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Analysis of water quality factors influencing the speciation of inorganic nitrogen using GRA

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Abstract

Based on the water quality data from 2006 to 2008, grey relational analysis (GRA) is used to analyze factors that may have influence on the speciation of inorganic nitrogen in the Chengdu section of middle Min river. The results show that water temperature, changing from 20.2±2.7, 13.4±5.7 and 16.8±5.6°C, is the first restrictive factor for the speciation of inorganic nitrogen; it is negatively correlated with the ratio of total ammonia nitrogen to total inorganic nitrogen contents [*m*(AN)/*m*(TIN)] in three different periods of wet season, dry season and year-round. The average pH values for years, in wet and dry periods are 7.6±0.4, 7.3±0.3 and 7.8±0.2, respectively, and have different influences in different seasons. It is the second restrictive factor and positive correlation between pH and *m*(AN)/*m*(TIN) in wet season and through the year yet it is the fourth factor in dry seasons. The values of dissolved oxygen (DO), which are 4.6±1.4, 4.6±2.4, 4.6±2.0 respectively, is the third factor and negatively correlates with *m*(AN)/*m*(TIN) in third different periods. The chemical oxygen demand (COD) indirectly inhibits the nitrifying bacteria because the DO is depleted in the decomposition of organic matter by heterotrophic bacteria, showing the positive correlation. As the alkalinity can meet the requirement of nitrification in wet season and through the year, it is not restrictive factor. However, it is the second restrictive factor in dry season because of low content of alkalinity inhibiting the growth of nitrifying bacteria.

Key words

Ammonia nitrogen (AN), Total inorganic nitrogen (TIN), Grey relational analysis (GRA), Min river

Introduction

Nitrogen pollution in aquatic ecosystems is becoming more and more serious since humans continue to interfere with the global nitrogen cycle now (Galloway et al., 2008). Excessive nitrogen entering water bodies has lead to human health problems, eutrophication and other environmental problems (Ryther and Dunstan, 1971; Anderson *et al.*, 2002; An *et al.*, 2003). Nitrogen in water bodies exists mainly in two forms of fixed nitrogen and free nitrogen. Fixed nitrogen exists in the form of organic-nitrogen (ON) in the animals and plants. Free nitrogen in water exists in the inorganic form of ammonia-nitrogen (AN), nitrite-nitrogen (NIN), nitrate-nitrogen (NAN). Total inorganic nitrogen (TIN) is the sum of the AN, NIN and NAN. Moreover, the existence of different forms of nitrogen leads to different environmental effects, for example ammonia toxicity to aquatic organisms is relatively large (Arthur *et al*., 1987; Randall and Tsui, 2002). The study of the nitrogen content and analysis of form composition in water, especially for the *m*(AN)/*m*(TIN) research, contribute to evaluation of contaminated water and the situation of self-purification (Michal *et al.*, 2004; Li and Xia, 2005).

The nitrogen cycle in water bodies is a very complex process involving a series of reactions (Chestérikoff *et al.*, 1992; Yu *et al*., 2008; Zhao *et al.*, 2009). The processes of ammonification (conversion of organic N to NH_4^+), nitrification (conversion of NH_4^+ to NO_3^-) and denitrification (conversion of NO_3^- to N_2O or molecular N_2) affect considerably the speciation of nitrogen in natural water conditions. In addition, such environmental factors as temperature, DO, pH, alkalinity, COD, and so on, also affect the behavior of nitrogen through affecting the transformation process of nitrogen. In the controlled conditions of laboratory simulation, the individual process can be understood better. However, it is impossible to reflect the whole migration and transformation of nitrogen as well as the leading role of some environmental factors when a number of processes coexist in natural water bodies. At the same time, the content and composition of nitrogen in the rivers are also impacted by other such factors as sources of pollution and environmental conditions. Hence, it is very necessary to analyze comprehensively the single factor for identifying the key impact factor from the various factors. GRA is a kind of method of factor analysis and of quantitative comparative analysis of the development trend between factors (Deng, 1989). Based on the comparison of geometric relationship between the statistical sequences in the river system (Li and Xia, 2005), it can analyze the degree of correlation between factors affecting the nitrification in the river system, such as water temperature, DO, pH, etc., rank order correlation and screen out factors which limit nitrification in the river. Moreover, the obtained results using GRA can provide some theoretical support for the treatment of ammonia-nitrogen pollution in the river (Li and Xia, 2005). In addition, this method does not require the typical distribution and large-sized samples. The analysis results generally coincide with the qualitative analysis. Therefore, it is with a wide range of practicality in the field of environment research (Cheng and Wang, 2004; Liu and Yu, 2007; Zeng et al., 2007).

The Min river, one of the most important tributaries of the Upper Yangtze river, located in Sichuan province, Southwest China. It is a main lifeline of water resource for the Chengdu plain. The middle reach of Min river flows through the Chengdu city. Now, these regions are facing a severe water shortage due to the increasing water demand for the economy development. Moreover, the situation is becoming more serious due deterioration of water quality. According to the bulletin of environmental quality of Sichuan province based on the National Environmental Quality Standards for Surface Water in the People's Republic of China (SEPA, GB-3838-2002, 2002), nitrogen, especially AN, is one of the major pollutants in the Min river. The objective of this study is to analyze simultaneously the effect of multi-factors such as water temperature, dissolved oxygen, pH, alkalinity and chemical oxygen demand on the nitrification in the middle Min river using GRA method.

Materials and Methods

Water quality analysis: Water samples were collected at 14 stations along the Chengdu section in the middle Min river from 2006 to 2008. At each station, the temperature, DO and pH of water were measured in situ with one Model 52 oxygen probe (Yellow Spring Instruments, Ohio, USA). Aliquots of water samples were filtered through 0.45 μm filters before the analysis. The potassium dichromate method was applied to the COD determination in water. The water's alkalinity was measured with the acid-base titration method. Concentrations of AN, NIN and NAN in water samples were also examined. The Nesslerization colorimetric method was applied to the AN analysis, NIN was determined by colorimetric method through formation of a reddish purple azo dye produced at pH 2.0-2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine. NAN was determined by the phenol disulfonic acid ultraviolet spectrophotometric method. Their detection limits were 0.02, 0.003 and 0.08 mgl^{-1}, respectively (National Environmental Protection Agency, 2004). After excluding the outliers from the above data and averaging them according to 14 sections, they then proceed to the GRA.

Selected time: Since the hydrological characteristics of the wet, dry seasons in the Chengdu section of the middle Min river may have different effect on the factors of water quality, the impact of factors on the *m*(AN)/*m*(TIN) in wet and dry seasons are analyzed respectively. In the group of dry season, the average value of 14 different sections in the fourth quarter of 2006, the second quarter of 2007 and the first quarter of 2008 is analyzed, whereas the average data in 14 different sections in the third and fourth quarter of 2007 and the second quarter of 2008 is applied for the GRA.

Selected sequences: Ammonia, one of the main pollutants in the Chengdu section of middle Min river, cannot be oxidized completely in nearly 100 km long river. Considering the effect of coastal sewage disposal, river flow seasonal changes and such environmental factors as temperature, DO, pH, COD and alkalinity on the concentration of AN, where the ratio of total ammonia-nitrogen to total inorganic nitrogen contents (*m*(AN)/*m*(TIN)) was used as reference sequence because of little effect from wastewater discharge and water flow. Moreover, it is believed that the composition of discharged wastewater retains stable in a year. The factors affecting the ratio of *m*(AN)/*m*(TIN) was selected as the compared sequences.

Grey relational analysis (GRA): The GRA, as for Cheng and Wang, 2004, Zeng *et al.*, 2007, was followed to derive correlation coefficient as absolute value (Tzeng and Tsaur, 1994).

Results and Discussion

Temperature: The optimum temperature of nitrification is 25-30°C. The growth of nitrifying bacteria slows down while the temperature is below 25°C or above 30°C (Painter, 1970). The water temperature listed in the Table 2 in the Chengdu section of middle Min river, changing from 20.2±2.7, 13.4±5.7 and 16.8±5.6°C in three different periods of wet season, dry season and year-round, is far below the optimum temperature and therefore one of the main limiting factors of the nitrification. Correlation analysis also shows that whether it is in the wet season, dry season, or throughout the year, the water temperature and ratio of *m*(AN)/*m*(TIN) are negatively correlated. Moreover, the entire correlation grade is the largest in three different

Table - 1: *m*(AN)/*m*(TIN) and affecting factors in the middle Min river for selected quarters

Environmental factors	The grey correlation grade and correlative pole					
	Wet season	Correlative pole	Dry season	Correlative pole	Year-round	Correlative pole
Temperature	0.7871	-	0.6855	-	0.7363	-
pH	0.7526	+	0.4951	+	0.6201	+
DO	0.6883	-	0.5198	-	0.6041	-
Alkalinity	0.5919	*	0.5945	-	0.5932	-
COD	0.5388	-	0.4876	+	0.5170	*

+ Positive correlation; - Negative correlation; * No correlation.

Table - 2: The content of ammonia nitrogen and other environmental factors in the Chengdu section of middle Min river (mgl^{-1})

Factors	Wet season	Dry season	Year-round	Normal value
AN	2.4±1.3	6.2±2.1	4.3±2.6	1 mg l^{-1}
NIN	0.2±0.2	0.2±0.1	0.2±0.2	-
NAN	2.2±3.9	2.3±2.3	2.7±3.2	-
T	20.2±2.7	13.4±5.7	16.8±5.6	25-30°C
pH	7.3±0.3	7.8±0.2	7.6±0.4	7.3-8.5
DO	4.6±1.4	4.6±2.4	4.6±2.0	1.5-2.0 mg l^{-1}
Alkalinity	154.4±21.1	158.6±62.7	156.5±46.3	7.14g/1gAN20
COD	8.1±4.6	25.2±12.4	16.5±12.7	mg l^{-1}

Values are mean±standard deviation of water quality factors analysis. Not to be requested in the National Environmental Standard for Surface Water

periods, indicating that water temperature is the first limiting factor of the five factors.

pH: The optimum pH of nitrifying bacteria for the whole nitrification process is 7.3-8.5 (Antoniou et al., 1990). As for the ammonia oxidizing bacteria (AOB), they choose to the upper limit of this range. When the pH is between 8.0-8.4, the nitrification rate is at the maximum at this time. The nitrification in the system will stop when the pH is below 5.0 (Burton and Prosser, 2001). The average pH value in the Chengdu section of middle Min river for years, in wet and dry periods are 7.6±0.4, 7.3±0.3 and 7.8±0.2, respectively, which are not in the optimum range of pH and not suitable for the growth of AOB. As shown in the Table 1, the pH value is the second factor influencing the ratio of *m*(AN)/*m*(TIN) in two periods of wet seasons and year-round. Moreover, it is positive correlation between pH and *m*(AN)/*m*(TIN). Therefore, the reaction of AN transformed into NIN will be restricted. However, the pH value is the fourth influencing factor in dry seasons, fully indicating that the impact of such factors as water temperature, DO, alkalinity, and so on, on the nitrification is more than that of pH.

DO: The DO concentration in water affect the growth of nitrifying bacteria and nitrification process (Céron et al., 2004). In the nitrifying system of activated sludge, it is appropriate to make DO maintain at 1.5-2.0 mgl^{-1} in the stage of nitrification. The nitrification tends to stop when DO is lower than 0.5 mgl^{-1}. The nitrification is not impacted by DO when it is greater than 2 mgl^{-1}. As shown in the Table 1, DO is the third factor influencing the ratio of *m*(AN)/*m*(TIN) in three different periods of wet season, dry season and year-round. Moreover, DO and the ratio of *m*(AN)/*m*(TIN) are negatively correlated. From the monitoring data listed in the Table 2 in the Chengdu section of the middle Min river, the DO values are 4.6±1.4, 4.6±2.4, 4.6±2.0, respectively, in three different periods. Therefore, the nitrification in the middle Min river is not impacted by the change of DO. In addition, the Min river is an open body of water, water bodies and atmosphere can carry out gas exchange effectively when river water flows downstream.

Alkalinity: From the results showed in the Table 1, alkalinity is the fourth influencing factor in the two periods of wet season and year-round. Moreover, from the data in the water column of the middle Min river listed in the Table 2, we can see that the alkalinity in water bodies is able to meet the consumption requirements of nitrification. Then, the change of alkalinity will not affect the nitrification process in the Min river. So, there is no correlation between alkalinity and *m*(AN)/*m*(TIN) listed in the Table 1. However, the fact that alkalinity is the second factor influencing the ratio of *m*(AN)/*m*(TIN) in dry season may be explained that low concentration of alkalinity inhibit the nitrification because of low water flow.

COD: COD is an index representing the content of reducing substances in water bodies. The reducing substances include a variety of organic substances, nitrite, sulfide, ferrous salt, and so on, in which organic matters are the most important reducing substances. Therefore, COD is also often used to be an indicator to measure the content of organic matter in water. The greater COD show that organic matters pollute water bodies more seriously. Nitrifying bacteria belong to the typical autotrophic bacteria. The impact of organic matters on nitrifying bacteria is mainly that the existence of organic matters stimulates the rapid growth of heterotrophic bacteria, so that heterotrophic bacteria and nitrifying bacteria compete for O_2, making nitrobacteria inhibited. The organic matter itself does not directly affect the growth of nitrifying bacteria and nitrification (Garnier et al., 1992, 2001; Cébon *et al.*, 2004). It can be seen from the Table 1 that COD and m(AN)/m(TIN) are positively correlated in three different periods of wet season, dry season and year-round. Moreover, the correlation grade is the smallest, showing that COD is the smallest limiting factor of five investigated factors that affect nitrification in the river.

Not all the compared sequences considered in this study are independent, by introducing the distinguishing coefficient ρ, whose role is to diminish the distortional effect away from a big absolute error and to improve the prominence difference of the obtained correlation coefficient (Liu and Yu, 2007). Thus, these sub-sequences in GRA may be considered as approximately independent. Water temperature is the largest factor in three different periods; the second factor is pH value in different periods of wet seasons and year-round and alkalinity in dry seasons. The third is the DO. The COD indirectly impedes the growth of nitrifying bacteria because the DO is consumed in the decomposition of organic matter by heterotrophic bacteria. As the alkalinity can meet the requirement of nitrification in wet season and through the year, it is not restrictive factor.

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