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Significant Changes in Chemistry of Fine Particles in Wintertime Beijing from 2007 to 2017: Impact of Clean Air Actions

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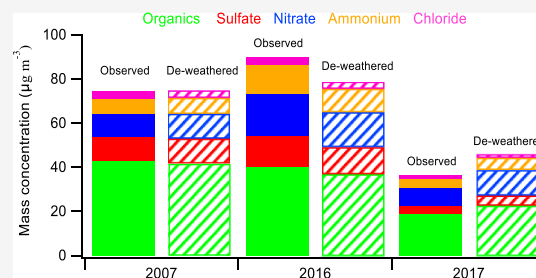
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Supporting Information

ABSTRACT: The Beijing government implemented a number of clean air action plans to improve air quality in the last 10 years, which contributed to changes in the concentration of fine particles and their compositions. However, quantifying the impacts of these interventions is challenging as meteorology masks the real changes in observed concentrations. Here, we applied a machine learning technique to decouple the effect of meteorology and evaluate the changes in the chemistry of nonrefractory PM₁ (particulate matter less than 1 μm) in winter 2007, 2016, and 2017 as a result of the clean air actions. The observed mass concentrations of PM₁ were 74.6, 90.2, and 36.1 μg m⁻³ in the three winters, while the deweathered concentrations were 74.2, 78.7, and 46.3 μg m⁻³, respectively. The deweathered concentrations of PM₁, organics, sulfate, ammonium, chloride, SO₂, NO₂, and CO decreased by -38, -46, -59, -24, -51, -89, -16, and -52% in 2017 in comparison to 2007. On the contrary, the deweathered concentration of nitrates increased by 4%. Our results indicate that the clean air actions implemented in 2017 were highly effective in reducing ambient concentrations of SO₂, CO, and PM₁ organics, sulfate, ammonium, and chloride, but the control of nitrate and PM₁ organics remains a major challenge.



INTRODUCTION

Frequent haze pollution in China has drawn great attention because of its adverse impacts on visibility, public health,¹ and complex interaction with the climate.² Beijing was one of the most polluted megacities in the world and has suffered persistent severe haze episodes in last two decades.^{3–6} During the severe haze episode, the hourly PM_{2.5} concentration reached 500–600 μg m⁻³.^{5,7} Haze events are formed primarily because of the unfavorable meteorological conditions limiting the dispersion of pollutants, rather than due to sudden increase in emissions.

A series of air pollution control measures were implemented since the late 1990s. Most important regulations were related to energy system restructuring and vehicle emissions.⁸ Because coal combustion has always been a major air pollution source in Beijing, many interventions were put into place to reduce the air pollutant emissions from this source. These include the

desulfurization retrofit, coal to gas in urban areas and denitrification retrofit for power plants since 2005, reduced coal combustion by nearly 11 million tons by 2017, and renovation of coal-fired boilers and old one-story houses in core areas in the mid-2000s. By the end of 2017, coal-fired boilers with a capacity below 7 MW in the whole city and those with a capacity below 25 MW were basically eliminated in urban areas; there is no longer coal combustion in industry fields, and no residential coal use in the core area in the six districts and the southern plains.⁹ Importantly, the “no-coal zone” policy in 2017 has been suggested to play a major role in reducing the air pollution levels in Beijing.⁸ Focusing on new

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vehicles, in-use vehicles, and fuel quality, a series of local emission and fuel quality standards for light-duty gasoline and heavy-duty diesel vehicles have been implemented in Beijing from 2008 to 2017. Moreover, comprehensive control measures as well as strengthened traffic management since 2008 such as driving restriction on light-duty passenger cars once a week, subsidized scrappage of yellow-labeled vehicles, and odd-even vehicle restriction for temporary measures. By the end of 2017, the most stringent standards for vehicles and fuels were implemented, and all yellow-labeled vehicles were scrapped.⁹ Under these control measures, annual average concentration of PM_{2.5} dropped to 58 and 51 $\mu\text{g m}^{-3}$ in 2017 and 2018, respectively, and decreased by 36 and 43% compared with that in 2013.^{10,11} In contrast, there was evidence that the mass concentration of submicron aerosol (PM₁) showed no significant reductions from 2005 to 2016.¹² Considering that PM₁ is the dominant contributor to the impacts of PM on human health and visibility,¹³ it is essential to quantify the variation chemistry and emissions of PM₁ in order to evaluate the impact of pollution control measures.

Temporal variation of the concentration of nonrefractory chemical species in PM₁ in Beijing was studied extensively^{4,5,12,14,15} to understand heavy haze formation mechanisms and/or to apportion the sources of PM₁. Previous studies reported that the mass concentration of PM₁ in the winter of 2008 was 73 $\mu\text{g m}^{-3}$,¹⁵ 66.8 $\mu\text{g m}^{-3}$ in winter 2011,¹⁶ 89.3 $\mu\text{g m}^{-3}$ in winter 2013,¹⁷ 64 $\mu\text{g m}^{-3}$ in winter 2014,¹⁴ and 92.9 $\mu\text{g m}^{-3}$ in winter 2016.¹² These data show that mass concentration of PM₁ fluctuated from 2007 to 2016, including the four years when the Clean Air Action Plan was implemented (2013–2016). These studies also provided data for understanding the changes in concentration of PM₁. Unfortunately, such data cannot be directly used to understand the real change in PM₁ concentrations as a result of the emission reductions (i.e., because of air pollution control). However, it is of great interest to the government, policymakers, and general public to know whether the specific action plan is working to meet the set targets. This is highly challenging because the measured concentrations of chemical species in PM₁ are determined by both emissions and meteorology.^{10,18} Therefore, to evaluate the link between pollution emissions and interventions, it is essential to decouple the effects of meteorology on measured concentrations.

Air quality modeling is the most commonly used method to study the effects of meteorology on air pollution levels and evaluate the effectiveness of pollution control measures.¹⁹ Chemical transport models are widely used to evaluate the response of air quality to emission control policies.²⁰ Atmospheric circulation and dynamic mechanism were also applied to identify the importance of meteorological conditions and its contributions to the improvement of air quality for the period 1960–2012, 1980–2013, and 2013–2017, respectively.^{11,21,22} Li et al. selected similar local and regional meteorological conditions before and during the parade to elucidate the net effectiveness of emission restrictions on PM₁ aerosol chemistry.²³ These studies examined the impact of meteorological conditions and emission control on the changes of the concentrations of particulate matter. However, there are major uncertainties in emission inventories and in the models themselves.⁸

Others applied statistical methods to decouple the effects of meteorology to evaluate the impact of measures on air quality.

For example, during Beijing Olympic Games, the mean atmospheric compositions under two similar stable weather pattern stages were used to quantify the outcomes of banning the 300 000 yellow-tag vehicles by removing meteorological influences as much as possible.²⁴ Recently, comprehensive parameters linking air quality to meteorological conditions index based on the mass concentration of PM_{2.5} were employed to estimate the contribution of meteorological conditions to the improvement of air quality in Beijing during Asia Pacific Economic Cooperation (APEC) in 2014, China's V-Day parade in 2015.²⁵

Machine learning models, including the boosted regression trees and random forest (RF) algorithms generally show higher prediction accuracy because of their strength in modeling complex relationships between response and predictor variables²⁶ and have a better performance compared to traditional statistical and air quality models by reducing variance/bias and error in high-dimensional data sets.⁸ Deep learning algorithms such as the kernel methods, which include support vector machines and artificial neural networks, have been used widely but it is hard to interpret the working mechanisms as well as the results within these models.^{18,27,28} RF has the advantage of not being a “black-box” method,²⁹ where the learning process can be explained, investigated, and interpreted. Recently, a novel machine learning technique based on an RF algorithm and the latest R-packages were used to quantify the real trend in criteria pollutants in order to evaluate the effectiveness of the Action Plan in Beijing.⁸

Here, we applied the same technique to a unique data set of nonrefractory submicron (NR-PM₁) species determined by an aerodyne aerosol mass spectrometer (Q-AMS) as well as PM₁ precursor gases (SO₂ and NO₂) in the winters of 2007, 2016, and 2017. This enabled us to quantify the real change in the concentrations of NR-PM₁ species from 2007 to 2017 and thus evaluate the effectiveness of air pollution interventions in reducing the concentration of NR-PM₁ species in Beijing for the first time.

■ MATERIALS AND METHODS

Sampling Site, Instrumentation, and Data Sources.

PM₁ chemical species data in this study were obtained from three independent campaigns at the China Meteorological Administration (CMA, 116°19.395'E, 39°56.916'N) campus. This is a typical urban background site. A detailed description of the sampling site is given by Zhang et al.¹⁵ The three campaigns were conducted in winter 2007 (11th November to 12th December 2007 and 4th January to 31st January 2008), 2016 (26th October 2016 to 2nd January 2017), and 2017 (28th October 2017 to 20th January 2018). Air was sampled through a PM₁₀ cyclone (16.7 L min⁻¹) to remove the particles larger than 10 μm . The Q-AMS as well as other instruments were located inside a container on the roof of a 13-floor building. An automatic aerosol dryer unit³⁰ was installed on top of the container to dry the inlet air with relative humidity (RH) < 30%. All of the aerosol instruments shared a common sampling inlet to maintain the consistency and comparability of aerosol studies with other works. Organics (Org), sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), and chloride (Chl) were measured by Q-AMS every 5 min. Furthermore, supplementary data including PM₁ concentrations were measured concurrently by GRIMM180 (Aerosol Technik Inc., USA), PM_{2.5} mass concentrations were downloaded from the Guanyuan station data set in the Chinese Environ-

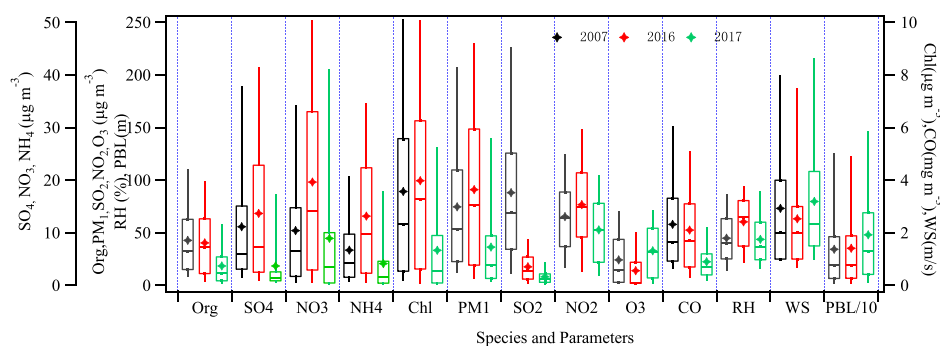


Figure 1. Boxplot of the PM₁ chemical components, gaseous pollutants, and meteorological variables in winters of 2007, 2016, and 2017 in Beijing, with mean (line in the middle of boxes), median (cross in the middle of boxes), 5, 25, 75, and 95% percentiles.

Table 1. Average Mass Concentrations of Chemical Species and Gaseous Pollutants (Observed and Deweathered) for Three Winters (2007, 2016, and 2017) in Beijing (Mean \pm Standard Deviation); Organics, Sulfate, Nitrate, Ammonium, Chloride, and PM₁, SO₂, NO₂, and O₃ in $\mu\text{g m}^{-3}$, CO in mg m^{-3} ^a

year	organics		sulfate		nitrate		ammonium	
	Obs	Norm	Obs	Norm	Obs	Norm	Obs	Norm
2007	42.7 \pm 33.5	41.0 \pm 18.5	11.1 \pm 12.0	11.2 \pm 2.0	10.4 \pm 11.5	11.1 \pm 2.7	6.7 \pm 6.7	7.2 \pm 1.5
2016	40.3 \pm 33.3	36.7 \pm 7.7	13.9 \pm 14.8	12.3 \pm 2.4	19.1 \pm 17.7	15.7 \pm 3.6	12.9 \pm 11.7	10.5 \pm 2.0
2017	18.8 \pm 18.8	22.6 \pm 4.4	3.5 \pm 6.2	4.6 \pm 1.1	8.5 \pm 13.6	11.5 \pm 3.6	4.0 \pm 5.7	5.5 \pm 1.2
year	chloride		NR-PM ₁		SO ₂		NO ₂	
	Obs	Norm	Obs	Norm	Obs	Norm	Obs	Norm
2007	3.6 \pm 3.7	3.5 \pm 0.9	74.6 \pm 63.1	74.2 \pm 13.6	88.1 \pm 69.2	86.6 \pm 25.4	65.3 \pm 34.3	70.3 \pm 10.4
2016	3.9 \pm 3.6	3.3 \pm 0.9	90.2 \pm 77.3	78.7 \pm 15.0	17.7 \pm 13.4	15.3 \pm 3.4	76.7 \pm 41.7	66.6 \pm 10.9
2017	1.4 \pm 1.8	1.7 \pm 0.4	36.1 \pm 44.2	46.3 \pm 8.7	8.1 \pm 6.8	9.4 \pm 2.2	52.6 \pm 32.2	59.1 \pm 9.3
year	O ₃		CO					
	Obs	Norm	Obs	Norm				
2007	24.2 \pm 24.5	25.1 \pm 10.3	2.2 \pm 1.8	2.3 \pm 0.6				
2016	13.9 \pm 17.2	18.0 \pm 8.1	2.1 \pm 1.7	1.8 \pm 0.3				
2017	32.9 \pm 24.5	25.7 \pm 7.3	0.9 \pm 0.7	1.1 \pm 0.2				

^aNotes: Obs=Observed, Norm=Deweathered

mental Protection Agency (CEPA) website (<http://zx.bjmemc.com.cn/>), and daily PM_{2.5} concentrations obtained from the filter samples³¹ were utilized to verify the final collection efficiency for AMS during three campaigns.

Trace gaseous pollutants, including NO₂, SO₂, CO, and O₃, were also monitored at the same site by Thermo Environmental Instruments (CO, NO₂, SO₂, and O₃) for winter of 2007³² and were downloaded from the Guanyuan station data set CEPA website for winters of 2016 and 2017. The Guanyuan station is a typical urban background site and was only 2 km away from the study site. The surface hourly meteorological data, including temperature, RH, pressure, precipitant, wind speed, and wind direction, were provided by Beijing airport meteorological observation station, which were measured at 30 m above the ground. The boundary layer height data was acquired from WRF simulation (WRF-ARW 3.9). Three nested domains with a horizontal resolution of 25, 5, and 1 km were configured. The initial and boundary conditions were provided by the NCEP FNL data available at 1 \times 1° in longitude and latitude at every 6 h. The Yonsei University (YSU) planetary boundary layer (PBL) parameterization was employed. A more detailed description on boundary layer height estimation from the YSU PBL parameterization scheme can be referred to Hong et al.³³

Deweathering Using RF Algorithm. An RF algorithm, based on an ensemble of decision trees, was employed to

model the concentration of chemical species by time variables (yearly, day of the year, day of week, and hourly) and meteorological variables (wind speed, wind direction, RH, temperature, and atmospheric pressure).^{18,30,34} The algorithm describes the relationship between hourly concentrations of an air pollutant and its predictor variables. The RF model was first constructed from a training data set (e.g., 70% of all data available) of observed concentrations of a pollutant and its predictor variables and then validated by unseen data set (testing data set accounting for 30% of all data points).

The original data sets contain hourly concentration of organics, sulfate, nitrate, ammonium, and chloride in PM₁, NO₂, SO₂, O₃, and CO for gaseous pollutants as well as their predictor variables, which include time variables (t_{trend}) represented by Unix Epoch time, hour (0–23), day of week (Monday to Sunday), and meteorological parameters (wind speed, wind direction, pressure, temperature, and RH). The testing data sets were randomly chosen for studying the correlation coefficient between daily observed and predicted values (Figure S1).

The weather normalized technique predicts the concentrations of an air pollutant at a specific measured time point but with varying meteorological conditions (deweathered concentration). The deweathering technique was first introduced by Grange et al.¹⁸ Both time variables (month, week, and hour) and meteorological parameters, except the trend

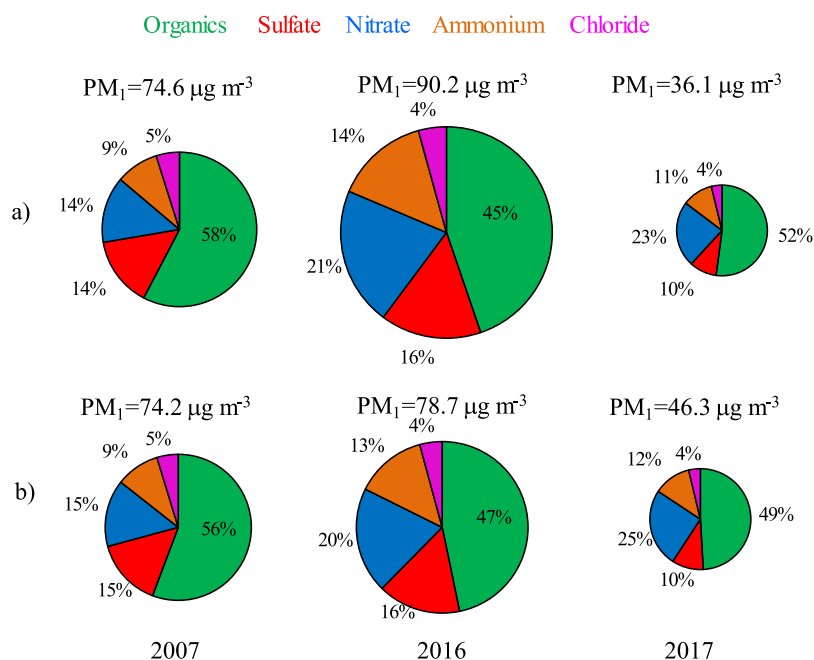


Figure 2. Average mass concentrations of PM₁ and their chemical components based on observed (a) and deweathered (b) data sets in winters of 2007, 2016, and 2017.

variable, were resampled randomly and were added into the RF model as input variables to predict the concentrations of chemical species and gaseous pollutants.³⁴

In our algorithm, only weather data (MET data) sets were resampled from the 10 year meteorological conditions in Beijing (2007–2017) rather than MET data during the study periods to better represent the average conditions. Meteorological data variables at a specific selected hour of a particular day in the input data sets were replaced randomly by the meteorological data at that hour for a period of 2 weeks before and after that selected data for all the 10 year meteorological data sets (called deweathered concentrations).⁸ For example, the new input weather data at 01:00 15/12/2016 are randomly selected from the observed data at 01:00 am on any date from 1st to 29th December of any year in 2007–2017. The selection process was repeated 1000 times to generate a final input data set. Each of the 1000 data was then fed to the RF model to predict the concentration of a pollutant or a PM₁ species; the 1000 predicted concentrations were then averaged to calculate the final weather-normalized concentration for that particular hour, day, and year.⁸

RESULTS

PM₁ Chemical Species in Winter 2007, 2016, and 2017. Figure 1 shows the general characteristics of organics, sulfate, nitrate, ammonium, and chloride in PM₁ (NR-PM₁), gaseous pollutants (SO₂, NO₂, O₃, and CO), key meteorological variables (wind speed and RH) and PBL heights. High time-resolution variations for these parameters were shown in Figure S2. PM₁ mass concentration ($\pm 1\sigma$) in the winter 2007, 2016, and 2017 was 74.6 ± 63.5 , 90.2 ± 77.3 , and 36.1 ± 42.2 μg m⁻³, respectively (Table 1). The mass concentration of PM₁ in 2017 decreased by 52 and 60% compared with that in 2007 and 2016. This shows that there was a significant decline in PM₁ in 2017.

Organics, sulfate, nitrate, ammonium, and chloride in the three winters (Figure 1 and Table 1) displayed a similar

temporal pattern as PM₁, which was high in 2016 and low in 2017. In 2017, the mass concentration of organics, sulfate, nitrate, ammonium, and chloride was 18.8, 3.5, 8.5, 4.0, and 1.4 μg m⁻³, respectively. Compared to those in 2007, sulfate and chloride decreased by about 68 and 61%, respectively. From 2007 to 2017, the concentration of organics and ammonium decreased by 56 and 40%, but that of the nitrate decreased only by 18%.

Chemical compositions of PM₁ were somewhat different in the three winters (Figure 2a). Among the five chemical species, organics always dominated PM₁, but its contribution to PM₁ mass varied significantly—58, 45, and 52% in 2007, 2016, and 2017, respectively. The second most important species in PM₁ was nitrate, followed by sulfate and ammonium. Chloride contributed the least to PM₁. The proportions of nitrate to total PM₁ increased gradually from 14% in 2007 to 21 and 23% in 2016 and 2017, indicating a more and more prominent contribution to PM₁ from nitrate. On the contrary, the percentages of sulfate in PM₁ reduced from 14% in 2007 to 10% in 2017.

SO₂ decreased dramatically from 88.1 μg m⁻³ in 2007, to 17.7 μg m⁻³ in 2016, and 8.1 μg m⁻³ in 2017. This is equivalent to decrease of 91% from 2007 to 2017. NO₂ concentrations decreased from 65.3 μg m⁻³ in 2007 to 52.6 μg m⁻³ in 2017. Another gaseous pollutant CO, representing the primary emissions from combustion processes, was 2.3 and 2.1 mg m⁻³ in the winters of 2007 and 2016, respectively, but decreased to only 0.9 mg m⁻³ in 2017 (Figure 1 and Table 1).

RH in 2016 ($60.4 \pm 24.2\%$) was significantly higher than that in 2007 ($44.8 \pm 23.7\%$) and 2017 ($43.7 \pm 22.9\%$), while the wind speed in 2016 (2.9 ± 2.2 m s⁻¹) was higher than that in 2007 (2.5 ± 2.0 m s⁻¹) but lower than in 2017 (3.2 ± 2.5 m s⁻¹). The height of PBL in winter 2016 was also lower than that in the other two winters.

Deweathered PM₁ Chemical Composition. The deweathered mass concentration of PM₁, its chemical species, and the gaseous pollutants are listed in Table 1. In general, from

2007 to 2017, the deweathered PM₁ chemical species such as organics, sulfate, ammonium and chloride as well as SO₂, NO₂, and CO decreased but to a different extent. SO₂, sulfate, chloride, and CO declined by more than 50% from 2007 to 2017, but nitrate increased during the same period. Moreover, concentrations of PM₁, sulfate, nitrate, and ammonium were higher in 2016 than those in 2007, but a large decline was observed from 2016 to 2017. The observed concentrations of PM₁ and its chemical species were lower than deweathered ones in 2007 and 2017 but much higher in 2016.

The real mass concentrations of chemical species and gaseous pollutants would be 15% (9–19%) lower in winter 2016 if under the 10 year average meteorological conditions, suggesting an unfavorable weather conditions for pollutant dispersion. They would be 30% (12–38%) higher in winter 2017 if under the 10 year average meteorological conditions, suggesting a more favorable dispersion condition. This is consistent with Vu et al. and Li et al.^{8,35} In 2007, the observed values are comparable to that of deweathered values. The diurnal cycles of PM₁ chemical species before and after deweathering in the three winters showed the differences in more details (Figure S3).

Figure 2b displays the deweathered chemical compositions of PM₁ in the three winters. Organics was the dominant species, accounting for 56, 47, and 49% of PM₁ in winter 2007, 2016, and 2017, respectively. The contribution of nitrate to PM₁ increased from 15% in 2007 to 20% in 2016 and 25% in 2017 but that of the sulfate decreased from 15% in 2007 to 10% in 2017.

DISCUSSION

Evaluating Real Changes in PM Composition Due to Clean Air Actions. The results of deweathered chemical compositions allow us to evaluate the effectiveness of various clean air action plans to improve air quality in the wintertime Beijing. The observed concentrations of SO₂ in winter 2007 (88.1 μg m⁻³) and 2017 (8.1 μg m⁻³) were comparable to those of previous studies.^{32,35} The deweathered SO₂ concentrations decreased by 82% from 2007 to 2016 and 39% from 2016 to 2017. Multiresolution Emission Inventory for China (MEIC)³⁶ estimated that the average emission flux of SO₂ in heating seasons of Beijing dropped by 79% from 19 kt/month in 2008 to 4 kt/month in 2016, primarily because of reductions from industry and residential sectors (Figure S4). It estimated a major decrease in SO₂ emissions from power plants for neighboring provinces—Tianjin and Hebei since 2014 (Figure S4). Thus, the trend in MEIC SO₂ emission is consistent with that of deweathered SO₂ concentration, indicating that the clean air action implemented since 2013 and the adoption of clean coal technologies that were enforced by the “Action Plan for Transformation and Upgrading of Coal Energy Conservation and Emission Reduction (2014–2020)”⁸ worked effectively.

Although SO₂ reduced by 71.3 μg m⁻³ from 2007 to 2016, sulfate concentration actually increased by 1.1 μg m⁻³, and then decreased by 7.7 μg m⁻³ from 2016 to 2017. One possible reason is the control of SO₂ in Beijing was implemented effectively during 2007 to 2016,³⁷ but not in its surrounding regions especially from industrial and residential sectors (Figure S4). Cut in local emission does not necessarily lead to the same degree of decrease in sulfate because the regional-emitted SO₂ can be transformed into sulfate during long-range transport. Higher sulfate contribution from regional transport

was also reported by Sun et al. via the back trajectory method on the chemical species.⁴ In 2017, SO₂ emission control was more efficient in both Beijing and the neighboring provinces (the so-called “no coal zone policy”),¹⁰ which led to the lower concentration of sulfate in PM₁ (deweathered). Change in chemistry of SO₂ oxidation may be another reason, which is discussed below.

The observed NO₂ in winter 2007 (65.3 μg m⁻³) is similar to those reported in previous work (approximately 69 μg m⁻³).³² The deweathered NO₂ concentration decreased by 5% but that of nitrate increased by 41% in winter 2016 relative to that in 2007. MEIC estimates that NO_x emissions from power plants in wintertime of Beijing, Tianjin, and Hebei decreased by 50, 70, and 47% from 2008 to 2016, respectively, but emissions from industry increased by 36 and 19% in Tianjin and Hebei, with no declining trend from the residential sector (Figure S4). Furthermore, decrease in NO_x emission from individual vehicles was compromised by increasing number of vehicles in Beijing (from 3.12 million in 2007 to 5.71 million in 2016, <http://www.mep.gov.cn>). These data suggest that emission controls from power plant contribute largely to the NO₂ decrease in winter 2016 from 2007, while the NO_x emission controls from industry and residential sectors from neighboring provinces were less efficient.

In 2017, a number of control measures were put in place to control NO_x emissions including both on-road and off-road vehicles, improved end-of-pipe control such as the application of low nitrogen-burning technologies for the combustion equipment as well as enhanced management of heavily polluting vehicles,¹⁰ which resulted in the reduction of NO₂ and nitrate by 11 and 27%, respectively, in winter 2017 relative to 2016.

Deweathered ammonium reduced from 7.2 μg m⁻³ in winter 2007 to 5.5 μg m⁻³ (by 23%) in winter 2017. This is generally consistent with the MEIC, which estimated that NH₃ from agricultural emission, the predominant NH₃ source, reduced by 22% in 2016 in comparison to 2008.

Deweathered PM₁ organics decreased by 45.7% in winter 2007 (41.6 μg m⁻³) in comparison to 2017 (22.6 μg m⁻³), most of which was from 2016 to 2017. Emissions from vehicles, coal combustion, biomass burning, and cooking are considered as major primary sources of organics.^{5,12,16} Secondary organics is formed in the atmosphere through various oxidation reactions of volatile organic compounds (VOCs). MEIC showed that during the Beijing wintertime, integrated control of VOCs led to 11% reduction of emissions from 2008 to 2016. VOC emissions from transportation and residential sector decreased by 66 and 14%, respectively, while those from industry and power plant increased by 65 and 160% (Figure S4). The policies of replacing coal-fired boilers with electrical and natural gas boilers, strengthened controls on vehicle emissions,³⁵ and thorough forbiddance of biomass burning in late 2016^{10,35} worked effectively to reduce the primary organics and secondary organic aerosol precursors from 2016 and 2017.

In summary, the controlling measures from industries and power plants in Beijing and its neighboring provinces, replacement of coal-fired boilers in Beijing, and elimination of small, clustered, and polluting factories worked effectively in reducing the concentrations of PM₁ and its precursors (SO₂, NO₂, and VOCs), while the emissions from industries remain a big challenge.

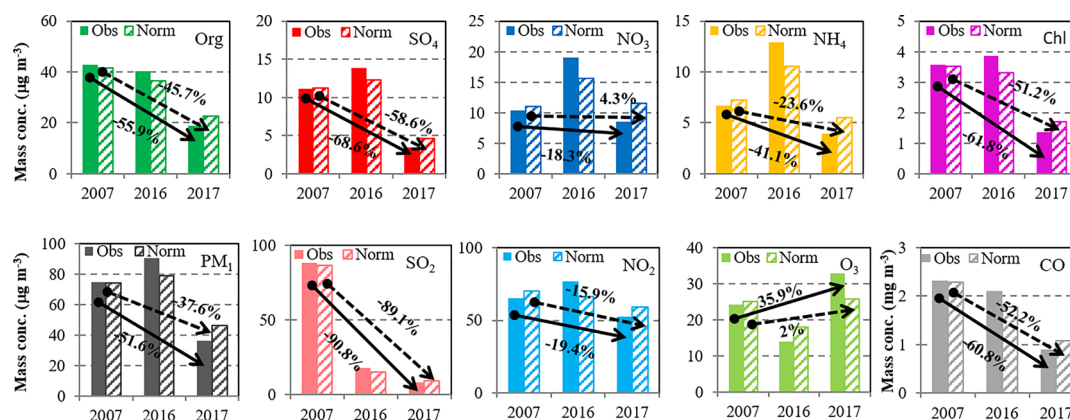


Figure 3. Average observed and deweathered (Norm) mass concentrations and changes of chemical species in PM₁ and gaseous pollutants in winters of 2007, 2016, and 2017.

Significance of Meteorology in Year-by-Year Variations of Air Pollutant Concentrations.

The observed PM₁ in 2016 is 2.5 times higher than in 2017 (Table 1), while deweathered PM₁ in 2016 is 1.7 times higher than in 2017. The observed and deweathered PM_{2.5} in 2016 (109.9, 91.2 µg m⁻³) is 2.5 and 1.5 times higher than those (44.8, 61.9 µg m⁻³) in 2017, respectively, which is consistent with our PM₁ results. Meteorology played an important role in the variations of PM in the winter. The impacts of RH, wind direction, wind speed, temperature, pressure, as well as the day of week, hourly variation, and the trends on the prediction performance of chemical species and gaseous compounds are shown in Figure S5. The results show that the most important variable impact on SO₂ was the trend (i.e., the variation pattern for species), indicating that the change in concentration of SO₂ is mainly due to its emission reduction. Mass concentration of all of the other species was very sensitive to RH, followed by its trend (except for NO₂). Wind speed affects the trend of NO₂, organics, chloride, PM₁, and CO more than that of the trend. Concentrations of sulfate, nitrate, and ammonium are correlated with hourly variations and temperature fluctuation, which are associated with the photochemical process and/or the changes of emissions from sources.

We also explored the time series of the ratios between observed and deweathered concentrations for the species (Figure S6). The ratios of particulate species display a similar variation trend, so do the gas phases including SO₂, NO₂ and CO. O₃ is an exception, which is not surprising considering its completely different formation mechanisms. Average ratios of the observed to deweathered concentrations of organics are slightly higher than those of the sulfate, nitrate, ammonium, and chloride. This indicates that the concentrations of organics are more sensitive to meteorological variations than the main inorganic ions. This is likely due to the differences in formation mechanisms rather than the emission changes. More modeling work is needed to fully understand this difference, which is out of the scope of this current study.

Higher RH and lower wind speed in 2016 contributed to the higher observed PM₁ concentration.^{5,12,38} The high RH was one prerequisite for the rapid sulfate formation via multiphase reactions.³⁹ Shen et al.,⁴⁰ found an exponential trend of the aerosol liquid water content (ALWC) with the RH. The high mass loading of ALWC promoted the secondary formation processes of the secondary inorganic aerosol (SIA). The SIA enhanced the ability of aerosol water uptake, which further

promoted the heterogeneous reactions. This was a self-amplifying process between the ALWC and SIA that could further enhance the particle mass loading in the ambient; lower wind speed leads to poorer dispersion conditions, contributing to the accumulation of air pollutants.³⁸ We showed that low RH and high wind speed in 2017 led to lower observed PM₁ concentrations,⁴⁰ consistent with Vu et al.⁸ and Cheng et al.¹⁰

Changes on PM₁ Chemistry and Challenges for Future Air Pollution Control.

With the implementation of clean air actions, the chemistry of PM₁ in the 10 years changed substantially. The contribution of organics to PM₁ in winter 2017 decreased significantly in comparison to 2007, which is consistent with studies during 2014–2016¹² and 2014–2017.³⁵ Sulfate increased by 1% in winter 2016 than in 2007. A previous study also suggested that the change in relative contribution of sulfate to PM₁ was relatively small (<2%) from 2014–2016.¹² The largest decline in concentration took place from 2007 to 2017 (by –59%) among all measured PM₁ chemical species. Meanwhile, the contribution of sulfate to PM₁ mass also decreased. This is consistent with the result by Xu et al. and Li et al. during 2014–2017.^{12,35} Deweathered data show that sulfate chemistry changed significantly in the winter from 2007 to 2017. The oxidation ratio for sulfate (SOR, the molar ratio of sulfate to the sum of sulfate and SO₂) was only 0.08 in winter 2007 but increased dramatically to 0.35 in 2016. Although lower than that in winter 2016, SOR in 2017 was still three times higher than in 2007. The high SOR in 2016 and 2017 explained the less dramatic decrease in sulfate concentrations from 2007 in comparison to SO₂ (Figure 3). There are a few possible mechanisms leading to this trend. The first one is the variation in RH. High RH (60.4%, and even 98% at times) in 2016 potentially enhanced the aqueous phase oxidation of SO₂ to form sulfate especially during severe haze events.^{41–43} A year-long study in Beijing from 2012 to 2013 also revealed that a rapid increase in the sulfur oxidation ratio at a RH threshold of 45%.³⁹ Li et al.⁴⁴ pointed out that ammonium bisulfate formation would occur readily on the surface of water via a loop-structure-promoted proton-transfer mechanism. In contrary, decreased SO₂ emissions and lower RH (40%) in winter 2017 suppressed the rapid formation of secondary sulfate through heterogeneous reactions³⁵ resulting in lower observed sulfate concentration. A second possible mechanism is a change in aerosol acidity. The ratio of NH₄⁺ and anions (SO₄²⁻, NO₃⁻, and Cl⁻) in 2007, 2016, and 2017 was 0.78, 0.97, and 0.92, respectively (Table 2), indicating

Table 2. SOR, C/A, and N/S in Three Winters^a

	SOR	C/A	NOR	N/S
2007	0.08	0.78	0.11	1.12
2016	0.35	0.97	0.15	4.48
2017	0.25	0.92	0.13	7.29

^aSOR = $[\text{SO}_4^{2-}]/[\text{SO}_2 + \text{SO}_4^{2-}]$, C/A = $[\text{NH}_4]/[\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-]$, N/S = $[\text{NO}_2 + \text{NO}_3^-]/[\text{SO}_2 + \text{SO}_4^{2-}]$, all of the values in the brackets are in molar.

aerosols were more acidic in 2007 than in 2016 and 2017. Higher acidity in PM₁ in winter 2007 may have inhibited the conversion of SO₂ to sulfate, whereas weaker acidity in PM₁ in 2016 promoted the conversion of SO₂ conversion. However, the exact mechanisms remain controversial.^{42,45} Furthermore, higher relative contribution of regional sulfur species to ambient levels in Beijing air may have led to the increase in the SOR in winter 2017, as mentioned above. More aged air masses are likely to have a higher SOR.³⁹ The above mentioned discussions suggest that a clearer understanding on the chemistry of SO₂ oxidation is needed to avoid further increase in SOR, which compromises the impact of emission reduction in SO₂ on PM₁ mass.

The deweathered concentration of nitrate in PM₁ showed a substantial increase in winter 2016 but slightly higher in winter 2017 in comparison to that in 2007 (Table 1). In the meantime, because of the substantial decrease in PM₁, the contribution of nitrate to PM₁ exhibited an increasing trend from 15% in winter 2007 to 25% in 2017. On the other hand, deweathered concentrations of NO₂ decreased by about 16% in winter 2017 compared to that in 2007. Accordingly, the oxidation ratio for nitrate (NOR, the molar ratio of nitrate to the sum of nitrate and NO₂) increased from 0.11 in winter 2007 to 0.13 in winter 2017. This suggests that the chemistry of NO₂ oxidation and/or regional transport may have contributed to the increasing trend of nitrate contribution to PM₁. Because of its short lifetime, NO_x emitted in adjacent regions would be largely transformed into particulate nitrates during transport. A higher contribution of regional transport to nitrates in PM₁ in Beijing would lead to an increase in NOR. In the atmosphere, NH₃ tends to react with H₂SO₄ to form ammonium sulfate first and excess NH₃ participates in ammonium nitrate formation.^{13,35} According to the aerosol thermodynamic equilibrium, less available ambient NH₃ favors more HNO₃ staying in the gas phase instead of partitioning into aerosols and then inhibits the formation of ammonium nitrate.¹³ In summary, secondary aerosol pollution in Beijing has gradually changed from sulfate- to nitrate-driven in recent years (Table 2). Reduction of nitrate concentration and its precursor, NO_x, is a major challenge.

Although the mass concentration and proportion of organics in PM₁ decreased from 2007 to 2017, organics concentration was still the highest contributor to PM₁ (49% in winter 2017). The mass concentration of organics (18.8 μg m⁻³) in 2017 is comparable to that in the Mexico City (17.3 μg m⁻³) and three times higher than that in Pittsburg (4.8 μg m⁻³).⁴⁶ Reducing the concentration of organics in fine particles requires mitigation measures to control primary organic emission as well as secondary organic aerosol precursors, VOCs.^{5,12,35}

Our results confirmed that the emission reduction due to the “Clean Air Actions”, rather than meteorology, is the main driver of the reduction in airborne concentrations of PM₁ and

its chemical components. However, there are still challenges for air pollution control, for example

- Increasing relative importance of nitrate in PM₁ pollution.
- Complex nonlinear chemistry of sulfate and nitrate formation, in the presence of high ammonia emissions.
- High contribution of organics to PM₁, as a result of both primary emissions and secondary formation from VOCs.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b04678>.

Detailed information about the performance of the RF model in predicting the daily mass concentrations of chemical species, time series of parameters in high time resolutions, diurnal cycles of observed and deweathered chemical concentrations in three winters, emission amount of gaseous pollutants of BTH in wintertime, relative importance of the predictor variables in the final RF submodel, and variations of the observed/deweathered for species (PDF)

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