



Integration of field observation and air quality modeling to characterize Beijing aerosol in different seasons



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H I G H L I G H T S

- Increases in sulfate/EC and WSOC/EC were observed under humid winter conditions.
- Formation of secondary organic and inorganic aerosols may be related.
- Large gaps existed between the observational and modeling results in winter.
- RH exhibited little influence on sulfate/EC and WSOC/EC in summer.
- The observed and modeled results were generally comparable in summer.

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A B S T R A C T

Fine particulate matter (PM_{2.5}) pollution in Beijing was investigated based on field observation and air quality modeling. Measurement results showed that when using elemental carbon (EC) as the reference component, concurrent increases were observed in the relative abundances of sulfate, nitrate, organic carbon (OC) and water-soluble organic carbon (WSOC) when RH exceeded ~65% during winter. The observed increases could not be explained by variations of primary biomass burning emissions, instead they likely pointed to heterogeneous chemistry and presumably indicated that formation of secondary inorganic and organic aerosols might be related during winter haze events in Beijing. Large gaps were found in winter when comparing the observational and modeling results. In summer, RH exhibited little influence on the observed sulfate/EC, OC/EC or WSOC/EC, and the observed and modeled results were in general comparable for the concentrations of sulfate, EC and OC. This study suggests that distinct yet poorly-understood atmospheric chemistry may be at play in China's winter haze events, and it could be a substantial challenge to properly incorporate the related mechanisms into air quality models.

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1. Introduction

Intensive measures have been taken in China to improve air quality and to control the fine particulate matter (PM_{2.5}) pollution in particular, following the "Action Plan on Prevention and Control of Air Pollution" and the "Three-Year Action Plan for Winning the

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Blue Sky Defense Battle" released by the State Council in 2013 and 2018, respectively (Wang et al., 2017; Cheng et al., 2019). Despite a nationwide decrease in PM_{2.5} concentration, 56% of the 338 cities at or above prefecture level still failed to meet the national air quality standard of PM_{2.5} (i.e., 35 µg/m³ for annual average) in 2018 and this percentage was as high as 83% for the 169 key cities identified by the Ministry of Ecology and Environment (MEE, 2019). In addition to the annual average concentration, another substantial concern on PM_{2.5} in China is the heavily-polluted episodes which typically occurred in winter (or autumn) and lasted a couple of days, e.g., the winter haze events in Beijing with hourly PM_{2.5} concentrations occasionally exceeding 500 µg/m³ (Wang et al., 2014a; Sun et al., 2016). These episodes gave rise to numerous studies, including international research initiatives (Shi et al., 2019), on formation mechanisms of the severe PM_{2.5} pollution (An et al., 2019). Focuses of these studies were extensive, including new particles (Guo et al., 2014; Yao et al., 2018), secondary organic and inorganic aerosols (Huang et al., 2014a; Cheng et al., 2016b), aerosol mixing state (Peng et al., 2016), aerosol phase (Liu et al., 2017b), meteorological conditions (Cai et al., 2017), interactions between aerosol and the planetary boundary layer (Ding et al., 2016; Zhong et al., 2019), etc. Interestingly, some studies suggested that the PM_{2.5} pollution in Chinese megacities (or city clusters) might be subject to distinct yet poorly-understood atmospheric chemistry (e.g., "haze chemistry"; Cheng et al., 2016b) that is rarely seen in North America or Europe and is missing in most air quality models. Therefore, haze in China undoubtedly merits further exploration.

Each step along the way between the source and fate of PM_{2.5} is complex, at least partially due to the difficult challenges in PM_{2.5} measurement and simulation. For example, although air quality models could in general reproduce the observed sulfate concentrations in the United States and Europe (Park et al., 2004; Walker et al., 2012; Shah et al., 2018), they were found to substantially underestimate sulfate during severe haze events in China (Wang et al., 2014b; Zheng et al., 2015a; Chen et al., 2016). This underestimation indicates atmospheric chemistry is more complex in China and may be due to many factors such as the catalytic effects of mineral dust (Dupart et al., 2012; He et al., 2014; Huang et al., 2014b; Nie et al., 2014; Park et al., 2017; Ma et al., 2018), reactions in aerosol water (Cheng et al., 2016b; Wang et al., 2016), reactions on droplet surface (Hung and Hoffmann, 2015) and misidentification of hydroxymethanesulfonate (HMS) as sulfate (Moch et al., 2018; Song et al., 2019). Discrepancies between the observational and modeling results are also considerable for nitrate, ammonium and carbonaceous components, not only in China but also elsewhere (Philip et al., 2014). This is particularly the case for carbonaceous components which have much larger uncertainties in observational data (e.g., separation of organic carbon and black carbon; Petzold et al., 2013) compared to the inorganic ions. Given that black carbon (BC) has not been unambiguously defined yet, here we use BC as a qualitative and descriptive term, and use other terms to specify BC results from different measurement principles (e.g., elemental carbon), as suggested by Petzold et al. (2013).

In this study, field observation and air quality modeling were integrated to investigate the PM_{2.5} pollution in Beijing. An improved measurement method was used to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC). Based on the refined OC and EC results, we started with the observed aerosol properties during winter in Beijing, followed by a comparison of the observational and modeling results on several major chemical components of PM_{2.5}. Results from summer were also investigated.

2. Methods

2.1. Field observation

Measurement results on PM_{2.5} chemical compositions, which were derived from two campaigns conducted during the summer (from 2 August to September 1; $N = 30$; Cheng et al., 2017) and winter (from 7 to 31 December; $N = 24$; Cheng et al., 2016a; Liu et al., 2019) of 2011 in Beijing, were re-visited in this study. Briefly, 24-h integrated PM_{2.5} samples were collected at an urban site (40.00° N, 116.32° E) located on the campus of Tsinghua University. The sampling was done by a high-volume sampler (Thermo Scientific, MA, USA) operated at a flow rate of 1.13 m³/min, using pre-baked quartz-fiber filters (8 in × 10 in, 2500 QAT-UP; Pall Corporation, NY, USA). Loaded filters were cut into punches with diameter of 47 mm and then used for the subsequent laboratory analyses. The chemical components quantified were OC, EC, water-soluble organic carbon (WSOC), water-insoluble organic carbon (WIOC, calculated as the difference between OC and WSOC), levoglucosan and water-soluble inorganic ions including sulfate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺). Compared to other studies, determination of OC and EC was improved in these two campaigns such that charring of OC, which has long been recognized as the major source of uncertainties in thermal-optical analysis, was significantly reduced by extracting the loaded filters using methanol. Details refer to Cheng et al., 2016a, 2017) and Liu et al. (2019). For the present study, it is expected that a better understanding of Beijing aerosol may be achieved by using the refined OC and EC measurement results.

2.2. Air quality modeling

A revised Community Multi-scale Air Quality (CMAQ) model (based on version 5.0.1; Hu et al., 2016a) was used to simulate the mass concentration and chemical composition of PM_{2.5} for the measurement period (i.e., August and December 2011). Compared to the original version, changes were made in the revised CMAQ to involve heterogeneous pathways for the formation of secondary organic aerosol (SOA) and secondary inorganic aerosol. The newly-added heterogeneous pathways were associated with reactive uptake of gaseous species, including (1) SO₂ for sulfate, (2) NO₂ for nitrate, (3) isoprene epoxydiols (IEPOX), methacrylic acid epoxide, glyoxal and methylglyoxal for isoprene SOA, and (4) glyoxal and methylglyoxal for SOA from other volatile organic compounds such as monoterpenes, alkanes and aromatics (Hu et al., 2016a). Exact heterogeneous mechanism was not identified in this study, instead the heterogeneous chemistry was parameterized based on apparent (i.e., bulk) reactive uptake coefficients (Hu et al., 2016a). Using the revised CMAQ, simulations were performed over East Asia with a horizontal resolution of 36 × 36 km as described in Hu et al. (2016a). To compare with the observational data, modeling results were obtained for the grid cell where the sampling site is located.

3. Results and discussion

3.1. Aerosol properties observed during winter in Beijing

For a receptor site such as that of the present study, temporal variations of aerosol properties can be driven by many factors such as the changes in primary emissions of particulate matter and gaseous precursors, atmospheric processes and meteorological conditions. It is essentially difficult, if not impossible, to robustly isolate the contribution of each factor. For the winter campaign, it

was found that the variations of aerosol sources could be partially revealed by the levoglucosan results. Despite some debates on its atmospheric stability (Hennigan et al., 2010) and its additional sources (e.g., coal combustion; Yan et al., 2018), levoglucosan has been and is still being widely used as a tracer for biomass burning. As shown in Fig. 1a, the winter samples could be separated into two groups according to their levoglucosan to OC ratios, which averaged $0.58 \pm 0.12\%$ ($N = 7$; Case A) and $1.23 \pm 0.14\%$ ($N = 17$; Case B) on a basis of carbon mass, respectively. EC concentrations were also much lower for Case A (averaging $3.35 \pm 0.62 \mu\text{g}/\text{m}^3$) compared to Case B (averaging $9.01 \pm 2.97 \mu\text{g}/\text{m}^3$) (Fig. 1b). In addition, these two cases were associated with quite different meteorological conditions. Case A had relatively low RH (averaging $33 \pm 4\%$) and was typically impacted by air coming from the northwest and descending from aloft, whereas Case B had substantially higher RH (averaging $53 \pm 13\%$) and was more strongly impacted by horizontal flow passing over the regions surrounding Beijing (including the south). Therefore, Cases A and B differed significantly in aerosol sources, source areas and meteorological conditions, indicating that they should be investigated separately.

Case A was relatively clean. Although $\text{PM}_{2.5}$ mass concentration was not measured in this study, it was constructed as the sum of organic matter (OM, calculated as $1.6 \times \text{OC}$; Turpin and Lim, 2001), EC and water-soluble inorganic ions (including five cations and three anions). Both the mass concentrations (averaging $19.91 \pm 1.68 \mu\text{g}/\text{m}^3$) and chemical compositions of the constructed $\text{PM}_{2.5}$ were found to be generally comparable among the Case A samples. The majority (i.e., 64%) of the constructed $\text{PM}_{2.5}$ could be attributed to the carbonaceous components, such that the contributions of EC, water-insoluble OM (calculated as $1.6 \times \text{WIOC}$) and water-soluble OM (calculated as $1.6 \times \text{WSOC}$) were 17, 28 and 19%, respectively (Fig. 2e). Sulfate, nitrate and ammonium (SNA) constituted another 24% of the constructed $\text{PM}_{2.5}$ while the contributions of chloride and metal cations (i.e., Na^+ , K^+ , Mg^{2+} and Ca^{2+}) were 4 and 8%, respectively (Fig. 2e). It was also noticed that when using EC as the reference component, the relative abundances of sulfate, nitrate, OC and WSOC were largely comparable among the Case A samples (Fig. 2a–d).

Case B was more polluted, with an average concentration of $88.43 \pm 37.26 \mu\text{g}/\text{m}^3$ for the constructed $\text{PM}_{2.5}$. Unlike Case A, the sulfate/EC, nitrate/EC, OC/EC and WSOC/EC ratios exhibited dependences on RH for Case B, as all the ratios increased substantially once RH exceeded $\sim 65\%$ (Fig. 2a–d). The Case B samples were further separated into two subgroups, i.e., Cases B1 and B2, using a

RH value of 65% as the threshold. Constructed $\text{PM}_{2.5}$ averaged 75.45 ± 22.29 and $119.57 \pm 49.68 \mu\text{g}/\text{m}^3$ for Cases B1 and B2, respectively. The contribution of carbonaceous components to the constructed $\text{PM}_{2.5}$ decreased from 61% for Case B1 to 54% for Case B2 whereas the contribution of SNA increased from 27% to 36% (Fig. 2e). The comparison between Cases B1 and B2 points to the links between high $\text{PM}_{2.5}$ concentrations, high RH levels and increased importance of SNA, which have been repeatedly observed during winter in Beijing (Sun et al., 2014; Zheng et al., 2015b; Elser et al., 2016; Hu et al., 2016b; Li et al., 2019).

Compared to Case B1, the large increases in both the sulfate/EC and nitrate/EC ratios observed for Case B2 (Fig. 2a and b) presumably indicated enhanced SO_4^{2-} and NO_3^- formation under the humid conditions, i.e., when RH was above $\sim 65\%$, during the winter campaign. For this enhancement, heterogeneous reactions might play an important role. Recently, a variety of studies have been conducted to investigate the sulfate formation mechanisms during winter in Beijing, with a focus on the high RH periods when enhanced sulfate formation was frequently observed. These studies indicated the presence of heterogeneous pathways that are missing in most air quality models (Zheng et al., 2015a; Chen et al., 2016), e.g., oxidation of SO_2 in aerosol water by NO_2 (Xie et al., 2015; Cheng et al., 2016b; Wang et al., 2016, 2018; Xue et al., 2016; Li et al., 2018; Chen et al., 2019), O_2 (catalyzed by transition metal ions; Fu et al., 2016; Li et al., 2017; Shao et al., 2019), H_2O_2 (Ye et al., 2018a; Fang et al., 2019), nitrate (after photolysis; Gen et al., 2019) and organic peroxides (Ye et al., 2018b). However, the relative importance of these reactions remains highly uncertain, leading to intense debates which are still ongoing. For example, several studies suggested that the heterogeneous sulfate formation was dominated by the NO_2 reaction pathway under the heavy haze conditions in winter (e.g., Cheng et al., 2016b; Wang et al., 2016), whereas the assumptions involved (e.g., about the acidity of the aerosol water and the ambient concentrations of H_2O_2) and therefore the conclusions derived were challenged by other investigators (Guo et al., 2017; Liu et al., 2017a; Ye et al., 2018a).

Similar to the sulfate/EC and nitrate/EC ratios, the OC/EC ratios were also considerably higher for Case B2 than B1 (Fig. 2c). The same pattern was observed for WSOC/EC (Fig. 2d), which were almost doubled for Case B2 (averaging 1.71 ± 0.29) compared to B1 (averaging 0.98 ± 0.11). It should be noted that this increase might not be attributed to changes in primary biomass burning emissions, as all the Case B samples had comparable levoglucosan to OC ratios (Fig. 1a). Given that WSOC was strongly associated with SOA during

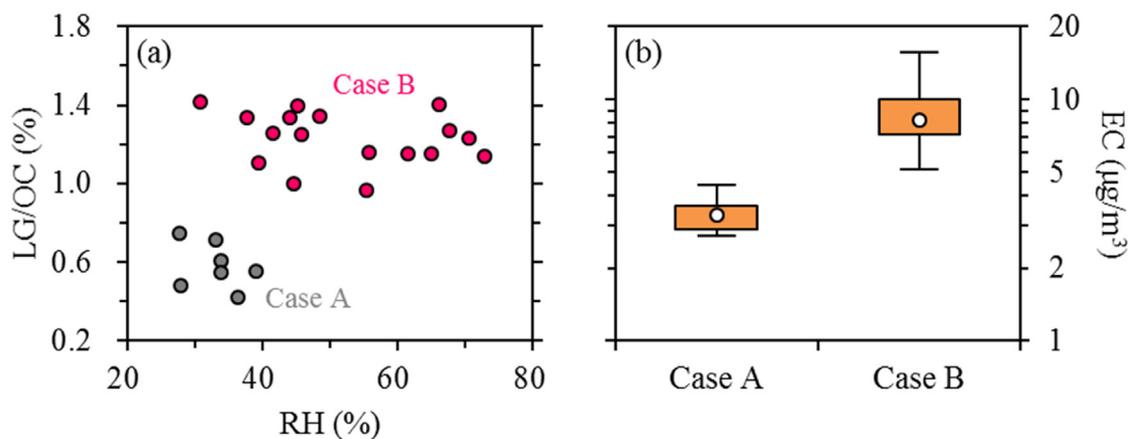


Fig. 1. (a) Levoglucosan to OC ratios (LG/OC; on a basis of carbon mass) and the corresponding RH values measured during winter in Beijing. (b) Comparison of observed EC concentrations between different groups of samples (i.e., Cases A and B) which were identified based on LG/OC. Lower and upper box bounds indicate the 25th and 75th percentiles, the whiskers above and below the box indicate the maximum and minimum, and the open circle within the box marks the median.

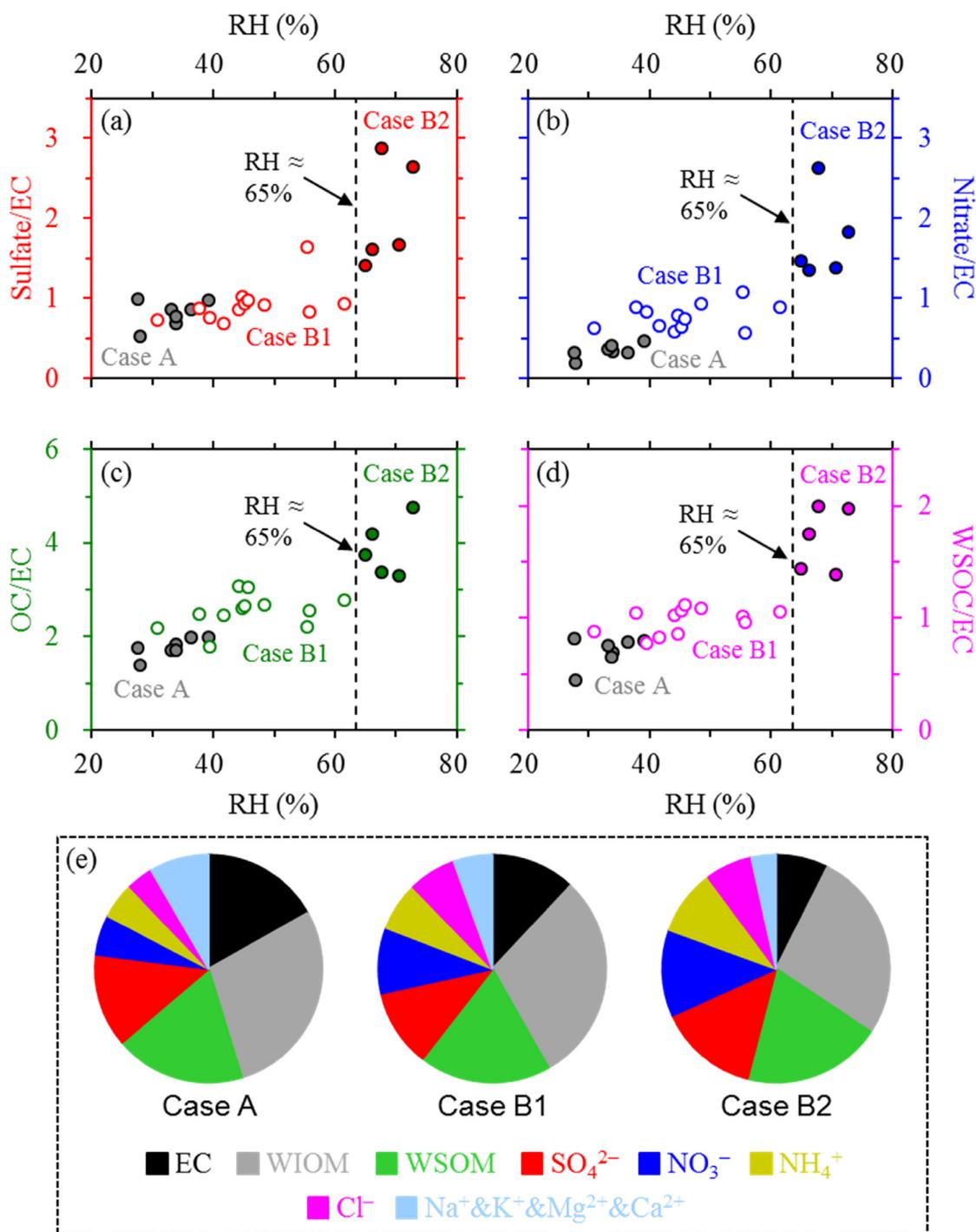


Fig. 2. Dependences of (a) sulfate/EC, (b) nitrate/EC, (c) OC/EC and (d) WSOC/EC on RH observed during winter in Beijing. The Case B samples were further separated into two groups (i.e., Cases B1 and B2) based on the dependences. Shown in (e) are the average PM_{2.5} compositions measured for the different groups of samples. Influences of EC measurement uncertainties on the comparisons shown here are discussed in Supplementary material (Section S1).

winter in Beijing (Zhang et al., 2018), SOA formation was likely also enhanced during Case B2 (i.e., under the conditions with RH above ~65%), and heterogeneous reactions might be largely responsible for this enhancement (Ziemann and Atkinson, 2012; Shrivastava et al., 2017). In addition to the present study, the concurrent increases in the relative abundances of sulfate, nitrate and SOA were also observed for the high RH conditions during December 2010 in Beijing (Hu et al., 2016b). In that study, observational results were derived from an aerosol mass spectrometer and an Aethalometer

for the non-refractory components and equivalent black carbon (eBC), respectively. The authors found that the sulfate/eBC, nitrate/eBC, OA/eBC and OOA/eBC ratios (OA and OOA stand for organic aerosol and oxygenated organic aerosol, respectively) increased by ~300%, 100%, 40% and 170%, respectively, during the winter periods with relatively high RH (above 60%) compared to the low RH (averaging ~30%) events. It seems that under humid winter conditions in Beijing, there may exist links between enhanced formation of secondary organic and inorganic aerosols (Ye et al., 2018b).

The discussions above do not necessarily mean that high RH will always enhance secondary inorganic and organic aerosols formation concurrently. For example, based on two campaigns conducted during the winters of 2014–2015 and 2017–2018 in Beijing, Li et al. (2019) found that the sulfate/eBC and nitrate/eBC ratios increased considerably under high RH conditions whereas the OOA/eBC ratio was largely unchanged. Similar results were observed by Zheng et al. (2015b) for January 2013. Regarding the influences of RH on SOA formation, the contrast between various studies indicates that atmospheric chemistry was rather complex during winter haze events in Beijing.

3.2. Comparison of field- and model-based aerosol properties during winter

The observed concentrations of sulfate, i.e., $(\text{SO}_4^{2-})_{\text{obs}}$, averaged 2.63 ± 0.18 , 8.32 ± 3.00 and $17.02 \pm 6.01 \mu\text{g}/\text{m}^3$ for Cases A, B1 and B2 when the average RH were 33 ± 4 , 46 ± 9 and $68 \pm 3\%$, respectively, indicating an increasing trend of sulfate concentration with increasing RH. This trend was also supported by results from Du et al. (2014), which covered the period included by the modeling but not involved in the field campaign (i.e., 1 to 7 December, 2011). During this period, the average RH and $(\text{SO}_4^{2-})_{\text{obs}}$ were as high as $86 \pm 10\%$ and $32.07 \pm 9.79 \mu\text{g}/\text{m}^3$, respectively. As shown in Fig. 3a,

for the whole month of December, the positive dependence of $(\text{SO}_4^{2-})_{\text{obs}}$ on RH could be approximated by an exponential relationship ($R^2 = 0.87$). However, this relationship could not be properly reproduced when using the modeled sulfate concentrations, i.e., $(\text{SO}_4^{2-})_{\text{mod}}$ (Fig. 3b). Most noticeably, $(\text{SO}_4^{2-})_{\text{mod}}$ were significantly higher than $(\text{SO}_4^{2-})_{\text{obs}}$ for the majority of the samples with RH above 60%, by as much as ~140–480%. This large discrepancy may be attributed to the parameters currently applied for heterogeneous SO_2 chemistry involved in the revised CMAQ, e.g., it seems that the assumed reactive uptake coefficient (γ) of SO_2 (i.e., 5×10^{-5} ; Hu et al., 2016a) should be scaled down. But $(\text{SO}_4^{2-})_{\text{mod}}$ were not always higher than $(\text{SO}_4^{2-})_{\text{obs}}$. Instead, they were comparable when RH was below 60%, and for two of the 11 sampling events when RH exceeded 60%. Thus a constant γ appeared not effective for the simulation of the wintertime sulfate. One may argue that the discrepancies between $(\text{SO}_4^{2-})_{\text{mod}}$ and $(\text{SO}_4^{2-})_{\text{obs}}$ might be able to be reduced by using RH-dependent γ rather than a constant value. As indicated by Fig. 3b, the currently used γ value (i.e., 5×10^{-5}) appeared suitable for the RH range of 0–60%. Given that a positive correlation is typically used to describe the dependence of γ on RH (Wang et al., 2012; Zheng et al., 2015a), γ values larger than 5×10^{-5} should be assigned for the RH range of 60–100% under the assumption that γ is RH-dependent. This will increase $(\text{SO}_4^{2-})_{\text{mod}}$ and therefore the discrepancies

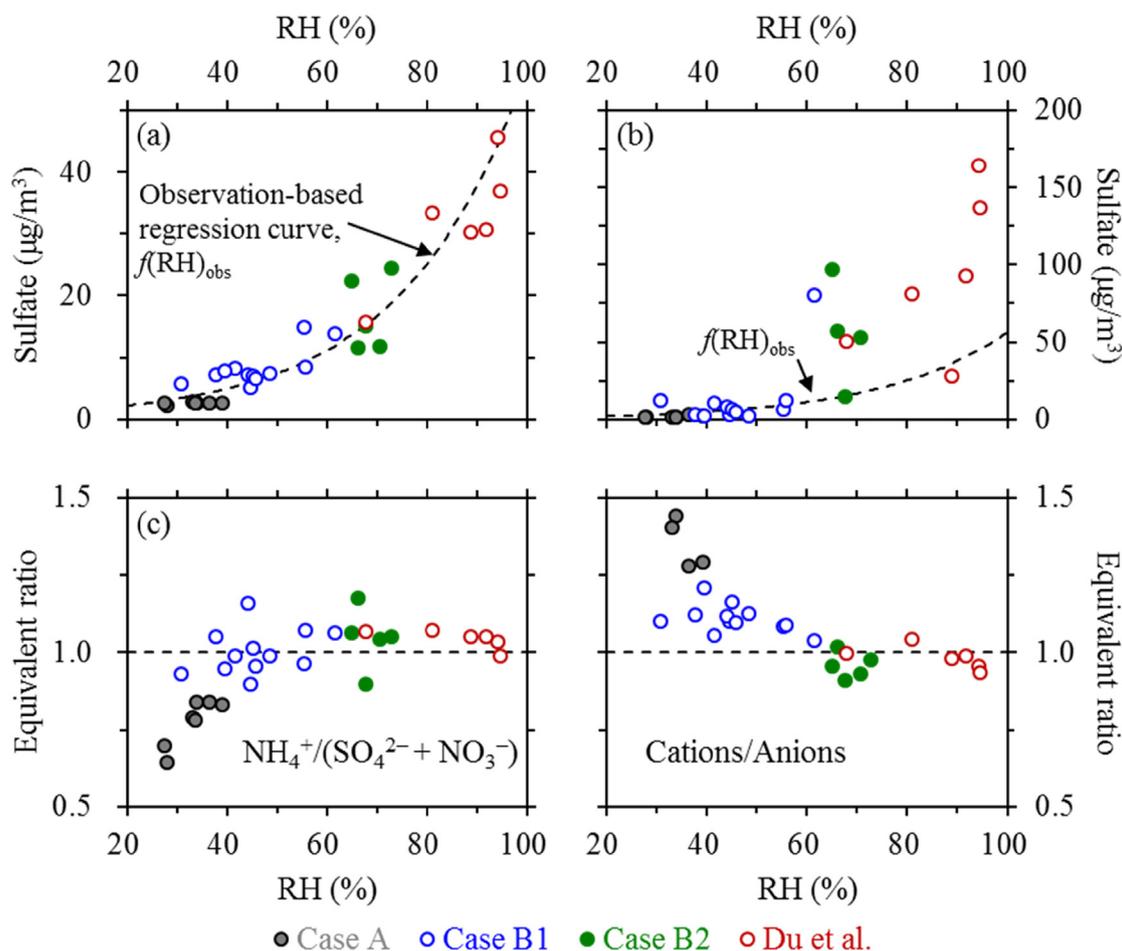


Fig. 3. Dependences of the (a) observed and (b) simulated sulfate concentrations on RH during winter in Beijing. Additional measurement results were taken from Du et al. (2014) for the winter period covered by the simulation but not involved in the field campaign. In (a), the dashed curve indicates the exponential regression result. This curve is also presented in (b) to show that the revised CMAQ model fails to reproduce the observed dependence of sulfate on RH. Also shown are (c) the equivalent ratios of ammonium to the sum of sulfate and nitrate and (d) the equivalent ratios of total cations to anions. The equivalent ratios are measurement-based. The dashed lines in (c) and (d) indicate an equivalent ratio of 1.

between $(\text{SO}_4^{2-})_{\text{mod}}$ and $(\text{SO}_4^{2-})_{\text{obs}}$ for the samples with RH above 60%, which does not support the use of RH-dependent γ . The discussions above point to the limitation of using the apparent γ (either constant or RH-dependent), although this approach was shown to be effective by some of the previous studies (e.g., Wang et al., 2014b; Zheng et al., 2015a). Exact heterogeneous mechanisms seem to be more appropriate for simulating wintertime sulfate. As shown in Fig. 3c and d, the cations were in general abundant enough to neutralize the anions during December in Beijing, which may favor the oxidation of SO_2 by NO_2 in aerosol water, i.e., the NO_2 reaction pathway (Cheng et al., 2016b; Wang et al., 2016). Additional discussions on heterogeneous sulfate formation are presented in Supplementary material (Section S2). Anyhow, the CMAQ model will be further modified in our future studies to quantitatively evaluate the relevance of various heterogeneous pathways for sulfate formation.

For the carbonaceous components, the modeled OC and EC concentrations (OC_{mod} and EC_{mod}) exhibited a strong positive correlation ($R^2 = 0.99$), leading to relatively constant OC_{mod} to EC_{mod} ratios during winter in Beijing. As shown in Fig. 4a for the measurement period of Cheng et al., 2016a), the OC_{mod} to EC_{mod} ratios, i.e., $(\text{OC}/\text{EC})_{\text{mod}}$, varied from ~ 1.7 to 2.0 with an average of 1.82 ± 0.09 . Unlike the observed OC/EC, i.e., $(\text{OC}/\text{EC})_{\text{obs}}$, the simulated ratio exhibited little dependence on RH (Fig. 4b). Importantly, the discrepancy between $(\text{OC}/\text{EC})_{\text{mod}}$ and $(\text{OC}/\text{EC})_{\text{obs}}$ was found to become more significant with increasing RH (Fig. 4c). For the Case A samples, $(\text{OC}/\text{EC})_{\text{mod}}$ were in general comparable with the observational results such that their differences averaged 0.05 ± 0.21 . However, $(\text{OC}/\text{EC})_{\text{mod}}$ were always lower than $(\text{OC}/\text{EC})_{\text{obs}}$ for Case

B1, by 0.76 ± 0.37 on average. The largest differences between $(\text{OC}/\text{EC})_{\text{mod}}$ and $(\text{OC}/\text{EC})_{\text{obs}}$ were observed for Case B2 when the modeling results were 1.71 ± 0.32 lower than the observational ones. It is noticed that the modeled contribution of secondary OC (SOC) to OC was as low as $\sim 10\%$, substantially lower than the observational results which were typically between 30 and 60% during winter in Beijing (Zhang et al., 2014; Hu et al., 2016b; Sun et al., 2016, 2018; Li et al., 2019). Thus the under-prediction of OC/EC by the revised CMAQ (Fig. 4c) should be largely associated with the underestimation of SOC by the model. It is for sure that the model had uncertainties in simulating primary particulate components (e.g., EC) as well (Fig. S6), which could be partially responsible for this under-prediction. Anyhow, Fig. 4 suggests that although the revised CMAQ had involved heterogeneous pathways for several VOCs, it still could not properly reproduce the observed abundance and temporal variation of organic aerosol during winter in Beijing, especially for the humid and heavily-polluted conditions like Case B2.

3.3. Comparison of field- and model-based aerosol properties during summer

The observed EC concentrations (EC_{obs}) averaged $3.96 \pm 1.35 \mu\text{g}/\text{m}^3$ during the summer campaign in Beijing, comparable with results from the relatively clean case in winter (i.e., Case A) but substantially lower than Cases B1 and B2. Unlike EC_{obs} , the average $(\text{SO}_4^{2-})_{\text{obs}}$ concentration was considerably higher in summer ($24.23 \pm 16.08 \mu\text{g}/\text{m}^3$) compared to all the three cases in winter. Therefore, the summer samples exhibited much higher $(\text{SO}_4^{2-})_{\text{obs}}$

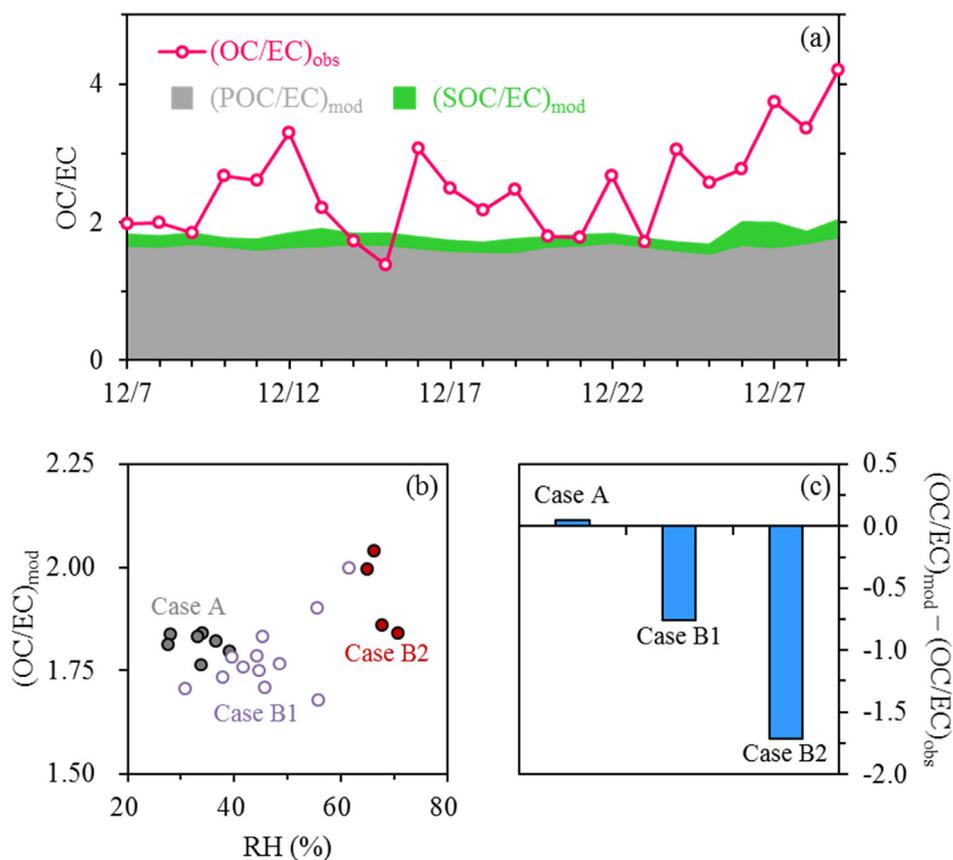


Fig. 4. (a) Daily variations of the observed and simulated OC/EC, i.e., $(\text{OC}/\text{EC})_{\text{obs}}$ and $(\text{OC}/\text{EC})_{\text{mod}}$, during winter in Beijing. $(\text{OC}/\text{EC})_{\text{mod}}$ is shown as the sum of the primary OC (POC) to EC ratio and the secondary OC (SOC) to EC ratio. (b) Dependence of $(\text{OC}/\text{EC})_{\text{mod}}$ on RH, which differs from the pattern observed for $(\text{OC}/\text{EC})_{\text{obs}}$ as shown in Fig. 2c. (c) Differences between the simulated and observed OC/EC for different groups of samples.

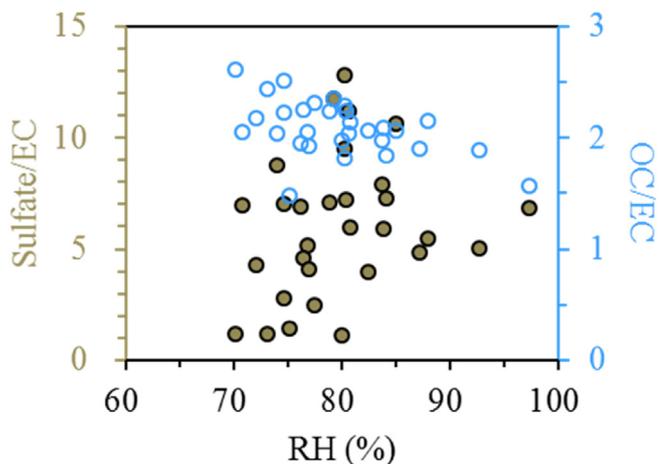


Fig. 5. Dependences of sulfate/EC and OC/EC on RH observed during summer in Beijing.

EC_{obs} ratios (varying between ~ 1 and 13 with an average of 6.01 ± 3.21 ; Fig. 5) than winter when $(SO_4^{2-})_{obs}/EC_{obs}$ averaged 0.81 ± 0.16 , 0.93 ± 0.25 and 2.04 ± 0.66 for Cases A, B1 and B2, respectively (Fig. 2a). Comparison of Figs. 2a and 5 also suggested that the summer and winter samples exhibited quite different relationships between $(SO_4^{2-})_{obs}/EC_{obs}$ and RH, i.e., the large increase in $(SO_4^{2-})_{obs}/EC_{obs}$ under high RH conditions observed during winter could not be seen in summer. Thus it was inferred that heterogeneous reactions may not be an important contributor for sulfate production during summer in Beijing. This inference was supported by the comparable $(SO_4^{2-})_{obs}$ and $(SO_4^{2-})_{mod}$ in August (Fig. 6a), given that the heterogeneous SO_2 chemistry involved in the revised CMAQ only had a minor contribution to $(SO_4^{2-})_{mod}$ during summer (Fu et al., 2016).

The observed OC concentrations (OC_{obs}) averaged $8.17 \pm 2.68 \mu gC/m^3$ in August, higher than Case A (averaging $5.85 \pm 0.68 \mu gC/m^3$) but considerably lower than Cases B1 and B2 in winter (averaging 22.88 ± 7.21 and $34.82 \pm 16.86 \mu gC/m^3$, respectively). Regarding $(OC/EC)_{obs}$, the ratios did not vary significantly during summer (Fig. 5), with an average of 2.09 ± 0.25 which was higher

than Case A (averaging 1.77 ± 0.21) but lower than Cases B1 and B2 (averaging 2.54 ± 0.36 and 3.87 ± 0.62 , respectively). Fig. 5 also suggests that $(OC/EC)_{obs}$ was largely independent of RH in summer while the same trend was found for the $(WSOC/EC)_{obs}$ ratio (Fig. S7), presumably indicating that heterogeneous chemistry did not contribute considerably to SOA formation during summer in Beijing. In addition, as shown in Figs. 6b and 7 for summer, the model could in general reproduce the magnitude of not only EC_{obs} but also $(OC/EC)_{obs}$ and, moreover, the modeled SOA/OA ratios were largely comparable with the observed WSOC/OC ratios. Thus the model's performance in simulating carbonaceous aerosol was much better in summer compared with winter, which may be associated with the seasonal difference in the relative importance of heterogeneous SOA chemistry.

4. Conclusions

Field observation and the CMAQ model were combined to investigate the $PM_{2.5}$ pollution in Beijing. For the winter samples with comparable levoglucosan to OC ratios (i.e., Cases B1 and B2), the observed sulfate/EC, nitrate/EC, OC/EC and WSOC/EC ratios increased substantially once RH exceeded $\sim 65\%$, indicating enhanced formation of secondary inorganic and organic aerosols possibly through heterogeneous pathways. In some of the previous studies conducted during winter in Beijing, however, no observational evidence could be found for enhanced SOA formation under high RH conditions, pointing to the complexity of atmospheric chemistry for China's winter haze events. This complexity could also be seen from the discrepancies between the observational and modeling results. In winter, the model failed to reproduce the observed dependence of sulfate on RH, although a heterogeneous pathway, which was parameterized using an apparent reactive uptake coefficient of SO_2 , had been involved for sulfate simulation. Maybe exact heterogeneous mechanism is required to properly simulate the wintertime sulfate. In winter, the model also failed to reproduce the observed magnitude and temporal variation of OC/EC, partially due to the underestimation of SOA. The gaps between the observational and modeling results were much smaller in summer, when heterogeneous chemistry appeared not that important. This study highlights the importance of heterogeneous

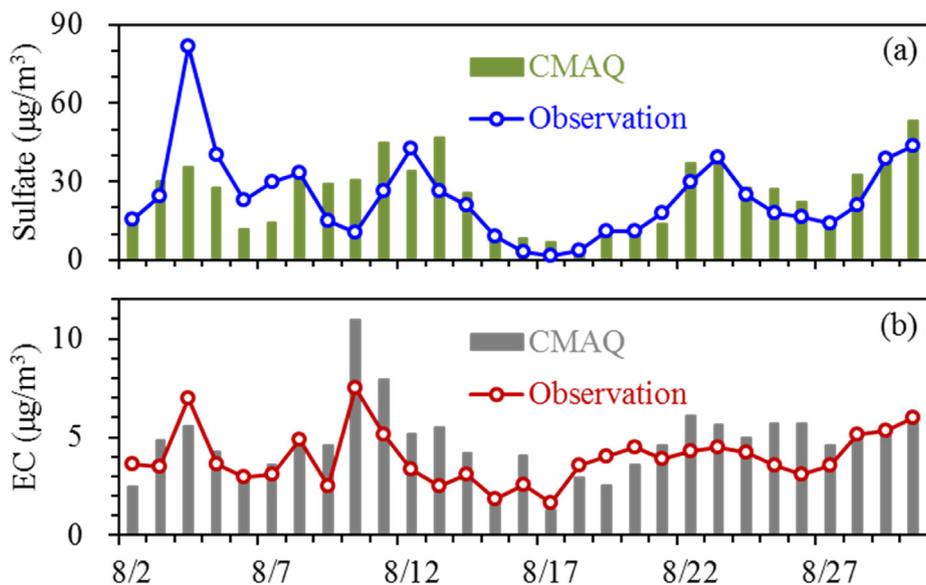


Fig. 6. Daily variations of the observed and simulated (a) sulfate and (b) EC concentrations during summer in Beijing.

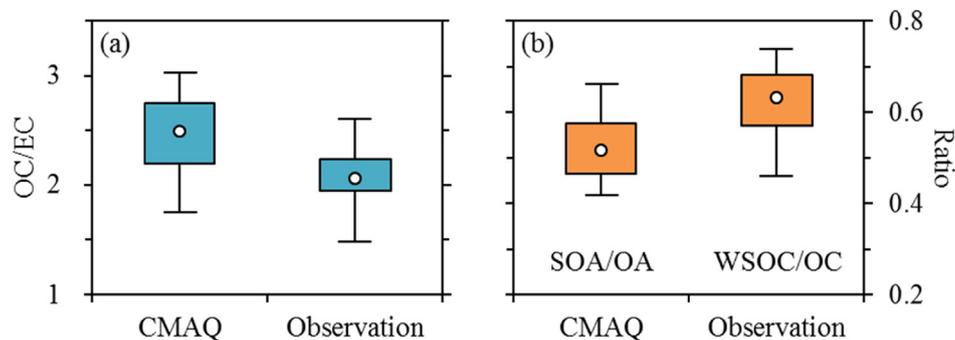


Fig. 7. (a) Comparison of field observation and the revised CMAQ model for the determination of OC/EC. (b) Comparison of the modeled SOA/OA and the observed WSOC/OC. Results in both (a) and (b) are for August. Box plot description is given in Fig. 1.

chemistry for understanding the winter haze events in China.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125195>.

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