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Characteristics of trace metals and phosphorus in seawaters offshore the Yangtze River

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This study presents the spatial distribution of total dissolved Cu, Zn, Co, and V during an autumn survey in the East China Sea (ECS). Dissolved Fe and its organic complexation were also investigated. The present study aimed to evaluate the relationship between Cu, Zn, Co, V, D-Fe and its organic ligands and total dissolved phosphate (TDP) in the coastal waters of the ECS. A correlation analysis shows that Cu, Zn and D-Fe were nutrient-like metals, whereas Co and V were non-nutrient-like metals. A multivariate statistical analysis showed that TDP was associated with D-Fe, Cu, Zn and Co, but was not associated with V. Furthermore, TDP was observed to be positively related with D-Fe, while negatively with Fe′, which indicated that the limitation of TDP decreased the uptake of Fe′. This paper improves our understanding of the association among trace metals, TDP and phytoplankton biomass in the ECS.

1. Introduction

Macro-nutrients, such as phosphate, nitrate and silicate, and trace metals, such as copper (Cu), zinc (Zn), cobalt (Co), and iron (Fe), are essential for marine ecosystems. The Redfield ratio demonstrated that to maintain a balance of the marine ecosystem, the ratio of N and P is 16:1 (Redfield, 1958). If the ratio is larger than this value, P limitation occurs and, as a result, the balance of the marine ecosystem is destroyed, which has been previously observed at many locations (Scavia et al., 2003; Smith, 1984; Zhang et al., 2004). However, the limitation of trace metals on the growth of marine phytoplankton was also observed in the global open ocean (Brand et al., 1983; Anderson et al., 1978; Sunda, 1989).

Phytoplankton in oceans may be limited by nutrients, both in open oceans and in coastal waters, which influences the growth of phytoplankton as well as the whole ecosystem. Dissolved inorganic phosphate (DIP) may be a limitation factor in open ocean, for example, in the western North Atlantic Ocean the concentration of DIP were only at 0.2–1.0 nmol/L, which is too low to support the growth of primary production (Wu et al., 2000). In coastal ecosystems, phytoplankton may be limited by both nitrogen (Shark Bay; Smith, 1984) and phosphorus (in most large rivers; Turner et al., 2003). In the Mississippi River and the Gulf of Mexico, phosphorus may be limited under high river water flow conditions and nitrogen is mostly limiting of blooms in summer (Rabalais et al., 2002; Scavia et al., 2003). Along with industrial activities and fertilizer applications in agriculture, nitrate loading has increased, which exceeds the uptake by phytoplankton (Turner et al., 2003). As a result, a high N:P ratio has been observed. Particular attention has been focused on this phenomenon, especially in Chinese coastal waters. In most of the large estuaries in China, high N/P ratios and a potential phosphorus limitation have been observed, such as in the Yangtze River estuary (Zhang et al., 2007; Li et al., 2009), the Yellow River estuary (Turner et al., 1990), and the Pearl River estuary (Harrison et al., 1990; Yin et al., 2004).

Furthermore, the influence of trace metals on the marine system has also been observed. Some studies have reported that low-dissolved Zn and Co concentrations in the open ocean could limit phytoplankton growth and carbon dioxide acquisition (Saito et al., 2004; Anderson et al., 1978; Sunda and Huntsman, 2005). However, high concentrations of Zn^{2+}, Cu^{2+} and vanadium (V) are toxic to marine phytoplankton (Sunda and Huntsman, 1998). Therefore, the distribution and chemical speciation of these metals controls and is being controlled by the growth and species of phytoplankton in oceans (Sunda and Huntsman, 1992). Certain links between trace metals and the phytoplankton community in oceans (Sunda, 1989; Sunda and Huntsman, 1992) have been observed. Trace metals, such as Fe, Cu, Zn, Co and V, have been demonstrated to be essential for the growth of marine phytoplankton. Most of these trace metals play an important role in algal physiology (Sunda, 1989). For example, Fe is present in cytochromes (Mehta et al., 2005), chlorophyll (Römheld and Marschner, 1991) and iron-sulfur proteins (Beinert, 2000); Zn is present in the replication and transcription of nucleic acids (Coleman, 1992); Cu is present in plastocyanin and cytochrome (Merchant and Bogorad, 1986); and Co is present in vitamin B12 (Rickes et al., 1948). Phytoplankton, in turn, could fix trace metals and control their distribution, which might result in the correlation between macro-nutrients, such as nitrogen and phosphorus, and trace metals (Mills et al., 2004; Bruland, 1980; Wu et al.,

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2000). Studies have shown that iron (Fe) controls primary productivity in the major regions of high nutrient low chlorophyll (HNLC), such as the north Pacific Ocean (Kondo et al., 2012; Martin and Fitzwater, 1988), the Southern Ocean (Tréguer and Jacques, 1993) and the equatorial Pacific Ocean (Rue and Bruland, 1997; Coale et al., 1996).

According to these research reports, the relationship between trace metals and nutrients (phosphate, nitrate or silicate) was found to be important for marine ecosystems (de Baar et al., 1994), which might provide evidence for the biological control of trace metals (Sunda and Huntsman, 1992). Previous studies regarding open oceans demonstrated that the vertical distribution of many trace metals was similar to the macro-nutrients, and a correlation between metals and nutrients was observed. For example, Zn was correlated with silicate, while Cu and Cd were also correlated with phosphate in the North Atlantic (Bruland, 1980) and other areas (de Baar et al., 1994). In these studies, the Zn:Si atom ratio was 5.4×10^{-5} and the Cd:P:N atom ratio was 3.47×10^{-4}:15.2:1. Although trace metal concentrations in coastal waters were orders of magnitude higher than those in open oceans, like major nutrients, the same correlations with trace metals and nutrients were also observed in coastal waters. For example, Fe was strongly correlated with nitrate and silicate (Fe:N:Si = 1:13.7:4.7) in the Gulf of Alaska (Martin et al., 1989), as well as the Peru upwelling region, Co was correlated with nitrate and phosphate (Saito et al., 2004). However, studies regarding to both trace metals and nutrients in marginal seas are scarce, especially in the area with high primary productivities, for example the East China Sea (ECS).

In addition to co-absorption with macro-nutrients, the distribution of trace metals were influenced by the movement of currents. Current transport takes particulate and dissolved trace metals into other regions, furthermore, the movement of water masses might induce to very different distributions of trace metals and macro-nutrients (Loscher et al., 1997). In ocean circulation, the concentrations of dissolved trace metals, for example, Cd, Zn, Cu, Ni and macro-nutrients, were increased with increasing age from the deep Atlantic to deep Pacific waters, which indicated transport of the current (Bruland, 1980; de Baar et al., 1994). In the Polar Frontal region, the Antarctic Circumpolar Current input dissolved Fe, which was the main source of Fe this area (Loscher et al., 1997). In the upwelling region of central California Current System, D-Fe and macronutrients from deep waters was upwelled, which increased the concentrations of trace metals and macro-nutrient, as a result diatom blooms occurred in this area (Biller et al., 2013). For Chinese marginal seas, trace metals, such as Al (Ren et al., 2011), Cu (Abe et al., 2003), D-Fe (Su et al., 2015), and Pb (Li et al., 2014), were influenced by the Kuroshio Current, Taiwan Warm Current, coastal currents and fresh waters.

River inputs may be another important source of macro-nutrients and trace metals. Higher trace metal concentrations were observed in the estuary and coastal areas than those in open oceans. Dissolved iron values ranged from 2.6 to 128 nmol/L in the East China Sea (Su et al., 2015), which was much higher than those of open ocean, for example, in the Central North Pacific area, the total dissolved Fe were only ranged from 0.09 to 0.77 nmol/L (Rue and Bruland, 1995). Dissolved lead values ranged from 0.13 to 1.86 nmol/L in the East China Sea (Li et al., 2014), however, in the Indian Ocean concentration of lead was only from 0.10 to 0.14 nmol/L (Danielsson, 1980). At the same time, major nutrients in coastal waters were also higher than those in the open oceans (de Baar et al., 1994; Rabalais et al., 2002). Eutrophication and harmful algal blooms have become an overwhelming phenomenon in the coastal environment from large estuaries (Li et al., 2009; Zhang et al., 2007). In phosphorus-limited Chinese coastal waters, high trace metal and high major nutrient concentrations may be observed and result in different correlations from those in open oceans, especially in the East China Sea (ECS).

The ECS is one of the largest marginal seas in the world which included very complex water masses. The Yangtze River, the third largest river in the world, entered into the ECS. The main terrestrial inputs of nitrogen, phosphorus and trace metals, such as Fe, Pb and Zn to the ECS were

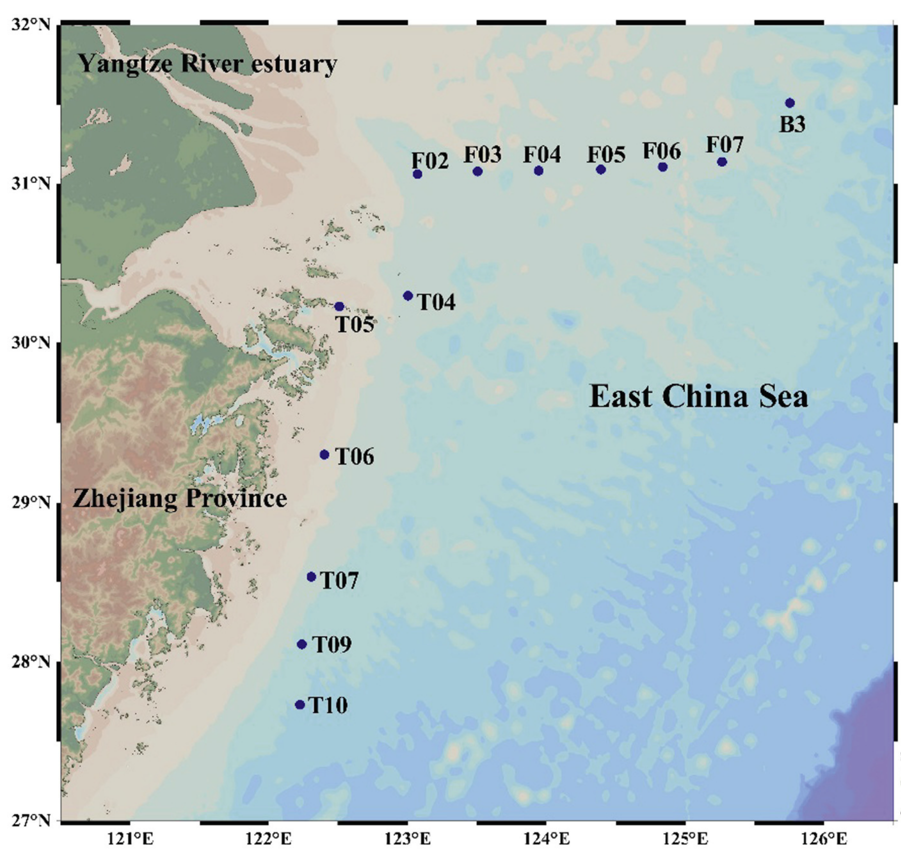

Fig. 1. Locations of seawater sampling points for the autumn cruise in the ECS.

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