

A point-by-point response to the reviews

Thank you for your valuable comments. The followings are our responses to your comments.

Response to Reviewer #3

Comment 1: The article aims to analyze the seasonal variation characteristics of the typical WSIs (WSIs) in the PM_{2.5} collected at an urban site in Beijing as well as a rural site in Baoding. The results from ion chromatography analysis of daily samples through the year of 2014 were presented in this study, the field and lab experiment is laborious. The data collected at the two sites were analyzed well and new ideas were given. The authors proposed the possible contribution of the periodic emissions from farmers' activities in the North China Plain (NCP) to the WSIs in Beijing, and the influence of fertilization events and crop straw had important influence on the regional air quality during the harvest seasons periods. Also, the maize harvest and soil ploughing in autumn in NCP were suspected to make contribution to the atmospheric Ca²⁺ in Beijing, which has not been explained well by previous studies. Since the influence of fertilization events and crop straw on the air quality have been neglected by most previous studies and only a small part of studies focused on the variation characteristics of WSIs in the four seasons, the detailed data of the daily variations of WSIs in this article are helpful for further identification of the pollution sources and how meteorological factor affect the accumulation of atmospheric pollutants.

Answer: Thank you for your extremely positive evaluation of our work. The followings are our responses to your comments.

Comment 2: The data in this article are collected at analyzed from two sites in Beijing and Baoding, and the major findings in this study is the possible contribution of the periodic emissions from farmers' activities in the NCP, such as crop harvest, crop straw burning, and coal combustion, to the WSIs in Beijing, while the title of this paper is "The variation characteristics and possible sources of atmospheric water-soluble ions in Beijing", the title is confusing and I wonder whether it is accurate. Maybe the inspiring points about the possible contribution of the periodic emissions from farmers' activities in the NCP could be highlighted.

Answer: Thank you for your valuable comments. The title has been replaced with "The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing".

Comment 3: There are some confusing expressions in this article.

Line 657: residential coal stoves,

Line 666: after harvest of the winter wheat in June-July?

Line 673-674: the serious pollutant emissions from the chimney of the farmers' coal stoves can be easily imagined by the strong smog,

Line 842: intensive farmers' activities,

Line 915: Tham et al., 2016

Answer: These confusing expressions as well as other mistakes have been corrected in our revised

44 manuscript:
 45 “Line 657: farmers’ coal stoves;
 46 Line 666: after the wheat harvest (in June-July);
 47 Line 673-674: heavy smoke from the chimneys of the farmers’ coal stoves can be seen everywhere
 48 in rural areas of the NCP due to heating supply;
 49 Line 842: during the period of farmers’ activities;
 50 Line 915: Tham et al. (2016)”

51
 52 **Response to Co-Editor**

53 **Comment 1:** In my opinion, the revised version of the manuscript has improved quite a bit. The
 54 authors have done a good job addressing the multiple concerns raised by the reviewers. I have a few
 55 remaining comments, mostly of technical nature:

56
 57 **Answer:** Thank you for your appreciation. The followings are our responses to your comments.

58
 59 **Comment 2: Throughout the text:** insert spaces between values and their units, for example,
 60 170km → 170 km

61
 62 **Answer:** Thank you for your valuable guidance. Spaces have been inserted between values and
 63 their units throughout the text.

64
 65 **Comment 3: Figures:** some of the figures in the PDF appear to have low resolution and are difficult
 66 to read without zooming into the figures. In particular, some of the axis labels, axis tick labels, and
 67 legends appear blurry. I would work on optimizing the resolution as well as size of the text used for
 68 annotating the figures. Figures 5 and 10 are especially difficult to read because of its large
 69 information content.

70
 71 **Answer:** Thank you for your comments. All of the figures have been optimized: The axis labels,
 72 axis tick labels and legends have been enlarged and in bold for reading easily without zooming into
 73 the figures. Some unrelated information (such as MGL, the values of the increasing rates of NO₃⁻
 74 and SO₄²⁻) in figures 5 and 10 has been delated and the necessary annotations have been added in
 75 the caption (figure 5) in our revised manuscript.

76

The number of the figure	Action	Treatment
1	Optimize	Change the display order of figures
2	Optimize	Change the display order of figures
3	Optimize	Enlarge the sizes of the axis labels and legends
4	Optimize	Enlarge the sizes of the axis labels and legends
5	Revise and annotate	Delate the unrelated information, change the display order and add the annotations
6	Revise	Change the colors and increase the font sizes
7	Optimize	Change the arrows in bold
8	Optimize	Change the symbols in bold
9	Optimize	Enlarge the sizes of the axis labels and legends

10	Revise	Delate the unrelated information, change the colors and enlarge the sizes of the axis labels and legends
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77

78 **Comment 4:** Line 84: the “intensity” of the emission is ambiguous; it is better to compare actual
79 emissions factors in g pollutants per kg of burned coal. I am sure those have been measured.

80

81 **Answer:** The emissions factors of typical pollutants have been compared and added in our revised
82 manuscript: “...the emission factors of typical pollutants such as PM_{2.5}, organic carbon (OC) and
83 polycyclic aromatic hydrocarbons (PAHs) from farmers’ coal stoves (about 1054-12910 mg/kg for
84 PM_{2.5}, 470-7820 mg/kg for OC and 58.5-229.1 mg/kg for PAHs) are usually about 1-3 orders of
85 magnitude greater than those from coal power plants or industries boilers (about 16-100 mg/kg for
86 PM_{2.5}, 0.3-17.1 mg/kg for OC and 0.8-12.8 µg/kg for PAHs) (Zhang et al., 2008; Xu et al., 2006;
87 Geng et al., 2014; Chen et al., 2005; Revuelta et al., 1999; Yang et al., 2016)...”

88

89 **Comment 5:** Line 107: what is meant by “artificial intelligence” here? I looked up the info about
90 the Laoying 2034 sampler, it appears to be a normal sampling instrument.

91

92 **Answer:** Thanks for your comments. “Artificial intelligence” has been delated in our revised
93 manuscript.

94

95 **Comment 6:** Line 132: please confirm that the station is only 20 m away. Do you perhaps mean 20
96 km?

97

98 **Answer:** The Beijing urban ecosystem research station is indeed 20 m away from our sampling site
99 of RCEES because the station is also located in our institute (RCEES) and the distance between
100 them is the spacing (about 20m) between two laboratory buildings.

101

102 **Comment 7:** Line 141: I think you should define what you mean by the “total cation concentration”
103 in this sentence. Do you consider the different charge states of the ions [total positive] = [Na⁺] +
104 [NH₄⁺] + 2*[Mg²⁺] + 2*[Ca²⁺] + [K⁺]? Also, since your positive and negative ions appear to be
105 balanced, does it mean that your PM_{2.5} is always neutralized (not acidic, with very low [H⁺])? If so
106 this would be worth discussing because particle acidity is an important parameter in controlling
107 SOA growth on particles.

108

109 **Answer:** Yes, the different charge states of the ions had been considered in our manuscript.
110 Although the positive and negative ions appear to be balanced, it doesn’t mean that the PM_{2.5} is
111 always neutralized because of the unknown concentrations of CO₃²⁻ and HCO₃⁻ (Hennigan et al.,
112 2015). If we consider the unknown concentrations of CO₃²⁻ and HCO₃⁻, the PM_{2.5} should be acidic
113 (with [H⁺]). In addition, several studies have estimated the concentrations of H⁺ by using the formula
114 below (with the exception of Mg²⁺ and Ca²⁺) (Zhang et al., 2007; Behera et al., 2015):

115 $[H^+] = [Cl^-] + [NO_3^-] + 2 \times [SO_4^{2-}] - [NH_4^+]$ (1)

116 or

117 $[H^+] = [Cl^-] + [NO_3^-] + 2 \times [SO_4^{2-}] - [NH_4^+] - [Na^+]$ (2)

118 It is evident that the PM_{2.5} in this study will be acidic based on the two methods. Particle acidity is
119 indeed an important parameter in controlling SOA growth on particles, which has been reported by
120 previous studies (Zhang et al., 2004; Hu et al., 2014). According to your valuable comments, the
121 “total cation concentration” and “total anion concentration” have been defined as “[Na⁺] + [NH₄⁺]
122 + 2 × [Mg²⁺] + 2 × [Ca²⁺] + [K⁺]” and “[F⁻] + [HCOO⁻] + [Cl⁻] + [NO₃⁻] + 2 × [SO₄²⁻]” in our revised
123 manuscript, respectively.

124

125 **Comment 8:** Line 156: The proposed explanation for the lower than expected PM_{2.5} mass measured
126 with TEOM needs more support. Instead of citing the Finlayson-Pitts book, please provide
127 references proving that NH₄NO₃ and other volatiles are indeed depleted from PM_{2.5} measured with
128 TEOM. I find it difficult to believe that 50 °C would deplete things other than water from particles
129 to a measurable extent. I suspect that other readers will also have doubts about that. So more
130 references here would definitively help.

131

132 **Answer:** Thank you for your recommendation. Another definitive reference (Charron et al., 2004)
133 has been found to confirm our proposed explanation for the lower than expected PM_{2.5} mass
134 measured with TEOM. Charron et al. (2004) carried out a comparison of PM₁₀ and PM_{2.5} mass
135 measured simultaneously by TEOM and filter-based gravimetric methods. The results confirmed
136 the expected large difference between the two methods and large differences between measurements
137 are associated with high particulate ammonium nitrate concentrations. According to your comments,
138 this reference has been added in our revised manuscript and uploaded in the system as the
139 supplement for your check.

140

141 **Comment 9:** Line 158: is the 20% value based on your measurement done in this work or on
142 measurements done by Yang et al. (2015)?

143

144 **Answer:** The 20% value is based on your measurement done in this work. This part has been made
145 clear in our revised manuscript: “...whereas they were found to only account for about 20% in the
146 filters of the TEOM 1405 Monitor in this study...”

147

148 **Comment 10:** Line 163: the variation is **not** periodic, please see the suggested correction in the
149 table below.

150

151 **Answer:** The mistake has been corrected in our revised manuscript based on your valuable comments.
152 Thank you very much.

153

154 **Comment 11:** Lines 206 and 212: you are using molar ratios in some cases and mass ratios in others.
155 It would help to be more uniform to avoid confusion.

156

157 **Answer:** Thank you for your valuable comments. Molar ratios were employed in most cases in the
158 paper, thus mass ratios (the mass Cl⁻/K⁺ ratios in Line 212 and the mass concentration ratios of NO₃⁻
159 /SO₄²⁻ in Table 3) have been replaced with molar ratios in our revised manuscript.

160

161 **Comment 12:** Line 222: specify the amount burned in kg (or another appropriate SI unit) per year;

162 use an appropriate unit modifier to get rid of the trailing zeros in the number. Example: 42 Tg/year

163

164 **Answer:** Thank you for your valuable guidance. 42,000,000 Tons (line 222) and 1,174,000 Tons
165 (line 232) have been replaced with 42 Tg/year and 1.174 Tg.

166

167 **Comment 13:** Line 232: since you are attributing high Cl^- to the use of NH_4Cl fertilizer, it would
168 be useful to discuss a correlation between the chloride and ammonium ions in this period compared
169 to other periods.

170

171 **Answer:** The correlation between Cl^- and NH_4^+ might be not significant in this period compared to
172 other periods, because NH_4^+ was not only from the direct emission of NH_4Cl fertilizer but also
173 dominated by the concentrations of atmospheric NH_3 . The soil source (microbial activities) and the
174 animal wastes mainly contributed to atmospheric NH_3 , especially during the summer with high
175 temperatures (Krupa, 2003). Therefore, it might be difficult to discuss the correlation between Cl^-
176 and NH_4^+ for recognizing the source of NH_4Cl fertilizer.

177

178 **Comment 14:** The use of English in this paper will need to be improved before the paper can appear
179 in its final form in ACP. The table below lists some of the mistakes but it is not a comprehensive
180 list. Given the high number of mistakes I am going to have to request a proof-reading service from
181 the journal.

182

183 **Answer:** We think it is an excellent arrangement for requesting a proof-reading service from the
184 journal. According to your comments, both the revised manuscript (marked) and a clean one have
185 been uploaded in the system. Thank you very much.

186

187 **Comment 15:** (from the Table in the review)

188 Line 82: Rephrase "...imagined by the strong smog..."

189 Line 218: Replace the http link with a reference to one

190 Line 262-269: Spilt this very long sentence in 2-3 sentences

191

192 **Answer:** Thank you very much for your careful reviews. These sentences have been corrected in
193 our revised manuscript:

194 "Line 82: heavy smoke from the chimneys of the farmers' coal stoves can be seen everywhere in
195 rural areas of the NCP due to heating supply;

196 Line 218: the http link has been replace with the reference of Ma et al. (2015);

197 Line 262-269: The back trajectory cluster analysis also supported the above conclusion: (1) the
198 extremely high concentrations of Ca^{2+} in Beijing occurred during the period of 6-25 October (Fig.
199 3 and Fig. 4) when the air parcels were mainly from the southwest/south regions (Fig. 5) where the
200 vast areas of agricultural field were being under intensive maize harvest and soil ploughing. (2)
201 Although the concentrations of Ca^{2+} in the rural area remained at high levels during the period of 2-
202 14 November (Fig.3 and Fig. 4), the relatively low concentrations of Ca^{2+} in Beijing were observed
203 during the period when the air parcels were mainly from the northwest region (Fig. 5) where
204 agricultural activities are relatively sparse."

205 In addition, other revisions such as "replace" and "delate" listed in the Table have been done in our

206 revised manuscript. Thank you for all you've done for us.

207

208 **References**

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249 The possible contribution of the periodic emissions from farmers'
250 activities in the North China Plain to atmospheric water-soluble ions
251 in Beijing

252 ~~The variation characteristics and possible sources of atmospheric~~
253 ~~water-soluble ions in Beijing~~

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262 Abstract: The North China plain (NCP), ~~which includes including~~ Beijing, is currently suffering
263 from severe haze events due to high pollution level of PM_{2.5}. To mitigate the serious pollution-~~status~~
264 ~~problem~~, identification of the sources of PM_{2.5} is urgently needed for the effective control measures.
265 Daily samples of PM_{2.5} were collected in Beijing city ~~as well as~~ and in a rural area in Baoding,
266 Hebei Province through the year of 2014, and the seasonal variation ~~characteristics~~ of water-soluble
267 ions (WSIs) in ~~the~~ PM_{2.5} were comprehensively analyzed ~~for recognizing to determine~~ their possible
268 sources. The results indicated that the periodic emissions from farmers' activities made ~~evident~~
269 ~~contribution a significant contribution~~ to the atmospheric WSIs in Beijing. The relatively high
270 concentration of K⁺ in winter and autumn at the two sampling sites confirmed that crop straw
271 burning ~~made evident contribution contributed~~ to atmospheric K⁺ in Beijing. The remarkable
272 elevation of Cl⁻ at the two sampling sites as well as the evident increase of the Cl⁻/K⁺ ratio and the
273 Cl⁻ proportion in WSIs during the winter in Beijing ~~were reasonably could be~~ ascribed to coal
274 combustion for heating by farmers. The unusually high ratio of Cl⁻ to Na⁺ in summer, the obviously
275 high concentrations of Cl⁻ in the rural sampling site and the elevation of Cl⁻ proportion in WSIs in
276 Beijing during the maize fertilization could be ~~rationally~~ explained by the use of the prevailing
277 fertilizer of NH₄Cl in the vast area of NCP. The abnormally high concentrations of Ca²⁺ at the two
278 sampling sites and the elevation of Ca²⁺ proportion during the period of the maize harvest and soil
279 ploughing in Beijing provided convincing evidences that the intensive agricultural activities in
280 autumn ~~made evident contribution contributed~~ to the regional mineral dust. The most serious
281 pollution episodes in autumn were coincident with significant elevation of Ca²⁺, indicating that the
282 mineral dust emission from the harvest and soil ploughing not only increased the atmospheric
283 concentrations of the primary pollutants, but also greatly accelerated formation of sulfate and nitrate
284 through heterogeneous reactions of NO₂ and SO₂ on the mineral dust. The backward trajectories
285 also indicated that the highest concentrations of WSIs usually occurred in the air parcel from

286 southwest/south regions ~~with, which have a~~ high density of farmers. In addition, the values of
287 nitrogen oxidation ratio (NOR) and the sulfur oxidation ratio (SOR) were found to be much higher
288 under haze days than under non-haze days, implying that formation of sulfate and nitrate was greatly
289 accelerated through heterogeneous or multiphase reactions of NO₂ and SO₂ on PM_{2.5}.

290 1. Introduction

291 The North China plain (NCP) is frequently suffering from severe haze pollution in recent years
292 (Chan and Yao, 2008;Liang et al., 2016), which has aroused great attention from the general public
293 (Zhang et al., 2014;Guo et al., 2014;Huang et al., 2014a;Yang et al., 2015b;Zhang et al.,
294 2015b;Zheng et al., 2015b;Sun et al., 2006). The severe haze pollution is mainly ascribed to
295 elevation of fine particulate matter with dynamic diameter less than 2.5 μm (PM_{2.5}) (Huang et al.,
296 2014a). PM_{2.5} can directly reduce atmospheric visibility by scattering or absorbing solar light
297 (Seinfeld and Pandis, 1998;Buseck and Posfai, 1999;Cheng et al., 2006) and is harmful to human
298 health (Finlayson-Pitts and Pitts, 2000;Nel, 2005;Poschl, 2005;Peplow, 2014).

299 To mitigate the serious pollution ~~status problem~~, identification of the sources of PM_{2.5} is urgently
300 needed for the effective control measures. Based on field measurements, positive matrix
301 factorization (PMF) (Yu et al., 2013;Wu et al., 2014;Huang et al., 2014a), principal component
302 analysis (PCA) (Wang et al., 2015) and chemical mass balance (CMB) (Huang et al., 2014a;Guo et
303 al., 2012) have been widely used for identifying the sources of PM_{2.5}. However, the results of the
304 source apportionment are still not convincing because there are large uncertainties about the
305 indicators, dominant factors and emission inventories used for the identification. For example, some
306 studies suggested traffic emissions in Beijing contributed about 15~20% to the PM_{2.5} (Yu et al.,
307 2013;Wu et al., 2014), while only 4% of the contribution was also reported (Zhang et al., 2013).
308 Additionally, the current source apportionment can only present gross contribution of each source
309 classification, but there are markedly different emissions from individual sources in the same

310 classification. For example, due to the strict control measures and highly efficient combustion, the
311 emissions of pollutants from power plants and big boilers fueled by coal must be totally different
312 from the ~~emissions of residential-farmers'~~ coal stoves ~~in on~~ both the emission intensity and
313 composition of pollutants. Finally, most studies about source apportionment mainly focused on
314 emissions from traffic, industry, construction and secondary formation, whereas the emissions from
315 farmers' activities in the NCP were ~~often almost~~ neglected.

316 There are about 300,000 km² ~~of~~ agricultural fields and 0.16 billion farmers in the NCP (Zhang et
317 al., 2011). The farmers' activities in the NCP are ~~very~~ seasonal, e.g., the fertilization events and
318 harvests mainly ~~occur in focus on~~ June-July and October-November and ~~residential-farmers'~~ coal
319 stoves are prevailingly used for heating in winter. The seasonal activities of farmers in the NCP were
320 suspected to make significant contribution to deteriorate the regional air quality, e.g., the most
321 serious pollution events (or haze days) in the NCP were usually coincident with the three seasonal
322 activities of farmers in recent years (Yang et al., 2015b;Huang et al., 2012;Li et al., 2014;Li et al.,
323 2011;Liu et al., 2013;Sun et al., 2013). The serious pollution events during harvest seasons were
324 widely ascribed to crop straw burning (Huang et al., 2012;Li et al., 2014), but the influence of
325 fertilization events and crop straw returning to fields on the regional air quality during the harvest
326 seasons periods was mostly neglected. Strong ammonia (NH₃) emission from the vast agricultural
327 fields in the NCP has been found during fertilization events just after ~~the wheat harvest (in June-~~
328 ~~July) of winter wheat in June-July~~ (Zhang et al., 2011), which must accelerate atmospheric
329 ammonium formation. Although crop straws burning by stealth is still ~~prevalent-prevailing~~, most
330 residual crops are being returned into the agricultural fields under the advocacy of government for
331 protecting the air quality. Because crop leaves absorbed large quantities of atmospheric particles

332 during crop growing season (Bealey et al., 2007; Ji et al., 2013), the abrupt release of the particles
333 by smashing crop straw for returning in the vast area of the NCP must also make ~~striking a~~
334 contribution to atmospheric particles in the region during the seasonal harvest seasons. In winter,
335 ~~heavy smoke the serious pollutant emissions~~ from the chimneys of the farmers' coal stoves can be
336 ~~easily imagined by the strong smog seen everywhere in rural areas of the NCP due to heating supply.~~
337 Although residential coal consumption only accounts for a small fraction of the total, e.g., ~11% in
338 Beijing-Tianjin-Hebei area (<http://hbdczx.mep.gov.cn/pub/>), the emission ~~intensity factors~~ of
339 ~~typical pollutants such as PM_{2.5}, organic carbon (OC) and polycyclic aromatic hydrocarbons (PAHs)~~
340 from farmers' coal stoves ~~(about 1054-12910 mg/kg for PM_{2.5}, 470-7820 mg/kg for OC and 58.5-~~
341 ~~229.1 mg/kg for PAHs) is-are~~ usually about 1-2-3 orders of magnitude greater than those from coal
342 power plants or industries boilers ~~(about 16-100 mg/kg for PM_{2.5}, 0.3-17.1 mg/kg for OC and 0.8-~~
343 ~~12.8 µg/kg for PAHs) (Zhang et al., 2008; Xu et al., 2006; Geng et al., 2014; Chen et al., 2005;~~
344 ~~Revuelta et al., 1999; Yang et al., 2016)~~, and the coal consumption by farmers mainly concentrates
345 on the four months in winter.

346 In this study, to understand the possible influence of farmers' activities on the regional air quality in
347 the NCP, filter samples of PM_{2.5} were ~~daily~~-collected ~~daily~~ in Beijing city as well as a rural area in
348 Baoding, Hebei Province for a whole year of 2014, and the seasonal variation characteristics of the
349 water-soluble ions (WSIs) in the PM_{2.5} samples were comprehensively investigated in relation to
350 the farmers' activities. The scientific evidences found in this study will be helpful for future control
351 measures in reducing pollutant emissions from rural areas in the NCP.

352 2. Materials and methods

353 2.1. Sampling sites

354 ~~A-The~~ sampling site in Beijing city was ~~chosen~~ on a rooftop (about 25_m above ground) in the
355 Research Center for Eco-Environmental Sciences (here referred to as RCEES, 40°00'29.85"N,
356 116°20'29.71"E), which is located between the north fourth-ring road and the north fifth-ring road
357 of Beijing and surrounded by some institutes, campuses, and residential areas (Pang and Mu, 2006).
358 Another sampling site in a rural area was selected on the rooftop of a field station (about 5_m above
359 ground) which is located in the agricultural field of Dongbaituo village (here referred to as DBT,
360 38°39'37.36"N, 115°15'16.05"E), Baoding, Hebei Province. The rural sampling site is far away
361 from industries, traffic and commercial emissions. The distance between the two sampling sites is
362 about 170_km and the detailed location of the two sampling sites is presented in Fig. 1.

363 2.2. Sample collection

364 PM_{2.5} samples at the two sites were both collected on Millipore PTFE filters (90_mm) by ~~an artificial~~
365 ~~intelligence's~~ a PM_{2.5} sampler (LaoYing-2034) and the sampling flow rate was set to 100_L min⁻¹.
366 The duration of each sampling was 24 hours, started at 3:00 p.m. every day and ended at 3:00 p.m.
367 on the next day. All the samples were put in dedicated filter storage containers (90_mm, Millipore)
368 after sampling and preserved in a refrigerator till analysis. For the sampling site of RCEES, a total
369 of 235 PM_{2.5} samples were collected from January to November of 2014, in winter (Jan 9- Mar 15),
370 spring (Mar 16- May 31), summer (Jun 1- Jun 30, Aug 9- Aug 21) and autumn (Sep 19- Nov 14).
371 To explore the possible influence of farmers' activities, PM_{2.5} samples at DBT were mainly collected
372 during the periods of periodic farmers' activities: heating season in winter (Jan 9- Feb 25), harvest
373 seasons in summer (Jun 9- Jun 22, Aug 9- Aug 17) and autumn (Sep 19- Oct 18, Oct 28- Nov 14).

374 2.3. Sample analysis

375 Each sample filter was extracted ultrasonically with 10_mL ultrapure water for half an hour. The

376 solutions were filtered through ~~water-a~~ micro-porous membrane (pore size, 0.45 μm ; diameter, 13
377 mm) before analysis and the ~~water-soluble ions~~ (WSIs) in the treated filtrates were analyzed by Ion
378 Chromatography (IC, WAYEE IC6200). Five anions (F^- , HCOO^- , Cl^- , NO_3^- and SO_4^{2-}) were
379 separated by using an anion column (IC SI-52 4E, 4 mmID*250 mm) with the eluent (3.6 mmol L⁻¹
380 Na_2CO_3) flow rate of 0.8 mL min⁻¹ and column temperature of 45 °C. Five cations (Na^+ , NH_4^+ ,
381 Mg^{2+} , Ca^{2+} and K^+) were separated by using a cation column (TSKgelSuperIC-CR, 4.6 mmID*15
382 cm) with the eluent (2.2 mmol L⁻¹ MSA and 1 mmol L⁻¹ 18-crown-6) flow rate of 0.7 mL min⁻¹ and
383 column temperature of 40 °C. The relative standard deviation (RSD) of each ion was less than 0.5%
384 for the reproducibility test. The detection limits (S/N=3) were less than 0.001 mg L⁻¹ for the anions
385 and cations. At least three filter blanks were analyzed for 60 filter samples, and the average blank
386 values were about 0.03 mg L⁻¹ for Na^+ , Ca^{2+} , F^- , NO_3^- and SO_4^{2-} , 0.02 mg L⁻¹ for NH_4^+ and Cl^- , 0.01
387 mg L⁻¹ for Mg^{2+} , K^+ and HCOO^- . The concentrations of all the ions were corrected for blanks.

388 **2.4. Meteorology, trace gases and back trajectory**

389 The meteorological data, including temperature, wind speed, wind direction, relative humidity (RH),
390 visibility and Air Pollution Index of $\text{PM}_{2.5}$, SO_2 , NO_2 , O_3 at RCEES were from Beijing urban
391 ecosystem research station (<http://www.bjurban.rcees.cas.cn/>), which is about 20m away from our
392 sampling site of RCEES.

393 To identify the potential influence of air parcel transport, the air mass backward trajectories were
394 calculated for 72_h through the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT
395 4) Model of the Air Resources Laboratory of NOAA with NCEP Final analyses data. The backward
396 trajectories arriving at 500_m above sampling position were computed at 0:00_h, 6:00_h, 12:00_h and
397 18:00_h (UTC) in each sampling day, respectively. A total of 940 backward trajectories with 72

398 hourly trajectory endpoints in four seasons were used as input for further analysis.

399 3. Results and discussion

400 The ratios of total cation concentration (defined as $[Na^+] + [NH_4^+] + 2 \times [Mg^{2+}] + 2 \times [Ca^{2+}] + [K^+]$)
401 to total anion concentration (defined as $[F^-] + [HCOO^-] + [Cl^-] + [NO_3^-] + 2 \times [SO_4^{2-}]$) in different
402 seasons are illustrated in Fig. 2a. The near unity of the ratios indicated excellent charge balance in
403 PM_{2.5} and high quality of the data. The mass concentrations of WSIs and PM_{2.5} at the sampling site
404 of RCEES during the period of Jan 1- Jan 24, 2015 were also simultaneously measured by the filter
405 sampling method and the TEOM 1405 Monitor, respectively. As shown in Fig. 2b, the variation
406 trends of the WSIs and PM_{2.5} were almost the same with a correlation coefficient (R^2) of 0.91,
407 implying that the concentration of WSIs measured could be used as an indicator of the pollution
408 level, well reveal the pollution status of PM_{2.5}. The average mass concentration of WSIs contributed
409 about 80% to the mass of PM_{2.5} measured by the TEOM 1405 Monitor, which was much greater
410 than the values of 50-60% reported by previous studies in the NCP (Shen et al., 2009; Li et al., 2013).
411 It was possible that ~~Therefore,~~ the mass concentration of PM_{2.5} measured by the TEOM 1405
412 Monitor was ~~suspected to be largely~~ underestimated because the volatile even semi-volatile
413 component in PM_{2.5} can be easily lost at 50 °C which is designed in the TEOM 1405 Monitor for
414 avoiding water condensation on the filter (Charron et al., 2004; Grover et al., 2005; Liu et al., 2014).
415 It is well documented that temperature is a key factor affecting the distribution of NH₄NO₃ on
416 particle phase due to its thermal decomposition, e.g., at temperature greater than 35 °C, little
417 NH₄NO₃ is expected under typical ambient conditions (Finlayson-Pitts et al., 1986). The total mass
418 proportions of NO₃⁻ and NH₄⁺ in WSIs usually accounts for about 50% in Beijing city (Yang et al.,
419 2015a), whereas they were found to only account for about 20% in the filters of the TEOM 1405

420 Monitor in this study, confirming the serious loss of NH_4NO_3 under the high temperature adopted
421 by the TEOM 1405 Monitor.

422 3.1. Daily variations of WSIs in Beijing city

423 The daily variations of WSIs at RCEES in each season ~~are is~~ illustrated in Fig. 3 and the ~~statistic~~
424 average mass concentrations of the WSIs at RCEES are summarized in Table 1. It is evident that
425 the concentration of the WSIs varied greatly on timescale of days, daily variations of the WSIs at
426 ~~RCEES exhibited significantly periodic fluctuation~~, indicating meteorological conditions played a
427 pivotal role in accumulation and dissipation of atmospheric pollutants. For example, the ~~most~~
428 frequently high highest frequency pollution levels of the WSIs in winter were mainly ascribed to
429 the relatively stable meteorological conditions with the low height of boundary layer which ~~favors~~
430 favored pollutants' accumulation (Wang et al., 2013; Quan et al., 2014; Tian et al., 2014; Wang et al.,
431 2014; Zhang et al., 2015a). Besides meteorological conditions, the extremely high levels of the WSIs
432 during the pollution episodes revealed strong sources of the pollutants around Beijing.

433 The mean concentrations ($\mu\text{g m}^{-3}$) of WSIs at RCEES in spring, summer, autumn and winter were
434 50.5 ± 37.3 , 44.2 ± 28.9 , 78.3 ± 92.6 , and 78.7 ± 61.2 , respectively. NO_3^- , SO_4^{2-} and NH_4^+ were
435 found to be the principal ions, accounted for about 80% to the total WSIs in each season, which
436 were in line with previous studies (Hu et al., 2014; Yang et al., 2015a; Huang et al., 2016; Yang et al.,
437 2015b). The three principal ions were mainly ascribed to secondary formation as discussed in the
438 following section. Although the most intensive photochemical reactivity in summer favors sulfate
439 and nitrate formation, the relatively low SO_2 concentration, the reduced gas-to-particle partitioning
440 ~~fast thermal decomposition~~ of ammonium nitrate and the frequent scavenging by rain events must
441 greatly counteract the contribution of the secondary formation, resulting in the lowest pollution

442 levels of the WSIs in summer. In comparison with other seasons, the ~~remarkable-large~~ elevation of
443 atmospheric SO₂ and NO_x (see section 3.2.3) in winter would result in large sulfate and nitrate
444 formation rates despite the lower concentrations of oxidizing species~~override the relatively low~~
445 ~~atmospheric photo-oxidants for their oxidation rates~~ and ~~resulted in~~ cause the highest mean
446 concentration of WSIs. Although the atmospheric concentrations of SO₂ and NO_x in autumn were
447 much smaller than in winter and in spring (see section 3.2.3), the mean concentration of WSIs in
448 autumn was almost the same as that in winter and nearly twice as those in spring and summer,
449 indicating that special mechanisms dominated the secondary formation of the atmospheric principal
450 ions (see section 3.2.3).

451 **3.2. The possible sources for the WSIs**

452 To explore the possible contribution of the periodic emissions from farmers' activities to the WSIs
453 in Beijing, the concentrations seasonal variation characteristics~~of typical WSIs at the urban and~~
454 rural sites are ~~comparatively illustrated~~ compared in Fig. 4. It is evident that the seasonal variation
455 of the typical WSIs at the two sites exhibited the similar trend, indicating the similar regional
456 meteorological conditions. The concentrations of the typical WSIs at DBT were generally higher
457 than those at RCEES during the periods of ~~intensive~~ farmers' activities (heating in winter,
458 fertilization in summer and maize harvest in autumn). To reveal the air mass transport influence on
459 the WSIs in Beijing, three-day backward trajectories for clusters and the corresponding mass
460 concentrations of WSIs during the four seasons in Beijing were analyzed, and the results are
461 illustrated in Fig. 5. It could be seen that the highest concentrations of the typical WSIs were usually
462 observed in the air parcels from southwest/south regions with high density of population.
463 Considering the large fraction (~30%) of air parcels from the southwest/south regions in each season,

464 the human activities in the southwest/south regions ~~made evident contribution~~ contributed to the
465 atmospheric WSIs in Beijing. Besides the industries, the emissions from the high density of farmers
466 in the southwest/south regions of Beijing was also suspected to ~~make evident contribution~~ affect to
467 the atmospheric WSIs in Beijing.

468 3.2.1. The sources of K⁺ and Cl⁻

469 ~~With the exception of~~ Without considering the extremely high concentrations of K⁺ on 1 February
470 and 16 February (Fig. 4) due to firework for celebrating Spring Festival and Lantern Festival (Jiang
471 et al., 2015;Kong et al., 2015), the concentrations of Cl⁻ and K⁺ were much higher in winter and
472 autumn than in spring and summer at the two sites (Fig. 4). The molar ratio of Cl⁻ to Na⁺ at the two
473 sites measured by this study (Fig. 6) in each season was above 1.30 which was greater than the value
474 of 1.18 in fresh sea-salt particles (Brewer, 1975), indicating sources other than sea-salt dominated
475 atmospheric Cl⁻. The pronounced correlation coefficients ($r > 0.6$, $p < 0.01$) between K⁺ (the
476 indicator for biomass burning, Gao et al., 2011) and Cl⁻ in winter and autumn indicated that crop
477 straw burning was a common source for K⁺ and Cl⁻ (Li et al., 2014). However, only crop straw
478 burning couldn't explain the relatively high concentrations of Cl⁻ in winter (Fig. 4), because the
479 average ~~mass-molar~~ Cl⁻/K⁺ ratio of ~~7.17.8~~ 7.17.8 (except for firework event during the Spring Festival) in
480 winter was about a factor of 2 greater than the value of ~~3.84.2~~ 3.84.2 in autumn when straw burning was
481 prevailing in the region. Besides straw burning and sea-salt, coal combustion (Yu et al., 2013;Wu
482 et al., 2014) and biofuel burning (Christian et al., 2010) have been also recognized as the sources
483 for atmospheric Cl⁻. Coal have almost been replaced with natural gas and electricity for heating
484 during the winter before 2013 in Beijing city
485 (~~<http://www.radiotj.com/gnwyw/system/2014/07/22/000485853.shtml>~~—Ma et al., 2015).

486 Considering the relatively stable Cl⁻ emissions from coal combustion of industries and power plants
487 as well as biofuel burning during the whole year, the obviously higher Cl⁻ concentrations measured
488 in winter than in other seasons (Fig. 4) should be ascribed to the additional coal combustion by
489 farmers because of the large amount of residential coal consumption (about ~~42,000,000 tons~~ 42
490 Tg/year) in Beijing-Tianjin-Hebei region and extremely high emission factors of Cl⁻ (80-300 ~~mg~~
491 /kg coal) from the coal combustion (Huang et al., 2014b). The obviously higher Cl⁻ proportion in
492 winter than in early spring (Fig. 7) provided further evidence for the above conclusion, because the
493 proportion largely counteracted the influence of meteorological factors.

494 It is interesting to ~~note be noted~~ that the remarkably higher Cl⁻/Na⁺ ratio was observed in summer
495 than in other seasons at RCEES (Fig. 6), which couldn't be explained by the Cl⁻ sources mentioned
496 above. Fertilization events in the vast agricultural fields of the NCP were suspected to contribute
497 ~~make contribution~~ to atmospheric Cl⁻ in Beijing because volatile NH₄Cl fertilizer are prevailingly
498 used as the basal fertilization for maize in summer. Based on yearbook of China fertilizer industry
499 (2012), national production of NH₄Cl fertilizers was about 1.174 Tg ~~1,174,000 tons~~ in 2011, which
500 was mainly used as the basal fertilization for maize in summer. The obviously high concentrations
501 of Cl⁻ at DBT (Fig. 4) were indeed observed during the basal fertilization period for maize in June.
502 Compared with the periods before and after maize fertilization, the proportion of Cl⁻ during maize
503 fertilization in summer increased about 3%-4% (Fig. 7), confirming the influence of maize
504 fertilization on atmospheric Cl⁻ in Beijing. The extremely high concentration (about 2 ppbv) of
505 Nitryl chloride (ClNO₂) observed by Tham et al. (2016) at the same rural site in June indirectly
506 indicated the high concentrations of Cl⁻ during the period of basal fertilization for maize. Because
507 fertilization is an important source for atmospheric NH₃, the elevation of Cl⁻ (as a tracer for

508 fertilization) revealed that fertilization in the rural areas around Beijing could also make obvious
509 contribution to atmospheric NH_4^+ in Beijing.

510 3.2.2. The sources of Ca^{2+}

511 The remarkably high concentrations of Ca^{2+} occurred in both spring and autumn at RCEES (Fig. 3
512 and Fig. 4), which were in good agreement with previous studies (Fig. 8). The evident elevation of
513 Ca^{2+} concentrations in spring has been usually ascribed to the frequent dust storms (Zhao et al.,
514 2013b), but there was still no explanation about the extremely high Ca^{2+} concentrations in autumn
515 (Zhao et al., 2013b; Zhang et al., 2013). The intensive maize harvest and soil ploughing in autumn
516 in the vast agricultural fields of the NCP were suspected to ~~make contribution~~ contribute to
517 atmospheric Ca^{2+} in Beijing. Because abundant atmospheric mineral particles were absorbed by
518 crop leaves (Bealey et al., 2007; Ji et al., 2013) during crop growing season, especially in the North
519 China where atmospheric mineral dust is always at high level (Zhang et al., 2013; Zhao et al., 2013b),
520 a large fraction of the mineral dust absorbed on the leaves of crop could be released into the
521 atmosphere during harvest with crop straw being crushed into pieces for returning to fields which
522 is a prevailing ~~method cultivation manner~~ under the advocacy of governments for reducing the
523 influence of crop straw burning on the air quality. Additionally, the soil ploughing can also cause
524 the suspension of particles (Fang et al., 2006; Chen et al., 2015). The remarkably high concentrations
525 of Ca^{2+} during the autumn at DBT (Fig. 4) should be ascribed to the above agricultural activities
526 because there are few construction activities in the rural area. Compared with the periods before and
527 after maize harvest and soil ploughing, the proportion of Ca^{2+} during maize harvest and soil
528 ploughing in autumn increased about 5%-7% (Fig. 7), confirming the influence of maize harvest
529 and soil ploughing on atmospheric Ca^{2+} in Beijing. The back trajectory cluster analysis also

530 supported the above conclusion: (1) the extremely high concentrations of Ca^{2+} in Beijing occurred
531 during the period of 6-25 October (Fig. 3 and Fig. 4) when the air parcels were mainly from the
532 southwest/south regions (Fig. 5) where the vast areas of agricultural field were being under intensive
533 maize harvest and soil ploughing;-. (2) ~~although~~ Although the concentrations of Ca^{2+} in the rural
534 area ~~were still kept~~ remained at high levels during the period of 2-14 November (Fig.3 and Fig. 4),
535 the relatively low concentrations of Ca^{2+} in Beijing were observed during the period when the air
536 parcels were mainly from the northwest region (Fig. 5) where agricultural activities are relatively
537 sparse.

538 3.2.3. The sources of NH_4^+ , SO_4^{2-} and NO_3^-

539 The remarkably high concentrations of NH_4^+ , SO_4^{2-} and NO_3^- also appeared in both winter and
540 autumn at the two sites (Fig. 4). NH_4^+ was mainly from the reactions of NH_3 with acid gases (such
541 as HNO_3) and acid particles, and hence its variation trend was the same as those of SO_4^{2-} and NO_3^- .
542 Although atmospheric NH_3 has long been considered to be mainly from agricultural activities, their
543 emissions mainly concentrate on warmer seasons (Krupa, 2003), which cannot explain the
544 frequently high concentrations of NH_4^+ observed in winter. Besides the increased gas-to-particle
545 partitioning slow thermal decomposition of ammonium nitrate at lower temperatures, strong NH_3
546 emission sources other than agricultural activities were suspected to be responsible for the
547 frequently high concentrations of NH_4^+ in the cold winter. Besides NH_3 emission from vehicles (Liu
548 et al., 2014), strong emission of NH_3 from residential farmers' coal stoves (the NH_3 emission factor
549 was 0.62-1.10 g/kg coal) was indeed found by our preliminary measurements, which was in line
550 with the latest study (Li et al., 2016). During the serious pollution episodes, the concentrations of
551 SO_2 at RCEES in autumn were almost the same as those in summer and about one order of

552 magnitude lower than in winter (Fig. 9), but the peak concentrations of SO_4^{2-} in autumn were about
553 a factor of 2 greater than those in summer and at almost the same level as those in winter. The
554 gaseous phase reaction with OH (Zhao et al., 2013c; Quan et al., 2014), the heterogeneous reaction
555 on mineral dust (He et al., 2014; Nie et al., 2014), and multiphase reactions in the aerosol water-~~of~~
556 ~~particulate-matters~~ (Zheng et al., 2015a) of SO_2 have been recognized to be responsible for
557 atmospheric SO_4^{2-} formation. The significant elevation of both Ca^{2+} and SO_4^{2-} in autumn implied
558 that the heterogeneous reaction of SO_2 on the mineral dust might greatly accelerate the conversion
559 of SO_2 to SO_4^{2-} . Although evidently high concentrations of Ca^{2+} occurred (Fig. 3 and Fig. 4) in
560 spring and SO_2 concentrations were much greater in spring than in autumn (Fig. 9), the SO_4^{2-}
561 concentrations were about a factor of 2 less in spring than in autumn. Atmospheric humidity was
562 suspected to play an important role in the heterogeneous reaction, e.g., the relative humidity was
563 much higher in autumn than in spring during the serious pollution events (Fig. 9). Similar to SO_4^{2-} ,
564 the relatively high concentrations of NO_3^- during the serious pollution events in autumn were also
565 ascribed to the heterogeneous reaction of NO_2 on the mineral dust. Therefore, the emission of
566 mineral dust from maize harvest and soil ploughing in autumn also played important roles in
567 secondary formation of nitrate and sulfate in Beijing.

568 The nitrogen oxidation ratio $\text{NOR} = n\text{NO}_3^- / (n\text{NO}_3^- + n\text{NO}_x)$ (n refers to molar concentration) and
569 the sulfur oxidation ratio $\text{SOR} = n\text{SO}_4^{2-} / (n\text{SO}_4^{2-} + n\text{SO}_2)$ have been used to estimate the degree of
570 secondary formation of NO_3^- and SO_4^{2-} , which can counteract the interference of meteorological
571 factors (Chan and Yao, 2008; Yu et al., 2013; Guo et al., 2014; Huang et al., 2014a; Yang et al.,
572 2015b; Zheng et al., 2015b). The values of NOR and SOR during haze days and non-haze days in
573 four seasons are listed in Table 2. Both the values of NOR and SOR on non-haze days were found

574 to be the highest in summer and the lowest in winter, ~~well~~ reflecting the seasonal variation of
575 photochemical intensity. Although sunlight intensity greatly reduced at ground level during haze
576 days, the values of NOR and SOR were about a factor of 2 greater during haze days than during
577 non-haze days in the four seasons, implying again that the heterogeneous or multiphase reactions of
578 SO₂ and NO₂ on atmospheric particles made significant contribution to atmospheric sulfate and
579 nitrate.

580 3.2.4. The variation characteristics of NO₃⁻ and SO₄²⁻ during serious pollution episodes

581 As shown in Fig. 9, the serious pollution episodes with noticeable elevation of various pollutants
582 usually occurred under slow wind speed (less than 2 m s⁻¹) and high relative humidity. In comparison
583 with their precursors of SO₂ and NO_x, the detailed variation trends of SO₄²⁻ and NO₃⁻ were different,
584 indicating that the elevation of SO₄²⁻ and NO₃⁻ was not simply ascribed to the physical process of
585 accumulation. It is interesting to ~~be noted~~ note that the increasing rates of SO₄²⁻ during some serious
586 pollution events especially with elevation of Ca²⁺ (such as in spring and autumn) were much slower
587 than those of NO₃⁻ (Fig. 10), implying that the atmospheric heterogeneous reaction of NO₂ on the
588 mineral dust was faster than that of SO₂. Compared with summer and winter, the relatively high
589 ratios of NO₃⁻/SO₄²⁻ in spring and autumn (Fig. 6) also supported the above conclusion.

590 3.3. Comparison with previous studies

591 The mean concentrations of the three principal ions and some related indicators in Beijing over the
592 past decade are summarized in Table 3. The seasonal variations of the three principal ions reported
593 were quite different, e.g., Huang et al. (2016) found the maximal mean concentrations of SO₄²⁻ and
594 NH₄⁺ in the summer and of NO₃⁻ in the autumn of 2014, whereas in this study all the maximal mean
595 concentrations of the three principal ions appeared in autumn. The mean concentrations of the three

596 ions in autumn in this study were in good agreement with the values reported by Yang et al. (2015).

597 For the ~~mass-molar~~ concentration ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ (denoted as N/S), all the investigations
598 exhibited relatively high values in autumn and spring, further confirming that the heterogeneous
599 reaction of NO_2 on mineral dust favored nitrate formation (as discussed above). For NOR and SOR,
600 all investigations were in good agreement, with the highest values in summer, the lowest in winter
601 and higher values during haze days than during clean days. Compared with the investigations of
602 2003, the evident increase of both the concentration of NO_3^- and the ratio of N/S in recent years
603 revealed the fast increase of vehicle numbers in the decade made significant contribution to
604 atmospheric nitrate.

605 **4. Conclusions**

606 The ~~conspicuous-large~~ daily fluctuation of the WSIs in each season confirmed that meteorological
607 factors played an important role in governing the accumulation and dispersion of the pollutants. The
608 extremely high concentrations of the WSIs during the serious pollution episodes indicated there
609 were strong sources of the pollutants in Beijing. Based on the comprehensive analysis of the data of
610 the WSIs, the ~~strongly periodic activities of farmers~~farmers' activities, such as crop harvest, crop
611 straw burning, and coal combustion for heating, were found to ~~make evident contribution~~contribute
612 to the atmospheric WSIs in Beijing. To mitigate the currently serious pollution status in the NCP
613 including Beijing, the strong emissions of pollutants from the periodic activities of farmers should
614 be ~~aroused great~~paid greater attention.

615 **Author contribution**

616 **Y. J. Mu** designed the experiments and prepared the manuscript. **P. F. Liu** carried out the
617 experiments and prepared the manuscript. **C. L. Zhang** carried out the experiments. **C. T. Liu, C.**

618 **Y. Xue, C. Ye, J. F. Liu and Y. Y. Zhang** were involved in part of the work. **H. X. Zhang** provided
619 the meteorological data and trace gases.

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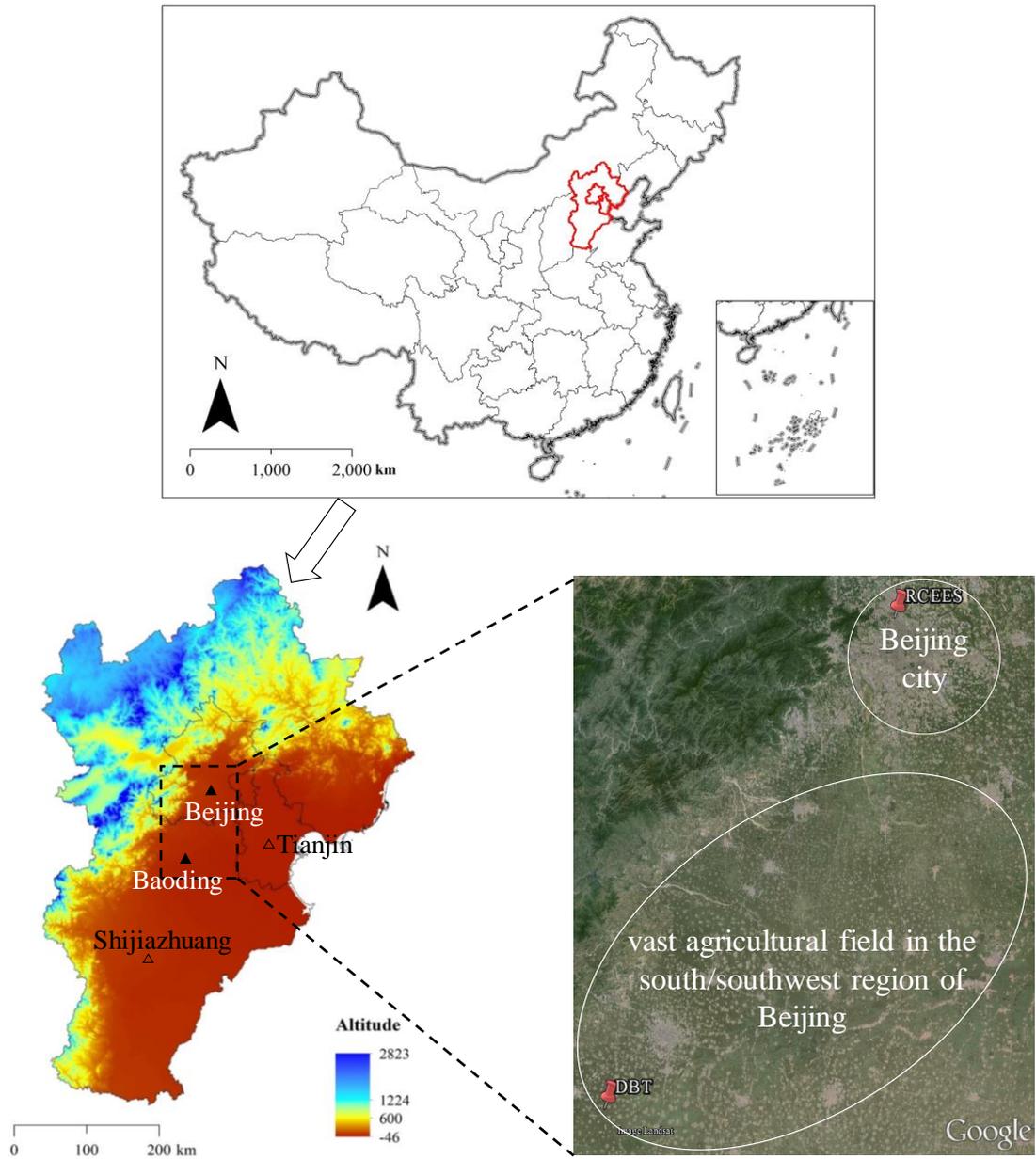
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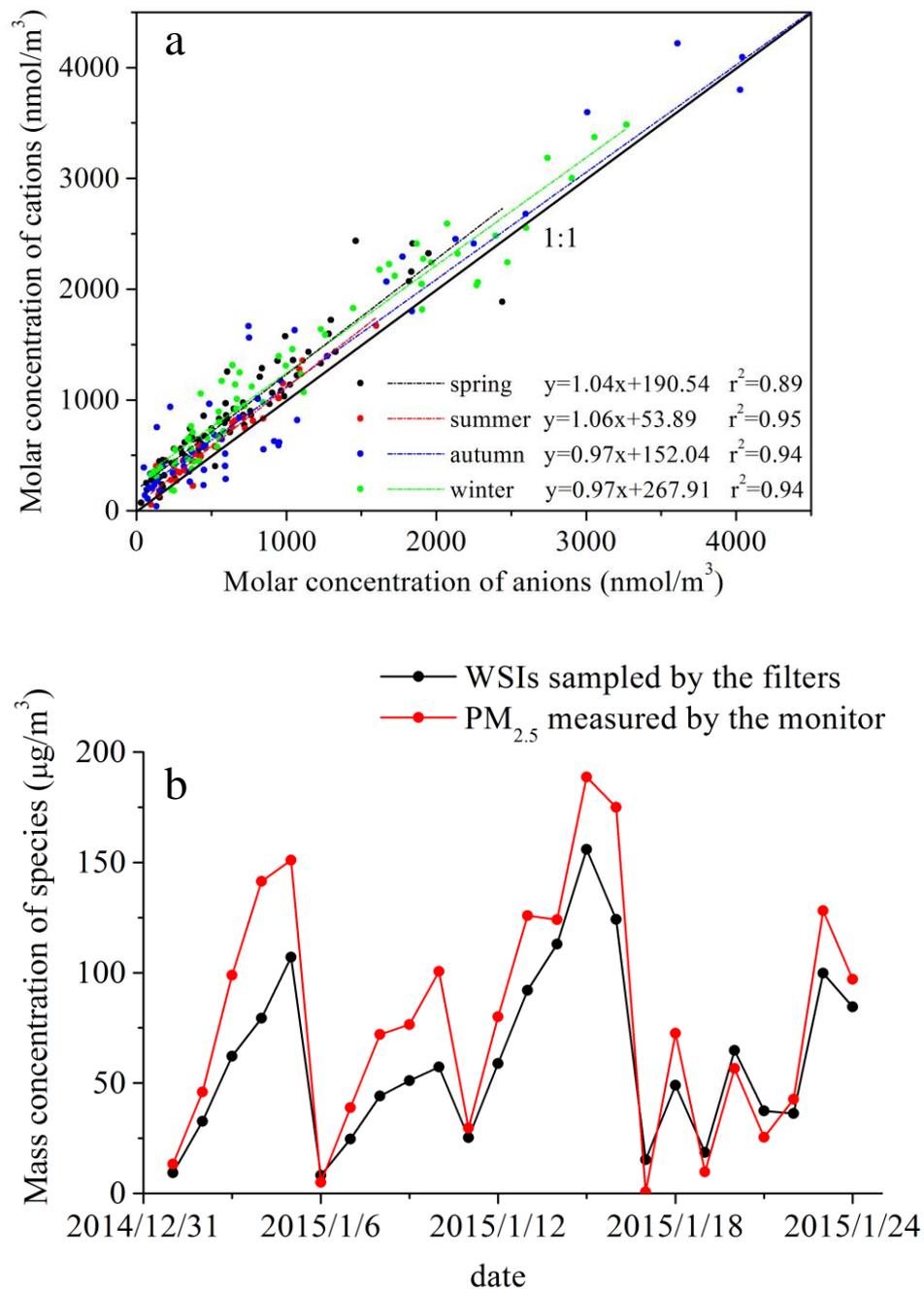
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Fig. 1 Sampling sites (the urban site in Beijing city and the rural site in Baoding, Hebei Province) in the NCP.



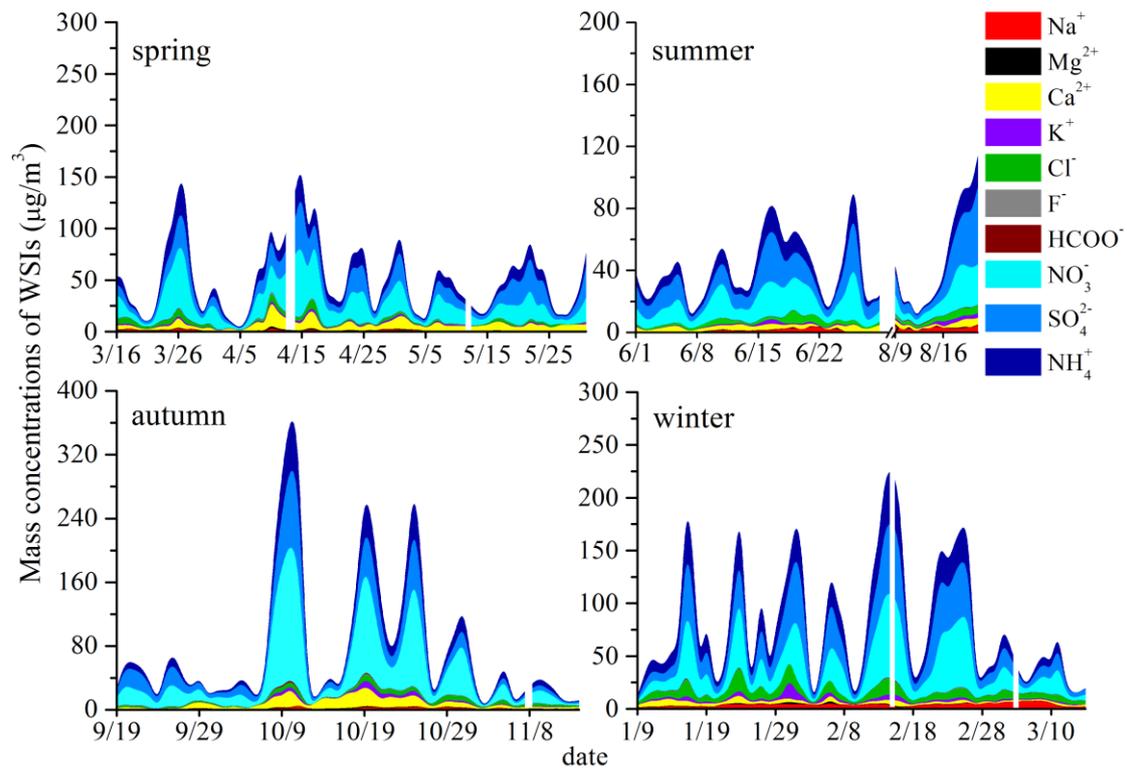
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867 **Fig. 2** The ratios of cations to anions in the four seasons of 2014 in Beijing (Fig. 2a), and the comparison between

868 WSIs sampled by the filters and $\text{PM}_{2.5}$ measured by the TEOM monitor (Fig. 2b, 1-24 January, 2015).

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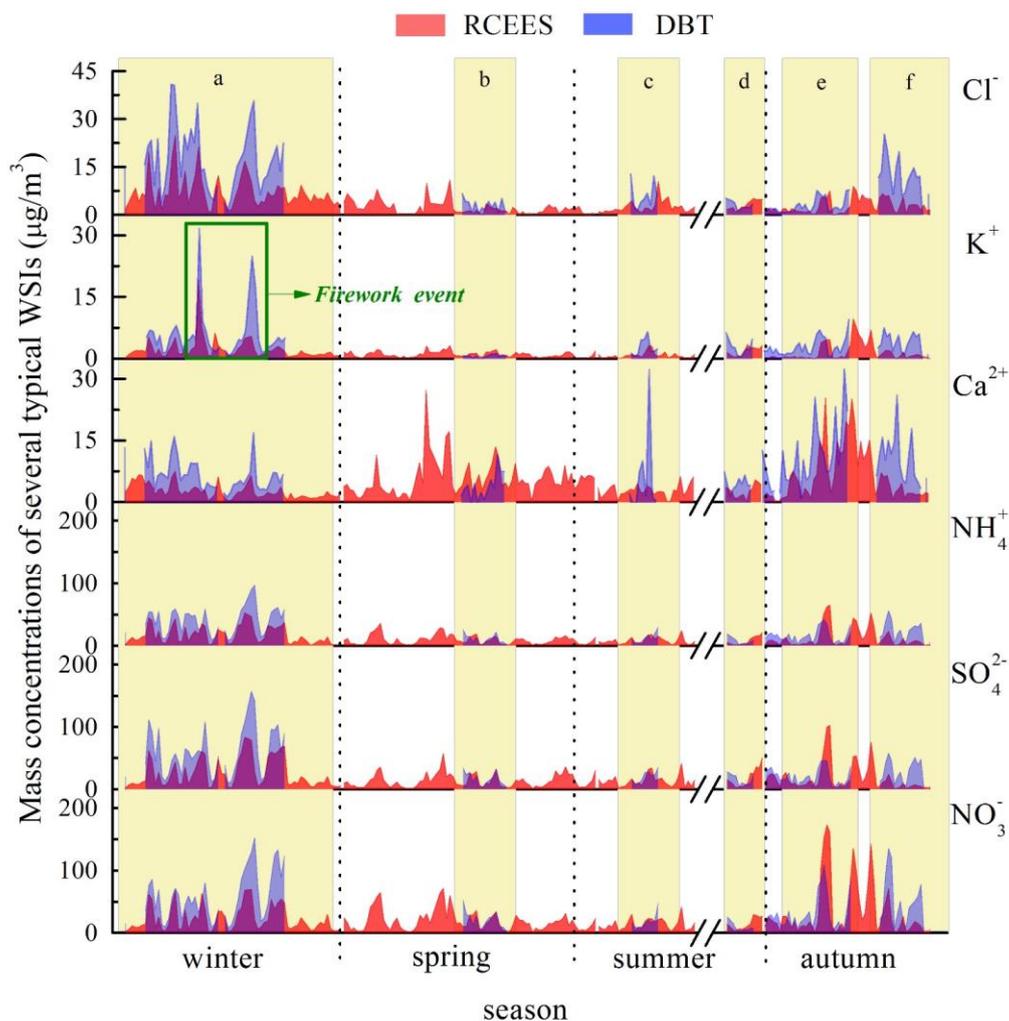


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872 **Fig. 3** Daily variations of WSIs in each season at RCEES (The smooth lines for the WSIs were drawn
 873 between the points of the daily data.).

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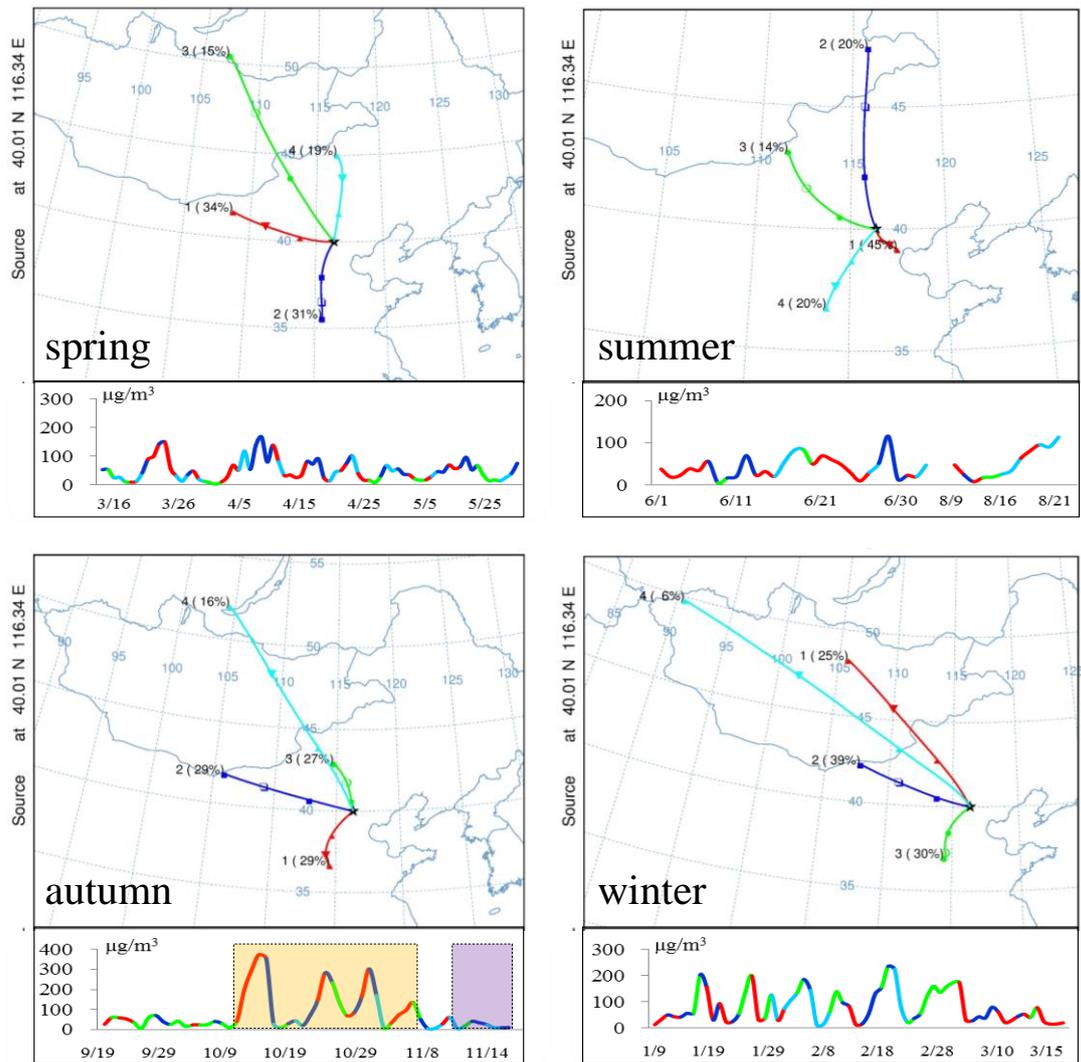


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877 **Fig. 4** Seasonal variations of the several typical Concentrations of selected WSIs in the year of 2014. (The mass
 878 concentrations of Cl^- , K^+ , Ca^{2+} , NH_4^+ , SO_4^{2-} and NO_3^- were presented at RCEES and DBT. The green square
 879 showed shows the firework event during the period of the Spring Festival. The gray square areas shaded in yellow
 880 represented farmers' activities, including residential coal combustion for heating (a), top dressing for wheat (b),
 881 wheat harvest and basal fertilization for maize (c), top dressing for maize (d), maize harvest and soil ploughing (e)
 882 and straw burning (f).)

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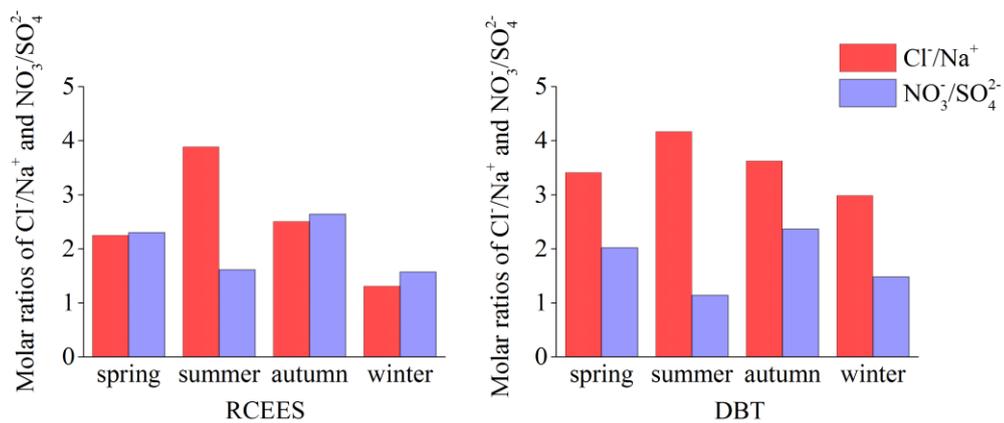
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Fig. 5 The back trajectory cluster analysis and the corresponding overall ion mass concentration during the four seasons in Beijing. (The area shaded in yellow represents the period with the high concentrations of Ca^{2+} both at RCEES and DBT. The area shaded in purple represents the period with the high concentrations of Ca^{2+} at DBT but the low concentrations of Ca^{2+} at RCEES (See Fig. 4).)



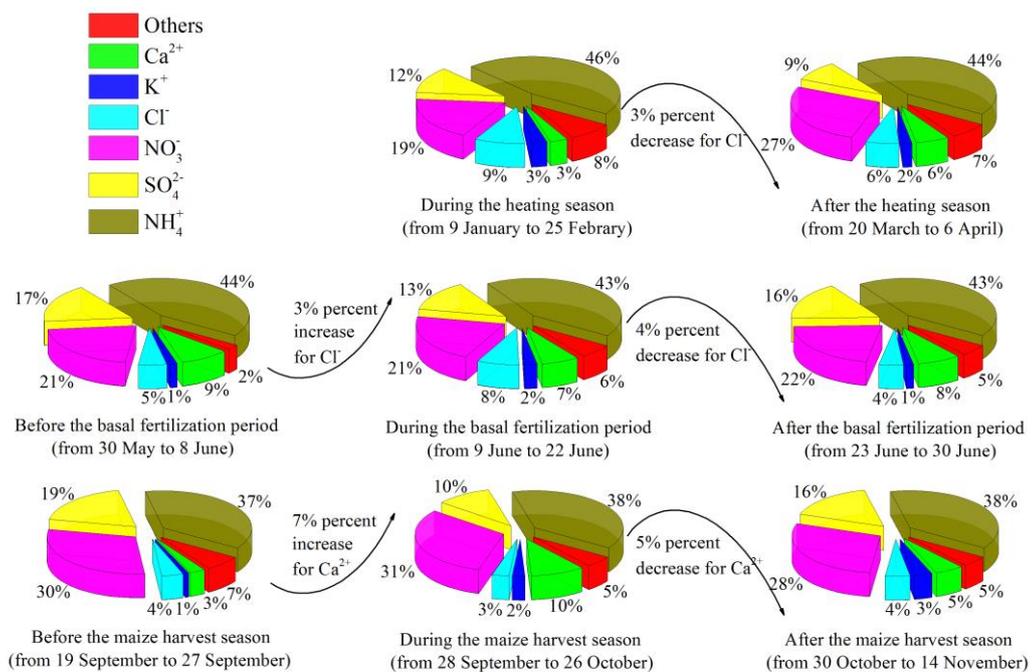
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Fig. 6 The average molar ratios of Cl⁻/Na⁺ and NO₃⁻/SO₄²⁻ in each season at the two sites.

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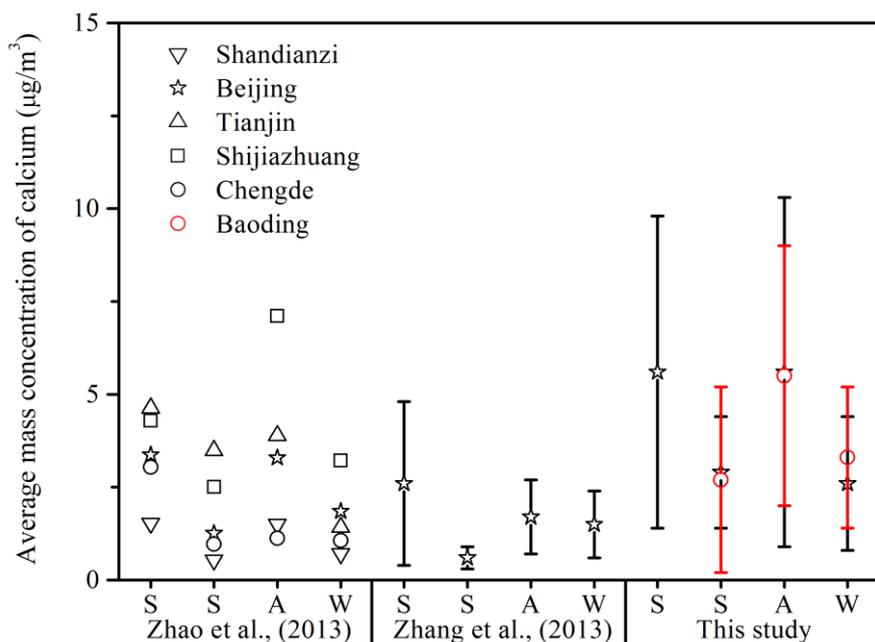
Fig. 7 Molar proportions-fractions of atmospheric WSIs at RCEES before, during and after the periods of heating in winter, maize fertilization in summer, and maize harvest and soil ploughing in autumn.

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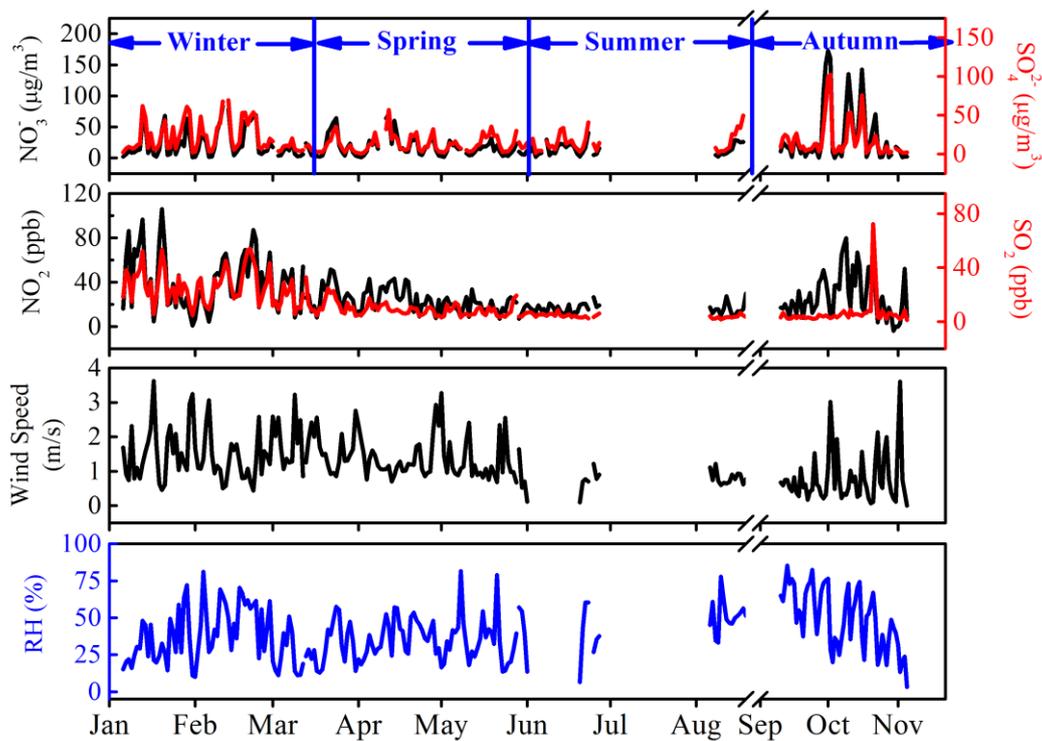
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902 **Fig. 8** Comparison of average mass concentration of calcium in four seasons between previous studies and this
 903 study for several cities in the NCP (S, S, A and W represent spring, summer, autumn and winter, respectively. The
 904 black symbols represent the urban sites and the red symbol represents the rural site (DBT).).
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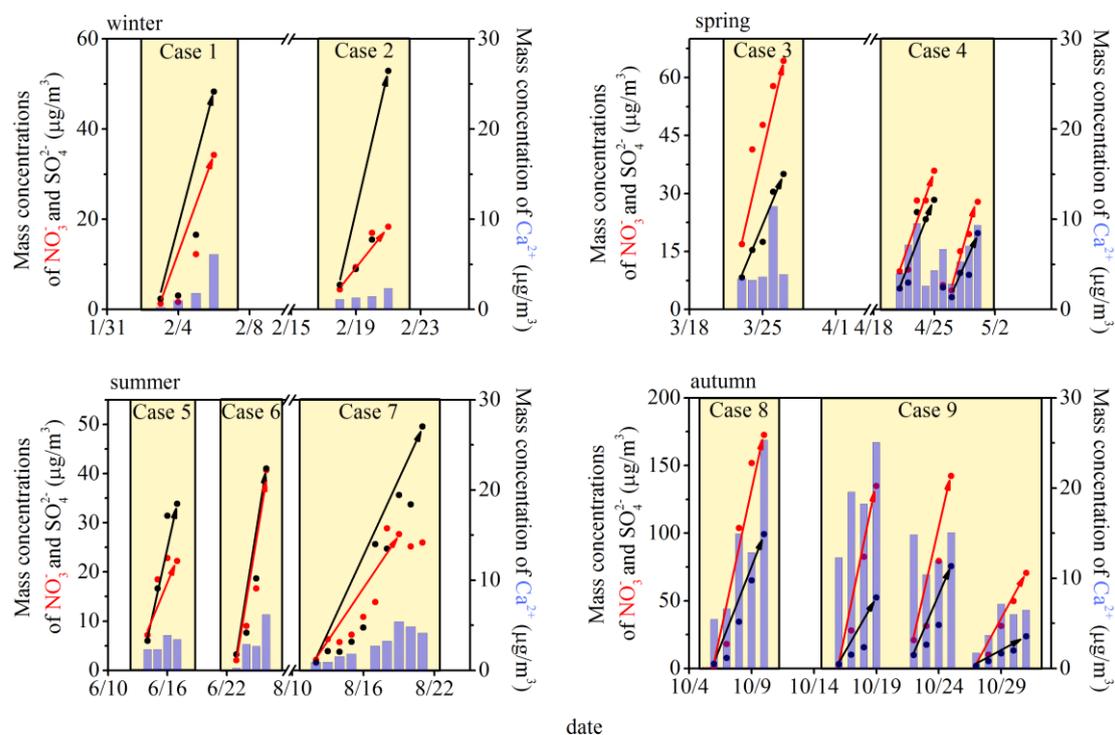
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Fig. 9 Time series of NO_3^- , SO_4^{2-} , NO_2 and SO_2 and meteorological data (wind speed and relative humidity) during the four seasons in Beijing for 2014



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Fig. 10 Case studies about the increasing rates of NO_3^- and SO_4^{2-} with the elevation of Ca^{2+} during serious pollution events in the four seasons.

Table 1 Concentrations ($\mu\text{g m}^{-3}$) of the WSI (mean concentrations and standard deviation (SD)) in four seasons at RCEES.

Species	Spring (N=74)		Summer (N=41)		Autumn (N=56)		Winter (N=64)		Annual (N=235)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
F ⁻	0.3	0.3	0.2	0.1	0.4	0.2	0.2	0.2	0.3	0.2
HCOO ⁻	0.2	0.1	0.2	0.1	0.4	0.5	0.3	0.2	0.3	0.3
Cl ⁻	2.4	2.2	2.6	1.9	2.8	2.3	7.0	4.9	3.9	3.7
NO_3^-	18.4	16.0	13.4	9.3	34.3	45.2	23.8	22.8	22.8	27.7
SO_4^{2-}	13.0	10.9	14.6	11.6	18.1	22.8	22.2	19.6	17.0	17.3
Na ⁺	1.2	0.8	2.1	1.4	1.6	1.1	3.8	1.7	2.3	1.8
NH ₄ ⁺	8.8	7.4	7.6	6.0	12.3	16.3	16.5	13.6	11.5	12.2
Mg ²⁺	0.5	0.4	0.3	0.2	0.4	0.3	0.5	0.5	0.4	0.4
Ca ²⁺	5.6	4.2	2.9	1.5	6.8	6.4	2.6	1.8	4.6	4.4
K ⁺	1.0	0.7	1.1	1.0	1.6	2.2	2.2	2.7	1.5	1.9
Mass	50.5	37.3	44.2	28.9	78.3	92.6	78.7	61.2	63.7	62.0

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921 **Table 2** SOR and NOR during haze days and non-haze days in four seasons at RCEES.

	Spring		Summer		Autumn		Winter	
	SOR	NOR	SOR	NOR	SOR	NOR	SOR	NOR
Haze days	0.3	0.3	0.7	0.4	0.6	0.4	0.2	0.3
Non-haze days	0.2	0.2	0.3	0.2	0.3	0.2	0.1	0.1
Ratio	1.8	1.8	2.0	2.3	2.0	2.6	2.3	2.5

922 The ratio of values in Haze days to that in Non-haze days.

Table 3 Summary of three principal ions ($\mu\text{g m}^{-3}$), the mass-molar concentration ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ (denoted as N/S), NOR and SOR for four seasons at RCEES.

Year	Spring						Summer						Autumn						Winter						Reference
	NO_3^-	SO_4^{2-}	NH_4^+	N/S ^a	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	NO_3^-	SO_4^{2-}	NH_4^+	N/S	NOR	SOR	
2014	18.4	13.0	8.8	<u>1.422</u>	0.2	0.2	13.4	14.6	7.6	<u>0.914</u>	0.2	0.4	34.3	18.1	12.3	<u>1.929</u>	0.2	0.4	23.8	22.2	16.5	<u>1.177</u>	0.2	0.2	This work
2014(haze)	30.2	21.6	14.5	<u>1.422</u>	0.3	0.3	25.0	28.8	15.3	<u>0.914</u>	0.4	0.7	73.6	36.0	26.5	<u>2.031</u>	0.4	0.6	37.7	34.5	25.4	<u>1.177</u>	0.3	0.2	This work
2014(clean)	7.8	5.2	3.5	<u>1.523</u>	0.2	0.2	8.6	8.7	4.4	<u>1.015</u>	0.2	0.3	8.9	6.5	3.2	<u>1.422</u>	0.2	0.3	5.9	6.4	4.5	<u>0.914</u>	0.1	0.1	This work
2014													35.5	20.0	16.7	<u>1.828</u>	0.2	0.4							Yang et al., 2015b
2013-2014(haze)	14.7	9.0	10.3	<u>1.625</u>	0.2	0.4	33.9	32.7	24.0	<u>1.015</u>	0.3	0.7	40.0	17.4	22.2	<u>2.336</u>	0.2	0.6	22.0	20.4	18.8	<u>1.177</u>	0.2	0.2	Huang et al., 2016
2013-2014(clean)	3.6	2.4	4.4	<u>1.523</u>	0.1	0.2	8.8	8.1	11.7	<u>1.177</u>	0.1	0.4	5.5	4.5	5.6	<u>1.219</u>	0.1	0.4	6.6	5.2	6.0	<u>1.320</u>	0.1	0.1	Huang et al., 2016
2013(haze)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	26.1	33.3	24.1	<u>0.812</u>	-	-	Tian et al., 2014
2013(clean)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.9	5.0	4.9	<u>1.015</u>	-	-	Tian et al., 2014
2010(haze)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	0.3	Zhao et al., 2013a
2010(clean)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.2	Zhao et al., 2013a
2009-2010	15.5	14.7	7.5	<u>1.177</u>	-	-	11.8	23.5	11.0	<u>0.508</u>	-	-	10.7	7.9	4.7	<u>1.422</u>	-	-	7.3	8.5	4.5	<u>0.914</u>	-	-	Zhang et al., 2013
2009	-	-	-	-	-	-	12.7	26.1	9.1	<u>0.508</u>	0.2	0.7	6.1	20.1	4.3	<u>0.305</u>	0.1	0.6	-	-	-	-	-	-	Hu et al., 2014
2005	-	-	-	-	-	-	9.9	22.6	4.7	<u>0.406</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Pathak et al., 2009
2001-2003	11.9	13.5	6.5	<u>0.914</u>	0.1	0.1	11.2	18.4	10.1	<u>0.609</u>	0.1	0.4	9.1	12.7	6.3	<u>0.711</u>	0.1	0.2	12.3	21.0	10.6	<u>0.609</u>	0.1	0.1	Wang et al., 2005
2002-2003	-	-	-	-	-	-	12.2	16.0	10.4	<u>0.812</u>	-	-	-	-	-	-	-	-	17.0	30.4	12.9	<u>0.609</u>	-	-	Sun et al., 2004

Quantitative interpretation of divergence between PM₁₀ and PM_{2.5} mass measurement by TEOM and gravimetric (Partisol) instruments

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Abstract

An intercomparison of PM₁₀ and PM_{2.5} mass measured simultaneously by tapered element oscillating microbalance (TEOM) instruments and Partisol samplers, with laboratory gravimetric determination of particle mass from the latter, has been carried out at a rural site in Oxfordshire, UK. The TEOM gives lower readings of both PM₁₀ and PM_{2.5} mass and the underestimation is greater at high concentrations. The strong day-to-day variation between instruments is the result of the variability of the particle composition and the influence of temperature and relative humidity. Results show that most of the particulate material not measured by the TEOMs belongs to the PM_{2.5} fraction and suggest that the loss of semi-volatile compounds constitutes an important part of the difference between instruments; even though it is not the only cause of divergence. Ammonium nitrate is one of the major particulate compounds lost in the inlet of the TEOMs located at Harwell. Its volatilisation can explain a significant part of the difference between TEOMs and filter-based Partisol methods. At Harwell, events of high concentrations are often events of high concentrations of semi-volatile compounds including particulate nitrate and as a consequence, the TEOM instrument may miss events above the daily air quality standard of 50 µg m⁻³. The influences of temperature and relative humidity are demonstrated. The difference between measurements decreases with increasing temperature and with decreasing relative humidity. This result is consistent with the mass deficit being associated with loss of semi-volatile substances such as NH₄NO₃ whose formation is temperature and humidity-dependent. It may also be related to positive artefacts associated with the filter-based method such as particle-bound water and adsorbed semi-volatile components.

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1. Introduction

Under European Directive 1999/30/CE, limit values for PM₁₀ have been set. These require a daily average concentration of 50 µg m⁻³ with 35 annual exceedences

permitted, and a maximum annual average of 40 µg m⁻³. These concentrations should be measured by the European gravimetric reference method or a method shown as equivalent. Member states that cannot fulfil this obligation have to establish a relationship between their method and the reference method necessary to convert data for the purposes of reporting under the above-mentioned directive.

PM₁₀ concentrations have been measured using tapered element oscillating microbalance (TEOM)

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instruments for many years at more than 350 sites in the UK, including the 50 urban background, kerbside, industrial and rural sites belonging to the Automatic Urban and Rural Network (AURN). The TEOM instrument has the advantage over conventional gravimetric methods of particle mass monitoring to provide data on an almost real-time basis and to be a cost and labour-effective method. Their introduction in the UK has led to significant improvements in knowledge of the sources and behaviour of particulate matter (QUARG, 1996; APEG, 1999). In comparison, 24-h measurements with filter-based gravimetric methods are costly and time consuming. The filter handling involves a large number of steps including pre-conditioning, weighing of blanks, filter installation and filter removal on the sampling site, post-conditioning and weighing of dust-loaded filters.

However, many studies comparing various filter-based PM₁₀ (or PM_{2.5}) samplers with TEOM instruments have shown that TEOMs report lower particle mass values than the collocated filter-based samplers (Allen et al., 1997; Ayers et al., 1999; Soutar et al., 1999; APEG, 1999; Salter and Parsons, 1999; Williams and Bruckmann, 2001; Cyrus et al., 2001). This is attributed to heating of the inlet of the TEOM system, usually to 50°C, conducted initially in order to minimise interferences from the evaporation and condensation of water onto the filter and to provide a stable and reproducible measurement (Patashnick and Rupprecht, 1991). The particulate material lost in the inlet of the TEOM is thought to be mainly semi-volatile particulate matter and particle-bound water, both of which partition between condensed and vapour phases in the atmosphere. The major such components are expected to be ammonium nitrate and semi-volatile organic compounds.

It is important to highlight that filtration-based mass measurements are not artefact-free. They can also lead to significant volatilisation losses of the same semi-volatile components during collection, due to changes in temperature, relative humidity, composition of the aerosol or pressure drop across the filter, and after collection—due to filter handling, transport and storage (see Chow, 1995). Artefacts in the measurement of particle mass concentrations from gravimetric methods also arise from the adsorption of semi-volatile organic gases onto or from collected particulate matter and filter media (Turpin et al., 2000) and the neutralisation of acid or basic gases on either filter media, or collected particulate matter (Tsai and Huang, 1995). Artefacts may also be associated with particle-bound water that may constitute a significant part of particulate matter. The variability of the water content of particles and the hysteresis in the water adsorption–desorption pathways of some major atmospheric compounds (Seinfeld and Pandis, 1996) complicate the mass measurement. In recent works, Speer et al. (2003) show that water associated with both inorganic and hygroscopic organic

components of PM_{2.5} can contribute significantly to mass and Price et al. (2003) reveal that particle-bound water may be the major cause of difference between TEOM and reference gravimetric measurements.

The amounts of semi-volatile compounds and particle-bound water vary both temporally and spatially. As a consequence, the extent of the difference between TEOMs and filter-based gravimetric methods is not universal, and spatial and seasonal differences have been shown by many studies (Allen et al., 1997; APEG, 1999; Williams and Bruckmann, 2001) implying that the relationship between TEOMs and filter-based gravimetric methods should be examined for each site. This also implies that the relationship between TEOMs and gravimetric methods may not be proportional or linear and may be complex.

This paper describes a study of the relationship between PM₁₀ and PM_{2.5} mass measurements by TEOM and Partisol (gravimetric) instruments at a rural site, and an investigation of the causal factors.

2. Material and methods

2.1. Description of the site

The monitoring station is within a self-contained, air-conditioned building located in the Harwell Research Science Centre in Oxfordshire. The nearest road is for access to buildings within the Science Park only. The manifold inlet is approximately 3 m above ground level. The surrounding area is generally open with agricultural fields. The nearest trees are at a distance of 200–300 m from the monitoring station. The station is a rural site that may be influenced by the London urban plume and possibly the busy A34 highway at a distance of 2 km to the east.

2.2. Description of instruments and gravimetric measurements

2.2.1. Tapered element oscillating microbalance

Two 1400A series TEOMs (Rupprecht and Patashnick Co., Inc.) have been providing measurements of PM₁₀ and PM_{2.5} at Harwell on an almost real-time basis for a number of years. The particle mass is determined by continuous weighing of particles deposited onto a filter. The filter is attached to a vibrating hollow tapered glass tube. The frequency of mechanical oscillation of this tube is a function of its mass. Deposition of particles on the filter leads to changes in the mass of the system and results in changes of its frequency of oscillation. A microprocessor directly converts the vibration frequency to mass concentrations.

The flow rate through the analyser is controlled using thermal mass flow controllers and is automatically

measured to determine the mass concentration. Air at 16.671min^{-1} ($1.002\text{m}^3\text{h}^{-1}$) is sampled through the sampling head and divided between the filter flow (31min^{-1}) and an auxiliary flow (13.671min^{-1}). The inlet is heated to 50°C prior to particles being deposited onto the filter in order to eliminate the effect of condensation or evaporation of particle water. An identical impactor is used as a size-selective inlet for PM_{10} on both instruments. For $\text{PM}_{2.5}$, the Partisol and the TEOM after 23 January 2002 were fitted with a Sharp-Cut Cyclone inlet; prior to that date the TEOM was fitted with a URG $\text{PM}_{2.5}$ cyclone inlet.

2.2.2. Partisol Plus Model 2025

The Partisol Plus Model 2025 from Rupprecht and Patashnick Co., Inc. is a microprocessor controlled measuring device for the sampling of particulate matter. Two Partisol instruments were installed on the Harwell site in order to measure simultaneously the PM_{10} and $\text{PM}_{2.5}$ particles on a daily basis. These instruments use the same size-selective inlet designs as the ones used on the TEOM with the same flow rate of 16.671min^{-1} ($1.002\text{m}^3\text{h}^{-1}$). In contrast to the TEOM instrument, the inlet is not heated and air is sampled at ambient temperature and pressure.

The Partisol has a fully automatic filter exchange mechanism that provides unattended monitoring for up to 16 consecutive days for 24-h sampling prior to filter change. Temperature and pressure sensors are provided in the instrument with internal regulators to maintain the temperature within $\pm 5^\circ\text{C}$ of ambient temperature. The total volume of air sampled, total measuring time, average temperature and pressure are recorded by the microprocessor. The Partisol Plus Model 2025 is equivalent to the gravimetric reference method according to the European standard prEN 12341 for the collection of PM_{10} (see Mückler, 2000).

Quartz fibre filters (Whatman QMA 47 mm diameter filters, $0.6\mu\text{m}$ pore size) have been used for the collection of particulate matter. Pre-conditioning and post-conditioning of filters were undertaken in accordance with the requirements of prEN 12341. Blank and dust-loaded filters are handled according to the same protocols. Filters are equilibrated for 48 h within an air-conditioned weighing room at a temperature of 20°C and a relative humidity of 50% before weighing on a balance with a resolution of $10\mu\text{g}$.

2.3. Data for inclusion in the comparison

The TEOM concentrations as reported by the instrument include a built-in calibration factor of $1.03 \times \text{TEOM reading} + 3\mu\text{g}$. This calibration factor has been determined through intercomparison of data from TEOMs and filter-based reference instruments sampling a standard Arizona road dust in order to

achieve US EPA certification (Patashnick and Rupprecht, 1991). The values corrected by the US EPA calibration factor correspond to data as supplied by the UK network (AURN data).

Examination of the influence of this calibration factor on the relationships between TEOM and Partisol PM_{10} data for seven sites in the UK has shown that the calibration factor applied to TEOM values explains a large component of intercepts significantly higher than zero (results not shown). These intercepts have no physical meaning. On the contrary, linear models computed with raw TEOM readings have intercepts close to zero (for the relationship of Partisol versus TEOM with $R^2 > 0.70$). In this paper, the raw TEOM readings (i.e. with the calibration factor removed) have been used because they correspond to the true mass collected with the TEOM instrument.

PM_{10} and $\text{PM}_{2.5}$ have been measured at the Harwell site using two collocated TEOMs for a number of years. Gravimetric data from two Partisol Plus 2025 have been derived from samples from September 2000. Data from 30 September 2000 to 2 July 2002 for the PM_{10} and from 7 September 2000 to 19 June 2002 for the $\text{PM}_{2.5}$ are included in the comparison. A total of 436 paired 24-h PM_{10} data and 461 paired 24-h $\text{PM}_{2.5}$ data are available for this study.

Particulate nitrate data used in this paper have been derived from samples collected using a collocated Partisol Plus Model 2025 instrument with PTFE filters and measured by ion chromatography.

Meteorological data (temperature and dew point used to compute relative humidity data) have been provided by the British Atmospheric Data Centre (BADc).

3. Results

3.1. Comparison of TEOM with gravimetric Partisol particle mass

Table 1 presents the mean and median PM_{10} and $\text{PM}_{2.5}$ particle mass concentrations collected with the filter-based Partisol samplers and TEOMs. Standard deviations and interquartile ranges are computed to give an estimation of how the particle mass concentrations are spread out. Robust estimators (median and interquartile range) are also presented because they are not influenced by occasional high concentrations like the mean and the standard deviation.

In agreement with other studies (Allen et al., 1997; Ayers et al., 1999; Soutar et al., 1999; APEG, 1999; Salter and Parsons, 1999; Williams and Bruckmann, 2001; Cyrus et al., 2001), the results show that the TEOMs give lower particle mass than the filter-based gravimetric methods. The median relative differences

Table 1

Average PM₁₀ and PM_{2.5} concentrations and number of exceedence days for PM₁₀ for the period September 2000–July 2002 ($N = 436$ for PM₁₀; $N = 461$ for PM_{2.5})

	PM concentrations		Ratios Partisol/TEOM
	Partisol	TEOM ^a	
<i>PM₁₀</i>			
Arithmetic mean ± SD	18.1 (±10.2)	10.2 (±5.3)	1.8 (±0.51)
Median ± IQR ^b	15.7 (±9.9)	9.2 (±5.5)	
Daily concentration > 50 µg/m ³	8	0	
<i>PM_{2.5}</i>			
Arithmetic mean ± SD	12.3 (±9.9)	6.5 (±4.2)	2.1 (±2.7)
Median ± IQR	9.0 (±8.8)	5.3 (±4.4)	

^aTEOM data are raw mass with USEPA correction removed.

^bIQR = interquartile range.

between Partisol and TEOM particle mass concentrations are, respectively, 42% for PM₁₀ and 48% for PM_{2.5}.

The median PM₁₀ and PM_{2.5} concentrations show smaller differences between Partisol and TEOM data than the means, indicating that some high concentrations measured by the Partisol instruments contribute to the higher difference in the means. The higher standard deviations (or interquartile ranges) for Partisol data than for TEOM data lead to the same conclusion. This means that the TEOMs read lower to a greater extent at high concentrations and suggests that higher amounts of semi-volatile compounds characterise events of high particulate matter concentrations.

The mean ratio Partisol/TEOM and the corresponding standard deviation for the whole studied period are presented in Table 1. Ratios of 1.8 for PM₁₀ data and of 2.1 for PM_{2.5} data are found, both with high standard deviations, showing that a large range of ratios occurs. This result is in agreement with other studies (King et al., 2000; Cyrus et al., 2001; Green et al., 2001) showing the variability of the difference between measurements from TEOMs and gravimetric methods from one day to another.

The European Limit Value for particles measured as PM₁₀ is 50 µg m⁻³ (24 h mean) with up to 35 permitted exceedences per year. The number of days exceeding this daily standard for the September 2000–July 2002 period is also presented in Table 1. No exceedence days were measured by the TEOM, while the gravimetric Partisol method gives a total of 8 days exceeding 50 µg m⁻³. Most of these events corresponded to daily Partisol concentrations above 60 µg m⁻³, while the corresponding TEOM particle mass concentrations were generally below 30 µg m⁻³. Seven of these events corresponded to cold days (temperature below 10°C) including four to very cold days (temperature below 5°C) and three of these events corresponded to days with high relative humidity (above 90%). This suggests that semi-volatile

compounds and occasionally particle-bound water on Partisol filters are responsible for large differences between instruments. For all these events, the PM_{2.5} fraction represented more than 80% of the PM₁₀ fraction (and often more than 90%); while the average PM_{2.5}/PM₁₀ ratio for the studied period is 60%. This means that episodes of high concentrations of PM₁₀ concentrations at Harwell are driven by high PM_{2.5} concentrations. The mean ratio Partisol/TEOM for these events of high concentrations is 2.1, which is higher than the mean ratio for the whole study period, confirming the greater difference at high concentrations.

The best fitting curves for the TEOM-Partisol relationships are linear despite the higher differences at high concentrations (see Fig. 1). Some studies have actually found nonlinear relationships due to higher amounts of volatile species at higher particle mass concentrations; resulting in higher divergences at higher concentrations (Salter and Parsons, 1999; APEG, 1999). Despite the scatter of the data, reasonable linear regressions between TEOMs and Partisol data can be established (Fig. 1). These linear regressions have been computed using the reduced major axis (RMA) regression method. Unlike the least square regression method that assumes that observations of the independent (X) variable are accurate, this method makes no assumption about the set of X -variable observations. A recent paper from Ayers (2001) has shown that the least square regression analysis is not appropriate for an instrument comparison exercise and leads to biased evaluations of the relationship between two instruments.

The relationships found for Harwell are not improved using nonlinear models and not really improved nor changed by removing outlier points. These results show that a large part of Harwell particle mass collected with the Partisol is vaporized in the inlet of the TEOMs. Almost all TEOM particle mass concentrations are lower than the Partisol particle mass concentrations.

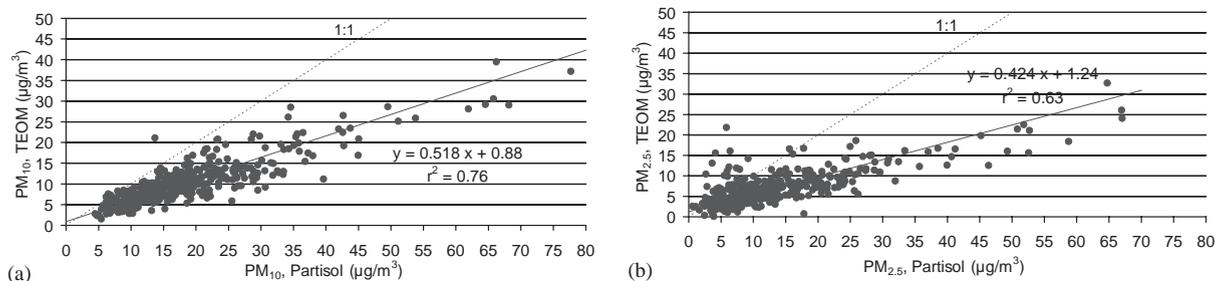


Fig. 1. TEOM versus Partisol for (a) PM_{10} and (b) $PM_{2.5}$ ($N = 436$ for PM_{10} ; $N = 461$ for $PM_{2.5}$).

Possible explanations for these substantial underestimations are examined below.

3.2. Origins of the divergence and influencing parameters

The results suggest that some semi-volatile compounds are lost in the inlet of the TEOMs. The major inorganic semi-volatile compound is thought to be particulate ammonium nitrate. Its gas–particle partitioning depends on the atmospheric temperature and relative humidity (Stelson and Seinfeld, 1982a, b). Particulate ammonium chloride is another well-known semi-volatile inorganic compound (Pio and Harrison, 1987a, b). Except in specific polluted areas, the concentrations of ammonium chloride in the atmosphere are generally too low to lead to condensation, and particulate ammonium chloride is considered negligible in this study. A large range of semi-volatile organic compounds in small amounts but of non-negligible total mass are contained in particulate matter. The gas–particle partitioning of these organic semi-volatile compounds depends on a large number of parameters such as their concentration, the total particle surface area, the particle composition, the total particulate matter concentration, the atmospheric temperature and the relative humidity (US EPA, 1996). Semi-volatile compounds are expected to be mainly in the fine fraction of particles. Particulate ammonium nitrate and semi-volatile organic compounds are thought to be the main compounds lost in the inlet of the TEOM instrument.

Particle-bound water associated with particles collected with the Partisol constitutes another explanation for the difference between the two instruments. The equilibration of Partisol filters to a relative humidity of 50% does not remove all particle-bound water. The examination of the particle water content as a function of relative humidity shows a significant increase for humidity larger than 30% (US EPA, 1996). Due to hysteresis effects the mass of water is greater in samples collected at high humidity (as generally prevails in the UK) and transferred to a lower humidity environment. A recent study (Price et al., 2003) concluded that the retention of water by the filter of the gravimetric method

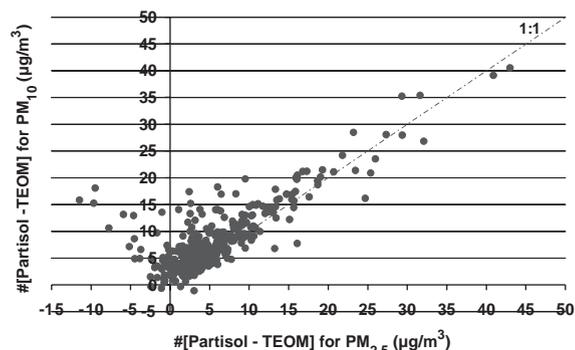


Fig. 2. Difference between Partisol and TEOM for PM_{10} data versus difference between Partisol and TEOM for $PM_{2.5}$ data ($N = 370$)—data in $\mu\text{g}/\text{m}^3$.

was the major cause of differences with the TEOM for their site in Northern England.

Finally, adsorption of organic vapour by the Quartz filters used in the Partisol instruments may contribute to the difference between the two instruments. Quartz fibre filters have a large specific surface area upon which adsorption of gases can occur. A large positive artefact due to adsorption of organic gases onto Quartz fibre filters is now well-known (Turpin et al., 2000). The importance of this artefact associated with the sampling of particulate matter with Quartz fibre filters cannot be estimated in this study. The contribution of particulate ammonium nitrate and the influence of temperature and relative humidity are examined, since appropriate data were available.

The close agreement between the difference between Partisol and TEOM data for PM_{10} and for $PM_{2.5}$ shows that most of the material not measured by the TEOMs is contained in the $PM_{2.5}$ fraction (see Fig. 2). The series of negative values of differences for $PM_{2.5}$ (i.e. TEOM data higher than Partisol data) are considered as suspicious. These values are not associated with negative values of differences for PM_{10} . They may be the result of artefacts with the $PM_{2.5}$ TEOM sampler. Allen et al. (1997) have observed large fluctuations in the $PM_{2.5}$ mass concentrations measured with the TEOM due to rapid changes

in the composition of air masses (pollutant concentrations and ambient relative humidity) affecting the equilibrium of particles collected on the TEOM filter and then responsible for adsorption or desorption of particulate material. They did not observe the same phenomenon for the simultaneous PM_{10} TEOM measurements and assumed that the coarse fraction of particles stabilises the semi-volatile particulate matter collected simultaneously. If these suspicious values are removed, a close linear relationship of $y = 0.973x + 2.167$, $r^2 = 0.78$ is found between the difference for PM_{10} and difference for $PM_{2.5}$. A slope close to 1 with a small systematic difference of about $2 \mu\text{g m}^{-3}$ (intercept) is shown by this relationship. About the same difference is found comparing the average differences between Partisol and TEOM data for PM_{10} and $PM_{2.5}$ (median of differences for $PM_{2.5}$, $4.0 \mu\text{g m}^{-3}$; for PM_{10} , $6.3 \mu\text{g m}^{-3}$). This suggests that a small part of the difference between the two methods is in general associated with the PM_{coarse} fraction. Nevertheless, a few much larger differences between Partisol and TEOM data for PM_{10} than for $PM_{2.5}$ are observed for low values of differences for $PM_{2.5}$. These much larger differences (above $15 \mu\text{g m}^{-3}$) occurred during damper

days (relative humidity above 90%) and might be the result of particle-bound water associated with PM_{coarse} particles (e.g. a major compound, NaCl is very hygroscopic and is mainly found in the coarse fraction of particulate matter).

The particulate ammonium nitrate mass was computed from the particulate nitrate assuming that all the particulate nitrate is associated with ammonium ions. In practice involatile nitrates (e.g. sodium nitrate) may make an important contribution to airborne nitrates. The particulate ammonium nitrate is compared to the difference between the two instruments and also used to correct the TEOM particle mass concentrations. Fig. 3 represents the relationships between the sums of TEOM particle mass data and calculated particulate ammonium nitrate with Partisol particle mass data; and in Fig. 4, the relationships between the difference between Partisol and TEOM data with the calculated particulate ammonium nitrate are plotted.

Both PM_{10} and $PM_{2.5}$ TEOM data are significantly improved by adding the particulate ammonium nitrate. The slopes of the relationships with the Partisol data are closer to the 1:1 line and the correlation coefficients are better showing that the data are less scattered. For the

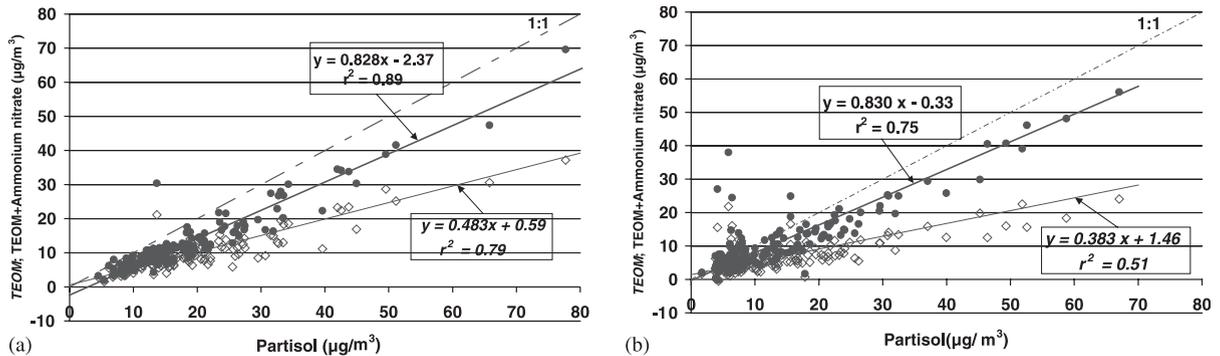


Fig. 3. TEOM PM data (empty dots) and TEOM PM data + particulate ammonium nitrate (full dots) versus Partisol PM data: (a) PM_{10} ($N = 146$) and (b) $PM_{2.5}$ ($N = 161$).

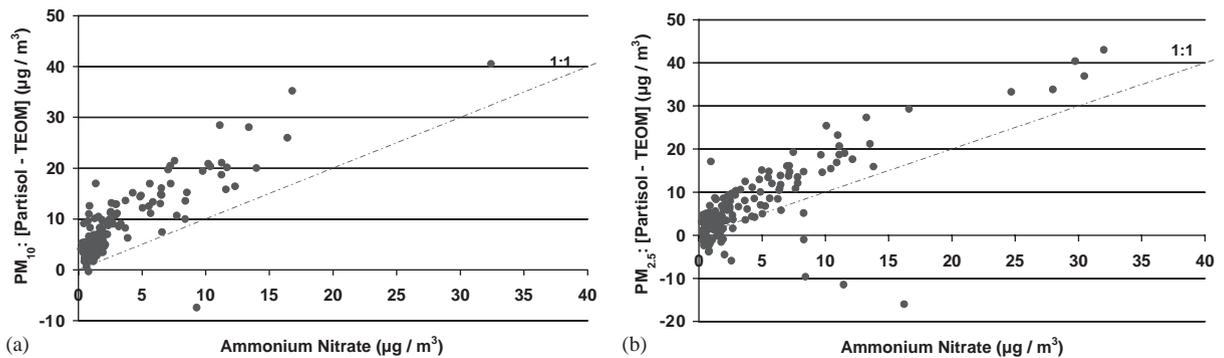


Fig. 4. Difference between Partisol and TEOM PM data versus calculated ammonium nitrate: (a) PM_{10} ($N = 146$) and (b) $PM_{2.5}$ ($N = 161$)—data in $\mu\text{g m}^{-3}$.

concentrations of particulate ammonium nitrate higher than $2\text{--}3\ \mu\text{g m}^{-3}$, the relationships between the difference between Partisol and TEOM data and the particulate ammonium nitrate are fairly linear (see Fig. 4); while for the concentrations lower than $2\text{--}3\ \mu\text{g m}^{-3}$, the relationship is poor indicating a significant relative contribution of other species. The remaining differences between Partisol and TEOM data are on average about 2.7 and $4.9\ \mu\text{g m}^{-3}$, respectively, for $\text{PM}_{2.5}$ and PM_{10} and seem to be constant for the higher differences. Particulate ammonium nitrate (median concentration about $1.9\ \mu\text{g m}^{-3}$, during the study period) is lost in the inlet of the TEOMs and contributes substantially to the lower reading of the TEOM, but its volatilisation does not explain the whole difference between Partisol and TEOM data. It corresponded on average to about 26% of the material lost in the PM_{10} fraction and about 40% of the material lost in the $\text{PM}_{2.5}$ fraction at Harwell. Different results in other studies reflect the different aerosol composition at different sites and explain the wide range of relationships between TEOM and gravimetric reference method found in the literature. Allen et al. (1997) found that the entire difference between a TEOM and a manual filter-based method for the Rubidoux site (California) can be attributed to particulate ammonium nitrate. On the contrary, Cyrus et al. (2001) have a small contribution of ammonium nitrate at their site. Harwell lies between these two extremes.

At the Harwell site, particulate ammonium nitrate represents an important part of the particulate material not measured with the TEOM instruments during episodes of high particulate pollution. Particulate nitrate data are available for three out of the eight episodes for which the gravimetric PM_{10} particle mass exceeded $50\ \mu\text{g m}^{-3}$. These three events were all associated with a high concentration of particulate nitrate (equivalent NH_4NO_3 concentrations above $16\ \mu\text{g m}^{-3}$) and the particulate ammonium nitrate represented more than 50% of the particulate material lost. For two of them, the TEOM data are successfully corrected by adding the particulate ammonium nitrate; while for the last one, the loss of the particulate ammonium nitrate does not explain the entire difference between the two instruments (about 18% is still uncorrected). The five other episodes with $\text{PM}_{10} > 50\ \mu\text{g m}^{-3}$ measured with the gravimetric Partisol method and not measured with the TEOM have ratios Partisol/TEOM above the mean ratio Partisol/TEOM and occurred during cold days, indicating that high amounts of semi-volatile compounds were lost. These results suggest that episodes dominated by high secondary particulate pollutants are not measured by the TEOM at the Harwell site.

The amount of semi-volatile compounds associated with the particles is expected to depend on the temperature and the relative humidity. Additionally,

the relative humidity has a significant impact on the growth of particulate matter. Comparisons between TEOMs and reference gravimetric methods in different countries have shown that for warmer and dryer regions the agreement is better than for colder and damper regions (Williams and Bruckmann, 2001; Noack et al., 2001). Similarly, other studies have shown that the agreement is better during the warmer months of the year than during the colder months (Allen et al., 1997; Williams and Bruckmann, 2001). Price et al. (2003) reveal that the divergence at their sampling site is higher on damper and/or rainy days. All these studies seem to confirm the influence of these meteorological parameters, but a previous study (Cyrus et al., 2001) did not find any relationship between the underestimation of the TEOM and the temperature or the relative humidity.

Because of the seasonal variation of the underestimation of the TEOM, Williams and Bruckmann (2001) recommend in their "Guidance to member states on PM monitoring and intercomparisons with the reference method" examination of the seasonal variations of factors and equations to amend the TEOM data. This examination for the Harwell site is not very helpful because of the small contrast between the seasons (ratio Partisol/TEOM for summer, 1.73; for winter, 1.88).

The relative differences (differences between the gravimetric Partisol mass and the TEOM mass divided by the Partisol mass) versus the temperature and versus the relative humidity are presented, respectively, in Figs. 5a and b. These results confirm that the differences between the TEOM and the Partisol for PM_{10} mass concentrations measured at Harwell depend on both the temperature and the relative humidity. The difference between the two instruments decreases with the temperature and increases with relative humidity. However, a large range of relative differences is associated with each temperature and relative humidity bin, suggesting a simultaneous influence of the particle composition. The same results are found for the $\text{PM}_{2.5}$ at Harwell and for other sites in the UK (results not shown).

Fig. 5a clearly shows that the differences between Partisol and TEOM data are higher than 40% for lower temperatures (below 2°C) and lower than 25% for higher temperatures (above 18°C). Fig. 5b shows that half of the differences between Partisol and TEOM data are below 30% for relative humidity lower than 70% and higher than 50% for relative humidity higher than 90%. The examination of the ratio Partisol/TEOM with both temperature and relative humidity leads to similar conclusions. The mean ratio for colder and damper weather ($T < 10^\circ\text{C}$ and $\text{RH} > 80\%$) is 1.98 and for warmer and drier weather ($T > 10^\circ\text{C}$ and $\text{RH} < 80\%$) is 1.63.

The decrease of the difference between the TEOM and the Partisol with temperature is likely to be related to a decrease in the amount of semi-volatile compounds in

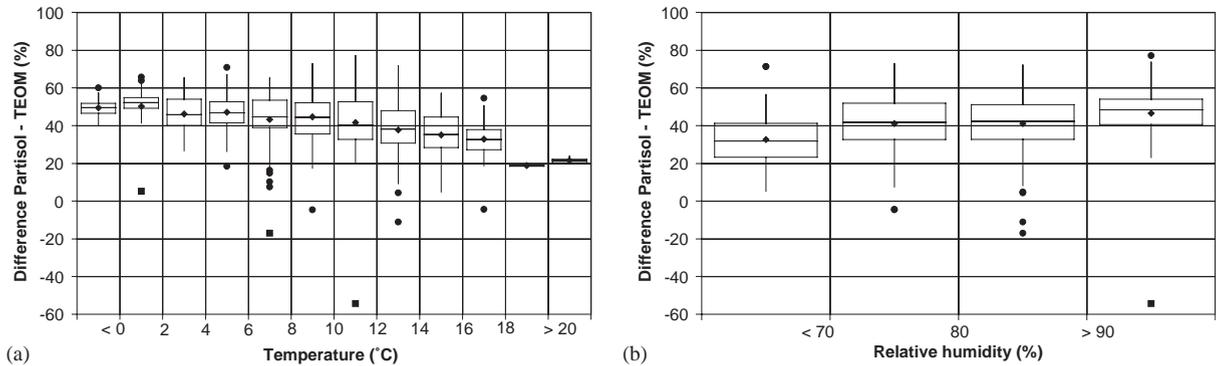


Fig. 5. Box plots of relative differences between Partisol and TEOM PM_{10} data for different (a) temperature ranges and (b) relative humidity ranges.

the particles or to an increase of the semi-volatile material volatilised from the Partisol filters, while the increase with relative humidity is likely to be related to the increase of the water content of particles and possibly also to the increase of semi-volatile compounds in particulate matter (as an example, the equilibrium of the ammonium nitrate between gaseous and condensed phases depends on the relative humidity, see [Stelson and Seinfeld, 1982a, b](#)). The influence of relative humidity on the difference between TEOM and gravimetric data seems to be less important than the influence of the temperature. The larger range of percentages associated with each range of humidity might be the result of the variation of particle composition. It might also be the result of the hysteresis of some major particulate compounds (e.g. $(NH_4)_2SO_4$) responsible for complicated relationships between particles and water ([Speer et al., 2003](#)). The significant influence of the temperature suggests that the lower reading of the TEOM is mainly due to the loss of semi-volatile compounds in the TEOM inlet.

4. Conclusion

An intercomparison between two TEOMs and two Partisol samplers for the monitoring of particles as PM_{10} and $PM_{2.5}$ has been carried out at a rural site located in Oxfordshire, UK. Results confirm the expected large difference between TEOM reading and particle mass from filter-based gravimetric methods. On average almost half of the particle mass derived from the Partisol instruments is not measured by the TEOMs. Because most of the particulate material not measured by the TEOMs is in the $PM_{2.5}$ fraction of particulate matter, the relative difference between the two methods is larger for $PM_{2.5}$ than for PM_{10} . Strong day-to-day variations of the difference between TEOM and Partisol particle mass are observed. This variability leads to

difficulty in establishing statistical relationships that successfully amend TEOM data.

Results suggest that the major semi-volatile compound lost in the inlet of the TEOMs is ammonium nitrate. Adding the calculated ammonium nitrate mass to the TEOM mass significantly improves the mass estimate, accounting for about 40% of the $PM_{2.5}$ mass deficit. Loss of other particulate material such as semi-volatile organic compounds and water must also contribute since the loss of particulate ammonium nitrate does not explain the entire difference. Large differences between measurements are associated with high particulate ammonium nitrate concentrations. As a consequence, episodes of high particulate matter concentration dominated by secondary pollutants at Harwell are not measured by the TEOMs.

The influences of temperature and of relative humidity on the difference between TEOMs and Partisol particle mass have been demonstrated. Elevated temperatures or lower relative humidities reduce the divergence between measurements. This is in agreement with previous studies showing that in summer or in areas with warm and dry climates, the agreement between TEOMs and reference gravimetric methods is better than in winter or in areas with colder and damper climates. These influences are consistent with the material lost in the inlet of the TEOMs being semi-volatile compounds and particle-bound water. The loss of semi-volatile substances from the Partisol filters reducing the divergence between the two methods during elevated temperatures is not precluded.

The establishment of a model to correct the TEOM particle mass by including influential variables such as particle composition, temperature and relative humidity would be a better alternative than statistical models. However, this study suggests that semi-volatile organic compounds may constitute a significant part of the particulate material lost in the TEOMs. This component of particulate matter includes a large range of

compounds that cannot be measured on a daily basis and moreover, the physico-chemical properties of the vast majority of such compounds are poorly quantified. On the other hand, artefacts from filter-based gravimetric methods possibly contribute to the difference and should be quantified.

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