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Key words: CODMn, NH3-N, remote sensing satellite, surface waters pollution, lake taihu.

ABSTRACT

The transport of pollutants into freshwater resources depends on the relationships between pesticide/fertilizer application, local topography and rainfall. These relationships are investigated at Lake Taihu, China, where the cropland around the basin is devoted to growing rice. Our aim is to study the effects of the rainfall and non-point source contamination on surface water quality, with a specific focus on Nitrate Potassium Permanganate Chemical Oxidant (CODMn) and Nitrates (NH3-N), and using satellite remote sensing to construct a pollution estimation model by using satellite data and surface data from 7 monitoring station surveys in 2008-2015. Comparing measured values and remote sensing predicted values, the average of CODMn relative deviation is -0.775 and the average of NH3-N relative deviation is -0.030, both within a reasonable range. Experimental data shows that the lower concentrations of NH3-N occurred when rainfalls are high, the CODMn's temporal and spatial distributions have high variability, and the interaction between seasons and rainfall rate explains variability of NH3-N and CODMn concentrations in surface waters.

I. INTRODUCTION

During previous decades, the application of pesticides has resulted in increased environmental and health hazards (Wyckhuys et al., 2013). In the case of lakes, the degree of surface water contamination depends on the soil properties, the presence of (organic and inorganic) fertilizers, flow rate and depth, and climate (rainfall and monsoon) (Neumann et al., 2002). Physical, chemical and biological processes occur, which depend on pesticide's mobility in the soil (such as volatilization, adsorptiondesorption), together with chemical and physical degradation (Vryzas et al., 2011). In a rice crop test field studied herein, the application of organic and inorganic fertilizers (nitrogen; phosphorus and potassium). The crop's high irrigation rates cause most of soil pollutants to flow to Lake Taihu via spray drift, runoff and drainage mechanisms. Within the gentle slopes of the Taihu basin, the pollutants' movement mainly depends on drainage through the soil. In many cases, high Nitrate (NH3-N) concentrations in Lake Taihu and shallow groundwater levels, prompt farmers to use fungicides and avoid crop yield losses.

Some studies have shown that inland waters' pollution distributions can be mapped through satellite remote sensing (Zhang et al., 2014). For continuously monitoring of NH3-N and CODMn levels in Lake Taihu, models have been developed to estimate pollution using satellite remote sensing data. This approach provides a latent capacity for monitoring pollution during coastal and inland surface water flows (Lian et al., 2014; Petus et al., 2014). However, to date there is an absence of systematically conducted studies which use satellite data to obtain the long-term distribution patterns of NH3-N and potassium permanganate (CODMn) at Lake Taihu. Such pollution distribution patterns are required for evaluation of the environment and ecological conservation measures at the lake.

In a previous study (Andrade and Stigter, 2009) into NH3-N, CODMn, dissolved oxygen (DO) and pH levels within experimental plots located at Lake Taihu, NH3-N was found to be the most important pollutant detected in rice crops and in water used for irrigation on account of its high mobility. As a consequence of the high mobility of NH3-N in surface water and soil, NH3-N concentrations are typically high in the Lake Taihu basin. An improved understanding of the impact of climate conditions on pesticide pollution levels is needed for sustainable management of water resources. Therefore, the aim here is to develop a pollution estimation model using satellite remote sensing to study the effects of rainfall and non-point source contamination on surface water quality.

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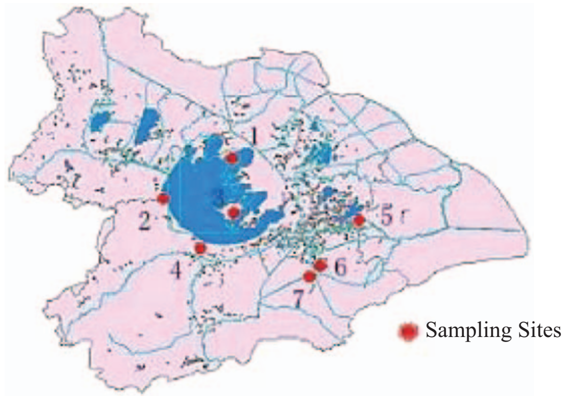

Fig. 1. Seven automatic water sampling sites of Lake Taihu basin.

II. EXPERIMENTAL

1. Study Area

Lake Taihu, which is located on Yangtze River delta, is the third-largest freshwater lake in China, and influenced by the East Asian monsoon climate. The Lake Taihu basin belongs to the subtropical monsoon climate zone, which has a humid climate and distinct seasons. The mean annual temperature is between 15°C-17°C.

In recent years, increased agricultural development and production have led to severe water pollution problems at Lake Taihu. From 1981 to 1991, the total nitrogen content of the Lake Taihu water layer had increased nearly twofold, and the algae volume had increased 38 times (Kun et al., 2014). Since 2000, the accumulation of ammonia nitrogen pollutants has led to blue-green algae blooms from March to September every year. This resulted in enormous social and agricultural disruptions within the local region.

The authors used seven automatic water sampling sites in the Lake Taihu basin as shown in Fig. 1. Water samples were collected from these sites as described below.

2. Crop Cultivation

This study's main (rice crop) agricultural concerns include soil water efficiency, effectiveness of management of fertilizers and crop diseases. Locks exist along on the main drainage canals and are operated to retain a level of water and manage droughts in summer. The accumulated water is used to irrigate the rice crops. Conversely, rising water tables cause extensive floods in areas during monsoon rain periods. As rice crops require a large quantity of nutrients and fertilizer (organic and inorganic), manure is primarily applied in the pre-planting fertilization period (López-Periago, 2002). According to the local climatic conditions, rice crops are planted between March and May, and Nitrogen (N) fertilizer is applied during the tillering stage (Wyckhuys et al., 2013). Fig. 3 shows the planting, fertilization and harvest cycles of rice crops.

3. Water Sample, Remote Sensing Data and Meteorological Data

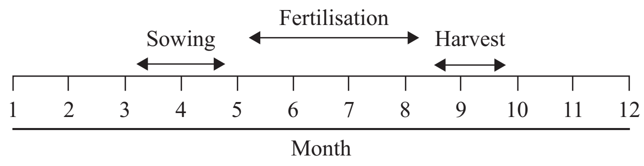

Fig. 3. Agronomic treatments throughout the rice crop growing cycle.

All water samples were collected from the river centers at a depth of 0.5 m below the surface. In particular, a telescopic water sampler was used to collect water in HCl-pre-washed glass bottles (1.5 l). The sampling bottles were washed with 500 ml water collected at each of the sampling locations. A flow meter was setup at the water outlet for the purpose of recording the volume of water outflow.

Spatial and temporal satellite image data was also collected over Lake Taihu. The satellite data was collected at a frequency of 1 image per week from 2006 at no cost. The maximum spatial resolution of the satellite image sensor is 250 nm. This data enables monitoring of the Lake Taihu basin in multi-annual periods and at moderate resolution. The satellite data (in raw digital counts) between 2006 and 2015 was collected from the Ministry of Environmental Protection of China. SeaDAS 6.0 was used for calculating the calibrated at sensor radiance. In the study of the basin, over 3500 data granules are covered between Jan. 2006 and Dec. 2015. Among them, 364 high quality scenes were selected after visual examination for the purpose of excluding those that were affected by clouds and thick aerosols.

The monthly mean of wind speed data from 2008 to 2015 was collected from a meteorological station, and the data could be downloaded on the internet (Shi et al., 2014).

4. Chemical Characterization

The water samples' CODMn concentration was measured based on standard methods (China National Environmental 1991). These analyses were performed using UV-220 spectrophotometry.

To extract NH3-N from the water samples, acetone was mixed with a water sample (500 ml) which was contained in a decanting funnel. Then the mixtures were twice shaken for 15 min. These organic mixtures were all collected into a volumetric flask of 250 ml. Then evaporation of the liquid of 250 ml was done with the aid of nitrogen. Thereafter it was re-dissolved in acetone (1 ml). Finally, it was transferred to a vial [12].

5. Statistical Analysis and Significant Assessment

Parametric statistics were used to estimate the statistical significance of group means' differences. Least significant difference tests, as well as linear and non-linear regressions were conducted on SPSS 17.0. To study the relationships between the variables, a correlation analysis was carried out. Significant (when $p \leq 0.05$) and non-significant (when $p > 0.05$) were used to report the significance levels. (Azrauzo et al., 2011).

Table 1. The pollutant CODMn weekly concentration of basic statistics in locations of Lake Taihu 2011.

Station	1	2	3	4	5	6	7
Average	3.60	4.05	4.04	4.59	4.00	6.17	7.96
Standard deviation	0.59	1.49	0.900	1.15	0.63	1.32	0.52
Sum	187.00	210.80	209.80	229.40	207.90	320.60	413.70
Observation count	52	52	52	50	52	52	52

Average: the annual data of weekly average concentration of pollutant, unit: mg/L;
Standard deviation: the average of the distances of each data from the average;
Sum: the sum of weekly average pollutant concentration in 2011, unit: mg/L;
Observation count: the number of collected samples at a location at a time.

Table 2. The pollutant NH3-N weekly concentration in locations of Lake Taihu in 2011.

Station	1	2	3	4	5	6	7
Average	0.012	0.836	0.161	0.431	1.769	1.617	1.363
Standard deviation	0.008	0.573	0.079	0.188	0.571	0.632	0.662
Sum	47.330	43.490	8.390	22.390	91.970	84.100	70.900
Observation count	52	52	52	52	52	52	52

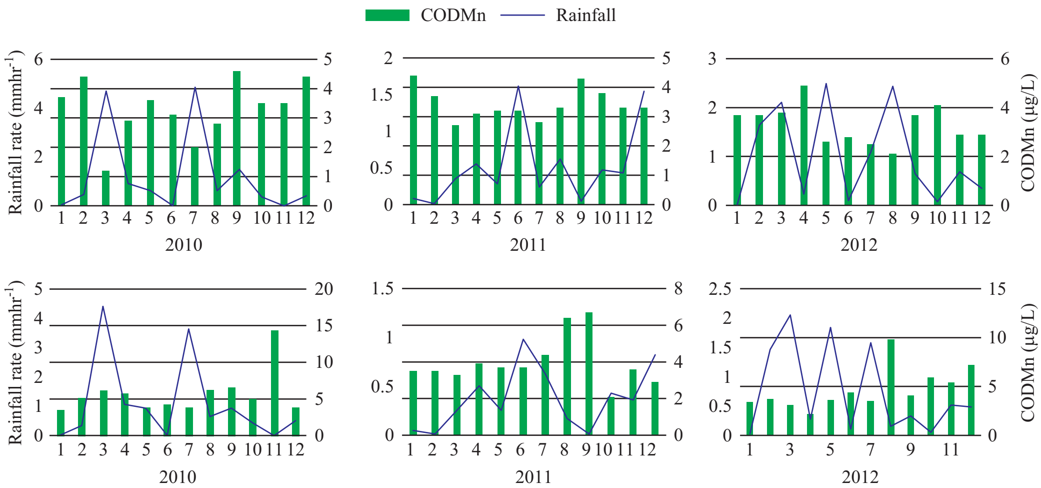

Fig. 4. CODMn concentrations at two stations and monthly precipitation from 2010 to 2012.

III. RESULTS

1. CODMn Concentrations

In all sampling sites where samples were analyzed, the pollutant CODMn was found within most of samples (Table 1). The monitoring location at the area where the pollutant concentration was the most serious is Monitoring Station 7. During the 12 months of this study, the sum of CODMn concentrations was 413.700 mg/l. In the case of Monitoring Station 6, the sum of CODMn concentrations was 320.600 mg/l. At Monitoring Stations 1 and 2, CODMn concentrations were measured from January to November. In the lake entrance, the junction of the river with the canal (Monitoring Stations 5), the sum and maximum of the CODMn pollutant appears to be independent of those at other monitoring sites. The fact that the CODMn was less in the canal junction suggests that partial pollutant release occurs either by sequestration within river sediments or by rapid degradation in the river.

Fig. 4 shows the distribution of CODMn concentrations for Monitoring Stations 1 and 2. This indicates that pollutant concentrations increase when the rainfall rates are low. Conversely, when the rainfall rates are high, pollutant concentrations decline. That is, the relationship between CODMn and rainfall rate is negatively correlated.

2. NH3-N Concentrations

The observed NH3-N concentrations in the waters of Lake Taihu are shown in Table 2. The NH3-N concentrations have a heterogeneous distribution in time and spatial domains. For the spatial distribution, the average value during 12 months at

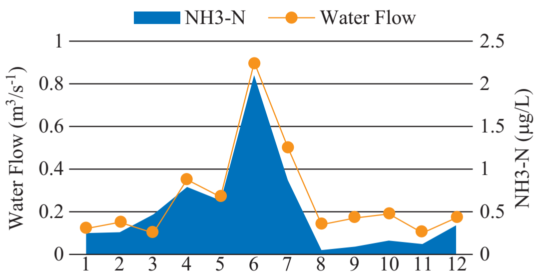

Fig. 5. Relationship between NH3-N concentration and flow rate (measured at monitoring station 1).

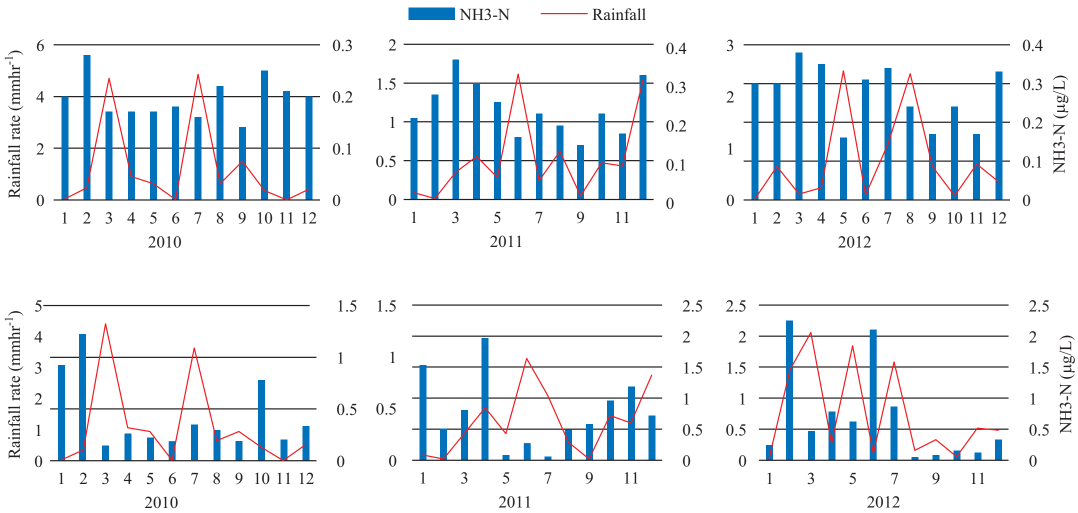

Fig. 6. NH3-N concentrations at two monitoring stations and monthly precipitation from 2010 to 2012.

7 monitoring stations ranged from 0.012 mg/l (Monitoring Station 1) to 1.769 mg/l (Monitoring Station 5) in Table 2. The standard deviations were low, between 0.008 (Monitoring Station 1) and 0.632 (Monitoring Station 6) mg/l. The maximum value (3.580 mg/l) was observed at Monitoring Station 5. High spatial variation of NH3-N can also be studied by analyzing the coefficients of variation so that NH3-N is measured in surface water samples (not shown).

According to monitoring stations data (Fig. 5), we can locate a water channel to relate the flow to the NH3-N. Clearly, the variation of NH3-N concentration depends on the level of water flow rate change. Nevertheless, these peaks of NH3-N concentration are also consistent with crop planting seasons. Fig. 6 shows data from 2 monitoring stations which exhibit similar behavior, namely, NH3-N concentrations peak when rainfall increase and vegetative development reduce.

For the spatial and temporal variability, using an analysis of variance, we find that the CODMN and NH3-N concentrations vary within a season's sampling year and a sampling area. The interplay between the area of runoff and the rainfall during season results in significant changes of pollutant concentrations.

IV. DISCUSSION

1. CODMn Concentrations

The study of farm chemical transport in agricultural surface water is of great importance. However, the nonhomogeneity of surface water research samples in topography and climate make model construction difficult. Over all satellite bands, it is found that find B_5 and B_8 offer good opportunities for estimating CODMn pollutant levels. The results presented below indicate that only the B_5 satellite band data correlates well with the original CODMn observations.

R. Square represents the ratio of the variance explained by the model to the total variance of the original data. The higher the value, the stronger the correlation with the model.

The standard deviation reflects the degree of discrepancy between individuals within the group of estimate.

Sig is the significant level.

Table 3 indicates that high values of R^2 occur for fitted Quadratic and exponential functions, and lower standard deviation of estimation occur for fitted quadratic and exponential functions. The other standard deviation of estimations are too large to meet our modelling requirements. The results show the significance level for the quadratic, power and exponential functions are less than 0.05. Therefore, the quadratic function was chosen for the model.

In Fig. 8, Comparing and analyzing the CODMn's measured values and remote sensing predicted values, the difference between them are in a reasonable range. From the measured

Table 3. The correlation table between CODMn and B_5.

Function type	Linear function	Quadratic function	Power function	Exponential function
R^2	0.837	0.908	0.854	0.882
The standard deviation of estimate	0.428	0.062	0.099	0.091
Sig	0.29	0.002	0.025	0.015

Table 4. The CODMn estimates precision analysis table in 2014.

Estimating model	P	AD	ARD	RMSE
CODMn = $0.006B5^2$-0.623B5 + 19.617	0.002	-9.433	-0.775	6.903

P: The significant level. A P value less than 0.01 means that the two groups of data have a clear relationship.

ARD: the ratio of the mean deviation of all measured values to the average of these measurements. This is used to compare the average deviation of the measured values of different substances.

AD: The difference between a single measured value and an average value. This reflects the magnitude of the deviation of the single measured value between the mean values.

RMSE: the square root of the sum of the squared and observed times n of the observed and true values.

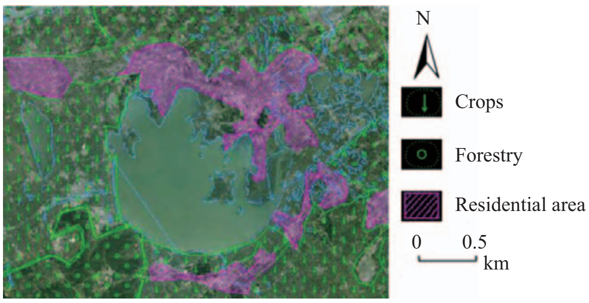

Fig. 2. Lake Taihu land use of watershed.

data comparisons shown in Fig. 7, the value of forecasted data had general correlate with the field monitoring data. From the estimate accuracy analysis (Table 4), the predictive value's P value (P) is 0.002 which was less-than 0.005. The predictive value's average relative deviation (ARD) is -0.775, the predictive value's absolute deviation (AD) is -9.433 and the predictive value's root mean square deviation (RMSD) is 6.903. That is, the two sets of data are significantly correlated.

The analysis of the CODMn observations in the Lake Taihu basin suggest that it is important to select multiple water monitoring sites. In areas where there are abundant human interferences, many aquifers and/or water displacement mechanisms, multiple monitoring of surface water CODMn concentrations must be carried out (Fig. 2). The soils in the studied basin have a higher organic material content compared to other soils. Thus, soil characteristics do not seem to have significant impact on the formation of channel pollutants.

The highest concentration of CODMn appears when the runoff is low. The concentration of CODMn decreases in the wet-seasons, owing to the dilution effect of the mixture observed in the water. The absence of CODMn at other monitoring stations, could be due to dilution effect of movement of the soil by periodic flooding.

2. NH3-N Concentrations

Similarly to CODMn, NH3-N concentrations also display

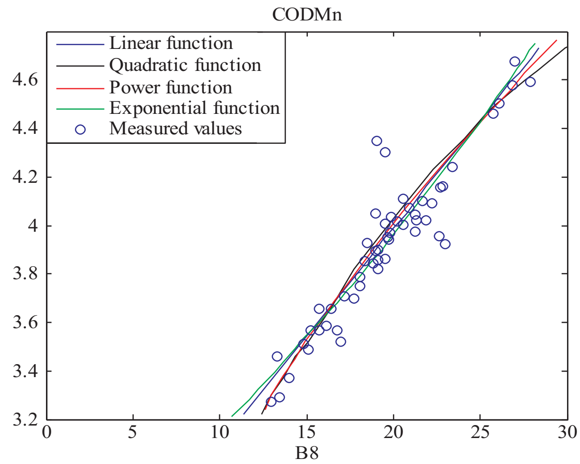

Fig. 7. The estimation model between CODMn and B_8.

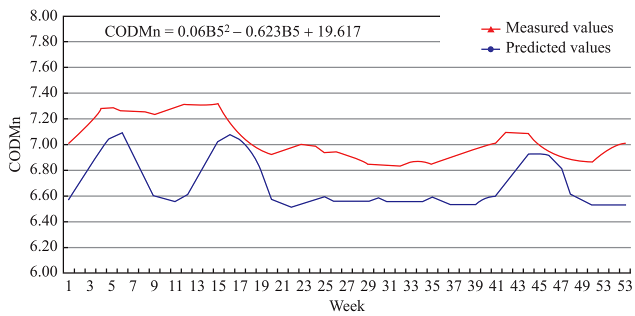

Fig. 8. Yixing Mt Mouth Station CODMn test model results measured data comparison chart in 2014.

high temporal and spatial variation. Previous experiments dispute that this diversification is derived from the high stage of nitrogen fertilization with raining leading to the reduction of NH3-N concentration (Andrade, 2009). This study result points to the NH3-N concentration being raised with increasing flow (Fig. 5). Water flow rates can influence the NH3-N concentration: higher water flows support the movement and attenuation

Table 5. The correlation table between NH3-N and B_4.

Function type	Linear function	Quadratic function	Power function	Exponential function
R^2	0.783	0.862	0.76	0.728
The standard deviation of estimate	0.17	0.151	0.218	0.232
Sig	0.008	0.019	0.011	0.015

Table 6. The NH3-N estimates precision analysis table in 2014.

Estimating model	P	AD	ARD	RMSE
NH_3-N=0.271-0.003B4	0.008	0.251	-0.030	0.226

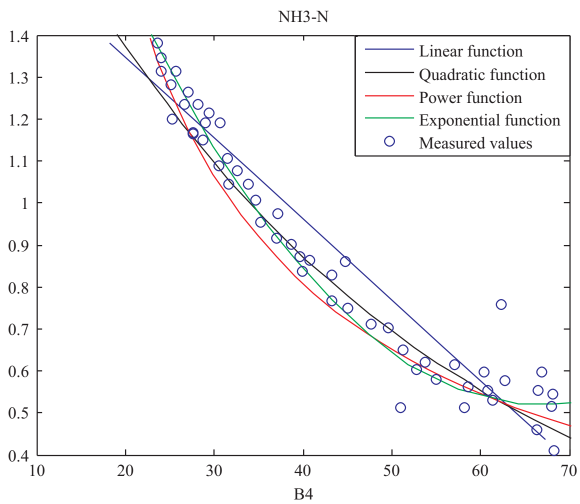

Fig. 9. The estimation model between NH3-N and B4.

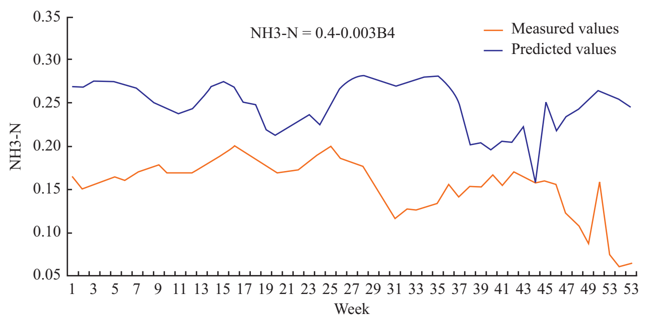

Fig. 10. The estimates of NH3-N model comparison chart from in 2015.

procedures of NH3-N, and low water flows support NH3-N accretion. This observation has previously been reported by Arauzo et al. (2011).

Consequently, the highest NH3-N concentration occurs in winter and the lowest concentration occurs in late stages of summer. During this research, we noted that the NH3-N concentration declines in autumn-winter for the reason that crop activity declines and the NH3-N assimilation decreases by crops at the same time.

Finally, the trends of NH3-N, CODMn and other pollutant (such as pH) concentrations in Lake Taihu are consistent with the recognized impacts of people on surface waters and ground waters in their immediate region. We hope our developed models can provide a scientific basis for future project scheduling and operational management.

V. CONCLUSIONS

Monitoring surface water pollutants within low-slope areas subject to intensive rice crop agriculture showed a high variability in time and space. The runoff in the studied area is negligible because of the low slopes. Therefore, the distribution through the soil becomes the main mechanism for transport of pollutants such as CODMn and NH3-N into the Lake Taihu basin.

It was found from the pollutant concentration observations that the maximum safe limits set for the standards of the Ministry of environmental protection of China were exceeded. Analysis of variance indicate that when rainfall decreased steadily, the highest concentrations of pollutant would occur in studied basin. The interaction between sampling site and rainfall can explain the variability in CODMn concentrations. The spatial and temporal distributions of NH3-N also shows a high variability, with the interaction between runoff and rainfall being responsible for the observed levels of NH3-N. By developing the model to characterize water quality, we hope to provide a scientific basis for future project scheduling and operational management.

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