1 **Emission factor for atmospheric ammonia from a typical**
2 **municipal wastewater treatment plant in South China**

3 Chunlin Zhang^a, Xuesong Geng^a, Hao Wang^{b*}, Lei Zhou^a, Boguang Wang^{a**}

4 ^a *Institute for Environmental and Climate Research, Jinan University, Guangzhou 511443, PR China*

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11 **Corresponding author*

12 *E-mail address:* hao.wang@uef.fi ; haowang201314@126.com

13 ***Corresponding author*

14 *E-mail address:* tbongue@jnu.edu.cn

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Abstract:

Atmospheric ammonia (NH_3), a common alkaline gas found in air, plays a significant role in atmospheric chemistry, such as in the formation of secondary particles. However, large uncertainties remain in the estimation of ammonia emissions from nonagricultural sources, such as wastewater treatment plants (WWTPs). In this study, the ammonia emission factors from a large WWTP utilizing three typical biological treatment techniques to process wastewater in South China were calculated using the US EPA's WATER9 model with three years of raw sewage measurements and information about the facility. The individual emission factors calculated were 0.15 ± 0.03 , 0.24 ± 0.05 , 0.29 ± 0.06 , and $0.25 \pm 0.05 \text{ g NH}_3 \text{ m}^{-3} \text{ sewage}$ for the adsorption-biodegradation activated sludge treatment process, the UNITANK process (an upgrade of the sequencing batch reactor activated sludge treatment process), and two slightly different anaerobic-anoxic-oxic treatment processes, respectively. The overall emission factor of the WWTP was $0.24 \pm 0.06 \text{ g NH}_3 \text{ m}^{-3} \text{ sewage}$. The pH of the wastewater influent is likely an important factor affecting ammonia emissions, because higher emission factors existed at higher pH values. Based on the ammonia emission factor generated in this study, sewage treatment accounted for approximately 4% of the ammonia emissions for the urban area of South China's Pearl River Delta (PRD) in 2006, which is much less than the value of 34% estimated in previous studies. To reduce the large uncertainty in the estimation of ammonia emissions in China, more field measurements are required.

Keywords: Atmospheric ammonia; wastewater treatment plant; emission factor; pH value; WATER9 model

Capsule abstract:

The atmospheric ammonia emissions from WWTPs might have been overestimated in South China, and the ammonia inventory should be reevaluated to reduce its large uncertainty.

1. Introduction

Atmospheric ammonia (NH_3) is involved in many chemical processes in the atmosphere that result in major air pollution problems such as acid deposition (Aneja et al., 2001; Asman, 2001), low visibility (Battye et al., 2003), greenhouse effect (Hellsten et al., 2008), and secondary aerosol formation (Erisman and Schaap, 2004; Wang et al., 2011; Behera and Sharma, 2012). Secondary aerosols have been regarded as an important component of fine particulate matter ($\text{PM}_{2.5}$), which is harmful to human health as indicated by increasing incidences of pulmonary disease, cardiac arrest, and premature death and reductions in lung function (Pinder and Adams, 2007). When deposited in ecosystems, NH_3 and particulate ammonium (NH_4^+) may cause nutrient imbalances, biodiversity loss, and eutrophication (Stevens et al., 2004; Bergström and Jansson, 2006).

The main sources of ammonia in the atmosphere are agricultural activities, but nonagricultural sources are also important (US EPA, 2002). To assess the impact of ammonia on regional air quality better, it is important to increase understanding about all the important sources of ammonia emissions. Quantifying the magnitude of nonagricultural sources emissions is uncertain because of the lack of required experimental data (Sutton et al., 2000). Several ammonia emission factors were developed for various nonagricultural emission sources, such as on-road mobile sources (Huai et al., 2003; Liu et al., 2014), biomass burning (EC/R, 2002), and wastewater treatment plants (WWTPs) (Kogan and Torres, 1997; Gu et al., 2010). WWTPs able to process a large quantity of nitrogen-rich wastes may generate a significant amount of ammonia under certain conditions (Chinkin et al., 2003). It was reported that WWTPs are the fifth major source of atmospheric ammonia after animal wastes, biological processes in soils, ammonia-based chemical fertilizers, and biomass burning (Bouwman et al., 1997). Recently, studies on nitrogen-rich wastewater focused mainly on agricultural sources, such as stored animal wastewater (Sommer et al., 2005) and swine lagoons (De Visscher et al., 2002; Bajwa et al., 2006; Blunde and Aneja, 2008). As such, only scarce data about atmospheric NH_3 emission from WWTPs have been reported in the last decade.

With its rapid industrialization and urbanization, South China, especially the Pearl River Delta (PRD) region, has been experiencing severe air pollution problems such as acid rain, photochemical smog, and haze (Zhang et al., 2007; Liu et al., 2008). Ammonia has been linked to some of these air pollution problems, and it has been shown that ammonia in the atmosphere plays an important role in regional

particulate air pollution (Hu et al., 2008). Atmospheric ammonia emissions contribute to approximately 8–11% of PM_{2.5} concentrations in the PRD region, comparable with SO₂ (9–11%) and NO_x (5–11%) emissions (Wang et al., 2011). Considerable effort has been devoted to estimate ammonia emissions in the PRD region in recent years. Most of these studies have focused on the ammonia emissions from livestock, fertilizer uses, and other agricultural sources (Gong et al. 2013; Li, 2013). Little effort, however, has been devoted to nonagricultural sources, especially those sources in urban areas (Liu et al., 2014), such as WWTPs, which are major ammonia sources in the urban PRD region (Zheng et al., 2012).

Concentrations of ammonia emissions from sewage treatment plants are quite uncertain, with estimations varying from 1.0 kt yr⁻¹ (Shen et al., 2014) to 6.4 kt yr⁻¹ (Zheng et al., 2012; Yin et al., 2010) in the PRD region, because of the large uncertainty in the available emission factors. For example, Gu et al. (2012) obtained an emission factor of 0.28 g NH₃ m⁻³ sewage for a WWTP via lab simulation of aerated processes in South China. This emission factor is relatively close to the value (0.15 g NH₃ m⁻³ sewage) used by Battye et al. (2003), who evaluated the ammonia inventory for the state of North Carolina and the San Joaquin Valley in the state of California, USA. However, the Emission Inventory Improvement Program (EIIP) in the United States recommends an emission factor for WWTPs in the range of 0.02 to 0.003 g NH₃ m⁻³ sewage (Roe et al., 2004). In China, a national technical manual for atmospheric ammonia inventory, which is similar to that of the EIIP (PRC NEPM, 2014), recommends a single ammonia emission factor of 0.003 g NH₃ m⁻³ sewage for WWTPs. Therefore, a large discrepancy exists among the recommended ammonia emission factors for WWTPs found in the literature and standard technical manuals. To develop more accurate ammonia inventories and to understand the effect of ammonia on PM_{2.5} formation and acid deposition in the region better, additional research, including on measurement and model estimation of the emission factor, is required.

To estimate the emission factor of volatile gases from wastewater treatment systems, various mathematical models have been developed, including TOXCHEM+ and the US EPA's WATER9. WATER9 is probably the most comprehensive among the available models (Oskouie et al., 2008). It is based mainly on the mass balance for each unit operation facility in the WWTP. For air emissions, such as of ammonia, hydrogen sulfide, volatile organics, and methane from hazardous waste management processes, the model can provide scientifically sound estimates (Zhang, 2010). To obtain emission rates, influent ammonia concentration and plant operational parameters are required as inputs to the

model, which is then able to estimate facility-level emissions using detailed information about each facility and the influent chemistry (EPA, 2001).

In this study, the main objective was to estimate sewage-based ammonia emission factors ($\text{g NH}_3\text{m}^{-3}\text{sewage}$) using the WATER9 model based on three years of raw sewage measurements and information about the facility of a typical WWTP in South China. The influences of process units on ammonia emissions are discussed in this paper. Moreover, total ammonia nitrogen (TAN) concentrations in the wastewater along the treatment processes were measured in a strengthened observation period to investigate the spatial variation of ammonia-nitrogen.

2. Material and methods

2.1 Experimental

2.1.1 Location

Lie De municipal wastewater treatment plant (LD) is the second largest WWTP in the city of Guangzhou, one of the most developed and important cities in the PRD region, South China. LD is located in the center of the city. The plant treats residential sewage and part of the industrial effluent from a district north of the Pearl River. The maximum treatment capacity in 2010 was 1.2 million m^3 per day, accounting for more than 25% of the total wastewater generated by the city. The service area of the plant covers 143.3 km^2 , and its service population is approximately 2.26 million. Wastewater is processed at LD by three typical biological treatment technologies, including adsorption-biodegradation activated sludge technology (A-B), sequencing batch reactor activated sludge technology (SBR), and anaerobic-anoxic-oxic technology (A-A-O). According to the available statistical data on WWTPs in the PRD region, biological processes treated over 93% of the sewage in 2015, with approximately 64% by A-A-O processes and almost 7% by SBR processes. The A-B process has also been widely applied in the PRD region for many years, though its exact percentage in the market is unclear.

2.1.2 Water treatment processes

LD consists of four different sewage treatment processes, including one A-B process, one UNITANK process (an upgrade of the SBR activated sludge process), and two slightly different A-A-O processes.

A schematic diagram of the four wastewater treatment processes is shown in Fig. 1. Technical properties of the key units in the four processes are listed in Table 1. All processes share the bar screens and the lift pump stations. Wastewater from the municipal pipe network was distributed to the four processes through the lift pumps after passing through the coarse screen.

Fig. 1 Schematic diagram of the four wastewater treatment processes at LD

Table 1 Technical properties of the key units in the four wastewater treatment processes

Properties	A-B	UNITANK	A-A-O-1	A-A-O-2
Grit chamber				
Number of tanks	1	1	1	3
Water depth (m)	5.0	6.5	8.3	6.3
Total water surface (m ²)	854	525	353	1,033
Biological reactors				
Number of tanks	2(A)+2(B)	4	2	3
Water depth (m)	5.0	5.8	9.0	9.0
Total water surface (m ²)	600(A)+4,884(B)	19,848	11,125	26,100

<i>Sludge loading</i>	1.8–3.6 (A)	0.18	0.004–0.01	0.004–0.01
(kg BOD ₅ /kg MLSS.d)	0.15–0.27 (B)		(Anoxic zone)	(Anoxic zone)
			0.17–0.20	0.17–0.20
			(Anaerobic zone)	(Anaerobic zone)
<i>Aeration system</i>	Diffused air	Diffused air	Diffused air	Diffused air
<i>Air supply capacity</i>				
(Nm ³ min ⁻¹)	195	230	195	520
Clarifier				
<i>Number of tanks</i>	2	-	2	3
<i>Water depth (m)</i>	5.0	-	4.6	5.5
<i>Total water surface (m²)</i>	4,422	-	9,570	23,445

A-B treatment process: After screening of coarse solids, fine grits were settled by a vortex grit chamber. The grit chamber was followed by a biological treatment system consisting of two aerated reaction tanks (tanks A and B with high and low sludge loads, respectively) and two clarifiers. Fine bubble aerators were employed for aeration. A part of the biologically active sludge discharged from the clarifier was continuously recycled during the process. The capacity of this process was around 0.22 million m³ per day.

UNITANK treatment process: This system consisted of three rectangular tanks; while one tank was aerating and filling, the others were in settle or anaerobic mode. A series of baffles was employed to direct the flow from side to side in the tanks, helping to mix the incoming influent and the returned activated sludge. After filtration and disinfection, the treated water was discharged directly to surface waters. The capacity of this process was also 0.22 million m³ per day.

Two A-A-O treatment processes: The biological reaction units in these processes consisted of an anaerobic zone, an anoxic zone, and an oxic zone. After preliminary treatment, 70–90% of the effluent was fed to the anaerobic zone, and the rest was fed to the anoxic zone. The main difference between the two similar processes was that A-A-O-2 had more biological reaction tanks than A-A-O-1 did. The treatment capacities of the two processes were 0.2 and 0.56 million m³ per day for A-A-O-1 and A-A-O-2, respectively.

2.1.3 Sampling and analytical procedures

The TAN concentrations of the raw sewage were measured at LD every day from 2011 to 2013, and the sewage's pH and water temperature were measured once a week. The TAN concentrations at multiple sites within LD were measured during a strengthened observation period in May 2014 to explore its spatial variation along the treatment processes. Twelve water sampling points were selected along the four wastewater treatment trains (as shown in Fig. 1). W1 represents the raw wastewater. In the A-B process, samples were also collected from tank A (W2), tank B (W3), and clarifier B (W4). In the UNITANK process, samples were taken at the outlet of the reaction tank (W5) and the rotary disk filtration (W6). For the A-A-O processes, samples were collected from the anaerobic zones (W7/W10), the oxic zones (W8/W11), and the clarifiers (W9/W12).

Water samples were collected near the surface with brown glass bottles, and then acidified to a pH value of <2 with sulfuric acid before being stored at 2–5 °C for later lab analysis. For each sampling site, two duplicate samples were taken together with a blank for each batch. Nessler's reagent spectrophotometry was used to analyze the ammonia in the water samples after filtration (PRC NEPA, 2009). During the experiment, the water used at the lab was free of ammonia, the absorbance of the reagent blanks was no more than 0.030, and the amount of HgCl₂ added was strictly controlled to ensure good color rendering of the Nessler's reagent. In addition, the pH of the raw wastewater was determined using the glass electrode method (PRC NEPA, 1987), and the water temperature was measured with a thermometer (PRC NEPA, 1992).

2.2 Modeling and important input parameters

2.2.1 WATER9 model

The WATER9 model was developed by the US EPA to estimate emissions of volatile compounds via various pathways from wastewater and waste management units. The model made separate emission estimates for each individual compound identified as a constituent of the wastewater. It accounts for emissions via volatilization, biodegradation, adsorption, photodecomposition, and hydrolysis. Volatilization and biodegradation are considered important emission pathways for surface impoundments, aerated and nonaerated wastewater treatment plants, land treatment areas, and landfills (US EPA, 1994).

In this study, a number of units were selected from WATER9 to model the corresponding units with similar function in the four wastewater treatment processes at LD. The modeled units in WATER9 and the corresponding units at the WWTP are listed in Table 2 (US EPA, 2001; Zhang, 2010). For the A-B process, tanks A and B were modeled by a diffused air biotreatment unit with high or low activated sludge biomass, respectively. For the UNITANK process, the reaction tanks were simulated by the combination of a diffused air biotreatment unit with aerated air and a similar unit without air, as well as a rectangular clarifier. For the A-A-O process, the anaerobic zone was modeled by a diffused air biotreatment unit with zero air input, whereas the anoxic zone and oxic zone were modeled by diffused air biotreatment units with low or high-activated sludge loading, respectively.

Table 2 Summary of original and modeled operation units

Original operation units at LD	Modeled units by WATER9
Bar screen	Bar screen
Lift pump station	Lift pump or station
Grit chamber	Grit separator
Biological reactors	Diffused air biotreatment
Clarifier	Circular/rectangular clarifier
Sludge thickener	Circular clarifier
Sludge dewatering	Open trench
Landfill	Landfill

2.2.2 Free ammonia in wastewater

The concentration of free ammonia in the wastewater is the most important input parameter for the WATER9 model for simulating ammonia transport from liquid to air. For the calculation of free ammonia, a TAN measurement is needed.

It is assumed that, in aqueous ammonium solutions, NH_3 , NH_4^+ , and hydrogen ions (H^+) exist in equilibrium. The fraction of TAN that is free ammonia in solution can be expressed as (De Visscher et al., 2002):

$$F_{\text{NH}_3} = \frac{[\text{NH}_3 - \text{N}]_{\text{solution}}}{([\text{NH}_3 - \text{N}]_{\text{solution}} + [\text{NH}_4^+ - \text{N}]_{\text{solution}})} = \frac{1}{1 + 10^{-\text{pH}(1 + K_{\text{ads}})/K_{\text{a,w}}}} \quad (1)$$

where $[\text{NH}_3 - \text{N}]_{\text{solution}}$ is the concentration of dissolved $\text{NH}_3 - \text{N}$ in solution, $[\text{NH}_4^+ - \text{N}]_{\text{solution}}$ is the concentration of $\text{NH}_4^+ - \text{N}$ in solution, $K_{\text{a,w}}$ is the dissociation constant for NH_4^+ in pure water, and K_{ads} is the equilibrium constant for ammonia adsorption. K_{ads} is important in determining

203 F_{NH_3} (Ro et al. 2008), and based on the pH values of the wastewater at LD, $K_{ads} = 0$ was used for
204 this calculation.

205 $K_{a,w}$ can be calculated by the following experimental equation (De Visscher et al., 2002):

206
$$\text{p}K_{a,w} = 0.0897 + 2729/T \quad (2)$$

207 where T is the water temperature in Kelvin.

208 After obtaining the concentration of $\text{NH}_3\text{-N}$ in the wastewater, the concentration of free NH_3 in the
209 wastewater can be calculated as:

210
$$[\text{NH}_3]_{\text{solution}} = \frac{M_{\text{NH}_3}}{M_{\text{NH}_3\text{-N}}} [\text{NH}_3\text{-N}]_{\text{solution}} \quad (3)$$

211 where M_{NH_3} is the molar mass of ammonia, and $M_{\text{NH}_3\text{-N}}$ is the molar mass of ammonia-N.

212 **2.3 Sensitivity analysis**

213 A sensitivity analysis was performed to determine the relative changes in flux with respect to changes
214 in the model input parameters. If X is the output of the model and θ is the input parameter to the model,
215 then X is the function of θ , that is,

216
$$X = f(\theta) \quad (4)$$

217 The sensitivity S of the output can be expressed as:

218
$$S = \left(\frac{dX}{d\theta} \right)_{\theta_0} \frac{\theta_0}{f(\theta_0)} \quad (5)$$

219 where θ_0 is the mean of the input parameters.

220 The first-order derivative can be calculated as follows:

221
$$f'(\theta_0) = \frac{f(\theta_2) - f(\theta_1)}{\theta_2 - \theta_1} \quad (6)$$

222 where θ_1 and θ_2 are the perturbed input values on either side of the mean.

223 **3. Results and discussion**

3.1 Monthly variation in the long term measurements

The monthly variations in the pH, temperature, and TAN concentration of the raw wastewater, based on the three-year measurements at LD, are shown in Fig. 2. The monthly average temperature of the influent was 24.9 °C and ranged from 20 to 32 °C. The monthly average pH varied from 7.08 to 8.27 over the study period, indicating a weak alkaline influent. The annual average pH was approximately 7.46, which is consistent with what Chen et al. (2006) found. The TAN concentration varied from 12.5 to 30.8 mg L⁻¹, with an average value of 22.2 mg L⁻¹. The highest TAN concentration was observed in winter, with the lowest values detected in summer, which is consistent with the findings for highway rest area sewage (Chen et al., 2016). In addition, it was shown that both pH and TAN concentration were lower during rainy seasons (from April to September) than they were during dry seasons (Fig. 2). This is probably a result of the dilution effect from increasing amounts of rainwater and residential water during summer time.

Fig. 2 Variations in wastewater pH, TAN concentration, and temperature from 2011 to 2013

3.2 TAN variation along the processes

The spatial variation in the TAN concentration in water along the treatment processes was investigated using the data collected in the strengthened observation period. The TAN concentrations for specific treatment units are shown in Fig. 3. The results clearly demonstrate that the ammonia concentrations in the water constantly decreased along each process.

The TAN concentration immediately decreased after the raw water (W1) passed through the grit chambers for all processes. The vortex-type grit chamber used in each process favors an increase in dissolved oxygen due to intensive turbulence. With the increase of dissolved oxygen, nitrification reactions decrease the ammonia concentration in the water by converting NH_4^+ into NO_2^- and NO_3^- .

The TAN concentration also decreased significantly after the water flowed through the aeration tanks or oxic zone (i.e., W3 to W4 in the A-B process, W7 to W8 in the A-A-O-1 process, and W10 to W11 in the A-A-O-2 process). There are two possible reasons for this decrease. One may be the enhanced nitrification reactions that occurred because of the increased dissolved oxygen and the nitrifying bacteria in the biological aeration units. Another possible reason is the physical effect of the aerated air, which promotes the escape of ammonia gases out of the water via intensive turbulence diffusion and air stripping.

Surprisingly, a significant decrease in the TAN concentration was observed for the water moving from the oxic zone to the clarifier in the A-A-O processes (i.e., from W8 to W9 and W11 to W12 in A-A-O-1 and A-A-O-2 respectively). As residual oxygen originating from the oxic zone will be consumed very rapidly in the clarifier, nitrification is unlikely taking place in the subsequent clarifiers. The drop might be explained partly by the uneven vertical distribution of the TAN concentration in the oxic zone and the selection of a single sampling location. Fresh air is supplied to the bottom of the aeration basins to increase the dissolved oxygen concentration at the bottom. Thus, the nitrification effect is likely weaker at the surface than at the bottom in the dynamic aeration tanks. Unfortunately, the effluents were moving out of the aeration tanks to the clarifiers through the bottom, whereas all the water samples were collected from the surface. This issue should be considered in future field sampling.

Fig. 3 Concentrations of TAN along the four wastewater treatment processes

3.3 Ammonia emission rates of the processes

During the wastewater treatment process, nitrogen can exist in any of the following forms: organic nitrogen, NH_3 , NH_4^+ , NO_2^- , or NO_3^- . The amount of nitrogen emitted into the air varies substantially depending upon a number of biological, chemical, technological, and meteorological factors (Kogan and Torres, 1997). To investigate the unit-specific characteristics of ammonia emission from WWTPs further, ammonia emission rates of each process at LD were estimated using the WATER9 model, based on the annual averages of influent pH (7.46), TAN concentration (22.2 mg L^{-1}), and water temperature (24.9°C) for 2011–2013.

Table 3 Calculated ammonia emission rates (t yr^{-1}) for the four wastewater treatment processes

Process	Lift pump	Grit chamber	Biological reactors	Clarifier	Dewatering	Total emission rates
A-B	0.104	0.031	9.244	1.870	0.006	11.255
UNITANK	0.109	0.034	18.281	-	0.006	18.430
A-A-O-1	0.036	0.706	16.968	1.058	0.005	18.773
A-A-O-2	0.118	1.014	46.038	2.533	0.018	49.721
Total	0.367	1.785	90.531	5.561	0.035	98.179

Table 3 shows the calculated ammonia emission rates for the key units of each process. The ammonia emission rates varied from 11.255 t yr⁻¹ (A-B) to 49.721 t yr⁻¹ (A-A-O-2), with a total emission rate of 98.179 t yr⁻¹ for the whole plant.

The biological reactors contributed approximately 90% w/w to the total ammonia emissions among all the key units in the processes. The ammonification in the biological reactors can convert organic nitrogen to free aqueous ammonia, which can escape easily to the atmosphere through air stripping, diffusion, or evaporation. Some studies (Chinkin, 2003) have suggested that ammonia-nitrogen is under heavy biological demand because of uptake and consumption by microorganisms under aerobic conditions. However, air stripping in aeration basins is a very important mechanism for ammonia emissions from a WWTP. In this study, the modeling results suggest that more than half of the contribution of the biological reactors to TAN comes from the aerobic units. Warn et al. (1990) even estimated that approximately 82% of the total ammonia emissions came from aeration tanks with air stripping. Anaerobic processes in the wastewater treatment system have also been considered an important source of NH₃ emission from sewage (Chinkin et al., 2003; Harmel et al., 1997). Under anaerobic conditions, ammonia-nitrogen (one of the biodegradation products of organic nitrogen) is able to enter the air via diffusion or evaporation. For example, in the UNITANK process, approximately 35% of the ammonia emissions was from the anaerobic tank, with an emission rate of 6.582 t yr⁻¹, and in the A-A-O process, approximately 30% was from the anaerobic tank, with emission rates of 5.005 and 14.962 t yr⁻¹ for A-A-O-1 and A-A-O-2, respectively.

In addition to the biological reactors, processing sludge is considered an important source for atmospheric ammonia emissions from wastewater treatment. For example, the highest concentration of NH₃ was observed around the sludge drying beds when Sonama Technology, Inc. was measuring ammonia emissions in the San Joaquin Valley (STI, 1998). Kogan and Torres (1997) demonstrated that most of the NH₃ emissions during biosolids treatment came from dewatering sludge, though the contribution from dewatering in this study was only 0.04% (Table 3). In addition, high levels of ammonium (usually 1.0–1.5 g L⁻¹) have been found in the digested liquid during the anaerobic digestion of sludge, which probably led to high emissions of ammonia (Wang et. al., 2015, 2016).

3.4 Ammonia emission factor of the processes

The monthly emission factors of atmospheric ammonia emitted from each process at LD were also calculated using the WATER9 model based on the three-year measurements of the influent. The results are presented in Table 4.

Table 4 Emission factors (Ef)* for the four processes ($\text{g NH}_3\text{m}^{-3}$ sewage)

	Month												Average
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	
Ef, A-B	0.18	0.19	0.12	0.13	0.15	0.11	0.15	0.13	0.12	0.11	0.18	0.19	0.15 ± 0.03
Ef, UNITANK	0.30	0.31	0.19	0.20	0.25	0.18	0.25	0.21	0.19	0.18	0.30	0.31	0.24 ± 0.05
Ef, A-A-O-1	0.34	0.38	0.24	0.26	0.31	0.23	0.32	0.26	0.24	0.22	0.34	0.38	0.29 ± 0.06
Ef, A-A-O-2	0.32	0.33	0.21	0.22	0.27	0.19	0.27	0.22	0.20	0.19	0.32	0.33	0.25 ± 0.05
Ef, average	0.29	0.31	0.19	0.21	0.25	0.18	0.25	0.21	0.19	0.18	0.29	0.31	0.24 ± 0.05

*Emission factor = total emission rate/treated sewage.

The average emission factor varied from 0.18 to 0.31 $\text{g NH}_3\text{m}^{-3}$ sewage, with an average of 0.24 $\text{g NH}_3\text{m}^{-3}$ sewage, which is close to the result obtained from lab aeration experiments (0.28 $\text{g NH}_3\text{m}^{-3}$ sewage) (Gu et al., 2012) and the recommended emission factor (0.15 $\text{g NH}_3\text{m}^{-3}$ sewage) by the California Air Toxics Emission Data System (ATEDS) (Coe et al., 1998; Battye et al., 2003). The maximum average emission factors were recorded in February and December when the pH values and TAN concentrations were also relatively high. A possible reason for this is the increase in volatilization of ammonia at high pH values and high TAN concentrations.

The ammonia emission factors reported previously for WWTPs are listed in Table 5, which shows that these values differ significantly from each other. Battye et al. (1994) recommended an emission factor of 2.28 $\text{g NH}_3\text{m}^{-3}$ sewage in a report to the US EPA. However, a much lower emission factor (0.15 $\text{g NH}_3\text{m}^{-3}$ sewage) was used later when Battye et al. (2003) evaluated the ammonia emission inventories. Chinkin et al. (2003), based on actual measurements for the Los Angeles County Sanitation District and the Country Sanitation Districts of Orange County, considered that using the US EPA emission factor would lead to an overestimate of ammonia emissions from WWTPs, and thus recommended an emission factor of 0.014 $\text{g NH}_3\text{m}^{-3}$ sewage. Roe et al. (2004) recommended an emission factor between 0.0032 and 0.020 $\text{g NH}_3\text{m}^{-3}$ sewage in the US EIIP. Zheng et al. (2012) and Yin et al. (2010) used an emission factor of 3.2 $\text{g NH}_3\text{m}^{-3}$ sewage the largest when compared to the others, to develop an ammonia emission inventory in the PRD region, South China. Moreover, the Ministry of Environmental Protection (MEP) in China recommends an emission factor of 0.003 $\text{g NH}_3\text{m}^{-3}$ sewage for WWTPs, which is the smallest of all the reported emission factors of this kind.

Considering the differences in structure, operational conditions, and wastewater quality of WWTPs and in climatic characteristics across China, it would be inappropriate to use only one emission factor. Furthermore, the effect of atmospheric ammonia on particulate air pollution based on such low emission factors might be underestimated, especially in urban areas where WWTPs are an important source of atmospheric ammonia.

Table 5 Ammonia emission factors from various studies, including this one ($\text{g NH}_3\text{m}^{-3}$ sewage)

Year	Location	Emission Factor	References
1994	USA	2.28	Battye et al., 1994
1994	USA	1.93	Battye et al., 1994
2003	USA	0.15	Battye et al., 2003
2004	USA	0.02–0.003	Roe et al., 2004
2010	China	3.2	Zheng et al., 2012, Yin et al., 2010
2012	China	0.28	Gu et al., 2012
2014	China	0.003	PRC MEP, 2014
2016	China	0.24	This study

Based on compiled comprehensive ammonia emission inventories (Zheng et al., 2012; Yin et al., 2010) in the PRD region, WWTPs contribute approximately 34% in the urban PRD region, if only industrial sources (1.6 kt yr^{-1}), sewage treatment (6.4 kt yr^{-1}), waste treatment (3.6 kt yr^{-1}), fuel combustion (2.3 kt yr^{-1}), and on-road mobile source (4.9 kt yr^{-1}) are considered as urban emission sources. That means WWTPs are one of the most important ammonia sources in urban areas and the control of their emissions should be considered a high priority. However, if we incorporate the results from this study, the emissions from WWTPs would be 0.48 kt yr^{-1} , a contribution of only 4%. Therefore, the ammonia emissions from WWTPs possibly were overestimated in previous studies. On the other hand, if we use the emission factor recommended by the PRC MEP, the amount of annual ammonia will be just 0.006 kt yr^{-1} , which accounts for merely 0.05%, making WWTPs quite insignificant sources.

3.5 Sensitivity of emission factor to pH value

Studies have shown that factors, such as pH, temperature, and TAN, have significant effects on ammonia emissions from wastewater (Roe et al., 2004; Bajwa, 2006). The pH strongly influences the

equilibrium between ammonia and ammonium ions in wastewater (Ro et al., 2008). Results of the sensitivity analysis indicated that in the range of average pH values recorded at LD, the sensitivity of ammonia emission rate to pH reached 17.8. The ammonia emission rate sensitivity was 2.71 for changes in water temperature and 1.0 for changes in TAN. Therefore, the sensitivity analysis results suggest that pH had the greatest influence on the rate of ammonia emissions from the wastewater.

The wastewater pH values at LD ranged from 7.08 to 8.27, and within this range, the ammonia concentration increased by a factor of 30 or more. Therefore, knowledge of the pH variation of WWTPs is important for obtaining plant- or region-specific ammonia emission factors, which is crucial for establishment of a reliable high-resolution emission inventory.

To examine the influence of pH on ammonia emission from WWTPs further, the overall emission factors of LD were calculated using WATER9 based on monthly pH values with annual average TAN concentration and temperature of the wastewater. The linear relationship between the calculated overall emission factors and the varied pH values, with a correlation coefficient of 0.85, is shown in Fig. 4. The difference between an emission factor obtained from the fitted equation and one obtained from the WATER9 calculations is within 10%, suggesting that the equation can be used as a simple approach for estimating ammonia emission factors from WWTPs.

Fig. 4 Emission factors versus pH for atmospheric ammonia emissions

4 Implications

WWTPs are relatively concentrated in urban areas where fewer agricultural activities occur. In these areas, ammonia emissions from WWTPs would be important and thus greatly influence the near-surface atmospheric chemistry. Two to three orders of magnitude difference among the available ammonia emission factors for WWTPs may cause huge uncertainty in estimation of atmospheric ammonia emissions. In the present study, based on the US EPA WATER9 model, three-year measurement data, and facility information from a typical WWTP in the PRD region, the overall emission factors were obtained for four wastewater treatment processes (A-B process, UNITANK process, and two slightly different A-A-O processes) that are typically used in South China. The calculated emission factors ranged from 0.15 ± 0.03 to $0.29 \pm 0.06 \text{ g NH}_3 \text{ m}^{-3} \text{ sewage}$, and the average overall emission factor of the WWTP was $0.24 \pm 0.06 \text{ g NH}_3 \text{ m}^{-3} \text{ sewage}$. The results suggest that ammonia emissions from sewage treatment might have been significantly overestimated in previous studies. WWTPs probably only account for approximately 4% of the ammonia emissions in the urban PRD region, much less than the 34% estimated by Zheng et al. (2012). Furthermore, the results indicate that the emission factor should be chosen cautiously when developing an ammonia inventory, and that the contribution of ammonia emissions from WWTPs to particulate air pollution needs reevaluation. With the increases in sewage treatment capacity, policy makers should start regulating the emissions or, at least, improve the emission inventory. More measurement campaigns are required to make the emission factor more precise.

Acknowledgements

This work was supported by the Chinese National Science Foundation (Grant No. 40975077) and Chinese National Key Technology R&D Program (No. 2014BAC21B04). We thank Mr. Dejun Zhao for his assistance with the measurement.

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