



# Simultaneous Speciation Analysis of Trace Heavy Metals (Cu, Pb, Cd and Zn) in Seawater from Sishili Bay, North Yellow Sea, China

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## Abstract

Different species of trace heavy metals (HMs) in seawater samples were simultaneously analyzed by anodic stripping voltammetric method, an analytical technique that does not require sample pre-concentration or the addition of reagents. The effects of the crucial parameters, deposition potential and time, on the determination of HMs were investigated. Concentrations of the total dissolved, dissolved active, and dissolved inert HMs were obtained through different analysis processes. The three species of Cu, Pb, Cd and Zn in seawater samples collected in different locations across Sishili Bay, North Yellow Sea, China were studied. The relative concentration of the dissolved active Cu, Pb, Cd and Zn in the total dissolved concentrations is 59.0%, 69.6%, 87.3% and 84.1%, respectively. The concentrations of different HMs species in Sishili Bay could be affected by the discharged effluent, sea current, and uptake of marine organism.

**Keywords** Speciation analysis · Trace heavy metals · Seawater · Sishili Bay · Anodic stripping voltammetry

The past decades were characterized by the globally rapid economic and industrial developments, which resulted in a large number of pollutants such as heavy metals (HMs) to be dumped into the marine environment (Maity et al. 2017). The study of HMs in marine environment has received considerable attention because of their possible damage to ecosystem and human health (Zhang et al. 2014). Meanwhile, it has been demonstrated that HMs such as copper (Cu), lead (Pb), cadmium (Cd) and zinc (Zn) also play important roles in regulating the biogeochemical processes (Milne et al. 2010; Peers et al. 2005; Shaked et al. 2006). Cu, Cd and Zn behave similarly as macronutrients, while Pb is an important tracer of possible natural or anthropogenic inputs (Di Carlo et al. 2017; Illuminati et al. 2010; Milne et al. 2010). The

vital or toxic roles of HMs mainly depend on their concentrations (Herrero et al. 2014).

Traditionally, environmental measurements only established the total concentration of target in samples (Kot and Namiesnik 2000), which later proved to be insufficient in evaluating their bioavailability, behaviour and toxicity (Huang et al. 2003). Therefore, it is essential to determine the occurrence and relative abundance of HMs species in marine environment with the new and effective methods and approaches.

Most of the current speciation analysis methods for HMs combine both separation and detection techniques. Separation techniques include gas chromatography (Wang and Cui 2016), supercritical fluid chromatography (Henry 2006), capillary zone electrophoresis (Kubán and Timerbaev 2014), and so on. As to the detection techniques, atomic absorption spectrometry (Ribeiro et al. 2017), atomic emission spectrometry (Vidal et al. 2016), and inductively coupled plasma mass spectrometry (Zhu et al. 2017) are most widely used. Although these methods have many advantages, a major limitation is their requirements for a series of complex pre-treatments, which are time and labour consuming.

Electrochemical techniques are the most promising methods for speciation analysis due to their high levels of convenience, rapid and straightforward analytical processes. van den Berg proposed the electrochemical method for

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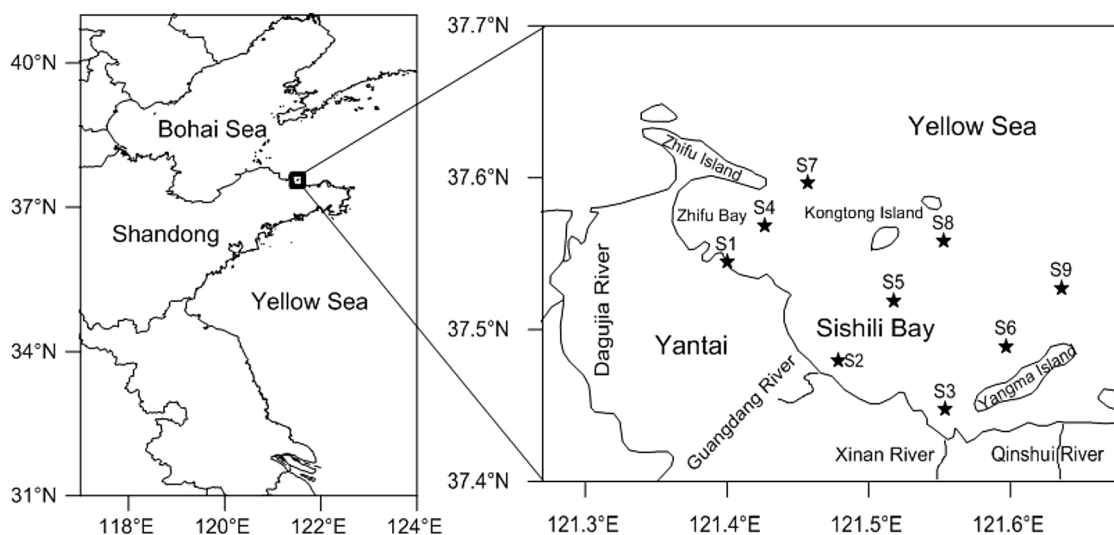
the measurement of redox speciation of iron in seawater in 1995 (Gledhill and van den Berg 1995). In that work, the concept of active ions was introduced and the stripping voltammetry was used for their detection. After that, van den Berg implemented the speciation analysis of different metal elements, such as iron, lead, copper and so on, through the electrochemical methods (Bi et al. 2013; van den Berg 2006; Whitby and van den Berg 2015). Anodic stripping voltammetry (ASV, mercury electrode) is the mostly used electrochemical method for the speciation analysis of metal elements. Vyskočil and Barek reviewed the advantages and limitations of mercury electrodes in environmental analysis in 2009 (Vyskočil and Barek 2009). It was considered that mercury electrode had some drawbacks like mercury reservoir requirement, precise generation and disposal of mercury, potential risks of poisoning and contamination with the use of mercury, and limited selectivity by the width of the potential window. But with the development of voltammetric analyser, e.g. 797 VA (Metrohm, Switzerland), there is no need to consider more on the safety and convenience with the use of ASV. And ASV has been successfully adopted for the speciation analysis of metal elements, especially for labile species. To simplify the processes, the dissolved HMs is divided into three species groups, namely, dissolved active HMs, dissolved inert HMs and total dissolved HMs. Dissolved active HMs is the fraction directly detected by ASV after filtration (0.45  $\mu\text{m}$ ). Although the concentration of this fraction is generally low, it is associated with high bio-availability and toxicity in the marine environment. The total dissolved HMs is the fraction electrochemically detected after filtration and subsequent UV digestion. Lastly, the dissolved inert HMs is defined as the fraction permanently coupled with inorganic/organic complexes and colloids, and

determined as the difference between the total dissolved and dissolved active HMs.

The aim of this study was to propose a voltammetric method for the simultaneous speciation analysis of HMs in seawater, which did not require pre-concentrations and additional reagents. Sishili Bay in the North Yellow Sea, China, a typical marine aquaculture bay, was chosen as the study area for the speciation analysis of HMs. Parameters have been investigated in terms of deposition potential and time for electrochemical detection. Different species of Cu, Pb, Cd, and Zn, were quantified and analyzed in seawater samples collected in different locations across the Bay area using ASV.

## Materials and Methods

Sishili Bay is an important harbour in Shandong Province, mainly used for marine aquaculture supplying local seafood markets (Fig. 1). As a mariculture area, the bay has a long history of seafood cultivation and remains the most important aquaculture area in Yantai City. However, over the last 2 decades, it has been subjected to intense human activities from the surrounding city. The increased population, aquaculture, urban sewage discharge and the cargo throughput of Yantai Port have placed in great stress on the marine ecosystem of Sishili Bay (Zhang et al. 2012). Anthropogenic inputs have been suggested as the main sources of HMs in the marine and coastal environments of the bay. Several publications are now available about the HMs contamination in the surface sediments of Sishili Bay (Sheng et al. 2012; Zhang et al. 2012). However, fewer studies have been done



**Fig. 1** Locations of sampling sites in Sishili Bay

to investigate the species and concentrations of HMs in the surface seawater of this area.

Here, seawater samples were collected in nine different locations across Sishili Bay area (Fig. 1) in February 25–26, 2017. Selected sites covered a wide range of environments exhibiting various biogeochemical processes, which was useful for the obtainment of information about the species and concentrations of HMs in different types of habitats in Sishili Bay. A 2.5 L sample collector was used to collect seawater into polypropylene containers which were washed with hydrochloric acid (HCl, 1 mol L<sup>-1</sup>) and rinsed with double distilled water thoroughly. All bottles and containers used for standards and samples were soaked in nitric acid (HNO<sub>3</sub>, 5 wt%) at least for 24 h prior to use, and then thoroughly washed using double distilled water before starting the experiments. All the reagents (HCl, HNO<sub>3</sub> and so on) were guarantee grade and purchased from Sinopharm Chemical Reagent Co. Ltd., China. Seawater samples were immediately processed after collection as summarized in Fig. 2. Filtration was carried out using 0.45 μm cellulose acetate membrane (Whatman). Filtered samples were transferred to quartz tubes and digested for 45 min under a low-pressure mercury vapour lamp to destroy the complexes and compounds, providing the concentrations of total dissolved HMs (Achterberg and van den Berg 1994). The concentrations of dissolved active HMs were obtained from the direct electrochemical analysis of the samples after filtration. The concentrations of dissolved inert HMs were then derived by calculating the dissolved active HMs fraction subtracted from the total dissolved HMs fraction (Florence 1986).

The speciation analysis of HMs was performed in seawater samples using ASV. A 797 VA Computrace analyzer (Metrohm, Switzerland) was used for all voltammetric measurements. The analyzer consists of a 797 VA Computrace Stand and was fully controlled with a 797 VA Computrace Software 1.3. In electrochemical experiments, hanging drop mercury electrode (HDME) was employed as the working electrode while the platinum (Pt) was used as the counter electrode and Ag/AgCl as the reference electrode. Before

determination, 10 mL samples were injected into the voltammetric cell and bubbled with high purity nitrogen (0.1 MPa) for 5 min to exclude the dissolved oxygen. The first step of the ASV analysis was the accumulation step, where the deposition potential and time were determined for Cu, Pb, Cd and Zn in seawater samples at -1.15 V and 60 s, respectively. After the accumulation step and an equilibration period of 10 s, differential pulse voltammetry (DPV) was performed from -1.15 to 0.02 V with sweep rate of 0.03 V s<sup>-1</sup>.

Figure 3 shows the typical DPV curves for the simultaneous determination of Cu, Pb, Cd and Zn with the peaks observed at -0.17, -0.41, -0.58 and -1.00 V, respectively. The concentrations of HMs were detected by the standard addition method (Illuminati et al. 2010). Briefly, the DPV curves were obtained after two successive additions of standard solution (Cu, Pb, Cd, Zn), and at least two replicates were conducted with every addition. Then the quantification was carried out using the peak currents of the sample before and after additions. Detection limits of 28.87, 1.06, 2.97

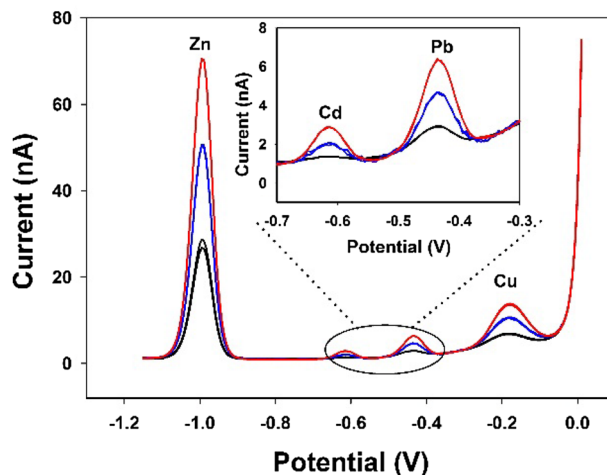


Fig. 3 Simultaneous analysis of Cu, Pb, Cd and Zn by differential pulse voltammetry (DPV) in seawater samples

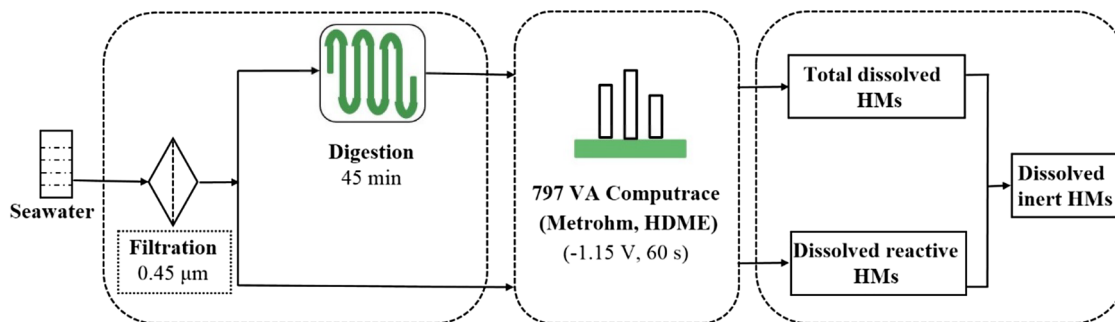


Fig. 2 Schematic diagram showing processes involved in analyzing different species of trace heavy metals (HMs)

and 12.70 ng L<sup>-1</sup> and quantification limits of 96.23, 3.50, 9.80 and 42.34 ng L<sup>-1</sup> were obtained for Cu, Pb, Cd and Zn, respectively. The accuracy of the analytical procedure was checked by analyzing certified reference materials for trace metals in seawater (NASS-6) and nearshore seawater (CASS-6) from the National Council of Research Canada. The concentrations of Cu, Pb, Cd and Zn obtained by the procedure are in agreement with the reference values; the results are compared in Table 1.

### Results and Discussion

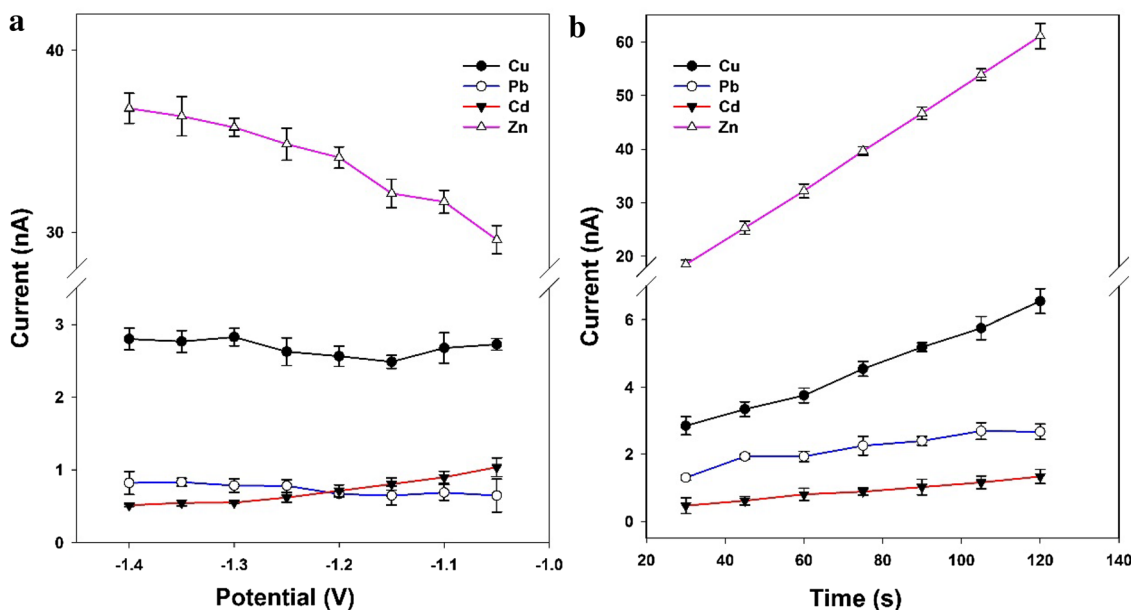
The deposition potential of HMs in seawater samples was investigated at the potential ranging from -1.40 to -1.05 V. Figure 4a shows the stripping current responses of Cu, Pb, Cd and Zn at various deposition potential with the deposition time of 60 s in seawater samples. When the deposition potential shifts from -1.40 to -1.05 V, different HMs ions have different responses. Specifically, Zn slowly decreases and Cd is the opposite, while Cu and

Pb almost have no changes with the deposition potential shift. The more negative the deposition potential, the more easily HMs ions be reduced, thereby causing the obvious increase of the peak current of Zn. However, with the deposition potential becomes more negative, unfortunately hydrogen evolution and reduction of other chemicals become significant which lead to the decrease in current signals of Cd (Huang et al. 2014). As to the Cu and Pb, the influence of deposition potential becomes relatively stable considering that the potential range of -1.40 to -1.05 V is much negative than their peak potentials (0.17 V for Cu, -0.41 V for Pb). In this work, a reduction potential of -1.15 V was chosen as the best compromise for the current signals and hydrogen evolution.

The influence of deposition time on the stripping peak currents by fixing the deposition potential of -1.15 V was summarized in Fig. 4b. The peak currents of all the Cu, Pb, Cd and Zn increased gradually with the deposition time. The deposition time of 60 s was used throughout the experiments since in previous research (Maity et al. 2017)

**Table 1** Results of the analysis of two seawater reference materials by means of differential pulse voltammetry (μg L<sup>-1</sup>, n=6)

Reference material	Cu	Pb	Cd	Zn
CASS-6				
Analyzed	0.532 ± 0.035	0.0108 ± 0.0050	0.0220 ± 0.0031	1.275 ± 0.150
Reference	0.530 ± 0.032	0.0106 ± 0.0040	0.0217 ± 0.0018	1.270 ± 0.180
NASS-6				
Analyzed	0.250 ± 0.030	0.006 ± 0.003	0.0310 ± 0.0022	0.255 ± 0.023
Reference	0.248 ± 0.025	0.006 ± 0.002	0.0311 ± 0.0019	0.257 ± 0.020



**Fig. 4** Effects of the deposition potential (a) and deposition time (b) on the stripping current responses of Cu, Pb, Cd and Zn in seawater samples

it showed to be enough to carry out the speciation analysis of Cu, Pb, Cd and Zn in the seawater samples.

In order to investigate the contamination level of HMs in the environment where the samples were collected, the concentrations of different species of Cu, Pb, Cd and Zn were determined (Fig. 5). Generally, the concentrations of HMs in Sishili Bay follow the decreasing order: Zn > Cu > Pb > Cd. Concentrations of the total dissolved Cu, Pb, Cd and Zn vary from 2.71 to 7.34  $\mu\text{g L}^{-1}$ , 1.12–2.00  $\mu\text{g L}^{-1}$ , 0.06–0.13  $\mu\text{g L}^{-1}$  and 7.18–21.22  $\mu\text{g L}^{-1}$ , respectively. The mean concentrations of Cu, Pb, Cd and Zn in the locations of S4, S7 and S8 are 5.95, 1.83, 0.13 and 15.96  $\mu\text{g L}^{-1}$ , respectively, which are clearly higher than the others. In comparison, Cu, Pb, Cd and Zn concentrations in the other six locations are only 3.51, 1.40, 0.08 and 9.34  $\mu\text{g L}^{-1}$ , respectively.

It should be noticed that there is the largest sewage treatment plant (STP) of Yantai located at the Zhifu Island. Lots of the industrial sources (including plating and leather industry, approximately 70%) and sewage (approximately 30%) wastewaters are discharged through the STP every year (Sheng et al. 2012). Additionally, for the sea current, Sishili Bay is basically characterized by the flow of Bohai Sea Coastal Current (BSCC) roughly from site S7 to S8 (Zhang et al. 2013). The sites S4 and S7 are along the channel of Yantai port, and can be impacted by the cargo vessels

and the pollutants from the sewage discharge area under the action of tidal currents (Liu et al. 2012). The site S8 is also influenced by the pollutants carried by the coastal current from the sewage discharge area (Liu et al. 2012). These could be the reasons that the total dissolved HMs concentrations at these three sites to be slightly higher than others in Sishili Bay area. Relatively, the sites with less effects by the sewage discharge and ship activities show lower concentration of HMs.

Available literature data for Sishili Bay with respect to HMs is insufficient for comparisons, but our findings are in line with the typical results from the adjacent sea areas (Table 2). Our results for all the dissolved concentrations of Cu, Pb, Cd and Zn show values which are in the same order of magnitude as those reported for Bohai Sea (Gao et al. 2014), North Yellow Sea (Tian et al. 2009), Bohai Bay (Meng et al. 2008; Zhang et al. 2010), Laizhou Bay (Li et al. 2015), and Jinzhou Bay (Wang et al. 2012). Through comparisons we find relatively high Pb values in Bohai Bay than those reported in the other Bohai Sea and North Yellow Sea areas, including the area we studied (Meng et al. 2008). This highlights a direct effect of river water on dissolved Pb concentration in seawater. As regards the comparison with legal limit, the sea water quality was assessed by comparing detected dissolved HMs concentrations to the

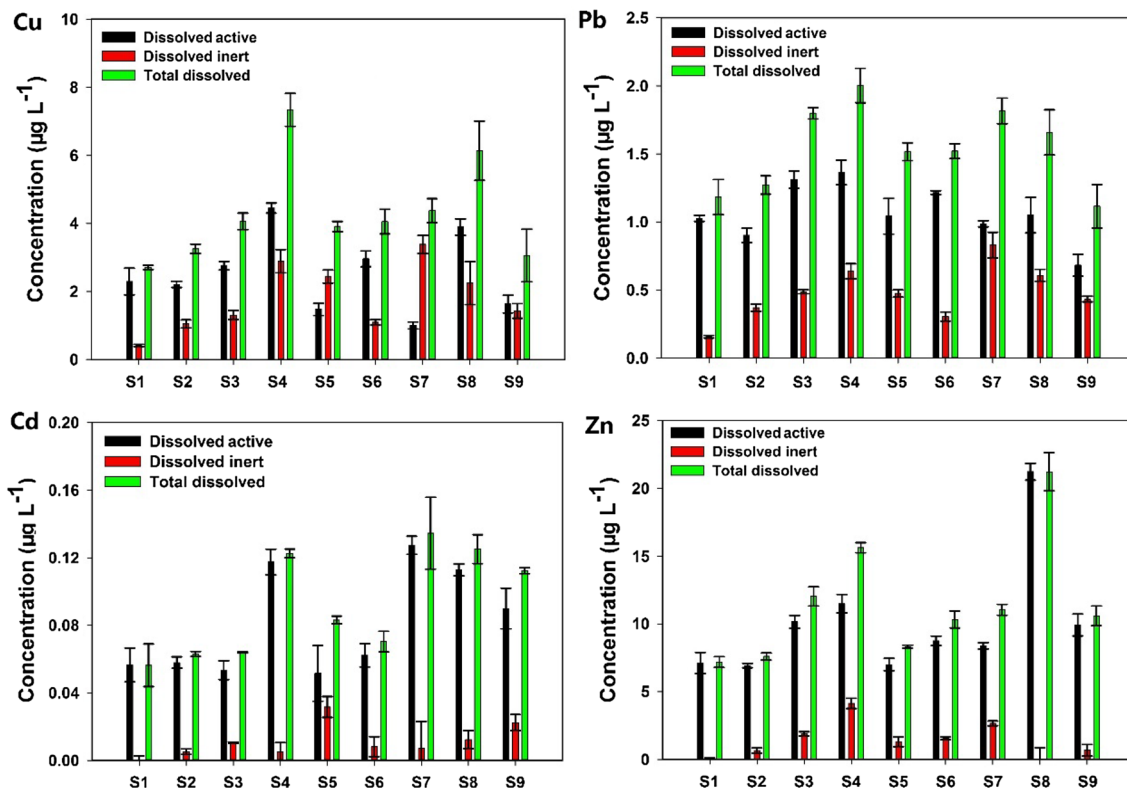


Fig. 5 Distributions of different species of Cu, Pb, Cd and Zn in seawater of Sishili Bay

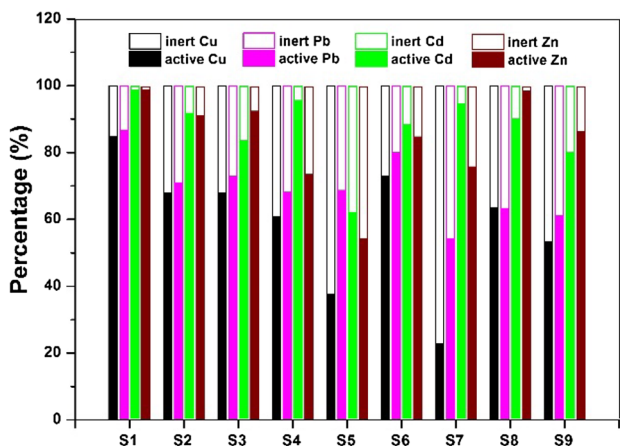


**Table 2** Selection of literature data for dissolved heavy metals concentrations in seawaters

Location, sampling year	Cu	Pb	Cd	Zn	References
Sishili Bay, 2017	2.71–7.34	1.12–2.00	0.06–0.13	7.18–21.22	This work
Bohai Sea, 2007	1.33–6.92	0.87–5.67	0.08–0.40	14.80–35.40	Gao et al. (2014)
Laizhou Bay, 2011	1.13–1.93	0.01–0.04	0.10–0.15	0.04–2.16	Li et al. (2015)
Bohai Bay, 2003	1.60–4.10	3.63–12.65	0.08–0.19	3.00–55.00	Meng et al. (2008)
Bohai Bay, 2008	–	–	0.11–0.18	15.20–24.30	Zhang et al. (2010)
North Yellow Sea, 2007	0.80	0.35	0.14	3.80	Tian et al. (2009)
Jinzhou Bay, 2009	1.26–2.49	0.21–1.39	0.56–2.04	1.58–25.73	Wang et al. (2012)

**Table 3** Sea water quality standard of China for some heavy metals ( $\mu\text{g L}^{-1}$ )

Heavy metals	Cu	Pb	Cd	Zn
Grade-I	5	1	1	20
Grade-II	10	5	5	50
Grade-III	50	10	10	100



**Fig. 6** Percentage of the dissolved active and inert concentrations of Cu, Pb, Cd and Zn in seawater samples collected in Sishili Bay

sea water quality standard of China (GB 3097-1997, China; SWQSC), which is shown in Table 3 (SEPA 1998). It can be seen that the concentration of the dissolved Cd in Sishili Bay was much lower than the grade-I sea water quality standard of China. However, the concentrations of Cu, Pb and Zn range from grade-I to grade-II sea water quality standard of China. Generally, the contamination of HMs in the seawater of Sishili Bay is light.

The percentage of the dissolved active concentrations of Cu, Pb, Cd and Zn in the total dissolved concentrations is presented in Fig. 6. The mean percentage of the dissolved active concentrations of Cu, Pb, Cd and Zn is 59.0%, 69.6%, 87.3% and 84.1%, respectively, following an order of  $\text{Zn} \approx \text{Cd} > \text{Pb} > \text{Cu}$ . The active HMs detected by ASV is classed as the free ions, inorganic complexes

and weak organic complexes (Achterberg et al. 2003). Only the free HMs ions, some inorganic complexes, and small amount of organic complexes are responsible for the uptake processes by cells of organisms (Huang et al. 2003). The complexation of HMs with organic ligands will reduce the free ions activity in the aqueous phase and thus reduce the potential of metal uptake by organisms (Huang et al. 2003). According to the literature (Muller 1996), Cu has the largest and Cd (Zn) the smallest fraction of organic complex species which is consistent with our results here. Results show that the dissolved active HMs result in their high bioavailability and toxicity to organism in the marine environment.

It can also be concluded that the percentage of the active HMs in sites S5, S7 and S9 is much lower than the others. Chlorophyll *a* concentrations of all the sampling sites were determined to investigate the relationship between the active HMs percentage and phytoplankton biomass. The concentrations of chlorophyll *a* (S1–S9) were 1.14, 0.79, 0.93, 1.25, 1.23, 0.67, 1.01, 0.83, and 2.78  $\mu\text{g L}^{-1}$  respectively. Considering the highest chlorophyll concentration of S9, the phytoplankton uptake could explain the low percentage of the active Cu and Pb in this site (Su et al. 2015). As to the site S5, which is exactly in the area of intensive scallop mariculture of Sishili Bay, the uptake by the bivalves would account for the low percentage of the active HMs due to the high accumulative ability of mollusks (especially to Zn and Cd) (Zhang et al. 2012). The decrease of the active Cu and Pb in site S7 might be caused by the treatment of free Cu ions and effluent of complexed Cu species.

In summary, an efficient and straightforward method has been proposed for the simultaneous speciation analysis of HMs in seawater. This work will contribute to the studies on relationship between the HMs species and bioavailability or toxicity. Different species of Cu, Pb, Cd, and Zn were analyzed in seawater samples collected in different locations across the Sishili Bay, north Yellow Sea, China with this method. Benefiting from this work, the speciation analysis and distribution of HMs in different water samples (freshwater, seawater) or other sea areas will also be studied in the future.

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