

Assessment of the Secondary PM_{2.5} Related to Ammonia
Emission in Kanto Region of Japan by Atmospheric Simulation

January 2018

Mengqian LU

Assessment of the Secondary PM_{2.5} Related to Ammonia
Emission in Kanto Region of Japan by Atmospheric Simulation

A Dissertation Submitted to
The Graduate School of Life and Environmental Sciences,
University of Tsukuba
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Environmental Studies
(Doctoral Program in Sustainable Environmental Studies)

Mengqian LU

Abstract

Ammonia has been widely applied in agricultural and industrial sectors. In recent years, it also developed new applications in energy sector. Thanks to the rise of creation technology, ammonia production expanded during the last century. However, volatilization and poor use efficiency lead to ammonia emission. In addition to being toxic, gaseous ammonia is a precursor of secondary fine particulate matters (PM_{2.5}). PM_{2.5} not merely obstructs the atmospheric visibility, but also negatively affects public health by inducing respiratory/cardiovascular diseases.

To alleviate PM_{2.5}-related environmental problems, the government of Japan has enacted an air quality standard in 2009. However, limited achievement has been obtained. Compared with other PM_{2.5} precursors (SO₂ and NO_x), there is still a lack of policies for controlling ammonia emission, especially from the perspective of secondary inorganic PM_{2.5}.

Therefore, appropriately understanding the current situation of the ammonia emission and ammonia-related PM_{2.5} would be very important. With a better understanding of the recent situation, effective emission abatement options for controlling ammonia-related PM_{2.5} should be explored.

To achieve the above-mentioned objectives, in this study, atmospheric models were used to conduct the atmospheric simulations. PM_{2.5} resulted from the chemical reactions among the precursors was estimated by a chemical transport model: ADMER-PRO (modified version). ISORROPIA II, which is now embedded in ADMER-PRO, was used to simulate the thermodynamic equilibriums among the secondary inorganic PM_{2.5} (nitrates, sulfates and ammonium). Typical weather patterns in July to August and December to January were selected as the study periods, which reflect the meteorological conditions in winter and summer. Kanto Region was selected as the study domain, for the large population and energy consumption compared with other areas throughout Japan.

Firstly, a comparative study was conducted on ammonia emission and ammonia-related PM_{2.5} in 2000 and 2010 in Kanto Region. According to the results, annual ammonia emission slightly decreased during 2000-2010 by 13%. Adversely, SO₂ and NO_x enormously decreased by 32.5% and 32.9%, respectively. Responding to the declines of the precursor emissions in this decade, the average PM_{2.5} concentration reduced by 44.8% in summer and 16.1% in winter. However, the achievements might be benefitted from the reduction of SO₂ and NO_x.

The next study aimed to explore the most efficient emissions control and abatement options. The first scenario was established to investigate the PM_{2.5} reduction efficiency of the individual precursor emissions (SO₂, NO_x and ammonia). It could be obtained that when same emission abatement policy was applied to the secondary PM_{2.5} precursors, SO₂ abatement showed the best efficiency in reducing PM_{2.5} concentrations. Additionally, ammonia abatement also showed a certain efficiency of PM_{2.5} reduction. Controlling NO_x emission indicated an unstable

performance, especially in winter. The second scenario was established to investigate the $PM_{2.5}$ reduction efficiency of ammonia emission discharged from different emission sources (all sources, agricultural sources, urban sources). Although agriculture has been always regarded as the major emission source, when applied the same emission reduction strategy, cutting down agricultural emissions presents a very low efficiency of $PM_{2.5}$ reduction. Adversely, controlling the ammonia emission from vehicle sources would be very effective for reducing $PM_{2.5}$ concentrations.

Although the current ammonia emission is mainly contributed by agricultural sources, in the future, ammonia would expand new applications in energy sector. Therefore, we then investigated the potential $PM_{2.5}$ -related health impacts of utilizing ammonia for power generation. When using ammonia-hydrogen energy to supply 20% of the energy in Kanto Region, the $PM_{2.5}$ would increase by 11.7% ($0.16 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{y}^{-1}$) in winter and 3.5% ($0.08 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{y}^{-1}$) in summer, resulting in 351 premature deaths per year.

The results of this study proved that controlling ammonia emission showed a certain efficiency in lowering secondary $PM_{2.5}$ levels, which would be even more effectively than controlling NO_x emission. When compared with the limited potential for further controls of SO_2 and NO_x emission, the policy for ammonia emission is still extensible. Since ammonia has extended its applications as one of the renewable energy sources, further in-depth research on the establishment of safety standards in energy sector is necessary.

Based on the results, further suggestions could be given and contribute to the establishment of ammonia-related strategies. Since ammonia has extended the application in electric power generation, this study is also helpful to assess the future trends and potential impacts of ammonia emission discharged from energy sector.

Keywords: ammonia; fine particulate matters; atmospheric simulation; environmental risk

Contents

Abstract	i
Contents	iii
List of Tables	v
List of Figures	vi
Chapter 1 Introduction	1
1.1 Background	1
1.2 Problems related with ammonia emission	2
1.2.1 Current situation of ammonia emission and ammonia-related PM _{2.5}	2
1.2.2 Lack of integration policies and experiences of ammonia-related PM _{2.5} abatement	3
1.2.3 Expanding applications and potential risks of ammonia in energy sector	5
1.3 Influence factors on ammonia-related PM _{2.5}	6
1.3.1 Meteorological conditions	6
1.3.2 Gas ratio	7
1.4 Necessity of atmospheric models and the existing assessments of ammonia-related PM _{2.5}	8
1.4.1 Necessity of atmospheric models.....	8
1.4.2 Existing assessments of ammonia-related PM _{2.5}	8
1.5 Objectives and originalities of this research	9
1.6 Structure of this research	9
Chapter 2 Current Situation of Ammonia emission and PM_{2.5} Reduction in Kanto Region	18
2.1 Introduction.....	18
2.2 Materials and methods	19
2.2.1 Study domain	19
2.2.2 Emission estimation	20
2.2.3 Atmospheric modeling	20
2.3 Results and discussion	21
2.3.1 Ammonia emission in Kanto Region	21
2.3.2 Inorganic PM _{2.5} in Kanto Region.....	23
2.4 Summary	24
Chapter 3 Analysis of Efficient Abatement Options for PM_{2.5} Reduction by Controlling Ammonia Emission in Kanto Region	35
3.1 Introduction.....	35
3.2 Materials and methods	36
3.2.1 Scenario establishment based on different ammonia precursors and ammonia emission sources	36
3.2.2 Emission inventories	37
3.2.3 Atmospheric simulation	37

3.3 Results and discussion	37
3.3.1 PM _{2.5} reductions respond to precursors	37
3.3.2 The PM _{2.5} reductions respond to ammonia emission sources.....	39
3.3.3 The uncertainty of weather pattern selection	41
3.4 Summary	42
Chapter 4 Impact Assessment of the PM_{2.5} Resulted from the Application of Ammonia-hydrogen Energy in Kanto Region.....	53
4.1 Introduction.....	53
4.2 Materials and methods	54
4.2.1 Focus and design.....	54
4.2.2 Ammonia emission estimation	55
4.2.3 NO _x and SO ₂ emission estimation.....	56
4.2.4 Atmospheric modeling	56
4.2.5 Health impact analysis	56
4.3 Results and discussion	57
4.3.1 Emission estimation	57
4.3.2 Incremental PM _{2.5} concentration.....	59
4.3.3 Health impacts	60
4.4 Summary	61
Chapter 5 Conclusions and Future Research.....	72
5.1 Current situation of ammonia emission and PM _{2.5} reduction in Kanto Region	72
5.2 Analysis of efficient abatement options for PM _{2.5} reduction by controlling ammonia emission in Kanto Region	72
5.3 Impact assessment of the PM _{2.5} resulted from the application of ammonia-hydrogen utilization in Kanto Region.....	73
5.4 Further research	74
References	75
Acknowledgements	88

List of Tables

Table 1.1 Annual ammonia emission from the major emission sources in Japan.....	12
Table 1.2 Major atmospheric reactions for the formation of ammonia-related PM _{2.5} , summarized by Behera <i>et al.</i>	13
Table 2.1 Summary of the existing air quality standards for PM _{2.5}	26
Table 2.2 Summary of the short-term planning for domestic PM _{2.5} abatement strategies of Japan	27
Table 2.3 Annual emissions of the PM _{2.5} precursors in Japan	28
Table 3.1 Basic emissions of the PM _{2.5} precursors in Kanto Region.....	43
Table 3.2 Annual average reductions and population-weighted average concentrations of PM _{2.5} reduction after applied the 5% abatement policy to different ammonia sources (all sources, agricultural sources, vehicles)	44
Table 4.1 The 21 LNG thermal power plants in Kanto Region and their estimated ammonia emission	63
Table 4.2 The number of LNG thermal power plants and the annual premature deaths for each prefecture in Kanto Region	64

List of Figures

Figure 1.1 The increase of annual PM _{2.5} concentration caused by food export in U.S..	14
Figure 1.2 PM _{2.5} sensitivity (defined as [d(PM)/d(ammonia)]) responses to GR at 298 K and 90% rh	15
Figure 1.3 NO ₃ ⁻ responses to the changes of NO _x and NH ₃ emissions, monthly average result in Beijing, July, 2005 (μg·m ⁻³)	16
Figure 1.4 The structure of this research.	17
Figure 2.1 Seven prefectures (Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, and Kanagawa) in Kanto Region	30
Figure 2.2 Spatial distribution map of ammonia emission in 2000, winter (left) and summer (right)	31
Figure 2.3 Spatial distribution map of ammonia emission in 2010, winter (left) and summer (right)	32
Figure 2.4 Spatial distribution map of PM _{2.5} reductions during 2000-2010, winter (left) and summer (right)	33
Figure 2.5 Spatial distribution map of PM _{2.5} reduction ratio of 2010 to 2000, winter (left) and summer (right)	34
Figure 3.1 PM _{2.5} reductions after applied the 5% abatement policy to the precursors in summer (left) and winter (right). 5% abatement of total ammonia emission (a) 5% abatement of total NO _x emission (b) and 5% abatement of total SO ₂ emission (c)	45
Figure 3.2 GR in the base case. Simulated data in summer (July to August) (a) and winter (December to January) (b)	46
Figure 3.3 PM _{2.5} reductions when reduce every 1,000 t of the precursors in summer (left) and winter (right). 1,000 t of ammonia emission (a) 1,000 t of NO _x emission (b) and 1,000 t of SO ₂ emission (c)	47
Figure 3.4 PM _{2.5} sensitivities of cell-grids (GR<10) respond to the corresponding gas ratios when applied the 5% precursor abatement strategy in summer. The scatter chart of 5% ammonia abatement scenario (a), the scatter chart of 5% NO _x abatement scenario (b) and the scatter chart of 5% SO ₂ abatement scenario (c)	48
Figure 3.5 PM _{2.5} sensitivities of cell-grids (GR<10) respond to the corresponding gas ratios when applied the 5% precursor abatement strategy in winter. The scatter chart of 5% ammonia abatement scenario (a), the scatter chart of 5% NO _x abatement scenario (b) and the scatter chart of 5% SO ₂ abatement scenario (c)	49
Figure 3.6 Ammonia emission cut down from different emission sources in summer (left) and winter (right). 5,200 t from all the ammonia emission sources (a) 5,200 t from agricultural sources (b) and 5,200 t from vehicle exhausts (c)	50

Figure 3.7 PM _{2.5} reductions after cutting down the same amount of ammonia emission from different ammonia emission sources in summer (left) and winter (right). 5,200 t from all the ammonia emission sources (a) 5,200 t from agricultural sources (b) and 5,200 t from vehicle exhausts (c)	51
Figure 3.8 Average PM _{2.5} concentrations under different weather patterns in 2010. In winter (December to January) (a) and summer (July to August) (b)	52
Figure 4.1 Seven prefectures (Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, and Kanagawa) and the geographical locations of the 21 LNG thermal power plants in Kanto Region.....	65
Figure 4.2 The flow chart of ammonia emission estimation	66
Figure 4.3 Estimated annual changes in emissions of ammonia (a) and NO _x and SO ₂ (b) under the conditions of the ammonia-hydrogen energy system.....	67
Figure 4.4 Incremental PM _{2.5} caused by ammonia emission from the LNG thermal power plants utilizing ammonia-hydrogen power generation systems. Simulated data in winter (December to January) (a) and summer (July to August) (b)	68
Figure 4.5 Ingredients of the incremental PM _{2.5} . Simulated data winter (December to January) (a) and summer (July to August) (b)	69
Figure 4.6 Premature deaths caused by incremental PM _{2.5} resulted from utilizing ammonia-hydrogen energy in Kanto Region. Annual chronic death (a) and daily acute death in winter (upper) and summer (below), respectively (b)	70
Figure 4.7 Performance comparison between the log-linear function and the linear function	71

Chapter 1 Introduction

1.1 Background

Ammonia has been widely applied in agricultural and industrial sectors. As the third abundant nitrogen containing gas, ammonia is attracting a great deal of attention [1]. Thanks to the rise of creation technology, ammonia production has been expanded during the last century. Nevertheless, volatilization and poor use efficiency lead to ammonia emission [2]. Major ammonia emission sources include livestock industries, synthetic nitrogen fertilizers and human excreta. Simultaneously, power plants, field burning and vehicle exhaust also make a contribution to the gross emissions [46]. Due to the development of fuel technologies, energy sector has also been regarded as one of the potential sources of ammonia emission [5].

Excessive atmospheric ammonia poses a direct threat to human health because of its toxicity [6], and accumulated ammonia in arable soils or atmosphere continuously alters the nitrogen cycle, which is a planetary phenomenon that could be severely damaged by anthropic activities [7-9]. Another costly impact caused by ammonia would be the formation of fine particulate matters (PM_{2.5}). PM_{2.5} refers to microscopic solid or liquid matters in atmosphere, of which the diameter would be less than 2.5 micrometers, at about 1/20th the width of a human hair [10]. According to the generating mechanisms, PM_{2.5} could be divided into primary particles (directly emitted from the emission sources) and secondary particles (produced from the chemical reactions of the precursors) [11]. Ammonia can react with SO₂ or NO_x to yield secondary inorganic PM_{2.5} comprising sulfates and nitrates [12, 13], which are regarded as an important constituent of secondary PM_{2.5} mass. The inorganic secondary particles represent half of the gross PM_{2.5} in East United States and account for more than 30% of PM₁₀ and PM_{2.5} in Europe [14, 15]. In Tokyo, the secondary particles account for 67% of all the PM_{2.5} mass, and the vast majority of them are composed of sulfates, nitrates and ammoniums [16].

PM_{2.5} not merely obstructs the atmospheric visibility, but also negatively affects public health by inducing respiratory/cardiovascular diseases [17]. However, was not well-controlled in Japan. In 2015, the achievement rate of the Environmental Quality Standards for PM_{2.5} (15

$\mu\text{g}\cdot\text{m}^{-3}$ for annual average $\text{PM}_{2.5}$ concentration, $35\ \mu\text{g}\cdot\text{m}^{-3}$ for daily $\text{PM}_{2.5}$ concentration) was less than 40% [18]. Furthermore, although the ammonia-related $\text{PM}_{2.5}$ accounts for 29%-32% of the total $\text{PM}_{2.5}$ mass in Tokyo and the surrounding area (capital-cycle), there are still no relevant policies for ammonia controls from the perspective of atmospheric pollution [16]. Therefore, for the environmental studies on ammonia-related $\text{PM}_{2.5}$, appropriately understanding the current situation and assessing the future trends of the ammonia emission sources are very important. In addition, it is also necessary to explore effective emission abatement strategies for controlling ammonia-related $\text{PM}_{2.5}$.

1.2 Problems related with ammonia emission

1.2.1 Current situation of ammonia emission and ammonia-related $\text{PM}_{2.5}$

About 60% of the global ammonia emission is considered to be contributed by anthropogenic sources [19]. Based on the research of Kannari *et al.*, anthropogenic ammonia emission in Japan has been classified into two categories: agricultural emissions and urban emissions [20]. According to the previous studies, the major anthropogenic ammonia emission sources would be agriculture, including the livestock industry and the application of chemical fertilizer. Meanwhile, the contribution rates of urban emission sources, especially ammonia emission from vehicle exhausts, have increased in recent years [4, 20-23]. The annual ammonia emission from the major emission sources in 1994-2010 are summarized in Table 1.1, the results indicated a slight decline in all sectors.

However, there is still a lack of the latest data, which could accurately reflect the current situation of ammonia emission. The statistical results from the Ministry of Agriculture, Forestry and Fisheries indicate that the livestock industry has expanded in recent years. During 2016-2017, laying hen husbandry increased 1.7% while pig husbandry and beef cattle husbandry increased 0.4% and 0.8%, respectively [24]. Kouyama conducted that in Japan, about 97% of the agricultural ammonia emission are contributed by livestock industry [25]. According to his result, the total agricultural emissions would be greatly influenced by the development of animal husbandry. On the other hand, due to the Unipolar Concentration in Tokyo (a phenomenon that the population and regional economic systems became intensively concentrated in Tokyo area since 1980s), the expansion of urbanization proved to

be inevitable in the last decade [26]. As investigated by the Ministry of Internal Affairs and Communications, the population in Tokyo has increased by 2.7% during 2010-2015, which would inextricably link to an apparent rise in urban emissions [27].

Furthermore, limited research focused on the ammonia-related secondary PM_{2.5}. Both the observed and simulated data which could reflect the PM_{2.5} distribution status are sparse even if in Kanto region, the core study area of the PM_{2.5} research in Japan. Kato and Nakanishi estimated the PM_{2.5} concentrations in Kanto region. In this study, they also made a component comparison between the simulated data and observed data from several specific observation points [28]. However, urban emissions were not regarded as one of the major sources of ammonia, and their emission inventory was established based on the data collected in 1998. Tokyo Metropolitan Research Institute for Environmental Protection conducted the component analysis of PM_{2.5} from four observation points (Koto, Komae, Higashiyamato, Ome) in Tokyo [29]. Although their results represented how PM_{2.5} and ozone respond to the concentration of NO_x in summer and winter, the relationship between ammonia and ammonia-related PM_{2.5} was not discussed. Takakura N *et al.* aimed to investigate the chemical composition of PM_{2.5} in Kyoto, a detailed description of how the concentration and components of PM_{2.5} changed throughout the year was conducted in their research [30]. Nevertheless, the majority of their data was selected from only one observation point (National Route 171), which could not represent the spatial and temporal distribution of PM_{2.5} pollution in Kyoto. Fushimi A summarized the original emission sources and the components of PM_{2.5} in Kanto Region [31]. Although his results proved that secondary inorganic particles accounts for more than 50% of the total PM_{2.5} in summer, the conditions in winter or other seasons were not shown in this research.

1.2.2 Lack of integration policies and experiences of ammonia-related PM_{2.5} abatement

As important precursors of secondary PM_{2.5}, there are strict standards of SO₂ and NO_x in worldwide. Emissions of these two precursors should follow the policies and strategies enacted by respective countries [32, 33]. Adversely, little effort has been devoted to regulate ammonia emission. Offensive Odor Control Law enacted by the Government of Japan slackly limits ammonia emission in consideration of the annoying odor [34]. United States

Environmental Protection Agency's (EPA) Integrated Nitrogen Panel to the Science Advisory Board has not petitioned to put ammonia as a criteria pollutant until year 2014 [35].

Although there has been a lack of corresponding policies and regulations to control the emission level, nowadays, ammonia pollutions presented increasing social importance. In some developed countries, it indicates a declining tendency of ammonia emission. There was a 28% ammonia emission reduction in Europe between the years 1990 and 2010 [36]. In Japan, 13% ammonia emission was cut down from 2000 to 2010, benefiting from the improved efficiency of agricultural activities and decreasing utilization rate of pit latrines [4, 37]. However, the situation is far worse in developing countries. China, for instance, which contributes approximately 20% of global ammonia emission, shows an increase of 13-16 Tg ammonia emission in year 2005, compared with an annual emission of 12-14 Tg in year 2000 [33,38]. In addition, the national emissions in China have doubled between 1980 and 2005 [8]. Thus the level of global ammonia emission does not show a declining tendency for the past few years [19, 39, 40]. Based on the result of Behera *et al.*, the global year-wise ammonia emission trends even increased during 1970-2005 [22].

According to the above-mentioned reasons, it is necessary to consider how to manage and reduce ammonia emission effectively. Many previous researches are focusing on this topic. Pinder *et al.* [41] set up a series of scenarios for reducing atmospheric PM_{2.5} in the Eastern United States. A conclusion was drawn that compared with SO₂ and NO_x, applying the current available control technologies to ammonia would be a cost-effective strategy. Ansari and Pandis [42] investigated PM sensitivities respect to the precursor concentrations over various temperatures and relative humidities. When the generated results were applied to two urban polluted areas, reducing ammonia emission proved to be most effective on PM control. Wang *et al.* [33] conducted a scenario-based impact assessment of ammonia emission on inorganic PM aerosols in East China. Their result suggested that a multipollutant strategy was necessary to reduce the emission level of ammonia, as same as current SO₂ and NO_x controls. However, the analyses are limited to a single area with different time periods or an annual comparison in parallel with various countries. Their researches neither classified emission sources, nor gave specific suggestions of high-efficiency emission control

corresponding to seasonal pollutions. The scenario of PM_{2.5} abatement presented Wakamatsu S *et al.* confirmed the importance of making policies according to the regional emission sources [43]. On the other hand, although they indicated that sulfates accounted for a large percentage of PM_{2.5} particles in Japan, the influence of ammonia emission on PM_{2.5} formation was not considered in their research.

1.2.3 Expanding applications and potential risks of ammonia in energy sector

Even though traditional agricultural and urban sources always contribute the vast majority of ammonia emission, the status of ammonia emission inventory might change since ammonia has emerged as a promising energy source in recent years.

The Fukushima Nuclear Power Station accident in March 2011 caused the nuclear power occupancy rate to drop from 31.7% to 1.3% within 32 months [44]. However, between 2011 and 2013, the average energy demands of the manufacturing industry increased by 21.7% [45]. To alleviate the energy burden, Japan's Agency for Natural Resources and Energy suggested that 30% of national energy consumption should be supplied by renewable energy by 2030 [46]. However, before 2010, only 10% of the total energy consumption was supplied by renewable sources. Furthermore, because of seasonal and regional limitations, domestic renewable primary energy is difficult to develop [47]. Energy storage is another complex problem. Indeed, satisfying 30% of the domestic energy consumption for 1 month would require at least 2×10^8 t of sodium-sulfur cells [5].

The development of ammonia energy seems to be a key to this problem. It has been proved that ammonia could directly supply the ammonia motors and gas-turbine power generators. As one of the hydrogen carriers, it also plays an important role in hydrogen energy [5]. In 1982, Bomelburg has already pointed out that ammonia could be a major factor in satisfying the energy demand in future [48]. The relatively low boiling point of ammonia indicates its convenience and low cost of storage [49]. Benefitted from the development of the Haber-Bosch process, ammonia production has undergone rapid commercialization over the last decade [2]. Moreover, the existing infrastructure could support the promotion of ammonia energy.

However, incomplete combustion/decomposition could lead to excess ammonia emission to the atmosphere. To the best of our knowledge, the potential impacts of the secondary PM_{2.5} particles produced from ammonia in energy-related applications have not yet fully explored in the previous studies. As noted by Eguchi, the residual ammonia density resulted from the incomplete decomposition of ammonia fuel cells could be as high as 1000 ppm if there is no treatment [50]. Iki *et al.* proposed a set of ammonia-powered electric generator, due to the incomplete combustion, even after the removal system, a small percentage of ammonia was still detectable in the exhaust [51]. The environmental impacts of these ammonia emissions were not discussed in their results. Miura *et al.* conducted a comparative study of ammonia energy systems applied to vehicles. In their research, it was noted that safety measurements should be enhanced in case of the potential ammonia leakage, while the risk of secondary products was never mentioned [52]. Satomi *et al.* made a performance comparison between ammonia-fueled solid oxide fuel cell (SOFC) and hydrogen-fueled SOFC. They concluded that ammonia would be a good substitute for hydrogen and ammonia-fueled SOFC could achieve almost the same performance as the hydrogen one [53]. Despite all the advantages, they did not evaluate the risk caused by potential ammonia emission.

1.3 Influence factors on ammonia-related PM_{2.5}

The formation of ammonia-related PM_{2.5} is controlled by a large number of atmospheric reactions. Table 1.2 summarized the major reactions involved in this process [22]. There are many impact factors which could influence the chemical equilibriums.

1.3.1 Meteorological conditions

Meteorological conditions would have important effects on the formation of PM_{2.5}. Temperature and humidity are closely related to the efficiency of atmospheric reactions. The wind speed and direction could affect the transport and dispersion of PM_{2.5}. Precipitation and rainfall are also proved to be important meteorological variables for PM_{2.5} concentration. Wang and Ogawa analyzed the relationship between PM_{2.5} concentration and the meteorological conditions obtained in Nagasaki, Japan. They concluded that the temperature shows a negative correlation when the precipitation has a positive one with PM_{2.5} concentration. Simultaneously, the effects of humidity and wind speed are depending on the

interval of threshold [54]. Goverdhan Rathla *et al.* recorded the meteorological data in Belagavi, Karnataka, India, and made a comparison with PM_{2.5} concentrations. Their result still indicated a weakly positive relationship among temperature and PM_{2.5} concentration [55]. Tai *et al.* studied the correlations of PM_{2.5} components with the 11-year observed meteorological data in the United States. They found that the influences of temperature and humidity were depending on the region and PM_{2.5} components, when precipitation was negatively corresponding to all PM_{2.5} components [56]. Cheng *et al.* investigated the influences of meteorological conditions on PM_{2.5} concentrations at a highway toll station in Taipei, Taiwan. Their result showed a significantly positive relationship between wind speed and PM_{2.5} level, by the reason of the re-suspension under well dispersed conditions [57].

1.3.2 Gas ratio

In addition to meteorological factors, the changes in ammonia-related PM_{2.5} are considered to relate to the concentration of PM_{2.5} precursors (ammonia, NO_x and SO₂). Paulot *et al.* noted that the sensitivity of PM_{2.5} to ammonia could be indicated by the gas ratio (GR), which was an important factor affects the increases in PM_{2.5} in response to ammonia emission. GR in their research was estimated using Eq. (1.1) [12]:

$$GR = \frac{[NH_x] - 2[SO_{4T}]}{[NO_{3T}]} \quad (1.1)$$

where NH_x is the total amount of ammonium and gaseous ammonia (units: mol), SO_{4T} is the total amount of sulfates and gaseous sulfuric acid (units: mol), and NO_{3T} is the total amount of nitrates and gaseous nitric acid (units: mol). Figure 1.1 represents the relationship between the increased PM_{2.5} concentration caused by ammonia emission from food export and GR [12]. As shown in Figure 1.1, GR<1 indicates that insufficient ammonia is available to neutralize NO_{3T} and SO_{4T}. Thus, any increase in inorganic PM_{2.5} would be strongly limited by the amount of ammonia. Conversely, when GR>1, ammonia emission would have little effect on the formation of inorganic PM_{2.5} (ammonium sulfate and ammonium nitrate). A same result was obtained by Ansari and Pandis [42]. In their research, GR was defined as Eq. (1.2):

$$GR = \frac{[NH_3^F]}{[HNO_3^T]} \quad (1.2)$$

where NH_3^{F} is the free ammonia [total ammonia - (2 × [sulfate])] and HNO_3^{T} is the total (gas + aerosol) nitrate concentration (units: ppb). Although Eq. (1.1) and Eq. (1.2) used different equations and units, both of them defined GR as the ratio of free ammonia and total nitrate concentration. As shown in Figure 1.2, $\text{PM}_{2.5}$ sensitivity decreases significantly when $\text{GR} > 1$. As shown in Figure 1.3, since GR would make great influence on $\text{PM}_{2.5}$ sensitivities, nonlinear relationship occurs among ammonia emission and its products [33].

1.4 Necessity of atmospheric models and the existing assessments of ammonia-related $\text{PM}_{2.5}$

1.4.1 Necessity of atmospheric models

Many researches have noted the potential impacts of ammonia-related $\text{PM}_{2.5}$ on the environment and public health. Due to the complexity of chemical reactions and thermodynamic equilibrium involved in atmosphere, atmospheric simulation is most commonly used. Makar *et al.* [58] studied the regional air quality problem caused by ammonia emission from fertilizer and livestock breeding in North America using the air quality-modeling system known as A Unified Air-quality Modelling System (AURAMS). Behera *et al.* [59] addressed the atmospheric transportation of ammonia and acid gases using chemical and meteorological simulations. Bu using the Community Multiscale Air Quality Modeling System (CMAQ), Paulot *et al.* [12] discussed ammonia emission from U.S. agriculture exports and the health impacts related to fine particles. In Japan, the chemical transport and secondary products estimation model ADMER-PRO are also widely used [60, 61].

1.4.2 Existing assessments of ammonia-related $\text{PM}_{2.5}$

Unlike ammonia's direct health impacts, $\text{PM}_{2.5}$ can diffuse far from the emission source and cause widespread premature mortality [62]. Lelieveld *et al.* [63] noted that in 2010, agriculture-related air pollution caused 3.8×10^4 premature deaths in Japan, with notable contributions from $\text{PM}_{2.5}$. Occasionally, the financial loss caused by $\text{PM}_{2.5}$ -related health impacts can even exceed the benefits associated with ammonia utilization [12]. Fann *et al.* [64] characterized $\text{PM}_{2.5}$ -related health impacts in the U.S. and attempted to minimize the related financial losses by reducing SO_2 and NO_x emissions. Paulot *et al.* [12] discussed ammonia

emission from U.S. agriculture exports and the health impacts related to $PM_{2.5}$. Because ammonia is a promising energy source, similar to hydrogen, Rouleau *et al.* [65] conducted a human health-impact analysis on biodiesel popularization. Their results indicated that among all of the pollutants in diesel exhaust, $PM_{2.5}$ most strongly affected the financial cost associated with human health, especially by increasing premature deaths. However, little of these previous researches focused on the problems mentioned in 1.2.

1.5 Objectives and originalities of this research

As mentioned above, ammonia-related $PM_{2.5}$ is one of the major components of $PM_{2.5}$. From the perspective of $PM_{2.5}$ reduction, evaluating and controlling ammonia emission would be important and even more urgent than other secondary $PM_{2.5}$ precursors.

In this study, an appropriately understanding of the situation of the ammonia emission and ammonia-related $PM_{2.5}$ was developed based on the current available data base. Due to the lack of existing ammonia-related strategies, effective emission abatement options for controlling ammonia-related $PM_{2.5}$ were explored. Based on our results, further suggestions were given and contribute to the establishment of ammonia-related strategies. In addition, since ammonia has extended the application in electric power generation, an impact assessment of potential ammonia emission discharged from energy sector was also conducted.

The specific objectives of this research are listed as follows:

(1) To find out the current situation of ammonia emission and ammonia-related $PM_{2.5}$, clarify the changes in last decade, based on the 10-year database EAGrid-Japan.

(2) To explore an effective abatement option for ammonia emission and ammonia-related $PM_{2.5}$.

(3) To evaluate the potential risk of excessive ammonia-related $PM_{2.5}$ caused by the extended ammonia applications in future.

1.6 Structure of this research

In order to achieve above-mentioned objectives, the main body of this thesis is divided into the following chapters:

Chapter 1 introduced the background and the current problems related with ammonia emission. Until now, there is still a lack of integration policies and experiences of ammonia-related PM_{2.5} abatements. Furthermore, the expanded applications of ammonia in energy sector would lead to potential environmental impacts.

Chapter 2 illustrated the current situation of ammonia emission and PM_{2.5} reduction. A comparative study on ammonia emission and ammonia-related PM_{2.5} in 2000 and 2010 in Kanto Region, the most populated area in Japan was conducted. The sources and concentrations of ammonia emission and ammonia-related PM_{2.5} were calculated and illustrated as distribution maps. The achievements of controlling secondary PM_{2.5} precursors in last decade (including SO₂ and NO_x) were discussed.

Chapter 3 represents an integrated spatial and temporal study on ammonia emission abatement options in Kanto Region. The total ammonia emission are divided to agricultural emissions and urban emissions, respectively they represent the combination of emissions discharged from agricultural sources (livestock, fertilizers, field burning) and urban sources (human excreta, vehicles, industries). Multiple ammonia emission strategies are applied to the scenarios, collaborated with the existing regulations of NO_x and SO₂ in Japan.

Chapter 4 evaluated the health impacts of utilizing ammonia-hydrogen energy, one of the promising ammonia-related energy systems in Japan. The scenario was originally used in the Japan National Sustainable Energy Development Project and focuses on Kanto Region [46]. We estimated the incremental PM_{2.5} density by assuming that 20% of the energy consumption in Kanto Region was supplied by ammonia-hydrogen energy. The PM_{2.5}-related health impacts are represented by premature deaths among the elderly population (individuals over 65 years old).

Chapter 5 summarizes the major results of this study, future work plans related with cost-benefit analysis of the ammonia abatement options are also represented in this chapter.

The relationships among these chapters are illustrated in Figure 1.4.

Table 1.1 Annual ammonia emissions from the major emission sources in Japan

Year	Livestock (kt)	Fertilizer (kt)	Vehicle (kt)	Energy (kt)	Reference
1989	249.51	96.58	N/A	316.96	Zhao and Wang 1994 [23]
1998	314.68	28.34	12.13	2.24	Kannari <i>et al.</i> 2001 [20]
2000		304.68	29.46	3.56	Fukui <i>et al.</i> 2014 [4]
2005		272.44	29.30	2.77	Fukui <i>et al.</i> 2014 [4]
2010		265.07	25.63	3.10	Fukui <i>et al.</i> 2014 [4]

Table 1.2 Major atmospheric reactions for the formation of ammonia-related PM_{2.5}, summarized by Behera *et al.* [22]

Reaction details	Reference
$\text{NO}_2(\text{g}) + h\nu \rightarrow \text{NO}(\text{g}) + \text{O}(\text{g})$	Lin <i>et al.</i> [66]
$\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	Lin <i>et al.</i> [66]
$\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$	Lin <i>et al.</i> [66]
$\text{NO}_2(\text{g}) + \text{OH}(\text{g}) + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	Lin <i>et al.</i> [66]
$\text{HNO}_3(\text{g}) + h\nu \rightarrow \text{OH}(\text{g}) + \text{NO}_2(\text{g})$	Seinfeld <i>et al.</i> [67]
$\text{HNO}_3(\text{g}) + \text{OH}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{NO}_3(\text{g})$	Seinfeld <i>et al.</i> [67]
$\text{NO}_2(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{O}_2(\text{g})$	Seinfeld <i>et al.</i> [67]
$\text{NO}(\text{g}) + \text{HO}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{OH}(\text{g})$	Calvert <i>et al.</i> [68]
$\text{NO}_3(\text{g}) + h\nu \rightarrow \text{NO}_2(\text{g}) + \text{O}(\text{g})$	Calvert <i>et al.</i> [68]
$\text{NO}_3(\text{g}) + \text{NO}_2(\text{g}) + \text{M} \rightarrow \text{N}_2\text{O}_5(\text{g}) + \text{M}$	Calvert <i>et al.</i> [68]
$\text{N}_2\text{O}_5(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HNO}_3(\text{g})$	Calvert <i>et al.</i> [68]
$\text{SO}_2(\text{g}) + \text{OH}(\text{g}) + \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{g}) + \text{HO}_2(\text{g})$	Bufalini [69]
$\text{SO}_2(\text{g}) + \text{O}(\text{g}) + h\nu \rightarrow \text{SO}_3(\text{g})$	Bufalini [69]
$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{g})$	Phillips [70]
$\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_3(\text{aq})$	Clegg <i>et al.</i> [71]
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$	Clegg <i>et al.</i> [71]
$2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s}) \text{ or } (\text{aq})$	Finlayson-Pitts <i>et al.</i> [72]
$\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{NH}_4\text{HSO}_4(\text{aq})$	Finlayson-Pitts <i>et al.</i> [72]
$\text{NH}_3(\text{g}) + \text{NH}_4\text{HSO}_4(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{aq})$	Finlayson-Pitts <i>et al.</i> [72]
$\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{s})$	Finlayson-Pitts <i>et al.</i> [72]
$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \leftrightarrow \text{NH}_4\text{Cl}(\text{s}) \text{ or } (\text{aq})$	Zhang <i>et al.</i> [73]
$\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$	Mozurkewich [74]
$\text{NH}_3(\text{g}) + \text{OH}(\text{g}) \leftrightarrow \text{NH}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	Diau <i>et al.</i> [75]

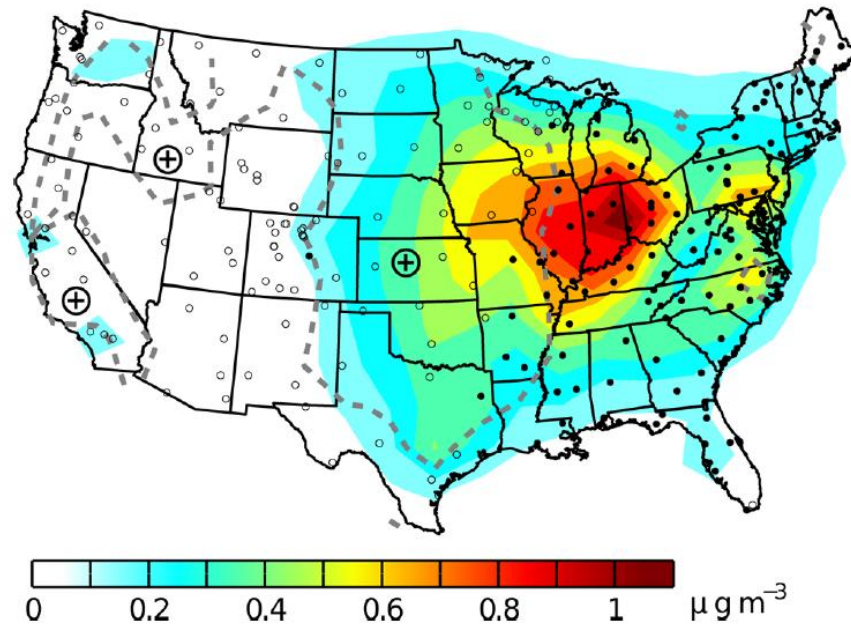


Figure 1.1 The increase of annual $PM_{2.5}$ concentration caused by food export in U.S. Black dots indicates indicate the regions with lower GR values when white dots indicate the regions with higher GR values [12]

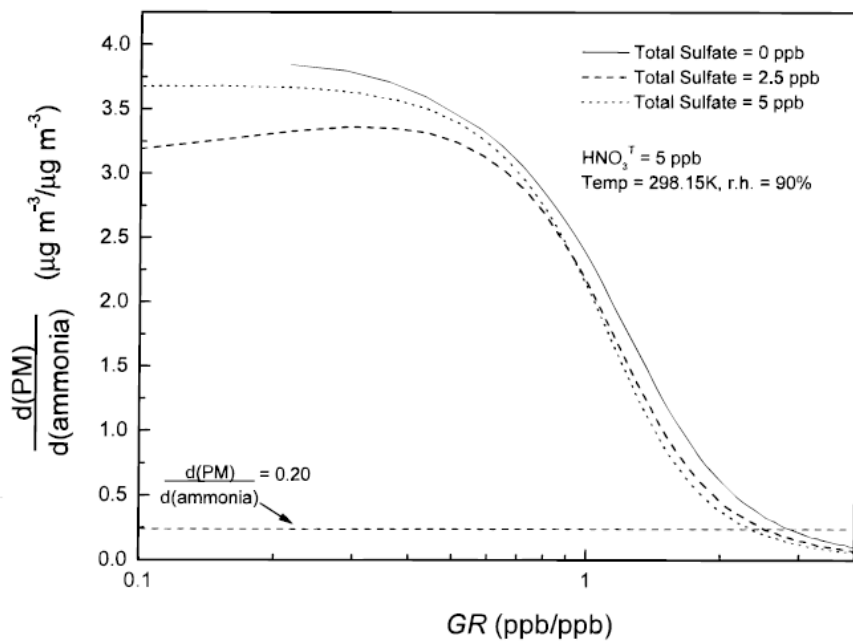


Figure 1.2 $\text{PM}_{2.5}$ sensitivity (defined as $[d(\text{PM})/d(\text{ammonia})]$) responses to GR at 298 K and 90% rh [42]

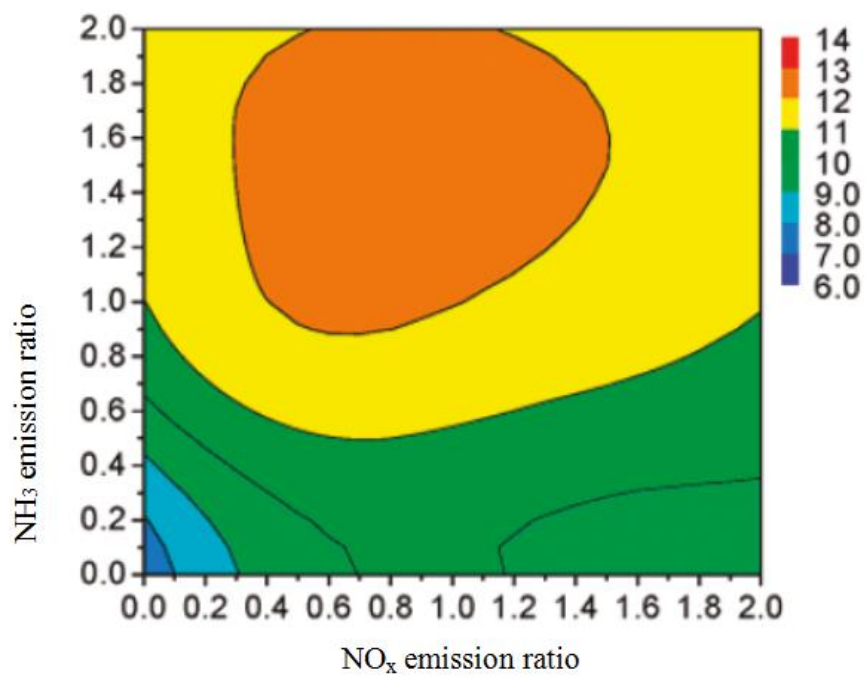


Figure 1.3 NO₃⁻ responses to the changes of NO_x and NH₃ emissions, monthly average result in Beijing, July, 2005 (μg·m⁻³) [33]

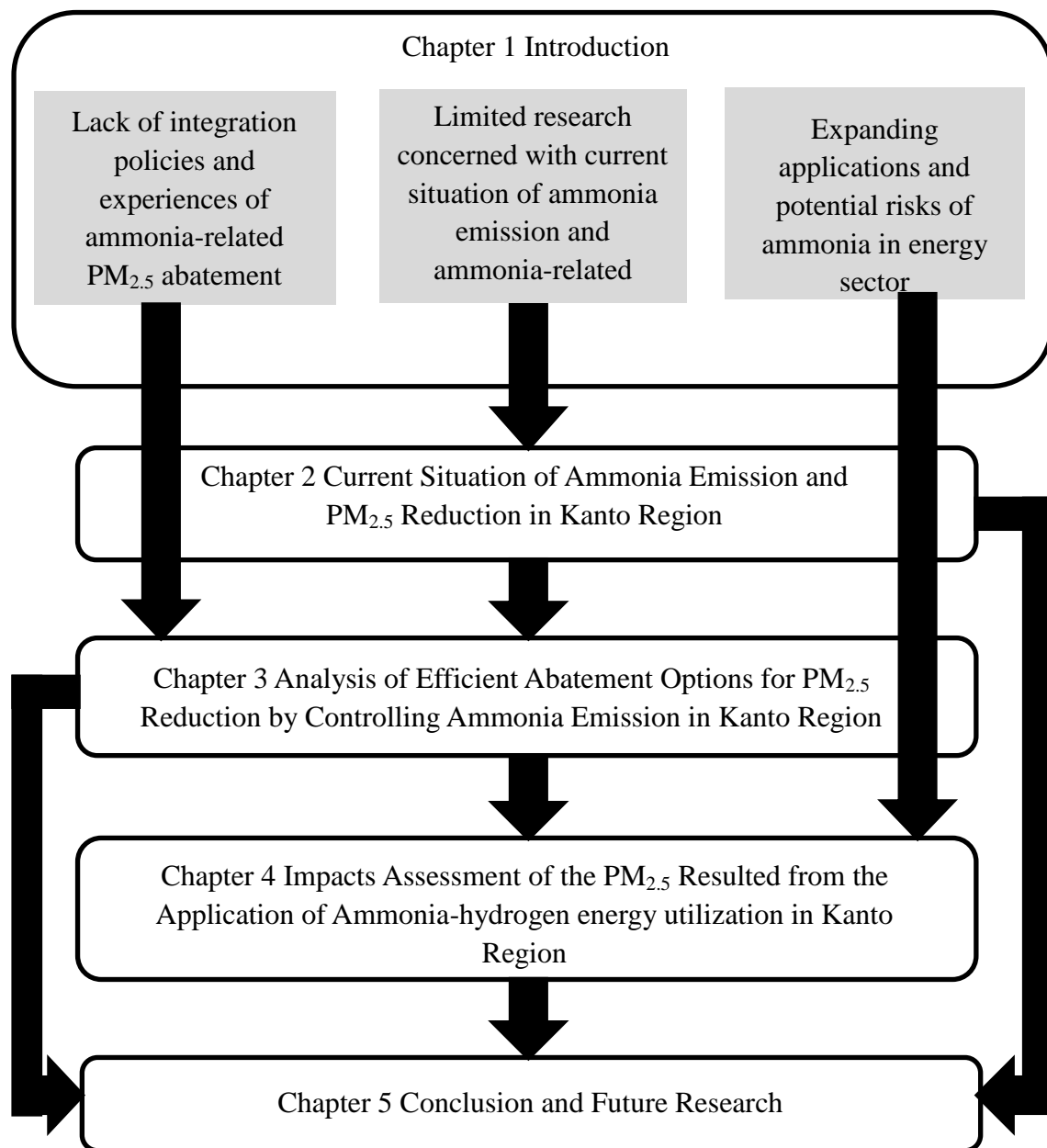


Figure 1.4 The structure of this research

Chapter 2 Current Situation of Ammonia emission and PM_{2.5}

Reduction in Kanto Region

2.1 Introduction

According to the results from Zhao and Wang, Japan made an annual contribution of 699.99 kt ammonia emission during 1989-1991, which accounts for 2.8% of the total emissions from Asian countries [23]. Agriculture is always regarded as the major source of ammonia emission. Due to the low efficiency of N-fertilizers (<50% in the tropics and <70% in temperate areas), 23% of the global gaseous ammonia losses is derived from the fertilizer application [76, 78]. Livestock and poultry also contribute a large amount of ammonia emission. The waste/slurry could lead to great ammonia volatilization in a small-region when spread on the surface of the ground [79]. In total, more than 50% of the atmospheric ammonia is discharged from agricultural sectors [80]. The respiration and excretion of human and pets are also one of the major sources of ammonia emission. The emission amount is closely dependent on the population size, with an emission factor of about 0.3 kg capita⁻¹·y⁻¹ for human, and 6.9 g capita⁻¹·d⁻¹ for dogs [81, 82]. Besides, vehicles are regarded as an important source of urban ammonia emissions, including both gasoline vehicles (>10 mg·km⁻¹) and diesel vehicles (>1 mg·km⁻¹) [4]. Gaseous ammonia could also be emitted from fuel combustion, the relative emission factors were calculated as 2.51 kg·tce⁻¹ (t of coal equivalent) for coal, 0.183 kg·tce⁻¹ for oil and 0.00912 kg·tce⁻¹ for gas [23]. In addition, industrial sectors (fertilizer production facilities, flue gas denitration facilities, sewage treatment facilities, etc.) also contribute to ammonia emission [20].

Benefited from the improvement of the utilization efficiency of chemical fertilizers and removal technologies, the annual emission of Japan decreased to 463.24 kt in 2000 and 404.39 kt in 2010 [4]. In 2010, the premature mortality of Japan related with outdoor air pollution, was still proven to be 25,000, ranking 15th in the world. In fact, 38% of the deaths were linked to agricultural emissions, which were dominated by ammonia emission discharged from fertilizers and domesticated animals [63]. Atmospheric ammonia could

directly threat human health by its toxicity. On the other hand, it could also cause adverse health effects by reacting with other PM_{2.5} precursors (SO₂ and NO_x) and producing secondary PM_{2.5} products. As investigated by United States Environmental Protection Agency (USEPA), the overall premature mortality rate will increased by 0.3-1.2% and 6-13% for short- and long-term exposure, if PM_{2.5} concentration is increased by 10 µg·m⁻³ [83,84]. To control the PM_{2.5} level, many countries and organizations have established relative air quality standards. Some of the existing air quality standards for PM_{2.5} are summarized in Table 2.1 [83]. Based on the investigation conducted by the Government of Japan, the achievement of the standard was less than 40% in 2015 [18].

Reducing NO_x and SO₂ emissions are generally considered to be the key to solve PM_{2.5} problem. However, Pinder *et al.* found that controlling ammonia emission would be a more cost-effective method of reducing PM_{2.5} in the eastern U.S. [41]. As shown in Table 2.2, most of the PM_{2.5} abatement strategies proposed by Japan government are focusing on SO₂ and NO_x. Still, it only pointed out that reducing agricultural ammonia emission could be one of the solutions to PM_{2.5} problem [83, 91]. To the best of our knowledge, limited research concatenated the current ammonia emission to the secondary PM_{2.5} products in Japan. Therefore, it is important to present the current situation of ammonia emission and how PM_{2.5} responds to the changes in the emissions over recent years. This chapter conducted a comparative study on ammonia emission and ammonia-related PM_{2.5} in 2000 and 2010 in Kanto Region, the most populated area in Japan. The sources and concentrations of ammonia emission and secondary inorganic PM_{2.5} were calculated and illustrated as distribution maps. The achievements of controlling secondary PM_{2.5} precursors in last decade (including SO₂ and NO_x) were represented.

2.2 Materials and methods

2.2. 1 Study domain

As shown in Figure 2.1, Kanto Region comprises seven prefectures (Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, and Kanagawa) in the southeast of Japan. It was selected as the region of interest for this study for the following three reasons: (1) In 2010, the population of Kanto Region rose to 42.6 million, while this area occupies only 1/10 of the country's

territory [92]. Dense population could lead to a relative higher ammonia concentration in Kanto Region. In fact, according to the results provided by Kannari *et al.*, Kanto Region contributed 17.2% of the domestic ammonia emission, ranking the 3rd among all the 10 geographical regions (Hokkaido, Tohoku, Kanto, Koshu, Hokuriku, Tokai, Kinki, Chugoku, Shikoku, Kyushu&Okinawa) of Japan [20]. (2) Represented by Tokyo City, Tokyo Metropolitan Area (TMA) is located in Kanto Region, and the rest of the region contributes a large scale of agriculture production [93]. This area has diverse emission sources, including both agricultural and urban sectors. (3) Only 39% of the PM_{2.5} in Kanto Region is related with transboundary pollution, which has been proven to be lowest throughout Japan [83, 94]. In other words, the PM_{2.5} concentration in Kanto Region is dominated more by domestic emission sources than other regions.

2.2.2 Emission estimation

Gaseous ammonia can react with NO_x and SO₂, as important precursors of inorganic PM_{2.5}, which would lead to ammonium sulfate and ammonium nitrate. In this study, the incremental PM_{2.5} was assumed to be comprised by ammonium sulfate and ammonium nitrate, resulted from the above-mentioned precursors.

The major chemical reaction between ammonia and acidic gases is shown in Eq. (2.1):



In this study, 2 scenarios were established to represent the respective situations of ammonia emission and ammonia-related PM_{2.5} in 2000 and 2010. The basic emission inventories of 2000 were obtained from EAGrid2000-Japan by Kannari *et al.* [95]. The 2010 emission inventories of PM_{2.5} precursors (ammonia, SO₂ and NO_x) were calculated from the 2000 database by multiplying the relative coefficients of variation [4]. Other emissions irrelevant to the secondary ammonium sulfate and ammonium nitrate (such as CO) were supposed to remain unchanged as in the 2010 case. Table 2.3 summarized the annual emissions of the PM_{2.5} precursors in Japan [4, 95].

2.2.3 Atmospheric modeling

Atmospheric simulation is an important method for assessing ammonia emission and its secondary products. In this study, the PM_{2.5} produced from incremental ammonia emission

was estimated by ADMER-PRO (modified version) [21], while weather predictions were simultaneously acquired from the Regional Atmospheric Modeling System (RAMS) 4.4. The NCEP/NCAR Reanalysis data set (ds083.2, 6 hour intervals) that represented the state of the earth's atmosphere, incorporating observations and numerical weather prediction (NWP) model output was applied to this study [22]. ISORROPIA II was incorporated to simulate the thermodynamic equilibrium between nitrates, sulfates and ammonium [23]. The vertical space between surface and up to 20 km in the atmosphere was divided into 29 layers, with the bottom layer thickness being 50 m. Dry deposition velocities for a part of gases were calculated by the existing multiple resistance analogy model, while the other gases and particles were considered to occur at a constant velocity (0.1cm/s: default value in ADMER-PRO). Wet deposition was simulated by the non-steady-state meteorological and air quality-modeling system CALPUFF [24].

The target domain (Kanto Region, as shown in Figure 2.1) was two-way nested with the parent domain, which covered almost all of Japan. The simulations were driven with the horizontal resolutions of 20 km × 20 km and 5 km × 5 km, respectively, in the parent domain and target domain. Based on the forecasting method developed by Yoshikado *et al.* [25], 16 days in July to August and December to January were selected as the study period, which reflect the typical weather patterns in winter and summer with an occurrence frequency over 50% in Kanto Region, respectively. The spatial variation of PM_{2.5} concentration was obtained after a 51-hour spin-up time by comparison between the 2000 case and 2010 case.

2.3 Results and discussion

2.3.1 Ammonia emission in Kanto Region

As shown in Figure 2.2, in 2000, the daily average ammonia emission from Kanto Region were proved to be 543.54 t·d⁻¹ in summer, four times larger than in winter (121.55 t·d⁻¹). Compared with the results of 2000, the amount of ammonia emission was slightly decreased in 2010. As indicated as Figure 2.3, the daily average ammonia emission were 472.88 t·d⁻¹ in summer and 105.75 t·d⁻¹ in winter. Based on the above mentioned results, July contributed the largest daily average ammonia emission (565.35 t·d⁻¹ in 2000 and 491.85 t·d⁻¹ in 2010) while January contributed the smallest (105.05 t·d⁻¹ 2000 and 91.39 t·d⁻¹ in 2010).

According to Table 2.3, agriculture is regarded as the major contributor of ammonia emission. Over recent years, there has been a general decline in livestock industry in Kanto Region. Based on the distribution statistics conducted by Ministry of Agriculture, Forestry and Fisheries, the broiler production decreased by 25.27% during 2000-2009. For the dairy cattle, the headcount reduced from 265,000 to 229,200 between 2006 and 2010. At the same time, the beef industry also indicated a slight decline from 354,800 to 353,600 [99]. The reduction of the animal husbandry could be one of the main reasons for the declined ammonia emission.

During 2000-2010, the population in Kanto Region grew from 40.43 million to 42.6 million, especially among the TMA (Tokyo, Kanagawa, Chiba and Saitama) [27, 96]. The size of population could influence the ammonia emission from human's respiration and excretion. According to Table 2.3, a large percent (22.9% in 2000 and 18.3% in 2010) of the annual ammonia emission of Japan was contributed by human and pets. Despite the increase of the national population, the annual ammonia emission related with the population decreased from 101,278 t to 73,936 t (-27%) between 2000 and 2010 [4, 95]. As proposed by Fukui *et al.*, The main reason for this is that more and more households were connected to municipal sewer and resulted in a higher efficiency of sewage treatment during the decade [4]. In 2000, the average penetration rate of flush toilet and septic tank in Kanto Region was less than 90.1%, which was increased to 95% in 2010 [97]. The data indicated that 3.06 million residents in Kanto Region have benefited from the popularization of sewer systems, which reduced ammonia emission and even offset the influences caused by the expanded population.

Vehicle exhaust is another source of ammonia emission, especially for the catalyst equipped vehicles, which has been proven to have a higher emission level than the precatalyst ones [1]. Benefited from the enforcement of the regulation on vehicle emissions, emissions of the major pollutants (including CO, NO_x, NMVOC, PM_{2.5} and SO₂) were reduced to extremely low levels during 2000-2010. For instance, on-road NO_x was reduced by 48% while on-road SO₂ reduced by 97% [4]. However, due to the lack of an appropriate standard to regulate the on-road ammonia emission, the vehicle-related ammonia emission even increased in the decade. Another reason for the increased vehicle-related ammonia emission

would be the amount of retained vehicles. In 2000, there were 74.58 million retained vehicles in Japan, while after ten years, the number rose to 78.69 million. According to the latest data in 2017, there are more than 81.23 retained vehicles in Japan, and 28.29% belongs to Kanto Region [98]. However, the vehicle-related ammonia emission only accounted for a very limited percentage of the total ammonia emission. Due to the large reduction in agricultural sector, the total ammonia emission still reflected a decreasing tendency among 2000-2010.

2.3.2 Inorganic PM_{2.5} in Kanto Region

Figure 2.4 shows the PM_{2.5} decrease in Kanto Region during 2000-2010. For the 2000 case, the PM_{2.5} concentration was calculated to be 1.25 $\mu\text{g}\cdot\text{m}^{-3}$ in summer (average result of 9 patterns in July and August) and 1.37 $\mu\text{g}\cdot\text{m}^{-3}$ in winter (average result of 7 patterns in December and January). In 2010, the seasonal average PM_{2.5} concentration declined to 0.69 $\mu\text{g}\cdot\text{m}^{-3}$ and 1.15 $\mu\text{g}\cdot\text{m}^{-3}$, with a reduction rate of 44.8% in summer and 16.06% in winter. The distribution map of the PM_{2.5} reduction ratio is shown in Figure 2.5. In winter, PM_{2.5} slightly declined among the southeast parts of Kanto Region (Ibaraki and Tokyo Bay Area), with the maximum decrease in grid-cell PM_{2.5} concentration indicated as 0.09 $\mu\text{g}\cdot\text{m}^{-3}$. Different from PM_{2.5} concentrations, the reduction rate seems to be higher in the west. In other words, the result indicates that PM_{2.5} declines are greater in the west than in other parts of Kanto Region. Although southeast areas represent a larger decrease of PM_{2.5} concentration among 2000 to 2010, when compared with the basic PM_{2.5} concentration in 2000, the reduction rates of most cell-grids were less than 15%. In summer, the PM_{2.5} decreases mainly concentrated in the northeast areas. The maximum decrease was up to 5.3 $\mu\text{g}\cdot\text{m}^{-3}$, dozens of times more than that in winter. In contrast to winter, the reduction rates in summer indicate a higher value over Kanto Region. In most of the northern areas, the reduction rates were greater than 45%.

The large difference between the PM_{2.5} reductions in summer and winter might be caused by the seasonality of the emission sources. Unlike the ammonia emission discharged from the agricultural sources, the emissions from road exhausts are believed to remain unchanged throughout the year [20]. Based on the results of Chapter 2.3.1, due to the expanding number of retained vehicles and lack of regulations for vehicle-related ammonia emission, ammonia-related PM_{2.5} would get limited seasonal influence from the vehicle

exhausts during the decade. For the agriculture sources, ammonia emission from animal husbandry show edstrong seasonality between winter and summer. Mukhtar *et al.* calculated the seasonal ammonia emission discharged from ground-level area sources of dairy operation. Their results indicated the ammonia emission factors were $11.6 \pm 7.1 \text{ kg head}^{-1} \cdot \text{y}^{-1}$ in summer and $6.2 \pm 3.7 \text{ kg head}^{-1} \cdot \text{y}^{-1}$ in winter [100]. Fertilizer is regarded as another important agricultural source. Being same as the emissions from animal husbandry, ammonia volatilizations from arable lands also present a higher level in summer than in winter [20]. According to the above mentioned reasons, the declines of agricultural productions in Kanto Region would make greater influences on ammonia-related $\text{PM}_{2.5}$ in summer. However, as shown in Figure 2.5, the difference of $\text{PM}_{2.5}$ ratios between urban areas and agricultural areas in summer is not significant as winter. This result indicated that the seasonality of agricultural ammonia emissions would not be the only impact factor of different $\text{PM}_{2.5}$ reductions in winter and summer. Thus a further investigation related with the other impact factors would be conducted in the following chapter.

The sensitivity of $\text{PM}_{2.5}$ to ammonia emission are also closely related with the concentration of other $\text{PM}_{2.5}$ precursors (SO_2 and NO_x). From 2000 to 2010, the concentration of NO_x and SO_2 declined by 34% and 30%, respectively. Although the relationship between $\text{PM}_{2.5}$ sensitivity and the concentration of precursors are proved to be nonlinear, there is no doubt that the declines of NO_x and SO_2 would also contribute to $\text{PM}_{2.5}$ decrease. Further discussions related with the abatement efficiency of $\text{PM}_{2.5}$ precursors in summer and winter would be conducted in Chapter 3.

2.4 Summary

In this chapter, a comparative study on ammonia emission and secondary inorganic $\text{PM}_{2.5}$ in 2000 and 2010 in Kanto Region was conducted. Based on the results, it could be concluded that: (1) Annual ammonia emission was decreased during 2000-2010 by 13%. (2) The $\text{PM}_{2.5}$ was found decreased in Kanto Region during the last decade, which might be mainly benefitted from the reduction of SO_2 and NO_x . The establishment of the controlling policies for ammonia emission would still be very necessary. (3) Due to the different $\text{PM}_{2.5}$ reduction ratio in winter and summer, further investigations on $\text{PM}_{2.5}$ reduction efficiency of

each precursor should be conducted. (4) It is also important to investigate how $PM_{2.5}$ concentration responds to different ammonia emission.

Table 2.1 Summary of the existing ambient air quality standards for PM_{2.5} [83]

Country	Annual standard ($\mu\text{g}\cdot\text{m}^{-3}$)	Daily standard ($\mu\text{g}\cdot\text{m}^{-3}$)	Reference
United States (2013)	12	35	USEPA [85]
European Union (EU) (2008)	20	-	EU [86]
China (2012)	35	75	Ministry of Environmental Protection of the People's Republic of China [87]
Korea (2011)	25	50	Government of South Korea [88]
Japan (2009)	15	35	Ministry of the Environment, Government of Japan [89]
World Health Organization (WHO) (2006)	15	35	WHO Regional Office for Europe [90]

Table 2.2 Summary of the short-term planning for domestic PM_{2.5} abatement strategies of Japan [83, 91]

Target emission source	Key point for the short-term plan
Soot, dust and NO _x from industrial sectors	Promote additional discharge control measures on the basis of the Air Pollution Control Law
VOC from energy sectors	Establish the measurements for fuel evaporative emission
NO _x and PM from vehicles	Enhance the exhaust emission regulation, introduce low-emission vehicles
SO _x and PM from ships	Reduce the sulfur content in fuel
NH ₃ from agricultural sectors	Promote the policies related with groundwater contamination and lake eutrophication
PM from field burning	Prohibit the field burning in principle

Table 2.3 Annual emissions of the PM_{2.5} precursors in Japan [4, 95]

Emission source	Ammonia (t)		NO _x (t)		SO ₂ (t)	
	2000	2010	2000	2010	2000	2010
Large-scale combustion sources						
Power plants (H<25m)	49	57	6,497	6,818	2,910	3,167
Power plants (25≤H<100m)	12	20	21,965	24,223	18,606	22,070
Power plants (H≥100m)	2,543	3,019	152,737	186,946	120,511	134,447
Waste incineration facilities (H<25m)	3	2	12,265	9,635	12,675	5,027
Waste incineration facilities (25≤H<100m)	80	61	39,187	30,326	165,87	6,453
Waste incineration facilities (H≥100m)	61	50	6,289	4,949	2,191	843
Other combustion facilities (H<25m)	41	53	158,371	101,095	127,408	74,041
Other combustion facilities (25≤H<100m)	289	267	259,157	177,148	182,011	99,777
Other combustion facilities (H≥100m)	208	192	154,394	114,220	110,051	71,538
Grid-unspecified facilities	13	118	24,424	17,242	24,534	14,911
Small-scale combustion sources						
Combustion facilities			83,495	70,461	64,485	32,028
Waste incineration facilities			1,249	390	501	155
Agricultural field burning	2,135	1,750	4,481	3,740	657	538
Mobile sources						
Vehicles: exhaust pipe	13,605	26,525	945,682	535,668	25,811	828
Vehicles: evaporation						
Vehicles:						

wearabrasion of tire and brake						
Navigation			332,830	242,528	159,142	122,204
Aviation			20,074	17,179	128	107
Off-road vehicles			185,638	74,327	35,76	51
Other sources						
Agriculture	285,661	265,071				
Human and pet	101,278	73,936				
Other ammonia	37,037	34,173				
Sources						
Total	443,014	404,393	2,408,705	1,616,894	871,784	588,183
H: height of stack						

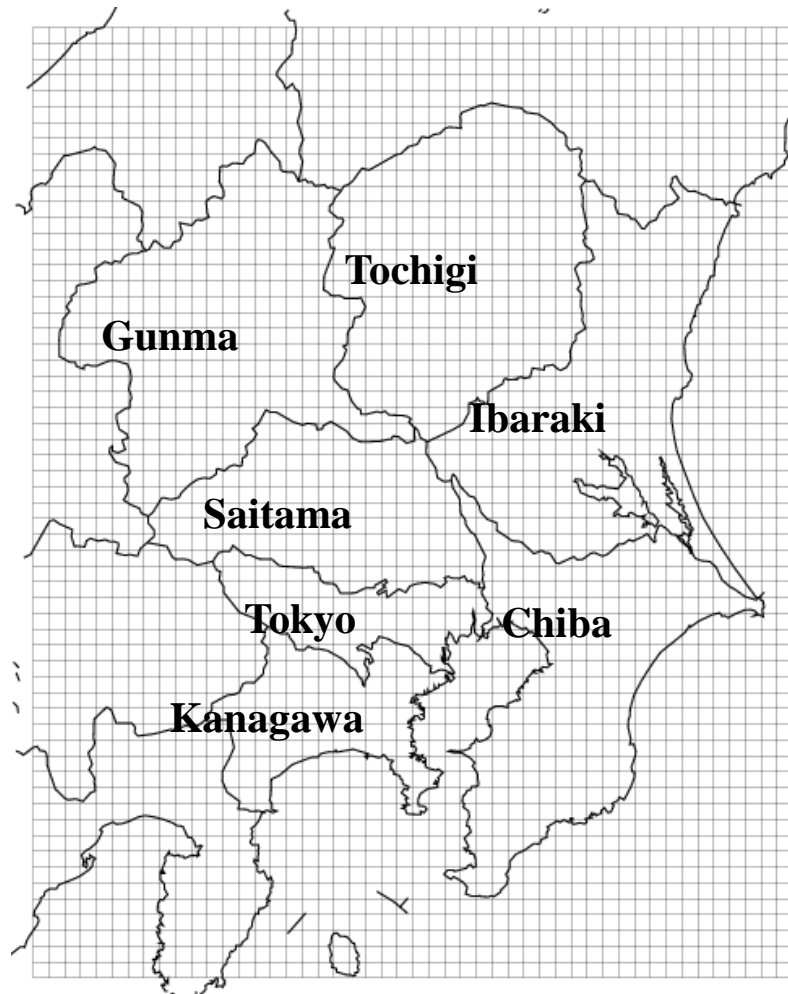


Figure 2.1 Seven prefectures (Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, and Kanagawa) in Kanto Region

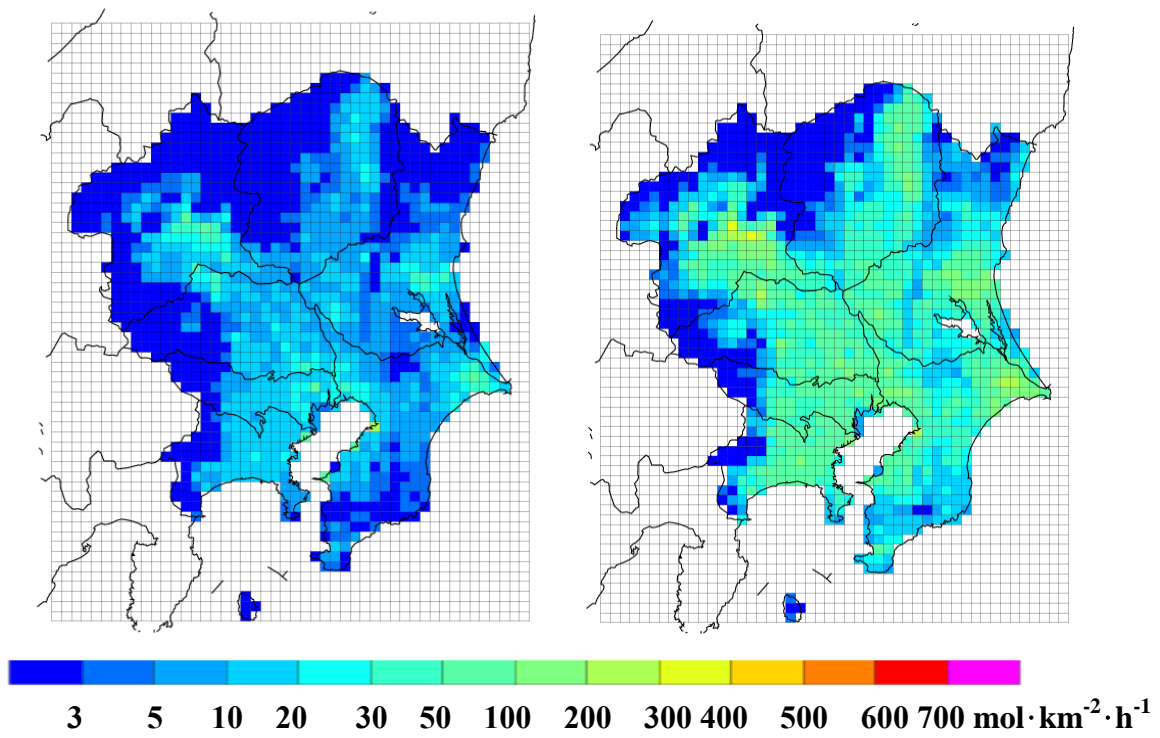


Figure 2.2 Spatial distribution map of ammonia emission in 2000, winter (left) and summer (right).

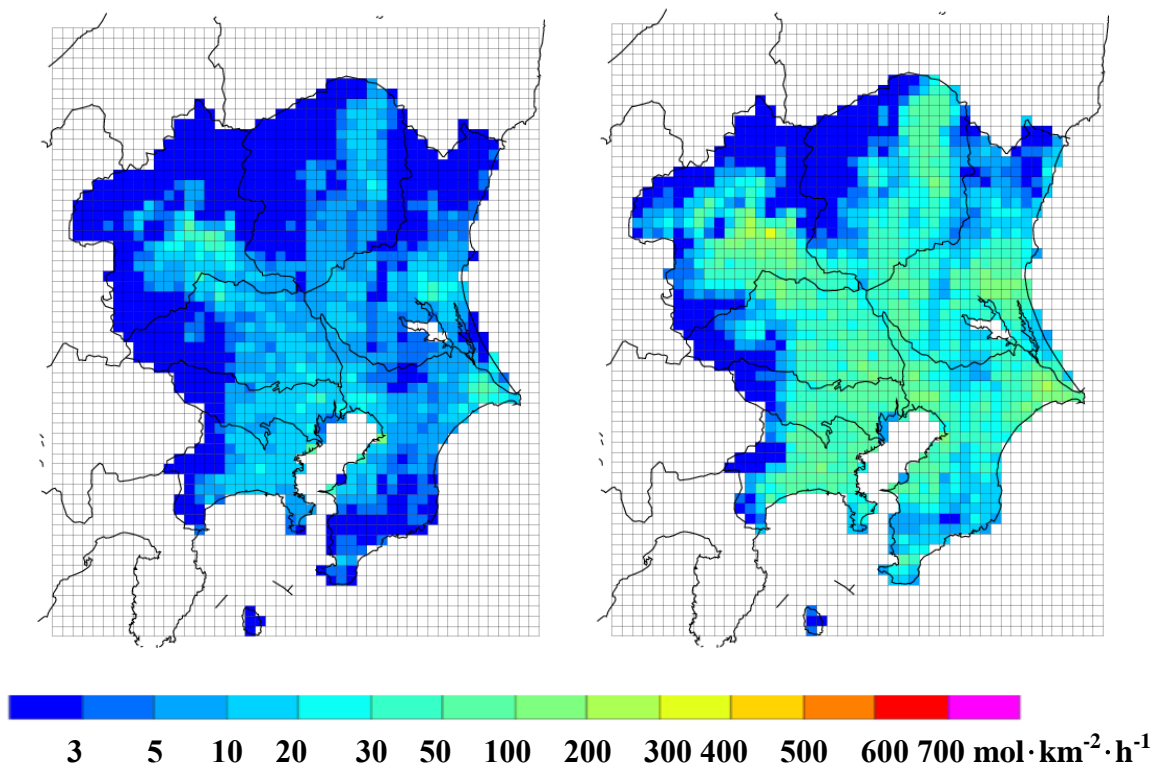


Figure 2.3 Spatial distribution map of ammonia emission in 2010, winter (left) and summer (right).

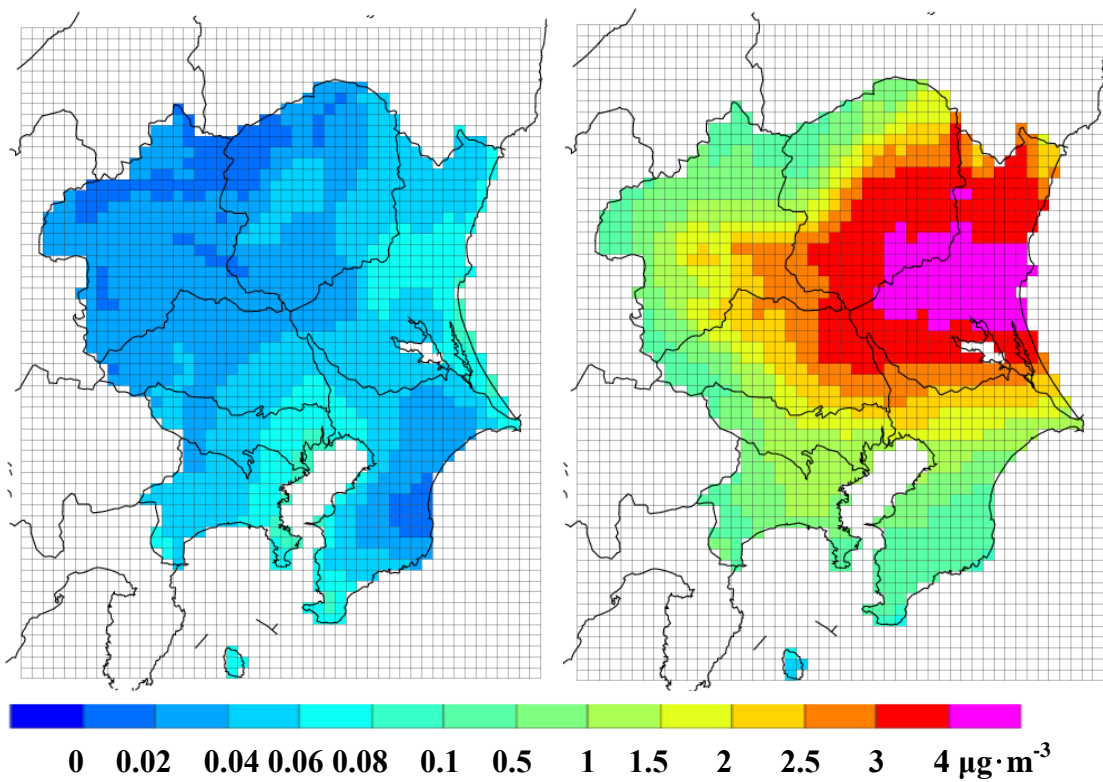


Figure 2.4 Spatial distribution map of PM_{2.5} reductions during 2000-2010, winter (left) and summer (right).

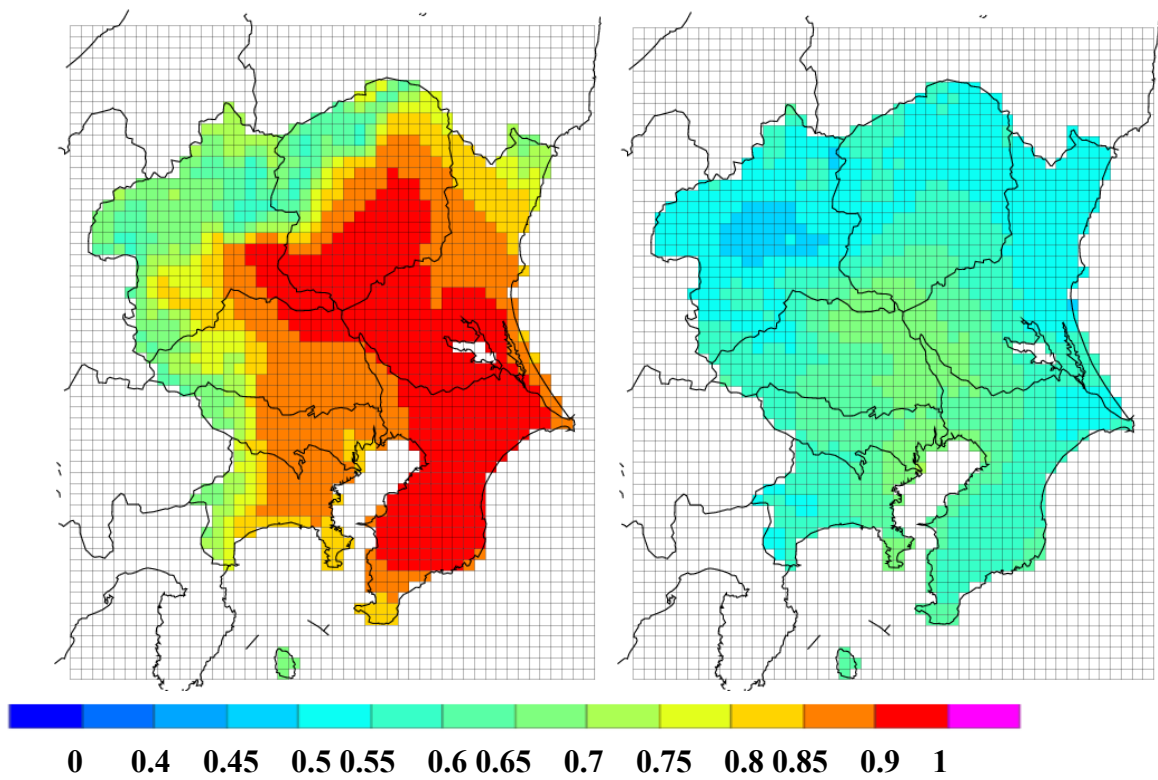


Figure 2.5 Spatial distribution map of PM_{2.5} ratio of 2010 to 2000, winter (left) and summer (right).

Chapter 3 Analysis of Efficient Abatement Options for PM_{2.5} Reduction by Controlling Ammonia Emission in Kanto Region

3.1 Introduction

As introduced in Chapter 1, excessive anthropogenic ammonia continuously influences the nitrogen cycle by accumulating in arable soils or volatilizing to atmosphere, which lead to a series of global environmental problems [6-9]. Furthermore, ammonia is one of the important precursors of secondary inorganic PM_{2.5} [12, 13]. Reactions between ammonia, SO₂ and NO_x, result in ammonium sulfate and ammonium nitrate, which are regarded as two of five major constituents of PM_{2.5} mass [101]. As shown in Table 2.1, PM_{2.5} limitations of 15 $\mu\text{g}\cdot\text{m}^{-3}$ for annual average concentration and 35 $\mu\text{g}\cdot\text{m}^{-3}$ for daily average concentration have enacted by Japan government in 2009 [83-89]. According to the results of Chapter 2 and the investigation conducted by the Ministry of the Environment, even though domestic PM_{2.5} level keeps decreasing for the past few years, current status indicates that no more than 40% of the nationwide monitoring stations achieved the qualified PM_{2.5} limitations [91].

Different from ammonia, there are strict regulations to control the SO₂ and NO_x emissions in Japan. In recent years, the emission levels of SO₂ and NO_x have nearly met the emission standards [91]. Adversely, limited regulation focuses on ammonia emission. As indicated in Chapter 1.2.3, Offensive Odor Control Law would be the only standard related with ammonia emission. However, it does not regulate ammonia concentrations from the perspective of air pollution, but in consideration of the annoying odor [34].

As noted above, there is no doubt that ammonia would be an important factor for the secondary PM_{2.5}. Compared with the well-conducted regulations of SO₂ and NO_x, there is a lack for appropriate standards for controlling the level of atmospheric ammonia. Thus, it is necessary to consider how to manage and control ammonia emission effectively. To the best of our knowledge, none of the previous researches have investigated the efficiencies of PM_{2.5} reduction responding to different sources of ammonia emission [102].

Responding to the PM_{2.5} abatement guidance proposed by the Ministry of Environment, this chapter represents an integrated spatial and temporal study on ammonia emission abatement options. Firstly, a 5% ammonia emission abatement strategy was applied to Kanto Region, collaborated with the same reduction scenarios of SO₂ and NO_x. Within the same reduction ratio, PM_{2.5} reduction efficiencies of the above-mentioned precursors were investigated. After that, a comparative study was conducted to indicate which ammonia emission source would be most effective in lowering PM_{2.5} levels. We believe the results would be an important step forward for the localization and seasonalization of low-emission development strategies.

3.2 Materials and methods

3.2.1 Scenario establishment based on different ammonia precursors and ammonia emission sources

To investigate the efficiency of PM_{2.5} reductions that respond to the emission reduction strategies, two scenarios were established in this study. In the first scenario, a strategy of overall 5% emissions reduction was applied to the precursors of secondary PM_{2.5} (SO₂, NO_x and ammonia), respectively. From the results, it could be further interpreted that how PM_{2.5} reduction respond to the decline in the individual precursor, and which precursor would be the most significant factor in controlling PM_{2.5} levels in Kanto Region. In the second scenario, it was assumed that the overall 5% emission reductions were cut down from agricultural or urban sources. In this presented scenario, seasonal variation and dependence of PM_{2.5} concentrations on different types of ammonia sources could be obtained. In addition, the results could also indicate when cut down the same amount of ammonia emission, which ammonia source would be the most effective to apply the PM_{2.5} reduction strategies.

Kanto Region was selected as the study area for the following reasons: 1) As mentioned in Chapter 2.2.1, compared with other areas which might get an influence from foreign anthropogenic sources, the sensitivity of PM_{2.5} concentration in this region significantly response to domestic emission sources. 2) As mentioned in Chapter 1.1, ammonium–sulfate–nitrate salts account for a large proportion of PM_{2.5} particles. 3) In the

dense-populated area, the urban sources have a larger contribution to PM_{2.5} concentration [102].

3.2.2 Emission inventories

According to the ammonia emission inventory established by Kannari *et al.*, all the anthropogenic ammonia emission sources in Japan were divided into urban sources (fertilizer industries, flue gas denitrification apparatuses, vehicles, sewage treatment facilities, pit-latrines, human perspiration and respiration, pets) and agricultural sources (fertilizer application and livestock farming) [20].

In this study, agricultural sources are regarded as the combination of the emissions caused by fertilizer volatilization and animal husbandry. Since it is hard to control the ammonia emission discharge from perspiration, respiration and excrement, the probability and applications of the policy would be very limited. Therefore, vehicle exhausts were considered as the only urban ammonia sources in this research.

The scenarios were established on the 2010 emission inventories. The emission data of all the precursors (NO_x, SO₂, and ammonia) were calculated as Chapter 2.2.2, other emissions and conditions irrelevant to the secondary PM_{2.5} were supposed to remain unchanged as EAGrid2000-Japan [4].

3.2.3 Atmospheric simulation

The calculation methods of atmospheric modeling (including the details of the models, nesting information, vertical layer, reanalysis data, dry/wet deposition, spin-up time, etc.) are the same as represented in Chapter 2.2.3. Different from Chapter 2, 10 patterns in July to August and December to January were selected to present the representative weather conditions in summer and winter, with an occurrence frequency of 35.59% and 41.5%, respectively.

10 patterns in winter and summer which reflects the results of the base case without applying any emission reduction strategies were obtained from Chapter 2.3.2.

3.3 Results and discussion

3.3.1 PM_{2.5} reductions respond to precursors

As indicated in Chapter 3.2.1, a 5% emission reduction strategy was applied to PM_{2.5} precursors (SO₂, NO_x and ammonia). In this scenario, when one of the precursor emissions was assumed to decline to 95%, the others would remain unchanged as the basic emissions of 2010. Table 3.1 summarized the basic emissions of the study period (July and August in summer, January and December in winter). As discussed in Chapter 2.3.1, ammonia emission proved to be higher in summer, which would mainly result from the seasonal agricultural activities. Oppositely, higher levels of NO_x emission occurred in winter, which was in accordance with the results of Huang *et al.* [103]. Compared with ammonia and NO_x, there was no significant difference between the SO₂ emission of summer and winter. In other words, SO₂ emission was relatively stable throughout the year.

Figure 3.1 shows the PM_{2.5} reductions after applied the 5% abatement policy to the precursors. When cutting down 5% of overall emissions, SO₂ shows the highest efficiency in reducing secondary PM_{2.5}, with an average annual reduction of 0.11 μg·m⁻³. As shown in Figure 3.1 (c), in summer, the PM_{2.5} reduction is concentrated in the north parts, while the PM_{2.5} decreases greatly throughout the Kanto Region in winter.

The 5% decline in ammonia emission also indicates a certain efficiency in annual PM_{2.5} reduction of 0.019 μg·m⁻³. In summer, the average PM_{2.5} reduction is 0.015 μg·m⁻³. The maximum PM_{2.5} reduction (0.19 μg·m⁻³) appears in the center of Kanto Region. In winter, the average PM_{2.5} reduction is 0.023 μg·m⁻³. PM_{2.5} slightly decreases in north Ibaraki, south Chiba and west Kanagawa, with the maximum PM_{2.5} reduction of 0.1 μg·m⁻³. The following reason could be summarized to explain the seasonal variation of PM_{2.5} reduction: according to Figure 2.3 and Table 3.1, the ammonia emission in Kanto Region was proved to be on a higher level in summer (4.5 times compared with the average emissions in winter). In another word, benefited from the 5% emission reduction strategy, there would be a greater reduction of ammonia emission in summer, which would lead to a greater decline in secondary PM_{2.5}.

Compared with SO₂ and NO_x, the 5% NO_x emission reduction strategy did not approach an ideal efficiency of PM_{2.5} reduction. When cutting down 5% of the overall NO_x emission, the average PM_{2.5} reduction proved to be 0.03 μg·m⁻³ in summer. However, it shows an increase tendency of 0.11 μg·m⁻³ in winter. The research conducted by Tsimpidi *et al.*

indicated the similar result. In their study, the Particulate Matter Comprehensive Air Quality Model with Extensions (PMCAMx) was used to investigate how PM_{2.5} responded to 50% reduction of NO_x emission. Although cutting down NO_x emission lowered the PM_{2.5} concentrations in summer, it resulted in a rather complicated response in winter, due to the changes of the oxidant levels. In some areas, the PM_{2.5} concentration was proved to negatively response to the NO_x decrease [104].

In fact, there is a large difference between the basic emission amounts of PM_{2.5} precursors. Based on Table 3.1, the 5% emission reduction strategy indicates 6,400 t decline in SO₂ emission, 5,200 t decline in ammonia emission and 20,400 t decline in NO_x emission (average amount of summer and winter). Figure 3.3 shows the PM_{2.5} reductions when reduce every 1,000 t of the precursors. Same as the results presented in Figure 3.1, cutting down SO₂ emission proved to be the most effective in controlling secondary PM_{2.5}, following is ammonia. The reduction of NO_x emission indicates an unstable performance in lowering PM_{2.5} concentration, especially in winter.

GR were calculated as Eq. (1.1) [12]. Figure 3.4 and 3.5 shows the PM_{2.5} sensitivities of 2,782 cell-grids (GR<10) responding to the corresponding GR when applied the 5% precursor abatement strategy in summer and winter. Based on Figure 3.4 and 3.5, it could be clearly indicated that in summer (Figure 3.4), the values of GR were uniformly distributed across the interval (0 to 10). Meanwhile, the PM_{2.5} sensitivity responds weakly to GR in all the three abatement scenarios. Adversely, GR were proved to be lower in winter (Figure 3.5), and negative values even occurred in some of the cell-grids. Compared with SO₂ and NO_x, PM sensitivities significantly responded to GR in the ammonia abatement scenario, which indicated that in the grid cells with lower GR, controlling ammonia emission could stably reduce PM_{2.5} levels than other precursors.

3.3.2 The PM_{2.5} reductions respond to ammonia emission sources

Based on the results of Chapter 3.3.1, we conducted a further investigation of how PM_{2.5} reductions respond to different ammonia sources. In this scenario, the 5% of the overall ammonia emission (5,200 t) were assumed to be reduced from all sources, agricultural source and urban (vehicle) sources, respectively. When the ammonia emission was assumed to be cut

down from one of the above-mentioned emission sources, the emissions of other sources would remain unchanged as the basic inventory of 2010. Figure 3.6 illustrated the ammonia emission cut down from each emission source. As shown in Figure 3.6 (b), the largest emissions occur in south Gunma, north Tochigi, east Ibaraki and east Chiba, where agricultural-centered economy are in domination. The agricultural emissions also indicate significant seasonality, due to the different intensities of agricultural activities in summer and winter. Figure 3.6 (c) shows the emission reductions from the urban sources, in which the 5% overall ammonia emissions are assumed to be cut down from vehicle exhausts. Different from the agricultural sources, in EAGrid2000-Japan, the emissions related with vehicles are considered as unchanged all over the year. Thus the emission reductions in Figure 3.6 (c) present a same value in summer and winter.

Figure 3.7 shows the PM_{2.5} reductions after cutting down the 5,200 t ammonia emission from different ammonia emission sources. In Figure 3.7 (a), it was assumed that 5,200 t ammonia emission were reduced averagely from all the ammonia sources, which lead to an annual PM_{2.5} reduction of 0.018 µg·m⁻³. Discussions related with seasonality and GR were conducted in 3.3.1. Although agriculture contributes the largest ammonia emission, the PM_{2.5} reduction efficiency proves to be the lowest among all the three cases (overall sources, agricultural sources, urban sources). As shown in Figure 3.7 (b), the annual PM_{2.5} concentration declines 0.017 µg·m⁻³, responding to the reduction of 5,200 emissions from agricultural sources. Compared with on-road NO_x and SO₂ emissions, ammonia emission discharged from vehicles are very limited and does not account for a large proportion of the gross emission. However, controlling vehicle exhausts presents the highest efficiency in reducing PM_{2.5}, with an annual PM_{2.5} reduction of 0.021 µg·m⁻³.

To further investigate how the residents of Kanto Region could benefit from the emission reduction strategies, the population-weighted average concentrations of the PM_{2.5} reductions (R_p, units: µg·m⁻³) were calculated by Eq. (3.1):

$$R_p = \sum_{n=1}^{3100} C_n P_n \quad (3.1)$$

where n is the number of an individual grid square ($n=1-3100$). P_n is the population in the corresponding cell-grid, which was estimated by the database of the Ministry of Environment of Japan in 2000 (units: capita) [112]. C_n is the annual $PM_{2.5}$ reduction of the corresponding grid-cell (units: $\mu\text{g}\cdot\text{m}^{-3}$), averaged from summer and winter. The results of R_p are summarized in Table 3.2, note a higher R_p indicates could benefit more from the reduction strategies of ammonia emission. Still, the agriculture case presents the lowest R_p of $0.012 \mu\text{g}\cdot\text{m}^{-3}$, two times less than the overall case ($0.022 \mu\text{g}\cdot\text{m}^{-3}$) and the urban case ($0.026 \mu\text{g}\cdot\text{m}^{-3}$). According to the Eq. (3.1), R_p is not only concerned with the concentrations of $PM_{2.5}$ reductions, but also closely related with the population density of the corresponding cell-grid. As shown in Figure 3.7 (b), the $PM_{2.5}$ reductions resulted from the declines in agriculture emissions are concentrated in Ibaraki, where the population would be limited when compared with TMA. As the largest emission contributor, the agricultural sources are considered as the first choice for the policy making. However, this study provides the evidence controlling the ammonia emission from other sources (especially vehicles) could achieve a higher efficiency of reducing $PM_{2.5}$ concentrations.

3.3.3 The uncertainty of weather pattern selection

According to Chapter 2, July, August, December and January were regarded as the study period. From the above-mentioned four months, the meteorological conditions of 7 weather patterns in winter and 9 patterns in summer were selected to conduct the atmospheric simulation, with an occurrence frequency over 50% in Kanto Region. Due to the inordinately long simulation time (about 72 hours to complete one pattern), instead the 16 patterns' simulation, we selected 10 patterns (5 for winter and 5 for summer) to conduct the studies in this chapter. The occurrence frequencies are proved to be 35.59% in winter and 41.5% in summer. To verify the performance of the weather patterns, the $PM_{2.5}$ concentrations of the base case which calculated under 1 patterns, 5 patterns and 7 patterns were summarized in Figure 3.8. The results of Figure 3.8 indicate that whether it's in winter or summer, the average $PM_{2.5}$ concentrations turn to be stable when 5 or more patterns were selected for the simulation. Thus 10 patterns selected in winter and summer were enough and reasonable for conducting this study.

3.4 Summary

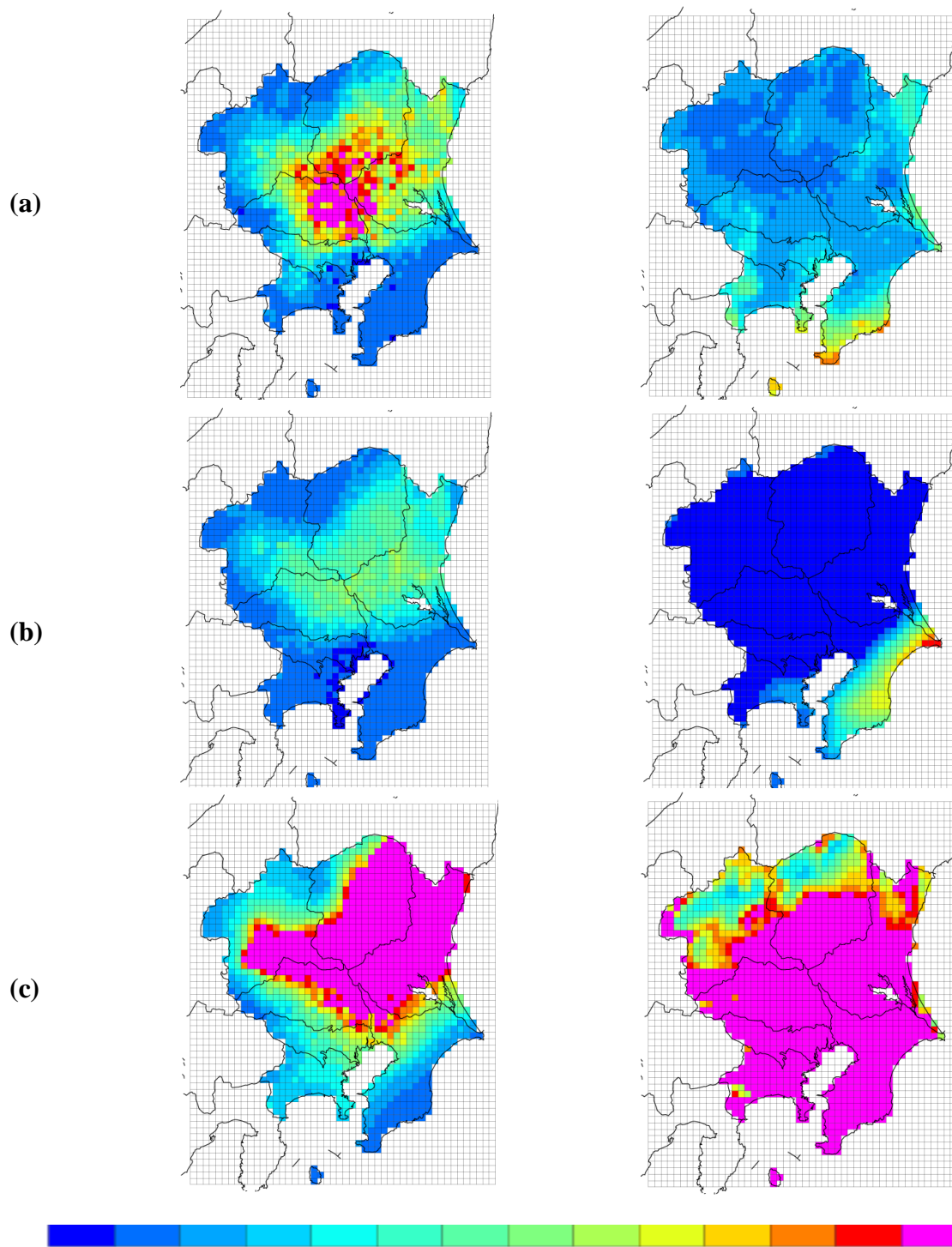
In this Chapter, an integrated spatial and temporal study on ammonia emission abatement options in Kanto Region was conducted. In spite of the potential uncertainties, it could be concluded that: (1) when same emission abatement policy was applied to the secondary PM_{2.5} precursors, SO₂ showed the best efficiency in cutting down PM_{2.5} levels, following that would be ammonia and NO_x. (2) Strict limits are set O₂ and NO_x in worldwide, while little effort has been devoted to regulate ammonia emission. Controlling ammonia emission might be the most available option for the current situation, especially in winter. (3) Although agriculture is always regarded as the major emission source, when applied the same emission reduction strategy, it presents a very low efficiency of PM_{2.5} reduction. Adversely, controlling the ammonia emission from vehicle sources would be very effective for reducing PM_{2.5} concentration. Based on the above-mentioned results, it would be more important to control the ammonia emission discharged in energy sector and dense populated areas.

Table 3.1 Basic emissions of the PM_{2.5} precursors in Kanto Region

Precursors	Jan. (t)	Jul. (t)	Aug. (t)	Dec. (t)
NO ₂	85.19	74.4	74.46	87.87
NO	1125.36	934.87	939.35	1151.14
SO ₂	344.97	345.63	348.19	372.05
Ammonia	91.39	491.85	453.91	120.11

Table 3.2 Annual average reductions and population-weighted average concentrations of PM_{2.5} reduction after applied the 5% abatement policy to different ammonia sources (all sources, agricultural sources, vehicles)

	Overall sources (5200 t·y ⁻¹)	Agricultural sources (5200 t·y ⁻¹)	Vehicles (5200 t·y ⁻¹)
PM _{2.5} average decrease (µg·y ⁻¹)	0.018	0.017	0.021
Population-weighted average decrease (R _p , µg·y ⁻¹)	0.022	0.012	0.026



0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 $\mu\text{g}\cdot\text{m}^{-3}$
 Figure 3.1 PM_{2.5} reductions after applied the 5% abatement policy to the precursors in summer (left) and winter (right). 5% abatement of total ammonia emissions (a) 5% abatement of total NO_x emissions (b) and 5% abatement of total SO₂ emissions (c)

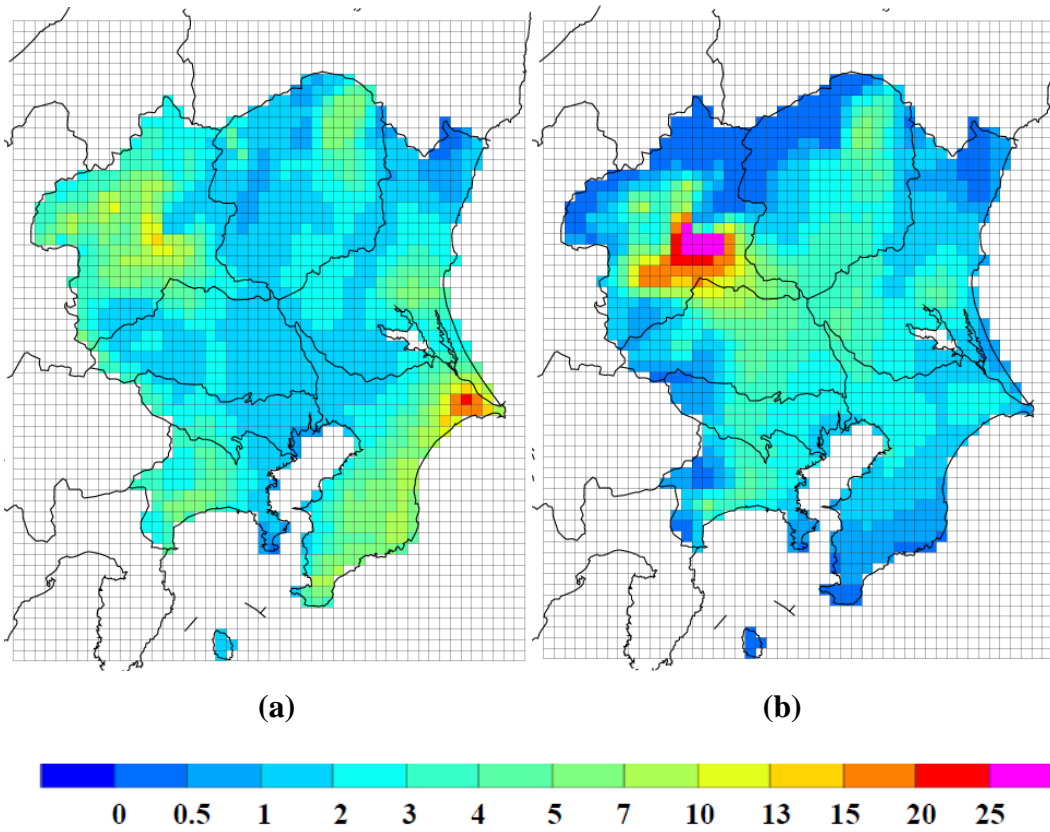


Figure 3.2 GR in the base case. Simulated data in summer (July to August) (a) and winter (December to January) (b)

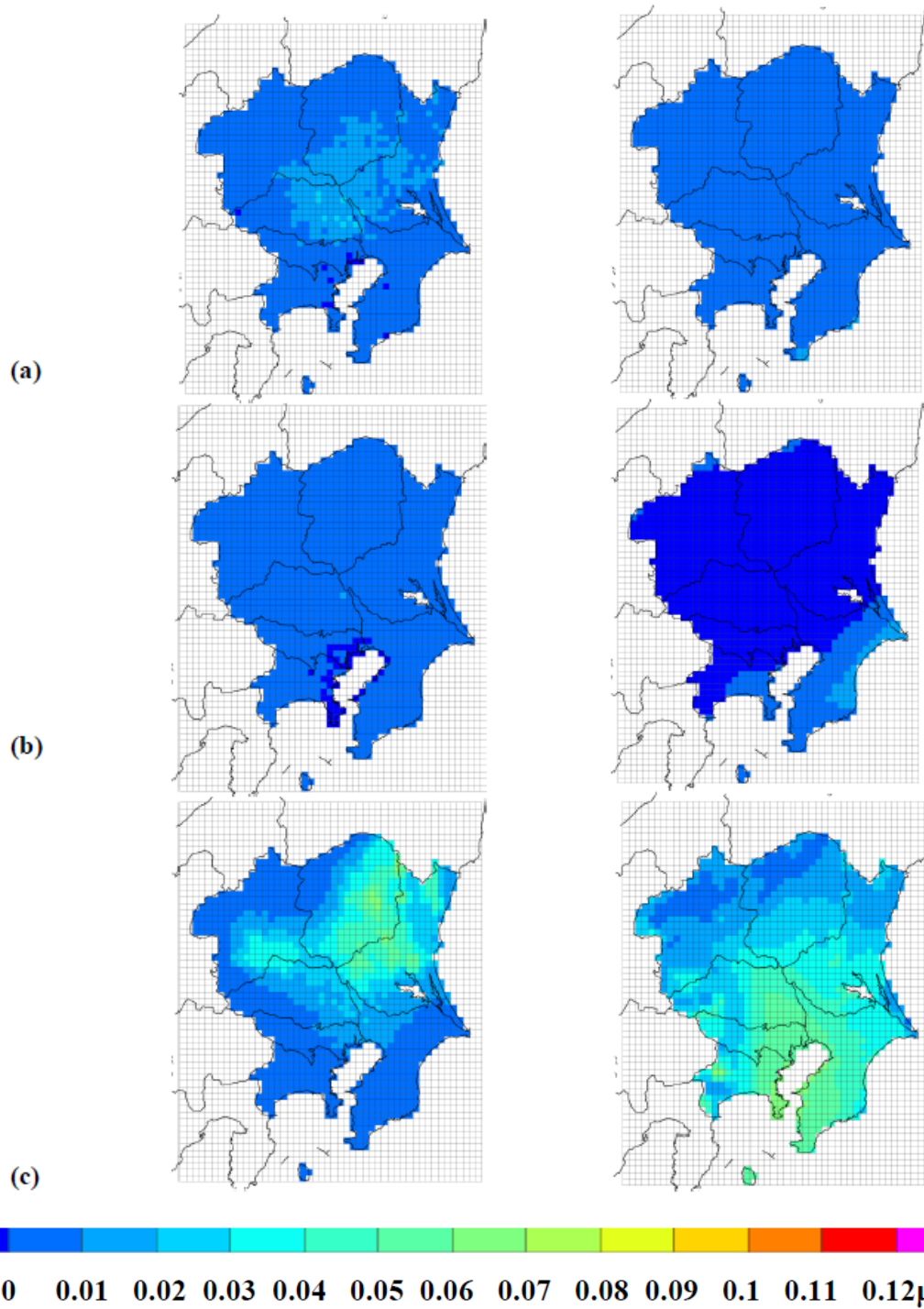


Figure 3.3 $PM_{2.5}$ reductions when reduce every 1,000 t of the precursors in summer (left) and winter (right). 1,000 t of ammonia emission (a) 1,000 t of NO_x emission (b) and 1,000 t of SO_2 emission (c)

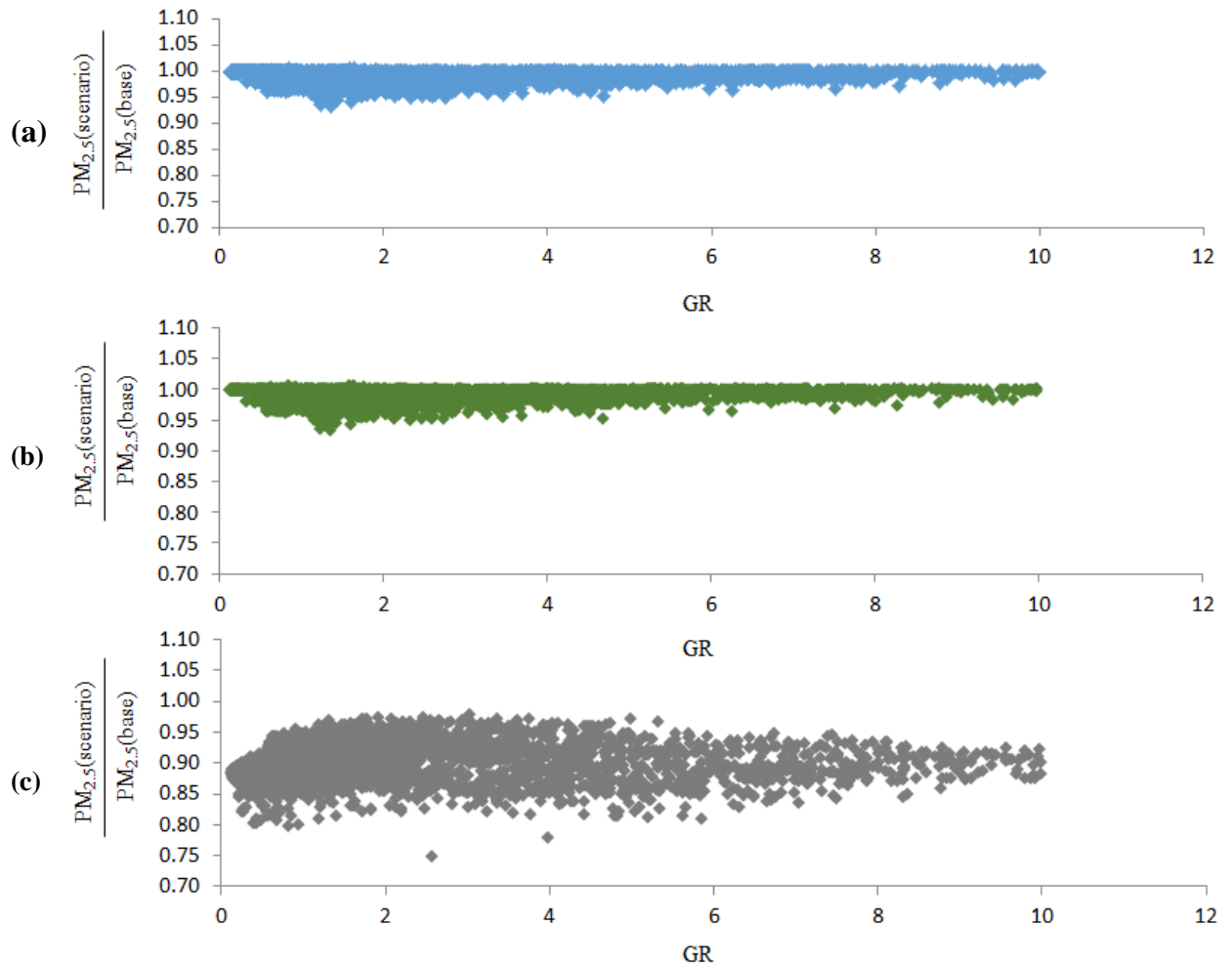


Figure 3.4 $PM_{2.5}$ sensitivities of cell-grids ($GR < 10$) responding to the corresponding gas ratios when applied the 5% precursor abatement strategy in summer. The scatter chart of 5% ammonia abatement scenario (a), the scatter chart of 5% NO_x abatement scenario (b) and the scatter chart of 5% SO_2 abatement scenario (c)

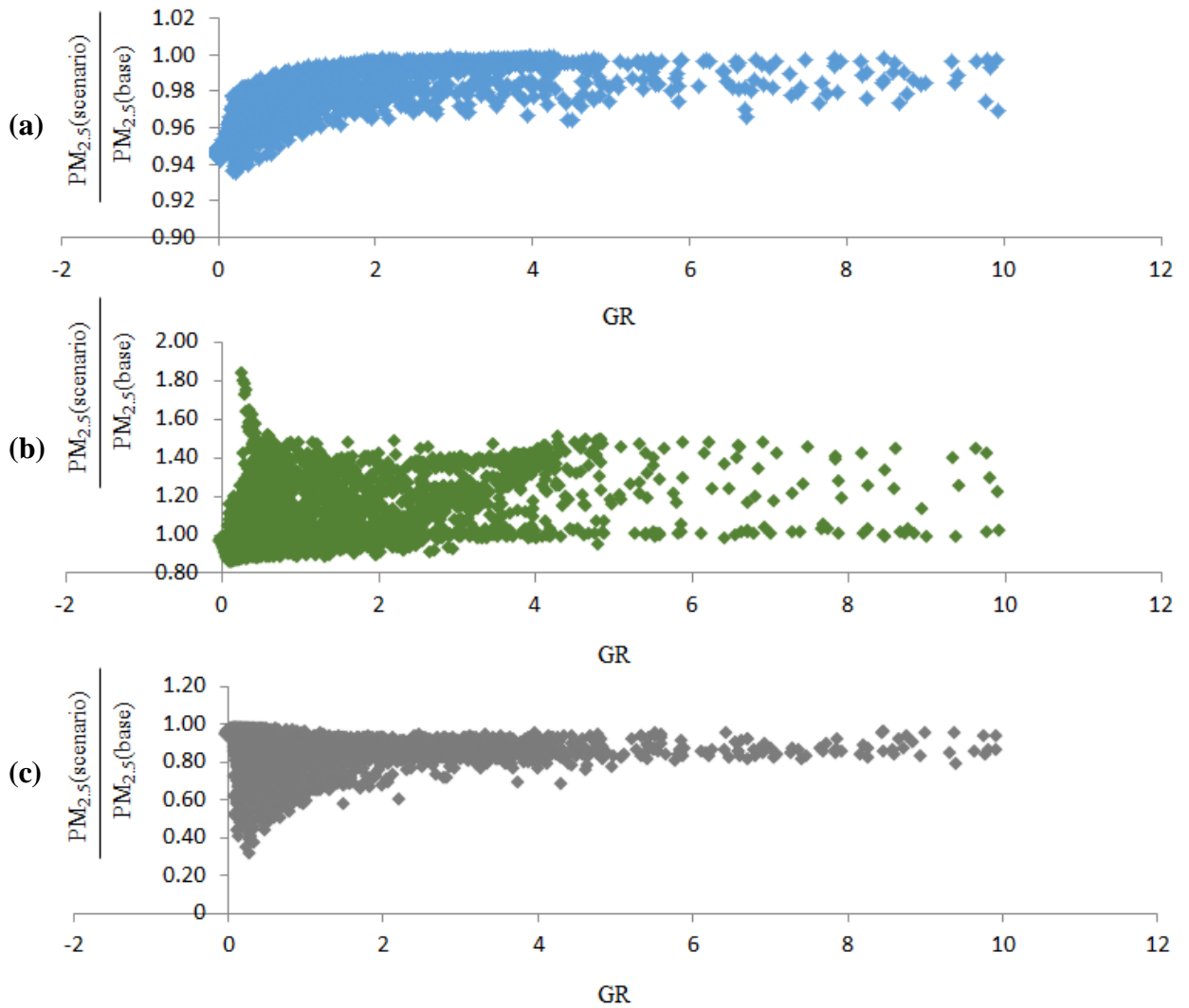
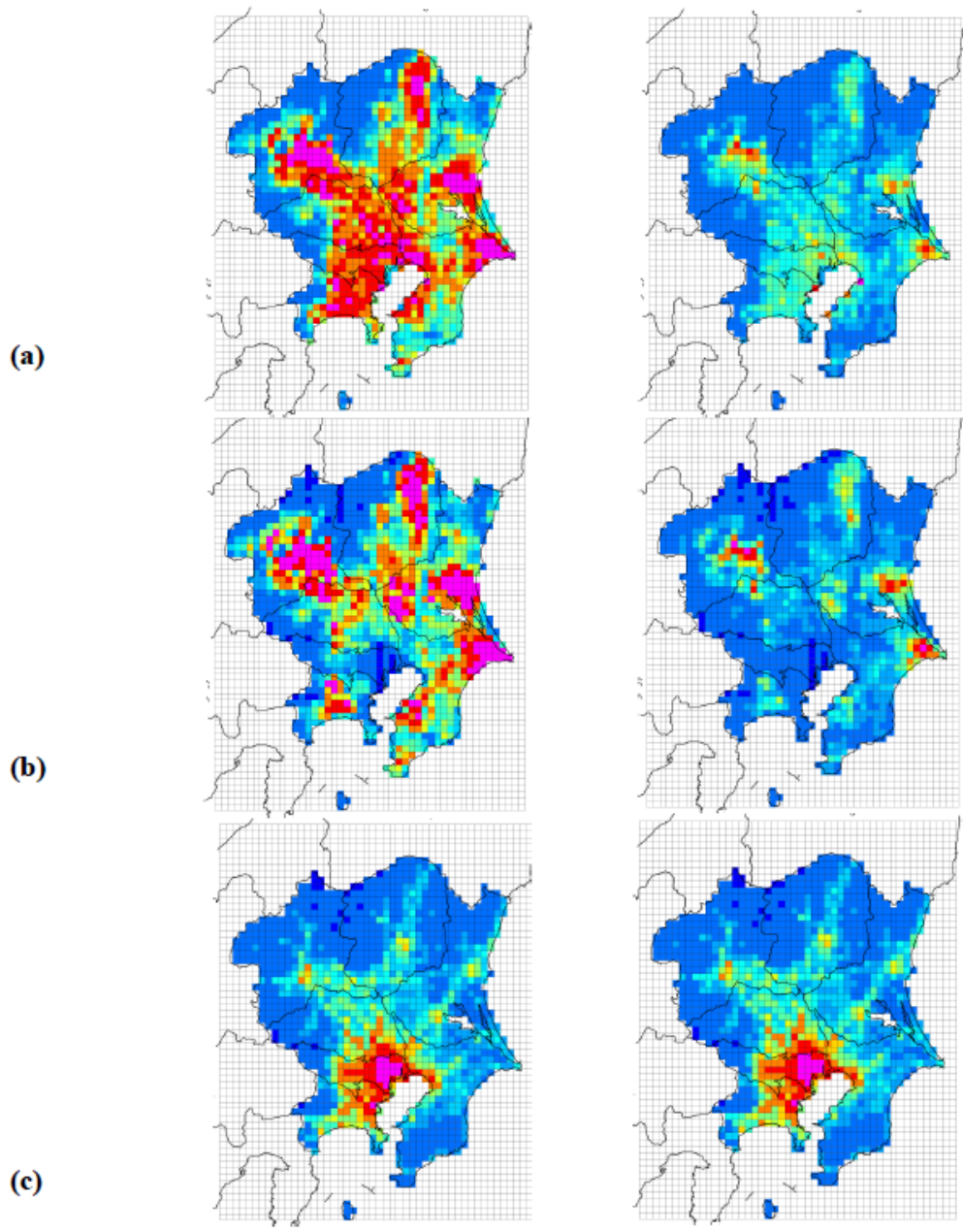


Figure 3.5 $PM_{2.5}$ sensitivities of cell-grids ($GR < 10$) responding to the corresponding gas ratios when applied the 5% precursor abatement strategy in winter. The scatter chart of 5% ammonia abatement scenario (a), the scatter chart of 5% NO_x abatement scenario (b) and the scatter chart of 5% SO_2 abatement scenario (c)



0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2 3 5 mol·km⁻²·h⁻¹

Figure 3.6 Ammonia emissions cut down from different emission sources in summer (left) and winter (right). 5,200 t from all the ammonia emission sources (a) 5,200 t from agricultural sources (b) and 5,200 t from vehicle exhausts (c)

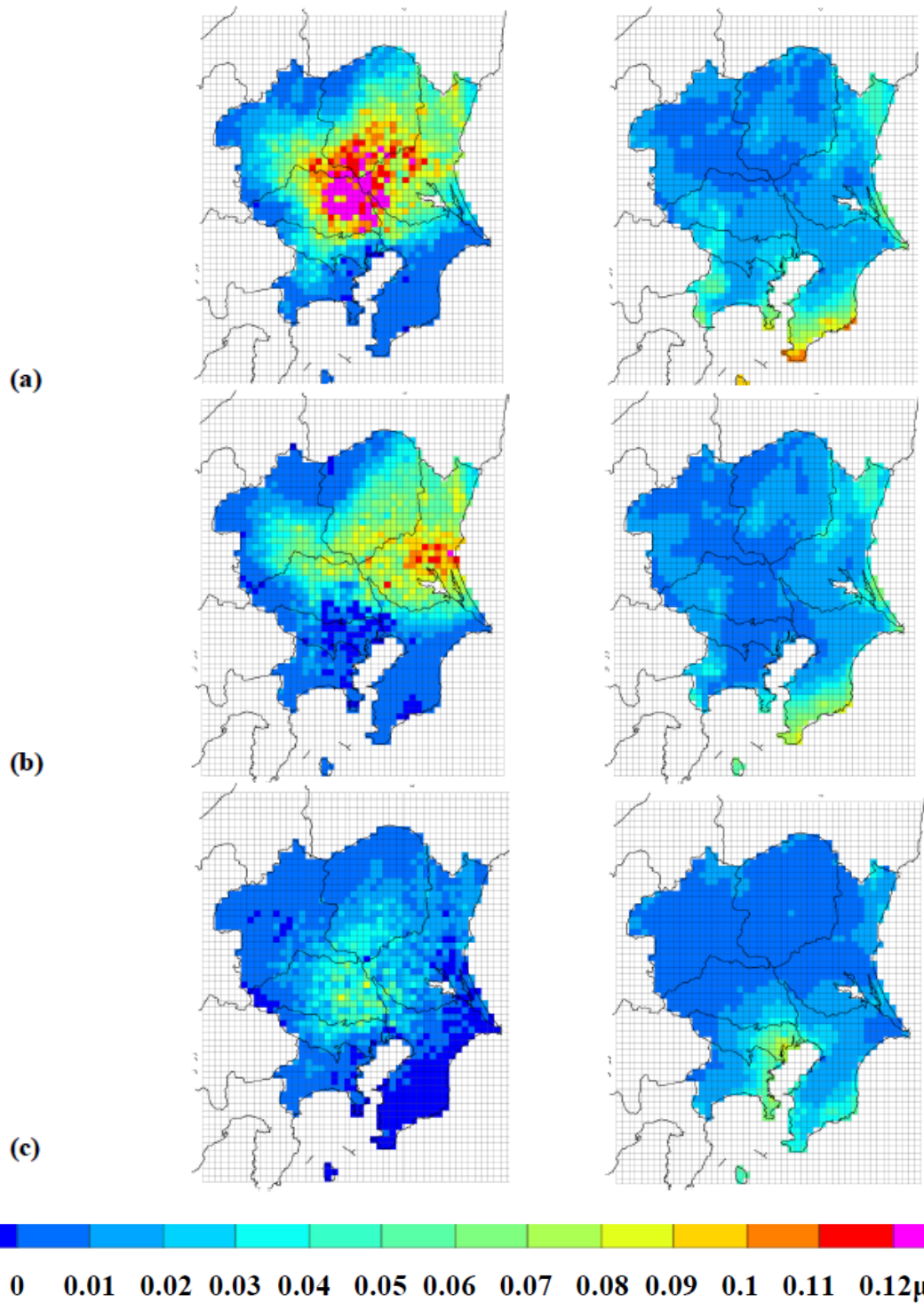
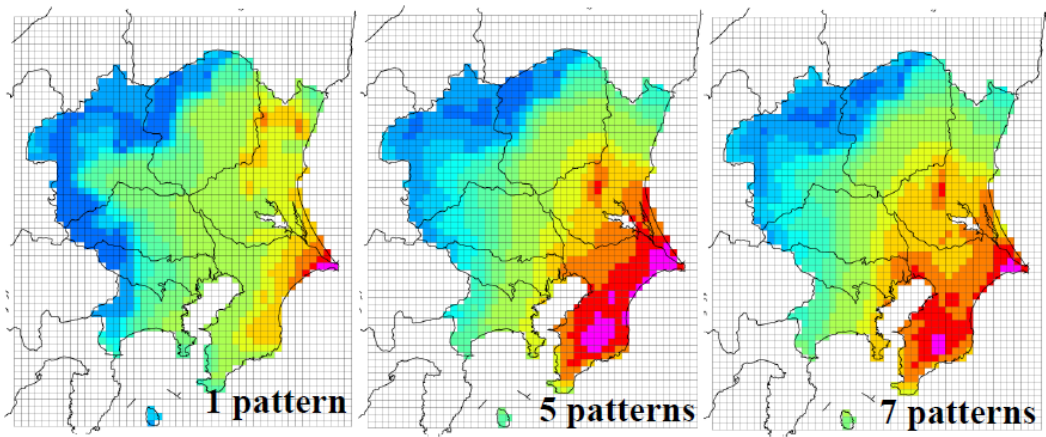
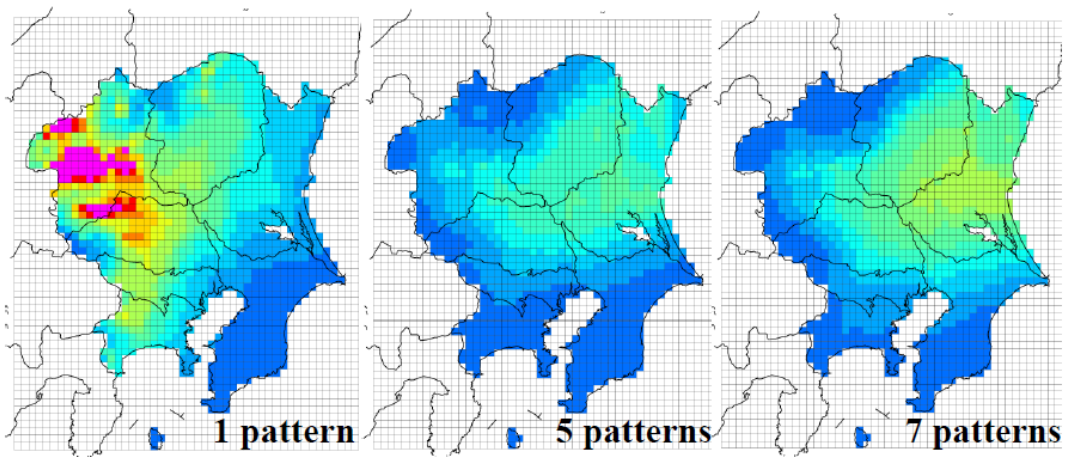


Figure 3.7 PM_{2.5} reductions after cutting down the same amount of ammonia emission from different ammonia emission sources in summer (left) and winter (right). 5,200 t from all the ammonia emission sources (a) 5,200 t from agricultural sources (b) and 5,200 t from vehicle exhausts (c)



(a)



(b)



0 0.2 0.4 0.6 0.8 1 1.3 1.5 2 2.2 2.4 2.6 2.8 $\mu\text{g} \cdot \text{m}^{-3}$

Figure 3.8 Average $\text{PM}_{2.5}$ concentrations under different weather patterns in 2010. In winter (December to January) (a) and summer (July to August) (b)

Chapter 4 Impact Assessment of the PM_{2.5} Resulted from the Application of Ammonia-hydrogen Energy in Kanto Region

4.1 Introduction

As introduced in Chapter 1.2.3, after the Fukushima accident, there has been a need for clean energy. Due to the limitation of developing domestic energy, importing renewable energy seems to be a practical solution for the energy shortage problem of Japan. For instance, Chubut Prefecture in Argentina has a wind power-generating capacity of 4,430 billion kWh·y⁻¹, which exceeds Japan's domestic demand by 4.5 times [105]. Renewable primary energy (wind, solar, etc.) can be converted to hydrogen through water electrolysis. Because of its high heat value, only 7×10⁵ t of hydrogen would be needed to satisfy 30% of the domestic energy requirement [5]. After the Fukushima accident, thermal power depending on fossil fuels became the backbone of the energy industry, accounting for 47% of the domestic electricity supply [44]. Previous cases in Japan have demonstrated that hydrogen could be used for large-scale, multi-fuel power generation [106].

Unlike liquefied natural gas (LNG), hydrogen is a convenient source of safe and stable energy. However, gaseous hydrogen is difficult to liquefy, and high-quality equipment is required for hydrogen storage. Thus, long distances represent a fatal disadvantage associated with importing hydrogen energy on a massive scale [107]. To achieve its safe and efficient transportation, ammonia is the most promising and useful chemical carrier. Additionally, it is completely carbon free, with a gravimetric hydrogen density of 17.8 wt% [46]. The relatively low boiling point of ammonia indicates its convenience and low cost of storage. Because of the development of the Haber-Bosch process, ammonia production has undergone rapid commercialization over the last decade [37]. Moreover, the existing infrastructure supports the promotion of ammonia-hydrogen energy.

Although ammonia is a useful hydrogen carrier, excessive atmospheric ammonia poses a direct threat to human health. Furthermore, PM_{2.5} resulted from ammonia emission can diffuse far from the emission source and cause widespread premature mortality. From the

results of Paulot *et al.* [12], the financial loss caused by PM_{2.5}-related health impacts can even exceed the benefits associated with ammonia utilization. Rouleau *et al.* [65] conducted a human health-impact analysis on biodiesel popularization, which was considered as a promising energy source as ammonia. Their results indicated that among all of the pollutants in diesel exhaust, PM_{2.5} most strongly affected the financial cost associated with human health, especially by increasing premature deaths.

However, to the best of our knowledge, no study has considered the public health impacts of the secondary products resulted from ammonia emission as energy carriers. Additionally, the results obtained in Chapter 3 indicated the importance of controlling ammonia emissions in energy sector and dense populated areas. This study aimed to evaluate the health impacts of utilizing ammonia-hydrogen energy in Japan. The scenario was originally used in the Japan National Sustainable Energy Development Project and focused on Kanto Region, the most populated area in Japan [46]. We estimated the incremental PM_{2.5} concentration by assuming that 20% of the energy consumption in Kanto Region was supplied by ammonia-hydrogen energy. The PM_{2.5}-related health impacts were represented by premature deaths among the elderly population (individuals over 65 years old).

4.2 Materials and methods

4.2.1 Focus and design

Based on the national target, 30% of domestic energy consumption should be supplied by renewable energy by 2030. Given that 10% is already supplied by the existing renewable energy infrastructure, the remaining 20% was assumed to be supplied by importing ammonia-hydrogen energy [46]. According to the above-mentioned scenario, the national target could be achieved. In this process, hydrogen is converted to ammonia for storage and long-distance transportation from overseas exporters and is eventually recovered by decomposing ammonia in domestic power plants to satisfy local energy demands. Our study focused on this renewable energy proposal of the Japanese government and aimed to evaluate the health impacts caused by the PM_{2.5} resulted from incomplete ammonia decomposition in the above-mentioned scenario.

Kanto Region was selected as the region of interest for this study for the following three reasons: (1) As mentioned in Chapter 2.2.1, in 2010, the population of Kanto Region rose to 42.6 million, equivalent to approximately 1/3 of the national population, occupying only 1/10 of the country's territory [92]. Because of this dense population, many potentially affected individuals reside in this area. (2) The electricity consumption of Kanto Region accounted for almost 1/3 of the national gross consumption in 2010 [92]. Because of this region's high electricity demand, ammonia-hydrogen power generation systems would create high ammonia emission. (3) In Kanto Region, there are 21 thermal power plants with LNG gas turbines, which could utilize ammonia-hydrogen energy and have enough capacity to supply the 20% energy consumption. Furthermore, benefited from the geographical locations (coastal areas, e.g. Tokyo Bay), they shall have convenient access to utilize imported ammonia-hydrogen energy. The geographical locations of the 21 LNG thermal power plants are shown in Figure 4.1.

4.2.2 Ammonia emission estimation

Based on the scenario assumed, the total ammonia emission (V_A , in ton) in Kanto Region was calculated using Eq. (4.1):

$$V_A = \frac{V_H R \rho_A}{\eta \rho_H} \quad (4.1)$$

where V_H is the amount of hydrogen needed to supply 20% of domestic energy consumption estimated based on the proposal of Japan's Agency for Science and Technology [5] (units: t), and R is the ratio of ammonia remaining after incomplete decomposition. Although the ammonia dissociation rate varies based on the conditions and catalysts used, in this study, R was set to be 0.1% according to the value determined for the high-purity, hydrogen-production system proposed by Eguchi *et al.* [50] η is the thermal efficiency of hydrogen for power generation (51%) estimated by Japan's Agency for Natural Resources and Energy [106]. ρ_A and ρ_H represent the densities of ammonia ($0.73 \text{ g} \cdot \text{L}^{-1}$) and hydrogen ($0.0899 \text{ g} \cdot \text{L}^{-1}$), respectively.

As shown in Table 4.1, the incremental ammonia emission was distributed among 21 LNG thermal power plants with LNG gas turbines according to their power-generation

capacities [108]. Ammonia emission from stacks is regulated by Japan's Offensive Odor Control Law (OOCL) [34]. The maximum emission flow rate of an individual power plant (q_n in $\text{Nm}^3 \cdot \text{h}^{-1}$) was calculated using Eq. (4.2):

$$q_n = 0.108C_m \text{He}_n^2 \quad (4.2)$$

where He_n is the effective stack height of the thermal power plants ($n=21$) [109] (in m), and C_m is the maximum emission density of a property defined by OOCL [34] (1 ppm). Assuming 24-hour continuous operation, all 21 LNG thermal power plants satisfied the ammonia emissions restriction. The flow chart of ammonia emission estimation is shown in Figure 4.2.

4.2.3 NO_x and SO_2 emission estimation

The basic emission inventories of NO_x and SO_2 were obtained from EAGrid2000-Japan by Kannari *et al.* [4]. Instead of utilizing ammonia-hydrogen energy, 20% of domestic energy consumption was assumed to be supplied by fossil fuels in the base cases. Thus NO_x and SO_2 emissions would have a decline in the ammonia-hydrogen energy applied scenarios, benefiting from introducing ammonia-hydrogen energy system. The reduced emissions of NO_x and SO_2 (20% of the emissions discharged from thermal power generation sector based on EAGrid 2000-Japan) were distributed to all fire power plants in Kanto Region by their generating capacities.

4.2.4 Atmospheric modeling

Corresponding to our scenarios, base cases were set without introducing ammonia-hydrogen energy to the 21 LNG thermal power plants.

The calculation methods related with atmospheric modeling (including the details of the models, nesting information, vertical layer, reanalysis data, dry/wet deposition, spin-up time, etc.) are represented in Chapter 2.2.3.

4.2.5 Health impact analysis

$\text{PM}_{2.5}$ exposure strongly affects premature mortality resulting from lung and heart diseases, leading to acute and chronic deaths, especially among the elderly [64]. In this study, we selected residents of Kanto Region who were over 65 years old to calculate the health impacts. $\text{PM}_{2.5}$ -related mortality was assumed to respond linearly to the increased $\text{PM}_{2.5}$

concentration. The premature deaths (P , units: $\text{capita} \cdot \text{y}^{-1}$ or $\text{capita} \cdot \text{d}^{-1}$) resulted from both long- and short-term exposure to $\text{PM}_{2.5}$, were calculated by Eq. (4.3). The chronic and acute deaths are assumed to be associated with annual and daily $\text{PM}_{2.5}$ increases, respectively:

$$P = \sum_{n=1}^{3100} m M P_n D_n \quad (4.3)$$

where n is the number of an individual grid square ($n=1-3100$). m , which is an impact parameter that describes how the overall premature deaths respond to the increasing $\text{PM}_{2.5}$ concentration by $10 \mu\text{g} \cdot \text{m}^{-3}$, was estimated according to Shi *et al.* [110] as follows: 2.14% (95% CI: 1.38%-2.89%) for acute mortality and 7.52% (95% CI: 1.95%-13.4%) for chronic mortality. The research [110] is focusing on the premature mortality occurring under low-concentration $\text{PM}_{2.5}$, which is appropriate for the current $\text{PM}_{2.5}$ situation in Kanto Region. M , the proportionate mortality of the elderly (86.6%), was obtained from the Statistics Association of Health, Labor and Welfare of Japan in 2012 [111]. P_n is the annual or daily death in the corresponding grid square and was estimated using the database of the Ministry of Environment of Japan in 2000 [112]. Finally, D_n is the incremental $\text{PM}_{2.5}$ concentration of the corresponding grid square (units: $10 \mu\text{g} \cdot \text{m}^{-3}$). The annual $\text{PM}_{2.5}$ increase is calculated as the average result of summer and winter.

The human health impacts caused by $\text{PM}_{2.5}$ -related premature deaths were converted to financial losses by the value of statistical life (VSL). VSL is defined as the amount of money that people would pay to save one life. In this study, a VSL of 4.8 million USD was used to estimate the health cost associated with $\text{PM}_{2.5}$ pollution [12].

4.3 Results and discussion

4.3.1 Emission estimation

Based on Eq. (4.1), the incremental ammonia emissions in Kanto Region were estimated to be $3 \times 10^4 \text{ t} \cdot \text{y}^{-1}$, indicating a 6.7% increase compared with the total ammonia emission in base case. Table 3.1 summarizes the estimated emissions of the 21 LNG thermal power plants in Kanto Region.

Meanwhile, there were reductions of NO_x and SO_2 emissions due to the decreased occupancy of fossil fuels in power generation sector. According to the supply capacity of

ammonia-hydrogen energy in Kanto Region, NO_x and SO_2 were assumed to have a reduction of 0.4% (8,736 t) and 0.6% (4,910 t) compared with the total emissions in base cases, respectively [4].

Figure 4.3 (a) illustrates the incremental ammonia emission contributed by the 21 LNG thermal power plants in Kanto Region. The increased emissions are mainly concentrated along the southern coast (Kanagawa and Chiba), especially around Tokyo Bay, because of the geographical locations of the power plants. Figure 4.3 (b) figures out the reduced NO_x and SO_2 emissions benefited from introducing ammonia-hydrogen energy system.

In this study, it was estimated that up to 30,000 t of ammonia was discharged from ammonia-hydrogen energy systems, leading to an average $\text{PM}_{2.5}$ increase of $0.16 \mu\text{g}\cdot\text{m}^{-3}$ in winter and $0.08 \mu\text{g}\cdot\text{m}^{-3}$ in summer. As shown in Chapter 4.3.2, ammonia was assumed to discharge directly to the atmosphere without exhaust gas treatment systems. Although the emission quantity seems to be within standards, gas-purification units could be a convenient solution to mitigate its negative impacts. Previous researchers have stated that in addition to its usage as a hydrogen carrier, ammonia could be directly used as an energy source for fuel cells or power generation [50]. Iki *et al.* even proposed that ammonia could be used to generate electricity without hydrogen as an intermediate product [51]. However, using ammonia for power generation would not overcome the emission problem. Indeed, incomplete combustion could lead to NO_x emission, and even after NO_x removal, a small percentage of ammonia was found to be detectable in the exhaust [61]. As noted by Eguchi [50], exhaust treatment could decrease this amount to 0.1 ppm. However, such treatment would contribute to the hidden costs and financial losses attributable to $\text{PM}_{2.5}$ -related deaths.

In this scenario, we suggested that total ammonia emission were distributed among the 21 LNG thermal power plants in Kanto Region according to their power-generation capacities. However, once ammonia-hydrogen energy generation is established, such emissions might be concentrated in a few hydrogen power plants. Prefectures with LNG thermal power plants would incur dozens or more times the health cost compared with those without LNG thermal power plants. Thus, concentrated emission sources would seriously and negatively influence surrounding areas.

On the other hand, the ammonia emission discharged from power plants were assumed distributed equally throughout each month. In fact, there might be an extreme energy demand in winter and summer, thereby the actual annual $PM_{2.5}$ concentration might be less than the predicted average of the two seasons in this study.

4.3.2 Incremental $PM_{2.5}$ concentration

Figure 4.4 (a) and (b) show the incremental $PM_{2.5}$ concentrations in winter (December to January) (a) and summer (July to August) (b), respectively. Figure 4.4 (a) shows the result in winter. Influenced by the north wind, $PM_{2.5}$ increase is mainly concentrated in the southern areas. In spite of the slight decrease in northwest, there is an average increase of 11.7% ($0.16 \mu\text{g}\cdot\text{m}^{-3}$) compared with the base cases. $PM_{2.5}$ concentration is more closely related with ammonia emission in winter, which is corresponding to the results obtained in Chapter 3. As shown in Figure 4.4 (b), even though the mean $PM_{2.5}$ concentration is generally lower in summer, an increase tendency of 3.5% ($0.08 \mu\text{g}\cdot\text{m}^{-3}$) is still existing. Different from winter, in which the $PM_{2.5}$ increase greatly occurs among the southernmost parts of Kanto Region (Kanagawa and Chiba), summer patterns indicate the maximum $PM_{2.5}$ increases responding to the emissions sources (Tokyo Bay areas). The increased concentrations of sulfates, nitrates and ammonium are presented individually in Figure 4.5.

Simultaneously with the increased ammonia emission, NO_x and SO_2 slightly decreased in our scenarios. Lower NO_x and SO_2 levels will generate a weaker $PM_{2.5}$ response to ammonia emission. However, in consideration of the proportion of total emission, the influence on GR could be very limited.

As indicated in our result, despite the slight reduction of NO_x and SO_2 , only the incremental $PM_{2.5}$ response to the increased ammonia emission was involved in the GR discussion. Actually, any change in the emissions sources of NO_x and SO_2 leads to a fluctuation in GR. Furthermore, the emission inventories for the base cases were estimated from Kannari *et al.* in 2000 [4]. After the Fukushima Accident, the domestic reliance on thermal power generation increased from 29% to 43% [113], increasing NO_x and SO_2 emissions from energy sector. In fact, due to the implementation of relative policies and regulations, the emissions seem to be better controlled in other sectors. The total emission of

NO_x and SO₂ shows a decreasing tendency during 2000-2010 [4]. Unfortunately, because few databases relevant to the current emissions status are available, the NO_x and SO₂ emissions were assumed to remain at the same levels as 2000 in this study.

4.3.3 Health impacts

Figure 4.6 shows the premature deaths caused by the incremental PM_{2.5} resulted from utilizing ammonia-hydrogen energy in Kanto Region. The increased PM_{2.5} level could lead to an annual premature mortality of 351 deaths, including 71 acute deaths and 280 chronic deaths. Based on a VSL of 4.8 million US\$, the total health cost would be 1,684.8 million US\$, or 56 US\$·kg⁻¹ of ammonia emissions.

As shown in Table 4.2, although only one power plant is located in Tokyo, the estimated impacts in this area may be as serious as 174 premature deaths, far exceeding the values determined for Chiba and Kanagawa. This discrepancy may be attributable to Tokyo's dense population and geographical location. The prefectures with no LNG thermal power plants also bear health costs from the incremental PM_{2.5} concentration, although their losses may be less than those of prefectures with LNG thermal power plants. Compared with the increase of PM_{2.5} concentration, premature death largely depends on population density. As shown in Figure 4.4 and Figure 4.6 (b), despite higher PM_{2.5} increase in winter, the acute death in summer (0.40 capita·d⁻¹) turns out to be ten times more than in winter (0.04 capita·d⁻¹), mainly because of the PM_{2.5} increase concentrated on dense-populated areas.

As shown in Figure 4.6, 42 million people in Kanto Region would be at risk of PM_{2.5}-related disease. Indeed, the incremental PM_{2.5} concentration will likely cause 351 acute and chronic deaths, corresponding to a health cost of 56 US\$ kg⁻¹ of ammonia emission.

In our health impact evaluation, the PM_{2.5}-related acute/chronic mortalities were based on the results of a study performed in New England that estimated the health effects of low-concentration PM_{2.5} [110]. Before the establishment of ammonia-hydrogen energy, the average PM_{2.5} concentration in Kanto Region is approximately 3 µg·m⁻³, as estimated by Kato and Nakanishi [28]. The PM_{2.5} concentration might have increased in recent years because of economic development and industrialization, altering the rate of PM_{2.5}-related mortalities [110].

In this research, we assumed there was a linear relationship among the incremental PM_{2.5} concentration and premature deaths. However, log-linear function is more widely applied to previous researches related with health impact evaluations [12]. Therefore, we did a performance comparison between the log-linear function and the linear function, the result were shown in Figure 4.7. According to the results from our atmospheric simulation, which indicates the incremental PM_{2.5} concentration is less than 0.16 $\mu\text{g}\cdot\text{m}^{-3}$, the maximum error between the two functions proves only to be 0.75%.

Stokstad evaluated the health costs of PM_{2.5} originating from the overuse of fertilizer and livestock breeding in the U.S. by considering the progressive emission of ammonia to the atmosphere. According to their results, these health costs ranged from 10 US\$·kg⁻¹ to 73 US\$·kg⁻¹ [115]. Additionally, Paulot and Jacob estimated an annual health cost of 100 US\$·kg⁻¹ of ammonia for food export in the U.S [12]. Unlike previous works, we only estimated the health impacts on the elderly (those over 65 years old) because of the limitations of the databases we used. However, when considering the potential risks faced by the whole population, the health costs would be greater. Japan's Ministry of Economy, Trade and Industry claimed that domestic electricity consumption would rise to 1,260 billion kWh·y⁻¹ in 2030 [116]. Furthermore, although energy consumption is increasing by 1% per year, the population is continuously decreasing. In 2030, it is estimated that more than 30% of the Japanese population will be over 65 years old [117]. Compared to the current situation, this aging society will face increased health impacts and financial losses. Due to the lack of data on mortality, we did not take this population decline into consideration. However, premature mortality might vary by county and population composition. Similarly, the health cost is also limited by VSL, with larger VSLs leading directly to greater financial losses [65]. It is difficult to determine and use a domestic VSL to evaluate the health impacts on the Japanese population. In addition to premature deaths, an increasing PM_{2.5} concentration could trigger other health effects, such as diabetes or nervous system damage. As demonstrated by Rouleau *et al.* [65], PM_{2.5}-related nonlethal diseases could incur tremendous health costs.

4.4 Summary

In this Chapter, PM_{2.5}-related health impacts of utilizing ammonia as hydrogen carrier in the energy sector were investigated. Despite all the limitations of this scenario-based study, our results indicated that: (1) the ammonia emission discharged from ammonia-hydrogen energy system increased PM_{2.5} by 11.7% (0.16 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{y}^{-1}$) in winter and 3.5% (0.08 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{y}^{-1}$) in summer, resulting in 351 premature deaths per year. (2) Cost-effective emission control or treatment and appropriate land planning should be considered when new applications of ammonia are extended in energy sector. (3) Further research on the establishment of safety standards in energy sector is necessary.

Table 4.1 The 21 LNG thermal power plants in Kanto Region and their estimated ammonia emission

No.	LNG power plant	Generating capacity (10 ⁴ kW)	Emission amount (t·y ⁻¹)	Location
1	Anusaki Thermal Power Plant	361	3,373	Chiba
2	Ichihara Power Plant	11	103	Chiba
3	Ougishima Power Station	81	757	Kanagawa
4	Kashimaminami Cooperative Power Plant	21	196	Ibaraki
5	Kanasaki Power Plant	200	1,869	Kanagawa
6	JR Eastern Japan Kanasaki Power Plant	14	131	Kanagawa
7	Kawasaki LNG Power Plant	85	794	Kanagawa
8	Goi Thermal Power Plant	189	1,766	Chiba
9	Samitto Mihama Power Chiba Power Plant	5	47	Chiba
10	JFE Chiba Power Plant	87	813	Chiba
11	Shinagawa Thermal Power Plant	114	1,065	Tokyo
12	Sodegaura Thermal Power Plant	360	3,363	Chiba
13	Chiba Thermal Power Plant	438	4,092	Chiba
14	Japan Tech Sodegaura Greenpower	11	103	Chiba
15	Ougishima Thermal Power Plant	200	1,869	Kanagawa
16	Futtsu Thermal Power Plant	540	5,045	Chiba
17	Bay Side Energy Ichihara Power Plant	11	103	Chiba
18	South Yokohama Thermal Power Plant	115	1,074	Kanagawa
19	Mihama Seaside Power Shinkou Power Plant	11	103	Chiba
20	Yokoshika Power Station	24	224	Kanagawa
21	Yokohama Thermal Power Plant	333	3,111	Kanagawa
	Total	3,211	30,001	

Table 4.2 The number of LNG thermal power plants and the annual premature deaths for each prefecture in Kanto Region

Prefectures	Power plants	Annual premature deaths
Ibaraki	1	4
Tochigi	0	0
Gunma	0	0
Saitama	0	35
Chiba	11	63
Tokyo	1	174
Kanagawa	8	75

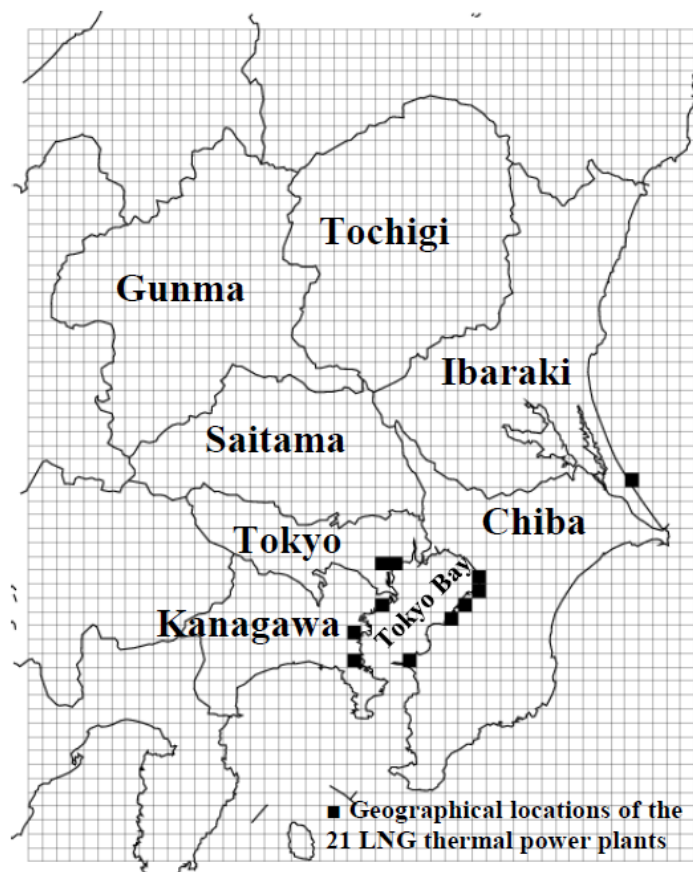


Figure 4.1 Seven prefectures (Ibaraki, Tochigi, Gunma, Saitama, Chiba, Tokyo, and Kanagawa) and the geographical locations of the 21 LNG thermal power plants in Kanto Region

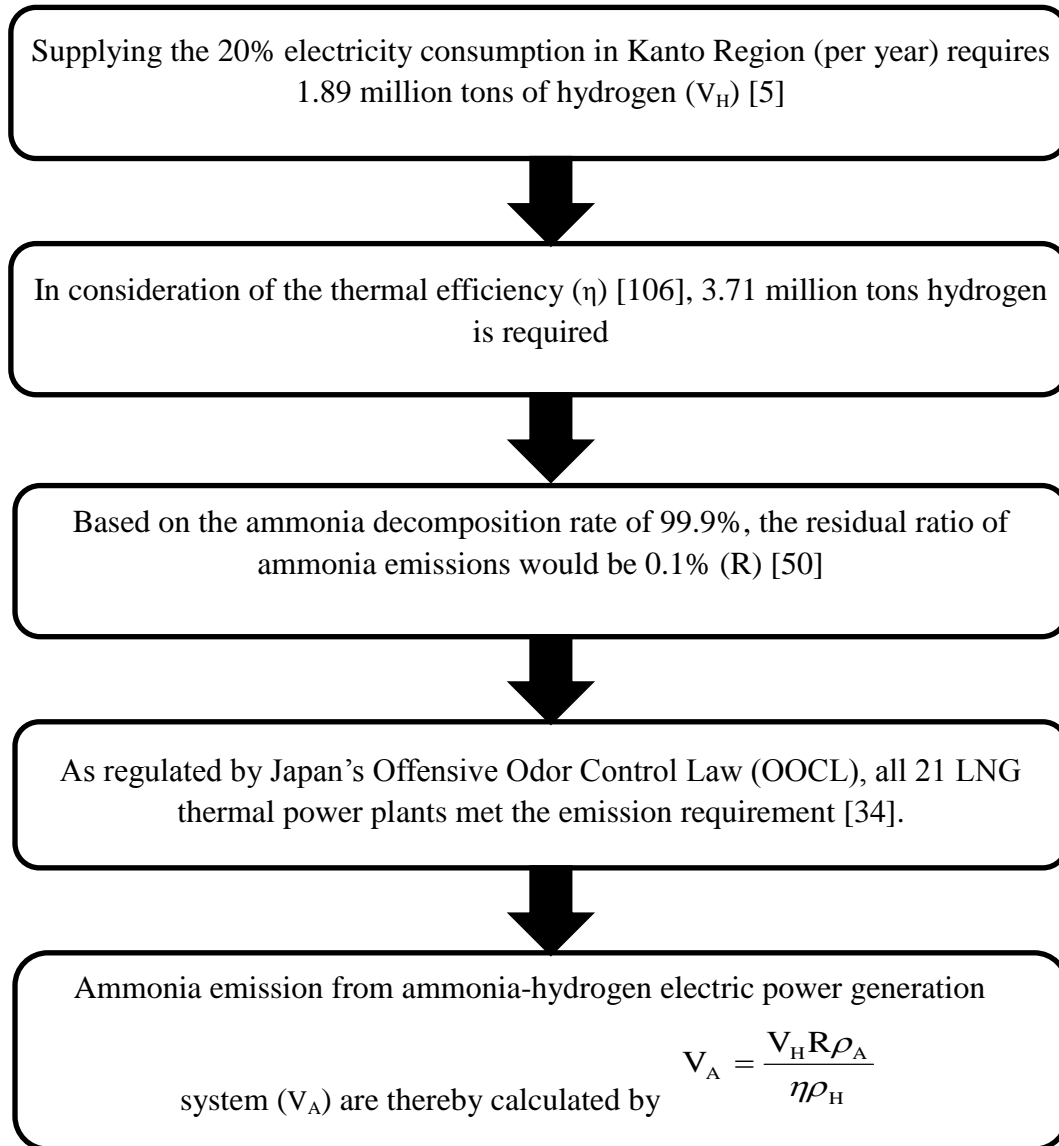


Figure 4.2 The flow chart of ammonia estimation

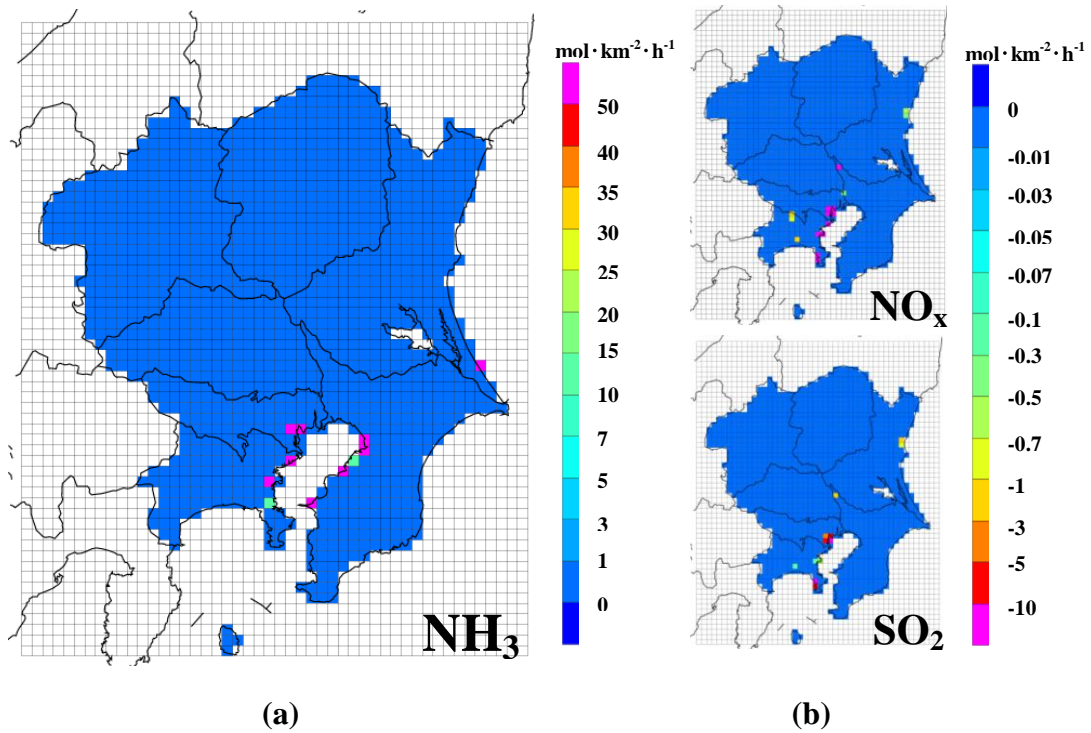
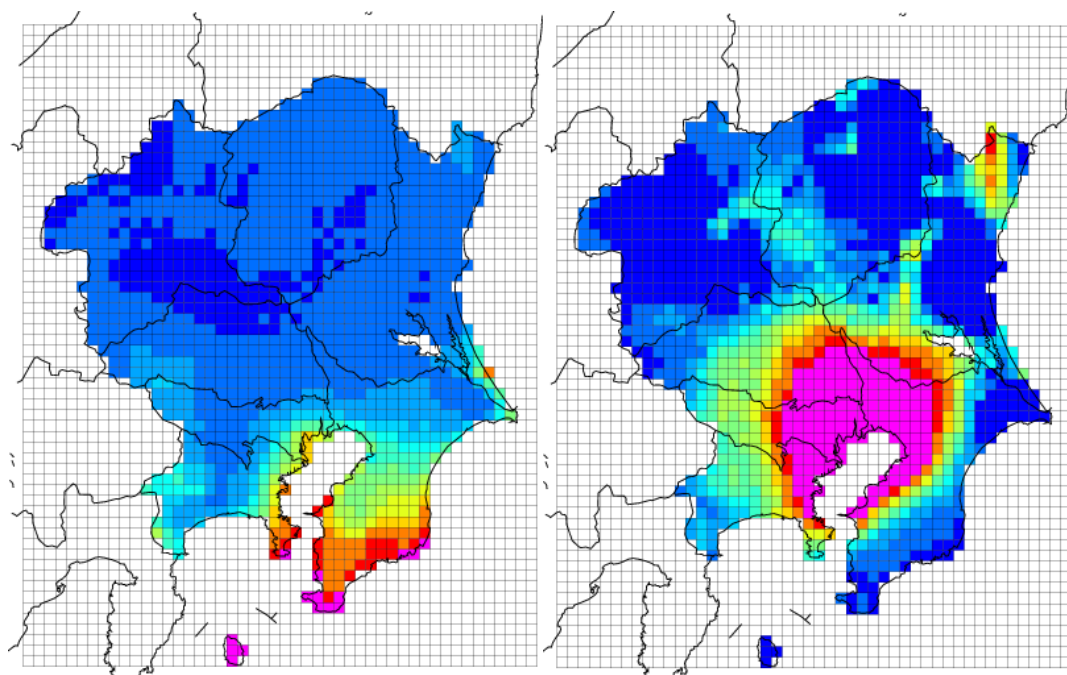
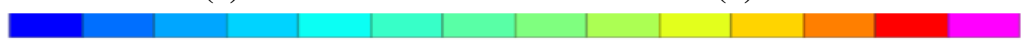


Figure 4.3 Estimated annual changes in emission of ammonia (a) and NO_x and SO_2 (b) under the conditions of the ammonia-hydrogen energy system



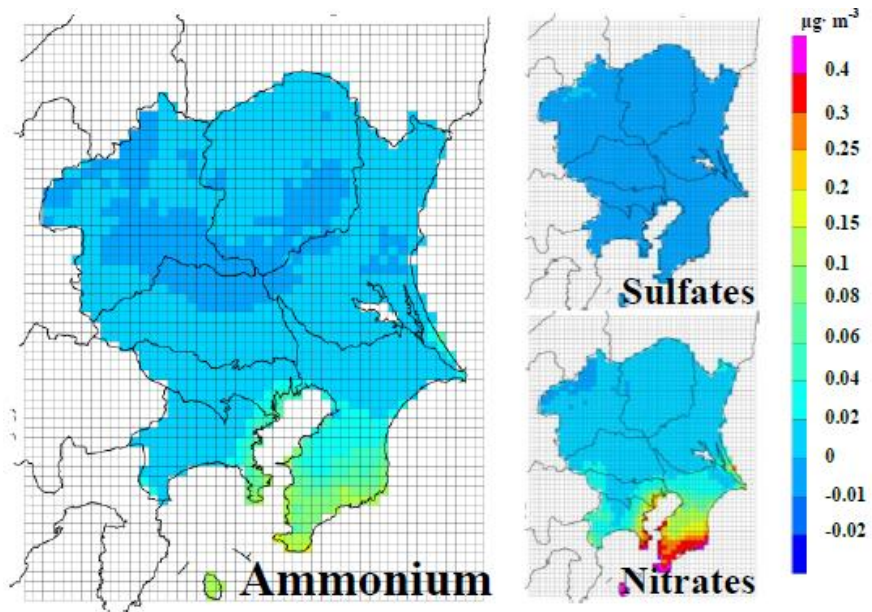
(a)

(b)

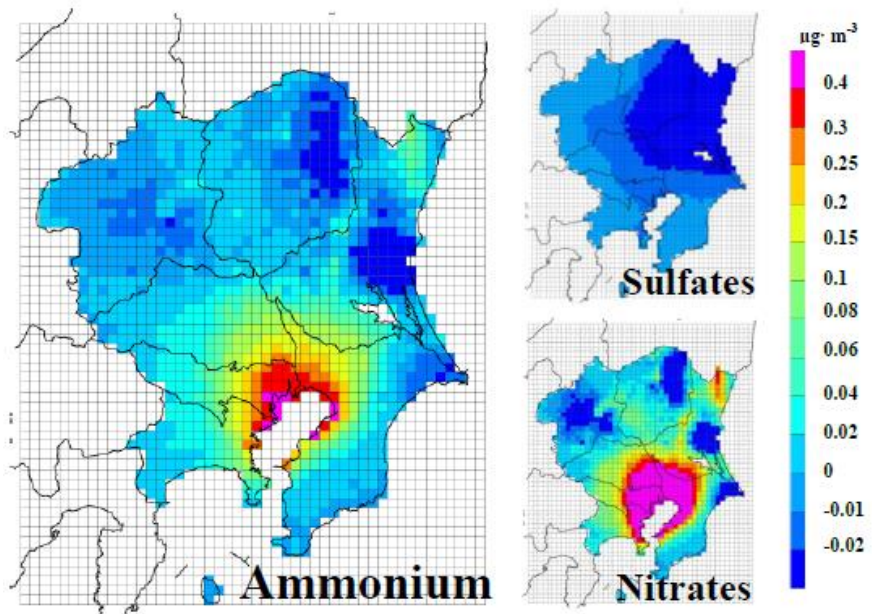


0 0.02 0.04 0.06 0.08 0.1 0.12 0.15 0.2 0.25 0.3 0.4 0.5 $\mu\text{g}\cdot\text{m}^{-3}$

Figure 4.4 Incremental $\text{PM}_{2.5}$ caused by ammonia emission from the LNG thermal power plants utilizing ammonia-hydrogen power generation systems. Simulated data in winter (December to January) (a) and summer (July to August) (b)



(a)



(b)

Figure 4.5 Ingredients of the incremental $PM_{2.5}$. Simulated data winter (December to January) (a) and summer (July to August) (b)

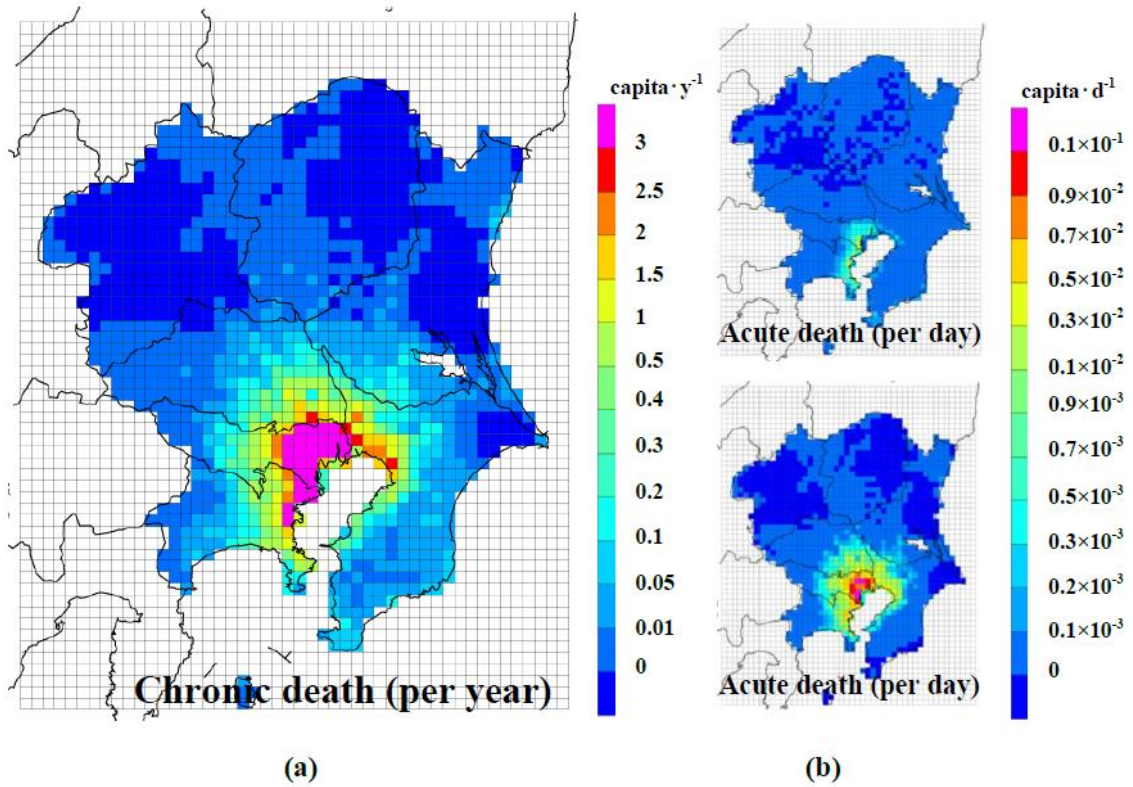


Figure 4.6 Premature deaths caused by incremental PM_{2.5} resulted from utilizing ammonia-hydrogen energy in Kanto Region. Annual chronic death (a) and daily acute death in winter (upper) and summer (below), respectively (b)

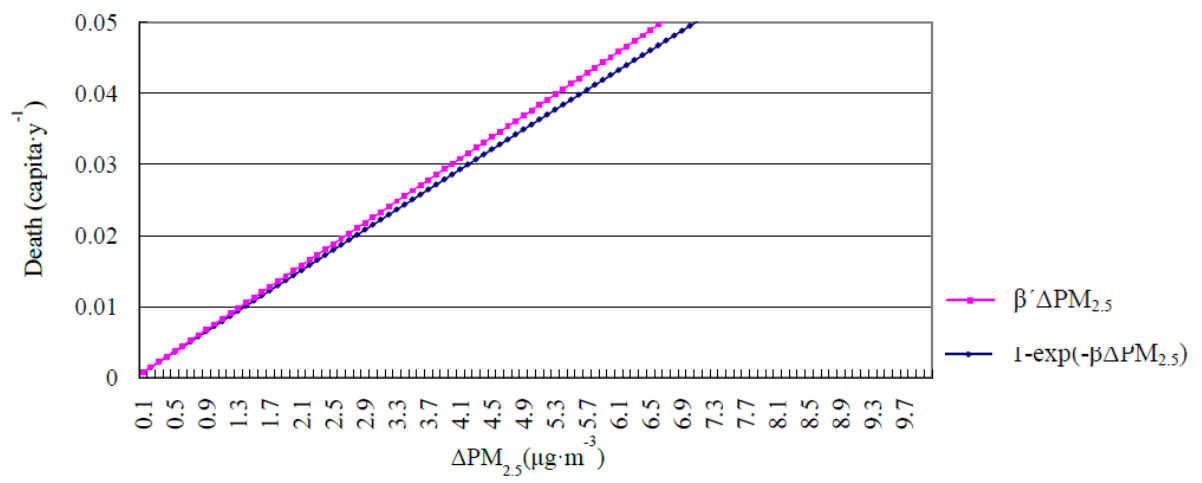


Figure 4.7 performance comparison between the log-linear function and the linear function

Chapter 5 Conclusions and Future Research

In this study, a series of simulation experiments were conducted to develop a better understanding of ammonia emission and ammonia-related secondary PM_{2.5} in Kanto Region, Japan. According to the results, the following issues have been noted and discussed: (1) the emission status of PM_{2.5} precursors (SO₂, NO_x and ammonia) in 2000 and 2010, (2) changes in ammonia emission and ammonia-related PM_{2.5} according to the existing emission sources, (3) the efficiency of PM_{2.5} reductions respond to the three of precursors, (4) the efficiency of PM_{2.5} reductions respond to different ammonia sources, (5) the potential PM_{2.5}-related health impacts caused by the possible applications of ammonia in energy sector.

5.1 Current situation of ammonia emission and PM_{2.5} reduction in Kanto Region

In this study, a comparative investigation on ammonia emission and ammonia-related PM_{2.5} in 2000 and 2010 in Kanto Region was conducted. Based on the results, the following conclusive results were obtained:

(1) In 2000, the daily average ammonia emission of Kanto Region were proved to be 543.54 t·d⁻¹ in summer and 121.55 t·d⁻¹ in winter. In 2010, the daily emission declined to 472.88 t·d⁻¹ in summer and 105.75 t·d⁻¹ in winter.

(2) In 2000, the seasonal PM_{2.5} concentration proved to be 1.25 μg·m⁻³ in summer and 1.37 μg·m⁻³ in winter. In 2010, it declined to 0.69 μg·m⁻³ and 1.15 μg·m⁻³, with a reduction rate of 44.8% in summer and 16.06% in winter.

(3) The PM_{2.5} declines in Kanto Region would be attributed to the achievement of controlling the SO₂ and NO_x emissions. Another reason might be the depression of agricultural sectors. The large difference of the reduction rates might be caused by the seasonality of the emission sources.

5.2 Analysis of Efficient Abatement Options for PM_{2.5} Reduction by Controlling Ammonia Emission in Kanto Region

In this study, an integrated spatial and temporal research on ammonia emission abatement options in Kanto Region was conducted. Firstly, a 5% emission reduction strategy

was applied to the precursors of secondary PM_{2.5} (SO₂, NO_x and ammonia), to verify which one would be most effective in controlling PM_{2.5} concentrations. After that, a further investigation was carried out to show how PM_{2.5} reductions respond to different ammonia sources. The 5% of the overall ammonia emission (5,200 t) were assumed to be reduced from all sources, agricultural source and urban (vehicle) sources, respectively. Based on the results, the following conclusive results were obtained:

(1) When applied the same reduction strategy (cut down 5% of the overall emission), SO₂ shows the highest efficiency in reducing secondary PM_{2.5}, with an average annual reduction of 0.11 μg·m⁻³. Following that, ammonia also indicates a certain efficiency in annual PM_{2.5} reduction of 0.018 μg·m⁻³. NO_x emission indicates an unstable performance in lowering PM_{2.5} concentration, especially in winter.

(2) When cutting down 5,200 t ammonia emission, controlling vehicle exhausts presents the highest efficiency in reducing PM_{2.5}, with an annual PM_{2.5} reduction of 0.021 μg·m⁻³. Agriculture proves the lowest efficiency of 0.017 μg·m⁻³.

(3) In consideration of the population density, controlling the agriculture sources would present a far more less efficiency than other sources.

5.3 Impact Assessment of the PM_{2.5} resulted from the application of ammonia-hydrogen energy utilization in Kanto Region

In this study, PM_{2.5}-related health impacts of utilizing ammonia-hydrogen energy in Kanto Region, Japan, were investigated. It was assumed that 20% of the electricity consumption in Kanto Region, the most populated area in Japan, was supplied by ammonia-hydrogen energy. Based on the incremental PM_{2.5} concentration, health impacts on the elderly (individuals over 65 years old) were quantitatively evaluated. Based on the results, the following conclusive results were obtained:

(1) Using ammonia-hydrogen energy for power generation could lead to increased PM_{2.5} concentrations (11.7% in winter and 3.5% in summer).

(2) Higher rates of related human health impacts would occur (up to 351 per year).

(3) The PM_{2.5}-related health impact is just one facet of the multi-faceted problem of using ammonia-hydrogen energy. To develop ammonia-hydrogen as a sustainable energy

source, further in-depth research on the cost-benefit ratio and the establishment of safety standards is necessary.

5.4 Further research

To give further suggestions on the reduction strategies of ammonia emission, the future work will focus on the following directions:

(1) Although ADMER-PRO has been widely applied to the domestic atmospheric studies in Japan [61], the simulation on secondary inorganic fine particles is still an extended application. In future, a detailed discussion about the model performance should be conducted.

(2) Cost and efficiency of current-available control technology should be estimated.

(3) Multiple combination options of the emission control technologies should be applied and assessed to achieve the most cost-effective $PM_{2.5}$ reductions.

References

- [1] Kean A J, Harley R A. On-road measurement of ammonia and other motor vehicle exhaust emissions. *Environmental Science & Technology*, 2000, 34: 3535–3539
- [2] Galloway J N, Townsend A R, Erismann J W, Bekunda M, Cai Z, Freney J R, Martinelli L A, Seitzinger S P, Sutton M A. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. *Science*, 2008, 320(5878): 889–892
- [3] Bouwman A F, Lee D S, Asman W A H, Dentener F J, Van Der Hoek K W, Olivier J G J. A global high-resolution emission inventory for ammonia. *Global Biogeochemical Cycles*, 1997, 1130: 561–587
- [4] Fukui T, Kokuryo K, Baba T, Kannari A. Updating EAGrid2000-Japan emissions inventory based on the recent emission trends. *Journal of Japan Society for Atmospheric Environment*, 2014, 4928: 117–125
- [5] Center for Research and Development Strategy, Japan Science and Technology Agency. Technology infrastructure of energy carrier for the transportation, storage, utilization of renewable energy. 2012. Available online at: <https://www.jst.go.jp/crds/pdf/2012/WR/CRDS-FY2012-WR-04.pdf>. (accessed 30, January 2017)
- [6] Tokyo Metropolitan Government. Air pollution and odor measurement. 2012. Available online at: <http://www.kankyo.metro.tokyo.jp/air/>. (accessed 16 August, 2017)
- [7] Lin B L. Anticipation and apprehension of nitrogen through biomass energy generalization. *Petrotech*, 2011, 34 (8): 45–52
- [8] Xuejun L, Fusuo Z. Nitrogen fertilizer induced greenhouse gas emissions in China. *Current Opinion in Environmental Sustainability*, 2011, 3 (5): 401–473
- [9] Rockström J, Steffen W, Noone K, Persson Å, Chapin F S, Lambin E F, Lenton T M, Scheffer M, Folke C, Schellnhuber H J, Nykvist B, Wit C A, Hughes T, van der Leeuw S, Rodhe H, Sörlin S, Snyder P K, Costanza R, Svedin U, Falkenmark M, Karlberg L, Corell R W, Fabry V J, Hansen J, Walker B, Liverman D, Richardson K, Crutzen P, Foley J A. A safe operating space for humanity. *Nature*, 2009, 461(7263): 472–475

- [10] Charanya V. Development of a source-meteorology-receptor (SMR) approach using fine particulate intermittent monitored concentration data for urban areas in Ohio. Dissertation for the Doctoral Degree. Toledo: The University of Toledo, 2007
- [11] Gelencser A, May B, Simpson D, Sanchez O A, Kasper G A, Puxbaum H, Caseiro A, Pio C, Legrand M. Source apportionment of PM_{2.5} organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin. *Journal of Geophysical Research*, 2007, 112: 1–12
- [12] Paulot F, Jacob D J. Hidden cost of U.S. agricultural exports: particulate matter from ammonia emissions. *Environmental Science & Technology*, 2014, 48(2): 903–908
- [13] Cao J J, Zhang T, Chow J C, Watson J G, Wu F, Li H. Characterization of atmospheric ammonia over Xi'an, China. *Aerosol and Air Quality Research*, 2009, 9 (2): 277–289
- [14] Putaud J P, Raes F, Van Dingenen R, Brüggemann E, Facchini M C, Decesari S, Fuzzi S, Gehrig R, Hüglin C, Laj P, Lorbeer G, Maenhaut W M, Mihalopoulos N, Müller K, Querol X, Rodriguez S, Schneider J, Spindler G, Ten B H, Tørseth K, Wiedensohler A. A European aerosol phenomenology²: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmospheric Environment*, 2004, 38: 2579–2595
- [15] Tslmpldl A P, Karydls V A, Paandls S N. Response of inorganic fine particulate matter to emission changes of sulfur dioxide and ammonia: The Eastern United States as a case study. *Journal of the Air & Waste Management Association*, 2007, 57: 1489–1498
- [16] Ministry of Environment, Government of Japan. The directionality for the abatement policy of domestic PM_{2.5}. 2015. Available online at: <http://www.env.go.jp/council/07air-noise/yoshi07-08.html>. (accessed 16 August, 2017)
- [17] Sun Y, Zhuang G, Tang A, An Z. Chemical Characteristics of PM 2.5 and PM10 in Haze-Fog Episodes in Beijing. *Environmental Science & Technology*, 2006, 40: 3148–3155
- [18] Ministry of Environment, Government of Japan. Air pollution situation in 2015. 2017. Available online at: <http://www.env.go.jp/press/102152.html> (accessed 16 August, 2017)

- [19] Asman W A H, Sutton M A, Schjorring J K. Ammonia: emission, atmospheric transport and deposition. *New Phytologist*, 1998, 139: 27–48
- [20] Kannari A, Baba T, Hayami H. Estimation of ammonia emissions in Japan. *Journal of Japan Society for Atmospheric Environment*, 2001, 36(1): 29–38
- [21] Ogino A, Orito H, Shimada K, Hirooka H. Evaluating environmental impacts of the Japanese beef cow–calf system by the life cycle assessment method. *Animal Science Journal*, 2007, 78(4): 424–432
- [22] Behera S N, Sharma M, Aneja V P, Balasubramanian R. Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environmental Science and Pollution Research*, 2013, 20:8092–8131
- [23] Zhao D, Wang A. Estimation of anthropogenic ammonia emissions in Asia. *Atmospheric Environment*, 1994, 28(4): 1352–2310
- [24] Ministry of Agriculture, Forestry and Fisheries, Government of Japan. Basic data of agriculture, forestry and fisheries. 2017. Available online at: <http://www.maff.go.jp/j/tokei/sihyo/index.html> (accessed 16 August, 2017)
- [25] Kouyama K. Occurrence state of agricultural ammonia emissions. In: *Proceedings of the 32nd Symposium of Japan Acid Rain*, Tokyo, Japan. Japan Acid Rain Monitoring Network, 2010, 1–4
- [26] Morikawa H. Seeking revitalization of declining small and medium-sized cities in non-metropolitan regions of Japan: a comparison with German cities. *Geographical Sciences*, 2016, 71(1):1–18
- [27] Ministry of Internal Affairs and Communications, Government of Japan. Population by prefecture. 2017. Available online at: <http://www.stat.go.jp/data/nihon/02.htm> (accessed 16 August, 2017)
- [28] Kato H, Nakanishi J. Estimation of PM_{2.5} concentrations in Kanto Region and its mortality risk. In: *Proceedings of the Council of Japan Society for Risk Analysis 2002*, Kyoto, Japan. Japan Society for Risk Analysis, 2002, 1–6

- [29] Tokyo Metropolitan Research Institute for Environmental Protection. The formation mechanism of secondary PM_{2.5}. 2011. Available online at: https://www.kankyo.metro.tokyo.jp/air/attachement/014_nijiseisei.pdf (accessed 16 August, 2017)
- [30] Takakura N, Taniguchi N, Otake S, Tsuji A, Kitano R, Hioki T, Saito Y. PM_{2.5} Chemical Composition Observed in Kyoto Prefecture. Annual report of Kyoto Prefectural Institute of Hygienic and Environmental Sciences, 2014, 59:63–70
- [31] Fushimi A. The origin and dispersion of primary and secondary particle during summer season in Kanto Region. In: Proceedings of the 39th Symposium of Japan Acid Rain, Tokyo, Japan. Japan Acid Rain Monitoring Network, 2013, 1–4
- [32] Graus W H J, Worrell E. Effects of SO₂ and NO_x control on energy-efficiency power generation. Energy Policy, 2007, 35: 3898–3908
- [33] Wang S X, Xing J, Jang C, Fu J S, Hao J M. Impact assessment of ammonia emissions on inorganic aerosols in East China using response surface modeling technique. Environmental Science & Technology, 2011, 45: 9293–9300
- [34] Government of Japan. Offensive odor control law. 2011. Available online at: <http://law.e-gov.go.jp/htmldata/S46/S46HO091.html>. (accessed 09 May, 2016)
- [35] United States Department of Agriculture. Official white paper of the USDA agricultural air quality task force. 2016. Available online at: <https://www.nrcs.usda.gov/wps/portal/nrcs/main/national/air/taskforce/>. (accessed 16 August, 2017)
- [36] European Environment Agency. Emission trends of ammonia (EEA member countries, EU-27 member states). 2011. Available online at: <http://www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1/assessment-2>. (accessed 16 August, 2017)
- [37] Kannari A, Tonooka Y, Baba T, Murano K. Development of multiple-species 1km×1km resolution hourly basis emissions inventory for Japan. Atmospheric Environment, 2007, 41 (16): 3428–3439
- [38] Zhang Y, Dore A J, Ma L, Liu X J, Ma W Q, Cape J N, Zhang F S. Agricultural ammonia emissions inventory and spatial distribution in the North China Plain. Environmental Pollution, 2010, 158: 490–501

- [39] Paulot F, Jacob D J, Pinder R W, Bash J O, Travis K, Henze D K. Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3). *Journal of Geophysical Research: Atmospheres*, 2014, 119: 4343–4364
- [40] Riddick S, Ward D, Hess P, Mahowald N, Massad R, Holland E. Estimate of changes in agricultural terrestrial nitrogen pathways and ammonia emissions from 1850 to present in the Community Earth System Model. *Biogeosciences*, 2016, 13: 3397–3426
- [41] Pinder R W, Adams P J, Pandis S N. Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the Eastern United States. *Environmental Science & Technology*, 2007, 41(2): 380–386
- [42] Ansari A S, Pandis S N. Response of inorganic PM to Precursor concentrations. *Environmental Science & Technology*, 1998, 32: 2706–2714
- [43] Wakamatsu S, Okazaki Y, Kanda I. A summarize of current researches related with secondary air pollutants (ozone and PM_{2.5}). The Japan Institute of Marine Engineering, 2014, 49(6): 54–59
- [44] Agency for Natural Resources and Energy, Government of Japan. Present situation of thermal power generation. 2013. Available online at: http://www.enecho.meti.go.jp/committee/council/basic_problem_committee/013/pdf/13-7.pdf. (accessed 30 January, 2017)
- [45] Agency for Natural Resources and Energy, Government of Japan. Strategic plan of energy and environment. 2013. Available online at: <http://www.enecho.meti.go.jp/about/whitepaper/>. (accessed 30 January, 2017)
- [46] Agency for Natural Resources and Energy, Government of Japan. Options associated with energy and environment. 2012. Available online at: https://www.env.go.jp/council/06earth/y060-110/mat01_2.pdf. (accessed 30 January, 2017)
- [47] Strategy Japan Science and Technology Agency. Renewable energy storage and carriage Center for Research and Development. 2013. Available online at:

- <http://www.jst.go.jp/crds/pdf/2012/WR/CRDS-FY2012-WR-04.pdf>. (accessed 16 August, 2017)
- [48] Bomelburg H J. Use of ammonia in energy-related applications. *Process Safety Progress*, 1982, 1(3): 175–180
- [49] Mitsushima S. Energy storage and transportation technology for huge scale renewable energies. *GS Yuasa Technical Report*, 2013, 10 (1): 1–6
- [50] Eguchi K. Development of ammonia fuel cell based on energy carrier project. 2013. Available online at http://www.jst.go.jp/pdf/pc201311_eguchi.pdf. (accessed 30 January, 2017)
- [51] Iki N, Kurata O, Matsunuma T, Inoue T, Suzuki M, Tsujimura T. Micro gas turbine firing ammonia. In: *Proceedings of the NH₃ Fuel Conference 2015*, Chicago, U.S. NH₃ Fuel Association, 2015, 1–39
- [52] Miura D, Tezuka T. A comparative study of ammonia energy systems as a future energy carrier, with particular reference to vehicle use in Japan. *Energy*, 2014, 68:428–436
- [53] Satomi E, Iwai H, Suzuki S, Koide T, Takahashi Y, Eguchi E. Development of ammonia-fueled SOFC. *ECS Transactions*, 2017, 78 (1): 2537–2540
- [54] Wang J, Ogawa S. Effects of meteorological conditions on PM_{2.5} concentrations in Nagasaki, Japan. *International Journal of Environmental Research and Public Health*, 2015, 12: 9089–9101
- [55] Goverdhan Rathla K S, Sankarappa T, Ashwajeet J S, Ramanna R. Effect of temperature, humidity and other physical parameters on air pollution in and around Belagavi, Karnataka, India. *International Research Journal of Environment Sciences*, 2015, 4(7), 55–62
- [56] Tai A P K, Mickley L J, Jacob D J. Correlations between fine particulate matter (PM_{2.5}) and meteorological variables in the United States: Implications for the sensitivity of PM_{2.5} to climate change. *Atmospheric Environment*, 2010, 44: 3976–3984
- [57] Cheng Y H, Li Y S. Influences of traffic Emissions and meteorological conditions on ambient PM₁₀ and PM_{2.5} levels at a highway toll station. *Aerosol and Air Quality Research*, 2010, 10: 456–462

- [58] Makar P A, Moran M D, Zheng Q, Cousineau S, Sassi M, Duhamel A, Besner M, Davignon D, Crevier L P, Bouchet V S. Modelling the impacts of ammonia emissions reductions on North American air quality. *Atmospheric Chemistry and Physics*, 2009, 9(18): 7183–7212
- [59] Behera S N, Sharma M. Transformation of atmospheric ammonia and acid gases into components of PM_{2.5}: an environmental chamber study. *Environmental Science and Pollution Research*, 2011, 19 (4): 1187–1197
- [60] National Institute of Advanced Industrial Science and Technology. ADMER-PRO Version 0.8 β Website. 2011. Available online at: <http://www.aist-riss.jp/software/admer-pro/>. (accessed 16 August, 2017)
- [61] Inoue K, Higashino H. Development and verification of the atmospheric model ADMER-PRO applicable for secondary formation. *Journal of Japan Society for Atmospheric Environment*, 2015, 50 (6): 278–291
- [62] Ji S, Cherry C R, Zhou W, Sawhney R, Wu Y, Cai S, Wang S, Marshall J D. Environmental justice aspects of exposure to PM_{2.5} emissions from electric vehicle use in China. *Environmental Science & Technology*, 2015, 49 (24): 13912–13920
- [63] Lelieveld J, Evans J S, Fnais M, Giannadaki D, Pozzer A. The Contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*, 2015, 525(7569): 367–371
- [64] Fann N, Lamson A D, Anenberg S C, Wesson K, Risley D, Hubbell B J. Estimating the national public health burden associated with exposure to ambient PM_{2.5} and Ozone. *Risk Analysis*, 2011, 32(1): 81–95
- [65] Rouleau M, Egyed M, Taylor B, Chen J, Samaali M, Davignon D, Morneau G. Human health impacts of biodiesel use in on-road heavy duty diesel vehicles in Canada. *Environmental Science & Technology*, 2013, 47(22): 13113–13121
- [66] Lin Y, Cheng M. Evaluation of formation rates of NO₂ to gaseous and particulate nitrate in the urban atmosphere. *Atmospheric Environment*, 2007, 41: 1903–1910
- [67] Seinfeld J H, Pandis S N. *Atmospheric chemistry and physics: from air pollution to climate change*. 2nd ed. Wiley, New York, 2006

- [68] Calvert J G, Stockwell W R. Acid generation in the troposphere by gas-phase chemistry. *Environmental Science & Technology*, 1983, 17(9): 428–443
- [69] Bufalini M. Oxidation of sulfur dioxide in polluted atmospheres—a review. *Environmental Science & Technology*, 1971, 5(8): 685–700
- [70] Phillips J A, Canagaratna M, Goodfriend H, Leopold K R. Microwave detection of a key intermediate in the formation of atmospheric sulfuric acid: the structure of H₂O-SO₃. *The Journal of Physical Chemistry*, 1995, 99: 501–504
- [71] Clegg S L, Brimblecombe P. Solubility of ammonia in pure aqueous and multicomponent solutions. *The Journal of Physical Chemistry*, 1989, 93(20): 7237–7248
- [72] Finlayson-Pitts B J, Pitts J N. *Chemistry of the upper and lower atmosphere*. 1st ed. Academic Press, San Diego, 2006
- [73] Zhang Y, Wu S, Hu J, Krishnan S, Wang K, Queen A, Aneja V P, Arya P. Modeling agricultural air quality: current status, major challenges, and outlook. *Atmospheric Environment*, 2008, 42(14): 3218–3237
- [74] Mozurkewich M. The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size. *Atmospheric Environment*, 1993, 27A:261–270
- [75] Diau E W G, Tso T L, Lee Y P. Kinetics of the reaction hydroxyl + ammonia in the range 273–433 K. *The Journal of Physical Chemistry*, 1990, 94(13):5261–5265
- [76] Bouwman A F, Boumans L J M. Estimation of global NH₃ volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands. *Global Biogeochemical Cycles*, 2002, 16(2): 1–11
- [77] Malhi S S, Grant C A, Johnston A M, Gill K S. Nitrogen fertilization management for no-till cereal production in the Canadian Great Plains: a review. *Soil & Tillage Research*, 2001, 60: 101–122
- [78] Sommer S G, Schjoerring J K, Denmead O T. Ammonia emission from Mineral Fertilizers and Fertilized Crops. *Advances in Agronomy*, 2004, 82: 577–622
- [79] Yang Z, Niimi H, Kanda K, Suga Y. Measurement of ammonia volatilization from a field, in upland Japan, spread with cattle slurry. *Environmental Pollution*, 2003, 121: 463–467

- [80] Schlesinger W H, Hartley A E. A global budget for atmospheric NH₃. *Biogeochemistry*, 1992, 15(3): 191–211
- [81] Kiaasson G. Past and future emission of ammonia in Europe. Part 1 of a report to Ministry for Public Housing Physical Planning and Environment, Project No. 64.19.23.01, International Institute for Applied Systems Analysis: A-2361 Laxenburg, Austria, 1991
- [82] Gharib S, Cass G R. Ammonia emissions in the South Coast Air Basin 1982. Open file report 84-2, Environmental Quality Laboratory, California Institute of Technology: Pasadena, California, 1984
- [83] Endou M. Current status and countermeasure for air pollution related with PM_{2.5}. 2015. Available online at: http://dl.ndl.go.jp/view/download/digidepo_9275297_po_0866.pdf?contentNo=1. (accessed 13 September, 2017)
- [84] U.S. Environmental Protection Agency. Integrated science assessment for particulate matter. 2009. Available online at: <https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=216546>. (accessed 13 September, 2017)
- [85] U.S. Environmental Protection Agency. National ambient air quality standards for particulate matter. *Federal Register*, 2013, 78(10): 3086, 2090–3091
- [86] European Union. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. *Official Journal of the European Union*, 2008, 152: 35
- [87] Ministry of Environmental Protection of the People's Republic of China. The announcement on the application of Environmental Air Quality Standard (GB3095-2012). 2012. Available online at: <http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqhjzlbz/201203/W020120410330232398521.pdf>. (accessed 24 November, 2017)
- [88] The Government of South Korea. Order for Enforcement of the Basic Law for Environmental Protection. 2011. Available online at: <http://www.law.go.kr/LSW/lsInfoP.do?lsiSeq=111442#0000>. (accessed 13 September, 2017)

- [89] Ministry of the Environment, Government of Japan. The environmental standard for air pollution caused by fine particulate matters. 2009. Available online at: <http://www.env.go.jp/kijun/taiki4.html>. (accessed 26 November, 2017)
- [90] WHO Regional Office for Europe. Air Quality Guidelines: Global Update 2005: Particulate matter, ozone, nitrogen dioxide and sulfur dioxide. 2006. Available online at: http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf?ua=1. (accessed 13 September, 2017)
- [91] Ministry of the Environment, Government of Japan. Abatement strategies for domestic PM_{2.5}. 2015. Available online at: <http://www.env.go.jp/council/toshin/t09-h2605.pdf>. (accessed 13 September, 2017)
- [92] Ministry of the Environment, Government of Japan. Prefectural population, land area, gross product and electricity consumption. 2012. Available online at <http://www.env.go.jp/doc/toukei>. (accessed 30 January, 2017)
- [93] Sato Y, Higuchi A, Takami A, Murakami A, Masutomi Y, Tsuchiya K, Goto D, Nakajima T. Regional variability in the impacts of future land use on summertime temperatures in Kanto region, the Japanese megacity. *Urban Forestry & Urban Greening*, 2016, 20: 43–55
- [94] Kanaya Y. Transboundary pollution of PM_{2.5} in Japan. 2013. Available online at: <https://www.env.go.jp/council/07air-noise/y078-01/ref03.pdf>. (accessed 13 September, 2017)
- [95] Kannari A, Tonooka Y, Baba T, Nomura K. An outline of the EAGrid2000 (East Asian Air Pollutant Emission Grid Database). 2006. Available online at: http://www.cger.nies.go.jp/db/eagrid/data/Introduction_j.pdf. (accessed 13 September, 2017)
- [96] Ministry of Internal Affairs and Communications, Government of Japan. Population by prefecture. 2000. Available online at: <http://www.stat.go.jp/data/kokusei/2000/kihon1/00/13.htm>. (accessed 16 August, 2017)

- [97] Ministry of the Environment, Government of Japan. Survey results of general waste process. 2015. Available online at: http://www.env.go.jp/recycle/waste_tech/ippan/stats.html. (accessed 16 August, 2017)
- [98] Japan Automobile Service Promotion Association. The statistical information of the retained vehicles in Japan. 2017. Available online at: <https://www.jaspa.or.jp/member/data/owned.html>. (accessed 16 August, 2017)
- [99] Ministry of Agriculture, Forestry and Fisheries, Government of Japan. Distribution statistics of stock farm products. 2017. Available online at: <http://www.maff.go.jp/j/tokei/kouhyou/kensaku/hin8.html>. (accessed 16 August, 2017)
- [100] Mukhtar S, Mutlu A, Capareda S C, Parnell C B. Seasonal and spatial variations of ammonia emissions from an open-lot dairy operation. *Journal of the Air & Waste Management Association*, 2012, 58: 369–376
- [101] PM_{2.5} precursor demonstration guidance. United States Environmental Protection Agency. 2016. Available online at: <https://www.epa.gov/pm-pollution/draft-pm25-precursor-demonstration-guidance>. (accessed 30 January, 2017)
- [102] Ministry of Environment, Government of Japan. The direction of domestic PM_{2.5} emissions abatement strategies. 2014. Available online at: <http://www.env.go.jp/council/07air-noise/y078-04/mat-04.pdf>. (accessed 30 January, 2017)
- [103] Huang H, Akustu Y, Arai M, Tamura M. Analysis of photochemical pollution in summer and winter using a photochemical box model in the center of Tokyo, Japan. *Chemosphere*, 2011, 44: 223–230
- [104] Tslmpidl A P, Karydls V A, Pandls S N. Response of fine particulate matter to emission changes of oxides of nitrogen and anthropogenic volatile organic compounds in the Eastern United States. *Journal of the Air & Waste Management Association*, 2008, 58: 1463–1473
- [105] Mitsubishi Heavy Industries. Probability of wind power utilization in Patagonia. 2008. Available online at https://www.mhi.co.jp/products/pdf/wind_sonota_0606_01.pdf. (accessed 30 January, 2017)

- [106] Agency for Natural Resources and Energy, Government of Japan. The importance of hydrogen fueled electricity generation. 2014. Available online at http://www.meti.go.jp/committee/kenkyukai/energy/suiso_nenryodenchi/suiso_nenryodenchi_wg/pdf/004_02_00.pdf. (accessed 30 January, 2017)
- [107] Kojima Y, Ichikawa T. Green hydrogen carrier using ammonia. *Hydrogen Energy Systems*, 2011, 36(4): 34–41
- [108] Electrical Japan website. Power plants in Kanto Region. 2013. Available online at: <http://agora.ex.nii.ac.jp/earthquake/201103-eastjapan/energy/electrical-japan>. (accessed 30 January, 2017)
- [109] Tower Map. Stack heights of thermal power plants. 2016. Available online at: <http://tower.30maps.com/>. (accessed 30 January, 2017)
- [110] Shi L, Zanobetti A, Kloog I, Coull B A, Koutrakis P, Melly S J, Schwartz J D. Low-concentration PM_{2.5} and mortality: estimating acute and chronic effects in a population-based study. *Environmental Health Perspectives*, 2016, 124(1): 46–52
- [111] Ministry of Health, Labor and Welfare, Government of Japan. Mortality statistics by cause of death. 2012. Available online at <http://www.mhlw.go.jp/toukei/saikin>. (accessed 30 January, 2017)
- [112] Statistics Bureau, Ministry of Internal Affairs and Communications, Government of Japan. Grid square statistics in 2000. 2000. Available online at http://www.stat.go.jp/data/mesh/teiky_3s.htm. (accessed 30 January, 2017)
- [113] Agency for Natural Resources and Energy, Government of Japan. Issues associated with thermal power generation. 2015. Available online at: http://www.enecho.meti.go.jp/committee/council/basic_policy_subcommittee/mitoshi/005/pdf/005_07.pdf. (accessed 30 January, 2017)
- [114] Manabe T. General feature of the JHFC Kawasaki hydrogen station. *Hydrogen Energy Systems*, 2004, 29(2): 50–53
- [115] Stokstad E. Ammonia pollution from farming may exact hefty health costs. *Science*, 2014, 343(6168): 238–238

- [116] Ministry of Economy, Trade and Industry, Government of Japan. An outlook of the domestic energy consumption in 2030. 2010. Available online at: <http://www.meti.go.jp/report/>. (accessed 09 May, 2016)
- [117] Ministry of Internal Affairs and Communications, Government of Japan. White paper on local public finance ministry of internal affairs and communications. 2012. Available online at: http://www.soumu.go.jp/menu_seisaku/hakusyo/index.html. (accessed 30 January, 2017)

Acknowledgements

I would like to show my heart felt gratefulness to my supervisor Prof. Zhang, Prof. Lei and Prof. Shimuzu for having enlarged my knowledge and horizon during my graduate school study.

Extend my sincere gratitude to Dr. Lin and Dr. Inoue from AIST for giving me kind comments and suggestions. Dr. Lin inspired the basic ideas of this research and Dr. Inoue helped a lot during atmospheric simulation.

I am also deeply indebted to my thesis committee members, for generously offering their time, support, guidance and good will throughout the preparation and review of this document.

I offer my thanks to the fellow students of water group, the members of Tsunemi Group, and all the people who have helped me to complete this research.

Many thanks to my dearest friends Mingyue, Hongjia, Xuewei and Gezhu, whenever I felt stressed out and turned to them, they were always there. Special thanks to Daniel and Chen, for helping me to get through all the tough days. This dissertation would not have been completed without their love and support.

Finally, I would like to express my great appreciation to the funding I received towards my PhD from the Asahi Glass Scholarship Foundation. Without the support and financial help, it would not have been possible for me to pursue and to complete this PhD project successfully.

It will not be enough to express my gratitude in words to all those people who helped me. I owe my every achievement to every one of them.