Wet deposition and scavenging ratio of air pollutants during an extreme rainstorm in the North China Plain

Pan Yue-Peng, Zhu Xia-Ying, Tian Shi-Li, Wang Li-Li, Zhang Guo-Zhong, Zhou Yan-Bo, Xu Peng, Hu Bo and Wang Yue-Si

State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China; National Climate Center, China Meteorological Administration, Beijing, China

ABSTRACT
Atmospheric wet deposition plays an important role in the supply of nutrients and toxic substances to terrestrial and aquatic environments. Although long-term (e.g. annual, multi-year) wet deposition is recorded well, pronounced and short-term changes in precipitation chemistry are less well investigated. In the present study, the precipitation chemistry and scavenging ratio of air pollutants were observed during an extreme torrential rain event (325.6 mm at the observation site) that occurred over 19–21 July 2016 in the North China Plain (NCP). The scavenging ratio of particles showed a similar spatial distribution to that of the precipitation amount in the NCP, indicating the efficient removal of particulate matter due to the large amount and precipitation intensity of the storm. In addition, the scavenging ratio of water soluble ions was larger than that of organics and gaseous pollutants such as SO2 and NO2, likely due to their differences in water solubility. Consequently, raindrops incorporated more aerosol sulfate than gaseous compounds. Due to the heavy precipitation amount, almost all species in rainwater during this storm showed their lowest concentration but the highest flux compared with other rain events, indicating an important role played by this storm in terms of the substances received by the terrestrial and marine ecosystems of the region. However, the contribution of this storm to the annual chemical flux was lower than that of precipitation amount, indicating that the atmospheric compounds were scavenged below-cloud first and were then diluted by the cloud/rainwater. Future studies are needed in the context of the occurrence of extreme rainfall events in the NCP from the perspective of climate variability.

1. Introduction
The removal of pollutants via wet deposition is considered an important pathway in cleansing the atmosphere (Bourcier et al. 2012), and equally important as dry deposition in terms of the inputs of nutrients and toxic substances to the affected terrestrial and marine ecosystems (Dentener et al. 2006; Pan and Wang 2015). Wet deposition of air pollutants is also known to be episodic, i.e. a small proportion of events contribute a large portion of the annual deposition (Smith and Hunt 1978). This episodic nature of wet deposition has been investigated over western Europe, Scandinavia, and eastern North America (Brook 1995; Smith and Hunt 1978), with highly episodic areas tending to be downwind of major emission regions. In the global emissions hotspot of East Asia, however, previous reports have tended to focus on the long-term (e.g. annual, multi-year) wet deposition flux (Pu et al. 2017; Wang et al. 2012; Li et al. 2010), with less attention paid to the basic characteristics of pronounced and short-term changes in precipitation chemistry. Thus, there is a need to address this knowledge gap, particularly with respect to the occurrence of extreme rainfall events in the context of climate variability (Pei et al. 2016), but also considering that episodic wet deposition can have a significant biological impact too (Davies et al. 1992).
On 19–21 July 2016, an extreme torrential rain event swept across the North China Plain (NCP), resulting in the daily precipitation record being broken at Fangshan station, Beijing, where the amount reached 381.7 mm. This event was named the Beijing ‘720’ rainstorm, and provided a unique opportunity to examine the episodic features of rainstorms in the NCP. The primary goal of the present study was to investigate the spatial distribution of particle removal during this rainstorm event in the NCP. The in situ surface measurements from rainwater, particle composition, and gaseous pollutants in Beijing were also used to examine the scavenging efficiency of the compounds in the air and to provide insight into the wet deposition features of various species during this extreme rainstorm. Overall, our expectation was to provide results that are useful for determining the important sources contributing to wet deposition, validating the removal mechanisms for atmospheric chemistry models, and setting a baseline against which rainstorm chemistry changes can be assessed.

2. Experimental details

2.1. Measurement site

The rainwater sampling for chemical analysis was performed at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, in urban Beijing (39°58′ N, 116°22′ E). The site description is detailed in Pan et al. (2012).

2.2. Rainfall sampling and chemical analysis

Rainwater was sampled using an automatic collector (APS-2B, Changsha Xianglan Scientific Instruments Co., Ltd.), equipped with a 707-cm² aperture. The pretreatment and chemical analysis of the rainwater samples is described in Pan et al. (2010, 2013).

2.3. Supporting data

The submicron aerosol composition of PM₁ at the IAP site was measured with HR-ToF-AMS (Aerodyne Research, Inc., USA), following previously reported procedures (Zhang et al. 2014). In addition, the concentrations of PM₂.₅, SO₂, O₃, and NO₂ in the NCP were derived from the urban air quality real-time publishing platform of the China National Environmental Monitoring Centre (http://106.37.208.233:20035/) and the Beijing Municipal Environmental Protection Bureau (http://zx.bjmemc.com.cn/).

The rainfall amount in the NCP was obtained from the meteorological observation stations available at http://cdc.cma.gov.cn/. In addition, an automatic meteorological observation instrument (Millos520, Vaisala, Finland) at the IAP site was used to observe meteorological parameters, including relative humidity, temperature, wind direction, and wind speed.

3. Results and discussion

3.1. Spatial distribution of the removal of PM₂.₅ in the North China Plain

The extreme ‘720’ rainstorm covered the main NCP, as illustrated in Figure 1. The accumulated precipitation amounts ranged from 98.5 to 381.7 mm, averaging 231.7 mm from 20 stations in the Beijing region (Figure 1). To examine how the air pollutants were reduced due to this storm, the scavenging ratio (SR) of PM₂.₅ was calculated based on the equation below:

\[
\text{SR of PM}_2.5 = \left( \frac{C_b - C_a}{C_b} \right) \times 100\%.
\]

Here, \(C_b\) and \(C_a\) represent the concentration of air pollutants before and after the rain event, respectively. Since aerosol pollution in the NCP is regional in nature, the SR estimated here represents the overall reduction of aerosol concentrations at a large scale in addition to the local site. Regional transport/dispersion contributes approximately 30% of aerosol mass concentrations in Beijing (Tian, Pan, and Wang 2016), and this contribution was expected to have decreased during the storm due to the washing effect on aerosol loading in source regions, even though the wind speed was high.

The spatial distribution of the SR of PM₂.₅ is also shown in Figure 1 (dotted). As is apparent, the SR of PM₂.₅ in Hebei, Shandong, and Beijing was 75.8%–97.8%, 53.7%–95.8% and 89.4%–97.3%, respectively. The lower values in

Figure 1. Spatial distribution of the precipitation amount and scavenging ratio of fine particles during the ‘720’ rainstorm in 2016.
Shandong Peninsula were due to the lower precipitation amount. In contrast, the higher values were almost all located in the regions with high rainfall in the NCP. These findings indicate the efficient removal of particulate matter due to the storm. This is further evidenced from previous records in Beijing that short-term rainstorms have a stronger washing effect on PM$_{2.5}$ than that of light rain (Ouyang et al. 2015).

To examine the influences of rainfall on the concentrations of various air pollutants during the ‘720’ rainstorm, Figure 2 shows the time series of chemical species in the air and the meteorological parameters before, during, and after the storm at the Beijing site where chemical data were available. As shown, both the aerosol composition (PM$_{2.5}$ and PM$_{1}$, as well as organics, SO$_{4}^{2-}$, NO$_{3}^{-}$, NH$_{4}^{+}$, and Cl$^{-}$ in PM$_{1}$) and gaseous pollutants (SO$_{2}$, NO$_{2}$ and O$_{3}$) decreased rapidly after the storm began. In addition, most of these species shared a similar temporal pattern, with the exception of SO$_{2}$. The high wind speeds during the rain event may have brought air masses from outside Beijing into the IAP site and thus supplemented the levels of SO$_{2}$ (Guo et al. 2014). The precipitation scavenging ratio of various chemical species was also calculated, and is discussed below.

### 3.2. Scavenging ratio of air pollutants in urban Beijing

In general, the SRs of the mass concentrations and chemical compositions were higher than those of gaseous pollutants during the ‘720’ rainstorm (Table 1). For the PM$_{1}$ compositions, the SRs of NO$_{3}^{-}$, NH$_{4}^{+}$, Cl$^{-}$, and SO$_{4}^{2-}$ (~0.95) were higher than that of organics (0.85). The difference in the SR between the water soluble species and carbonaceous aerosols may have been due to their differences in water solubility (González and Aristizábal 2012; Pan and Wang 2015). However, the SRs of gaseous pollutants were lower than 0.65, except for O$_{3}$ (0.92). The large SR of O$_{3}$ may be attributable to the removal of precursors and the limited photochemical production of O$_{3}$.

We also calculated the SR for seven other rain events in July 2016 and found that the SRs of most species (except SO$_{2}$) correlated well with the rain intensity being greater than 2 mm h$^{-1}$. This finding indicates that rain intensity plays a more important role than the precipitation amount in the removal of air pollutants (González and Aristizábal 2012).

To further quantify the relative contributions of aerosol and gaseous pollutants to rainwater chemistry, we assumed that all the scavenged aerosol SO$_{4}^{2-}$ and SO$_{2}$ gas was incorporated into the rainwater collected at the surface site, and we then calculated the scavenging amount (SA) of sulfur in the air as follows:

\[
SA \text{ of SO}_4^{2-}-S = (C_b - C_a) \times 1.88/96;
\]

\[
SA \text{ of SO}_2-S = (C_b - C_a)/64.
\]

Here, $C_b$ and $C_a$ represent the concentrations of SO$_4^{2-}$ or SO$_2$ before and after the rain event, respectively; and 1.88 is the

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**Figure 2.** Hourly variation of precipitation, wind speed (WS), wind direction (WD) and concentrations of aerosol and gaseous pollutants during 18–22 July 2016.
The results show that the SA of SO$_4^{2-}$-S was 7.17 times that of SO$_2$-S, indicating that aerosol SO$_4^{2-}$ contributed 88% to rainwater sulfur during this storm. We also calculated the contribution of aerosol SO$_4^{2-}$ to rainwater sulfur during other events in July and found that the values ranged from 0.20 to 7.17. The values depended on both the precipitation amount ($R^2=0.59$, $p<0.05$) and rain intensity ($R^2=0.86$, $p<0.05$), indicating heavy rainfall removed more aerosol sulfate than gaseous SO$_2$. Due to the higher solubility of SO$_4^{2-}$, it was found that high sulfate SRs were associated with increased rain intensity in a mid-sized Andean city (González and Aristizábal 2012).

### 3.3. Wet deposition of water soluble species in urban Beijing

Figure 3 shows the concentrations and fluxes of water soluble ions in rainwater during the ‘720’ rainstorm and other rain events in July. The concentrations of ions during the ‘720’ storm were all lower than the other rainfall events recorded between December 2015 and November 2016 at the IAP site, due to the dilution effect of the extreme rainfall amount. With the exception of Mg$^{2+}$ and Ca$^{2+}$, the concentrations of ions during the ‘720’ storm are lower than the values observed in recent decades at the regional background site of Shangdianzi in the NCP (Pu et al. 2017; Li et al. 2010) and are comparable to the global background site of Waliguan in China (Pu et al. 2017). Thus, the precipitation chemistry observed in this study can serve as a baseline against which rainstorm chemistry changes in Beijing in the future can be assessed. The major ions during this storm were Ca$^{2+}$, NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$, with concentrations of 6.1, 1.7, 1.1, and 0.8 mg L$^{-1}$ (Table 2), respectively, which are orders of magnitude higher than those observed at high-altitude Himalayan stations in eastern India (Roy et al. 2016) and a southwest site of Mexico City, Mexico (Báez et al. 2007) or the background EMEP station in Víznar (Granada, Spain) (Calvo et al. 2010). This finding indicates that, although the major ions during this storm were the lowest on record at the IAP site, the rainwater chemistry in Beijing is significantly affected by anthropogenic emissions.

As shown in Table 2, the wet deposition fluxes of Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ were 18.8, 539.9, 0.8, 199.2, 1987.2, 31.52, 270.3, and 351.6 mg m$^{-2}$ d$^{-1}$, respectively, which contributed 3%, 21.8%, 0.4%, 22.1%, and
quality. On the other hand, various chemical species were simultaneously deposited via rainfall into the receiving terrestrial and marine ecosystems. As a result, wet deposition of this storm ranked the highest in 2016 and contributed substantially to the annual flux. In addition, the chemical compounds in rainwater collected during this storm originated both from below-cloud and in-cloud processing. This suggests, assuming that the occurrence of rainstorm events depends mainly on meteorological conditions, that decreases in annual wet deposition amounts due to future emissions reduction measures, could be offset by increases in the frequency of meteorological conditions conducive to such episodes (Brook 1995).

Disclosure statement
No potential conflict of interest was reported by the authors.

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Table 2. Concentrations and fluxes of water soluble species in rainwater collected during the '720' rainstorm and from December 2015 to November 2016.

| Unit   | Date        | Rain (mm) | Na⁺ | NH₄⁺ | K⁺ | Mg²⁺ | Ca²⁺ | Cl⁻ | NO₃⁻ | SO₄²⁻ |
|--------|-------------|-----------|-----|------|----|------|------|-----|------|-------|
| Conc.  | '720' rainstorm | 325.6     | 0.06| 1.66 | 0.00| 0.61 | 6.10 | 0.10| 0.83 | 1.08  |
| Conc.  | 2015–2016 mean | 3.1      | 4.8 | 8.0  | 2.2 | 17.2 | 9.9  | 28.7| 29.2 |
| Flux   | '720' rainstorm | 18.75 | 539.87 | 0.78 | 199.19 | 1987.20 | 31.52 | 270.31 | 351.62 |
| Flux   | 2015–2016 sum  | 787.5   | 615.3 | 2472.1 | 200.9 | 899.5 | 7330.9 | 1692.3 | 7150.4 | 6822.1 |
| %      |             | 41.4%    | 3.0% | 21.8% | 0.4% | 22.1% | 27.1% | 1.9% | 3.8% | 5.2% |

27.1%, 1.9%, 3.8%, and 5.2% of the annual deposition of these species between December 2015 and November 2016. This finding highlights that wet deposition during this storm had a more important influence on cations than anions. In addition, the wet deposition of inorganic nitrogen (NH₄⁺ and NO₃⁻) during this storm was even higher than the annual flux observed at five remote sites in the Tibetan Plateau (Liu et al. 2015) and in mountainous heathland ecosystems in northwestern Spain (Calvo-Fernández, Marcos, and Calvo 2017), indicating the importance of the nitrogen input during this storm for the receiving terrestrial and marine ecosystems.

The rainy season of the Beijing area is concentrated mainly in summer, and rainstorms often occur in late July and early August (Guo et al. 2015). During 1980–2010, the accumulated precipitation amounts in July contributed one-third of the annual precipitation in Beijing. The precipitation amount of the '720' rainstorm was 325.6 mm at the IAP site, which was 41.4% of the annual precipitation from December 2015 to November 2016. If the major source of certain pollutants dissolved in rainwater was entirely from cloud processing, the contribution of wet deposition of these species to the annual flux would be similar to that of the precipitation amount (41.4%). However, the contributions of these species were all lower than 41.4% (Table 2), indicating that the air pollutants were likely scavenged below-cloud first and then diluted by the cloud/rainwater (Celle-Jeanton et al. 2009). In future, we suggest the application of a sequential sampling technique to record detailed changes of precipitation chemistry during rainstorms at high temporal resolution (e.g. 5–10 min), thus allowing the differentiation of the in-cloud and below-cloud contribution to be determined.

4. Implications
In recent years, extreme torrential rainfall has often hit the NCP during the summer (Guo et al. 2015; Pei et al. 2016). During the period 19–21 July 2016, Beijing received approximately 232 mm of precipitation, averaged over 20 stations; and in the storm center, over 382 mm was recorded. On the one hand, the air pollutants were removed from the atmosphere efficiently during this storm, contributing significantly to the improvement of air
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