

General Comments:

The manuscript by Cheng et al. investigated the characteristics of haze pollution during two sequential heating seasons in the central city of the Harbin-Changchun (HC) metropolitan area, with a focus on the major drivers responsible for the observed inter-annual variations of aerosol composition. Compared to traditional hotspots of air pollution studies in China (e.g., the North China Plain), HC is unique with respect to both meteorological conditions (e.g., the extremely cold winter) and anthropogenic emissions (e.g., those from the intensive energy use for central and space heating). Therefore, observational results from this region may provide additional insights into haze pollution in China. However, PM_{2.5} in HC remains largely unexplored with limited studies, which may explain the relatively slow improvement of air quality in HC compared to the North China Plain. In this context, the authors did a good job of unfolding the chemical compositions and sources of PM_{2.5} in HC. Many in the community of atmospheric science would be interested in the results presented. My overall assessment is that this manuscript could be considered for publication in ACP given the following concerns (mostly technical) could be properly addressed.

Specific comments

(1) Line 54, suggest changing “aerosol” to “aerosols”.

Our responses: The change was made as suggested (see line 54).

(2) Line 58, “its effects on SOA...” should be better.

Our responses: The change was made as suggested (see line 58).

(3) Line 97, suggest removing the “the” after “with”; in addition, references should be provided for “limited studies”.

Our responses: The changes were made as suggested (see lines 98-99).

(4) Line 177, as indicated by the PMF source profiles, it seems that zero EC was apportioned into the two factors representing secondary aerosols. Please confirm and revised the description if necessary.

Our responses: Yes, zero EC was apportioned into the secondary-aerosol factors. This point was clarified in the revised manuscript (see line 168).

(5) Lines 207-208, I think the “during 2019-2020” here is redundant and unnecessary.

Our responses: The phrase was removed as suggested (see lines 274-275).

(6) Lines 227-228, rephrase “the same OC average concentrations”.

Our responses: The phrase was revised to “the same OC levels” (see lines 294-295).

(7) Line 235, references should be provided for the ISORROPIA model.

Our responses: References were added as suggested (see line 148).

(8) Line 249, suggest adding a “usually” before “not”.

Our responses: The change was made as suggested (see line 332).

(9) Line 261, suggest adding a “the” before “positive”.

Our responses: The change was made as suggested (see line 344).

(10) Line 287, the meaning of “those” is not clear enough.

Our responses: “Those” was changed to “the corresponding values” for clarity (see line 370).

(11) Line 291, references are necessary for this statement.

Our responses: Reference was added as suggested (see line 375).

(12) Line 307, suggest adding an “In addition” before “an obvious difference...”

Our responses: The change was made as suggested (see line 391).

(13) Line 318, suggest changing “emission” to “emissions”.

Our responses: The change was made as suggested (see line 402).

(14) Line 332, please note that the more rapid decrease of SO₂ emissions compared to NO₂ is valid only for recent years in China.

Our responses: This point was clarified in the revised manuscript: “...*which typically indicated a more rapid decrease of SO₂ emissions compared to NO₂ during recent years in China*” (see lines 416-417).

(15) Line 637, change “contribution” to “contributions”.

Our responses: The change was made as suggested (see lines 755-756).

(16) Line 647, suggest adding an “an” before “ambient”, and changing “with” into “at”.

Our responses: The changes were made as suggested (see line 765).

(17) Annotation in Figure 8, suggest changing “Stronger impact of...” to “Stronger impacts of...”

Our responses: The change was made as suggested (see Figure 8).

(18) Caption of Figure S4, suggest using “increasing strengths of biomass burning impact”.

Our responses: The change was made as suggested (see Page 9 in supporting information).

(19) Caption of Figure S6, I guess something was missing after “Relationship between OC/EC”.

Our responses: It should be “Relationship between OC/EC and sulfate”. This mistake was corrected in the revised manuscript (see Page 11 in supporting information).

(20) Caption of Figure S7, rephrase the sentence “For the 2019-2020 campaign, $(OC/EC)_{pri}$ and OC^* were determined as the slope...”

Our responses: This sentence was re-written as: “*For the 2019–2020 campaign, $(OC/EC)_{pri}$ and OC^* were determined based on linear regression of OC on EC ($r = 0.98$), with $(OC/EC)_{pri}$ as the slope (2.13) and OC^* as the intercept (3.11), respectively, using low-RH samples (i.e., those with RH below 60%)*” (see Page 12 in supporting information).

(21) Captions of Figures S9 and S10, it is unnecessary to repeat the definition of “D” and “H” conditions.

Our responses: The duplicated definitions were removed as suggested (see Pages 14 and 15 in supporting information).

(22) Caption of Figure S11, suggest changing “temperature” to “temperatures”.

Our responses: The change was made as suggested (see Page 16 in supporting information).

1 **Dramatic changes in Harbin aerosol during 2018–2020: the roles of open burning policy and**
2 **secondary aerosol formation**

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15 **Abstract**

16 Despite the growing interest in understanding haze formation in Chinese megacities, air
17 pollution has been largely overlooked for the Harbin-Changchun (HC) metropolitan area located in
18 the severe cold climate region in Northeast China. In this study, we unfolded significant variations
19 of fine particulate matter (PM_{2.5}) in HC's central city (Harbin) during two sequential heating seasons
20 of 2018–2019 and 2019–2020, and explored major drivers for the observed variations. The two
21 campaigns showed comparable organic carbon (OC) levels but quite different OC sources. The
22 biomass burning (BB) to OC contribution decreased substantially for 2019–2020, which was
23 attributed primarily to the transition of local policies on agricultural fires, i.e., from the “legitimate
24 burning” policy released in 2018 to the “strict prohibition” policy in 2019. Meanwhile, the
25 contribution of secondary OC (OC_{sec}) increased significantly, associated with the much more
26 frequent occurrences of high relative humidity (RH) conditions during the 2019–2020 measurement

27 period. Similar to OC_{sec} , the major secondary inorganic ions, i.e., sulfate, nitrate and ammonium
28 (SNA), also exhibited RH-dependent increases. Given the considerable aerosol water contents
29 predicted for the high-RH conditions, heterogeneous reactions were likely at play in secondary
30 aerosol formation even in the frigid atmosphere in Harbin (e.g., with daily average temperatures
31 down to below $-20\text{ }^{\circ}\text{C}$). In brief, compared to 2018–2019, the 2019–2020 measurement period was
32 characterized by a policy-driven decrease of biomass burning OC, a RH-related increase of OC_{sec}
33 and a RH-related increase of SNA, with the former two factors generally offsetting each other. In
34 addition, we found that open burning activities were actually not eliminated by the “strict prohibition”
35 policy released in 2019, based on a synthesis of air quality data and fire count results. Although not
36 ~~evident throughout~~ occurred during the 2019–2020 measurement period, agricultural fires broke out
37 within a short period before crop planting in spring of 2020, and resulted in off-the-chart air
38 pollution for Harbin, with 1- and 24-hour $PM_{2.5}$ concentrations peaking at ~ 2350 and $900\text{ }\mu\text{g}/\text{m}^3$,
39 respectively. This study indicates that sustainable use of crop residues remains a difficult challenge
40 for the massive agricultural sector in Northeast China.

41 1. Introduction

42 Despite nationwide reductions in anthropogenic emissions (Zhang et al., 2019), severe haze
43 pollution characterized by high concentrations of fine particulate matter (PM_{2.5}) is far from being
44 effectively controlled in China, e.g., haze episodes were observed in Beijing even during the
45 COVID-19 lockdown (Lv et al., 2020). This reveals the complex yet poorly understood responses
46 of air pollution to changes of primary emission. While secondary aerosol production has been
47 thought to be largely responsible for this lack of understanding, the chemical mechanisms remain
48 vague (Le et al., 2020; Wang et al., 2020b; Huang et al., 2021). For example, state-of-the-art models
49 incorporating gas-phase and cloud chemistry frequently underestimated sulfate and secondary
50 organic aerosol (SOA) concentrations for winter haze events in Beijing (Wang et al., 2014; Zheng
51 et al., 2015a; Cheng et al., 2016; Liu et al., 2020a). The underestimation was more significant with
52 increasing relative humidity (RH) or aerosol water content (AWC) levels, pointing to the importance
53 of aqueous-phase reactions in aerosol water (Wang et al., 2016; Shrivastava et al., 2017; Su et al.,
54 2020; Liu et al., 2021b). On the other hand, quantitative prediction of secondary ~~aerosol~~ aerosols
55 formed through aqueous-phase reactions remains challenging, partially due to uncertainties in
56 aerosol pH (Guo et al., 2017b; Song et al., 2018; Zheng et al., 2020) and oxidant concentrations (Ye
57 et al., 2018; Wang et al., 2020a). In addition, despite the role of heterogeneous chemistry has been
58 widely accepted for sulfate formation, ~~the~~ its effects on SOA remain unclear, with more evidences
59 indicating an enhancement effect (Hu et al., 2016; Kuang et al., 2020; Liu et al., 2020a; Wang et al.,
60 2021a) overwhelming those suggesting little influence of RH or AWC on SOA formation (Zheng et
61 al., 2015b). In all, there is a growing interest in understanding haze pollution in Chinese megacities
62 (Shi et al., 2019), especially regarding the driving factors responsible for the spatio-temporal

63 variations, since these factors are essential for the development of efficient air pollution control
64 strategies.

65 Studies on haze in China have been historically concentrated in the North China Plain (NCP),
66 especially around Beijing. Recently, new hotspots began to emerge, e.g., the Harbin-Changchun
67 (HC) metropolitan area. HC is located in the severe cold climate region in Northeast China, and
68 includes 11 cities in the two provinces of Heilongjiang and Jilin. Compared to NCP and other
69 traditional hotspots of air pollution research (e.g., the Yangtze River Delta), HC is characterized by
70 its extremely cold winter when the daily average temperatures could drop to below $-20\text{ }^{\circ}\text{C}$. Thus,
71 the heating season is usually as long as six months in HC, lasting from late fall through early spring
72 of next year. During this period, intensive energy use is expected, e.g., coal combustion for central
73 heating in urban areas and household biomass burning for space-heating in rural areas. The intensive
74 energy use, to a large extent, determines the relatively high baseline of $\text{PM}_{2.5}$ pollution in HC's
75 heating season. According to the open access air quality data routinely published by China National
76 Environmental Monitoring Center (<http://106.37.208.233:20035/>), the monthly averages of $\text{PM}_{2.5}$
77 measured during winter in Harbin stayed above $55\text{ }\mu\text{g}/\text{m}^3$ from 2013 throughout 2020, whereas the
78 corresponding value could drop to below $30\text{ }\mu\text{g}/\text{m}^3$ for Beijing.

79 Another feature of HC is that it is located in a main agricultural region in China. For example,
80 Heilongjiang Province provided $\sim 13\%$ and 15% of the national rice and corn productions in 2019,
81 respectively, with only $\sim 5\%$ of China's land area (National Bureau of Statistics of China, 2020).
82 The massive agricultural sector results in a huge amount of crop residues, which are produced after
83 harvesting in autumn and must be disposed before planting in spring of the next year. Although
84 nominally prohibited, open burning persists as an important approach for the disposal of crop

85 residues in Northeast China, with a time window largely overlapped with the heating season. These
86 agricultural fires frequently resulted in heavily-polluted PM_{2.5} episodes, e.g., with 24-hour PM_{2.5}
87 peaking at ~650 µg/m³ during early November of 2015 in Harbin (Li et al., 2019b). Given that the
88 agricultural fires were never eliminated, interim provisions were released by Heilongjiang Province
89 in 2018, which approved a window of approximately 3 months (from 11 December, 2018 to 9 March,
90 2019) for open burning of crop residues (Department of Ecology and Environment of Heilongjiang
91 Province, 2018). However, the interim provisions were amended in 2019, i.e., the “legitimate
92 burning” policy was terminated and was replaced by a toughest-ever policy on open burning, which
93 required that agricultural fires should be strictly prohibited for the period of 15 September, 2019 to
94 15 May, 2020. The rapid transition of open burning policy reflects the ongoing attempts of local
95 government to control the severe haze pollution caused by agricultural fires. However, the most
96 effective and reliable approach remains inconclusive, given that very little is known about the role
97 of biomass burning in PM_{2.5} pollution in Northeast China. Actually, PM_{2.5} in Northeast China is far
98 from being well characterized yet with ~~the~~ limited studies (e.g., Cao et al., 2016; Yang et al., 2017;
99 Li et al., 2019b; Zhang et al., 2020), especially regarding sources and chemical mechanisms of
100 aerosol formation.

101 In this study, we investigated the variations of Harbin aerosol during two sequential heating
102 seasons of 2018–2019 and 2019–2020, with focuses on the roles of (1) rapid transition of open
103 burning policy and (2) significant change of meteorological conditions (especially relative
104 humidity), which would influence primary emissions and secondary aerosol formation, respectively.
105 Policy implications for improving air quality in the HC region were also discussed.

106 2. Methods

107 **2.1 Field observation and additional data sets used**

108 Two campaigns were conducted at an urban site located in the campus of Harbin Institute of
109 Technology (HIT; 45°45'24" N, 126°40'49" E) during the heating seasons of 2018–2019 (from 16
110 October, 2018 to 14 April, 2019; $N = 180$) and 2019–2020 (from 16 October, 2019 to 4 February,
111 2020; $N = 112$), following the same sampling and analytical procedures. As described for the 2018–
112 2019 campaign (Cheng et al., 2021a), a low volume sampler (MiniVol; Airmetrics, OR, USA)
113 operated at a flow rate of 5 L/min was used to collect airborne $PM_{2.5}$ onto pre-baked quartz-fiber
114 filters (2500 QAT-UP; Pall Corporation, NY, USA), and the measured species included organic
115 carbon (OC), elemental carbon (EC), organic tracers for biomass burning (levoglucosan and
116 mannosan) and water-soluble inorganic ions (sulfate, nitrate, ammonium, etc.). Briefly, OC and EC
117 were determined by a thermal/optical carbon analyzer (DRI-2001; Atmoslytic Inc., CA, USA),
118 using the IMPROVE-A temperature protocol with transmittance charring correction. Precision of
119 the carbon analyzer was investigated by analyzing the samples using another protocol (NIOSH).
120 Comparisons of total carbon and optical attenuation results between the two protocols suggested
121 good repeatability for both the carbon and transmittance measurements (Figure S1). Levoglucosan
122 and mannosan were detected by a Dionex ion chromatography (IC) system (ICS-5000⁺; Thermo
123 Fisher Scientific Inc., MA, USA), using the high-performance anion-exchange chromatography
124 coupled to pulsed amperometric detection (HPAEC-PAD) method. In addition, the IC was also used
125 to measure the inorganic ions. Precision of the IC was evaluated by analyzing selected solutions 5–
126 10 times, and the relative standard deviations were found to be within 5% for all the water-soluble
127 species detected, either organic or inorganic. Based on the observed aerosol components, $PM_{2.5}$ mass
128 was reconstructed as the sum of organic matter (determined as $1.6 \times OC$), EC and inorganic ions.

129 The reconstructed $PM_{2.5}$ will be specified as $(PM_{2.5})^*$ in the following discussions.

130 Air quality data including $PM_{2.5}$, sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon
131 monoxide (CO), etc. were obtained from China's National Urban Air Quality Real Time Publishing
132 Platform (<http://106.37.208.233:20035/>). They were measured at monitoring sites operated by the
133 China National Environmental Monitoring Center (CNEMC), and could be accessed with a time
134 resolution of 1 hour. There are a total of 12 CNEMC sites in Harbin. Results from the nearest one
135 to the filter sampling site (~2.4 km apart), i.e., Taiping Hongwei Park, were used in this study. In
136 addition, hourly meteorological data including temperature and relative humidity (RH) were
137 obtained from Weather Underground (<https://www.wunderground.com>).

138 Using levoglucosan as the reference component, the relative abundances of water-soluble
139 potassium (K^+) were found to increase substantially for five samples collected during the Chinese
140 New Year periods in February of 2019 ($N = 2$; Cheng et al., 2021a) and in January of 2020 ($N = 3$;
141 Figure S2), pointing to significant influence of firework emissions. Given that such emissions may
142 result in primary sulfate and nitrate which are difficult to quantify, the firework events were
143 excluded, and the remaining sulfate and nitrate were considered secondary in the following
144 discussions. Then taking together observational results from the filter sampling and CNEMC sites,
145 the sulfur oxidation ratio (SOR) was determined as the molar ratio of sulfate to the sum of sulfate
146 and SO_2 , and the nitrogen oxidation ratio (NOR) was determined similarly based on nitrate and NO_2 .

147 **2.2 Thermodynamic simulation**

148 The ISORROPIA-II model (Fountoukis and Nenes, 2007) was used to predict aerosol water
149 content (AWC) and aerosol pH. The calculations were conducted in two ways, namely the “reverse”
150 and “forward” modes. For the “reverse” mode, the measured aerosol-phase data were deployed as

151 input to derive AWC and pH directly. For the “forward” mode, the model was run in an iteration
152 way (Liu et al., 2021a). Briefly, we used the measured aerosol-phase data as initial input, ran
153 ISORROPIA-II in the “forward” mode to predict gas-phase concentrations of semi-volatile species
154 (e.g., ammonia and nitric acid), and used the sum of predicted gas-phase and measured aerosol-
155 phase concentrations as the input for next round. The calculations were repeated until the simulated
156 results were stable and in line with the observational data. Although the “reverse” and “forward”
157 mode simulations showed comparable AWC levels for this campaign (Figure S3), the latter
158 approach has been suggested to give more accurate and robust estimation of pH (Guo et al., 2017a;
159 Song et al., 2018). Thus, AWC and pH results predicted by the iteration approach were used in the
160 following discussions.

161 **2.3 Source apportionment**

162 Source apportionment was performed using EPA’s Positive Matrix Factorization (PMF) model
163 (version 5.0), with times series of OC, EC, levoglucosan, chloride, nitrate, sulfate and ammonium
164 from both campaigns as inputs. A total of five factors were resolved, and their profiles were shown
165 in Figure S4. Two factors (BB-1 and BB-2) were strongly associated with primary biomass burning
166 emissions, since almost all the levoglucosan (~90%) were apportioned to these two factors whereas
167 neither of them was a major contributor to secondary ions. Another two factors were inferred to
168 represent secondary aerosols (SA-1 and SA-2), as they had zero EC but the majority of nitrate and
169 sulfate. The last factor (non-BB_{pri}) was attributed to primary emissions from non-BB sources,
170 because more than 50% of EC but little levoglucosan was found in this factor.

171 ~~Two campaigns were conducted at an urban site located in the campus of Harbin Institute of~~
172 ~~Technology (HIT) during the heating seasons of 2018–2019 (from 16 October, 2018 to 14 April,~~

173 2019; $N=180$) and 2019–2020 (from 16 October, 2019 to 4 February, 2020; $N=112$), following
174 the same sampling and analytical procedures. As described for the 2018–2019 campaign (Cheng et
175 al., 2021), a low-volume sampler operated at a flow rate of 5 L/min was used to collect airborne
176 $PM_{2.5}$ onto pre-baked quartz-fiber filters, and the chemical components quantified included organic
177 carbon (OC), elemental carbon (EC), organic tracers for biomass burning (levoglucosan and
178 mannosan) and water-soluble inorganic ions (sulfate, nitrate, ammonium, etc.). Based on the
179 measured species, $PM_{2.5}$ mass was reconstructed as the sum of organic matter (determined as $1.6 \times$
180 OC), EC and inorganic ions. The reconstructed $PM_{2.5}$ will be specified as $(PM_{2.5})^*$ in the following
181 discussions. In addition to the observational results from HIT, online data sets were used to obtain
182 hourly meteorological data such as temperature and relative humidity (RH), and air quality data
183 including $PM_{2.5}$, inhalable particles (PM_{10}), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon
184 monoxide (CO) and ozone (O_3). Refer to supplementary material for details on the field
185 measurement and collection of additional data.

186 Using levoglucosan as the reference component, the relative abundances of water-soluble
187 potassium (K^+) were found to increase substantially for five samples collected during the Chinese
188 New Year periods in February of 2019 ($N=2$; Cheng et al., 2021) and in January of 2020 ($N=3$;
189 Figure S1), pointing to significant influence of firework emissions. Given that such emissions may
190 result in primary sulfate and nitrate which are difficult to quantify, the firework events were
191 excluded, and the remaining sulfate and nitrate were considered secondary in the following
192 discussions. Correspondingly, the sulfur oxidation ratio (SOR) was determined as the molar ratio of
193 sulfate to the sum of sulfate and SO_2 , and the nitrogen oxidation ratio (NOR) was determined
194 similarly based on nitrate and NO_2 .

195 3. Results and discussion

196 3.1 Variation of biomass burning (BB) OC

197 Although comparable OC levels were observed during the 2018–2019 and 2019–2020
198 measurement periods (averaging 20.66 ± 18.17 and $20.64 \pm 16.76 \mu\text{gC}/\text{m}^3$, respectively), the former
199 campaign exhibited substantially higher contributions of levoglucosan to OC (Figure 1a). Here we
200 applied the levoglucosan to OC ratio (LG/OC) as the indicator for BB impact, given that the absolute
201 concentrations of ambient levoglucosan could be influenced by other factors in addition to biomass
202 burning (e.g., wind speed and planetary boundary layer height). LG/OC averaged 1.83 ± 1.18 and
203 $1.17 \pm 0.30\%$ (on a basis of carbon mass) during 2018–2019 and 2019–2020, respectively, indicating
204 that the influence of biomass burning was stronger during the former campaign. This difference was
205 mainly caused by the 2018–2019 samples collected during and after the “legitimate burning” periods
206 (periods of P-2 and P-3, with average LG/OC ratios of 2.09 ± 1.42 and $2.15 \pm 0.94\%$, respectively;
207 Figure 1b), whereas the LG/OC ratios observed before the onset of “legitimate burning” (P-1,
208 averaging $1.20 \pm 0.36\%$) were in general comparable with those during the 2019–2020 campaign.

209 Recalling the different open burning policies released in 2018 and 2019, the observed
210 variations of LG/OC appeared to be associated with agricultural fires. According to the relationship
211 between levoglucosan and OC, Cheng et al. (2021a) classified the 2018–2019 samples into three
212 groups (Cases A, B and C) with LG/OC ranges of $< 1.5\%$, $1.5\text{--}3.0\%$ and $> 3.0\%$, respectively.
213 Levoglucosan exhibited strong linear correlations with OC for all the three cases ($r \geq 0.95$), with
214 slopes, i.e., $\Delta\text{LG}/\Delta\text{OC}$ (approximately equivalent to LG/OC given the close-to-zero intercepts), of
215 1.1, 2.3 and 5.0%, respectively. The variation of LG/OC across the three cases was inferred to be
216 driven mainly by agricultural fires that had relatively low combustion efficiencies, based on a

217 synthesis of the following evidences (Cheng et al., 2021a): (1) the levoglucosan to K^+ ratios and
218 levoglucosan to mannosan ratios observed throughout the 2018–2019 campaign were in line with
219 the characteristics of BB smoke emitted by the burning of crop residues; (2) no dependence of
220 LG/OC on temperature was observed, indicating that the variations of LG/OC could not be
221 explained by biomass burning for household space-heating in rural areas; (3) elevated LG/OC ratios
222 were typically associated with intensive fire counts, i.e., open burning of crop residues, around
223 Harbin; (4) chemical signatures associated with combustion phase exhibited changes toward
224 smoldering-dominated burning from Cases A through C, e.g., $\Delta EC/\Delta CO$ (derived from linear
225 regression of EC on CO) decreased whereas the levoglucosan to K^+ ratios increased. Following
226 Cheng et al. (2021a), LG/OC ratios higher than 1.5% were considered an indicator for apparent
227 impacts of agricultural fires around Harbin. As shown in Figures 1c–1d, approximately 50% of the
228 2018–2019 samples exhibited LG/OC above 1.5%, with various fractions for the three periods, i.e.,
229 15, 64 and 71% for P-1, P-2 and P-3 samples, respectively. Thus, apparent impacts of agricultural
230 fires were frequently encountered in the 2018–2019 campaign, particularly after the onset of
231 “legitimate burning”. It is noteworthy that the agricultural fires did not actually disappear after the
232 ending of “legitimate burning” and instead extended to mid-April of 2019. For the 2019–2020
233 campaign, however, only less than 5% of the samples showed LG/OC larger than 1.5% (Figure 1c),
234 indicating ~~that the rare occurrence of agricultural fires were almost completely eliminated~~ during
235 the measurement period.

236 Comparison of source apportionment results between the two campaigns also indicated
237 substantial changes in the influence of agricultural fires. ~~In this study, source apportionment was~~
238 ~~performed using EPA’s Positive Matrix Factorization (PMF) model (version 5.0), with OC, EC,~~

239 ~~levoglucosan, chloride, nitrate, sulfate and ammonium from both campaigns as inputs. A total of~~
240 ~~five factors were resolved, and their profiles were shown in Figure S2. Two factors (BB-1 and BB-~~
241 ~~2) were strongly associated with primary biomass burning emissions, since almost all the~~
242 ~~levoglucosan (~90%) were apportioned to these two factors whereas neither of them was a major~~
243 ~~contributor to secondary ions. Another two factors were inferred to represent secondary aerosols~~
244 ~~(SA-1 and SA-2), as they had little EC but the majority of nitrate and sulfate. The last factor (non-~~
245 ~~BB_{PH}) was attributed to primary emissions from non-BB sources, because more than 50% of EC but~~
246 ~~little levoglucosan was found in this factor.~~ For the 2018–2019 campaign, both the OC mass
247 apportioned to BB-1 (OC_{BB-1}; Figure S5) and the contribution of BB-1 to OC (f_{BB-1} ; Figure 2)
248 increased substantially after the onset of “legitimate burning”, likely indicating that this factor was
249 representative of agricultural fire emissions. This inference was also supported by the comparison
250 of OC source apportionment results across the three cases (A–C) with increasing LG/OC ratios, i.e.,
251 with stronger impacts of agricultural fires. OC_{BB-1} increased drastically by ~25 folds (from 1.2 to
252 30.9 $\mu\text{gC}/\text{m}^3$) from Cases A through C, with OC attributed to other factors being largely unchanged,
253 and correspondingly, f_{BB-1} increased sharply from 9 to 69% across the three cases (Figure S6). In
254 addition, it was noticed that negligible EC was apportioned to the BB-1 factor (Figure S4), which
255 was the characteristic of smoldering-dominated combustion as supported by numerous BB source
256 emission studies (McMeeking et al., 2009; May et al., 2014; Pokhrel et al., 2016; McClure et al.,
257 2020; Wang et al., 2020c). This feature was consistent with the inference that the agricultural fires
258 had relatively low combustion efficiencies (Cheng et al., 2021a). During the 2018–2019 campaign,
259 the contribution of agricultural fires to OC was rather small (9%) before the onset of “legitimate
260 burning”, whereas after this time point, the contribution increased to ~40% (Figure 2). The overall

261 $f_{\text{BB-1}}$ was 34% for the entire measurement period of 2018–2019, suggesting agricultural fire
262 emissions as the dominant source of OC. For the 2019–2020 campaign, however, $f_{\text{BB-1}}$ was
263 substantially lower (9%; Figure 2), comparable with that determined for the 2018–2019 samples
264 collected during P-1, i.e., before the onset of “legitimate burning”. Regarding the temporal variation
265 of agricultural fire impacts, therefore, the same patterns were observed based on the comparisons of
266 LG/OC and PMF results across various measurement periods.

267 Unlike $\text{OC}_{\text{BB-1}}$, OC masses apportioned to the BB-2 factor ($\text{OC}_{\text{BB-2}}$) were comparable for the
268 2018–2019 samples collected before, during and after the “legitimate burning” periods (Figure S5).
269 $\text{OC}_{\text{BB-2}}$ was also largely unchanged across the three cases (A–C) with stronger impacts of
270 agricultural fires (Figure S6). Therefore, it seems that BB-2 was associated with biomass burning
271 activities that did not have significant daily variation, with the most likely candidate being
272 household combustion of crop residues (for cooking and heating). In addition, $\text{OC}_{\text{BB-2}}$ appeared to
273 be slightly higher for the 2019–2020 campaign compared to 2018–2019 (6.24 vs. 4.51 $\mu\text{gC}/\text{m}^3$;
274 Figure S5), presumably because more crop residues were consumed through household use ~~during~~
275 ~~2019–2020~~ in response to the “strict prohibition” open burning policy.

276 The two biomass burning factors constituted 57% of OC for the 2018–2019 campaign (Figure
277 2). Before the onset of “legitimate burning”, the total contribution of biomass burning (f_{BB}) was 46%
278 and was dominated by the BB-2 factor (i.e., household burning of crop residues), whereas after this
279 time point, f_{BB} increased to 59% and was dominated by BB-1 (agricultural fires). For the Case C
280 samples, i.e., under the strongest impacts of agricultural fires, f_{BB} was as high as 79% (Figure S6).
281 A prominent reduction in $\text{OC}_{\text{BB-1}}$, however, occurred for the 2019–2020 measurement period, and
282 f_{BB} dropped to 39% with BB-2 as the dominant ~~driver~~ contributor (Figures 2 and S5). It is

283 noteworthy that compared to the typical f_{BB} determined during winter in Beijing (~10–20%, derived
284 from field observations using aerosol mass spectrometer; Hu et al., 2016; Sun et al., 2018; Li et al.,
285 2019a; Xu et al., 2019), the BB contributions were much higher in Harbin even when the
286 contribution of agricultural fires was limited (e.g., during the 2019–2020 campaign, and P-1 in
287 2018–2019), pointing to strong emissions from residential burning of crop residues throughout the
288 heating season in Northeast China.

289 3.2 Variation of secondary OC

290 OC masses apportioned to the SA-1 and SA-2 factors (OC_{sec}) were considered secondary. OC_{sec}
291 were 3.9 and 7.6 $\mu\text{gC}/\text{m}^3$ for the 2018–2019 and 2019–2020 campaigns, respectively, constituting
292 19 and 37% of OC (Figures 2 and S5). It was noticed that for biomass burning OC and OC_{sec} , their
293 inter-campaign differences showed comparable absolute values but opposite signs. This explains
294 why the two heating seasons had significantly different OC sources but almost the same OC [levels](#)
295 [average concentrations](#).

296 As shown in Figure 3, OC_{sec} exhibited a positive dependence on RH, with an explosive increase
297 of OC_{sec} after RH exceeded 80%. Only ~6% of the 2018–2019 samples (10 out of 180) experienced
298 such humid conditions, whereas this fraction was as high as ~37% for 2019–2020 (corresponding
299 to 42 out of the 112 samples). Thus the potential influence of RH on SOA formation was primarily
300 investigated based on results from the 2019–2020 campaign. Figure 4 compares OC source
301 apportionment results across different RH ranges (< 60%, 60–80% and > 80%), which are termed
302 low-, medium- and high-RH conditions, respectively, for this measurement period. Not only OC_{sec}
303 but also its contribution to OC (f_{sec}) increased significantly from the low- through high-RH
304 conditions, by factors of 9.8 and 2.6, respectively. Although the 2019–2020 campaign experienced

305 much lower ambient temperatures (as low as $-20\text{ }^{\circ}\text{C}$) compared to Beijing's winter ($\sim 0\text{ }^{\circ}\text{C}$), the f_{sec}
306 of Harbin reached 42% for the RH range of $> 80\%$, generally comparable with the typical range of
307 oxygenated organic aerosol (OOA) contribution ($\sim 35\text{--}60\%$) determined under humid winter
308 conditions in Beijing (Sun et al., 2013, 2014, 2018; Hu et al., 2016; Xu et al., 2019). Given the
309 considerable AWC levels predicted for the high-RH conditions (typically above $50\text{ }\mu\text{g}/\text{m}^3$; Figure
310 3), it was inferred that heterogeneous reactions might be at play in the RH-dependent increase of
311 f_{sec} .

312 ~~As shown in Figure 3, OC_{sec} exhibited a positive dependence on RH, with an explosive increase~~
313 ~~of OC_{sec} after RH exceeded 80%. Only 6% of the 2018–2019 samples (10 out of 180) experienced~~
314 ~~such humid conditions, whereas this fraction was as high as 37% for 2019–2020 (corresponding~~
315 ~~to 42 out of the 112 samples). Therefore, the inter-annual variation of OC_{sec} was likely associated~~
316 ~~with the different RH levels between the two campaigns. Although the daily average temperatures~~
317 ~~could drop to below $-20\text{ }^{\circ}\text{C}$ during the measurement periods, simulation results based on the~~
318 ~~ISORROPIA-II thermodynamic model (Guo et al., 2017a; Song et al., 2018; see Supplement for~~
319 ~~details) still showed considerable amounts of liquid water in aerosol phase at high RH, e.g.,~~
320 ~~typically with AWC levels of above $50\text{ }\mu\text{g}/\text{m}^3$ when RH exceeded 80% (Figure 3). Therefore,~~
321 ~~heterogeneous reactions were presumably at play in the RH-dependent increase of OC_{sec} .~~

322 ~~Figure 4 compares OC source apportionment results across different RH ranges ($< 60\%$, 60–~~
323 ~~80% and $> 80\%$), which are termed low-, medium- and high-RH conditions, respectively, for the~~
324 ~~2019–2020 campaign. Both OC_{sec} and its contribution to OC (f_{sec}) increased significantly from the~~
325 ~~low- through high-RH conditions, by factors of 9.8 and 2.6, respectively. Although the 2019–2020~~
326 ~~campaign experienced much lower ambient temperatures compared to Beijing's winter ($\sim 0\text{ }^{\circ}\text{C}$), the~~

327 ~~f_{sec} of Harbin reached 42% for the RH range of > 80%, generally comparable with the typical range~~
328 ~~of oxygenated organic aerosol (OOA) contribution (~35–60%) determined under humid winter~~
329 ~~conditions in Beijing (Sun et al., 2013, 2014, 2018; Hu et al., 2016; Xu et al., 2019).~~

330 The OC to EC ratio (OC/EC) is also a commonly used indicator for SOA, giving rise to the
331 EC-tracer method for the estimation of OC_{sec} mass. However, it has long been recognized that SOA
332 formation is usually not the only factor that can increase OC/EC, and another factor that could be
333 playing a crucial role is the biomass smoke with relatively high emission ratios of OC to EC. Among
334 the three primary factors resolved in this study, OC/EC for the primary emissions of BB-1
335 (extremely high as negligible EC was apportioned to this factor; Figure S4) and BB-2 (3.5) were
336 both larger than that of non-BB_{pri} (2.8). Thus the influences of not only SOA but also biomass
337 burning emissions need to be considered when interpreting the observed OC/EC. For the 2018–2019
338 campaign, the temporal variation of OC/EC was mainly driven by biomass burning emissions
339 (especially the BB-1 factor), as can be seen from the positive dependence of OC/EC on levoglucosan
340 and the comparison of OC/EC across the three cases with increasing LG/OC (Figure S7). In this
341 case, the EC-tracer method should be used with caution, since the basic assumption, i.e., variation
342 of OC/EC can be attributed primarily to SOA formation, was invalid. Unlike 2018–2019, SOA was
343 the dominant driver for the variation of OC/EC during the 2019–2020 measurement period, as
344 indicated by the positive dependence of OC/EC on sulfate and the comparison of OC/EC across the
345 low- through high-RH conditions (Figure S8). During the 2019–2020 campaign, similar patterns of
346 temporal variation were observed for OC_{sec} retrieved using the EC-tracer method and PMF approach,
347 and both results supported the RH-dependent increase of OC_{sec} (Figure S9). However, compared to
348 the PMF-based f_{sec} , the EC-tracer method resulted in a higher contribution of OC_{sec} to OC for the

349 high-RH conditions (60% vs. 42%). This is not surprising, as variation of biomass burning emissions
350 could also contribute to the elevated OC/EC of the high-RH conditions (Figure S8), but this
351 contribution could not be distinguished from that of SOA by the EC-tracer method. Nonetheless,
352 enhanced SOA formation was evident for the high-RH conditions, which mainly occurred within
353 the coldest months (December and January) during the 2019–2020 measurement period.

354 **3.3 Variation of secondary inorganic aerosol**

355 Both sulfate and SOR exhibited increasing trends as RH became higher (Figure 5), e.g., SOR
356 averaged 0.09 ± 0.04 and 0.20 ± 0.07 for the RH ranges of below and above 80%, respectively. The
357 apparent increase of SOR after RH exceeded 80% pointed to enhanced sulfate formation,
358 presumably through heterogeneous reactions given the high AWC levels (as can be seen from Figure
359 3). In addition, NO_2 appeared to be at play in the heterogeneous conversion of SO_2 to sulfate,
360 because the RH-dependent increase of SOR was more significant for the samples with relatively
361 high NO_2 concentrations (e.g., above $30 \mu\text{g}/\text{m}^3$; Figure 6). Based on the observational results
362 available, however, it was inconclusive whether NO_2 was the dominant oxidant for the
363 heterogeneous formation of sulfate. Simulation results by ISORROPIA-II suggested moderately
364 acidic aerosols (pH of 4.2 ± 1.1) for the high-RH conditions, and the importance of other oxidants
365 (e.g., H_2O_2) could be comparable with or even overwhelm NO_2 for the oxidation of SO_2 in aerosol
366 water at such pH levels (Guo et al., 2017b; Liu et al., 2017; Ye et al., 2018; Wang et al., 2021b).
367 Nonetheless, the relationship between SOR and RH observed in Harbin was in general consistent
368 with the wintertime results from Beijing. However, the threshold RH for sharp increase of SOR was
369 higher in Harbin (80%) than that in Beijing (~40–70%), and the SOR in Harbin with RH above 80%
370 (averaging 0.2) were at the lower end of ~~these~~ the corresponding values observed during winter in

371 Beijing (typically with averages of ~0.2–0.6) (Sun et al., 2013; Zheng et al., 2015b; Zhang et al.,
372 2018; Li et al., 2019a; Liu et al., 2020b). ~~These differences indicated that heterogeneous formation~~
373 ~~of sulfate was less efficient in this study, and a likely cause~~ A likely cause for these differences was
374 the relatively low temperatures during the measurement period, which would reduce the rate
375 coefficients of relevant aqueous-phase reactions (Cheng et al., 2016).

376 The 2018–2019 and 2019–2020 campaigns exhibited comparable sulfate concentrations for the
377 RH range of below 80%, with median values of 3.72 and 3.39 $\mu\text{g}/\text{m}^3$, respectively (Figure S10).
378 RH-dependent increase of sulfate was evident for both campaigns but was less significant for the
379 former one, e.g., the median sulfate were 5.32 and 15.84 $\mu\text{g}/\text{m}^3$ for the high-RH conditions of 2018–
380 2019 and 2019–2020, respectively. As mentioned earlier, only 10 out of the 180 samples from the
381 2018–2019 campaign fell into the high-RH conditions. Among these 10 samples, the RH-dependent
382 increase of sulfate was observed for only three ones with NO_2 concentrations of above 60 $\mu\text{g}/\text{m}^3$,
383 but was not evident for the remaining samples which had much lower NO_2 (mostly below 30 $\mu\text{g}/\text{m}^3$;
384 Figure 7). For the 2019–2020 campaign, however, the majority of the samples with RH above 80%
385 showed NO_2 concentrations of above 60 $\mu\text{g}/\text{m}^3$, accompanied with elevated sulfate. Therefore, the
386 different NO_2 levels under high-RH conditions between the two campaigns (with median
387 concentrations of 21.27 and 72.41 $\mu\text{g}/\text{m}^3$ during 2018–2019 and 2019–2020, respectively; Figure
388 S11) was a likely cause of the more significant RH-dependent increase of sulfate observed during
389 the 2019–2020 campaign.

390 The 2019–2020 campaign also exhibited more significant RH-dependent increase of nitrate,
391 similar to sulfate (Figure S12). In addition, an ~~An~~ obvious difference between the two campaigns
392 was that the nitrate to sulfate ($\text{NO}_3^-/\text{SO}_4^{2-}$) ratios tended to be higher during 2019–2020 (Figure

393 S13), with an average of 1.28 ± 0.51 (compared to 1.10 ± 0.66 for 2018–2019). This trend was
394 somewhat surprising, as the 2019–2020 measurement period experienced substantially lower
395 temperatures than 2018–2019 (Figure S13) and consequently was expected to be impacted by
396 stronger heating-induced coal combustion emissions, which were a large source of SO₂. However,
397 SO₂ were actually lower for the 2019–2020 campaign, presumably due to the implementation of
398 clean air actions targeting pollutants from coal combustion. On the other hand, NO₂ were higher
399 during 2019–2020. Factors responsible for this increase were unclear, while a possible explanation
400 was that the meteorological conditions of 2019–2020 were generally less favorable for dispersion
401 of air pollutions, as indicated by the frequent occurrences of high RH. In this case, the decrease of
402 SO₂ ~~emission~~ emissions in 2019–2020 was inferred to be more significant after accounting for the
403 unfavorable meteorological conditions. In general, the 2019–2020 campaign exhibited higher NO₂
404 to SO₂ ratios (Figure S13), which were in line with the observed variation of nitrate to sulfate ratios.

405 In addition to the relative abundances of NO₂ and SO₂, the influence of their gas-to-particle
406 conversion ratios should also be considered when comparing NO₃⁻/SO₄²⁻ across different conditions.
407 The two campaigns differed with respect to humidity levels and biomass burning emissions, both
408 of which could influence SNA formation. Although NOR and SOR were indeed influenced by RH,
409 NO₃⁻/SO₄²⁻ did not show clear dependence on RH (Figure S14). In addition, there were
410 observational evidences indicating that biomass burning emissions could enhance photochemical
411 oxidation of NO₂ whereas this effect was much weaker for SO₂ (Akagi et al., 2012; Collier et al.,
412 2016), i.e., stronger BB impacts favor the increase of NO₃⁻/SO₄²⁻. Therefore, the larger NO₃⁻/SO₄²⁻
413 during the 2019–2020 campaign could not be explained by the reduced BB influences or the
414 elevated RH levels, and instead should be attributed primarily to the higher NO₂ to SO₂ ratios. The

415 increasing trend of NO₂/SO₂ observed in this study was consistent with inventory results which
416 typically indicated a more rapid decrease of SO₂ emissions compared to NO₂ during recent years in
417 China (Zheng et al., 2018).

418 3.4 Variation of aerosol composition

419 The discussions above indicated significant differences between the two campaigns regarding
420 the characteristics of both primary emissions and secondary aerosol formation. This in turn resulted
421 in substantially different aerosol compositions between the two measurement periods, with the
422 dominant drivers for the variation of aerosol composition being different as well (Figure 8).

423 For the 2018–2019 campaign, the contribution of OA to (PM_{2.5})^{*} was much higher than that of
424 SNA (60 vs. 28%). The variation of (PM_{2.5})^{*} composition was driven mainly by biomass burning
425 emissions (especially those from agricultural fires), which tended to increase the OA contribution
426 and correspondingly decrease the relative abundance of SNA. During the most intensive BB
427 episodes (with LG/OC above 3.0%), the OA contribution reached 66% whereas the SNA
428 contribution dropped to 23%. For the 2019–2020 campaign, however, the contribution of SNA to
429 (PM_{2.5})^{*} was largely comparable with OA (41 vs. 49%), and heterogeneous chemistry became the
430 dominant driver for the variation of (PM_{2.5})^{*} composition. The relative abundances of both SNA and
431 SOA increased considerably from the low-RH through high-RH conditions, with their total
432 contributions reaching 62% for the RH range of above 80%.

433 During the 2019–2020 measurement period, significantly higher levels of major secondary ions
434 were observed than 2018–2019, i.e., the total concentrations of sulfate, nitrate and ammonium (SNA)
435 averaged 27.30 and 15.53 μg/m³, respectively. This difference was largely explained by the RH-
436 dependence. For the 2019–2020 campaign, the sampling events with RH above 80% were mainly

437 encountered in January of 2020 ($N = 20$) as well as in December of 2019 ($N = 17$), when the daily
438 average temperatures were typically below -10°C . The frequent occurrences of high RH were
439 uncommon for Harbin's winter, as can be seen from the comparison of RH in January across the
440 past twenty years (Figure 9). Thus, the 2019–2020 campaign provided a unique opportunity to
441 explore heterogeneous chemistry in Chinese cities located in the severe cold climate region, and
442 might be considered as an upper limit regarding the RH-dependent enhancement of secondary
443 aerosols. On the other hand, the effective increase of SNA and SOA under high-RH conditions
444 implied the abundances of gaseous precursors, both organic and inorganic. To avoid the occurrence
445 of extreme pollution events, a more fundamental solution would point to the effective control of
446 gaseous pollutants.

447 **3.5 Agricultural fires missed by the 2019–2020 campaign**

448 The 2019–2020 campaign was designed to cover the entire heating season but was interrupted
449 by the outbreak of COVID-19. Although there was no observational result on aerosol composition
450 after 5 February, 2020, a severe $\text{PM}_{2.5}$ episode caused by agricultural fires was identified during 17–
451 18 April, 2020, as indicated by the intensive fire counts recorded for Harbin and the surrounding
452 areas (Figure 10). According to the open-access air quality data, the 24-hour $\text{PM}_{2.5}$ in Harbin reached
453 ~ 500 and $900 \mu\text{g}/\text{m}^3$ on these two days, respectively, with the hourly concentrations peaking at
454 $\sim 2350 \mu\text{g}/\text{m}^3$. During this period, similarly high $\text{PM}_{2.5}$ levels were observed for a nearby city, Suihua,
455 which is located in the same region (the Song-Nen Plain) as Harbin. Based on a synthesis of air
456 quality data and air mass trajectory, we found that the massive amounts of air pollutants in the
457 Harbin-Suihua region, which were emitted by the agricultural fires within a concentrated period of
458 two days, could be transported ~ 500 km northward to Heihe, a city located on the border between

459 China and Russia. As shown in Figures 10 and S15, $PM_{2.5}$ in Heihe started to increase when the
460 back trajectory suggested air masses passing over the Harbin-Suihua region, resulting in an episode
461 with a peak $PM_{2.5}$ concentration of $\sim 310 \mu\text{g}/\text{m}^3$. The discussions above indicated that although
462 agricultural fires were not evident during the 2019–2020 measurement period, they were postponed
463 to late April of 2020. Thus, agricultural fires were not actually eliminated by the toughest-ever
464 policy on open burning, but broke out within a short period before the planting of crops in spring
465 instead. It is noteworthy that the intensive open burning activities resulted in not only off-the-chart
466 air pollutions for the nearby cities but also heavily-polluted episodes for downwind regions far away
467 from the source areas. We suggest that transboundary transport of agricultural fire emissions from
468 the Northeast Plain, especially the two provinces of Heilongjiang and Jilin, deserves more attention.

469 **4. Conclusions and implications**

470 Significant differences were observed between aerosol properties measured during two
471 sequential heating seasons in the central city of the HC metropolitan area, i.e., Harbin. Briefly, the
472 differences were caused by ~~inter-annual~~ inter-campaign variations of both primary emissions and
473 secondary aerosol formation. The 2018–2019 measurement period was characterized by (i) frequent
474 occurrences of agricultural fires, which were boosted by the “legitimate burning” policy, and (ii)
475 overall low RH levels which were unfavorable for heterogeneous formation of secondary aerosols.
476 Correspondingly, the observed $(PM_{2.5})^*$ was dominated by organic aerosol, with a substantially
477 higher contribution than SNA (60 vs. 28%). Biomass burning emissions were the largest OC source
478 for this measurement period. The BB to OC contribution (f_{BB}) was 46% before the onset of
479 “legitimate burning” primarily due to household burning of crop residues, and increased to 59%
480 after the onset of “legitimate burning” with the major contribution from agricultural fire emissions.

481 In addition to OC, the temporal variations of $(\text{PM}_{2.5})^*$ mass concentration and chemical composition
482 were mainly driven by biomass burning as well, especially by agricultural fires. The average
483 $(\text{PM}_{2.5})^*$ reached $\sim 100 \mu\text{g}/\text{m}^3$ for the most intensive BB episodes, with an enhanced OA contribution
484 of 66% and a reduced SNA contribution of 23%.

485 Compared to 2018–2019, the 2019–2020 campaign was influenced by (i) a transition of open
486 burning policy, i.e., agricultural fires were strictly prohibited, and (ii) frequent occurrences of high-
487 RH conditions. In this case, no evidence was observed to indicate apparent influence of agricultural
488 fires, and correspondingly, the f_{BB} (39%) was dominated by household burning of crop residues. In
489 addition, both SNA and secondary OC (OC_{sec}) exhibited significant RH-dependent increases. For
490 the RH range of above 80%, SOR and the OC_{sec} to OC contribution reached 0.2 and 42%,
491 respectively, despite the low ambient temperatures encountered (averaging about -16°C in terms of
492 daily average). Unlike 2018–2019, organic aerosol and SNA showed comparable contributions to
493 $(\text{PM}_{2.5})^*$ for the 2019–2020 campaign (49 vs. 41%), and the variations of $(\text{PM}_{2.5})^*$ during this
494 measurement period were mainly driven by secondary components.

495 **5. Implications**

496 This study has crucial implications for further improving the air quality in HC region. First, f_{BB}
497 remained relatively high for the heating season of Harbin (e.g., compared to the wintertime results
498 from Beijing), even without apparent influence of agricultural fires. This highlights the importance
499 of reducing domestic use of crop residues, on top of previous clean air actions implemented for the
500 residential sector primarily focusing on coal combustion. Second, driven by the transition of open
501 burning policy, agricultural fires exhibited different patterns but were never eliminated. For example,
502 although there was no “legitimate burning” period during 2019–2020 and agricultural fires did not

503 occur as frequently as during 2018–2019, burning did break out in spring of 2020 before crop
504 planting. Thus, neither the “legitimate burning” policy released in 2018 nor the toughest-ever “strict
505 prohibition” policy released in 2019 could be considered successful for the effective control of
506 agricultural fires. More studies are necessary to design a new roadmap towards sustainable use of
507 crop residues in Northeast China, which may contribute to the dual targets of air quality
508 improvement and climate change mitigation. Third, it is noteworthy that $(PM_{2.5})^*$ averaged ~ 115
509 $\mu\text{g}/\text{m}^3$ for the high-RH conditions of 2019–2020, even higher than results from the most intensive
510 BB episodes during 2018–2019. This reveals the need for effective control of gaseous precursors,
511 both organic and inorganic, of secondary aerosols. Given the increasing trends of NO_2/SO_2 and
512 $\text{NO}_3^-/\text{SO}_4^{2-}$ observed between 2018 and 2020, control of the NO_2 -related sources should be
513 strengthened.

514 It should be noted that the discussions on heterogeneous formation of SOA and SNA did not
515 necessarily exclude the reactions in fog/cloud water. Actually, based on the observational results
516 available, we could not robustly distinguish the relative importance of various aqueous-phases
517 pathways for secondary aerosol formation. To address this problem, air quality modeling with a
518 focus on HC should be conducted in future studies, which could also quantitatively evaluate the
519 contributions of various factors (e.g., meteorology, emissions and regional transport) to long-term
520 trends of $PM_{2.5}$ concentration and chemical composition. An essential precondition is that the model
521 could properly re-produce the observational results, which appears a substantial challenge for
522 Harbin as indicated by the limited inter-comparison studies, especially for the periods with intensive
523 agricultural fires or high RH levels (Cheng et al., 2021b).

524 **Data availability.**

525 Data are available from the corresponding author upon request (jiumengliu@hit.edu.cn).

526 **Author contribution**

527 YC and JL designed the study and prepared the paper with inputs from all the coauthors. QY, XC,
528 YZ, ZD and LL carried out the experiments. GG provided the air quality data. WM and HQ
529 participated in the field campaign and data analysis. QZ and KB supervised the study.

530 **Competing interests.**

531 The authors declare that they have no conflict of interest.

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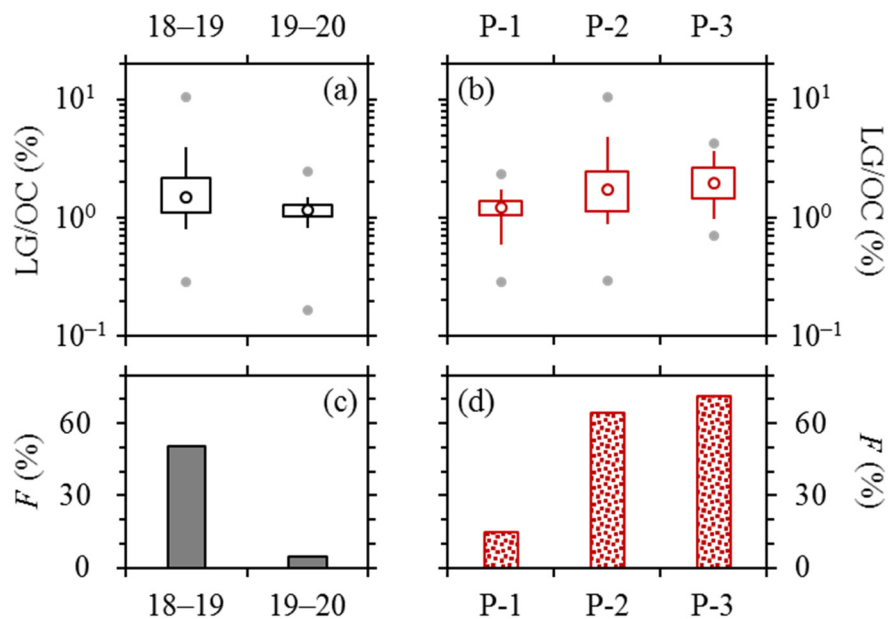
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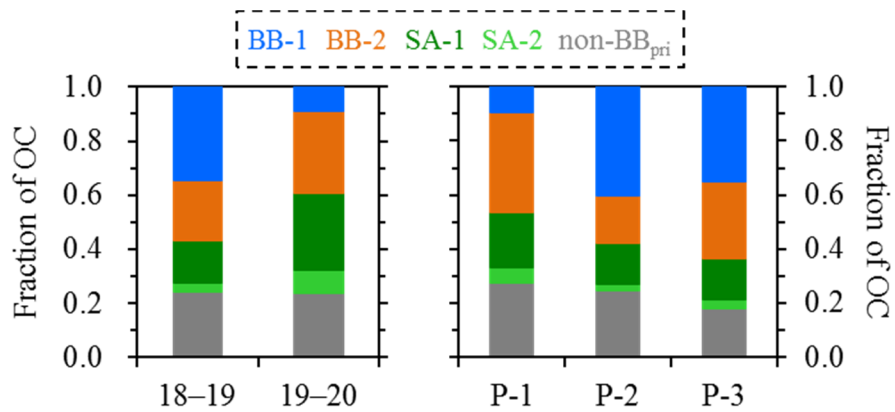
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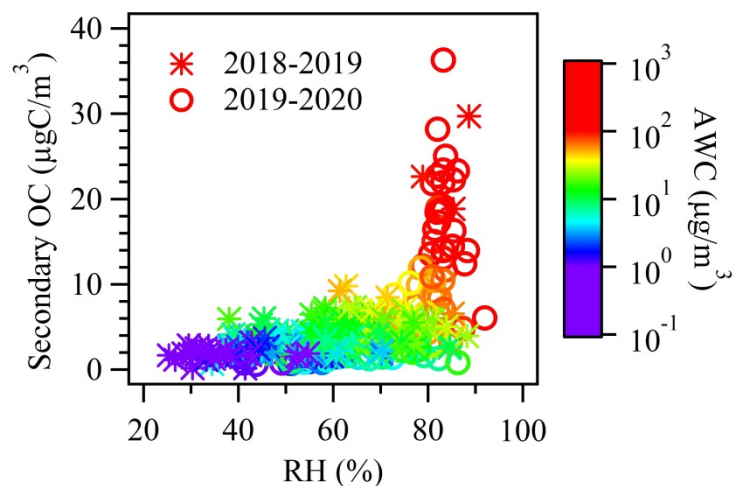
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737 **Figure 1.** Comparisons of levoglucosan to OC ratios, i.e., LG/OC (on a basis of carbon mass), and
 738 the fractions of samples with LG/OC above 1.5% (denoted as F), **(a, c)** between the 2018–2019 and
 739 2019–2020 campaigns, and **(b, d)** across the 2018–2019 samples collected before (P-1), during (P-
 740 2) and after (P-3) the “legitimate burning” periods. Lower and upper box bounds indicate the 25th
 741 and 75th percentiles, the whiskers below and above the box indicate the 5th and 95th percentiles, the
 742 solid circles below and above the box indicate the minimum and maximum, and the open circle
 743 within the box marks the median (the same hereinafter).



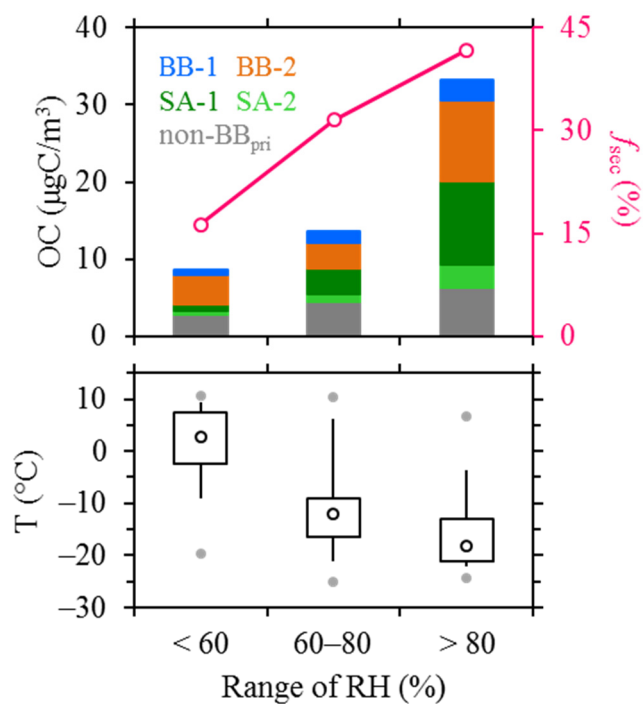
744

745 **Figure 2.** Comparison of OC source apportionment results between the 2018–2019 and 2019–2020
 746 campaigns (left panel), and across the 2018–2019 samples collected before (P-1), during (P-2) and
 747 after (P-3) the “legitimate burning” periods (right panel).



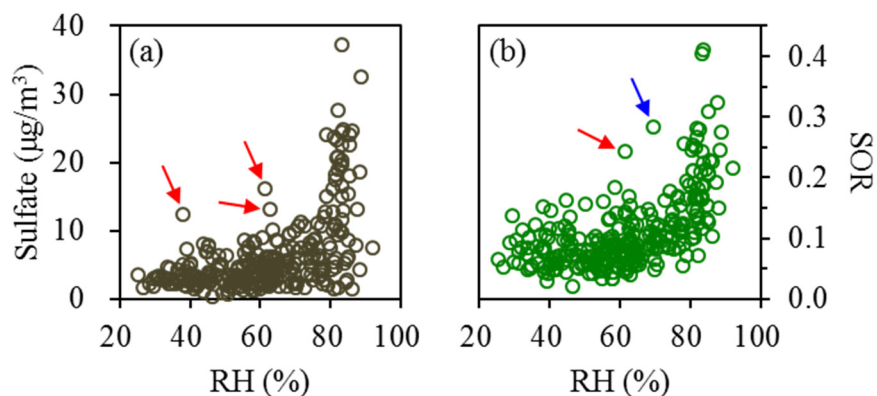
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749 **Figure 3.** Dependence of secondary OC (OC_{sec}) on RH among the two campaigns, color-coded by
 750 AWC levels. Results from the 2018–2019 campaign and 2019–2020 campaign were marked using
 751 stars and circles, respectively. The majority of the data points with RH above 80% were observed
 752 during 2019–2020. RH exceeded 80% for only ten samples collected during 2018–2019, and only
 753 three out of these ten samples showed RH-dependent increase of OC_{sec}.



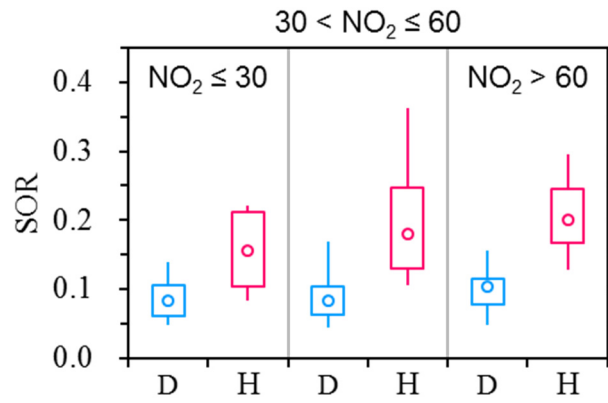
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755 **Figure 4.** Comparisons of OC source apportionment results (upper panel, left axis), the **contribution**
 756 **contributions** of PMF-based OC_{sec} to OC (f_{sec} ; upper panel, right axis), and ambient temperatures
 757 across different RH ranges (lower panel) for the 2019–2020 campaign.



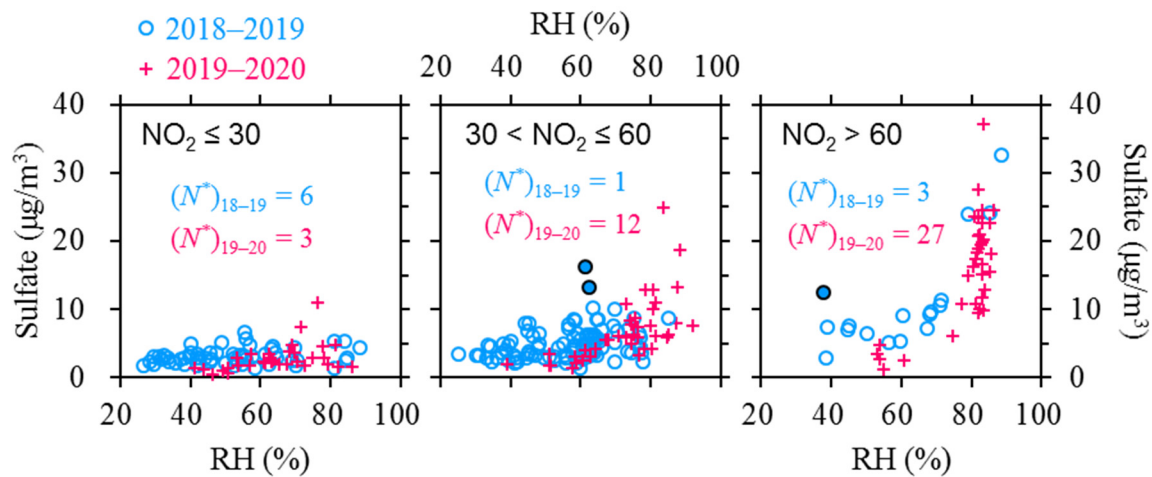
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759 **Figure 5.** Dependences of **(a)** sulfate and **(b)** SOR on RH. Results from the 2018–2019 and 2019–
 760 2020 campaigns are combined. Relatively high sulfate are typically observed for the conditions with
 761 RH above 80%, which is also the case for SOR. There appear to be several outliers showing
 762 considerably higher sulfate or SOR than other samples at similar RH. All the outliers occurred
 763 during the 2018–2019 measurement period, and most of them were accompanied with extremely
 764 high levoglucosan concentrations (above 5 $\mu\text{g}/\text{m}^3$), as highlighted by the red arrows. The outlier
 765 highlighted by the blue arrow was observed ~~with~~ at an ambient temperature of above 10 °C, which
 766 was uncommon for the heating season. The outliers indicate that factors other than RH were also at
 767 play in sulfate formation, but the influences were evident for only several samples.



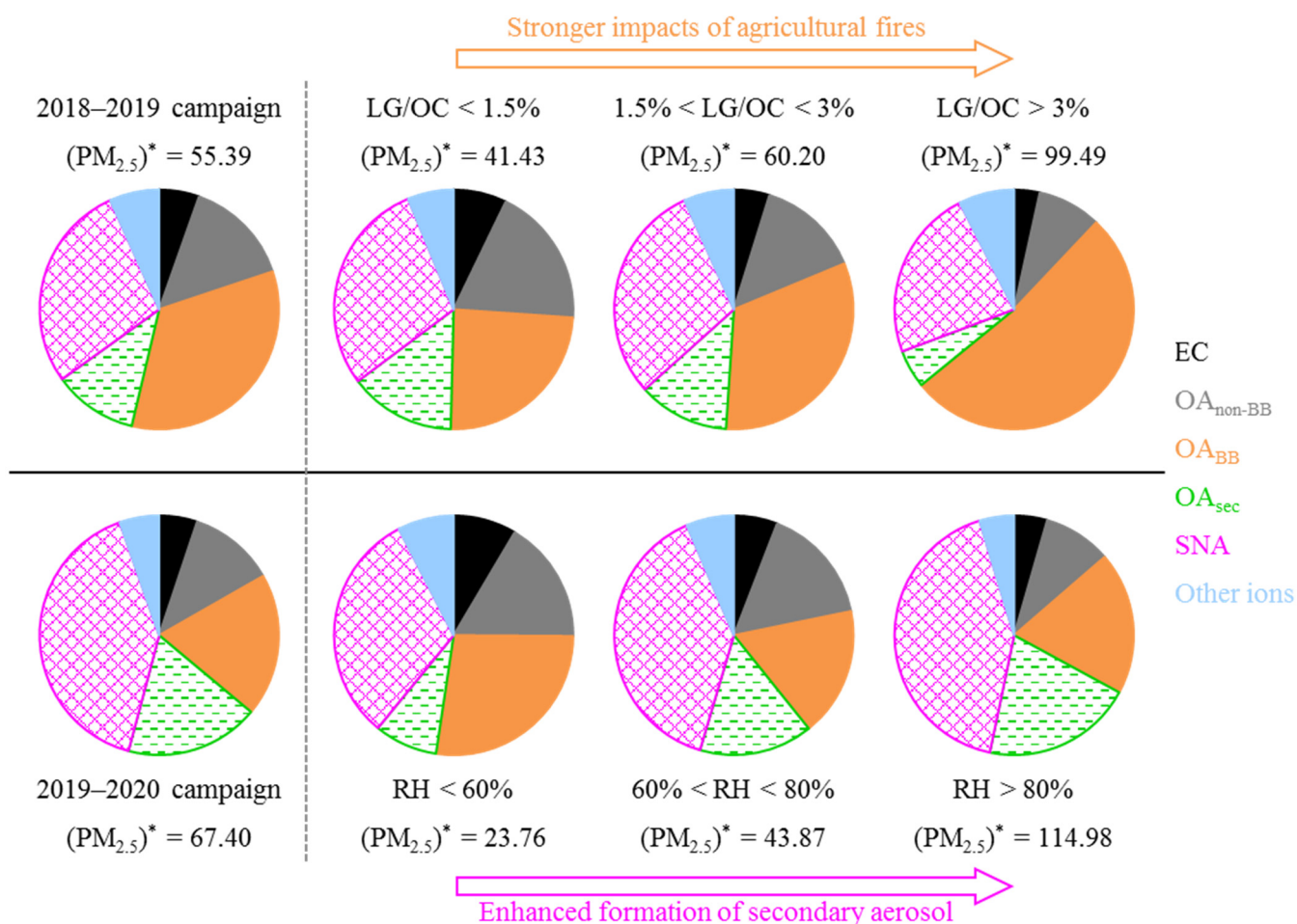
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769 **Figure 6.** Comparisons of SOR between different RH levels, with results from different NO₂ ranges
 770 (below 30, 30–60 and above 60 μg/m³) shown separately. Results from both the 2018–2019 and
 771 2019–2020 campaigns are included. The terms “D” and “H” indicate relatively dry (RH below 80%)
 772 and more humid conditions (RH above 80%), respectively.



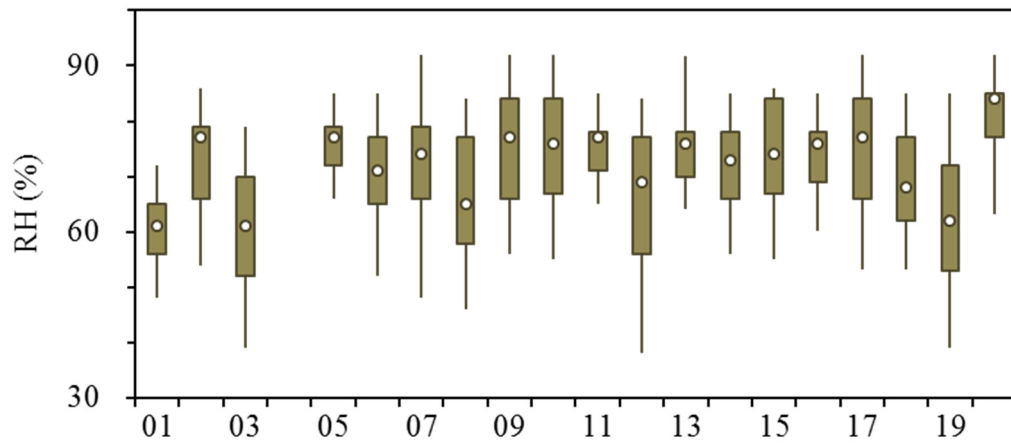
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774 **Figure 7.** Dependences of sulfate on RH in different NO₂ ranges (below 30, 30–60 and above 60
 775 µg/m³). Results from the 2018–2019 and 2019–2020 campaigns are shown using different markers.
 776 The outliers in Figure 5a are highlighted by the solid circles. N^* indicates the number of samples
 777 with RH above 80%. High-RH conditions were typically accompanied with NO₂ concentrations of
 778 below 30 µg/m³ during 2018–2019, and NO₂ above 60 µg/m³ during 2019–2020, respectively.



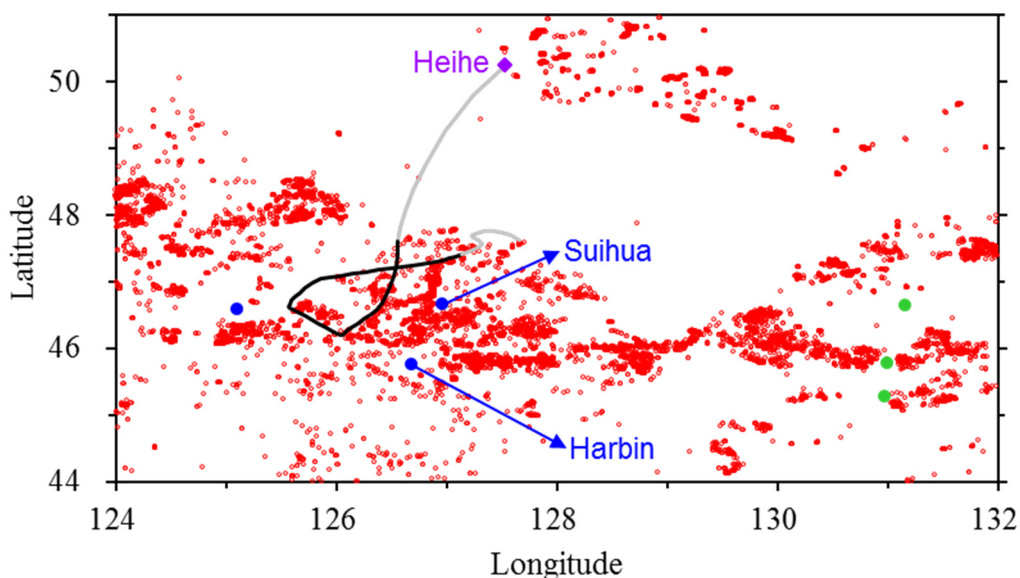
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780 **Figure 8.** Comparison of aerosol compositions measured for the 2018–2019 and 2019–2020 campaigns. The 2018–
 781 2019 measurement period experienced relatively dry meteorological conditions (with RH levels rarely exceeding
 782 80%) and was characterized by a wide window of ~3 months for “legitimate burning”. Correspondingly, variations
 783 of (PM_{2.5})^{*} concentration (in µg/m³) and aerosol composition observed during 2018–2019 were mainly driven by
 784 agricultural fires. However, the “legitimate burning” policy was terminated in 2019, and the 2019–2020 campaign
 785 did not show clear evidence for apparent influence of agricultural fires. On the other hand, high-RH conditions
 786 occurred much more frequently during the 2019–2020 measurement period compared to 2018–2019.
 787 Correspondingly, variations of (PM_{2.5})^{*} concentration and aerosol composition observed during 2019–2020 were
 788 mainly driven by RH-dependent increase of secondary aerosols.



789

790 **Figure 9.** Comparison of RH measured during January in Harbin across the past twenty years (from
 791 2001 through 2020). Time resolution is 1-h for the RH data. No observational result is available for
 792 January of 2004.



793

794 **Figure 10.** Active fires (red circles) detected by the joint NASA/NOAA Suomi-National Polar
 795 orbiting Partnership (S-NPP) satellite for Heilongjiang Province during 17–18 April, 2020. Three
 796 cities located in the Song-Nen Plain are shown using blue dots (the unlabeled city is Daqing), and
 797 three cities located in the San-Jiang Plain (i.e., Shuangyashan, Qitaihe and Jixi with decreasing
 798 latitudes) are shown using green dots. The two plains, separated by mountains, are the main
 799 agricultural regions in Heilongjiang. Intensive agricultural fires are evident for both plains during
 800 the two-day episode, indicating the open burning activities are province-wide, although prohibited.
 801 The agricultural fires resulted in severe $PM_{2.5}$ pollution for nearby cities, e.g., the 24-hour
 802 concentrations peaked at ~ 900 and $675 \mu\text{g}/\text{m}^3$ in Harbin and Jixi, respectively. A $PM_{2.5}$ episode
 803 was observed even for Heihe (~ 500 km away from Harbin) on 19 April, 2020, which was attributed to
 804 the pollutants transported from the Harbin-Suihua region. The solid line indicates the 72-hour back
 805 trajectory ending at 7:00 in Heihe, accompanied with the highest 1-hour $PM_{2.5}$ observed on 19 April,
 806 2020 ($\sim 310 \mu\text{g}/\text{m}^3$). The trajectory indicates transport pathway of air masses impacting Heihe,
 807 with the segment in black showing locations of the air masses during 17–18 April, 2020.

Supporting Information for:

Dramatic changes in Harbin aerosol during 2018–2020: the roles of open burning policy and secondary aerosol formation

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SI-1. Field observation.

Two campaigns were conducted at an urban site in Harbin during the heating seasons of 2018–2019 (from 16 October, 2018 to 14 April, 2019; $N = 180$) and 2019–2020 (from 16 October, 2019 to 4 February, 2020; $N = 112$). The sampling was performed in the campus of Harbin Institute of Technology ($45^{\circ}45'24''$ N, $126^{\circ}40'49''$ E), using a low volume sampler (MiniVol; Airmetrics, OR, USA) operated with pre-baked quartz fiber filters (2500 QAT-UP; Pall Corporation, NY, USA) at a flow rate of 5 L/min. As described in Cheng et al. (2021), the samples were analyzed for organic carbon (OC), elemental carbon (EC), organic tracers for biomass burning (levoglucosan and mannosan) and water-soluble inorganic ions. Briefly, OC and EC were measured by a thermal/optical carbon analyzer (DRI-2001; Atmoslytic Inc., CA, USA), using the IMPROVE-A temperature protocol with transmittance charring correction. Levoglucosan and mannosan were detected by a Dionex ion chromatography (IC) system (ICS-5000⁺; Thermo Fisher Scientific Inc., MA, USA), using the high performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC-PAD) method. The IC was also used to determine the inorganic ions including sulfate, nitrate, ammonium, etc.

Hourly air quality data (e.g., CO), which were measured at a nearby monitoring site (Taiping Hongwei Park, about 2.4 km away from the filter sampling site) operated by the China National Environmental Monitoring Center (CNEMC), were obtained from China's National Urban Air Quality Real Time Publishing Platform (<http://106.37.208.233:20035/>). Hourly meteorological data including temperature and relative humidity were obtained from Weather Underground (<https://www.wunderground.com>).

SI-2. Aerosol water content (AWC) and aerosol pH estimated using ISORROPIA-II

To estimate AWC and aerosol pH during the two campaigns, ISORROPIA-II was run with daily-integrated data (including concentrations of aerosol-phase species, ambient temperature and relative humidity) as input. To simplify the simulations, ISORROPIA-II was run assuming particles are “metastable”. It is also assumed that the particles are internally mixed and that pH does not vary with particle size (so that bulk properties represent the overall aerosol pH).

Because of limitations in input data, e.g., no gas phase data available directly on site, the calculation was done in two ways, the “reverse” and “forward” mode. For the “reverse” mode, the measured aerosol-phase data were deployed as input to retrieve AWC and pH directly. For the “forward” mode, the model was run in an “iteration” way, that we used the measured aerosol-phase data as initial input, ran ISORROPIA-II in the “forward” mode to predict gas-phase concentrations of NH_3 , HNO_3 and HCl , and used the sum of predicted gas-phase and measured aerosol-phase

concentrations as the input for next round. The calculations were repeated until the simulated results were stable and in line with the observational data. Both the reverse and forward modes showed comparable AWC levels (Figure S14). For pH, we specifically deployed results using the forward mode, as studies have suggested that the forward mode gives more accurate and robust results than the reverse mode (e.g., Guo et al., 2017, 2018; Song et al., 2018).

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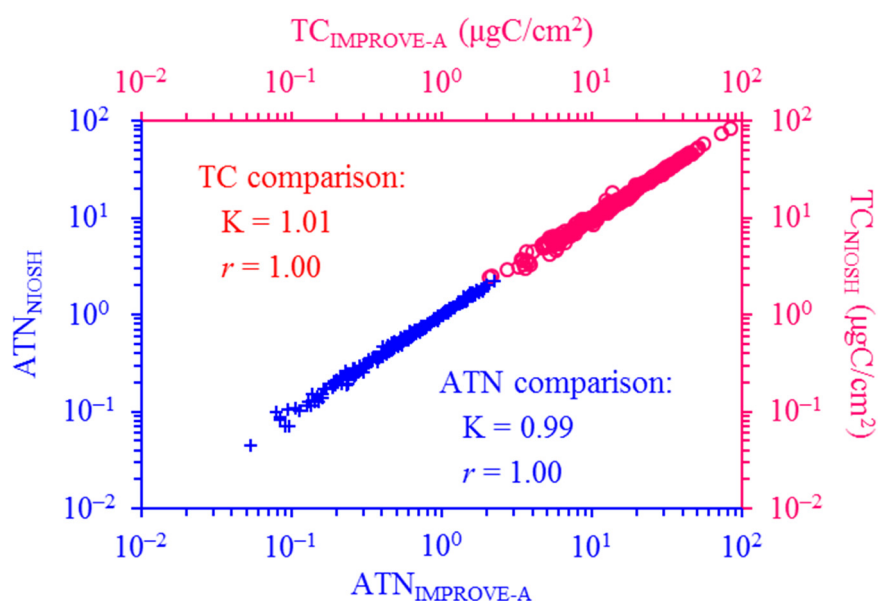


Figure S1. Comparisons of total carbon (TC) and optical attenuation (ATN) measured by different temperature protocols. Results from both campaigns are included. ATN is calculated as $\ln(I_{\text{final}}/I_{\text{initial}})$, where I_{initial} and I_{final} indicate filter transmittance signals measured at the beginning (i.e., when the loaded filter has not been heated) and end (i.e., when all the deposited carbon has been combusted off the filter) of thermal-optical analysis, respectively. Linear regression results are shown with K as slope (intercept was set as zero). TC and ATN agreed well between different protocols, demonstrating good precisions for both the carbon and transmittance measurements.

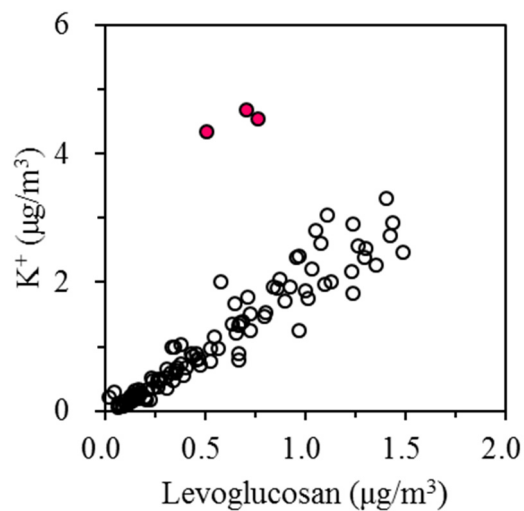


Figure S2. Relationship between K^+ and levoglucosan during the 2019–2020 campaign. Three samples collected during the Chinese New Year period exhibit substantially higher K^+ to levoglucosan ratios (as highlighted by the solid circles), pointing to significant influence of firework emissions.

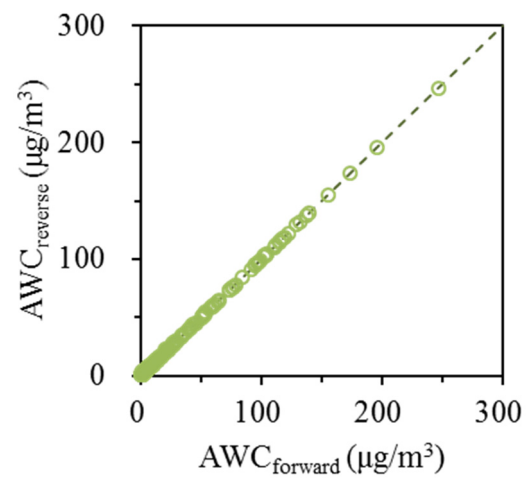


Figure S3. Comparison of AWC results predicted by reverse and forward modes. The dashed line indicates one-to-one correspondence.

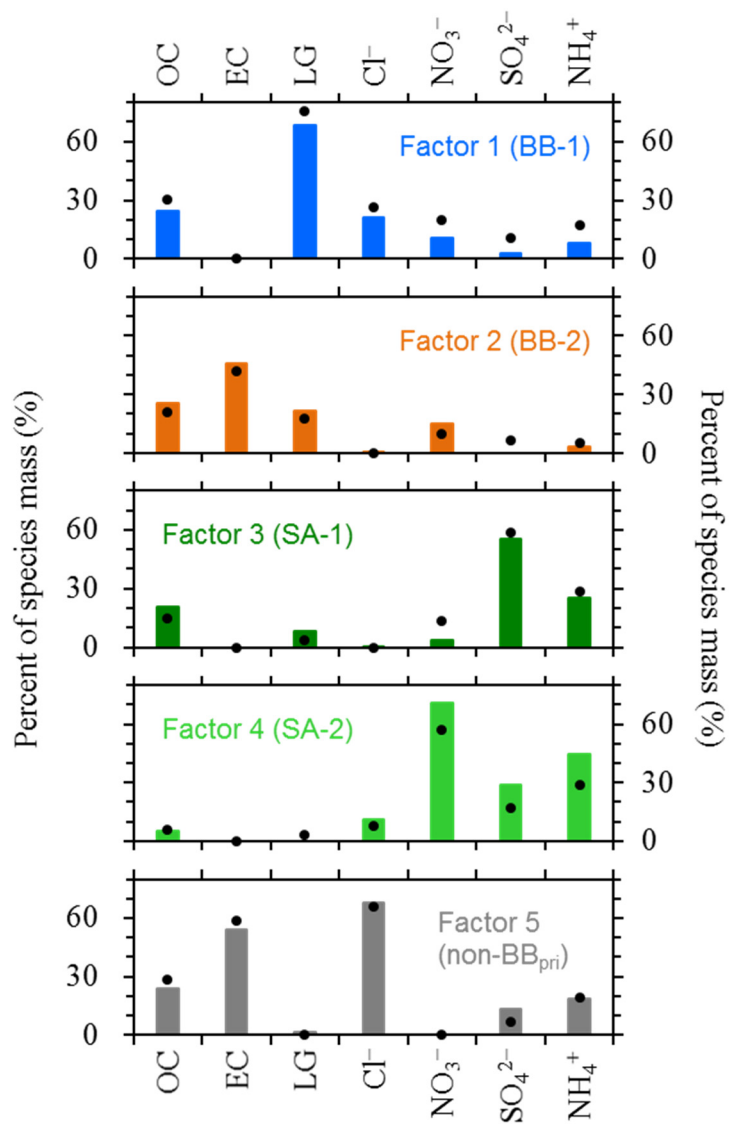


Figure S4. Source profiles resolved by PMF. The solid bars and circles indicate results obtained by this study and Cheng et al. (2021a), respectively. For this study, aerosol compositions measured during the 2018–2019 and 2019–2020 campaigns were combined and used as the PMF inputs, whereas Cheng et al. (2021a) was based only on the former campaign. In general, similar profiles were resolved by the two studies, despite the different measurement periods covered.

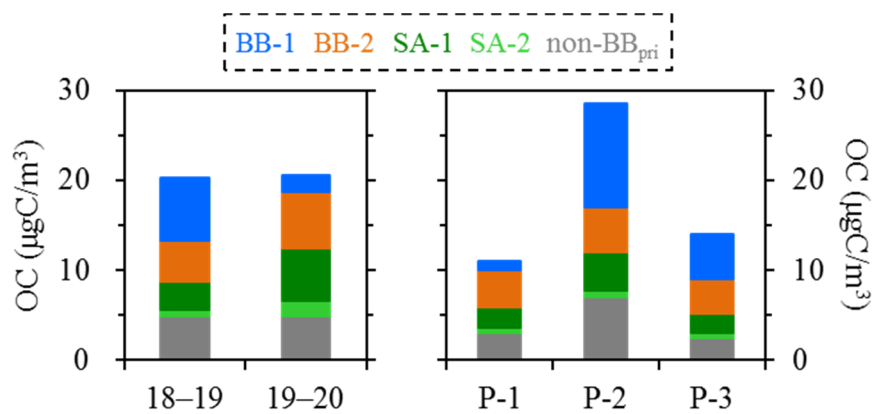


Figure S5. Comparisons of OC source apportionment results between the 2018–2019 and 2019–2020 campaigns (left panel), and across the 2018–2019 samples collected before (P-1), during (P-2) and after (P-3) the “legitimate burning” periods (right panel).

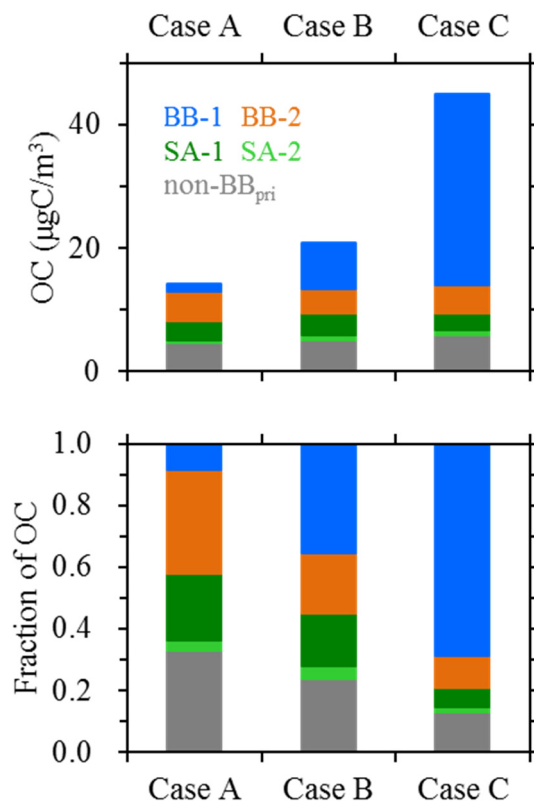


Figure S6. Comparison of OC source apportionment results across the 2018–2019 samples with increasing ~~strength~~ strengths of biomass burning ~~impacts~~ impact. Cases A, B and C correspond to LG/OC ranges of < 1.5%, 1.5–3.0% and > 3.0%, respectively.

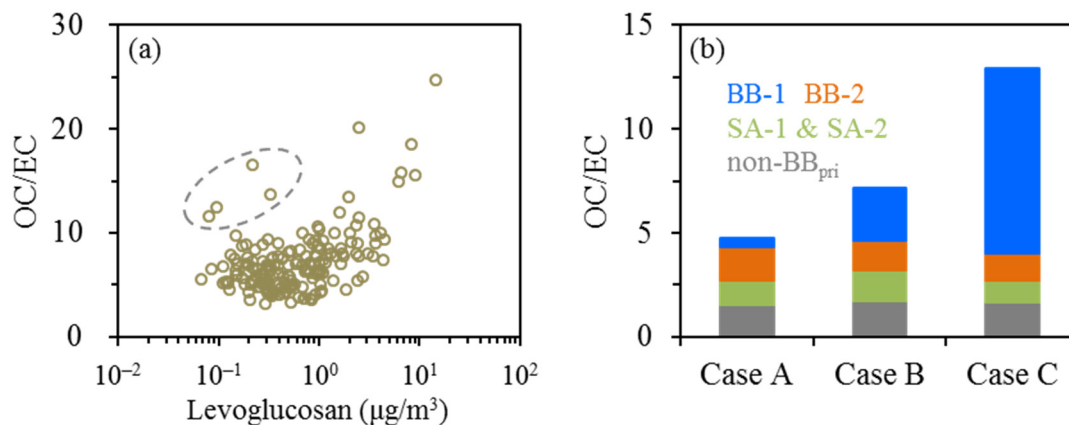


Figure S7. (a) Relationship between OC/EC and levoglucosan, and (b) comparison of OC/EC among Cases A–C, for the 2018–2019 campaign. OC/EC ratios in (b) are based on results from PMF analysis, i.e., for each case, OC/EC is presented as the sum of source-resolved OC to total EC ratios (e.g., $\text{OC}_{\text{BB-1}}/\text{EC}$ and $\text{OC}_{\text{BB-2}}/\text{EC}$). The two factors representing secondary aerosols are not distinguished in (b). In general, OC/EC showed a positive dependence on levoglucosan, although there appeared to be several outliers (as highlighted by the dashed oval) which had the lowest EC concentrations of the measurement period (below $\sim 0.5 \mu\text{g}/\text{m}^3$). Thus, biomass burning is considered the dominant driver for the temporal variation of OC/EC during the 2018–2019 campaign. This inference is also supported by (b), as OC/EC exhibited an increasing trend from Case A through Case C, which cannot be explained by SOA or non-BB emissions.

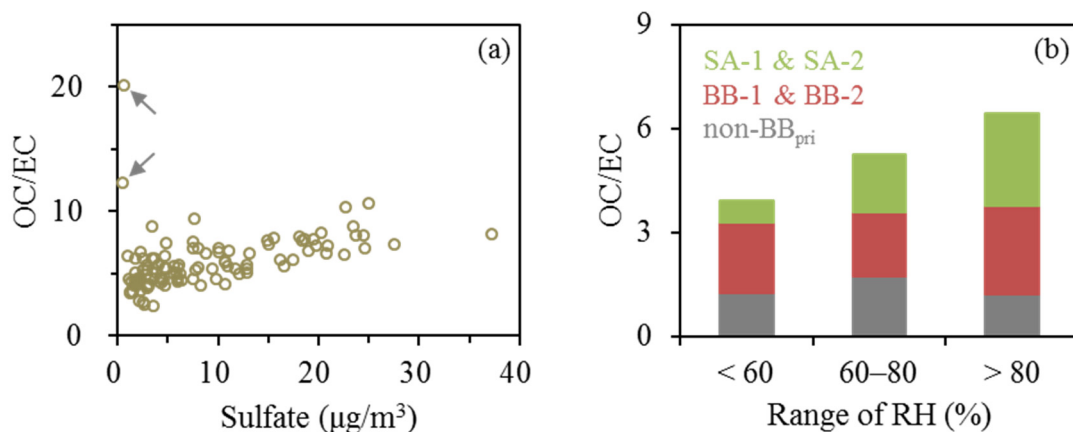


Figure S8. (a) Relationship between OC/EC and sulfate, and (b) comparison of OC/EC with increasing RH levels, for the 2019–2020 campaign. In general, OC/EC showed a positive dependence on sulfate, although there were two outliers (as highlighted by the arrows) which had the lowest EC concentrations of the measurement period (below $0.3 \mu\text{g}/\text{m}^3$). Thus, SOA is considered the dominant driver for the temporal variation of OC/EC during the 2019–2020 campaign. This inference is also supported by (b), as with increasing RH, OC/EC exhibited an increasing trend, which cannot be explained by the primary factors (either BB or non-BB).

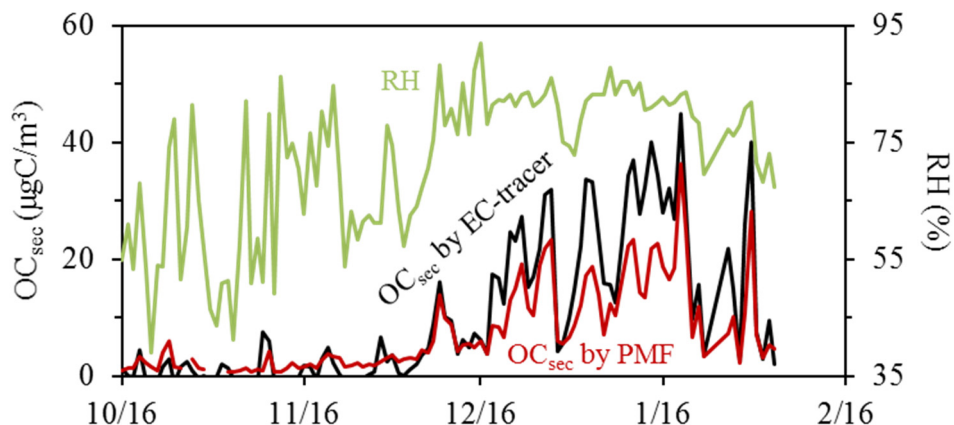


Figure S9. Temporal variations of OC_{sec} and RH during the 2019–2020 campaign. The PMF-based OC_{sec} was calculated as the sum of OC masses attributed to the SA-1 and SA-2 factors. For the EC-tracer method, OC_{sec} was calculated as: $OC_{sec} = OC - EC \times (OC/EC)_{pri} - OC^*$, where $(OC/EC)_{pri}$ is the OC to EC ratio representative of combustion sources and OC^* indicates primary OC from non-combustion sources. ~~For the 2019–2020 campaign, $(OC/EC)_{pri}$ and OC^* were determined as the slope (2.13) and intercept (3.11) from the linear regression of OC on EC ($r = 0.98$), respectively, based on the low RH samples (i.e., those with RH below 60%).~~ For the 2019–2020 campaign, $(OC/EC)_{pri}$ and OC^* were determined based on linear regression of OC on EC ($r = 0.98$), with $(OC/EC)_{pri}$ as the slope (2.13) and OC^* as the intercept (3.11), respectively, using low-RH samples (i.e., those with RH below 60%). Compared to the PMF-based results, OC_{sec} calculated by the EC-tracer method showed a similar pattern of temporal variation. Results from both methods showed RH-dependent increase of OC_{sec} .

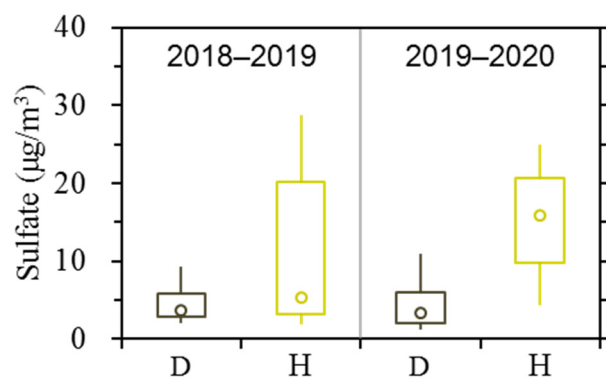


Figure S10. Comparison of sulfate between different RH levels for the 2018–2019 and 2019–2020 campaigns. The terms “D” and “H” indicate relatively dry and more humid conditions with RH below and above 80%, respectively.

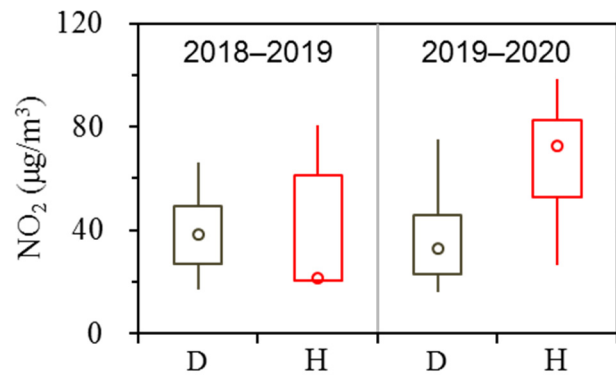


Figure S11. Comparison of NO₂ between different RH levels for the 2018–2019 and 2019–2020 campaigns. ~~The terms “D” and “H” indicate relatively dry and more humid conditions with RH below and above 80%, respectively.~~

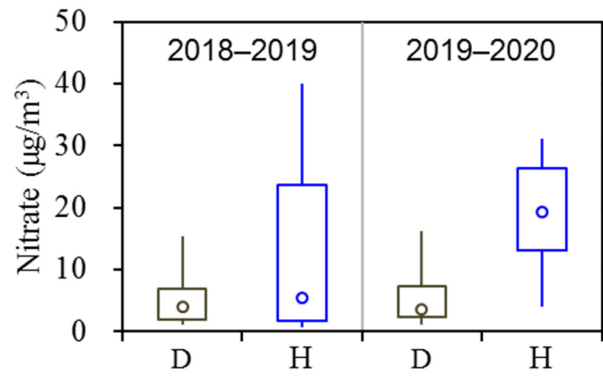


Figure S12. Comparison of nitrate between different RH levels for the 2018–2019 and 2019–2020 campaigns. ~~The terms “D” and “H” indicate relatively dry and more humid conditions with RH below and above 80%, respectively.~~

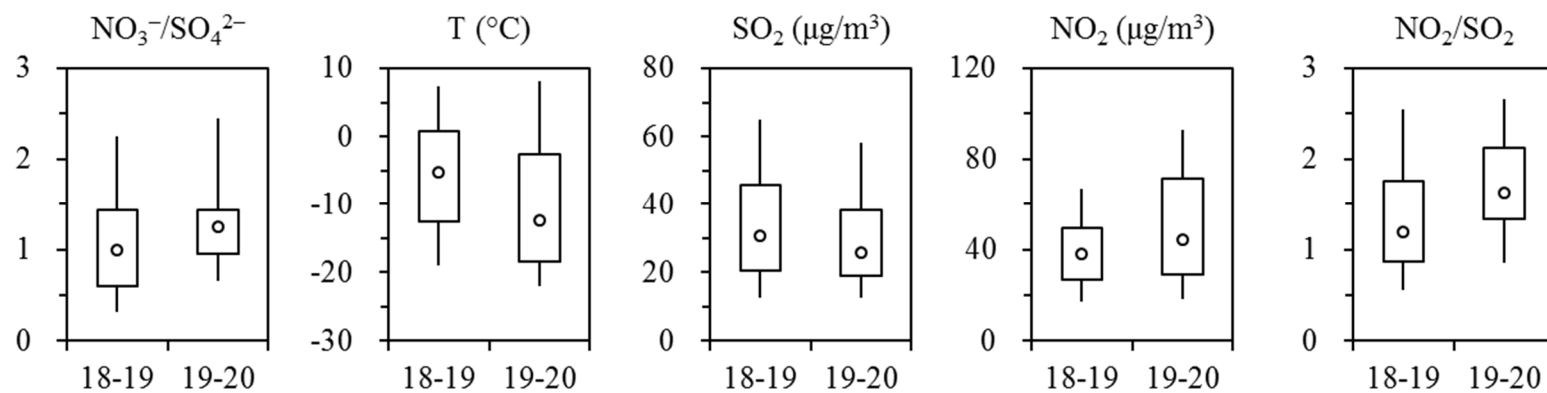


Figure S13. Comparisons of the nitrate to sulfate ratios, ~~temperature~~ temperatures, SO₂, NO₂ and the NO₂ to SO₂ ratios between the 2018–2019 and 2019–2020 campaigns.

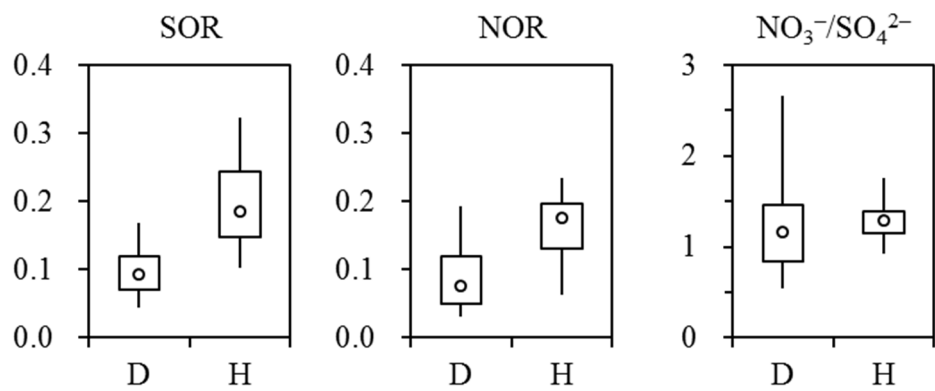


Figure S14. Comparisons of SOR, NOR and the nitrate to sulfate ratios at different RH levels for the 2019–2020 campaign.

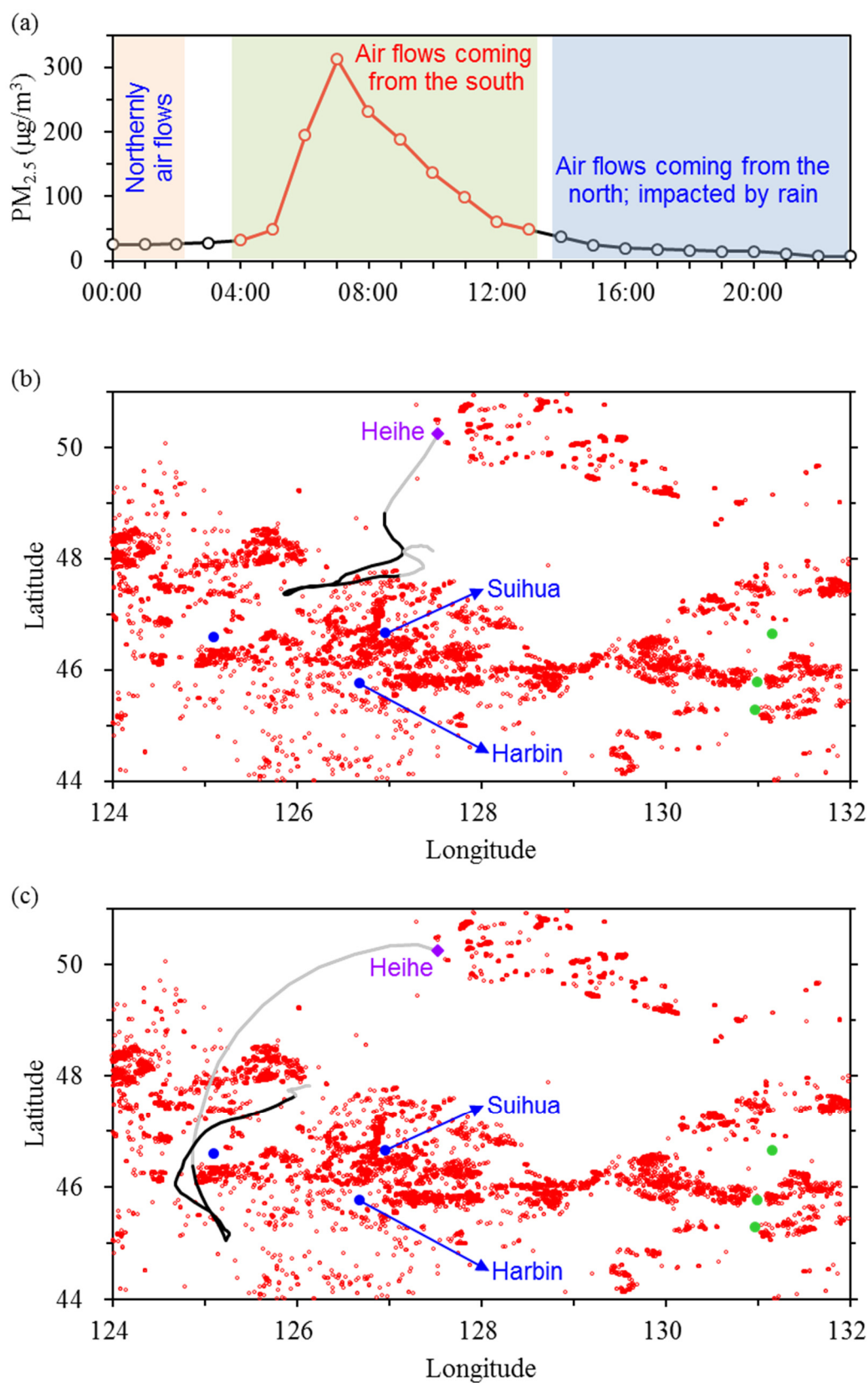


Figure S15. (a) Temporal variation of 1-h $PM_{2.5}$ observed in Heihe on 19 April, 2020. (b–c) 72-hour back trajectories ending at 4:00 and 13:00, respectively, in Heihe, overlaid with active fires detected during 17–18 April, 2020 as red circles. $PM_{2.5}$ were relatively low between 0:00 and 3:00,

when the air flows came from the northwest, moved fast and descended sharply. $PM_{2.5}$ started to increase at 4:00, with the trajectory from the south and impacted by the region with agricultural fires (as shown in b). The increase of $PM_{2.5}$ continued as the trajectory path moved towards Harbin and Suihua, where the impacts of open burning were inferred to be extremely strong based on their off-the-chart $PM_{2.5}$ concentrations. The maximum $PM_{2.5}$ was observed at 7:00, and then $PM_{2.5}$ started to decrease although the air masses still passed over the Harbin-Suihua region (or the nearby area) before arriving at Heihe. A likely cause for the decrease of $PM_{2.5}$ after 7:00 was the increase of planetary boundary layer height from morning through noon time. The trajectory left the Harbin-Suihua region at 13:00 (as shown in c) and returned to the north at 14:00. In addition, there was rain in Heihe after 14:00, and correspondingly, $PM_{2.5}$ gradually decreased to below $10 \mu\text{g}/\text{m}^3$.