Urban Haze in the North China Plain

Observations from NACMON

*** The average concentrations of $PM_{2.5}$ mass and chemical compositions at 31 NACMON stations, October 2017 to September 2018.**

China contributes approximately 18%–35% of global air pollutant emissions. The Northern China Plain (NCP), one of the country's major emissions regions, has extremely high $PM_{2.5}$ pollution (haze) frequency in winter. The haze mainly forms in stagnant weather with high relative humidity.

Over the last decades, many studies have characterized aerosols and quantified the potential sources of $PM_{2.5}$ in haze. These studies have found many reasons for the NCP haze. Anthropogenic emissions such as burning coal for power supply and residential heating contributed 54% of the $PM_{2.5}$. Secondary aerosols contributed about half of the $PM_{2.5}$ in Beijing during winter 2013, suggesting that efficient transformation of secondary aerosols is also an important factor in haze formation, especially under high relative humidity. On the other hand, regional transport of polluted air, and the calm conditions that favor accumulation of air pollution, also result in extremely high $PM_{2.5}$ pollution in this region.

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Many studies have investigated individual cities (often Beijing and Tianjin). Therefore, the source apportionment results are often limited to the megacities, while understanding of nearby cities is scarce. Furthermore, haze occurs on a regional scale, and regional transport can be important in forming pollution. The regional effects and chemical evolution of haze events will not be well understood without a long-term and comprehensive observational network.

To improve the air quality in the NCP, the Chinese government has implemented a “2 + 26” regional strategy since early 2017, targeting Beijing and 27 other major NCP cities to strictly reduce airborne $\text{PM}_{2.5}$ concentrations. To evaluate this strategy, China’s National Aerosol Composition Monitoring Network (NACMON) selected 31 sites, including the “2 + 26” cities, to sample aerosols daily and provide measurements of other air pollutants online. All of the daily aerosol sampling has been set up since March 2017, but the online component was not installed until the end of 2018.

The scientific objectives of taking NACMON observations are 1) to investigate the source and formation of $\text{PM}_{2.5}$ -driven haze pollution, 2) to establish long-term databases to access the trends in aerosol chemical composition at a national and regional scale, 3) to validate model results, 4) to help the Chinese government make better decisions on air quality control and management, and 5) to evaluate the effect of the “2 + 26” strategy. The ultimate objective is to reduce the frequency of haze and improve air quality in the region. This brief introduction to NACMON includes preliminary results of offline measurements from October 2017 to September 2018.

NACMON OBSERVATIONS

To implement the “2 + 26” strategy, NACMON conducted comprehensive offline (since March 2016) and online measurements (since late 2018) in 31 cities of the NCP to obtain the chemical composition and optical properties of aerosols. Water-soluble ions, inorganic gases (SO_2 , NH_3 and HNO_3), carbonaceous aerosols including organic and elemental carbon (OC and EC), and trace metal concentrations were monitored online at 1-h resolution. Aerosol optical properties were monitored online at all the stations using lidar with 1-min and 7.5-m vertical resolutions; the lidar also provides the

atmospheric extinction coefficient, polarization ratio profile, and mixing layer height. Size distributions, trace metals, and mixing states of aerosols were determined in 7 cities. For offline measurements, daily concentrations of $\text{PM}_{2.5}$ mass, water-soluble ions, organic and elemental carbon, and metallic elements were obtained.

CHEMICAL COMPOSITIONS OF $\text{PM}_{2.5}$

The October 2017–September 2018 average $\text{PM}_{2.5}$ mass concentrations at the various offline sampling sites ranged from 53.5 to 112.5 $\mu\text{g m}^{-3}$. Despite efforts to reduce emissions, the $\text{PM}_{2.5}$ mass concentrations at all monitoring sites still exceeded the Chinese Grade I Standard annual mean of 35 $\mu\text{g m}^{-3}$. The higher $\text{PM}_{2.5}$ levels were usually observed in winter whereas lower $\text{PM}_{2.5}$ concentrations were found in the summer. This is a typical seasonal cycle in China. Stagnant weather and temperature inversions are unfavorable for diluting air pollution, while fossil fuel combustion and biomass burning is enhanced in winter. Interestingly, in Beijing, the average $\text{PM}_{2.5}$ concentration in the winter (43 $\mu\text{g m}^{-3}$) was much lower than during summer (65 $\mu\text{g m}^{-3}$). As part of Chinese government strategies to reduce anthropogenic emissions, Beijing Gas Group has reduced coal consumption by substituting with natural gas, for residential heating year by year since 2013. In Tianjin, the average $\text{PM}_{2.5}$ mass during the winter (55 $\mu\text{g m}^{-3}$) was roughly the same as in summer (53 $\mu\text{g m}^{-3}$) and autumn (50 $\mu\text{g m}^{-3}$) and lower than in spring (64 $\mu\text{g m}^{-3}$). In earlier studies, dramatic enhancements of sulfates accompanied high winter $\text{PM}_{2.5}$ concentrations in Tianjin, suggesting that coal combustion was a major source. Annual coal consumption in Tianjin decreased 2.6 million tons in 2017, which may partly explain the low $\text{PM}_{2.5}$ concentrations in the winter.

Organic matter, which is mainly emitted from combustion or through secondary transformation by volatile organic compounds (VOCs), constituted a major fraction (17%–30%) of the total $\text{PM}_{2.5}$ mass in all cities, followed by nitrate (7%–23%), sulfate (9%–18%), ammonium (4%–13%), elemental carbon (3%–7%), mineral dust (2%–8%), trace element (2%–4%) and chloride (1%–4%). Secondary inorganic aerosols (a summation of SO_4^{2-} , NO_3^- and NH_4^+) accounted for 19%–53% of $\text{PM}_{2.5}$ mass. Backward trajectory calculations

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revealed that $\text{PM}_{2.5}$ mass with enriched secondary aerosol was higher when the air parcels were from the southwest, south, and southeast. The air from these regions usually traveled slowly, had high relative humidity, and passed over regions with high anthropogenic emissions, facilitating the transformation of gas to particles.

Comparisons with two decades of data in Beijing show organic matter has constituted a major fraction (21%–51%) of $\text{PM}_{2.5}$ mass but show no significant annual trends. In addition, secondary inorganic aerosol was also a main chemical component in $\text{PM}_{2.5}$. The contribution of these inorganic aerosols to $\text{PM}_{2.5}$ mass varied from 23% to 45%. Before 2014, SO_4^{2-} was the most predominant species of secondary inorganic aerosol. However, nitrate

▲ Source apportionments of $\text{PM}_{2.5}$ in the six selected cities under various air quality conditions, ranging from low concentrations of $\text{PM}_{2.5}$ to very high concentrations (in haze).

has dominated this category of aerosols since 2015. Mineral dust (such as road dust and soil) seemed to be the third largest contributor to $\text{PM}_{2.5}$ at 2%–24%. Elemental carbon, mainly produced from combustion, contributed 2%–11% to $\text{PM}_{2.5}$ mass. Unlike nitrate, mineral dust and elemental carbon did not show any trends in the past 20 years. Due to an upward trend of nitrate from 2000 to 2018, the enhancements of nitrate-to-sulfate mass ratios were also found over the NCP region. Several recent studies indicated that the mass ratio of nitrate-to-sulfate in $\text{PM}_{2.5}$ was higher than 1.0 in the NCP region, as opposed to 0.3–0.9 in the last decade. In the NCP region, annual SO_2 emissions were cut down from ~1,000 to ~400 Gg between 2008 and 2016, resulting in a ~35% decrease of sulfate aerosol. NO_x emissions reductions

TABLE 1. Information of observed items in NACMON sites over the NCP region.								
Cities/ observations	Optical properties	Online measurements				Offline measurements		
		OC/EC	Ions	Metals	Mixing states	OC/EC	Ions	Metals
Beijing	•	•	•	•	•	•	•	•
Tianjin	•	•	•	•	•	•	•	•
Hebei Province								
Shijiazhuang	•	•	•	•	•	•	•	•
Baoding	•	•	•			•	•	•
Langfang	•	•	•			•	•	•
Zhangjiakou	•	•	•			•	•	•
Xiongan	•	•	•	•	•	•	•	•
Cangzhou								
Tangshan	•	•	•			•	•	•
Qinhd	•	•	•			•	•	•
Henshui	•	•	•			•	•	•
Xingtai	•	•	•			•	•	•
Handan	•	•	•			•	•	•
Henan Province								
Zhengzhou	•	•	•	•	•	•	•	•
Jiaozuo	•	•	•			•	•	•
Xinxiang	•	•	•			•	•	•
Kiafeng	•	•	•			•	•	•
Hebi	•	•	•			•	•	•
Puyang	•	•	•			•	•	•
Shandong Province								
Jinan	•	•	•	•	•	•	•	•
Heze	•	•	•			•	•	•
Jining	•	•	•			•	•	•
Liaochen	•	•	•			•	•	•
Dezhou	•	•	•			•	•	•
Zibo	•	•	•			•	•	•
Binzhou	•	•	•			•	•	•
Shanxi Province								
Taiyuan	•	•	•	•	•	•	•	•
Yangquan	•	•	•			•	•	•
Changzi	•	•	•			•	•	•
Jingchen	•	•	•			•	•	•
Anyang	•	•	•			•	•	•

(–17%) were much smaller than SO₂ emissions reductions (–62%).

NITRATE ON HAZE DAYS

The relative abundances of organic matter, elemental carbon, chloride, and mineral dust, as well as trace elements, decreased significantly during the

haze days (but increased in some cities). The relative contribution of sulfates to PM_{2.5} typically remained constant or decreased during PM haze. Most cities had enhanced absolute concentrations and relative abundances of nitrate and ammonium during haze days. Hydrolysis of N₂O₅ on water aerosols (e.g., in high relative humidity) is considered an important

pathway for nitrate formation in the NCP region. Case analysis indicates that a threshold RH value for nitrate formation was lower than for sulfate. This can partly explain why increases of nitrate contribution were in general found during haze periods. Case analysis in Beijing also shows that high winds favoring dilution of PM pollution and lower RH (in the 60%–70% range) did not facilitate the conversion of SO_2 to SO_4^{2-} , resulting in low concentrations of both $\text{PM}_{2.5}$ and sulfate. Yet earlier, when relative humidity remained at 80% for several days, both absolute concentrations and relative abundances of sulfate in $\text{PM}_{2.5}$ increased.

Unlike previous studies in northern China that suggested the ratio of sulfate in haze events increased much faster than that of nitrate, these new observations indicate that NO_3^- and NH_4^+ are major contributed species to $\text{PM}_{2.5}$ haze. Again, this implies that reduction of NO_x/NH_3 emissions is crucial to improving air quality in NCP.

SOURCES OF $\text{PM}_{2.5}$

Using a common mathematical modeling technique (positive matrix factorization, or PMF) for identifying pollution sources and their relative contributions from varied observations showed that secondary aerosols were the predominant source, contributing 23%–39% to $\text{PM}_{2.5}$, followed by traffic emissions (17%–27%), mineral dust (11%–18%), coal combustion (10%–16%), steel industry (6%–20%), and biomass burning (7%–19%). Previous studies using PMF have similarly found secondary aerosols to be a dominant source of $\text{PM}_{2.5}$ in Beijing with a positive trend ($2.2\% \text{ yr}^{-1}$; $p < 0.05$). Inorganic species dominated the secondary aerosol sources, demonstrating that control of NO_x and SO_2 emissions is an important way to decrease PM levels. Among primary sources, coal combustion and traffic emissions were major contributors of $\text{PM}_{2.5}$ in Beijing.

Coal is the primary energy source in China, and the use of coal ranges from power plants to industries to domestic households. In this study, the contribution of coal combustion (18%) was half of that found in 2014 and 2015. This might reflect the effectiveness of controls on SO_2 emissions in Beijing in 2017. Biomass burning, another emission source of $\text{PM}_{2.5}$, is experiencing a significant negative trend ($-1.3\% \text{ yr}^{-1}$; $p < 0.05$), as the Chinese

government prohibited the burning of harvest residuals in the 2010s. Mineral dust and industries were minor sources of $\text{PM}_{2.5}$ in Beijing; however, mineral dust contained enriched transition metal ions, an important catalyst of sulfate formation in clouds. Steel manufacturing was the only industrial source estimated (7.5% contribution in Beijing), but SO_2 , NO_x , and volatile organic compounds emitted from industry emissions would transform into secondary aerosols. Because sources of secondary aerosols were not estimated, the relative contribution of industry emissions to $\text{PM}_{2.5}$ might be underestimated in this study.

Contributions of mineral dust decreased evidently with increasing $\text{PM}_{2.5}$ levels in all cities, and the contributions of biomass burning and traffic emissions stayed constant or decreased in high $\text{PM}_{2.5}$ levels. Furthermore, coal combustion contributions to $\text{PM}_{2.5}$ decreased obviously with increasing $\text{PM}_{2.5}$ levels in the most cities. However, in Beijing, the contribution of coal combustion increased from 15% on clear days to 22% on haze days—nonetheless a much smaller absolute contribution than in an earlier study (57%). Significant enhanced contributions of steel pollution in haze were only found in Shijiazhuang, suggesting that control of steel manufacturing emissions could decrease $\text{PM}_{2.5}$ concentrations in this city.

The fraction of secondary aerosols increased substantially with increasing $\text{PM}_{2.5}$ levels in all selected cities. For instance, in Beijing, secondary aerosols contributed 14% to $\text{PM}_{2.5}$ during low PM days and 19% under moderate air quality conditions, and rose to 38% and 58% when $\text{PM}_{2.5}$ concentrations exceeded 75 and 150 $\mu\text{g m}^{-3}$, respectively. Other cities also had abrupt enhancements of secondary aerosols in the haze days, highlighting that secondary aerosols were the dominant source of $\text{PM}_{2.5}$ and triggered PM haze formation over the NCP region. Secondary inorganic aerosol is mainly transformed from NO_x and SO_2 emitted by vehicle and industrial emissions, and its emission sectors are not well understood yet.

Identification of potential sources of secondary aerosols will be important for alleviation of haze. Due to regional transport, meteorological conditions and emission sources influence the evolution of aerosol composition in haze events. Because secondary aerosols are the dominant component, control of gas emissions, in addition to primary PM

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Control of gas emissions, in addition to primary particulate emissions, will be an important strategy to improve air quality in the North China Plain.

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BAMS: What would you like readers to learn from this article?

Yan-Lin Zhang: Haze pollution frequently occurs in the North China Plain (NCP) during winter. In response, the Chinese government has made a big effort to reduce anthropogenic emissions of $PM_{2.5}$ for many years. However, the influence of such emission control on chemical compositions and source apportionments of $PM_{2.5}$ has not been explored. We attempt to answer these scientific questions.

BAMS: What were the limitations of past studies?

Y-LZ: Previous aerosol studies had been in individual cities (often one or two sites such as Beijing and Tianjin). Based on these observations, scientists could not understand the formation processes of haze pollution or the spatial distributions of aerosol compositions and source apportionments of $PM_{2.5}$ in the haze.

BAMS: What surprised you about your findings?

Y-LZ: I am surprised by an upward trend of contributions of secondary aerosols to $PM_{2.5}$ in Beijing over the last two decades since the clean air activities were implemented in 2010. According to our results, the increasing trend of secondary aerosols is due to increases of particulate nitrate, which is mainly in a form of NH_4NO_3 . This implies that effective control of NO_x and NH_3 emissions is important to decreasing PM pollution in the NCP region.

BAMS: What was the biggest challenge you encountered while doing this work?

Y-LZ: In this work, simultaneous aerosol sampling is conducted for 1 year with a daily resolution at 31 sampling sites in the NCP. We spend a lot of human resources maintaining the NACMON work, storing each aerosol sample and doing a good QA/QC procedure.

Yu-Chi Lin: This means that 31 scientists have to change the filters every day. After sampling, the filtered samples are placed into aluminum foils and stored in

the refrigerator at each sampling site. The scientists have to send the filter samples back to the laboratory of the China National Environmental Monitoring Station every week for chemical analysis, and all the chemical analyses have to be finished within three weeks after sampling. The water-soluble ion analyses have to be pretreated by extraction with Milli-Q water and are then determined by ion chromatography. On the contrary, organic and elemental carbons are determined by OC/EC analyzer and the elements are analyzed by x-ray fluorescence. We can imagine that these are high loading laboratory tasks.

BAMS: The result of that hard work is impressive!

Y-LZ: All measurements have their own standard operating procedures, which followed the national operating standard of China. This provides accurate and precise data for further scientific research.

emissions, will be an important strategy in decreasing secondary aerosol formation and improve air quality in the NCP region.

IMPLICATIONS

This project is the first systematic summary of the chemical compositions and source apportionments of aerosols in the NCP through multistation observations. In the haze pollution, nitrate-dominant or sulfate-dominant aerosols were driven by ambient as well as precursor gases. Primary particle sources such as coal combustion and biomass burning revealed downward trends while secondary aerosols, especially for NO_3 , showed upward trends over the last two decades. Almost 70% of the nitrate was in secondary products

(mainly NH_4NO_3). Therefore, control of both NO_x and NH_3 would decrease nitrate concentrations. NO_x emissions have been reduced ~20% in China. Meanwhile, fossil fuel combustion could be an important source of gaseous and particulate NH_3 in urban pollution, so control of NH_3 emissions from nonagricultural activities needs more attention.

Unfortunately, NACMON field observations alone cannot quantitatively estimate the influence of regional transport on high $PM_{2.5}$ pollution without model simulations. In addition, aerosols, meteorological conditions, and climate change are linked together. NACMON observations and data, combined with model simulation, can resolve many of these interactions, and ultimately questions of human health, in the future. ☪