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# Numerical Models for Predicting the Fate of Ammonia Nitrogen for Biological Treatment Processes in Urbanized Rivers in China

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## Abstract

One of the sustainable approaches towards polluted urbanized rivers restoration is the use of biological treatment method. The method has been successfully used in China since the past decade and has received growing recognition among university and government authorities. Field campaigns during biological treatment methods to measure water quality variables are expensive as in most water quality measurements. Therefore, the availability of mathematical models helps to provide a basis for forecasting and planning for such campaigns. Ammonia-nitrogen is a key variable supporting eutrophication of rivers. In this research, mathematical models were developed to describe the fate of ammonia-nitrogen given a set of water quality variables (i.e. transparency, water temperature, COD, DO, total nitrogen and total phosphorus). Selected six models were chosen based on adjusted R2, Akaike Information Criterion (AICc) and Bayesian Information Criterion (BIC). The selected models were tested with independent dataset. The results show that the prediction errors range from ±20% to ±36%. The errors found in this research are comparable to previous studies and are considered to be largely due to the large sampling and measurement errors usually encountered in water quality testing and measurements. The results in this research support on-going numerical modelling in wastewater treatment, water quality modelling and water resources planning and management.

**Keywords:** Fate; Ammonia-nitrogen; Numerical models; Biological treatment method

## Introduction

Developing economies face the challenge of poor surface water quality of water bodies. Environmental degradation coupled with industrial growth and infrastructural development further adds more challenge to water planners and managers in urban communities. China for instance, is undergoing water related challenges due to urban expansion and the rapid growing industrial activity. It is also partly because the transport of household and industrial wastewater from both point and non-point sources into rivers have increased their vulnerability and support for aquatic life [1]. In most of the cases, eutrophication is one of the key problems as a result of the large amounts of nitrogen and phosphorus from surface runoff. These sources have contributed more pollution compared to agricultural areas [2]. These polluted rivers, apart from reducing their surface aesthetics, also reduce their capacities to withstand storms and floods. The study of transport and nutrient dynamics has been conducted in several parts in the world [3].This is to support the growing need of mankind for clean surface water to support both human and aquatic life. Countries with heavily polluted rivers resort to river restoration campaigns through either hydraulic, chemical or biological means. In China, the use of biological treatment has received laudable credits from both civil and government authorities as an efficient, cost-effective and sustainable approach towards river restoration. This is in part to support campaigns from urban wastewater planners to meet the needs of a rapid urban water system [4]. Some literatures agree that river restoration campaigns could support efforts on Agenda and current talks at COPs on Climate Change [5,6].

River restoration campaigns involved several different techniques usually a function of cost, technology availability and expertise present at the time of operation. In the most general scenario, the use of weirs, changing effluent discharge positions, oxygenator for aeration and use of engineered wetlands have been used. Among these, wetlands happened to have received considerably research, popularity and found to remove over 70% of nutrients during restoration exercises. The growing technology, Biological Treatment Method (BTM) is not new to history but it is beginning to receive attention in river and wastewater treatment nowadays. The BTM has been successfully used in many countries worldwide including China for domestic and industrial wastewater treatment. For instance, the method has been used in urban streams in Shenzen, Rui'an and Wuxi of China. This method has been known to rapidly reduce the concentrations of effluent BOD and COD [7]. The spatio-temporal measurement of water quality variables involved in BTM are tedious and require an efficient workforce to be able to carry out the treatment process. The measurements of water quality variables during BTM by regular sampling method require enormous work. Moreover, BTM is not a regular operation but necessary for populated riverine systems.

There is however lack of requisite mathematical algorithms to support the forecasting and monitoring of water quality variables under the BTM. Nutrient flux in urban rivers is very important for monitoring water quality. Nitrogen is one of these nutrients that promote cellular growth and thus eutrophication in water bodies. In wastewater, nitrogen has the capability to exist in different forms - ammonia, organic, nitrate and nitrite. In this particular case, the ammonia-nitrogen widely known to contribute towards eutrophication is considered. Mathematical algorithms are developed and tested to determine their predicative

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power and practical applications. With a given measurements of water temperature, transparency, COD, total nitrogen, total phosphorus; the predicted estimate of ammonia-nitrogen can be obtained. In other related studies, mathematical expressions developed by Vollenweider were used to estimate the fate of phosphorus in water bodies [8]. In another study, statistical models were successfully used to investigate the Escherichia coli flux in beaches in Lake Michigan [9]. Regression models were also used to predict and monitor nutrient and bacteria flux of lakes in the U.S [10]. A general critical review of these previous algorithms revealed that there were concentrated in lakes and beaches study and the measured parameters used for forecasting differ totally from those involved in BTM. Therefore, mathematical algorithms developed in this paper support the prediction of ammonia-nitrogen. This paper aims to undergoing efforts in water quality monitoring, environmental modelling and water resources planning for urban cities. The research also supports the development of decision support systems for planning using these standard algorithms and can provide useful planning tool for eutrophication management in rivers.

## Methods

### Study Area

The Xuxi River is derived from the mouth of Jing-Hang and flows into the ancient canal towards the end of its lower reach. It is located in the Chang Nan District of Wu Xi city of China. The total length of the river is 1.36km with an upstream surface width of 4.5m and a depth of about 1.4m. The river is characterized by muddy sediments sometimes up to 1.6m. This river is located in a north sub-tropical humid zone. This zone is affected by the monsoon circulation phenomenon and thus, has four distinct seasons. The recorded annual precipitation is generally higher than the annual evaporation. The hydrodynamics of the river are generally poor. For instance, natural river siltation, indiscriminate rubbish dumping and unstable slopes of river make it hydrodynamic conditions poor and inhabitable for aquatic life. It was estimated in an independent research that about 10,000m3 of sewage was discharged daily into the river [7]. This was partly due to the non-existence of a common wastewater treatment facility in the city. The background sampling results are shown in Table 1 below. The information obtained from the background information indicates that, most of the quality variables are worse than the Class V of the Chinese National Standard (CNS) for Surface Water Quality (GB2828-2002). The Class V is the poorest water quality standard specified by the Chinese National Standard board. This means that the river water is highly unsuitable for drinking, irrigation and industrial purposes. The Ministry of Environmental Protection 2009 report on surface water quality reported that, the seven big rivers in China (the Yangtze River, Yellow River, Pearl River, Songhua River, Huaihe River, Haihe River and Liaohe River) were under polluted in general. According to the CNS 2002, 408 sections of the 203 rivers under national monitoring with water quality ranges from Grade I to III, Grade IV to V and inferior grade V represented respectively 57.3%, 90 24.3% and 18.4% [11]. This implies that about 42.7% of most rivers in China are not suitable for aquatic life and domestic uses. Therefore, we selected the Xuxi River as a representative case for majority of the rivers which are in the inferior category of Class V in China. This means that, results from this research were appropriate for use for rivers in the Class V and other highly polluted systems compared to this class.

### Biological treatment method

Figure 2 schematise the Xuxi River system and sampling points. Five sampling points were used for the collection of the data. These included the Small Bridge of Rong Lane (No.1), Xuxi Bridge (No.2), Xishan New Village Bridge (No.3), Wuai Road (No.4) and Small Wood Bridge (No.5). There is a weir about 50cm high which on No.5. This weir controls the flow of the river system for low and high discharges. In this way, it was able to maintain a steady condition to allow for the bacteria to purify the polluted river. During the biological treatment process, there was no control of sources of pollution and any artificial oxygenation. The selected bacteria and microbial accelerator were directly injected into the river to activate the native bacteria in original river system. In all, thirty-four buckets each containing 150kg of bacteria were used for restoring the quality of the Xuxi River. In the process, the bacteria were cultured nearby the river and injected into the five sections.

### Data

The derivation and evaluation of the models were done with two different datasets obtained for the same study area. The data used for the derivation of the mathematical algorithms were obtained with BTM data for October 2009. The evaluation data was obtained for November 2008 (Table 4 in appendix). The datasets contained measurements of Total Phosphorus (TP), Ammonia (NH3-N), Transparency (T), Water Temperature (WT) and Total Nitrogen (TN). Due to the scarce nature of the data, it was practically assumed that the derived mathematical algorithms ability to forecast the fate of ammonia-nitrogen (NH3-N) with reasonable accuracy meant that it was practically applicable for future BTM applications. This scientific judgment was not out the box assumption but follows other research methodology discussed statistically by Helsel and Hirsch [12].

### The Virtual Beach (VB) MLR model

The VB Multiple Linear Regression (MLR) Tool by USGS was used to support the work of this study. The study employed the statistical capability of the package to handle multiple linear regressions. This was used to develop the model for predicting the fate of TP against a given set of water quality variables.

The MLR model [12] is given by

$$y=\gamma_0+\gamma_1 x_1+\gamma_2 x_2+...+\gamma_k x_k+\varepsilon \tag{1}$$

Where y is the predicted water quality variable (ammonia-nitrogen)

| Sampling point | Temperature (°c) | Transparency (cm) | DO (mg/l) | COD (mg/l) | TP (mg/l) | TN (mg/l) | NH3-N (mg/l) |
|---|---|---|---|---|---|---|---|
| Small Bridge of Rong Lane (No.1) | 16.3 | 20 | 1.2 | 11.0 | 0.95 | 24.8 | 13.6 |
| Xuxi Bridge (No.2) | 18.0 | 20 | 0.2 | 11.2 | 0.58 | 24.8 | 11.2 |
| Xishan New Village Bridge (No.3) | 16.8 | 20 | 0.3 | 12.9 | 0.92 | 24.6 | 13.8 |
| Wuai Road (No.4) | 16.6 | 10 | 0.3 | 13.9 | 1.10 | 23.0 | 15.8 |
| Small Wood Bridge (No.5) | 16.6 | 10 | 0.1 | 14.2 | 1.17 | 22.9 | 16.4 |
| National standard | | | | | | | |
| GB3838-2002 | | | 2 | 15 | 0.4 | 2.0 | 2.0 |
| | Class V | More than Class V | Class V | More than Class V | More than Class V | More than Class V | |

**Table 1:** Background data of Xuxi River sampled by the Wuxi Environmental Monitoring Centre on November 12th, 2008

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γ 0 is the intercept

γ1 is the slope coefficient for the first explanatory variable

γ2 is the slope coefficient for the second explanatory variable

γk is the slope coefficient for the kth explanatory variable, and

ε is the remaining unexplained noise in the data – error.

The MLR analysis is dependent on least squares method to fit models. It is therefore subject to many considerations i.e. variable interactions, multicollinearity and model selection [13]. The VB uses backward elimination method to help the user select the best appropriate model with the specified explanatory variables. The VB model facilitates model development and offers better chances for developing good models with limited datasets. The VB has been successfully used to develop models for the fate of biological contaminants in beaches [13-15]. The VB has a function to perform data transformations. By default, MLR equations are linear and this has the tendency to limit value of explanatory variables. VB offers a number of transformation methods such as square root and square.

### Model Evaluation

VB offers several options for checking the fits of the selected models and the forecasts. In general, goodness of fit and predicative capacity is important to describe a model's ability to predict. In this particular paper, emphasis was laid on the use of adjusted R2 (R2a), Prediction Sum of Squares (PRESS), Corrected Akaike Information Criterion (AICc), Bayesian Information Criterion (BIC) and Root Mean Square Error (RMSE). The (R2a), AICc and BIC were applied to choose the most suitable model for description of the fate of ammonia-nitrogen. The PRESS and RMSE were used to determine the predictive power and accuracy, respectively, of each model. The VB tool uses Genetic Algorithm (GA) too effectively and efficiently search for the best possible MLR model [16]. GA uses a class of stochastic search procedures called evolutionary algorithms. These algorithms use computational models of natural processes to develop computer-based problem solving systems [17]. The process mimics the natural biological phenomena where organisms produce successive generations. The application of GAs in hydrological and water quality modelling is receiving attention in recent times [18-21].

## Results and Discussion

### Model Development

The ammonia-nitrogen (NH3-N) was modelled as an independent variable against other parameters (TN, TP, WT, T, COD and 155 DO). This produced 12 different mathematical models. The mathematical expression of each of these models is provided in Table 1. The corresponding statistics (AICc and BIC) for each of the mathematical model has been provided also in Table 1. See Wolfe et al. [16] for detail understanding the permutation logic used to derive the algorithms. All the models show a relatively high Ra2 of above 85%. Ranking the models, show that NM8 and NM9 have an adjusted R2 of 0.896. Except NM12 and NM11, the rest of the models show an adjusted R2 of above 89%. The AICc validates the goodness of fit of the mathematical expression by penalising out the addition of independent variables. Based on AICc criterion, the mathematical model with the lowest value is preferred. Table 1 shows that, NM 1 show best results but has a relatively small adjusted R2 (0.894). Others that show relatively low AICc include NM2, NM3, NM6, NM4, NM5, NM7, NM8, NM9, NM10, NM12 and NM11. BIC is also another appropriate technique for model selection, the lower the value, the better the results. The ranking of BIC show

| Model No. | Description of Model | Evaluation Statistics | | |
|---|---|---|---|---|
| | | $R_a^2$ | AICc | BIC |
| NM1 | $[NH_3-N]=-77.0375e-01+93.3067e-02*\sqrt{(TP)*(TN)}-15.7915-04$ $*[(COD)]*(WT)]+30.6424e-03*(T)+38.3081e-01*\sqrt{(TN)}$ | 0.894 | 34.903 | 9.620 |
| NM2 | $[NH3-N]=-80.2138e-01+94.1416e-02*\sqrt{(TP)*(TN)}+37.7342e-01$ $*\sqrt{(TN)}+31.1467e-03*(T)$ | 0.894 | 35.040 | 9.758 |
| NM3 | $[NH3-N]=-83.2092e-01+95.2719e-02*\sqrt{(TP)*(TN)}+37.428e-01$ $*\sqrt{(TN)}+15.1695e-02*\sqrt{(T)*(DO)}$ | 0.892 | 35.437 | 10.155 |
| NM4 | $[NH3-N]=-64.9137e-01+91.7595e-02*\sqrt{(TP)*(TN)}-31.5105e01$ $*INV[(T)*(WT)]+39.3491e-01*\sqrt{(TN)}-22.4571e04*[(COD)*(WT)]$ | 0.891 | 37.870 | 12.297 |
| NM5 | $[NH3-N]=-50.5474e-01+86.8854e-02*\sqrt{(TP)*(TN)}-30.1865e01$ $*INV[(T)*(WT)]+38.1515e-01*\sqrt{(TN)}-54.3122e-03*(WT)$ | 0.891 | 37.88 | 12.306 |
| NM6 | $[NH3-N]=23.6176e-01-32.6788e-02*(WT)+73.978e-02$ $*\sqrt{(TN)*(WT)}+68.2419e-02*\sqrt{(TP)*(TN)}$ | 0.890 | 35.918 | 10.636 |
| NM8 | $[NH3-N]=-77.0375e-01+93.3067e-02*\sqrt{(TP)*(TN)}-15.7915e-04$ $*[(COD)]*(WT)]+30.6424e-03*(T)+38.3081e-01*\sqrt{(TN)}$ | 0.896 | 38.283 | 12.710 |
| NM9 | $[NH3-N]=-67.3899e-01+93.4659e-02*\sqrt{(TP)*(TN)}-31.2644e01$ $*INV[(T)*(WT)]+39.1559e-01*\sqrt{(TN)}-40.4196e-03*(COD)$ | 0.896 | 38.286 | 12.714 |
| NM10 | $[NH3-N]=-62.1001e-01+90.686e-02*\sqrt{(TP)*(TN)}-31.2594e01$ $*INV[(T)*(WT)]+39.3318e-01*\sqrt{(TN)}-66.6498e-02*LOG[(COD)*(DO)]$ | 0.895 | 38.310 | 12.738 |
| NM11 | $[NH3-N]=-46.3988e-01+46.5421e-01*\sqrt{(TN)}-79.1775e-03*(WT)$ $-29.2869e-02*INV(TP)$ | 0.874 | 39.207 | 13.924 |
| NM12 | $[NH3-N]=-46.3988e-01+46.5421e-01*\sqrt{(TN)}-79.1775e-03*(WT)$ $-29.2869e-02*INV(TP)$ | 0.876 | 38.853 | 13.570 |

**Table 2:** Derived models and evaluation statistics of each model

the same results for AICc. This means that according to BIC, NM1 is most appropriate just as the AICc ranking. AICc integrates the bias in regression for small sample sizes. Therefore, BTM projects are still in preliminary implementation in China and obtaining long term series of data is difficult and in most cases impossible. Thus, the AICc becomes a good model selection. In other case, the use of complex models in practice does not always necessarily provide the best answers in practical. Simple models are generally preferred. The use of BIC penalises the effect of complex models and give preference to simpler models. Based on this discussion, AICc and BIC were considered most appropriate for the model selection. This also confirms with related research that AICc and BIC were best choice for model selection [22]. The NM1, NM2, NM3, NM6, NM4 and NM5 are respectively the most appropriate models for use. These models were further tested with independent datasets another BTM project conducted in November 2008.

## Evaluation

Six of the mathematical models derived were selected for evaluation for their predictive power and reliability for practical forecasting under the BTM programs. The selected models were used to predict the ammonia-nitrogen concentrations of independent dataset taken during November 2008 in the same study area. The results of the predictions are provided graphically and Table 2 for further details for comparison of data.

The results indicate that NM2 is most appropriate when tested with independent datasets with a RMSE of +2.12. However, the significant difference between PRESS statistics for NM2 and NM3 is negligible and the RMSE of NM3 is +2.12. This means that both NM2 and NM3 are most appropriate for forecasting of NH3-N. In general, all the other models show a relative RMSE below +2.16 with slight variations among them when comparing values to an accuracy of 4-decimal places. The graphical behaviour of the NM2 and NM3 show a relative close match with the observed data especially towards the tail-end. In some cases, the predictions are lower than the observed and in other cases higher. In few cases though, both predictions and observed matches. The measurement of ammonia-nitrogen is difficult due to the fast chemical transformation of this compound to other nitrogen complexes. Sampling errors, instrumental errors, laboratory errors and observer's mistakes accumulate errors in measurement of biological variables in rivers. Now, since datasets for this case study were conducted in entirely two different years (2008 and 2009), the compliance and attention to detail by experts differs and this could heavily reflect in the results shown here. This is because, these measurements conducted in the different years though for the same project were analysed and tested by different persons involved. 196 Hence, this difference could have affected the accuracy of the prediction.

Sampling and measurements in water quality have typical errors in the range of 15-20% for most water quality variables, and sometimes higher (30-40%) for BOD [23,24]. This implies prediction errors for mathematical models are bound to be much higher. For instance, in related research, it was found out that the prediction error were 30%-40% for total phosphorus or total nitrogen for measured annual loading [25-27]. In the same study, it was realized that prediction errors were also much higher when models were derived statistically and for cases in which measurements from Secchi disk transparency were involved. The research findings are comparable to the findings in this research. The prediction error for all models is between ±21% and ±36%. In all cases except the NM6, measurements of Secchi disk transparency are included. However, the measurements with transparency measurements included show a relatively lower prediction error as was found out in Reckhow 1992 and 1994. Scientific uncertainties are unavoidable but provides a means for decision makers for selecting alternative measures and if possible consider other experimentation and observation [28]. The mathematical models derived here are therefore acceptable and can be applied to support decision making but are not explicit in replacing traditional field measurements.

| Model No. | PRESS | RMSE | Prediction error (%) |
|---|---|---|---|
| NM 1 | 443.74 | 2.1339 | ±23 |
| NM 2 | 438.10 | 2.1204 | ±19 |
| NM 3 | 438.44 | 2.1200 | ±21 |
| NM 4 | 452.43 | 2.1543 | ±36 |
| NM 5 | 448.13 | 2.1443 | ±32 |
| NM 6 | 454.75 | 2.1585 | ±33 |

**Table 3:** Evaluation statistics for models

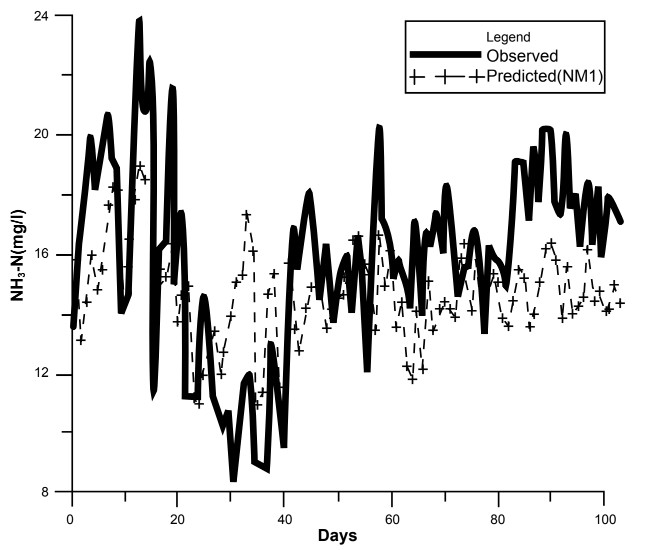


**Figure 1:** Prediction of ammonia-nitrogen concentrations for NM1

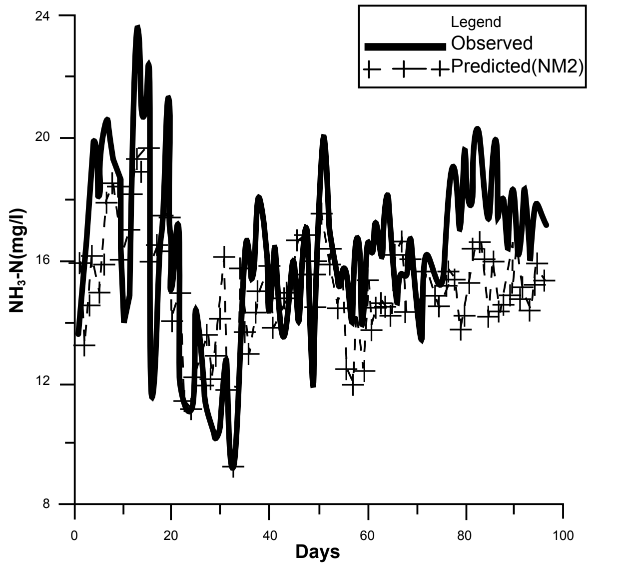


**Figure 2:** Prediction of ammonia-nitrogen concentrations for NM2

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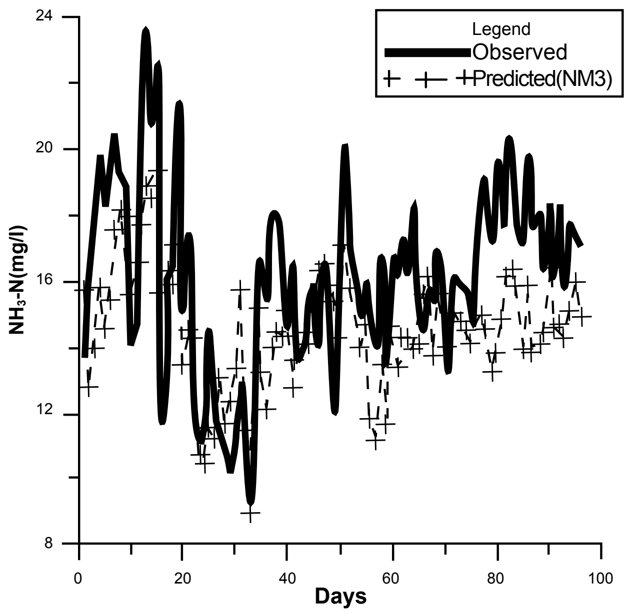


**Figure 3:** Prediction of ammonia-nitrogen concentrations for NM3

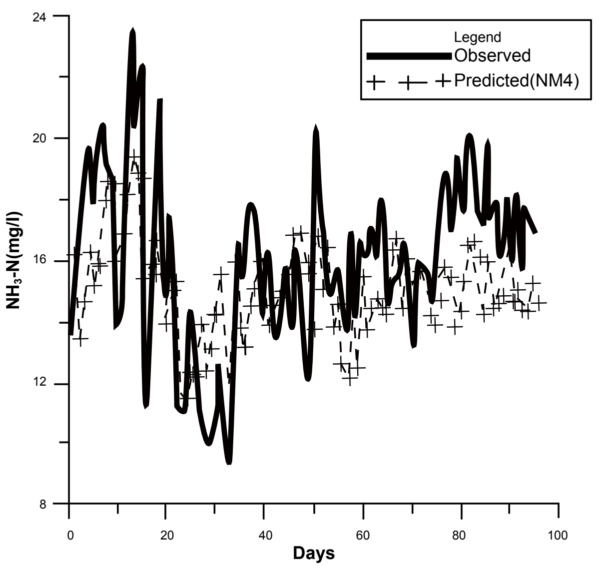


**Figure 4:** Prediction of ammonia-nitrogen concentrations for NM4

## Conclusions

The Biological Treatment Method (BTM) for polluted urbanized rivers is a creative and innovative on-going development in China. During such campaigns, water quality variables sampling is conducted to verify the purification process of the river system. However, it is expected that to support future planning, monitoring and management of such schemes, mathematical models describing the fate of nutrients during the treatment process are necessary and crucial. In view of this, the fate of ammonia-nitrogen (NH3-N) was modeled given a set of other water quality variables such as transparency, water temperature, COD, DO, total nitrogen and total phosphorus. It was found out that six of the models were appropriate for further testing and evaluation for practical use. The selection of the mathematical models was done using standard statistics i.e. AICc, adjusted R2 and BIC. The six models were evaluated using independent datasets from the year 2008. The results show that prediction errors are in the range of ±20%~±36%. This prediction error fall within related research conducted in water quality modelling. However, the large sampling and measurement errors typical of water quality variables explain the errors obtained in this research. Notwithstanding, the mathematical models are to serve as a guide for further planning, forecasting and management of BTM pilot projects. This research would also be useful to other numerical modelling in wastewater treatment, water quality modelling and water resources planning and management.

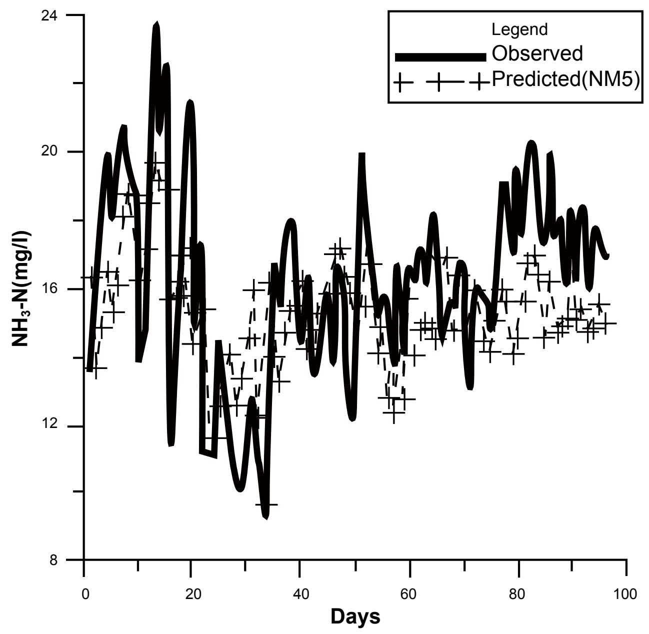


**Figure 5:** Prediction of ammonia-nitrogen concentrations for NM5

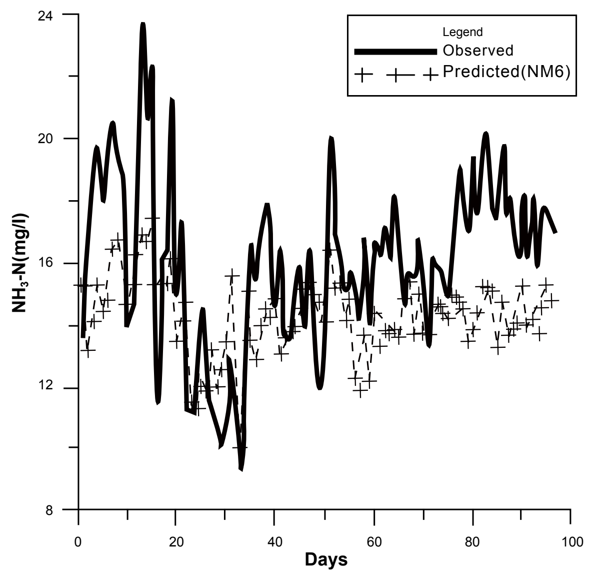


**Figure 6:** Prediction of ammonia-nitrogen concentrations for NM6

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