Dissolved inorganic tin sources and its coupling with eco-environments in Bohai Bay

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**Abstract** Dissolved inorganic tin (DISn) and its spatial variation were examined in Bohai Bay seawaters to understand the DISn behavior and pollution in this area. DISn concentration gradually increased with the distance from the coast and showed a slight decrease with the increasing depth from surface water, suggesting the scavenged behavior of tin with an atmospheric input to surface water. Besides, the higher DISn values also were found near the Haihe Estuary inferring that the riverine input was a source of DISn. Based on the data in this study, a preliminary estimate of the tin budget via riverine input and atmospheric deposition has been established. According to our estimate, about $2 \times 10^6$ and $8.47 \times 10^5$ g/year of tin reach Bohai Bay via rivers and atmosphere. Environmental factors such as suspended particulate material, salinity, total organic matter, pH, nutrients, and phytoplankton had the important influences on DISn distribution. Among them, the negative correlation between DISn and phytoplankton at most stations might indicate the biological uptake of tin.

**Keywords** Dissolved inorganic tin · Distribution · Environmental factors · Source · Bohai Bay

**Introduction**

Tin (Sn) is considered an essential element for organisms, even humans. In nature, tin occurs both in inorganic and organic forms. A good deal of research on biogeochemical processes in aquatic environment has been, and continues to be, devoted to organic tin. Rather less attention has been focused on inorganic tin, especially on the aquatic geochemical characteristics and behaviors of inorganic tin. Inorganic tin may be taken up by both passive diffusion and active transport across the cell membrane (Pawlik-Skowrońska et al. 1997). However, tin is a toxic cumulative element and moderate level of tin may inhibit the growth of organism and lead to harmful environmental effects. Thus, the geochemical characteristics and behaviors of inorganic tin should be of global interest and be much accounted for (Arambarri et al. 2003).

The distribution and behavior of DISn have been examined in estuaries, coastal waters, and open oceans (Andreea et al. 1983; Arambarri...
These studies indicate that the marine biogeochemical cycle of DISn includes: the transport from the continent to the sea by rivers and atmosphere, the uptake by phytoplankton, regeneration from organic detritus, adsorption–desorption by particulate, removal from seawater to marine sediments, and release from sediment resuspension.

The factors controlling the DISn distribution remarkably include the sources and modes whereby tin enters the environment; the physical, chemical, and biological activities; the seawater characteristics (i.e., suspended particulate material (SPM), salinity, total organic carbon (TOC), depth, temperature, and pH); and ocean currents (Andreae et al. 1983; Pawlik-Skowrońska et al. 1997).

Tin is like other metals and its compounds are introduced in the environment naturally as well as from a variety of human activities (Le et al. 1999). The approaches possible for tin to enter an aquatic environment include atmospheric deposition, riverine input, and sediment resuspension. Byrd and Andreae (1986a) found that the major flux of tin to the oceans in the northern hemisphere was from the atmospheric deposition. They also estimated a global riverine DISn flux of 90.44 t/year which was substantially smaller than the atmospheric continent-to-ocean flux of tin (ca. 357 t/year) (Byrd and Andreae 1986a, b). In addition, Neal and Davies (2003) found that the riverine input of tin into the North Sea was 3.77 t/year.

On the other hand, the seawater characteristics also affect the tin distribution and behavior to some extent. For example, besides the increasing tin concentration, tin toxicity grows with the augmenting of both pH values and duration in aquatic systems. Especially, the bioavailability of tin is highest at neutral and slightly alkaline pH and is reduced in the presence of humic acid (Pawlik-Skowrońska et al. 1997). At low pH, in view of the low water solubility, the tin is poorly adsorbed and its bioavailability is low (Bulten and Meinema 1991). In addition, due to the adsorption–desorption processes, the tin concentration in seawater also relates to the SPM, which mainly originates from rivers and resuspended sediments and detritus (Byrd and Andreae 1986b). Other characteristics (e.g., TOC and Eh) also can affect or indicate the tin distribution, source, and behavior indirectly (Pawlik-Skowrońska et al. 1997).

Overall, three geochemical characteristics make tin an element of unique interest. (1) Its mobilization by human activities, as evidenced by an annual production of about $250 \times 10^9$ g, exceeds tenfold the natural rate of mobilization of tin by erosion. (2) Tin is one of the three most highly enriched metals (after lead and tellurium) in the atmospheric particulate matter as compared the earth’s crust (Byrd and Andreae 1982). (3) Tin can be involved in biological cycling. Since tin has so many interesting characteristics, and because of its contribution to environmental pollution, the geochemical characteristics and behaviors of tin in Bohai Bay seawaters were studied, which would provide a basis for comparison with other oceans and for future monitoring of this area. The objectives of our study were to: (1) determine spatial distribution of DISn in Bohai Bay seawaters; (2) evaluate if the sources, distributions, and behaviors of DISn in the seawaters were associated with the seawater characteristics, nutrients, and phytoplankton species; and (3) estimate the sources of DISn to Bohai Bay.

Materials and methods

Study area

Bohai Bay is a semi-enclosed shallow water basin located in the western region of the Bohai Sea in the northeastern part of China, with a surface area of $1.6 \times 10^4$ km², which is 20% of Bohai Sea’s surface area. Bohai Bay receives a vast amount of freshwater from the Haihe River Basin, the Luanhe River Basin, and the Huanghe River Basin. Among them, the Haihe River Basin is the major freshwater source discharging directly to
Bohai Bay from the top of the western bay. The Haihe River Basin draining into Bohai Bay mainly includes the Haihe River, the Tuhaihe River, the Majiahe River, the Dehuixinhe River, the Nanpaiwuhe River, and the Beipaihe River. Bohai Bay is shallow, having a depth of \( \leq 32 \) m, and the mean water depth of 12.5 m. The water exchange between Bohai Bay and the central Bohai Sea is quite slow and weak because of its semi-enclosed position, thus most of pollutants from riverine input accumulate gradually.

Sample collection

In order to achieve the projected objective, a population of 20 sample stations were designated according to their latitudes from 38\(^\circ\)14'04" N to 38\(^\circ\)58'00" N (Fig. 1). Water samples were collected during 21 to 28 April 2008 with the cruise of “Hai Jian 11”. The samples were taken at the surface and bottom layers using 10 L Niskin bottles deployed by a CTD rosette. Water samples for tin and heavy metals were filtered immediately on board through pre-cleaned and weighing 0.45 \( \mu \)m Nuclepore filters. The filters were folded twice with the loaded surface inside, returned to the plastic Petri dishes, stored at \(-20^\circ\)C, dried, and re-weighed in the land laboratory for suspended particulate material determinations. The filtrates were immediately stored at 4\(^\circ\)C in 1 L acid-cleaned high-density polyethylene bottles, and preserved with ultrapure HCl to a pH < 2. Water samples for analysis of Hg were filtered immediately with pre-cleaned silica fiber filter and then stored in Pytex bottles which were pre-acidified to give a final concentration of 2% HNO\(_3\), kept at 4\(^\circ\)C after acidifying them to pH < 2 with ultrapure HNO\(_3\). Another water samples for nutrients and chlorophyll \( a \) (Chl-\( a \)) were filtered immediately on board through pre-cleaned Whatman GF/F glass fiber filters; the filtrates were transferred to polyethylene bottles and stored frozen, and the filter samples containing chlorophyll \( a \) were stored in dark at \(-20^\circ\)C until analysis. Phytoplankton samples were collected at all stations using the plankton net (mouth diameter 31.6 cm, mesh size 76 \( \mu \)m). After dragging, the concentrates were collected from the plankton net bucket to a glass bottle and were fixed with buffered formalin at a final concentration about 2.0% in seawater, and then stored in the dark until analysis.

![Fig. 1](image-url)  The location of the stations in Bohai Bay, 2008
Analytical methods

**Tin determination**

DISn was pre-treated within 2 weeks of collection using the methods of co-precipitation of ferric hydroxide. The analytical technique for DISn has been described elsewhere (Qin et al. 2007). Briefly, the amount of DISn was determined by hydride generation and atomic fluorescence (HG-AFS: XGY-1011A). Tin was determined by acidifying samples to 0.06 M HNO\(_3\). To explicitly evaluate analytical precision, all samples were determined in triplicate (precision as relative standard deviation better than 7%). Accuracy was assured using the standard addition method of calibration with recoveries of 85–110%. The detection limit of the method for DISn was 0.05 ng/ml. Recoveries of pre-concentration, checked by co-precipitation of 0.4 ng/ml tin standard with ferric hydroxide, were 98 ± 5%.

**Physico-chemical studies**

The physico-chemical parameters (i.e., pH, salinity, total organic carbon, dissolved inorganic nitrogen (DIN), phosphate, and silicate) of 40 batches of water samples (triplicate of each batch) were performed by standard methods “The specification for marine monitoring (GB 17378.4-1998)” (SBQTS1998a). The TOC values were determined by potassium persulfate oxidation method. Phosphate (PO\(_{4}^{3-}\)) and silicate (SiO\(_2^{3-}\)) were measured using phosphorus molybdenum blue method and silicon molybdenum blue method, respectively. DIN was calculated as the sum of nitrate, nitrite, and ammonia. Nitrate was reduced to nitrite by zinc–cadmium metal and determined (as nitrate plus nitrite) using N-(1-naphthalin group) diaminoethane photometric method, and ammonia was measured by the alkaline phenol method to form indophenol blue.

**Chlorophyll a and phytoplankton biomass**

In the preparation for spectrophotometric analysis, the filter samples were immersed in 10 ml of 90% acetone solution and then placed in cool, dark chambers for about 24 h to ensure the extraction of Chl-a. The soaked solution was centrifuged at 3000 r/min for 10 min, and the supernatant was analyzed with the fluorescence spectrophotometer (Cary Eclips, Varian) at 436 nm (Ex) and 670 nm (Em) wavelength.

Phytoplankton cell enumeration was performed by using an inverted microscope at ×100–400 magnification after sedimentation of 0.5 ml subsamples for 24 h in 25 ml Utermöhl chambers (Utermöhl 1958).

**Heavy metals determination**

Zn, Cu, Pb, Cd, Cr, and Hg were detected. The Hg concentration was determined through the cold-vapor atomic fluorescence method (XGY-1011A). The remaining five metals were measured in seawater by atomic absorption spectrometry (Thermo Scientific iCAP 6300 Radial). Zn, Cu, Pb, Cd, and Hg were performed following the method previously described in detail by Kremling et al. (1999). Cr was analyzed by standard methods following “The specification for marine monitoring (GB 17378.4-1998)” (SBQTS1998a). The relative standard deviations were better than 7% for all heavy metals. The detection limits for Zn, Cu, Pb, Cd, Cr, and Hg were 4.55, 3.2, 1.04, 0.67, 40, and 0.05 ng/l, respectively.

**Statistical analyses**

Multivariate analysis methods such as multiple regression analysis, principal component analysis (PCA), and Pearson correlation analysis have been used to extract information from the chemical analysis in order to find the relationships between DISn and environmental factors (Capelli et al. 2000; Lucila Lares et al. 2002; Szefer et al. 2002). In this work, a value of \(p < 0.05\) was considered to indicate a significant difference in all statistical analysis. Multiple regression analysis was used to estimate the coefficients of the linear equation, which best predicted the value of the dependent variable. Principal component analysis was executed on the analytical data in order to obtain a visual representation of the main characteristics of relationship among heavy metal concentrations in the study water. The combined plot of scores and loadings allowed us to recognize groups of
heavy metals with similar behavior and the existing correlation among heavy metals. Usually, the principal components (PCs) are obtained by their eigenvalues >1. All statistical calculations in this paper were conducted using SPSS 13.0.

Results and discussion

Distribution of DISn

**Horizontal distribution**

DISn concentration was chosen to reflect the tin pollution level. The DISn concentrations in the surface and bottom waters of Bohai Bay are shown in Fig. 2. It displayed that the DISn concentration in the surface waters ranged from 0.208 to 0.503 ng/ml, with an average of 0.314 ng/ml. The sequence of DISn concentrations in the bay was: the western bay (0.341 ng/ml) > the central bay (0.310 ng/ml) > the bay mouth (0.275 ng/ml), with a maximum value of 0.503 ng/ml at station B2 and minimum value of 0.208 ng/ml at station D1. DISn concentrations at stations A4, A5, A6, A8, B2, and B3 were grouped into higher value team, the values of which exceeded 0.350 ng/ml. The sharp increase of DISn concentration at station B2 seemed to be attributed to the inputs of the Haihe River Basin, including several rivers (e.g., the Chaobaixinhe River, the Haihe River, the Beipaihe River, the Nanpaiwuhe River, the Maji-}

![Fig. 2](image)

**Fig. 2** The DISn concentrations in the surface and bottom waters of Bohai Bay

aché River, and the Tuhahei River shown in Fig. 1), the river directions of which pointed to station B2. DISn was carried by these rivers to Bohai Bay and finally arrived at the river junction station B2. Therefore, the DISn concentration in the surface water of station B2 was higher than other stations in Bohai Bay. However, the relatively low DISn concentrations appeared at C line and station D1, where the values were lower than 0.250 ng/ml.

Compared to those reported by world coastal regions (Table 1), the average DISn concentration in Bohai Bay was close to those in Kagoshima Bay and inshore water of Fukiagehama (Kiriyama and Kuroda 1991). However, DISn concentration in Bohai Bay was higher than those in the Tejo Estuary, Atlantic Ocean, and inshore waters of Shibukawa and Ajino (Andreae et al. 1983; Nakashima 1979; Smith and Burton 1972). In addition, DISn concentration in inshore water of Japanese, Pacific Ocean, and Caspian Sea were higher than that in Bohai Bay (Hamaguchi et al. 1964; Nagiev et al. 2005; Shimizu and Ogata 1963). These different levels of DISn in different aquatic regions may be caused by several reasons, such as the different determine methods, locations, and pollution levels.

**Vertical distribution**

Data from the surface and bottom waters of Bohai Bay were used to investigate the vertical distribution of DISn. Figure 2 exhibited that the DISn concentrations in the bottom waters ranged from 0.206 to 0.381 ng/ml. The DISn concentrations at stations A2, A4, A8, A10, B2, B3, and D2 were higher in the surface waters than the bottom ones. The highest difference of DISn concentration between the surface and bottom waters was found at station B2. As discussed above, station B2 located at the river junction of the Haihe River Basin received a lot of DISn from several rivers resulting in the high DISn concentration in the surface water. Besides, the vertical hydrodynamic of station B2 was weak resulting in the weak exchange between the surface water and bottom water, thus the DISn concentration in the surface water of station B2 was considerably higher than that in bottom water. However, the DISn concentrations at stations A1, A3, A5, A6, A7, A9,
Table 1  Comparison of DISn concentrations in the sea waters of different aquatic areas

<table>
<thead>
<tr>
<th>Aquatic areas</th>
<th>DISn concentration (ng/ml)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kagoshima Bay</td>
<td>0.45</td>
<td>Kiriyama and Kuroda (1991)</td>
</tr>
<tr>
<td>Fukiagehama inshore water</td>
<td>0.59</td>
<td>Kiriyama and Kuroda (1991)</td>
</tr>
<tr>
<td>Japanese inshore water</td>
<td>1.8</td>
<td>Shimizu and Ogata (1963)</td>
</tr>
<tr>
<td>Shibukawa, Okayama</td>
<td>0.139</td>
<td>Nakashima (1979)</td>
</tr>
<tr>
<td>Ajino, Okayama</td>
<td>0.068</td>
<td>Nakashima (1979)</td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>0.30–1.22</td>
<td>Hamaguchi et al. (1964)</td>
</tr>
<tr>
<td>Caspian Sea</td>
<td>1.55</td>
<td>Nagiev et al. (2005)</td>
</tr>
<tr>
<td>Atlantic Ocean</td>
<td>0.009</td>
<td>Smith and Burton (1972)</td>
</tr>
<tr>
<td>Tejo Estuary</td>
<td>0.003</td>
<td>Andreae et al. (1983)</td>
</tr>
<tr>
<td>Bohai Bay</td>
<td>0.311</td>
<td>This study</td>
</tr>
</tbody>
</table>

A11, B1, B4, C1, C2, and C3 were higher in the bottom waters than surface ones. In addition, the DISn concentration at station D1 was the same in the surface water and bottom one. Generally, the vertical variation of DISn concentrations between the surface and bottom waters did not present a uniform tendency, which was likely attributed to the different location, riverine input, sediment resuspension, atmospheric deposition, and biological activities. Furthermore, although there was not a uniform tendency for vertical variation of DISn, the average DISn concentration in Bohai Bay generally decreased from 0.314 ng/ml in the surface waters to 0.308 ng/ml in the bottom ones.

The relationships of DISn to environmental parameters

Suspended particulate material

Due to the adsorption–desorption process, the DISn concentration was related to the SPM. The SPM of Bohai Bay was in the range of 45.00–124.15 mg/l, with an average of 84.57 mg/l. SPM was generally higher in the bottom layers than that in the surface layers. The desorption of trace metals during estuarine mixing has been found (Li et al. 1984b). Thus, the DISn in Bohai Bay may partly come from desorption of SPM. This was supported by the positive relationship between DISn concentration and SPM, with the correlation coefficient of 0.659 ($p < 0.01$; Fig. 3). This correlation suggested that the DISn concentration increased with the SPM increase. However, the rate of the adsorption reaction was much higher than the rate of desorption (Zhang and Sparks 1990). Therefore, although some tin was desorbed and released into the seawaters from SPM, the SPM was not a large repository for tin to the water column.

The SPM in Bohai Bay mainly originated from sediment resuspension, continental weathering, riverine input, and atmospheric deposition. There was evidence that some tin was mobilized during sediment diagenesis and resuspension processes in the bay. Another part of tin that was weathered from the continents reached the bay locked in particulates, which deposited on the continental margins and were removed from further consideration in the geochemical tin cycle. Besides, most of SPM was carried into Bohai Bay by riverine input and atmospheric deposition. Consequently, the sediment resuspension, continent weathering, riverine input, and atmospheric deposition contributed to tin source in the water column of Bohai Bay.

Salinity

The DISn behavior can be estimated through the function of salinity and tin concentration. Salinity is an important factor influencing aquatic ecosystem and is easily affected by river runoff. Studies on the horizontal and vertical distributions of salinity in Bohai Bay showed differences of 30.0–32.1‰ between the surface and bottom waters.
Seawater entered Bohai Bay from the central Bohai Sea and the Yellow Sea from the east with a counterclockwise gyre along the coast, while the freshwater discharges from the Haihe River, the Jiyunhe River, the Luanhe River, and the Huanghe River were pushed coastwise, which resulted in the gradient of salinity in Bohai Bay. There was a horizontal gradient of salinity across the A line, salinity at western side was higher than that at eastern part.

The circulation pattern, which had important consequences for the dynamic of tin cycling in Bohai Bay, was governed by the mixing of freshwater from rivers with seawater from the central Bohai Sea and the Yellow Sea. The surface salinity distribution was taken as an indicator for the mixing processes. This distribution was dependent on the amount of runoff as well as wind direction. Less freshwater flow would reduce freshwater/seawater mixing areas in an estuary. Among various rivers, as the largest river discharging to the Bohai Sea, the Huanghe River delivered $4.10 \times 10^9$ m$^3$/year freshwater discharges, accounting for 50% of freshwater into the Bohai Sea (Yao and Zhang 2005). Hence, the large inflow of the Huanghe River resulted in the lower salinity of the bay mouth. The Haihe River was an important freshwater source to the western part of Bohai Bay. However, the Haihe River contributes a lesser freshwater discharge to Bohai Bay nowadays, since it was greatly modified by anthropogenic activities. Hence, the salinity near the Haihe Estuary was higher than that near the Huanghe Estuary.
The behavior of DISn varied among different estuaries and bays. DISn behaved conservatively along a salinity gradient of 0.36–22.92‰ in Suwannee Estuary and along a salinity gradient of 0.20–23.87‰ in the Chesapeake Bay (Byrd and Andreae 1986b). However, DISn behaved non-conservatively along a salinity gradient of 0.09–26.30‰ in the Delaware Bay (Byrd and Andreae 1986b). In Bohai Bay, the tin inputs of Bohai Bay may be due to pollutant sources or desorption from suspended particles or biological behaviors. There was no obvious relationship between DISn concentration and salinity in the whole bay (Fig. 3b), so the DISn likely behaved non-conservatively along the salinity gradient in Bohai Bay. However, since the range of salinity was narrow, the DISn behavior in Bohai Bay could not be accurately quantified.

Total organic carbon

The TOC not only can indicate the DISn sources but also can affect the bioavailability of tin. The TOC concentration in Bohai Bay seawaters was higher within 20 km from the coast (4.33 mg/l), followed by that within 20–30 km from the coast (3.84 mg/l), and diminished beyond 30 km from the coast (2.68 mg/l), with a maximum value of 10.40 mg/l at station A1 and minimum value of 0.33 mg/l at station D2. The TOC concentration within the bay was obviously higher than that at the bay mouth. The negatively linear relationship between TOC concentration and DISn concentration was found, with \( r = -0.508 \) (\( p < 0.01 \); Fig. 3), suggesting that they originated from different sources.

Organic matters in seawaters were mainly terrigenous and biogenous. The atomic ratio of C/N could be used to define the general characteristics of organic matter input. In this respect, C/N > 12 was taken as being from a terrigenous input (Muller and Mathesius 1999). Plankton organisms had lower C/N ratios with values between 4 and 7 (Pereira et al. 1996), with phytoplankton having an average ratio of 5–6 (Muller and Mathesius 1999). The average C/N ratio in Bohai Bay was 20, more than 12, confirming that the majority of organic matter in Bohai Bay seawaters came from terrestrial material and the phytoplankton biomass acted as an assistant source. Chl-a concentration and cell abundance of phytoplankton in seawater were commonly used as indicators of phytoplankton biomass and regarded as important parameters to describe ocean ecosystem and environmental characteristics. The horizontal distributions of Chl-a concentration and phytoplankton biomass in Bohai Bay are shown in Figs. 4 and 5, respectively.

From the above figures, it could be found that the Chl-a concentration and phytoplankton biomass were higher in shore than that in the middle area, and especially higher near the Haihe Estuary. Their distributions were similar to the TOC distribution. Consequently, the distributions of TOC and phytoplankton biomass in Bohai Bay were quite opposite of DISn distribution. Thus, the discrepancy between phytoplankton biomass and DISn distribution indicated that phytoplankton biomass was not a key source of tin in Bohai Bay or that the decrease of DISn in the seawaters was due to the phytoplankton uptake.

On the other hand, the bioavailability and toxicity of tin towards organisms was reduced in the presence of humic acid (Pawlik-Skowrońska et al. 1997). The humic acid was a natural complexing agent, which could compete with organisms to combine with DISn. Therefore, the uptake of tin by organisms was reduced and the bioavailability and toxicity of DISn was effectively lessened correspondingly. TOC concentration was used to estimate humic acid concentration. Thus, the more
the humic acid concentration was, the higher the TOC concentration was and the less the bioavailability and toxicity of DISn was.

**The pH**

The pH value of seawater is one of the most important factors influencing the tin bioavailability and toxicity (Campbell and Stokes 1985; Pawlik-Skowrońska et al. 1993; Skowroński et al. 1991). Availability of DISn to the microorganism cells changed with the pH increase and DISn entered the cells more effectively in the alkaline environment. The aquatic medium presents alkaline, which is a common phenomenon during photosynthesis. Besides, the alkaline medium has been considered as an essential condition for the form of the intact cells of algae and cyanobacteria (Shiraiwa et al. 1993). Pawlik-Skowrońska et al. (1997) had reported that inorganic tin exerted toxic effects on the cyanobacterium only at alkaline pH. These viewpoints seemed to be explained by the solubility of inorganic tin in different pH medium. Under neutral and acidic conditions (pH 5–6) inorganic tin existed in aqueous solution mainly as undissolved hydroxides. At pH 7, inorganic tin existed as cationic or neutral chemical species like Sn(OH)$^+$, Sn(OH)$_2^+$, Sn(OH)$_2$, and SnO, which were not available to the microorganism cells or were taken up in very small amounts (Pawlik-Skowrońska et al. 1997). Moreover, tin at pH 7 liquid medium could precipitate, so that it was not involved in the toxicity towards the microorganism populations (Halas and Cooney 1981). Thus, tin lacked inhibiting effects on the growth of microorganisms at pH 7. At high pH, inorganic tin existed as dissolved forms: SnO$_3^{2-}$, SnO$_2^{2-}$, and Sn(OH)$_2^-$ (Pawlik-Skowrońska et al. 1997). These chemical forms of inorganic tin could enter the microorganism cells easily and exert stronger toxic effects. Generally, the tin toxicity increased with the increase of tin concentration, time of exposure, and pH value of the medium. In this respect, the pH values of Bohai Bay were in the range of 8.10–8.28, with an average of 8.17. It was obvious that Bohai Bay seawater was an alkaline medium, which was useful to photosynthesis of microorganisms and in which DISn existed as dissolved forms. So, DISn in Bohai Bay was available to microorganisms and could be taken up effectively by microorganisms, resulting in that tin exerted toxic effects on microorganisms and inhibited the growth of microorganisms at last. Thus, with the pH increase, the availability of tin increased and the toxic effects on phytoplankton enhanced, resulting in the decrease of phytoplankton biomass ultimately. Consequently, since pH could affect the solubility and behavior of tin in aquatic environment, the pH in Bohai Bay influenced the DISn concentration and distribution directly.

**Nutrients**

Both tin and nutrients are considered essential elements for organisms. Thus, there must be close relationships between tin and nutrients. Phosphate, DIN, and silicate concentrations in Bohai Bay seawaters were in the ranges of 4.9–27.4, 137.4–278.2, and 292–656 ng/ml, with averages of 15.0, 186.7, and 461 ng/ml, respectively. There was a lack of relationship between DISn and silicate, but DISn correlated well with phosphate ($r = 0.660$, $p < 0.01$) and DIN ($r = 0.630$, $p < 0.01$; Fig. 3). That was:

\[
\text{DISn (ng/ml)} = 0.005 \text{PO}_4 \text{(ng/ml)} + 0.0011 \text{DIN (ng/ml)} + 0.066 \\
(r = 0.779, n = 40, p < 0.01)
\]

Generally speaking, the Si/P and DIN/P ratios can be used to identify the nutrient-limiting...
factors for the growth of phytoplankton. In this study, the Si/P and DIN/P ratios of seawaters were higher than 16 in Bohai Bay, so it seemed that the phosphate was the limiting factor for phytoplankton growth. This was consistent with the conclusions of Jiang et al. (2005), Yu et al. (2001), and Zhang et al. (2007). So DISn behavior seemed to be more related to phosphate rather than silicate and DIN. Moreover, the significant correlations between DISn and nutrients suggested that tin had been involved in biological cycling.

In conclusion, because the environmental parameters (e.g., SPM, salinity, pH, TOC, nutrients, and Chl-a) had intensive interactions among themselves and these interactions from station to station also were different, the final distribution of DISn in Bohai Bay seawaters was influenced by these environmental parameters together.

Phytoplankton

Being an essential element for phytoplankton, tin is taken up by these organisms probably due to incorporation through a nutrient pathway. Thus, tin can be removed by biological uptake in seawaters. Diatom and dinoflagellate were the major components of the phytoplankton community in Bohai Bay. The biomasses of diatom and dinoflagellate were 0.67 × 10^2–8.70 × 10^4 and 0–2.6 × 10^2 cells/l, accounting for 92.95% and 7.05% of total phytoplankton, respectively.

According to our investigation, Chaetoceros castracanei karsten (30.2% of total count), Melosira sulcata (Ehrenberg) Cleve (22.0%), Nitzschia pungens Grunow (10.4%), Noctiluca scintillans Swerzy (7.0%), Ditylum brightwellii (West) Grunow (6.4%), Chaetoceros curvisetus Cleve (5.1%), Coscinodiscus sp. (3.5%), and Coscinodiscus radiatus Ehrenberg (2.0%) were dominant species in April 2008. So, in order to realize the biological behavior of DISn, the relationships between DISn and phytoplankton species were analyzed (Table 2).

Comparison of DISn concentration with phytoplankton biomass in Bohai Bay suggested that DISn negatively correlated with diatom (r = −0.356, p < 0.05), dinoflagellate (r = −0.486, p < 0.01), and phytoplankton (r = −0.356, p < 0.05) at most stations (Table 2). Although the specific biochemical role of tin was not well understood, it was recognized that tin has been involved in the biological cycle. Accumulation of tin by primary producers, such as aquatic angiosperm plants, macroalgae, and microalgae had been reported (Falke and Weber 1993; Mushrifah and Peterson 1991; Rossbach 1993; Wright and Weber 1991). Wong et al. (1984) reported that at tin concentration of 46 ng/ml, microalgae could accumulate tin (at pH 8) to a concentration factor 9.1 × 10^4.

Aquatic microalgae at the base of the food web accumulated tin compounds, transferred them to higher trophic levels, and could also contribute to tin transformations by alkylation and dealkylation (Cooney 1988). If tin was actively consumed by

<table>
<thead>
<tr>
<th>Category</th>
<th>DISn</th>
<th>Proportion (%)</th>
<th>Samples number (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corethron hystrix Hensen</td>
<td>−0.372^a</td>
<td>0.14</td>
<td>17</td>
</tr>
<tr>
<td>Noctiluca scintillans Swerzy</td>
<td>−0.577^b</td>
<td>7.0</td>
<td>11</td>
</tr>
<tr>
<td>Chaetoceros spp.</td>
<td>−0.409^a</td>
<td>1.2</td>
<td>12</td>
</tr>
<tr>
<td>Nitzschia pungens Grunow</td>
<td>−0.314</td>
<td>10.4</td>
<td>17</td>
</tr>
<tr>
<td>Melosira sulcata (Ehrenberg) Cleve</td>
<td>−0.367</td>
<td>22.0</td>
<td>20</td>
</tr>
<tr>
<td>Chaetoceros laciniosus Schutt</td>
<td>−0.476^a</td>
<td>2.4</td>
<td>10</td>
</tr>
<tr>
<td>Chaetoceros castracanei karsten</td>
<td>−0.389^a</td>
<td>30.2</td>
<td>17</td>
</tr>
<tr>
<td>Diatoms</td>
<td>−0.356^a</td>
<td>92.95</td>
<td>14</td>
</tr>
<tr>
<td>Dinoflagellates</td>
<td>−0.486^b</td>
<td>7.05</td>
<td>12</td>
</tr>
<tr>
<td>Total of phytoplankton</td>
<td>−0.356^a</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

^aCorrelation is significant at the 0.05 level (two-tailed)
^bCorrelation is significant at the 0.01 level (two-tailed)
organisms, biological uptake may be one of the possible removal mechanisms of tin. However, the relationship between the DISn concentration and phytoplankton biomass at station B2 did not accord with the negative correlation. Although the higher phytoplankton biomass at station B2 could take up more DISn, the riverine input of DISn from the Haihe River Basin to the river junction station B2 was large. It seemed that the riverine input of DISn to the surface water of station B2 could compensate for the loss of DISn by biological uptake.

In particular, the estimation of the uptake of tin by phytoplankton was related to phytoplankton species. In this respect, DISn especially correlated well with Corethron hystrix Hensen ($r = -0.372$, $p < 0.05$), N. scintillans Swerzy ($r = -0.577$, $p < 0.01$), Chaetoceros spp. ($r = -0.409$, $p < 0.05$), Chaetoceros lacinius Schutt ($r = -0.476$, $p < 0.05$), and C. castracanei karsten ($r = -0.389$, $p < 0.05$). It seemed that DISn had more significant relationships with these phytoplankton species than others in Bohai Bay. In addition, because phytoplankton was such a rich source of tin in the water column, although it was not a key source, its dynamics could have a profound effect on the DISn distribution in Bohai Bay. Tin may be also released from the decomposition of phytoplankton and fairly stable in the surface water.

The sources of DISn

The relationships of DISn to heavy metals

Six heavy metals, Zn, Cu, Pb, Cd, Cr, and Hg, were determined. Their concentration ranges were 14.7–25.1, 2.18–3.12, 1.25–2.02, 0.107–0.184, 2.28–3.35, and 0.035–0.068 ng/ml, respectively. The higher values of heavy metals were obtained at stations A1, A2, and B1, adjacent to the Haihe Estuary and the coast. It suggested that these heavy metals in Bohai Bay seawaters came mainly from the continental input and riverine input.

To investigate the relationships between DISn and heavy metals, PCA was employed to simplify the dataset (Fig. 6). The analysis showed that there were three PCs, which described 75.2% of the total variances. It may indicate the different origins or controlling factors of DISn and heavy metals in Bohai Bay seawaters.

The first group (PC1) was highly correlative element, represented by Hg and Cr. The average concentrations of Hg and Cr were 0.050 and 2.89 ng/ml. The Hg concentrations at stations A1, A2, A3, and B1 were higher than the value of the grade-one seawater quality standard of China (SWQSC-1, 0.05 ng/ml), while the Cr concentration at each station was less than the value of SWQSC-1 (50 ng/ml) (SBQTS 1998b). It implied

Fig. 6 Plot of the factor loadings of the variables on three PCs
that the sources of Hg and Cr may include Hg polluted rivers as well as the continental weathering.

The second group (PC2) also had great correlation, represented by Sn, Zn, and Pb. It suggested that they had the same source and the factors controlling DISn distribution also worked on Zn and Pb. The average concentrations of Zn and Pb were 20.2 and 1.63 ng/ml, which were slightly higher than the values of SWQSC-1 (20 and 1 ng/ml, respectively) (SBQTS1998b). It indicated that these elements mainly originated from the riverine input with terrestrial discharge of wastewater from industrial and agricultural activities, accounting for Zn, and atmospheric transport and deposition, exemplified by Pb.

The last group (PC3) was Cu and Cd. The average concentrations of Cu and Cd were 2.69 and 0.160 ng/ml, which were less than the values of SWQSC-1 (5 and 1 ng/ml, respectively). There was no station with concentrations higher than the values of SWQSC-1 (SBQTS1998b). It implied that they mainly came from the natural input.

Tin was widely used in industrial processes and had the potential for environmental pollution. The perturbation of the oceanic cycle of tin by anthropogenic inputs should be similar to that of lead (Schaule and Patterson 1981, 1983). The transport of tin into Bohai Bay could be either by lateral advection of tin originating from rivers or diffusing out of shelf sediments or by atmospheric transport. Nevertheless, its sediments were not a large repository for tin to the water column. Thus, atmospheric deposition and riverine input were considered as the major sources of tin in Bohai Bay.

Riverine input

Rivers were mainly carriers of anthropogenic as well as natural nutrients and metals, increasing the human impacts on the whole aquatic system of Bohai Bay. The riverine input was the main source of phosphate, DIN, and silicate in Bohai Bay (Zhang et al. 2004). DISn corrected well with phosphate and DIN in the whole bay, which indicated that the riverine input was one of major sources of DISn in Bohai Bay.

The main rivers that discharge directly into Bohai Bay include the Haihe River, the Jiyunhe River, the Zhangweixinhe River, the Dehuixinhe River, the Tuhaihe River, and the Majiahe River. The riverine input to Bohai Bay was estimated at ca. 6.5 × 10⁹ m³/year of freshwater, with an amount of suspended matter of 6.0 × 10⁶ t/year (Lei et al. 2007; Li et al. 1995). The river fluxes of tin by the Haihe River Basin were not monitored due to logistic problem. However, although tin input was hard to quantify, it was necessary to throw some light on the amount of tin discharged from rivers to Bohai Bay, through modeling.

The flux of DISn from a river into Bohai Bay is simply $F_{ED} = V_{ED} \cdot C_{ED}$, where $V_{ED}$ is the river discharge (cubic meters per year) and $C_{ED}$ is the estuary concentration of tin (nanograms per milliliter) (Andreae et al. 1983; Cutter and Cutter 2004; Yao et al. 2006).

Because of non-conservative behavior of tin in the whole bay, the tin concentrations of the estuaries could not be acquired through function of tin and salinity. Taking into consideration the water discharge and geographical conditions, the average tin concentration (0.311 ng/ml) in Bohai Bay was assumed to be the average value of major rivers. The riverine flux of DISn to Bohai Bay was about 2 × 10⁶ g/year.

Atmospheric deposition

Tin is one of the ten most highly enriched elements in atmospheric particulates (Rahn 1976). Soil dust and forest fires are the main natural sources for emission of tin into the atmosphere (Byrd and Andreae 1982). However, metal smelting and combustion processes are the major anthropogenic sources for emission of tin into the atmosphere (Bjerregaard and Andersen 2007). Tin emitted this way is generally bound in small particles with a potential for atmospheric long-range transport and contamination. In view of average atmospheric concentration of tin near 1 ng/m³ in the northern hemisphere and the normally much higher values in urban atmosphere, a higher input might have been expected on the basis of atmospheric deposition alone (Byrd and Andreae 1982; Rahn 1976). In conclusion, the natural inputs of tin into the atmosphere except biomethylation were relatively unimportant when compared to the anthropogenic flux.
In the study, the surface water concentrations of tin increased from a value of 0.261 ng/ml in shore to 0.503 ng/ml beyond 31 km from the coast in Bohai Bay. Besides, tin concentration in Bohai Bay generally showed a slight decrease with the increasing depth. These patterns provided evidence that the transport of some tin from continents to Bohai Bay was via the atmospheric long-range transport.

The atmospheric deposition onto the ocean surface occurs by both dry and wet deposition. Dry deposition can be defined as the process by which chemicals are transferred from the atmosphere to the ocean in gaseous form of solid phases. Wet deposition is defined as chemical transfer by rainfall. Because the deposition velocity is influenced by the grain size, wind speed, relative humidity, and surface physico-chemical characteristics of atmospheric particle and so on, both forms of deposition are difficult to measure directly. Indirect approaches are often used to estimate air–sea fluxes. In this study, dry deposition flux \( F_p \), wet deposition flux \( F_r \), and the total deposition flux \( F_t \) of Sn in Bohai Bay were estimated according to the following equations: 

\[
F_p = V_p \times C_p, \quad F_r = V_r \times C_r, \quad F_t = F_p + F_r.
\]

\( V_p \) and \( V_r \) were the average atmospheric particulate matter and rainfall discharges to Bohai Bay, with \( 1.16 \times 10^{11} \) g/year and \( 1.32 \times 10^9 \) m\(^3\)/year, respectively (Dai et al. 1987; Li et al. 1984a). \( C_p \) and \( C_r \) were the tin concentrations in atmospheric particulate matter and rainfall, with 3.76 μg/g and 0.311 μg/l, respectively, assumed by the tin concentrations in sediments and seawaters.

Dry deposition flux and wet deposition flux of tin to Bohai Bay were about 4.36 × 10\(^5\) and 4.11 × 10\(^5\) g/year, respectively. Thus, the total deposition flux throughout the year in this area was 8.47 × 10\(^5\) g/year, which was so abundant that almost corresponded with the riverine flux.

Conclusions

The DISn concentration in Bohai Bay seawaters displayed the higher concentrations in the central bay waters and the lower concentrations in shallow coastal waters, which were indicative of atmospheric transport and deposition of tin to the surface waters. Besides, the DISn concentration also displayed higher values near the Haihe Estuary, which inferred that the riverine input was another main source of tin. Moreover, chlorophyll \( a \) concentration and phytoplankton biomass had quite opposite distributions with DISn, suggesting that phytoplankton was not a key source of tin to Bohai Bay. Thus, because atmospheric deposition and riverine input were such rich sources of DISn in the water column, their dynamics had a profound effect on the DISn distribution in Bohai Bay. The relationships between DISn and nutrients suggested that tin had been involved in biological cycling. Besides, the DISn concentration negatively correlated with phytoplankton biomass at most stations supporting the idea of being taken up by phytoplankton.

Overall, the behaviors and sources of DISn in Bohai Bay have been introduced. These provided information and evidence for forecasting the future behavior of DISn in Bohai Bay. Its sediments were not a large repository for tin to the water column, leaving systems that were dominated by atmospheric deposition and riverine inputs. Although these rivers were dominated by tin, future studies should evaluate the potential effects of this input on estuarine systems that quickly responded to change in tin flux. In addition, the quantifiable effects of phytoplankton on DISn also should be studied further.

Acknowledgements This paper was supported by Fund for Creative Research Groups by NSFC (no. 40821004), the National Key Project for Basic Research of China (no. 2007CB407305, no. 2011CB403602), and the Knowledge Innovation Program of the Chinese Academy of Sciences (KZCXZ-YW-Q07–02).

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