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ORIGINAL ARTICLE

Spatial and seasonal variation of potential toxic elements in *Adocia pigmentifera*, seawater and sediment from Rameswaram, southeast coast of India

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Abstract The concentrations of potential toxic elements (PTEs) such as cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) were measured in five different stations of Rameswaram (RM) coast, Gulf of Mannar (GoM), India, in coastal waters in sediments and tissues of *Adocia pigmentifera*. Concentration of PTEs (Cd, Cu, Pb and Zn) was found to be highest in sediments followed by *A. pigmentifera* and seawater samples collected from the different stations of RM coast. The pattern of accumulation of PTEs in the three sample types is of the following order Zn $<$ Pb $<$ Cu $<$ Cd. The seasonal variation of these PTEs also followed the same pattern. One-way analysis of variance (ANOVA) with Tukey's HSD post hoc test has revealed significant differences among stations S1–S4 when compared with the station S5 which is considered as the reference site. Correlation coefficient study showed no significant correlation in the concentration of PTEs in *A. pigmentifera*, seawater and sediment samples. The concentration of all the PTEs in different sample types has exceeded the FAO/WHO/sediment background values, except for the concentration of Zn in *A. pigmentifera* and sediment sample, which did not exceed the limits. The contamination factor (CF) and geoaccumulation index (I_{geo}) values indicated significant contamination of PTEs in the sediments from different stations of RM coast, India. Variations found between the sample types during the studies could be due to changes in levels of pollution discharge over time, availability of PTEs for adsorption as well as variations in the sampling season. Increasing urban sprawl and release of effluents both from domestic and industrial sources are the main sources of pollution at RM coast and are the prime reasons for the loss of existing diverse ecosystem.

Keywords Potential toxic elements · Seasonal variation · Gulf of Mannar · *A. pigmentifera* · Rameswaram

Introduction

Every year a new chemical is seen entering the market and most of them are seen finding their way into the marine environment (Rao et al. 2006). The ever increasing list of chemical pollutants released into the marine ecosystem on the whole includes potential toxic elements (PTEs), hydrocarbons both aliphatic, aromatic, and radio nucleotides. Among all these contaminants, the pollution by PTEs such as cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) is considered potentially hazardous to human health (Cachada et al. 2012). The contamination of the marine environment by PTEs has become a global phenomenon because of their persistence and accumulation in the tissues of the inhabiting organisms (Gochfeld 2003). These PTEs belong to the priority of contaminants according to the European Water Framework Directive 2000/60/EC (Mylopoulos et al. 2008; Arsene et al. 2009). The concentration of the PTEs is usually low in the marine environment, but due to the anthropogenic activity their concentrations are increasing significantly and causing a threat to the aquatic environments. Our previous studies have clearly revealed that marine sponges serve as ideal biomonitors for the

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evaluation of PTEs in the coastal ecosystems (Rao et al. 2006, 2007, 2009) and studies by other researchers have also proved that sponges are the best model organisms for evaluating the health status of the marine environment (Pan et al. 2011; de Mestre et al. 2012; Genta-Jouve et al. 2012). *Adocia pigmentifera* is a violet marine repent sponge that has large oscula and that often grows as an encrusting form on other organisms. *A. pigmentifera* is also known for its diuretic and insecticidal properties (Rao et al. 2008). It is found in the subtidal zones of southeast coast of India. Individual sponges have a length ranging from 2.5 to 20 cm and are suitable for collection. Most of the demosponges serve as ideal biomonitors for monitoring contaminants in the marine environment. Until now no reports on the behavior and monitoring of PTEs have been reported on this sponge, which is the prime reason of choosing this species in the current research. The widespread distribution of *A. pigmentifera* in the coastal regions of GoM also makes it one of the most feasible sponges for biomonitoring. Gulf of Mannar is at the tip of the southeast coast of India and consists of 21 islands starting from Rameswaram (RM) to Tuticorin. The gulf is declared as the Marine Biosphere Reserves (GoMBR) by the Ministry of Environment and Forest, Government of India (Rao et al. 2009). It is one of the natural harbours for various marine flora and fauna such as oysters, coral reefs, various fishes and different types of sea grasses, seaweeds which are seen inhabiting the coast. During recent past there has been vast increase in the tourism facilities around RM and existence of a number of small and large scale industires which have contributed to significant increase in the level of contaminants around the coast. The sediments of RM are dominated by carbonates and poor in silicates which consists of dune sands flaky, rock-forming minerals like chlorite, biotite and muscovite. The sands are underlain by calcareous sandstones. The entire coastal tract consists of gypsum, limestone and magnesium compounds. The RM island consists of freshwater aquifers which dry up quickly in summer. The ground water quality usually varies from alkaline to highly saline. The saline aquifers in coastal tract occur to a depth of up to 80 m below ground level. The great challenges which are experienced by the existing diverse ecosystem at RM coast are due to overexploitation, mismanagement and the entry of untreated sewage both from domestic and industries surrounding the coast (Sulochanan et al. 2007; Rao et al. 2009). The concentrations of PTEs in seawater are Cd (0.07), Cu (0.82), Pb (0.13) and Zn (0.24) µg/l, and in tissues of *Sigmadocia fibulata* are Cd (0.4), Cu (5.53), Pb (0.45) and Zn (0.62) µg/g, which have been reported from our earlier studies (Rao et al. 2007). Similar studies on marine sediments conducted by Sulochanan et al. (2007) from the same coast have indicated an increase in the concentrations of PTEs such as Cd (1.66), Cu (3.61), Pb (15.56) and Zn (2.82) µg/g dry weight of sediment. Previous studies conducted by us involved only the measurement of PTEs in seawater and sponge tissues only (Rao et al. 2007, 2009) from a different coast of GoM, India. The current study highlights the monitoring of seasonal variation of Cd, Cu, Pb and Zn concentrations in the three sample types collected from different stations of RM coast and also to evaluate the degree of contamination in the chosen area in comparison to others. Interestingly, there is lack of information on the seasonal distribution of PTEs in the coastal region of RM, India. There exists paucity on the distribution of PTEs in different seasons among the three sample types (seawater, *A. pigmentifera* and sediment) from the coastal regions of RM.

Materials and methods

Marine sponge *A. pigmentifera* (Family: Chalinidae, Order: Haplosclerida, Class: Demospongia) were collected along the coastal regions of Rameswaram coast, India. *A. pigmentifera* was collected by snorkeling and skin diving during the months of March to December (premonsoon, monsoon and post monsoon). The collected sponges are from five different stations which are as follows: station S1 is bath ghat (9.17°N 79.24°E); S2 shankumaal (9.20°N 79.22°E); S3 sewage outlet (9.13°N 79.23°E); S4 is boat house (9.13°N 79.25°E) and S5 station is opposite to television tower (9.20°N 79.17°E) (Fig. 1). *A. pigmentifera* samples after collection were washed thoroughly with natural seawater to remove all the intact mud and other particles; later the samples were frozen by placing them in liquid nitrogen container until the analytical work was initiated. The voucher specimens were submitted to National Institute of Oceanography (NIO), Goa for depository purpose and were identified by Dr. P. A. Thomas as *A. pigmentifera* at Vizhinjam Research Centre of Central Marine Fisheries Research Institute (ICAR), Vizhinjam, Thiruvananthapuram, India. The collected sponges before analysis were removed from the liquid nitrogen cans and dried in oven before further processing was carried out.

Water and sediment sampling

Seawater samples from chosen stations were collected in fresh autoclaved and acid-rinsed bottles labelled appropriately and immediately preserved at 4 °C to prevent further changes in the PTEs concentration. Freshly deposited marine surface sediments from the upper 5 cm layer were

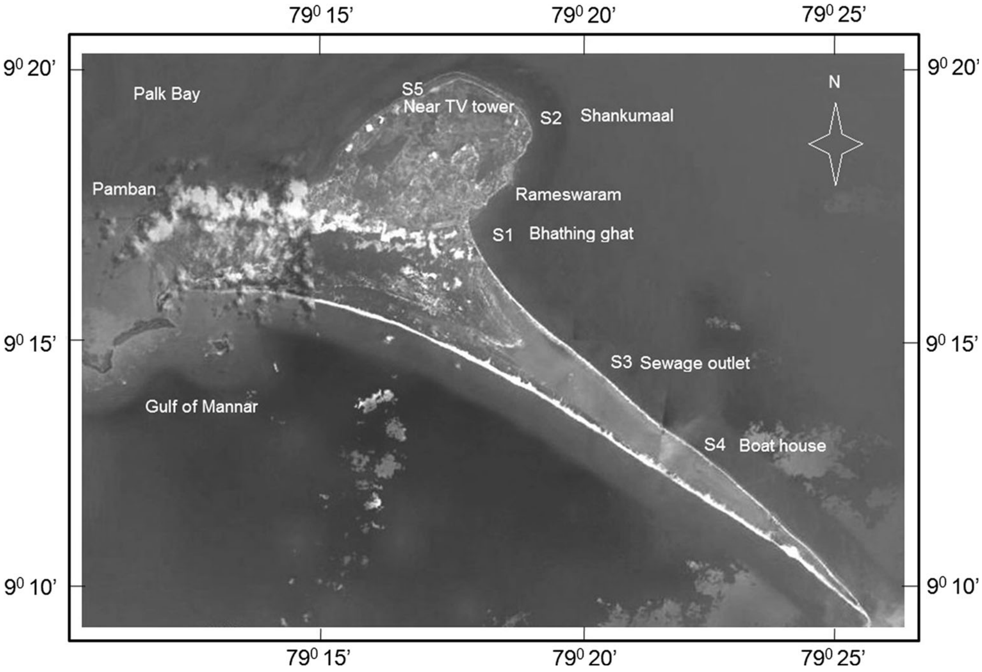

Fig. 1 Map showing the collection sites of the study area, Rameswaram coast of Gulf of Mannar, India

collected. The sediment samples were collected using a stainless steel scooper, with an internal diameter of 9 cm. The collected sediments were then placed in polyethylene bags, labelled appropriately and refrigerated at 4 °C immediately to avoid changes in PTEs distribution. These samples were then carried to the work station until further analysis. These samples were then wet fractionated using <63 μm sieve (USA Standard Testing Sieve, A.S.T.M.E-11 specification, OH, USA); before this process the large calcareous debris and rock fragments were carefully removed using plastic tweezers.

Treatment of tissue samples for PTEs analysis

The oven dried and weighed samples of *A. pigmentifera* each were used for the analysis of PTEs by the method of Mc Carthy and Ellis (1991). The samples were placed in Teflon® beakers and digested with 10 ml of 70 % nitric acid (HNO_3) in microwave vessel in an IFB (Indian Fine Blanks Ltd.) microwave oven, India. The programme was repeated once again to ensure the total digestion of all samples. After completing the heating programme, the vessel was cooled to room temperature and carefully vented in fume hood. The contents of each vessel were quantitatively transferred to another Teflon® beaker and evaporated to incipient dryness. The residues were re-dissolved in 5 ml of 1:1 HNO_3: milli-Q water and brought to a final volume of 50 ml. Clear solutions were obtained in all cases, simultaneously blanks and standards were prepared.

Open acid digestion of marine sediments for PTEs analysis

The sediment samples of <63 μm were analyzed for PTEs by the method of Begum et al. (2007). Briefly, 0.5 g of the sample was added to Teflon® beaker. Each sample was moistened with a few drops of milli-Q water, and then 10 ml of acid mixture containing hydrofluoric acid, nitric acid and perchloric acid (HF: HNO_3: $HClO_4$) in the following ratio (7:3:1) was added to each sample. All the chemicals used were of analytical grade. Samples were swirled until completely moist. The beakers were covered with lids and kept overnight for digestion after adding 5 ml of 1 μg/ml ^{103}Rh (rhodium) solution (as an internal standard). The following day the beakers were heated on a hot plate at 220 °C for about 1 h, the lids were removed and the contents were evaporated to incipient dryness until a crystalline paste was obtained. The evaporation process was repeated after adding 5 ml of the above acid mixture in each case. The remaining residues were then dissolved using 20 ml of 1:1 HNO_3: milli-Q water. Clear solutions were obtained for all samples. After cooling to room temperature, the volume was made up to 250 ml with milli-Q water and stored in polyethylene bottles until analysis was performed. A procedural blank solution was also prepared.

Seawater analysis

The PTEs in seawater is determined by a simple and rapid method by complexation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutylketone (MIBK), following the method of Brooks et al. (1967). In this study, after the APDC/MIBK extraction of PTEs from seawater, samples were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS). The collected seawater samples were passed through 0.4 µm filter paper prior to analysis to eliminate the additional contribution of metal concentration in seawater. The pH of filtered seawater was adjusted to 2 with dilute HNO_3 followed by the addition of 1 ml of 1 % APDC and 5 ml of MIBK. The samples are shaken vigorously for 2 min and allowed to stand for 10 min for phase separation. The aqueous phase was drained and the MIBK was transferred in a separating funnel. Five milliliters of 25 % HNO_3 was added and shaken for back extraction. After phase separation, the aqueous phase was transferred in a test tube for further analysis by ICP-MS (Model: Perkin-Elmer SCIEX, Model ELAN® DRC II ICP-MS (Toronto, ON, Canada). The inter-elemental effects during analysis were taken care of using built in Elan 2.1 version software. The ICP-MS used in the present study is the most precise and highly sensitive instrument for the detection of PTEs even at nanogram concentration. The concentration of Cd, Cu, Pb, and Zn was highest, and the other PTEs were below the detection limit, hence only these PTEs are considered in the present study. A total of 19 numbers of samples were seen collected during sampling and are analyzed for the existing concentration of PTEs. The salinity of seawater samples collected at different stations were measured using a hand held salinity refractometer (Atago, Japan, S/Mill-E 2442-W06), temperature in the seawater samples was recorded using thermal sensitive probe attached to multimeter (Consort, Belgium, Model C932) and conductivity was measured using calibrated electrode (Consort, Belgium, SK10T JJ7) attached to multimeter.

The accuracy and precision of all the analytical methods was assessed by multi-replicate analysis using NBS marine sediment standard reference materials (MESS-3, PACS-4 and DORM-2 obtained from Canada) and blanks. Standards and blanks were digested and analyzed using the same procedure as the experimental samples were performed; measured values were of 99 % within the standards range values.

Statistical analysis

All values are presented as mean ± SE. The statistical difference between PTEs concentration in the tissues of *A. pigmentifera*, seawater and sediment samples collected from different stations of Rameswaram coasts was determined using one-way analysis of variance (ANOVA) with Tukey's HSD post hoc test using Origin 8.5 version software. Results were considered with significance levels of 5 % on each PTEs to test the significant differences between the stations among the PTEs.

Table 1 Physicochemical parameters of seawater collected from different stations of Rameswaram coast, India

Sample location	pH	Salinity (psu)	Temperature (°C)	Electrical conductivity (mS/cm)
S1	7.4–8.2	32–34	20–22	51.78–55.02
S2	7.0–8.0	26–34	18–25	51.24–55.02
S3	7.4–8.0	28–34	16–25	50.18–55.02
S4	7.0–8.0	26–34	18–26	48.05–55.02
S5	7.4–8.2	30–34	16–24	51.24–55.02

Results

Physiochemical properties of seawater

The pH, salinity, temperature and electrical conductivity of the seawater samples collected at different stations of Rameswaram are presented in the Table 1. The pH of seawater samples in stations S1 and S5 are seen ranging from 7.4 to 8.2, moreover the pH at stations S2 and S4 are varying from 7.0 to 8.0. At station S3 the pH is in the range of 7.4–8.0. The salinity among the different stations of RM is ranging from 26 to 34 practical salinity units (psu) at the same time temperature recorded in the different station is 16–26 °C. The electrical conductivity was varying from 48 to 55 mS/cm.

Concentration of PTEs in seawater

Cadmium concentration in seawater samples is varying from 3.13 to 9.02 µg/l. The lowest concentration of Cd 3.13 µg/l was recorded at station S1 in October month, whereas the highest concentration 9.02 µg Cd/l was noticed in station S4 during the month of March with a mean value of 6.43 µg/l. The concentration of Cu in the seawater collected from the different stations of RM coast ranged between 4.23 and 6.21 µg/l, with the highest concentration recorded at station S3, moreover the lowest value recorded at station S5 during the month of March. The concentration of Pb 3.23 µg/l which is highest at station S3 during the month of March and the least value being 1.01 µg Pb/l recorded at station S2 in the month of November (Fig. 2). Concentration of Zn in seawater samples is varying from 0.28 to 0.62 µg/l, with a mean value of 0.346 µg/l, with highest being recorded at station S1 and the least at station S3 both the highest and least values are recorded in the same month (October). The concentration of PTEs in the seawater decreased in the following pattern Zn < Pb < Cu < Cd (Table 2).

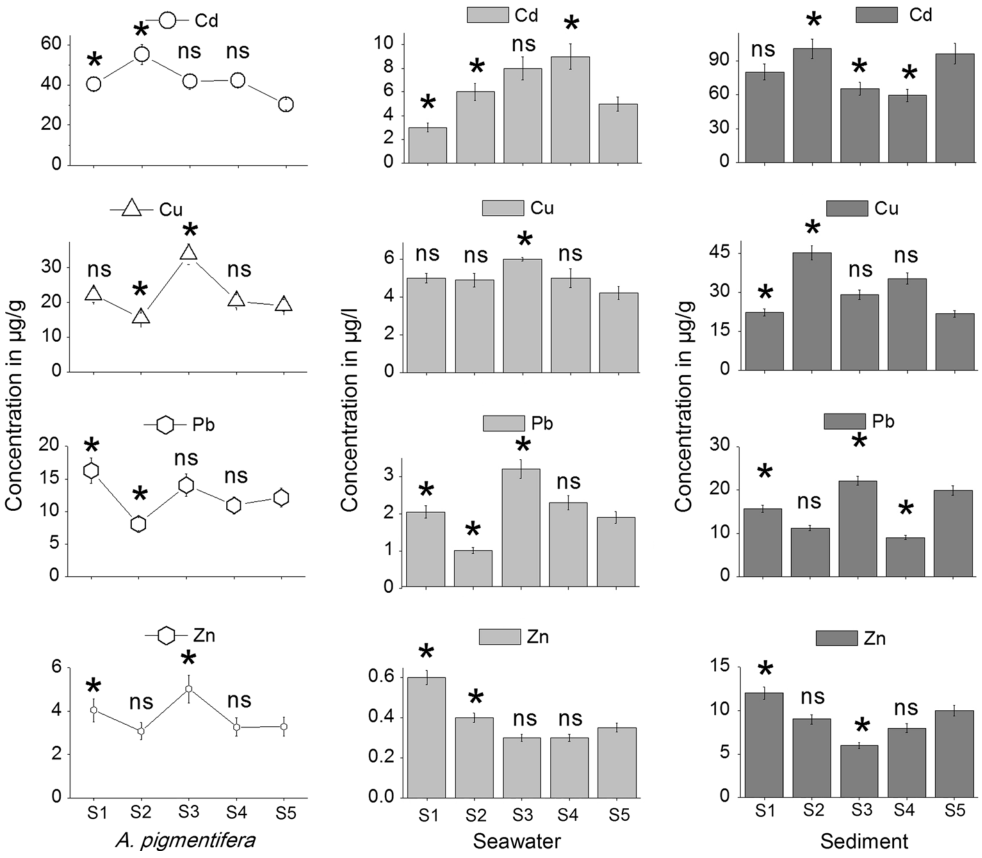

Fig. 2 The concentration of potential toxic elements in the tissues of *Adocia pigmentifera* (µg/g), seawater (µg/l) and sediment (µg/g) samples in the five different stations of Rameswaram coast, Gulf of Mannar, India. *Asterisk* in the *graph* represents significant difference among stations when compared with S5, ns represents not significant among the stations when compared with S5

Table 2 Potential toxic elements from the five locations of Rameswaram coast, India, in different seasons in *A. pigmentifera* (µg/g), seawater (µg/l) and sediment (µg/g)

Sample type	Metal	No. of samples	Range	Mean	Standard error	[a]Threshold limits
A. pigmentifera	Cd	19	30.21–55.21	42.841	±8.49	0.1
	Cu	19	15.48–33.85	23.475	±3.03	20
	Pb	19	8.09–16.31	12.166	±1.51	0.5
	Zn	19	3.07–5.01	3.872	±0.32	50
Seawater	Cd	19	3.13–9.02	6.432	±1.92	0.01
	Cu	19	4.23–6.21	5.188	±0.44	0.01
	Pb	19	1.01–3.23	2.153	±0.09	0.10
	Zn	19	0.28–0.62	0.346	±0.06	0.10
Sediment	Cd	19	59.27–100.45	80.277	±12.72	0.38
	Cu	19	21.81–45.24	31.510	±9.45	17
	Pb	19	9.05–22.09	15.687	±4.31	14
	Zn	19	6.04–12.01	9.211	±1.64	67

[a] Threshold limit concentrations of metals in tissue, sediment are presented in µg/g and in seawater µg/l according to tolerance level in fish (FAO/WHO 1989; ITS 2000). Sediment from sediment background concentration (Bervoets and Blust 2003)

Concentration of PTEs in *A. pigmentifera*

The accumulation pattern of PTEs in the tissue of *A. pigmentifera* is as follows Zn < Pb < Cu < Cd (Table 2). The Cd concentration is ranging from 30.21 to 55.21 µg/g dry tissue weight. Higher concentration of Cd 55.21 µg/g was recorded at station S2 in the month of October and the least value of 30.21 µg/g recorded at Station S5 during the month of March. Concentration of Cu varied between 15.48 and 33.85 µg/g dry tissue weights. Station S2 recorded the highest concentration in the month of March, moreover the lowest is recorded at station S2 during the month of October (Fig. 2), with a mean value of 23.47 µg/g. Lead concentration in the tissues of *A. pigmentifera* is seen ranging from 8.09 to 16.31 µg/g, the highest concentration was noticed during the month of October at station S1 and minimum was observed during the month of March at station S2. Of all the studied PTEs the concentration of Zn is seen recorded least

Fig. 3 Images showing the sewage effluent site (**a**). The sewage effluent seen entering into the open sea at Rameswaram coast (**b**)

in the tissues of *A. pigmentifera,* which is ranging from 3.07 to 5.01 µg/g. The least concentration was recorded in the station S2, whereas the highest concentration was recorded in station S3 which is the sewage disposal site (Figs. 2, 3).

Concentration of PTEs in sediment

The order of accumulation of all the four PTEs analyzed in all the three sample types (*A. pigmentifera*, seawater and sediment) followed the same pattern without any deviation Zn < Pb < Cu < Cd (Table 2). The concentration of PTEs was highest in the sediment samples when compared to seawater and tissue of *A. pigmentifera* and the pattern among the sample types is as follows (seawater < *A. pigmentifera* < sediment). The highest concentration of Cd 100.45 µg/g dry weight of sediment was observed at station S5 during October month, whereas the lowest (59.27 µg Cd/g) is recorded at station S4 in the month of April. Concentration of Cu varied between 21.81 and 45.24 µg/g with the highest concentration being noticed at station S2, whereas the lowest being noticed at station S1, with a mean value of 31.51 µg Cu/g dry weight of sediment. The concentration of Pb was ranging from 9.05 to 22.09 µg/g dry weight of sediment. The highest concentration of Pb 22.09 µg/g was recorded in the month of October at station S5, whereas the lowest value was recorded at station S4 with a mean value of 9.05 µg Pb/g during March. The concentration of Zn noticed at station S1 is 12.01 µg/g and the least value 6.04 µg/g is seen recorded at station S3 with a mean value of 9.21 µg/g Table 2.

Correlation coefficient of metals in seawater, sediment and *A. pigmentifera*

Correlation coefficient for seawater samples among the stations showed no significant difference among the locations ($p < 0.05$), the two PTEs Pb and Zn have shown positive correlation ($p < 0.05$) with *A. pigmentifera* and also with seawater and sediment samples collected along the coast of RM, similar results were observed with Cu and Pb in relation to *A. pigmentifera* and sediment samples collected from the different sites of RM coast (Fig. 4a–c). There was no significant correlation among the PTEs in *A. pigmentifera*, sediment and seawater samples (Table 2).

Discussion

The current study is an attempt to present the seasonal distribution of PTEs (Cd, Cu, Pb and Zn) and the degree of contamination in seawater, *A. pigmentifera* and sediment samples collected from different stations (S1–S5) of RM coast, India. The concentration of Cd, Cu, Pb and Zn followed the same trend in the three sample types analyzed, but their distribution varied among different seasons (months). Seasonal changes were observed in all the stations with respect to PTEs. These changes are the result of fluctuation in environmental parameters of the *A. pigmentifera* habitat (salinity, temperature, pH, electrical conductivity, dissolved oxygen etc.). Similar observation was noticed in the *Ulva rigida* species by Ustunada et al. (2011). Significant difference in the concentration of Cu, Cd, Pb and Zn was noticed among different stations of RM coast (Fig. 2). The difference in distribution of PTEs in five stations is due changes in levels of pollution discharge over time, availability of PTEs for adsorption as well as variations in the sampling season. Concentration of PTEs in seawater is usually high during the months of March/May and our results are in agreement to the results of Sulochanan et al. (2007) and Rao et al. (2007, 2009). Similar findings were noticed in the coastal waters of Kalpakkam which indicated high concentration of other PTEs during the month of March (Satpathy et al. 2008). But our results were contradictory to that of Chakraborty et al. (2009) who noticed high concentration of PTEs during the moths of September/October and low concentration during the period of march/may. There exists several reasons which attribute to the high concentration of PTEs which include huge run off from the surrounding locations and also several other properties of seawater which are seen influencing

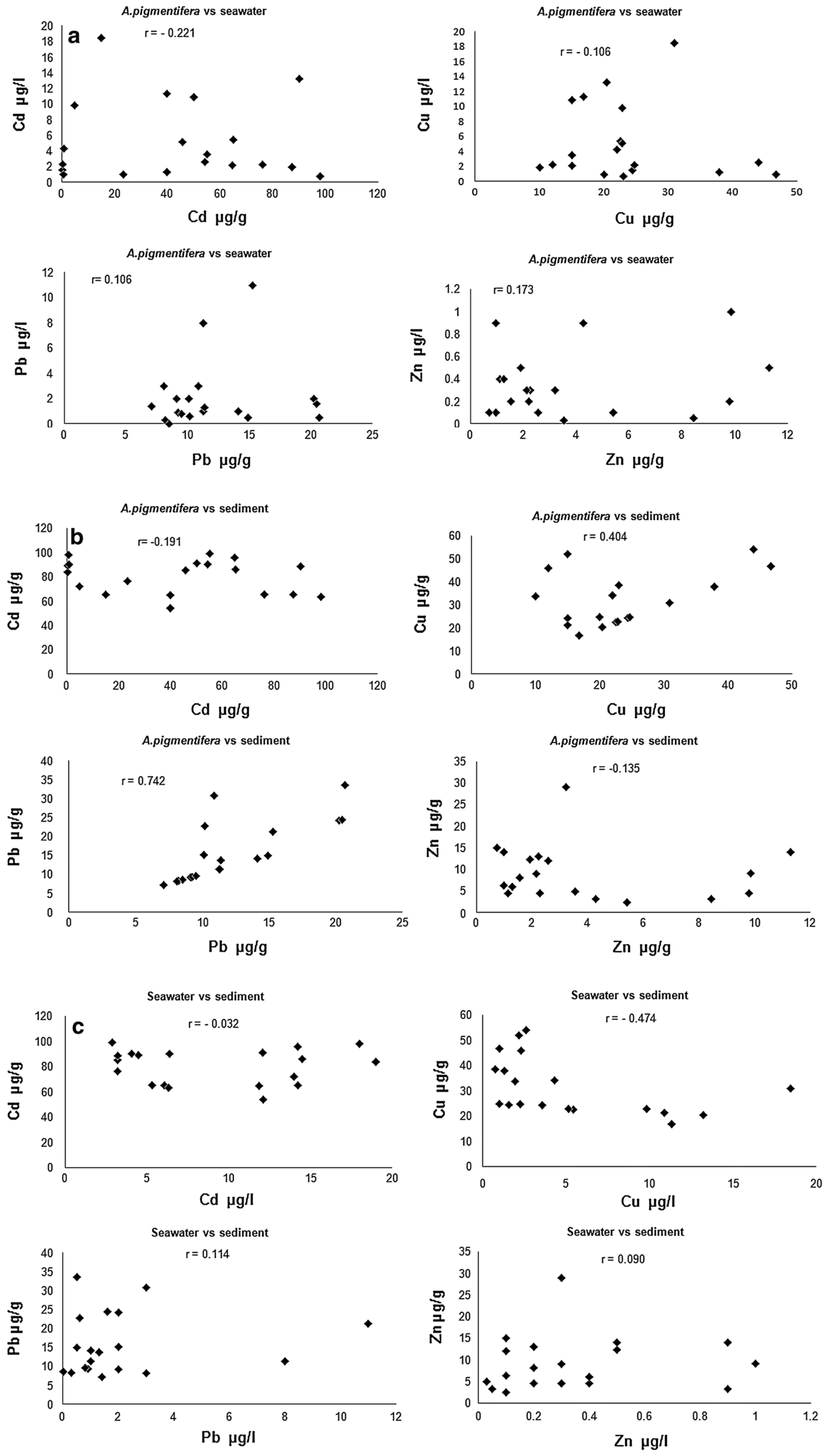

Fig. 4 Correlation coefficient of potential toxic elements between *A. pigmentifera* and seawater (**a**); *A. pigmentifera* and sediment (**b**) and seawater and sediment (**c**)

the distribution of PTEs in different seasons (Chakraborty et al. 2009; Barua et al. 2011). The seasonal variation of the PTEs in seawater samples collected at different stations are significantly influenced by the physiochemical properties of seawater such as pH, temperature, salinity, electrical conductivity and dissolved oxygen (Wong et al. 2000). At the same time the solubility of PTEs is mainly regulated by the seawater pH, concentration and nature of the organic ligands, metal oxidation state and redox conditions existing in the environment (Lalah et al. 2008). In the current study the concentration of PTEs in seawater are significantly higher in the month of March this high concentrations could be due to the increase in the rate of PTEs accumulation due to the increase in temperature and decrease in salinity at the same time lower concentration in the month of October might be due to the lower temperature and sedimentation which results in decrease in the concentration of PTEs (Coulibaly et al. 2012). The concentration of PTEs in seawater exceeded the environmental impact assessment reports, FAO/WHO limits (Yigit et al. 2002; Bashir et al. 2012) indicating significant contamination of PTEs in the seawater samples during all the studied seasons.

Sediment samples revealed high concentration of PTEs at different stations in the month of October in the current study which is entirely contradictory when compared among other coastal regions (Gaspic et al. 2009; Wang et al. 2010; Fang and Yang 2011). Monsoon season in the coastal regions of RM begins during the month of October and ends in December (Krishna Kumar et al. 2010); during this period there is heavy rainfall in the coast. Turbulent conditions appear in the monsoon season during which the fresh water stream from different sources dilutes the sea. Due to the dilution of the seawater, variation in salinity is seen occurring, which is complicated by mixing of waters brought into the region by currents causing turbulent exchange. The sea becomes turbid due to the resuspension of sediment which results in the enhancement of PTEs concentration in the environment (Jonathan et al. 2004; Barua et al. 2011; Rajan et al. 2012; Jagadeesan et al. 2013). Further, increase in the concentration of nutrients, phosphates, organic compounds, organic matter and changes in the salinity during monsoon period causes increase in the concentration of PTEs in the ambient medium and leads to the deposition in the sediments (Martin et al. 2012). Earlier reports have indicated high concentration of PTEs in the core sediments of GoM, India, during the month of December (Sundararajan and Srinivasalu 2010). High concentrations of Cu, Pb and Zn are reported from other coastal regions (Ravera et al. 2003; Franca et al. 2005; Papastergios et al. 2010). Contrary to the present results, the concentrations of the following PTEs were relatively low in the month of October in the west coast regions of India (Chakraborty et al. 2009). Natural background levels of PTEs exist in the majority of sediments due to mineral weathering and natural soil erosion. It is due to the anthropogenic activities which accelerate or antagonize this process that the background levels are increased resulting in pollution of the environment (Koigoora et al. 2013). When comparing among different stations one should be aware of many factors (grain size) influencing their distribution and mineralogical composition of the sediment (Koigoora et al. 2013). The contamination of sediment with Cd, Cu, Pb and Zn is reported from the coastal regions of Palk Bay, GoM and RM, India, by Sulochanan et al. (2007), but the reported concentrations were relatively low for Cd and Cu, but at the same time the concentrations of Pb and Zn were higher in the same station irrespective of the season. The concentration of Cd and Cu presented in the current study is several times higher when compared to the previous studies from the southeast coast of India (Jonathan and Ram Mohan 2003; Jonathan et al. 2004; Stephen-Pichaimani et al. 2008; Sankar et al. 2010). Except for the concentration of Zn, rest of all the PTEs concentrations exceeded the sediment background values (Bervoets and Blust 2003) in all the seasons indicating significant contamination of these PTEs in the marine sediments of RM coast of India. The contamination factor (CF) as reported by Turekian and Wedepohl (1961), is an effective tool in the evaluation of significant contamination over certain period of time. High CF value for Cd revealed significant enrichment of these PTEs in the sediments of RM coast. The contamination levels of Cu and Pb are moderate and moreover the contamination of Zn was significantly low in the coast of RM as presented in the Table 3. The current CF values measured for the PTEs are in agreement with the sediment background values which indicated the same pattern of contamination. Geoaccumulation index (I_{geo}) originally defined by Muller (1969), is a quantitative measure of the PTEs pollution in the marine sediments (Koigoora et al. 2013). It is used to determine the contamination levels in the study area. The measured I_{geo} values for the different PTEs in the sediments of RM coast indicate high contamination of Cd followed by unpolluted levels of rest of the PTEs (Table 3).

Table 3 Contamination factor (CF) and geoaccumulation index (I_{geo}) values for the sediment samples collected from different stations of Rameswaram coast, India

Potential toxic elements	CF	Contamination level	I_{geo}	Pollution level
Cd	8.0	Very high	5.35	High
Cu	1.28	Moderate	0.84	Unpolluted
Pb	1.06	Moderate	0.71	Unpolluted
Zn	0.17	Low	0.11	Unpolluted

The uptake of PTEs in *A. pigmentifera* was higher when compared to *Sigmadocia fibulata* and *Haliclona tenuiramosa* collected from GoM, India (Rao et al. 2007, 2009). The concentrations of Cd, Cu and Pb are higher in the present study when compared to those reported in *Suberites cf. diversicolor* reported from Australia (de Mestre et al. 2012) and in *Spongia officinalis* collected from the coast of Antarctica (Negri et al. 2006). Similar kind of studies performed in France reported higher concentrations of Cu, Pb and Zn in *S. officinalis* (Perez et al. 2005). The relative abundance of PTEs in the tissues of *A. pigmentifera* reflects uptake in proportion to that of the PTEs in sediments and seawater. High concentration of PTEs in the tissues of *A. pigmentifera* reflects the capacity of the sponge to accumulate these PTEs. Similar kind of observation in other sponge species was noticed from our earlier studies conducted at GoM, India (Rao et al. 2006, 2007, 2009). Coral skeletal tissues displayed high concentration of Cd and Pb

Table 4 Comparison of metal concentrations in sponge species (µg/g), Seawater (µg/l) and sediment (µg/g) observed by different authors

Sample	Location	Potential toxic elements				Author
		Cd	Cu	Pb	Zn	
Suberites cf. diversicolor	Australia	2–14	3–23	0.8–2	100–235	de Mestre et al. (2012)
S. officinalis	France	0.3–0.5	33.3–71.3	0.6–15.6	46.1–80.3	Perez et al. (2005)
Six species of sponges	S. Arabia	0.03–0.75	4.5–25.3	0.24–2.07	5.6–201	Pan et al. (2011)
S. officinalis	Antarctica	8–42	3.8–22.1	0.1–7	22–86	Negri et al. (2006)
H. tenuiramosa	India	0.01–1	0.01–3	Np	Np	Rao et al. (2009)
S. fibulata	India	0.25–5.0	3.0–5.5	0.3–0.45	0.39–0.58	Rao et al. (2007)
Seawater	India	Np	0.82	0.13	0.24	Rao et al. (2007)
Seawater	Malaysia	0.004–0.006	0.013–0.042	0.01–0.1	0.031–0.043	Abdullah et al. (2007)
Seawater	Turkey	0.009–0.7	0.79–1.15	0.72–21.6	0.40–3.60	Ustunada et al. (2011)
Seawater	Iran	0.07–0.09	1.41–1.78	4.39–6.94	0.22–0.44	Khoshnoud et al. (2011)
Seawater	Turkey	0.17 ± 0.27	0.36 ± 0.39	0.41 ± 0.27	1.051 ± 1.751	Demirak et al. (2006)
Seawater	S. Arabia	95–100	300–1,000	300–2,500	100–200	Alyahya et al. (2011)
Sediment	Croatia	0.086–0.121	21.1–51.9	29.9–67.3	21.9–65.4	Gaspic et al. (2009)
Sediment	India	4.6–7.5	385–657	24.9–40	71.3–201	Raj and Jayaprakash (2008)
Sediment	India	Np	24.80	33.21	180.37	Sundararajan and Srinivasalu (2010)
Sediment	India	0.23	18.1	20.8	113.4	Stephen-Pichaimani et al. (2008))
Sediment	India	0.240	18.1	21.6	115.2	Janaki-Raman et al. (2007)
Sediment	Hong Kong	0.1–2.5	1.1–194.8	0.2–107.5	0.1–88.2	Choi et al. (2006)
Seawater	India	6.432	5.188	2.153	0.346	Present study
Sponge	India	42.841	23.475	12.166	3.872	Present study
Sediment	India	80.277	31.510	15.687	9.211	Present study

collected from coastal regions of GoM, India (Krishna Kumar et al. 2010). Urban sprawl, storm water runoff and sewage inputs both from domestic and industrial sources have resulted in the high concentrations of Cd and Pb in the coral tissues (Krishna Kumar et al. 2010). Our results are in agreement with the results of Krishna Kumar et al. (2010) who observed high concentrations of Cu and Zn from the coastal regions of GoM, India. Seasonal variation of PTEs (Cd, Cu, Pb and Zn) in *A. pigmentifera* is also associated with growth dynamics. The concentrations of PTEs were low during the months March–April and higher concentrations have been reported during the months October–December; this is due to the presence of young individuals of *A. pigmentifera* which are seen growing very fast during their young stage and similar increase in growth rate was observed in several species of sea grass (Ward 1987; Nobi et al. 2010; Manikandan et al. 2010). Seasonal variation of PTEs in *A. pigmentifera* might be due to the fact that these are loosely bound to the suspended particulate fraction and at the same time existing low pH has also caused the increased solubility and mobility of PTEs which increase their availability (Violante et al. 2010). The variation of PTEs is also affected by the total concentration in seawater and sediments; it seems that some of the PTEs are found to be cleaned from the surface of the sediments by sponge tissues and some from the suspended seawater particles. A comparative study of PTEs concentration in different species of sponges that are in other geographical areas has been presented in Table 4. The concentration of Zn in the present study is lower when compared to all the other studied areas, whereas the concentration of Cu are reported to be higher in the tissue of sponges from Australia, France and Saudi Arabia, whereas the Pb concentration was higher only at France (Table 4).

Conclusion

Rameswaram is one of the marine biosphere reserve hotspots of the southeast coast of India with a diverse ecosystem. With the obtained current results, it is apt that RM is contaminated with PTEs in sediment, *A. pigmentifera* and seawater samples. This initial finding supports the notion that *A. pigmentifera* can differently accumulate PTEs from seawater and sediment of the RM coast during different seasons, even though the concentration of PTEs in *A. pigmentifera* at different stations was changing widely, reflecting contamination in both sediment and seawater column. The difference in the concentration of PTEs in the different sample types is due to changes in the level of pollution discharge over time, availability of PTEs for adsorption as well as variation in the sampling seasons will contribute to the variation in their concentration. Except the concentration of Zn in *A. pigmentifera* and sediment rest of all the PTEs have exceeded the FAO/WHO/sediment background values representing a significant contamination of these PTEs to the inhibiting biota and could be at potential risk. Proper measures need to be taken in order to protect the fragile ecosystem of RM from contaminants and also reduce environmental risk. The current study provides a base line data on RM coast for future research.

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