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Influence of mariculture on the distribution of dissolved inorganic selenium in Sanggou Bay, northern China

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ABSTRACT: Selenium is known as a 'double-edged sword' element on account of its dual beneficial and toxic effects on organisms, depending on its concentration and chemical form. Dissolved inorganic selenium (DISe) concentration in the water column and selenium content in biological species were investigated in a typical aquacultural area in Sanggou Bay, China. In addition to sampling within Sanggou Bay, the main sources of DISe into Sanggou Bay were sampled to estimate selenium transport from different sources. Results showed that DISe and selenite [Se(IV)] concentrations averaged, respectively, 0.69 nmol l^{-1} and 0.28 nmol l^{-1}, with ranges 0.21 to 1.36 nmol l^{-1} and 0.07 to 0.58 nmol l^{-1}, in the surface water of Sanggou Bay. The DISe in Sanggou Bay remained well below the toxic levels. The DISe and Se(IV) concentrations varied temporally, with lows in summer and highs in spring and autumn. Concentrations showed strong horizontal gradients from the coast to offshore areas within the bay, as significantly influenced by the intensive and widespread seaweeds and bivalves aquaculture activity in the bay. The highest selenium content (mean ± SD) was observed in scallops (3.6 ± 0.7 µg g^{-1}), followed by oyster (1.6 ± 0.4 µg g^{-1}), phytoplankton (0.9 ± 0.3 µg g^{-1}), *Gracilaria lemaneiformis* (0.063 ± 0.008 µg g^{-1}) and kelp (0.032 ± 0.005 µg g^{-1}). The main source of DISe in Sanggou Bay was water exchange with the Yellow Sea, whereas the most important sink was biological activity, which removed 53 ± 12 % of the incoming selenium from bay waters.

KEY WORDS: Dissolved inorganic selenium · Aquaculture · Seaweed · Bivalve · Sanggou Bay

INTRODUCTION

Selenium is known to be a 'double-edged sword' element, having one of the narrowest ranges of beneficent effects of all elements, varying between dietary deficiency (<40 µg d^{-1}) and toxicity (>400 µg d^{-1}) (Price et al. 1987, Fernández-Martínez & Charlet 2009). Selenium is an essential trace element required in the diets of many organisms for normal growth and physiological functions (Lin & Shiau 2005, Lobanov et al. 2009). It serves as a component of the enzyme glutathione peroxidase to protect cell membranes against oxidative damage (Rotruck et al. 1973). However, excess dietary selenium behaves as an analogue to sulfur, erroneously replacing sulfur atoms in proteins; this leads to distortion of the structure and eventual dysfunction of enzymes and proteins (Simmons & Wallschläger 2005). The biogeochemical cycle of selenium in aquatic systems has attracted considerable attention in recent decades (Cutter & Bruland 1984, Cutter & Cutter 1995, 2001, Abdel-Moati 1998, Yao & Zhang 2005).

Similar to other trace elements, the chemical form has an important influence on the fate of the sele-

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nium. To understand the biological function of selenium in aquatic organisms, it is necessary to know the levels of different selenium species in the water column. The behavior of selenium in natural waters is complicated by the presence of several oxidation states (−II, IV, VI) and organic species (Conde & Sanz Alaejos 1997). Selenite [Se(IV)] and selenate [Se(VI)] are depleted in surface water and enriched in deep water, and exhibit a nutrient-type profile consistent with other bioactive trace elements in the ocean (Cutter & Bruland 1984, Cutter & Cutter 1995, 2001).

China is one of the largest marine shellfish and seaweed producers in the world (Zhang et al. 2009). Sanggou Bay, located in Shandong Province, is an important aquacultural production area in China (Guo et al. 1999) (see Fig. 1), and is mainly used to culture seaweed and bivalves (Fang et al. 1996). Sanggou Bay has been the focus of research for ~20 yr, and extensive studies have been conducted on hydrodynamic characteristics (Zhao et al. 1996), sediment chemistry (Cai et al. 2003), nutrients (Liu et al. 2004), heavy metals (Jiang et al. 2008), ecosystem services (Zheng et al. 2009), and the sustainable management of aquaculture (Zhang et al. 2009, Shi et al. 2011). Until now, however, little research has been conducted on selenium in the aquacultural areas. Studies have indicated that selenium can stimulate the growth of seaweed (Fries 1982, Horne 1991) and that, through metabolism, seaweed can accumulate over 50 times more inorganic selenium in Se(IV) enriched culture medium than in seawater (Yan et al. 2004). In addition, the selenium assimilation efficiency of bivalves can be as high as 70 to 95% when feeding on the cytoplasm of the prey alga (Wang & Fisher 1996, Reinfelder et al. 1997); these levels may be threatening to upper trophic level birds and fish (Lemly 1995). Further studies are necessary to investigate the distributions of selenium species in aquaculture areas like Sanggou Bay, and to understand the mechanisms controlling the speciation of selenium in natural waters more generally.

The goal of this research was to investigate the distribution of dissolved inorganic selenium (DISe), selenite [Se(IV)] and selenate [Se(VI)] in Sanggou Bay, and in the river and groundwater along the coastline of the bay, in order to (1) determine the distribution of inorganic selenium species under different aquaculture conditions, and (2) estimate the input and output fluxes of selenium species. The results of this study will improve understanding of how the mariculture of seaweed and bivalves affects selenium biogeochemistry in aquacultural areas.

MATERIALS AND METHODS

Study area

Sanggou Bay is situated on the eastern tip of Shandong Peninsula to the northwest of the Yellow Sea (37° 01′ to 37° 09′ N, 122° 24′ to 122° 35′ E), with a total area of approximately 144 km^2 and mean depth of 7.5 m (Zhang et al. 2009). The bay has been used for aquaculture with seaweed and bivalves in different regions for >30 yr. Monoculture of seaweeds, including kelp *Saccharina japonica* and *Gracilaria lemaneiformis*, occurs mainly near the mouth of the bay (hereafter 'S-region') from December to May (winter and spring) and from June to November (summer and autumn), respectively. Monoculture of bivalves (in the 'B-region'), including scallops (*Chlamys farreri*) and oysters (*Crassostrea gigas*), is mainly located near the end of the bay, while the middle part of the bay is occupied by seaweed–bivalve polyculture ('SB-region') (Fig. 1). The annual production of kelp and *G. lemaneiformis* is approximately 84.5 × 10^3 and 25.4 × 10^3 t dry weight, respectively, while the annual production of bivalves is approximately 75 × 10^3 t (Rongcheng Fisheries Technology Extension Station 2012). The rivers that enter the bay include the Gu (Chinese name: Guhe), Yatou (Yatouhe), Sanggan (Sangganhe), and Shili (Shilihe) rivers, as well as several other smaller creeks. The annual discharge of these seasonal rivers is from 0.17 × 10^9 to 0.23 × 10^9 m^3 (Editorial Board of Annals of Bays in China 1991).

Sample collection

Samples were collected from marine areas in and adjacent to Sanggou Bay and from major rivers and groundwater along the coastline of the bay. Marine samples were collected during cruises in Sanggou Bay from 22 to 26 April (spring), 21 to 29 July (summer), and 17 to 20 October (autumn) of 2013, to investigate selenium levels in different seasons and various aquacultural activities. During each cruise, approximately 21 marine stations (Stns SG1 to SG19) were sampled (Fig. 1). Surface water was collected upstream and to the side of the boat while the boat moved forward, using a plastic pole sampler 3 to 4 m in length with an acid-cleaned polyethylene bottle attached to the end. Near-bottom water samples were taken with a 5 l organic glass hydrophore. Sediment cores (about 0 to 4 cm depth) were collected using a box core (15 × 15 cm) at Stns SG5 and SG6 in July 2013. Porewaters were extracted and filtered
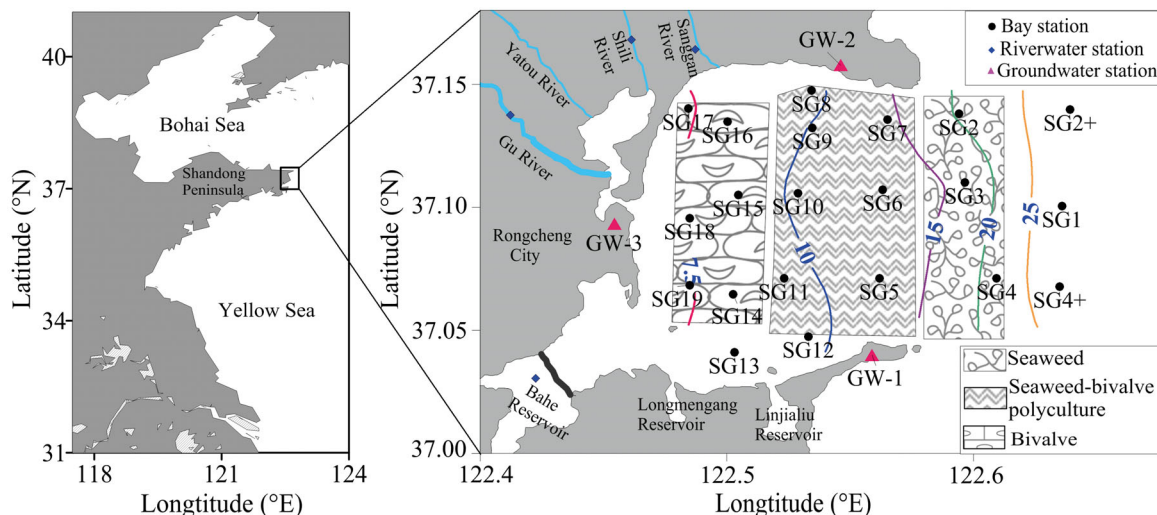
Fig. 1. Locations of field sampling and observation sites in Sanggou Bay in April, July and October 2013

from the sediment cores using 19.21.23F Rhizon CSS soil moisture samplers (Liu et al. 2011) and were frozen until analysis. River water and groundwater sampling was undertaken in April and July 2013 (Fig. 1). On each occasion, a total of 5 river water samples (from the Gu River [2 stations], Shili River, Yatou River, and Bahe Reservoir; Fig. 1) were collected using a 5 l clean plastic bucket from relatively fast-moving areas located away from urban regions. Three groundwater samples (from Stns GW-1, GW-2 and GW-3; Fig. 1) were collected from wells along the coastline of Sanggou Bay. Water temperature and salinity were measured *in situ* using an YSI Professional Plus meter at the time of sample collection. Water samples were filtered in the laboratory within 8 h of collection through precleaned 0.40 µm Nuclepore filters on a class 100 clean bench. The filtrates were placed in acid-cleaned polyethylene bottles and kept frozen until analysis.

Phytoplankton were collected by net tows using a net with a mesh size of 70 µm in April 2015. After the trawl, the plankton were filtered through a 200 µm mesh to remove the zooplankton and then were stored in plastic bottles previously decontaminated with dilute HCl solution. These bottles were kept from the sun and heat in an insulated box containing ice throughout the sampling process and transported to the laboratory. Phytoplankton were collected on the weighed 0.40 µm Nuclepore filters and freeze dried until analysis. Kelp, *G. lemaneiformis*, scallops and oysters samples were also collected in the bay during April, July, July and October 2013, respectively, stored in zip-closure plastic bags and kept in an insulated box containing ice throughout the sampling process. The seaweeds were washed with distilled water

to remove salts and small invertebrates and freeze dried. The muscle was collected from bivalves and freeze dried. Dried samples were ground into powder to pass through an 80 mesh (180 µm) sieve before analysis.

Analytical methods

Measurement of dissolved selenium concentrations

The analytical techniques for Se(IV) and Se(VI) by hydride generation combined with sector field inductively coupled plasma mass spectrometry (HG-ICP-MS) (Element 2™ ICP-MS, Thermol) have been described elsewhere (Zhang & Combs 1996, Chang et al. 2014). Briefly, Se(IV) at an acidity of 2 mol l^{-1} HCl was reacted with $NaBH_4$ to produce hydrogen selenide and was then quantified using HG-ICP-MS. Se(VI) was quantitatively reduced to Se(IV) by heating a sample acidified with 3 mol l^{-1} HCl to 97°C for 75 min, then quickly cooling the sample to room temperature using an ice-water bath, and finally following the steps for Se(IV) determination to yield the concentration of dissolved inorganic selenium (DISe). The reduction recovery ranged from 95 to 103%. This reduction method avoided the problematic variation in Se(VI) reduction behavior with different matrices, and kept the reduction rate at nearly 100% for a longer period of time than previous methods (e.g. Cutter et al. 1978, Yao & Zhang 2003). The Se(VI) concentration was calculated as the difference between DISe and Se(IV). The detection limits for Se(IV) and Se(VI) were 0.025 and 0.030 nmol l^{-1}, respectively. The measurement precisions for Se(IV) and Se(VI) in

river water were 3.4 and 3.9%, respectively, and those in seawater were 3.1 and 3.4%, respectively. The spiked standard Se(IV) or Se(VI) recovery ranged from 97 to 103%. The accuracy of the methods was tested with standard solutions, Se(IV) 50031-94 and Se(VI) GBW10032, and showed differences within −3.0 and 0.7%, respectively. The concentration of chlorophyll *a* (chl *a*) was measured using an ACLW-RS chlorophyll turbidity temperature sensor.

Measurement of selenium content of biological tissues

For total selenium content determination, complete digestion of the biological species tissues was performed with a microwave digestion system (MARSX-press, CEM). Samples (about 0.2 g) of dry tissue were soaked in 6 ml concentrated HNO_3. The digestion program was as follows: the sample was heated to 100°C for 10 min, held for 5 min, and then heated to 150°C for 5 min, held for 5 min, and finally heated to 180°C within 5 min and held for 45 min. After cooling, the solution was evaporated at 150°C to dryness using a heating block within about 2.5 h. Subsequently, the residue was dissolved in 5 ml 4 mol l^{-1} HCl, and heated in 110°C using the heating block to reduce Se(VI) to Se(IV) for 45 min. After cooling, samples were added 15 ml H_2O and diluted with 1 mol l^{-1} HCl to 50.0 ml in volumetric flask. The selenium concentration was determined by HG-ICP-MS. The biological standard reference materials GBW010024 (sea scallop), GBW010025 (spiral algae) and GBW010050 (prawn) were measured, with results of 1.49 ± 0.05, 0.23 ± 0.008 and 5.12 ± 0.05 µg g^{-1} (2σ, n = 6), respectively, with relative error −0.6, +3.8, and +0.3%, respectively, confirming the accuracy of the method.

Data statistics and analysis

The statistics software package Statistical Package for the Social Sciences version 16.0 (SPSS) was used for all data analyses. Differences were tested for significance using 1-way and 2-way analysis of variance (ANOVA), and p < 0.05 was taken to indicate significant difference. Mean values are presented with standard deviation throughout.

Flux estimates

A steady-state box model based on the Land-Ocean Interactions in the Coastal Zone (LOICZ) Biogeo-

chemical Modeling Guidelines was used to construct a DISe budget for Sanggou Bay from water budgets and non-conservative distribution of DISe, which were in turn constrained by the salt balance under steady-state conditions (Gordon et al. 1996).

The vertical diffusional flux of dissolved selenium from the bottom sediment was estimated using a modified form of Fick's first law (Meseck & Cutter 2012):

$$J = \theta^m D_o \left(\frac{\Delta Se}{\Delta z} \right) \qquad (1)$$

where J is the diffusional flux, θ is the porosity, m has a value of 3 for surface sediments (Ullman & Aller 1982), D_0 is the effective diffusion coefficient (−4.87 × 10^{10} m^2 s^{-1}) (Meseck & Cutter 2012), and $\Delta Se/\Delta z$ is the observed concentration gradient of porewater selenium. The selenium concentration at $z = 0$ m (Se_0) in water from the near-bottom of the core was used as the initial point in the concentration gradient. A negative value of J indicates that dissolved selenium is fluxing out of the sediments, while a positive J results from dissolved selenium fluxing into the sediments. The value of θ in Sanggou Bay was 0.7 (Ning et al. 2016, this Theme Section).

RESULTS

Hydrographic properties in Sanggou Bay

The water temperature in the Sanggou Bay displayed a significant horizontal gradient, decreasing from the coast to offshore in spring and summer, with a reversed gradient occurring in autumn (Fig. 2a–c). Mean water temperatures ranged from 7.7 to 20.7°C between seasons, reflecting a remarkable seasonal variation (Table 1). The salinity increased from the coast to offshore (Fig. 2d–f) as a result of water exchange with the Yellow Sea. The mean salinity varied slightly, from 28.3 to 31.4, with lows in July and October due to rainfall and freshwater discharge (Table 1). The average concentrations of phytoplankton biomass, measured as chl *a*, varied between 0.83 µg l^{-1} in spring and autumn, and 6.9 µg l^{-1} in summer (Table 1).

Seasonal variations of inorganic selenium species

Concentrations of DISe ranged from 0.21 to 1.36 nmol l^{-1} for all surface water samples in the bay, with a mean of 0.69 nmol l^{-1} (Table 1). The critical selenium limit in water is classified as 126 nmol l^{-1} in China,
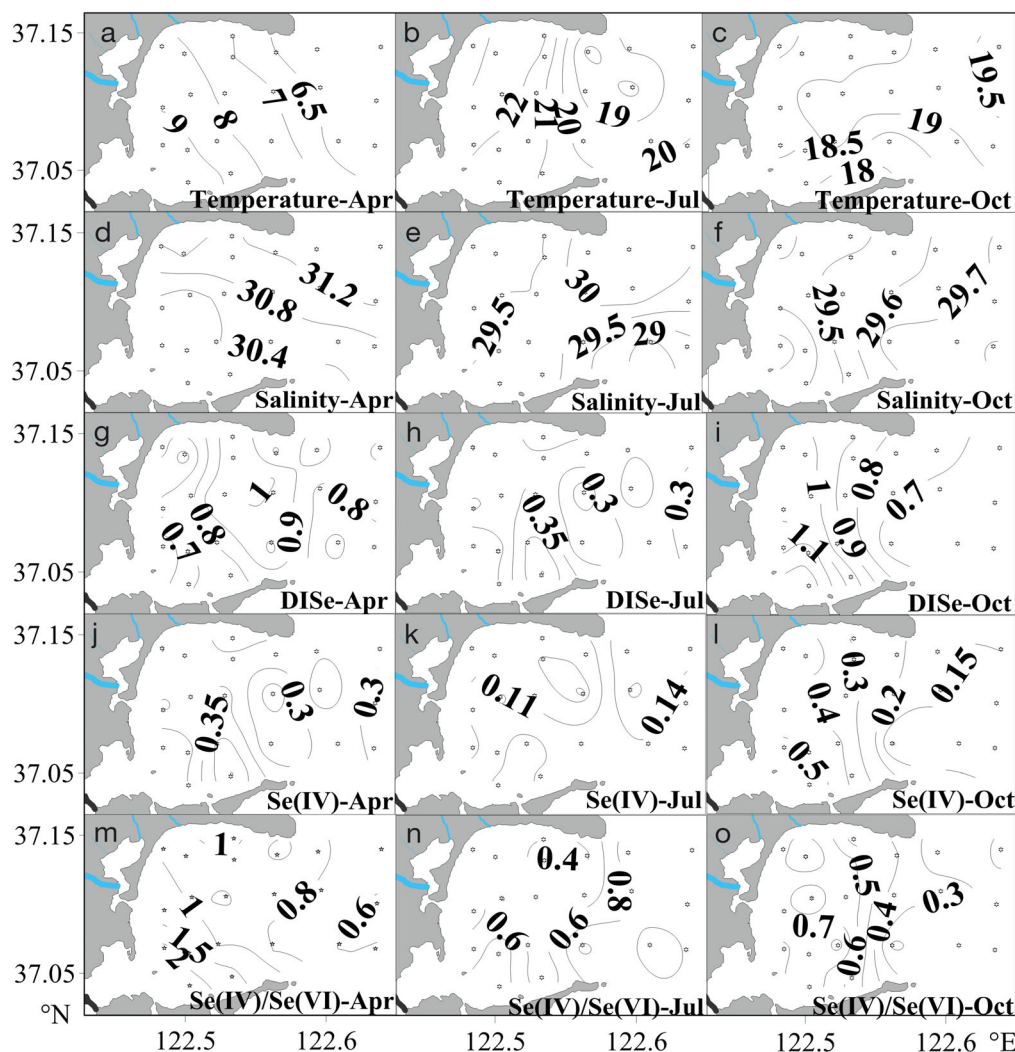
Fig. 2. (a–c) Temperature, (d–f) salinity, (g–i) dissolved inorganic selenium (DISe) concentration, (j–l) Se(IV) concentration and (m–o) Se(IV)/Se(VI) ratio distributions at the surface of Sanggou Bay in April, July, and October 2013 (left, centre and right columns, respectively)

Table 1. Mean values (with ranges in parentheses) of temperature, salinity, chl *a*, dissolved inorganic selenium (DISe) and Se(IV) concentration and Se(IV)/Se(VI) ratio in the surface water of Sanggou Bay in April, July and October 2013

	Spring (April)	Summer (July)	Autumn (October)
Temperature (°C)	7.7 (6.0–9.9)	20.7 (17.7–24.5)	18.5 (16.6–19.6)
Salinity	30.7 (30.1–31.4)	29.6 (28.3–30.5)	29.5 (29.3–29.8)
Chl *a* (µg l^{-1})	0.83 (0.59–2.3)	6.9 (0.86–20)	0.83 (0.36–2.0)
DISe (nmol l^{-1})	0.79 (0.47–1.02)	0.33 (0.21–0.46)	0.89 (0.61–1.36)
Se(IV) (nmol l^{-1})	0.39 (0.24–0.51)	0.12 (0.07–0.18)	0.30 (0.10–0.58)
Se(IV)/Se(VI) ratio	1.07 (0.59–2.30)	0.64 (0.30–1.06)	0.51 (0.18–0.85)

(State Environmental Protection Administration of China 2002); the dissolved selenium in Sanggou Bay remained 2 orders of magnitude below toxic levels.

The minimum mean concentrations of DISe occurred during summer (0.33 nmol l^{-1}), while the maximum occurred during autumn (0.89 nmol l^{-1}) (Table 1). The minimum mean concentrations of Se(IV) also occurred during summer (0.12 nmol l^{-1}), but the maximum occurred during spring (0.39 nmol l^{-1}) (Table 1). One-way ANOVA showed that the concentrations of DISe and Se(IV) were not significantly different between spring and autumn ($p > 0.05$), but that the values in summer were significantly lower than those in spring and autumn ($p < 0.0001$). It is clear from Table 1 that mean concentrations of DISe and Se(IV)

showed similar seasonal patterns, with low values in summer and high values in spring and autumn. The mean Se(IV)/Se(VI) ratios for spring, summer, and autumn were 1.07, 0.64, and 0.51, respectively (Table 1). One-way ANOVA showed that the Se(IV)/Se(VI) ratio was not significantly different between summer and autumn (p = 0.25), whereas values in spring were significantly higher than those in summer and autumn (p < 0.0001). The Se(IV)/Se(VI) ratio indicated that Se(VI) was the dominant species of inorganic selenium in the bay during summer and autumn, but Se(IV) was the dominant species in the large proportion along the coast of the bay during spring.

Horizontal distributions of inorganic selenium species

The horizontal distributions of DISe, Se(IV), and the Se(IV)/Se(VI) ratio in surface waters of Sanggou bay show similar features, such as a strong horizontal gradient from the coast to offshore (Fig. 2g−o). The concentrations of DISe along the coast during spring were lower than concentrations in the rest of the bay (Fig. 2g). While DISe showed a strong zonal distribution along the coast during autumn, decreasing offshore from 1.2 to 0.6 nmol l^{-1}, it was rather evenly distributed in summer (Fig. 2h,i). The distribution of Se(IV) in the bay exhibited a similar pattern to DISe in spring, summer, and autumn (Fig. 2j−l). The Se(IV)/Se(VI) ratio had a zonal distribution along the coast during spring and autumn, decreasing offshore from 2 to 0.6 and 0.7 to 0.3, respectively (Fig. 2m,o); however, during summer, the ratio was higher along the coast and at the mouth of the bay (0.8) as compared with in the central region (0.4) (Fig. 2n).

A 2-way ANOVA was conducted that examined the effect of season and space (i.e. S-region, B-region and SB-region, representing the 3 main types of aquaculture in Sanggou Bay) on Se(IV) and Se(VI) distribution. Both season and space significantly affected Se(IV) and Se(VI) concentrations (p = 0.0001). There was also significant interaction between season and space (p = 0.0001). Se(IV) concentrations in the S-region and B-region were significantly less than those in the SB-region in spring (p = 0.046) (Fig. 3a). In contrast, Se(VI) concentrations during spring in the B-region were significantly lower than those in the S-region and SB-region (p = 0.007) (Fig. 3b). During summer, Se(IV) concentrations in the S-region were slightly higher than those in the SB-region and B-region (p = 0.015) (Fig. 3a). There was no significant difference in Se(VI) concentrations between different regions during summer (p = 0.235). In autumn, Se(IV) concentrations in the bay increased in the following order: S-region, SB-region and B-region (p < 0.0001) (Fig. 3a). Se(VI) concentrations shared the same pattern (p < 0.02), with low values in the S-region and high values in the B-region (Fig. 3b).

Riverine input of selenium to Sanggou Bay

As shown in Table 2, the DISe and Se(IV) concentrations in 4 riverine waters were not significantly different between spring and summer (p > 0.2). Overall, DISe concentrations in riverine water ranged from 0.69 to 1.5 nmol l^{-1} with a mean of 1.0 nmol l^{-1}; these were slightly higher than those observed in the water column in Sanggou Bay (0.68 ± 0.29 nmol l^{-1}) during this study (Tables 1 & 2). The mean concentration of Se(IV) was 0.14 nmol l^{-1} in both spring and
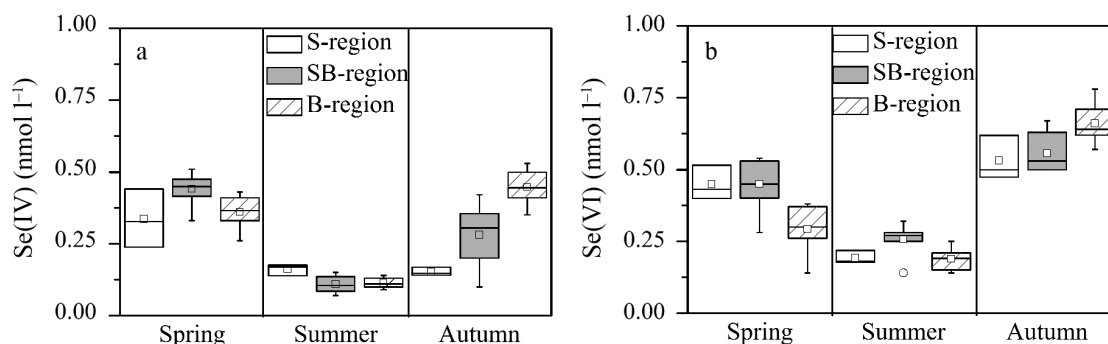

Fig. 3. Box plots of (a) Se(IV) and (b) Se(VI) concentrations in seaweed monoculture (S-region), seaweed-bivalve polyculture (SB-region) and bivalve monoculture (B-region) in spring, summer and autumn of 2013. The ends of the box and the ends of the whiskers, and the line across the box represent the 25th and 75th percentiles, the 1st and 99th percentiles and the median, respectively; the open square inside the box indicates the mean value. A circle represents an outlier

Table 2. Concentrations of dissolved inorganic selenium (DISe) and Se(IV) and Se(IV)/Se(VI) ratio in major rivers that enter into Sanggou Bay and in groundwater (GW) along the coastline of Sanggou Bay, measured in April and July 2013

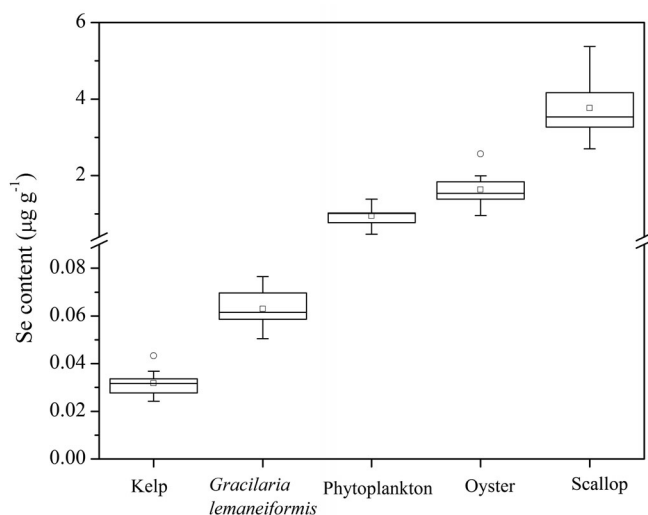| Water source	Sampling location / station number	DISe (nmol l^{-1})	Se(IV) (nmol l^{-1})	Se(IV)/Se(VI) ratio
Spring (April 2013)				
River	Gu River	1.21	0.18	0.17
	Sanggan River	0.69	0.17	0.21
	Shili River	1.12	0.08	0.18
	Bahe Reservoir	0.91	0.12	0.10
Groundwater	GW-1	34.9	1.36	0.04
	GW-2	3.14	0.60	0.24
	GW-3	3.49	0.26	0.08
Summer (July 2013)				
River	Gu River	1.49	0.11	0.08
	Sanggan River	0.84	0.21	0.18
	Shili River	1.03	0.12	0.25
	Bahe Reservoir	1.16	0.13	0.11
Groundwater	GW-1	27.5	2.76	0.11
	GW-2	5.45	0.49	0.10
	GW-3	3.54	0.89	0.34

Fig. 4. Selenium (Se) content in kelp (n = 11), *G. lemaneiformis* (n = 9), phytoplankton (n = 6), oysters (n = 9) and scallops (n = 9). Box plot details as in Fig. 3

summer; this concentration was comparable to the one observed in the water column in Sanggou Bay during summer, but was lower than those observed during spring and autumn (Tables 1 & 2). The mean Se(IV)/Se(VI) ratio was 0.16, with a range of 0.08 to 0.25, indicating that Se(VI) was the major inorganic species in riverine water. The DISe concentrations in the Sanggan River during spring and summer were lower than those in the Gu River, the Shili River and Bahe Reservoir; however, concentrations of DISe and Se(IV) varied only slightly among rivers.

Groundwater input of selenium to Sanggou Bay

The salinity values of groundwater samples were <0.1, indicating that they are freshwater. The DISe and Se(IV) concentrations in groundwater showed little temporal variation and were not significantly different between spring and summer (p > 0.1). DISe was >25 nmol l^{-1} in the sample from Stn GW-1, while it was <6 nmol l^{-1} in samples from Stns GW-2 and GW-3 (Table 2). The low concentrations of ^{226}Ra in sample GW-1 (Wang et al. 2014) indicates the low activity of rock–water interactions. Moreover, the dissolved inorganic arsenic concentration was nearly 10 times higher in sample GW-1 than samples GW-2 and GW-3 (Li et al. 2014). Stn GW-1 was excluded from the calculation of average selenium concentration. The mean DISe and Se(IV) concentrations were 3.91 ± 1.05 nmol l^{-1} and 0.56 ± 0.26 nmol l^{-1}, respectively. The mean Se(IV)/Se(VI) ratio was 0.15, indicating that Se(VI) was the predominant species in the groundwater. The mean DISe concentration in groundwater (3.91 nmol l^{-1}) was nearly 4 times higher than that in riverine water (1.0 nmol l^{-1}). Compared with surface water, groundwater usually contains higher content due to greater contact time for rock–water interactions (Fordyce 2013).

Selenium content in aquaculture species

The lowest content of Se was present in kelps (0.032 ± 0.005 µg g^{-1}), followed by *G. lemaneiformis* (0.063 ± 0.008 µg g^{-1}) (Fig. 4) these values were in the range of selenium content (0.01 to 0.6 µg g^{-1}) reported elsewhere in seaweed (Liu et al. 1987, Maher et al. 1992, Barwick & Maher 2003). These seaweeds accumulated selenium to concentrations 3 to 4 orders of magnitude above the ambient concentration in the seawater. The Se content for phytoplankton (0.9 ± 0.3 µg g^{-1}) was 10 to 30 times higher than for seaweeds (Fig. 4), and the value was within the range of those previously published for marine phytoplankton (0.5 to 4.5 µg g^{-1}) (Liu et al. 1987, Baines & Fisher 2001, Sherrard et al. 2004). The highest mean Se contents were observed in bivalves, i.e. scallops (3.6 ± 0.7 µg g^{-1}) and oysters (1.6 ± 0.4 µg g^{-1}); these values were consistent with

the range in bivalves reported elsewhere (0.24 to 4.6 µg g^{-1}) (Liu et al. 1987, Baldwin & Maher 1997, He & Wang 2013).

DISCUSSION

Influence of phytoplankton on selenium distribution

As shown in Table 1, Se(IV) concentrations were lower in summer and higher in spring, while the opposite was true for chl *a* concentrations. Studies have indicated that Se(IV) and Se(VI) can both be assimilated by phytoplankton, with Se(IV) being the preferred species for phytoplankton uptake (Apte et al. 1986, Vandermeulen & Foda 1988, Baines & Fisher 2001). Moreover, as illustrated in Fig. 2m,o, Se(IV)/Se(VI) ratios along the coast decreased towards offshore. In the coastal regions of the bay, the ratio was >0.5 during all 3 seasons, while the ratio in the freshwater end member (river and groundwater) was normally <0.2 (Table 2). There has been a paucity of investigations on selenium species in the Yellow Sea; the mean Se(IV)/Se(VI) ratio for Bohai Sea is 0.45 (Yao & Zhang 2005) and the value for East China Sea was 0.32 (Y. Chang et al. unpubl.). The relatively high Se(IV)/Se(VI) ratios in the bay compared to rivers and surrounding marine basins suggest that either Se(IV) is produced or Se(VI) is preferentially consumed in the bay. Both anions can be assimilated into biomass, but phytoplankton usually has a higher affinity for Se(IV) than for Se(VI) (Fig. 5). Therefore, preferential uptake of Se(VI)
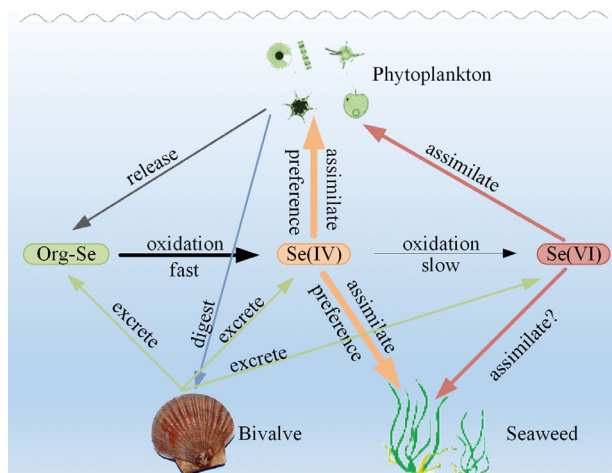

Fig. 5. A conceptual diagram of the biological effects of phytoplankton, seaweed and bivalves on selenium speciation (based on Vandermeulen & Foda 1988, Besser et al. 1994, Hu et al. 1997, Baines & Fisher 2001, present study)

probably cannot explain the observed pattern. However, the organic selenium is later released into the water column where it oxidizes to Se(IV) (Cutter & Bruland 1984), as dissolved oxygen is high in the bay. In contrast, the rate constant of the oxidation from Se(IV) to Se(VI) was 8.7 × 10^{-4} yr^{-1}, which means it takes >1000 yr to oxidize Se(IV) to Se(VI) (Cutter & Bruland 1984); therefore, this process can be ignored. This may also be the reason why Se(IV)/Se(VI) ratios are elevated at the mouth of the bay during summer, as large amounts of algae would release organic selenium, which would then be oxidized to Se(IV) (Fig. 2n).

Influence of mariculture species on selenium distribution

The distribution of selenium was greatly affected by the mariculture species, as shown in Fig. 3. Laboratory studies have indicated that both Se(IV) and Se(VI) can increase the growth of macroalgae, with Se(IV) taken up more readily than Se(VI) (Fries 1982, Horne 1991). Kelp can bioaccumulate >50 times more inorganic selenium in a Se(IV) enriched culture medium than in seawater (Yan et al. 2004). The kelp in the bay is generally cultivated in November and is harvested in late May. Thus, due to the fast growth of kelp, Se(IV) would be preferentially taken up by the seaweed (Fries 1982). This would explain the relatively low concentrations of Se(IV) in the kelp monoculture region (S-region) in spring (Fig. 3a). Utilization of Se(VI) is more limited compared with Se(IV) (Fries 1982), resulting in the high levels of Se(VI) present in the S-region during spring (Fig. 3b). Moreover, the elevated Se(VI) may be caused by the Yellow Sea input. The *G. lemaneiformis* monoculture is planted after the harvest of kelp in late May. The assimilation of selenium by *G. lemaneiformis* is similar to that of kelp (Fries 1982).

Bivalves mainly accumulate selenium from particulate sources by ingestion and assimilation, while passive uptake from dissolved phases is negligible (Wang & Fisher 1996, Griscom & Fisher 2004, Luoma & Presser 2009). Bivalves have been observed to accumulate ingested selenium to concentrations markedly higher than those present in the algal diet, due to high assimilation rates of cytosolic selenium (Wang & Fisher 1996, Reinfelder et al. 1997). After ingestion, bivalves excrete selenium as dissolved phases probably in the forms of inorganic selenium, including Se(IV) and Se(VI), and organic selenium (Wang & Fisher 1996), and the organic selenium can then be

oxidized to Se(IV) (Cutter & Bruland 1984). These processes probably resulted in the high Se(IV) and Se(VI) concentrations in the bivalve monoculture region (B-region) during autumn (Fig. 3a,b). Another possible reason for elevated Se(VI) concentrations in B-region was the input from river or groundwater.

The intensive kelp and bivalve aquaculture activities occurring over large areas of Sanggou Bay have a significant influence on the distribution of selenium in the bay. A conceptual diagram of the biological effects of phytoplankton, seaweed and bivalves on the selenium species in Sanggou Bay is shown in Fig. 5. Phytoplankton and seaweeds (kelp and *G. lemaneiformis*) preferentially assimilate Se(IV) and convert it to organic selenium (Fries 1982, Vandermeulen & Foda 1988, Horne 1991, Besser et al. 1994, Hu et al. 1997, Baines & Fisher 2001). Dissolved organic selenium regenerated from biogenic particles (as phytoplankton cells die and/or bivalves excrete) is quickly oxidized to Se(IV) in the oxygenated water (Cutter & Bruland 1984, Wang & Fisher 1996, Luoma & Presser 2009). However, neither Se(IV) nor organic selenium are reconverted to Se(VI), as these reactions have a half reaction time of hundreds of years (Cutter & Bruland 1984). Thus, the seaweeds assimilate both Se(IV) and Se(VI), resulting in low levels in the water column, while the bivalves assimilate particulate selenium but excrete dissolved selenium, replenishing selenium levels in the water column.

DISe budget for Sanggou Bay

Inputs of selenium to Sanggou Bay

The riverine input of DISe into Sanggou Bay (Y_Q) can reach 15 ± 4 kg yr^{-1} (see Fig. 6) by multiplying the mean DISe concentrations with the annual mean river water discharge.

The submarine groundwater discharge into the bay during summer is $(9.45$ to $11.20) \times 10^9$ m^3 yr^{-1}, as determined by calculation based on the non-conservative inventory of ^{226}Ra and ^{228}Ra (Wang et al. 2014). As submarine groundwater discharge includes recycled seawater (75 to 90%) as well as fresh groundwater (Moore 1996), the hypothesis of groundwater discharge over the whole bay—instead of just along the shoreline—overestimates the discharge volume. Therefore, we assumed that 5% of the submarine groundwater discharge represented a best estimate of the fresh groundwater discharge, resulting in a value of 0.47×10^9 m^3 yr^{-1}. The annual input of DISe from fresh groundwater (Y_G) into the bay was then estimated by multiplying the mean DISe concentrations of groundwater and annual fresh groundwater discharge, giving a value of 146 ± 39 kg yr^{-1}.

The diffusional flux of DISe from the sediment was calculated for the bay using Eq. (1). The DISe concentrations in near-bottom water and porewater for Stn SG5 were 0.32 nmol l^{-1} and 0.45 nmol l^{-1}, respectively, and DISe concentrations in near-bottom water and porewater for Stn SG6 were 0.3 and 0.41 nmol l^{-1}, respectively. Calculations demonstrate that there can be a -0.68 and a -0.58 nmol m^{-2} yr^{-1} flux of DISe between the sediment and water column at Stns SG5 and SG6, respectively. The negative values indicate flux of DISe out of the sediment. The diffusional flux from the sediment to the water column in the bay was estimated by averaging the diffusional flux from each of the different regions. The DISe flux from the sediments (Y_S) was $(7.2 \pm 0.8) \times 10^{-3}$ kg yr^{-1}.

The selenium concentration in rainwater ranges from 1.3 to 2.6 nmol l^{-1} in China (Zhu & Tan 1988). A rainwater sample was collected during summer in the Bay with a selenium concentration of 1.7 nmol l^{-1}, which is within the range of rainwater values in China (Zhu & Tan 1988). Thus, the annual wet deposition of DISe was estimated to be 17.5 kg yr^{-1}, by multiplying the selenium concentration in rainwater with the amount of annual rainfall. The amount of selenium in dry deposition is not known for this region; therefore, the value for the East China Sea (soluble dry deposition of 0.27 ± 0.48 μg m^{-2} d^{-1}) (Hsu et al. 2010) has been adopted to estimate the annual dry deposition of selenium into the bay. Accordingly, the total atmospheric input (wet and dry deposition) of selenium into the bay (Y_P) was 32 ± 25 kg yr^{-1}.

Biological utilization of selenium

The elemental Se:C ratio for phytoplankton in seawater was $(8.5 \pm 3.0) \times 10^{-6}$, which were within the range of those previously pubished for marine phytoplankton (Liu et al. 1987, Baines & Fisher 2001, Sherrard et al. 2004), and the carbon fixed by phytoplankton in Sanggou Bay is 9.5×10^6 kg yr^{-1} (Jiang et al. 2015). Utilization of selenium by phytoplankton in Sanggou Bay was estimated to be -81 ± 29 kg yr^{-1} (negative values indicate removal of selenium from the bay through assimilation by biological organisms; see Fig. 6) by multiplying the carbon fixed by phytoplankton and the elemental Se/C ratio for phytoplankton in Sanggou Bay.

Intensive aquaculture activities have a large influence on selenium levels in Sanggou Bay. The amount of selenium removed from the bay by aquaculture activities was calculated by multiplying aquacultural production in the bay (Rongcheng Fisheries Technology Extension Station 2012) and the selenium content in the cultured species, including kelp, *G. lemaneiformis*, scallops, and oysters. Thus, the amount of selenium fixed by kelp, *G. lemaneiformis*, scallops and oysters was 2.7 ± 0.4, 1.6 ± 0.2, 54 ± 11, and 98 ± 54 kg yr^{-1}, respectively. The highest selenium utilization was by scallops and oysters (151 ± 30 kg yr^{-1}), followed by phytoplankton (81 ± 29 kg yr^{-1}) and seaweed (4.31 ± 0.5 kg yr^{-1}), and the total selenium utilization was estimated to be about 236 ± 42 kg yr^{-1} (see Fig. 6).

Selenium budget for Sanggou Bay

The steady-state box model, illustrated in Fig. 6, calculates the water and salt budgets, and then estimates the mass balance of DISe in Sanggou Bay, including exchange with the Yellow Sea. Freshwater inputs from river discharge (V_Q), groundwater discharge (V_G) and precipitation (V_P) are 0.19×10^9 (Editorial Board of Annals of Bays in China 1991), 0.47×10^9

(Wang et al. 2014) and 0.13×10^9 m^3 yr^{-1} (Shandong province Rongcheng City the Local Chronicles Compilation Committee 1999), respectively. These inputs are reduced by evaporation (V_E), which is 0.15×10^9 m^3 yr^{-1} (Shandong province Rongcheng City the Local Chronicles Compilation Committee 1999). From the water mass balance, net water exchange (V_R) is from Sanggou Bay to the Yellow Sea, with a residual flow of -0.64×10^9 m^3 yr^{-1} (positive values indicate transport into the bay, negative values export from the bay to the Yellow Sea). Using a salinity of 0 for freshwater input, and salinities of 30 and 32 for Sanggou Bay and the Yellow Sea (Lin et al. 2005), respectively, the water exchange flow from the Yellow Sea to Sanggou Bay (V_X) is 9.96×10^9 m^3 yr^{-1}, based on the salt balance in the bay. When calculating the net DISe transport from the Yellow Sea to Sanggou Bay, the mean the DISe concentration (1 ± 0.44 nmol l^{-1}) of Bohai Sea (Yao & Zhang 2005) and the East China Sea (Y. Chang et al. unpubl. data) was used as the value for the Yellow Sea, where DISe data are lacking. The net transport (Y_R) from Sanggou Bay to the Yellow Sea is -42 ± 12 kg yr^{-1} (positive values indicate transport into the bay, negative values export from the bay to the Yellow Sea), and the exchange (Y_X) between Yellow Sea and Sanggou Bay is 253 ± 71 kg yr^{-1}. The data obtained in this study allow for the calculation of selenium budgets in Sanggou Bay (Fig. 6). Atmospheric dry and wet depositions (Y_P), riverine input (Y_Q), groundwater influx (Y_G), exchange between Yellow Sea and Sanggou Bay (Y_X), net transport from the Yellow Sea to Sanggou Bay (Y_R), sediment diffusion (Y_S), and biological fluxes are all shown in Fig. 6. The exchange between Sanggou Bay and the Yellow Sea (Y_X) was the major source of selenium to Sanggou Bay, contributing $57 \pm 19\%$ of total DISe inputs. Groundwater discharge (Y_G) accounted for $33 \pm 10\%$ of the total DISe input, making it the second largest source of selenium into the bay. However, the exchange of DISe flux ($0.002 \pm 0.0004\%$) between the sediment and the water column was negligible compared with other sources. The sediment–water exchange of selenium is also a negligible source in San Francisco Bay, as indicated by stable isotope ratios (Johnson et al. 2000) and sediment porewater values (Meseck & Cutter 2012). The net transport of DISe from Sanggou Bay to the Yellow Sea accounted for $10 \pm 3\%$ of the DISe export.
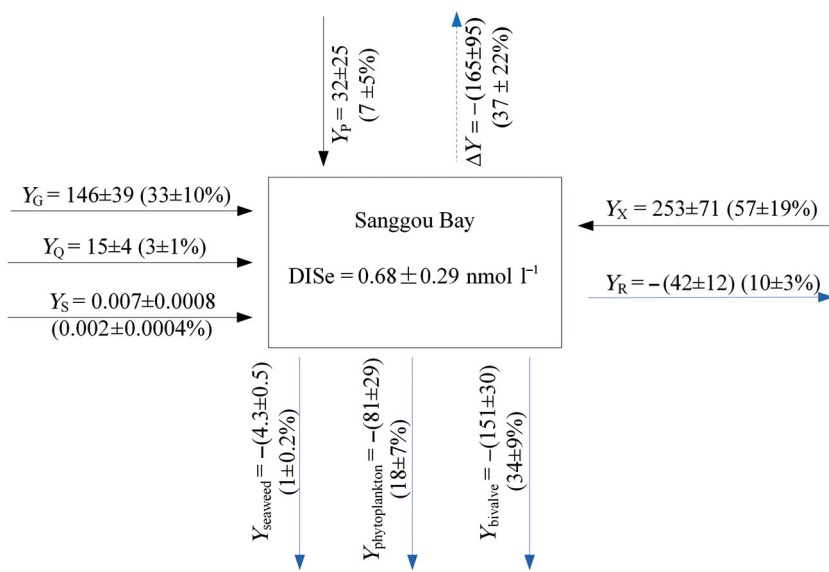

Fig. 6. Selenium budget in Sanggou Bay, showing inputs and outputs (*Y*) as absolute values (kg yr^{-1}; mean ± SD) and as percentages of total input. Positive values of *Y* indicate transport into Sanggou Bay; negative values indicate export of dissolved inorganic selenium (DISe) from Sanggou Bay or assimilation by biological organisms. Y_P: atmospheric deposition; Y_Q: riverine input; Y_G: groundwater input; Y_X: exchange between Sanggou Bay and Yellow Sea; Y_R: net transport from Yellow Sea to Sanggou Bay; Y_S: sediment/diffusion; ΔY: net internal sink

The amount of selenium utilized by bivalves was 151 ± 30 kg yr^{-1}. This amount was 34 ± 9% of the total DISe input (Fig. 6), making bivalves the most important selenium sink. Phytoplankton assimilation was another sink of selenium, using 18 ± 7% of the total DISe input, while the seaweed assimilated only 1 ± 0.2% of the total DISe input (Fig. 6). Thus, biological activity removed nearly 53 ± 12% of the DISe out of the water column and was the major sink of DISe in Sanggou Bay. This means with the harvesting of marine products, nearly half of the selenium was removed out of the bay.

The input of DISe was 445 ± 85 kg yr^{-1}, and output of DISe was 280 ± 42 kg yr^{-1} in the bay. There was a net imbalance between the input and output of dissolved selenium, however. The selenium budgets in Sanggou Bay are only approximations, which depend on the accuracy of the freshwater, water exchange fluxes between Sanggou Bay and the Yellow Sea. If these flux estimates are valid, however, there is a net internal sink of −165 ± 95 kg yr^{-1} (37 ± 22%) in the bay (Fig. 6). Studies have shown that algae can form dimethylselenide and dimethyldiselenide, which can be volatilized and released into the atmosphere (Ansede & Yoch 1997). The selenium flux of dimethylselenide to the atmosphere was estimated to be 60 to 260 kg yr^{-1} in Gironde Estuary (Ansede & Yoch 1997), and methylation was estimated to account for 10 to 30% of the selenium removed from San Francisco Bay (Hansen et al. 1998). Thus, internal sinks of DISe in Sanggou Bay might include emission from the water column into the atmosphere as volatile selenium, dissimilatory reduction of Se(VI) and Se(IV) to inorganic reduced phases (Se0, Se-II) (Stüeken et al. 2015), and/or transformation to other organic and particulate forms of selenium. To better constrain the uncertainty of budget calculations, more observations are required to understand the biogeochemical process of selenium in Sanggou Bay.

Sensitivity analysis

Box model sensitivity analysis were exampled by changing model parameters by 10% in order to evaluate model response. The sensitivity was quantified by calculating a normalized sensitivity defined as the percentage change in a variable produced by a percentage change in the parameter.

Table 3. Normalized parameter sensitivity of the net internal sink of dissolved inorganic selenium (DISe) (ΔY) for each parameter

Parameter	Treatment (%)	Normalized sensitivity (%)
River discharge (V_Q)	10	4.7
Groundwater discharge (V_G)	10	18
Precipitation (V_P)	10	3.6
Evaporation (V_E)	10	−3.0
DISe concentration in Yellow Sea	10	47
DISe concentration in Sanggou Bay	10	−33
DISe concentration in rivers	10	0.9
DISe concentration in groundwater	10	8.8
DISe concentration in rainwater	10	1.1
Soluble dry deposition	10	0.9
DISe flux in sediments (Y_S)	10	1.1
Se content in phytoplankton	10	−4.9
Se content in kelp	10	−0.2
Se content in *G. lemaneiformis*	10	−0.1
Se content in oysters	10	−5.9
Se content in scallops	10	−3.3
Carbon fixed by phytoplankton	10	−4.9
Production of kelp	10	−0.2
Production of *G. lemaneiformis*	10	−0.1
Production of oysters	10	−5.9
Production of scallops	10	−3.3

Ten percentage changes in parameters of DISe concentration for Yellow Sea, DISe concentration for Sanggou Bay and groundwater discharge result in changes in net internal sink (ΔY) yield of 47, −32 and 18%, respectively, while changes in other parameters result in changes in ΔY yield of <10% (Table 3). There has been a paucity of investigations on selenium species in the Yellow Sea; the DISe concentration in Yellow Sea which was used to calculate the net DISe transport from the Yellow Sea to Sanggou Bay (Y_X) was obtained by averaging the values of Bohai Sea (Yao & Zhang 2005) and the East China Sea (Y. Chang et al. unpubl. data). The sensitivity analysis showed that DISe concentration in the Yellow Sea was the most critical parameter and therefore in cases where selenium data are available, it would be worth using a more accurate parameterization of DISe concentration in the Yellow Sea. The DISe concentrations in Sanggou Bay presented significantly variation between seasons and the relative annual mean variation was 42%, which is greater than the 10% changes for sensitivity analysis. Therefore, in future selenium budget calculation, it may be possible to reduce uncertainty in calculating the budget in seasonal levels. Moreover, the box model's sensitivity to changes in groundwater discharge suggested that any improvement in estimates of groundwater discharge is likely to improve the model accuracy. Finally, the budgets were relatively insensitive to riverine input (Y_G), atmospheric

deposition (Y_P), sediment diffusion (Y_S), and to biological fluxes. This suggested that inaccuracies in riverine, atmospheric deposition, sediment diffusion and biological data sets have relatively minor impacts on selenium budget calculation, especially in comparison with inaccuracies associated with other model inputs.

CONCLUSION

Distributions of dissolved inorganic selenium species observed in Sanggou Bay provide relevant information that can be linked to the dynamics and biological reactions that take place in the region. Average concentrations of DISe and Se(IV) in surface waters of the bay were 0.67 and 0.28 nmol l^{-1}, respectively, with ranges of 0.21–1.36 and 0.07–0.58 nmol l^{-1}, respectively. The average Se(IV)/Se(VI) ratio was 0.74, indicating that Se(VI) was the predominate inorganic selenium species in large proportion of the bay. DISe concentrations in Sanggou Bay remained 2 orders of magnitude below the critical selenium limit for water in China. The highest selenium content was observed in scallops (3.6 ± 0.7 μg g^{-1}), followed by oyster (1.6 ± 0.4 μg g^{-1}), phytoplankton (0.9 ± 0.3 μg g^{-1}), *G. lemaneiformis* (0.063 ± 0.008 μg g^{-1}) and kelp (0.032 ± 0.005 μg g^{-1}).

The DISe and Se(IV) concentrations were low in summer and high in spring and autumn. The distribution of DISe and Se(IV) in the bay showed strong horizontal gradients from the coast to offshore. The intensive seaweed and bivalve aquaculture present over large areas had a strong influence on selenium distribution. The Se(IV) concentrations in the seaweed monoculture region were low in spring due to the uptake by the seaweed. While the Se(IV) and Se(VI) concentrations in the bivalve monoculture region were high in autumn, probably caused by the bivalves assimilating particulate selenium but excreting dissolved selenium, thereby replenishing selenium levels in the water column.

A simple budget for DISe in Sanggou Bay was estimated in this study. The major source of DISe into Sanggou Bay was water exchange with the Yellow Sea. Groundwater discharge was the second largest source of selenium into the bay. However, intensive bivalve aquaculture removed 34 ± 9% of the DISe input, making it the most important sink.

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