are to: (1) assess the concentrations of Cd and Pb in the bivalve *T. lacunosum* shells and the sediments, (2) compare the levels of these metals in Nayband Bay as a “contaminated” site with Lavar-e Saheli as a “control” site, (3) assess the relation between the metal contents in the samples of the sediment and shells in Nayband Bay (contaminated site), and (4) assess the feasibility of using the bivalve *T. lacunosum* shell as a bioindicator for controlling trace metal contaminations in the marine environmental media. This study was carried out partly at the laboratory of Persian Gulf Studies Center and Marine Ecology (Persian Gulf Research Center) and partly at the environmental chemistry laboratory of Bushehr University of Medical Sciences in 2014.

Materials and methods

Sampling

Lavar-e Saheli region was chosen as the control site because there is a long distance between its coastal area and the contaminated industrial region. Moreover, high distribution and abundance of bivalve *T. lacunosum* were observed in both Lavar-e Saheli (control site) and Nayband Bay (contaminated site). Figure 1 shows a shell of bivalve *T. lacunosum*. The concentration levels of Cd and Pb in the bivalve *T. lacunosum* shells and surface sediment were measured in two different sites including Nayband Bay and

Fig. 1 Shell of bivalve *Trachycardium lacunosum*

Lavar-e Saheli in the region of Asaluyeh. The number and location of the study stations were selected based on the geographic orientation map. Figure 2 shows the sampling points. The geographical coordinates of the forty sampling points within the study areas range from 27°23′43.78″N, 052°39′27.46″E to 28°13′45.59″N, 051°17′12.51″E, accordingly (Table 1).

Sampling was done in the tidal zone to collect sediment and bivalve *T. lacunosum* shell samples from a total of 40 stations located on two sites: Nayband Bay a "contaminated" site and Lavar-e Saheli a "control" site (20 stations in each site) in summer 2013. Forty samples of sediments from contaminated and control sites were collected with a hand-driven soil auger from 0 to 10 cm of surface sediment.

Bivalve *T. lacunosum* shells were collected by hand. A caliper (0.02 mm accuracy) was used to measure the length of the bivalves' shell. The shell sizes selected from both sites were similar. Transfer to the laboratory was done in polyethylene containers using an icebox (ASTM 1991). Samples were kept at − 20 °C prior to analysis (Gavrilovic et al. 2007).

Reagents

All suprapure grade quality chemicals were used (Merck, Germany), and all solutions were prepared by ultrapure water.

Sample preparation

An oven (at 105 °C) was used to dry the samples, and foreign objects were discarded afterward. The sediments were screened through a 25-micron sieve for maintaining homogeneity and were kept in polyethylene containers until digestion (Delman et al. 2006).

The frozen shells were thawed in room temperature, to prepare bivalve *T. lacunosum*. They were then rinsed with 0.5% HNO_3 and deionized water. The washed shells were put in an oven (105 °C) for 72 h to dry. They were powdered by a porcelain mortar. After mixing the prepared samples, they were kept in polyethylene containers until analysis (Yap et al. 2003a).

For a sample digestion, 10 mL of HNO_3 (65%) and $HClO_4$ (60%) at a 4:1 ratio was added to 1 g of the sediment sample and then heated on a hot plate digester (HC: 6040, UK). Initially, the sediments and shells were digested

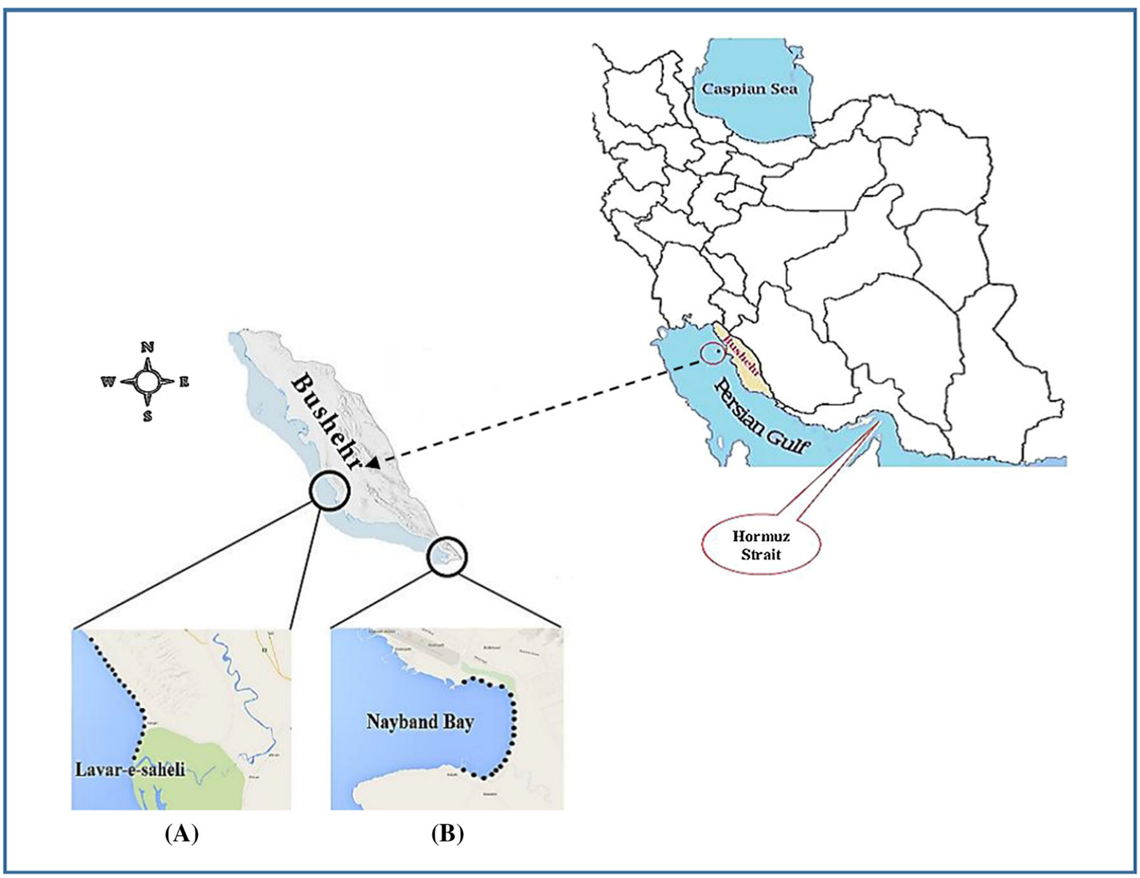


Fig. 2 Locations of sampling points. **a** Lavar-e Saheli as control site, **b** Nayband Bay as contaminated site

Table 1 Geographical coordinates of sampling stations at the study areas

	N	E
Stations in Lavar-e Saheli (control site)		
1	28°13′45.59″N	51°17′12.51″E
2	28°13′42.77″N	51°17′13.12″E
3	28°13′40.38″N	51°17′13.37″E
4	28°13′38.14″N	51°17′13.72″E
5	28°13′36.13″N	51°17′13.94″E
6	28°13′34.10″N	51°17′14.12″E
7	28°13′33.77″N	51°17′14.45″E
8	28°13′32.27″N	51°17′14.67″E
9	28°13′30.01″N	51°17′15.02″E
10	28°13′27.49″N	51°17′15.31″E
11	28°13′24.97″N	51°17′15.76″E
12	28°13′22.36″N	51°17′16.18″E
13	28°13′19.04″N	51°17′16.46″E
14	28°13′16.31″N	51°17′17.74″E
15	28°13′14.09″N	51°17′17.81″E
16	28°13′12.08″N	51°17′17.68″E
17	28°13′5.35″N	51°17′17.71″E
18	28°13′2.74″N	51°17′17.86″E
19	28°12′59.71″N	51°17′17.64″E
20	28°10′39.25″N	51°17′17.34″E
Stations in Nayband Bay (contaminated site)		
21	27°26′39.57″N	52°40′32.36″E
22	27°26′21.06″N	52°40′34.43″E
23	27°26′2.91″N	52°40′36.37″E
24	27°25′48.69″N	52°40′35.29″E
25	27°25′33.86″N	52°40′35.21″E
26	27°25′21.54″N	52°40′33.93″E
27	27°25′11.54″N	52°40′32.18″E
28	27°25′1.77″N	52°40′29.43″E
29	27°24′52.85″N	52°40′25.78″E
30	27°24′45.36″N	52°40′22.32″E
31	27°24′36.78″N	52°40′18.48″E
32	27°24′27.10″N	52°40′14.73″E
33	27°24′19.29″N	52°40′9.73″E
34	27°24′11.30″N	52°40′5.49″E
35	27°24′4.09″N	52°40′0.34″E
36	27°23′57.01″N	52°39′52.23″E
37	27°23′50.64″N	52°39′41.26″E
38	27°23′49.45″N	52°39′4.93″E
39	27°23′46.16″N	52°39′15.78″E
40	27°23′43.78″N	52°39′27.46″E

for 1 h at a low temperature (40 °C). Then, they were completely digested for 3 h at 140 °C. Samples were cooled at room temperature. In order to make a 25 ml solution, distilled water was added to the cool digested samples. The prepared solution was filtered using a Whatman 42 filter paper. The prepared samples were kept in a refrigerator prior to atomic absorption spectrophotometer analysis. The concentrations of Cd and Pb in the samples were measured using atomic absorption spectrophotometer (AASS Model Varian 240, USA) (Yap et al. 2002). All the data were displayed in µg/g of sample dry weight (µg/gdrw).

Two blanks were also analyzed in each batch to check the concentration of heavy metals in the samples. In addition, standard reference materials SRM-1646a (NIST, USA) were employed to validate the proposed analytical method. The percent of recoveries for Cd and Pb were 93.1 and 93.5%, respectively.

The accumulation of metals in sediment and its contamination level was determined by enrichment factor (EF) and geoaccumulation index (I_{geo}) along with comparing the trace metal concentrations according to sediment quality guidelines (SQGs).

In order to assess the source of contamination, iron was used as the reference metal to identify differences between natural and man-made sources. As shown in the following equation, the EF is determined by dividing the ratio of metal and Fe concentrations in the sample $[M/Fe]_{Sample}$ over its background ratio $[M/Fe]_{Background}$ (Ergin et al. 1991)

$$EF = \frac{\left[\frac{M}{Fe}\right]\text{sample}}{\left[\frac{M}{Fe}\right]\text{Background}}$$

In this study, the background concentrations of metals (Pb = 20 µg/gdrw, Cd = 0.3 µg/gdrw, and Fe = 47,000 µg/gdrw) in the average shale obtained were used from Turekian and Wedepohl (1961). If the value of EF falls within the range of 0.5 and 1.5, then the source of metal is natural and higher than 1.5 shows the metal source is man-made (Zhang and Liu 2002).

The following equation was applied to calculate geochemical index (I_{geo}) for metal content in the sediments of the contaminated site:

$$Igeo = \log_2(C_n/1.5B_n)$$

where metal n concentration in the sediment was measured as C_n, and background value and variations in the metal were B_n and 1.5, respectively (Turekian and Wedepohl 1961). The level of contamination is classified according to González-Macías et al. (2006). The range of I_{geo} is from 0 to 6 classified from uncontaminated to strongly contaminated, respectively.

The biota-sediment accumulation factor (BSAF) is determined by the ratio of the concentration of the metal in shell (C_M) over the metal concentration in sediment (C_S) as expressed by the following equation.

$$\text{BSAF} = C_S/C_M$$

A BSAF greater than 1 (> 1) indicates the occurrence of accumulation and biomagnification of examined pollutants.

To evaluate the accumulation of metal in the bivalve shell, the bioaccumulation ratio on the studied species (BARz) is calculated (Ferguson and Chandler 1998; Mackay et al. 2000; Ruus et al. 2005; Somerset et al. 2015):

$$\text{BARz} = \left[C_{\text{organism,polluted}}\right]/\left[C_{\text{organism,controlled}}\right]$$

where Z is the studied species, $C_{\text{organism, polluted}}$ is the concentration of selected accumulated metal in the polluted site and $C_{\text{organism, controlled}}$ is the concentration of metal in a crab in the unpolluted site used as a control species.

Data analysis

Data analysis was done using SPSS software (version 18). The relationship between the variables and data and parameters relations were determined by Mann–Whitney *U* test and Spearman's test, respectively.

Results and discussion

All figures are based on the mean of three replications. The highest and lowest content levels of Pb in the sediments of Nayband Bay were related to stations 15 (7.19 ± 1.22 µg/gdrw) and 14 (2.28 ± 1.49 µg/gdrw), respectively (Fig. 3). Moreover, the highest and lowest content levels of Pb in the sediments of Lavar-e Saheli site were observed at stations 24 (4.97 ± 1.48 µg/gdrw) and 30 (2.11 ± 1.25 µg/gdrw), respectively (Fig. 4).

The highest and lowest content levels of Cd in the sediments of Nayband Bay were related to stations 6 (1.92 ± 1.44 µg/gdrw) and 12 (0.81 ± 1.26 µg/gdrw), respectively (Fig. 3). Moreover, the maximum and minimum concentrations of Cd in Lavar-e Saheli sediments belonged to stations 22 (1.35 ± 1.22 µg/gdrw) and 34 (0.04 ± 1.75 µg/gdrw), respectively (Fig. 4).

The EF values of Pb in Nayband Bay (0.11–0.43) and Lavar-e Saheli (0.1–0.25) indicate no metal enrichment and the source of metal is natural. According to the geoaccumulation index, Nayband Bay is not contaminated (I_{geo} - $\leq 0 = 0$). The EF values of Cd for some stations in Nayband Bay were in the range of 1.7–6.51 indicating minor to moderately severe metal enrichment. The contamination level in Nayband Bay is moderate to strongly contaminated ($I_{geo} = 2.90$). Higher EF values and enrichment have been observed in stations closer to industries. However, the EF values in Lavar-e Saheli regions exhibit no to minor degrees of Cd enrichment (EF = 0.14–4.5) with no contamination level ($I_{geo} = -3.49$).

Our results showed that the concentration of Pb in Nayband Bay sediments (3.56–5.25 µg/gdrw) is much higher than that in Qatar, Oman, Bahrain, Kuwait, Kish, and Hendurabi Islands, but less than the concentration reported for Mahshahr Bay, Bushehr, and Chabahar coasts (Beg et al. 2001; Dehghan Mediseh 2007; Islami Andargoli 2008; SabzAli Zadeh 2008). Moreover, the concentration levels of Cd in the sediments (1.16–1.44 µg/gdrw) were higher than that in Bahrain, Qatar, Mahshahr Bay, Imam Khomeini port, and Hendurabi Island (De Mora et al. 2004; Dehghan Mediseh 2007; SabzAli Zadeh 2008). However, the content levels of Cd and Pb in sediments of Cochin Backwaters (India), Annaba Gulf (Algeria), and Lake Timsah (Egypt) were higher than that Nayband Bay and the enrichment factor values of more than 2 exhibited a high

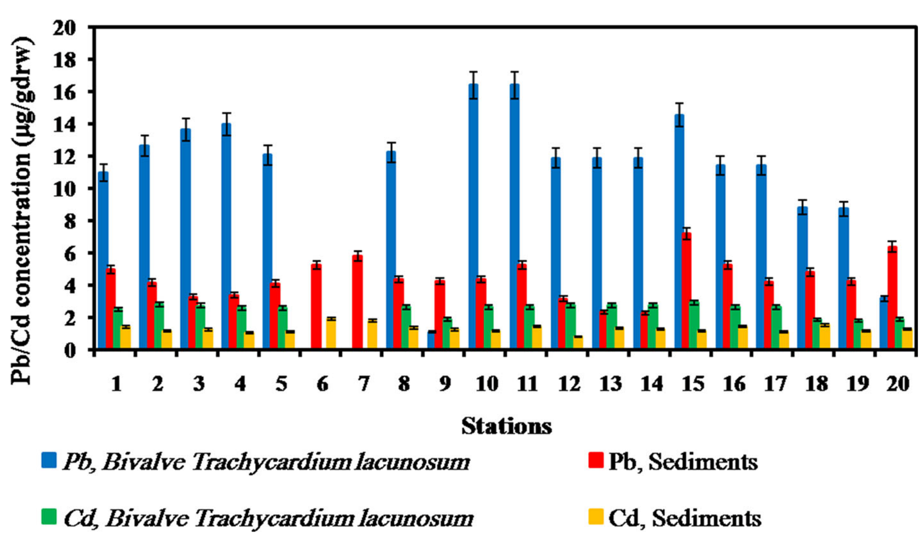
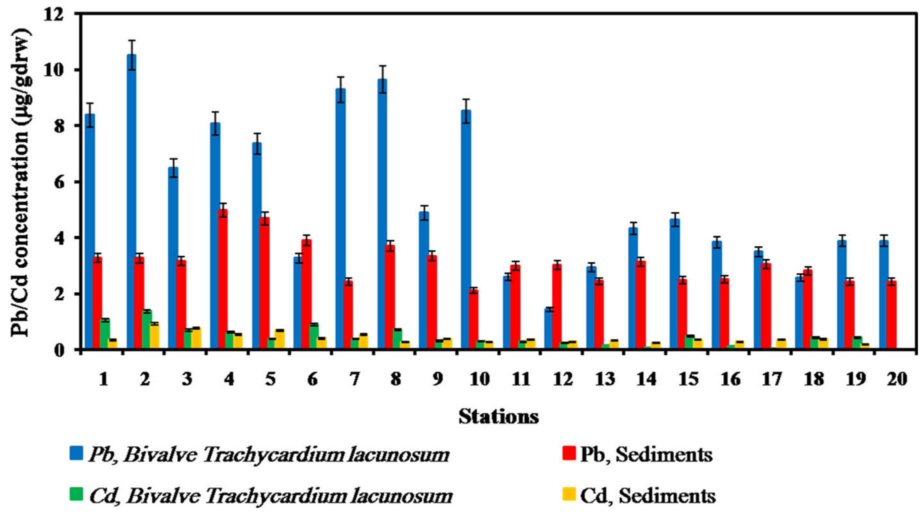


Fig. 3 Concentration levels of Pb and Cd in the sediments and bivalve *Trachycardium lacunosum* shells in different stations in Nayband Bay ("contaminated" site)

Fig. 4 Concentration levels of Pb and Cd in the sediments and bivalve *Trachycardium lacunosum* shell in different stations in Lavar-e Saheli ("control" site)



anthropogenic impact of the trace metals due to industrial and agricultural discharge (Martin et al. 2012; Bourhane-Eddine et al. 2013; EL-Shenawy et al. 2016).

Data demonstrated that the average concentration level of Pb in the bivalve shells at Nayband Bay was in the range of 11.30–13.71 μg/gdrw and maximum (16.38 ± 1.03 μg/gdrw) and minimum (1.11 ± 2.22 μg/gdrw) concentration levels were related to sampling stations 10, 11, and 9, respectively (Fig. 3). Maximum and minimum concentration levels of Cd in the shell samples in Nayband Bay were related to stations 15 (2.94 ± 1.01 μg/gdrw) and 9 (1.91 ± 1.03 μg/gdrw), respectively, and the concentration levels ranged from 2.38 to 2.75 μg/gdrw (Fig. 3).

Unfortunately, all the organisms in the bivalve *T. lacunosum* obtained from the contaminated zone in Nayband Bay found dead, demonstrating a severe contamination of the studied zone. Many studies reported that the heavy metals contents in the soft tissue were much greater than the shell because of the bioaccumulation (Huanxin et al. 2000b, Islami Andargoli 2008; Shirneshan and Riyahi Bakhtiari 2012). By comparing the uptake level of Pb and the accumulation levels in the bivalve *T. lacunosum* shells in Nayband Bay (11.3–13.71 μg/gdrw) with other regions, it was concluded that the Pb contents in the bivalve *T. lacunosum* shells were much higher than former studies in Bahrain, the UAE, Oman, Saudi Arabia, Mexico, Qatar, Nigeria, Kuwait, Hendurabi island, India, and Algeria (De Mora et al. 2004; Fowler et al. 1993; Sadig and Zaidi 1985; Martin et al. 1998–99; Olayan-Bu and Subrahmanyam 1996; Rejomon et al. 2013; Bourhane-Eddine et al. 2013). Nevertheless, the content levels of Pb in the shells were lower compared with the reported concentration levels in Egypt (Gabr and Gab-Alla 2008). But the contents of Cd in the shells (2.38–2.75 μg/gdrw) were higher than the reported concentration levels of studied shells in Qatar, Senegal, Caledonia, Nigeria, Hendurabi Island, and Egypt (De Mora et al. 2004; Sidoumou et al. 2006; Hédouin et al. 2009; Etim et al. 1991; EL-Shenawy et al. 2016), but less than the recorded levels of studied shells in the UAE, Bahrain, and Egypt (De Mora et al. 2004; Sidoumou et al. 2006; Gabr and Gab-Alla 2008).

The average concentration levels of Pb in the bivalve shells of Lavar-e Saheli were in the range of 3.31–8.29 μg/gdrw. Highest and lowest content levels of Pb in the bivalve shells of different stations in Lavar-e Saheli site were related to stations 2 (10.51 ± 1.23 μg/gdrw) and 12 (1.43 ± 1.03 μg/gdrw), respectively (Fig. 4). Moreover, the highest and lowest content levels of Cd in the bivalve shells of different stations of Lavar-e Saheli site were related to stations 2 (0.92 ± 1.22 μg/gdrw) and 17 (0.18 ± 1.03 μg/gdrw), respectively, and the concentration levels ranged from 0.26 to 0.48 μg/gdrw (Fig. 4).

The BSAF values for Pb in Nayband Bay are in the range of 0.49–2.07 which exhibit the occurrence of accumulation and biomagnification of metal in some stations. However, the BSAF in the all studied stations in Nayband Bay for Cd showed that biomagnifications of pollutant occurred (> 1).

In addition, the BARz values of Pb and Cd are in the range of (1.29–1.48) and (4.29–10.61), respectively, which

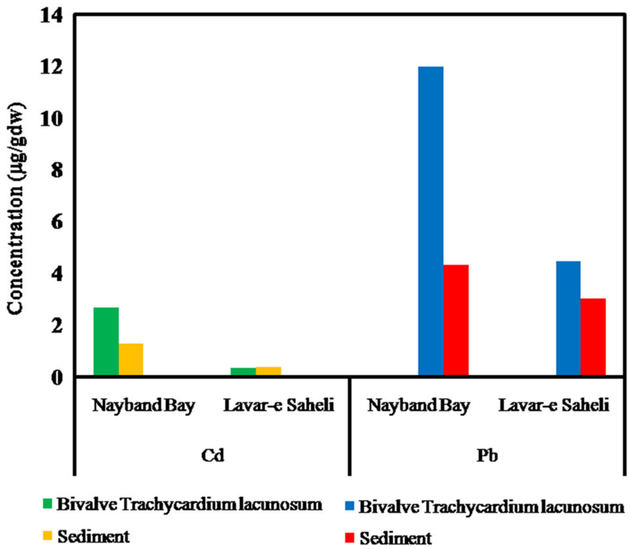


Fig. 5 Comparison of Cd and Pb concentrations in the bivalve *Trachycardium lacunosum* shell and sediment in the Nayband Bay (contaminated site) and Lavar-e Saheli (control site)

demonstrate the accumulation of trace element in bivalve shell in Nayband Bay in comparison with Lavar-e Saheli site.

The bivalve has the ability to uptake and bioaccumulate heavy metals (Kanakaraju et al. 2008a, b). Therefore, it is necessary to assess the correlations between heavy metals contents in bivalve *T. lacunosum* shell and sediments in the study regions. We found a significant relation between Pb content in the sediments and bivalve *T. lacunosum* shells in Nayband Bay ($n = 38$, $r = 0.76$, $P < 0.0001$). In addition, the relationship was statistically significant between Cd and Pb amount in Nayband Bay sediments (contaminated site) ($n = 39$, $r = 0.63$, $P < 0.0001$).

The comparisons of the amount of Cd and Pb in the shells and sediments in the contaminated site (Nayband Bay) with the control site (Lavar-e Saheli) showed significant difference and abundance of heavy metals contamination in Nayband Bay due to oil and gas industries and refining activities in this area (Fig. 5). The BSAF and BARz for the metals (Pb and Cd) in the contaminated site confirmed the occurring of metal biomagnifications. The positive significant relationship between the amounts of Pb and Cd in bivalve *T. lacunosum* shells and sediments indicated that aerosol deposition and local runoff and liquid inputs from the surrounding industries are the major origins for the metals uptake of in the shell tissues. The increased amount of these metals in the sediments has led to their bioaccumulation in the bivalve shell (Ferguson and Chandler 1998; Mackay et al. 2000; Ruus et al. 2005; Somerset et al. 2015). Also, in two studies on *Solen spp* shell in Malaysia (Kanakaraju et al. 2008a, b) and bivalve *Perna viridis* in Peninsular coast in Malaysia (Yap et al. 2003b), significant correlations between Pb and Cd contents in the shells and surface sediments were reported which are consistent with our results. The significant correlation between heavy metals in the shell and the sediment is because the metal in the shell binds to metallothioneins in soft tissue (Apti et al. 2005). Our results were also in agreement with Rainbow study (2006) which indicated that shell of oyster *S. cucullata* was a good heavy metal bioindicator (Rainbow 2006).

Conclusion

Cd and Pb concentrations in the bivalve *T. lacunosum* shells and surface sediments in the contaminated site (Nayband Bay) were much higher than the control site (Lavar-e Saheli). The source of Pb in the contaminated site was natural and no enrichment has occurred, but the source of Cd was anthropogenic indicating minor to moderately severe enrichment. There was a significant positive relationship between Cd and Pb concentrations in bivalve *T. lacunosum* shells and the sediments in Nayband Bay. We can conclude that the high level of the trace metals in the sediments has contributed to the bioaccumulation of these metals in the bivalve shell.

Acknowledgements We gratefully thank the Vice-Chancellor for Research and Technology of Shiraz University of Medical Sciences for supporting the research project No. 92-6649. Also, the facilities and excellent technical assistance provided at Persian Gulf Studies Center and Marine Ecology (Persian Gulf Research Center), the Department of Toxicology, and Department of the Food and Drug Administration are highly appreciated.

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