Identification of Seawater Quality by Multivariate Statistical Analysis in Xisha Islands, South China Sea

Mei-Lin Wu, Jun-De Dong and You-Shao Wang

Abstract

Xisha waters are considered to be in pristine condition, while facing the fast increasing stress under anthropogenic activities. Water quality around Yongxing Island (YX) has been measured in May, 2012. The results show that the water quality is of the first class standards as compared to the water quality of China, with insignificant difference among the monitoring stations. Robust principal component analysis (PCA) was used to identify the spatial pattern of water quality. YX is characterized by high DO, salinity, and Chl-a with low nutrients, indicating phytoplankton photosynthesis is stronger in YX island waters than the rest of the study areas. Beidao (BD) is characterized by high NH$_4$-N and COD, and low pH, implying that these areas may have higher organic matter decomposition than rest of the areas. The water quality monitoring stations should cover spatially and temporally around Xisha waters for protecting the marine environment.

Keywords: water quality, Xisha, principal component analysis, marine environment protection, nutrients

1. Introduction

Isolated oceanic islands with limited area are surrounded by seawater, without sitting on the continental shelves. They may be a natural experimental area to examine the ecological changes and impacts that accompany human arrival [1]. The island’s ecosystems have pristine environmental conditions, but the interference of humans poses serious threats to the delicate and vulnerable ecological processes of the island [2]. Anthropogenic loading of
polluted materials from urbanized and industrialized land to the isolated islands cannot be directly performed, but it may be brought to these open waters by ocean currents and atmospheric deposits. Human activities in the island including tourism, overfishing, and aquaculture farms have determined influence on the water quality around the islands. To some extent, natural progress including hydrodynamics, typhoons, and other weather conditions also have significant influence on the water quality.

Xisha Islands located in the northern South China Sea (nSCS), consist of more than 20 islands and atolls. The Chinese government established Sansha city on Yongxing Island of the Xisha Islands in 2012. Sansha is the smallest prefecture-level city, by both population and land area in China. The residents in Sansha are about 1443, while the floating population was up to 2000 by the end of December, 2013 (http://www.sansha.gov.cn/). The total land area of Sansha is less than 13 km$^2$. Because Sansha government pays attention to environmental protection, about 2.92 million dollars will be spend to build desalination systems and grow trees on Xisha in the hope of turning the island into a new oasis (http://www.news.xinhuanet.com). In view of this, it is necessary to conduct the environmental and ecological monitoring in Xisha waters, in order to suggest the better management activities to protect environment around the islands. The ecological conditions in the islands were intensively attracted worldwide. The decline in number of seabirds and the remaining birds are caused by increasing human disturbance [3]. The coverage of living hermatypic corals have sharply reduced, while the dead coral coverage had sharply increased from 2005 to 2009 [4]. Coral species dramatically decreased in the past several decades in Yongxing Island [5]. Fish resources are abundant in Xisha waters, which can be exploited to a certain extent [6]. Even though the coral reefs of Xisha islands are considered to be the healthiest and most resilient in the northern South China Sea, it is facing living environmental problems including coral bleaching events, diseases and natural disasters, especially due to anthropogenic activities. Because coral reefs thrive in oligotrophic conditions, pristine water quality is a crucial contributor for the growth of coral reefs. However, water quality characteristics in these islands have not been reported so far. Consequently, it is lack of related information on understanding variation influence on physicochemical properties and phytoplankton under the human activities.

The purpose of this study is to present data on the water quality in Xisha waters. The spatial pattern of water quality was assessed by multivariate statistical analysis. Meanwhile, the key driving factors that control the water quality have been identified. From all these information not only do the people recognize the water quality status, but also give suggestion to establish an effective way for further environmental and ecological assessment of Xisha waters.

2. Materials and methods

This study was conducted in May 2012, around Yongxing Islands (YX), connected with the Beidao (BD), Shidao (SD) and Zhaoshu (ZS) islands with rich coral reef community.
Twelve sampling stations (Table 1) were selected along the coast of the above-mentioned study area (Figure 1). Physical parameters such as salinity and pH were measured in situ using a quanta water quality monitoring system (Hydrolab Corporation, USA). Discrete water samples were taken at 0.5 m below the surface, and 1 m above the sea bottom using 5-L GO FLO bottles. The surface water was only taken when the water depth was less than 5 m. Water from the surface and bottom layers were taken when the depth was more than 5 m. Water quality parameters including nutrients (nitrite, nitrate, ammonia, phosphate, and total phosphate), chemical oxygen demand (COD), and chlorophyll (Chl-a) were estimated using standard methods from “The specialties for oceanography survey” (GB17378.4-1998, GB17378.4-2007, China). Dissolved oxygen (DO) (mg·L⁻¹) was determined using Winkler titrations.

| Stations | Sampling depth (m) | Longitude | Latitude |
|----------|--------------------|-----------|----------|
| ZS1      | 1/8                | 112.2609  | 16.9722  |
| ZS2      | 1/10               | 112.2641  | 16.9694  |
| ZS3      | 1/6                | 112.2719  | 16.9716  |
| BD1      | 1/8                | 112.3003  | 16.9659  |
| BD2      | 1/6                | 112.3101  | 16.9601  |
| BD3      | 1/7                | 112.3149  | 16.9571  |
| SD1      | 1/8                | 112.3409  | 16.8493  |
| SD2      | 1/4                | 112.3465  | 16.8494  |
| SD3      | 1/4.6              | 112.3515  | 16.8473  |
| YX1      | 1/4                | 112.3592  | 16.8364  |
| YX2      | 1/6.5              | 112.3560  | 16.8335  |
| YX3      | 1/4.5              | 112.3503  | 16.8264  |

Symbol “1/number” in the column of sampling depth displays the sampling layer. For example, string “1/8” exhibits sampling was conducted in surface layer-1m below the surface and bottom layer-8 m, respectively.

Table 1. Sampling stations and their locations.

Descriptive statistics and multivariate statistical analysis were carried out for coastal water samples using MATLAB 2014. Since the ratio of samples to the variables is 2:1, the classical principal component analysis might fail. Robust principal component analysis (RPCA) is still effective even if there are a few anomalous observations and even observation samples are less than number of variables [7–9]. Thus, RPCA is employed to understand the spatial pattern of water quality.
Descriptive statistics of nine water quality parameters is shown in Table 2. The NO$_2$-N level at most of sampling stations is below the detected limit (data not shown). pH ranged from 8.00 to 8.06, with the narrow range. Chl-a has a relatively low value in the range from 0.02 to 0.06 μg L$^{-1}$. COD varied from 0.16 to 0.31 mg L$^{-1}$, with the mean value of 0.24 mg L$^{-1}$. Nutrients display a big change with higher standard deviation than pH and COD. According to the seawater quality standard of China (GB 3097–1997), all these water quality (pH, DO, COD, and nutrients) ranges from the first class quality standard scale. Thus, Xisha waters belong to the first class water quality, which is namely, the pristine water.

![Monitoring stations in the studying area. Four sampling areas are Yongxing south (YX), Shidao (SD), Beidao (BD) and Zhaoshu (ZS), respectively.](image)

### Table 2. Descriptive statistics of nine water quality parameters.

| Parameter | pH  | salinity | DO (mg L$^{-1}$) | COD | PO$_4$-P (μmol L$^{-1}$) | NO$_2$-N | NH$_4$-N | Chl-a (μg L$^{-1}$) | TP (μmol L$^{-1}$) |
|-----------|-----|----------|------------------|-----|------------------------|----------|----------|---------------------|------------------|
| Mean      | 8.04| 33.35    | 6.61             | 0.24| 0.07                   | 0.68     | 0.97     | 0.03                | 0.20             |
| Min       | 8.00| 32.99    | 6.02             | 0.16| 0.03                   | 0.36     | 0.43     | 0.02                | 0.13             |
| Max       | 8.06| 33.50    | 7.81             | 0.31| 0.29                   | 2.25     | 1.79     | 0.06                | 0.45             |
| Std       | 0.02| 0.12     | 0.45             | 0.04| 0.06                   | 0.47     | 0.39     | 0.01                | 0.08             |
In this study, different water quality parameters display different spatial characteristics (Figure 2). From the graph, it is observed that pH and Chl-a are higher in YX than the rest of the study stations. Salinity, COD, NH$_4$-N, and TP are maximum in SD. The maximum of NO$_3$-N is observed in ZS, with the minimum of DO also in ZS. However, results of one-way analysis of variance show the insignificant difference among the four sampling areas, suggesting the water quality mainly affected by the natural progress, with the least disturbed anthropogenic activities.

pH is significantly and positively correlated with DO ($r = 0.71$, $p$-value = 0.00). It is possible that in an environment with low levels of organic matter and low levels of respiration, any hydrogen ions released are being absorbed by the alkalinity of the surrounding seawater [10]. COD is lower than the threshold limit of the first class water quality standard and is insignificantly related with other water quality parameters, implying the low organic matter in this environment. On the other hand, the chemoautotrophic process of nitrification is also associated with DO and pH. The process uses up oxygen and also releases hydrogen ions which can cause a fall in pH. However, NO$_3$-N is insignificantly related with NH$_4$-N and DO. It implies that nitrification is not a main controlling factor on dissolved nitrogen for transformation. That is to say, other physical-biochemical processes play an important role in dissolved nitrogen cycle. NH$_4$-N is significantly negatively related with Chl-a ($r = −0.50$, $p$-value = 0.02), while NO$_3$-N is insignificantly related with Chl-a. NH$_4$-N may be the preferred N source for phytoplankton growth in the study area. NH$_4$-N is assimilated primarily by phytoplankton in Pearl River Estuary, nSCS [11].

Robust principal component analysis rendered the first three significant factors (eigenvalue >1.0) that explained 67.02% of the total variance of data set. The results of the RPCA were visualized in the form of ordination diagrams based on PC1 and PC2. The parameter lines were obtained from the factor loadings of the original variable (Figure 3a). The closer the two-parameter lines lie together, the stronger the mutual positive correlation is [12]. pH and DO have the highest positive correlation coefficients, so the two lines are very close with acute angle between them. Similarly, an obtuse angle between two lines represents a negative correlation, etc., NH$_4$-N and Chl-a. The lengths of the parameters represent the relative explanatory power of sampling stations within the ordination in PC1 and PC2 (Figure 3b). In the fourth quadrant, sampling stations in YX are characterized by high DO, salinity and Chl-a, and low nutrients, as these parameter lines are located in this quadrant. It suggests that this area may have a high photosynthesis rate and high primary production. According to Redfield ratio, the average ocean photosynthesis and aerobic respiration can be expressed as follows:

$$106 CO_2 + 16 NH_3 + H_3PO_4 + 122 H_2O \rightarrow (CH_2O)_{106} (NH)_{16} (H_3PO_4) + 106 O_2 \quad (1)$$

Due to photosynthetic activities, nutrients (NH$_4$-N and PO$_4$-P) are quickly taken up by the algae, which result in a shift of the equilibrium [Eq. (1)]. That is to say, phytoplankton photosynthesis is stronger in YX island waters than rest of the areas, suggesting phytoplankton consumes more nutrients from the water, and then produces more oxygen. Photosynthetic organisms release O$_2$ and assimilate nutrients, thereby community respiration attenuating the pH and DO decline. It suggests that photosynthesis keeps balance with respiration, therefore leaving the system without extra organic matter in these areas. The loading of COD is negative in PC1, indicating less organic matter in these areas than rest of the areas (Figure 3).
Figure 2. Spatial distributions of water quality, (a) pH, (b) salinity, (c) DO, (d) COD, (e) phosphate, (f) nitrate, (g) ammonia, (h) chlorophyll and (i) total phosphate. ZS, BD, SD, and YX denote Zhaoshu, Beidao, Shidao, and Yongxing, respectively.
On the other hand, sampling stations in ZS1, SD1 and most of sampling stations in BD are characterized by high NH$_4$-N and COD, and low pH (Figure 3). From this phenomenon, it implies that these areas may have higher organic matter decomposition than rest of the areas. Algal debris and other organic matters can be converted into carbon dioxide and NH$_4$-N [Eqs. (2) and (3)] under biochemical oxidation, resulting in the increase of NH$_4$-N and a decrease in pH.

\[
(CH_2O)_{106}(NH)_{16}(H_3PO_4) + 106O_2 \rightarrow 106CO_2 + 16NH_3 + H_3PO_4 + 122H_2O \quad (2)
\]

\[
NH_3 + H^+ \rightarrow NH_4^+ \quad (3)
\]

NH$_4$-N in these stations is insignificantly related with NO$_3$-N \(r = -0.31, p\text{-value} > 0.10\), while ammonia concentration is higher than NO$_3$-N except in ZSB1, ZSS2, and SDS1. NH$_4$-N production has excess ammonia reduction during nitrification process, resulting in that nitrification may be secondary biochemical progress. This is in disagreement with the study [13]. In this study, the presence of nitrate is mainly due to processes such as nitrification. Water quality may be associated with coral community in Xisha waters. Different dominant coral species reside in the different areas around Yongxing Island, with different species index and cover [5].

As the abovementioned, Xisha waters have spatial variations due to different ecological characteristics. Nutrient levels are below the threshold of the first class water quality of China, Xisha waters are considered in pristine environment so far. However, Sansha city on central Yongxing Island of the Xisha islands was built up by China in 2012. With the development of Sansha, more and more infrastructure has been built in Xisha islands. Special marine features have a great deal of potential for attracting various types of tourists. The elevated nutrient level may promote negative responses such as an increase in bleaching susceptibil-
ity of coral community [14]. Consequently, Xisha islands is intensively facing the stress of anthropogenic activities.

4. Conclusion

In this study, only summer water samples were taken at the several limited islands around Yongxing Island. Results from multivariate statistical analysis shows that Xisha waters are considered to be in pristine condition, while facing the increasing stress under anthropogenic activities. Thus, in the next environment and ecological monitoring plan of Xisha waters, more islands around Yongxing will be integrated into one unit. Xisha Deep Sea Marine Environment Observation Station, South China Sea Institute of Oceanology, Chinese Academy of Sciences have been established in 2007, which is a good platform to conduct the ecosystem observation focusing on Xisha waters. This organization will help us to obtain the information on the variability where water quality will be easily polluted. The present collected data can present a baseline for future studies in Xisha waters, and even in other isolated island waters.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Nos. 31270528, 41430966 and 41206082), Natural Science Foundation of Guangdong (No. S2013020012823), Scientific Research Project of Guangzhou (Nos. 201504010005 and 201504010006), the project of Guangdong Provincial Department of Science and Technology (No. 2012A032100004) and the projects of knowledge innovation program of State Key Laboratory of Tropical Oceanography (No. LTOZZ1604).

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