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Procedia Environmental Sciences 13 (2012) 1069 - 1075

The 18th Biennial Conference of International Society for Ecological Modelling

Degradation of Inorganic Nitrogen in Beiyun River of Beijing, China Y. Yu, J. Wu, X. Y. Wang^{*}, Z. M. Zhang

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Abstract

Nitrogen pollution characteristics of Beiyun River and the migration of inorganic nitrogen in sediment-water were studied using laboratory experiment. Extract NH₄-N was the dominant pollutants in Beiyun River that caused the severe harm to aquatic system. NH_4 -N exchange in sediment-water system was observable at different sites. The calculating of NH₄-N degradation coefficients showed there was little difference of NH₄-N degradation rate at three sites of Beiyun River. Nitrification process was mainly occurred in 12 days and NH₄-N can rapidly in the degradation without input.

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Keywords: River; Nitrogen; water; sediment; degradation coefficient

1. Introduction

Anthropogenic inputs of nitrogen from municipal, industrial and farming wastewater to river contributes significantly to eutrophication. One of the crucial mechanisms for N loss in aquatic system is through biological oxidation and reduction of N species in the aerobic and anaerobic sediment zones, coupled with exchange processes between these zones [1]. Ammonium, nitrate could diffuse to the overlying water or to deeper anoxic sediment layers which it can be reduced by denitrifying microorganisms. But in some natural water high levels of inorganic nitrogen cannot be assimilated.

In most cases, nitrate is the predominant nitrogen form in water of many study areas and has been the focal point of regional and national surveys to identify aquifer susceptibility to pollution [2, 3]. However, ammonium also is found in ground/surface water in many situations [4]. High concentration of ammonia (NH_4^+) would destroy aquatic ecological system. A typical feature of the Beiyun River is high ammonium and organic matter lead to aquatic ecosystems degradation seriously. Nitrification occurs in the upper

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oxygenated sediment layer, where nitrifying bacteria oxidize ammonium to nitrate [5-7]. The extent of the N biochemical processes in one ecosystem is different from that in another, so processes must be evaluated on an individual ecosystem basis.

In this study, Beiyun River was selected for water quality assessment as it reflects typically urban river in northern China. The objectives of this study are to (1) assess water N pollution characteristics of urban river; (2) examine the rates of degradation of NH_4^+ in water column and (3) reveal the process of nitrification of NH_4^+ in the aerobic zone of the sediment – water interface.

2. Materials and Methods

2.1. Study areas

Beiyun River is an urban river from Beiguan sluice gate to Yangwa sluice gate (Beijing boundary) is about 42 km which includes two major reaches, Tonghui River, Liangshui River in Tongzhou district of Beijing, China. The average annual rain fall is 643 mm, with the majority of the precipitation occurring from June to September. The average annual temperature is approximately 11.3 °C. Beiyun River is currently served as the most important drainage in Beijing. This river is relatively polluted by organic substances and ammonia nitrogen.

2.2. Sampling and parameters

Water samples of Beiyun River had collected monthly at 9 monitoring sites during April - November 2009. The water quality parameters Dissolved Oxygen (DO) in water was monitored on site using a portable water quality instrument (Hydrolab Datasonde). Total nitrogen (TN), ammonia nitrogen (NH₄-N), nitrate nitrogen (NO₃-N), Nitrite nitrogen (NO₂-N) in water measured using Spectrophotometry [8].

The sediments samples were collected by an ETC-1 grab sampler at three points SGD, SL and YWZ. SGD located in the upstream of Beiyun River where Liangshui River merge into, and SL lies on the downstream. YWZ was the important floodgate on Beiyun river where flow out from Beijing borders. Isolation sediments and pore water from three points through centrifuge 6000rpm/min then analyze the concentration of NH₄-N after extract using potassium chloride (2mol/L).

2.3. Simulating Experiment

Simulating experiment was perform with sediment and overlying water at three sites into a plexiglas column (20 cm * 40 cm) in lab to analyze the transformation of NH_4^+ , NO_3^- and NO_2^- with 2 days intervals for 30 days and paralleled.

2.4. degradation coefficient

It is generally acknowledged that degradation of ammonia followed first-order kinetics formula, (1)

$$C = C_{o} \mathcal{C}^{(\Lambda)}$$
(1)

where: c- concentration of NH4⁺; c0- initial concentration of NH4⁺; K- degradation coefficient; t- time

Degradation coefficient cumulated according slope of (2) [9].

$$K = \frac{\ln Co / Ct}{t}$$
(2)

3. Results and Discussions

3.1. Basic Characteristics of Water Quality

Characteristics of nitrogen and DO of Beiyun River from April to November are shown in Fig 1. The concentrations of NH_4^+ range from 12.7mg/L~15.8mg/L that account for 78% of TN. Some reports supporting that NH_4 -N content of sewage treatment plant in tributary of Tonghui river was varied between 0.8 and 28.8 mg/L [10] that close to NH_4 -N of Beiyun river. This indicated ammonia was the dominant form of nitrogen which was mainly come from sewage discharge. Its presence in water causes a serious pollution and potential threat to ecosystem.

The result illustrated the trending of TN form April to November was opposite with DO content. DO is important to nitrification what is the oxidation to reduce nitrogen. TN and NH_4^+ was lowest in August and its might be uptake by phytoplankton or diffuse to sediment, corresponding to the highest DO concentration in the water might produced by photosynthesis. Whereas, DO value reduced to the lowest in September may be consumption by a lot of microbial death. Organic nitrogen can be seen from differences of TN and NH_4^+ in water that increased gradually in July. The Nitrate was increasing in October and November while NH_4^+ and TN without much change. Therefore Nitrate accumulated in winter that indicated denitrification slows down at low temperature.



Fig.1. TN, NH4+, NO3- and DO in water column

3.2. Ammonia in sediment/water

The concentration of NH_4^+ of sediment, pore water and overlying water sampling from three sites in July and August were determined. NH_4^+ in sediments was higher than pore water and overlying water. The highest NH_4^+ concentration of 25.0 mg/L in sediment was observed at site SL in August meanwhile concentration of NH_4^+ in pore water was the highest. And the highest in overlying water was 15.5 mg/L appeared at YWZ in July.



Fig.2. Ammonium in overlying water, pore water rand sediment of Beiyun River

Some research consider that in shollow waters, DIN exchanges at the sediment-water interface may provide a large part of nitrogen for phytoplankton, however, at greater depth, bottom water characteristis are less varible[11, 12]. Beiyun river is a shollow, slow-moving river because of insufficient rainful and small gradient. NH_4^+ concentration of overlying water in August is generally lower than which in July, just as NH_4^+ variation showed in Figure 1. Simultaneously NH_4^+ concentrations of pore water and sediment in SL and YWZ were increasing in August. That might be occurred NH_4^+ diffuse into the sediments in SL and YWZ but didn't showed in SGD. Particularly, in SGD, the concentrations of NH_4^+ in overlyingwater, pore water and sediments in august were lower than which in July. That might can be concluded NH_4^+ in SGD transport to other forms or emission to air. By contrast, the environment of August may be more benificial to NH_4^+ removal.

3.3. Degradation coefficient

It is often assumed that nitrification occurs in the water column and that the process follows first-order water column kinetics with rates calculated as a function of water [13, 14]. In the present study degradation coefficients of ammonium in overlying water was calculated to compare the degradated rate of inorganic nitrogen in river (Table. 1). NH_4^+ degradation coefficient of overlying water was ranged from 0.1330 to 0.1483 d⁻¹. The value of degradation coefficient in SGD was lower than in SL and YWZ

slightly. The results of NH_4^+ concentration in sediment and overlying water also poved that NH_4^+ exchange in SL and YWZ was stronger than SGD.

Sites	Kinetics Formula	Coefficients	\mathbb{R}^2
SGD	Y = 0.1330 x - 0.0218	$0.1330(d^{-1})$	0.8406
SL	Y = 0.1483 x - 0.1019	$0.1483(d^{-1})$	0.7671
YWZ	Y = 0.1480 x - 0.0121	$0.1480(d^{-1})$	0.7650

Table.1. Degradation coefficients of ammonia in Beiyun River

3.4. Degradation of inorganic nitrogen in water column

Gujer [15] considered that short retention times and high sediment surface to water volume ratios benefit sediment-based nitrification in shallow, fast-moving River. In Beiyun river there are have much difference from river bottom with sediment and concrete. The NH_4^+ concentration variation was investigated in three sites with sediment.



Fig.3. Varies of inorganic nitrogen in simulating experiment

Under normal conditions, the reaction of ammonia oxidation to nitrite is a velocity-limiting step; in contrast, nitrite is oxidized rapidly to nitrate [16]. In the simulating process, ammonia is reduced in the first of 20 days and much lower than Nitrate in the later 10 days. The concentration of Nitrite at the beginning of 12 days is very active which varied from 0.31mg/L to 3.01mg/L and then decreased to the low level. The Nitrate concentration was considerably lower than Ammonia at beginning and then increasing constantly. The trend of Ammonia showed degradation and release from the sediment was happened at the beginning of the simulating. The release of ammonia from sediment was fluctuating. As the

content of ammonia in sediment of sites SL and YWZ were higher than SGD, ammonia releasing presented more obvious in SL and YWZ. Along with nitrifying bacteria community to be steady the degradation would to be dominant at the 20th day. After 20 days, Nitrate was the main form of nitrogen and the concentration was stable because the denitrification process was very slow for the accumulation of nitrate. Nitrification process came to be dominant with nitrifying bacteria acclimation.

4. Conclusions

Laboratory experiments were used to monitoring the degradation process of inorganic nitrogen in the water column and estimate the rates of NH₄-N degradation. The ammonia was degrading $94.7\% \sim 97.8\%$ at the experiment there was absent of external pollution sources. Degradation coefficients of ammonia were $0.1330 \sim 0.1483 \text{ d}^{-1}$ that revealed nitrification process in overlying water was active, especially in the first 12^{th} days when nitrite was large fluctuation. The increasing of NH₄-N content in sediments proved that NH₄-N might transport from water column into sediments. Sediments was very important to adsorb N of river, although that process might be effected by other environmental factors, such as DO which to be considered a reactant to nitrification present opposite trending with TN in this study.

Acknowledgments

This study was supported by the National Key Research Program on Water Pollution Control and Remediation (2008ZX07209) and National Natural Science Foundation Project (40971258), P.R. China.

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