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Received: 28 January 2000

Amended: 30 June 2000

Accepted: 23 August 2000

Limnol. Oceanogr., 45(8), 2000, 1871–1878
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Evidence of trace metal limited photosynthesis in eutrophic estuarine and coastal waters

Abstract—Based on field observations and incubation experiments, this study provides evidence that trace metal limited (e.g., Fe) photosynthesis may function in eutrophic coastal waters. In the Zhujiang (Pearl River) Estuary and the adjacent coastal area, analyses of water samples indicate that phytoplankton photosynthesis is apparently phosphorus limited in the freshwater and upper estuary and nitrogen and/or silica limited in the coastal waters farther offshore. The incubation experiments using in situ water samples show, however, that in both cases photosynthesis can be enhanced by addition of trace elements (e.g., Fe and Cu). This is presumably because exogenous influx of major plant nutrients has skewed the primary production toward trace-element limitation, which in turn limits the increase in chlorophyll biomass and full consumption of major nutrients in eutrophic coastal waters as compared to the nutrient-poor oligotrophic open ocean.

Recent studies have shown that addition of trace amounts of iron may dramatically increase photosynthesis in the open ocean, at both the equator and high latitudes (e.g., Martin and Fitzwater 1988; De Baar et al. 1995; Coale et al. 1996a,b; Takeda 1998), and in coastal high nutrient and low chlorophyll (HNLC) upwelling regions (Hutchins and Bruland 1998). If such an Fe-limited photosynthesis is an important mechanism that regulates the marine autotrophic production and associated draw-down of atmospheric CO₂, a fundamental challenge is to characterize the variability of Fe limitation along the nutrient gradients between the eutrophic coast (including estuaries) and the interior of the ocean.

The coastal ocean is nutrient enriched and has altered nutrient ratios as a result of changed riverine input due to land-use change and anthropogenic nutrient emission over the last century (Nixon 1995; Paerl 1997). Coastal water ecosystems respond to such changes in nutrient budgets by shifting population dynamics of phytoplankton and hence of the rest of the food web, leading to changes in top-down as well as bottom-up control of community structures (Landry et al. 1997). Current research on coastal eutrophication largely concerns the response to the increased plant nutrient (N, P, and Si) loadings from land, and trace metals (e.g., Fe) are usually considered to be in excess in coastal waters due to natural weathering and, most recently, pollution drainage from land source (De Jonge et al. 1994; Pelley 1998). In

eutrophic coastal waters, photosynthesis is traditionally believed to be limited by one of the major plant nutrients (e.g., N or P) due to a distorted nutrient ratio and enhanced influx (Turner and Rabalais 1994; Humborg et al. 1997). Trace metal limitation (e.g., Fe) in coastal waters has only received attention in recent years (cf. Sunda and Huntsman 1995; Schmidt and Hutchins 1999; Wells 1999). Evidence from the Zhujiang (Pearl River) Estuary and South China Sea indicates, however, that trace-metal-fertilized photosynthesis could be an important feature of eutrophication in coastal waters. Our conceptual model of coastal eutrophication should consider the potential impacts of trace elements as additional regulators of phytoplankton production and community composition.

The Zhujiang (Pearl River) is the largest river draining South China. It discharges 350×10^9 m³ yr⁻¹ of freshwater with a sediment load of 85×10^6 tons yr⁻¹ into the South China Sea (Fig. 1). The land use of the drainage area is very complex, including agriculture over the whole watershed plus urban activities in the lower reaches and delta region (e.g., Guangzhou, Hong Kong, and Macao). The adjacent coastal area (21.5–23°N, 112.5–114.5°E) is eutrophic, with elevated riverine nutrient inputs, i.e. 60–100 μM for DIN (DIN = NO₃⁻ + NO₂⁻ + NH₄⁺), 0.5–1.0 μM for phosphate, and 100–150 μM for dissolved silica (H₂SiO₃), respectively, into the South China Sea via eight channels/streams of the Zhujiang (Zhang et al. 1999).

The estuary of the Zhujiang (the Lingdingyang) is characterized by a microtide: the tidal range is 1–2 m with current of 1–2 m s⁻¹. The high salinity water enters the Lingdingyang from the southeastern side (i.e., Hong Kong), whereas the freshwater effluents from various channels move southward mainly via the western part of Lingdingyang (Fig. 1). The residual current shows a counterclockwise pattern, with a surface velocity of 10–30 cm s⁻¹ (Zhang et al. 1999).

This study attempts to increase understanding of nutrient dynamics in the Zhujiang Estuary in relation to photosynthesis and eutrophication of the South China Sea. The knowledge was gained from cruises in the wet (August–September 1996) and dry (January–February 1997) seasons and in situ nutrient additions (August–September 1996) in the Zhujiang Estuary and the adjacent shelf region.

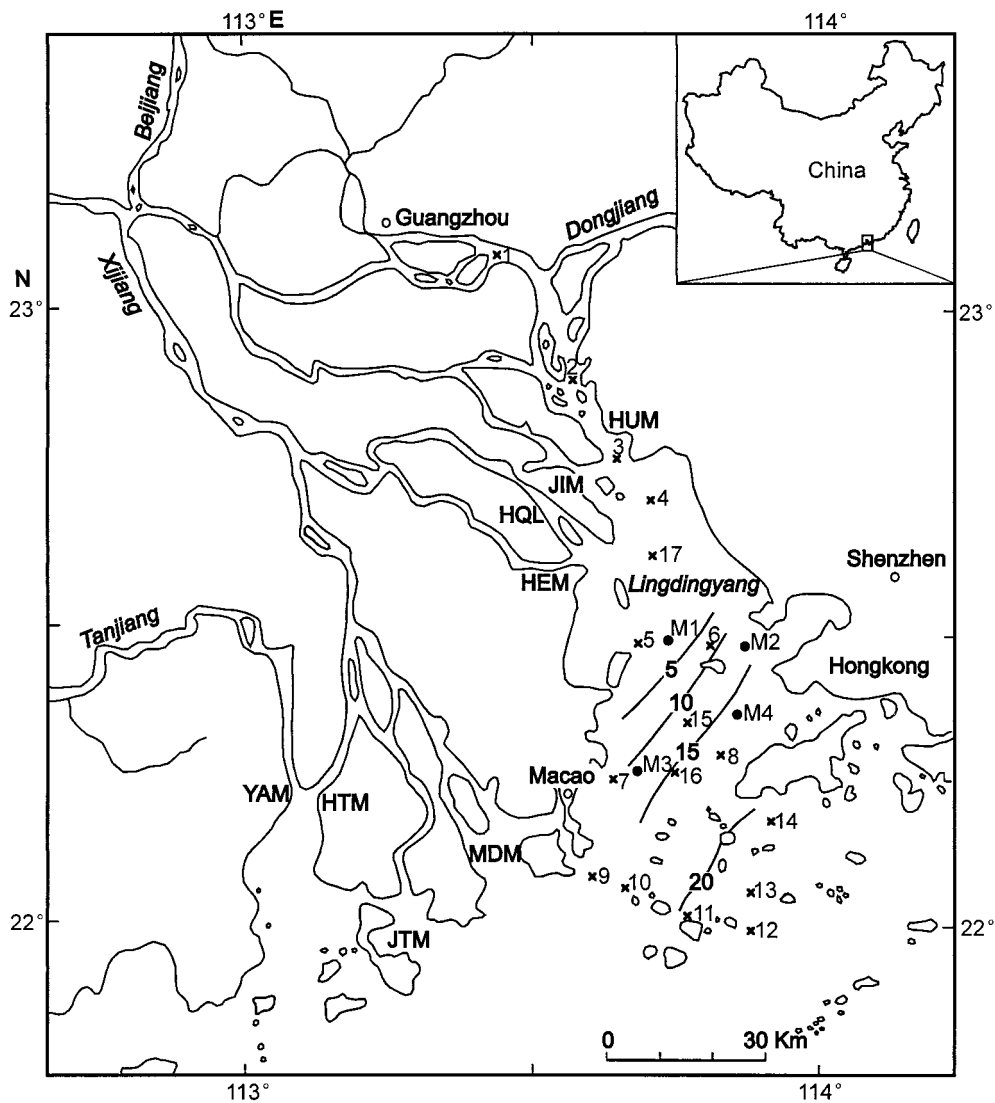


Fig. 1. Map of the Zhujiang Estuary (Lingdingyang) in South China. The figure shows the field observation area with grid and anchor (M1 and M3) stations taken in both August–September 1996 and January–February 1997 cruises. The eight channels of Zhujiang emptying into the South China Sea include Humen (HUM), Jiaomen (JIM), Hongqili (HQL), Hengmen (HEM), Modaomen (MDM), Jitimen (JTM), Hutiaomen (HTM), and Yamen (YAM). Also shown in the figure are the surface salinity isopleths in the Lingdingyang in flood tide in summer cruise where significant stratification was found. The incubation experiments were undertaken at stations M1 and M3 in August–September 1996 cruise.

The field observations were carried out in August–September 1996 and January–February 1997. The riverine discharge during the summer cruise was in the falling stage of the flood period with a water flow of $5,000\text{--}10,000\text{ m}^3\text{ s}^{-1}$. Discharge was low ($2,000\text{--}3,000\text{ m}^3\text{ s}^{-1}$) during the winter cruise. Water samples were taken from various depths at 25–30 stations in the Zhujiang Estuary and the adjacent coastal region until a salinity of 34.5 was reached. Surface water samples were collected with precleaned 2-liter polyethylene bottles attached to the end of a 5-m glass fiber-reinforced pole on board a small boat. Deep-water samples were taken with 5-liter Niskin bottles according to salinity gradients. Samples were filtered immediately on board within a clean

plastic tent through acid-cleaned $0.45\text{-}\mu\text{m}$ pore-size Sartorius filters. After filtration, the filtrate was poisoned by HgCl_2 and stored at $0\text{--}4^\circ\text{C}$ in the dark for H_2SiO_3 and deep frozen for other nutrient species (e.g., N and P) analyses. Samples for dissolved and particulate organic carbon (DOC/POC) and nitrogen (PON), and chlorophyll *a* (Chl *a*) were filtered through precleaned (450°C overnight) Whatman GF/F filters with a Millipore Glass Filtration Set® (Millipore). This filtrate was also poisoned by HgCl_2 and stored in the dark ($0\text{--}4^\circ\text{C}$). Filters were kept deep-frozen before analysis.

The incubation samples (M1 and M3) were collected from the subsurface (1–3 m) in the upper estuary (salinity: 1.0–5.0) and coastal (salinity: 25–30) waters, using precleaned

Table 1. Concentration (μM) of nutrients and Chl *a* (mg m^{-3}) at incubation stations (M1 and M3) in August–September 1996 and January–February 1997 cruises. The values of nutrients and Chl *a* in the table cover vertical profiles of flood and ebb tides in each cruise. Data of salinity (psu) at these stations were also given for comparison. The location of incubation stations is given in Fig. 1.

Station	Salinity	NH_4^+	$\text{NO}_3^- + \text{NO}_2^-$	PO_4^{3-}	H_2SiO_3	Chl <i>a</i>
August–September 1996						
M1	0.1–4.5	0.16–8.70	55.6–72.5	0.11–0.46	120–147	0.95–3.71
M3	13.7–30.5	2.45–9.83	15.3–22.3	0.30–0.68	9.80–22.5	0.32–0.81
January–February 1997						
M1	22.9–29.9	9.60–17.8	17.3–35.3	0.06–0.95	21.8–56.1	
M3	24.2–31.6	1.55–10.3	4.50–20.1	0.09–0.61	9.80–33.5	

5-liter Niskin bottles on the September 1996 cruise. Large particles and grazers (e.g., zooplankton) were removed by a 60- μm pore-size nylon mesh. The incubations were made for ca. 12 h with 1.25-liter polycarbonate incubation bottles suspended at the sea surface, attached to a line from the ship. The nutrient treatment (amendment) was adjusted to make the initial concentration of each nutrient species roughly twice the ambient concentrations, because the concentrations in the estuary may change by a factor of two between dry and wet seasons (Zhang et al. 1999). Control and dark bottles were incubated along with each series of nutrient-amended treatments. The incubation bottles were cleaned with HCl (1:5 v/v) and rinsed thoroughly with Milli-Q water before use, and incubations were undertaken using clean technique to avoid contamination (Fitzwater et al. 1982; Martin and Fitzwater 1990). Triple incubations were made with each nutrient species of interest, which gave an uncertainty of 10–20% to the final chemical and biological analyses. After incubation, the samples were filtered immediately in the dark under careful pressure control to avoid damage to phytoplankton cells. The sample preparation was carried out in a Class-100 clean bench to minimize contamination. Dissolved oxygen in water samples was measured before and after incubation by Winkler titration with a precision of 1–2.5%. The photosynthetic rate was estimated by the change in dissolved oxygen rather than by the ^{14}C method (Strickland and Parsons 1972), for logistic reasons and the constraint of field observations (Zhang et al. 1999).

In the laboratory, samples were analyzed by colorimetry for nutrients (NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , and H_2SiO_3) (Zhang et al. 1997a), POC and PON were determined by PE-240 C-H-N Analyzer (Zhang et al. 1997b), DOC was determined by UV/persulphate oxidation and high temperature combustion and oxidation (HTCO) in combination (Wang et al. 1997). Chlorophyll *a* (Chl *a*) was measured for incubation samples by a fluorescence method after extraction with acetone (90% v/v) (Parsons et al. 1984). Data quality was controlled by repeated analysis of national and/or international standards and frequent intercalibration/comparison practice.

All apparatus and laboratory ware for sample collection, incubation, and analysis were carefully cleaned before use, and care was taken in both field observation and laboratory analysis to avoid contamination and loss (Zhang 1995; Zhang et al. 1997a). High quality reagents were selected, and if necessary reagents were purified to reduce blanks.

At two mooring stations (M1 and M3) where the incubations were undertaken, salinity covers a wide range in

flood and ebb tides with a strong stratification in the summer cruise (Table 1). Nutrients vary considerably at these two sites, indicating the influence of freshwater effluents at the surface and marine waters at near bottom (Web table: <http://www.aslo.org/lo/pdf/vol.45/issue.8/1871al.pdf>). The winter cruise showed a higher concentration and a well-mixed vertical structure of salinity in the estuary relative to the summer. Concentrations of nutrients are lower at the mooring stations in winter than summer, owing to a reduced riverine input and hence the high salinity there. In the Zhujiang Estuary, concentrations of DIN vary between 60 and 80 μM for freshwater end members (Fig. 2). DIN decreases with higher chlorinities in the estuary and reaches ca. 5–10 μM in marine waters, although data are scattered (Fig. 2). Phosphate does not show any simple relationship with chlorinity; its concentration is close to 0.5 μM in the river channels and increases up to 0.5–1.0 μM in the coastal waters farther offshore, with an apparent regeneration in the mixing zone (Fig. 2). Dissolved silica illustrates almost a linear dilution in the Zhujiang Estuary, riverine concentrations of silica (ca. 150 μM) fall with higher chlorinities and reduce to ca. 10 μM in the coastal waters of South China Sea (Fig. 2). The DIN/ PO_4^{3-} ratio (DIN = $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) in the Zhujiang and its estuary could be as high as 100–1,000, indicating phosphorus limitation of photosynthesis in low-salinity waters. DIN/ PO_4^{3-} decreases almost log-linearly in the estuarine mixing zone, and N/P approaches 10–20 farther offshore on the shelf region, suggesting that photosynthesis is nitrogen limited there (Fig. 3). Similarly, the DIN to H_2SiO_3 ratio averages 0.5 at the freshwater end members and reaches up to 1.5 in coastal waters, indicating a potential photosynthetic limitation by H_2SiO_3 relative to nitrogen, although the data are scattered (Fig. 3). The taxonomic data indicate that diatoms are not uncommon in the estuary and become dominant species in coastal waters.

Figure 4 summarizes the results of incubation experiments conducted in the upper estuary (salinity: 2.4) and coastal waters (salinity: 27.1), including net photosynthesis ($\text{mg C m}^{-3} \text{ d}^{-1}$) and the corresponding change (NP) in chlorophyll *a* (mg m^{-3}) in incubation. Light measurements are used to generate a depth-integrated productivity for water column (cf. Zhang et al. 1999). In the upper estuary, incubation results confirm that phosphate is a photosynthesis-limiting nutrient; photosynthesis is twofold higher with PO_4^{3-} -addition than with NO_3^- -addition (Fig. 4). Such a nutritional regime facilitates blooms of dinoflagellates (Qi et al. 1993). Experiments with macronutrient and micronutrient species, like

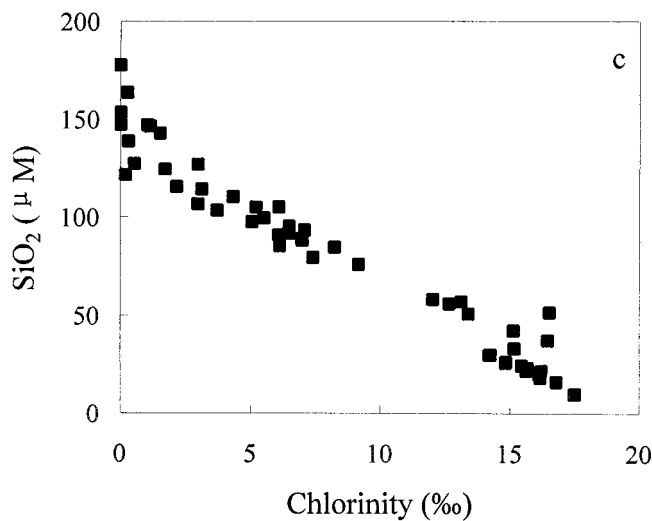
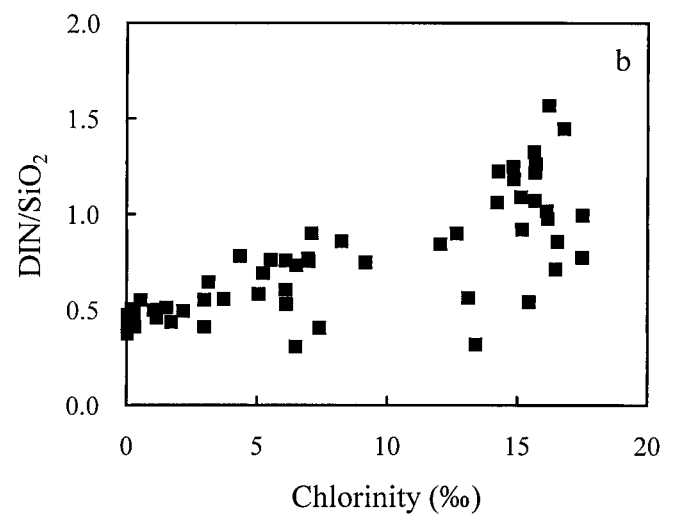
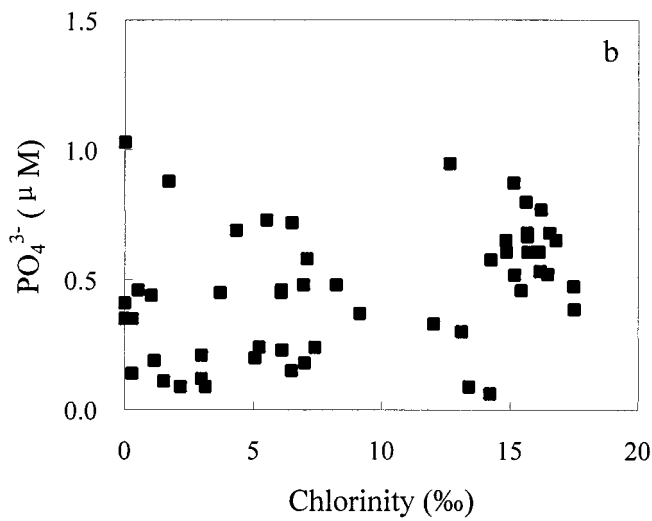
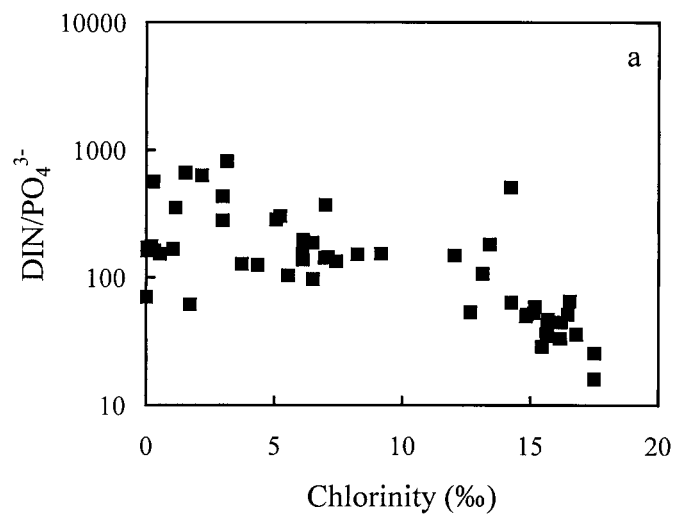
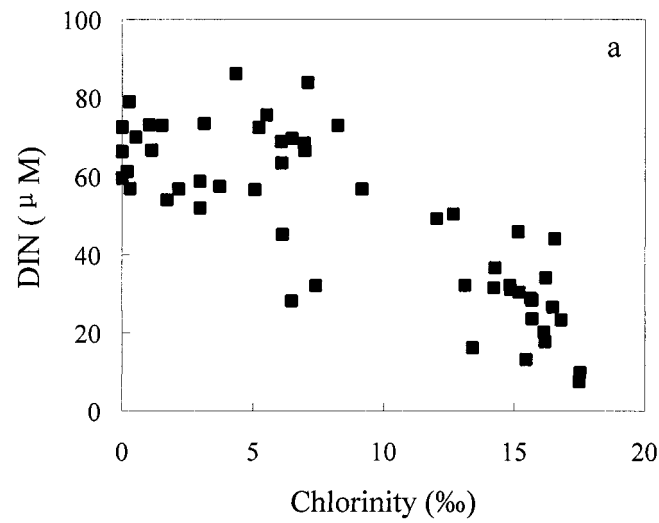


Fig. 3. Nutrient status of Zhujiang (Pearl River) Estuary and South China Sea, which show (a) $\text{DIN}/\text{PO}_4^{3-}$ and (b) DIN/SiO_2 against chlorinity. Apparently, the elevated $\text{DIN}/\text{PO}_4^{3-}$ values show the character of phosphorus limitation in low-salinity areas. The photosynthesis turns out to be nitrogen and silica limited in the offshore region. Winter sample data have chlorinity $\geq 12.5\text{‰}$ and hence combined with those of summer cruise. Samples from surface and bottom waters are not discriminated to show the trend of element ratio against chlorinity gradients.

dissolved silica and Cu, show no statistical difference (t -test, $p = 0.05$) as compared to controls. In the lower estuary and coastal waters, the incubation data show that nitrogen becomes an apparent limiting factor for photosynthesis. Autotrophic cells respond also to the addition of silica and Cu

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Fig. 2. Concentrations (μM) of nutrient species are plotted against chlorinity in the Lingdingyang, which shows the longitudinal profiles of (a) DIN, (b) PO_4^{3-} , and (c) SiO_2 in the estuarine zone.

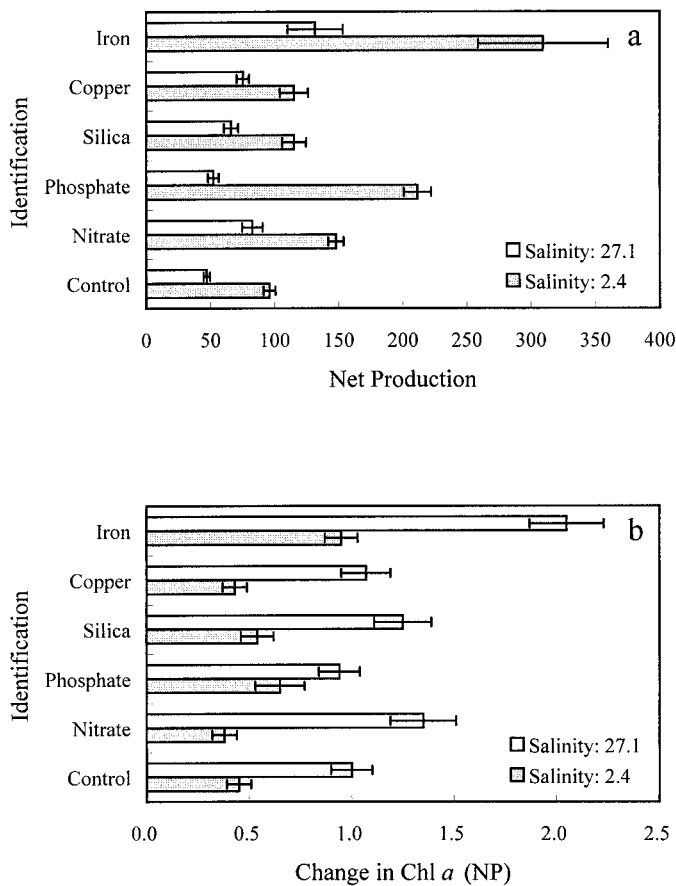


Fig. 4. Comparison of (a) net primary productivity ($\text{mg C m}^{-3} \text{d}^{-1}$) and (b) corresponding change (NP) in chlorophyll *a* (mg m^{-3}) in the upper Zhujiang Estuary (M1 salinity: 2.4) and South China Sea coastal waters (M3 salinity: 27.1). The data in the figure are based on the nutrient-addition incubations. The comparison of nutrient-spiked incubations with batch control underlines the significance of various nutrients and trace species on coastal photosynthesis (t -test, $p = 0.05$). In both cases, the Fe-addition series show the highest net production and Chl *a* change relative to batch control and other limiting nutrients.

(t -test, $p = 0.05$), and an exogenous silica source favors the activities of diatoms (Fig. 4). The added copper could be toxic to micrograzers that remained in the screened samples of incubation. Microscopic identification indicates that diatoms, notably *Chaetoceros* and *Coscinodiscus*, are the dominant autotrophic species in this region, contrasting with other coastal areas where nonsiliceous organisms (e.g., dinoflagellates) are more abundant. However, in both the upper estuary and coastal waters, the phytoplankton species show a greatest response to the exogenous Fe, compared to plant nutrients and other trace elements (e.g., Cu). Incubation experiments show that the photosynthesis rate and chlorophyll *a* could be twofold to threefold higher in the Fe series than in the controls. The Fe-incubation data show 50–100% higher photosynthetic rates and chlorophyll *a* content compared to the incubations with phosphate in the upper estuary and nitrate/silica in coastal waters (Fig. 4). Moreover, the community growth rate, as estimated by Chl *a*, is twice as high in the Fe case compared to other nutrient-addition incubations (Table 2). These data support the hypothesis that the autotrophic community in coastal waters may not be limited by a single nutrient, but rather by a number of nutrient species to different extents.

Fe addition makes other nutrients more available for photosynthesis. In a similar experiment in the Zhujiang Estuary, incubation with rainwater samples (i.e., Fe addition of 31.5 nM) resulted in a production and biomass that could be doubled relative to batch control and higher than a single nutrient (e.g., Fe) addition (Zhang et al. 1999). It should be indicated, however, that the net carbon fixation in the Fe incubation is ca. <10–20% of the potential production expected from a C:Fe ratio (C:Fe $\sim 10^5$), compared to a value of 10–30% in open ocean (Takeda 1998). The coastal eukaryotic plankton may have a higher Fe requirement in photosynthesis, hence a lower C:Fe ratio as compared to the oceanic species (Raven 1988). This suggests a higher Fe-limiting threshold for coastal and brackish water communities. Moreover, Fe limitation can also be affected by the nitrogen source, and it was reported that Fe requirement in photosynthesis is much lower in the case of NH_4^+ assimilation than NO_3^- (Raven 1988).

This study suggests low efficiency of Fe use in the eutro-

Table 2. Community growth rate (d^{-1}) and net production (NP) to chlorophyll *a* (Chl *a*) ratio of incubation experiments in summer cruise. The growth rate was estimated by the change in Chl *a* of incubation samples. The net production ($\text{mg C m}^{-3} \text{d}^{-1}$) to corresponding Chl *a* (mg m^{-3}) ratio was assumed to reflect the character of productivity of autotrophic community in the upper estuary and coastal waters. Errors show standard deviations of three incubation measurements. The significant increase in growth rate and different NP:Chl *a* ratio indicates that different phytoplankton species respond to Fe addition to various extents. Similar situations occur in the incubations with other nutrients. The net production was estimated via changes in dissolved oxygen of incubation experiments. The net production to Chl *a* ratio was obtained from the data of Fig. 3.

Identification	Community growth rate (d^{-1})		Net production to Chl <i>a</i> ratio	
	2.4	27.1	2.4	27.1
Salinity (psu)	2.4	27.1	2.4	27.1
Temperature ($^{\circ}\text{C}$)	29.2	29.4	29.2	29.4
Control	2.52 ± 0.50	3.22 ± 0.46	183 ± 26	41.3 ± 4.6
NO_3^- (100 μM)	2.14 ± 0.34	3.90 ± 0.46	332 ± 42	53.5 ± 6.8
PO_4^{3-} (1.0 μM)	3.37 ± 0.62	3.08 ± 0.32	280 ± 38	48.8 ± 6.4
H_2SiO_3 (80 μM)	2.94 ± 0.38	3.73 ± 0.70	183 ± 20	46.3 ± 6.4
Cu^{2+} (75 nM)	2.43 ± 0.44	3.37 ± 0.34	229 ± 27	61.8 ± 8.6
Fe^{2+} (85 nM)	4.25 ± 0.67	4.85 ± 0.72	281 ± 36	56.2 ± 7.2

phic coastal ocean, where abundant particles could effectively remove biologically available Fe from the water column. It is still unclear whether such a low efficiency of Fe use provides evidence that once Fe limitation is relieved, other major/micro nutrients become limiting, or the incubation is too short to allow the full uptake of available Fe, or both. Some of the Fe in the incubation is probably not available to photosynthetic uptake due, for example, to fast chemical reactions (e.g., adsorption and oxidation/precipitation) for this particle-active element (Johnson et al. 1997). The competition for Fe among autotrophic and mixotrophic/heterotrophic communities in the water column further reduces the Fe available in photosynthesis (Tortell et al. 1996; Maranger et al. 1998). The dissolved Fe in the river and upper estuary was ca. 50 nM, representing 10^{-4} – 10^{-6} of total Fe influx (i.e., dissolved plus particulate forms) to the estuary; much of this iron source (>90%) is chelated or colloidal bound and consequently not directly available to phytoplankton uptake. Dissolved iron was reduced to 1–2 nM in coastal waters, with abundant colloidal and organically bound Fe pools in the fraction passing through 0.4- μ m pore-size filters (Edmond et al. 1985; Li et al. 1988; Zhang 1995). Some 99% of Fe in oceanic waters is organically complexed, and 30% or more of the world ocean shows a characteristic of Fe limitation (Rue and Bruland 1995; Behrenfeld and Kolber 1999; Geider 1999).

It should be remembered, however, that in the eutrophic coastal waters of the South China Sea (e.g., Lingdingyang) a large amount of Fe is bound to particles as a labile fraction (e.g., precipitation as oxides on the surface of particles and/or surface bound by adsorption) along with total suspended matter (TSM: 10–350 mg L⁻¹). This could considerably reduce the bioavailability of this element in the euphotic zone where aerobic condition dominates but provides a potential Fe pool in solution under the oxygen-depleted situation. Some of the dissolved trace metals (e.g., Fe) carried by the river could be considerably scavenged (~70–90%) from the water column in the estuary, further reducing their availability to biota (Zhang 1995). Though total Fe is higher in coastal waters, this does not necessarily indicate the relief of Fe limitation, as the presence of particles and exogenous chelators (e.g., from a land source) could effectively shut down the biological Fe uptake and consequently community growth (Table 2). The increase of community growth with Fe addition in this study indicates the lack of biologically available Fe, even though the total Fe could be far higher than the limiting threshold in the Zhujiang Estuary.

In the Zhujiang Estuary, incubation for 12 h results in a significant increase in Chl *a*, partly due to the high biomass and removal of predators by use of the net. In a very similar experiment off the Yangtze River Estuary, 1 d of incubation induced an increase of Chl *a* from 5 mg m⁻³ to 40 mg m⁻³. In these two coastal regions, a severalfold increase of Chl *a* can be found once the grazing pressure is released by removal of predators. This implies that, compared to the open ocean, the grazing pressure may well regulate (top-down) the moderate biomass in coastal waters even though photosynthesis can be increased by Fe addition.

In the incubation experiments, the removal of plant nutrients in sustaining the net production is <5–10% of the total

amendment, which suggests again that major nutrients are less limiting compared to trace metals (e.g., Fe). The growth rate can be higher in coastal water than in the upper estuary, even though the major nutrients are more abundant in the low-salinity region. Our results show a rapid consumption–regeneration cycle and/or more efficient use of nutrients in the shelf region than in the estuary (Table 2 and Fig. 4). The ratio of net production to Chl *a* was fourfold to sixfold higher in the low-salinity region compared to coastal waters farther offshore; different autotrophic communities respond to the exogenous supply of nutrients to various extents (Table 2).

Compared to previous studies, in which diatoms are shown to respond most to trace Fe additions to HNLC provinces (e.g., Hutchins and Bruland 1998; Takeda 1998), the present work provides evidence that both siliceous and non-siliceous species respond to an increment of 50–100 nM of Fe and other metals (e.g., Cu) in eutrophic coastal waters. It was suggested that at a dissolved Fe level of 1.5–2.5 nM, the phytoplankton community is not Fe stressed; however, the incubation data from the coastal upwelling region show that autotrophic species respond to Fe addition at >10 nM dissolved Fe (Hutchins and Bruland 1998). A concentration of 10 nM of Fe is a factor of 5 higher than is needed to saturate growth rate from the equatorial Pacific upwelling regime (Coale et al. 1996a). Again, the mixotrophic community responds to the Fe addition at a much higher concentration, up to several micromolar Fe (Maranger et al. 1998). The dilemma is probably that Fe limitation in the ocean results from either the depletion of the absolute concentration (e.g., the oligotrophic province) or the low availability of Fe, and the distorted ratio of Fe relative to other major and/or trace nutrient species (e.g., the eutrophic province), or both, depending upon the time and space. Taking into account that primary production is not proportional to the extremely high plant nutrient influx in eutrophic coastal waters compared to the oceanic interior, notably the Northwest Pacific (Ning et al. 1998; Shiomoto et al. 1998), trace metals, especially Fe, appear to be limiting factors to the autotrophic community because of their low bioavailability. This in turn affects the capacity for uptake of abundant plant nutrients. Thus the mechanism of Fe limitation may operate in both oligotrophic oceanic and eutrophic coastal regimes, but through different channels. This phenomenon was probably omitted in previous studies of coastal eutrophication and harmful algal blooms, since Fe and other trace species were often not included and/or data obtained are not convincing (Qi et al. 1993; Turner and Rabalais 1994; Vollenweider et al. 1996; Anderson and Garrison 1997). The possible interpretation is that the supply of biologically available trace metals (e.g., Fe) is below the requirement to fully use the limiting macronutrients, thus leaving an excess of these nutrients in the water column.

The harmful algal blooms at Hong Kong and adjacent coastal waters in March–April 1998 have caused a collapse of over 50% of the fisheries, with an economic damage of 40–50 × 10⁶ US\$. These blooms, however, were not directly linked with nutrient discharge from the Zhujiang. The dissolved oxygen (DO) in the Lingdingyang and Hong Kong coastal waters varies from 7.5 mg L⁻¹ at surface to 2.4 mg L⁻¹ in vertical profiles, with an oxygen saturation of 30–

35% in near-bottom waters in the summer cruise. Thus, iron bound to particles and organic materials can be remobilized under the oxygen-depleted condition in near-bottom waters, providing a potential pool of Fe for the photosynthesis of the euphotic zone. While the blooming of plankton cells is permitted by added trace nutrients (e.g., Fe), Fe addition is not necessarily related to riverine influx; the system can be driven by upwelling and circulation, or chemical reactions (e.g., redox event and mineralization), in both time and space, providing available Fe to support photosynthesis.

The coastal phytoplankton community differs from oceanic species in their higher Fe requirements (Brand 1991; Sunda and Huntsman 1995), and our results confirm a higher Fe-limiting threshold in eutrophic coastal waters. The role of Fe in the physiology of coastal ecosystems illustrates a further difference relative to oceanic systems in that eukaryotic phytoplankton (e.g., diatoms), which are dominant in coastal waters (e.g., Zhujiang Estuary), may readily uptake Fe bound to porphyrin ligands relative to siderophore-complexed iron, whereas iron bound to siderophores is relatively more available to cyanobacteria, which are more abundant in the open ocean (Hutchins et al. 1999). This implies that in the eutrophic coastal waters, where porphyrin is more abundant than in the open ocean, Fe uptake by eukaryotic plankton is a favored mechanism, compared to uptake by prokaryotic picoplankton that prefers the siderophore-bound Fe. At a given Fe level, phytoplankton (e.g., diatoms) in the Zhujiang Estuary tend to show a more noticeable syndrome of Fe limitation, as they require higher Fe levels for growth than do the picoplankton.

The Fe-mediated photosynthesis in eutrophic coastal waters has global biogeochemical implications. Major nutrient ratios (e.g., N/P and N/Si) cited in the literature and shown in Fig. 3 may not necessarily identify the real situation of limiting resource for the autotrophic community. An increase in major plant nutrients will skew the primary production further toward limitation by trace nutrients. Such unbalanced nutrient ratios will not only affect the primary productivity (Table 2), but may also have profound influence on the species composition of plankton and hence the biodiversity and structure of the food web. For example, the shift of dinoflagellate to diatom blooms, and/or vice versa, can also be affected by the availability of trace metals (i.e. Fe), given that major nutrients are not limiting.

The hypothesis of trace metal limited photosynthesis was examined through the comparison of nutrient ratios and mesocosm-type simulation approach using eutrophic Zhujiang Estuary as an example. In the Zhujiang Estuary and adjacent coastal environment where NO_3^- is the dominant N source for photosynthesis, phytoplankton may illustrate a much greater syndrome of Fe deficiency than N assimilation using NH_4^+ as N source. Following an increase in NO_3^- to NH_4^+ ratio of riverine input, the Fe-limitation syndrome can be expected to be more serious in coastal waters, making the N assimilation in photosynthesis more costly. The results obtained support the idea that trace metal could considerably enhance the growth of the autotrophic community in eutrophic coastal waters. Since the major nutrient inputs to the coastal ocean will continue to increase due to an accelerated land use and population growth, the understanding of Fe limitation in photosynthesis in the coastal ocean is of pri-

mary significance with respect to environmental protection, economics, and human health issues in the 21st century, as the coastal ocean represents an anthropogenically disturbed environment with a fragile and over-stressed ecosystem, compared to the open ocean.

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Acknowledgements

I appreciate the thoughtful advice and critical comments of two anonymous reviewers; such comments helped the study and improved the manuscript. Z. G. Yu, L. Y. Wei, S. Q. Gao, and L. X. Dong assisted in the field observation and laboratory work. J. E. Cloern, P. J. Wangersky and J. A. Raven carefully read the manuscript and improved the English usage. Funding for this study was provided by the Natural Science Foundation of China through grants 49576297 and 49525609.

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Received: 9 July 1999

Accepted: 10 July 2000

Amended: 26 July 2000