Energy and Earth Science
Vol. 2, No. 1, 2019
www.scholink.org/ojs/index.php/ees
ISSN 2578-1359 (Print) ISSN 2578-1367 (Online)

Original Paper

Ammonia Nitrogen Pollution Characteristics of Natural Rainfall in Urban Business District in Southern China: A Case Study of Chengdu City

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Received: March 28, 2019 Accepted: April 12, 2019 Online Published: April 23, 2019

doi:10.22158/ees.v2n1p15 URL: http://dx.doi.org/10.22158/ees.v2n1p15

Abstract

Chengdu city was chosen as the representative of southern cities in China in this work, characteristics of ammonia nitrogen (NH_3-N) pollution in natural rainfall were analyzed by measuring the concentration in 15 natural rainfalls from April to September in 2017. The influence of ammonia emission from toilet vent of building on NH_3-N pollution in rainfall was investigated, and the variation of total NH_3-N pollutants and its influencing factors were expounded. The results showed that the average concentration of NH_3-N in first rainfall was the highest, reaching 18.2mg/L, the average concentration of NH_3-N in the subsequent 14 rainfalls was between 2.0 and 5.0mg/L, which is higher than Grade V (≤2mg/L) of Environmental Quality Standards of Surface Water (GB 3838-2002), and was an important source of NH_3-N pollution in water. The concentration of NH_3-N in natural rainfalls decreased with the increase of the distance between the sampling point and the toilet vent, indicating that the ammonia discharged from toilet exhaust is a major source of NH_3-N pollution in urban atmosphere. The main factors affecting total NH_3-N pollutants in natural precipitation include rainfall

intensity, rainfall duration and drought days. The total amount of NH_3-N pollutants in surface runoff is less than that in natural rainfall.

Keywords

southern city in China, natural rainfall, ammonia nitrogen pollution, total pollutant amount, pollution characteristics

1. Introduction

Rainfall is a natural way to clean the atmosphere (Wang & Xu, 2009), so the air pollutants are an important source of pollution in rainwater. At present, the air pollution in cities of China has turned to the complex air pollution formed by fine particulate matter ($PM_{2.5}$) and polluted gases (O_3, SO_x, NO_x, NH_3) (Cao, 2014; Samen J M et al., 2000; Gao, 2012). Some researches (Ge et al., 2015)pointed out that water-soluble inorganic ions (WSII) like SO_x, NO_x and NH_3 are important chemical components of $PM_{2.5}$, secondary water-soluble inorganic ions like SO_4^{2-}, NO_3^-, NH_4^+ are the most important chemical species in the process of regional particulate matter pollution. Among them, $(NH4)_2SO_4$ and NH_4NO_3 formed by reaction of the secondary pollutants such as sulfuric acid or nitric acid with NH_3 have become the main water-soluble secondary pollutants in the atmosphere; Yang (Yang et al., 2007) observed atmospheric aerosols in Jinan city and found that secondary ions in $PM_{2.5}$ mainly exist in the form of $(NH_4)_2SO_4$ and NH_4NO_3, nitrogen deposition has been taken into account as an important nitrogen source in the study of nitrogen cycle in river basins; Huang (Huang et al., 2016) studied nitrogen deposition in Huanghuai Plain from May 2008 to April 2012. It was found that NH_3-N was the main type of nitrogen deposition and the proportion of NH_3-N in nitrogen deposition was 6%-79%, with an average of 53%; Zhu (Zhu et al., 2015) considered 41 ecological research sites in China, and found that particulate nitrogen, ammonia nitrogen and nitrate nitrogen accounted for 24%, 40% and 33% of total nitrogen, respectively, indicating that ammonia nitrogen was the main component of atmospheric deposition; Zheng (Ge et al., 2017) studied three ammonia-rich areas in Korea, and found that, $(NH_4)_2SO_4$ and NH_4NO_3 were the main forms of water-soluble ions in $PM_{2.5}$; The atmospheric $(NH_4)_2SO_4$ and NH_4NO_3 can enter urban water body through rainfall, becoming an important source of NH_3-N in water body, aggravating water eutrophication and destroying water ecosystem balance (Ding et al., 2007; Neal et al., 2006); Wang Jin jie (Wang et al., 2014) carried out a 1-year study on nitrogen wet deposition in Jinshui River Basin. It was found that the concentration of total nitrogen in rainwater ranged from 0.24mg/L to 2.89mg/L, ammonium nitrogen, nitrate nitrogen and organic nitrogen accounted for 42.8%, 13.3% and 43.9% respectively, nitrogen concentration of rainwater decreased with the increase of rainfall, and was obviously diluted by rainfall; Relevant studies (Wang et al., 2014) indicated that compared with nitrate nitrogen, attached algae are easier to absorb and utilize ammonia nitrogen, leading to algae and other aquatic plants to proliferate in large numbers, resulting in blooms.

In this work, Chengdu is taken as a representative city of southern China to study the characteristics of ammonia nitrogen natural rainfall caused by air pollution sources. Chengdu is a subtropical humid

monsoon climate area with mild climate, distinct seasons, long frost-free period, abundant rainfall and less sunshine. The annual total precipitation is 918.2mm, mainly in July to August (Chengdu Statistical Yearbook, 2016).

15 natural rainfalls in Chengdu city from April to September 2017 were collected and detected. The characteristics of NH_3-N pollution in natural rainfalls were analyzed and the temporal and spatial variation of NH_3-N pollution in rainfalls near toilet vents of buildings was emphasized. Because there are no industrial enterprises in urban business area, and residential buildings or office buildings are the main structures, the ventilation outlets of the buildings are only toilet vents.

Total amount of NH_3-N in rainfall and land surface runoff was also discussed. The purpose of this work is to provide theoretical support for source analysis and control of ammonia nitrogen pollution in water.

2. Method

2.1 Sample Collection

From the beginning of obvious precipitation to the end of the rainy season (April to September) in 2017, a total of 15 rainfall samples were collected in Chengdu urban area. The natural rainfall sampling sites were located near the author's working unit, which is Environmental Protection Building. The sampling sites of surface runoff process were located on the roads and pavement near the building. The sampling points were arranged as shown in Figure 1 and the attributes of each point are shown in Table 1. Natural rainfall samples were collected by a 2000mL barrel. Rainfall runoff samples are collected manually by pumping devices.

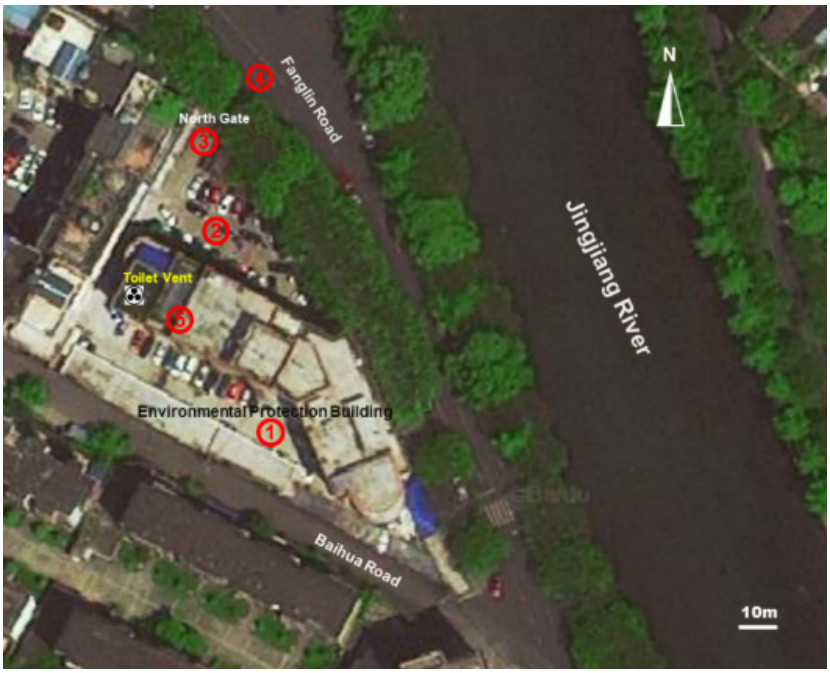

Figure 1. Satellite Map of Sampling Layout

Table 1. Attributes of Sampling Points

Serial number	Location	Sampling type		Pavement attribute
		Rainfall	Runoff	
①	Opening space in yard	√		/
②	Parking lot ground	√	√	Cement
③	Ground near north gate	√	√	Concrete
④	Automobile Lane	√	√	Asphalt
⑤	Roof of building	√	√	Waterproof coating

2.2 Monitoring and Detection

Rainfall monitoring results were recorded with a dump rain gauge (JDZ02-1) combined with real-time rainfall data published by Chengdu Meteorological Bureau. The concentration of NH_3-N was determined by Nessler's reagent spectrophotometry (HJ535-2009). All samples were detected within 24 hours after collection.

3. Result and Discussion

3.1 Variation of NH_3-N Concentration in Natural Rainfall

The NH_3-N concentration of all rainfall samples in Chengdu urban area from April to September in 2017 was monitored and results are shown in Figure 2. It can be seen that the concentration of NH_3-N in the first rainfall in 2017 was the highest, reaching 18.2mg/L. According to Environmental Quality Standards for Surface Water (GB3838-2002), it was far worse than Grade V (≤2mg/L), which is the minimum requirement of water quality evaluation.

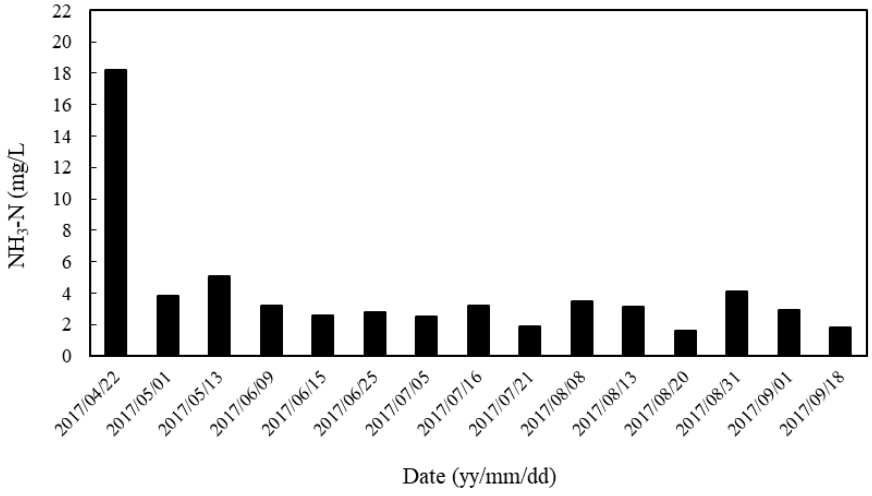

Figure 2. Ammonia Nitrogen Concentration in Natural Rainfall (April to September in 2017)

The first rainfall in 2017 occurred on April 22, around the Grain Rain Day which is the 6th solar term of the 24 divisions of solar year in traditional Chinese calendar. The higher concentration of NH_3-N in

rainwater is due to the increase of motor vehicle travel in winter and frequent human in indoor activities like catering, bathing, heating, etc. The use of natural gas, fuel and other energy causes the increase of SO_2 and NO_x emissions, which promotes the formation and accumulation of $(NH_4)_2SO_4$ and NH_4NO_3 in atmosphere. The lower temperature in winter is also conducive to the accumulation of NH_4NO_3 in the atmosphere in granular form (Meng et al., 2015). Meanwhile, the atmosphere structure is stable in winter, pollutants are not easy to diffuse. Therefore, during the first rainfall, accumulated $(NH_4)_2SO_4$ and NH_4NO_3 in atmosphere dissolved into the rainwater, resulting in a higher concentration of NH_3-N.

NH_3-N concentration decreased significantly in the following 14 rainfalls, ranging from 1.6mg/L to 5.1mg/L, with an average concentration of 3.1mg/L. It can be seen that atmospheric pollutants are the main source of ammonia nitrogen in natural rainfall. The first rainfall has a distinct effect on the scouring and purification of $(NH_4)_2SO_4$ and NH_4NO_3 accumulated in winter atmosphere, which makes the concentration of NH_3-N in subsequent rainfall decrease significantly. During the study period, NH_3-N concentration of natural rainfall in Chengdu city was mostly higher than that of Grade V in standard GB3838-2002 (except for rainfall on July 21, August 20 and September 18).Excessive ammonia nitrogen from rainfall flows into urban rivers, which may make water quality exceed the standard requirement and further cause the eutrophication of water body.

3.2 Effect of Toilet Vent in Buildings on NH3-N Concentration of Rainfall

The formation of $(NH_4)_2SO_4$ and NH_4NO_3 in the atmosphere depends on NH_3 emissions. It is reported that the main sources of NH_3 in atmosphere include livestock and poultry sources, nitrogen fertilizer application, synthetic ammonia production and human feces, accounting for 64%, 17%, 1% and 18% respectively (Li, 2012). NH_3 in Chengdu urban area mainly comes from human excrement, almost all of which are discharged into atmosphere through toilet vents in buildings. Therefore, sampling points were arranged near the vent (0, 5, 10 and 15m) on the roof of Environmental Protection Building, as shown in ⑤ in Figure 1, and NH_3-N concentration in rainfall were detected.

3.2.1 Characteristics of Rainfall

The concentration of pollutants in precipitation is influenced by many factors, and there is a large spatial-temporal difference (Zhang et al., 2010; Pu et al., 2010). In this study, NH_3-N concentration in two rainfall events (May 13, 2017 and June 9, 2017) was monitored, and the effect of toilet vent on the concentration was analyzed. These two rainfall events belong to light and moderate rain and the rainfall amounts were 8.2 mm and 23.5 mm, respectively. The rainfall process line is shown in Figure 3.

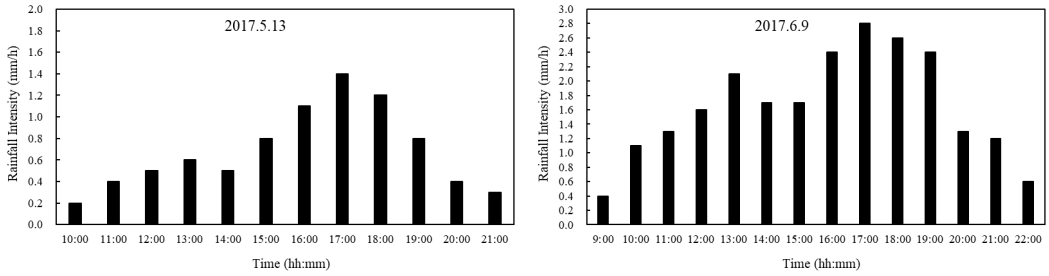

Figure 3. Rainfall Process Line on May 13, 2017 and June 9, 2017

3.2.2 Temporal and Spatial Variation of NH_3-NConcentration in Rainfall

The variation of NH_3-N concentration during rainfall process at different sampling points in two rainfall events on May 13, 2017 and June 9, 2017 is shown in Figure 4. It can be seen that with the prolongation of rainfall duration at different places, NH_3-N concentration of the rainfall decreases in varying degrees. At the beginning of rainfall, NH_3-N concentration decreases significantly with time, but at the later stage, the concentration decreases slowly. This is due to the accumulation of ammonia nitrogen pollutants in atmosphere during earlier drought period, and the initial scouring effect of rainfall makes NH_3-N concentration in the initial rainfall higher. However, ammonia nitrogen in atmosphere mainly comes from toilet vent in the late stage of rainfall, ammonia gas discharged directly or after secondary reaction dissolves into natural precipitation rapidly, so the NH_3-N content in late rainfall is relatively lower. In addition, due to the moderate rain on June 9, 2017, the rainfall was larger and the initial scouring effect was stronger, so the ammonia nitrogen in rainfall decreased more obviously.

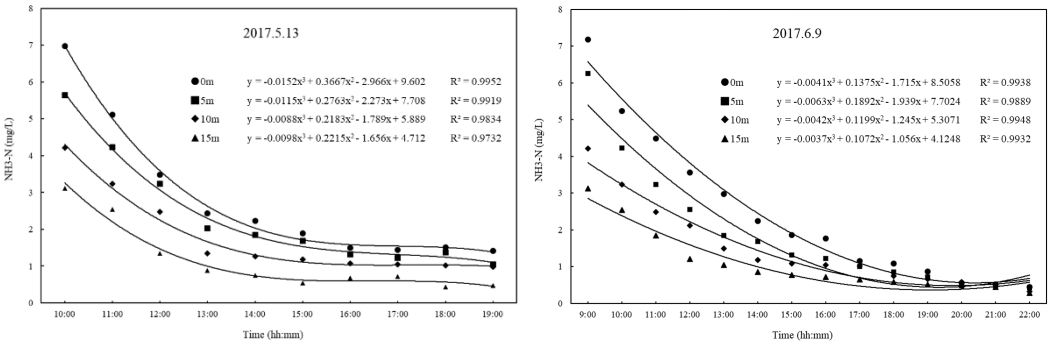

Figure 4. Variation of NH_3-N Concentration in Rainwater at Different Distance from Toilet Vent

By analyzing the variation of NH_3-N concentration with time, it was found that ammonia nitrogen in natural rainfall at the same sampling point showed a decreasing trend. As the distance from the toilet vent increased, the ammonia nitrogen in rainwater decreased, while the attenuation rate raised. In the case of larger rainfall, such as the moderate rain on June 9, 2017. NH_3-N concentration in the middle and late stages was less affected by distance to the vent, and all the values tended to minimum.

3.3 Total Analysis of Ammonia Nitrogen Pollutants

Because NH_3-N concentration in rainwater can cannot reflect the pollution degree in urban water, the ammonia nitrogen pollution in rainfall and surface runoff was further assessed by the total amount of pollutants measurement method.

3.3.1 Rainfall Analysis

Three typical rainfalls on April 22, 2017, June 25, 2017 and August 13, 2017 were selected to analyze the total amount of ammonia nitrogen pollutants in rainwater and surface runoff. Three typical rainfalls on April 22, 2017, June 25, 2017 and August 13, 2017 were selected to analyze the total amount of ammonia nitrogen pollutants in rainfall and surface runoff. According to the 24-hour hyetal grade standard, the three precipitations belong to light, moderate and heavy rain. On April 22, 2017, the rainfall intensity was small and the duration was short; on June 25, 2017, the rainfall intensity was low and the duration was long; on August 13, 2017, the rainfall was intense and lasting for a long time, each rainfall was 9.26, 21.25 and 34.33mm, respectively.

3.3.2 Total Ammonia Nitrogen Pollution Analysis

The total amount of ammonia nitrogen pollutants per unit area in natural rainfall was calculated by multiplying the average NH_3-N concentration by amount of rainfall per unit area. The calculation results are expressed in grams per square meter as shown in Table 2.

Table 2. Total Amount of Ammonia Nitrogen Pollutant in Three Typical Rainfalls in 2017 (g/m^2)

Date	Opening space in yard (Rainfall)	Parking lot ground (Runoff)	Ground near north gate (Runoff)	Automobile Lane (Runoff)	Roof of building (Runoff)
2017/04/22	100.5	88.7	97.8	78.3	85.4
NH_3-N loss rate		11.7%	2.7%	22.1%	15.0%
Average NH_3-N loss rate			12.9%		
2017/06/25	77.1	52.5	56.8	69.2	44.1
NH_3-N loss rate		31.9%	26.3%	10.2%	42.8%
Average NH_3-N loss rate			27.8%		
2017/08/13	129.1	82.9	101.8	94.1	80.1
NH_3-N loss rate		35.8%	21.1%	27.1%	38.0%
Average NH_3-N loss rate			30.5%		

The total amount of ammonia nitrogen pollutants per unit area of surface runoff can be calculated by formula (1), as in

$$W_T = \frac{\sum_{t=0}^{T} C_t \times P_t}{1000 \times A} \tag{1}$$

$W_T$is the total amount of pollutants per unit area, g/m^2; C_t is the concentration of pollutants in each period, mg/L; P_t is the rainfall in each period, L; A is catchment surface area, m^2.

The total amount of ammonia nitrogen pollutants in natural rainfall and surface runoff at different

sampling points were calculated. The variation of NH_3-N concentration in rainfall and surface runoff is shown in Figure 5 with corresponding rain intensity.

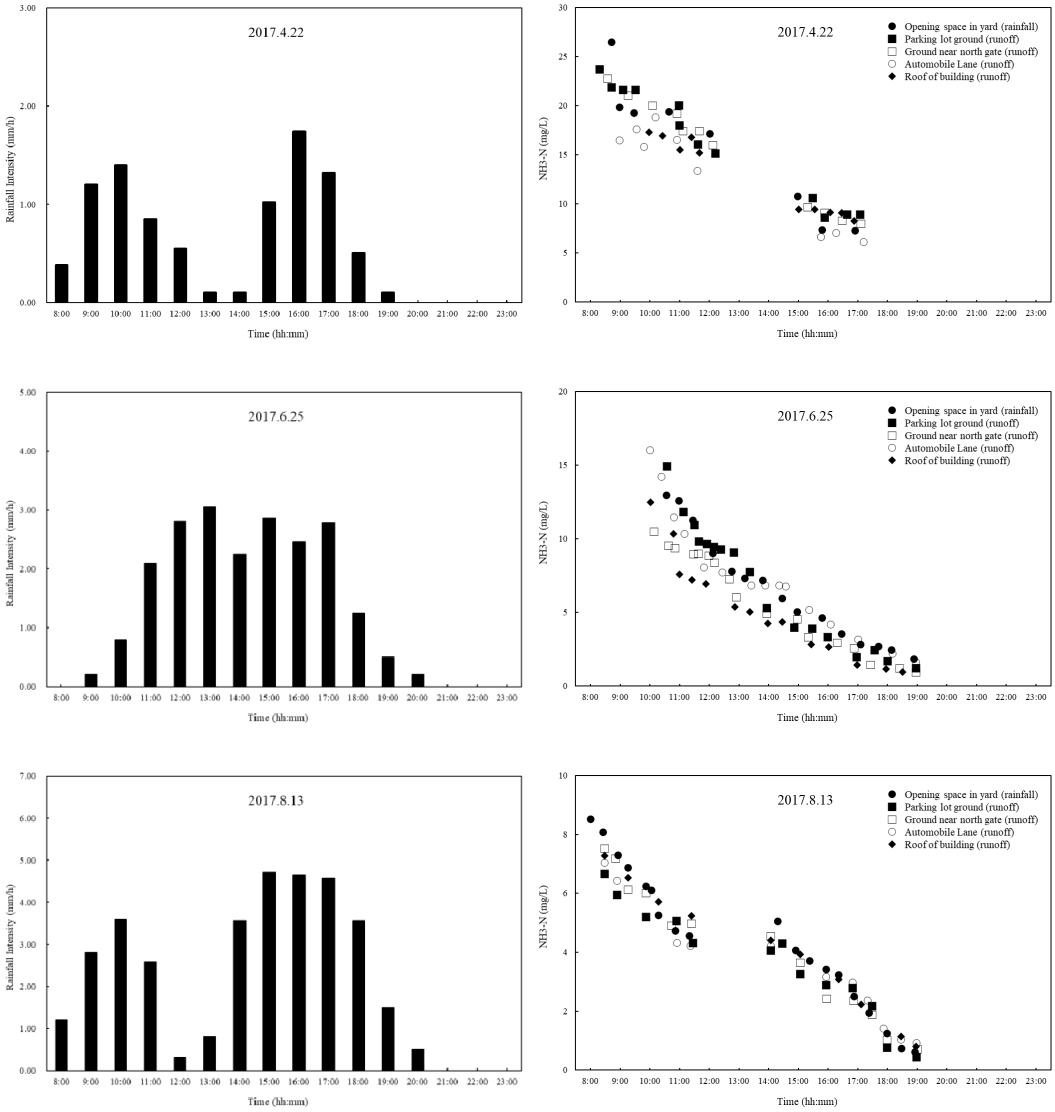

Figure 5. Variation of Rainfall Intensity and NH_3-N Concentration in Rainfall and Surface Runoff

According to results of monitoring and calculation, the total amount of ammonia nitrogen pollutants in natural rainfall is sorted as follows: June 25, 2017<April 22, 2017<August 13, 2017. On August 13, 2017, the rainfall intensity was strong and lasted for a long time, ammonia nitrogen pollutants in atmosphere was fully washed and absorbed by rainwater, the total amount of ammonia nitrogen pollutants in the rainfall was the largest. It also showed that rainfall intensity and duration were one of the main factors affecting total amount of ammonia nitrogen in rainfall. On the other hand, although the intensity of rainfall on June 25, 2017 was greater than that on April 22, 2017, because the rainfall on April 22 was the first rainfall in 2017, the accumulation of pollutants in the atmosphere was very large,

and the total amount of ammonia nitrogen pollutants dissolved in rainwater was relatively large, which also showed that the number of dry days before rainfall is another major factor affecting ammonia nitrogen in natural rainfall.

Moreover, ammonia nitrogen in rainwater is greater than that in surface runoff. The reason is that pollutants in rainwater was adsorbed on impervious surface during runoff, which reduces the total amount of ammonia nitrogen. During these 3 rainfall periods, the ammonia nitrogen of surface runoff at each sampling point has different degrees of loss compared with that in rainfall, as detailed in Table 2. The average NH_3-N loss rate in surface runoff was 12.9%, 27.8% and 30.5% respectively, which indicate that the greater rainfall intensity, the longer duration and runoff time, the more ammonia nitrogen can be lost in the process of runoff.

4. Conclusion

(1) Among the 15 natural rainfalls monitored in 2017, the NH_3-N concentration of 14 rainfalls was higher than the value of Grade V (≤2mg/L) of Environmental Quality Standards for Surface Water (GB3838-2002). NH3-N concentration of the first rainfall was the highest, reaching 18.2 mg/L, and then began to decrease in the subsequent 14 events, basically between 2.0 and 5.0 mg/L. Ammonia nitrogen accumulated in the atmosphere is an important source of ammonia nitrogen pollutants in urban surface water.

(2) NH_3-N concentration in natural rainfall decreases with the increase of the distance between sampling point and toilet vent. Ammonia discharged from toilet is an important source of ammonia nitrogen in urban atmosphere.

(3) The main factors affecting the total amount of ammonia nitrogen pollutants in natural rainfall include rainfall intensity, time duration and the number of dry days before rainfall. Because of the adsorption effect on ground surface, the total amount of ammonia nitrogen pollutants in surface runoff is less than that in natural rainfall. Urban ground surface cleaning and emission reduction are the fundamental ways to reduce pollution.

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