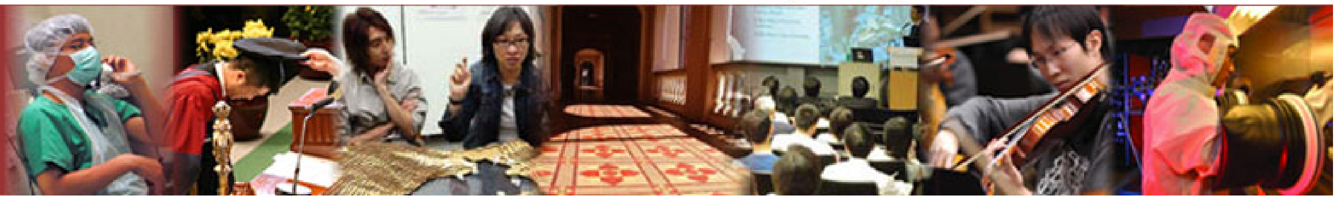

Title	Long-term and seasonal changes in nutrients, phytoplankton biomass, and dissolved oxygen in deep bay, Hong Kong
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Long-Term and Seasonal Changes in Nutrients, Phytoplankton Biomass, and Dissolved Oxygen in Deep Bay, Hong Kong

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Abstract Deep Bay is a semienclosed bay that receives sewage from Shenzhen, a fast-growing city in China. NH_4 is the main N component of the sewage (>50% of total N) in the inner bay, and a twofold increase in NH_4 and PO_4 concentrations is attributed to increased sewage loading over the 21-year period (1986–2006). During this time series, the maximum annual average NH_4 and PO_4 concentrations exceeded 500 and 39 μM, respectively. The inner bay (Stns DM1 and DM2) has a long residence time and very high nutrient loads and yet much lower phytoplankton biomass (chlorophyll (Chl) <10 μg L^{-1} except for Jan, July, and Aug) and few severe long-term hypoxic events (dissolved oxygen (DO) generally >2 mg L^{-1}) than expected. Because it is shallow (~2 m), phytoplankton growth is likely limited by light due to mixing and suspended sediments, as well as by ammonium toxicity, and biomass accumulation is reduced by grazing, which may reduce the occurrence of hypoxia. Since nutrients were not limiting in the inner bay, the significant long-term increase in Chl *a* (0.52–0.57 μg L^{-1} $year^{-1}$) was attributed to climatic effects in which the significant increase in rainfall (11 mm $year^{-1}$) decreased salinity, increased stratification, and improved water stability. The outer bay (DM3 to DM5) has a high flushing rate (0.2 day^{-1}), is deeper (3 to 5 m), and has summer stratification, yet there are few large algal blooms and hypoxic events since dilution by the Pearl River discharge in summer, and the invasion of coastal water in winter is likely greater than the phytoplankton growth rate. A significant long-term increase in NO_3 (0.45–0.94 μM $year^{-1}$) occurred in the outer bay, but no increasing trend was observed for SiO_4 or PO_4, and these long-term trends in NO_3, PO_4, and SiO_4 in the outer bay agreed with those long-term trends in the Pearl River discharge. Dissolved inorganic nitrogen (DIN) has approximately doubled from 35–62 to 68–107 μM in the outer bay during the last two decades, and consequently DIN to PO_4 molar ratios have also increased over twofold since there was no change in PO_4. The rapid increase in salinity and DO and the decrease in nutrients and suspended solids from the inner to the outer bay suggest that the sewage effluent from the inner bay is rapidly diluted and appears to have a limited effect on the phytoplankton of the adjacent waters beyond Deep Bay. Therefore, physical processes play a key role in reducing the risk of algal blooms and hypoxic events in Deep Bay.

Keywords Eutrophication · Nutrients · Phytoplankton biomass · Dissolved oxygen · Sewage · Hong Kong · Deep Bay

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Introduction

Eutrophication has been considered to be a major threat to marine ecosystems for several decades (Ryther and Dunstan 1971; Rosenberg 1985; Nixon 1995; Bachmann et al. 2006) since nutrient enrichment can disrupt biological communities and ecosystem processes in the coastal areas (Cloern 1999). In weakly flushed waters, the increased loading of N and P increases phytoplankton biomass and oxygen demand due to the decomposition of more organic matter, leading to hypoxia or anoxia in some cases (Cooper and Brush 1991; Boynton et al. 1995; Malakoff 1998; Fisher et al. 2006). In contrast, increased nutrient loading has less effect in turbid waters (Cloern 1999, 2001; Le Pape et al. 1996) where phytoplankton growth is often light-limited all year (Heip et al. 1995), or algal biomass is diluted due to high mixing and flushing rates (Ball et al. 1995).

Climatic change also affects ecological responses to coastal eutrophication (Howarth et al. 2000). Freshwater inputs can increase nutrient loads and stratification of the water column and lead to an increase in phytoplankton biomass and a subsequent potential depletion of bottom dissolved oxygen (DO; Justić et al. 1997). On the other hand, increased freshwater discharge could decrease phytoplankton growth due to light limitation caused by an increase in the load of the suspended solids (SS) and reduce residence time of the embayment, leading to low phytoplankton biomass (Le Pape et al. 1996; Howarth et al. 2000).

A number of water quality monitoring programs have been established to analyze long-term trends and changes in water quality in many regions of the world. Long-term measurements provide evidence for the evolution of eutrophication impacts and the ecosystem response to changes in nutrient supply in coastal areas (e.g., O'Shea and Brosnan 2000; Gowen et al. 2002; Paerl et al. 2006).

In Hong Kong waters, anthropogenic nutrient loads are from seasonally varying inputs from the Pearl River and year-round inputs from Hong Kong sewage. Presently, there is little information on whether the high nutrient

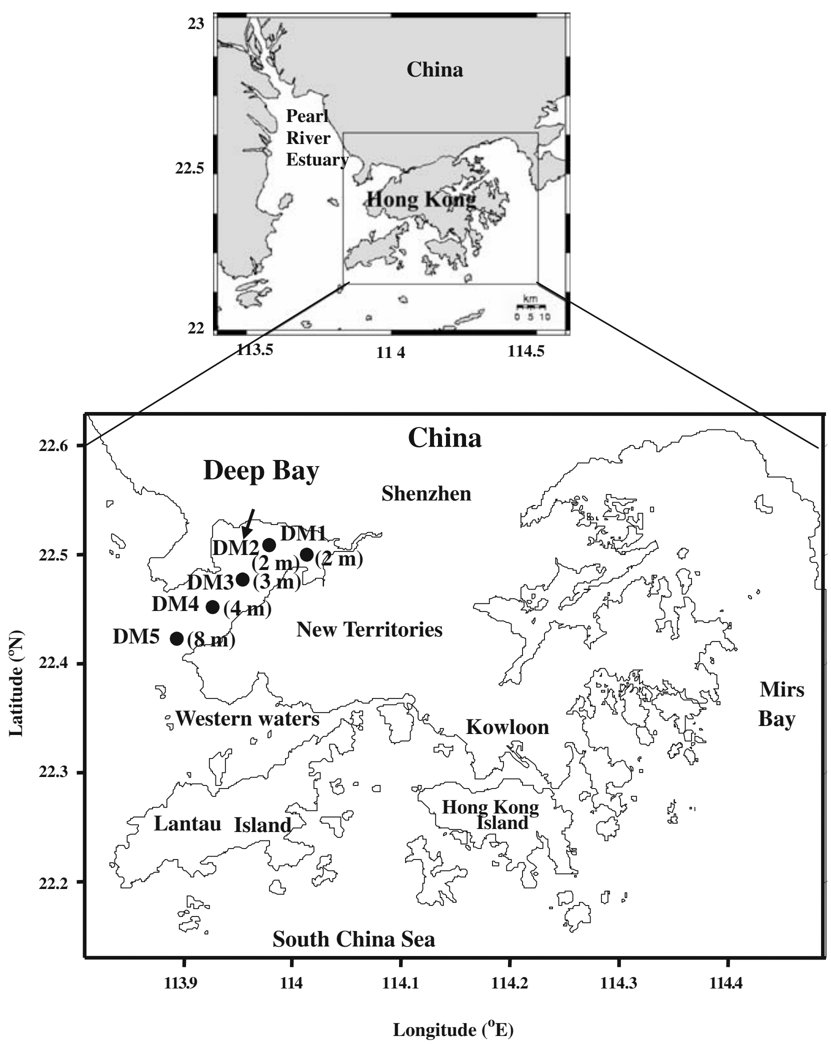

Fig. 1 Location of the sampling stations in Hong Kong waters. These five stations are the same as the EPD monitoring stations. The *number* in the bracket represents the water depth

concentrations (NH_4>400 μM) from sewage inputs into Deep Bay also influence Hong Kong waters.

Deep Bay is a shallow semienclosed bay which is surrounded by a large megacity, Shenzhen, to the north and the New Territories of Hong Kong to the south (Fig. 1). It is influenced by four rivers with very small discharges. The entrance of the bay is located to the southwest where it joins the Pearl River estuary. Deep Bay has suffered from extensive anthropogenic pollutant inputs such as unsewered villages and livestock farms (Environmental Protection Department (EPD) 2004). The results of a recent evaluation indicated that the water quality of Deep Bay was the worst among all the waters of Hong Kong in terms of nutrient concentrations (EPD 2006), with threats to sensitive ecosystems (wetland reserves) and oyster culturing in the bay (Lee and Qian 2003). However, little is known about the long-term response of this ecosystem to nutrient enrichment in Deep Bay in terms of phytoplankton biomass and DO in the bottom water. The objective of this paper was to evaluate the 21-year long-term trends and seasonal variations in nutrients, phytoplankton biomass, and DO in Deep Bay due to a twofold increase in nutrient loading. This is the first comprehensive analysis of water quality parameters for Deep Bay. From this time series analysis, we were also able to determine that the high nutrient loading in the inner bay is diluted by the Pearl River as the water exits the bay, and therefore this nutrient load from Deep Bay has little influence on the immediate surrounding Hong Kong waters.

Materials and Methods

The EPD of the Hong Kong government has maintained a comprehensive sampling program to monitor water quality at >76 monitoring stations in the territorial waters since the late 1980s (website: www.epd.gov.hk). Five stations located in the Deep Bay were grouped into two sections: the inner bay (DM1 and DM2) and the outer bay (DM3, DM4, and DM5; Fig. 1). Bimonthly sampling in 1986 and 1987 and monthly sampling since 1988 were conducted by EPD during the 21-year time series in Deep Bay, except for DM5 where monthly sampling was conducted from 1991 to 2006. The dry season was defined as October to March, and the wet season was from April to September. The year was divided into four seasons: spring (March to May), summer (June to August), fall (September to November), and winter (December to February). Water samples were taken only at the surface (1 m below the surface) at DM1, DM2, and

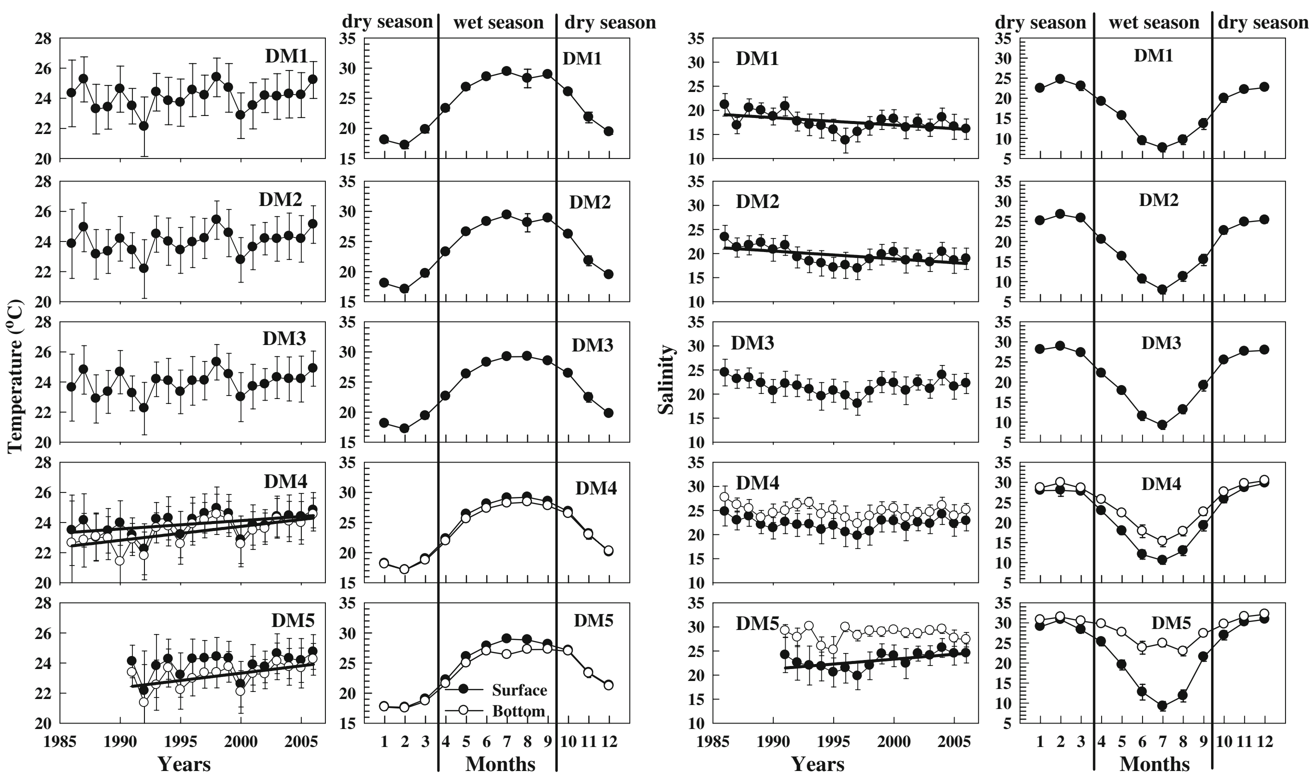

Fig. 2 Annual average temperature and salinity and monthly average temperature and salinity at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The *line* represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data

Table 1 Long-term trends in 15 variables in Deep Bay during 1986–2006

Stations	Layer	Variables	Slope	r^2	Number	Stations	Layer	Variables	Slope	r^2	Number
DM4	S	Temp	0.06	0.23	21	DM1	S	Salinity	−0.15	0.26	21
	B		0.09	0.43	21	DM2			−0.16	0.32	21
DM5	S		0.10	0.35	16	DM5			0.2	0.34	16
DM1	S	NH_4	8.2	0.26	21	DM2	S	TN	8.5	0.46	21
DM2			8.2	0.55	21	DM4	S		2.15	0.46	21
DM4	S		1.3	0.73	21		B		1.83	0.37	21
	B		1.1	0.68	21	DM1	S	PO_4	−0.56	0.25	21
DM5	S		1.07	0.81	16	DM1	S	TP	−1.76	0.21	21
	B		0.67	0.71	16	DM5	S		−0.12	0.75	16
DM3	S	NO_2	0.37	0.37	21		B		−0.13	0.64	16
DM4	S		0.38	0.44	21	DM1	S	DIN to PO_4	0.84	0.36	21
	B		0.39	0.74	21	DM2			0.82	0.51	21
DM5	S		0.47	0.74	16	DM4	S	DIN to SiO_4	0.07	0.61	21
	B		0.3	0.68	16		B		0.06	0.66	21
DM2	S	NO_3	0.77	0.43	21	DM5	S		0.06	0.55	16
DM4	S		0.91	0.41	21		B		0.05	0.69	16
	B		0.94	0.67	21	DM1	S	Chl *a*	0.57	0.19	21
DM5	S		0.45	0.30	16	DM2			0.52	0.21	21
DM1	S	DIN	7.4	0.28	21	DM3	S	SS	0.71	0.32	21
DM2			8.3	0.63	21	DM1	S	DO	−0.08	0.3	21
DM3			2.6	0.41	21	DM2			−0.09	0.39	21
DM4	S		2.6	0.75	21	DM3			−0.07	0.31	21
	B		2.4	0.83	21	DM4			−0.08	0.63	21
DM5	S		1.98	0.84	16	DM5	S		−0.13	0.61	16
	B		1.3	0.57	16		B		−0.07	0.48	16
DM1		SDD	−0.03	0.48	9	DM2	S	BOD	0.11	0.52	21
DM4			−0.07	0.53	9						

Trend evaluated by a linear regression at a significance level of $p<0.05$. Minus sign denotes a significant decreasing trend

S surface, *B* bottom layer

DM3, due to their shallow depth, and were assumed to be representative of the whole water column, especially in reference to DO. In contrast, water samples were taken at three depths: surface (1 m below the surface), middle (data not shown), and bottom (1 m above the bottom) at the deep stations (DM4 and DM5). Methods for sampling and routine water quality measurements are reported by EPD (EPD 2006), and the methods during the 21-year time series were standard methods for the examination of water and wastewater by the American Public Health Association and Annual Book of American Society for the Testing and Materials standards for nutrients, DO, biological oxygen demand, SS, and chlorophyll (Chl). Chlorophyll was extracted with 90% acetone and measured using a spectrophotometer at 664, 647, and 630 nm. The optical density at 750 nm is a correction for turbidity. Chl *a* concentrations were calculated according to the equations proposed by Jeffrey and Humphrey (1975).

Table 2 Long-term trends analyzed by a linear regression for summer and winter temperatures in outer Deep Bay during 1986–2006

Stations	Layer	Seasons	Slope	r^2	Number
DM3	S	Summer	0.08	0.19	21
DM4	S	Summer	0.08	0.26	21
		Winter	0.08	0.20	21
	B	Summer	0.09	0.28	21
		Winter	0.09	0.22	21
DM5	S	Summer	0.14	0.53	16
	B	Winter	0.23	0.27	16

S surface, *B* bottom layer

Statistical Analyses

Linear regressions were used to analyze the time series using Sigmaplot 9.0 (n=number of sampling months in a year for

Table 3 pH values at the surface in Deep Bay during 1986–2006

Month	DM1	DM2	DM3	DM4	DM5
1	7.61±0.12	7.79±0.10	8.03±0.07	8.06±0.06	8.10±0.06
2	7.53±0.07	7.66±0.07	7.88±0.06	8.04±0.04	8.05±0.06
3	7.48±0.06	7.68±0.08	7.78±0.09	7.99±0.05	8.01±0.05
4	7.55±0.08	7.66±0.06	7.83±0.08	7.92±0.08	7.94±0.08
5	7.47±0.07	7.60±0.08	7.77±0.11	7.93±0.07	7.88±0.12
6	7.46±0.09	7.59±0.08	7.93±0.09	7.96±0.06	7.83±0.07
7	7.37±0.14	7.49±0.14	7.74±0.13	7.91±0.13	7.91±0.14
8	7.68±0.09	7.68±0.09	7.87±0.10	7.98±0.07	7.89±0.08
9	7.53±0.10	7.59±0.11	7.82±0.08	7.90±0.08	7.80±0.09
10	7.48±0.12	7.64±0.10	7.91±0.08	8.02±0.05	7.98±0.06
11	7.10±0.40	7.26±0.41	7.84±0.08	7.98±0.06	8.03±0.04
12	7.52±0.07	7.62±0.07	7.76±0.09	7.97±0.06	8.01±0.08

Error bar represents ±1 SE, n=21 for DM1, DM2, DM3, and DM4 and n=16 for DM5

the annual average data and number of sampling years for the monthly average data). Correlations of NH_4 vs salinity and DO vs temperature were analyzed by the SPSS Program (Pearson test). A t test analysis was conducted to determine any significant difference between variables ($p<0.05$).

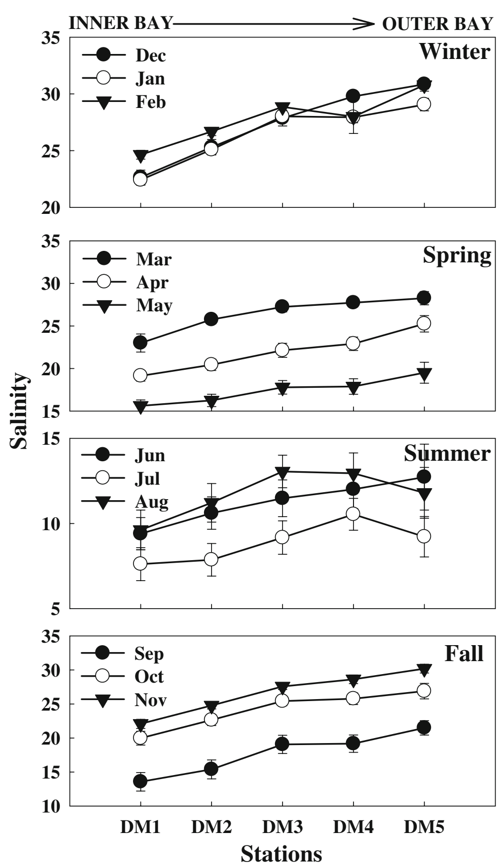

Fig. 3 Monthly average salinity at the surface along the transect from the inner bay to outer bay in four seasons during 1986–2006. *Vertical bars* indicate ±1 SE and n=21 for DM1 to DM4 and n=16 for DM5. Note the change in the scale on the *y-axis*

Results

Temperature, Salinity, and pH

Annual average surface temperature exhibited no significant trends at DM1, DM2, and DM3 but rose significantly at the surface and bottom at DM4 and at the surface at DM5 at the rate of 0.06–0.1°C year^{-1} (Fig. 2, Table 1). In summer, there was a long-term increase in temperature at the surface at DM3 and at the surface and bottom at DM4 by 0.08–0.09°C year^{-1}. In winter, temperature increased at the surface and bottom at DM4 and at the bottom at DM5 at the rate of 0.08–0.23°C y^{-1} (Table 2). Surface temperature fluctuated from a low of 17–21°C in winter to a high of 28–30°C in summer (Fig. 2). The pH value increased from 7.1–7.8 in the inner bay to 7.8–8.1 in the outer bay (Table 3).

Annual average surface salinity decreased significantly by 0.15 year^{-1} at DM1 and 0.16 year^{-1} at DM2 and increased by 0.2 year^{-1} at the surface of DM5 (Fig. 2, Table 1). Surface salinity fluctuated seasonally with high salinity (22–31) in the winter and low salinity (7.5–13) in the summer at all stations (Fig. 2). Surface salinity increased along the transect from DM1 to DM5 during March to June and September to December. In July, the highest surface salinity occurred at DM4 (10.5), significantly ($p<0.05$, t test) higher than that at DM5 (9.2) due to dilution by the Pearl River discharge at DM5 (Fig. 3).

Nutrients and Nutrient Ratios

Annual average NH_4 concentrations exhibited a significant increase in the water column in the inner bay (DM1 and DM2) by 8.2 μM year^{-1} and at the surface and bottom in the outer bay (DM4 and DM5) at the rate of 0.67 to 1.3 μM year^{-1} (Fig. 4, Table 1). Seasonal patterns of NH_4 were observed with high concentrations (up to 400 μM at

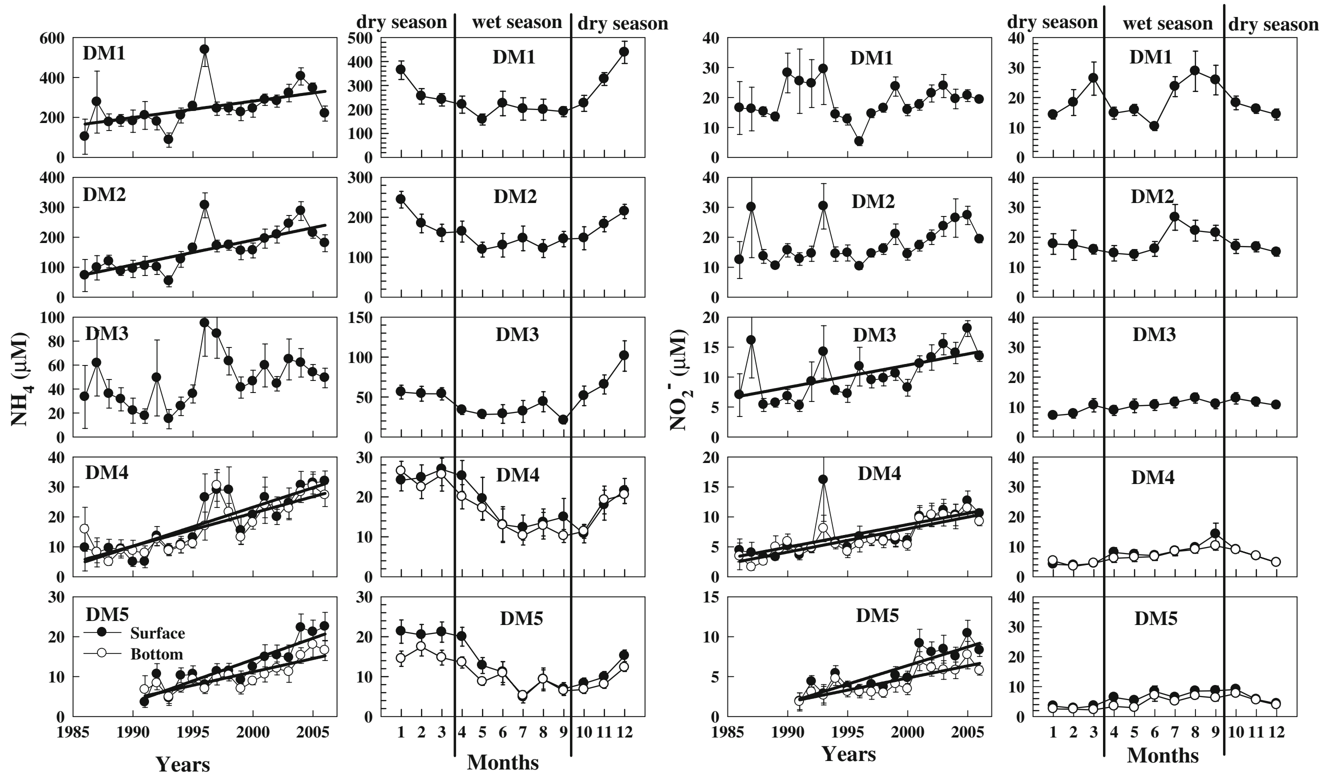

Fig. 4 Annual and monthly average NH_4 and NO_2^- concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

DM1) in the dry season and lower values in wet season throughout the bay. NH_4 concentrations decreased markedly along the bay's axis. The monthly average NH_4 values of 200 to 400 μM at DM1 were one order of magnitude higher than the monthly average of <25 μM at DM5. Annual average NO_2^- concentrations doubled from ~5 to >10 μM during the 21-year period in the outer bay (DM3, DM4, and DM5; Fig. 4).

There was a significant ($p<0.05$) long-term increase in NO_3 at the surface at the rate of 0.45 to 0.94 μM year^{-1} in the outer bay (DM3, DM4, and DM5) where strong seasonal variations in NO_3 were observed at the surface, with high concentrations (40 to 80 μM) in the wet season and low values (10 to 40 μM) in the dry season (Fig. 5). Annual average DIN ($NH_4 + NO_2^- + NO_3$) concentrations increased significantly ($p<0.05$) in the water column in the inner bay by 7.4 to 8.3 μM year^{-1} and at the surface and bottom in the outer bay at the rate of 1.3 to 2.6 μM year^{-1} and doubled from about 35 to 70 μM in the water column throughout the bay during the last two decades. In contrast to the seasonality of NH_4 and NO_3, there were no obvious seasonal patterns for DIN and TN at DM2 and DM3, but DIN and TN were significantly ($p<0.05$, t test) higher at DM1 in the dry season and at DM4 and DM5 in the wet season due to the invasion of Pearl River water at DM4 and DM5 (Fig. 6, Table 1). No long-term trends were observed for SiO_4 at all stations. However, SiO_4 concentrations demonstrated the same seasonality pattern as NO_3 (Fig. 5).

Annual average PO_4 concentrations declined significantly ($p<0.05$) by 0.56 μM year^{-1} at DM1 (Fig. 7, Table 1). A significant ($p<0.05$) long-term decreasing trend in TP concentration was observed at the rate of 0.12 to 1.76 μM year^{-1} at DM1 and at the surface and bottom at DM5 (Fig. 7, Table 1). There was no obvious seasonal variability in PO_4 and TP. PO_4 and TP concentrations exhibited the same inshore–offshore decreasing gradient as NH_4.

DIN to PO_4 molar ratios increased significantly and more than doubled from 12 to 25:1 during the 21-year period in the inner bay where DIN to PO_4 ratios had no seasonal variability and fluctuated between 16:1 and 32:1 (Fig. 8). DIN to PO_4 ratios increased from the inner to the outer bay in summer, with the lowest ratio (22:1) at DM1 and the highest ratio (87:1) at DM5. In contrast, DIN to PO_4 ratios varied seasonally in the outer bay, with low ratios (19:1 to 45:1) in winter and high ratios (37:1 to 87:1) in summer. There was a significant ($p<0.05$) long-term increase in DIN to SiO_4 at the surface and bottom in the outer bay driven by the twofold increase in DIN in the Pearl River water during the 21-year period (Fig. 8).

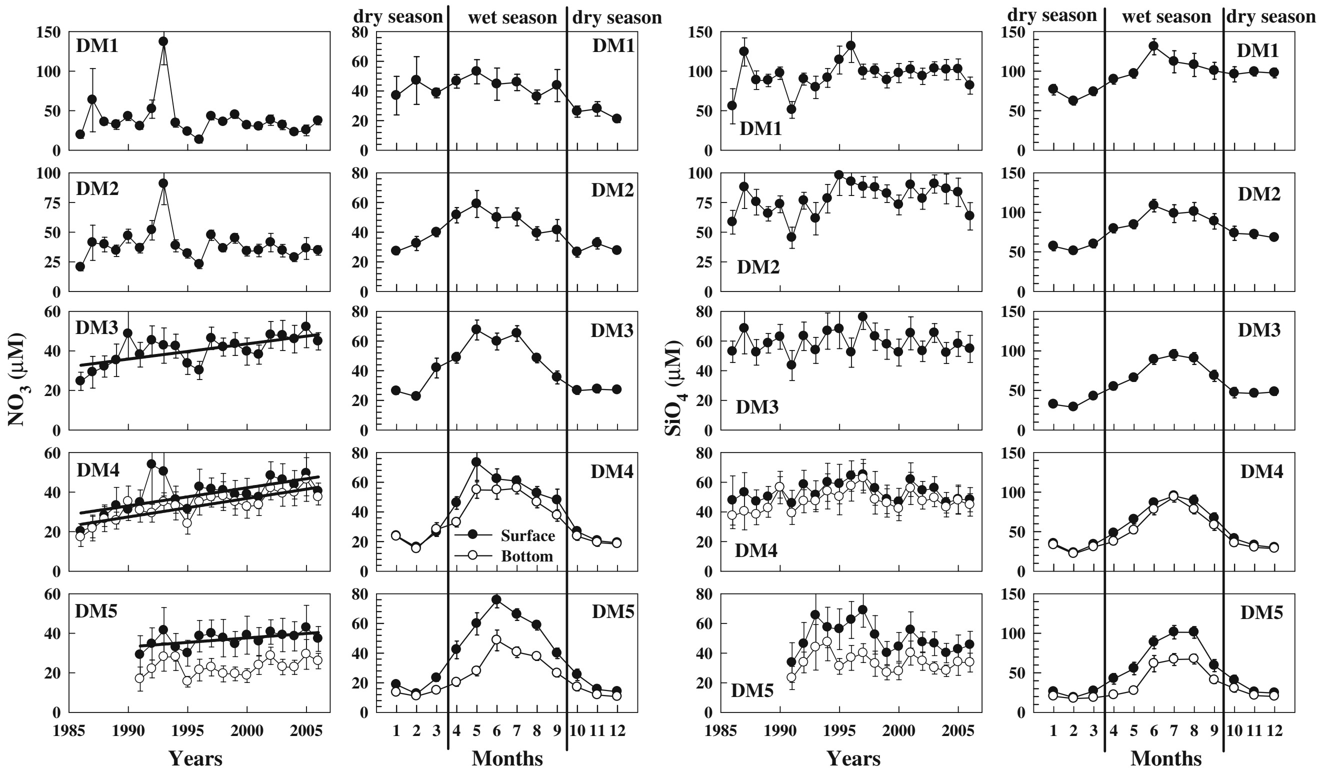

Fig. 5 Annual and monthly average NO_3 and SiO_4 concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

Chlorophyll and Suspended Solids

There was a significant increase in Chl *a* concentrations in the inner bay (DM1 and DM2) at the rate of 0.52–0.57 μg L^{-1} $year^{-1}$ (Table 1). In contrast, no trend was observed in the outer bay. Monthly water column average Chl *a* concentrations were <5 μg L^{-1} at DM4 and DM5 (Fig. 9). There was significantly higher Chl *a* in summer and surprisingly high Chl *a* in January in the inner bay.

There was a significant ($p<0.05$) long-term trend in SS only at DM3. No seasonal variation in SS was observed at any of the stations. SS decreased spatially along the transect from the inner to the outer bay (Fig. 9).

Dissolved Oxygen and Biochemical Oxygen Demand

Annual average DO concentrations at the surface decreased significantly throughout the bay at the rate of 0.07 to 0.13 mg L^{-1} $year^{-1}$, as well as at the bottom at DM5 by 0.07 mg L^{-1} $year^{-1}$ (Fig. 10, Table 1). Likewise, seasonal variations in DO occurred at all stations with the lowest concentrations occurring in late summer, but hypoxia was seldom detected. DO concentrations increased from 3.0–6.4 mg L^{-1} in the inner to 3.9–7.8 mg L^{-1} in the outer bay (Fig. 10). There was a significant ($p<0.05$) increasing trend in biochemical oxygen demand (BOD) at DM2 over the 21-year time series (Fig. 10, Table 1).

Secchi Disk Depth

Annual average Secchi Disk Depth (SDD) decreased significantly at DM1 and DM4 by 0.03 and 0.07 m $year^{-1}$, respectively (Fig. 11, Table 1). The monthly average SDD was very shallow and approximately 25% of the water depth. SDD increased along the bay's axis with the shallowest (usually <0.6 m) at DM1 and DM2, moderate (<0.8 m) at DM3, and the deepest (<2 m) at DM4 and DM5. Even if Chl *a* and SS in the inner bay varied over summer, the monthly average of SDD did not vary accordingly.

Rainfall

Annual average rainfall increased significantly by 11 mm $year^{-1}$ in Hong Kong during 1960–2006, but there was no significant increase during the 21-year period from 1986 to 2006 (Fig. 12a, b). There was a significant negative correlation between surface salinity and rainfall at DM1 and DM2 (Fig. 12c, d).

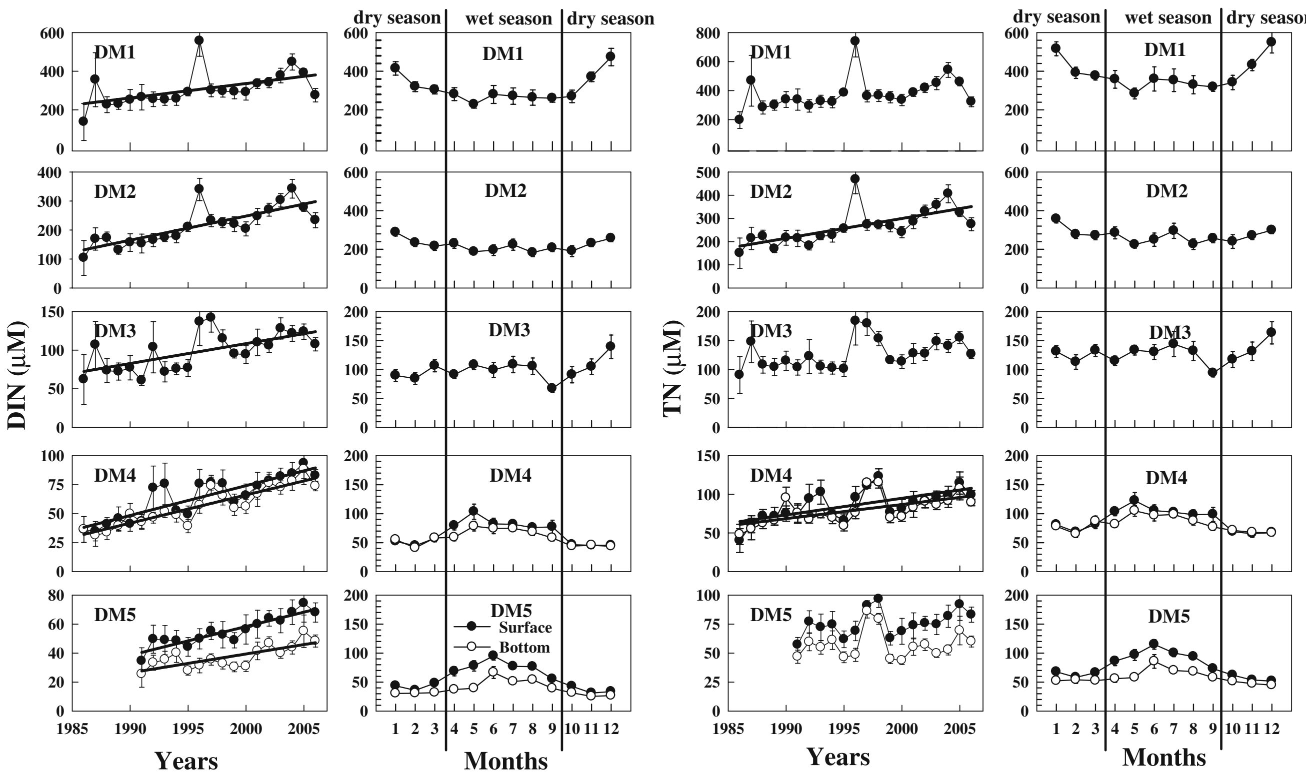

Fig. 6 Annual and monthly average DIN (=NH_4 + NO_2^- + NO_3) and TN concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

Discussion

Hong Kong waters experience seasonal variations with the invasion of coastal/oceanic water induced by the northeast monsoon winds in winter and by the typical two-layer estuarine circulation with the outflow of the Pearl River plume at the surface and the deep oceanic inflow at the bottom due to the southwest monsoon winds in summer (Watts 1983; Yin et al. 1999). As a result, there are marked seasonal and temporal variations in nutrients and phytoplankton biomass (Yin 2002; Xu et al. 2008). The outer part of Deep Bay is connected with the western edge of the Pearl River estuary and the western waters of Hong Kong. It is essential to understand the effects of the Pearl River discharge and the coastal/oceanic water on water quality of the Deep Bay for future management of the bay.

Inner Bay (DM1 and DM2): Long-Term and Seasonal Changes

Seasonal variations in salinity occurred throughout the bay. In winter, relatively high salinity (22–30) and a salinity gradient (up to 8) are evident along the bay's axis from 22–24 at DM1 to 29–31 at DM5, suggesting that the bay is subjected to the invasion of the coastal water from the China Coastal current with low nutrient concentrations (generally <5 μM DIN and <0.5 μM PO_4; Yin et al. 1999; Yin 2002). In summer, when rainfall is maximal, the salinity in the inner bay reaches a minimum due to dilution by rainfall and land runoff. Previous studies have shown that sewage effluent can be detected by NH_4 and PO_4 concentrations, as well as by low DIN to PO_4 ratios (~10:1; Xu et al. 2008). In the inner bay that received high sewage discharge, monthly averaged DIN to PO_4 ratios were generally within Redfield proportions (16:1 to 32:1) and exhibited no seasonality, implying that the Pearl River discharge, with a high DIN to PO_4 ratio of ~100:1 had little influence on the inner bay (DM1 and DM2). The low flushing rate (0.04 day^{-1} or a residence time of ~25 days) in the inner bay (Lee and Qian 2003) likely explains the lack of influence by the invasion of Pearl River water in summer and coastal water in winter.

The shallow (2 m) inner bay is vertically well mixed and most strongly affected by the sewage discharge at DM1. NH_4 was the main contributor (>50%) to the total nitrogen, as indicated by a significant correlation between NH_4 and TN, and the intercept of <123 μM (Fig. 13). The same results were observed for the correlation between TP and

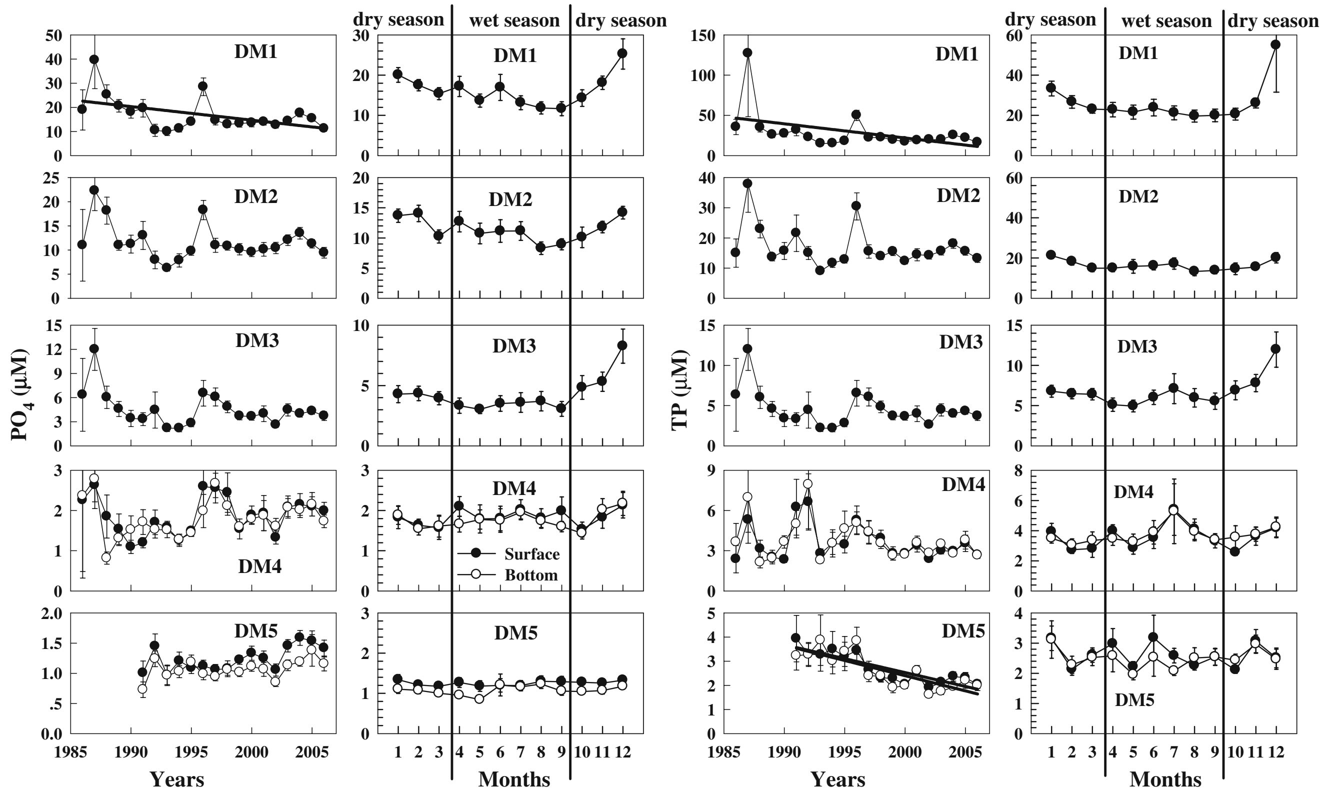

Fig. 7 Annual and monthly average PO_4 and TP concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

PO_4 (Fig. 13). Elevated NH_4 and PO_4 concentrations are good indicators of inputs from sewage discharge (Xu et al. 2008). The long-term increase in NH_4 concentration of 8.2 μM year^{-1} at DM1 is due to the increase in the sewage discharge and the increased human population of Shenzhen from ~310,000 in 1980 to over eight million today. The long-term PO_4 reductions are related to the P-containing detergent ban in the 1990s and the improvement in sewage treatment. In turbid estuaries, sorption onto particles and colloidal aggregation often removes phosphate, especially when phosphate is high (>5 μM; Sanders et al. 1997; Soetaert et al. 2006). As a result of the PO_4 reduction and NH_4 increase, the annual average DIN to PO_4 ratio increased by over four times from 6:1 in 1986 to 25:1 in 2006. Based on the Redfield ratio of 16N:1P, the potential limiting nutrient shifted from N to P limitation after the phosphate detergent ban. Similar increases in stoichiometric ratios of DIN to PO_4 have been reported in many other estuaries following the improved treatment of sewage (Philippart et al. 2000; Nedwell et al. 2002; Soetaert et al. 2006).

In general, NH_4 and PO_4 loading from the sewage should remain relatively constant among all seasons. However, seasonal patterns showed that there was a sharp decline in NH_4 and PO_4 concentrations by 200 and 10 μM, respectively, in summer, relative to winter (Figs. 4 and 7). This was most likely due to dilution by rainfall and land runoff which is clearly evident by the very low salinity in July at DM1 and DM2. We estimate that the contribution of the phytoplankton uptake component to the observed decrease in NH_4 and PO_4 was very low: based on Redfield ratios, only ~25 μM N and <2 μM PO_4 would be required to produce the 25 μg Chl L^{-1} of algal biomass measured in the water column in summer. The DON and PON concentrations, estimated from the intercept in the plots of TN vs DIN (Fig. 14), were relatively low (20–22 μM). Hence, we speculated that a minor fraction of NH_4 was converted to organic N through phytoplankton and bacterial uptake. The low pH value in the inner bay was more likely related to the input of low pH sewage. Unfortunately, this time series data set does not have bacterial abundance estimates. In addition, the decrease in NH_4 due to nitrification, derived from the total increase of 30 μM N from NO_3 and NO_2^- in summer, did not explain the 200-μM reduction in NH_4 (Fig. 4). Therefore, the reductions in NH_4 and PO_4 in summer were likely due mainly to dilution by rainfall and land runoff. This suggestion is also supported by the observation that TN

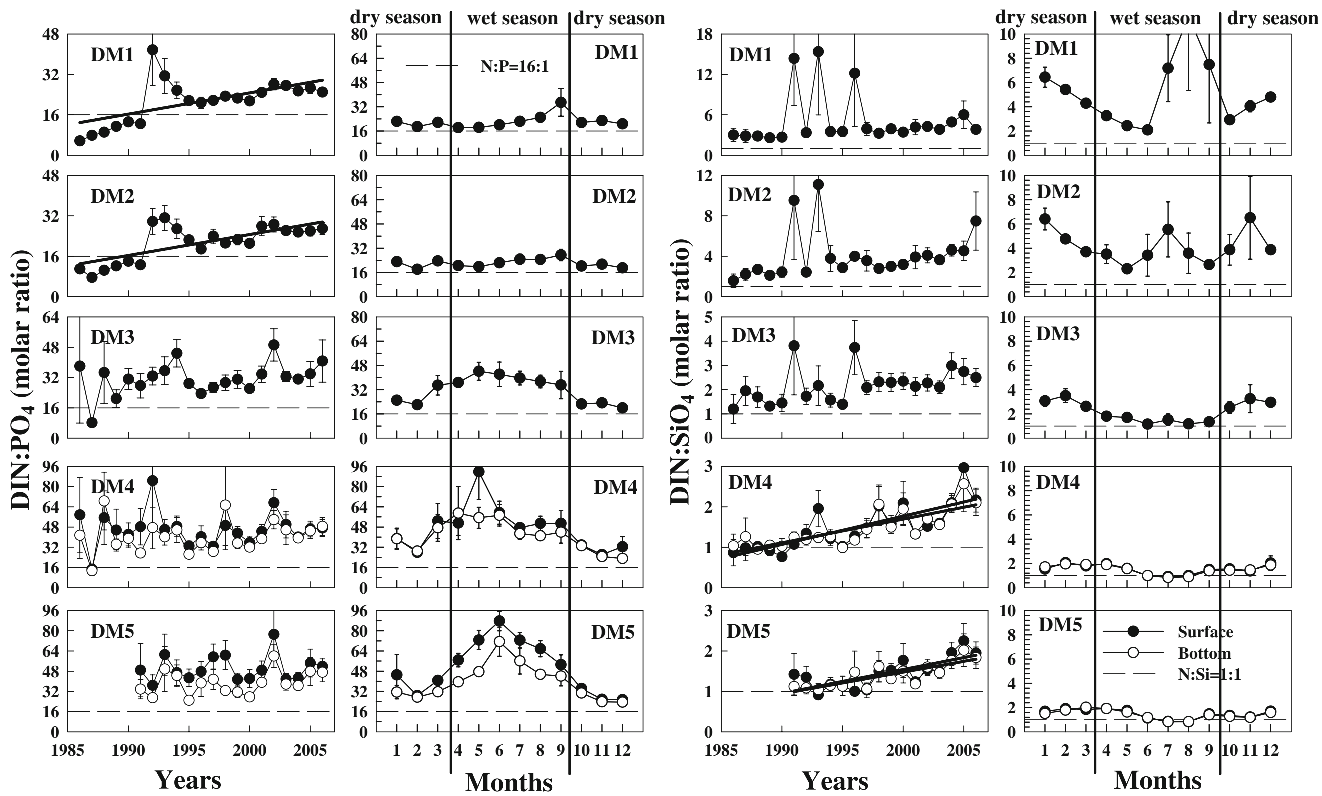

Fig. 8 Annual and monthly average DIN to PO_4 ratios and DIN to SiO_4 ratios at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

concentrations were lower in the wet season than the dry season despite the increased input of NO_3 from the land runoff in the wet season. The significant positive correlation between monthly average NH_4 and salinity implied that freshwater input played an important role in the dilution of the sewage (Table 3).

Silicate is also an indicator of the freshwater inputs since it comes from terrestrial inputs through runoff. In summer, a maximum Si concentration of 140 μM at DM1 and 120 μM at DM2 was observed in the inner bay, higher than those (~100 μM) in the outer bay, implying that the summer maximum of Si concentrations in the inner bay was due to the high inputs from land runoff around the inner bay caused by the maximal rainfall during this period, rather than input from the Pearl River discharge. The runoff inputs also led to the similar increase in NO_3 concentrations in summer. The lower peak in NO_3 concentrations (~60 μM) in the inner bay than the 60–80 μM in the outer bay (Fig. 5) was associated with a smaller contribution of nitrogen from agriculture to NO_3 concentrations rather than from the Pearl River discharge. In summer, rainfall reaches a maximum monthly average value of 400 mm, about ten times higher than winter (http://gb.weather.gov.hk/). The significant ($p<0.05$, t test) seasonal increase in Si concentrations suggested that the contribution of freshwater inputs into the inner bay increased dramatically in summer. The freshwater inputs resulted in a rapid decrease in salinity in the inner bay that is relatively enclosed and weakly flushed (Lee and Qian 2003). As a result, salinity was low (~5) in summer (Fig. 3). Similar findings have been reported in the Scheldt estuary in Belgium (Soetaert et al. 2006).

High Chl *a* concentrations are a good indicator of eutrophication impacts (Pinckney et al. 1999; Paerl et al. 2006; Wong et al. 2009). Based on a N to Chl ratio of 1 μmol:1 μg, Chl *a* concentrations were expected to be at least 200 μg L^{-1} all year, if no factors other than nutrients limited algal growth. Nonetheless, the maximum monthly average Chl *a* concentrations were <40 μg L^{-1} in the inner bay, much lower than expected. In addition, Chl *a* concentrations were overestimated as the analytical method is sensitive to chlorophyll *b* from chlorophytes. In this area, the SS concentrations were 20–100 mg L^{-1}, much higher than a threshold value of 10 mg L^{-1} above which primary production starts to become light-limited (Ragueneau et al. 2002; Soetaert et al. 2006). We speculate that phytoplankton growth was limited by light because of vertical mixing (wind

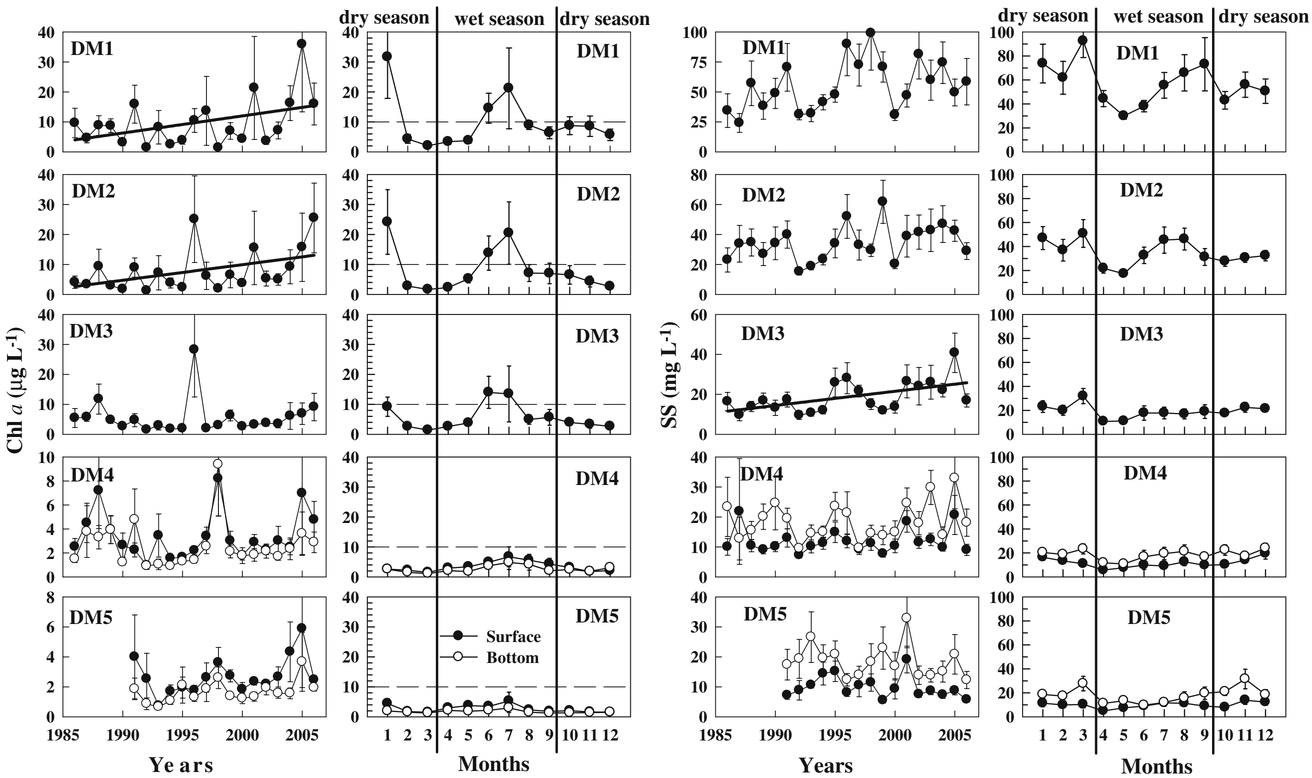

Fig. 9 Annual and monthly average Chl *a* and SS (SS) concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. The *dashed horizontal line* represents the Chl *a* concentration (10 µg L^{-1}) that indicates an algal bloom. Note the change in the scale on the *y-axis*

and tides) and the relatively high SS concentrations, since nutrients were not limiting in the inner bay and any change in DIN to PO_4 ratios from 5–10:1 to ~26:1 had little effect on phytoplankton growth. The resuspension of the sediment due to the shallow depth reduces the light penetration into the water column, as indicated by the shallow Secchi disk depth (Fig. 11). Light limitation for phytoplankton growth has often been reported in other turbid estuaries and coastal areas (Soetaert et al. 1994; Fisher et al. 1999; Colijin and Cadée 2003). In addition, the high phaeopigment to Chl *a* ratio (1.1 to 7.4 µg/µg; Table 4) suggested active grazing, and bacterial consumption made an important contribution to Chl *a* decomposition. A recent study indicates that micro-zooplankton grazing is one of the important factors regulating the phytoplankton growth in western waters next to Deep Bay (Chen et al. 2009). In the inner bay, the extremely high NH_4 concentrations of 200 to 400 µM also very likely inhibited phytoplankton growth to some extent based on previous studies that have shown that the inhibition of the algal growth occurs at 36 µM NH_4 or lower (Natarajan 1970; Admiraal 1977; Thomas et al. 1980; Chang and McClean 1997; Yoshiyama and Sharp 2006). It is possible that the inner bay was in a hypereutrophic state where net heterotrophy (bacterial production) dominates rather than autotrophy (algal production), but, without bacterial abundance data, it is not possible to confirm this hypothesis.

It is not clear why there was a significant long-term increase in Chl *a* since nutrients were never limiting. It is possible that the increase in Chl *a* is attributed to the decrease in salinity that was most likely caused by a combination of the increase in the freshwater sewage discharge from Shenzhen and the increase in rainfall by 28 mm $year^{-1}$ over the 21-year period. The increased freshwater discharge generally produces two contrasting effects on the phytoplankton biomass. The increased freshwater discharge improves water stability by reducing vertical mixing and increasing stratification, which favors the accumulation of phytoplankton biomass. On the other hand, high freshwater discharge dilutes the phytoplankton biomass. The former was responsible for the increasing trend in Chl *a* since modeling results showed that there was a low flushing rate (0.04 day^{-1}) in the inner bay (Lee and Qian 2003). A more rapid decline in salinity in the inner bay relative to the outer bay generated a pronounced salinity gradient along the axis of the bay and probably increased the residence time by weakening water circula-

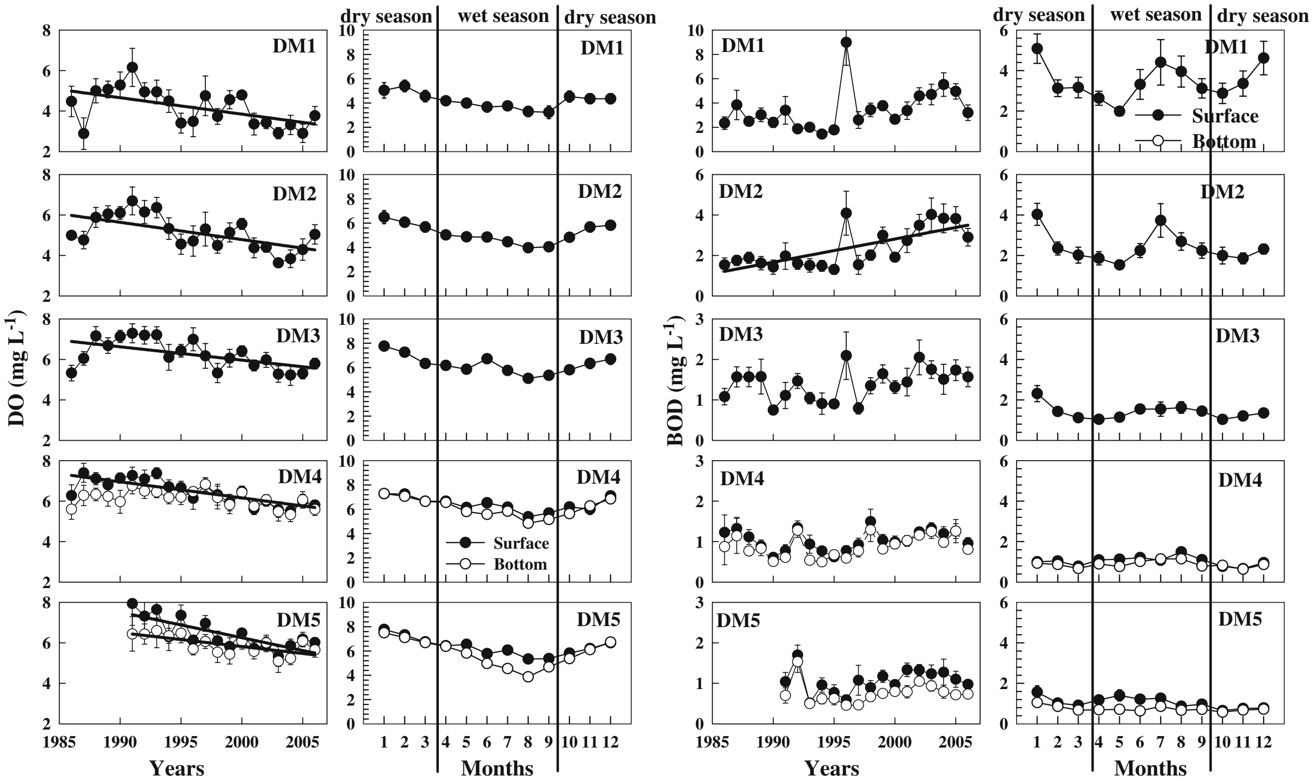

Fig. 10 Annual and monthly average dissolved oxygen (*DO*) and BOD concentrations at the surface (DM1, DM2, and DM3) and surface and bottom (DM4 and DM5) at five stations in Deep Bay during 1986–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=6$ during 1986–1987 and $n=12$ during 1988–2006 at all stations for the annual average data and $n=21$ for DM1 to DM4 and $n=16$ for DM5 for the monthly average data. Note the change in the scale on the *y-axis*

tion. In summer, salinity reached a minimum and increased water stability. Furthermore, the invasion of the Pearl River discharge has little effect in the inner bay. By comparison, the invasion of the relatively high salinity coastal water in winter into the outer bay produced a pronounced salinity gradient along the bay's axis, which increased the residence time in the inner bay. Thus, relatively high monthly averaged Chl *a* concentrations (>20 μg L^{-1}) occurred in both summer (June/July) and winter (January).

In the inner bay, hypoxic events (<2 mg DO L^{-1}) did not appear to be frequent (<10% of total sampling times). However, in this study, samples were taken at 1 m above the sediment during the daytime, and therefore near-bottom hypoxic events were probably underestimated since hypoxic events could develop just above the sediment and be more pronounced at nighttime. Despite this fact, the extent of hypoxia was overall not as severe as expected, and long-term hypoxic events were absent, which is mainly attributed to the shallow depth (~2 m). Fisher et al. (1999) found that the extent of hypoxia was inversely correlated with the mean depth in regions of Chesapeake Bay. The long-term DO reductions were due to the increased domestic sewage loading with already low oxygen and high organic matter. More organic matter inputs into this area due to the increased sewage effluent stimulated bacterial respiration, leading to lower DO, as indicated by the increasing trend in BOD at DM2. Enhanced BOD was considered to be responsible for the decrease in DO in many other estuaries (St. John 1990; Brosnan and O'Shea 1996). Meanwhile, an increase in the freshwater loading was partially responsible for the decreased DO by weakening water circulation and increasing the water stratification. The significant decreasing trend in DO concentration indicates the need for further sewage treatment for Shenzhen.

Seasonal variations in DO were observed with low concentrations in summer and maximum values in winter. The DO minimum in summer was related to higher temperature, as indicated by a significant correlation between monthly average DO and temperature (Table 5). In summer, the high water temperature resulted in elevated bacterial respiration, as well as a decrease in solubility of DO in the water column (Truesdal et al. 1955; Carpenter 1966).

Outer Bay (DM3 to DM5): Long-Term and Seasonal Changes

At the deeper stations (DM4 and DM5) in the outer bay, the bottom temperature rose significantly in summer and winter

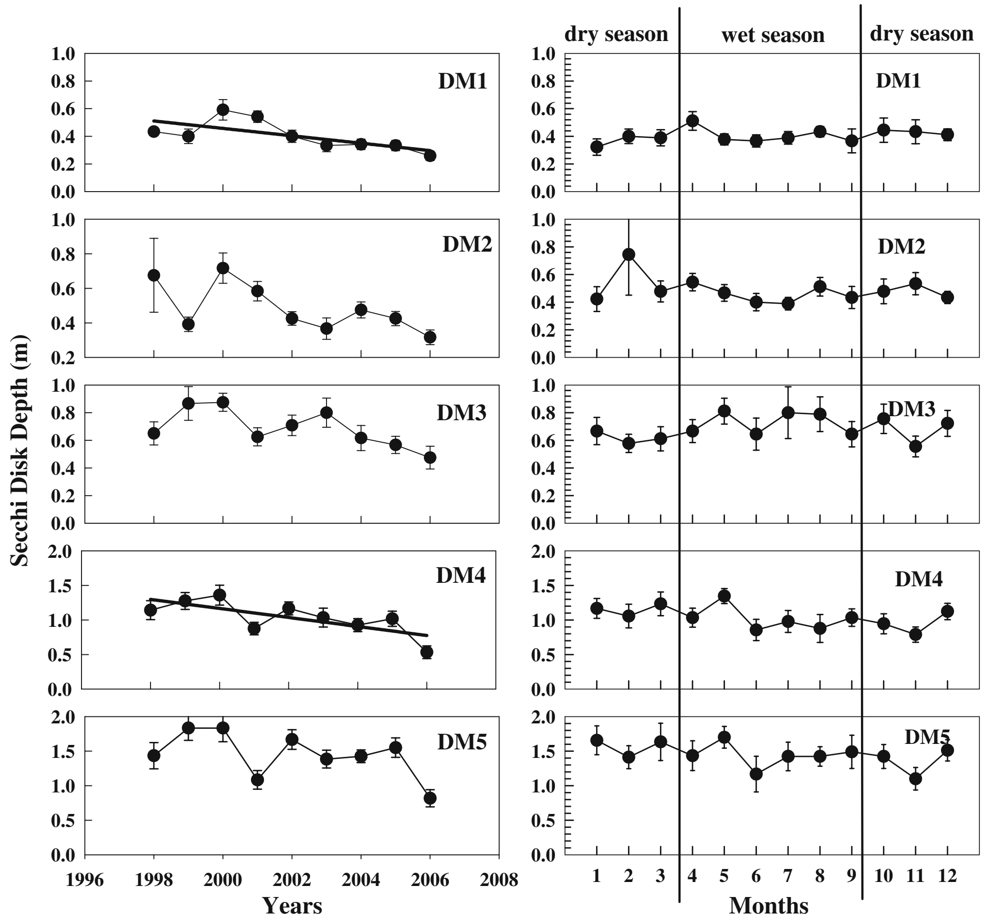

Fig. 11 Annual and monthly average Secchi disk depths at five stations in Deep Bay during 1998–2006. The linear regression line represents a significant linear regression trend ($p<0.05$). *Vertical bars* indicate ±1 SE and $n=9$

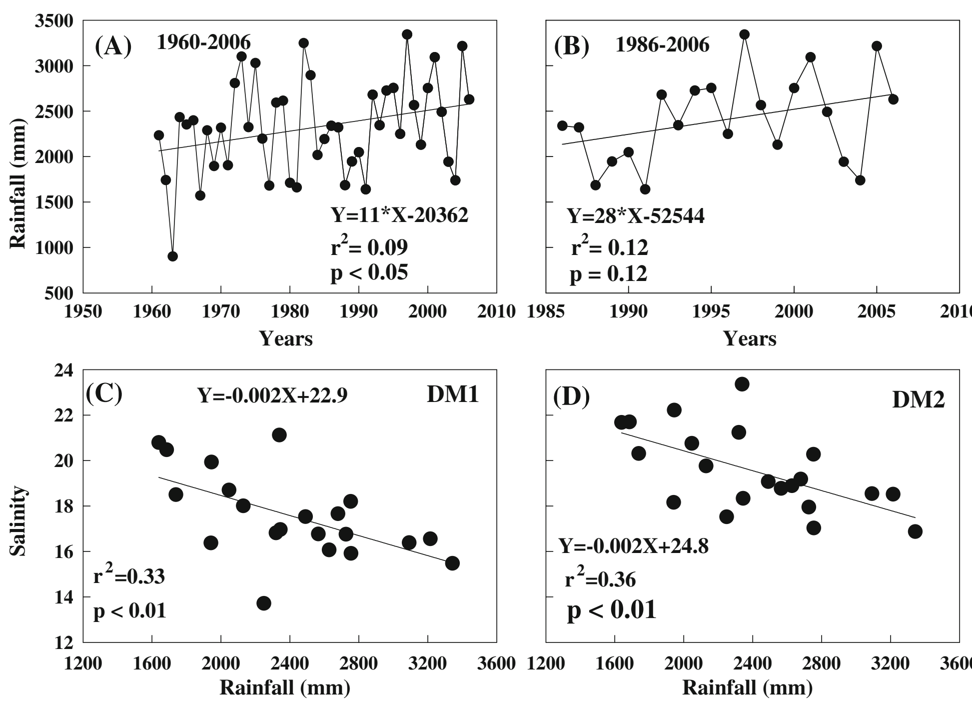

Fig. 12 Annual average rainfall in Hong Kong waters during 1960 to 2006 (**a**) and 1986–2006 (**b**). A significant linear regression trend is denoted by $p<0.05$. Concentrations and linear regressions of annual average salinity vs rainfall for the surface in the inner bay at DM1 (**c**) and DM2 (**d**) during 1986–2006

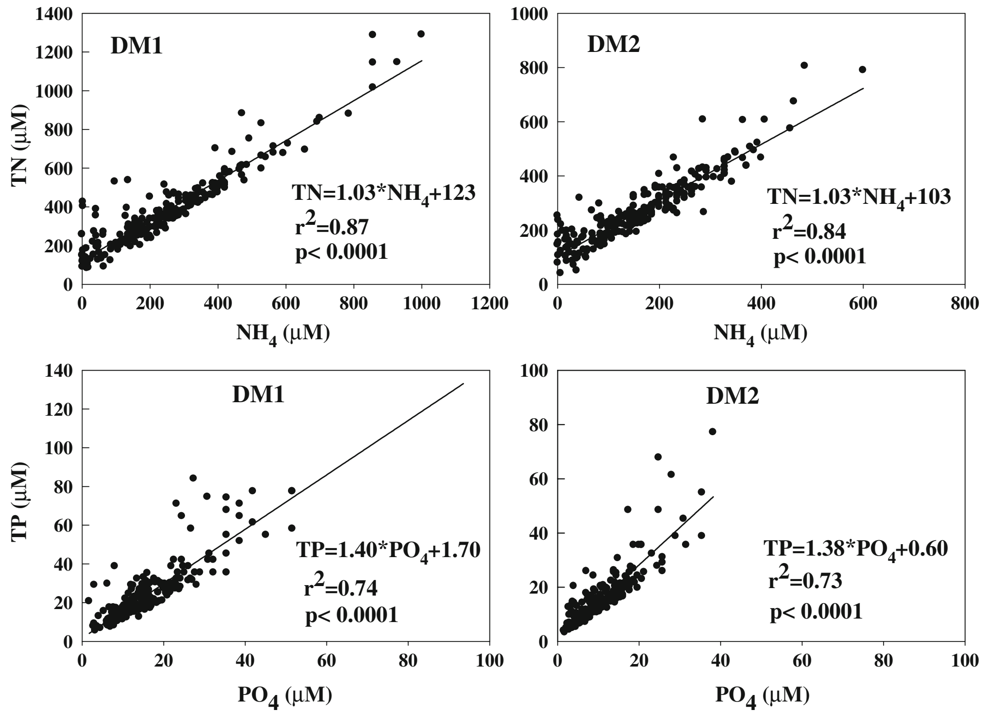

Fig. 13 Concentrations and linear regressions of TN vs NH_4 and TP vs PO_4 for the surface in the inner bay (DM1 and DM2) from the time series from 1986 to 2006

during the last two decades, and the largest increase occurred in winter, as indicated by the higher rate of increase (0.23°C year^{-1}) at DM5. The long-term increase (0.5–2°C) in the surface and bottom temperature during the last two decades was observed in other waters (e.g., western and southern waters, Victoria Harbor) of Hong Kong (Ho 2007). The rate of increase (0.14 in summer and 0.23°C year^{-1} in winter) in the bottom temperature at DM5 was greater than at DM4 (Table 2). The slower rate of increase at DM4 was possibly attributed to strong vertical mixing due to shallow depth (4 m), as indicated by the small difference between surface and bottom salinity (Fig. 2). The long-term increase in temperature reflected climatic changes in Hong Kong waters which affects ecological responses to eutrophication (Howarth et al. 2000).

In July, when the Pearl River discharge is maximal, the salinity reached a minimum due to dilution by the Pearl River discharge in the outer bay, especially at DM5. The Pearl River discharge has high NO_3 (~100 μM) and SiO_4 (>100 μM) concentrations, as well as high DIN to PO_4 ratios (~100:1; Yin et al. 2000), since the nutrient inputs are from agriculture, rainfall, and groundwater as well as sewage. In the outer bay, monthly averaged DIN to PO_4 ratios demonstrated strong seasonal variability with a maximum DIN to PO_4 ratio of ~90:1 in June at DM5 (Fig. 8). These results indicated that the outer bay is influenced by the Pearl River discharge with high DIN in summer. However, in winter, it is influenced by the invasion of coastal water with low DIN. This suggestion is supported by the high flushing rate (0.2 day^{-1} or a residence time of ~5 days) in the outer bay (Lee and Qian 2003).

A threefold or more increase in NH_4 at the surface was observed (from 3–10 to 20–31 μM) at the outer bay stations (DM4 and DM5, respectively) in response to the increased sewage loading during the last 21 years. PO_4 concentrations exhibited no seasonal pattern in the outer bay. At DM5, PO_4 concentrations (~1 μM) were similar to that in the Pearl River discharge (Yin et al. 2000).

The increase in NO_3, but no increase in SiO_4, is consistent with the recently documented long-term increasing trend for NO_3 in the Pearl River discharge during the last two decades (Xu et al. 2008). Significant correlations between salinity and NO_3 or SiO_4 in the outer bay (Fig. 15) suggest that these nutrients come from the Pearl River discharge and that they have both behaved conservatively during the last two decades. NO_3 and SiO_4 concentrations in the Pearl River discharge, estimated by the intercept concentrations, are similar to the observed values (NO_3 75–100 μM; SiO_4 130–140 μM) in the near-zero salinity end member in the Pearl River estuary (Yin et al. 2000, 2001; Cai et al. 2004). These results also agree with the observations in the adjacent western waters (Xu et al. 2008). The long-term increasing trend in DIN, accompanied by the increase in DIN to SiO_4 ratios as a result of the increase in NH_4 and NO_3, suggests that eutrophication impacts are becoming more severe, and nutrient ratios are being altered in this area during the last two decades. Similar to the inner bay, DIN was the main component

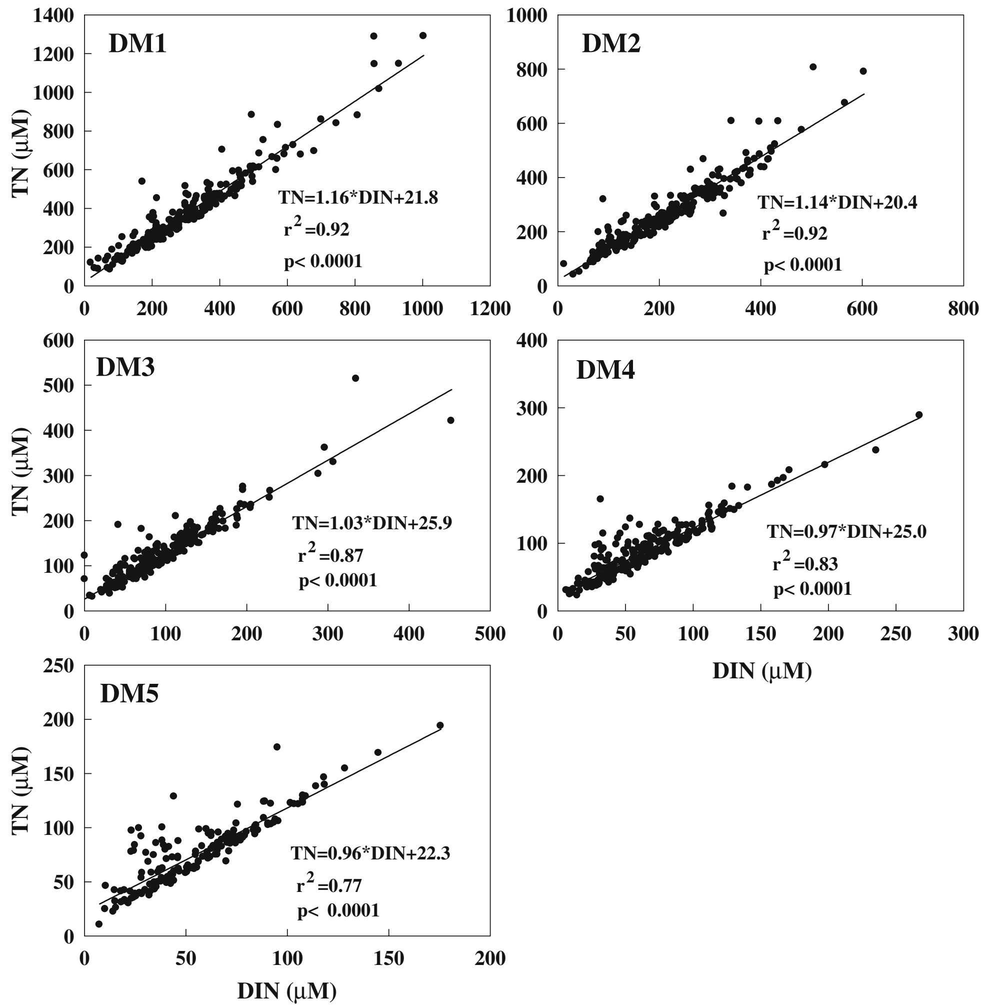

Fig. 14 Concentrations and linear regressions of TN vs DIN for the surface for five stations from the time series from 1986 to 2006. Intercept=DON + PON

(>50%) of TN in the outer bay, indicating that there was little contribution from particulate organic N. Annual and monthly average DIN to PO_4 ratios were greater than the Redfield ratio of 16N:1P, suggesting that P was deficient relative to N in this region. However, the ambient PO_4 concentrations remained >1 µM, well above the threshold value for P limitation (PO_4≈0.1 µM, Justić et al. 1995), implying that actual P limitation rarely occurred.

Table 4 Phaeopigment to Chl *a* ratio (µg/µg) at the surface in Deep Bay during 1986–2006

Month	DM1	DM2	DM3	DM4	DM5
1	4.29±1.68	4.61±1.76	1.37±0.51	1.74±0.75	1.63±0.72
2	3.61±0.91	3.19±0.81	2.11±0.87	0.87±0.24	0.57±0.15
3	4.23±1.34	3.64±1.40	1.83±0.69	1.03±0.27	0.60±0.09
4	4.23±1.81	1.97±0.58	1.02±0.24	1.04±0.37	0.52±0.13
5	1.94±0.61	1.11±0.24	0.78±0.15	1.07±0.29	1.06±0.26
6	1.72±0.57	2.09±0.58	1.40±0.61	1.03±0.22	1.60±1.04
7	4.61±2.12	2.19±0.59	1.83±0.71	2.91±0.83	1.56±0.59
8	1.62±0.57	2.04±0.48	0.89±0.23	1.66±0.43	1.12±0.43
9	7.44±4.23	3.31±1.19	2.07±0.90	1.03±0.27	1.83±0.71
10	1.68±0.71	1.82±0.77	1.86±1.05	0.94±0.29	1.62±0.71
11	5.45±4.42	2.56±0.92	0.83±0.16	1.24±0.64	1.40±0.54
12	2.32±0.54	2.24±0.60	2.22±0.95	1.04±0.27	0.92±0.36

Error bar represents ±1 SE, n=21 for DM1, DM2, DM3, and DM4 and n=16 for DM5

Table 5 Correlation coefficients, *r*, derived from a Pearson test, between monthly average NH_4 and salinity and DO and temperature for the inner bay (DM1 and DM2) from 1986 to 2006; $n=12$ (months in a year)

Stations	Variable	Salinity		Variable	Temperature	
		n	*r*		*n*	*r*
DM1	NH_4	12	0.59[a]	DO	12	−0.86[b]
DM2		12	0.71[a]		12	−0.94[b]

[a] Significant correlation at the 0.05 level

[b] Significant correlation at the 0.01 level

In the outer bay, annual and monthly average Chl *a* concentrations in the water column were usually <10 µg L^{-1} and lower than expected. Phytoplankton biomass exhibited no long-term or seasonal trends, as well as no response to long-term and seasonal changes in nutrients. Organic nitrogen (DON and PON) was 22 to 26 µM (Fig. 14), comparable to those in the inner bay and <50% of the total N. These results indicated that the factor regulating phytoplankton growth and biomass accumulation was not nutrient concentrations but physical processes and grazing. This suggestion was supported by the conservative mixing in the transport of NO_3 and SiO_4. In the outer bay, the high flushing rate was likely responsible for low phytoplankton biomass (Lee and Qian 2003). The influence of physical processes on the regulation of phytoplankton growth was also observed in the nearby western waters of Hong Kong (Xu et al. 2008, 2009).

In the outer bay, the long-term and seasonal patterns of DO were similar to the inner bay, suggesting that DO concentrations were mainly affected by the advection of low oxygen water from the inner bay. The decrease in DO is not as severe as observed in the inner bay. The lowest bottom DO occurred in summer because of the strong thermohaline stratification and higher bacterial respiration induced by higher water temperatures.

Spatial Variations in Water Quality

There was a strong gradient in water quality from the inner to the outer bay in response to the sewage inputs from Shenzhen. High NH_4, PO_4, and BOD were observed, as well as low DO concentrations in the inner bay where the maximum annual water column averaged NH_4 and PO_4 concentrations exceeded 500 and 39 µM, respectively. In contrast, NH_4 and PO_4 concentrations decreased sharply from the inner to the outer bay because of dilution due to the invasion of Pearl River water in summer and coastal water in winter. At DM5 (outer bay), NH_4 and PO_4 concentrations were only ~5% of those at DM1 (inner bay), implying that the sewage discharge at DM1 had little effect on the water quality outside the bay. This suggestion is supported by the relatively low NH_4 and PO_4 concentrations in western Hong Kong waters adjacent to Deep Bay (EPD 2006). Correspondingly, DO concentrations increased from an annual and monthly average value of 3 mg L^{-1} in the inner bay to >4.5 mg L^{-1} in the outer bay, possibly because of mixing with high oxygen water from the Pearl River discharge in summer and the coastal water in winter.

Summary

Deep Bay can be divided into the inner bay (DM1 and DM2) and the outer bay (DM3 to DM5). The inner bay has a relatively small volume of water since it is only 2 m deep and a long residence time of about 25 days. Therefore, high rainfall and runoff in summer reduces the salinity from ~25 in winter to 7 in July. Similarly, the climatic effect of the significant increase in rainfall (11 mm $year^{-1}$) over the last 45 years increased stratification and reduced light limitation, which explained the increase in Chl over the 21-year period, since nutrients are not limiting. Phytoplankton growth was likely limited by grazing and light due to vertical mixing and SS, as well as by ammonium toxicity. The lowest DO (monthly average of ~3.0 mg L^{-1}) occurred in the inner bay near the sewage effluent discharge site.

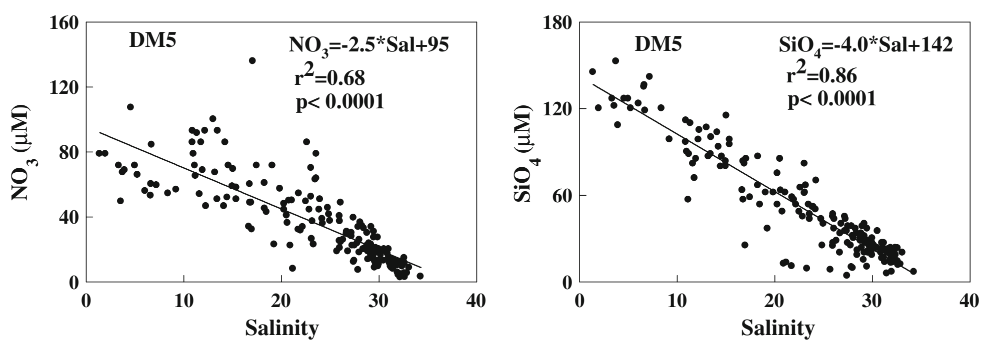

Fig. 15 Concentrations and linear regressions of NO_3 and SiO_4 versus salinity for the surface for the outer bay (DM5) from the time series from 1991 to 2006

Long-term hypoxic events were not frequent (<10%) throughout the bay due to the shallow depth and mixing. Information on bacterial biomass should also be considered in future monitoring.

The outer bay experienced seasonal exchange between the Pearl River discharge with high DIN to PO_4 ratios in summer and the coastal water with low DIN to PO_4 ratios in winter. The twofold increase in NO_3 and DIN and no significant increase in PO_4 in the outermost station in the bay confirm previous findings that the >20-year increase in the N loading from the Pearl River has shifted the receiving waters of the Pearl River into potential P limitation especially in summer. Phytoplankton growth was primarily regulated by the dilution of the Pearl River discharge and possibly grazing in the outer bay. Hypoxia seldom occurred in the outer bay. However, DO concentrations showed a significant long-term reduction from 0.07 to 0.13 mg L^{-1} $year^{-1}$ throughout the bay in response to the increase in sewage loading and suggests that further sewage treatment is warranted in the future. Thus, in order to understand the long-term changes in Deep Bay, it is necessary to consider the climatic effects of increased rainfall along with the increase in anthropogenic nutrient loading.

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