Nitrate inversion based on remote sensing in the Pearl River Estuary, China

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Abstract. Against a background of ongoing economic and industrial development, the impact of human activities on the offshore environment has become increasingly significant in recent years. In many regions, contamination of the marine environment necessitates the need for dynamic, real-time and wide-coverage water quality monitoring and satellite remote sensing, such that multi-temporal and spatial scale observation of various oceanic parameters are realized. In this paper, using salinity, in situ spectral data, nitrate and other water quality data from five sampling campaigns in the Pearl River Estuary and adjacent waters, studies on the inversion of nitrate concentrations using an artificial neural network were performed. Two inversion models, based on input of the measured salinity and field spectral data and just the field spectral data, were investigated. After comparing the accuracy of the two models, it was considered that the nitrate model with salinity and field spectral data as input performed best. Finally, the selected model was applied to MODIS data to achieve inversion of the nitrate concentrations in the estuary waters and obtain the temporal distribution of nitrate concentrations as a means to monitor and evaluate water quality in the estuary.

Keywords. MODIS; Pearl River Estuary; nitrate remote sensing; model inversion; artificial neural network

1. Introduction
The estuary constitutes the intersection of two different water bodies, the ocean and the river, and belongs to the near-shore second-class water body. Usually, the chromogenic composition and other
water quality parameters of estuaries are very complicated. On the one hand, the estuary, which is connected to the incoming rivers and the ocean, is an important geographical hub and home to a large number of organisms that support human activities. On the other hand, the estuary is very fragile. The estuary marks the confluence of rivers and marine sediments, and contaminants are readily attached to sediments. Thus the concentrations of pollutants in the estuary can be high and the residence time can be long[1]. In recent years, the impact of human activities on the offshore water environment has become a cause for concern. A large number of untreated industrial byproducts and domestic sewage do not meet environmental discharge standards, and in notable cases, have caused serious eutrophication of some coastal and estuarine areas in China. Eutrophication may lead to algal blooms, water anoxia, biological community damage and other ecological disasters, which seriously affects the quality of the marine environment and the safety of human and marine life. Given the high service function and value of the estuarine ecosystem, the high development and utilization of coastal areas, and the high sensitivity of the estuary to pollution, measures are needed to protect the estuarine environment[2].

Eutrophication caused by high concentrations of inorganic nitrogen and active phosphate in coastal waters is one of the most prominent environmental problems in China. Nitrogen, not only plays an important role in biological activities as a key ecosystem source element, but is also an indispensable parameter in water quality monitoring. Traditional field sampling methods based on hydrological station and ship sampling, have limited distribution points, and can only reflect the water quality information for the location at the time of sampling. Moreover, such methods typically require a long analysis time and have high equipment maintenance costs. Combining conventional field observations with remote sensing to obtain water quality data represents not only a “clean” technology approach that conforms to the ideal concept of environmental protection, but also promises to overcome the above deficiencies and retrieve a wide range of spatial distribution characteristics of water quality parameters, which would be an effective means to identify and better understand the early onset of eutrophication in the estuary[3-6].

As a general nonlinear approximation method, artificial neural networks have been widely applied to ocean water color inversion in recent years. The method can fully utilize the information of each band of the satellite sensor and other a priori conditions, so that all kinds of information can be comprehensively utilized, and at the same time, high calculation efficiency can be achieved[7]. In this paper, taking the Pearl River Estuary as a typical study site and nitrate as the detection index, a nitrate inversion model based on an artificial neural network method was established by using the field data for salinity, nitrate and surface reflectance for five separate voyages in the Pearl River Estuary and its adjacent waters.

2. Materials and Methods

2.1. Overview of the study area

The Pearl River Estuary is located in the subtropical marine monsoon climate zone. It is an estuary where the river delta network and the estuary bay coexist. The estuary has a north-south trumpet shape. Several main rivers of the Pearl River system interlink with each other in the lower reaches of the river.
After entering the delta network, the rivers flow into the South China Sea in eight radial channels, forming a unique water system characteristic of “Three Rivers converging and the eight rivers diverging.” The average rainfall in the area is typically 1600-2300 mm, and the river runoff is large, which makes the hydrological conditions of the estuary complex and variable. In recent years, eutrophication of the Pearl River Estuary has become more and more serious. Shenzhen and Hong Kong lie on the east bank of the river, while Zhuhai and Macao are located on the west bank, and to the north is Guangzhou. A large amount of industrial sewage and domestic wastewater are discharged into the sea, making the water composition of the estuary complex[8]. The Pearl River Estuary is a typical second-class water body. The variable hydrodynamic conditions and complex hydrological environment make the marine water color remote sensing application for this area quite challenging.

2.2. Sample collection

The field data were obtained from five voyages in the Pearl River Estuary and its adjacent waters, conducted in July 2006, December 2006, November 2013, February 2014 and May 2014. After removal of the sampling station data with poor spectral quality, a total of 97 sampling points covering water salinity, nitrate concentration and surface remote sensing reflectance (Rrs) (calculated from synchrotron radiation data) were used for the experiments. The field investigation area and layout of the 97 stations are shown in Figure 1. The nitrate concentrations ranged from 0.0034 to 1.54 mg/l. The nitrate concentrations of the two voyages in July 2006 and December 2006 were determined in the field using a flow injection analyzer (LACHAT QC8500) (Detection limit, 0.003 mg/l). For the other three voyages, samples were transported to the laboratory and nitrate concentrations were determined according to a standard colorimetric method (GB 17378.4-2007) featuring cadmium column reduction (Detection limit, 0.0007 mg/l).

![Figure 1. Sampling stations in the estuary of the Pearl River system.](image-url)
At the same time of sampling, the surface reflectance spectrum of the water was measured according to NASA’s water spectrum measurement specification. The spectrometer measurement range for the voyages in July 2006 and December 2006 was 325-1075 nm, and the range for the remaining voyages was 350-2390 nm. In the course of the experiment, to ensure consistency with the band channel set by the MODIS satellite, the actual utilization range was restricted to 380–1100 nm. This was because the spectral response function in the range of 1075-1100 nm was very small, thus there was little difference between the calculated equivalent reflectivity and the zero assigned to it. Therefore, in 2006, the missing bands for the two voyages were all supplemented by zero. Figure 2 shows the surface spectral reflectance curves corresponding to various nitrate concentrations in the estuary and adjacent waters.
Figure 2. The measured remote sensing reflectance for waters in the visible and near-infrared bands. (a) Spectral curves for voyages in November 2013, February and May 2014; (b) Spectral curves for voyages in July and December 2016.

2.3. Nitrate Remote Sensing Inversion

The correlations between different single bands, the band ratio and the band difference with nitrate concentration were studied for the 380-800 nm region using remote sensing reflectance. As shown in Figures 3-5, it can be seen that band (597 nm)/band (450 nm) correlates well with nitrate, the $R^2$ value being 0.65; in addition, band (490 nm)-band (450 nm) and the single band near 490 nm also gave relatively high correlation, the $R^2$ values being 0.5734 and 0.433, respectively.

Figure 3. $R^2$ values for different wavelengths and different nitrate concentrations.
Figure 4. Correlation analysis between band difference and nitrate concentration.
The main goal of correlation analysis is to establish an inversion model that can be applied to satellite data. Therefore, the channel settings for MODIS were further examined. The correlations between 10 single-bands, the band ratios and the band difference combinations for MODIS and nitrate were calculated. The band types with high $R^2$ values are listed in Table 1 below; the highest $R^2$ value was 0.61 (B8/B2).

| Band       | $R^2$    | Band       | $R^2$    |
|------------|----------|------------|----------|
| B6         | 0.3808   | B8/B1      | 0.6064   |
| B7         | 0.3921   | B8/B2      | 0.6100   |
| B8         | 0.3931   | B8/B3      | 0.5886   |
| B3-B6      | 0.5529   | B8/B4      | 0.5603   |
| B4-B6      | 0.5594   | B9/B1      | 0.5771   |
| B6-B4      | 0.5532   | B9/B2      | 0.5669   |
| B7-B3      | 0.5529   | B10/B1     | 0.5810   |
| B7-B4      | 0.5594   | B10/B2     | 0.5647   |

The above results indicate that it is feasible to estimate nitrate concentrations using satellite remote sensing reflectance. This methodology features a three-layer feedforward back propagation network (referred to as a BP network), and the network structure is shown in Figure 6. As can be seen, the BP neural network has three layers, and includes the input layer, the hidden layer and the output layer. The full connection is achieved between several types of layers, and there is no connection between each layer of neurons. When a pair of learning samples are provided for the network, the activation value of neurons propagates from the input layer to the output layer through each hidden layer, and each propagation is controlled by an assigned weight and a threshold value. Finally, each neuron in the output layer gets the input response of the network. Next, according to the direction of the target
output and the actual direct error reduction output, the connection weight is corrected layer by layer from the output layer through each hidden layer, and finally returns to the input layer. With reverse of the error propagation correction, the accuracy of the network response to the input mode also rises[9-11].

**Figure 6.** Schematic of the BP neural network structure.

Any continuous function in a closed interval can be approximated by a BP neural network in a hidden layer, so a BP neural network in three layers can complete any mapping from the n-dimension to the m-dimension. Thus this study used a network with a hidden layer for training. The spectral and salinity data were used as input parameters and then only the spectral data were used for input, respectively, and the corresponding nitrate concentrations as the output were obtained. After normalizing the data, the network was trained by the Levenberg-Marquardt method which used the digital optimization technique to obtain the model. The updating formula for the Levenberg-Marquardt weight and threshold is:

$$X_{k+1} = X_k - (J^T J + uI)^{-1} J^T e$$  \(1\)

where \(J\) is the Jacobian matrix of the error-to-weight differential, \(e\) is the error vector, and \(u\) is a scalar. Depending on the magnitude of \(u\), the method varies smoothly between two extremes: the Newton method (when \(u\) goes to zero) and the well-known steepest descent method (when \(u\) tends to infinity). Using the Levenberg-Marquardt optimization method, the learning time can be shortened which is of benefit in practical applications[12].

For the neural network inversion process, the selection of the number of cells in the hidden layer is a very complicated problem. If the number is too small, the information that the network can obtain to solve the problem cannot be fully utilized; if the number is too large, not only will the training time be increased, but also the fault tolerance will be poor, resulting in over-fitting. To determine the hidden node problem, an empirical formula is first used to determine the range of nodes as in Equation (2), and then the change of the root mean square difference between the inverted nitrate concentration and the measured nitrate concentration of the test set is used to determine the final number of hidden nodes.

$$m = (n - l)^{1/2} + \alpha$$ \(2\)

Here, \(m\) is the number of hidden layer nodes and \(n\) and \(l\), respectively, represent the number of input layer and output layer nodes and \(\alpha\) is an empirical calibration coefficient, which is usually an integer between \([0, 10]\)[13].

In addition to the parameters mentioned above, the other parameters of the neural network model keep the default values of MATLAB software. The training data, the test data and the verification data were randomly assigned according to the ratio 0.7 : 0.15 : 0.15. The Levenberg-Marquardt method was selected for the training algorithm, and the maximum number of iterations to terminate the
training was 6, and the root-mean-square error is used as the criterion to evaluate the performance of the model and adjust the weight between nodes.

The training results showed that when the equivalent reflectivity and salinity data of the MODIS band were the input parameters, the number of hidden nodes required to achieve high precision was eight; when the spectral data were the input, the number of hidden nodes required to achieve high precision was six. Most of the randomly initialized networks produced better inversion accuracy. Finally, the network with highest precision was selected as the inversion model, as shown in Figures 7-8.

![Figure 7. Mixed nitrate model based on salinity and spectral data.](image)

\[ R^2 = 0.8463 \]
\[ \text{RMSE} = 0.1466 \]
3. Results

Using the nitrate, the salinity and the remote sensing reflectance data, the model was established and through application of the neural network method, the sea surface nitrate concentrations over a large scale and long time span were obtained. In this study, the monthly average remote sensing reflectance data for 10 bands of MODIS and the salinity data of SMAP in September 2014 were used to retrieve the distribution map of nitrate concentration in the Pearl River Estuary and its surrounding waters using the above-mentioned hybrid model, as shown in Figure 9.

Figure 8. Nitrate model based on spectral data.

The correlation between the nitrate inversion result and the measured value, calculated for the spectral data and salinity as the model input, reached 0.8463, the root mean square error being 0.1466. The correlation for the model established by input of only the spectral data attained a value of 0.6512, the root mean square error being 0.2573. Thus, according to the statistical indices, the model for nitrate inversion, in which both the spectral data and salinity were used as the input parameters achieved best results.
Figure 9. Nitrate concentration distribution obtained from model inversion (September 2014).

It can be seen from the distribution map that for the period in question, the overall trend for the sea surface nitrate concentration near the Pearl River mouth was high near the shore and lower in the main body of the sea; the highest concentration for nitrate, 1.2 mg/l, appearing just outside the mouth of the Pearl River. For the near shore data, the nitrate concentration appeared to be distributed in strips along the coast, reflecting the characteristics that the nitrate in the mouth of the Pearl River is mainly from land. Due to the large differences in the field measurement times for the ship-based data used to establish the model, and the inconsistencies in the observation times and the space between the neural network inversion values and the measured values, the inversion accuracy of the model was affected. The inversion values for the neural network are based on the average data for September 2014, in which the resolution of the salinity data is relatively low being about 40 km, while the actual measured values are the sampling point data for 2006, 2013 and 2014, respectively.

4. Summary
Using measured data for water quality such as salinity, field spectral data and nitrate concentrations from five sampling campaigns in the Pearl River Estuary and adjacent waters and a neural network method, two inversion models, based on the input of salinity and spectral data, and the input of just spectral data, were simulated and the respective results were analyzed. The main conclusions were as follows:

1) The feasibility of using hyperspectral remote sensing to retrieve a non-optically active parameter, that is, the nitrate concentration in a near shore water body was demonstrated. 2) The Pearl River Estuary belongs to the second class of water body, and the water color elements are complex. From the perspective of the $R^2$ values for the correlation analysis reaching 0.8, the performance of the neural
network methodology in extracting the water quality element was confirmed. 3) From comparative analysis of the statistical indices for the models, it was demonstrated that the use of salinity in the input layer does improve the accuracy of the model. 4) The study has combined field data with remote sensing data, and the remote sensing method for estimation of nitrate concentration in the waters of the Pearl River estuary has been studied in a quantitative manner. It has been confirmed that the approach is highly appropriate for monitoring the dynamic changes of nitrate concentrations and also abnormal water quality changes that would be difficult to monitor by conventional measurement methods. 5) The accuracy of the model generated by the input of just salinity and spectral data is not sufficiently high, and this may reflect the wide differences in the field measurement times for the five voyages and the dispersion of the sampling stations.

In addition, the paper still has the following problems to be further solved:

1) limitations of satellite products. The spatial resolution of SMAP salinity satellite data is 40km, far lower than that of MODIS satellite (4km). In addition, the microwave radiation at the sea surface is highly interfered with the land signal, so there is often a lack of data in the inshore areas. Therefore, most of the inshore areas in the inversion map for September 2014 were blank, and there was also a lack of data in some far-sea areas. Using the data of MODIS and SMAP together as the model input will sacrifice the spatio-temporal resolution advantage of the SMAP satellite, so that the final nitrate water quality products cannot reflect small-scale changes. In addition, the atmospheric correction accuracy of the optical satellite in the near-shore second-class water body needs to be further improved.

2) Nitrate, as a dissolved small molecule, has no significant spectral characteristics. The nitrate model in the paper is mainly based on the statistical relationship between the nitrate concentration, the spectral characteristics, and the salinity of seawater in the Pearl River Estuary. Such a model inevitably has regional limitations, and it is difficult to extend the same model to other areas. If similar methods are used in other sea areas, it is necessary to use local measured data to conduct model training again.

Acknowledgments
This study is supported by the National Key R&D Program of China (No. 2017YFC1405300 &2018YFB0505005), Key research and development plan of Zhejiang Province under contract no. 2017C03037, the National Natural Science Foundation of China under contract no. 41476157, and Southern Marine Science and Engineering Guangdong Laboratory (Zhanjiang)(Zhanjiang Bay Laboratory) ZJW-2019-08. We thank the satellite ground station, satellite data processing & sharing center, and marine satellite data online analysis platform (SatCO2) of SOED/SIO/MNR for their help on data collection and processing.

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