


Dissolved iodine in the Changjiang River Estuary, China

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ABSTRACT

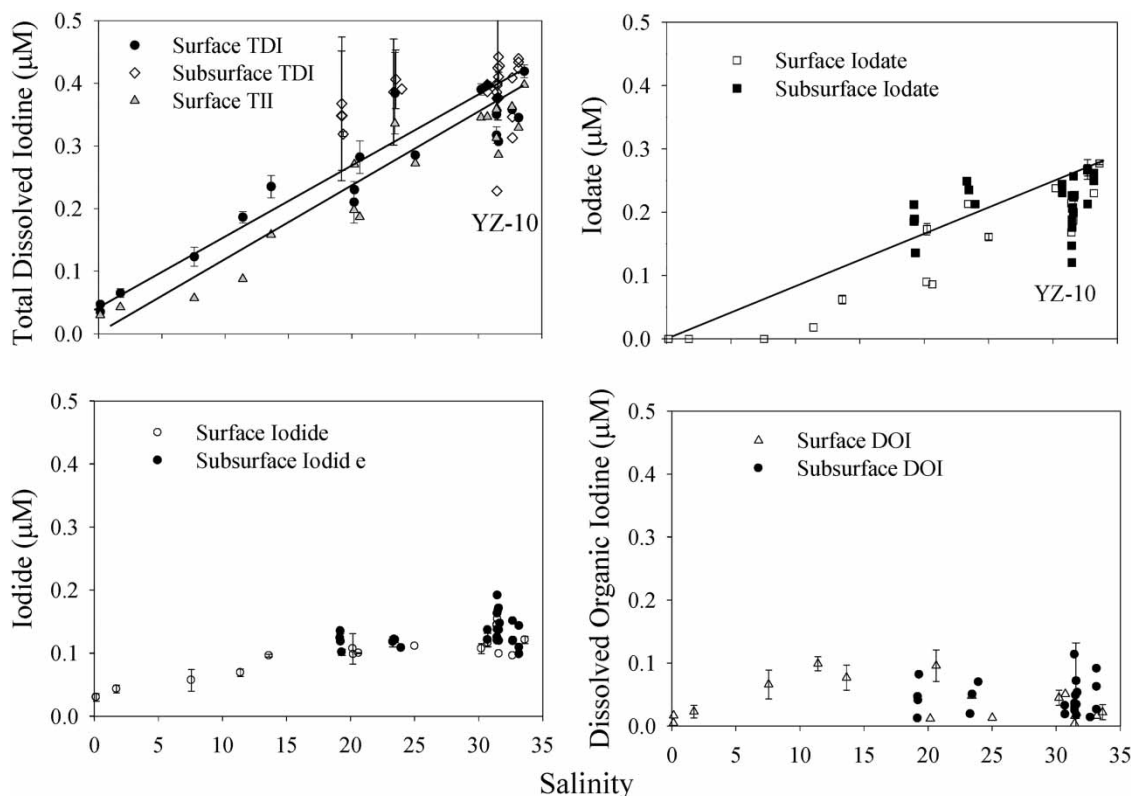
The distribution and behavior of total dissolved iodine (TDI) and its species-iodate, iodide, and dissolved organic iodine (DOI) in the Changjiang River Estuary (CJE) surface and subsurface waters were studied along the salinity gradient. Results showed that TDI concentration in the freshwater endmember of CJE was 0.037 μM and existed as iodide. Although the transformation of dissolved iodine forms was active, TDI showed a conservative behavior, ranging from 0.037 μM to 0.42 μM in the estuary. Iodate showed removal behavior (ranging within 0–0.277 μM), iodide showed additive behavior (ranging within 0.037–0.131 μM), whereas DOI showed additive ($0 < \text{salinity} < 20$) (ranging within 0–0.099 μM) and removal ($20 < \text{salinity} < 33.5$) behavior (ranging within 0.099–0.022 μM). The iodine atoms in DOI were supplied primarily by iodide when salinity was < 10 but by iodate when salinity was > 10 . The iodine–carbon ratios in DOI from different sources were more than 10 times different. The annual flux of iodine in the Changjiang River was $4.0 \times 10^9 \text{g}$, accounting for about 4% of the global river iodine flux.

Key words: dissolved organic iodine, iodate, iodide, total dissolved iodine

HIGHLIGHTS

- Total dissolved iodine concentration in the freshwater endmember of the Changjiang River Estuary was 0.037 μM .
- Iodate and iodide showed removal and additive behaviors in the estuary.
- The iodine atoms in dissolved organic iodine are mainly supplied by iodide when salinity is > 10 but by iodate in waters of salinity between 10 and 33.5.
- The annual flux of iodine in the Changjiang River was $4.0 \times 10^9 \text{g}$.

GRAPHICAL ABSTRACT



1. INTRODUCTION

An estuary is located in a regional environment with land–sea interaction, which is rich in nutrients and high in productivity (Nedwell *et al.* 1999). It also has a great influence on the transportation, migration, and transformation of biogenic elements (Windom *et al.* 1989; Bedsworth & Sedlak 1999; Zhang *et al.* 1999; Ye *et al.* 2021). Among various biogenic elements, iodine exists primarily in dissolved form in estuaries as iodate, iodide, and dissolved organic iodine (DOI) (Truesdale 1975; Smith & Bulter 1979; Takayanagi & Cossa 1985; Francois 1987; Luther *et al.* 1988; Ullman *et al.* 1988; Upstill-Goddard & Elderfield 1988; Guo & Peng 1989; Wong 1991; Zimmermann 2009; Wadley *et al.* 2020; MacKeown *et al.* 2022).

Studies on iodine in estuaries are mostly about its inorganic forms, namely, iodate and iodide. Iodine behaves differently in various estuaries. Iodate in estuaries may be conservative (Takayanagi & Cossa 1985; Guo & Peng 1989) or nonconservative (Abdel-Moati 1999; Cook *et al.* 2000). In some estuaries, the water residence time is too short (Wang *et al.* 2004) for iodate to change its state, whereas, in other estuaries, several factors such as phytoplankton, humus, and sunshine can change the iodate to iodide (Smith & Bulter 1979; Wong 1982; Takayanagi & Cossa 1985; Francois 1987; Luther *et al.* 1988; Cook *et al.* 2000). For example, in the Yarra Estuary, the behavior of iodate radical and total iodine is conservative, and $[IO_3^-]/[I^-]$ decreases with increased salinity, and almost all iodine exists in the form of iodine ion at 0.134 μM given the fresh-water nature of the river (Smith & Bulter 1979). However, in the St. Lawrence River, although the iodate and total iodine concentrations are conservative, they primarily exist in the form of iodate (>90%) (Takayanagi & Cossa 1985). Meanwhile, in the James River Estuary, the iodate concentration falls below the detection limit in the moderate-salinity region, whereas the total iodine concentration is 0.130 μM at zero salinity (Wong 1982).

The study of DOI began in the 1970s (Truesdale 1975). In coastal bays and estuaries, the proportion of DOI in total dissolved iodine (TDI) is very high (reaching 80%) (Wong & Cheng 2001a, 2001b; Wong & Hung 2001a; Wong & Zhang 2003; Schwehr *et al.* 2005). Overall, the status and role of DOI in the iodine biogeochemical cycle remain unclear (Wong & Cheng 1998, 2001a).

In the present study, the contents of iodide, iodate, and DOI in the Changjiang River Estuary (CJE) are systematically studied for the first time. The relationships of the concentrations of various iodine species and salinity with Chlorophyll *a* (Chl. *a*) were studied. The migration and transformation of dissolved iodine in the CJE were also analyzed and discussed.

2. STUDY AREA AND METHODS

2.1. Study area

Surface-water samples (sampling depth: 0.5 m) and subsurface-water samples (sampling depth: 5–46 m) were collected from stations in the CJE in April 2009 (Figure 1). Surface-water salinity was monitored using an underway pumping system. In the freshwater–seawater mixing zone, sampling was performed at salinity values of 0, 3, 9, 12, 15, 18, 20, 26, 30, and 33; in the sea area, sampling was conducted at gridded stations of 0.5° (Table 1).

2.2. Sampling methods

The sampling bottles used were made from high-density polyethylene or polypropylene. They needed to be pretreated before sampling. The steps were as follows: (1) soaking in reverse osmosis (RO) water for at least 24 h, (2) washing with detergent (2% micro) (Cole Parmer Company) and then rinsing with RO water, (3) washing with RO water after soaking in 10% HCl for 24 h, and (4) drying in a clean room. The filter membrane was soaked in 0.5 mol/L HCl solution for 12 h, washed with Milli-Q water to neutral, and dried in a clean room. After sampling, the cap was tightened and immediately stored at $-20\text{ }^{\circ}\text{C}$ in a refrigerator. The cap was confirmed to still be tight after several hours when the sample had frozen. TOC samples filled the pretreated 40-mL Pyrex glass bottles (450 $^{\circ}\text{C}/4\text{ h}$) up to ca. two-thirds to three-fourths full and were stored at $-20\text{ }^{\circ}\text{C}$ in a refrigerator.

2.3. Measuring methods

Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined by a high-temperature combustion oxidation method. The instrument was a Shimadzu TOC-VCPH. The volume of injection was set at 100 μL , and the coefficient of variation was set at $<2\%$. Measurements were made three times for each sample. If the coefficient of variation exceeded the prescribed range, the instrument automatically added the number of injection times to enable the determination to meet the standard. Iodide was determined by cathodic stripping square wave voltammetry. At -0.15 V (relative to standard calomel) potential, Hg initially lost electrons and then iodine was deposited onto the suspended mercury electrode in the

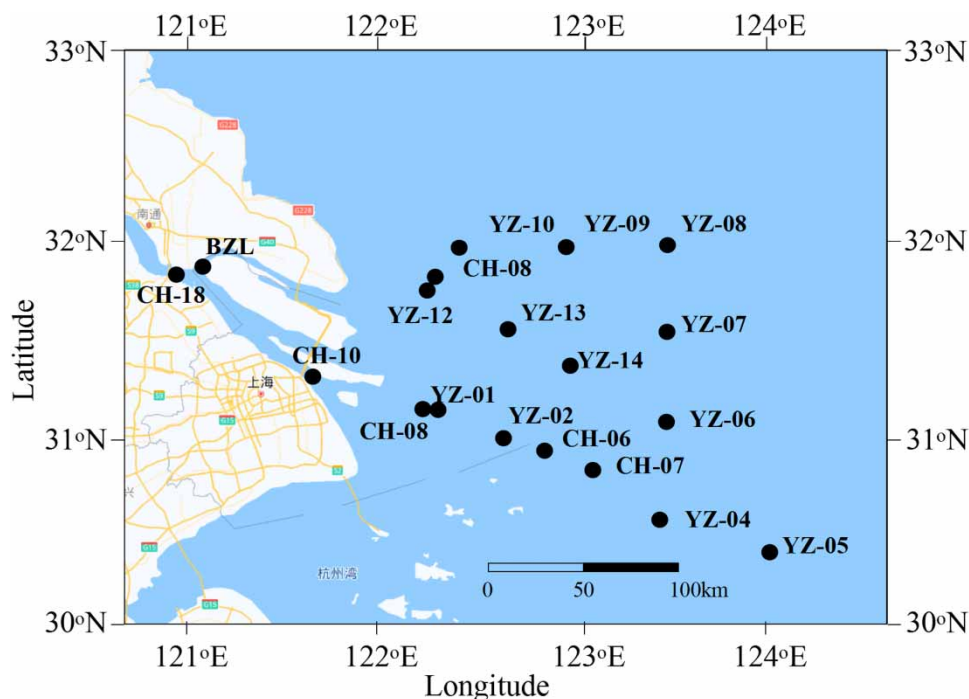


Figure 1 | Distribution of sampling stations in the CJE in spring.

form of Hg_2I_2 for a certain time. The effect of adding Triton X-100 in the solution was to make the peak current significant, and the peak height was positively correlated with the iodide concentration. Quantitative analysis was carried out by adding different iodide concentrations to the solution. Dissolved oxygen (DO) was removed by aeration with high-purity argon. Sulphite was added to the solution to remove oxygen quickly. Iodate was measured by the spectrophotometric method with a Shimadzu UV1700 spectrophotometer (Figure 2).

Table 1 | Salinity of the surface and subsurface samples in the CJE

| Station | Depth (m) | Salinity | Station | Depth (m) | Salinity |
|--------------------|-----------|----------|---------|-----------|----------|
| Surface samples | | | | | |
| CH-01 | 0.5 | 1.7280 | YZ-07 | 0.5 | 31.4342 |
| CH-02 | 0.5 | 7.5660 | YZ-08 | 0.5 | 31.4725 |
| CH-03 | 0.5 | 11.4000 | YZ-09 | 0.5 | 31.5858 |
| YZ-01 | 1 | 13.6400 | YZ-10 | 0.5 | 31.4300 |
| YZ-02 | 1 | 20.6317 | CH-08 | 0.5 | 20.2133 |
| CH-06 | 0.5 | 25.0150 | YZ-12 | 0.5 | 20.1742 |
| CH-07 | 0.5 | 30.2133 | YZ-13 | 0.5 | 23.4125 |
| YZ-04 | 0.5 | 33.6192 | YZ-14 | 0.5 | 30.7125 |
| YZ-05 | 0.5 | 32.6600 | CH-10 | 0.5 | 0.1500 |
| YZ-06 | 0.5 | 33.1758 | CH-18 | 0.5 | 0.1400 |
| Subsurface samples | | | | | |
| YZ-05 | 8 | 32.6867 | YZ-13 | 5 | 23.4733 |
| YZ-05 | 22 | 32.6800 | YZ-13 | 15 | 23.3083 |
| YZ-06 | 8 | 33.1700 | YZ-14 | 5 | 30.6975 |
| YZ-06 | 25 | 33.1700 | YZ-14 | 15 | 30.7108 |
| YZ-07 | 8 | 31.5833 | YZ-05 | 46 | 32.6725 |
| YZ-07 | 20 | 31.6642 | YZ-06 | 48 | 33.1700 |
| YZ-08 | 8 | 31.4675 | YZ-07 | 37 | 31.5333 |
| YZ-08 | 20 | 31.4750 | YZ-08 | 41 | 31.4717 |
| YZ-09 | 15 | 31.6000 | YZ-09 | 32 | 31.5900 |
| YZ-10 | 8 | 31.4475 | YZ-10 | 23 | 31.4642 |
| YZ-12 | 3 | 19.2375 | YZ-12 | 20 | 19.3175 |
| YZ-12 | 5 | 19.1925 | YZ-13 | 28 | 23.9467 |
| YZ-12 | 10 | 19.2125 | - | - | - |

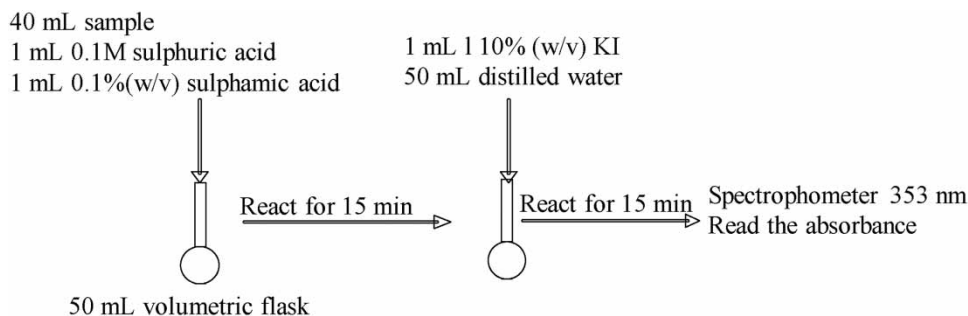


Figure 2 | Measurement process of iodate determined by the spectrophotometric method.

DOI was measured according to the method developed by Wong & Cheng (1998) as reduced iodide (Wong & Cheng 1998).

Longitudes and latitudes were received with a Global Positioning System (GPS) receiver in real-time and recorded with cruise conductivity, temperature, depth (CTD) data. The precision was accurate to 0.00001°. Estuary voyage salinity and dissolved oxygen (DO) were primarily measured using an underway pumping system. The salinity precision was 0.01. Chl. a was determined by the national standard GB17378.7-1998 of the People's Republic of China.

3. RESULTS

3.1. Distribution of TDI, total inorganic iodine (TII), and iodate

The TDI of the CJE in spring was 0.034 μM at the river freshwater endmember and 0.42 μM at the sea endmember (Figure 3). The two-endmember model is often used to study the element addition or removal behavior in the estuary (Burton & Liss 1976). The relationship between surface TDI and salinity (S) can be expressed as follows:

$$\text{TDI } (\mu\text{M}) = 9.8(\pm 0.7) \times 10^{-3}S + 0.056(\pm 0.019), R^2 = 0.9014, N = 20 \quad (1)$$

Here, S represents salinity, R represents the relative coefficient, and N represents the sample numbers.

Results showed a good linear relationship between TDI and salinity ($R^2 = 0.9014$). Surface TDI conservatively indicates that TDI was transformed into other phases, i.e., granular iodine or gaseous iodine, and that the amount removed from the water body was very small.

The average surface [TDI]/ S was 0.0098 μM . This result was similar to those found in other estuaries, such as the Nile and Hune (i.e., 0.0098 and 0.012 μM , respectively) (Ullman *et al.* 1988; Guo & Peng 1989; Abdel-Moati 1999; Cook *et al.* 2000).

Surface TII was also close to conservative behavior (Figure 3). The relationship between TII and salinity can be expressed as follows:

$$\text{TII } (\mu\text{M}) = 1.05(\pm 0.7) \times 10^{-2}S + 0.013(\pm 0.017), R^2 = 0.9303, N = 20 \quad (2)$$

The relationship between TII and salinity was close to linear ($R^2 = 0.9303$). The surface TII regression line was slightly lower than that of TDI, and the difference between the two regression lines represented DOI. DOI concentration increased in low-salinity areas and decreased in high-salinity ones. A detailed distribution of DOI is shown in the following section.

Iodate concentration in the CJE ranged within 0–0.277 μM (Figure 4). Iodate was removed in all surface-water samples (except for several samples) of the whole estuary, which was similar to that in the Nile River Estuary, Huon River Estuary, and James River Estuary (Abdel-Moati 1999; Cook *et al.* 2000; Wong & Cheng 2001a). Iodate concentration below 10 salinity was 0 μM , which was also similar to the above three estuaries, but the salinity of iodate disappearance differed from each other (Luther *et al.* 1991; Abdel-Moati 1999; Cook *et al.* 2000; Wong & Cheng 2001a).

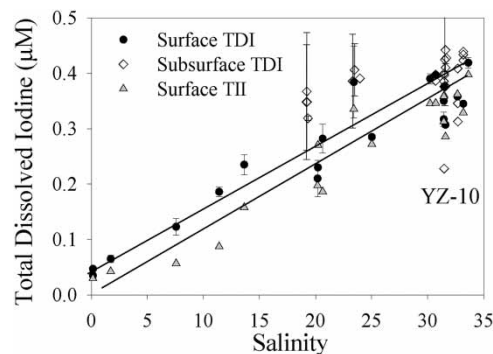


Figure 3 | Relationship between salinity and TDI in surface and subsurface water samples in the CJE in spring.

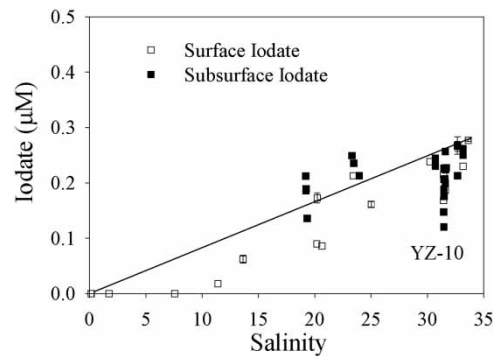


Figure 4 | Relationship between salinity and iodate in surface and subsurface water samples in the CJE in spring.

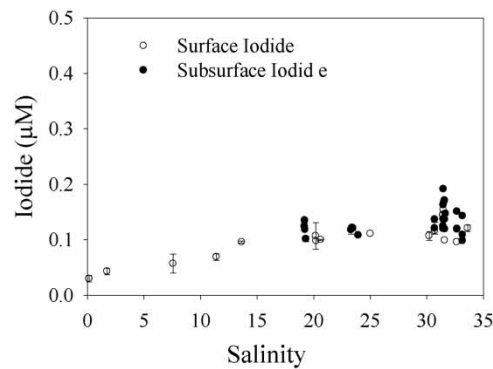


Figure 5 | Relationship between salinity and iodide in the surface and subsurface water samples in the CJE in spring season.

3.2. Iodide distribution in surface and subsurface layers

The correlation between iodide and salinity was as follows:

$$[I^-] = 0.0026S + 0.0406, R^2 = 0.7610 \quad (3)$$

Iodide of the freshwater endmember ($S = 0$) and seawater endmember was 0.031 and 0.124 μM , respectively (Figure 5). The main form of iodine at freshwater endmember was iodide, whereas in seawater endmember, it accounted for one-third. This finding differed from those in the James Estuary and Chesapeake Bay, in which iodine was DOI-dominated in the low-salinity area (Wong & Cheng 1998).

3.3. Distribution of DOC and DOI in surface and subsurface layers

With increased salinity from 0 to 33.6, DOC decreased from 154 to 71 μM , showing conservative mixing (Figure 6).

DOI in the surface layer of the CJE differed from that of iodate and iodide. It had the characteristics of 'two small ends and a large middle' (Figure 7). DOI decreased with increased salinity, reaching 0.022 μM at a salinity of 33.6. This trend was similar to that of the James River Estuary, but the salinity varied when DOI reached its maximum of ~ 20 in the James River Estuary (Wong & Cheng 2001a).

The fitting equation of surface DOI with salinity was as follows:

$$\text{DOI} (\mu\text{M}) = -2.0 \times 10^{-3}S^2 + 5.4 \times 10^{-3}S + 2.5 \times 10^{-2}R^2 = 0.4262 \quad (4)$$

Different from the good relationship between iodate or iodide with salinity (both $R^2 > 0.9$), no good linear relationship existed between DOI and salinity ($R^2 = 0.4262$). DOI in the subsurface layer greatly varied, and the range was approximately

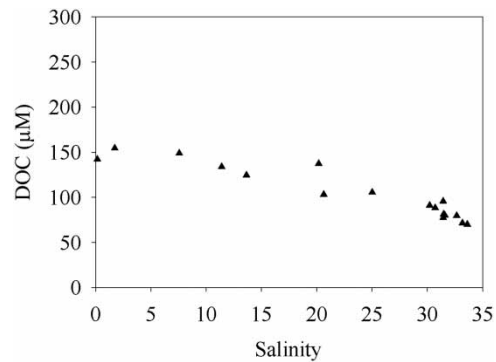


Figure 6 | Relationship between salinity and DOC in surface water in the CJE in spring.

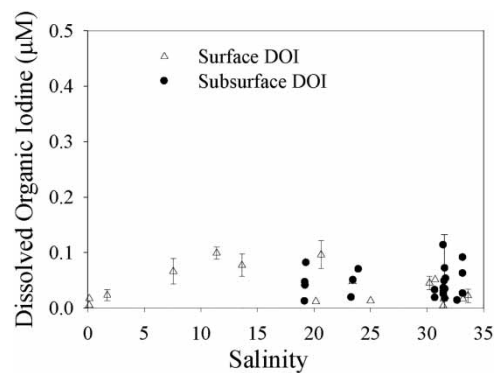


Figure 7 | Relationship between salinity and DOI in surface water in the CJE in spring (when salinity was between 0.1 and 11.4, DOI concentration increased with increased salinity, from 0 µM to the highest value of 0.099 µM).

between 0.02 and 0.1 µM. No samples had salinity of <15 in the subsurface layer, and the relationship between DOI and salinity in the subsurface layer above moderate salinity was not obvious.

4. DISCUSSION

4.1. Annual flux and transport form of TDI

The surface TDI of the CJE was 0.037 µM at 0.2 salinity, which was close to the average concentration of river iodine in the world (0.04 µM) (Turekian 1971; Wong 1991). Although this paper showed data only for spring, according to the previous studies, the seasonal variation of TDI concentration at freshwater endmember did not largely vary with the season (Abdel-Moati 1999; Cook *et al.* 2000). This finding may be related to the low iodine content of soil in the river basin, i.e., the iodine concentration in the water body was similar to whether the soil iodine entered the water body primarily by leaching in the dry season or by washing in the wet season. Therefore, we assumed that the concentration of TDI in the CJE was basically unchanged throughout the year, and the annual flux of dissolved iodine in the Changjiang River can be obtained accordingly (Table 2). The annual flux of iodine in the Changjiang River was 4.0×10^9 g, accounting for about 4% of the global river iodine flux (Wong 1991).

4.2. Transformation of iodine among different forms

Subsurface samples in the CJE were more active than surface samples, so the transformation of iodine in different forms was primarily discussed in the subsurface layer. The relationship between salinity and TDI in the subsurface layer was similar to that in the surface layer, but the variation of iodate was larger. The possible reasons were as follows. First, the subsurface layer actually originated from different water sources, and the depth of the subsurface layer greatly varied due to the different depths of the stations. The biological production may have been affected by different light levels and biological factors.

Table 2 | Iodine species and annual flux in the Changjiang River freshwater endmember

| | Year | Freshwater flux $\times 10^{11} \text{ m}^3$ | TDI μM | Iodine flux $\times 10^8 \text{ g}$ | Species | Reference |
|-------------------|-----------|---|----------------------|--|--------------------|----------------------------|
| Changjiang River | 2009 | 9.3 | 34.7 | 40 | I^- | This study |
| Nile River | 1993 | 0.1 | 81 | 1 | I^- , DOI | Abdel-Moati (1999) |
| Mississippi River | 1996–1998 | 7 | 66 | 82 | DOI | Oktay <i>et al.</i> (2001) |

Second, the subsurface layer may be affected by the sediments, which may react with iodate by releasing humus (Francois 1987; Reifenhauer & Heumann 1990). Once the sediments settled down again, iodine followed with the sediments and entered the diagenesis process (Upstill-Goddard & Elderfield 1988).

Iodide showed additive behavior in the subsurface of the stations with moderate to high salinity, whereas iodate did not decrease in the moderate-salinity region. Therefore, the increase in iodide may have originated only from the release of bottom sediments, rather than from the transformation of iodate, consistent with TDI.

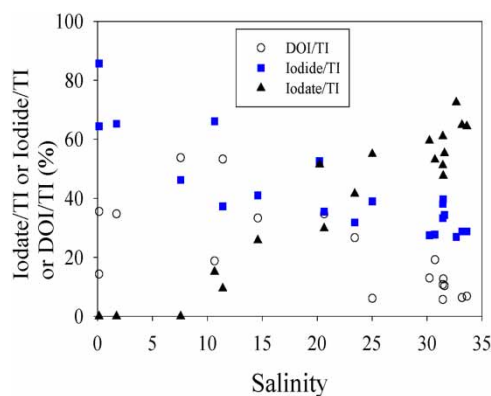
4.3. Relationship between salinity and ratio of iodine species

The values of $[\text{IO}_3^-]/[\text{TDI}]$, $[\text{I}^-]/[\text{TDI}]$, and $[\text{DOI}]/[\text{TDI}]$ varied with salinity, and results are shown in Figure 8. At the endmember of the river, $[\text{I}^-]/[\text{TDI}]$ was the highest, with an average of 70% for two samples with 0 salinity and 30% for $[\text{DOI}]/[\text{TDI}]$, contrary to the James River Estuary where $[\text{DOI}]$ and $[\text{I}^-]$ accounted for 80 and 20%, respectively (Wong & Cheng 2001a). The $[\text{DOI}]/[\text{TDI}]$ in the CJE was about 10% when the salinity was above 30, which was the same as that in the James Estuary and similar to that in most sea areas (Wong & Cheng 2001a; Wong & Zhang 2003; Wong *et al.* 2004). $[\text{DOI}]/[\text{TDI}]$ increases first and then decreases with increased salinity, reaching a maximum of about 55% at a salinity of 10, and then decreases with increased salinity. This result was also different from that of the James Estuary. The trend of $[\text{I}^-]/[\text{TDI}]$ in the CJE decreases linearly with increased salinity. The trend of $[\text{I}^-]/[\text{TDI}]$ in the CJE initially increased with increased salinity, reading the highest point of 60% at a salinity of 25, and then it decreased with increased salinity. The $[\text{I}^-]/[\text{TDI}]$ of the CJE was about 30% when the salinity exceeded 30%, differing slightly from that of about 50% in the James Estuary.

Although iodide and DOI are both products of iodate, they behave differently in various estuaries, which may be related to the latitude (Campos *et al.* 1999), discharge, productivity, and human influence. Figure 8 also shows that $[\text{IO}_3^-]/[\text{TDI}]$ in the CJE was 0 in water samples which had 0–10 salinity, and did not appear until salinity exceeded 10. Subsequently, iodide increased with increased salinity, reaching its maximum at salinity above 30.

4.4. Relationship between DOI and DOC

DOI can be produced by the following three reactions: (1) iodate reduced by biology to produce DOI (Formula (5)) (Wong & Cheng 2001b); (2) iodate involved in photoreaction to produce DOI (Formula (6)) (Spokes & Liss 1996); and (3) after iodide formed iodine molecules and hypoiodic acid, DOI was produced (Formula (7)) (Luther 1991; Luther & Campbell 1991;

**Figure 8** | Relationships of $[\text{IO}_3^-]/[\text{TDI}]$, $[\text{I}^-]/[\text{TDI}]$, and $[\text{DOI}]/[\text{TDI}]$ in the CJE in spring.

Truesdale *et al.* 1995a, 1995b).



where DOM is dissolved organic matter.

The above formulas revealed that the reactant iodate or iodide can produce DOI because iodate was 0 nM in the water body with salinity between 0 and 10 (Figure 8). DOI production was similar to that of Formula (7) and given that iodide and iodate existed in the water body where the salinity between 10 and 20, DOI production was similar to that of Formulas (5)–(7). Biomass and PAR increased with increased salinity (Ning *et al.* 2004), and phytoplankton and light can play important roles in DOI production; consequently, [DOI]/[TDI] increased (Figure 9).

The DOI/DOC, i.e., the iodine–carbon ratio (I/C) in DOI (Figure 10), showed that with increased salinity from 0 to 20, I/C increased from about 1:10,000 to 1:1,000, reaching the highest ratio. Subsequently, salinity decreased from 20 to 33.6, and the range of variation was larger when salinity exceeded 30.

5. CONCLUSIONS

- (1) TDI concentration in the freshwater endmember of CJE was 0.037 μM . TDI showed a conservative behavior, ranging within 0.037–0.42 μM in the estuary. Iodate showed removal behavior (ranging within 0–0.277 μM), iodide showed

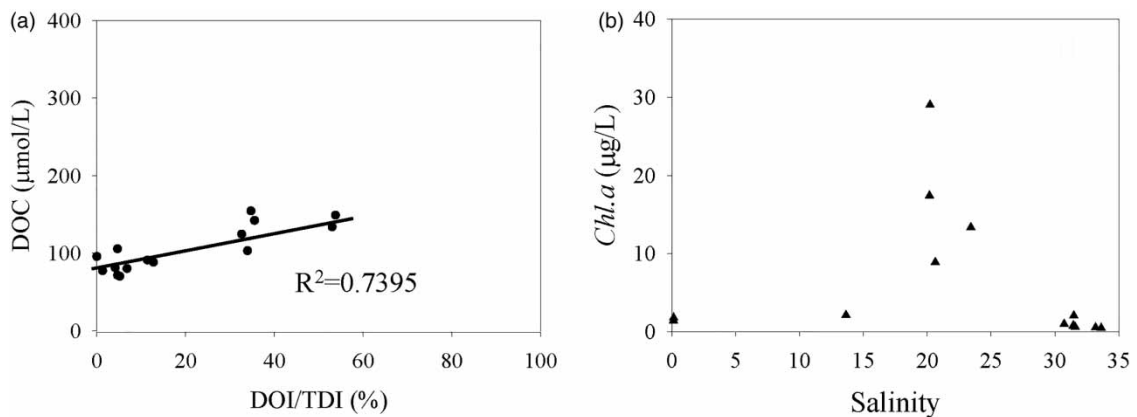


Figure 9 | Relationships (a) between DOC and [DOI]/[TDI] and (b) between salinity and Chl. a in the CJE in spring.

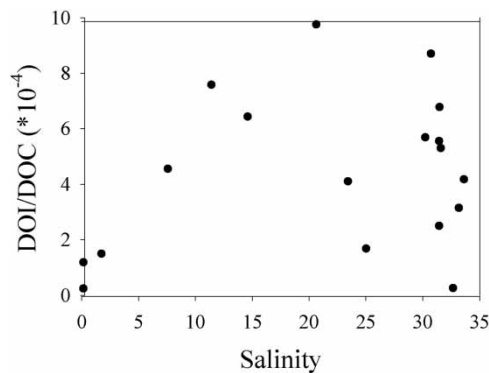


Figure 10 | Relationship between salinity and DOI/DOC in the CJE in spring.

- additive behavior (ranging within 0.037–0.131 μM), and DOI shows additive ($0 < \text{salinity} < 20$) (ranging within 0–0.099 μM) and removal ($20 < \text{Salinity} < 33.5$) behaviors (ranging within 0.099–0.022 μM).
- (2) The flux of iodine in the CJE was 4.0×10^8 g/a, accounting for about 4% of the global flux, imported into the estuary as iodide.
 - (3) The I/C ratio increased by an order of magnitude in water with a salinity of 0 to ~ 20 .
 - (4) The iodine atoms in DOI may be primarily supplied by iodide in water with a salinity of 0–10. The mechanism of DOI production was the reaction between iodide and DOM. Iodine atoms in DOI were primarily supplied by iodate at > 10 salinity, and the mechanism of DOI was primarily from biological production.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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