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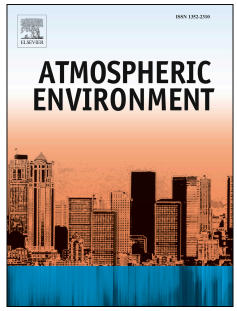

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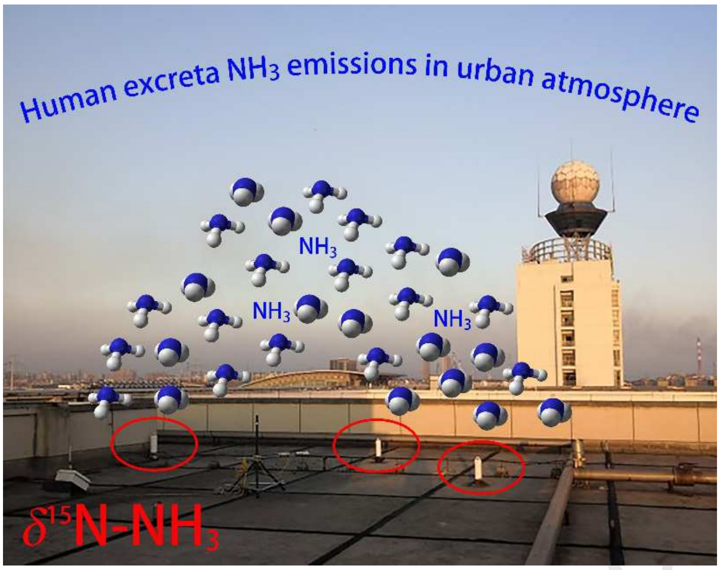
YZ designed the study. SS, YH and YC performed the research. SS analyzed the data. SS, YL and YC wrote the paper, with inputs from YZ, FC, AM.


Human excreta NH3 emissions in urban atmosphere
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Online characterization of a large but overlooked human excreta source of ammonia in China's urban atmosphere

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ABSTRACT

In urban China, human excreta are mostly stored in septic tanks beneath various buildings, and the generated NH_3 are emitted to the atmosphere through ceiling ducts on rooftops. Here we performed highly time-resolved measurements of NH_3 concentrations and auxiliary parameters in the ceiling duct of a typical building complex during different seasons with varying temperature and population, allowing an in-depth investigation of the driving forces in terms of governing NH_3 emissions. Extremely high levels of NH_3 concentration (1013±793 μg m^{-3}) were observed throughout the campaign. Seasonally, the NH_3 concentration during summer vacation (1377±1072 μg m^{-3}) was significantly higher than during school time in fall (796±432 μg m^{-3}) and winter (661±267 μg m^{-3}). Moreover, the diurnal variation of NH_3 during summertime was highly correlated with temperature (R^2=0.95, p<0.01), while it was not the case for school time with dense population (R^2=0.47, p<0.01, R^2=0.57, p<0.01 in fall, winter, respectively). The highest temperature was 35.9 ^oC, with an emission intensity peak of 4.1 mg s^{-1} while the lowest temperature was 1.3 ^oC with an emission intensity of 0.8 mg s^{-1}. The nitrogen stable isotopic composition of NH_3($\delta^{15}N-NH_3$) may be a useful tool to trace NH_3 sources. Here we report the $\delta^{15}N-NH_3$ measured from ceiling duct collected directly, which constrains human excreta source $\delta^{15}N-NH_3$ values ($mean_{min}^{max}$) ‰ to $-35.6‰_{-39.8‰}^{-31.9‰}$. These results support that temperature is the key factor in controlling NH_3 emissions from human excreta and demonstrate the importance of using human excreta emitted $\delta^{15}N-NH_3$ to quantify excreta NH_3 contribution in urban atmospheres. Our findings highlight opportunities to limit NH_3 emissions from human excreta that will bring co-benefits to the air quality and human health in urban China.

Key words: human excreta; ammonia; seasons; emission intensity; isotopic signature

1 Introduction

Gaseous ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. It can be released into the environment from both agricultural and non-agricultural sources. Agricultural NH_3 sources mainly include fertilizer application and livestock production, accounting for over 80 % of the global NH_3 emissions(He et al., 2011; Vitousek et al., 2008). Despite the dominant role of agricultural NH_3 at global or regional scales, non-agricultural NH_3 with miscellaneous sources (e.g., on-road traffic(Chang et al., 2016b; Nowak et al., 2010; Pandolfi et al., 2012), urban green land(Chan and Yao., 2008), NH_3 slips from coal-fired power plants(Pan et al., 2018), wastewater(Häni et al., 2018; Yin et al., 2010) and solid waste(Häni et al., 2018)) exert disproportionately important contributions to the total NH_3 emissions of urban areas. Although non-agricultural sources contribute a small part of the global NH_3 emissions, they are more locally concentrated, particularly on an urban scale. Besides, urban areas are generally featured with NO_x and SO_2 rich atmospheres, gaseous NH_3 partitions is transformed into aerosol phase by reacting with sulfuric and nitric acids; then forms ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$), and ammonium bisulfate (NH_4HSO_4), which are major chemical component of fine particulate matter ($PM_{2.5}$) (An et al., 2019; Butler et al., 2016; Durbin et al., 2002; Su et al., 2016).

A lot of evidence suggests that nonagricultural activities like wastewater treatment (Pennisi et al.,2012; Guo et al., 2020), coal combustion (Fan et al., 2019), solid garbage (Hironori et al., 2011), vehicular exhaust (Zhang et al., 2020), and urban green space are also important sources to ambient NH_3. For example, the emission rate of NH_3 from vehicle exhaust was 1300 tons in Shanghai in 2014, which accounted 12% of total NH_3 emissions in this mega-city (Chang et al., 2019). Yao et al. (Yao et al 2008) suggests that NH_3 from vehicular emissions can be neglected and they proposed that urban green spaces are the dominant contributor to urban atmospheric NH_3 in North American and Northern China. On the other hand, volatilization of digested sludge is another important source of atmospheric NH_3, which accounts for 27% of the total NH_3 emissions in England. Sutton et al. (Sutton et al., 2000) considered NH_3 emission under sludge injection as 75% less than spreading. In addition, Pan et al.(Pan et al., 2018) suggests that coal-fired power plants is an crucial source of NH_3 at urban site with a contribution as high as 16%. This clearly indicates that the non-agricultural emissions and sources of NH_3 deserve a more comprehensive discussion in the scientific community.

It has been documented that NH_3 emissions from human excrement exist all over the world(Chang et al., 2015; Sutton et al., 2000), and in most developed countries, including their rural areas(Healy et al., 1970; Williams, 2005). But unlike Europe or the U.S, human excrements are mostly stored in septic tanks beneath various buildings in Chinese cities. Human excrements that are stored in septic tanks are not directly discharged into sewer pipes, but are discharged into the atmosphere through a ceiling duct connected to the roof(Driscoll et al., 2003). Therefore, human excrements from urban buildings in China may be a significant source of NH_3 emission. As a product of microbial decomposition in septic tanks due to prolonged septic tanks, a large amount of gas (including NH_3) in the septic tank is directly released into the atmosphere through the ceiling duct on the roof. This unique and potentially important source of NH_3 in Chinese cities has received little attention in previous studies (Chang et al., 2015).

The application of stable nitrogen (N) isotopes as a potential tracer of origin of NH_3 has been proposed (Elliott et al., 2019), which might help constrain regional NH_3 budgets. Zhang et al. (2007) has been proven very helpful for characterizing NH_3 emission sources(Chang et al., 2016a; Felix et al., 2013b; Ti et al., 2018). For example, field-observed $\delta^{15}N$ signatures of NH_3 emitted from volatility-driven sources (i.e., -31.7‰ to -27.1‰, -30.8‰ to -26.9‰, and -51.2‰ to -47.1‰ for livestock, waste, and fertilizer) are distinct from combustion-related sources (i.e., -10.21‰ to 0.20‰), highlighting the potential of N isotope measurements to trace agricultural versus non-agricultural NH_3 emission sources, especially in urban areas(Chang et al., 2016a; Chang et al., 2019a; Felix et al., 2017). One challenge, however, is that the large variability of the observed $\delta^{15}N$-NH_3 values, may partly reflect the influence of atmospheric processes (not solely the emissions source) that are associated with N isotope fractionation(Walters et al., 2019; Walters and Hastings, 2018). Indeed, once released into the atmosphere, NH_3 undergoes a number of potential physical (e.g., deposition) and chemical processes (e.g., particle nucleation and condensation) that can alter their primary isotopic “fingerprints” and the isotopic composition of their reaction products (e.g., aqueous and solid NH_4^+)(Altieri et al., 2014; Asman et al., 1998; Hastings et al., 2013; Xiao et al., 2012).

NH_3 can be detected by both active and passive sampling (Anderson et al., 2013; Chang et al., 2016b; Meng et al., 2011; Ru-Jin et al., 2014; Wentao et al., 2011). Previously, passive sampling methods have reported extremely high concentrations of NH_3 in the ceiling ducts of various buildings in the urban areas(Chang et al., 2015). However, the emission mechanism behind those high concentrations and the emission intensity have not been carefully studied. The current passive sampling methods suffer from several weaknesses including but not limited to low time resolution. The collected passive samples cannot be stored for a long time because of contamination (M.J Roadman, et al., 2003). To this end, this study uses an online instrument that is capable of continuously monitoring NH_3 concentrations emitted from the ceiling duct, with high time resolution (1 hour) and a high degree of accuracy.

In this research, a typical ceiling duct in a teaching building with varying population and temperature are selected to thoroughly investigate its NH_3 emission characteristics and potential driving factors. During the summer vacation, there are fewer human activities in the teaching building and temperature is much higher compared to those of school time. This study aims at clarifying the relationships between the different factors and providing a theoretical basis for clearing NH_3

emission channels of Chinese characteristics and quantifying the atmospheric human excreta sources of NH_3 in urban atmospheres.

2 Materials and methods

2.1 Site description

Measurements of human excreta-emitted NH_3 were performed in a ceiling duct on the rooftop of a six-floor teaching building in Nanjing (Fig. 1a), a typical megacity in eastern China. The teaching building (Wendelou or WDL in short; 32.20°E, 118.42°N) is located on the campus of Nanjing University of Information Science and Technology (NUIST), which has 248 classrooms, 62 toilets, and 1 septic tank (60 m^3 in volume). The septic tank for human excreta was built in the bottom of WDL. In total, there are four ceiling ducts (16 cm in diameter and length about 20 m) on the rooftop, connected with the septic tank. (Fig. 1b).

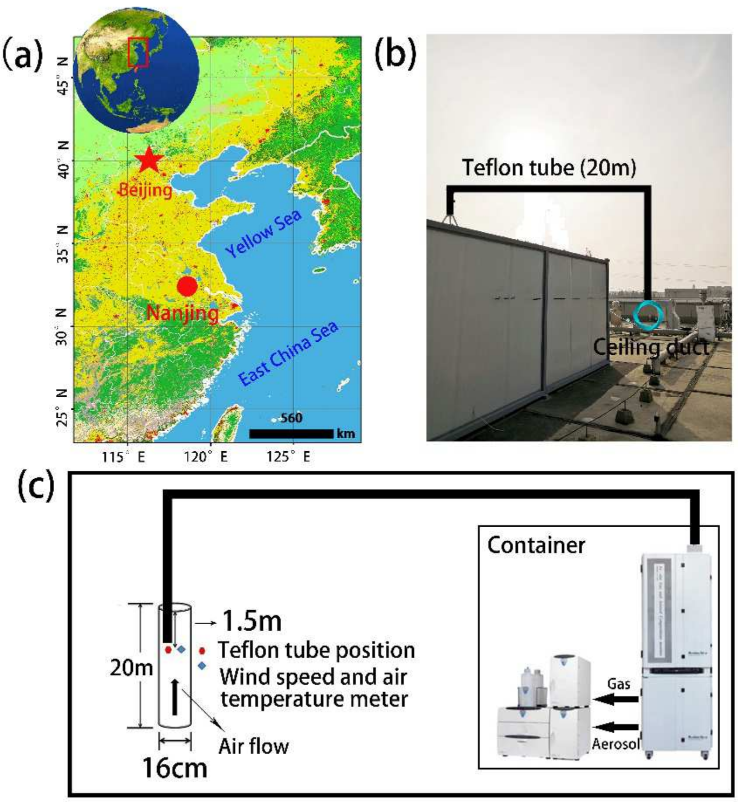

Figure 1. The location of Nanjing city (a). Field picture of instruments set-up on the rooftops of WDL (b). A sketch of the collection between ceiling duct and IGAC instrument (c).

2.2 NH_3 measurements

The sampling campaign was conducted from July to December 2018. The hourly NH_3 measurements in the ceiling duct were divided into three periods, i.e., vacation time in summer (14/7 14:00 to 20/7 19:00; high temperature and almost no people), school time in fall (6/9 12:00 to 17/9 9:00; relatively low temperature and dense population), and school time in winter (6/12 10:00 to 8/12 12:00; very low temperature and dense population), with the aim to identify the driving forces controlling NH_3 emissions from human excreta. As a comparison, ambient NH_3

concentrations were also measured during three periods, i.e., 1:00 21/7 to 9:00 27/7, 1:00 18/9 to 1:00 28/9, and 19:00 2/12 to 23:00 4/12.

Hourly NH_3 concentrations were measured by an In-situ Gas and Aerosol Compositions monitor (IGAC; Fortalice International Co; Taiwan). Specifically, the IGAC platform is composed of three subsystems: a particle collection unit, an annular denuder, and an ion chromatograph analyzer (IC)(Tian et al., 2017). Air was pumped into a sharp-cut cyclone operating at a flow rate of 16.7 L min^{-1}. The air was drawn through the annular denuder which wetted with dilute H_2O_2 solution. The aerosol-collecting device, a Rapid Capture Fluid Particle (PCFP), was placed downstream of the denuder. It employs the mechanism of wet scrubbing, particle condensation growth, and impaction to capture particles. The gas and aerosol liquid extracts from denuder and PCFP are subsequently injected into the two ICS once an hour for cations and anions. Since the sampling Teflon tube was directly placed into the exhaust vent of the ceiling duct (see in Figure S2), the interference of the ambient air is eliminated. The NH_4^+ concentration is a low in the pre-experiment so it ignored here. The performance of IGAC has been widely validated in previous work(Chang et al., 2007; Young et al., 2016).

The exhaust vent of the ceiling duct and the $PM_{2.5}$ cutting head of the IGAC were connected by a Teflon tube (6.5 mm in diameter and length about 20 m) (Fig 1c). To avoid potential interference from the ambient atmosphere, the Teflon tube was inserted into the exhaust tube (1.5 m in length). The sampling site of the ambient atmosphere is located at the same location (Figure S1 and Figure S2). The cutting head is transformed into the sampling of the ambient atmosphere, and the system was cleaned once after the transformation.

Meteorological parameters including relative humidity, temperature, wind speed, and wind direction, were hourly observed by a co-located Met station one (HMP155 U.S) at the same building.

2.3 NH_3 emission intensity

The NH_3 emission intensity (EI) is the mass of the substance discharged per unit time. Since the concentration in the ceiling duct is greater than the concentration in the ambient atmosphere and the septic tank is constantly releasing gas, the ceiling duct can be regarded as a one-way passage of NH_3 from the septic tank to the ambient atmosphere. The amount of NH_3 discharged from the septic tank to the ambient atmosphere via the ceiling duct per unit time is expressed in mg hr^{-1}. Accordingly, the EI based on the flow transmission flux can be established. Specifically, for a particular building, the NH_3 EI of urban human settlements building is related to the air flux (indicated by wind speed), sampling time, and NH_3 concentration in the ceiling duct:

$$\mathrm{EI} = \pi \times r^2 \times C \times \frac{W \times 3.6 \cdot 10^3}{1 \cdot 10^3} \quad (1)$$

Where EI is the emission intensity (mg NH_3 hr^{-1}); r represents the inner diameter of the ceiling duct (0.08 m); C represents hourly average NH_3 concentration in the ceiling duct (μg m^{-3}); W stands for the wind speed (m s^{-1}) inside the ceiling duct; $1\cdot10^3$ represents the coefficient of mass unit converted from μg to mg; $3.6\cdot10^3$ is a constant, which is converted from second to hour.

In order to quantify the discharge flux of the ceiling duct and calculate the emission intensity, the WFWZY-1 universal wind speed recorder was also placed in the ceiling duct (1.5 m from the exhaust vent; Fig. 1c) to measure the interior wind speed per second. The accuracy of the measurements of wind speed is 0.01m s^{-1}.

2.4 Nitrogen isotopic analysis

A newly developed chemical method for $\delta^{15}N$-NH_4^+ of low NH_4^+ samples was used in the current work. The detailed analytical procedures are given elsewhere (Liu et al., 2014). Briefly, this method is based on the $\delta^{15}N$ isotopic analysis of N_2O, which is much less abundant in the atmosphere than N_2 and thus causes minimal atmospheric contamination. The filtered samples were firstly extracted with ultra-pure water (18.2 MΩ cm). Concentrations of NH_4^+ were then analyzed using an ion chromatographic system (883 Basic IC plus, Metrohm Co., Switzerland) equipped with a Metrosep C4/4.0 cation column. In this analysis, we used 1.0 mmol L^{-1} HNO_3+0.5 mmol L^{-1} pyridine dicarboxylic acid as eluent and the detection limit of NH_4^+ was 0.0028 mg L^{-1}. After the measurement of the NH_4^+ concentration, the extracted sample was oxidized to NO_2^- by hypobromite (BrO^-) in a vial. NO_2^- was then quantitatively converted into N_2O by hydroxylamine (NH_2OH) under strongly acid conditions. The produced N_2O was subsequently analyzed $\delta^{15}N$- N_2O by a purge and cryogenic trap system (Gilson GX-271, IsoPrime Ltd., Cheadle Hulme, UK) coupled to an IRMS (PT–IRMS) (IsoPrime 100, IsoPrime Ltd., Cheadle Hulme, UK) at the Yale-NUIST Isotope Atmoschemistry Lab for N isotopic analysis within one month.

Isotope ratio values are reported in parts per thousand relatives to atmospheric N_2 as follows:

$$\delta^{15}N(100\%) = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{N_2}}{(^{15}N/^{14}N)_{N_2}} \times 1000 \quad (2)$$

Three international standards (IAEA N1, USGS 25, and USGS26 with $\delta^{15}N$ values of +0.4, −30.4, and +53.7 ‰, respectively) were used to correct the reagent blank and drift during isotope analysis. The standard deviation of $\delta^{15}N$ measurements is less than 0.3 ‰.

To minimize isotope fractionation of $\delta^{15}N$-NH_3 during the sampling process, an active sampling method was used to collect NH_3 samples from the ceiling duct emission source. Due to the high concentration of emission sources, active sampling (absorption efficiency is close to 100%) was conducted from the source to avoid interference from the external environment. In the preliminary experiment, the other ion concentration was lower than the blank approximation, which can be ignored. Therefore, this method also applies to the collection of vehicle exhaust, biomass combustion and other samples (Pan et al 2018, Chang et al 2016). On the other hand, human excreta samples were collected using a modified version of the United States Environmental Protection Agency (US EPA) Method 7. Briefly, human excreta samples were collected by a double-pneumatic air sampler (flow rate ~ 2 L min^{-1}), which contain two 25 ml borosilicate bottles. When collection NH_3 samples emitted from the ceiling duct, the sampler was placed near the exit (~1.5m) of the ceiling duct and each sampling was conducted for 2 hours in summer (i.e., 6:00-8:00, 12:00-14:00, 18:00-20:00, for three days; n=9) and winter (i.e., 6:00-8:00, 12:00-14:00, 18:00-20:00, for two days; n=6). The sampling bottles contained 15 mL 0.05 mol L^{-1} H_2SO_4 as NH_3 absorbing solution. During the sampling process, NH_3 would be absorbed by acidic solution. After sampling, the samples were sent back to the laboratory and conditioned for 5 days. During the conditioned process, the samples have to be shook 3-5 times per day to facilitate the conversion of NH_3 to NH_4^+. After that, the NH_4^+ concentration in the absorbing solution was determined using an ion chromatography (Thermo Fisher Scientific, Sunnyvale, USA) and the $\delta^{15}N$ were analyzed by the IRMS as mentioned above.

3 Results and discussion

3.1 Human excreta as an important NH_3 source to influence ambient NH_3

As depicted in Fig. 2, 863 hourly NH_3 concentrations were successfully measured throughout the sampling campaign, 449 and 414 were measured inside and outside the ceiling duct, respectively. The NH_3 concentrations ($\text{mean}_{\text{min}}^{\text{max}} \pm 1\sigma$) we measured in the ceiling duct ($1013_{123.6}^{4304.9} \pm 793$ μg m^{-3}) were two to three orders of magnitude higher than that of the ambient air ($15.6_{4.6}^{37.2} \pm 5.6$ μg m^{-3}), indicating that human excreta are an important source of NH_3. Our results are consistent with Chang et al. (2015) that also reported extremely high concentrations of NH_3 in the ceiling ducts of various buildings across Shanghai ($1128_{148.0}^{5937.0} \pm 404$ μg m^{-3} in summer). Given that septic tanks are a dominant sanitation system in urban China, human excreta thus can be regarded as a ubiquitous NH_3 source in China's urban atmospheres.

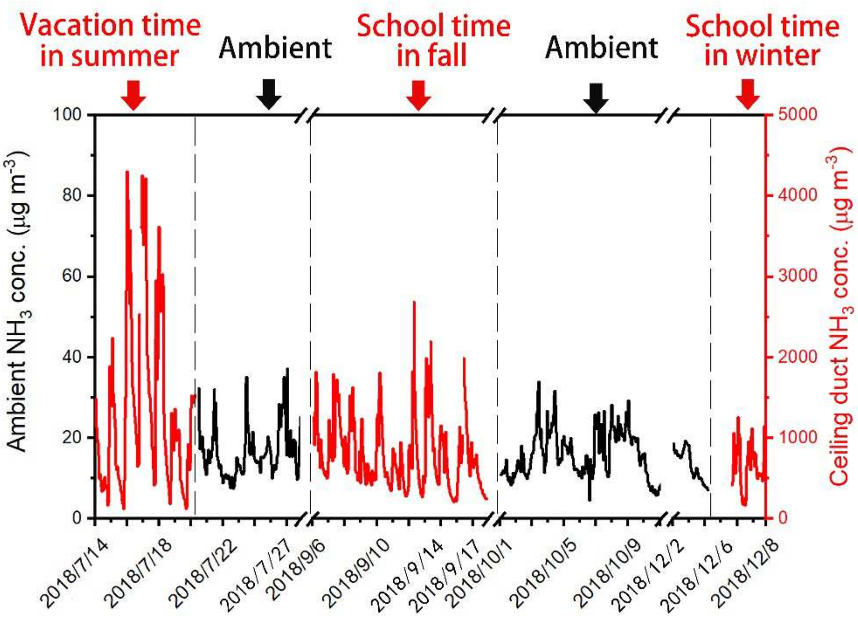

Figure 2. The overall change in NH_3 concentration (yyyy/mm/dd) (Red is the NH_3 concentration in the ceiling duct, blank represent the NH_3 concentration on ambient).

Using a variety of chemical, physical, and optical techniques, there is an increasing number of studies in terms of investigating the influences of NH_3 source emissions (e.g., livestock waste, fertilizer application, traffic, industrial processes) on ambient

NH_3 concentrations in China (Table 1). Although the main source of NH_3 is agriculture, field monitoring results in Table 1 show that the concentrations of NH_3 in urban areas are generally higher than that in rural areas, indicating that urban areas are a hot spot of NH_3 emissions. In the present study, the average ambient NH_3 concentration (mean±1σ) measured at WDL was 15.6±5.6 μg m^{-3}, which is not only higher than all the sites in rural areas but higher than most sites in urban areas. Previous studies suggested that on-road traffic and NH_3 slip from the coal-fired power plant are the major non-agricultural sources contributing to the high levels of NH_3 in urban atmospheres. However, both performed in Nanjing, our measured NH_3 concentration at WDL was much higher than that measured in downtown area(Pan et al., 2018; Wang et al., 2016; Zheng et al., 2015). Moreover, the NH_3 concentrations measured at the roadside and industrial sites were less than half of our measured NH_3 concentration. We thus infer that the high NH_3 concentration at WDL can be attributed to the strong influence of NH_3 emissions from the ceiling duct.

Table 1. Ambient NH_3 concentration measurements in China

Location	Period	Land use types	methodology	Time resolution	NH_3 (μg m^{-3})	Reference
WDL, Nanjing	7-12/2018	urban	IGAC	hourly	15.6±5.6	This study
Nanjing	6-7/2015	urban	MARGA	monthly	9.5	(Pan et al., 2018)
Nanjing	8-11/2012	urban (near industrial)	HRTOF-CIMS	1 Hz	1.3±1.8	(Zheng et al., 2015)

Nanjing	7-8/2013	urban (near road)	Portable NH_3 online detector	Hourly	6.7	(Wang et al., 2016)
Beijing	2/2009-7/2009	urban	Ogawa	weekly	18.1±13.8	(Meng et al., 2011)
Shanghai	4/2014-7/2015	urban	MARGA	weekly	6.4±2.3	(Chang et al., 2019b)
Guangzhou	11/2010	urban	OP-DOAS	2.5 min	1.6	(Wang et al., 2012)
Guangzhou	9-11/2015	urban	Diffusive sampler	monthly	4.9	(Pan et al., 2018)
Shanghai	4/2014-4/2015	urban	MARGA	hourly	5.6±3.9	(Chang et al., 2016a)
Tianjin	6-8/2015	urban	Diffusive sampler	monthly	14.5	(Pan et al., 2018)
Chengdu	6-8/2015	urban	Diffusive sampler	monthly	10.5	(Pan et al., 2018)
Xian	4/2006-4/ 2007	urban	Ogawa	daily	12.9	(Zhang et al., 2002)
Huanjiang	2-3/2015	background	Diffusive sampler	monthly	3.6	(Pan et al., 2018)
Changzhou	2-3/2015	suburban	Diffusive sampler	monthly	6.0	(Pan et al., 2018)
Linze	3-5/2015	rural	Diffusive sampler	monthly	3.7	(Pan et al., 2018)
Beijing	8-9/2015	rural	ALPHA	daily	14.0±1.6	(Xu et al., 2015)
Shanghai	4/2014-7/2015	rural	MARGA	weekly	5.1±3.1	(Chang et al., 2019b)
Linyi	8-12/2015	rural	ALPHA	daily	5.5	(Xu et al., 2015)
Baoding	8-12/2015	rural	ALPHA	daily	11.8	(Xu et al., 2015)

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278 **3.2 Driving factors in controlling NH_3 concentrations in the ceiling duct**

In order to further understand the driving factors controlling NH_3 emissions in the ceiling duct, the whole sampling campaign was divided into three periods with varying temperature and population to compare their NH_3 concentrations and emission rates. The time-series variations of NH_3 concentrations in and out of the ceiling duct during different periods are illustrated in Figure 2, in which most NH_3 concentration spikes were concentrated in the summertime. Specifically, the highest NH_3 concentration (4304.9 μg m^{-3}) has occurred 17/7 12:00 when temperature also reached at a very high level (37 ^{o}C). During summer vacation, apart from the on-duty staff, there were almost no other people to use the toilet. Thus, NH_3 emissions in this period were largely driven by temperature rather than human activities. In Table 2, the descriptive statistics of all measured parameters in different periods are reported, in which the average NH_3 concentrations both in and out of the ceiling duct were the highest during summer, followed by that during fall and winter. This is also the case for NH_3 emission intensity in the ceiling duct and ambient temperature. These results highlight the importance of temperature in terms of controlling NH_3 emissions from a ceiling duct.

Table 2. Comparison of NH_3 concentration and temperature in and out of the ceiling duct during different periods.

		Time	**T (□)**	**NP[a]**	**NH_3 (μg m^{-3})**	**N[b]**	**EI[c] (mg hr^{-1})**
Vacation in summer	Ceiling duct	2018.7.14 13:00- 2018.7.20 19:00	31.8±2.8	1-2	1377±1072	151	3.6±1.8

	Ambient	2018.7.21 1:00-2018.7.27 9:00	30.1±2.8	/	17±7	151	/
School time in fall	Ceiling duct	2018.9.6 12:00-2018.9.17 9:00	24.5±2.3	1000-1200	796±432	247	2.5±1.3
	Ambient	2018.10.1 1:00-2018.10.11 1:00	21.1±3.2	/	16±6	212	/
School time in winter	Ceiling duct	2018.12.6 10:00-2018.12.8 12:00	2.4±2.5	1000-1200	661±267	51	2.2±1.1
	Ambient	2018.12.2 19:00-2018.12.4 23:00	11.7±2.6	/	12±3	53	/

Notes: a: Estimated number of people at the WDL. b: The number of samples. c: Emission intensity

In our study, hourly observations of NH_3 concentrations in the ceiling duct over long-term periods offer a unique opportunity to provide robust diurnal profiles, which can be used to further examine the effects of natural and anthropogenic factors in terms of influencing NH_3 emissions. Figure 3 depicts the diurnal variations of NH_3 concentration and temperature measured during different periods in the ceiling duct. Different from the results measured during fall and winter, the diurnal profile of NH_3 concentration during summer shows a unimodal variation, with the maximum occurred on 13:00 (Fig. 3a), which is generally consistent with the variation of temperature. Indeed, Fig. 3b reveals that, NH_3 concentrations in the ceiling duct were highly correlated with temperature (r^2 = 0.95), confirming that without the interference of people using the toilet, the temperature is almost the only factor in terms of controlling NH_3 emissions from human excreta during summertime.

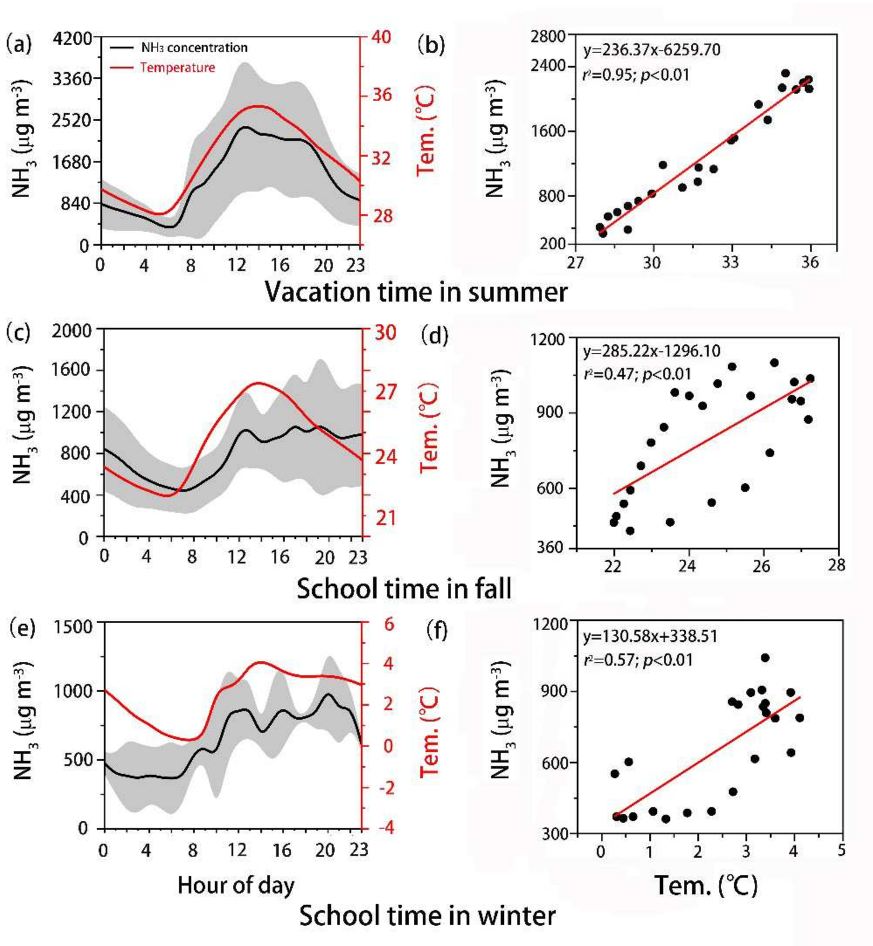

Figure 3. Diurnal variations of the average NH_3 in the ceiling duct and ambient temperature and their correlation analysis during vacation in summer (a and b), school time in fall (c and d), and school time in winter (e and f) (the gray shaded area represent the range of observed values during each period).

Correlation analysis between NH_3 concentration and temperature during fall (Fig. 3d) and winter (Fig. 3f) also suggest a potentially important influence of temperature. However, increased from 8:00, their diurnal profiles of NH_3 characterized by relatively flat variation at a high level during the afternoon. This can be explained the intensive using of toilets during school time, indicating that human activities can be another important factor in terms of controlling NH_3 emissions from human excreta. Nevertheless, their NH_3 concentrations were still significantly lower than that during summer. Therefore, the temperature is the most important factor in regulating NH_3 concentrations in the ceiling duct.

3.3 Temperature-driven variability in NH_3 emission intensity

As discussed above, NH_3 concentrations in the ceiling duct are mainly controlled by temperature. However, NH_3 emission intensity (EI) is the function of NH_3 concentration and wind speed in the ceiling duct. Therefore, it is not clear if NH_3 EI is also governed by temperature. Fig. 4 illustrates the diurnal profiles of NH_3 EI from the ceiling duct, wind speed in the ceiling duct, and ambient temperature, during different periods. Among the three periods, on the whole, the emission intensity of all three seasons showed a trend of fluctuation and increase after 8:00 am, and gradually decreased with the change of seasons. NH_3 EI varied within the largest ranges during the vacation in summer (Fig. 4a), followed by the school time in fall (Fig. 4b) and winter (Fig. 4c). Among each period, there was also a larger variation range during daytime than during nighttime. As shown in figure 4, the correlation coefficients between (R^2) emission intensity and temperature were 0.69 (p<0.01), 0.49 (p<0.01) and 0.62 (p<0.01) in summer vacation, school time in fall and school time in winter, respectively. Previous work has proven that temperature was an important factor that effected NH_3 emission from waste slurries (Génermont, S., and P. Cellier et al., 1997), wind speed on aerodynamic conductance (Roelle, P.A et al., 2002; Beuning, J.D et al., 2008.) and the effects of temperature on volatilization through the Henry constant (Montes, F et al., 2009). In this work, emissions peak of NH_3 (EI up to 4.1 mg s^{-1}) was found at 13:00-15:00 in summer vacation. Meanwhile, higher levels of temperature (35.9 ^{o}C) was also observed during this time. Thus, the high NH_3 EI was due to high temperature, which was favorable for microbial activities in the septic tanks, leading to more production of NH_3. We estimated based on the emission intensity, these data suggest that emissions of NH_3 from human excreta for urban population of ~8 million people in Nanjing contribution 1289 Mg NH_3 annually to the atmosphere within the city, which correspond to 8.9% of the total NH_3 emission in the Nanjing urban areas.

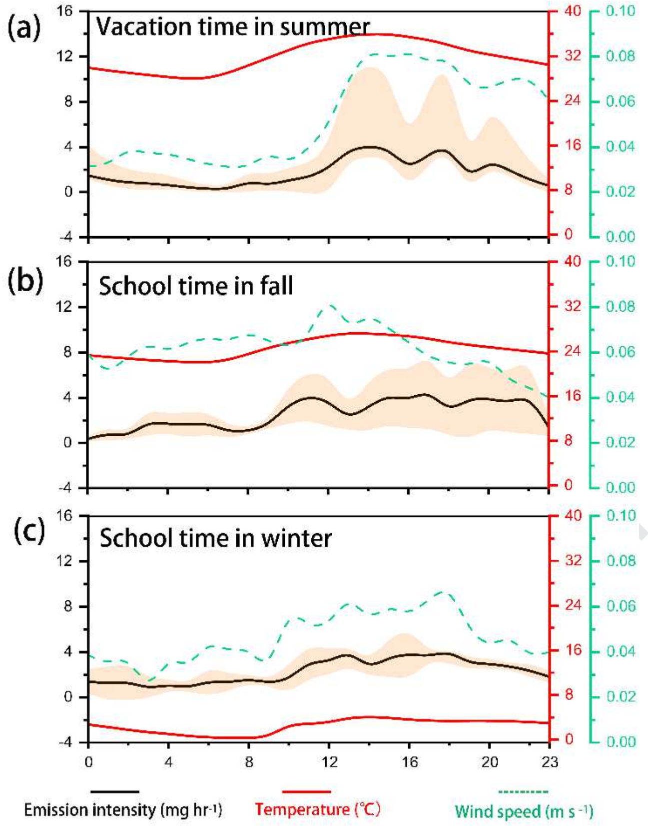

Figure 4. Emissions intensity comparison in Summer (a) /Fall(b)/Winter(c). Emission intensity is calculated from the average hourly ammonia concentrations and wind speed measured in the ceiling duct

3.4 δ^{15}N values of human excreta NH_3

Using δ^{15}N as a tool to discriminate the contribution of various sources to ambient NH_3 requires well-representative isotopic signatures of NH_3 emission sources. Direct ceiling duct measurements of human excreta allow us to evaluate δ^{15}N-NH_3 without interference from other NH_3 sources. The δ^{15}N-NH_3 from human excreta samples (15 in total) greatly varied from -39.8 to -32.3‰ in summer (n=9), -37.9 to -31.9‰ in winter (n=6) where the NH_3 concentration ranged from 224 to 1450 μg m^{-3}, 321.3 to

646.5 μg m^{-3} and the average δ^{15}N value ($\bar{x} \pm 1\sigma$) of ceiling duct emitted NH_3 was -36.9 ± 2.5‰, -33.7 ± 2.2‰, respectively. There is no significant correlation was found between δ^{15}N values and ambient temperature in summer (R^2=0.18,$P > 0.05$) and winter (R^2=0.11,$P > 0.05$), indicating that δ^{15}N-NH_3 at the receptor site was not influenced by ambient temperature. In other words, the emission source (ceiling duct) was likely the main factor to control δ^{15}N in atmospheric NH_3. The δ^{15}N-NH_3 values of human excreta emissions collected in this study are similar to the livestock waste (Freyer, 2010; Hristov and Huhtanen, 2009; Lynch et al., 2006), Due to different sampling methodology, there may be differences in δ^{15}N-NH_3. For different NH_3 emission sources, the fluctuation of its δ^{15}N-NH_3 is in a certain range (Figure 5) (livestock waste (-43‰ to -9‰)). NH_3 emitted from volatilized sources has relatively low δ^{15}N values, allowing them to be distinctly differentiated from NH_3 emitted from human excreta sources that are characterized by relatively high δ^{15}N values (Heaton, T.H et al., 1986).

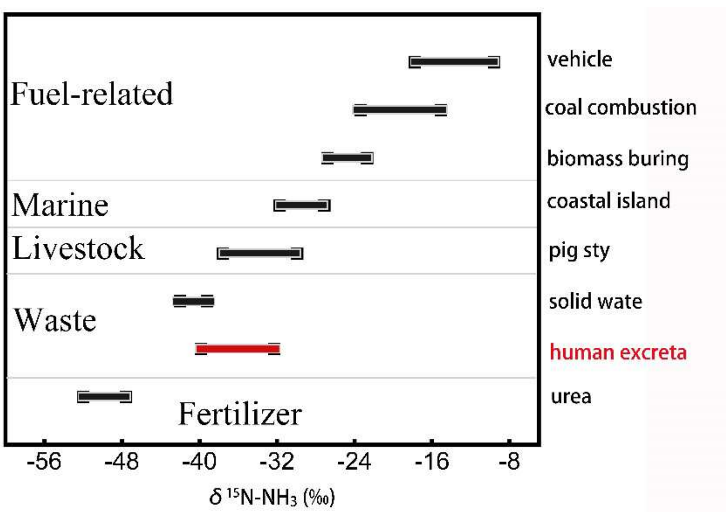

Figure 5. The $\delta^{15}N-NH_3$ values in five different NH_3 emission sources. In this figure, $\delta^{15}N-NH_3$ of human excreta are obtained in this work and others are acquired form the literatures.

As a comparison, the $\delta^{15}N$ values of human exhaust and other various NH_3 sources were compiled and their variation ranges are reported by Felix(Felix et al., 2013a). These NH_3 sources can be classified into four categories based on their $\delta^{15}N$ values and initial characteristics (Figure 5), i.e., fertilizer, waste, livestock, marine, and fuel-related sources. The distribution of their variation ranges comes to a conclusion: NH_3 emitted from vehicle exhausts has the highest $\delta^{15}N$ values, allowing them to be distinctly differentiated from NH_3 emitted from other sources (especially volatilization-related sources). Therefore, we confirm that ceiling duct measurements of $\delta^{15}N-NH_3$ values can be ideally considered as the isotopic signature of human excreta source. Collectively, the distinct $\delta^{15}N$ values of excreta-emitted NH_3 determined in this study can be used as a representative endmember of human excreta source to discriminate the contribution of livestock waste to ambient NH_3 in urban atmospheres.

4 Conclusions

This paper presents detailed results of NH_3 concentrations and auxiliary parameters in the ceiling duct of a typical building complex during different seasons with varying temperature and population. High concentrations of NH_3 were observed in and out of the ceiling duct with high time resolution, confirming human excreta is a ubiquitously important source of NH_3 in urban China and may strongly affect ambient NH_3 concentrations. Further studies found that the NH_3 concentration during summer vacation (1377±1072 μg m^{-3}) was significantly higher than that of school time in fall (796±432 μg m^{-3}) and winter (661±267 μg m^{-3}). Our findings show that temperature as the most important factor in terms of controlling NH_3 concentrations in the ceiling duct. This can be explained by the fact that a high temperature could facilitate the microbial decomposition of human excreta in the ceiling duct. Furthermore, High NH_3 emission intensity was also observed in the ceiling duct and mainly governed by temperature. Using direct ceiling duct measurements, we shows that the amount of NH_3 emission determines the expected range in δ^{15}N-NH_3. Our approach constrains human excreta source δ^{15}N-NH_3 values ($mean_{min}^{max}$) to $-35.6‰_{-39.8‰}^{-31.9‰}$. This result particularly relevant for tracing sources and transport of NH_3 that contribute to ammonium salt formation in urban environments. Given the importance of human excreta-emitted NH_3 in China's urban areas, we urge the scientific community to modify ceiling ducts so that they do not influence NH_3 measurements.

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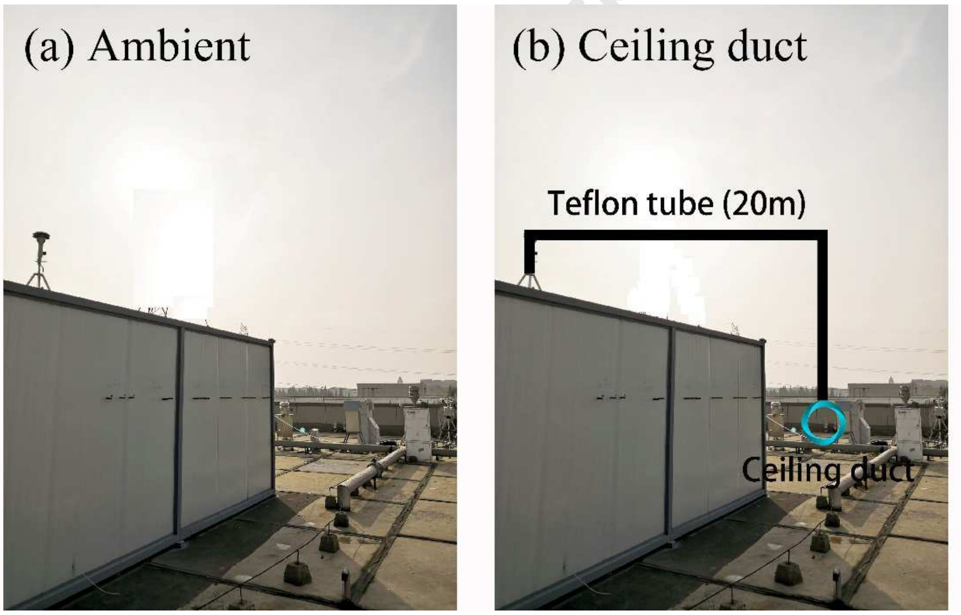

Figure S1. Field picture of instruments set-up on the rooftops of WDL.

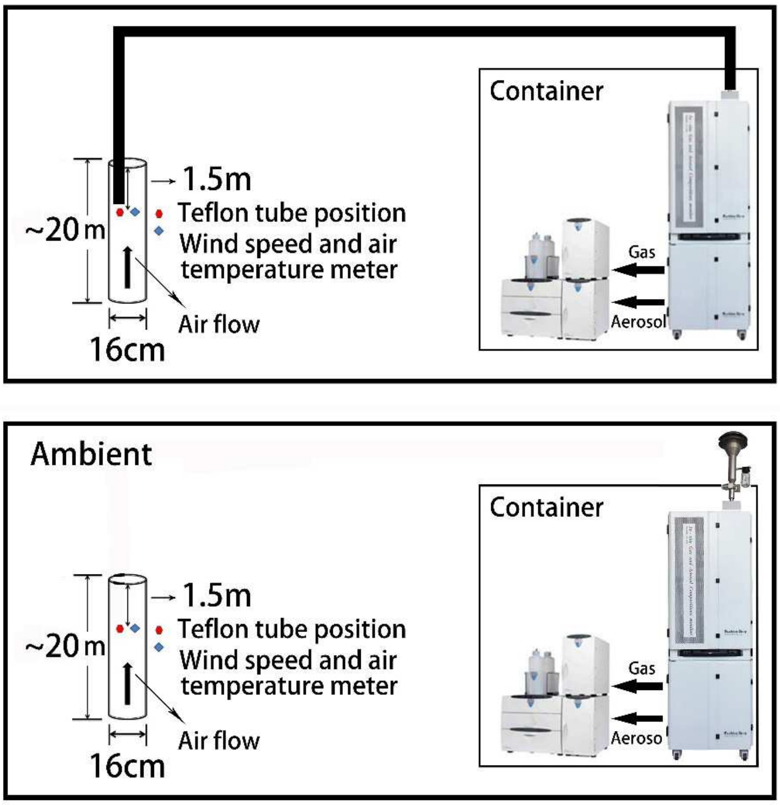

Figure S2. A sketch of the collection between ceiling duct and IGAC instrument.

Highlights

1. We performed highly time-resolved measurements of NH_3 concentrations and auxiliary parameters in the ceiling duct of a typical building

2. Temperature is the key factor in controlling NH_3 emissions from human excreta.

3. Here we report the $\delta^{15}N$-NH_3 measured from ceiling duct collected directly.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: