MODELING THE IMPACT OF AMMONIA ON THE FORMATION OF ATMOSPHERIC PARTICLES IN LOW SULFUR ENVIRONMENT IN BEIJING-TIANJIN-HEBEI, CHINA

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by

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LIST OF SYMBOLS

β	Sensitivity factor
B_{sp}	Extinction coefficient
C_{H^+}	The concentration of H^+
˚C	Degrees centigrade
ε	Distribution coefficient
cm	Centimetre
K_e	Thermodynamic equilibrium constant
km	kilometer
mg m^{-3}	milligram per cubic meter
m s^{-1}	Meters per second
nmol m^{-3}	Nanomoles per cubic meter
pH	Acidity
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
γ	Activity coefficient
t	Ton
Tg	Million tons
µg m^{-3}	Microgram per cubic meter
µm	One thousandth of a millimeter or 10^{-6} meter
v_p	Particulate-phase deposition velocity

LIST OF ABBREVIATIONS

ACSA-14	Aerosol chemical speciation analyzer made in 2014
AQI	Air Quality Index
AWC	Aerosol water content
BC	Black carbon
BFM	Brute Force method
CAMx	Comprehensive Air Quality Model with Extensions
CB05	Carbon Bond mechanism 2005
CMAQ	Community Multiscale Air Quality
CMB	Chemical mass balance
CO_2	Carbon dioxide
CO	Carbon monoxide
DDM	Decoupled direct method
ESRL	Earth System Research Laboratories
F-TUV	Fast Troposphere Ultraviolet Visible
GDP	Gross Domestic Product
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
HONO	Nitrous acid
MB	Mean Bias
MEGAN	Model of emission of gases and aerosol from nature
MOSAIC	Model for Simulating Aerosol Interactions and Chemistry
NCDC	National Climatic Data Center
NCL	National Center for Atmospheric Research Command Language
NCP	North China Plain
NH_3	Ammonia
NMB	Normal Mean Bias
NME	Normal Mean Error
NMVOC	Non-methane volatile organic carbon
NO_2	Nitrogen dioxide
NOAA	National Oceanic and Atmospheric Administration

NOR	Nitrogen oxidation ratio
NO_X	Nitrogen oxides
NPF	New particle formation
O_3	Ozone
OC	Organic carbon
PBL	Plant boundary layer scheme
$PM_{2.5}$	Fine particulate matter
PM_{10}	Particulate matter with aerodynamic diameter of 10 μm or less
PMF	positive matrix factorization
PRD	Pearl River Delta
PSAT	Particulate matter source apportionment technology
QA	Quality assurance
QC	Quality control
RH	Relative humidity
RMSE	Root Mean Square Error
SAPRC-99	The 1999 version of the Statewide Air Pollution Research Center mechanism
SNA	Sulfate, nitrate, and ammonium
SO_2	Sulfur dioxide
SOA	Secondary organic aerosols
SOR	Sulfur oxidation ratio
TSSA	Tagged species source apportionment
UNMIX	Unmixing receptor model
USA	United States of America
USGS	United States Geological Survey
VBS	Volatility Basis Set
VOCs	Volatile Organic Compounds
WPS	WRF Pre-processing System
WRF	Weather Research and Forecasting
WRF-Chem	Weather Research and Forecasting model with Chemistry model
YRD	Yangtze River Delta

PEMODELAN IMPAK AMMONIA KE ATAS PEMBENTUKAN PARTIKEL ATMOSFERA DALAM PERSEKITARAN SULFUR RENDAH DI BEIJING-TIANJIN-HEBEI, CHINA

ABSTRAK

Pencemaran jerebu ialah cabaran alam sekitar utama yang dihadapi di China, dan usaha baru-baru ini telah memberi tumpuan kepada pengurangan kepekatan bahan zarahan, terutamanya $PM_{2.5}$. Mengurangkan bahan pencemar primer dianggap sebagai kaedah utama untuk mengurangkan $PM_{2.5}$ dan komponen sekundernya, terutamanya hari ini apabila mengurangkan ammonia (NH_3) dianggap lebih berkesan. Kajian ini menggunakan Model Penyelidikan dan Ramalan Cuaca dengan Model Kimia (WRF-Chem) yang digabungkan dengan Kaedah Brute Force (BFM) untuk menjalankan analisis sensitiviti untuk mengukur kesan pengurangan pelepasan bahan pencemar terhadap $PM_{2.5}$ dan sumbangan komponen sekundernya di rantau Beijing-Tianjin-Hebei. Seterusnya, objektif kedua penyelidikan ini adalah untuk menganalisa artikel ini ciri-ciri pencemaran pH kota Handan dan kesannya terhadap pembentukan komponen sekunder $PM_{2.5}$. Akhirnya, berdasarkan kesan perubahan pH ke atas pembentukan komponen sekunder, objektif ketiga adalah strategi pengurangan pelepasan di rantau Beijing-Tianjin-Hebei telah ditambah baik. Keputusan menunjukkan bahawa 30%_SO_2_40%_NH_3_40%_NO_X mempunyai sumbangan terbesar kepada $PM_{2.5}$ (6.8%), diikuti oleh 30%_SO_2_60%_NH_3_60%_NO_X dengan 3.8% dan 30%_SO_2_40%_NH_3 dengan 3.4%. Mengambil langkah kawalan yang diselaraskan untuk NH_3, NO_X dan SO_2 bukan sahaja dapat mengurangkan kepekatan $PM_{2.5}$, tetapi juga mengawal pembentukan aerosol tak organik sekunder. Nilai pH purata di Bandar Handan dari Mac 2015 hingga Februari 2016 ialah 4.3, menandakan

tahap keasidan yang sederhana, yang membolehkan lebih banyak NO_3^- memasuki fasa zarah. Nisbah nitrogen oksida (NOR) dipengaruhi oleh kandungan lembapan aerosol (AWC) dan nilai pH, manakala nisbah sulfur oksida (SOR) dipengaruhi oleh kandungan lembapan aerosol atau nilai pH. Apabila senario garis dasar menurun kepada 30%_SO_2_40%_NH_3_40%_NO_X, nilai pH turun sebanyak 0.7, yang menunjukkan bahawa nilai pH $PM_{2.5}$ berubah sedikit, dan mungkin terdapat beberapa bahan dalam $PM_{2.5}$ yang menampan perubahan pH nilai. Mengikut kesan perubahan pH ke atas pembentukan komponen sekunder, dengan mengambil kira saiz bandar yang berbeza dan ciri pelepasan setiap bandar, 30%_SO_2_40%_NH_3_40%_NO_X sesuai untuk Beijing dan Tianjin, dan 30%_SO_2_60%_NH_3_60%_NO_X sesuai untuk Shijiazhuang dan Tangshan manakala bandar lain menggunakan 30%_SO_2_60%_NH_3_60%_NO_X. Keputusan ini memberikan asas baharu dan penting untuk orang ramai memahami ciri dan proses penjanaan bahan zarahan atmosfera, dan membantu China dan negara lain yang mengalami masalah pencemaran yang serius untuk merangka pelan kawalan pencemaran yang berkesan.

MODELING THE IMPACT OF AMMONIA ON THE FORMATION OF ATMOSPHERIC PARTICLES IN LOW SULFUR ENVIRONMENT IN BEIJING-TIANJIN-HEBEI, CHINA

ABSTRACT

Haze pollution is a significant environmental challenge in China, with recent efforts focusing on reducing particulate matter concentrations, especially $PM_{2.5}$. Reducing primary pollutants is recognized as a crucial approach to lower $PM_{2.5}$ and its secondary compositions, especially now that ammonia (NH_3) reduction is considered more efficient. This work applied the Weather Research and Forecasting model with Chemistry model (WRF-Chem) combined with the Brute Force Method (BFM) for sensitivity analysis to quantify the contribution of pollutant reduction to $PM_{2.5}$ and its secondary compositions in January 2016, in Beijing-Tianjin-Hebei region. The second objective of this study is to analyze the characteristics of pH pollution in Handan and its influence on the formation of secondary components of $PM_{2.5}$. The third objective is to refine the emission reduction strategies in the Beijing-Tianjin-Hebei region based on how pH variations affect the formation of secondary compositions. The results showed that the 30%_SO_2_40%_NH_3_40%_NO_x contributed the largest contribution (6.8%) to $PM_{2.5}$, followed by 3.8% of 30%_SO_2_60%_NH_3_60%_NO_x and 3.4% of 30%_SO_2_40%_NH_3. A synergistic control measure for NH_3, NO_X, and SO_2 would not only reduce $PM_{2.5}$ concentrations, but also controlled the formation of secondary inorganic aerosol. The average pH of Handan city was 4.3 during March 2015 to February 2016, indicating a moderate level of acidity, which made more NO_3^- to enter the particulate phase. Nitrogen oxidation ratio (NOR) was affected by Aerosol water content (AWC) and pH, while sulfur oxidation ratio (SOR) was affected by AWC or

pH. pH decreased by 0.7 when the base case was reduced to 30%_SO_2_40%_NH_3_40%_NO_X, suggesting that the change in pH of $PM_{2.5}$ is small and that there may be something in $PM_{2.5}$ that buffers the change in pH. According to the influence of pH change on the formation of secondary compositions, taking into account the different city sizes and the emission characteristics of each city, Beijing and Tianjin are suitable for 30%_SO_2_40%_NH_3_40%_NO_X, Shijiazhuang and Tangshan are suitable for 30%_SO_2_60%_NH_3_60%_NO_X, while the other cities take 30%_SO_2_60%_NH_3_60%_NO_X. The results offer important new understandings of the properties and creation processes of atmospheric particulate matter, which will help China and other countries with serious pollution problems design effective pollution control programs.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the past twelve years, haze pollution occurred frequently in China, especially in Northern China. Fine particulate matter ($PM_{2.5}$) has become the main culprit of haze pollution. $PM_{2.5}$ is defined as particulate matter in the atmosphere with an aerodynamic equivalent diameter less than or equal to 2.5 micrometers. Because of its tiny diameter, $PM_{2.5}$ can enter the human body, which negatively affect the health of the human body and lead to respiratory diseases; meanwhile $PM_{2.5}$ can alter the scattering and absorption of light in the atmosphere, indirectly affecting the climate. The source of $PM_{2.5}$ include primary emissions from pollution sources, but a large portion of it is transformed by gaseous pollutants in the atmosphere through chemical reactions, such as sulfate, nitrate, and ammonium (SNA) and secondary organic aerosol (SOA) and other secondary composition. The content of secondary composition in $PM_{2.5}$ varies due to meteorological conditions, precursor concentration, chemical reaction rate, and surface properties of particles, etc. In major cities in Northern China, secondary compositions can exceed 50% in $PM_{2.5}$ during heavy pollution processing (Wang et al., 2014e). Among them, the formation mechanism of SNA is a hot spot in China and international academic circles.

SNA in $PM_{2.5}$ are mainly generated through complex chemical reactions of primary pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_X), and ammonia (NH_3) emitted into the atmosphere. These secondary particulate matters have significant small particle size characteristics and are capable of being suspended in the air for long periods of time and transported to long-distance areas through air currents, forming regional pollution. In addition, high concentration of SNA result in high hygroscopicity and light scattering capacity of $PM_{2.5}$ make haze formation easier and exacerbate the deterioration of regional air quality.

In order to effectively control $PM_{2.5}$ pollution, it is crucial to develop scientifically emission reduction measures. Reducing primary pollutant is an important way to control $PM_{2.5}$ concentration. But it cannot be achieved by controlling primary pollutants. This is because $PM_{2.5}$ pollution is influenced by the formation of secondary composition, regional transport and other factors. Therefore, controlling $PM_{2.5}$ pollution not only requires precise quantification of emission reductions, but also an assessment of the potential impacts of emission reduction measures on atmospheric chemical processes. Considering the control of $PM_{2.5}$ pollution by studying the formation of SNA, there should pay attention to several aspects. On the one hand, scientific calculations and rational planning can ensure the effectiveness of emission reduction measures; on the other hand, emission reduction measures must be prevented from adversely affecting the balance of other chemical components in the atmosphere, so as to avoid the generation of secondary pollution or the waste of economic resources. For example, reducing sulfate generation may increase the concentration of nitrate in the atmosphere, which in turn affects the overall chemical properties of $PM_{2.5}$. In addition, reducing the NH_3 may cause the acid-base balance of the aerosol, thus affecting the change of pH, which in turn may influence the formation of secondary particulate matter. Therefore, the control of $PM_{2.5}$ pollution is a dynamic process that should shift with the changes in meteorological conditions, pollution emission characteristics, physical and chemical properties of $PM_{2.5}$, and other conditions. In recent years, with the control of SO_2 and NO_X emission, NH_3 emission reduction may have become an important initiative to help control $PM_{2.5}$ pollution. This chapter will introduce the need for NH_3 reduction in terms of research background, the statement of problems, research objectives, research significance.

1.2 Research Background

Haze pollution control entered the fast lane with the formulation and promulgation of a series of policy documents since 2013 in China (as shown in Figure 1.1). In the process of haze pollution control, China has accumulated a lot of experience and addressing a series of issues (Sheehan et al., 2014). $PM_{2.5}$ concentration showed a clear downward trend, dropping by 30% or more in some cities (Zhai et al., 2019). The “Ten Air Pollution Prevention and Control Action Plan” has achieved initial success in China (as shown in Figure 1.1), but it is just the beginning of air pollution prevention and control. To achieve the goal of a beautiful China by 2035, there is still much work to be done. As China still faces multiple problems such as large emissions, outdated energy and industry structure, and traffic congestion, etc. Presently, the atmosphere still be subject to heavy or even severe haze pollution in China, especially in North China Plain (NCP) region, Yangtze River Delta (YRD), Pearl River Delta (PRD), Sichuan province and Chongqing city, and parts of the Fenwei Plain. These places are experiencing the dual threat of particulate matter and ozone (O_3), highlighting the long journey ahead in air pollution control efforts (Wang et al., 2022a; Wang et al., 2023).

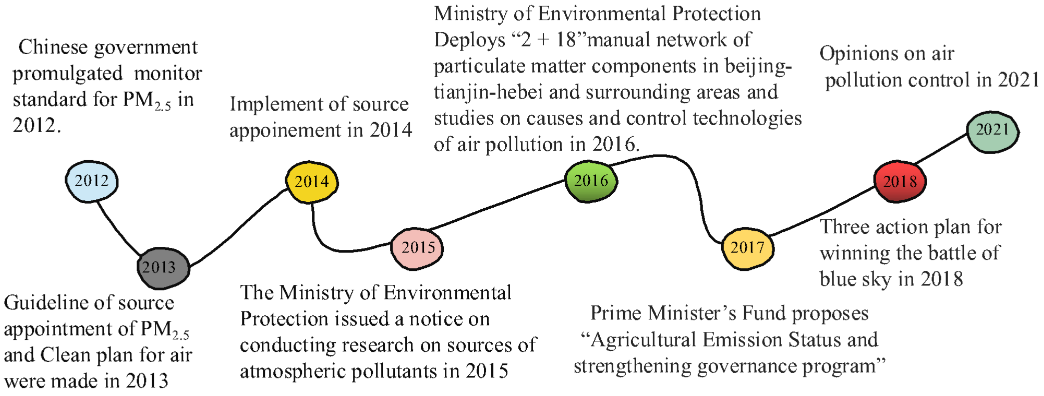

Figure 1.1 A series of air pollution control measures in China since 2013

Air pollution presents combined pollution in China, characterized by high concentrations of $PM_{2.5}$, accompanied by high O_3 concentrations (He et al., 2002; Hu et al., 2015b; Ren et al., 2017; Song et al., 2017; Han et al., 2018). $PM_{2.5}$ is the main cause in the formation of haze, which not only reduces visibility and negatively affects people's visual senses, but also affects climate change, and most of all jeopardizes human health (Pope III et al., 2002; Ramanathan and Feng, 2009; Turner et al., 2020). In Beijing-Tianjin-Hebei region, our concern revolves around the issue of $PM_{2.5}$. For instance, the severe haze event in January 2013 have attracted widespread public attention because of its wide range of pollution, long lasting, and serious pollution level, which made it became another air pollution event after haze smog event in London and photochemical smog event in Los Angeles, and some studies have confirmed that poor meteorological conditions, high emissions, and the generation of secondary pollutants are important reasons for haze pollution (Wang et al., 2014b; Wang et al., 2014c; Wang et al., 2014e; Zheng et al., 2015a; Peng et al., 2019). The daily concentration of $PM_{2.5}$ in Handan, a city located in Beijing-Tianjin-Hebei region, reached top to 643.0 $\mu g\ m^{-3}$ (Wei et al., 2014). Similarly, during that period, Beijing, Tianjin, Shijiazhuang, Baoding, Xingtai, Cangzhou, Hengshui, Tangshan, and Langfang frequently experienced $PM_{2.5}$ concentrations that exceeded the maximum limit of 500 on the Air Quality Index (AQI). This indicates that 10 out of the 13 cities in Beijing-Tianjin-Hebei were affected by high $PM_{2.5}$ concentration. The daily averaged concentrations of $PM_{2.5}$ in those cities were several or even tens of times higher than the national secondary threshold of 35 µg m^{-3}. Therefore, reducing $PM_{2.5}$ concentration and mitigate haze pollution has been an important and meaning task in this region.

1.2.1 Overview of Air Pollution in the Beijing-Tianjin-Hebei Region

1.2.1(a) Environmental Pressure in the Beijing-Tianjin-Hebei Region

Beijing-Tianjin-Hebei region covers Beijing city, Tianjin city and Hebei province, with an area of about 216,000 square kilometers and a population of more than 110 million, and its Gross Domestic Product (GDP) accounts for about 10% of the national GDP. It is an important economic zone in northern China, the regional economic activities show obvious industrialization and energy-intensive characteristics, heavy industry (steel, cement, glass and other traditional industries) accounted for a high proportion of the iron and steel, especially in Hebei Province. There is a world of iron and steel to see China, Chinese iron and steel to see Hebei said. The energy structure is dominated by coal burning, which emits a large amount of SO_2, NO_X and particulate matter during the production process. And coal-fired heating in winter often causes an increase in SO_2 and $PM_{2.5}$ emissions. In 2019, the total annual energy consumption will be 4.86 billion tons of standard coal in China, an increase of 3.3% from the previous year, and it will grow to 4.96 billion tons of standard coal by 2020 (China Statistical Yearbook, 2020; 2021). Energy consumption is still continuing to grow without seeing the peak indicates that total energy demand will continue to grow, air pollution prevention and control and air quality improvement is still facing a serious challenge.

While the Beijing-Tianjin-Hebei region is experiencing rapid economic development, it is facing complex and severe environmental pressures, with the main problems focusing on outdate industrial technology, high energy consumption, increase in motor vehicle ownership and weak regulation on disorganization enterprises. For example, there has a huge number of motor vehicles in Beijing-Tianjin-Hebei region, especially in Beijing city, where vehicle emissions have become a primary source of $PM_{2.5}$. Transportation emission contributed 31.1% in Beijing (http://www.bj.xinhuanet.com/bjyw/2014-04/17/c_1110289403.htm; last access on 1st January 2025) and 20% in Tianjin (http://news.enorth.com.cn/system/2014/08/23/012101467.shtml; last access on 1st January 2025), respectively. At the same time, emissions from transit freight vehicles further contribute pollution, especially heavy-duty diesel vehicles, which increase emission of NO_X and particulate matters. In addition, the Beijing-Tianjin-Hebei region is highly urbanized and densely populated, and urban domestic emissions such as restaurant fumes, construction dust and garbage incineration place an additional burden on air quality. Therefore, the Beijing-Tianjin-Hebei region urgently needs to optimize its industrial structure, adjust its energy structure, and collaborate on regional governance to cope with the increasing environmental pressure and achieve a balance between economic development and ecological protection. Although regional synergistic governance has begun to bear fruit in recent years, long-term efforts are still needed to realize the coordination of environmental protection and economic development, especially in terms of energy structure transformation and industrial upgrading.

1.2.1(b) Characteristics and Causes of $PM_{2.5}$ Pollution

$PM_{2.5}$ pollution has long been one of the most significant environmental problems in the Beijing-Tianjin-Hebei region. This mainly stems from the regional economic structure characterized by heavy industry as the pillar industry, with a large number of high energy-consuming and highly polluting industries such as iron and steel, cement, and chemicals concentrated in this region. In earlier years, when heavy haze weather occurred, the $PM_{2.5}$ concentration can reach 600 $\mu g\ m^{-3}$, almost tenfold greater than China's secondary standard. In China's air pollution ranking, seven of the ten cities with the highest pollution levels are situated within Beijing-Tianjin-Hebei (Hu et al., 2015b). As a result, the Beijing-Tianjin-Hebei region is the most polluted area for $PM_{2.5}$ and has also received widespread attention.

In previous studies, it has been found that $PM_{2.5}$ comes from various sources, with industrial sources dominating in Hebei Province and transportation emission accounting for a larger share in Beijing and Tianjin (Wang et al., 2014b; Wang et al., 2014c; Wang et al., 2014e). In analysing and studying their pollution characteristics, it was found that $PM_{2.5}$ showed sawtooth-shaped change characteristics (Wei et al., 2014), and the static and stable conditions at night made it easier for $PM_{2.5}$ to accumulate. $PM_{2.5}$ is higher in winter than in summer, but the hot weather in summer makes the secondary composition of $PM_{2.5}$ account for a larger proportion (Wang et al., 2014b; Zheng et al., 2015a; Peng et al., 2019). Secondary compositions were important composition of $PM_{2.5}$. Heavy pollution episodes in Beijing-Tianjin-Hebei region involve the accumulation of secondary composition, especially in the accumulation phase of the pollution process. Therefore, $PM_{2.5}$ pollution in this case is actually a secondary pollution process.

As a result of the efforts of the emission reduction measurements (Including coal-to-electricity and coal-to gas conversions, the prohibition of small boilers, and the ban on bulk coal usage), $PM_{2.5}$ has shown a significant decline. Satellite data revealed that $PM_{2.5}$ present slight fluctuations during 2013-2014, underwent a rapid decline from 2015 to 2017, and maintain a steady decrease from 2018 to 2020 (Yang et al., 2022). Real-time monitoring data from 26+2 cities between 2015 and 2018 also confirmed a decline in $PM_{2.5}$, leading to Jiang's conclusion that more stringent winter control strategies should be implemented in this region (Jiang et al., 2020). Wang et al. (2019) found that $PM_{2.5}$ decline from 98.9 $\mu g\ m^{-3}$ in 2013 to 64.9 $\mu g\ m^{-3}$ in 2017, achieving a 25% reduction in $PM_{2.5}$ as planned. However, Beijing-Tianjin-Hebei region still experiences an annual mean $PM_{2.5}$ value about 1.5 times higher than the national threshold. Haze pollution still occurred in north China, i.e., Hebei, Henan, Shandong, Shanxi, and Shaanxi (Zheng et al., 2018). For example, the annual average $PM_{2.5}$ concentration was 56 $\mu g\ m^{-3}$ in Hebei province and 51 $\mu g\ m^{-3}$ in Beijing in 2018 despite they reached the goal of Air Pollution Prevention and Control Action Plan (below 60 $\mu g\ m^{-3}$ in 2017), respectively, yet which was 1.6 and 1.5 times of the state secondary standard.

According to previous studies (Wang et al., 2014b; Wang et al., 2014c; Wei et al., 2014; Zheng et al., 2015a; Peng et al., 2019), $PM_{2.5}$ annual concentration of Beijing-Tianjin-Hebei ranked number one. There are some reasons as following context.

(1) Terrain. Occurrence of severe/heavy haze days is closely associated with orographic wind convergence zones along Yanshan Mountains and Taihang Mountains in Beijing-Tianjin-Hebei. They can slow down the wind speed. On one

hand, they can slow down the clean air from the northwest. Additionally, they can continuously accumulate particles from the southern of Hebei.

(2) Industrial emission. The region abounds in natural mineral resources, such as coal, iron, and petroleum. A lot of industrial construction located in this region, including steel and iron manufacturing, glass plants, and power plants, and porcelain manufacturing. All of them are local or regional backbone industries with high-emission factories. For example, Hebei province produces nearly 200 million tons of steel, accounting for 25% of the whole output in China.

(3) Coal combustion. The major energy consumption in the NCP depended largely on coal combustion as its low cost. It is the reason that most northern residents use coal for heating and cooking in past years. Coal combustion emits lots of PM and gas-phase pollutants.

(4) Meteorological conditions. NCP experiences a moderate monsoon with hot, humid summers and cold, dry winters. $PM_{2.5}$ concentration are negatively correlated with wind speed, and elevated temperature, and positively correlated with RH as higher humidity is conducive to the transformation of secondary components of PM by aqueous phase reactions. In winter, low planet boundary layer height caused by low pressure system is prone to form stable weather, which leads to the accumulation of PM.

1.2.2 Causes and Trends of Low Sulfur Environment

1.2.2(a) Sources and Control of SO_2 Emissions

SO_2 is a common gaseous pollutant in the atmosphere, and its main sources are the combustion of fossil fuels and some industrial production processes. In Beijing-Tianjin-Hebei region, there are a large number of thermal power plants and industrial boilers, which consume a large amount of coal, which contains about 0.5%-3% sulfur that is emitted into the atmosphere when coal is burned. Metallurgical and chemical industries also release SO_2 when they process sulfurous ores at high temperatures. Additionally, domestic, industrial, and transportation source are also important sources of SO_2. Low-quality bulk coal is widely used for winter heating in rural areas, which is burned without any purification treatment and becomes an important supplementary source of SO_2 in the Northern China.

In China, to reduce SO_2 emissions, the control methods of SO_2 mainly include fuel pre-desulfurization, combustion desulfurization and flue gas desulfurization. Fuel pre-desulfurization controls SO_2 emissions at source mainly by treating coal to reduce sulfur content before combustion, in-combustion desulfurization technology directly reduces SO_2 generation during coal combustion, and flue gas desulfurization removes SO_2 by treating flue gases after combustion is completed, and it is the most widely used desulfurization method. Each of the three desulphurization methods has its own advantages and disadvantages, and the selection of a suitable desulphurization method needs to be considered comprehensively according to fuel characteristics, emission requirements and economic conditions in order to achieve a balance between environmental and economic benefits.

1.2.2(b) Implementation of SO_2 Emission Control Measures in China

Over the past few decades, China has undergone four stages of air pollution control: eliminating smoke and dust to establish the theory of atmospheric environmental capacity (1972-1990), implementing zoning control to combat acid rain and SO_2 pollution (1991-2000), implementing comprehensive control measures to reduce SO_2 (2001-2010), and overcoming challenges to achieve the goal of protecting the blue sky (2011-2020). In order to reduce the concentration of SO_2 in the atmosphere, the Chinese government has implemented a series of control measures, and the control of SO_2 emissions was mainly concentrated in the phases of 1991-2000 and 2001-2010, and continues to this day.

Control measures of SO_2 in China have primarily focused on desulfurization and denitrification since the Twelfth Five-Year Plan, resulting in a significant decrease in SO_2 concentrations across all regions. SO_2 concentration have decreased by about 16% due to use of desulphurization facilities during 2006-2015 (Wang et al., 2013). Zhai et al. (2019) found that SO_2 concentration in Beijing-Tianjin-Hebei region decreased by 76% from 2013 to 2018, with current annual average concentrations controlled to be less than 15 $\mu g\ m^{-3}$. By the end of 2019, the annual mean value of SO_2 decreased by 50% compared to 2015, reaching 11 $\mu g\ m^{-3}$ in 337 cities. None of the 337 cities exceeded the national secondary threshold of 60 $\mu g\ m^{-3}$ (http://www.cnemc.cn, last access on 20th January 2025). Consequently, controlling SO_2 emissions has yielded significant results, with low atmospheric SO_2 concentrations. This achievement is attributed to long-term implication of SO_2 control measurements. Coal consumption, which accounted for 57.7% of total energy consumption, has been significantly reduced due to unprecedented control measures on residential coal combustion. It is worth mentioning that the government has taken strict control measures on coal consumption by local residents in the Beijing-Tianjin - Hebei region, resulting in elimination of bulk coal combustion.

1.2.2(c) Effects of Low SO_2 Concentration on Atmospheric Chemical Process

This study considers that there are three possible impacts of low SO_2 environment. The first impact is on acidic gaseous pollutants like SO_2 in the atmosphere, such as NO_X. Significant progress has been made in decreasing SO_2 concentrations in the atmospheric, with NO_X surpassing SO_2 as the main pollutant in certain cities (Zheng et al., 2018). NO_X and SO_2 are both important acid gases in the air, and they react with NH_3 to form sulfate and nitrate. When the SO_2 concentration decreases, more NO_X may be involved in the acid-base neutralization reaction, leading to the formation of more nitrate. Xu et al. (2019a) found nitrate accounted for 32.8% of $PM_{2.5}$ and the nitrate to sulfate ratio was 3.33 during moderately polluted days. The reduction in SO_2 decreases the OH radicals' share of the reaction with SO_2, making more OH radicals available for reaction with NO_X, which may accelerate the NO_X conversion rate and thus change the chemical behavior of NO_X in the atmosphere. In some cities of Northern China, nitrate have become the highest composition and dominated urban haze pollution using the online monitoring datasets (Li et al., 2018a; Wen et al., 2018; Xu et al., 2019a). West et al. (1999) and Chen et al. (2016) found that the decrease of SO_2 would not effectively reduce the concentration of particles as more NH_3 and nitric acid (HNO_3) reaction to produce NH_4NO_3 which offset the decrease of sulfate.

The second impact is on alkaline gaseous pollutants in the atmosphere, such as NH_3. NH_3 is a main alkaline gas in the atmosphere (Kuang et al., 2020), and it reacts with acidic gases like SO_2 and NO_X to produce SO_4^{2-}, NO_3^-, and NH_4^+, contributing to atmospheric secondary pollution (Jiang & Xia, 2017; Meng et al., 2022). When SO_2 is reduced, acidic gases are reduced, making the atmosphere more likely to be alkaline. Also, since there are no effective control measures for NH_3, the atmosphere is in an NH_3-rich condition, resulting in higher free concentrations of NH_3 in the atmosphere, and the unconsumed NH_3 may remain in the gaseous state, increasing the life cycle and transport range of NH_3. In previous study, Chu et al. (2016) found that NH_3 reacted with sulphuric acid, then the excess-NH_3 reacted with HNO_3. But now elevated free concentrations of NH_3 are more likely to react with NO_X to produce nitrate.

Additionally, NH_3 is highly soluble in water, where it can raise the aerosol pH, and pH changes can also affect the formation of secondary composition.

The third impact is on secondary composition, such as sulfate. SO_2 is the main precursor pollutant of sulfate in the atmosphere and generates sulfuric acid (H_2SO_4), and thus sulfate, through gas-phase reactions or liquid-phase reactions. When the concentration of SO_2 in the atmosphere decreases, it leads to a decrease in the production of sulfate. The decrease in sulfate concentration changes its proportion in $PM_{2.5}$. This is common knowledge that we all know. Interestingly, some studies have found that sulfate still plays an important role in $PM_{2.5}$, despite the decreasing concentrations of SO_2 (Wang et al., 2015b; Zhang et al., 2016). The percentage of sulfate in Wuhan experienced a slight increase of 19.5% (Yin et al., 2020). High initial emission levels have not significantly altered the percentage of sulfate in $PM_{2.5}$ in Beijing (Wang et al., 2015b; Zhang et al., 2016). Now, the annual concentration of SO_2 continued to decline from 15 $\mu g\ m^{-3}$ in 2018 (Zhai et al., 2019) to 9 $\mu g\ m^{-3}$ among 169 prefecture-level cities in China (CMEE, 2021). A new research perspective has emerged with the rapid decrease in SO_2 concentration: how is sulfate produced in large quantities under low SO_2 concentration, and is it related to the excess NH_3 in the atmosphere?

1.2.3 Characteristics of NH_3 Emissions in Beijing-Tianjin-Hebei Region

High emissions are one of the important characteristics of NH_3 emissions in China. China is the largest contributor to global NH_3 emissions, with annual emissions reaching 14 Tg, accounting for 20% of global emissions and 55% of Asian emissions (Clarisse et al., 2009). NH_3 emission are higher in NCP (Beijing-Tianjin-Hebei belongs to NCP) than in other regions because Henan, Shandong, and Hebei are large agricultural provinces (Huang et al., 2012a). In 2011, nearly 3.0 Tg of NH_3 was emitted into the atmosphere due to nitrogen fertilizer application, with higher NH_3 emissions observed in NCP (Wang et al., 2013). Among the provinces, Henan, Shandong, and Hebei accounted for 11.1%, 9.9%, and 8.8% of the national NH_3 emissions, respectively (Wang et al., 2013). According to Zheng et al. (2018) and Zhai et al. (2019), the change in NH_3 from 2013 to 2017 was small. Relevant studies showed that NH_3 emissions remained at about 9.6 million tons in China in 2020, which was twice the total emissions of European and American countries (Streets et al., 2003). Zhao et al. (2017) predicted that the emission of NH_3 will increase by 33% in 2030 in comparison with 2012 if effective control strategies are not adopted in NCP region. Therefore, China should make effectively measurement to control NH_3 emissions in northern China, and here we will pay special attention to the Beijing-Tianjin-Hebei region, which exhibits intensive agricultural production and high population density.

However, implementing precise control measures for NH_3 is particularly challenging because its wide range of sources, including agriculture, human activities, motor vehicle emissions, and so on (Liu et al., 2015a; Zhou et al., 2016; Chang et al., 2019). In China, NH_3 mainly originate from agricultural sources, which is a collective term for emission sources that emit NH_3 directly from agricultural activities, including livestock and poultry farming, fertilizer application, biomass burning, straw composting, soil background, and human waste. Livestock farming (37.0-45.5%) and fertilizer application (33.4-42.7%) are the major contributors to NH_3 emissions (Xu et al., 2016). However, some studies in recent years have found that motor vehicles in megacities contribute significantly to NH_3 emissions (Wang et al., 2016c; Chang et al., 2019), while others have confirmed that motor vehicles in cities make negligible contributions to NH_3, and urban green spaces are actually important sources of NH_3 (Teng et al., 2017; Yao et al., 2013). There is ongoing debate about the sources of NH_3

in urban areas, but it is undeniable that high NH_3 concentrations do exist in cities. In order to figure out the sources of NH_3, most of the studies still adopt the emission factor approach for NH_3 inventory. In addition, Fu et al. (2015) developed a more accurate NH_3 emission inventory by combining online NH_3 monitoring with the Community Multiscale Air Quality (CMAQ) model. Zhang et al. (2021) used δ15N-NH_3 to estimate NH_3 concentrations before and after the COVID-19 lockdown period, employing an isotopic passive sampling method that resulted in a deviation of 15.4‰ (Pan et al., 2020).

1.3 Statement of Problem

1.3.1 Key issues in NH_3 Emission Reduction

For a considerable period, China has primarily focused on preventing and controlling acid gases like SO_2 and NO_X to combat acid rain (Wu, 2006; Xie et al., 2009; Liu et al., 2018b; Ren et al., 2024). More recently, their attention has shifted towards addressing emissions from motor vehicle exhaust and Volatile Organic Compounds (VOCs), which can lead to the production of secondary organic compounds (Wu et al., 2017; Wu et al., 2020b; Li et al., 2022). However, there hasn't been a particular emphasis on alkaline gases. The National Prime Minister's Fund introduced the "Agricultural Emission Status and Strengthening Governance Program in 2017," highlighting the need to address NH_3 emissions. The State Council issued the "Opinions of the Communist Party of China Central Committee and State Council on Deepening the Battle against Pollution Prevention and Control in November 2021." This document specifically called for a 5% reduction in total NH_3 emissions from large-scale farms in Beijing-Tianjin-Hebei and neighbouring regions by 2025 compared to 2020. This marks the first inclusion of NH_3 emission reduction in the agenda for atmospheric environmental issues.

However, most regions have not yet made relevant emission reduction strategies. And the development of NH_3 abatement measures must be scientific. NH_3 reduction is a complex challenge that requires effective design based on balancing atmospheric chemical processes and environmental benefits. First, NH_3 has complex and diverse emission sources. Agriculture, human activities, motor vehicle emissions contribute to NH_3 concentrations. If we control all NH3 emission sources, it will make the work heavy and disorderly. Because agricultural sources contribute more than 90% of total NH_3 emissions, this study primarily focuses on NH_3 abatement measures for agricultural sources to evaluate its role to $PM_{2.5}$ formation and potential impacts. Second, blind emission reduction of NH_3 may cause a series of environmental problems. For example, it reduces the amount of NH_3 washed to the ground by rainwater and increases the occurrence of H_3O^+ in rainwater. NH_3 reduction makes it easier for SO_2 to react with NH_3, resulting in the formation of more acidic ammonium bisulfate, which contributes to acid rain ($pH<5.6$) (Liu et al., 2019). The emergence of acid rain offsets the economic benefits of $PM_{2.5}$ reduction and nitrogen deposition resulting from NH_3 abatement, increasing the marginal cost. Third, in most of the previous studies, the effects of emission reduction of pollutant concentration on $PM_{2.5}$ and its compositions at that time were addressed, and the interactions between SO_2, NO_X, and NH_3 were not considered (Kulmala et al., 2015; Liu et al., 2019; Ye et al., 2022). Kulmala et al. (2015) found that control only one pollutant may increase the concentration of others. Therefore, the contribution of NH_3 and NH_3/NO_X to $PM_{2.5}$ and its secondary components after 70% reduction of SO_2, respectively, was considered in this study.

NH_3 emission reduction strategies should be tailored to local conditions. The sources of NH_3 are complex, and NH_3 reduction strategies need to take into full consideration the specific conditions of different cities to realize precise management tailored to local conditions. The sources of NH_3 emissions are complex and diverse, closely related to agricultural activities, industrial emissions, transportation and urban life, and also significantly affected by factors such as population density, economic structure and land use patterns. Within a region, the scale, functional positioning, and pollution characteristics of different cities often vary significantly, resulting in a significant impact of NH_3 emission reduction on $PM_{2.5}$ and its secondary inorganic constituents (e.g., SNA) to be spatially heterogeneous. In past studies, Liu et al. (2019) suggested that synergistic emission reduction or NH_3 reduction is effective in reducing $PM_{2.5}$ concentrations. Their studies focused on modeling and analysis at the national level and did not address the characterization of pollution at the regional level, much less delve into the specific problems of urban areas. Chen et al. (2017a) confirmed that NH_3 reduction could inhibit the production of SNA in winter in Baoding city. However, his study only made calculations for a third-tier city, lacked spatial comparative analysis, and did not involve comparative studies on emission reduction of different pollutants, which has significant shortcomings in the formulation of emission reduction measures. Therefore, when designing regional emission reduction strategies, it is necessary to formulate differentiated emission reduction policies based on quantitative analysis and with full consideration of the scale, economic structure and pollution characteristics of cities. This will not only improve the efficiency of policy implementation, but also maximize the promotion of $PM_{2.5}$ concentration decline and achieve synergistic optimization of regional air quality.

1.3.2 Impact of NH_3 Emission Reduction on Aerosol Acidity

NH_3 abatement should consider chemical mechanisms. Aerosol acidity is a key fundamental property in atmospheric chemical processes and is closely related to a variety of activities such as new particle formation (NPF), aging processes, gas-solid partitioning, dry deposition, toxicity, and nutrient transport. Aerosol acidity not only affects the formation of sulfate and nitrate (Guo et al., 2017a), but also interferes significantly with the gas-solid partitioning and dry deposition processes of semivolatile aerosols such as HNO_3/NO_3^- and NH_3/NH_4^+ (Nenes et al., 2020; Nenes et al., 2021). In China, the pH of aerosols is usually maintained around 4.0, which is significantly higher than the aerosol acidity (usually below 3.0) in the United States and European countries (Weber et al., 2016; Guo et al., 2015; Guo et al., 2017b). It has been shown that this difference is mainly attributed to the significantly higher atmospheric NH_3 concentration in China than in the United States and European countries, which results in a higher alkaline level of aerosols.

Aerosol acidity is often represented by pH value. Factors affecting aerosol acidity include aerosol component content, atmospheric temperature, atmospheric relative humidity (RH) and AWC (Jia et al., 2020). In previous studies, there have been many studies exploring the changes in aerosol acidity and its influencing factors (Nah et al., 2018; Ding et al., 2019). For example, an increase in AWC promotes the hydrolysis of water-soluble salts such as ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3), which changes aerosol acidity; meanwhile, an increase in AWC absorbs more atmospheric pollutants to participate in the aqueous phase reaction (Ge et al., 2019). However, Battaglia Jr. et al. (2019) concluded that soluble organic matter has a small effect on pH of 0.2 pH, but at 70% humidity, the change in pH increases to 0.6 pH. In the study of Guo et al. (2017b), they concluded that a 10-

fold change in NH_3 induces a change in pH of ~1 pH. From these data, an effect of ~0.2 pH on aerosol acidity means a 20% change in atmospheric NH_3, which is not a big difference for Europe and the United States, where NH_3 concentrations are very low, only a few micrograms (Wang et al., 2016a). However, China has large NH_3 emissions and high atmospheric NH_3 concentrations, especially in the Beijing-Tianjin-Hebei region, with average annual NH_3 emissions of more than 720,000 tons (data from: http://meicmodel.org.cn). In Beijing in 2015, the concentration of NH_3 could reach 38 $\mu g\ m^{-3}$ (Wang et al., 2016a). The annual average NH_3 concentration of NH_3 in Handan was 15.2 $\mu g\ m^{-3}$ in 2015 (Tan et al., 2021). It is an indisputable fact that changes in atmospheric NH_3 concentrations affect changes in aerosol acidity, and changes in acidity affect gas-solid partitioning (Ahrens et al., 2012). However, how the change in acidity affects the formation and transformation of the secondary components of aerosols needs to be explored in further studies, and there are relatively few studies analyzing the effect of the change in aerosol pH on the activity coefficients (γ) of SNA, and even fewer studies characterizing the partitioning of semivolatile components.

1.3.3 Optimizing NH_3 Emission Reduction Strategies

Optimizing regional NH_3 abatement strategies is an important work. Although some studies have focused on the importance of synergistic abatement (More detailed explanation can be found in section 2.4.4) (Fu et al., 2017; Zhao et al., 2017; Xu et al., 2022), no studies have emerged to analyze the optimization of abatement strategies based on the effects of chemical mechanisms generated by abatement, taking into account the effects of NH_3 abatement on pH. In this study, by simulating and analyzing the change of pH under different pollutant abatement cases and its important regulatory role in the generation, transformation and deposition of particulate matter, we quantify that the abatement of different pollutants may change the physicochemical properties and concentration levels of particulate matter by altering the acidity and alkalinity of the aerosol, which affects the efficiency of the generation of SNA salts. To further investigate in depth the effects of synergistic emission reduction of multiple pollutants on $PM_{2.5}$ and its secondary inorganic constituents in an integrated manner, thus providing scientific and technical support for further in-depth research on the combined effects of multiple pollutant abatement on $PM_{2.5}$ and its secondary inorganic constituents, and thus optimizing regional abatement strategies.

In addition, this type of modeling study is able to identify potential environmental risks in the process of synergistic emission reduction of multiple pollutants. For example, excessive reduction of NH_3 may increase aerosol acidity. Therefore, by comprehensively evaluating the emission reduction effects under different cases, quantitative support can be provided for the development of more scientific, differentiated and regionalized emission reduction strategies for different city scales. The realization of $PM_{2.5}$ effective control can also minimize the negative environmental effects of emission reduction, thus promoting the overall improvement of air quality and the sustainable development of the regional ecosystem.

In summary, this study strongly advocates addressing the following urgent issues:

(1) What is the source contribution of emission reduction of NH_3 and NH_3/NO_X to $PM_{2.5}$ at low SO_2 concentrations? Additionally, what are the differences in the impact of NH_3 abatement on emissions in large, small, and medium-sized cities?

(2) What are the characteristics of pH changes and how do pH changes affect nitrate and sulfate?

(3) How does pH change in different cities under different abatement cases? How can these changes be combined with emission reduction contributions to optimize emission reduction strategies?

1.4 Research Objectives

Combining the above three issues, the main objective of this study is to investigate the effect of NH_3 abatement on $PM_{2.5}$ and its secondary inorganic compositions under low SO_2 concentration conditions. To achieve this, this study focuses on three objectives.

Firstly, quantifying the contribution of NH_3 and NH_3/NO_X emission reductions to $PM_{2.5}$ at lower SO_2 concentrations. Discuss and analyze the differences in the impact of NH_3 emission reduction on megacities, medium cities and small cities.

Secondly, studying the characteristics of pH change, figure out the factors those affecting pH change, and discuss the impact of pH change on the formation of nitrate and sulfate.

Thirdly, analysing pH changes in different cities under different abatement cases. pH change mechanisms are combined with emission reduction contributions to optimize and develop emission reduction strategies.

1.5 Research Significance

The research significance of this study is to provide a scientific basis and quantitative support for regional air quality management. It explores the mechanism of pollutant interactions by examining the impact of various pollutant reduction cases on $PM_{2.5}$ and its secondary inorganic elements in Beijing-Tianjin-Hebei region. Compared with traditional single pollutant emission reduction assessments, this study analyzes the coordinated emission reduction of multiple pollutants and demonstrates how emission reduction policies vary in different cities. This theoretically supports the development of more targeted and effective emission reduction measures.

This study also examines how pH variations affect $PM_{2.5}$, particularly how nitrate and sulfate are formed. The generation and transformation of particulate matter are significantly influenced by the pH of aerosols; variations in pH can also alter the pace at which secondary pollutants are produced, which can impact efforts to improve air quality.

Finally, this study can provide a valuable resource for optimizing abatement technologies by simulating the effects of various abatement cases on pH, which help develop NH_3 abatement control strategies in the Beijing-Tianjin-Hebei region. It will also provide guidance for national decisions and approaches related to NH_3 emission reduction. It will help support the synergistic improvement of regional air quality, promote long-term sustainable improvement of air quality, and provide a basis for the development of region-specific emission reduction plans.

1.6 Layout of This Study

This study focuses on the haze pollution problems in the Beijing-Tianjin-Hebei region, and the overall structure includes the following parts: Chapter 1 is the introduction, which describes the background of the study, the problem statement, and the objectives and significance of the study; Chapter 2 is the literature review, which summarizes the progress of relevant research within China and internationally; Chapter 3 is the research methodology, which introduces the data sources, experimental design, model tool, and analysis methods; Chapter 4 is the results and analysis, which calculate the contribution of primary pollutants to $PM_{2.5}$ concentration, followed by the effect of aerosol acidity on secondary compositions, and optimizing pollution reduction strategies based on the research results. Finally, Chapter 5 is the conclusion and outlook, which summarizes the main research findings and makes suggestions for future research directions.

1.7 Summary

This chapter presents the background, problem statement, research objectives and significance of the study, focusing on air pollution in the Beijing-Tianjin-Hebei region. First, an overview of the environmental pressures in the region is presented, and in-depth analyses of the characteristics and causes of particulate matter pollution, trends and impacts of low-sulfur environments, and ammonia (NH_3) emission characteristics and control are presented. Next, key research questions are identified, including the main challenges of ammonia emissions, the impact of emission reduction on aerosol acidity, and methods to optimize emission reduction strategies. Finally, the research objectives and their significance in improving regional air quality and facilitating environmental policy formulation are presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Air pollution is one of the environmental problems globally. In China, haze pollution occurred frequently in recent years, of which $PM_{2.5}$ is regarded as the main factor. To address the issue of haze pollution, this chapter will focus on investigating the role of atmospheric NH_3 and aerosol acidity in the formation process of $PM_{2.5}$, to identify the current research gaps. Firstly, this study sorted out the sources and compositions of $PM_{2.5}$, and its formation mechanisms and source apportionment. Secondly, it summarized the definition and measurement methods of aerosol pH, along with on the formation of $PM_{2.5}$. Thirdly, the sources and sinks of atmospheric NH_3 were investigated, its impact on the formation of $PM_{2.5}$ were evaluated, and relevant research on NH_3 emission reduction measures was reviewed. Based on the investigation, this chapter pointed out the gaps in the current research and put forward the research innovation points and directions.

2.2 The Sources and Compositions of $PM_{2.5}$, its Formation mechanisms, and Source Apportionment

2.2.1 The Sources and Compositions of $PM_{2.5}$

The sources of $PM_{2.5}$ can be divided into two main categories in terms of the formation process: primary sources and secondary sources. Primary sources are $PM_{2.5}$ emitted directly into the atmosphere from pollution sources, which can be further divided into natural and anthropogenic sources. Natural sources include volcanic eruptions, forest fires, desert dust, and phenomena such as weathering and biological decay of rocks. Anthropogenic sources are sources of pollutant emissions that are