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Impacts of metal contamination and eutrophication on dinoflagellate cyst assemblages along the Guangdong coast of southern China

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A B S T R A C T

Fifty-one surface sediment samples were collected from eleven sea areas along the Guangdong coast in southern China. Biogenic elements, metals and dinoflagellate cysts were analyzed. Twenty-one cyst taxa in 12 genera were identified. The cyst concentrations ranged between 14 and 250 cysts/g, with an average of 69 cysts/g. The low cyst production was caused by coarse sediments, high sedimentation rates, and high anthropogenic disturbances. Biogenic elements were comparable with those reported. However, the metal concentrations were far lower than the sediment quality guidelines. Both biogenic elements and metals were higher in the Mid Coast and lower in the Western Coast. Eutrophication slightly enhanced the productivity of autotrophic dinocysts, and cysts of *Scrippsiella* indicated eutrophication. Cd had inhibitory effects on cyst production. *Alexandrium* and *Diplopsalis* cysts were sensitive to metal contamination; however, *Gyrodinium*, *Pheopolykrikos*, and *Lingulodinium* cysts had high resistance to metal contamination.

1. Introduction

Dinoflagellates constitute one of the key components of the marine phytoplankton community, and they play an important role in marine food webs. Dinoflagellates display a wide diversity of trophic strategies, including autotrophy, heterotrophy and mixotrophy. Approximately 13–16% of living dinoflagellates produce resting cysts as a part of their life history (Head, 1996). Dinoflagellate cysts (dinocysts) form because of sexual fusion of gametes, which are generated in response to certain conditions, such as low temperature, disturbance, metal contamination and nutrient depletion (Head, 1996; Tang and Gobler, 2012). Dinocysts consist of very resistant organic materials and are generally well preserved in sediments. However, temporary cysts are sometimes formed when motile vegetative cells are exposed to unfavorable conditions. Temporary cysts are not the product of sexual reproduction, and they can quickly re-establish the vegetative cells when conditions become favorable (Anderson et al., 2004). Temporary cysts are not easy to preserve in the sediment. Generally, a dinocyst refers to the dinoflagellate resting cyst. Studies on dinocyst assemblages have highlighted the importance of cysts as a signal for pollution related to human activities and the development of eutrophication (Sætre et al., 1997; Matsuoka, 1999; Pospelova et al., 2005, 2008; Pospelova and Kim, 2010; Liu et al., 2012).

Urbanization and anthropogenic discharge result in eutrophication in many estuarine and coastal waters (Zimmerman and Canuel, 2000). The accumulation of total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and biogenic silica (BSi) in sediments provides information about the deposition and preservation of these materials, which are regarded as signals of eutrophication and diatom productivity (Wang et al., 2015). The relationship between dinocysts and nutrient enrichment has been studied in worldwide sea areas (Matsuoka, 1999; Pospelova et al., 2005, 2008; Dale et al., 1999; Pospelova and Kim, 2010; Liu et al., 2012). However, different signals were reported for eutrophication in different areas. The proportion of cysts from heterotrophic dinoflagellates is generally considered a signal of cultural eutrophication in shallow well-mixed estuarine and coastal systems (Matsuoka, 1999; Pospelova et al., 2005; Pospelova and Kim, 2010). An increase in one autotrophic dinoflagellate, such as *Lingulodinium machaerophorum* (cyst of *Lingulodinium polyedrum*) (Dale et al., 1999) and *Scrippsiella trochoidea* (Wang et al., 2011a), may be a response to cultural eutrophication.

Heavy metals are among the most important pollutants from anthropogenic activities, and they have caused environmental deterioration in many sea areas (Zimmerman and Canuel, 2000; Pan and Wang, 2012; Popadic et al., 2013). When metals enter the marine environment, most will settle into the sediments. Sediments act as scavengers for metals and provide excellent information about the anthropogenic impacts (Guevara et al., 2005). Dinocysts can be an important strategy for surviving under metal stress conditions (Okamoto et al., 1999). However, the relationship between dinocysts

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and metal pollution remains poorly documented (Pospelova et al., 2005; Liu et al., 2012; Aydin et al., 2015).

Guangdong province is one of the most developed areas in China. This southern province has 3368 km of coastline along the South China Sea. The 2114-km long Pearl River, southern China's largest river, flows through the center of this region. Guangdong Province has experienced rapid industrialization and urbanization since the end of 1970s and it became one of the greatest economically developed regions and densely populated areas in China. The gross domestic product (GDP) of the Guangdong Province has ranked first among thirty-one provinces in China since 1989. Guangdong coast is an important maricultural area, which includes oyster, mussel, sea-ear, prawn culture, and caged-fish farms (Wang et al., 2008). Mariculture was introduced during the mid-1980s; it increased dramatically during the late 1990s, and now covers 208,000 hm^2 water area. Urbanization, industrialization, agriculture and mariculture result in eutrophication and pollution in Guangdong coastal zones. Previous studies have shown that these sea areas are severely contaminated by metals (Ip et al., 2007; Gao et al., 2010; Wang et al., 2013), particularly the Pearl River Estuary (PRE) and nearby embayment (Ip et al., 2007). High concentrations of metals were also found in the aquatic organisms in the PRE (Ip et al., 2005). Dinocyst assemblages were documented in sediments from some Guangdong sea areas, indicating high diversity and a wide distribution of potential harmful species (Wang et al., 2011a). However, none of these studies evaluated the impacts of metal contamination on dinocyst assemblages, and the cyst distribution in the Western Coast of Guangdong province has not been documented.

In this study, dinocysts; five metals (Cd, Cu, Hg, Pb, and Zn); and biogenic elements, including TOC, organic matter (OM), TN, TP, and BSi, were measured in the surface sediments from eleven sea areas of Guangdong coast. Correlation analysis (CA) and redundancy analysis (RDA) were applied to understand the response of dinocyst assemblages to environmental parameters as well as to differentiate the spatial distribution of dinocysts. The purposes of the study are as follows: (1) to evaluate the spatial variation in dinocyst assemblages in the Guangdong coast and (2) to understand dinocyst assemblages in relation to metal contamination and eutrophication.

2. Materials and methods

2.1. Study areas

The Guangdong coast is located at the northern part of the South China Sea. This region has a subtropical monsoon climate with massive rainfall, long summers and warm winters. The annual average water temperature ranges between 22 °C and 25 °C; the lowest is 12–16 °C and highest is 32–35 °C. The annual precipitation is between 1300 mm and 2500 mm. The Guangdong coast includes three regions according to their location, the Eastern Coast, Mid Coast and Western Coast. In this study, we collected sediment samples from fifty-one stations in eleven sea areas (Fig. 1); four belong to the Eastern Coast, three to the Mid Coast, and the other four to the Western Coast. The location and basic information of these sea areas are listed in Table 1.

The Eastern Coast is an important aquacultural area, within which Zhelin Bay is one of the most intensively managed sea areas in China, and more than half of the water areas are occupied by mariculture (Wang et al., 2008). Industries in the eastern area include petrochemical, electronic, ceramic, toy, and food industries. Phytoplankton communities mostly house small diatoms; however, blooms of *Phaeocystis globosa* have frequently occurred since 1997 (Qi et al., 2004).

The Mid Coast is surrounded by the most economically developed and populated regions, the Pearl River Delta. Nearby famous major cities include Hong Kong, Guangzhou, Shenzhen, and Macao. Three of the top ten largest ports in the world, the Guangzhou Port, Shenzhen Port, and Hong Kong Port, are in this region. Furthermore, one of the study areas, Daya Bay is the location of two nuclear power stations. Rapid economic growth and intense human activities have increased pressure on the environment, and algal blooms frequently occur in the PRE and surrounding sea areas (Qi et al., 2004).

The Western Coast is the main agricultural area in southern China, which is the largest producing area of litchi, banana, longan, and vegetables in China as well as an important area for mariculture and fishing. Furthermore, Maoming city, one of the largest petrochemical manufacturing bases in China, is also in this region.

2.2. Sediment collection

Surface sediments were collected by a Peterson grab from 51 stations between October and November 2007 in the eleven sea areas of the Guangdong coast (Fig. 1). Triplicate sediments were collected from each station, and the top 2-cm surface sediments were collected with a polyethylene spatula. The three replicate sediment samples were well mixed and separated into two subsamples. One subsample was stored at 4 °C in dark for dinocyst observation, and the other was stored at − 20 °C for analyses of biogenic elements and metals.

2.3. Analyses of the grain size

A fraction of the fresh sample was separated for grain size analysis by laser diffraction using a Mastersizer Micro (Malvern Instruments Corporate, UK). The four fractions with particles sizes > 2000 μm, 63–2000 μm, 2–63 μm, and < 2 μm represent gravel, sand, silt, and clay, respectively.

2.4. Analyses of biogenic elements and metals

Sediments for Hg analysis were freeze-dried, and others were dried at 40 °C until a constant weight was reached. Dry sediments were gently ground with agate pestle and mortar, sieved with 150-μm mesh sieve for homogenization and stored in plastic sealing-off bags.

The TOC and TN were measured by a Perkin-Elmer 2400 Series II CHNS/O Analyzer (Perkin Elmer Inc., USA). The OM was determined through Loss on Ignition (LOI) (Heiri et al., 2001). Dry ground sediments were incinerated at 550 °C for 5 h in a muffle furnace SG-XL1200, and the loss on ignition is the content of the OM. Dried powder sediments for BSi determination were weighed into a 50-mL polypropylene centrifuge tube. Then, 1 mol/L HCl and 10% H_2O_2 were added to remove the carbonate and organics followed by centrifugation and water washes. The tube precipitate was dried at 50 °C until a constant weight was reached, and 10 mL of 0.5 mol/L Na_2CO_3 solution was added. The tube was capped and well mixed; then, it was digested at 90 °C for 5 h. The BSi in the extracts was measured by the molybdate blue spectrophotometric method (Mortlock and Froelich, 1989).

The US EPA Method 200.2 protocols were adapted to analyse Cd, Cu, Pb, Zn and TP (USEPA, 1994). Precisely 0.5 g of dried and homogenized sediments was weighed; transferred to a 50-mL conical flask digestion vessel, in 2.8 mL (1:1) HNO_3 and 7 mL (1:4) HCl; covered with a watch glass and left undisturbed for 12 h. The vessel was then placed on a graphitic panel heater at 95 °C and refluxed for 80 min and allowed to cool. The extract was transferred into a 25-mL volumetric flask, diluted to 25 mL with ultrapure water and mixed thoroughly and kept undisturbed for 24 h. The sample extract was then analyzed for metals by an ICP/AES instrument (SPECTRO Spectro Ciros CCD inductively coupled plasma atomic emission spectrometry, Spectro Analytical Instruments, Germany). Hg was determined by combustion on a Direct Mercury Analyzer (Lumex Zeeman mercury RA-915 + Analyzer, Lumex-marketing JSC, Russia).

The QA/QC was assessed by the analyses of blank reagents and ten replicates of the certified reference material (Offshore Marine Sediment, GBW 07314, China). All reagents used in the analyses were ultrapure. The analytical results agree with the certified values for all studied elements. The analytical precision was controlled within 5% for