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Increased eutrophication offshore Hong Kong, China during the past 75 years: Evidence from high-resolution sedimentary records

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Abstract

Total organic carbon (TOC), total nitrogen (TN), stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), lipids and biogenic silica (BSi) from a high-resolution sediment core east of Hong Kong span the interval from 1925 to 2001. Organic matter (OM) within this core (E2) is derived from both marine phytoplankton and terrestrial material as deduced from the range of values of $\delta^{13}C_{org}$ (−24.0‰ to −22.4‰) and $\delta^{15}N$ (2.9‰ to 5.3‰) and lipid biomarkers. Diatom and dinoflagellate productivity which is reflected in the biogenic silica (BSi) and dinosterol concentrations respectively, increased gradually starting in 1940 and accelerated after 1965, especially between 1980 and 2000, indicating that algal blooms and/or red tides caused by eutrophication increased during this time. The abundance of coprostanol, which reflects domestic sewage discharge, and the terrestrial biomarkers (long-chain fatty acids and fatty alcohols and sitosterol) exhibit similar temporal changes with the primary production, showing that the enhanced eutrophication resulted from increased anthropogenic activities in the northern coastal waters of the South China Sea (SCS) in recent decades.

Keywords: High-resolution; Organic matter; Biogenic silica; Lipids; Eutrophication; Coastal waters; South China Sea

1. Introduction

Deforestation, urbanization and anthropogenic discharge are known to result in eutrophication in many estuarine and coastal waters (Ver et al., 1999; Zimmerman and Canuel, 2000; 2002; Geiss et al., 2002). In the Pearl River estuary and adjacent coastal and Pearl River Delta (PRD) area of the South China Sea (SCS), major cities of Hong Kong, Macao, Shenzhen and Zhuhai and others in northern Guangzhou occur. In these areas, rapid economic growth and human activities have increased pressure on the environment (Huang et al., 2004). As a result of these anthropogenic activities, eutrophication and algal blooms and/or red tides frequently occur in the northern coastal waters of the SCS (Qi et al., 1996; Liang et al., 2000; Yin, 2003), which have drawn significant attention because of their potential human health impacts and risk to the local mariculture and fishing industries (Holmes and Lam, 1985).

There is a major need to diagnose and monitor eutrophication and its impacts on local ecosystems

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within the SCS. However, such studies require an adequate time series of observations and monitoring incorporating local environmental factors (e.g. nutrients from anthropogenic disposal, agricultural runoff and airborne pollution) and ecosystem factors (e.g. phytoplankton species, primary production). There is a lack of adequate data available to permit identification of local eutrophication causes and mechanisms (Geiss et al., 2002).

Sediment cores provide a useful tool for evaluating and reconstructing historical records of anthropogenic sewage discharge, eutrophication and their impacts on local ecosystems including lakes and coastal environments (Hodell and Schelske, 1998; Meyers, 2003; Ver et al., 1999; Zimmerman and Canuel, 2000; 2002). The sedimentary organic matter (OM) in coastal areas mainly originates from primary and secondary production, terrestrial inputs and bacterial production in sediments. The relative significance of these sources is determined by local environmental factors such as climate, hydrodynamic conditions and nutrient supply. Changes in any of these factors are reflected in the abundance and composition of sedimentary OM (Meyers, 1997; Geiss et al., 2002; Zimmerman and Canuel, 2000; 2002). Algal blooms and/or red tides caused by eutrophication may leave their imprint as biomarkers within the sedimentary record (Geiss et al., 2002; Zimmerman and Canuel, 2000; 2002). Sedimentary OM in sediment cores in conjunction with other parameters (e.g. BSi and biolipids) can provide information on paleoproductivity and past ecosystems (Meyers, 1997; 2003; Zimmerman and Canuel, 2000; 2002), which makes it possible to assess eutrophication and related algal blooms and/or red tides (e.g. Jia et al., 2002; Turner and Rabalais, 1994; Geiss et al., 2002; Zimmerman and Canuel, 2000; 2002).

The content of BSi in marine sediments has a close link with biosiliceous (diatom) productivity in the overlying surface waters (Conley, 1998). High concentration of sedimentary lipids, especially algal sterol signatures may be linked to high inputs of terrigenous OM (Grimalt and Albaigés, 1990). Thus, changes in sterol composition and concentration may be used to indicate marine inputs and associated organic productivity.

The objectives of this study are: (1) to investigate the stratigraphic record for reconstructing the eutrophication history in the northern coastal areas of the SCS in context of eutrophication frequency accelerated during the past century, and (2) to examine whether the eutrophication is related to local anthropogenic activities.

2. Materials and methods

2.1. Sediment sampling

A cruise was conducted, 26–30 July, 2002, in the Pearl River estuary and adjacent northern SCS. Twelve sediment cores were collected in the region (Fig. 1), which was undisturbed by channel-dredging activities. A stainless steel static gravity corer (8 cm i.d.) was employed to minimize the disturbance of surface sediment layers. Samples were taken with normal gravity coring equipment. A sediment core for this study (Core E2, total length 50 cm) was selected from southeast of Hong Kong at a water depth of 26 m. The core was sectioned at 1 cm intervals, and the sediment sections were immediately stored at −30 °C for further analysis.

2.2. ^{210}Pb dating

The sediment core was dated using the ^{210}Pb radiometric technique. The ^{210}Pb activities in the sediment subsamples were determined by analysis of the α-radioactivity of its decay product ^{210}Po, on the assumption that the two radionuclides are in equilibrium. The Po was extracted, purified, and self-plated onto silver disks at 75–80 °C in 0.5 M HCl, with ^{209}Po used as the yield monitor. Counting was done by a computerized multi-channel α-spectrometry with Au–Si surface barrier detectors. The relative error for this method was <10%. Supported ^{210}Pb was obtained from the α-activity of the supporting parent ^{226}Ra, co-precipitated with $BaSO_4$.

2.3. Sample analysis

2.3.1. Analyses of organic carbon and total nitrogen and their isotopes

The samples were freeze dried and homogenized. After treatment with 4 N HCl (for details see Hu et al., 2006a), total organic carbon (TOC) and total nitrogen (TN) contents of the carbonate-free sediments were measured on a Vario EL-III elemental analyzer, and the δ^{13}C and δ^{15}N analyses were made using a thermo DELTA ^{plus} XL mass spectrometer after treatment. The isotope ratios are reported in parts per mil (‰) as:

$$\delta(‰) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000,$$

where δ(‰) stands for δ^{13}C (‰) or δ^{15}N(‰), and R_{sample} and R_{standard} are the isotopic ratios of the sample and

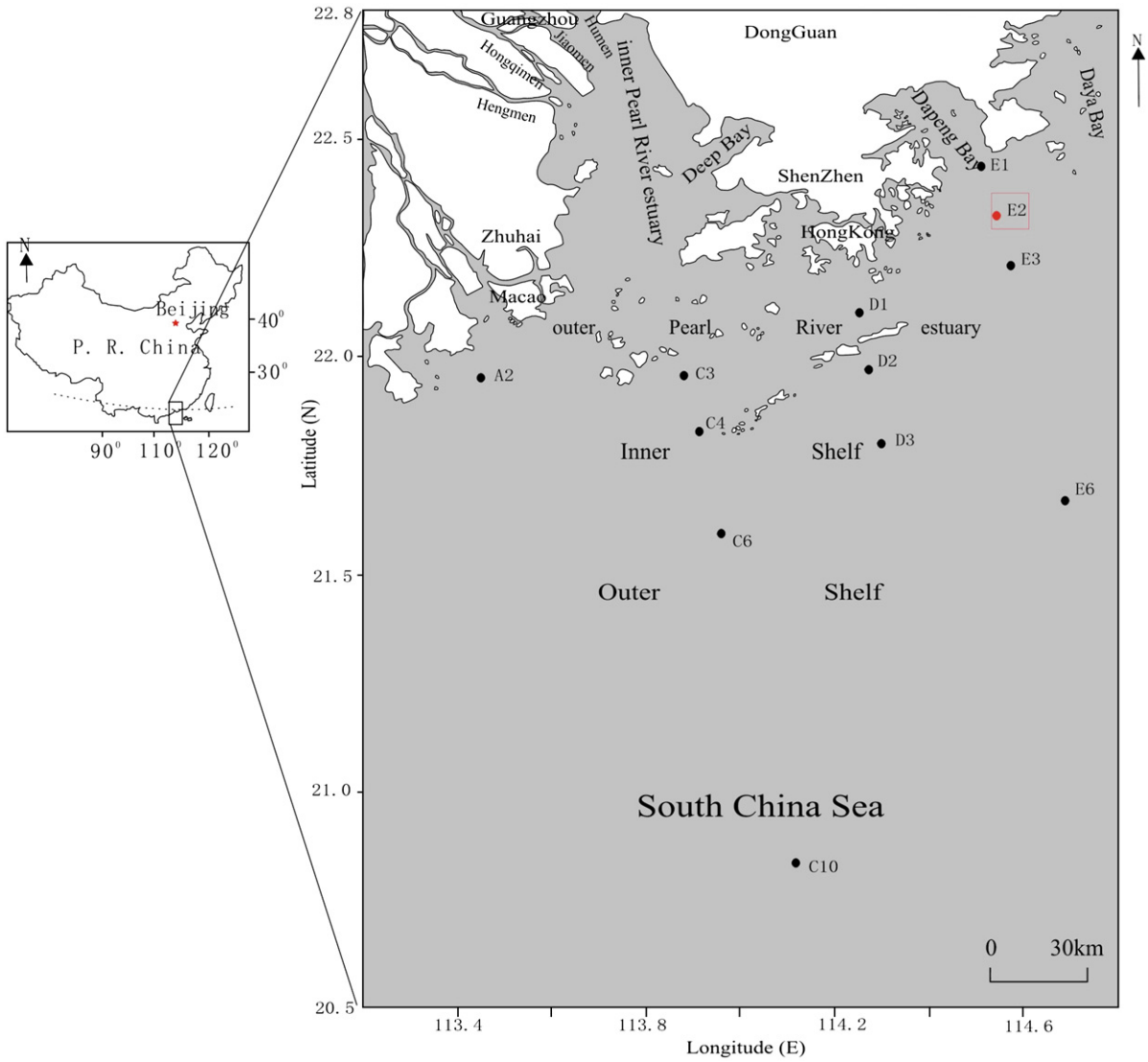

Fig. 1. The location of the sampling sites in the Pearl River estuary and adjacent coast of the South China Sea.

standard respectively. For carbon the standard is Peedee Belemnite (PDB) and for N it is air.

2.3.2. Biomarker analysis

The methods of Hu et al. (2006b) were used for extraction of the lipids of the sediments for this analysis. Sterols/*n*-alkanols and the fatty acid fraction were silylated with 50 μL BSTFA (*N*, *O-Bis* trimethylsilyltrifluoroacetamide).

All lipid biomarkers were analyzed with a Hewlett Packard gas chromatograph (GC, HP 6890) with a split/splitless injector and a flame ionization detector (FID). The gas chromatograph was fitted with a DB-5 (50 m, 0.32 mm i.d., 0.25 μm) capillary column (J&W). The GC oven was programmed from 70 °C (hold 2 min) to 290 °C at 3 °C/min and hold at 290 °C for 30 min. Hydrogen was used as the carrier gas.

Identification of compounds was achieved by GC retention times of unknown compounds with authentic standards and analysis by gas chromatograph/mass mass spectrum (GC/MS) using a Finnigan-MAT4515 GC–MS. The same column and temperature regime as for the GC were used. Helium was the carrier gas. The mass spectrometer was operated in EI model at 70 eV.

2.3.3. Biogenic silica measurement

Dried powder sediment was weighed into a 50-ml polypropylene centrifuge tube. 1 M HCl and 10% H_2O_2 were added to remove the carbonate and organics. Exactly 25 ml 2 M Na_2CO_3 solution was added to the

carbonate and organic-free samples, the tube was then capped, mixed well, and boiled at 85 °C for 5 h to extract BSi. BSi in the extracts was measured by the molybdate blue spectrophotometric method (Mortlock and Froelich, 1989). Duplicate analysis of the same sample suggested that the precision of this extraction procedure was better than ±3%.

3. Results

3.1. Chronology

The activities of ^{210}Pb, excess ^{210}Pb and ^{226}Ra are in the range 1.6 to 6.3, 0.8 to 5.6 and 0.45 to 0.85 (10^{-2}Bq g^{-1}), respectively (Fig. 2). The profiles of activities of ^{210}Pb and ^{226}Ra in the core extend to the unsupported/supported ^{210}Pb boundary. The $^{210}Pb_{exc}$ semi-log diagram is presented in Fig. 2B. A Constant Flux Model (Lin et al., 1998) was applied to date the core, which gave an average accumulation rate of 0.65 cm a^{-1}. Therefore, Core E2 represents more than 75 years of sediment deposition.

3.2. Stratigraphic variations of total organic matter

The TOC contents are in the range 0.39% to 0.63% in the sediments from Core E2 (with mean value 0.48%, Fig. 3A). The TOC remained relatively constant before the early 1940s. Overall, the TOC content shows a slight increasing trend, but exhibits small oscillations from the early 1940s to 1965. From 1965 to 1985, the TOC content increased gradually. For the past 15 years, TOC concentrations vacillate to reach a maximum that is nearly twice that from middle 1920s to early 1940s (Fig. 3A). The TN content ranged between 0.08% and 0.23% (with mean value 0.12%), and displayed relatively small variations. The variation trend of TN in the core sediments is similar to that of TOC. A small but oscillatory increase is observed from early 1940s to 1965 and there was also a relatively stable increase from 1965 to 1985, and an oscillationary increase after 1985 (Fig. 3B). The C/N ratios are in the range of 3.3 to 7.1 (with mean value 4.97) and show a general downcore trend towards lower values (Fig. 3C). However, the ratios exhibit abrupt oscillations between the early 1940s and 1965, varying from the lowest (3.3) in 1950 to 7.0 in 1959. From 1965 to 1985, the C/N ratios were relatively constant, but they became more variable after 1985 (Fig. 3C).

$\delta^{13}C_{org}$ values range between −24.0‰ and −22.4‰, and are rather constant in the pre-1940 samples (Fig. 3D). From the early 1940s to 1965, the $\delta^{13}C_{org}$ values become more variable, changing from −24.0‰ to −22.5‰. During the interval 1965 to 1985, the $\delta^{13}C_{org}$ values are less noisy and show a slightly increasing trend. In samples from 1985 to 2000, δ^{13}C values are more variable and show no net trend. The most positive value (−22.6‰) corresponds well to the lowest C/N ratio (3.3), but the net downcore trend of C/N ratio variation is not synchronous to the $\delta^{13}C_{org}$ profile (Fig. 3C, E). The δ^{15}N values range

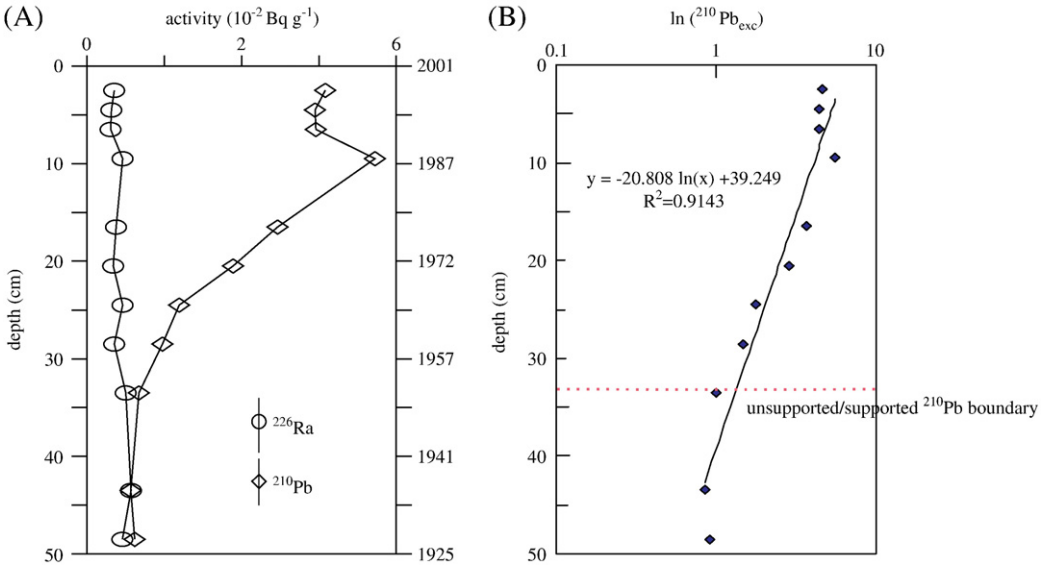

Fig. 2. A) ^{210}Pb and ^{226}Ra activities versus depth in the sediment core. Selected dates calculated by Constant Flux Model are shown to the right; B) distribution of excess ^{210}Pb activity in the sediment core.

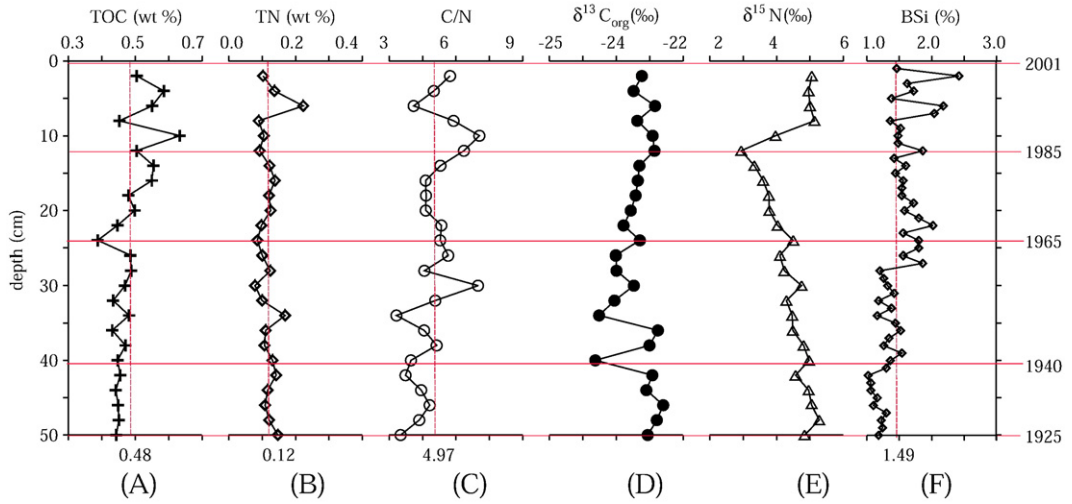

Fig. 3. Vertical variations in Core E2 of A) TOC (%), B) TN (%), C) C/N ratios, D) $\delta^{13}C_{org}$ (‰), E) $\delta^{15}N$ (‰) and F) BSi content (%) indicating diatom productivity. The right hand axis provides the age model (years AD). (– – – – indicates the mean values).

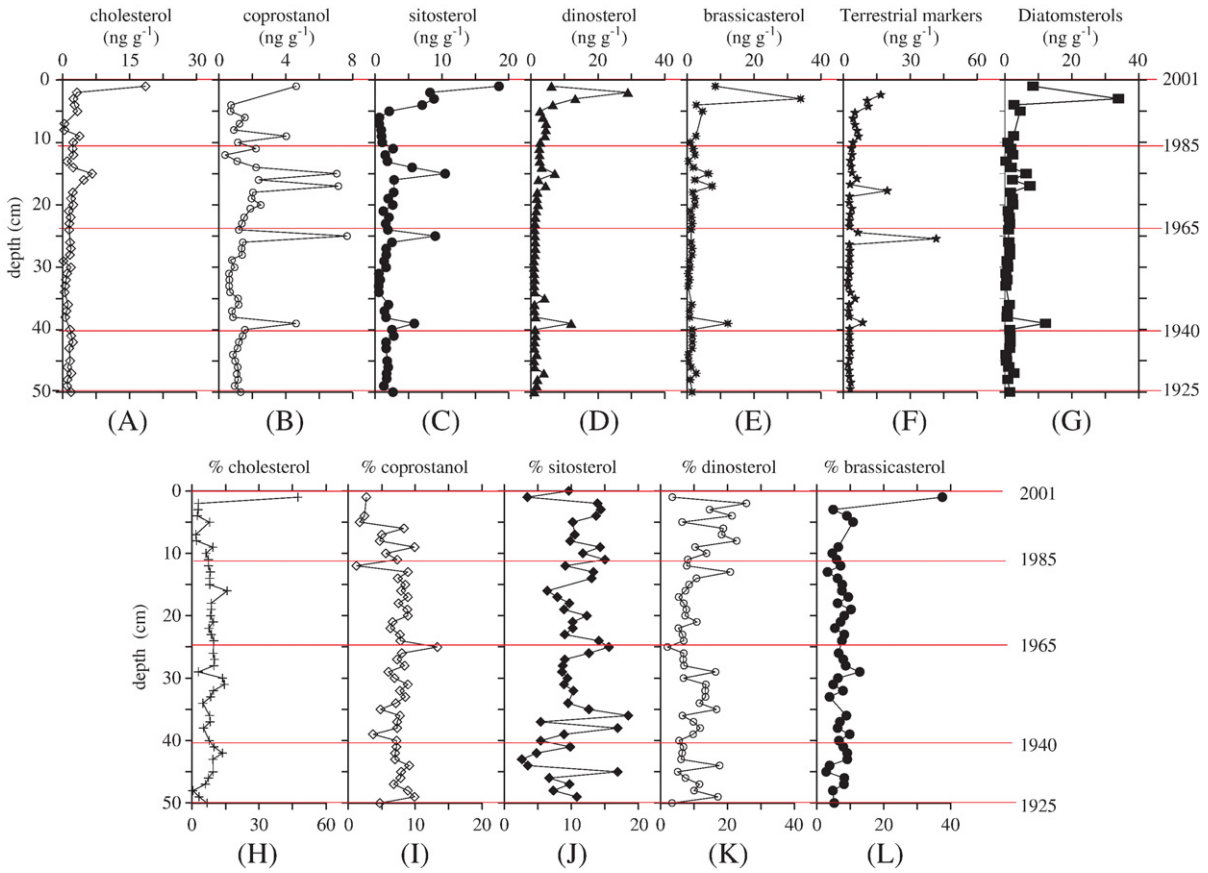

Fig. 4. Vertical variations of sterols in Core E2. A) cholesterol, B) coprostanol, C) sitosterol, D) dinosterol, E) brassicasterol, F) terrestrial markers (sum of $\geq C_{22}$ long-chain alcohols), G) diatom sterols, H) cholesterol as a proportion (%) of the total sterols, I) coprostanol as a proportion (%) of the total sterols, J) sitosterol as a proportion (%) of the total sterols, K) dinosterol as a proportion (%) of the total sterols, and L) brassicasterol as a proportion (%) of the total sterols.

from 2.9 to 5.3‰ and display a long-term decrease over 1940–1985, abruptly increasing thereafter to invariant values from 1991 to 2000 (Fig. 3E).

3.3. Summary of lipid biomarkers

Emphasis was placed on identifying the lipid classes because they are very useful in source identification. The core samples contain both fatty acids and alcohols/sterols.

3.3.1. Alcohols/sterols

The total alcohol concentrations are in the range 17.7 ng g^{-1} to 313.6 ng g^{-1}, and sterols range from 5.4 to 177.2 ng g^{-1}. The sterols are mainly composed of cholesterol, dinosterol, brassicasterol with lesser amounts of sitosterol and coprostanol (Fig. 4). These compounds account for 0.3–47.4%, 2.0–25.6%, 2.8–37.5%, 2.6–18.5% and 1.2–13.3% of the total sterols, respectively (Fig. 4H, I, J, K, L).

The downcore profiles of cholesterol, dinosterol and brassicasterol are similar to each other (Fig. 4A, D, E) whereas coprostanol and sitosterol have a different pattern but are similar to each other ($r^2=0.81$, Fig. 4B, C). The cholesterol content was low and nearly constant before the early 1980s. From 1980s to present, the cholesterol content was more variable and reached its maximum in 2001 (Fig. 4A). Dinosterol and brassicasterol show similar trends, they were relatively low and constant before 1940. They exhibited relatively stability from the 1940s to 1965 (Fig. 4D, E). Coprostanol and sitosterol were also relatively low and constant before 1940. From the 1980s to the present, coprostanol and sitosterol were more variable (Fig. 4B, C).

Long-chain ($\geq C_{22}$) fatty alcohol contents were relatively low and stable before 1940. They exhibited a slight increase from 1940 to 1965 and reached a maximum near 1963. After the 1970s, long-chain fatty alcohols increase significantly and more variably (Fig. 4F).

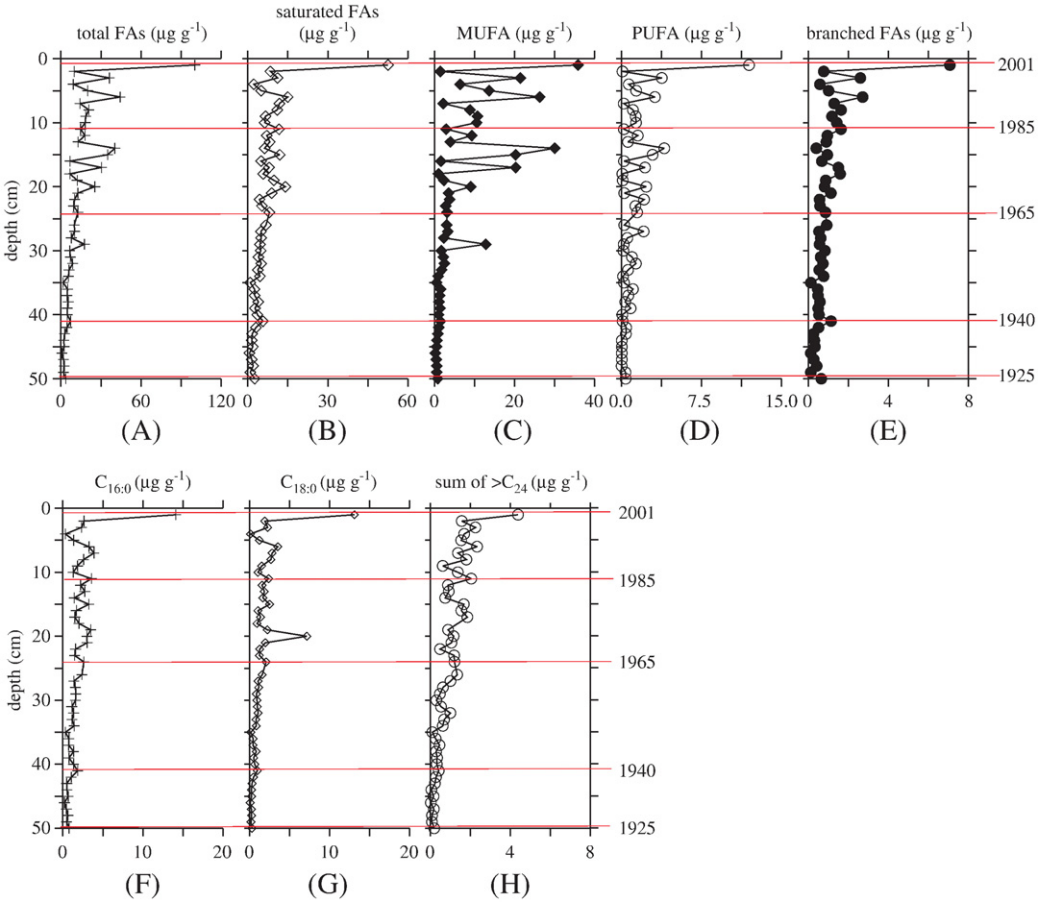

Fig. 5. Vertical variations of fatty acids in Core E2. A) total FAs, B) saturated FAs, C) monounsaturated fatty acids (MUFAs), D) polyunsaturated fatty acids (PUFAs), E) branched FAs, F) $C_{16:0}$, G) $C_{18:0}$, and H) sum of long-chain ($>C_{24}$) fatty acids.

3.3.2. Fatty acids

A total of 29 fatty acids (FAs) were identified in the core sediments, including saturated, monounsaturated fatty acid (MUFAs), polyunsaturated fatty acids (PUFAs) and branched fatty acids (Fig. 5). They account for 15.7–84.8%, 14.1–74.3%, 0.5–21.2% and 0.5–21.2% of total fatty acids, respectively. Saturated FAs are dominated by $C_{16:0}$ and the $C_{18:0}$ (accounting for 3.5–29.7% and 1.1 to 28.0% of total FAs, respectively). Few PUFAs ($C_{18:2\ \omega6}$ and $C_{20:3}$) were detected.

The profiles of total FAs, saturated FAs, MUFAs, PUFAs, branched FAs, $C_{16:0}$, $C_{18:0}$ and long-chain ($>C_{24}$) FAs are similar (Fig. 5). They were relatively stable and low before the 1940s. From 1940 to 1965, saturated, branched and long-chain FAs showed a slight increasing abundance (Fig. 5B, E and H), while MUFAs and PUFAs were relatively variable during this time (Fig. 5C, D). All the fatty acids increased the abundance and variability after 1965 (Fig. 5).

3.4. Vertical distribution of biogenic silica content

The biogenic silica content (%; BSi) ranges from 1.02 to 2.42. The vertical distribution of BSi is shown in Fig. 3F. It is clear that the BSi content increases gradually upcore. Before early 1940s, the BSi content was relatively low and stable. The BSi increased slowly and stably during the interval 1940 to 1965. The BSi content increased rapidly from 1965 to 1985. It was more variable and reached its maximum after 1985 (Fig. 3F).

4. Discussion

4.1. Organic matter origin

The $\delta^{13}C$ values are useful to distinguish the sources of bulk sedimentary OM (Meyers, 1997; 2003). Typically, OM derived from terrestrial C_3 plants has $\delta^{13}C$ values between −26‰ to −28‰ (with an average −27‰) and C_4 plants approximately −14‰ (O'Leary, 1988; Meyers, 1997). Marine OM has $\delta^{13}C$ values between −20‰ and −22‰ (Meyers, 1994). We do not further consider C_4 plant sources in this paper, because the natural hinterland ecosystem is subtropical C_3 forest and the dominant cultivated plant is rice (also a C_3 plant) in the studied coastal area (Jia and Peng, 2003). Typical $\delta^{15}N$ values for bulk terrestrial vascular plants range from −5‰ to +18‰ with an average value of ~3‰ and marine particulate organic matter (POM) range from 3‰ to 12‰ with a mean value ~6‰ (Müller and Voss, 1999; Maksymowska et al., 2000).

From the $\delta^{13}C_{org}$ and $\delta^{15}N$ values of the Core E2 sediment samples (Fig. 3D and E), we can conclude that the sedimentary OM consists of a mixture of two components, namely, terrestrial C_3 plants and marine phytoplankton.

The organic carbon to nitrogen (C/N) ratio is another useful indicator for elucidating the sources of sedimentary OM (Müller and Voss, 1999; Maksymowska et al., 2000). Generally, marine OM and terrestrial OM have C/N ratios of ~5–8 and >15, respectively (Meyers, 1997). However, post-depositional changes in this ratio can occur (Bordovskiy, 1965), and the presence of a significant fraction of inorganic nitrogen (adsorbed on clay minerals) can also limit the usefulness of C/N ratios as source indicators of OM in marine sediments. In our study, the C/N ratios (Fig. 3C) do not indicate specific OM sources as effectively as do the $\delta^{13}C_{org}$ values. If all of the sedimentary TN values exclusively reflect N bound to OM, a close covariance between TN and TOC of sediments is expected and regression of these two variables should result in a line that passes through the origin. Although a fairly strong correlation ($r^2=0.73$) exists between TN% and TOC% (Fig. 6A), a linear regression of these two variables does not pass through the origin. The positive intercept suggests the presence of poorly quantified inorganic N fraction (2.3% to 35% of the TN), presumably as NH_4^+ adsorbed on clays, Müller, 1977; Meyers, 1997), which might help to explain the relatively low C/N ratios. The parameters (C/N, $\delta^{13}C_{org}$ and $\delta^{15}N$) of bulk OM do not exhibit obvious correlation (Figs. 6B and C). The lack of correlations is likely due to the influence of inorganic N on TOC/TN and $\delta^{15}N$ values.

The lipid biomarkers constitute less than 1% of the total sedimentary OM and may not be representative of the total material (Meyers, 1997). The molecular compositions of the Core E2 sediments nonetheless reveal important details about changes in origins of the OM, which suggest that there are several sources of organic matter in the coastal area. These include marine phytoplankton, terrestrial higher plants, bacteria and domestic sewage, and which are considered in the following sections.

4.1.1. Phytoplankton

Polyunsaturated fatty acids (PUFAs) normally associated with phytoplankton, for example, 20:5ω3 and 16:4ω1 are typical diatom fatty acids (Colombo et al., 1996); 18:2ω6, 18:3ω3 and 18:3ω6 have been used as markers of green macroalgae (Meziane and Tsuchiya, 2000); 22:6ω3 is indicative of a dinoflagellate origin (Colombo et al., 1996; Budge and Parrish, 1998).

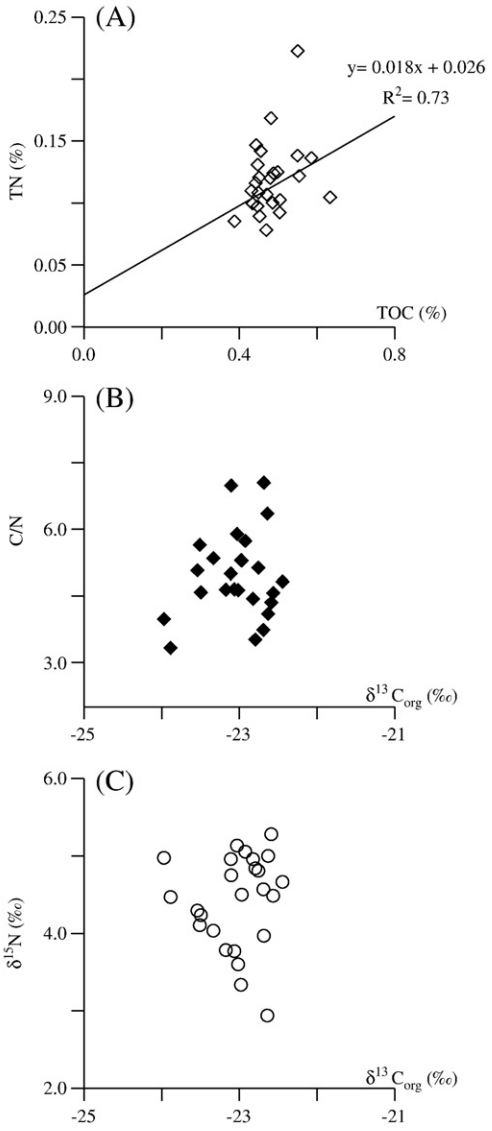

Fig. 6. Correlations among A) TOC and TN, B) $\delta^{13}C_{org}$ and C/N, and C) $\delta^{13}C_{org}$ and $\delta^{15}N$ in the sediments from Core E2.

However, none of these PUFAs except 18:2ω6 and 20:3 were detected in E2 core sediments, possibly because PUFAs are labile and are subject to rapid losses by bacterial degradation and/or via zooplankton grazing (Canuel and Martens, 1996). Thus, these PUFAs associated with phytoplankton would not necessarily be expected to be preserved in their original amounts, which may partially explain the absence of several diagnostic PUFAs in the E2 core sediments (Carrie et al., 1998). Therefore, it is not possible to easily assess the phytoplankton community structure by fatty acids alone in sediments (Carrie et al., 1998).

Sterols have been utilized to identify components of phytoplanktonic communities. 24-methylcholest-5-en-3β-ol, 24-methylenecholest-5-en-3β-ol and brassicasterol are diatom markers (Volkman et al., 1980; Volkman, 1986). These sterols detected in Core E2 sediments suggest the contribution of diatoms (Volkman, 1986). The presence of dinosterol indicates a dinoflagellate contribution to sedimentary OM (de Leeuw et al., 1983) and the observed concentration (Fig. 4D) indicates that of dinoflagellate production from the overlying water column.

BSi is extensively used as a palaeoindicator of diatom production and used to reconstruct changes in palaeoproductivity (Ragueneau et al., 1996). Comparing Fig. 3F with Fig. 4G, it can be seen that downcore profiles of BSi and diatom sterols show similar overall trends. Moreover, the BSi indicates more abundant and specific information. In our study, BSi is chosen as an indicator of diatom production.

4.1.2. Terrestrial higher plants

Long-chain fatty acids ($>C_{24}$) and alkanols ($\geq C_{22}$) are considered as indicators of terrestrial input in sediments (Colombo et al., 1996; Carrie et al., 1998). However, terrestrial plants generally contain large amounts of 18:2ω6 and 18:3ω3 acids (Budge and Parrish, 1998), while 18:3ω3 was not found in our sediment samples. The more labile fatty acid components of terrestrial detritus may not survive in the coastal environment (Carrie et al., 1998). Thus, it is not surprising that 18:3ω3 was not found in the E2 core sediments. In any case, the long-chain fatty acids and alkanols detected in the core sediments suggest terrestrial inputs to the sedimentary OM. Sitosterol is also a marker of land plants (Sangiorgi et al., 2005). However, it can also be derived from some diatom species (Volkman, 1986). In our study, the downcore profile of sitosterol is similar to the distribution of long-chain fatty alcohols, suggesting that it might originate from land plants in the study area (Fig. 4C, F).

4.1.3. Bacteria

Branched (*iso*- and *anteiso*-) fatty acids are representative of a bacterial origin (Volkman et al., 1980; Carrie et al., 1998; Budge and Parrish, 1998). We defined the sum of branched-chain fatty acids as the bacterial indicator in this paper. Notably, the bacterial biomass increased over the 1940–1985 period, and was highest during 1985–2000, consistent with increasing eutrophication over this period, with the highest levels in the most recent part of the record (Fig. 5E). MUFA 18:1ω7 is a well-known bacterial marker found both in

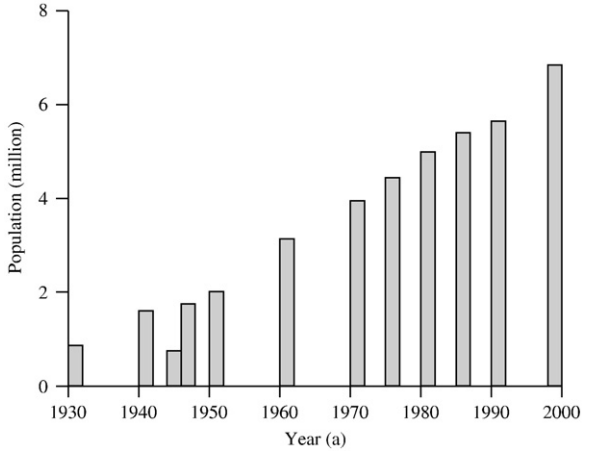

Fig. 7. The population of Hong Kong since 1930.

aerobic and anaerobic bacteria, and it is related to bacteria in the surface sediments more widely in the studied area (Hu et al., 2006b).

4.1.4. Sewage

Coprostanol has been applied successfully to trace sewage pollution in diverse environments due to its source specificity and environmental stability (Grimalt et al., 1990). In our samples, considerable amounts of coprostanol were detected (Fig. 4B and I), suggesting domestic sewage discharge into the coastal environment. The sedimentary pattern of coprostanol downcore in E2 could indicate the historical trends of sewage contamination in this area. The similarity of downcore profiles of coprostanol and sitosterol ($r^2=0.81$, Fig. 4B, C) suggests that coprostanol inputs to this area are related to terrestrial introduction. Anthropogenic discharge and deforestation are known as the main activities that trigger increases in terrestrial inputs, and are associated with population increases in the local system. As shown in Fig. 7, the population of Hong Kong (http://www.demographia.com) increased continuously from 1931 to 2000, except in 1945. However, the concentration of coprostanol did not exhibit a continuous increase from 1925 to 2000, especially after 1970s. This could be explained by improvements in sewage disposal in Hong Kong after 1970s (Marc and Adrian, 1996).

4.2. Evidence of eutrophication

4.2.1. Temporal variance of TOC and primary production

The sedimentary concentration of TOC and of individual biomarkers is influenced by a variety of environmental conditions and deposit processes, notably primary productivity, water column remineralization, sedimentation rate, bottom water oxygen concentration and exposure time (Hodell and Schelske, 1998), downcore diagenesis, the sedimentary TOC and biolipids still can be used to partially reconstruct the overlying marine production and the terrigenous inputs (Zhao et al., 2006).

The TOC, BSi related to diatom production and the dinosterol concentration indicating dinoflagellate production, were low and stable before 1940, which can be regarded as the "background" in the studied area. After 1940, all these indicators showed increasing concentrations, suggesting that low and stable primary production in the water column increased gradually after 1940. The enhancement of primary production could be one of the direct results of eutrophication in water. However, at different times, as presented in the core, the rate of eutrophication has varied. From 1940 to 1965, BSi and TOC increased slowly and stably, suggesting that the rate of eutrophication was more moderate. After 1965, eutrophication increased, especially from 1980 to 2000 (Fig. 3F, A), corresponding to the documented increasing frequency of red tides in this area (Yin, 2003). An increase in the frequency of red tides is also well documented, more broadly in coastal China (Table 1).

However, it would seem that individual sedimentary and geochemical biomarker indicators have responded

Table 1
Red tide frequency in the coastal waters of China

Year	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
F[a]	4	1				3	1	2	1	7	4	4	6	7
F[b]												7	7	6

Year	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
F[a]	9	12	13	12	34	38	50	39	22	25	20	24	22
F[b]	10	16	45	11	15	9	10	4	8	8	13	6	57

[a] Red tide frequency from Liang et al. (2000).
[b] Red tide frequency from Yin (2003).

differently to the eutrophication. Figs. 3A, F and 4 D, G suggest that BSi is more sensitive to the eutrophication in the studied area. Diatoms were the dominant phytoplankton species at the Pearl River estuary and adjacent coastal waters and *Skeletonema costatum* was the dominant red tide species in both dry and wet seasons (Huang et al., 2004). Therefore, eutrophication triggered the enhancement of diatom production first. By contrast, dinoflagellate production increased more slowly. The 1998 massive dinoflagellate red tide that occurred in Hong Kong and its surrounding waters (Yang and Hodgkiss, 2004) corresponds well, temporally, with the maximum value of dinosterol concentration in Core E2 (Fig. 4D). Thus we might tentatively suggest relatively higher concentration of dinosterol at about 1943 and 1980 might represent dinoflagellate red tides in the studied area.

4.2.2. Is eutrophication partly caused by anthropogenic activities?

We used coprostanol as a marker of domestic sewage pollution in this paper. Coprostanol abundance was low and stable before 1940 in Core E2, providing a background value. In the early 1940s and middle 1960s, coprostanol abundance increased, with a maximum value for the whole core in 1960s, which is similar, in timing, to the distribution of TOC, BSi and dinosterol (Figs. 3A, F and 4D). Due to the location of this core, the major influence on the sedimentary OM budget is from Hong Kong. The peak value in 1940s might be associated with the influx of wartime refugees and the maximum value in 1960s might be affected by the population increase in Hong Kong in this time (Fig. 7).

Presumably as a result of rapid urbanization and industrial development both in Hong Kong and neighbouring mainland China since the 1970s, coprostanol related to sewage discharge increased significantly during the last three decades, though with slight reductions at various times (Fig. 4B). This trend is quite similar to that of eutrophication discussed above. Therefore, human-induced impacts on eutrophication appear to have increased from 1970s. Further, soil and nutrient losses related to deforestation and increased runoff associated with urbanization and industrialization induced by human activity (Owen and Lee, 2004) would also trigger further terrestrial contributions to depositing OM.

The distribution of terrestrial markers (sitosterol, long-chain alcohols and long-chain FAs; Figs. 4C, F and 5H) indicate that terrigenous inputs increased after 1940. It can be shown from Fig. 4B, C, E that there has been a sharp increase in terrestrial input during the interval 1940 to 1985 and reaching maximum values at the same time as the peak in coprostanol abundance, suggesting that anthropogenic influences were enhanced during this stage. Increased terrestrial OM can also be inferred from the $\delta^{13}C_{org}$ and $\delta^{15}N$ values. The values varied from −24.0‰ to −22.6‰ and 5.0‰ to 2.9‰, respectively, during this period (Fig. 3D, E). Terrestrial inputs increased and variability increased in the last three decades (Figs. 4C, F and 5H), corresponding well with the rapid land reclamation and rapid urbanization both in Hong Kong and mainland China since the 1970s.

5. Conclusions

The high-resolution sedimentary records of the bulk OM, lipids and BSi reflect the increased eutrophication from 1925 to 2000 in the east of Hong Kong. The primary production indicated by BSi and dinosterol concentrations increased gradually and progressively from 1940 to 1965 and accelerated after 1965, especially in the period from 1985 to 2000, reflecting the fact that algal blooms and/or red tides caused by eutrophication increased. In addition, the synchronous temporal changes in the domestic sewage marker (coprostanol), terrestrial markers and primary production indicators in the sediments show that the enhanced eutrophication was related presumably to the increased anthropogenic activities in the northern coastal waters of the SCS in recent decades.

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References

Bordovskiy, O.K., 1965. Accumulation and transformation of organic substances in marine sediment. Mar. Geol. 3, 3–114.

Budge, S.M., Parrish, C.C., 1998. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. Org. Geochem. 29, 1547–1559.

Canuel, E.A., Martens, C.S., 1996. Reactivity of recently deposited organic matter: degradation of lipid compounds near the sediment-water interface. Geochim. Cosmochim. Acta 60, 1793–1806.

Carrie, R.H., Mitchell, L., Black, K.D., 1998. Fatty acids in surface sediment at the Hebridean shelf edge, west of Scotland. Org. Geochem. 29, 1583–1593.

Colombo, J.C., Silverberg, N., Gearing, J.N., 1996. Lipid biogeochemistry in the Laurentian Trough I. Fatty acids, sterols and aliphatic hydrocarbons in rapidly settling particles. Org. Geochem. 25, 211–225.

Conley, D.J., 1998. An interlaboratory comparison for the measurement of biogenic silica in sediments. Mar. Chem. 63, 39–48.

de Leeuw, J.W., Rijpstra, I.C., Schenck, P.A., Volkman, J.K., 1983. Free, esterified and residual bound sterols in Black Sea Unit 1 sediments. Geochim.Cosmochim. Acta 47, 455–465.

Geiss, L.P., Méjanelle, L., Dale, B., Karlsen, D.A., 2002. Lipids as indicators of eutrophication in marine coastal sediments. J. Microbiol. Methods 48, 239–257.

Grimalt, J.O., Albaigés, J., 1990. Characterization of the depositional environments of the Ebro Delta (western Mediterranean) by the study of sedimentary lipid markers. Mar. Geol. 95, 207–224.

Grimalt, J.O., Fernandez, P., Bayona, J.P., Albaigés, J., 1990. Assessment of fecal sterols and ketones as indicators of urban sewage inputs to coastal waters. Environ. Sci. Technol. 24, 357–363.

Hodell, D.A., Schelske, C.L., 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. Limnol. Oceanogr. 43, 200–214.

Holmes, P.R., Lam, C.W.Y., 1985. Red tides in Hong Kong waters – response to a growing problem. Asian Mar. Biol. 2, 1–10.

Hu, J., Peng, P., Jia, G., Mai, B., Zhang, G., 2006a. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. Mar. Chem. 98, 274–285.

Hu, J., Zhang, H., Peng, P., 2006b. Fatty acid composition of surface sediments in the subtropical Pearl River estuary and adjacent shelf, Southern China. Estuar. Coast. Shelf Sci. 66, 346–356.

Huang, L.M., Jian, W.J., Song, X.Y., Huang, X.P., Liu, S., Qian, P.Y., Yin, K.D., Wu, M., 2004. Species diversity and distribution for phytoplankton of the Pearl River estuary during rainy and dry seasons. Mar. Pollut. Bull. 49, 588–596.

Jia, G., Peng, P., Fu, J., 2002. Sedimentary records of accelerated eutrophication for the last 100 years at the Pearl River estuary (in Chinese with English abstract). Quat. Sci. 22, 158–165.

Jia, G.-D., Peng, P.-A., 2003. Temporal and spatial variations in signatures of sedimented organic matter in Lingding Bay (Pearl estuary), southern China. Mar. Chem. 82, 47–54.

Liang, S., Qian, H.L., Qi, Y.Z., 2000. Problem on the red ride in coastal China Sea (in Chinese with English abstract). Ecol. Sci. 19, 44–50.

Lin, R.F., Min, Y.S., Wei, K.Q., Zhang, G., Yu, F.J., Yu, Y.L., 1998. ^{210}Pb-Dating of sediment cores from the Pearl River mouth and its environmental geochemistry implication (in Chinese with English abstract). Geochimica 27, 401–516.

Maksymowska, D., Richard, P., Piekarek-Jankowska, H., Riera, P., 2000. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdansk (Southern Baltic Sea). Estuar. Coast. Shelf Sci. 51, 585–598.

Marc, S.-E., Adrian, D., 1996. Early experiences in monitoring the effects of Hong Kong's new generation of sewage outfalls on the marine environment. Mar. Pollut. Bull. 33, 317–327.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem. Geol. 144, 289–302.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org. Geochem. 27, 213–250.

Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Org. Geochem. 34, 261–289.

Meziane, T., Tsuchiya, M., 2000. Fatty acids as tracers of organic matter in the sediment and food web of a mangrove/intertidal flat ecosystem, Okinawa, Japan. Mar. Ecol. Prog. Ser. 200, 49–57.

Mortlock, R.A., Froelich, P.N., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Res. 36, 1415–1426.

Müller, A., Voss, M., 1999. The palaeoenvironments of coastal lagoons in the southern Baltic Sea, II. δ13C and δ15N ratios of organic matter – sources and sediments. Palaeogeogr. Palaeoclimatol. Palaeoecol. 145, 17–32.

Müller, P.J., 1977. C/N ratio in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochim. Cosmochim. Acta 41, 765–776.

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336.

Owen, R.B., Lee, R., 2004. Human impacts on organic matter sedimentation in a proximal shelf setting, Hong Kong. Cont. Shelf Res. 24, 583–602.

Qi, Y.Z., Lei, Z., Lu, S.H., Qian, H.L., 1996. The ecology and occurrence of harmful algal blooms in the South China Sea. Intergovernmental Oceanographic Commission of UNESCO, pp. 33–36.

Ragueneau, O., Leynaert, A., Treguer, P., DeMaster, D.J., Anderson, R.F., 1996. Opal studied as a marker of paleoproductivity. EOS (Trans. Am. Geophys. Union) 77, 491–493.

Sangiorgi, F., Fabbri, D., Comandini, M., Gabbianelli, G., Tagliavini, E., 2005. The distribution of sterols and organic-walled dinoflagellate cysts in surface sediments of the North-western Adriatic Sea (Italy). Estuar. Coast. Shelf Sci. 64, 395–406.

Turner, R.E., Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi River delta. Nature 368, 619–621.

Ver, L.M.B., Mackenzie, F.T., Lerman, A., 1999. Carbon cycle in the coastal zone: effects of global perturbations and change in the past three centuries. Chem. Geol. 159, 283–304.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. Org. Geochem. 9, 83–100.

Volkman, J.K., Johns, R.B., Gillan, F.T., Perry, G.J., 1980. Microbial lipids of an intertidal sediment I. Fatty acids and hydrocarbons. Geochim. Cosmochim. Acta 44, 1133–1143.

Yang, Z.B., Hodgkiss, I.J., 2004. Hong Kong's worst "red tide" – causative factors reflected in a phytoplankton study at Port Shelter station in 1998. Harmful Algae 3, 149–161.

Yin, K., 2003. Influence of monsoons and oceanographic processes on red tides in Hong Kong waters. Mar. Ecol. Prog. Ser. 262, 27–41.

Zhao, M., Mercer, J.L., Eglinton, G., Higginson, M.J., Huang, C.-Y., 2006. Comparative molecular biomarker assessment of phytoplankton paleoproductivity for the last 160 kyr off Cap Blanc, NW Africa. Org. Geochem. 37, 72–97.

Zimmerman, A.R., Canuel, E.A., 2000. A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. Mar. Chem. 69, 117–137.

Zimmerman, A.R., Canuel, E.A., 2002. Sediment geochemical records of eutrophication in the mesohaline Chesapeake Bay. Limnol. Oceanogr. 47, 1084–1093.