BIOGEOCHEMICAL DYNAMICS AT MAJOR RIVER-COASTAL INTERFACES

Linkages with Global Change

This volume provides a state-of-the-art summary of biogeochemical dynamics at major river-coastal interfaces for advanced students and researchers. River systems play an important role (via the carbon cycle) in the natural self-regulation of Earth’s surface conditions by serving as a major sink for anthropogenic CO₂. Approximately 90 percent of global carbon burial occurs in ocean margins, with the majority of this thought to be buried in large delta-front estuaries (LDEs). This book provides information on how humans have altered carbon cycling, sediment dynamics, CO₂ budgets, wetland dynamics, and nutrients and trace element cycling at the land-margin interface. Many of the globally important LDEs are discussed across a range of latitudes, elevations, and climates in the drainage basin, coastal oceanographic setting, and nature and degree of human alteration. It is this breadth of examination that provides the reader with a comprehensive understanding of the overarching controls on major river biogeochemistry.

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To our families for their unending support and patience through the years.

“No man ever steps in the same river twice, for it’s not the same river and he’s not the same man.”

– Heraclitus
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*T. S. Bianchi, M. A. Allison, and W.-J. Cai*

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*M. A. Allison, A. Kolker, and E. Meselhe*

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River plumes, typical of large freshwater discharges, may extend into the adjacent continental shelf hundreds of kilometers away from the estuarine mouth and become critical areas of land-ocean interaction both physically and biogeochemically (Hickey et al. 1998; Nash and Moun 2005; Dagg et al. 2008; Dai et al. 2008; Chen and Borges 2009; Gan et al. 2010; Cao et al. 2011; Bianchi et al. 2012; Han et al. 2012).

From a physical dynamic point of view, buoyancy input from freshwater discharge forms gravitational circulation, changes the course of flow direction, and modulates the mixing intensity in the estuary. After exiting into the ambient shelf, river plume often yields a right-tilted (in the northern hemisphere) quasi-stationary bulge of buoyant freshwater and associated circular currents over the shelf at the entrance to the estuary (Chao and Boicourt 1986; Zu and Gan 2008). With the existence of ambient coastal currents, the fate and characteristics of the plume, as well as the coastal currents themselves, are largely controlled by the interaction between the plume and coastal currents (Fong and Geyer 2002; Gan et al. 2009). The plume insulates surface coastal water from the water below and amplifies the efficiency of wind forcing near the surface (Lentz 2001) and may even generate internal waves (Nash and Moun 2005). At the same time, the lateral density gradient or pressure gradient formed between the buoyant plume and ambient seawater geostrophically alters the intensity of the wind-driven currents (Chao 1988; Gan et al. 2009). Therefore, the interaction between the plume and coastal circulations affect not only the advection but also the turbulence mixing on the shelf, thereby affecting significantly the biogeochemistry therein. At the same time, river plumes are often loaded with carbon, nutrients, and sediments (Dagg et al. 2004; McKee et al. 2004). Both the high nutrient discharge within the river plume and the low turbidity of its lower reach are favorable for phytoplankton growth and very often result in enhanced biological activity (Gaston et al. 2006 and references therein). River plumes are thus frequently sites of phytoplankton blooms and intensive carbon uptake in coastal seas.

It is therefore clear that river plumes, which are initiated by large river discharge, transported, and modulated by the estuarine and adjacent shelf circulation, make dynamical and biogeochemical links of the land-ocean interactions. However, the complexity of the interaction between the plume dynamics and estuarine/shelf circulation along with the associated biogeochemical alteration therein makes it challenge to elucidate their processes and mechanism. To make quantitative assessment of
these processes adds to the challenge. This chapter provides an overview of the basic characteristics of the Pearl River, Pearl River Estuary (PRE), and their adjacent northern South China Sea (NSCS). We focus on the physical and biogeochemical characteristics of the river plume off the PRE over the subtropical shelf sea in the NSCS. We emphasize the coupled physical-biogeochemical processes in this extremely dynamic and complex system impacted by river plumes. We also offer approaches to distinguish the biogeochemical rates from the complex water mass transport and/or mixing. Although this chapter is site-specific based on the regional studies, we are attempting to demonstrate that such integration between physical dynamics and biogeochemistry is a key to understanding these systems of similar nature, and the approach we have exemplified should have applicability to many coastal ocean settings in the world.

2. Basics of the Pearl River, estuary, and the shelf

2.1. The Pearl River

2.1.1. Basics

The Pearl River, or Zhujiang in Chinese, is an extensive river system in southern China, ranking as the third longest river in China after the Yangtze River and the Yellow River. It is mainly composed of three tributaries, the West River (Xijiang), the North River (Beijiang), and the East River (Dongjiang), all of which share a common delta, the Pearl River Delta (PRD) (Fig. 13.1A). Both the North and East Rivers originate from Jiangxi Province with a length of 573 and 562 km, respectively (Table 13.1). Originating from Yunnan province, the West River is the largest tributary of the Pearl River system, with a length of 2,214 km (Table 13.1).

The 450,000 km² Pearl River basin drains the majority of the south central (Guangdong and Guangxi provinces), as well as parts of the southwest (Yunnan, Guizhou, Hunan, and Jiangxi provinces) of China, and the northeast of Vietnam. The catchment areas of the West River, the North River, and the East River are 351,500, 44,700, and 25,300 km², respectively (Table 13.1). The entire drainage basin of the Pearl River is located south of 27°N. With a subtropical climate, the area has a long summer (wet season) and a short winter (dry season). The average annual rainfall is 1,470 mm (Dai et al. 2008a).

The West River basin is characterized by a “karst” landscape and thus is high in carbonate mineral content of ~80% (Cai et al. 2008 and references therein). The total ion content is 176.5 mg L⁻¹ in the West River (Table 13.1). The long-term average concentration of HCO₃⁻ is modest, being 118.3 mg L⁻¹ (1939 μmol L⁻¹) in the West River (Table 13.1), whereas the specific HCO₃⁻ flux (1279 × 10³ mol km⁻² yr⁻¹) is highest among all of the world large rivers because of the high weathering rate at its drainage basin (Cai et al. 2008). The West River is also characterized by high inorganic nitrogen concentration (DIN, NO₃⁻+NO₂⁻+NH₄⁺, ~126 μmol L⁻¹) and moderate silicate concentration (Si(OH)₄, ~120 μmol L⁻¹) (Table 13.1).

The North River is in the intermediate range in terms of carbonate content, with [HCO₃⁻] of 87.1 mg L⁻¹ (1,428 μmol L⁻¹) and the total ion content of 131.9 mg L⁻¹ (Table 13.1). Nutrient concentrations in the North River are slightly higher than those of the West River, with DIN of 151.8 μmol L⁻¹, PO₄ (DIP) of 0.41 μmol L⁻¹, and Si(OH)₄ of 133.2 μmol L⁻¹, respectively (Table 13.1).
In the eastern basin of the Pearl River, granites are abundant. The East River thus has characteristic higher silicate concentration (173.1 μmol L⁻¹) but lower bicarbonate ion concentration (31.8 mg L⁻¹ or 521 μmol L⁻¹) and total ion content (52.7 mg L⁻¹) (Table 13.1). Dissolved organic carbon, dissolved inorganic nitrogen, and phosphate are similar in all of the three tributaries of the Pearl River system.

On an annual basis, the West River discharges $6.68 \times 10^6$ ton yr⁻¹ of suspended sediment into the SCS, which accounts for ~90% of the total sediment flux of the Pearl River. The summation of the
### Table 13.1. Basic characteristics and hydrochemistry of the Pearl River system and its estuaries

<table>
<thead>
<tr>
<th>Major tributaries</th>
<th>West River</th>
<th>North River</th>
<th>East River</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (km)</td>
<td>2214</td>
<td>573</td>
<td>562</td>
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<tr>
<td>Basin area (10³ km²)</td>
<td>351.5</td>
<td>44.7</td>
<td>25.3</td>
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<td>421.5</td>
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<tr>
<td>Discharge (10⁹ m³ yr⁻¹)</td>
<td>219.7</td>
<td>42.1</td>
<td>23.4</td>
<td>–</td>
<td>285.2</td>
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<tr>
<td>Landscape</td>
<td>Karst</td>
<td>Karst</td>
<td>Granite</td>
<td></td>
<td></td>
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<tr>
<td>Chemical parameters (μmol L⁻¹)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIN (NO₃⁻+NO₂⁻+NH₄⁺)</td>
<td>125.9</td>
<td>151.8</td>
<td>145.4</td>
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<td></td>
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<tr>
<td>PO₄ (DIP)</td>
<td>NA</td>
<td>0.41</td>
<td>1.59</td>
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<td></td>
</tr>
<tr>
<td>Si(OH)₄</td>
<td>119.6</td>
<td>133.2</td>
<td>173.1</td>
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<td>DOC</td>
<td>108.9</td>
<td>82.6</td>
<td>86.7</td>
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<td>Major ions (mg L⁻¹)</td>
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<td>Ca²⁺</td>
<td>29.7</td>
<td>23.1</td>
<td>5.6</td>
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<tr>
<td>Mg²⁺</td>
<td>5.0</td>
<td>2.7</td>
<td>1.6</td>
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<td>Na⁺+K⁺</td>
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<td>7.6</td>
<td>6.8</td>
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<tr>
<td>Cl⁻</td>
<td>3.3</td>
<td>1.9</td>
<td>2.8</td>
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<tr>
<td>SO₄²⁻</td>
<td>10.4</td>
<td>9.4</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>118.3</td>
<td>87.1</td>
<td>31.8</td>
<td></td>
<td></td>
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<tr>
<td>Total dissolved solids</td>
<td>176.5</td>
<td>131.9</td>
<td>52.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total dissolved solids flux (10⁶ t yr⁻¹)</td>
<td>35.2</td>
<td>5.3</td>
<td>1.3</td>
<td>41.8</td>
<td></td>
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<tr>
<td>Suspended sediment flux (10⁶ t yr⁻¹)</td>
<td>66.8</td>
<td>5.4</td>
<td>2.5</td>
<td>74.7</td>
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<th>Sub-estuaries</th>
<th>Lingdingyang</th>
<th>Modaomen</th>
<th>Huangmaohai #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlets</td>
<td>HUM</td>
<td>JOM</td>
<td>HQM</td>
</tr>
<tr>
<td>Surface area (km²)</td>
<td>1180</td>
<td>350</td>
<td>440</td>
</tr>
<tr>
<td>Discharge (10⁹ m³ yr⁻¹)</td>
<td>57.8</td>
<td>54.1</td>
<td>20.0</td>
</tr>
</tbody>
</table>

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b Cai et al. (2004).
c Dai et al. (2009).
d Zhao (1990).
e X. Guo unpublished data (Jan. 2010); Sampled at 111.33°E, 23.47°N in the West River, 112.96°E, 23.56°N in the North River, and 114.29°E, 23.16°N in the East River.
f Zhang et al. (2007).
g Zhang et al. (2011).
h Wong and Cheung (2000).
* HUM: Humen; JOM: Jiaomen; HQM: Hongqimen; HEM: Hengmen; MDM: Modaomen; JTM: Jitimen; HTM: Hutiaomen; YM: Yamen.
# August 2005, unpublished data from X. Guo.

Pearl River has a total suspended sediment flux of $7.47 \times 10^8$ ton yr⁻¹, including the contribution from the North ($5.4 \times 10^6$ ton yr⁻¹) and East ($2.5 \times 10^6$ ton yr⁻¹) Rivers (Table 13.1). Such a sediment flux from the Pearl River system only accounts for $\sim 0.4$–$0.5\%$ of the global total flux to the ocean (15–20 Gt yr⁻¹, Zhang et al. 2011).

Regarding the total dissolved solids load, the Pearl River has a total flux of $4.18 \times 10^8$ ton yr⁻¹, 84% of which is delivered by the West River ($3.52 \times 10^8$ ton yr⁻¹), and only accounts for $\sim 1\%$ of the
2. Basics of the Pearl River, estuary, and the shelf

2.1. Precipitation and river discharge

According to Dai et al. (2009), the West River has a long-term average discharge of $219.7 \times 10^9$ m$^3$ yr$^{-1}$, and ranks as the 23rd world largest river in terms of water discharge. Among the three major tributaries that merge into the PRD, the West River contributes $\sim 76\%$ of the total discharge. The summation of the Pearl River system has a total discharge of $285.2 \times 10^9$ m$^3$ yr$^{-1}$, including the contribution of the East and North Rivers, which makes the Pearl River system the 17th largest river in the world (Table 13.1).

There is no significant interannual variation in water discharge during this long-term period between 1948 and 2004. Exception occurred, however, to the periods of relatively high flows around the 1950s and the later 1990s and low flows in the later 1980s (Fig. 13.2A). To explore the causes behind the discharge trends, Figure 13.2A shows the trends during the same period in precipitation and air temperature (both from Dai et al. 2007). Water discharge is significantly correlated with precipitation, suggesting that precipitation change is a major cause for the discharge trends and large interannual to decadal variations. Widespread decreases in precipitation in the mid-1960s, 1990, and 2005 coincide with the decrease in runoff in these periods, whereas the increase in precipitation in the years 1959, 1969, 1975, 1980, 1995, 1997, and 2000 are consistent with runoff increases. Although the droughts in mid-1960s, 1990, and 2005 are reflected by the increase in air temperature, the high flows period corresponds to the decreased air temperature.

Monthly average discharge of the West River distributes asymmetrically and is characterized distinguishably by peak values in July. Large upward trend is from April to September, during which $80\%$ of the annual water discharge takes place, and downward trend is from October to March, indicating the flood/wet season in summer and dry season in winter (Fig. 13.2B).

In addition to the significant monthly changes in the water discharge, there often occurs synoptic at a weekly time scale, typically forced by heavy precipitation at monsoonal season (Fig. 13.2C), which very much initiates the river plumes demonstrated in later sections (see Section 3).

2.2. Pearl River estuary

2.2.1. Basics

The Pearl River system empties into the SCS through three sub-estuaries, Lingdingyang, Modaomen, and Huangmaohai, via eight major outlets, namely Humen (HUM), Jiaomen (JOM), Hongqimen (HQM), Hengmen (HEM), Modaomen (MDM), Jitimen (JTM), Hutiaomen (HTM), and Yamen (YM) (Fig. 13.1B).

Lingdingyang, traditionally referred to as the PRE, is a funnel-shaped sub-estuary with a surface area of 1,180 km$^2$ (Table 13.1). Generally, the Lingdingyang sub-estuary is divided into two parts by two islands around the latitude of $22^\circ 25'$ N. The northern part is designated Inner Lingdingyang; the southern part, outer Lingdingyang (Han 1998).
Figure 13.2. River discharge of the Pearl River system at different time scales. (A) Long-term variability of the freshwater discharge of the West River, the largest tributary of the Pearl River, which accounts for \( \sim 76\% \) of the total freshwater discharge. Data in 1950–1984 recorded at Wuzhou gauge station are from Dai et al. (2009). Data in 1985–1999 recorded at Gaoyao gauge station are from Dai et al. (2007). Data between 2000–2009 (Wuzhou) are from xxfb.hydroinfo.gov.cn/. Data of precipitation and air temperature are collected from Dai et al. (2007). (B) Monthly average discharge of the West River in 2000–2009. (C) Daily water discharge of the West River in May 2001 and June–August 2008. The gray bar indicates values during the cruise periods in May 13–June 3, 2001, and in June 29–July 15, 2008; both cases are illustrated in this chapter showing the discharge initiated river plumes. The solid line shows the generally observed maximum value in the wet season.
2. Basics of the Pearl River, estuary, and the shelf

The topography of the Lingdingyang sub-estuary has mixed features of channels, shoals, and tidal flats (Figure 13.1B). The depth of the sub-estuary varies from 0 to 30 m. Humen is one of the outlets at the northern end of the PRE. Two deep channels with varying depths are located in the eastern half of the sub-estuary, providing important pathways for seawater intrusion and freshwater outflow. The east channel has a water depth of about 10 m, and the west channel is shallower. These geographic and topographic features exert dynamic influences on tidal cycles, water circulation, and the water column structure. Consequently, they affect water quality and estuarine ecosystems.

The four eastern outlets (HUM, JOM, HQM, and HEM) collect about 50–55% of the Pearl River freshwater from the East and North Rivers, as well as some branches of the West River, and discharge their waters into the Lingdingyang and eventually into the continental shelf of the NSCS.

Lingdingyang is a heavily perturbed area and surrounded by several metropolis, such as Guangzhou, Shenzhen, and Hong Kong. These metropolis have populations of several to >10 million and annual sewage discharge of ~700–1,000 million tons (Bu and Ye 2007).

The Modaomen sub-estuary receives most of the freshwater of the West River through the MDM and JTM outlets, which account for about 28% (Cheung et al. 2000) of the total discharge into the sea south of Macau. The Modaomen sub-estuary is an arc-like siltation zone with its apex at the MDM and JTM outlets, with a surface area of 350 km² (Table 13.1). The MDM outlet is very shallow, with a water depth of 1–2 m (Guo et al. 2009).

Huangmaohai, with a surface area of 440 km², is also a funnel-shaped sub-estuary similar to Lingdingyang (Table 13.1). The Huangmaohai sub-estuary collects the discharge from two branches of the West River and a local river (the Tanjiang) through the HTM and YM outlets.

In contrast to the Lingdingyang, the Huangmaohai and Modaomen sub-estuaries are surrounded by relatively less populated cities such as Jiangmen and Zhuhai. Populations of these two cities are 4 and 1.5 million and the sewage discharges are 150 and 120 million tons, respectively (Bu and Ye 2007).

2.2. Circulation in the estuary

2.2.2. Gravitational circulation

As a semi-enclosed coastal water body that connects with the Pearl River discharge at its upper reach and with the adjacent NSCS shelf sea at its lower reach, PRE has an estuarine circulation that is largely forced by tides and the river influx. Tides are mainly semi-diurnal (M2) and diurnal (K1) around PRE region and have ~1.0 m magnitude inside the PRE. They are amplified and modulated as they propagate back and forth in the estuary with spatially variable water depths. It strengthens vertical shear of the currents, reduces the vertical stability of the water column, and introduces stronger vertical mixing. Tides form a counterclockwise tidal residual circulation (Mao et al. 2004) and affect the estuarine circulation in both tidal and subtidal frequencies. Although the freshwater from Pearl River discharge pushes seawater beyond the river mouth, it forms the thermohaline forcing between the buoyant river water and dense seawater, leading to a gravitational circulation in the PRE. The circulation pattern is thus determined by the relative strength between freshwater volume $R$ and tidal volume $V$. In the wet season, $R$ is strong or the ratio $R/V$ is large. The circulation in PRE exhibits generally as a salt wedge estuary (Fig. 13.3A), in which the freshwater flushes seaward at the upper layer and seawater directs landward at the lower layer. It generates a density front that wedges
landward from the surface near the estuary mouth toward the bottom near mid-estuary. An upward transport of mass and salt (entrainment) enhances the estuarine circulation, and the vertical velocity shear near the front creates instability. The river discharge decreases dramatically in dry seasons as the ratio $R/V$ becomes smaller (Fig. 13.3B). With the additional strong northeasterly wind-stirring mixing, the circulation in the PRE is generally characterized as a slightly stratified estuary, in which turbulence is strong and water column is vigorously mixed in dry seasons.

2.2.2.2. Subtidal circulation

Besides the periodical motion of tidal flow within the time scale of tidal period, the PRE is greatly controlled by the subtidal currents that vary over the period beyond the tidal period. In fact, the subtidal currents, which are controlled by both tidal and subtidal forcing, play a dominant role in the net material transport in estuary. Unlike classical estuaries that have relatively small spatial scale with gravitational circulation, the subtidal circulation in the PRE may be controlled by the intrusion of local wind-driven shelf current, besides the tidal and freshwater discharge.

The southwesterly and northeasterly monsoonal winds prevail in NSCS during the wet and the dry seasons, respectively (Fig. 13.4). The magnitude of seasonally averaged wind stress is about 0.1 Pa in the dry season (Fig. 13.4B) and about 0.025 Pa in the wet season (Fig. 13.4A). They direct surface current westward and southeastward inside the PRE and form respective upwelling and downwelling circulations (see later) on the adjacent shelf. The wind-driven surface currents can be identified by the orientation of the river plume inferred from chlorophyll $a$ concentrations of satellite remote sensing (Figs. 13.4C and 13.4D) and by surface currents.

The plume mainly tilts southeastward inside the PRE and directs eastward by coastal current over the shelf in the wet season. It attaches along the west bank inside the PRE and flows westward after exiting the estuary in the dry season. The seasonal variation is mainly governed by the subtidal forcing induced by seasonal monsoon and the volume of the river discharge (Zu and Gan 2008). In the dry season, relatively strong wind and weak river discharge form westward moving of the freshwater. In the wet season, opposite conditions reduce the wind effect inside the estuary. Zu and Gan (2012) showed...
that the current directs eastward inside the estuary when southwesterly wind reaches $\sim 0.05$ Pa in the wet season.

2.2.2.3. Intra-tidal circulation

The strengths of tides, river discharge, and associated mixing jointly control the advancing/retreating of seawater/river water in the PRE at intra-tidal time scale. The results obtained from the numerical results of Zu and Gan (2012) were used to demonstrates the dynamic response to forcing during different tidal phases (Fig. 13.5). The model was forced with observed wind, river discharge, and tides in the wet season of July 2000, and the results on July 27 were presented.

At Phase 1 at the peak of ebbing, the strong southward currents occupied over the entire estuary; it lowered the water level in the PRE and the adjacent shelf, as tides retreated toward the South China Sea. Relatively high elevation was formed by the buoyant river discharge at the head of the estuary, which tended to force water southward. The opposite condition occurred at Phase 4 at the peak of
Figure 13.5. Variations of surface elevation (m, left column) and barotropic current vectors (m s$^{-1}$, right column) at four different tidal phases on July 27, 2000. The top panel (A) shows northward (>0)-southward (<0) depth-integrated velocity (m s$^{-1}$) at a station around Lingding Island in the middle of the Pearl River estuary.
flooding, whereas the conditions at Phases 2 and 3 showed the similar features with the respective weak flooding and ebbing events between Phases 1 and 4. During all phases, the tidal currents were amplified in the estuary, and the northeastward monsoon-driven currents prevailed over the shelf. The tidal effect was relatively weak over the shelf, and the shelf currents east of Hong Kong tended to be enhanced during ebbing current.

Perhaps the intra-tidal circulation in the estuary can be more clearly seen from the velocity and salinity distribution along the axial section A (Fig. 13.1B). During Phases 1 and 4, Figures 13.6A and 13.6D show the respective seaward and landward flows, dominated by tidal currents, in the weakly stratified estuary and strongly stratified adjacent shelf. Water column appeared more stratified at the ebbing phases as fresh river discharge flushing out of the estuary in the upper layer. The interesting response of circulation to tides occurred during Phases 2 and 3 (Fig. 13.6B and 13.6C), in which the $R/V$ ratio was comparable and the velocity in the water column was vertically sheared in the shelf and in the estuary as well at Phase 3. The intruded seawater, built up by the flooding current before Phase 3 and entrained from the lower layer, was pushed seaward in the upper layer, which created a highly unstable two-layer water column in the estuary. At Phase 2, the landward advancing seawater met the freshwater from the prior ebbing current and generated a salinity front ~8 km south of the estuarine entrance. The convergence in the front pushed the surface water downward while the flooding current advanced seawater landward in the lower layer.
In addition, Zu and Gan (2012) found that the salt water intrusion has a distinct spring-neap variation, as the distribution of the salinity gradient changes from a sharp front, separating the freshwater inshore with seawater offshore, during spring tide into a highly stratified water column during neap tide. The landward intrusion of salt water caused by tides cannot monotonically increase/decrease with the flooding/ebbing currents, but changes with the competing effects of tidal mixing and river discharge. The classical two-layer circulation is only one of the circulation modes in the PRE. Subtidal currents, such as wind-driven currents, tend to intensify/weaken the intensities of cross estuary-shelf circulation during the different tidal phases.

2.2.3. Hydrology and biogeochemistry of the PRE

The hydrology of the PRE as illustrated by the spatial distribution of salinity within the estuary is largely reflective of the river discharge pattern and the estuarine circulation. As previously described (Guo et al. 2009), we divided the PRE into three zones for ease of discussion, namely upper estuary upstream of Human outlet, mid-estuary in the Inner Lingdingyang and Huangmaohai (here as the case of Inner Lingdingyang), and lower estuary in the Outer Lingdingyang and its adjacent northern shelf waters of NSCS (Fig. 13.1B and Fig. 13.7).

As shown in Figure 13.8, the salinity near Humen Outlet (distance = 0 in Fig. 13.9) was 0–4.2 in the wet season as in the cases of August 2005 (summer) and April 2007 (spring), with the freshwater
Figure 13.8. Surface distributions (≤ 5 m) of salinity, dissolved inorganic carbon (DIC) (μmol kg$^{-1}$), TAlk (μmol kg$^{-1}$), dissolved inorganic nitrogen (DIN, NO$_3$+NO$_2$+NH$_4$) (μmol L$^{-1}$), dissolved inorganic phosphorus (DIP) (μmol L$^{-1}$), and silicate (Si(OH)$_4$) (μmol L$^{-1}$) in the Pearl River Estuary in spring (April 2007) (A), wet season (summer, August 2005) (B), and dry season (winter, February 2004) (C). Data of salinity, DIC, and TAlk in the dry season [February 2004] are from Dai et al., 2006 and Guo et al. 2008. Data of salinity, DIC, and TAlk in the wet season [August 2005] are from Guo et al. 2009. Data of salinity in spring [April 2007] are from Guo et al. 2009.
Figure 13.9. Salinity (A), DIC (μmol kg⁻¹) (B), TAlk (μmol kg⁻¹) (C), DOC (μmol L⁻¹) (D), DIN (μmol L⁻¹) (E), DIP (μmol L⁻¹) (F), and Si(OH)₄ (μmol L⁻¹) (G) vs. distance from Humen along the sampling transects in Lingdingyang sub-estuary during spring (April 2007), summer (August 2005), and winter (February 2004). The broken vertical lines represent the location of Humen. Positive numbers denote downstream and negative values are upstream of Humen. Data of salinity, DIC, and TAlk in the dry season [February 2004] are from Dai et al., 2006 and Guo et al. 2008. Data of salinity, DIC, and TAlk in the wet season [August 2005] are from Guo et al. 2009. Data of salinity in spring [April 2007] are from Guo et al. 2009.
end-member located at \( \sim 20 \) km upstream of Humen, whereas the salinity was \( 10-15 \) in the dry season in February 2004 (winter) when the zero salinity was located at \( \sim 40 \) km upstream of Humen. In the mid-estuary of the Lingdingyang sub-estuary, the spatial distribution of salinity was highly variable between seasons (Figs. 13.8 and 13.9), with high values in winter (\( \sim 15.0-\sim 34.0 \)) as compared with spring (\( \sim 4.0-\sim 20.0 \)) and summer (\( \sim 3.0-\sim 15.0 \)), reflective of the complexity of river discharge and estuarine circulations discussed earlier. In the lower estuary, average salinity was \( 30.0-34.0 \) in the dry season in February 2004, whereas it was \( 15.0-33.0 \) in the wet season in August 2005. The salinity in the lower estuary in spring was between that in summer and winter, with average values of \( 22.0-34.0 \).

The distributions of carbon and nutrients in the PRE and their controls have been examined in a number of studies (e.g., Cai et al. 2004; Zhai et al. 2005; Dai et al., 2006; Dai et al. 2008a; Dai et al. 2008b; Guo et al. 2008; He et al., 2010; Cao et al. 2011; Han et al. 2012; Yin et al. 2012), which are briefly summarized here.

Generally, among the three zones of the PRE, the upper estuary is biogeochemically characterized by extremely high nutrients, notably NH\(_4\), high DOC, and high \( p\text{CO}_2 \), but depleted O\(_2\) (Guo et al. 2009), although a significant seasonal variation occurs (Figs. 13.8 and 13.9). The mid-estuary is dominated by mixing between freshwater and seawater. Consequently, nutrients and DOC behave conservatively or apparently conservatively and display less seasonal variations. In the lower estuary, nutrients and DOC decrease and are controlled by net community production owing to low turbidity.

In the upper estuary, DIC concentration is very high in winter, with the value of \( \sim 2,500 \text{ mol kg}^{-1} \) at the freshwater end-member, and decreases rapidly to \( \sim 1,800 \text{ mol kg}^{-1} \) at \( \sim 25 \) km upstream of Humen. In contrast, in spring and summer, DIC is \( \sim 1,250-2,250 \text{ mol kg}^{-1} \) at \( \sim 40-70 \) km upstream of Humen and with the minimum values of \( \sim 550-1,100 \text{ mol kg}^{-1} \) at \( \sim 25 \) km upstream of Humen. The distribution patterns of TA\(_{\text{alk}}\) are similar to those of DIC, with values of \( \sim 2,146 \text{ mol kg}^{-1} \) in winter and \( 1,560-1,816 \text{ mol kg}^{-1} \) in summer and spring at the freshwater end-member. At \( \sim 25 \) km upstream of Humen, the minimum TA\(_{\text{alk}}\) are 688, 647, and 1,722 \text{ mol kg}^{-1} in spring, summer, and winter, respectively. DOC is also enriched in the upper estuary freshwater end-member as high as \( \sim 480 \text{ mol L}^{-1} \) in all seasons, which might be influenced profoundly by the wastewater input from upstream cities, and decreases rapidly to \( \sim 200 \text{ mol L}^{-1} \) in the vicinity of Humen. The upper estuary also has a very high DIN concentration in the freshwater end-member (760 \text{ mol L}^{-1} at \( 40 \) km upstream of Humen) in winter, but lower concentrations of 570 and 380 \text{ mol L}^{-1} in spring and summer, respectively. A highly variable DIN is observed in summer at \( 30 \) km upstream of Humen, but not in winter, which is apparently influenced by large branch inputs of the East River. A remarkable feature of the Pearl River estuary is that NH\(_4^+\) is the dominant species of inorganic nitrogen. There exists a year-round pattern of dramatic decrease in NH\(_4^+\), increase in NO\(_3^-\), and insignificant change in NO\(_2^-\) in the upper estuary, which is dominated by the nitrification. This process has been elaborated by Dai et al. (2008b) and is not discussed here. DIP is overall at a level of 1.0 \text{ mol L}^{-1} over the wide sampling distance in all seasons, except 3.5 and 5.6 \text{ mol L}^{-1} in freshwater end-member in spring and summer, respectively. Si(OH)\(_4\) concentration is always enriched in the upper estuary in all seasons. In the freshwater end-member, Si(OH)\(_4\) concentrations are \( \sim 179, 165, \) and 85 \text{ mol L}^{-1} in spring, summer, and winter, respectively. Note that there is a Si(OH)\(_4\) peak at \( \sim 30 \) km upstream of Humen, and Si(OH)\(_4\) displays great variable in the upper estuary zone, especially in spring and summer. This might be related to the increasing branch inputs from the East River, whose landscape is granite.
In the mid-estuary of the Inner Lingdingyang, DIC concentration increases from Humen, and is higher in winter, with the value of ~1,900 \( \mu \text{mol kg}^{-1} \), but lower in spring and summer, with the value of ~1,300–1,500 \( \mu \text{mol kg}^{-1} \). Similarly, TAlk also increases from Humen and is higher in winter (~1,900 \( \mu \text{mol kg}^{-1} \)) than that in spring and summer (~1,300–1,600 \( \mu \text{mol kg}^{-1} \)). DOC decreases from Humen to the Inner Lingdingyang and displays an apparently conservative behavior, with concentration in winter slightly higher than that in spring and summer. DIN in the mid-estuary is also controlled by mixing and decreases from ~180–300 \( \mu \text{mol L}^{-1} \) around Humen to ~100–220 \( \mu \text{mol L}^{-1} \) in the Inner Lingdingyang, with higher concentrations in spring and winter. As mentioned previously, DIP remains at the level around 1.0 \( \mu \text{mol L}^{-1} \) in all seasons. Si(OH)\(_4\) decreases from ~140–170 \( \mu \text{mol L}^{-1} \) at Humen to ~60–100 \( \mu \text{mol L}^{-1} \) in the Inner Lingdingyang in spring and summer, and from ~70 \( \mu \text{mol L}^{-1} \) to ~30–40 \( \mu \text{mol L}^{-1} \) in winter.

In the lower estuary, DIC concentration increases downstream, reaching 1,933 \( \mu \text{mol kg}^{-1} \) in spring and 1890 \( \mu \text{mol kg}^{-1} \) in summer. Also, TAlk keeps increasing in the lower estuary, with the values of ~2,210–2,280 \( \mu \text{mol kg}^{-1} \) in all seasons. DOC continues decreasing to 80–100 \( \mu \text{mol L}^{-1} \) at the downstream 100 km away from Humen. DIN decreases rapidly to below ~50–100 \( \mu \text{mol L}^{-1} \) in all seasons. DIP is still at the level of 1.0 \( \mu \text{mol L}^{-1} \) in all seasons. Si(OH)\(_4\) decreases from ~60–100 \( \mu \text{mol L}^{-1} \) in the Inner Lingdingyang to 2.5–30 \( \mu \text{mol L}^{-1} \) in the Outer Lingdingyang in spring and summer, and from ~30–40 \( \mu \text{mol L}^{-1} \) to 6.9 \( \mu \text{mol L}^{-1} \) in winter.

2.2.4. Conceptual summary and about the mixing behavior: Conservative and nonconservative PRE is such a complex estuarine system that the application of the classic two-end member mixing model should be done with caution. When taking into account the mixing scheme in the upper estuary (upstream of Human), the East River has distinct end-member values (e.g., of DIC/DOC) because of the drainage characteristics and the different extent of the local material sources (see Table 13.1 and description in Section 2.1.1). As a result, the mixing curve in the upstream of Humen should adopt a three end-member mixing scheme. An example of this has been demonstrated by Guo et al. (2008), which considers the highly variable end-member concentrations apparently influenced by different tributaries with different drainage basin chemistry and anthropogenic influences.

When considering the mixing scheme downstream of Humen, in particular in the mid-estuary, a two-end member mixing model may be applicable depending on the target chemical elements, which may or may not be different in other outlets, all of which discharge into the Lingdingyang. In this mixing dominated zone, most of the chemical parameters appear to be conservative at salinity >5 in winter. In summer, biological uptake of nutrients (DIN and Si(OH)\(_4\)) and DIC occurs in the outer estuary and inner shelf areas where salinity is 12–25 as indicated by the nonconservative mixing line and higher DOC concentration (Fig. 13.10).

2.3. Northern South China Sea Shelf

2.3.1. Basics

The shelf over NSCS stretches from the northwest to the southeast of mainland China and from the coast to roughly the 200 m isobath with an area of about 1.2 \( \times 10^6 \) km\(^2\) (Fig. 13.1C). The shelf
Figure 13.10. Salinity distributions of DIC ($\mu$mol kg$^{-1}$) (A), TAlk ($\mu$mol kg$^{-1}$) (B), DOC ($\mu$mol L$^{-1}$) (C), DIN (N+N: NO$_3$+NO$_2$) ($\mu$mol L$^{-1}$) (D), DIP ($\mu$mol L$^{-1}$) (E), and Si(OH)$_4$ ($\mu$mol L$^{-1}$) (F) in the Pearl River Estuary. Dashed lines indicate the conservation mixing line in summer. Data of salinity, DIC, and TAlk in the dry season [February 2004] are from Dai et al., 2006 and Guo et al. 2008. Data of salinity, DIC, and TAlk in the wet season [August 2005] are from Guo et al. 2009. Data of salinity in spring [April 2007] are from Guo et al. 2009.
topography in the NSCS is characterized by the complex coastline variation in the nearshore region and by the existence of a prominent eastward widened shelf formed by an abrupt offshore extension of isobaths east of the PRE and bounded by the 50 m isobath at its southern edge (Fig. 13.1C). A shallow bank, the Taiwan Shoals, is located between the 50-m isobath in the south and the 30-m isobath in the north at the eastern end of the widened shelf. Shelf circulation over the NSCS is mainly dominated by monsoonal wind-driven shelf circulation over the unique variable shelf topography (Gan et al. 2009a) and under the influence of buoyancy from river plume (Gan et al. 2009b).

2.3.2. Shelf circulation in the northern South China Sea

2.3.2.1. Upwelling circulation in summer (wet season)

In summer, coastal upwelling driven by strong prevailing southwesterly monsoon winds occurs over the near-shore NSCS (Gan et al. 2009a) and interplays with the buoyant river plume (Gan et al. 2009b) in the wet season. These two physical processes largely shape the nutrient dynamics and influence phytoplankton growth and the associated biological production (Gan et al. 2010; Cao et al. 2011; Han et al. 2012).

The coastal upwelling circulation in the NSCS is characterized by a strong upwelling jet regulated by the variable isobaths and coastline over the shelf with water depth less than 50 m (Fig. 13.11A). A distinct intensified upwelling occurred as a result of the unique widened shelf topography east of PRE at 115.5°E, as shown by the amplified alongshore current and associated cross-isobath transport at depths from a numerical simulation (Gan et al. 2009a). It is noteworthy that the intensified upwelling
over the widened shelf is a common phenomenon occurring to many shelf seas around the world, which may invoke the geostrophically amplified shoreward advection of dense deep waters over the widened shelf and strong and efficient upslope dense water advection in the bottom boundary layer by the converging isobaths at the head of the widened shelf.

The intensified cross-isobath transport at depths also existed near the entrance of PRE and at the lee of Hong Kong Island arising from local topographic effect (Gan and Allen 2002). These hotspots of intensified upwelling circulation shaped the river plume over the shelf east of PRE and enhanced the estuary (or bay)-shelf exchange rate.

2.3.2.2. Downwelling circulation in winter (dry season)

Forced by northeasterly monsoon during winter, or the dry season, the surface currents over the shelf direct southwestward, roughly following the shelf topography as a result of geostrophy (Fig. 13.11B). With the bottom frictional effect and the effect arising from the flow-topography (effect) interaction (Gan et al. 2009a, 2013), the current near the bottom deviated from the isobaths and directed seaward. Relatively strong seaward cross-isobath transport existed at the head of the widened shelf at 115.5°E and in the waters off PRE. Similar to the conditions in summer, the alone-shore component of downwelling circulation controlled the fate of the plume in both near and far fields after river water exited the estuary. The cross-shore component, particularly in the places where its magnitude was amplified, tended to move waters at depths over the inner shelf seaward and suppressed seaward expansion of the river plume in the surface.

3. Physical dynamics and biogeochemistry of the plume

3.1. Plume over the Shelf

The Pearl River freshwater exits the PRE and forms a river plume over the broad continental shelf in the northern part of the SCS. The nature of the plume over the shelf is governed by its intrinsic dynamics as well as by the wind-driven circulation over the shelf.

The plume first formed a bulge after leaving the estuary. In the absence of the coastal current, the bulge expanded seaward and reached a quasi-stationary when the total freshwater from the river discharge and in the bulge balanced each other. It generated a positive surface elevation anomaly and isohaline. The plume attached the coastline when the river discharge was small or overshot into the open shelf water when the discharge was large. It touched with the bottom in the near field or stayed in the upper part of the water column in the far field, respectively. Plume often propagated like a first mode baroclinic wave that resulted from the density difference between the river and seawater, as described by inviscid theory (Chao and Boicourt 1986; Garvin 1987; Rennie et al. 1999). In PRE, the plume is, however, subject to the control of earth rotation, tides, and wind-driven coastal circulation (Zu et al. 2008; Gan et al. 2009b).

After entering the shelf, the discharge moved westward under the Coriolis force, forming a freshwater bulge at the western side of the estuary entrance, when the coastal current was weak or absent. The plume re-hugged the coastline as it moved westward and tended to form an anti-cyclonic circulation (Zu et al. 2008). The structure of the plume can be greatly modified by the tidal forcing. The
seaward movement of the plume was deterred under the influence of tide, leading to more freshwater piling up at the head of the PRE, and forming a larger surface tilt (Fig. 13.5). The associated seaward pressure gradient increases and contributes to the formation of a stronger southward moving jet in the upper part of the estuary.

Over the shelf off PRE, the strongest forcing that controls the plume is the wind-driven coastal circulation. The plume swung westward and eastward during the wet and dry seasons, respectively (Figs. 13.11C and 13.11D). In the dry season, the co-effect of rotation and wind-driven current confined the plume to the western side of the estuary. Inside this strong and slender plume, the advection term was comparable to the Coriolis term, as the current is highly nonlinear, with a large value of the ratio of relative vorticity to planetary vorticity ($\zeta/f$) (Zu and Gan 2008). The river plume reached Hainan Island under the northeasterly driven shelf current (Fig. 13.11B). In the wet season, strong river discharge generated a strong plume and extended over a large area in the NSCS. It yielded a bulge of plume water near the entrance of the estuary and extended westward when upwelling wind relaxed or reversed direction. A fraction of the plume emanated from the outer part of the bulge, detached from the coast and the bottom, advected eastward with its central axis approximately directed 22.1°N over the shelf, and gradually turned toward the offshore side of the upwelling jet (Fig. 13.11C). It formed a widening and deepening buoyant plume over the shelf.

Unlike the plume in the absence of the coastal current, the freshwater in the outer part of the bulge flows downstream at the speed of the current (Gan et al. 2009b), rather than the first baroclinic wave as in Chao and Boicourt (1986) or Rennie et al. (1999). In this plume-current system, the fraction of the discharged freshwater volume accumulated in the bulge reached a steady state, and the volume of newly discharged freshwater was transported downstream by the upwelling current. There was no further plume water accumulation in the bulge afterward, and all newly discharged freshwater advected downstream. The coastal current was close enough to the bulge at the entrance of the PRE that it limited the growth of the bulge (Gan et al. 2009b). With the existence of wind-driven currents in the ambient coastal water, the fate and characteristics of the plume, as well as the currents, were controlled by the interaction between the plume and wind-driven circulation.

### 3.2. Plume effect on the shelf circulation

The coastal current is profoundly influenced by the stratification in the water column (Allen et al. 1995; Lentz 2001). With the increase of vertical stratification by the plume, the mixed layer thins, and the role of wind stress in the surface Ekman layer is enhanced. As a result, the intensity of surface alongshore currents and cross-shelf circulation is amplified, whereas the coastal wind-driven jet is located farther from shore.

The modulation of upwelling circulation by the buoyant plume over the NSCS shelf during the wet season can be seen from numerical results (Fig. 13.11C) obtained on day 30, with the model being forced with an upwelling favorable wind (Gan et al. 2009b). The less dense plume water and the seawater formed density fronts at the lateral edges of the plume, particularly on its northern flank, where the upwelled dense water over the inner shelf met the lighter plume water offshore. Enhancement of stratification by the plume thinned the surface frictional layer and enhanced the cross-shelf circulation in the upper water column such that the surface Ekman current and compensating
3. Physical dynamics and biogeochemistry of the plume

Net surface velocity vectors (m s\(^{-1}\)) and alongshore velocity (color contours, m s\(^{-1}\)) induced by river plume 30 days after the onset of upwelling. The red and blue contour lines are the 30 m and 50 m isobaths, respectively.

Figure 13.12. The simulated result of net surface velocity vectors (m s\(^{-1}\)) and alongshore velocity (color contours, m s\(^{-1}\)) induced by river plume 30 days after the onset of upwelling. The red and blue contour lines are the 30 m and 50 m isobaths, respectively.

flow beneath the plume were amplified, whereas the shoaling of the deeper dense water in the upwelling region changed minimally (Gan et al. 2009b). The pressure gradient generated between the buoyant plume and ambient seawater accelerated the wind-driven current along the inshore edge of the plume but retarded it along the offshore edge (Fig. 13.12).

During the dry season, the buoyant water attached along the coastline west of PRE and was expected to enhance the westward coastal current. Zu and Gan (2008) found that the co-effect of the river buoyancy and the surface Ekman transport generated a larger cross-shelf pressure gradient and resulted in a much stronger coastal current over the shelf off PRE in the dry season. Consequently, the magnitudes of the saltier water inflow on the eastern side and the freshwater outflow on the western side of the estuary were strengthened.

3.3. Biogeochemistry of the river plumes

The Pearl River plume has a profound impact on the biogeochemistry of the NSCS, primarily owing to the abundant nutrients that the plume carries to the shelf system. As being examined, the scale of the plume is clearly determined by the runoff in the upper stream, whereas the spatial pattern of the plume on the shelf is modulated by the shelf circulation manifested particularly by the upwelling.

The southwestern (SW) monsoon typically begins in April–May, and is followed by a rainy season, when potential river plumes may be formed under flood upstream. Here we present two cases studies of the Pearl River plume and its impact on the nutrient and carbon biogeochemistry. The first case is under relatively low river discharge observed in the PRE and the NSCS in May 2001 (see details in Dai et al. 2008a). In May 2001 (Fig. 13.2C), SW winds on May 1, 6–8, 13–14, and 19–22 induced significant precipitation on May 1–4, 8–9, 16–18, and 21–22. River discharge recorded showed a steady increase from 8,000 m\(^3\) s\(^{-1}\) to as high as ~20,000 m\(^3\) s\(^{-1}\). Another case is in summer of 2008 (Fig. 13.2C); as detailed in Han et al. (2012), continuous heavy rain caused water discharge peaked at ~43,000 m\(^3\) s\(^{-1}\) on June 16 and was down to ~22,000 m\(^3\) s\(^{-1}\) on July 15. Such river discharges were
Figure 13.13. MODIS color index (CI) in the Pearl River estuary in May 2001 showing the daily average on May 5 (A), 7 (B), 12 (C), and 14 (D), 2001. This color index represents the MODIS ocean color derived empirically. The approach has applicability even under severe sun glint. The color index is significantly correlated with Chl \( a \). See details in Hu (2011).

much higher than the annual mean water discharge of about 6,700 m\(^3\) s\(^{-1}\), or the monthly long-term average value of \( \sim 14,000 \) m\(^3\) s\(^{-1}\) from June to August.

### 3.3.1. Case of May 2001

Figure 13.13 shows the average MODIS ocean color index (CI) in PRE and in the adjacent SCS on May 5, 7, 12, and 14, 2001, which clearly suggests that the Pearl River plume stretched from the PRE and flowed southwestward. Notably, the plume expansion can be observable from the images of May 12 and 14 as compared with that on May 7. This is consistent with the field observation on May 8–9 (Fig. 13.2, see Fig. 2 in Dai et al. 2008a), suggesting again the plume development following the high precipitation upstream. The plume clearly brought a significant amount of nutrients into the region, as demonstrated by an increase in inorganic nitrogen concentration. At the river end during the survey, high Si(OH)\(_4\) (\( \sim 150 \) μmol L\(^{-1}\)) and NO\(_3\) (75–120 μmol L\(^{-1}\)) concentration were observed at levels very similar to those observed during summertime measurement (Figs. 13.8 and 13.9). The consequence of such delivery of nutrients was the phytoplankton bloom observed associated with the river plume. For example, a several-fold increase (from \( \sim 0.1–0.2 \) mg m\(^3\) to a maximum level of 1.8 mg m\(^3\), an order of magnitude higher than pre-bloom conditions) in biomass (Chl \( a \)) was observed. In addition to increased Chl \( a \), significant drawdown of pCO\(_2\) from \( \sim 350 \) to \( \sim 200 \) μatm,
biological uptake of DIC (decreased from $\sim 1,660$ to $\sim 1,500–1,560$ $\mu$mol kg$^{-1}$), and associated enhancement of DO (saturation from $\sim 95\%$ to $\sim 120–130\%$) and pH ($\sim 8.2–8.6$) were also observed.

Net DIC drawdown associated with the plume-induced bloom was assessed to be of 100–150 $\mu$mol kg$^{-1}$ and TAlk increase of 0–50 $\mu$mol kg$^{-1}$ (from $\sim 2,030–2,080$ to $\sim 2,030$ $\mu$mol kg$^{-1}$). For an average surface water depth of 5 m, a very high apparent biological CO$_2$ consumption rate (net community production, NCP) of 70–110 mmol m$^{-2}$ d$^{-1}$ was estimated. This value is 2–6 times higher than the estimated air-sea exchange rate ($\sim 18$ mmol m$^{-2}$ d$^{-1}$). POC concentrations in the surface waters reached 30–40 $\mu$mol L$^{-1}$, which was also an order of magnitude higher than the value in the pre-bloom period of $\sim 5$ $\mu$mol L$^{-1}$.

3.3.2. Case of August 2008

Following a continuous heavy rain in the upstream Pearl River as described previously, a strong plume that extended more than 300 km from the PRE mouth in summer 2008 was observed according to the temperature and salinity distributions (Fig. 13.14). This plume area was characterized by high nutrient concentrations ($\sim 0.1–14.2$ $\mu$mol L$^{-1}$ for DIN, $\sim 0.02–0.10$ $\mu$mol L$^{-1}$ for DIP, and $\sim 0.2–18.9$ $\mu$mol L$^{-1}$ for Si(OH)$_4$) and by low DIC (<1740 $\mu$mol kg$^{-1}$) and TAlk (<2010 $\mu$mol kg$^{-1}$).

In contrast, the near shore area (upwelling) had high nutrients (0.8–6.4 $\mu$mol L$^{-1}$ for DIN, $\sim 0.20–0.37$ $\mu$mol L$^{-1}$ for DIP, and 5.7–19.2 $\mu$mol L$^{-1}$ for Si(OH)$_4$) and high DIC and TAlk (higher than $\sim 1940$ $\mu$mol kg$^{-1}$ and $\sim 2210$ $\mu$mol kg$^{-1}$) apparently sourced from subsurface nutrient-replete waters through wind-driven coastal upwelling, higher than those in the outer shelf surface seawater. The consequence of biomass contributed by nutrient-enriched plume and upwelling was also significant, which was expatiated in Cao et al. (2011) and Han et al. (2012).

3.3.3. Comparison between 2001 and 2008

To put the preceding two cases into comparison, we see the similarity in between in terms of the precipitation-initiated enhanced river discharge and the subsequent river plumes formed. Table 13.2 demonstrates that the discharge of the Pearl River determined the river plume intensity (plume expansion). For example, the much higher river discharge in 2008 (Fig. 13.2C) induced a much larger plume extension away from the PRE mouth relative to that in 2001. However, the concentrations of nutrients, DIC, and TAlk in both cases were similar around the Pearl River plume bulge under
Table 13.2. Comparison of the river plume between 2001 and 2008

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Discharge (m$^3$ s$^{-1}$)</td>
<td>8,000 – ~20,000</td>
<td>peaked at ~43,000 and was down to ~22,000</td>
</tr>
<tr>
<td>Plume direction/extension</td>
<td>southwest</td>
<td>northeast</td>
</tr>
<tr>
<td>Plume area/extent</td>
<td>~109 km away from the PRE mouth</td>
<td>~400 km away from the PRE mouth to the southern Taiwan Strait</td>
</tr>
<tr>
<td>Nutrient</td>
<td>NO$_3^-$: 75–120 μmol L$^{-1}$ at the river end</td>
<td>NO$_3^-$+NO$_2^-$: from ~100 μmol L$^{-1}$ at near null salinity to ~8.0–1.5 μmol L$^{-1}$ at the river mouth</td>
</tr>
<tr>
<td>(Carbon) DIC/TAlk (μmol kg$^{-1}$)</td>
<td>DIC: ~1,660 – ~1,500–1,560; TAlk: ~2,030 – ~2,030–2,080</td>
<td>DIC: &lt;1,740; TAlk: &lt;2,010</td>
</tr>
<tr>
<td>NCP (mmol C m$^{-2}$ d$^{-1}$)</td>
<td>~70–110</td>
<td>~36±19</td>
</tr>
</tbody>
</table>

Data are from Dai et al. (2008) for the case of 2001, and from Cao et al. (2011) and Han et al. (2012) for the case of 2008.

**Different discharge conditions.** Nevertheless, the conservation of these chemical parameters might be variable in upper-mid-estuary during flood and/or after flood period in wet seasons, which has been illustrated by Han et al. (2012). In addition, the directions of the plume extension were different in the two cases.

Biological responses to both plume cases were also significant. However, the NCP value in the case of 2008 was much lower than in May 2001 on the NSCS shelf. This is primarily related to the plume extension. The location of the plume-induced bloom observed in the May 2001 case was limited to nearshore at the mouth of the PRE, whereas significant DIC removal extended to the far reaches of the plume in the 2008 case (Cao et al. 2011). In addition, the river plume in summer of 2008 was additionally impacted by the coastal upwelling over the NSCS shelf (see later).

### 4. Coupling the physical dynamics and biogeochemistry

Deconvolution of physical dynamics and biogeochemistry in complex systems such as river plumes is not an easy task, in particular when quantitative assessment is to be made. Numerical modeling is certainly a sophisticated approach that heavily relies on the rightness of the physical dynamics that the model can resolve. Alternatively, mass-balance–based end-member mixing model is a relatively straightforward way to use as far as the end-member values can be defined and quantified (Cao et al. 2011; Han et al. 2012). Here we first demonstrate how to establish the end-member mixing between different water masses and its subsequent application to quantify the biologically mediated processes.

#### 4.1. Mixing of different water masses

The mixing model used to differentiate biogeochemical rates on top of conservative physical mixing between different water masses involves essentially water masses and their end-member concentrations of targeted chemicals, estimation of concentrations under conservative mixing without biogeochemical alteration, and finally comparing the difference between the predicted concentrations
4. Coupling the physical dynamics and biogeochemistry

Figure 13.15. (A) The potential temperature ($\theta$) ($^\circ$C) vs. salinity scheme in the northern South China Sea (NSCS) collected from the conductivity-temperature-depth recorder per meter dataset in the whole water column (redrawn from Shu et al. 2011 and Han et al. 2012). $\theta$–S plots exhibit three water masses: river plume, SCS surface water, and SCS subsurface water. Biological mediated dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^-$) ($\Delta \text{DIN}$) ($\mu$mol L$^{-1}$) (B) and biological mediated dissolved inorganic carbon ($\Delta \text{DIC}$) ($\mu$mol kg$^{-1}$) (C) vs. salinity in coastal upwelling and in river plume (D, E) on the NSCS shelf in summer 2008. Data in Panels B, D were collected from Han et al. 2012; Panels C, E were redrawn from Cao et al. 2011).

and actually measured concentration, which estimates the biogeochemical alteration of the targeted chemicals.

First, we have to identify the water masses that can be easily derived based on the $\theta$–S (potential temperature-salinity) diagram. Taking the summer 2008 case as an example (Fig. 13.15A), we identified three primary water masses, namely, plume water, surface SCS water, and subsurface SCS water. Second, based on the mass balance equations for potential temperature, salinity, and the water
fractions originating from the three end-members, we may resolve the fractional contribution of each water mass and predict nutrient or carbon concentrations if no biogeochemical alteration occurred to the system. The mass balance equations are as follows:

\[ \theta_{RI} F_{RI} + \theta_{SW} F_{SW} + \theta_{SUB} F_{SUB} = \theta_{in situ} \]  
\[ S_{RI} F_{RI} + S_{SW} F_{SW} + S_{SUB} F_{SUB} = S_{in situ} \]  
\[ F_{RI} + F_{SW} + F_{SUB} = 1 \]  

where \( \theta_{in situ} \) and \( S_{in situ} \) represent the potential temperature and salinity in the samples; the subscripts \( RI, SW, \) and \( SUB \) denote the three different sources: Pearl River plume, the SCS surface water, and the subsurface water; and \( F_{RI}, F_{SW}, \) and \( F_{SUB} \) represent the fractions in the in situ water samples contributed by the three end-members, which were calculated from the potential temperature and salinity.

The conservative nutrient concentrations of DIN (DIN\(^{o}\)), DIP (DIP\(^{o}\)), and Si(OH)\(_4\) (Si(OH)\(_4\)^{o}) and DIC (DIC\(^{o}\)) by mixing of the end-members can then be derived as:

\[ \text{DIN}^{o} = \text{DIN}_{RI} F_{RI} + \text{DIN}_{SW} F_{SW} + \text{DIN}_{SUB} F_{SUB} \]  
\[ \text{DIP}^{o} = \text{DIP}_{RI} F_{RI} + \text{DIP}_{SW} F_{SW} + \text{DIP}_{SUB} F_{SUB} \]  
\[ \text{Si(OH)}_{4}^{o} = \text{Si(OH)}_{4RI} F_{RI} + \text{Si(OH)}_{4SW} F_{SW} + \text{Si(OH)}_{4SUB} F_{SUB} \]  
\[ \text{DIC}^{o} = \text{DIC}_{RI} F_{RI} + \text{DIC}_{SW} F_{SW} + \text{DIC}_{SUB} F_{SUB} \]  

where \( \text{DIN}_{RI}, \text{DIN}_{SW}, \text{DIN}_{SUB}, \text{DIP}_{RI}, \text{DIP}_{SW}, \text{DIP}_{SUB}, \text{Si(OH)}_{4RI}, \text{Si(OH)}_{4SW}, \text{Si(OH)}_{4SUB}, \text{DIC}_{RI}, \text{DIC}_{SW}, \) and \( \text{DIC}_{SUB} \) are the concentrations of the three end-members for DIN, DIP, Si(OH)\(_4\), and DIC.

Third, we may calculate the difference between the prediction based on conservative mixing and the field-measured values denoted as \( \Delta \), which reflected the amount of nutrients produced (negative) or removed (positive) associated with biological processes:

\[ \Delta \text{DIN} = \text{DIN}^{o} - \text{DIN}_{in situ} \]  
\[ \Delta \text{DIP} = \text{DIP}^{o} - \text{DIP}_{in situ} \]  
\[ \Delta \text{Si(OH)}_{4} = \text{Si(OH)}_{4}^{o} - \text{Si(OH)}_{4_{in situ}} \]  
\[ \Delta \text{DIC} = \text{DIC}^{o} - \text{DIC}_{in situ} \]  

where \( \text{DIN}_{in situ}, \text{DIP}_{in situ}, \text{Si(OH)}_{4_{in situ}} \), and \( \text{DIC}_{in situ} \) represent the nutrient concentrations measured during the cruise.

Based on the preceding model estimation, we derived that most of the \( \Delta \text{DIN} \) and \( \Delta \text{DIP} \) in coastal upwelling are positive, suggesting DIN and DIP consumption during the up-slope advection of the subsurface water from a depth of \( \sim 100 \) m until it outcropped nearshore (Fig. 13.15B, \( \Delta \text{DIP} \) is not shown here). However, a few negative \( \Delta \text{DIN} \) and \( \Delta \text{DIP} \) along the coast likely indicated DIN and
4. Coupling the physical dynamics and biogeochemistry

DIP additions sourced from organic matter degradation. Such regenerated DIN and DIP might have been consumed very quickly by phytoplankton given the oligotrophic nature of the ambient water, the process of which was however difficult to elucidate. We may further estimate the net community production based on the $\Delta$DIN in coastal upwelling to be $54\pm24$ mmol C m$^{-2}$ d$^{-1}$.

In the plume regions, overall $\Delta$DIN and $\Delta$DIP were positive, indicating net biological uptake (Fig. 13.15D). Based on the modeled consumption of individual nutrients, the nutrient uptake ratio was 16.7 in coastal upwelling area and agreed well with the classic Redfield ratio, and was $61.3\pm8.7$ in river plume, which an alternative non-DIP source likely contributed (see Fig. 10 in Han et al. 2012).

$\Delta$DIC in coastal upwelling displayed the combination of DIC addition and uptake along the upwelling current (Fig. 13.15C), indicating two processes of DIC regeneration and biological consumption. In addition, for stations involved in Shantou upwelling region during the entire sampling period, the average $\Delta$DIC value was $8\pm9$ $\mu$mol kg$^{-1}$, and the consequent NCP for upwelled waters on the NSCS shelf was estimated to be $23\pm26$ mmol C m$^{-2}$ d$^{-1}$. Positive $\Delta$DIC in river plume were observed, indicating the exclusively biological removal of DIC (Fig. 13.15E). The $\Delta$DIC displayed an overall trend decreasing with the increasing salinity, and the consequent NCP for the river plume was $36\pm19$ mmol C m$^{-2}$ d$^{-1}$. $\Delta$Si(OH)$_4$ displayed similar behaviors to that of $\Delta$DIC (see Figs. 8 and 9 in Han et al. 2012). We also found that both the DIC-derived NCP and nutrient-derived production were very well agreed in between and also were comparable to the primary production arrived at using numerical simulations (Gan et al. 2010), which suggests that our three end-member mixing model was able to estimate the biological alteration on top of the physical mixing between different water masses.

Taking together the physical dynamics and the simple mass balance, we were able to come up with the following mechanistic understanding of carbon and nutrients in such a complex system under the influence of both river plumes and coastal upwelling (Fig. 13.16). The upslope advection of subsurface waters intensified the cross-shelf advection off Shanwei and then subsequently transported northeastward by the upwelling coastal current and outcropped at the lee of the coastal cape off Shantou. Pearl River plume enhanced upwelling wind-driven current near surface, whereas it was advected eastward. Among these physical processes, organic matter appeared to be remineralized, and DIC and nutrients were regenerated along with the upslope advection of subsurface waters toward Shanwei. In the inner shelf along the upwelling coastal current from Shanwei to Shantou, there appeared a northward enhancement trend of DIC and nutrient consumption rates, although regeneration and consumption of DIC and nutrients (notably for Si(OH)$_4$) coexisted. DIN and DIP consumption followed the Redfield stoichiometry. In the plume areas, net consumption of nutrients and DIC were obvious, with an apparent non-Redfield DIN:DIP uptake ratio (Han et al. 2012).

4.2. Coupled physical-biogeochemical model

With a coupled three-dimensional physical model and a nitrogen-based dissolved inorganic nitrogen, phytoplankton, zooplankton, and detritus (NPZD) ecosystem model and field measurements, Gan et al. (2010) conducted a process-oriented study of the biological response to upwelling and
Pearl River plume in the NSCS during the wet season. They identified the two high chlorophyll centers that are typically observed over the NSCS shelf and stimulated by nutrient enrichment from intensified upwelling over the widened shelf and from the river plume. The nutrient enrichment has strong along-shore variability involving the variable cross-isobath nutrient transport between the middle and the inner widened shelf during the upwelling and an eastward expansion of the nutrient-rich plume. Only a relatively small portion of upwelled nutrient-rich deep water from the outer shelf reaches the inner shelf, where algal blooms occur. Nutrient enrichment in the plume stretches over a broad extent of the shelf and produces significant biomass on the NSCS shelf. The spatial dislocation and temporal variation of NO₃, phytoplankton (P), and zooplankton (Z) biomasses are found in the plume waters, in which Z and N have the largest and the smallest eastward and seaward extensions with P stays between them, respectively. This is jointly controlled by the eastward advection of the plume and by the different growth rates and growth time lag in P and Z.

Frequently observed subsurface chlorophyll maximum (SCM) contributes substantial biomass to the waters over the continental shelf of the NSCS. Based on the coupled physical-biological numerical model and validated by field measurements, Lu et al. (2010) showed the influences of physical forcing processes, the upwelling circulation and plume, on the SCM. They found that the depth and intensity
of the SCM are spatially variable regulated by the variable upwelling circulation and associated plume distribution over the NSCS shelf. Cross-shore component of upwelling circulation shoals and weakens the SCM toward the coast as a result of the upwelling of high-nutrient, low-chlorophyll deep water. The enhanced upwelling-favorable wind weakens the intensity of the SCM due to dilution by the enhanced mixing. In the vast region of NSCS that is covered by the plume, the SCM weakens because of the substantial reduction of photosynthetic active radiation (PAR) in the water column beneath the plume.

5. Summary and perspectives

We have demonstrated in this chapter that river discharge, wind forcing, tides, gravitational circulation, and shelf current intrusion jointly govern the circulation and water mass properties in the PRE, which largely regulates the physical and biogeochemical characteristics of freshwater discharged onto the continental shelf or of the plume in the NSCS. The motion of the plume and thus the cross-gradient material transport over the shelf are determined by plume dynamics of density front and stratification effect on the frictional transport, besides by the predominant wind-driven circulation. Therefore, the biogeochemical characteristics and evolutions in the PRE plume over the shelf are the synthesized response of biogeochemical dynamics in the plume and in the ambient shelf water to the physical forcing dynamics of the time-dependent, three-dimensional shelf circulation in the NSCS.

The dynamics of the Pearl River plume have predominant roles in stimulating primary production in the NSCS through delivery of a large quantity of nutrients into the shelf system otherwise oligotrophic in nature. We also demonstrated the approaches to differentiate the biogeochemical rate on top of complex physical dynamics of plume systems, which are often superimposed with many other coastal processes. One of the typical schemes is the coastal upwelling, which is often observable in the western boundary under southwest monsoon. We have shown that the plume is a very efficient reactor for biogeochemical processes as seen by high nutrient and inorganic carbon consumption rates, which apparently supported the enhanced biological productivity.

Site-specifically, coupled physical-biogeochemical processes have been much less studied for the river plume in other seasons in this particular system, for example, in the winter time. What is basically known is that the Pearl River plume is much less prominent in the dry season, when the northeastern monsoon prevails, which modulates the plume to the western part of the estuary.

Although this chapter has emphasized the interactive physical and biogeochemical processes, we must point out that the PRD has been one of the most rapid developing regions in the world during the past 30 years. As a consequence, the PRE has been experiencing intense anthropogenic disturbance (see also Chapter 11). For example, the PRE currently receives an annual wastewater discharge of recently \( \sim 5,000 \times 10^6 \) ton yr\(^{-1} \) from upstream cities such as Guangzhou, Foshan, and Dongguan (see the Environmental Status Bulletins of Guangdong Province, China: [www.gdepb.gov.cn](http://www.gdepb.gov.cn/)). Agricultural activities have given rise to increasingly high levels of pollution from fertilizers and pesticides. Associated with these waste/fertilizer discharges, the nutrients and inorganic carbon system might be greatly influenced in the lower reaches of the estuary, even to the NSCS shelf through the river plumes and estuary-shelf circulation, the effect of which on the shelf ecosystem system has however never been carefully examined. Added in more complexity is global change, which may
well be reflected in regional changes in temperature, CO$_2$, and circulation, the effect of this global scale multiple drivers are yet to be assessed for the PRE and NSCS regions.

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References

References


