



# Screening of seaweeds in the East China Sea as potential bio-monitors of heavy metals

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## Abstract

Seaweeds are good bio-monitors of heavy metal pollution and have been included in European coastal monitoring programs. However, data for seaweed species in China are scarce or missing. In this study, we explored the potential of seaweeds as bio-monitor by screening the natural occurring seaweeds in the “Kingdom of seaweed and shellfish” at Dongtuo Islands, the East China Sea. Totally, 12 seaweed species were collected from six sites, with richness following the sequence of Rhodophyta > Phaeophyta > Chlorophyta. The concentration of heavy metals (Cu, Cr, Ni, Zn, Pb, Cd, As) in the seaweeds was determined, and the bioaccumulation coefficient was calculated. A combination of four seaweeds, *Pachydietyon coriaceum*, *Gelidium divaricatum*, *Sargassum thunbergii*, and *Pterocladia capillacea*, were proposed as bio-monitors due to their high bioaccumulation capabilities of specific heavy metals in the East China Sea and hence hinted the importance of using seaweed community for monitoring of pollution rather than single species. Our results provide first-hand data for the selection of bio-monitor species for heavy metals in the East China Sea and contribute to selection of cosmopolitan bio-monitor communities over geographical large area, which will benefit the establishment of monitoring programs for coastal heavy metal contamination.

**Keywords** Seaweed · Heavy metal · East China Sea · Richness · Bio-monitor · Bioaccumulation coefficient

## Introduction

Heavy metals released from anthropogenic activities are affecting the coastal systems increasingly (Elsikaily et al.

2011; Gao and Chen 2012; Tamilselvan et al. 2013). The fact that heavy metals in coastal waters are persistent with no degradation opened the opportunity of identifying bio-monitors that denotes an anthropogenic impact (Reis et al. 2011). Bio-monitor needs to fulfill certain required characteristics including sedentary nature, widespread distribution with considerable biomass, easy to identify, etc., in addition to being pollutant accumulators (Rainbow 1995). Seaweeds are therefore considered to be good agents for bio-monitoring of heavy metals in seawater (Akcali and Kucuksezgin 2011; Chaudhuri et al. 2007; Murphy et al. 2007). By now, in Europe, seaweeds have been included as key organisms to classify and monitor the ecological status of coastal ecosystems with decades of studies (Reis et al. 2014; Viana et al. 2010), as documented in the European Water Framework Directive (Ballesteros et al. 2007; Juanes et al. 2008). For instance, the seaweed *Alaria esculenta* in Irish coast was suggested to be used in the European Real-Time Environmental Monitoring Networks, because of its accumulation efficiency of heavy metal contamination (As, Cd, Cu, Fe, Hg, Pb, and Zn) (Reis et al. 2016).

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Compared to progress made on Western world seaweed species, much less is known for their Eastern relatives, despite the need to identify cosmopolitan bio-monitor to allow intra-specific comparisons of bio-availabilities between geographical areas (Rainbow 1995). The bio-monitoring potential of seaweed species from the Eastern world includes a few case-studies from China (Caixue et al. 2010; Zhang et al. 2014), India (Chakraborty et al. 2014; Kumar et al. 2009), and Russia (Khristoforova and Kozhenkova 2002). For instance, brown algae (*Padina gymnospora* and *Dictyota bartayresiana*) and green algae (*Ulva lactuca* and *Enteromorpha intestinalis*) in the Gulf of Kutch (India) were suggested as bio-monitors for Cd, Ni, Cr, Cu, Zn, and Pb (Chakraborty et al. 2014), as well as *Gracilaria confervoides* in the Liusha Bay of South China Sea for As, Cu, Pb, Cr, and Fe (Caixue et al. 2010), *Cladophoropsis zollingeri* for Fe in the mangrove area of South China Sea (Zhang et al. 2014). The lack of investigation of seaweed potential as bio-monitor for heavy metal in China is surprising, taking into account that 47% of the world's seaweed production is derived from China (FAO 2017) representing a high biodiversity (Ding et al. 2011). Indeed, there is a need for screening the native seaweed species for potential use as bio-monitors in future.

Furthermore, large-scale seaweed aquaculture has been proved to be an important way of nutrient reduction in coastal water in China due to high nitrogen and phosphorus removal capacity (Xiao et al. 2017). Investigating the heavy metal concentrations of seaweed tissues will benefit the potential application of seaweeds as bio-monitor of coastal heavy metal contaminations. In addition, seaweed composition could also reflect and monitor the ecological status of coastal environments (Diez et al. 2009; Paraskevi et al. 2015; Pinedo et al. 2007). For instance, in the Northwestern Mediterranean, healthy coastal ecosystems were dominated by dense *Cystoseira* forests, comparing to those comprised by *Ulva* spp. and other green algae (Pinedo et al. 2007). In Hainan Island of China, seaweed species richness and composition were found closely related to a pollution gradient (Li et al. 2016).

Therefore, we conducted a survey in Dongtou Islands of the East China Sea, the so-called “kingdom of seaweed and shellfish” of China for its rich seaweed biodiversity. The objectives of this study are to (i) investigate the seaweed richness, (ii) quantify the seaweed tissue heavy metal concentrations, and (iii) calculate the bioaccumulation coefficient for heavy metals for cross-comparisons between seaweed species. Our study aims to fill the knowledge gap of biodiversity and bio-monitoring potential of seaweeds in East China Sea, as well as to bring new insights into a bio-monitoring program for heavy metal pollution in Chinese coastal waters.

## Materials and methods

### Study area

Dongtou Islands (120°59'45" E~121°15'58" E, 27°41'19" N~28°01'10" N), located in the East China Sea (China), has subtropical marine monsoon climate. Annual seawater salinity in Dongtou Islands ranges from 27 to 35 ‰. Annual average water temperature is 18.4 °C, where February has minimum temperature with average monthly water temperature of 8.5 °C, and August has maximum temperature with average monthly water temperature of 27.9 °C. The average tidal range is about 4.5 m. The seaweed community in this area is diverse due to the unique regional geographical and oceanographic conditions. This region is climatically influenced from the Taiwan warm ocean current and is affected by Oujiang River.

### Sampling

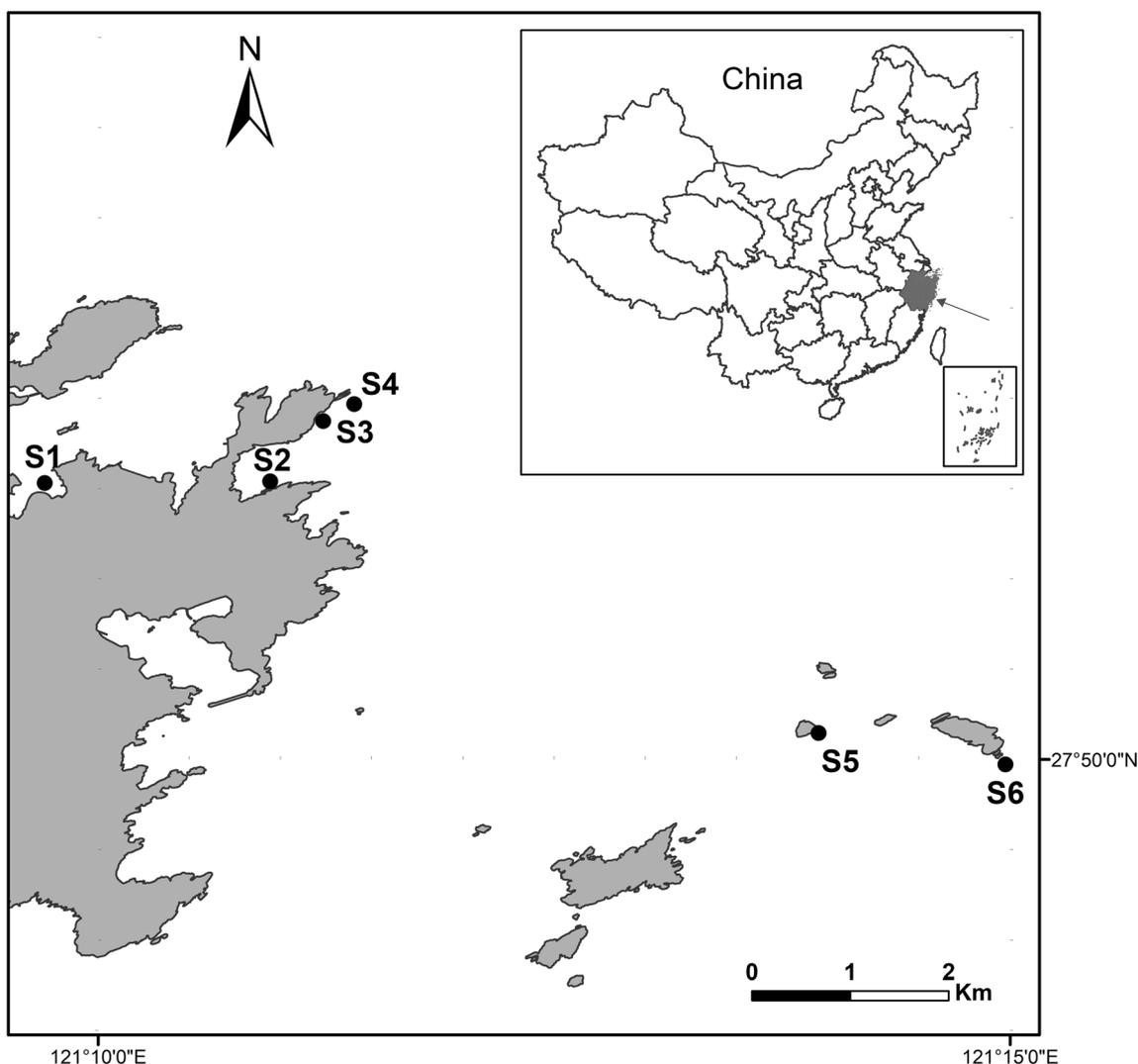
Seaweeds were collected from six sites in the Dongtou Islands (Fig. 1) during low tide period of May 2015. Sites 1–4 were located nearshore on the main island, and sites 5–6 were located in open sea. Site 1 and site 2 are close to fishery harbor and village, which are influenced by heavier pressure of human activity compared to the other sites. Seaweeds were collected from the intertidal and subtidal zone by free diving. The seaweed samples were carefully washed at the sampling site with seawater to remove the epiphytic organisms and trapped sediment, stored in polyethylene bags containing seawater, and then transferred to the laboratory in portable cooler at 4 °C.

### Seaweed identification

In the lab, the samples were washed with tap water and rinsed with Milli-Q water (Millipore, Milli-Q Advantage A10, France) and then wiped with dry towels. Sampled seaweeds were identified and classified based on their morphological features including the size, shape, and color.

### Chemical analysis

After the identification, the samples were dried at 60 °C for 48 h. The concentrations of heavy metals in seaweed samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent, 7900, USA) for Cu, Cr, Ni, Zn, Pb, Cd, and As (Caixue et al. 2010; La Rocha et al. 2009). For the detection of Cu, Cr, Ni, Zn, Pb, Cd, and As, the dried samples were homogenized in an agate mortar and reduced to a fine powder after sieving (200 µm) (Caixue et al. 2010) and then digested by microwaving (LabTech, ETHOS UP, Italy) with 7 ml 65% nitric acid and 1 ml 30% hydrogen peroxide; all the reagents used during procedure were of analytical grade (Caixue et al. 2010; Kamalakannan et al. 2008).



**Fig. 1** Field sampling sites (S1–S6) in Dongtou Islands, East China Sea (i.e., S1 represents the sampling site 1)

The digestion steps were as follows: (i) 0.2 MPa, 4 min; (ii) 0.5 MPa, 2 min; (iii) 0.8 MPa, 2 min; (iv) 1.0 MPa, 2 min; (v) 1.2 MPa, 2 min; and (vi) 1.5 MPa, 5 min (Caixue et al. 2010). The solution was transferred into a 50-ml volumetric flask and diluted with Milli-Q waters (Millipore, Milli-Q Advantage A10, France). Laver (35 g, Chinese National Standard Material No. GBW 10023), from the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Science, was used as certified reference material (Duan et al. 2015; Jiang et al. 2009; Wang et al. 2014). Three replicate detections were performed on the certified reference material. Analytical blanks were run in the similar way as that of the samples (Kamalakkannan et al. 2008). The recovery of the procedures was checked using the certified reference material (Giusti 2001). The detection results of certified reference material (Laver) by ICP-MS method proved the reliability of the detections for Cu, Cr, Ni, Zn, Pb, Cd, and As (Table 1).

### Bioaccumulation coefficient

The annual mean concentrations of heavy metals in seawater in Dongtou Islands in 2015 were derived from the bulletin of coastal environment released by the Ministry of Environment Protection, China (MEP 2015). The seawater quality monitoring frequency is two to three times a year in March to May, July to August, and October for in total 301 coastal water quality monitoring stations in China. The seawater sampling and detection method followed the technical specification for offshore environmental monitoring by the Ministry of Environmental Protection (HJ442–2008, (MEP 2008)). The seawater monitoring data from the monitoring site (No. ZJ0304, E: 121.2100, N: 27.8144), which is close to the study area, was used to calculate the bioaccumulation coefficient in the seaweeds. The concentration of Zn in seawater was below the detection limit of Zn (6.4  $\mu\text{g/L}$ ) (MEP 2008). The bioaccumulation coefficient was calculated as the ratio of the

**Table 1** Certified and detected tissue concentrations of heavy metals in the certified reference material Laver (GBW 10023)

Element	Certified concentration (mg/kg DW)	Detected concentration (mg/kg DW)	Recovery (%)
Cu	12.200 ± 1.100 <sup>a</sup>	11.490 ± 0.020 <sup>b</sup>	94
Cr	2.400 ± 0.400	2.250 ± 0.030	94
Ni	2.250 ± 0.180	2.190 ± 0.040	97
Zn	28.000 ± 2.000	28.170 ± 0.020	101
Pb	2.050 ± 0.150	1.980 ± 0.040	97
Cd	0.570 ± 0.050	0.580 ± 0.010	102
As	27.000 ± 6.000	26.890 ± 0.060	100

<sup>a</sup> The range of certified tissue concentrations of heavy metals

<sup>b</sup> Mean ± standard error from three replicate detections

seaweed tissue concentration to the concentration in the coastal waters.

### Statistical analysis

Principal component analysis (PCA) of tissue heavy metal concentrations in seaweed was performed in MATLAB (version 2016a). The concentrations of Cu, Cr, Ni, Zn, Pb, Cd, and As were used as discriminating variables. Cluster analysis of tissue heavy metal concentrations in seaweed was performed

by the Ward grouping method using SPSS (version 20).  $p < 0.05$  was considered as significant.

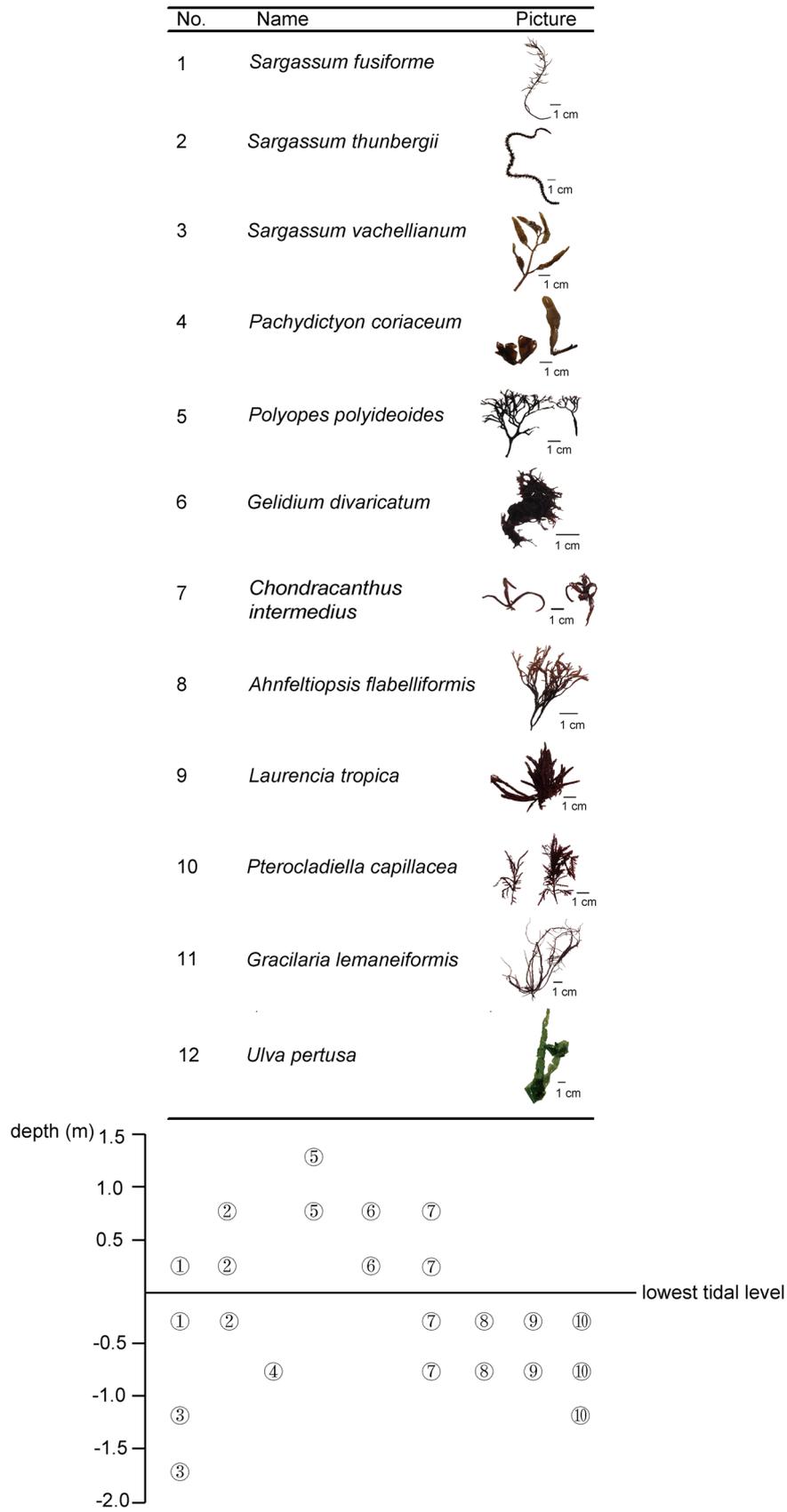
## Result and discussion

### Richness of natural seaweed species

In this study, we investigated the seaweed species distributed in Dongtou Islands in summer. Totally 12 seaweed species were found at the sampling sites (Table 2), belonging to three phyla—Phaeophyta (brown algae), Rhodophyta (red algae), and Chlorophyta (green algae). Two additional samples of *Gracilaria lemaneiformis* and *Ulva pertusa* were collected from floating seaweed cultivation raft. Rhodophyta showed highest richness in this survey, accounting for 59% of all the species, followed by Phaeophyta (33%) and Chlorophyta (8%). *Sargassum fusiforme*, *Sargassum thunbergii*, and *Chondracanthus intermedius* were found in both intertidal and sublittoral zone, from -1.0 to 1 m (Fig. 2). *Sargassum vachellianum*, *Pachydietyon coriaceum*, *Ahnfeltiopsis flabelliformis*, *Laurencia tropica*, and *Pterocladia capillacea* were confined to the sublittoral zone, which was no more than 2.0 m deep (Fig. 2). *Polyopes polyideoides* and *Gelidium divaricatum* were restricted to the intertidal zone (Fig. 2).

**Table 2** Seaweed species collected in the Dongtou Islands, East China Sea

	Latitude (°N)	Longitude (°E)	Phylum	Species
SITE 1	27.8588	121.1618	Phaeophyta	<i>Sargassum fusiforme</i>
SITE 2	27.8590	121.1824	Phaeophyta	<i>Sargassum fusiforme</i>
			Rhodophyta	<i>Gracilaria lemaneiformis</i>
			Chlorophyta	<i>Ulva pertusa</i>
SITE 3	27.8646	121.1872	Phaeophyta	<i>Pachydietyon coriaceum</i>
				<i>Sargassum thunbergii</i>
				<i>Sargassum vachellianum</i>
			Rhodophyta	<i>Ahnfeltiopsis flabelliformis</i>
				<i>Laurencia tropica</i>
				<i>Pterocladia capillacea</i>
				<i>Chondracanthus intermedius</i>
SITE 4	27.8661	121.1901	Phaeophyta	<i>Sargassum thunbergii</i>
				<i>Sargassum vachellianum</i>
				<i>Sargassum fusiforme</i>
			Rhodophyta	<i>Ahnfeltiopsis flabelliformis</i>
				<i>Polyopes polyideoides</i>
				<i>Gelidium divaricatum</i>
				<i>Pterocladia capillacea</i>
SITE 5	27.8357	121.2325	Phaeophyta	<i>Chondracanthus intermedius</i>
			Rhodophyta	<i>Sargassum thunbergii</i>
				<i>Gelidium divaricatum</i>
				<i>Pterocladia capillacea</i>
SITE 6	27.8329	121.2496	Phaeophyta	<i>Laurencia tropica</i>
				<i>Chondracanthus intermedius</i>
				<i>Sargassum thunbergii</i>
				<i>Sargassum vachellianum</i>
			Rhodophyta	<i>Sargassum fusiforme</i>
	<i>Polyopes polyideoides</i>			
	<i>Gelidium divaricatum</i>			
	<i>Chondracanthus intermedius</i>			



**Fig. 2** The seaweed species with specimen photos from field sampling, and their distributions in the tidal zones

Seaweed species richness increased significantly from offshore to the sea (Table 2, Fig. 1), which is similar to patterns reported from the South China Sea (Li et al. 2016). However, the seaweed species richness in our study was higher in sites 3 and 4 located on the main island comparing to the uninhabited islands (sites 5 and 6), which contradicts to the SW Atlantic, where coastal urbanization was found to lead to seaweed species loss and shifts in community structure (Schermer et al. 2013). A possible explanation is that nutrient inputs (i.e., domestic sewage) stimulated the growth of seaweeds on the coasts and increased the complexity of seaweed community composition. Several seaweed species appeared in a list of economic important seaweeds in the East China Sea about half a century ago, including *Sargassum fusiforme*, *Sargassum thunbergii*, *Gelidium divaricatum*, and *Ulva pertusa* suggesting that these species have been present in historic times (Tseng and Chang 1959). Due to lack of earlier documents in the region, it is difficult to evaluate potential changes of seaweed richness and composition over time emphasizing the need for baseline studies to be used for future research on regional marine ecosystem in response to global changes and human activities.

## Heavy metal comparison on the phylum level

### Phaeophyta

Phaeophyta has the highest concentrations of Cd (4.59 mg/kg DW) and As (44.02 mg/kg DW) among all seaweeds, and equal concentrations of Cr ( $2.25 \pm 0.10$  mg/kg DW) and Pb ( $1.95 \pm 0.10$  mg/kg DW) compared to Rhodophyta and Chlorophyta (Fig. 3). Similar to our study, Phaeophyta was found to absorb or accumulate significantly higher

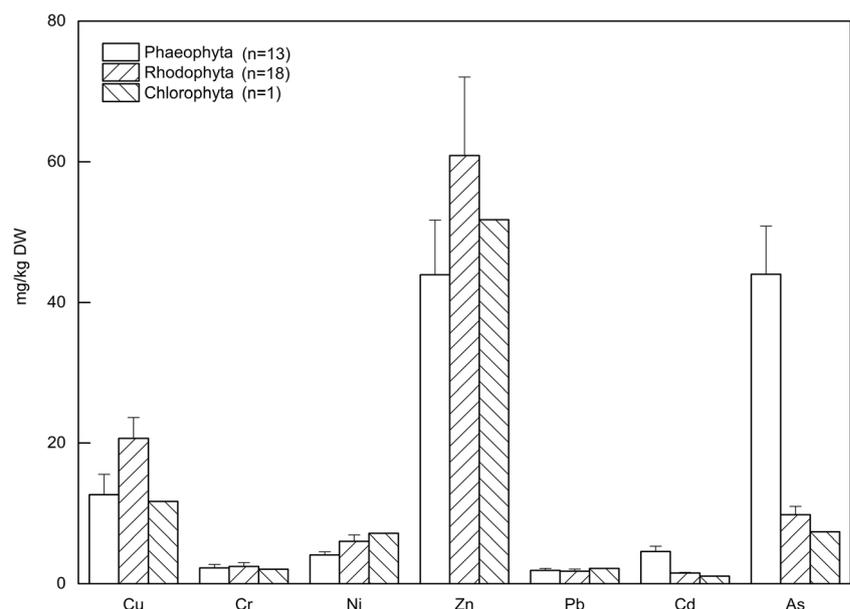
concentrations of Cd (Mata et al. 2009; Schintu et al. 2010) and As (Malea and Kevrekidis 2014; Ryan et al. 2012) compared to Rhodophyta and Chlorophyta from seawater. In general, brown seaweeds are resistant to marine pollutions (Costa et al. 2016), and at the same time, brown seaweeds have been proven to be effective and predictable in the biosorption of Pb from aqueous solutions (Davis et al. 2003). More specifically, *Sargassum filipendula* (Luna et al. 2010) and *Macrocystis pyrifera* (Cazon et al. 2012) showed high efficiency in biosorbing Cd. Similarly, *Lessonia nigrescens*—a brown seaweed in the Chilean coast—absorbed both Cd and As from seawater (Gutierrez et al. 2015; Hansen et al. 2006), and *Fucus vesiculosus* had been found to bioaccumulate heavy metals in estuaries and coastal waters throughout northwest Europe (Varma et al. 2011).

Our results suggest that in the East China Sea, Phaeophyta can be used as bio-monitor of Cd and As pollution. Indeed, various brown algae have been proposed as bio-monitors, including *Fucus spiralis* for Cd contamination in the northwest coast of Portugal (Reis et al. 2014), *Padina pavonica* (Schintu et al. 2010) and *Cystoseira* (Kravtsova et al. 2015) for both Cd and Pb contamination in the Mediterranean Sea and the Black Sea, respectively, and *Cystoseira barbata* for Fe, Mn, and Zn in Aegean Sea (Aydın-Önen and Öztürk 2017).

### Rhodophyta

Concentrations of Cu (20.66 mg/kg DW) and Zn (60.89 mg/kg DW) in Rhodophyta were significantly higher than those of Phaeophyta and Chlorophyta (Fig. 3) suggesting potential use of Rhodophyta as bio-monitor of Cu and Zn pollutions in the East China Sea. Similar to this study, Rhodophyta was an effective adsorbent or accumulator for Cu and Zn, i.e.,

**Fig. 3** Average concentrations of heavy metal determined in three seaweed phyla—Rhodophyta, Phaeophyta, and Chlorophyta, with the error bars showing the standard errors



*Pterocladia capillacea* for Cu (Elsikaily et al. 2011), *Polysiphonia lanosa* for Zn (Ryan et al. 2012), and *Gymnogongrus torulosus* for Cu and Zn (Areco and Dos 2010). Interestingly, Rhodophyta in the Gulf of Kutch were found to accumulate less Cu and Zn compared to Phaeophyta and Chlorophyta (Chakraborty et al. 2014), indicating that heavy metal accumulation in seaweeds is complex and regional scale study is needed before using the seaweed as bio-monitor in a specific area (Fig. 3, Table 3). Furthermore, Rhodophyta was found that it had effective biosorption capacity of Pb (Ibrahim 2011), i.e., *Chondracanthus chamissoi* (Yipmantin et al. 2011), *Gracilaria corticata varcartecala*, and *Grateloupia lithophila* (Tamilselvan et al. 2013).

### Chlorophyta

Chlorophyta has the highest concentration of Ni (7.14 mg/kg DW) (Fig. 3), which suggests potential use as bio-monitor for Ni pollution in the East China Sea, consistent with investigations of *Chaetomorpha aerea* in the Arabian Gulf (Alhomaidan 2008) and *Ulva reticulata* in India (Vijayaraghavan et al. 2005). Similar to this study, Chlorophyta were good bio-monitors of Pb, i.e., *Ulva lactuca* (Figueira et al. 2016) and *Caulerpa lentillifera* (Pavasant et al. 2006). Furthermore, the capacity of biosorption or bioaccumulation of Cu and Zn was highlighted for Chlorophyta, i.e., *Helimedea gracilis* (Jayakumar et al. 2015), *Chaetomorpha linum* (Ajjabi and Chouba 2009), and *Ulva* sp. and *Enteromorpha* sp. (Akcali and Kucuksezgin 2011).

The uptake behaviors of heavy metals are also different through the three seaweed phyla, which will help to explain why these seaweed phyla showed dramatically different patterns of heavy metal accumulation in addition to the species-specific favor of metals of seaweeds (He and Chen 2014; Sawidis et al. 2001). Similar to our suspicion, a study on the distribution of rare earth elements (REE) and silicon in seaweed showed that the uptake behavior of these elements dramatically differed in green, red, and brown algae. In details, the REE patterns similar to that of suspended particles for the green and red algae, but patterns closer to that of seawater solutions and relatively lower Si concentration for the brown algae (Fu et al. 2000).

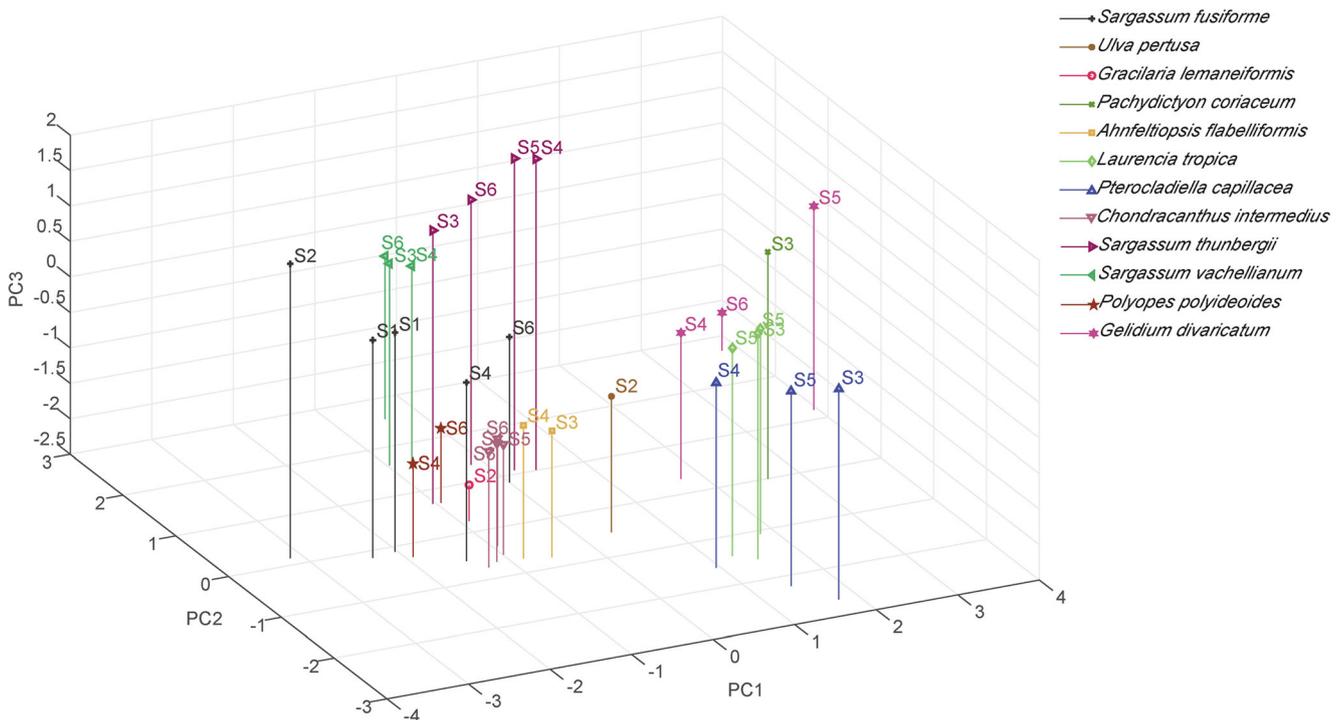
### Analysis on the species level

#### Principal component analysis (PCA) and cluster analysis

PCA analysis based on concentrations of heavy metals in the seaweed species showed that about 79% of the total variance was explained by three PCs (Fig. 4). PC1 is mostly associated with Cu, Cr, and Pb, and explains 41% of the total variance. *Gelidium divaricatum* shows the highest concentrations of Cr (6.83 mg/kg DW) and Pb (4.21 mg/kg DW) (Table 3). In

**Table 3** Mean concentration ( $\pm$  SE) of heavy metal in seaweed species collected in the Dongtou Islands, East China Sea

Phylum	Species	Heavy metal concentration (mg/kg DW)							
		Cu	Cr	Ni	Zn	Pb	Cd	As	
Phaeophyta	<i>Sargassum fusiforme</i> (n = 5)	7.93 $\pm$ 0.89	0.85 $\pm$ 0.11	2.87 $\pm$ 0.38	20.87 $\pm$ 6.69	1.50 $\pm$ 0.62	1.71 $\pm$ 0.17	57.71 $\pm$ 13.44	
	<i>Sargassum thunbergii</i> (n = 4)	12.81 $\pm$ 0.83	3.84 $\pm$ 0.47	6.04 $\pm$ 0.53	40.69 $\pm$ 4.67	2.00 $\pm$ 0.24	5.63 $\pm$ 0.12	49.08 $\pm$ 2.46	
	<i>Sargassum vachellianum</i> (n = 3)	8.59 $\pm$ 0.23	1.21 $\pm$ 0.12	3.11 $\pm$ 0.38	81.03 $\pm$ 12.90	1.90 $\pm$ 0.39	8.48 $\pm$ 0.29	23.77 $\pm$ 3.88	
Rhodophyta	<i>Pachydictyon cortaceum</i> (n = 1)	47.62	5.9	5.23	61.22	3.34	3.19	16.12	
	<i>Polyopes polydeoides</i> (n = 2)	3.89 $\pm$ 0.07	0.92 $\pm$ 0.25	1.57 $\pm$ 0.16	63.17 $\pm$ 15.69	1.32 $\pm$ 0.11	1.70 $\pm$ 0.17	15.41 $\pm$ 0.05	
	<i>Gelidium divaricatum</i> (n = 3)	23.76 $\pm$ 0.40	6.83 $\pm$ 1.11	6.58 $\pm$ 0.34	134.50 $\pm$ 40.88	4.21 $\pm$ 0.64	1.56 $\pm$ 0.30	8.89 $\pm$ 1.07	
	<i>Gracilaria lemaneiformis</i> (n = 1)	12.32	0.86	0.8	97.84	0.9	1.11	8.31	
	<i>Ahnfeltiopsis flabelliformis</i> (n = 2)	11.47 $\pm$ 0.82	1.16 $\pm$ 0.03	4.85 $\pm$ 0.18	32.25 $\pm$ 2.27	1.09 $\pm$ 0.09	1.93 $\pm$ 0.11	4.81 $\pm$ 0.74	
	<i>Laurencia tropica</i> (n = 3)	27.80 $\pm$ 1.31	3.01 $\pm$ 0.18	11.38 $\pm$ 0.44	44.79 $\pm$ 1.28	1.92 $\pm$ 0.19	1.92 $\pm$ 0.23	9.72 $\pm$ 2.70	
Chlorophyta	<i>Pterocladia capillacea</i> (n = 3)	41.87 $\pm$ 5.09	1.89 $\pm$ 0.23	9.68 $\pm$ 0.53	30.51 $\pm$ 2.04	1.58 $\pm$ 0.04	1.41 $\pm$ 0.03	3.35 $\pm$ 0.23	
	<i>Chondracanthus intermedius</i> (n = 4)	12.13 $\pm$ 0.26	1.04 $\pm$ 0.07	3.06 $\pm$ 0.09	44.48 $\pm$ 2.57	0.77 $\pm$ 0.12	1.10 $\pm$ 0.06	15.41 $\pm$ 0.25	
	<i>Ulva pertusa</i> (n = 1)	11.68	2.05	7.14	51.74	2.18	1.09	7.35	



**Fig. 4** PCA of the heavy metal concentrations of seaweed species. S1–S6 represent the sampling site 1 to site 6

addition to having the highest Cu concentration (47.62 mg/kg DW) (Table 3), *Pachydictyon coriaceum* also has relative high concentrations of Cr (5.9 mg/kg DW) and Pb (3.34 mg/kg DW) (Table 3). This suggests that these two seaweed species are more sensitive to the bioaccumulation of Cu, Cr, and Pb than other species, respectively. PC2 is mainly associated with Zn and Cd, explaining 23% of the total variance. *Gelidium divaricatum* has the highest Zn concentration (134.50 mg/kg DW) (Table 3), and *Sargassum vachellianum* has the highest Cd concentration (8.48 mg/kg DW) (Table 3), indicating that these two seaweed species are the most sensitive to the bioaccumulation of Zn and Cd, respectively. PC3 is clearly featured by As and explains 15% of the total variance. *Sargassum fusiforme* shows the highest As concentration (57.71 mg/kg DW) (Table 3), followed by *Sargassum thunbergii* (49.08 mg/kg DW) (Table 3), reflecting that these two species are more sensitive to accumulate As compared with other seaweed species. According to the PCA, the pattern of heavy metal concentrations in seaweeds is determined in the order PC1 (Cu, Cr, and Pb) > PC2 (Zn and Cd) > PC3 (As), and the concentrations of heavy metals in the seaweed species are more closely related to species rather than location (sampling site). Cluster analysis reflects the similarity in distribution of heavy metals and hence the comprehensive bioaccumulation ability of seaweed species, which were divided into five groups (Fig. 5). For instance, *Gelidium divaricatum* and *Pachydictyon coriaceum* are divided into the same group, showing that they have similar element distribution and bioaccumulation ability. This is consistent with the PCA result, which demonstrates

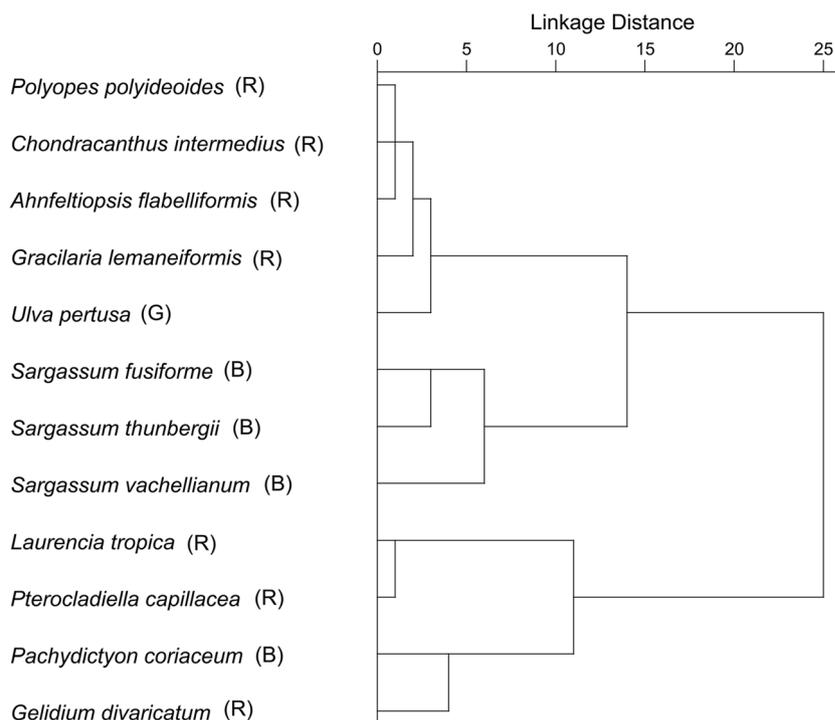
that both of them are sensitive to accumulate Cr and Pb. Similar finding is presented in the group of *Sargassum fusiforme* and *Sargassum thunbergii* for the bioaccumulation of As.

**Bioaccumulation coefficient of heavy metal in seaweed species**

The bioaccumulation coefficient showed that *Pachydictyon coriaceum* is the strongest accumulator of Cu, *Gelidium divaricatum* of Cr and Pb, *Sargassum vachellianum* of Cd, *Sargassum fusiforme* of As, and *Laurencia tropica* of Ni (Table 4). Thus, our data reveal seaweed species with the strongest accumulation of particular elements. For instance, our findings that *Sargassum* has a high ability to accumulate As are consistent to other studies, i.e., of *Sargassum* spp. in the Todos os Santos Bay, Brazil (Brito et al. 2012). Moreover, *Sargassum* sp. has high potential biosorption capacity of Pb, Zn, Cu, and Ni (Sheng et al. 2004), in addition to our findings of its high accumulation capacity of Cd and As. Therefore, our data suggest the identification of potential cosmopolitan bio-monitors for several heavy metal elements. Similarly, in addition to Cu, *Pachydictyon coriaceum* has high accumulation capacities for Cr and Pb. Other good potential cosmopolitan bio-monitors consist of (1) *Sargassum thunbergii* for Cd and As, and (2) *Pterocladia capillacea* for Cu and Ni.

Interspecific differences of bioaccumulation coefficient for heavy metals in seaweeds have usually been attributed to the binding sites for elements (Stengel et al. 2004) and

**Fig. 5** Cluster analysis on the heavy metal concentrations of seaweed species using Ward grouping method, B represents Phaeophyta (brown algae), R represents Rhodophyta (red algae), and G represents Chlorophyta (green algae)



biochemical composition (Malea and Kevrekidis 2014), which is determined by the species phylogeny (Hoek CVD et al. 1995). However, even in the same seaweed species, the bioaccumulation coefficient is often affected by the heavy metal concentrations in the coastal waters (Caixue et al. 2010; Ryan et al. 2012; Zhang et al. 2014). Similarly, it seems as the Cu concentration in seawater influenced the bioaccumulation coefficient, i.e., in the Liusha Bay, the Cu

concentration of seawater was 12.3  $\mu\text{g/L}$  and the bioaccumulation coefficient of *Sargassum thunbergii* was 1788 (Caixue et al. 2010), while in this study, the Cu concentration in seawater was 0.064  $\mu\text{g/L}$ , and the corresponding bioaccumulation coefficient of *Sargassum thunbergii* was 20,016. Therefore, research efforts are needed for elements and seaweed species where data are scarce or missing (Malea and Kevrekidis 2014), emphasizing the importance of the current

**Table 4** Bioaccumulation coefficient of heavy metal in seaweed species collected in the Dongtou Islands, East China Sea

Heavy metal	Cu	Cr	Ni	Pb	Cd	As
Concentration in seawater ( $\mu\text{g/L}$ ) <sup>a</sup>	0.640	0.700	0.670	0.032	0.036	1.430
<i>Sargassum fusiforme</i>	12,391	1214	4284	46,875	47,500	40,357
<i>Sargassum thunbergii</i>	20,016	5486	9015	62,500	156,389	34,322
<i>Sargassum vachellianum</i>	13,422	1729	4642	59,375	235,556	16,622
<i>Pachydictyon coriaceum</i>	74,406	8429	7806	104,375	88,611	11,273
<i>Polyopes polyideoides</i>	6078	1314	2343	41,250	47,222	10,776
<i>Gelidium divaricatum</i>	37,125	9757	9821	131,563	43,333	6217
<i>Gracilaria lemaneiformis</i>	19,250	1229	1194	28,125	30,833	5811
<i>Ahnfeltiopsis flabelliformis</i>	17,922	1657	7239	34,063	53,611	3364
<i>Laurencia tropica</i>	43,438	4300	16,985	60,000	53,333	6797
<i>Pterocladia capillacea</i>	65,422	2700	14,448	49,375	39,167	2343
<i>Chondracanthus intermedius</i>	18,953	1486	4567	24,063	30,556	10,776
<i>Ulva pertusa</i>	18,250	2929	10,657	68,125	30,278	5140

<sup>a</sup> The values are annual average value of heavy metal concentrations in seawater in 2015, from the bulletin of coastal environment quality, released by the Ministry of Environment Protection, China

study in the East China Sea. Moreover, our data will also contribute to the selection of bio-monitor species and the design of bio-monitoring programs over large geographical areas, as well as the interpretation of bio-monitoring data for coastal environment protection and management.

### Selection of seaweed species for bio-monitoring

The phylogeny of seaweeds usually determines the biochemical composition and binding sites for elements (Malea and Kevrekidis 2014) and thus contributes to the bioaccumulation coefficient of heavy metals (Figs. 4 and 5, Table 4). Our result revealed that some species are better bio-monitors for certain heavy metals. However, in coastal waters, the heavy metals are often present as multi-pollutions, rather than a single element. Nevertheless, bioaccumulation studies focus mostly on the accumulation of heavy metals from single metal solutions (Luna et al. 2010). Therefore, a better strategy of ecological monitoring and accumulation would be to combine several seaweed species and measure several heavy metals. The concept of using seaweed communities as bio-monitor has been applied in several European countries, such as Spain, Poland, Germany, and Denmark, for early detection of increased anthropogenic contaminations (Viana et al. 2010). Our results of the selective bioaccumulations of certain heavy metals by local seaweeds, and the concept of using a suite of bio-monitors will allow recognition of the presence and relative magnitude of heavy metal sources, and thus benefit the establishment of novel monitoring program for heavy metal-contaminated marine environment.

### Conclusion

1. The seaweed richness of this survey follows the sequence of Rhodophyta > Phaeophyta > Chlorophyta.
2. In the East China Sea, Phaeophyta are promising bio-monitor of Cd and As, as well as Rhodophyta for Cu and Zn and Chlorophyta for Ni.
3. PCA and cluster analysis, together with the bioaccumulation coefficient, suggest that *Pachydictyon coriaceum*, *Gelidium divaricatum*, *Sargassum thunbergii*, and *Pterocladia capillacea* have good potential to act as bio-monitors of heavy metals.
4. A single seaweed species does not reflect the comprehensive heavy metal pollutants in coastal environment, and combining seaweed species posing different bioaccumulation capacities will benefit the bio-monitoring of heavy metals.

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**Author contribution** Conceived and designed the analysis: X.X., T.W., and Y.P. Sampled and identified the seaweed: T.W., T.D., X.X., Y.P., K.L., F.L., J.W., and Y.Y. Wrote the paper: Y.P., X.X., M.H., and T.W. All authors analyzed, interpreted the results, and edited the manuscript.

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