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...
et al. 2003; Byrd and Andreae 1982, 1986b; Tao et al. 1999). 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 seawater; (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. To achieve these objectives, DISn distribution, the coupling relationships between DISn and the seawater characteristics (SPM, salinity, pH, and TOC), heavy metals, nutrients, and phytoplankton of Bohai Bay and sources were studied.

**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 $1.6 \times 10^4$ km$^2$, 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