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Development and uncertainty analysis of a high-resolution NH_3 emissions inventory and its implications with precipitation over the Pearl River Delta region, China

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Abstract. Detailed NH_3 emission inventories are important to understand various atmospheric processes, air quality modeling studies, air pollution management, and related environmental and ecological issues. A high-resolution NH_3 emission inventory was developed based on state-of-the-science techniques, up-to-date information, and advanced expert knowledge for the Pearl River Delta region, China. To provide model-ready emissions input, this NH_3 emissions inventory was spatially allocated to 3 km × 3 km grid cells using source-based spatial surrogates with geographical information system (GIS) technology. For NH_3 emissions, 9 source categories and 45 subcategories were identified in this region, and detailed spatial and temporal characteristics were investigated. Results show that livestock is by far the most important NH_3 emission source by contributing about 61.7 % of the total NH_3 emissions in this region, followed by nitrogen fertilizer applications (∼ 23.7 %) and non-agricultural sources (∼ 14.6 %). Uncertainty analysis reveals that the uncertainties associated with different sources vary from source to source and the magnitude of the uncertainty associated with a specific source mainly depends on the degree of accuracy of the emission factors and activity data as well as the technique used to perform the estimate. Further studies should give priority to the hog, broiler, goose subsectors of the livestock source and N fertilizer application source in order to reduce uncertainties of ammonia emission estimates in this region. The validity of the NH_3 emissions inventory is justified by the trend analysis of local precipitation compositions, such as pH values, the $Ca^{2+}+NH_4^+/SO_4^{2-}+NO_3^-$ ratios, and NH_4^+ concentrations which are directly or indirectly related to NH_3 emissions.

1 Introduction

Atmospheric ammonia (NH_3), which participates in the cycle of nitrogen (Sanhueza, 1982), is associated with several environmental issues, such as acid deposition (Pearson and Stewart, 1993), low-visibility (Battye et al., 2003), soil acidification (Asman et al., 1998), eutrophication (Erisman et al., 2003), and greenhouse effect (Hellsten et al., 2008) directly or indirectly. As the primary alkaline gas, NH_3 reacts with H_2SO_4 and HNO_3 to form ammonium sulfate and ammonium nitrate (Pinder et al., 2007), which are important constituents of airborne fine particulate matter ($PM_{2.5}$). These reactions and products determine the chemical compositions of dry and wet depositions.

Much effort has been made to understand NH_3 impacts on the formation of fine particulate matter in the atmosphere and wet depositions (Asman, 2001; Pavlovic et al., 2006; Pinder and Adams, 2007; Quan et al., 2008). These studies intensely rely on detailed inventories of precursor emissions (such as SO_2, NO_x, VOCs, NH_3, etc.), including their magnitudes, temporal and spatial characteristics, which are also

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indispensable components in formulating control policy for regional air pollution management using air quality models.

The Pearl River Delta (PRD) region locates in southern China with a special landscape surrounded by hills and coastlines with typical subtropical climate. Due to rapid economic development, quick industrialization and urbanization, regional air pollution problems such as acid rain, photochemical smog characterized by high concentrations of ozone (O_3) and haze characterized by high concentrations of $PM_{2.5}$ (Shao et al., 2006; Zhang et al., 2007; Liu et al., 2008) have emerged in this region. It has been a popular research topic to investigate and understand the pollution formation and its characteristics in this region in the past decade using field observations and modeling approaches (Wang et al., 2005; Wu et al., 2006; Streets et al., 2006; Chen et al., 2009; Kwok et al., 2010). Recent field studies have shown that $PM_{2.5}$ is associated with high level of ammonium concentrations in the atmosphere in this region (Lai et al., 2007; Niu et al. 2006; Hu et al., 2008). However, due to lack of a reliable and model-ready NH_3 emission inventory, few studies have reported how ammonia emissions may impact the $PM_{2.5}$ formation and acid deposition in this region using a modeling approach.

Emission inventories are indispensable information for understanding pollution formation and formulating control strategies. There are already model-ready regional emission inventories available for primary pollutants such as SO_2, NO_x, PM_{10}, CO and VOCs covering various emission sources in the PRD region (HG-JWGSDEP, 2005; Zheng et al., 2009b; He et al., 2011). Although a few ammonia emission inventories were developed for the PRD region (HG-JWGSDEP, 2005; Yang, 2008; Yin et al., 2010) in the past few years, these inventories are bulk annual emissions, lack spatial and temporal information, and typically cover part of ammonia emission sources. Furthermore, uncertainties in compiling and developing these inventories are not characterized and quantified. Therefore, current ammonia inventories are incapable of supporting air quality models to investigate the effects of ammonia emissions and its uncertainty on the formation and transport of $PM_{2.5}$ and acid deposition.

In recent years, PRD local government agencies have been taking strict measures to reduce SO_2 and NO_x emissions, and both SO_2 and NO_2 concentrations have shown decreasing trends as a result in the past five years (GDEMC and HKEPD, 2006–2010). However, no significant improvement of $PM_{2.5}$ and PM_{10} concentrations have been observed (GDEMC and HKEPD, 2006–2010), suggesting the complex atmospheric chemistry and transport processes for these species in the region (Zhang et al., 2008). The relationships between ammonia emissions, secondary $PM_{2.5}$ formation, and acid deposition are still not fully understood in this region, which reduces the effectiveness of SO_2 and NO_x reduction measures to some extent. In order to formulate evidence-based and sound multi-pollutant control policies for reducing both $PM_{2.5}$ pollution and acid deposition, there is a need for a comprehensive understanding of ammonia emissions and its spatial and temporal characteristics in this region.

The main objectives of this paper are: (1) to develop a model-ready NH_3 emission inventory with high-resolution temporal and spatial information in the PRD region for the base year of 2006; (2) to characterize uncertainties in NH_3 emission estimates using a quantitative approach (where possible) and to identify important uncertainty sources; (3) to investigate long-term variations in agricultural NH_3 emissions from 1998 to 2006 in the PRD region; and (4) to analyze the potential relationships between NH_3 emissions and NH_4^+ concentrations in precipitation.

2 Data and methodology

2.1 Study domain and source categorization

The study area, shown in Fig. 1, is set between the latitudes of 21.530° N and 24.580° N, and between the longitudes of 111.135° E and 115.669° E, covering the PRD region under the Lambert conformal projection. The domain covers nine cities in the PRD region: Guangzhou, Shenzhen, Dongguan, Zhuhai, Jiangmen, Foshan, Zhongshan and parts of Huizhou and Zhaoqing.

The anthropogenic NH_3 emissions are typically contributed by agricultural sources, but NH_3 emissions from non-agricultural sources cannot be neglected though they are typically small contributors (Battye et al., 2003). In this study, both agricultural and non-agricultural sources were investigated, which consist of 9 source categories and 45 subcategories. Details for source classification are shown in Table 1.

2.2 Data sources and study periods

A comprehensive data collection was conducted to estimate NH_3 emissions in this study that includes previous studies, agricultural statistics, and government or institute reports. Agricultural activity data were mainly based on available statistics from the Agricultural Statistical Yearbook of Guangdong (ASYG). The official statistical data provide a relatively complete data set for livestock headcounts, which includes the number of yellow cattle, buffalo, goat, hog and other subcategories, and the amount of nitrogen fertilizer application. Other miscellaneous non-agricultural activity data were obtained from Guangdong provincial pollutant statistical reports, official statistical yearbook and others. Detailed sources of activity data were also listed in Table 1.

The 2006-based activity data, land-use, road-network, population distribution, and other relevant information were used to identify temporal-spatial characteristics of NH_3 emissions. In order to achieve the third and fourth objectives of this study, activity data of agricultural NH_3 sources were collected from 1998–2006. The 1998–2006 precipitation data were collected from officially operated acid rain

Table 1. Anthropogenic NH_3 emission source categories and data sources.

Category	Subcategory	Category	Subcategory
Livestock[a]	yellow cattle	Biomass Burning	crop residues field burning[d]
	buffalo		domestic crop residue[e]
	dairy		domestic firewood[e]
	beef cattle		forest fire[a]
	goat	Sewage Treatment[f]	
	sow	Waste Treatment	waste incineration[b,g]
	hog		waste landfill[g]
	hen	Human Beings[d]	human breath
	broiler		human sweat
	laying duck		human excretion
	duck	Fuel Combustion	industrial coal combustion[b]
	goose		industrial oil combustion[b]
	pigeon		industrial gas combustion[b]
	rabbit		domestic coal combustion[d]
N Fertilizer Application[a]	urea		domestic oil combustion[d]
	ammonium nitrate		domestic gas combustion[h]
	ammonium sulfate	On-road Mobile Source[i]	light duty gasoline vehicle
	aqua ammonia		light duty diesel vehicle
	others		heavy duty gasoline vehicle
Industry Sources	ammonium synthesis[b]		heavy duty diesel vehicle
	nitrogenous fertilizer[c]		motorcycle
	nitric acid[b]		
	phosphoric acid[b]		

[a] Data from ASYG (2007). [b] Data from Guangdong Provincial Pollutant statistical reports. [c] Data from CIESY (2007). [d] Data from GSY(2007). [e] Data from CESY (2007). [f] Data from official websites of sewage treatment plants in the PRD region (2007). [g] Data from CUCSY (2007). [h] Data from CSYRE (2007). [i] Data from Che et al. (2009).

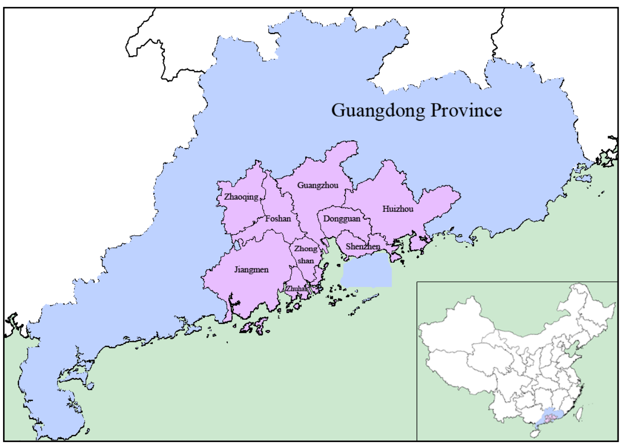


Fig. 1. The PRD region and its location.

monitoring stations in the PRD region directly. Samples were collected by using an automatic precipitation sampler equipped with a polyethylene bucket at each rainfall event. Each precipitation sample was analyzed for pH, rainfall, and ions of NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, F^- and Cl^-.

2.3 Methods for estimating ammonia emissions

The typical method for estimating emissions from a given source is to multiply an "activity level" with a representative "emission factor", shown in Eq. (1):

$$E = \mathrm{EF} \times \mathrm{AL}, \tag{1}$$

where E is the emission estimate for a source category, EF is the emission factor for the category, and AL is the activity level for the category.

The detailed methods for compiling activity data, determining environmental variables and estimating NH_3 emissions for each source were presented and discussed by Yin et al. (2010). The improvements and updates to the previous study are discussed in this section.

2.3.1 Livestock

NH_3 emissions from domestic livestock were estimated based on average waste nitrogen excretion and subsequent NH_3 volatilization during housing, storage of manure outside the building, application to grassland or arable land and grazing periods (Dragosits et al., 1998). A number of studies were performed on NH_3 emissions factors in other countries based on the gender, age, body weight, and purpose of livestock feeding (Misselbook et al., 2000; Faulkner et al., 2008; Reidy et al., 2008). However, since detailed activity data were limited in current study, the emission factors based upon the gender, age, and body weight cannot be used directly for estimating NH_3 emissions. In this study, the subsource category-based emission factors from the work by Yang (2008) were used, in which the emission factors with modifications in terms of the excretion rates, N excretion, feeding time, NH_3-N volatilization rates of domestic livestock were recalculated. Since NH_3 emissions from livestock mainly occur during different management stages of manure, such as housing, manure storage, land spreading and grazing, NH_3 emissions from livestock were estimated using the following equations:

$$\mathrm{ef}_1 = N_{\mathrm{X}1} V_1 \tag{2}$$

$$\mathrm{ef}_2 = N_{\mathrm{X}1}(1 - V_1) V_2 \tag{3}$$

$$\mathrm{ef}_3 = N_{\mathrm{X}1}(1 - V_1)(1 - V_2) V_3 \tag{4}$$

$$\mathrm{ef}_4 = N_{\mathrm{X}4} V_4 \tag{5}$$

$$\mathrm{EF} = \mathrm{ef}_1 + \mathrm{ef}_2 + \mathrm{ef}_3 + \mathrm{ef}_4 \tag{6}$$

where $\mathrm{ef}_{1,2,3,4}$ are NH_3-N loss at housing (1), storage (2), spreading (3), and grazing (4), respectively, $N_{\mathrm{X}1,4}$ are N excretion during housing (1) and grazing (4), $V_{1,2,3,4}$ are NH_3-N volatilization rates at different emission stages, EF is the final emission factor.

Owing to the lack of activity data about hens and laying ducks, their populations are given by the following equation:

$$A_i = \frac{Q_i}{M_i \times N_i} \tag{7}$$

where i represents hen or laying duck, A is the population for hen or laying duck, Q is the total yield of egg and duck egg (kg), M is the average single weight of egg or duck egg (kg/per egg or duck egg), and N is the average annual egg yield from hen or laying duck. Since there was only total egg production in 2006 from the ASYG (2007), in this study we estimated the proportion of the total yields of egg and duck egg in the PRD for the year of 2006 by using the yields of egg and duck egg during 1998–2003 (ASYG) in the PRD region.

2.3.2 Nitrogen (N) fertilizer application

The application of N fertilizer is known as another important source of the agricultural emissions (Zhang et al., 2010; Huang et al., 2012). NH_3 loss from N fertilizer depends on many factors, including chemical compositions of N fertilizer, soil properties (pH values, calcium content, water content, etc.), meteorological conditions (temperature, wind speed, and precipitation), timing, and methods of application (Bouwman et al., 2002; Goebes et al., 2003). However, due to limited information about the amount of various N fertilizers, a synthetic emission factor was estimated by using ratios of application of different fertilizers multiplied by their corresponding NH_3 loss per nitrogen fertilizer (Table 2). In China, widely used nitrogen fertilizers are represented by ammonium bicarbonate (ABC) and urea (Zhang et al., 2009). In this study, the NH_3 emission factors were updated with the use of newly measured NH_3-N emission rates by Dong et al. (2009) for ABC and urea.

2.3.3 Industrial process

Industrial processes such as the production of synthesis ammonia and N fertilizer are one of the main sources for NH_3 emissions (Lee et al., 2002). In addition to the two sub-source categories, production of nitric acid and phosphate fertilizer was also accounted for in this study though emissions from these processes may be relatively lower. Due to the lack of information on the production yields of these fertilizers and detailed production processes for individual plants, an average emission factor of 2 kg NH_3/t N fertilizer produced was assumed for the industrial processes over the whole PRD region.

2.3.4 Human beings

It is well documented that direct NH_3 emissions from humans occur from breath, sweat, excretion as normal metabolic processes, and also cigarette smoking (Sutton et al., 2000). In this study, NH_3 emission from cigarette smoking was neglected due to the lack of data about the population of smokers. The NH_3 emission factors from the human being source were quoted from foreign studies due to the lack of domestic measurements.

2.3.5 Biomass burning

Biomass burning has been considered an important source of atmospheric trace species and has significant effects on global atmospheric chemistry and climate change (Andreae, 2001). The biomass burning usually includes four types: grassland fire, forest fire, field burning of crop residues and domestic bio-fuel combustion (Yan et al., 2006). In this study, NH_3 emissions for the last three types of biomass burning were estimated. Detailed information about estimating activity amounts of type-based biomass burning for the PRD region can be found at He et al. (2011). Compared to our previous study (Yin et al., 2010), activity data for the last two types of biomass burning were recalculated using updated parameters for the domestic bio-fuel burning, and using modified variables for the crop residue, including the modification of crop-specific amount of crops produced, crop-specific production-to-residue ratio, dry matter content of crop-specific residue, percentage of residues that are burned in the field, and crop-specific burning efficiency ratio.

Table 2. Ratios of nitrogen fertilizer application and the emission factors.

Nitrogen fertilizer	ABC	Urea	Ammonium nitrate	Ammonium sulfate	Aqua ammonia	Others	Average
Using ratios (%)[a,b]	55.50	36.80	3.85	0.60	0.40	2.85	
Emission factor (NH_3 / %(N))	25.9 [c]	21.1 [c]	2.4 [d]	9.7 [e]	3.0[e]	3.6 [d]	22.4

[a] From Sun et al. (1997). [b] From Wang et al. (1997). [c] From Dong et al. (2009). [d] From Klimont. (2001). [e] From Bouwman et al. (1997).

2.3.6 On-road mobile source

NH_3 emissions from motor vehicle internal combustion processes cannot be ignored, though they are typically much smaller compared to other sources mentioned above. However, recent laboratory dynamometer studies show that advanced catalysts which are installed in most light-duty gasoline vehicles may produce much larger NH_3 emission rates stemming from an over-reduction of NO_x to NH_3 than those without such control devices (Kean et al., 2000; Tanner, 2009). Currently, all newly manufactured light-duty vehicles in China are equipped with a three-way catalyst (TWC). NH_3 emissions from motor vehicles may become significant, especially considering the rapid increase of vehicle population at a rate of about 10 % per year in the PRD region (Che et al., 2011).

The vehicle population data and vehicle kilometers traveled (VKT) were from the work done by Che et al. (2009). Vehicle types considered in this study include: light duty gasoline (LDG), light duty diesel (LDD), heavy duty diesel (HDD), heavy duty gasoline (HDG), and motorcycle (MC). The emission factors were taken from the Emission Inventory Improvement Program (EIIP) (Roe et al., 2004) due to the lack of domestic NH_3 emission measurements from motor vehicles.

2.3.7 Other sources

The inventories from domestic, power plant, and industrial fuel combustion sources (e.g. coal, heavy oil, diesels, and natural gas) were developed based primarily on emission factors reported about nonagricultural sources in the EIIP database.

NH_3 emissions from waste treatment mainly come from municipal solid waste (MSW) landfills and waste incineration for municipal and commercial waste. However, little information exists on NH_3 emission factors from landfill sources. Sutton et al. (2000) used the CH_4 emission rates to estimate NH_3 emission rates by using $NH_3 : CH_4$ mass ratio of 0.0073 from landfill source, and this same approach was adopted in this study.

Sewage treatment plants that process a large quantity of nitrogen-rich wastes may generate significant ammonia emissions under certain conditions, particularly through anaerobic processes (Chinkin et al., 2003). The fraction of NH_3 lost to the atmosphere is dependent upon the pH values of the solution and temperature (Roe et al., 2004). The emission factors adopted in this study for these sources are given in Table 3 based on the treatment capacity of an entire plant.

2.4 Spatial allocation

In order to investigate the spatial characteristics of ammonia emissions and to provide gridded emission inputs for air quality models, the bulky NH_3 emission inventory was spatially allocated to 3 km × 3 km grid cells with the aid of GIS technology using source-based spatial surrogates. In this study, large-scale livestock feeding operations (emissions from housing stage), sewage treatment plants, MSW incinerators and landfills, industrial processes, power plants and industrial stationary boilers were treated as point sources, and emissions from these sources were directly allocated to grid cells based on their latitude and longitude coordinates.

For area sources such as domestic fuel consumption and human being grid-cell-based population densities from 2006, Land Scan Asia Population (ORNL, 2007) were used to perform spatial allocation. NH_3 emissions from on-road mobile sources were spatially allocated with the use of "standard length" approach by Zheng et al. (2009a), taking into consideration of road network information and road type-based traffic flows.

The GIS-based land use data were used as surrogates to help spatially allocate NH_3 emissions from biomass burning, N fertilizer application, and livestock area sources based upon source characteristics and land types. NH_3 emissions from biomass burning were allocated as a function of rural residential area, arable land, and woodland for bio-fuel combustion, crop residues open burning and forest fire, respectively. The emissions from N fertilizer application were apportioned according to the distribution of arable lands within the study domain.

Since NH_3 emissions from livestock sources may occur in the stages of housing, manure storage, land spreading of livestock manures and grazing, which might happen at different locations, emissions from different stages were spatially allocated based upon where these emissions are produced. For example, in most cases, emissions from the housing and manure storage mainly occur in suburban areas, grazing NH_3 emissions take place at the forest and grassland, while spreading emissions happen onto arable land and grassland. However, compared to northern China, there is less forest and grassland for grazing activity in the PRD region, thus NH_3

Table 3. Emission factors used in this study (as: NH_3).

Source	Emission factor	Unit	Source	Emission factor	Unit
Livestock[a]			domestic crop residue	1.30	$g\,kg^{-1}$
yellow cattle	25.52	$kg\,a^{-1}$	domestic firewood	1.40	$g\,kg^{-1}$
buffalo	10.56	$kg\,a^{-1}$	**Human Beings**		
dairy	37.61	$kg\,a^{-1}$	human breath	3.64[f]	$g\,per^{-1}\,a^{-1}$
beef cattle	22.58	$kg\,a^{-1}$	human sweat	17.00[f]	$g\,per^{-1}\,a^{-1}$
sheep	4.93	$kg\,a^{-1}$	human excretion	0.76[g]	$kg\,per^{-1}\,a^{-1}$
sow	11.55	$kg\,a^{-1}$	**Sewage Treatment**	3.20[g]	$g\,m^{-3}$
hog	2.82	$kg\,a^{-1}$	**Fuel Combustion**		
hen	0.49	$kg\,a^{-1}$	industrial coal combustion	0.02[h]	$kg\,t^{-1}$
broiler	0.18	$kg\,a^{-1}$	industrial oil combustion	0.10 [h]	$kg\,(10^3\,l)^{-1}$
laying duck	0.35	$kg\,a^{-1}$	industrial gas combustion	51.30 [h]	$kg\,(10^6\,m^3)^{-1}$
duck	0.03	$kg\,a^{-1}$	domestic coal combustion	0.90[h]	$kg\,t^{-1}$
goose	0.24	$kg\,a^{-1}$	domestic oil combustion	0.12[h]	$kg\,(10^3\,l)^{-1}$
breast	0.01	$kg\,a^{-1}$	domestic gas combustion	320.51[f]	$kg\,(10^6\,m^3)^{-1}$
rabbit	0.24	$kg\,a^{-1}$	**Waste Treatment**		
N Fertilizers Application[b]	22.40	%t (N)	waste incineration	0.21[f]	$kg\,t^{-1}$
Industry Process			waste landfill	7.3 [h]	$kg\,kg^{-1}\,CH_4$
ammonium synthesis[c]	2.10	$kg\,t^{-1}$	**On-road Mobile Sources** [h]		
nitrogenous fertilizer[d]	2.00	$kg\,t^{-1}$	light-duty gasoline (LDG)	63.20	$mg\,km^{-1}$
nitric acid[c]	3.8	$kg\,t^{-1}$	light-duty diesel (LDD)	4.20	$mg\,km^{-1}$
phosphoric acid[c]	0.07	$kg\,t^{-1}$	heavy-duty gasoline (HDG)	28.00	$mg\,km^{-1}$
Biomass Burning[e]			heavy-duty diesel (HDD)	16.80	$mg\,km^{-1}$
forest fire	1.02	$g\,kg^{-1}$	Motorcycle (MC)	7.00	$mg\,km^{-1}$
crop residues field burning	0.53	$g\,kg^{-1}$			

[a] From Yang. (2008). [b] From Table 2. [c] From AP42 Fifth Edition: Chapter 8.1 table 8.1-1. [d] From Klimont.(2001). [e] From He et al. (2011). [f] From Sutton et al. (2000). [g] From HG-JWGSDEP. (2005). [h] From Roe et al. (2004).

emissions from grazing were quite small and were allocated to suburban areas instead of forest and grassland.

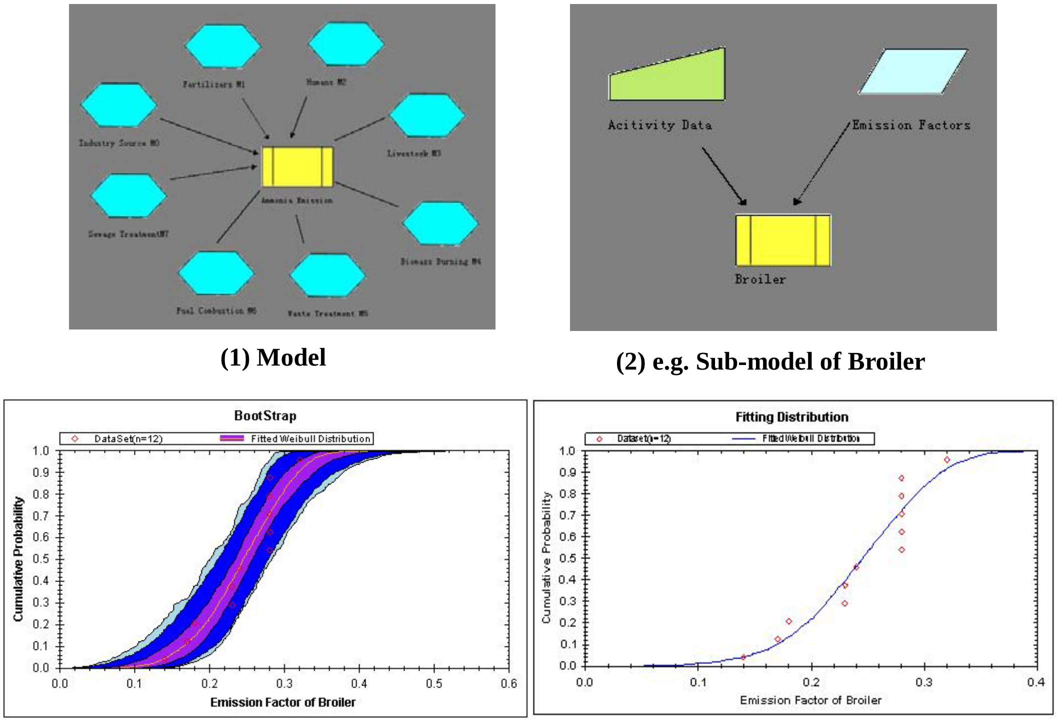
2.5 Temporal variation

By using some surrogates like energy consumption, electricity production, industrial product yields, traffic flows and fire count, the temporal variations of non-agricultural emission sources could be characterized (Zheng et al., 2009b; He et al., 2011). For the agricultural source, there are various novel approaches for analyzing temporal variations, including inverse methods (Gilliland et al., 2003), process-based models (Pinder et al., 2006), hybrid approaches (Skjøth et al., 2011) and others. However, seasonal characteristics in agricultural source emissions depend strongly on both local human farming activities and climate conditions (Pinder et al., 2006; Huang et al., 2012). Under the current circumstances of having no detailed agricultural registers and practices, reliable input parameters in the function of process driven description, and NH_3 observations in the air quality monitoring network in China, developing temporal profiles using the methods mentioned above is impractical.

In this study, temporal profiles of agricultural source were derived from field investigations by referring to other similar studies (Streets et al., 2003; Chinkin et al., 2003; Huang et al., 2012). In addition, various data sources were collected to help figure preliminary temporal profile in the PRD region. For livestock, we collected production information of animal husbandry in Guangdong province (Statistical Reports of Guangdong Province, 2007) and ambient meteorological data. For N fertilizer application, we investigated the farming seasons of different crops in the PRD region based upon the database of farming seasons for different crops, such as wheat, corn, rice, sugarcane, vegetables, and others, which are available at http://www.zzys.gov.cn/ (China's planting information network).

2.6 Uncertainty analysis

Various uncertainty sources may lead to uncertainties in emission estimates. These sources may arise from lack of knowledge or information in activity data, emission factors or related parameters (NARSTO, 2005). There are qualitative, semi-quantitative, and quantitative approaches which can be used to characterize uncertainties in emission inventories (NARSTO, 2005). The quantitative approach is preferred



(1) Model (2) e.g. Sub-model of Broiler

(4) Bootstrap Simulation (3) Fitting Distribution

Fig. 2. The model framework for analyzing uncertainty in emission estimates by the AuvToolPro.

since it can provide quantitative information to guide future emission inventory improvements (Zheng, 2002). In this paper, both qualitative and quantitative approaches were used for analyzing uncertainty in the PRD NH_3 emission inventory.

For most source categories, quantitative uncertainties are characterized with the aid of the uncertainty analysis tool AuvToolPro (Lau et al., 2010). The AuvToolPro is an extension version of AuvTool developed by Zheng and Frey (2002). The AuvToolPro is able to conduct quantitative variability and uncertainty analysis in model inputs and outputs for any user-defined models with the use of bootstrap simulation and Monte Carlo simulation, and to identify key sources leading to uncertainty in model outputs using sensitivity analysis approaches. A model framework for quantifying uncertainty in NH_3 emission estimates was shown in Fig. 2. In the uncertainty analysis, bootstrap simulation or expert judgment was used to quantify uncertainties in source-based emission factors or other model input parameters, depending on data availability (Zheng et al., 2010). The uncertainties in model input parameters that were analyzed by AuvToolPro for livestock and biomass burning sources are shown in Tables S1 and S2 in the Supplement as examples.

Uncertainties in source-based NH_3 emissions and the total NH_3 emissions are quantified using Monte Carlo simulation by propagating uncertainties in model inputs through source-based emission models and the overall emission model. For those categories such as the industrial process category in which quantitative uncertainty analysis cannot be conducted, uncertainties are qualitatively judged by assessing the reliability and accuracy of data sources, estimation methods used, and uncertainty in emission factors. Key uncertainty sources in estimating NH_3 emissions were identified by using correlation analysis method inherent in the AuvToolPro.

2.7 Data processing for precipitation samples

Sampling was carried out at the nine cities' environmental monitoring stations in the Pearl River Delta (PRD) region. In order to keep the H^+ balance, the pH values of the rainwater samples were measured immediately at the end of a rain event at sampling sites with a portable pH analyzer. Then they were filtered through 0.45 µm pore size membrane filters to remove the insoluble particles, and stored in a refrigerator at about 3–5 °C prior to chemical analysis. The collection and analysis of precipitation samples in the laboratory strictly followed the technical specifications required for acid deposition monitoring in China (HJ/T165-2004, State Environmental Protection Administration of China, 2004) to assure the analytic quality of precipitation samples.

The H^+ concentration in precipitation samples was calculated based upon measured pH values. The annual volume-weighted-mean (VWM) concentrations of chemical compositions were calculated based on Eq. (8). The average annual pH was converted from the negative logarithm of the annual VWM concentration of H^+.

$$\overline{C} = \frac{\sum_{i=1}^{n} Ci\,Pi}{\sum_{i=1}^{n} Pi} \tag{8}$$

where i represent the times of rainfall, n is the total number of sample, C is the concentrations of ion compositions (μeq l^{-1}), and P is the rainfall (mm).

The ionic balance of total anions ($\Sigma-$) with total cations ($\Sigma+$) for each precipitation sample was checked in Fig. 3. The results showed that the correlation coefficient between them was 0.99, within the range of 1.00 ± 0.25, indicating that the data qualities for these precipitation samples were acceptable (Zhang et al., 2000).

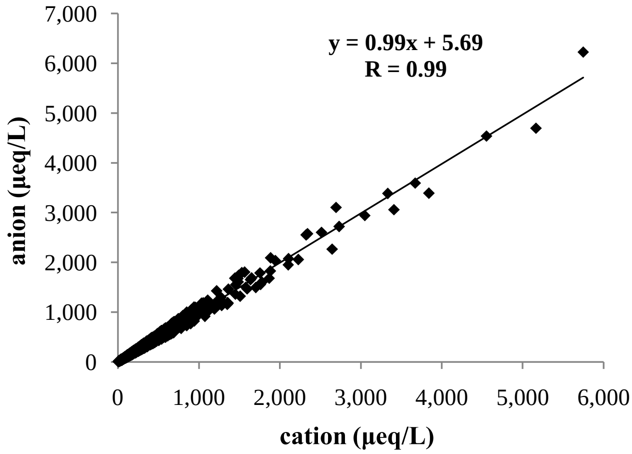


Fig. 3. Relationships between the sum of cations and that of anions.

3 Results and discussion

3.1 Ammonia emission inventories in 2006

Table 4 lists source-based NH_3 emission estimates and their corresponding contributions in the PRD region. The total NH_3 emissions in 2006 are estimated about 195.7 kt, in which 167.2 kt is from agricultural sources and 28.5 kt from non-agricultural sources.

3.1.1 Contributions by source and city

Source

Of the total anthropogenic NH_3 emissions, agricultural sources accounted for about 85.4 %, and non-agricultural sources for about 14.6 %. Biomass burning, sewage treatment, on-road mobile, and others were responsible for 3.7 %, 3.3 %, 2.5 % and 5.1 % of the total NH_3 emissions, respectively.

Livestock was the largest contributing source, being responsible for 61.7 % of the total NH_3 emissions. The contributions by sub-source categories for livestock source are given in Fig. 4. The results show that there were large differences among the different livestock species. Broiler, hog, goose, and others accounted for 43.4 %, 32.1 %, 6.5 %, and 18.0 % of the total livestock emissions, respectively. Broiler and hog were the two largest NH_3 emission sources, owing to their large consumption, and statistics from ASYG show that the production of pork and poultry accounted for approximately 66.3 % and 30.1 % of the total yield of meat, respectively. In addition, as for geese, the consumption in the PRD region was relatively higher than in other provinces in China, owing to the natural dense water systems suitable for raising geese as well as the traditional dieting habits of geese. Meanwhile, due to the shorter breeding cycle, smaller floor space, and higher stocking density for these three livestock, there

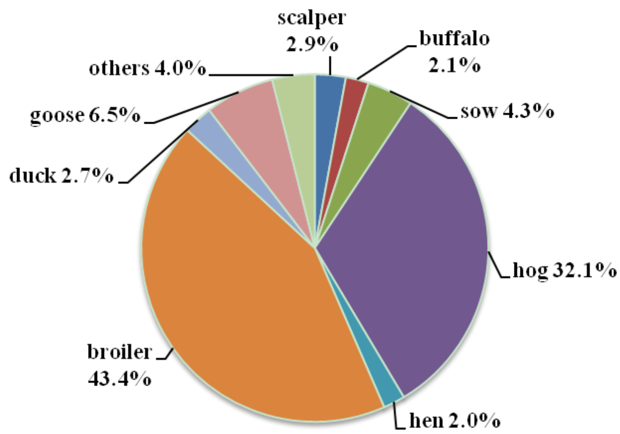


Fig. 4. Emission contributions by subcategories of livestock, 2006.

are larger yields and better developments in the PRD region. By contrast, the smaller contributions of other livestock (e.g. yellow cattle, beef cattle, buffalo, dairy, and goat) may be influenced by the lower level of activity data owing to their longer breeding cycle, larger floor space, and fewer livestock farms in this region.

The second largest NH_3 source was the application of N fertilizers represented by ABC and urea, which accounted for about 23.7 % of the total NH_3 emissions. Because both N fertilizers are characterized by high N content and high N loss after application (Tian et al., 2001), there are high ammonia emissions from these sources. China is the sole ABC manufacturer and user, and the combined consumption of ABC and urea in China is responsible for 90 % of the total N fertilizer application.

Of many non-agricultural sources, biomass burning, sewage treatment, and on-road mobile sources were ranked the top three for NH_3 emissions. Within the sub-source categories of biomass burning, domestic bio-fuel combustion was the major contributor, in that domestic crop residue and

Table 4. NH_3 emission inventory in the PRD region, 2006.

Agricultural sources	Emission (kt yr^{-1})	% of total	Non-agricultural sources	Emission (kt yr^{-1})	% of total
Livestock	**120.9**	**61.7 %**	**Industry Sources**	**1.6**	**0.8 %**
yellow cattle	3.5	1.8 %	**Biomass Burning**	**7.2**	**3.7 %**
buffalo	2.6	1.3 %	crop residues field burning	0.5	0.3 %
dairy	1.5	0.8 %	domestic crop residue	2.0	1.0 %
beef cattle	1.6	0.8 %	domestic firewood	4.6	2.4 %
goat	0.2	0.1 %	forest fire	0.0	0.0 %
sow	5.2	2.6 %	**Sewage Treatment**	**6.4**	**3.3 %**
hog	38.8	19.8 %	**Waste Treatment**	**3.6**	**1.8 %**
hen	2.4	1.2 %	waste incineration	0.6	0.3 %
broiler	52.5	26.8 %	waste landfill	3.0	1.5 %
laying duck	1.1	0.6 %	**Human Beings**	**2.6**	**1.3 %**
duck	3.3	1.7 %	human breath	0.2	0.1 %
goose	7.8	4.0 %	human sweat	0.7	0.4 %
pigeon	0.3	0.1 %	human excretion	1.7	0.9 %
rabbit	0.1	0.1 %	**Fuel Combustion**	**2.3**	**1.2 %**
N Fertilizer Application	**46.3**	**23.7 %**	**On-road Mobile Source**	**4.9**	**2.5 %**
ammonium bicarbonate	29.7	15.2 %	light duty gasoline vehicle	4.3	2.2 %
urea	16.1	8.2 %	light duty diesel vehicle	0.1	0.0 %
ammonium nitrate	0.2	0.1 %	heavy duty gasoline vehicle	0.1	0.0 %
ammonium sulfate	0.1	0.1 %	heavy duty diesel vehicle	0.2	0.1 %
aqua ammonia	0.0	0.0 %	motorcycle	0.4	0.2 %
others	0.2	0.1 %	**Total**	**195.7**	**100.0 %**

woody fuel shared 27.7 % and 64.6 % of total biomass burning emissions, respectively. In comparison, less than 0.3 % and 7.5 % of total biomass burning emissions were contributed by forest fire and field burning of crop residues. In the PRD region, many large sewage treatment plants use activated sludge process and they process a large quantity of sewage due to the large population. In this study, we assume that these plants operate 365 days yr^{-1}, which may overestimate contributions from municipal sewage treatment plants. Although NH_3 emissions per vehicle are quite small, there are a large number of vehicles (about 5.4 million) in the PRD region, which makes the motor vehicle one of the top three sources for NH_3 emissions in the non-agricultural category.

City

Figure 5 presented detailed city contributions of total NH_3 emissions and contributions from different sources in different cities in the PRD region. Guangzhou had the largest NH_3 emissions, then Jiangmen and Foshan, accounting for 23.3 %, 19.3 % and 17.9 % of the total NH_3 emissions, respectively.

Livestock and N fertilizer application are consistently the major sources in these nine cities. NH_3 emissions from livestock accounted for 40.0–76.1 % of the total emissions in different cities. The percentage is smaller in Shenzhen and Dongguan where second and third industry dominates, while bigger numbers are found in Foshan, Jiangmen, Zhaoqing, and Huizhou where large numbers of livestock are raised on their large geographical territories.

Emissions from N fertilizer applications constituted the second largest portion of the total NH_3 emissions in different cities, ranging from 8.0 % to 35.1 %, with the lowest ratio in Shenzhen and the highest in Zhongshan, followed by Huizhou and Zhaoqing. The large variations from one city to another are attributed to the magnitude of the agricultural land areas in different cities which determine the usage of fertilizers.

Owing to higher urbanization, larger population density, and smaller land areas, NH_3 emissions from non-agricultural sources such as sewage treatment, on-road mobile vehicles, and waste incineration are higher in Shenzhen than in other cities, where agricultural NH_3 emissions are low.

3.1.2 Comparisons with previous studies

Table 5 presents a comparison of NH_3 emission inventory developed in this study with other similar studies, including our previous study (Yin et al., 2010). Since studies on non-agricultural NH_3 emission sources in the PRD region or the Guangdong province are rarely available, only agricultural sources were included in the comparisons.

Estimates of NH_3 emissions are higher than that from Yin et al. (2010), and the differences are attributed to some revised and updated work and progresses that were made in calculation of activity data about hen, laying duck, domestic bio-fuel combustion, and rural human excretion. The

Table 5. Comparison with other studies.

Region/Source	PRD region			Guangdong province					
	This study	Yin[a]	HK-GD 2003-based EI[b]	Sun[c]	Wang[d]	Klimont[e]	Klimont[e]	Dong[f]	Huang[g]
Base year	2006	2006	2003	1992	1991	1990	1995	2006	2006
Livestock	120.9	121.0	35.4	214.8	267.3			126.5	143.5
N Fertilizer Application	46.3	42.3	53.7	184.3	94.5			382.6	107.9
Industry Process	1.6	1.6	2.1	5.0	2.2			0.3	0.5
Human Beings	2.6	7.3	12.5	84.5	85.0			56.5	4.7
Biomass Burning	7.2	8.0	5.7						2
Waste Treatment	3.6	3.6							11.9
Fuel Combustion	2.3	2.3							
Sewage Treatment	6.4	6.4							
On-road Mobile Sources	4.9	2.4	0.3						7.8
Total	195.7	194.8	109.8	488.6	448.9	597.0	638.0	565.9	278.3

[a] Yin et al. (2010). [b] HG-JWGSDEP. [c] Sun et al. (1997). [d] Wang et al. (1997). [e] Klimont. (2001). [f] Dong et al. (2010). [g] Huang et al.(2012).

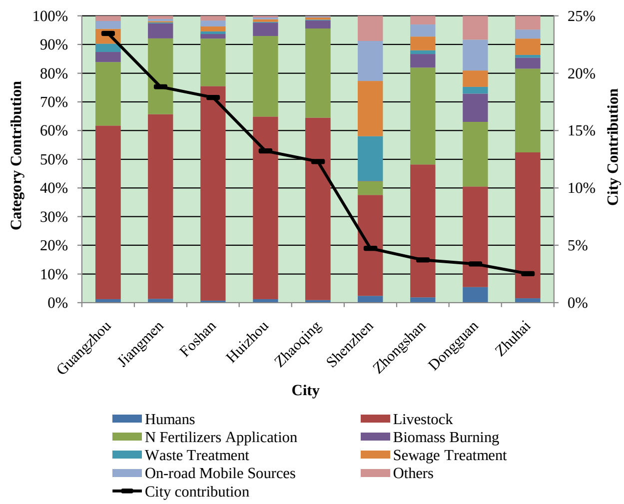


Fig. 5. Source contributions by cities in the PRD region, 2006.

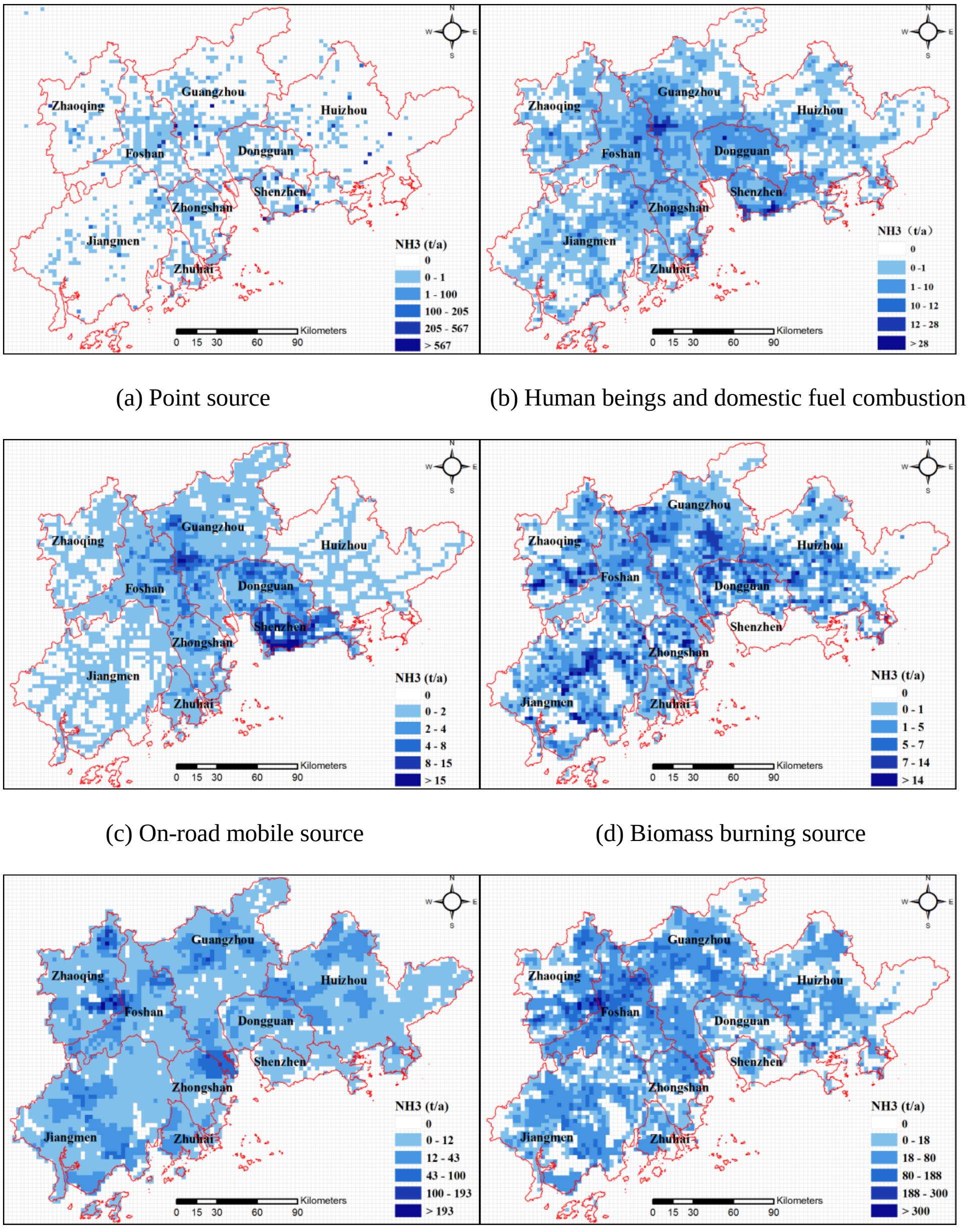
emission factors of N fertilizer application, field burning of crop residues, and LDG vehicle were also updated, and new sources of forest fire were added in this study.

Estimates of NH_3 emissions from livestock in this study are higher than those reported in HK-GD 2003-based EI (HG-JWGSDEP, 2005), and the main reason might be attributed to the use of different estimation methods, activity data, and emission factors in the two emission inventories in addition to the different base years used. In this study, the "bottom-up" method was used whenever possible by collecting the detailed information for livestock for each city, and there are 14 sub-source categories of livestock. While the HK-GD 2003-based EI adopted a "top-down" method to obtain the whole PRD regional activity data using the proportion of gross yield value of primary industry to Guangdong province, and only 5 sub-sources (i.e. yellow cattle, dairy, goat, pig, and poultry) were included. Also, our estimate was close to that for Guangdong province by Huang et al. (2012) and the disparity is mainly caused by uncertainties in emission factors and the detailed activity data sources.

NH_3 emissions from N fertilizer applications are lower than those reported in HK-GD 2003-based EI (HG-JWGSDEP, 2005) due to the reduced agricultural acreage from 2003 to 2006 and the overestimate of activity data by using the "top-down" method in the later. Large uncertainties exist in the estimate of emission from fertilizer application, and there are large differences among the different works by Sun et al. (1997), Wang et al. (1997), Dong et al. (2010) and Huang et al. (2012) for Guangdong province. Our estimates account for 40 % of those by Huang et al. (2012), and this is reasonable since the area of farm lands of the PRD region was about 31 % of the whole Guangdong province (GSY, 2007). The modified synthetic emission factor taking into consideration application ratio and emission rates of different N fertilizers was used in this study, and it is believed that there is less uncertainty in the NH_3 emission estimates from N fertilizer application than previous studies which used the single emission factor for total N fertilizer.

3.2 Spatial characteristics

The $3\,km \times 3\,km$ gridded PRD regional NH_3 emissions are presented in Figs. 6 and 7 for different emission sources and the total emissions, respectively. Point sources which comprise power plants, industrial stationary boilers, and processes scatter over urban areas. The large emissions from point sources are distributed over the grid cells where sewage treatment plants and livestock feeding operations are densely located (Fig. 6a). As seen in Fig. 6b, human being and domestic fuel combustion exhibit a relatively uniform distribution that focuses on the downtown areas with dense populations, especially in Guangzhou, Shenzhen, and Zhuhai.



(a) Point source

(b) Human beings and domestic fuel combustion

(c) On-road mobile source

(d) Biomass burning source

(e) N fertilizer application source

(f) Livestock area source

Fig. 6. Spatial distributions of NH_3 emissions by source category in the PRD region.

The bulk of on-road mobile emissions are contributed from Guangzhou, Foshan, Dongguan and Shenzhen where there are heavy traffic flows and crowded road networks, as shown in Fig. 6c. The spatial distribution of biomass burning emissions (Fig. 6d) is mainly distributed over rural residential areas, which is consistent with the patterns of emissions from domestic bio-fuel burning. The distribution of N fertilizer application presents intensive emissions on arable land in suburbs of Guangzhou, Zhaoqing, Foshan, and Jiangmen, and fewer emissions in the centers of PRD regional cities (Fig. 6e). Most emissions from livestock (Fig. 6f) were distributed over rural residential and crop areas in Huizhou, Guangzhou, Foshan, Zhaoqing, and Jiangmen due to the large amounts of livestock raised in these cities. Overall, anthropogenic NH_3 emissions are mainly distributed over the area where less urbanization develops, including outlying areas of the PRD region and less-developed areas of the economically developed cities, like Zengcheng and Huadu areas of Guangzhou, Sanshui area of Foshan, Zhaoqing, and Jiangmen (Fig. 7). The general characteristics are consistent with

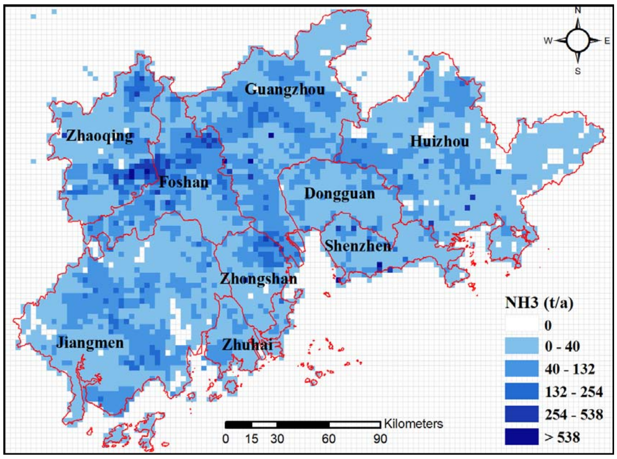


Fig. 7. Spatial distributions of total NH_3 emissions in the PRD region.

the patterns of agricultural emissions that contribute more than 80 % of the total emissions, and exhibit a large difference from the emissions of SO_2 and NO_x in the PRD region (Zheng et al., 2009a) which are mainly distributed over central-southern city clusters.

3.3 Temporal characteristics

Figure 8 shows the seasonal variations in livestock, N fertilizer application, NH_4^+ in precipitation and ambient temperature. For livestock sources, compared with other calendar months, the emissions are relatively higher from May to October because higher ambient temperatures may increase the volatilization of excretions (Shen et al., 2011; Huang et al., 2012). The lower NH_3 emissions were found from December to February during which there are relatively lower temperatures and infrequent agricultural activities.

Temporal variation in N fertilizer application emission was different from the one in livestock. The emission increases gradually from April, and peaks in July, then decreases. This may be partly attributed to N fertilizers being the most widely used fertilizers for farming in China. The N fertilizers were generally used at the beginning of March for early rice raising and seedling, in April for early rice sowing and transplanting, in late June for topdressing, and in early July for early rice grain filling and late rice raising and seedling in the PRD region. Also, they are used at the beginning of July for late rice sowing and transplanting, in early August for transplanting, in late September for topdressing, and in early October for late rice grain filling. In the meantime, high temperature and long daytime sunlight in summer in the PRD region may increase the NH_3 volatilization from N fertilizer application source. All of these factors may contribute to such temporal characteristics in the N fertilizer application source in this region.

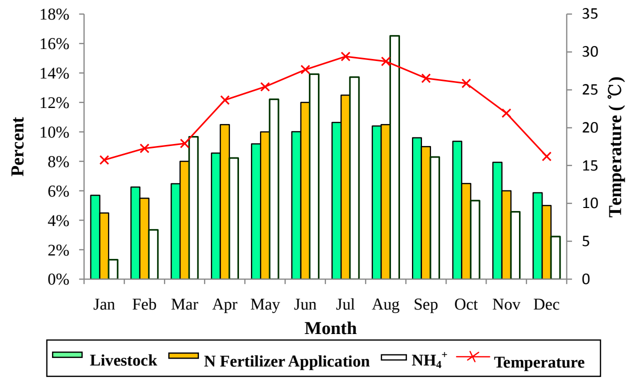


Fig. 8. Monthly variations in emissions from livestock and N fertilizer applications, NH_4^+ in precipitation and in temperature.

As shown in Fig. 8, we found that monthly variations of NH_4^+ in precipitation exhibited obvious seasonal peak to valley characteristics, with maximum in August and minimum in January, indicating an overall consistency with winter/summer difference in the agricultural NH_3 emission, despite that there were some discrepancies in March and April. The results were also consistent with the studies from Meng et al. (2010) and Shen et al. (2011), in which seasonal variations in ambient NH_3 concentrations peaked in warm seasons and bottomed in cold seasons based upon year-long observations of ammonia in China.

3.4 Uncertainties

3.4.1 Uncertainties in NH_3 emission estimates

Uncertainties in emission inventories are associated with the emission factors and the activity practices. To benefit future research, the major source categories are ranked in Table 6. The activity data that were acquired from the official statistics are assumed to be the most authoritative with less uncertainty. As shown in Table 6, there typically exist relatively high uncertainties in human beings, waste treatment, and fuel combustion, with approximately −64 % to 137 % , −75 % to 128 % , and −76 % to 140 % relative errors, respectively. The higher uncertainties in these sources can be attributed to the following reasons: (1) emission factors were usually calculated indirectly for human being excretion and landfill; and (2) emission factors of these sources were mainly obtained from foreign studies due to few NH_3 emission measurements available in China. It is obvious that further measurements are needed.

The uncertainty of livestock is relatively moderate, since the bottom-up approach was used for estimating emission in this study and the recalculated emission factors were taken from the work by Yang (2008) who modified the parameters (e.g. excretion rates, N excretion, feeding time, and NH_3-N volatilization rates) in China, which was considered more

Table 6. Uncertainty in NH_3 emission estimates by source category.

Sources	Emission ($kt\,yr^{-1}$)	Mean ($kt\,yr^{-1}$)	Uncertainty range* (%)
N Fertilizer Application	46.3	44.0	(−35 %, 30 %)
Human Beings	2.6	3.9	(−64 %, 137 %)
Livestock	120.9	139.9	(−31 %, 26 %)
Biomass Burning	7.2	6.6	(−25 %, 25 %)
Waste Treatment	3.6	2.2	(−75 %, 128 %)
Fuel Combustion	2.3	19.9	(−76 %, 140 %)
Sewage Treatment	6.4	5.9	(−22 %, 22 %)
Total	189.4	222.40	(−43 %, 50 %)

* 95 % Confidence Interval.

consistent with reality than simply using emission factors from elsewhere. For N fertilizer application, higher uncertainties in emission factors are anticipated because they are influenced by a large number of parameters such as fertilizer varieties, soil properties, meteorological conditions, timing, and method of application. However, because ABC and urea are the most widely used fertilizers and the domestic studies about NH_3 volatilization are rarely available, a relative error of −35 % to 30 % was assumed to represent the overall uncertainty in this study, and it may be even higher in reality.

Biomass burning and sewage treatment have shown lower uncertainties (Table 6) with a relative error of −25 % to 25 %, and −22 % to 22 %, respectively. The uncertainty associated with biomass burning mainly comes from the lack of emission factors and proper statistics of activity data, and the particular explanations that can be found in our previous study (He et al., 2011). The information on sewage treatment emissions is extremely sparse in China and more detailed investigation is needed. In this study, when emission factors are not available, the 30–50 % relative errors are assumed for these emission sources. The actual uncertainties may be higher than the values reported here.

The quantitative uncertainty analysis of on-road mobile and industry process emissions are not conducted due to the lack of available data, including local vehicle emission measurements, fleet characteristics, the discrepancy in vehicle classifications between annual statistical reports and the model use. Excluding these sources, the uncertainty of the total NH_3 emission inventory was estimated to be −43 % to 50 %, on the 95 % confidence interval.

3.4.2 Identification of important uncertainty emission sources

The correlation coefficients between the source-based NH_3 emission and the overall emission from all sources are listed in Table S3 in the Supplement. A large correlation coefficient (either positive or negative) indicates that the emission source makes significant contributions to uncertainties in model outputs, and therefore is a key uncertainty source (Cullen and Frey, 1999). As shown in Table S3, the hog, broiler and goose were dominant uncertainty emission sources leading to uncertainty in NH_3 emission estimates, implying that more data collection or measurements of emission factors for the three livestock types will help significantly reduce uncertainties in estimating NH_3 emissions in the PRD region. The N fertilizer application was another important uncertainty source as well, indicating that further studies are needed to investigate the volatilizations of N fertilizer application. It is worth mentioning that although industrial coal combustion was generally thought to be a small contributor to NH_3 emission, the results from this study showed higher uncertainties in the estimated NH_3 emissions. Reducing uncertainty in emission factors from the industrial combustion will help improve in NH_3 emission estimates, to some extent. To improve future NH_3 emission inventory in the PRD region, further studies should give priority to the above mentioned emission sources.

3.4.3 Uncertainties in spatial allocation

The spatial allocation processes introduce another area of uncertainty. It is affected by resolution of activity data and weight indexes for different sources, such as land use maps, pop density, and road network, etc. Theoretically, the NH_3 emissions from each city would be bottom-up according to the corresponding area based on the actual locality. For most point sources, the uncertainty associated with longitude and latitude coordinates is very small. The uncertainties of spatial allocation may come from the agricultural practices determining the weighted indexes of different land use classes. It was effective for N fertilizer application but more difficult for livestock sources, because ratios of four processes (i.e. housing, storage, spreading and grazing) could not be determined accurately due to the special traditional household managements in the PRD region. To simplify the ratios, some assumptions had to be made by finding an alternative coefficient according to the percentages of emission factors in the different four processes. The major uncertainties are not from the theoretical process, but rather associated with the local situations.

3.5 Trends in agricultural ammonia emissions

Emissions from PRD regional agricultural NH_3 sources were calculated from 1998 to 2006. Activity data were collected from Agricultural Statistical Yearbook of Guangdong (ASYG) 1999–2007. As shown in Fig. 9, steady rising trend of the total agricultural emissions was observed before it peaked in 2003 and then slightly decreased in 2004 and 2006. It is reasonable because atmospheric NH_3 is much less influenced by industrial activities, and agricultural sources generally do not change much (Shen et al., 2011). Based on the trend analysis for livestock and N fertilizer application, the decreasing trend after the year 2003 could be attributed to the

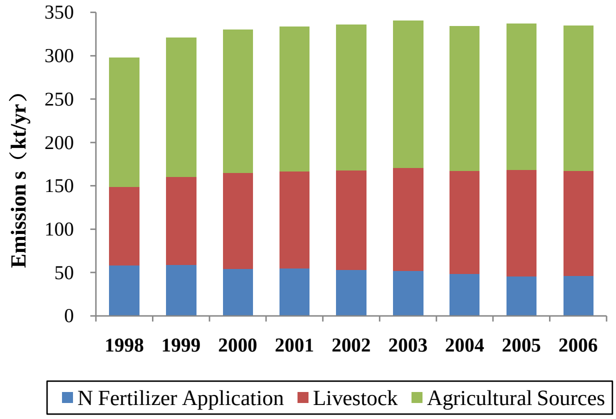


Fig. 9. NH_3 emissions from the categorical and total agricultural sources in the PRD region from 1998 to 2006.

changes of agricultural land use and the reduced application of N fertilizer. Meanwhile, due to the variations of the magnitude of livestock, a rising and decreasing trend was displayed in 2005 and 2006, respectively.

3.6 Characteristics of precipitation and its association with ammonia

3.6.1 Characteristics of precipitation

The average annual proportion of chemical compositions is shown in Fig. 10. SO_4^{2-} is the most abundant anion in precipitation due to the fact that coal is the major energy carrier in the PRD region. The ion of NH_4^+ that was generated with precursors of SO_2, NO_x and NH_3 emissions is the second abundant cation and contributes 27.1 % of the cations measured. As shown in Table 7, by analyzing the annual variation between agriculture NH_3 emissions and pH values, the discrepancies were found in the years 2002 and 2005. While it was observed that the annual variation of pH was consistent with Ca^{2+}+NH_4^+/SO_4^{2-}+NO_3^- (NP/AP) during the study period, it is worth noting that when NH_3 emissions came to the maximum in 2003, the value of NP/AP and pH values also reached their peaks (Table 7). The complex phenomenon was mainly attributed to the fact that pH values are affected by reactions between the acidic and alkaline constituents (Wang and Han, 2011).

3.6.2 Influence of NH_3 emissions on NH_4^+ concentrations

An exploratory linear regression between annual agricultural NH_3 emissions and observed annual average concentrations of NH_4^+ in precipitation was conducted for 2006 (Fig. 11). The natural log-transformed NH_4^+ concentration shows a positive correlation with natural log-transformed NH_3 emission densities ($R^2 = 0.203$), which was higher than

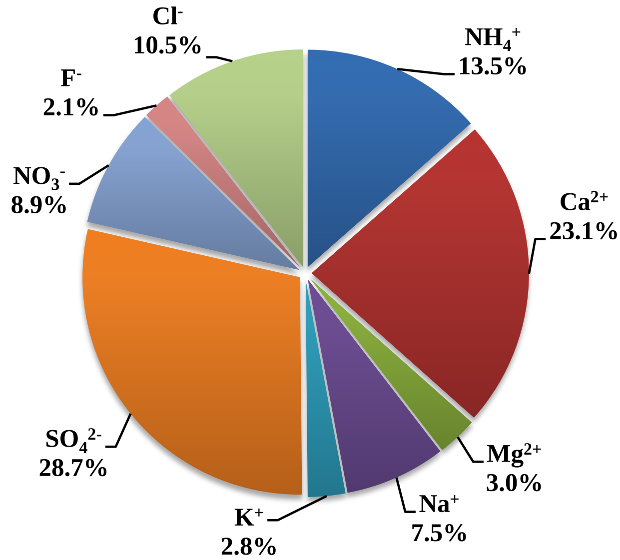


Fig. 10. Average chemical composition of precipitation in the PRD region, 2006.

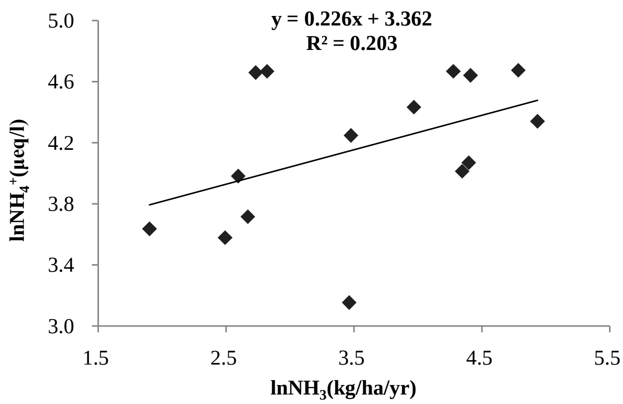


Fig. 11. Natural log-transformed annual average NH_4^+ concentrations in precipitation versus natural log-transformed annual county NH_3 emission densities.

that in the work by Aneja et al. (2003) for America. This indicates that PRD regional NH_3 emissions may partly impact local chemical compositions of precipitation, although the correlation is weaker than that between agricultural NH_3 emissions and NH_4^+ concentrations associated with aerosols ($R^2 = 0.86$) (Aneja et al., 2003). The primary reason is that the incorporation of NH_4^+ into rainfalls takes place on a larger spatial scale, and the majority of NH_4^+ observed in rainfall at a particular location originates from relatively distant sources (Shimshock and Pena, 1989). The NH_4^+ in precipitation would be expected to be influenced by a broader area than just local emissions.

Table 7. Agricultural NH_3 emission and chemical compositions of precipitation in the PRD region, 1986–2006.

Year	Agricultural NH_3 emission	pH	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	NO_3^-	F^-	Cl^-	$Ca^{2+}+NH_4^+/SO_4^{2-}+NO_3^-$
	$kt\,yr^{-1}$		$\mu eq\,l^{-1}$									
1998	149.0	4.79	57.0	64.9	6.4	37.4	9.9	111.6	33.3	5.0	24.5	0.84
1999	160.3	4.86	82.5	90.6	17.3	31.9	12.5	141.7	41.0	18.7	35.4	0.95
2000	165.1	4.84	57.3	84.0	9.1	22.3	12.1	117.6	32.1	13.7	28.0	0.94
2001	166.8	4.83	59.2	63.2	7.8	24.5	8.4	102.0	28.1	8.8	27.9	0.94
2002	168.0	4.54	62.7	70.4	10.4	19.0	20.3	105.4	37.7	10.0	49.6	0.93
2003	170.2	4.84	65.3	76.5	9.1	28.1	11.0	101.2	34.5	10.4	43.7	1.04
2004	167.0	4.66	62.5	138.4	13.0	30.3	13.2	150.6	49.9	14.5	46.9	1.00
2005	168.4	4.50	104.7	168.4	14.1	88.9	12.6	233.9	76.2	19.6	57.2	0.88
2006	167.1	4.65	67.8	115.7	14.9	37.7	14.0	144.0	44.5	10.3	52.7	0.97

4 Summary and recommendations

A high-resolution temporal and spatial anthropogenic NH_3 emission inventory for the PRD region was developed using the proper methods with the best available data, emission factors, and knowledge. The total NH_3 emissions for the year 2006 are 195.7 kt, of which livestock contributes about 61.7 %, N fertilizer application about 23.7 %, and non-agricultural sources about 14.9 %. The estimated results show that agricultural source is the largest contributor to NH_3 emissions in the PRD region.

The spatial distribution patterns of gridded emissions indicate that high NH_3 emissions are mainly distributed over the areas where less urbanization has developed, including rural areas of the PRD region and the arable land. The temporal variations of agricultural NH_3 emissions exhibit a seasonal pattern, in which larger emissions occur during summer and autumn and lower emissions during December to February for livestock; and for N fertilizer application, peak emission appears in July and the lowest emission in January. Assessments of uncertainty in emission estimates show that low uncertainties are associated with agricultural emission estimates, while high uncertainties are associated with non-agricultural emission estimates. The high uncertainty emission sources include hog, broiler, geese of livestock type, and N fertilizer application, and industrial coal combustion of non-agricultural source.

Multi-year agricultural NH_3 emission inventories in the PRD region from 1998 to 2006 were developed. A steady rising trend is observed before 2003 and a weak decreasing trend was noticed in 2004 and 2006, respectively, accompanying smaller discrepancies in total emission amounts during this period.

Analysis of the precipitation data in 2006 shows that SO_4^{2-} was the most abundant anion in precipitation, and the ion of NH_4^+ was the second abundant cation measured. It is observed that the trend of pH values was consistent with that of NP/AP during the study period, and when NH_3 emissions came to the maximum in 2003, the value of NP/AP and pH values were also at their peaks. And linear regression analysis indicates that regional NH_3 emissions may partly impact the local chemical compositions of precipitation.

Further improvements in the accuracy of regional ammonia emissions can be made by conducting local emission testing and investigating source-based temporal and spatial characteristics. For livestock, the detailed characterization of the behavioral patterns of different livestock is necessary; and for N fertilizer application, the collection of activity data about the various fertilizers is important. Additionally, sewage sludge incineration, non-road mobile sources, and natural sources need to be further investigated. Effort should also be made in monitoring atmospheric NH_3 concentrations at different sites in order to validate the ammonia emissions and their temporal and spatial characteristics.

Analysis of the agricultural NH_3 emissions and ammonium concentrations associated with precipitation indicates that there is a complicated relationship between precursors and the characteristics of rainfall. Further research shall look into how environmental parameters affect these relationships. Because of the mutual influence between precipitation and PM due to the reactions among atmospheric precursors, extensive research (both measurement and modeling) is warranted to investigate such seasonal dynamic NH_3/aerosol relationships and the influence of NH_3 on total $PM_{2.5}$.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/7041/2012/acp-12-7041-2012-supplement.pdf.

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