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Stable isotope geochemical characteristics of dissolved inorganic carbon in the Jiulong River Estuary, Fujian Province, China

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Abstract The isotopic composition of dissolved inorganic carbon (DIC) in estuarine environments has been studied for its significant role in determining the isotopic composition of inorganic/organic matter and its applications to the study of various natural processes. In this paper, based on the stable isotope geochemical characteristics of dissolved inorganic carbon in the Jiulong River Estuary, the following conclusions are drawn: (1) $\delta^{13}C_{DIC}$ values are mainly controlled by the mixing ratio of fresh water and sea water; (2) $\delta^{13}C_{phytoplankton}$ values are linearly related to the $\delta^{13}C_{DIC}$ values; (3) $\delta^{13}C_{POM}$ values for the Jiulong River Estuary are affected by anthropogenic pollution significantly; and (4) the comprehensive analysis of $\delta^{13}C_{phytoplankton}$, $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ shows that along with increasing salinity, the proportion of POM derived from the degradation of phytoplanktons gradually increases.

Key words Jiulong River Estuary; stable carbon isotope; dissolved inorganic carbon (DIC)

1 Introduction

Dissolved inorganic carbon (DIC) in natural waters consists of CO_2 (aq), H_2CO_3, HCO_3^-, and CO_3^{2-}. The isotopic composition of DIC in natural waters is controlled by the sources and sinks of carbon, and it results from isotope fractionation in solid, dissolved and gaseous phases and oxidation states. The major contributing sources of DIC in natural waters are atmospheric CO_2, which is derived from the decay of organic matter and dissolution of carbonates. In estuarine waters, more sources of DIC appear, such as fresh and marine inputs, as well as biogenic carbon from oxidation of organic matter, atmospheric carbon from dissolution of carbonate minerals, and anthropogenic carbon from municipal wastes or sewage.

The processes involved in the removal of DIC include photosynthesis, carbonate precipitation, and air-water exchange (Hélie et al., 2002; Mukherjee and Ray, 2013). Knowledge of the conservative or non-conservative mixing behavior of $\delta^{13}C$ values of DIC ($\delta^{13}C_{DIC}$) in estuaries is useful for understanding the cycling of carbon and provides information about the processes that govern the distribution of $^{13}C/^{12}C$ ratios in estuarine environments (Peterson et al., 1994; Hellings et al., 2001; Barth et al., 2003; Ahad et al., 2008; Miyajima et al., 2009; Meersche1 et al., 2011).

Estuaries are highly dynamic and complex ecosystems, which play a key role in our understanding of ecosystem functioning as a whole, and its connectivity with both terrestrial and coastal marine habitats. The Jiulong River, located in the subtropical zone, is the second largest river system of Fujian Province, China. It produces a large amount of terrigenous materials to be transported into the estuary and Taiwan Strait. The mean annual runoff of the Jiulong River is 11.7×10^9 m^3 and the yearly sediment load is about 2.5×10^6 t. Additionally, the Jiulong River Estuary has experienced rapid industrialization and urbanization within the second half of the last century and is now the largest economically developed and densely populated region of Fujian Province. So, the Jiulong River Estuary and Taiwan Strait have become the ideal research region for studying interaction between land and sea.

In this paper, we attempt to study the stable isotope geochemical characteristics of and factors affecting $\delta^{13}C_{DIC}$ in the Jiulong River Estuary. The results will contribute to a further study on the source, sink, and regulation mechanism of carbon in this region.

2 Materials and methods

The study was carried out in March, 2013 in the Jiulong River Estuary. Map of the study area and locations of sampling stations are shown in Fig. 1. The CTD data were *in-situ* measured. Water samples for $\delta^{13}C_{DIC}$ (30 mL) measurement were poisoned with 0.1 mL of saturated mercuric chloride ($HgCl_2$) solution immediately upon collection and stored at 4℃ in darkness to prevent further biological production of CO_2. The particulate organic matter (POM) and phytoplanktons were collected by means of GF/F (0.45 μm) glass fiber filters. The filters were decarbonated with 0.1 N HCl, dried at 60℃ and then stored in darkness at 4℃. In the laboratory, the filters were rinsed with distilled water, and dried at 60℃.

Carbon isotopic ratios in dissolved inorganic carbon (DIC) were determined using a modified method following Atekwana and Krishnamurthy (1998). 10 mL aliquots of the water samples were injected with a syringe into glass bottles that were pre-filled with 1 mL 85% phosphoric acid and magnetic stir bars. CO_2 was then extracted and purified after cryogenic removal of H_2O using a liquid nitrogen-ethanol trap. Carbon isotopic ratios in organic samples (POM and phytoplanktons) were measured in terms of CO_2 production by combustion in a sealed quartz tube with CuO at 900℃. All $\delta^{13}C$ samples were analyzed on a mass spectrometer (MAT252, Finnigan MAT, USA). The laboratory reference was calibrated against PDB; the analytical precision for perfectly homogenized samples was ±0.1‰. The results are expressed as $\delta^{13}C$ values: $\delta^{13}C\ (‰)=(R_{sample}-R_{reference})/R_{reference}\times1000$ ($R={}^{13}C/{}^{12}C$).

3 Results and discussion

3.1 Distribution of $\delta^{13}C_{DIC}$ in the Jiulong River Estuary

$\delta^{13}C_{DIC}$ values in surface sea waters are within the range of -1‰ to 2.2‰ all over the world. And the vertical distribution of $\delta^{13}C_{DIC}$ for various sea areas is essentially the same (Kroopnick, 1980; Lin et al., 1999; Takahashi et al., 2000; Quay et al., 2003). During photosynthesis, organisms preferentially take up the lighter isotope ^{12}C, and then the $\delta^{13}C_{DIC}$ values of surface water increase. With increasing water depth, as organic matter settles out of the water column and decomposes, it contributes isotopically light carbon (^{12}C) back to water, thus making the $\delta^{13}C_{DIC}$ values decrease.

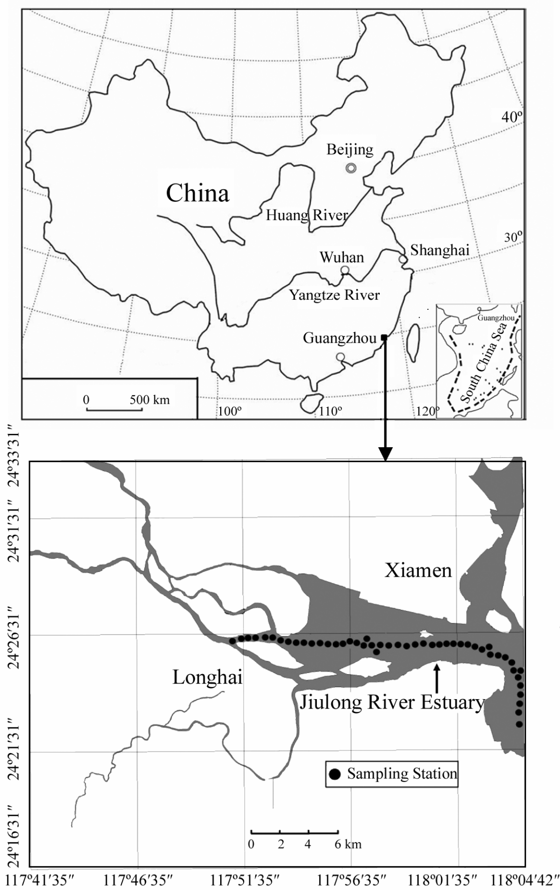

Fig. 1. Map of the study area and locations of sampling stations in the Jiulong River Estuary.

For estuarine environments, the $\delta^{13}C_{DIC}$ have two source (terrigenous supply and sea supply), and the $\delta^{13}C_{DIC}$ mixing ratio can be predicted by a conservative two-component mixing model (Tan and Strain, 1979). Assuming two-component mixing with conservative behavior, the $\delta^{13}C$ values of DIC can be obtained by the following equation:

$$\delta^{13}C=\frac{S\,(C_A\delta^{13}C_A-C_B\delta^{13}C_B)-(S_B\,C_A\delta^{13}C_A-S_A\,C_B\delta^{13}C_B)}{S\,(C_A-C_B)-(S_B\,C_A-S_A\,C_B)} \qquad (1)$$

where C=the concentration of DIC; A, B=characteristic values for the fresh and marine end members; and S=salinity.

It is obvious from equation (1) that three types of mixing behaviors can be depicted in a $\delta^{13}C$ versus salinity diagram. The mixing line will be straight if the

DIC contents of fresh and saline waters are identical. If the DIC contents of saline water are greater than those of fresh water, the mixing curve will be concave toward the horizontal salinity axis. An opposite direction of curvature for the mixing curve is expected when fresh water has a larger concentration of DIC than saline water.

In the Jiulong River Estuary, the $\delta^{13}C_{DIC}$ values are within the range of -11.315‰ to -0.946‰ with salinity ($\times10^{-12}$) varying from 0.61 to 30.29 in March, 2013 of surface sea water samples (Fig. 2). The distribution characteristics of relationship between $\delta^{13}C_{DIC}$ and salinity are very consistent (R^2=0.989). The data show that the $\delta^{13}C_{DIC}$ values for the Jiulong River estuary are mainly controlled by fresh water and sea water mixing ratios as shown in equation (1).

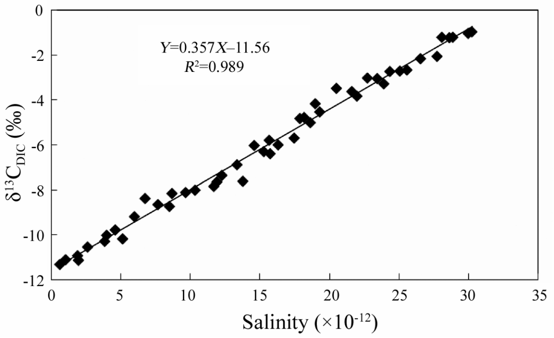

Fig. 2. The $\delta^{13}C_{DIC}$ values versus salinity in the Jiulong River Estuary.

3.2 $\delta^{13}C_{DIC}$ indicators of the carbon cycle in the Jiulong River Estuary

River systems have been recognized as a very important component of the global carbon cycle. Annual DIC supply through the world river systems represents a carbon flux of about 0.38×10^{15} g into the ocean (Richey et al., 2002). The isotopic composition of estuary DIC provides valuable insights into the carbon cycle kinetics between continents and oceans because $\delta^{13}C_{DIC}$ reflects the contributions of DIC from different sources with distinct isotopic compositions. Isotopic aspects of carbon cycling have been studied in several large river systems (Yang et al., 1996; Aucour et al., 1999; Barth et al., 2003; Brunet et al., 2005; Wachniew, 2006; Yu et al., 2010; Meerschel et al., 2011; Moyer et al., 2013). And this study attempts to isotopically characterize DIC in the Jiulong River Estuary.

3.2.1 Relationship between $\delta^{13}C_{phytoplankton}$ and $\delta^{13}C_{DIC}$

In seawater, during photosynthetic fixation of CO_2 into organic materials, organisms preferentially take up the lighter isotope of carbon (^{12}C) and makes surface ocean ^{13}C increase. As a result of this fractionation process, the $\delta^{13}C$ values of phytoplanktons ($\delta^{13}C_{phytoplankton}$) are depleted by 21‰ relative to $\delta^{13}C_{DIC}$. The $\delta^{13}C_{DIC}$ values for surface seawater are within the range of -1‰ to 2.2‰ worldwide (Kroopnick, 1980; Lin et al., 1999; Takahashi et al., 2000; Quay et al., 2003), and the $\delta^{13}C_{phytoplankton}$ values vary from -22‰ to -19‰ worldwide (Fry and sherr, 1984). In the estuary region, the $\delta^{13}C_{DIC}$ values are related greatly to salinity, and the corresponding $\delta^{13}C_{phytoplankton}$ values vary from -13‰ to -29‰ (Farquhar et al., 1989; Descolas-Gros and Fontugne, 1990; Gillikin et al., 2006).

In the Jiulong River Estuary, the $\delta^{13}C_{DIC}$ values vary from -11.315‰ to -0.946‰ with $\delta^{13}C_{phytoplankton}$ values ranging from -31.248‰ to -22.267‰ in March, 2013. The correlation can be expressed as: $\delta^{13}C_{phytoplankton}= 0.764\delta^{13}C_{DIC}-21.83$ (Fig. 3). The intercept (-21.83) was consistent with the isotope fractionation (averaging -21‰) between $\delta^{13}C_{phytoplankton}$ and $\delta^{13}C_{DIC}$ as reported in the literature (Fry and Sherr, 1984). The data show that the $\delta^{13}C_{phytoplankton}$ is linearly related to $\delta^{13}C_{DIC}$ (R^2=0.939) in the Jiulong River Estuary.

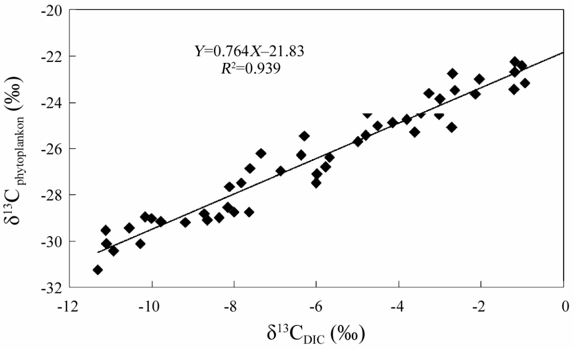

Fig. 3. $\delta^{13}C_{DIC}$ values versus $\delta^{13}C_{phytoplankton}$ values in the Jiulong River Estuary.

3.2.2 Relationship between $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$

Due to different dynamic mechanisms, the relationship between $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ is far more complex than that between $\delta^{13}C_{phytoplankton}$ and $\delta^{13}C_{DIC}$. The sources of POM in estuaries mainly come from photosynthesis and terrigenous input of organic detritus. Theoretically, the $\delta^{13}C_{POM}$ values that combined those of terrestrial organic debris and phytoplanktons in different proportions can be calculated by the following equation (Bouillon et al., 2011).

$$\delta^{13}C_{POM}=\delta^{13}C_0\cdot f+\delta^{13}C_{phytoplankton}\cdot(1-f) \qquad (2)$$

where $\delta^{13}C_0$=the $\delta^{13}C$ values of terrestrial organic debris and f=the percentage of terrestrial organic debris.

But, in this study, the calculated results differ significantly from those worked out from the above formula. The reason is that serious anthropogenic organic pollution makes the sources of POM not a simple binary mixing model in the Jiulong River Estuary. The $\delta^{13}C_{POM}$ values vary from -31.521‰ to -24.707‰, and the linear correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POM}$ can be expressed as: $\delta^{13}C_{POM}=0.595\delta^{13}C_{DIC}-25.10$ (Fig. 4). The linear correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POM}$ ($R^2=0.883$) is significantly lower than that between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{phytoplankton}$ ($R^2=0.939$). It is shown that the $\delta^{13}C_{POM}$ values for the Jiulong River Estuary are affected by anthropogenic pollution significantly.

3.2.3 Comprehensive analysis of $\delta^{13}C_{phytoplankton}$, $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$

The $\delta^{13}C_{phytoplankton}$ values are directly related to the $\delta^{13}C_{DIC}$ values as analyzed above and the $\delta^{13}C_{POM}$ values are affected by the degradation of phytoplanktons. So, the comprehensive analysis of $\delta^{13}C_{phytoplankton}$, $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ can help understanding the mixing and distribution characteristics of organic matter with differential salinity and will contribute to a further study on the source and sink of carbon and its regulation mechanism in the Jiulong River Estuary.

As shown in Fig. 5, the $\delta^{13}C_{phytoplankton}$ and $\delta^{13}C_{DIC}$ values were linearly related to salinity ($R^2=0.943$ and 0.989, respectively) in the Jiulong River Estuary. Relatively, due to the transport of terrigenous organic debris and anthropogenic pollution, the linear relationship between $\delta^{13}C_{POM}$ and salinity ($R^2=0.789$) has an obvious deviation in the low salinity region (salinity<18). As the proportion of POM derived from the degradation of phytoplanktons gradually increases, the $\delta^{13}C_{POM}$ values are linearly related to the salinity well in a high salinity region (>25).

4 Conclusions

(1) In the Jiulong River Estuary, the distribution characteristics of $\delta^{13}C_{DIC}$ and salinity are very consistent. It is shown that the $\delta^{13}C_{DIC}$ values are controlled mainly by the fresh water and sea water mixing ratio.

(2) The organic carbon of phytoplanktons comes from DIC. The $\delta^{13}C_{DIC}$ values vary from -11.315‰ to -0.946‰ with $\delta^{13}C_{phytoplankton}$ values within the range of -31.248‰ to -22.267‰. The $\delta^{13}C_{phytoplankton}$ values are linearly related to the $\delta^{13}C_{DIC}$ values.

(3) Based on the analysis of linear correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POM}$, the data show that the $\delta^{13}C_{POM}$ values for the Jiulong River Estuary are affected by anthropogenic pollution significantly.

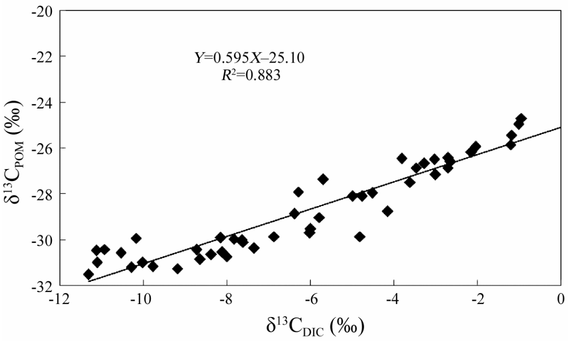

Fig. 4. $\delta^{13}C_{DIC}$ values versus $\delta^{13}C_{POM}$ values in the Jiulong River Estuary.

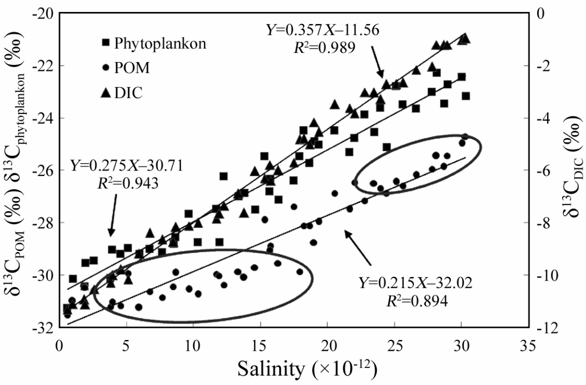

Fig. 5. $\delta^{13}C_{DIC}$, $\delta^{13}C_{POM}$ and $\delta^{13}C_{phytoplankton}$ values versus salinity in the Jiulong River Estuary.

(4) The comprehensive analysis of $\delta^{13}C_{phytoplankton}$, $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ shows that along with increasing salinity, the proportion of POM derived from the degradation of phytoplanktons will gradually increase.

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