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Original Research

Identification of Coastal Water Quality, Including Heavy Metals, in the South China Sea

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Abstract

Human activities and natural processes like mixing and/or upwelling driven by climate change have a strong influence on water quality in the coastal regions. Human activities are the dominant factor for water quality in the mouth of the Sanya River. This region exhibited the maximum influence of discharge from the Saya estimated by higher nutrient levels and chlorophyll *a* (Chl *a*). Natural processes are the dominant factor regarding water quality in outer bay. Both human activities and natural processes play important roles on water quality in Sanya Bay. Each hydrologic and ecological zone has a specific water quality response associated with the relative importance of both human activities and natural processes. Therefore, the information would be useful for regional agencies in developing a strategy to carry out scientific plans for resource use based on marine system functions.

Keywords: nutrients, heavy metals, monsoons, human activities, coastal ecosystem

Introduction

In coastal areas, environmental problems (such as water quality deterioration, eutrophication, and algae bloom) is produced by both natural and human activities. Coastal environmental problems show not only various patterns of spatial inshore-offshore and along-shore gradients, but often also considerable year-to-year variations in both intensity and extension, under the direct influence of both natural and human activities [1]. Environmental problems in coastal areas are determined by competing processes in the water. Anthropogenic influences as well as natural processes play a role in coastal water, and impair their use for industrial, agricultural, recreational, or other purposes. Therefore, researchers have been paying more attention to the effects of natural and human activities on water quality, in particular the key contributors of human activities to nutrients and heavy metals [2, 3].

People are becoming more aware of the complexity of nature and the delicate balance that exists within the global ecosystem [4]. The discharge of effluents and associated toxic compounds into aquatic systems represents an ongoing environmental problem due to their possible impact on communities in the receiving aquatic water, and the potential effect on human health [5]. Diffuse pollutants due to natural and human activities have been increasingly declining water quality, and pollution prevention requires a better understanding of water quality and the impact by natural and human activities in coastal areas.

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This study identified the temporal and spatial variations of water quality, including heavy metals, and particularly the impacts of natural and human activities on water quality in order to enact better management policies in coastal areas.

Materials and Methods

Study Area

Sanya Bay lies on the southern shore (from 109º20' to 109º30'E, 18º11' to 18º18'N) of Hainan Island, with a water area of 120 km^2 and an average depth of 16 m. It is a typical tropical bay in China. Dongmao Island, Ximao Island, and Luhuitou possess mostly coastal coral reefs. The Sanya River is in the eastern part of the bay (length 31.3 km, drainage area 337 km^2 and annual flow of 2.11×10^9 m^3) [6]. The wet and warm southwest monsoon prevails in the wet season from April to September, which brings humid air from low latitudes, resulting in gentle monsoonal rainfall in spring and heavy rainfall in summer. In contrast, a dry and cold northeast monsoon predominates in the dry season from October to the following March.

In order to evaluate the anthropogenic and natural effects in this bay, the thirteen monitoring stations are in Sanya Bay (Fig. 1).

Sampling and Analytical Method

Year-round sampling in the bay was conducted in winter (13 January), spring (25 April), summer (20 July), and autumn (20 October) in 2010. A Quanta® Water Quality Monitoring System (Hydrolab Corporation, USA) was employed to collect the data for temperature (T/ºC), pH, and salinity (S/psu) in the surface and bottom layers. Seawater samples for analysis of nutrients and heavy metal were taken using 5 L GO FLO bottles at surface layer, according to the methods and sampling tools of "The specialties for oceanography survey" (GB12763-91, China). Water samples from the surface layer were analyzed for nitrate (NO_3-N/μmol·L^{-1}), nitrite (NO_2-N/μmol·L^{-1}), and silicate concentrations (SiO_3-Si/μmol·L^{-1}) with a SKALAR auto-analyzer (Skalar Analytical B.V. SanPlus, Holland).

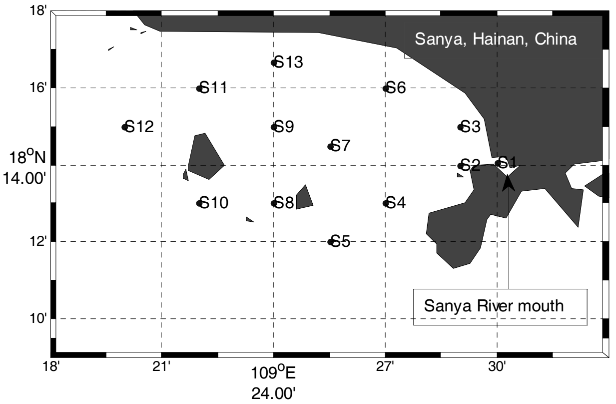

Fig. 1. Monitoring stations in Sanya Bay.

Ammonium concentrations (NH_4-N/μmol·L^{-1}) were analyzed with methods of oxidized hypobromite. Phosphorus concentrations (PO_4-P/ μmol·L^{-1}) were analyzed using oxidized methods by molybdophosphoric blue. Dissolved oxygen concentrations (DO/mg·L^{-1}) were determined using the method of Winkler titration. Total nitrogen (TN/μmol·L^{-1}), total phosphus (TP/μmol·L^{-1}), chlorophyll *a* (Chl *a*/μg·L^{-1}), chemical oxygen demand (COD/mg·L^{-1}), 5-day bio-chemical oxygen demand (BOD_5), and heavy metals (Zn/μg·L^{-1}, Pb/μg·L^{-1}, Cd/μg·L^{-1}, and Cu/μg·L^{-1}) were tested according to "specialties for marine monitoring" (GB17378.4-1998, China).

During the observation period, daily climatological data such as air temperature, precipitation, wind direction/speed, and solar radiation at the Sanya Meteorological Observatory Station of Tropical Marine Biological Research Station in Hainan, Chinese Academy of Sciences, were obtained.

Data Analysis

Principal component analysis (PCA) is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components, which are linear combinations of the original variables. The new axes lie along the directions of maximum variance [7]. It 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 (principal components or PCs) without losing much information [8-12]. The principal component (PC) can be expressed as:

$$z_{ij} = pc_{i1}x_{1j} + pc_{i2}x_{2j} + \cdots + pc_{im}x_{mj}$$

...where z is the component score, pc is component loading, x the measured value of variable, i the component number, j the sample number, and m the total number of variables.

All the mathematical and statistical computations were performed using MATLAB 2008b (Mathworks Inc., USA).

Results

Weather Condition

Rainfall patterns prior to the sampling dates differed between collection periods (Fig. 2a). The winter, spring and summer collections were made after a relatively dry period, while the autumn collections occurred after significant rain events in October. From 16-20 October, there was approximately 216 mm of precipitation, approximately 3 to 5 days prior to the autumn data collections.

Solar radiation levels and UV recorded were high from May to early September, and low from middle November to April (Fig. 2b and 2c). Transient decreases in solar radiation and UV were recorded for several days in 16-20 October due to rainfall.

Air temperature showed a similar trend to solar radiation with the high recorded in May, June, and July, and low in January, February, and December (Fig. 2d).

The prevailing winds were southerly from June to September, with a daily mean velocity of 1.75 m·s^{-1}, northerly to northwesterly from October to March with gusts of more than 2.30 m·s^{-1} (Fig. 2e and 2f). There was a strong northerly wind with a daily mean velocity of 1.80 m·s^{-1} (maximum 5.40 m·s^{-1}) associated with an autumnal rain front on 16-20 October.

General Hydrography

The surface water temperature at the three sampling stations reflected the seasonal change in air temperature (Fig. 3a). Surface salinity decreased due to precipitation on 20 October (Fig. 3b). Low salinity levels were recorded at S1 located near the mouth of the Sanya. Surface salinity was stable at 33 or more in January, April, and July.

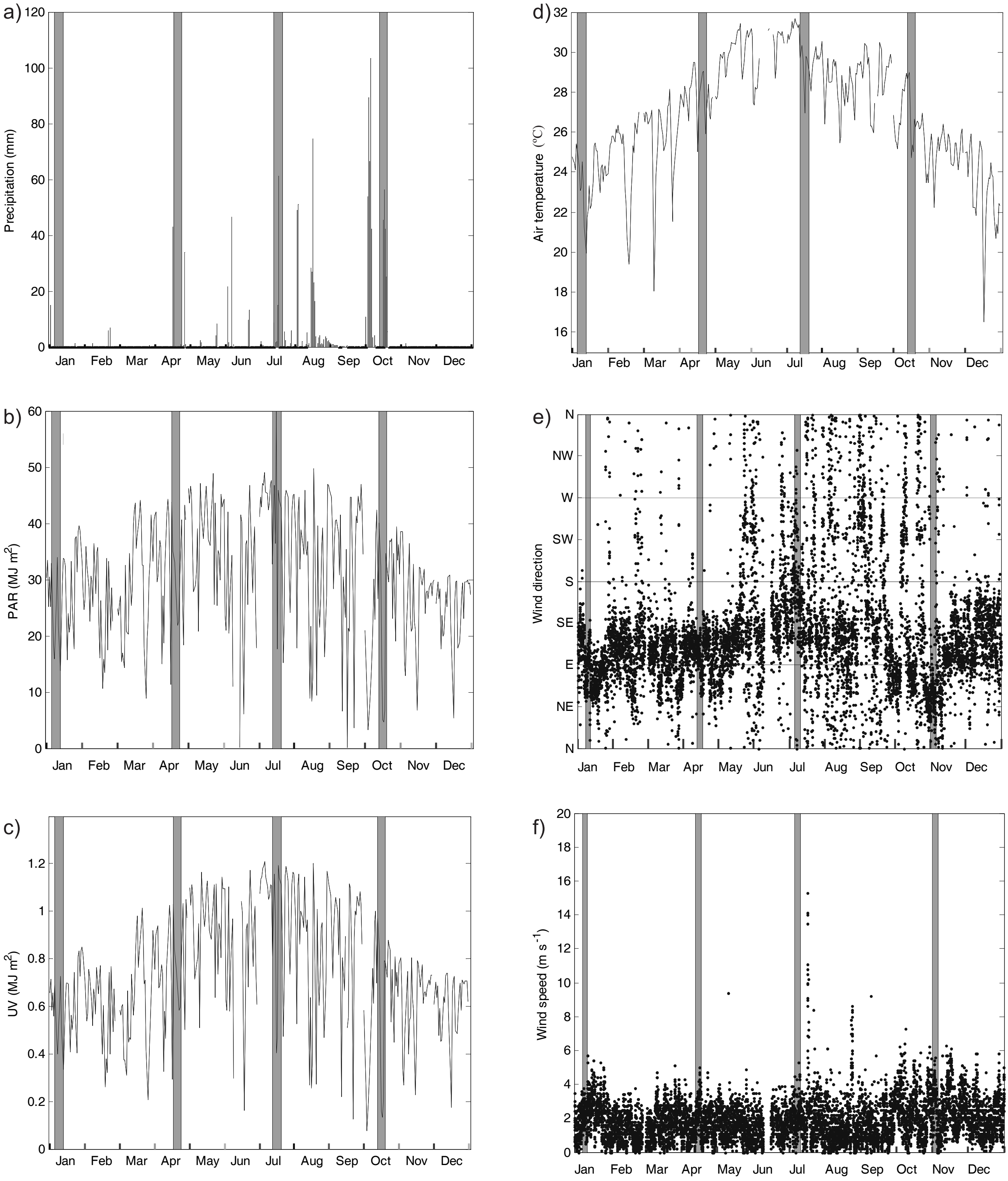

Fig. 2. Seasonal variation in precipitation (a), solar radiation (b), UV (c), air temperature (d), wind direction (e), and wind speed (f) from January 1, 2010 to December 31, 2010. Shaded bars highlight timing of 5 days prior to sampling time.

The vertical distributions of water temperature and salinity during the observation period are shown in Fig. 3a. Surface water temperature had a broad range (from 23 to 30ºC) with a maximum in July and a minimum in January (Fig. 3a). Bottom water temperature had a broad range (from 23 to 30ºC) with a maximum in July and a minimum in January (Fig. 3a). In July, the bottom water temperature dropped sharply to 24ºC, which was the lowest of the year. Remarkable thermocline was detected at stations S4, S5, and S6 (Fig. 3a). The temperature difference between winter and summer was significant.

Nutrients

Fig. 4 shows the temporal variations in nutrient concentrations at the sampling stations. Nitrite, nitrate, and ammonia concentrations varied between 0.07 and 1.85 μmol·L^{-1}, between 0.38 and 8.93 μmol·L^{-1}, and between 0.91 and 5.78 μmol·L^{-1}, respectively, during the study period (Fig. 4a-c). The concentration of each inorganic nitrogen species was higher at S1 than at other monitoring sites (S2-S13).

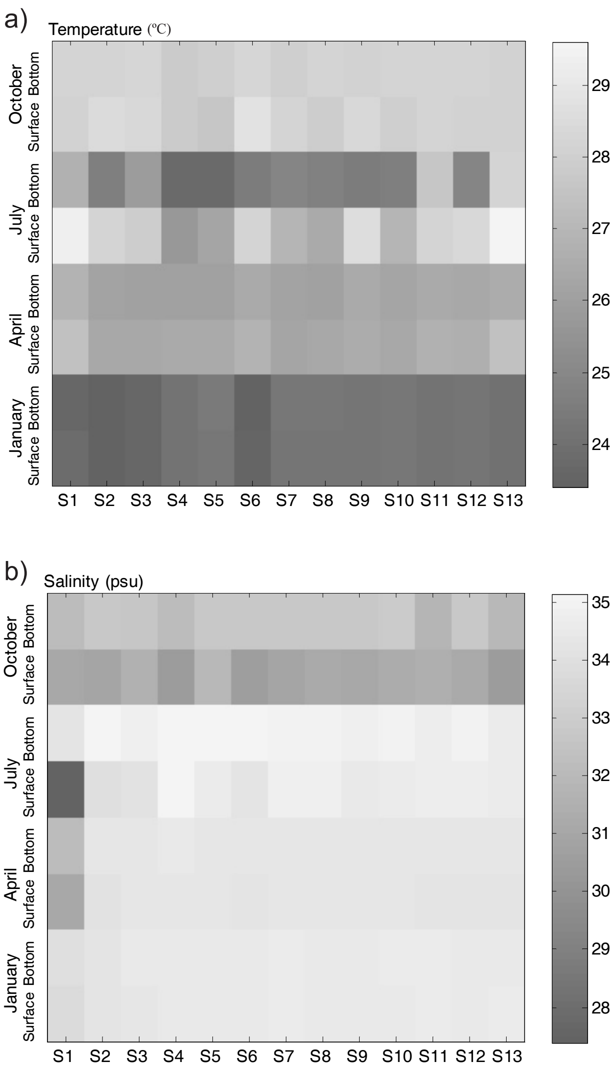

Fig. 3. The temporal and spatial distributions of temperature (a) and salinity (b).

Silicate and phosphate concentrations ranged from 3.00 to 5.45 μmol·L^{-1}, and from 0.08 to 0.96 μmol·L^{-1}, respectively (Fig. 4d and 4e).

The spatial distribution of the PO_4-P concentration shows that it decreases from the eastern to the western parts of the bay.

Chlorophyll

Chlorophyll concentration ranged from 0.19 to 53.31 μg·L^{-1}, and was higher at S1 than at other monitoring sites (S2-S13). It is obvious that chlorophyll *a* concentrations in the bottom layer increased sharply and much more than the surface layer (Fig. 5).

Heavy Metals

Heavy metal concentrations (Pb and Cu) in the water column of the bay exhibit a distinct seasonal change ($p<0.05$). The heavy metal concentrations (Zn, Cd, Pb, and Cu) decrease from the eastern to the western parts of the bay (Fig. 6).

Principal Component Analysis

By principal component analysis, a complex linear correlation between spatial and temporal variations of water quality was determined. Anthropogenic influences as well as natural processes play a role in coastal water quality (Fig. 7). The loading of nutrients were positive on the PC1 (Fig. 7a). The loading of heavy metals were positive on the PC2 (Fig. 7a). The scores of the monitoring sites (S1 and S2) stayed on the right side of the first principal component axis (Fig. 7b). The scores of the other monitoring sites stayed on the left side of the first principal component axis. In temporal pattern, water quality indicated the distinct seasonal change (different color) (Fig. 7b). In spatial pattern, the two distinguished groups (Sanya River mouth and outer bay) were identified (Fig. 7b). The water body in Sanya River mouth may receive pollutants from the Sanya River. Waters in the South China Sea may have strong influence on the water body in outer bay.

Discussion

The temporal and spatial variation of water quality in coastal waters is governed by human activities and natural processes. Anthropogenic inputs into coastal systems impact directly on the nutrient status and flux rates because of the loads of dissolved nutrients they carry and indirectly through the inputs of particulate nutrients, which can be remineralized in the water column or in the sediments [13]. It is well known that natural processes are driven by daily changes in air temperature, solar radiation, and wind and rainfall associated with the passage of meteorological fronts [14].

Temporal Variation of Water Quality

The combined influence of upwelling and river flow caused a change in zoning depending on the oceanographic characteristics. The vertical variations of water temperature suggest that thermocline occurred in summer (Fig. 3a). In May the thermocline was caused by solar irradiation and during June-August by an exotic coldwater upwelling, and disappeared from September to the following March, and the seawater mixed [6, 15]. The thermocline in Sanya Bay reveals that there was obvious vertical distribution and stratification in the bay (Fig. 3a). The difference in upwelling patterns were determined by the wind intensity and direction during the southwest monsoon in the northern South China Sea [16]. In Sanya Bay, the costal-upwelling forced by southwest monsoon (Fig. 2e) and the strong stratification

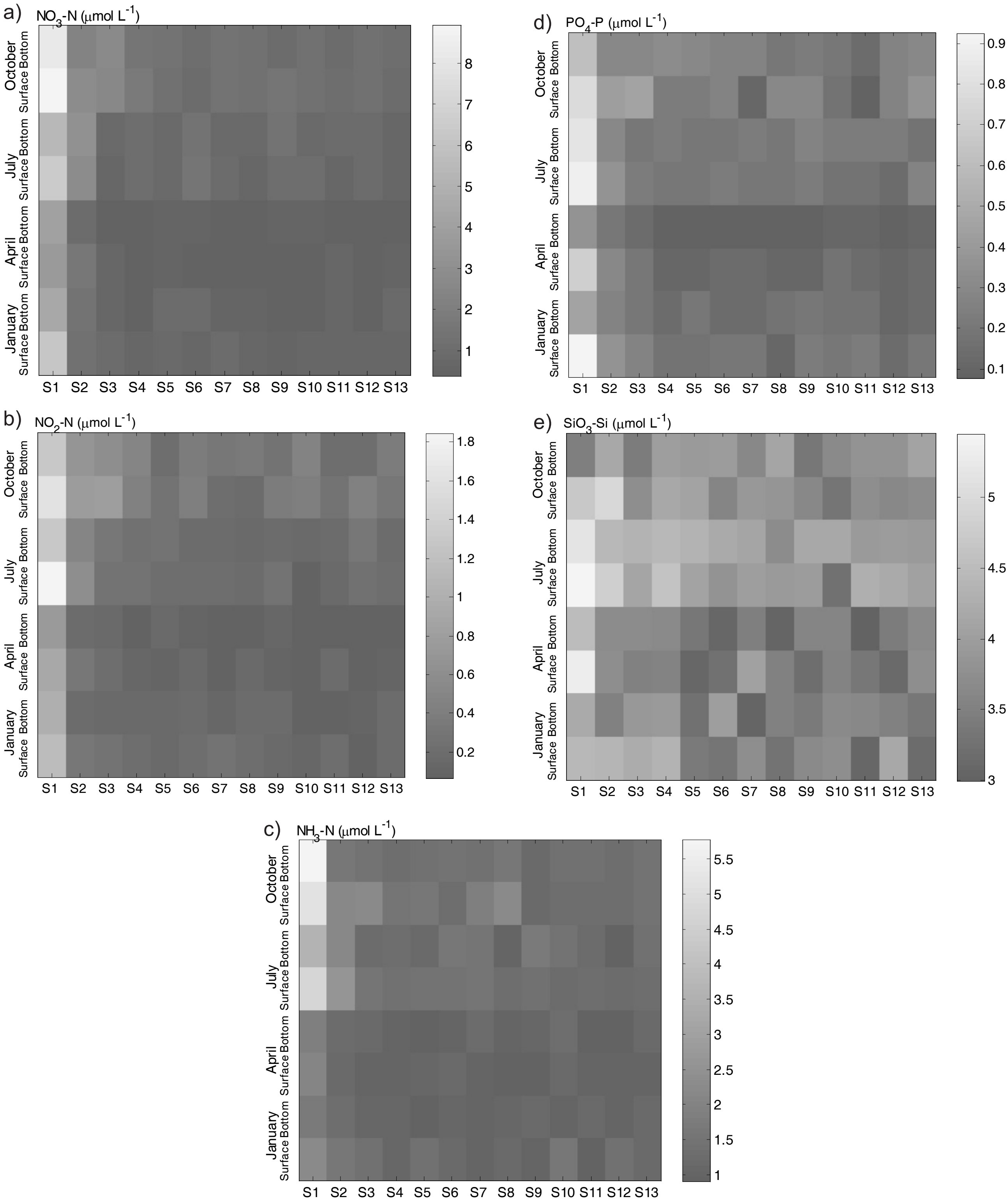

Fig. 4. The temporal and spatial distributions of NO_2-N (a), NO_3-N (b), NH_4-N (c), PO_4-P (d), and SiO_3-Si (e).

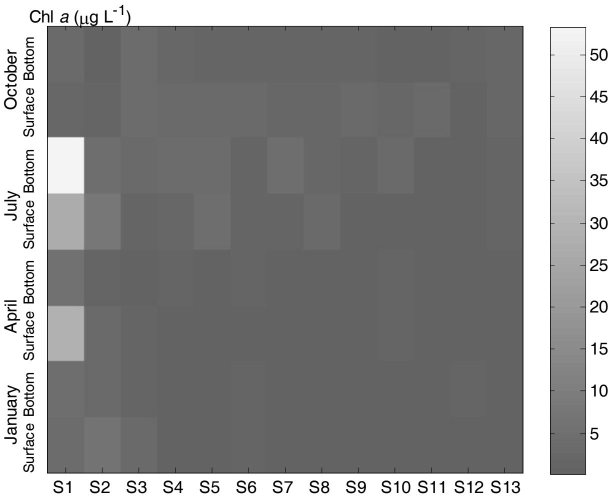

Fig. 5. The temporal and spatial distributions of Chl *a*.

events occurred at S3, S4, and S5, located in the outer and south area of the bay (Fig. 3a). During the upwelling events, the hydrodynamic, conditions of the bay are controlled by meteorological forcing. It is obvious that chlorophyll *a* concentrations in bottom layer increased sharply and much more than a surface layer (Fig. 4). During the stratification event (July), the total chlorophyll *a* concentration of deep layer was much higher than the surface [17]. The stable water in summer can help nutrients be released from the sediment to the overlying water supplying algal growth in the bottom layer [18]. In addition, the bay is also affected by cold-water upwelling occurring during June to August [6, 15].

From the score plot, the temporal distribution of the samples can be observed clearly (Fig. 7b). The sea surface salinity of S1 and S2 was less than that in other monitoring sites in April and July ($p<0.05$), respectively. Sea surface salinity of the monitoring sites was insignificant in January and October, respectively. Heavy rain dilutes the surface salinity in October (Fig. 3a). Rainfall is an important climatic indicator of changes in seasonal characteristics (Fig. 2a). The high metal concentration (Zn) in the rainfall days may be attributed to inputs of freshwater runoff and suspended matter from land. The seasonal variations in metal concentrations can also be related to cycles of convection or stratification within the bay. In addition, Nutrients are introduced in the bay by rivers and sewage discharge. The stochastic events (rainfall) had significant impacts on nutrient inputs into the estuarine systems, increasing the concentrations of all inorganic nutrients in an urbanized lagoonal estuary [19]. These descriptive

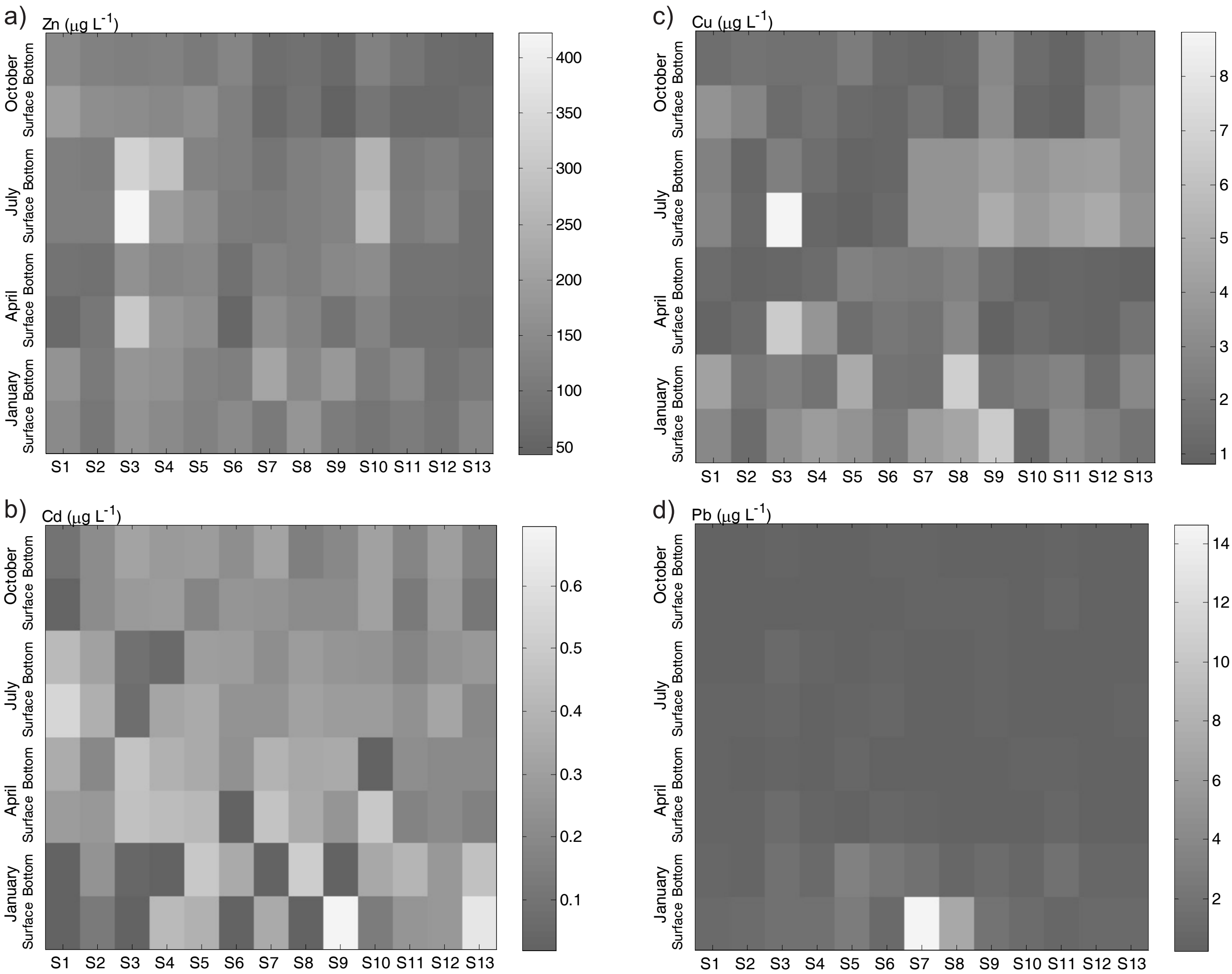

Fig. 6. The temporal and spatial distributions of Zn (a), Cd (b), Cu (c), and Pb (d).

studies are also of utmost importance when evaluating natural changes or anthropogenic effects in a particular area to determine the extent of associated environmental changes and biological processes, as has been considered by other authors [20]. In Sanya Bay, natural processes and water transport processes from the continent to the bay, nutrients, and heavy metal distribution in the bay may be related to point or non-point inputs like Sanya River inputs and exchange from the oceanic water.

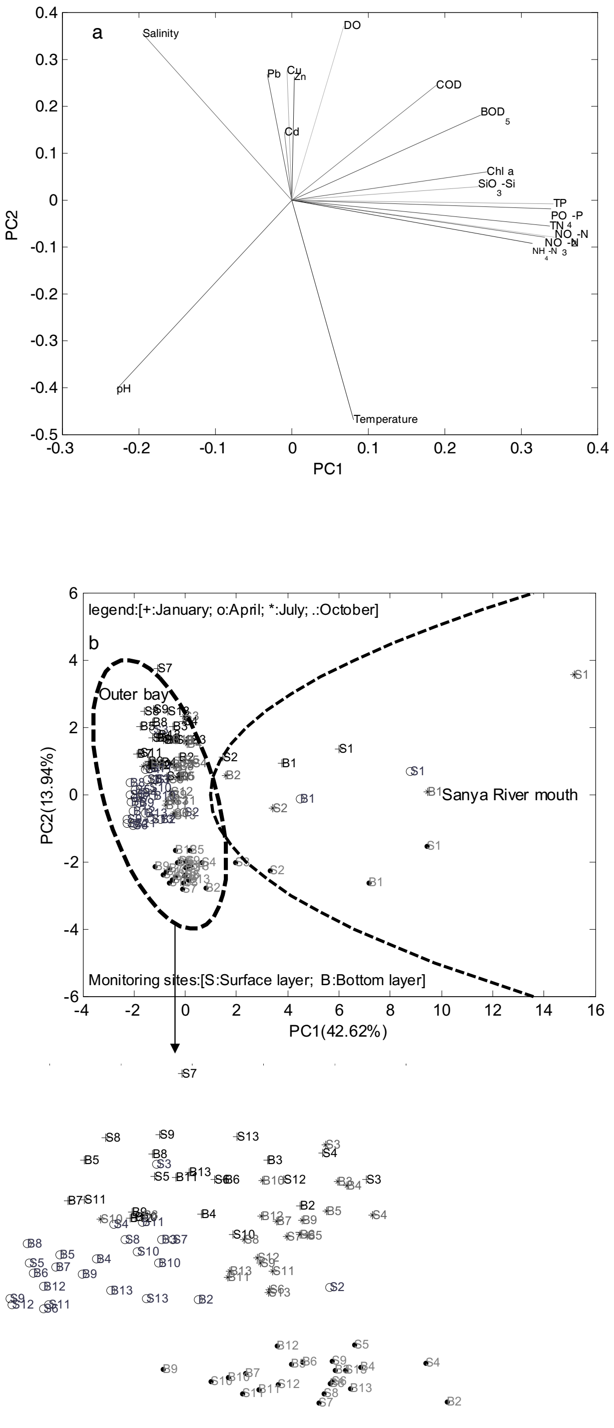

Fig. 7. The results of principal component analysis, loadings (a), and scores (b) on the first and second principal components.

Spatial Variation of Water Quality

The zonation was governed by a combination of specific date and hydrographic conditions with the intervention of meteorological events. The influences of river flow due to rainfall, mixing and wind-induced upwelling are of capital importance in the bay. The 19 July sampling showed a clear upwelling situation. The costal-upwelling forced by southwest monsoon and the strong stratification events occurred in the bay. During January and October there was a slight river supply. The salinity (about 34.00) was uniform in the bay (Fig. 3b), owing to the fact that it occurred during the mixing period.

These physical characteristics had a significant influence on large spatial variability, in which environmental processes as meteorological events and water exchange from the northern South China Sea represent exogenous inputs that strongly determine the spatial behavior of the system. In Sanya Bay, subsectors were defined within the bay and characterized by different hydrodynamic conditions (upwelling and mixing) and human activities. The area of the Sanya River mouth (S1 and S2) was affected by human activities (high nutrients and low salinity) in Fig. 7b. In contrast, the area in outer bay located around the western, northern, and eastern parts of the bay was affected by oceanic water in Fig. 7b. Water quality in Sanya River mouth was mainly influenced by the Sanya, and water quality in other areas were mainly influenced by the waters in the South China Sea [3, 21].

Conclusions

Human activities and natural processes act on a tropical bay, Sanya Bay, in the northern South China Sea. These lead to temporal and spatial differences of water quality in the bay. This study demonstrates that water quality exhibits two distinct hydrologic zones. Human activities are the dominant factor on water quality in the Sanya River mouth. This region exhibited the maximum influence of discharge from the Sanya estimated by higher nutrient levels and Chl *a*. natural processes like upwelling and mixing caused by monsoons are the dominant factor on water quality in outer bay. Each hydrologic and ecological zone has a specific water quality response associated with the relative importance of both human activities and natural processes.

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