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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 study, air pollution management, and related environmental and ecological issues. A high-resolution NH_3 emission inventory is developed based on the state-of-the-science techniques, the up-to-date information, and the advanced expert knowledge for the Pearl River Delta region, China. To provide model-ready emissions input, this NH_3 emissions inventory is 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 sub-categories are identified in this region, and detailed spatial and temporal characteristics are investigated. Results show that livestock is by far the most important NH_3 emission source that contributes 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. The validity of the NH_3 emissions inventory is justified by the trend analysis of local rainwater compositions, especially 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. Based on the analysis, recommendations for additional work to further improve the accuracy of the NH_3 emissions inventory are also discussed and proposed.

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 et al., 1993), low-visibility (Battye et al., 2003), soil acidification (Asman et al.,

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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 $PM_{2.5}$ in the atmosphere and wet depositions (Asman, 2001; Pavlovic et al., 2006; Pinder et al., 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 indispensable components in formulating control policy for regional air pollution management (Streets et al., 2003).

The Pearl River Delta (PRD) region locates in southern China, having a special landscape surrounded by hills and coast lines 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; Lu et al., 2009). 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). However, due to lack of a reliable and model-ready NH_3 emission inventory, few works are reported regarding how ammonia emissions may impact on 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., 2009a; 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 of 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 reduce 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 identify key 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 relationship between NH_3 emission and ammonium concentrations in precipitation and its implication for acid deposition control.

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2 Data and methodology

2.1 Study domain and source categorization

The study area is shown in Fig. 1 and 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 are investigated, which consist of 9 source categories and 45 sub-categories. The 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. These include examination of literatures, agricultural statistics, and government/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 with the number of scalper, buffalo, goat, hog and other sub-categories, and the amount of total nitrogen fertilizer application. Other miscellaneous non-agricultural activity data were obtained from the Guangdong provincial pollutant statistical reports, official statistical yearbook and others. The 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 are used to identify temporal-spatial characteristics of NH_3 emissions. In order to achieve the third and fourth objectives of this study, relevant activity data from agricultural NH_3 sources are collected from 1998–2006. The 1998–

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2006 precipitation data are collected from officially-operated acid rain monitoring stations in the PRD region. Each precipitation sample is analyzed for pH, rainfall, NH_4^+, SO_4^{2-}, NO_3^- and other ionic components.

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):

$$E = \mathrm{EF} \times \mathrm{AL} \quad (1)$$

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 work are discussed in this section.

2.3.1 Livestock

NH_3 emissions from domestic livestock are based on average waste nitrogen excretion (Yang et al., 2008) and subsequent NH_3 volatilization during housing, storage of manure outside the building, its application to grassland or arable land and grazing periods (Dragosits et al., 1998). A number of studies were performed on NH_3 emission factors in other countries based on the gender, age, body weight, and the purpose of feeding livestock (Misselbook et al., 2000; Reidy et al., 2008; Faulkner et al., 2008). However, since detailed activity data are not available in current study, the emission factors based upon the gender, age, and body weight cannot be used directly for estimating NH_3 emissions in the PRD region. In this study, the sub-source 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

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volatilization rates of domestic livestock are 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 are estimated using the following equations:

$$\mathrm{ef}_1 = \mathrm{N}_{\mathrm{X}1} \times V_1 \quad (2)$$

$$\mathrm{ef}_2 = \mathrm{N}_{\mathrm{X}1} \times (1 - V_1) \times V_2 \quad (3)$$

$$\mathrm{ef}_3 = \mathrm{N}_{\mathrm{X}1} \times (1 - V_1) \times (1 - V_2) \times V_3 \quad (4)$$

$$\mathrm{ef}_4 = \mathrm{N}_{\mathrm{X}4} \times V_4 \quad (5)$$

$$\mathrm{EF} = \mathrm{ef}_1 + \mathrm{ef}_2 + \mathrm{ef}_3 + \mathrm{ef}_4 \quad (6)$$

where $\mathrm{ef}_{1,2,3,4}$ are NH_3-N loss at housing (1), storage(2), spreading (3), and grazing (4), respectively. $\mathrm{N}_{\mathrm{X}1,4}$ are nitrogen (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 population is given by the following equation:

$$A_i = \frac{Q_i}{M_i \times N_i} \quad (7)$$

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 is 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 fertilizers is known as another important part of the agricultural emissions (Battye et al., 1994; Marian et al., 2003). The NH_3 loss from N fertilizer depends on many factors, including chemical compositions of N fertilizers, soil properties (pH value, calcium content, water content, etc.), meteorological conditions (temperature, wind speed, and precipitation), timing, and method of application (Bouwman et al., 2002; Song et al., 2003). However, due to limited information about the amount of various N fertilizers, a synthetic emission factor is estimated by using ratios of application of different fertilizers multiplying by their corresponding NH_3 loss per nitrogen fertilizer (Table 2). In China, widely used N fertilizers are represented by ammonium bicarbonate (ABC) and urea (Zhang et al., 2009), as shown in Table 2. In this study, the NH_3 emission factors are 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 is 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 is assumed for the industrial processes over the whole PRD region.

2.3.4 Human being

It is well documented that direct NH_3 emissions from humans occur from breath, sweat, excretion as a normal metabolic process, and cigarette smoking (Sutton et al., 2000). In this study, NH_3 emission from cigarette smoking is neglected due to the lack of data

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about the population of smokers. The NH_3 emission factors from the human being source are 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 re-calculated using updated parameters for the domestic bio-fuel burning, and using modified variables for the field burning of 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.

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 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).

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The vehicle population data, and vehicle kilometers traveled (VKT) are from the work done by Che et al. (2009). Vehicle types considered in this study include: light duty gasoline vehicle (LDGV), light duty diesel vehicle (LDDV), heavy duty diesel vehicle (HDDV), heavy duty gasoline vehicle (HDGV), and motorcycle (MC). The emission factors are 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) are developed based primarily on emission factors reported about non-agricultural sources in the EIIP database (Roe et al., 2004).

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 is 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 factor adopted in this study is 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 is 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 are treated as point sources, and emissions from these sources are directly allocated into 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) are used to perform spatial allocation. NH_3 emissions from on-road mobile sources are spatially allocated with the use of 'standard length' approach by Zheng et al. (2009b), taking into consideration of road network information and road type-based traffic flows.

The GIS-based land use data are used as surrogates to help spatially allocate NH_3 emissions from biomass burning, N fertilizer application, and livestock area sources based upon source characteristics. NH_3 emissions from biomass burning are 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 detailed description can be found in He et al. (2011). The emissions from N fertilizer application are apportioned according to the distribution of arable lands within the study domain (Zhang et al., 2010).

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, and 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 on 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 emissions from grazing are quite small and are allocated onto suburban areas instead of forest and grassland.

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2.5 Uncertainty analysis

Various uncertainty sources may lead to uncertainties in emission estimates, and 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). Quantitative approach is preferred since it can provide quantitative information to guide future emission inventory improvement (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 named AuvToolPro which were developed recently by our group. The tool 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 analyzing uncertainty in NH_3 emission estimates with the use of AuvToolPro was shown in Fig. 2. In the uncertainty analysis framework, bootstrap simulation or expert judgment is first used to quantify uncertainties in source-based emission factors or other model input parameters, depending on data availability (Zheng et al., 2010). Then, uncertainties in source-based NH_3 emissions and total NH_3 emissions are quantified using Monte Carlo simulation by propagating uncertainties in model inputs trough source-based emission models. For those categories such as 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.

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2.6 Data processing for precipitation samples

Precipitation samples were collected from the beginning of each rain event with a funnel sampler. In this study, data processing about the quality assurance/quality control (QA/QC) procedures for ionic balance of precipitation samples was made according to the technical specification HJ/T165-2004 published by State Environmental Protection Administration of China.

Since the charge balance is influenced by ion balances, before QA/QC, the units for concentration of chemical compositions should be expressed in the form of μeq l^{-1}. The H^+ concentration in precipitation samples 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^+.

$$\overline{C} = \frac{\sum_{i=1}^{n} C\mathrm{i}P\mathrm{i}}{\sum_{i=1}^{n} P\mathrm{i}} \tag{8}$$

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

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.

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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 source responsible for 61.7 % of the total NH_3 emissions and the contributions by sub-source categories for livestock source are given in Fig. 3. The results show that there are large differences among the different livestock species. Broiler, hog, goose, and others account for 43.4 %, 32.1 %, 6.5 %, and 18.0 % of the total livestock emissions, respectively. Broiler and hog are the two largest NH_3 emission sources owing to the need for their large consumption, and statistics from ASYG show that the production of pork and poultry account for approximately 66.3 % and 30.1 % of the total yield of meat, respectively. In addition, as for goose, the consumption in the PRD region is relatively higher than in other provinces in China, owing to the natural dense water systems suitable for raising goose as well as the traditional dieting habits for goose. Meanwhile, due to the shorter breeding cycle, smaller floor space, higher stocking density for these three livestock, there are larger yields and better developments in the PRD region. By contrast, the smaller contributions of other livestock (e.g. scalper, 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 is the application of N fertilizers represented by ABC and urea, which account 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 solely ABC manufacturer and user, and the combined consumption of ABC and urea in China is responsible for 90 % of the total N fertilizer application.

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Of many non-agricultural sources, biomass burning, sewage treatment, and on-road mobile sources are ranked the top three for NH_3 emissions. Within the sub-source categories of biomass burning, domestic bio-fuel combustion is the major contributor in that domestic crop residue and 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 are 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 processed a large quantity of sewage due to the large population and numerous 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 4 presents detailed city contributions of total NH_3 emissions and contributions from different sources in different cities in the PRD region. Guangzhou has 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 of the PRD region.

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.

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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 the PRD cities than in other cities, especially in Shenzhen 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 sources in the PRD region or Guangdong province are rarely available, only agricultural sources are 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 emission factors of N fertilizer application, field burning of crop residues, LDGV are 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. scalper, dairy, goat, pig, and poultry) were included.

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 N fertilizer application, and there are large differences among the different works by Sun et al. (1997), Wang et al. (1997), and Dong et al. (2010) for Guangdong province. The modified synthetic emission factor taking into consideration of 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 use the single emission factor for total N fertilizer.

3.2 Spatial characteristics

The 3 km × 3 km gridded PRD regional NH_3 emissions were presented in Fig. 5 and Fig. 6 for different emission sources and the total emissions, respectively. Point sources comprise power plants, industrial stationary boilers, and processes scattered over urban areas. The large emissions from point sources distributed over the grid cells where sewage treatment plants and livestock feeding operations are densely located (Fig. 5a). As seen in Fig. 5b, human being and domestic fuel combustion exhibited a relatively uniform distribution that focus on the downtown areas with dense populations, especially in Guangzhou, Shenzhen, and Zhuhai. 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. 5c. The spatial distribution of biomass burning emissions (Fig. 5d) is mainly distributed over rural residential areas, and that 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. 5e). Most emissions from livestock (Fig. 5f) were distributed over rural residential and crop areas in Huizhou, Guangzhou, Foshan, Zhaoqing, and Jiangmen due to the large amounts of livestock were raised in these cities. Overall, anthropogenic NH_3 emissions are mainly distributed over the area where less urbanization developed, including outlying areas of the PRD region and less-developed areas of the economically developed cities, like Zengcheng and Huadu

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areas of Guangzhou, Sanshui area of Foshan, Zhaoqing, and Jiangmen (Fig. 6). The general characteristics is consistent with the patterns of agricultural emissions that contribute more than 80 % of the total emissions, and it exhibits a large difference from the emissions of SO_2 and NO_x in the PRD region (Zheng et al., 2009a) that are mainly distributed over central-southern city clusters.

3.3 Temporal characteristics

Emissions in livestock are based on the analysis of monthly yields of livestock breeding and human consumptive activities, and the monthly product yields and consumptions are derived from the statistical reports of Guangdong province (GPBS, 2007). As shown in Fig. 7, compared to other months, the emissions are relatively higher from May to October, because the higher ambient temperatures increase the volatilization of excretions, and lower from December to February when temperatures are typically lower and the consumption of livestock for dairy life reduced due to the vast migrant workers returning home during the Chinese Spring Festival. Variations in the percentage of the averaged monthly NH_3 emissions from N fertilizer application were shown in Fig. 7. A common feature is that N fertilizer application was the lowest in February because of Chinese New Year occurring in this month. There are significant differences in the monthly profile compared with livestock emissions. It increases gradually from April and peaks in July and then decreases due to the change of crop types from early rice to late rice with a typical planting pattern including raising rice seedlings, transplanting, earing, grouting, topdressing, and harvest during March–September (http://www.zzys.gov.cn/, China's planting information network). In addition, other impacting factors including temperature and daytime sunlight durance during these months also play a role.

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3.4 Uncertainties

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 being, 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; (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 re-calculated 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 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 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

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and proper statistics of activity data that using the "top-down" method instead. 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 is estimated to be −43 % to 50 %, characterized on the 95 % confidence interval.

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 determined 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

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(ASYG) 1999–2007. As shown in Fig. 8, steady rising trend of the total agricultural emissions was observed before it peaked in 2003 and then slightly decreased in 2004 and 2006. Based on the trend analysis about the livestock and N fertilizer application, the decreasing trend after the year 2003 could be attributed to the 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

Figure 9 shows the annual average pH and acid rain frequency of rainwater at the nine cities in the PRD region for the base year 2006. All cities had annual average pH values less than 5.6. There was a zonal distribution with high acid rain frequency above 68.9 % that focus on the cities of Guangzhou, Zhaoqing, Foshan, and Shenzhen at the north-south axis of the PRD region. 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 precursor NH_3 emissions is the second abundant cation contributing 27.1 % of the cations measured, and mostly likely it is influenced by the NH_3 emissions.

As shown in Table 7, the pH values displayed a steady trend over time ranging from 4.50 to 4.86, with the lowest value in 2005 during 1998–2006. The situation of acid rain was not improved during this period, but the long-term variation of SO_4^{2-}/NO_3^- was between 2.9 and 3.7 close to that in the developed countries of Europe and North America (Polkowska et al., 2005; Ito et al., 2002; Glavas et al., 2002), which may suggest that the contribution of NO_x to acidification become more and more important due to the rapidly increasing number of motor vehicles.

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3.6.2 Impacts of ammonia emissions on precipitation properties

In Table 7, the mean long-term trend of the ratio Ca^{2+}+NH_4^+/SO_4^{2-}+NO_3^- (NP/AP) was around 0.94 during 1998–2006, which was lower than that of some northern Chinese cities (e.g. Beijing) (Yang et al., 2004). This indicates that more inputs of alkaline species like NH_3 into the precipitation in Beijing than that in the PRD region.

A significant correlation between agricultural NH_3 emissions and pH values is observed, and the concordant rising trend is found in most years except in the years of 2002 and 2005 (Fig. 11). Therefore, a simple relationship cannot explain the variation of rainwater pH values that affected by reactions between the acidic and alkaline constituents (Wang et al., 2011). While, as shown in Fig. 12, it is observed that the trend of pH values is consistent with NP/AP during the study period. It's 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, which may imply that local NH_3 emissions have an impact on the characteristics of rainwater.

3.6.3 Influence of NH_3 emissions on NH_4^+ concentrations

Figure 13 displays the long-term trend between agricultural NH_3 emissions and NH_4^+ concentrations associated with precipitation during 1998–2006 in the PRD region, and the variation of NH_4^+ concentrations is similar to that of agricultural NH_3 emissions except in 1999.

An exploratory linear regression between annual agricultural NH_3 emissions and observed annual average concentrations of NH_4^+ in precipitation was conducted for the base year (Fig. 14). The natural log-transformed NH_4^+ concentration in precipitation shows a positive correlation with natural log-transformed NH_3 emission densities within the corresponding county ($R^2 = 0.203$). And the value of R^2 was higher than that in the work by Aneja et al. (2003) for America indicating that PRD regional NH_3 emissions impact on the 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, so that the local signal may result from the relatively inefficient process of below-cloud scavenging of NH_3 and NH_4^+ (Shimshock et al., 1989).

4 Summary and recommendations

A high-resolution temporal and spatial anthropogenic NH_3 emission inventory for the PRD region is 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 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 February. 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.

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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 the annual average pH value was 4.65 and acid rain has a frequency of 68.9 % for the PRD region. SO_4^{2-} was the most abundant anion in precipitation and the ion of NH_4^+ was the second abundant cation measured.

The acid conditions in precipitations were not improved during 1998–2006 and the average NP/AP value of 0.94 is lower than that of some northern cities in China. A significant long-term correlation between agricultural NH_3 emission and pH value was observed reflecting the fact that the local NH_3 emissions influence the precipitation characteristics. 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 impact on the local chemical compositions of precipitation.

Further improvements for the accuracy of regional ammonia emissions are necessary and likely through local emission factor development, comprehensive collection of activity data, and temporal and spatial surrogate data. With 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.

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 the mutual influence between precipitation and PM due to the reactions among atmospheric precursors, extensive

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research (both measurement and modeling) is warranted to investigate such seasonal dynamic NH_3/aerosol relationships and the influence of NH_3 on total $PM_{2.5}$.

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

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

Note: [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.

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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

Note: [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).

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

Source	Emission factor	Unit	Source	Emission	Unit factor
Livestock[a]			domestic straw burning	1.30	$g\,kg^{-1}$
scalper	25.52	$kg\,a^{-1}$	domestic fuel wood burning	1.40	$g\,kg^{-1}$
buffalo	10.56	$kg\,a^{-1}$	**Humans Being**		
dairy	37.61	$kg\,a^{-1}$	human breath	3.64[f]	$g\,(per\,a)^{-1}$
cattle	22.58	$kg\,a^{-1}$	human sweat	17.00[f]	$g\,(per\,a)^{-1}$
sheep	4.93	$kg\,a^{-1}$	human excretion	0.76[g]	$kg\,(per\,a)^{-1}$
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	7.30[h]	$kg\,(kg^{-1}\,CH_4)^{-1}$
ammonium synthesis[c]	2.10	$kg\,t^{-1}$	**On-road Mobile Sources**[h]		
nitrogenous fertilizer[d]	2.00	$kg\,t^{-1}$	light-duty gasoline (LDGV)	63.20	$mg\,km^{-1}$
nitric acid[c]	3.80	$kg\,t^{-1}$	light-duty diesel (LDD)	4.20	$mg\,km^{-1}$
phosphoric acid[c]	0.07	$kg\,t^{-1}$	heavy-duty gasoline (HDGV)	28.00	$mg\,km^{-1}$
Biomass Burning[e]	1.30		heavy-duty diesel (HDDV)	16.80	$mg\,km^{-1}$
forest fire burning	1.02	$g\,kg^{-1}$	Motorcycle (MC)	7.00	$mg\,km^{-1}$
crop residues field burning	0.53	$g\,kg^{-1}$			

Note: [a] From Yang (2008). [b] From Table 3. [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 HK-GD 2003-based EI. [h] From Roe et al. (2004).

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Table 4. NH_3 emission inventory in the PRD region for the year of 2006.

Source	Category	Emission ($kt\,yr^{-1}$)	% of total
Agricultural source	**Livestock**	**120.9**	**61.7 %**
	N Fertilizer Application	**46.3**	**23.7 %**
	ammonium bicarbonate	29.7	15.2 %
	urea	16.1	8.2 %
	ammonium nitrate	0.2	0.1 %
	ammonium sulfate	0.1	0.1 %
	aqua ammonia	0.0	0.0 %
	others	0.2	0.1 %
Non-agricultural source	**Industry Sources**	**1.6**	**0.8 %**
	Biomass Burning	**7.2**	**3.7 %**
	field straw burning	0.5	0.3 %
	domestic crop residue	2.0	1.0 %
	domestic firewood	4.6	2.4 %
	forest fire	0.0	0.0 %
	Sewage Treatment	**6.4**	**3.3 %**
	Waste Treatment	**3.6**	**1.8 %**
	waste incineration	0.6	0.3 %
	waste landfill	3.0	1.5 %
	Human being	**2.6**	**1.3 %**
	human breath	0.2	0.1 %
	human sweat	0.7	0.4 %
	human excretion	1.7	0.9 %
	Fuel Combustion	**2.3**	**1.2 %**
	On-road Mobile Source	**4.9**	**2.5 %**
	light duty gasoline vehicle	4.3	2.2 %
	light duty diesel vehicle	0.1	0.0 %
	heavy duty gasoline vehicle	0.1	0.0 %
	heavy duty diesel vehicle	0.2	0.1 %
	motorcycle	0.4	0.2 %
	Total	195.7	100.0 %

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Table 5. Comparison with other studies.

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

Note: [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).

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 Being	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	222.4	(−43 %, 50 %)

Note: * 95 % Confidence Interval

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Table 7. pH and chemical compositions of precipitation in the PRD region, 1998–2006.

Year	pH	NH_4^+ (μeq l^{-1})	SO_4^{2-} (μeq l^{-1})	NO_3^- (μeq l^{-1})	SO_4^{2-}/NO_3^-	$Ca^{2+}+NH_4^+/SO_4^{2-}+NO_3^-$
1998	4.79	57.0	111.6	33.3	3.4	0.84
1999	4.86	82.5	141.7	41.0	3.5	0.95
2000	4.84	57.3	117.6	32.1	3.7	0.94
2001	4.83	59.2	102.0	28.1	3.6	0.94
2002	4.54	62.7	105.4	33.7	3.1	0.93
2003	4.84	65.3	101.2	34.5	2.9	1.04
2004	4.66	62.5	150.6	49.9	3.0	1.00
2005	4.50	104.7	233.9	76.2	3.1	0.88
2006	4.65	67.8	144.0	47.2	3.0	0.97

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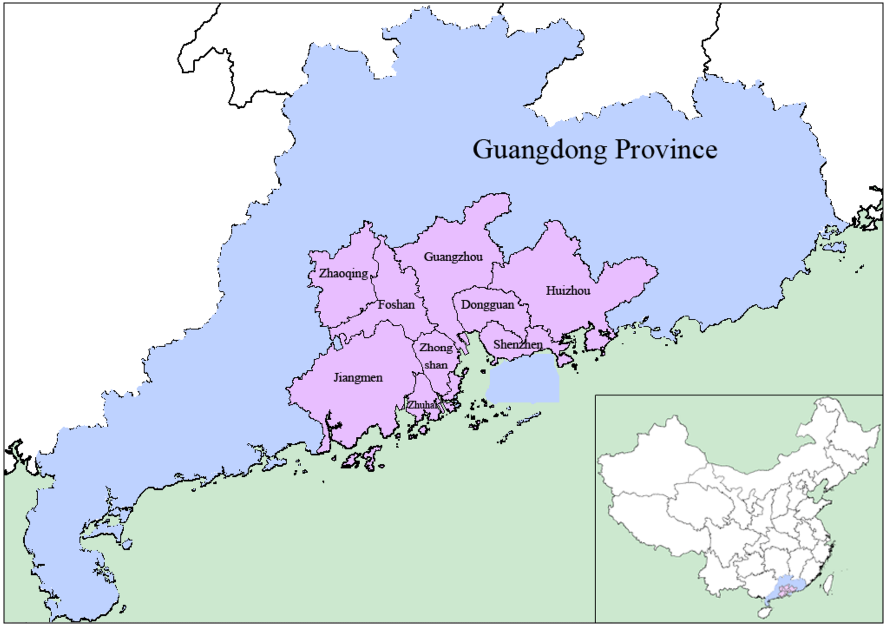

Fig. 1. The PRD region and its location.

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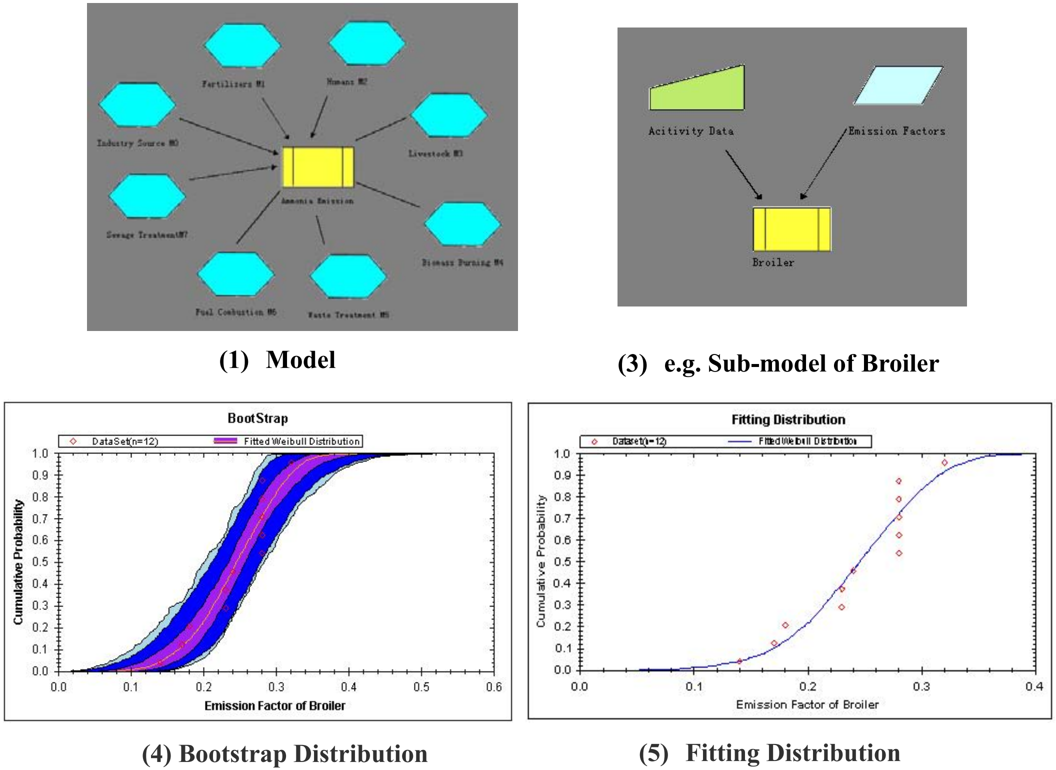

Fig. 2. The model framework for analyzing uncertainty in emission estimates by the AuvTool-Pro.

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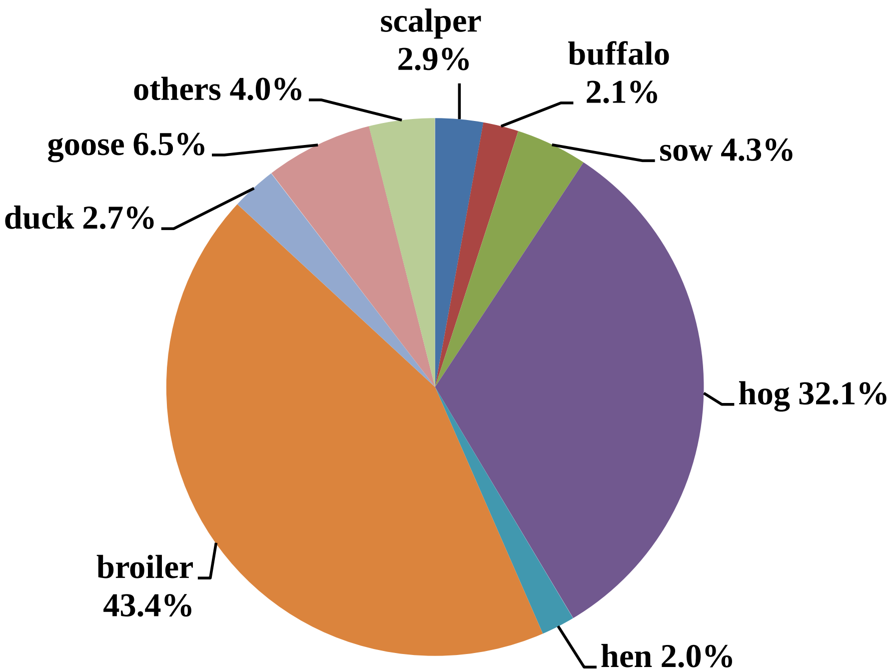

Fig. 3. Emission contributions by subcategories of livestock for the year of 2006.

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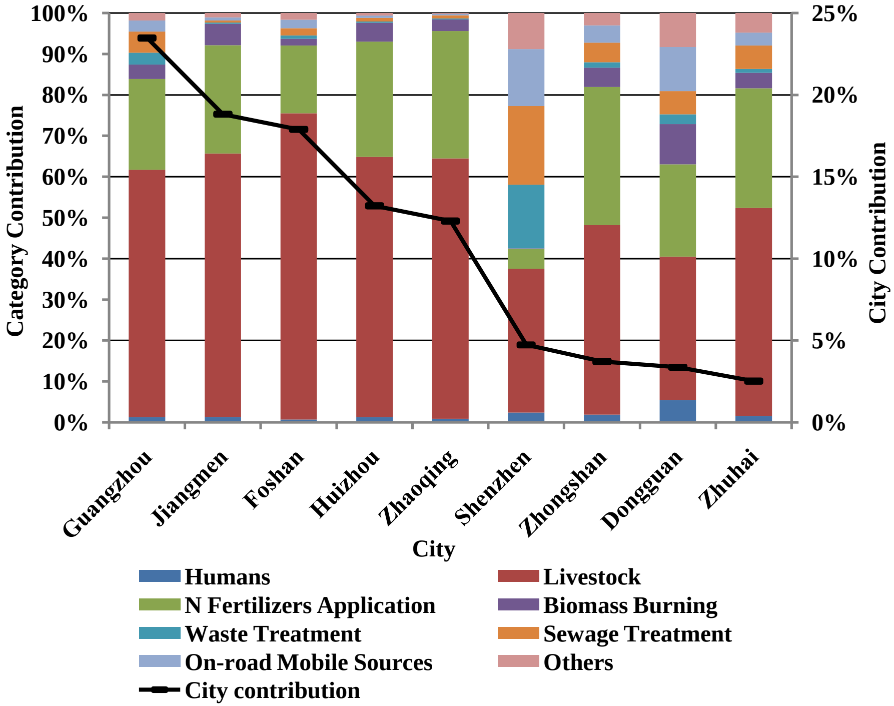
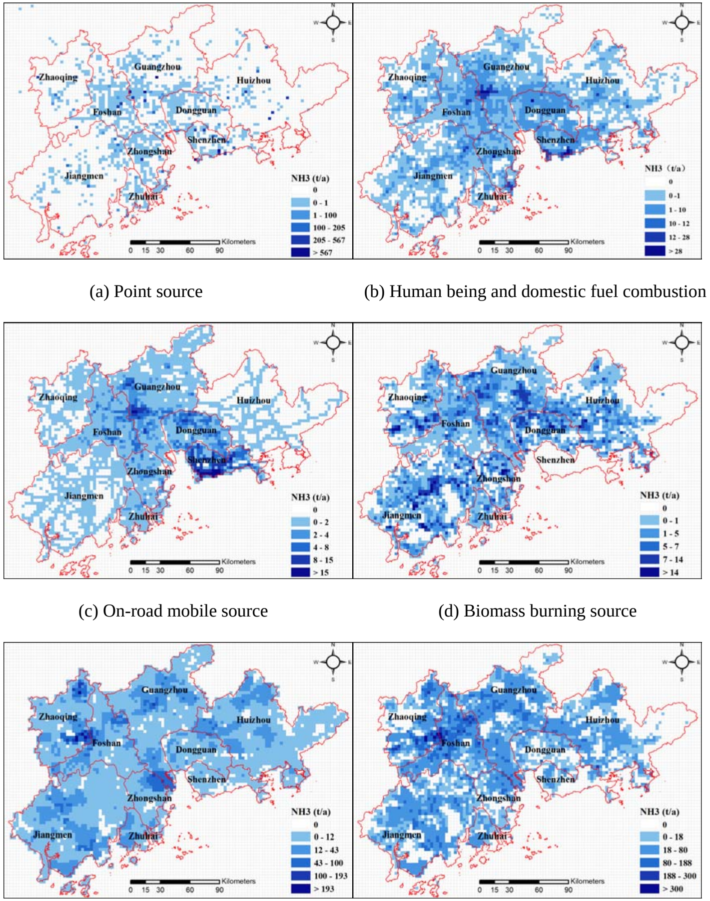


Fig. 4. Source contributions by cities in the PRD region for the year of 2006.



(a) Point source (b) Human being and domestic fuel combustion

(c) On-road mobile source (d) Biomass burning source

(e) N fertilizer applization source (f) Livestock area source

Fig. 5. Spatial distributions of NH_3 emissions by source category in the PRD region.

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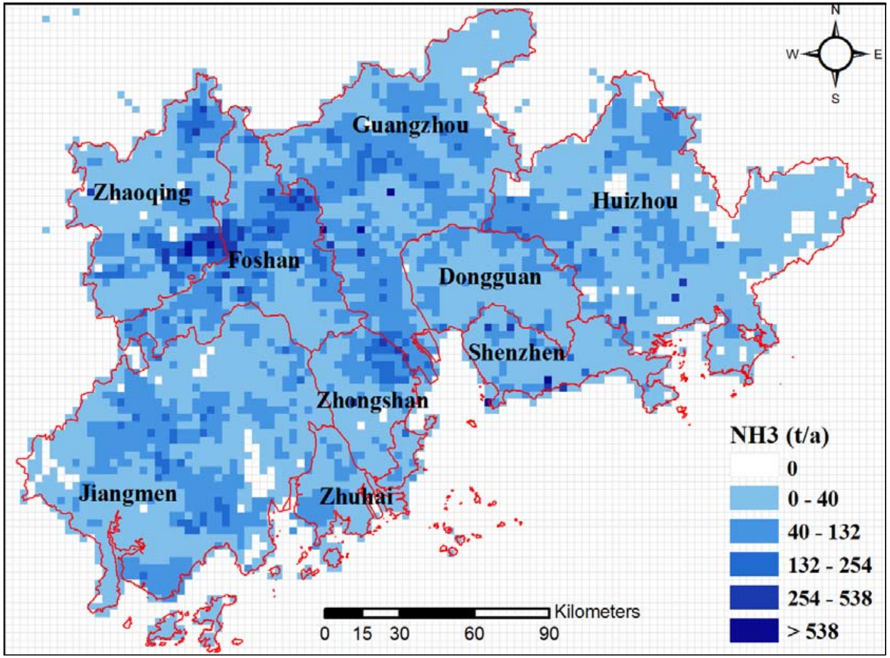

Fig. 6. Spatial distributions of total NH_3 emissions in the PRD region.

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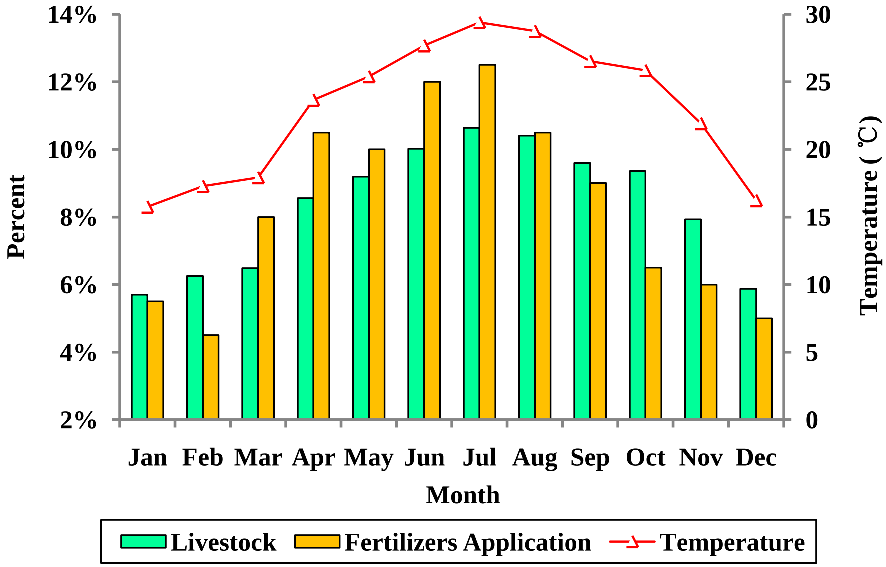

Fig. 7. Monthly variations in emissions from livestock population and N fertilizer applications, and in temperature.

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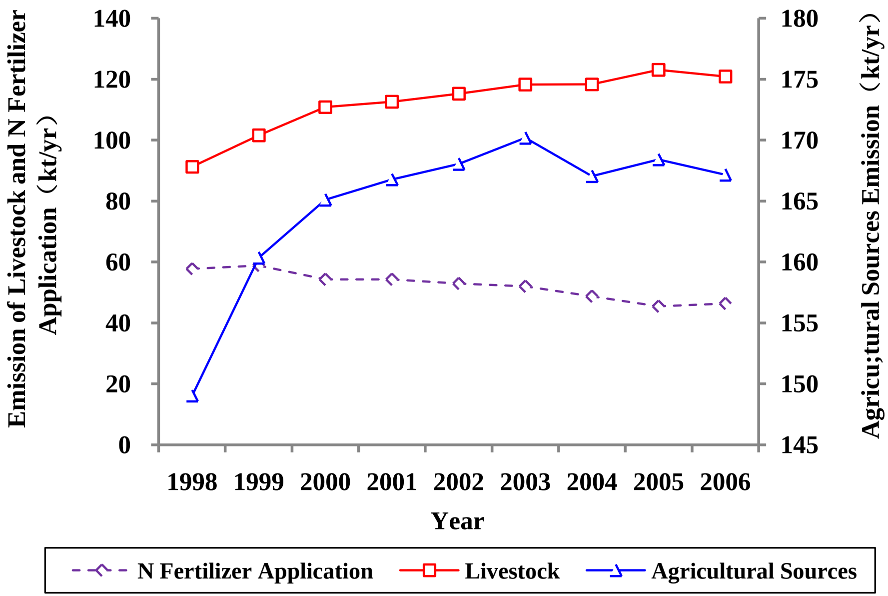

Fig. 8. NH_3 emissions from the categorical and total agricultural sources in the PRD region from 1998 to 2006.

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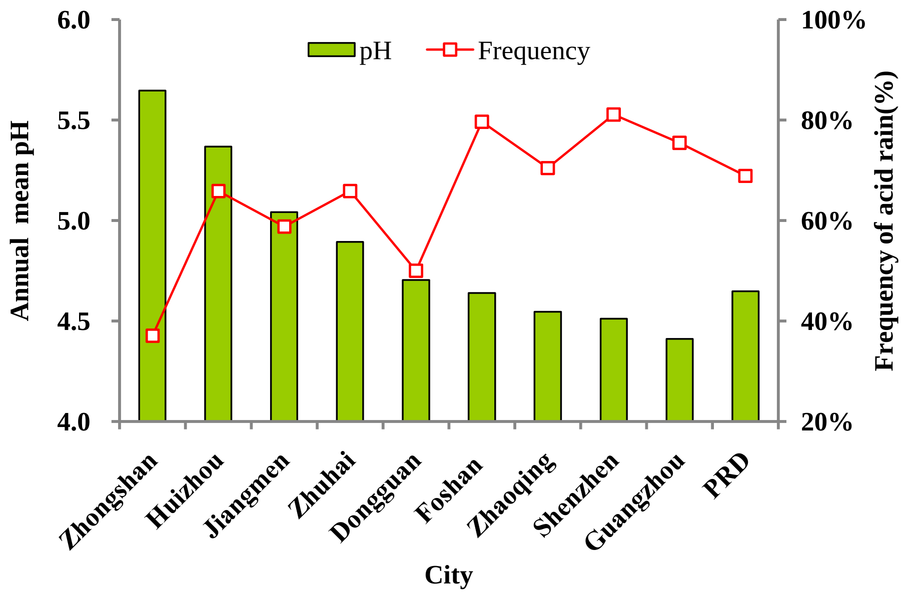

Fig. 9. Annual average pH and frequency of acid rain in the PRD region, 2006.

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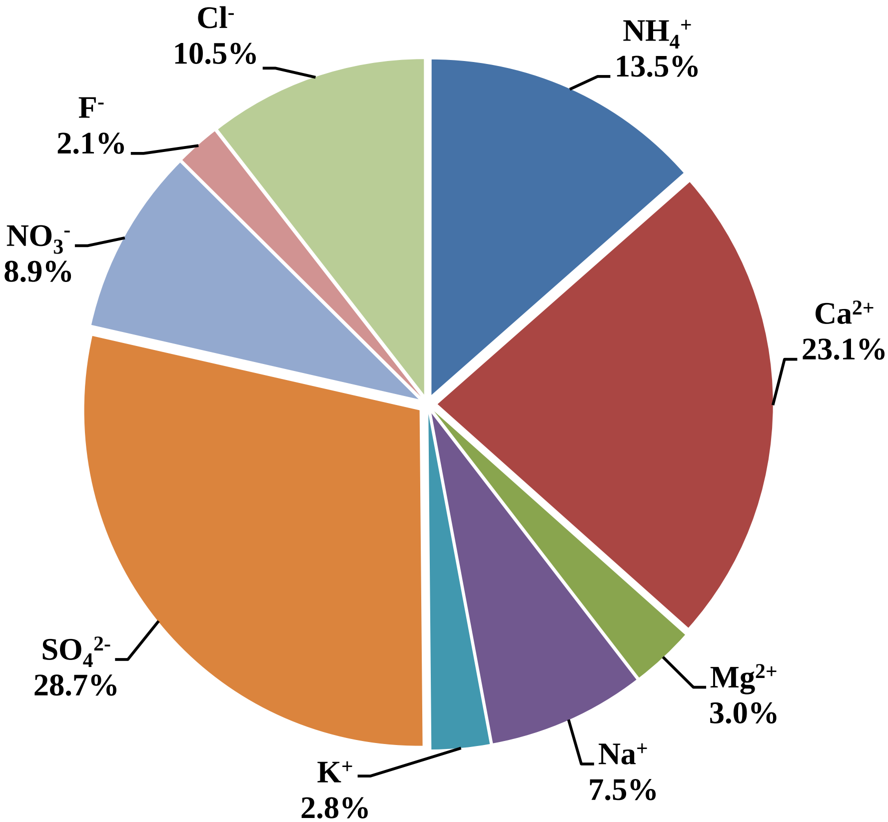

Fig. 10. Average chemical composition of precipitation in the PRD region, 2006.

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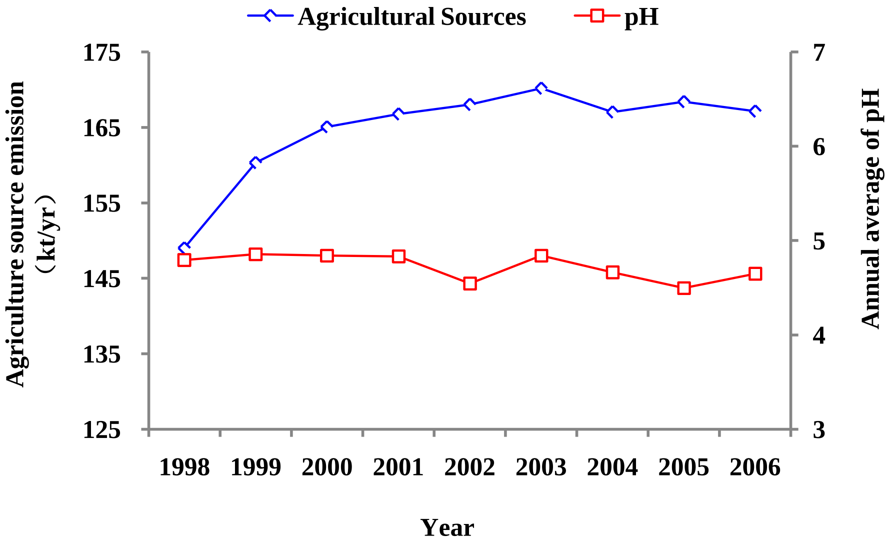

Fig. 11. Temporal variational trend of the relationships between agricultural NH_3 emission and pH of precipitation in the PRD region, 1998–2006.

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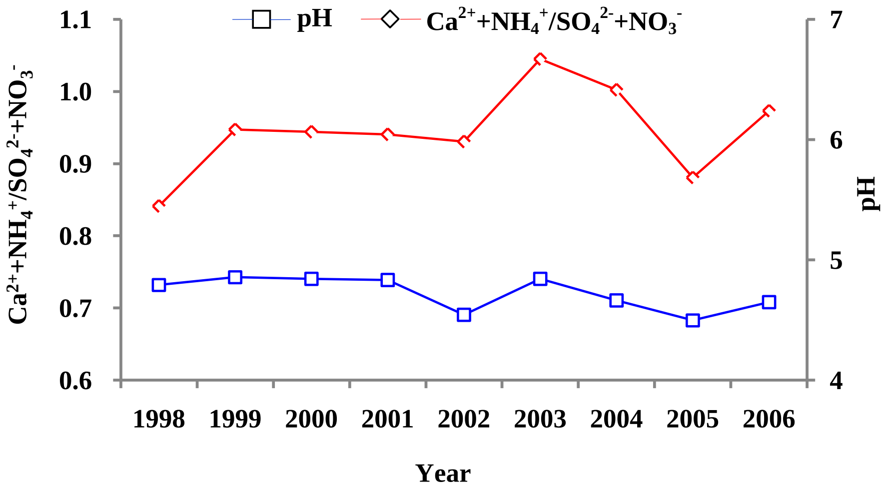

Fig. 12. Temporal variational trend of the relationships between $Ca^{2+} + NH_4^+/SO_4^{2-} + NO_3^-$ and pH of precipitation in the PRD region, 1998–2006.

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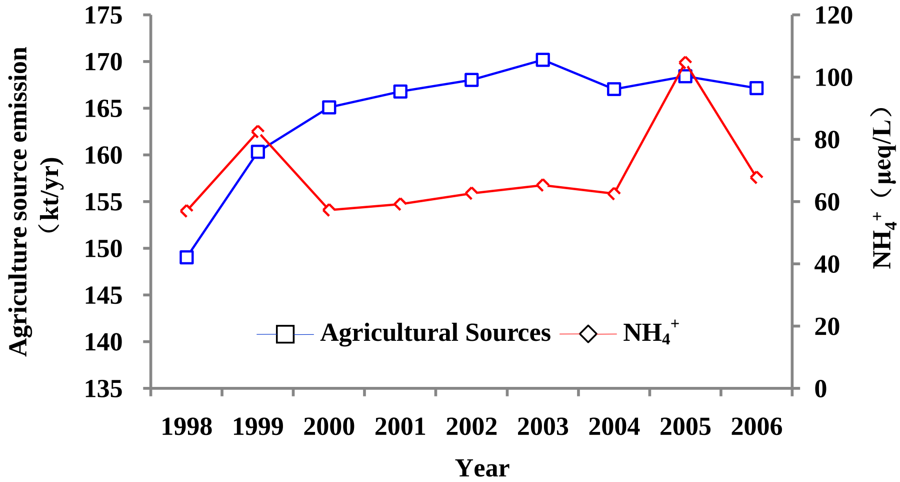

Fig. 13. Long-term trend of the relationships between agricultural NH_3 emission and NH_4^+ concentration of precipitation for the PRD region, 1998–2006.

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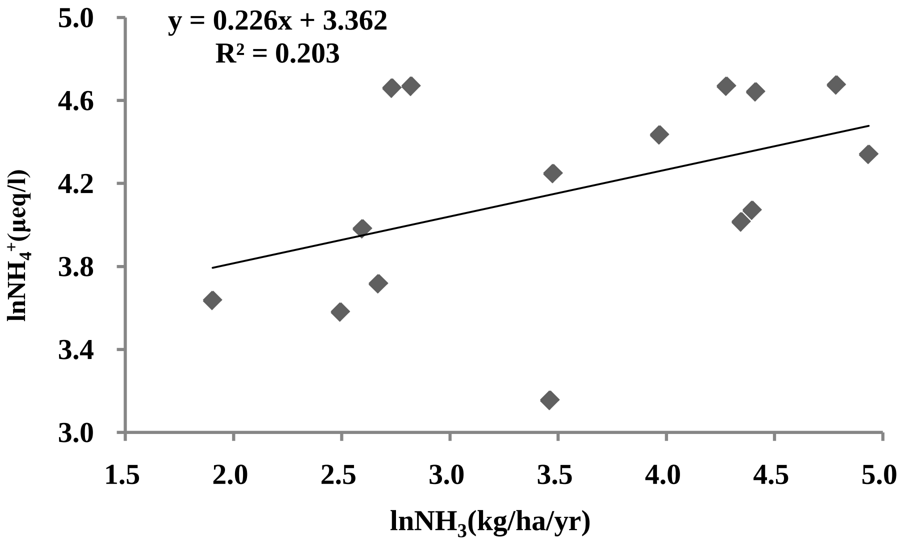

Fig. 14. Natural log-transformed annual average ambient NH_4^+ concentration versus natural log-transformed annual county NH_3 emission density.

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