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RESEARCH ARTICLE

Spatial assessment of water quality using chemometrics in the Pearl River Estuary, China

Meilin WU (✉)[1], Youshao WANG[1,2], Junde DONG[1], Fulin SUN[1,2], Yutu WANG[1,2], Yiguo HONG[1]

1 State Key Laboratory of Tropical Oceanography, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
2 Marine Biology Research Station at Daya Bay, Chinese Academy of Sciences, Shenzhen 518121, China

Abstract A cruise was commissioned in the summer of 2009 to evaluate water quality in the Pearl River Estuary (PRE). Chemometrics such as Principal Component Analysis (PCA), Cluster analysis (CA) and Self-Organizing Map (SOM) were employed to identify anthropogenic and natural influences on estuary water quality. The scores of stations in the surface layer in the first principal component (PC1) were related to NH_4-N, PO_4-P, NO_2-N, NO_3-N, TP, and Chlorophyll *a* while salinity, turbidity, and SiO_3-Si in the second principal component (PC2). Similarly, the scores of stations in the bottom layers in PC1 were related to PO_4-P, NO_2-N, NO_3-N, and TP, while salinity, Chlorophyll *a*, NH_4-N, and SiO_3-Si in PC2. Results of the PCA identified the spatial distribution of the surface and bottom water quality, namely the Guangzhou urban reach, Middle reach, and Lower reach of the estuary. Both cluster analysis and PCA produced the similar results. Self-organizing map delineated the Guangzhou urban reach of the Pearl River that was mainly influenced by human activities. The middle and lower reaches of the PRE were mainly influenced by the waters in the South China Sea. The information extracted by PCA, CA, and SOM would be very useful to regional agencies in developing a strategy to carry out scientific plans for resource use based on marine system functions.

Keywords principal component analysis, self-organizing map, estuarine water quality, the Pearl River Estuary, spatial variation

1 Introduction

The Pearl River is China's third longest river (2200 km), after the Yangtze and Yellow Rivers. The Pearl River has three principal tributaries, namely the Xijiang River, the Beijiang River, and the Dongjiang River (Chen et al., 2004). Its drainage basin is located in a sub-tropical climate zone with annual rainfall of 1600 – 2300 mm (Huang et al., 2003). The annual average river discharge is 10,524 $m^3 \cdot s^{-1}$, with 20% occurring during the dry season from October to March, and 80% during the wet season from April to September (Zhao, 1990). The Pearl River Estuary is located midway along the northern boundary of the South China Sea. The coast has a NE-SW orientation and the adjacent marine shelf is 150 – 250 km wide (Harrison et al., 2005). The Pearl River drains an area of 452,000 km^2 (Zhao, 1990). In recent years, rapid economic growth and anthropogenic stress from cities such as Guangzhou, Hong Kong, Macau, Shenzhen, Dongguan, Zhongshan, Jiangmen, and Zhuhai have greatly affected the water in the Pearl River Estuary.

The Pearl River flows into the Pearl River Delta which has become one of the leading economic regions and a major manufacturing center of China and the world. As a consequence of high population, the river receives much input from both natural and anthropogenic origins that may cause deterioration of water quality. Furthermore, an estuary is a very complex body of water where freshwater and seawater mix. The mixing of seawater with river discharge and the accompanying biogeochemical processes reduce the pollution within the estuary. The Pearl River Estuary is a wide body of water, which complicates the hydrodynamics and the ecosystem even further (Chen et al., 2004), since the upper reach of the Pearl River Estuary is comprised of narrow and shallow river channels and is primarily dominated by river discharges. The Pearl River Estuary is a complex system where several different circulation regimes coexist and various types of fronts form between these circulation regimes such as the river plume front and coastal temperature front (Wong et al., 2003; Hu and Li, 2009). No complete study has been performed on the water quality caused by human activities

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E-mail: mlwu@scsio.ac.cn

and natural processes in the estuary. Some authors have described local effects in the Pearl River Estuary caused by nutrients (Huang et al., 2003), heavy metals (Duzgoren-Aydin, 2007; Cheung et al., 2008; Dou et al., 2009; Wei and Huang, 2010), and persistent organic pollution (Li et al., 2010; Qiao et al., 2010).

The spatial distribution of water quality in the estuary may be related to the types of pollutant loadings in the river system, such as agriculture, industrial activities, and seawater intrusion. Water quality assessment is involved with the measurement of multiple parameters taken from many monitoring stations. Consequently, it is difficult to interpret these huge and complex data matrices comprised of a large number of physico-chemical parameters. Chemometrics is deemed the best approach to interpret latent meaningful information from the large data matrices. Chemometric methods such as principal component analysis and cluster analysis are widely used to identify the spatial and temporal distribution of water quality in coastal waters (Shrestha and Kazama, 2007; Wu and Wang, 2007; Zhou et al., 2007; Astel et al., 2008; Wu et al., 2010, 2012) . However, few studies have applied a self-organizing map to identify anthropogenic effects on water quality. Kohonen (1982) put forward the self-organizing map (SOM), a type of artificial neural network (ANN) with unsupervised learning which can provide a way of representing multidimensional data in a much lower dimensional space, usually one or two dimensions (Kohonen, 1982; Kohonen, 2001). SOM has been employed to interpret the temporal and spatial variations of water quality (Lu and Lo, 2002; Song et al., 2007; Astel et al., 2008; Cereghino and Park, 2009; Çinar and Merdun, 2009; Ye et al., 2009). SOM can present excellent visualization capabilities to illustrate water quality characteristics. This visual information will be useful for government and the public to know the water quality status. From a top-down perspective, these results will be an effective way for improving water quality; when management organizations are aware of the spatial pattern of deteriorated water quality and key factors, they can take effective measurements to deal with it. Meanwhile, it is very important to make the public know about related information on water quality, in order to address water environmental protection.

In this study, chemometrics such as PCA, CA, and SOM were employed to identify the spatial pattern of water quality in the Pearl River Estuary and the corresponding driving factors caused by the natural and anthropogenic activities in the Pearl River Estuary.

2 Materials and methods

2.1 Sampling and analytical method

The sampling stations were chosen along the main estuary course axis downstream (Fig. 1). Water samples were taken at the surface (1 m below the surface) and bottom (1 m above the bottom) layers of 28 observation stations in August 17 – 24, 2009 (Wang, 2013). A YSI 6600 V2 Sonde water quality monitoring system (YSI Incorporated, USA) was employed to collect the data for temperature (°C), turbidity (Turbid/ntu), pH, and salinity (psu) from the surface to bottom layers. Total suspended particulate matter ($SPM/(g\cdot L^{-1})$) was weighed after drying samples in a 50°C oven for 24 h. Seawater samples for analysis of nutrients and Chlorophyll *a* (Chl $a/(\mu g\cdot L^{-1})$) were taken using 5-L GO FLO bottles at surface and bottom layers. Water samples were analyzed for nitrate (NO_3-N/($\mu mol\cdot L^{-1}$)), ammonium (NH_4-N/($\mu mol\cdot L^{-1}$)), nitrite (NO_2-N/($\mu mol\cdot L^{-1}$)), dissolved phosphorus (PO_4-P/($\mu mol\cdot L^{-1}$)), total phosphorous (TP/($\mu mol\cdot L^{-1}$)), and silicate (SiO_3-Si/($\mu mol\cdot L^{-1}$)). The analytical parameters were determined in triplicate with reference to current official methods ("The specialties for oceanography survey" GB 17378.4-2007, China). Two replicates of 1.0-L samples from the surface and bottom layers were filtered through 0.45 μm GF/F filters and deep frozen immediately at −20°C. At the end of the cruise, all filters were transported to the shore laboratory in liquid nitrogen. Within a week, the chlorophyll was extracted in 10 mL 90% acetone in the dark for 24 h in a refrigerator and its concentration determined with 10-AU Fluorometry (Turner Designs, USA).

2.2 Data treatment

There are many studies in which environmental data are obtained from monitoring stations for hydro-chemical and biological variables. This result can be presented as a "two-way" table. In this study, the sampling data can be built with the unfolded matrix.

2.3 Cluster analysis

In this study, squared Euclidean distances and the Ward's method measuring the distance between clusters were performed on the normalized data set, and then the cluster tree was created (Wu et al., 2007).

2.4 Principal component analysis (PCA)

PCA is a statistical procedure that transforms the original variables into new, uncorrelated variables called the principal components (PCs), which are linear combinations of the originals. The new axes lie along the directions of maximum variance, that is to say, they account for as much of the variability in the data as possible. This reduces the dimensionality of the data set by explaining the correlation among a large number of variables in terms of a smaller number of underlying factors (PCs), without losing much information (Vega et al., 1998; Wu et al., 2010).

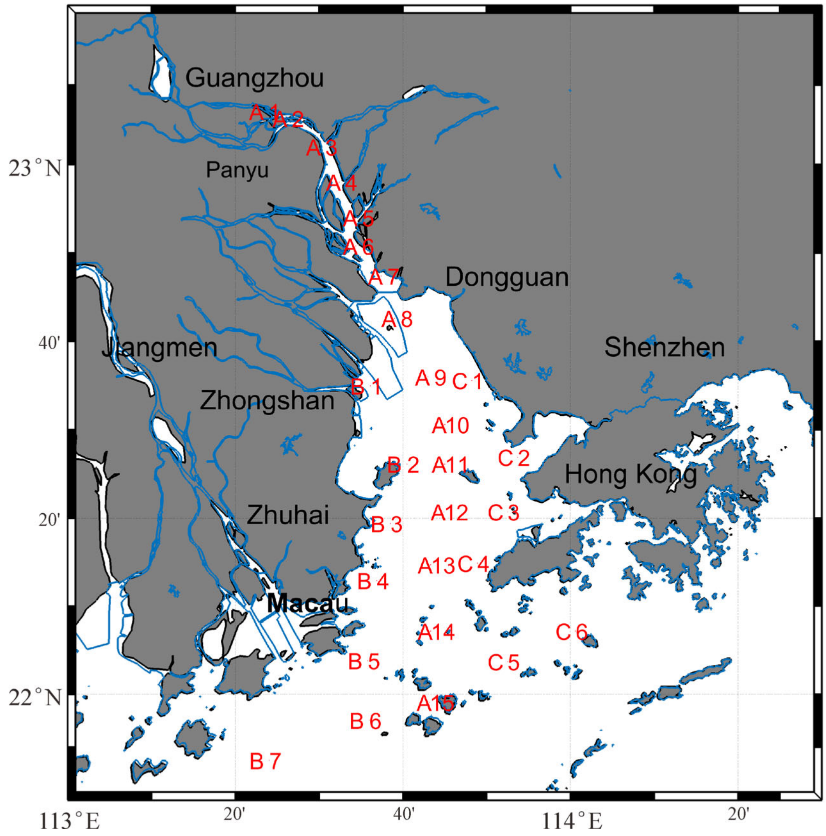


Fig. 1 Monitoring stations in the Pearl River Estuary.

2.5 Self-organizing map

A self-organizing map consists of components called nodes or neurons. Associated with each node is a weight vector of the same dimension as the input data vectors and a position in the map space. The usual arrangement of nodes is a regular spacing in a hexagonal or rectangular grid. SOM describes a mapping from a higher dimensional input space to a lower dimensional map space, and displays a high-dimensional signal manifold onto a much lower dimensional network in an orderly fashion (Astel et al., 2007). It is a good approach to produce "component planes" which are very convenient to explain the results of the SOM. A component plane is a representation of the map that shows the values that take the same component of the weight vectors in each of the map units. The map size or the number of output neurons of the SOM is crucial for optimum clustering analysis. There are two classical methods for the map size determination. The first one is an error evaluating the topographic quality of the trained SOM. The second one is the optimal number of map units close to $5\sqrt{n}$, where n is the number of training samples (Cereghino and Park, 2009).

Data was compared to standardized experiments in order to avoid misclassification due to wide differences in data dimensionality. The data was normalized with mean and variance of zero and one, respectively. Standardization tends to decrease the influence of the variances of variables. Moreover, before performing PCA, Kaiser-Meyer-Olkin (KMO) was used to examine the validity of PCA. The KMO for both the surface and bottom data is 0.84, indicating that PCA may be useful in dimensionality reductions.

All the mathematical and statistical computations were performed using MATLAB R2008b (Mathworks Inc., USA).

3 Results

3.1 Environmental factors

In the upper reaches of the Pearl River Estuary, the salinity of the surface waters was low, less than 0.60 psu. Salinity was less than 10.00 psu in middle reaches of the estuary, and presented high values ranging from 10.00 psu to 19.00 psu in the lower reaches. Salinity of the bottom samples was greater than in the surface samples in the same sites. Salinity in the bottom samples had a similar spatial distribution as that of the surface, with increasing values downstream (Figs. 2(a) and 2(b)). No clear stratification occurred in the upper reaches of the Pearl River Estuary,

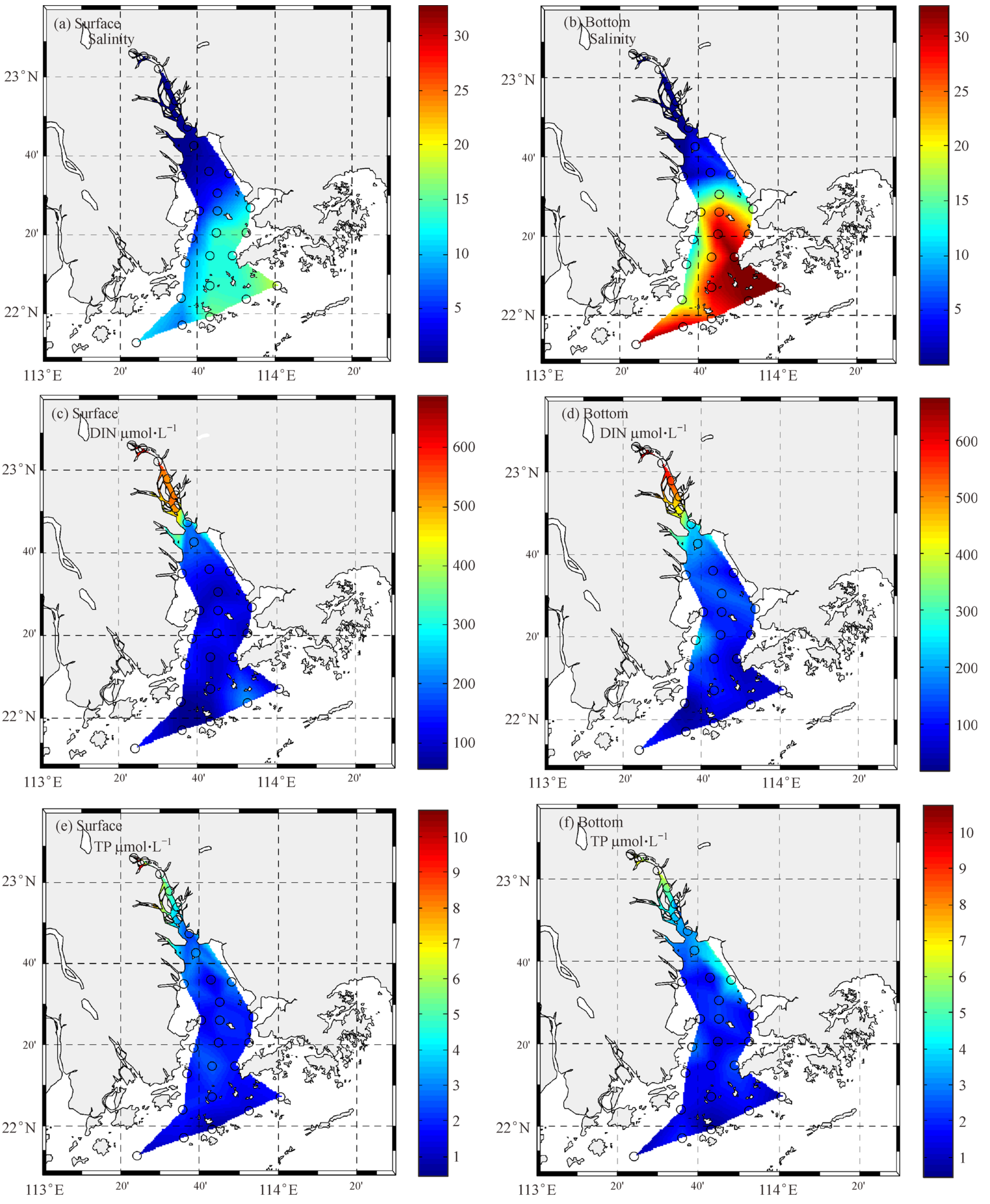


Fig. 2 Surface and bottom distributions of salinity (a), (b), DIN (c), (d) and TP (e), (f), respectively. Circles represent the sampling stations.

and little difference in hydrographic parameters was observed between surface and bottom water. However, there is a clear difference in salinity between the surface and the bottom waters in the lower reaches of the Pearl River Estuary (Figs. 2(a) and 2(b)).Salinity was relatively homogeneous throughout the water column in the Guangzhou reach of the Pearl River (sites: A1 – A3), with the salinity less than 0.6.

Chl *a* varied from 0.98 μg·L^{-1} in A14 to 176.69 μg·L^{-1} in A1. SPM ranged from 0.0004 g·L^{-1} in A11 to 0.15 g·L^{-1} in A3. Turbidity showed the broad range from 0.30 ntu in B7 to 91.50 ntu in A1. pH displayed a relatively narrow scale, ranging from 6.61 in A5 to 8.36 in A15. Silicate ranged from 10.00 $\mu g \cdot L^{-1}$ in B1 to 144.03 $\mu g \cdot L^{-1}$ in A5.

The spatial distribution of DIN concentration in the surface and bottom layers reveals that the DIN concentration decreases from the upper reaches to the lower reaches of the Pearl River Estuary (Figs. 2(c) and 2(d)). The spatial distribution of TP concentration in the surface and bottom layers is similar to that of the DIN concentration (Figs. 2(e) and 2(f)). In general, salinity and pH increased along the seaward side, while the rest water quality decreased.

3.2 Spatial patterns of water quality

Principal component analysis is applied to the matrix combined with the surface and bottom layers, respectively. Loadings of the two retained PCs with eigenvalues greater than 1 for the surface and bottom layers are shown in Table 1. To the surface water quality, PC1 (59.10% of the variance) positively contributes mainly by NH_4-N, PO_4-P, NO_2-N, TP, Chlorophyll *a,* and NO_3-N, namely, the “anthropogenic influence factor”, and negatively contributes mainly by salinity and pH, namely, the “natural characteristics factor”. PC2 (14.80% of the variance) is characterized by salinity, turbidity, and SiO_3-Si. To the bottom water quality, PC1 (65.51% of the variance) also positively contributes mainly by PO_4-P, NO_2-N, TP, and NO_3-N, and negatively contributes mainly by salinity and pH. PC2 (13.31% of the variance) is characterized by salinity, Chlorophyll *a,* NH_4-N, and SiO_3-Si. Thus, controlling factors on water quality in the surface may be generally similar to the bottom.

In the surface and bottom layers, the scores of stations in PC1 reveal that the Guangzhou urban reach of the Pearl River (A1 – A3) and the middle and lower reaches of the Pearl River Estuary are widely separated (Fig. 3(a) and 3 (c)). The scores of these sites (A1 – A3) are more than 4 and less than 0 in PC1 and PC2, respectively. They are mainly associated with NH_4-N, PO_4-P, NO_2-N, TP, Chlorophyll *a*, and NO_3-N. The first loading of these variables has contributed more to the scores of these sites than the others do.

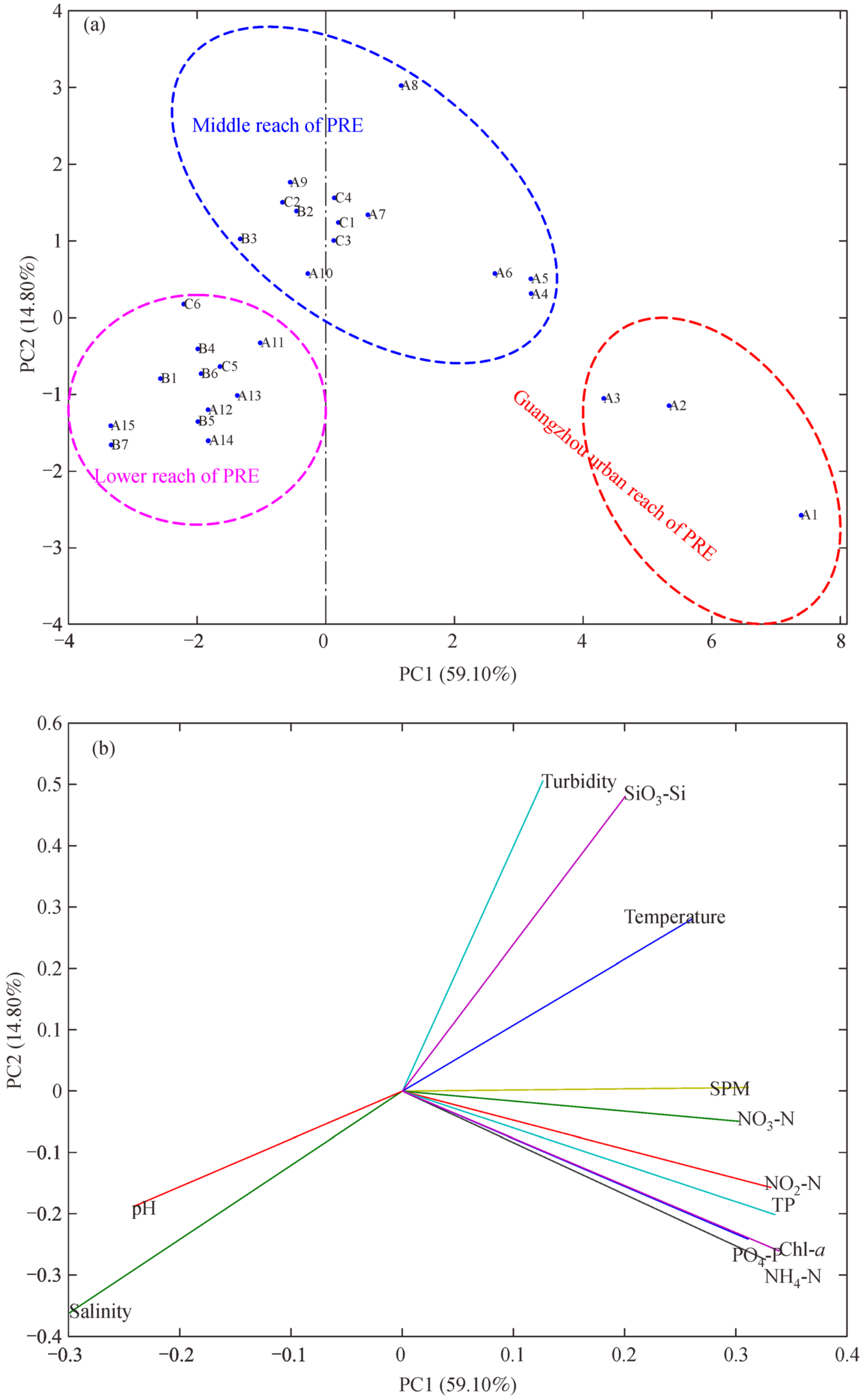
The loading plots of variables for the surface and bottom layers in the first two components are shown in Figs. 3(b) and 3(d), respectively. The loadings of nutrients in PC1 are positive. The loadings of salinity and pH are negative in both PC1 and PC2. Salinity may be an important indicator of marine character. High negative loadings on pH in PC1 can be explained by high levels of dissolved organic matter consuming large amounts of oxygen, then undergoing anaerobic fermentation processes which lead to the formation of ammonia and organic acids. Hydrolysis of these acidic materials causes a decrease of pH values (Vega et al., 1998; Singh et al., 2004).

In Figs. 3(a) and 3(c) the stations in the Guangzhou urban reach of the Pearl River (A1 – A3) show positive values in PC1, and these stations are related to nutrients with high values. The distribution of the stations along PC1 has a very strong correspondence with the geographical location, with the direction of high values to low values (high nutrients to low nutrients) roughly corresponding to the downstream direction. This direction also corresponds to an increase in salinity.

There are obvious differences between the scores of the surface waters and bottom waters at the same station in the lower reaches of the estuary in Fig. 3. The loadings of

Table 1 Loadings of 12 physical-chemical parameters on the first two PCs in the surface and bottom layers, respectively

	Surface layer		Bottom layer	
	PC1	PC2	PC1	PC2
Temperature	0.2602	0.2797	0.3278	0.2082
Salinity	−0.2992	−0.3612	−0.3090	−0.3273
pH	−0.2401	−0.1869	−0.3133	−0.2921
Turbidity	0.1265	0.5056	0.1962	−0.0251
SiO_3-Si	0.2005	0.4807	0.2325	0.5679
Total suspended matter	0.3111	0.0056	0.2638	−0.1251
NH_4-N	0.3267	−0.2752	0.2888	−0.4300
PO_4-P	0.3109	−0.2412	0.2956	−0.2113
NO_3-N	0.3031	−0.0498	0.3091	0.0042
NO_2-N	0.3313	−0.1570	0.2940	−0.0258
TP	0.3351	−0.2016	0.3211	−0.1311
Chlorophyll *a*	0.3389	−0.2606	0.2844	−0.4219
Eigenvalue	7.0915	1.7757	7.8611	1.5969
Variance/%	59.10	14.80	65.51	13.31
Cumulative/%	59.10	73.90	65.51	78.82


(a)
Middle reach of PRE
Lower reach of PRE
Guangzhou urban reach of PRE
A1
A2
A3
A4
A5
A6
A7
A8
A9
A10
A11
A12
A13
A14
A15
B1
B2
B3
B4
B5
B6
B7
C1
C2
C3
C4
C5
C6
PC1 (59.10%)
PC2 (14.80%)
−4
−2
0
2
4
6
8
4
3
2
1
0
−1
−2
−3
−4
(b)
Turbidity
SiO_3-Si
Temperature
SPM
NO_3-N
NO_2-N
TP
Chl-*a*
PO_4-P
NH_4-N
pH
Salinity
PC1 (59.10%)
PC2 (14.80%)
−0.3
−0.2
−0.1
0
0.1
0.2
0.3
0.4
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4

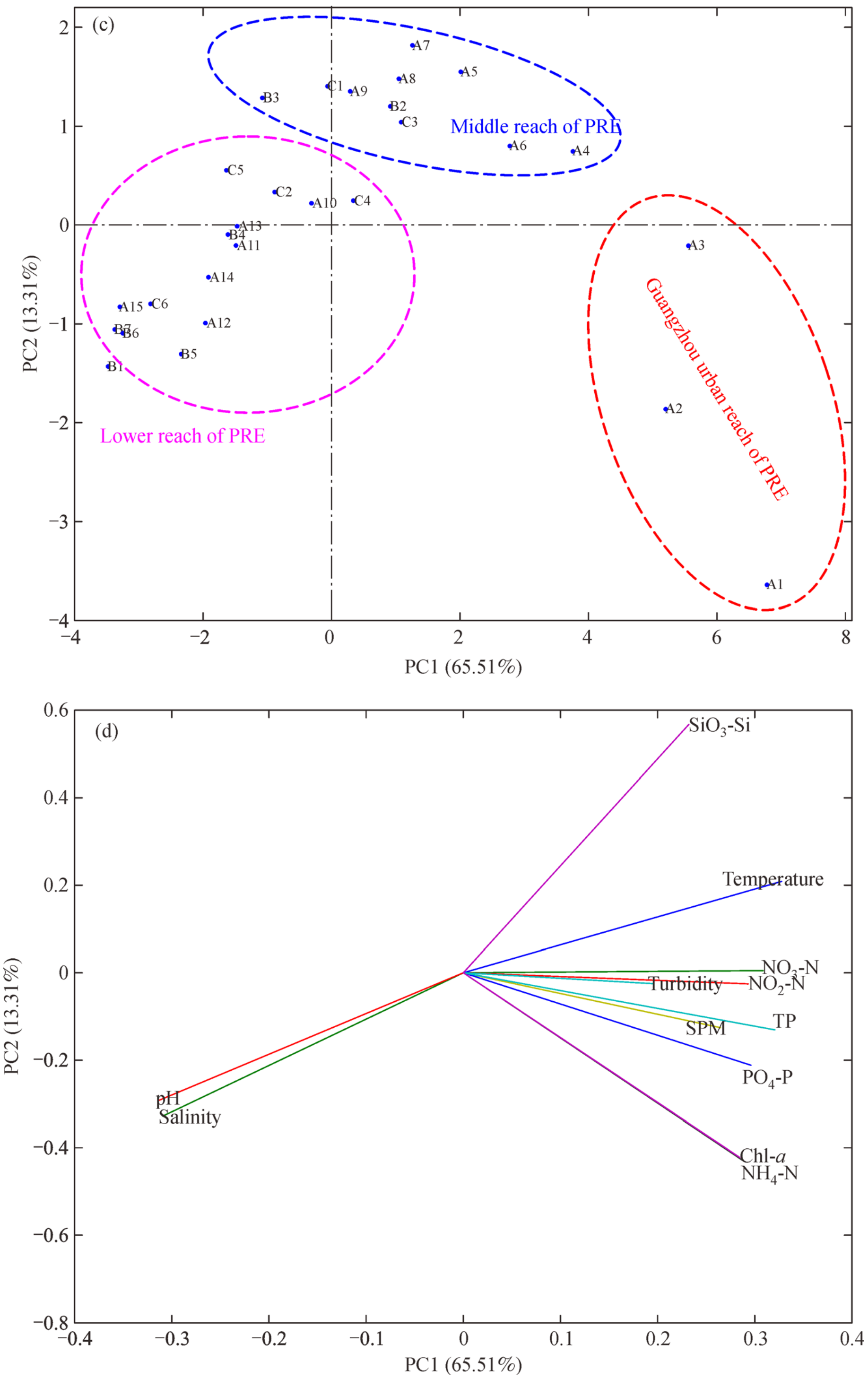


Fig. 3 Results of PCA to the surface and bottom layers. The scores (a) of sampling stations and loadings (b) of variables for the surface layer and in the first two PCs; The scores (c) of sampling stations and loadings (d) of variables for the bottom layer and in the first two PCs

salinity, pH, Chlorophyll a, NH_4-N, and SiO_3-Si in PC2 have largely contributed to the different scores of the sampling stations in the middle and lower reaches of the Pearl River Estuary. Clear stratification was observed in the lower reaches of the Pearl River Estuary during our cruise.

CA applied to water quality of the surface and bottom layers rendered a dendrogram where the monitoring stations were divided into three large clusters, respectively. The results may be a little different. Three large clusters had almost similar results with the Guangzhou and Dongguan reach, the middle and lower reaches of the

Pearl River Estuary in surface and bottom layers at $D_{\mathrm{link}}/D_{\max}*100 < 70$ (Figs. 4(a) and 4(b)).

SOM was employed to identify the spatial distribution of water quality; 40 output neurons were arranged in 5 rows and 8 columns, and the training results were satisfactory (Fig. 5). The results of SOM showed three distinguished spatial distributions of water quality (Fig. 5). The three main locations of the monitoring stations can be

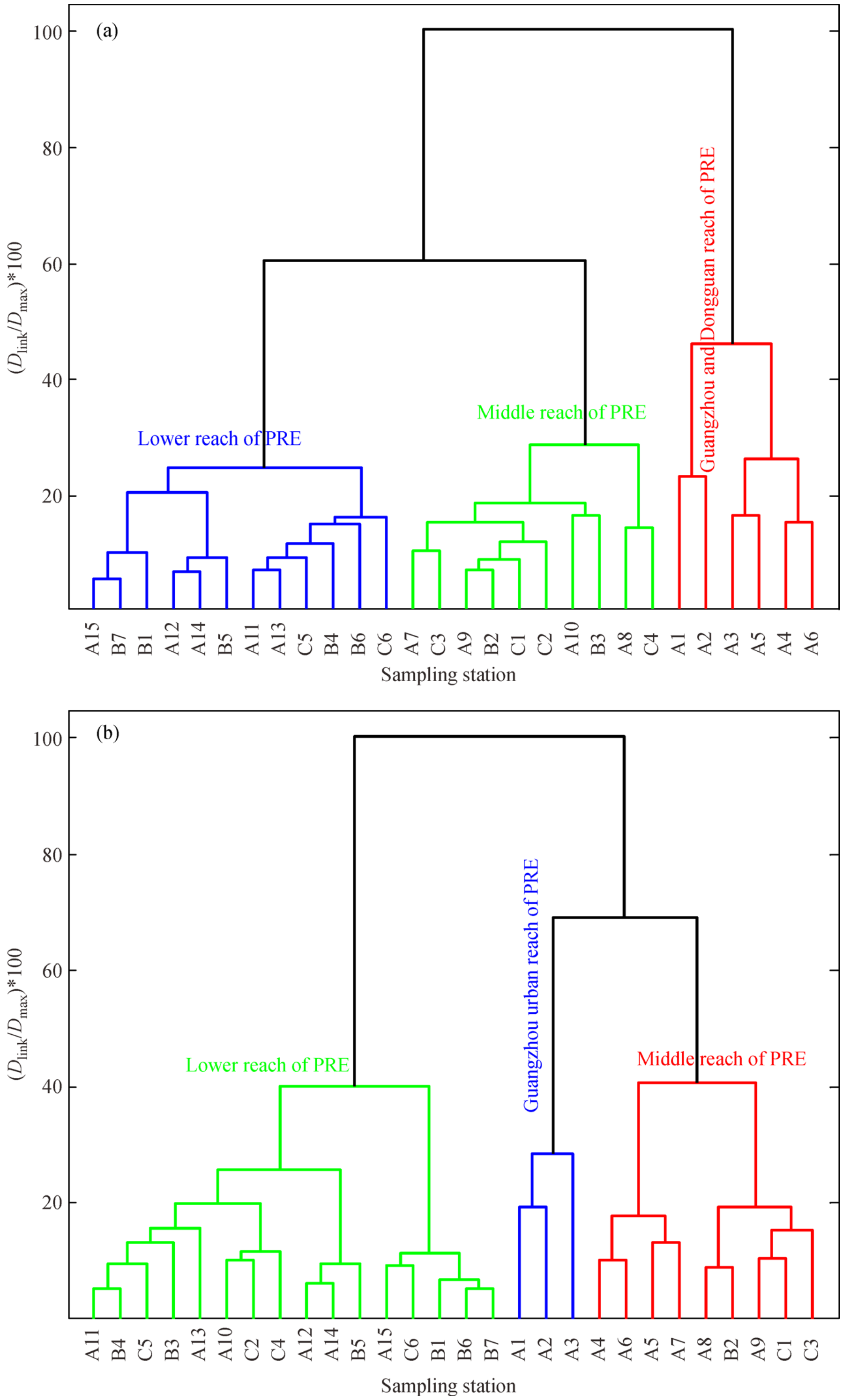


Fig. 4 Dendrogram based on Ward's method of clustering for the surface (a) and bottom (b) layers, respectively. $D_{\mathrm{link}}/D_{\max}$, which represents the quotient between the linkage distances for a particular case divided by the maximal linkage distance.

differentiated. Monitoring stations located at the middle estuarine reaches were ranked in the lower left corner, and urban stations were in the lower right corner, while stations at lower reaches were in the top right corner. The lower estuarine area is characterized by high salinity and low nutrients. In contrast, the urbanized upper reaches are associated with freshwater and high nutrients.

The component planes of the salinity and TP were shown in Fig. 6. The high and low concentrations of water quality parameters at the different monitoring stations are shown to have distinguished patterns. It may be helpful to identify the cluster characteristics and corresponding polluted water quality parameters. PCA is applied to the same dataset analyzed by SOM, coupling with the superimposed SOM grid to scores of sampling stations resutling from PCA (Fig. 7(a)), presents similar results to SOM. The first two PC explained 73.95% of the variance. From the loadings of variables, these three monitoring stations (A1 – A3) are located in the Guangzhou urban reaches of the Pearl River, which in general showed high concentrations of TP, Chl *a*, inorganic nitrogen (NH_4-N, NO_3-N, and NO_2-N) and low transparency while the stations in the lower reach of Pearl River Estuary have the higher salinity and pH values (Fig. 7(b)).

4 Discussion

The waters in the Pearl River Estuary are influenced by three water systems: the Pearl River discharge, oceanic water from the South China Sea, and coastal water from the South China Coastal Current (Zhao, 1990). The relative intensity and movement of these water masses as well as the interactions among them are significant factors controlling water quality in the Pearl River Estuary (Zhou et al., 2004). During the summer wet period, estuarine circulation is strong. Saline water enters the estuary as a salt wedge at the bottom and freshwater flows out of the estuary at the surface (Harrison et al., 2005). Stratification is strong in summer with haloclines at ~1 m and also near the bottom layer (Zhang, 1996). In the wet season, a stratified layer and a salinity gradient are observed in Lingdingyang, resulting from large river discharge (Li et al., 2006). In summer, the Pearl River discharge reaches its maximum and the river water contains high NO_3-N concentrations (~100 μmol/L) and high N:P ratios (> 100:1) (Yin et al., 2001), much higher than the 16N:1P ratio required for phytoplankton growth (Redfield et al., 1963). Generally, during summer (the wet season) when a southwesterly monsoon prevails, pollu-

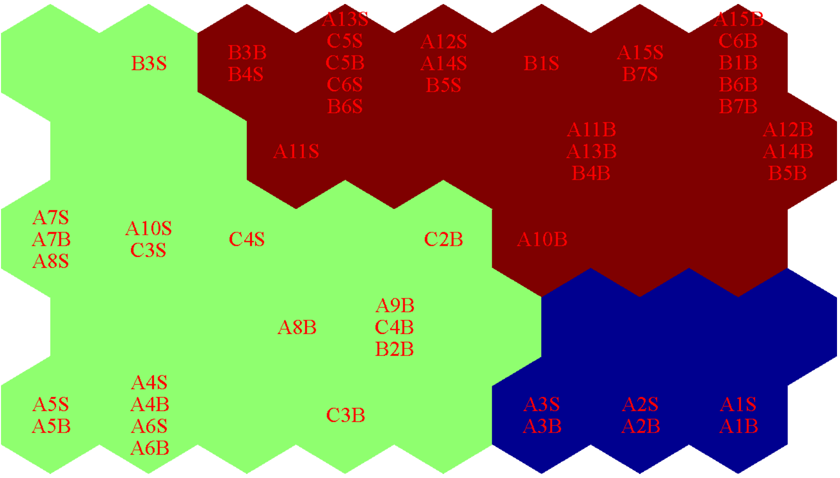


Fig. 5 The result of SOM clustering of the cells on the map plane. The first letter and number denote the monitoring stations. The second letter “S” or “B” denote surface layer or bottom layer, respectively.

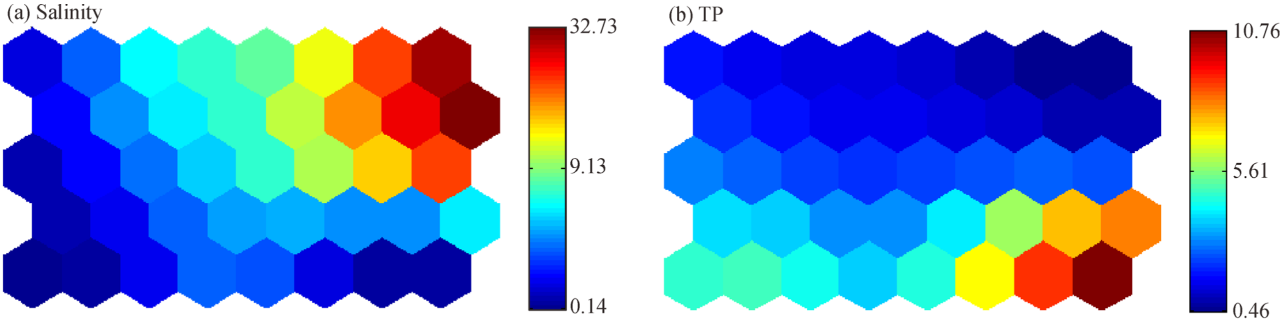


Fig. 6 The component planes for selective water quality parameters on SOM. (a) Salinity and (b) TP.

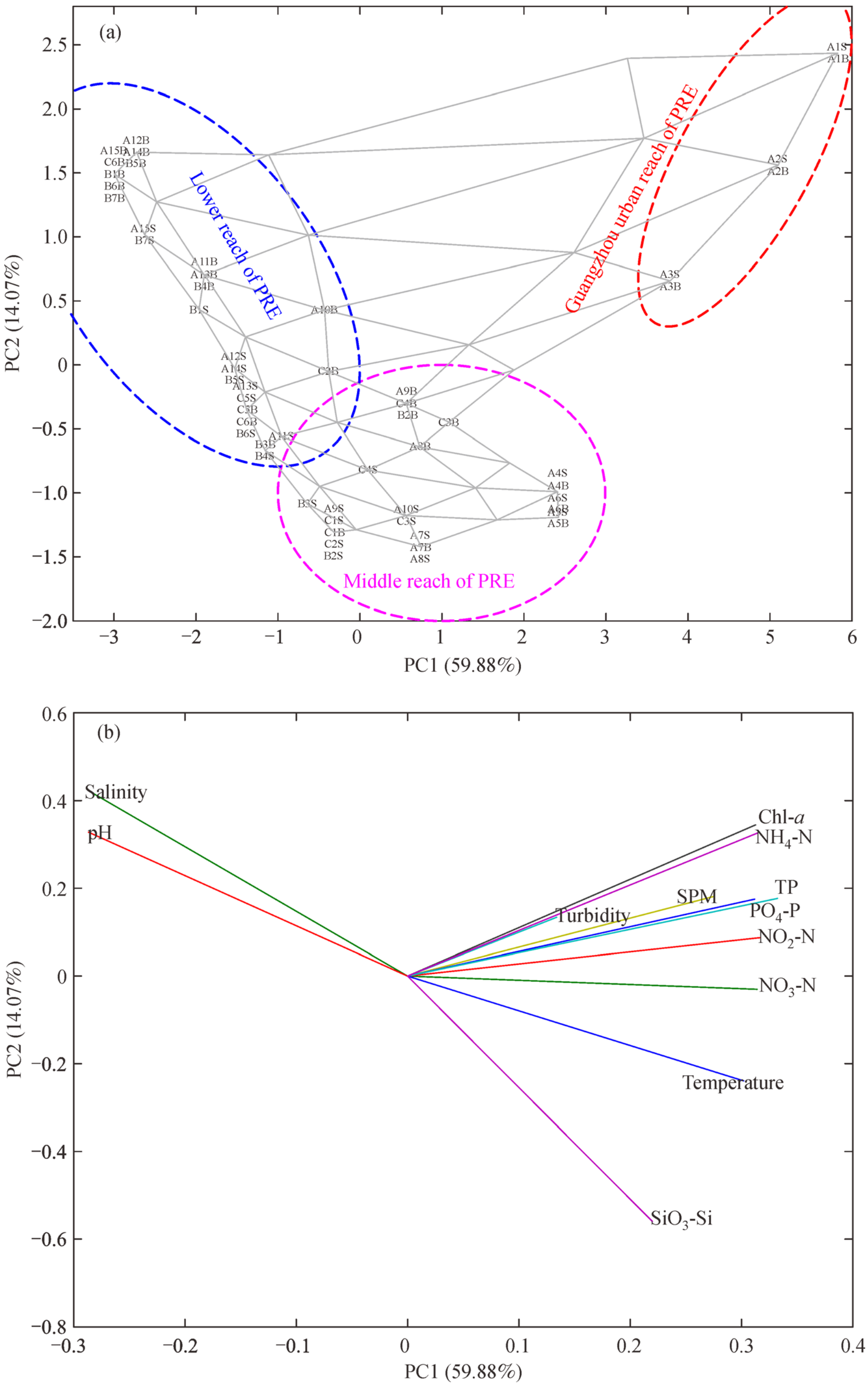


Fig. 7 Water quality of the surface and bottom layer projected on the subspace with the first two largest eigenvalues by PCA. (a) Scores of sampling stations in the first two PCs, SOM grid (Fig. 5) projected to the same subspace has been superimposed; (b) loading of water quality variables.

tants from domestic sewage, industrial wastewater, agriculture fertilizer, and marine culture, etc. are carried into the waters. The interaction between fresh water and marine water is very strong (Huang et al., 2003). Tide is also an important factor. Therefore, water environments are known to be dynamic. However, in this study, we focus on the general trend of spatial patterns of water quality. Tide function will be considered in a future study.

4.1 Anthropogenic input

The concentration of nutrients (NO_3-N, NH_4-N, PO_4-P, TP, and SiO_3-Si) in the upper reaches of the Pearl River Estuary from the Humen Outlet upward to the suburb of Guangzhou was significantly higher than that in the middle and lower reaches of the estuary (Fig. 7(b)). The nutrients in the Pearl River Estuary mainly came from domestic sewage, industrial wastewater, agriculture fertilizer, and marine culture (Huang et al., 2003). The Pearl River delta has nine main cities (Hong Kong, Macau, Guangzhou, Shenzhen, Foshan, Dongguang, Zhongshan, Zhuhai, and Jiangmen), with a population of more than 36 million and a population density of more than 1.0×10^4/km^2 (not including Hong Kong and Macau). Over 100 million people live in the entire watershed of the Pearl River, called the Pearl River Region (Chen et al., 2004). Fertilizer was widely used in the Pearl River basin, and was a source of nutrients for the estuary. Domestic and industrial sewage discharge in the Pearl River basin has been rising steadily in the past several years (Table 2). The waste discharge is characterized by heavy organic loads (Tao and Hills, 1999). In addition, there is significant marine culture in the Pearl River Estuary. The surplus feedstuff and the excretions from fish also contribute to nutrient load (Holby and Hall, 1991; Hall et al., 1992). Human activities result in high nutrient concentrations in the Pearl River Estuary. As a consequence, the aquatic environment of the Pearl River and its estuary has deteriorated dramatically in recent years.

NO_3-N is the main form of dissolved inorganic nitrogen. It contributes over 60% of the dissolved inorganic nitrogen; the second one is NH_4-N. NO_2-N is often less than 20% of the dissolved inorganic nitrogen in all stations. It is mainly related to the runoff from industries and sewage. High nitrogen concentrations resulted from the sewage input in Junk Bay, Hong Kong (Hodgkiss and Lu, 2004). High concentration of ammonia can be related to the decomposition of organic material and sewage inflow from the Balneario Camboriu city sewage treatment plants at the Camboriu River estuary (Pereira-Filhoet al., 2001). The dissolved inorganic nitrogen was mainly from the runoff of the Pearl River (Huang et al., 2003) and was mainly influenced by domestic wastewater. It may be related to the influence of domestic wastewater in Shenzhen (including the submarine wastewater discharge project in the west of Shenzhen) and Hong Kong near this area (Wen et al., 1995).

The domestic and industrial wastewater discharge enters the Pearl River and then the Pearl River Estuary. These stations (A1 – A3) were mainly influenced by human activities. Thus, domestic sewage, industrial wastewater, agriculture fertilizer, and marine culture play an important role in determining the local water quality (Wang, 2013).

4.2 Natural processes by seawater intrusion

The result from the scores of the stations in the first two axes demonstrated that the three different regions of stations were well distinguished (Fig. 3). The concentration of nutrients had an important contribution to the loading of sites (A1 – A3) in PC1. These sites (A1 – A3) are in the Guangzhou urban reach of the Pearl River. Results obtained from cluster analysis have also identified the similar spatial distribution of water quality in surface and bottom layers (Fig. 4). The average concentrations of nutrients (DIN) show similar spatial variations, decreasing from the suburb of Guangzhou to the lower reach of the Pearl River Estuary (Fig. 2).

The results obtained from PCA and SOM indicate that the nutrients are important factors controlling the spatial characterization of water quality in the Pearl River Estuary (Fig. 3, Fig. 4, Fig. 5, and Fig.7). These variables (NH_4-N, PO_4-P, NO_2-N, TN, TP, Chlorophyll *a*, and NO_3-N) are related to human activities (anthropogenic factor), and other variables (salinity and pH) are related to seawater incursions into river water (natural factor). The PCA results show that dissolved inorganic nitrogen (ammonia, nitrate, and nitrite) has an important contribution to loadings of the PC1 and PC2.

In this study, salinity and pH were used as tracers for natural processes, which had an important effect on the

Table 2 Quantity of wastewater discharge from Guangdong Province, China between 2000 and 2008

	2000	2001	2002	2003	2004	2005	2006	2007	2008
Total volume of wastewater discharged/(10^9 tons)	44.8	51.1	49	54.6	54.2	63.8	65.5	69.1	67.7
Domestic sewage/(10^9 tons)	11.4	11.3	14.6	14.9	16.5	23.2	23.5	24.6	21.3
Industrial effluent/(10^9 tons)	33.4	39.9	34.4	39.8	37.7	40.7	42.0	44.5	46.4
Total volume of COD emission in wastewater/(10^5 tons)	95.1	110.3	95.2	98.2	92.7	105.8	104.9	101.7	96.4
Total amount of ammonia/(10^5 tons)	–	9	8.5	9.3	8.7	10	9.3	12	12.2
Industrial effluent/(10^5 tons)	–	0.9	1	0.8	0.9	0.9	0.7	1.1	1
Domestic sewage/(10^5 tons)	–	8.1	7.6	8.5	7.7	9.1	8.6	10.9	11.2
Rate of industrial wastewater meeting discharge standard/%	81.8	84.1	78.3	82.9	83.9	83.9	84.9	86.1	89.7
Overall rate of domestic sewage treatment/%	17.2	16.6	21.2	24.7	35.7	40.2	45.3	50.2	55.9

The data based on Environmental Status Bulletins of Guangdong Province, China at http://www.gdepb.gov.cn/.

water quality characteristics. Salinity has strong negative loadings in PC1 and PC2. Fresh water discharge from the Pearl River diminishes the surface salinity in the middle and lower reach of the Pearl River Estuary – an important effect. The correlation coefficients between nutrients and salinity in the surface layer are more than -1.0, with minimum value (silicate: -0.79), and maximum value (PO_4-P: -0.48). Thus, all nutrients behaved in a non-conservative way in relation to theoretical dilution, suggesting that biological activities and the mixing of the Pearl River with South China Sea waters were responsible for the observed distribution of nutrients. Likely, they indicate the equal importance of mixing between polluted freshwaters and coastal saline waters and biological activities. This phenomenon needs to be investigated in a future study. Nutrients were introduced in the Pearl River Estuary by river and sewage discharges. Negative correlations between nutrients and salinity demonstrate that land sources are the main reason for high levels of nutrients (Liu et al., 2005). Anthropogenic activities could play a significant role on dissolved inorganic nitrogen in the Pearl River Estuary.

5 Conclusions

Nutrients were evidenced in the obtained graphs, and rationalized on the basis of anthropogenic pollution in heavily populated and industrialized areas. All of this information would be very useful to regional agencies in developing a strategy to manage water resources in the Pearl River Estuary. The mixing between polluted freshwaters and coastal saline waters may contribute to diluting the nutrient pollution from human activities. The second outcome of this study is the possibility to explore such complex information visually, by means of easy-to-see bi-dimensional graphs.

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