Anonymous Referee #1 Received and published: 9 April 2019

Comment 1

Carbonaceous aerosols are of great importance for air quality and climate. This manuscript presents long periods measurements of EC and OC in Beijing between 2013 and 2017. The results are informative under the background of China's Clean Air Act. Although the manuscript is well written generally, some conclusions are a little bit speculative, which could be improved in the revision. Specifically, Concentrations of atmospheric compositions are influenced by both meteorology and emissions. The observed decreasing trend of OC and EC could be also attributed to changes in meteorological conditions, which was not discussed.

Response: We thank the reviewer for the constructive comments and suggestions. According to the reviewer's suggestions, we have added some meteorological information in Table S1, which is referred to in line 220 of the revised manuscript, and it is now explained in lines 219-232 why the annual average OC and EC have decreased over the years. The revised part is as below:

Benefiting from the Air Pollution Prevention and Control Action Plan and increasing atmospheric self-purification capacity (ASC, shown in Table S1), a decline in annual average concentrations is on the whole recorded. In detail, the annual average concentrations of OC peaked in 2014 and then declined from 14.5 to 7.7 μg/m^3, whereas those of EC also peaked in 2014 and then declined from 4.3 to 2.6 μg/m^3 during the study period. The decline in OC and EC concentrations is closely associated with decreasing coal consumption, increasing usage of natural gases and the implementation of a strict vehicular emission standard and increasing atmospheric self-purification capacity (Tables S1- S3).

Comment 2

The strong correlation between OC and EC are not necessarily meaning they are from same source. Primary pollutants could correlate well with each other under same meteorology. Please prove these statements with more detailed analysis.

Response: Thank you for pointing this out. For better clarity, a more detailed discussion has been added in the revised manuscript.

Primary OC and EC share a variety of common sources including vehicular emissions, coal combustion, biomass burning, etc. (Bond et al., 2013). Besides, primary OC and EC can correlate well with each other under the same meteorological conditions, as these would have similar effects

on the carbonaceous aerosols in terms of atmospheric advection and convection. However, it should be noted that EC is more stable than OC (Bond et al., 2013); the correlation between OC and EC would become gradually less significant with the enhancement of secondary OC formation when the meteorology is more favorable for complex chemical conversion of volatile organic compounds (VOCs) and secondary VOCs via gas-to-particle partitioning or heterogeneous reactions. Hence, the OC/EC ratios/correlations can indicate the impact from source types and meteorological influences to some extent (Blando and Turpin, 2000).

The above modifications can be seen in lines 477-483 of the revised manuscript.

References:

Blando, J. and Turpin, B.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, Atmos. Environ., 34 (10), 1623–1632, 2000.

Bond, T. C., Doherty, S. J. Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, J. Geophys. Res-Atmos., 118(11), 5380–5552, 2013.

Anonymous Referee #2 Received and published: 9 April 2019

General Comments

This research is to investigate the OC and EC hourly concentration variation in Beijing, China from 2013 to 2018. Based on data, authors discussed the relationship between OC and EC, and with major air pollutants and sources via inter-annual, seasonal, weekly and diurnal variations. Finally NWR and PSCF were employed to evaluate the local and regional anthropogenic sources. In general, the data of this manuscript are informative and this paper fits the scope of ACP. Please modify the manuscript based on the following comment before ACP publication.

Response: We thank the reviewer for the constructive comments and suggestions. According to the reviewer's suggestions, we have done our best to revise our manuscript.

Comments:

1.Section 3.1, page 9, Table 2 contains a lot of data, and the source of data should be acknowledged. I could not see the importance of Table 2 in the main text, and suggest that Table 2 can be shifted to supporting information.

Response: We thank the reviewer for the comment. As suggested, Table 2 has been moved to the supplementary material.

2. Page 10, line 237, it should be "Table 3", not Table 2. In Table 3, what are the meaning for TOT and TOT? Please explain both of them by note in the table. (Same with Table 4).

Response: Thanks for pointing this out. As the original Table 2 has been removed, the original Table 3 is Table 2 now. In addition, the notes for the abbreviations TOT, TOR and EA have been added as footnotes of Tables 2 and 3 in the revised manuscript.

3. Page 10, lines 254-255, what criteria did authors classify PM2.5 different air quality levels as excellent, good, slightly polluted, moderately polluted, heavily polluted and severely polluted? Please specify in the text.

Response: Thanks for the comment. The criteria used to classify the air quality have been added in the revised manuscript. Air quality as Excellent, good, lightly polluted (LP), moderately polluted (MP), heavily polluted (HP) and severely polluted (SP) are based on the daily average $PM_{2.5}$ concentration, i.e., excellent ($0<PM_{2.5}\leqslant 35$ μg/m^3), good ($35<PM_{2.5}\leqslant 75$ μg/m^3), lightly polluted (LP, $75<PM_{2.5}\leqslant 115$ μg/m^3), moderately polluted (MP, $115<PM_{2.5}\leqslant 150$ μg/m^3), heavily polluted (HP, $150<PM_{2.5}\leqslant 250$ μg/m^3) and severely polluted (SP, $PM_{2.5}>250$ μg/m^3), respectively.

4. Page 10, line 254, in Fig. 2, "White Block" label is referring to PM2.5 in both two figures?

Response: Thanks for the comment. It is true that the "white block" refers to the $PM_{2.5}$ concentration in the top sub-figure in Fig. 2, while it means percentage of composition in $PM_{2.5}$ excluding OC and EC in the bottom sub-figure in Fig. 2. The legends in Fig. 2 have been revised for better clarity in the revised manuscript.

5. Section 3.2, page 11, Fig. 4 can be part of Fig. 3. Does Fig. 4 contain special information? If yes, some more discussion related to Fig. 4 should be added. Otherwise I recommended to remove this figure.

Response: As suggested, the original Fig. 4 has been removed in the revised manuscript as it presents partially repetitive information of Fig. 3.

6. Page 11, I found quite a lot of data in Fig. 3 including OC-EC during 2002-2012, SO2, NO2, fire spots, please specify the data sources of all these data.

Response: Thank you for pointing this out. As advised, the sources of the data, which were not included in this study, have been added in section 2 and in lines 309-310 (He et al., 2001; Zhao et al., 2013; Ji et al., 2016; Lang et al., 2017; Tao et al., 2017) in the revised manuscript.

References:

He, K. B., Yang, F. M., Duan, F. K., Ma Y. L.: Atmospheric particulate matter and regional complex pollution, Science Press, Beijing, China. 310-327, 2011.

Ji, D. S., Zhang, J. K., He, J., Wang, X. J., Pang, B., Liu, Z. R., Wang, L. L., and Wang, Y. S.: Characteristics of atmospheric organic and elemental carbon aerosols in urban Beijing, China, Atmos. Environ., 125, 293-306, 2016.

Lang, J. L., Zhang, Y. Y., Zhou, Y., Cheng, S. Y., Chen, D. S., Guo, X. U., Chen, S., Li, X. X., Xing, X. F., Wang, H. Y.: Trends of PM2.5 and chemical composition in Beijing, 2000-2015. Aerosol Air Qual. Res., 17, 412-425, 2017.

Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning $PM_{2.5}$ chemical composition, aerosol optical properties and their relationships across China, Atmos. Chem. Phys., 17, 9485-9518, https://doi.org/10.5194/acp-17-9485-2017, 2017.

Zhao, P., Dong, F., and Yang, Y.: Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China, Atmos. Environ., 71, 389-398, 2013.

7. Page 12, lines 302-305, authors claims that biomass burning could contribution a lot to OC and EC, please be noted that fire spots in 2012 were highest, please add some discussion in this section.

Response: Thanks for this comment. More discussion has been added in line 338-349 in the revised version: "In Fig. 3, it can be seen that the annual average EC concentration and the fire spot counts exhibit a rather similar variation from 2004 to 2017, except in the year 2012, which suggests that the EC levels are somewhat correlated with the biomass burning; this might indicate that biomass burning contributed somewhat to the EC levels. The reduction in fire spot counts from 2014 to 2017, which resulted from efforts to control the agricultural field residue burning since 2013, helped to reduce the EC concentrations to some extent, but the low EC levels during 2014-2017 are likely mostly due to the implementation of the clean air act. With regard to the anomaly in the year 2012, based on the MODIS data for this year, a very non-uniform distribution of fire spots in the BTH region was observed, with a distinct decrease of fire spot counts in Beijing, but higher fire spot counts in the southern Hebei Province; this may be ascribed to the fact that the policy of Banning Straw Burning in Summer and Autumn was executed to different degrees in the whole region, with

better implementation in the Beijing area and worse action in the other parts. (http://www.beijing.gov.cn/zfxxgk/110029/qtwj22/2012-12/11/content_357114.shtml). In addition, for the years from 2002 to 2017, the highest precipitation volume in Beijing was recorded in 2012, i.e., 733.2 mm, and the rainy days mainly occurred in the intensive straw burning periods, accounting for 76.4% of all rainy days in 2012. The frequent wet scavenging might have suppressed the EC concentrations during the intensive straw burning periods, so that the annual EC level for 2012 was comparable to those recorded from 2011 onward."

8. Section 3.3, pages 12-14, authors separately discussed monthly and seasonal variations. Actually, I found quite a lot of data explanations are similar for both monthly and seasonal variation. Is it possible for authors to combine both to simplify the discussion?

Response: Thank you for pointing this out. We have simplified the discussion in lines 360-416 in the revised manuscript and the revised text is as follows: "Fig. S1 shows the monthly mean OC and EC concentrations at our study site for the whole 5-year period. Similar variations are observed with generally higher mean OC and EC levels in the cold season (from November to March next year when the centralized urban residential heating is provided) and lower ones in the warm season (from April to October). The highest average OC and EC concentrations were 24.1 ± 18.7 μg/m^3 in December 2016 and 9.3 ± 8.5 μg/m^3 in December 2015, respectively. However, the lowest OC and EC levels were not observed in the warm months; they were 5.0 ± 4.6 μg/m^3 in January, 2018 and 1.5 ± 1.7 μg/m^3 in December, 2017, respectively; this was associated with both frequent occurrence of cold air mass and the implementation of a winter radical pollution control action plan (Chen and Chen, 2019) in Beijing from November, 2017. Overall, the increased fuel consumption for domestic heating in addition to unfavorable meteorological conditions (lower mixing layer height, temperature inversion and calm wind) in the colder months is considered to lead to higher OC and EC levels (Ji et al., 2014). In addition, the lower air temperature in the cold months led to shifting the gas-particle equilibrium of semi-volatile organic compounds (SVOCs) into the particle phase, leading to higher OC levels. In the cold months, the cold start of vehicles (5.64 million vehicles in Beijing at the end of 2017) also increased the emission of OC. In the warm season, lower OC and

EC levels were observed, which could be attributed to the following factors: no extra energy consumed for domestic heating, strong wet scavenging by frequent precipitation occurring in these months, and more unstable atmospheric conditions favorable for pollutant dispersion; in addition, during this period, the monthly mean OC and EC concentrations generally decreased from year to year. In contrast, for the cold season, the monthly mean OC and EC concentrations did not show a clear decreasing trend from year to year. In addition to the more intensive energy consumption in the cold season, the EC and OC levels could be also be enhanced strongly by regional transport and stagnant meteorology leading to ground surface accumulation in the autumn and winter (Wang et al., 2019; Yi et al., 2019), which would counteract the efficacy of the energy structure change in the Beijing-Tianjin-Hebei region of the past few years. It is worth pointing out that, on a year to year basis, the monthly average OC and EC concentrations in the cold seasons of 2017 and 2018 were generally lower than those in 2016, demonstrating to some extent the effectiveness of the execution of the radical pollution control measures for cities on the air pollution in the Beijing-Tianjin-Hebei region. The interquartile ranges of OC and EC in the warm months were narrower than in the cold months, indicating that there was more substantial variation in concentration in the latter months. The larger variation in the colder months could be caused by the cyclic accumulation and scavenging processes. In this region, due to the cyclic accumulation and scavenging process, the concentration of particulate matter increases rapidly when the air mass back trajectories change from the northwest and north to the southwest and south over successive days in Beijing; in contrast, the concentration of particulate matter declines sharply when a cold front causes the shift of back trajectories from the southwest and south to the north and northwest (Ji et al., 2012). The successive accumulation processes are closely associated with unfavorable meteorological conditions, which gives rise to higher OC and EC concentrations, while more scavenging of aerosols by cold fronts leads to lower levels.

As to the seasonality in OC and EC, similar seasonal variations are observed in the various years with generally higher mean concentrations in autumn and winter and lower levels in spring and summer (Fig. 4). Remarkably, the OC and EC concentrations in the autumn and winter of 2017 were lower than those in the previous years. This was due to the combined effect of controlling anthropogenic emissions strictly and favorable meteorological conditions. Since September 2017, a

series of the most stringent measures within the Action Plan on Prevention and Control of Air Pollution was implemented to improve the air quality; these measures included restricting industrial production by shutting down thousands of polluting plants, suspending the work of iron and steel plants in 28 major cities and limiting the use of vehicles and reducing coal consumption as a heating source in northern China. In addition, the air quality improvement in the autumn and winter of 2017 was closely tied to frequent cold fronts accompanied by strong winds, which was favorable for dispersing the pollutants. The average OC and EC concentrations in the winter were 1.69 and 1.14, 2.17 and 1.93, 1.49 and 2.14, 2.41 and 2.29 and 0.80 and 0.88 times higher than those in the summer for 2013, 2014, 2015, 2016 and 2017, respectively. The difference in the ratios for 2017 was due to the series of the most stringent measures taking effect and favorable meteorology. The Beijing municipal government in particular has made great efforts to replace coal by natural gases and electricity-powered facilities. Besides, new energy vehicles are increasingly used to replace the gasoline vehicles."

Reference:

Chen, H. and Chen, W.: Potential impact of shifting coal to gas and electricity for building sectors in 28 major northern cities of China, Appl. Energ., 236, 1049-1061, 2019.

9. Section 3.4, page 14, lines 365-367, EC concentrations increased starting from 17:00 because of evening rush hours, I am curious why morning rush hour did not result in the increase of EC?

Response: Thank you for this comment. As indicated in the manuscript, whereby 'other times' stands for 'non-night times', "At other times, both the higher PBL height and lower traffic intensity resulted in lower EC concentrations". It has been reported that morning peaks of OC and EC levels were higher than those during the nighttime in urban areas in the US (Rattigan et al., 2010, Kang et al., 2010), where there was no strong traffic emission of OC and EC during the nighttime. However, as regulated by the Beijing Traffic management Bureau (http://www.bjjtgl.gov.cn/zhuanti/10weihao/), HDV and HDDT are allowed to enter the urban area inside the 5th Ring Road from 0:00 to 06:00 (local Time) in Beijing. In addition to the nocturnal

PBL effect, these high emitters contribute significantly to the high levels of OC and EC from midnight to the early morning; the OC and EC originating from the morning rush hour is not sufficiently dominant to form peaks during the 6:00-8:00 period.

References:

Kang, C. M., Koutrakis P., and Suh, H. H.: Hourly measurements of fine particulate sulfate and carbon aerosols at the Harvard-U.S. Environmental Protection Agency Supersite in Boston, J. Air Waste Manage., 60:11, 1327-1334, 2010.

Rattigan, O. V., Felton, H. D., Bae, M. S., Schwab, J. J., and Demerjian, K. L.: Multi-year hourly $PM_{2.5}$ carbon measurements in New York: Diurnal, day of week and seasonal patterns, Atmos. Environ., 44(16), 2043-2053, 2010.

10. Section 3.5, similar to the above comment No. 6, please specify the data source of gaseous pollutants.

Response: Thank you for pointing this out. We have added the following text for the data sources of the gaseous pollutants in section 2.2 in the revised manuscript: "The analyzers/monitors for O_3, CO, SO_2, NO_x and $PM_{2.5,}$ and their precision, detection limits and calibration methods have been described in detail elsewhere (Ji et al., 2014). Briefly, O_3 was measured using an ultraviolet photometric analyzer (model 49i, Thermo Fisher Scientific (Thermo), USA), CO with a gas filter correlation nondispersive infrared method analyzer (model 48i, Thermo, USA), SO_2 using a pulsed-fluorescence analyzer (model 43i, Thermo, USA), NO-NO_2-NO_x with a chemiluminescence analyzer (model 42, Thermo, USA) and $PM_{2.5}$ using a US Environmental Protection Agency Federal Equivalent Method analyzer of $PM_{2.5}$ (SHARP 5030, Thermo, USA)."

11. Page 18, 2nd paragraph, authors discussed the relationship between ozone and OC. It is interesting to find that O3 at 50ug/m3 represented the highest OC, and OC increased with ozone for O3 concentration above 100ug/m3. More discussion of the potential reasons will definitely enhance the quality of manuscript.

Response: Thank you for pointing this out. We have added the following relevant discussion and explanation on the relationship between ozone and OC in lines 541-567 in the revised manuscript: "Emissions of primary air pollutants lead through multiple pathways to the formation of ozone and secondary organic carbon (SOC) (Seinfeld and Pandis, 1998), both of which are the principal components of photochemical smog. The relationship between OC and O_3 is of use for understanding their variation and formation. The OC concentrations were highest for an O_3 concentration of 50 μg/m^3, which is approximately the average O_3 concentration in Beijing in winter (Cheng et al., 2018). During the period of an O_3 concentration of 50 μg/m^3, low atmospheric temperature (9.4±9.9 ºC), relatively high RH (59.2±23.7 %), lower WS (1.1±0.8 m/s) and higher NO_x concentrations (72.7±57.5 ppb) were observed and a lower mixed layer height was recorded in winter (Tang et al., 2016), which were favorable for accumulation and formation of OC. A relatively lower temperature is beneficial for condensation/absorption of SVOCs into existing particles (Ji et al., 2019), which would then experience further chemical reactions to generate secondary organic aerosol (SOA). Note that a low temperature does not significantly reduce SOA formation rates (Huang et al., 2014) in the winter. In addition, processes including aqueous-phase oxidation and NO_3-radical-initiated nocturnal chemistry may contribute to or even dominate SOA formation during winter (Hallquist et al., 2009; Rollins et al., 2012; Huang et al., 2014). Hence, the above factors gave rise to the higher OC concentration at an O_3 concentration of 50 μg/m^3 particularly in winter. In addition, scattering and absorbing effects of aerosols that were trapped in the lower mixed layer height led to less solar radiation reaching the ground and further restrained the O_3 formation in the cold season (Xing et al., 2017; Wang et al., 2016b). OC declined when O_3 concentrations increased from 50 to 100 μg/m^3. Usually moderate O_3 concentrations accompanying lower OC concentrations are caused by increasing T (19.5±8.3 ºC), increasing WS (2.0±1.3 m/s) and less titration of relatively lower observed NO concentrations (6.4±14.6 ppb). It can also be seen that there was a concurrent increasing trend of OC and ozone when the O_3 concentration was above 100 μg/m^3, which generally occurred in the warmer season. Besides the impact of meteorological conditions, such a trend might not be dominated by gas-to-particle partitioning of low-volatility

organic compounds but by the oxidation of VOCs driven by hydroxyl radicals to generate both SOC and O_3 with relatively long lifetimes (>12 h; Wood et al., 2010)"

References:

Hallquist, M., Wenger, J., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics 9(14), 5155-5236, 2009.

Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Dällenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z. S., Szidat, S., Baltensperger, U., EI Haddad, I., and Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 2014.

Rollins, A. W., Browne, E. C., Min, K. E., Pusede, S. E., Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day, D. A., Russell, L. M., and Cohen, R. C.: Evidence for NOx control over nighttime SOA formation, Science 337(6099), 1210-1212, 2012.

Tang, G., Zhang, J., Zhu, X., Song, T., Münkel, C., Hu, B., Schäfer, K., Liu, Z., Zhang, J., Wang, L., Xin, J., Suppan, P., and Wang, Y.: Mixing layer height and its implications for air pollution over Beijing, China, Atmos. Chem. Phys., 16, 2459-2475, 2016.

Wood, E. C., Canagaratna, M. R., Herndon, S. C., Onasch, T. B., Kolb, C. E., Worsnop, D. R., Kroll, J. H., Knighton, W. B., Seila, R., Zavala, M., Molina, L. T., DeCarlo, P. F., Jimenez, J. L., Weinheimer, A. J., Knapp, D. J., Jobson, B. T., Stutz, J., Kuster, W. C., Williams, E. J.: Investigation of the correlation between odd oxygen and secondary organic aerosol in Mexico City and Houston. Atmos. Chem. Phys. 18(10), 8947-8968, 2010.

12. Section 3.6, page 19, line 493, no Fig. 14 and 15 are in the whole manuscript.

Response: Our apologies for this error. It has been corrected and all the joint probability data are presented in the right panels of Figs. 7 and 8 in the revised manuscript.

Anonymous Referee #3 Received and published: 12 March 2019

General comments

The manuscript describe how EC and OC concentrations changed at Beijing between 2013 and 2017. Hourly EC/OC data is important and informative. However, interpretation of data is not equally robust. In some parts, discussions are very speculative. This is the main weakness of this paper. Seasonal, diurnal and interannual variations are nicely discussed. Particularly discussion of long-term variations in EC and OC concentrations, using their own data is very informative, but the part where discussion of long-term variations are extended to 2002 using literature information is not that convincing. Authors applied nonparametric wind regression to locate local sources. This is a new tool and nicely applied in this work. They also applied PSCF to identify distant sources. I do not really think distant sources can be differentiated from local ones with PSCF, because every single trajectory ends up in Beijing, which is a huge source itself.

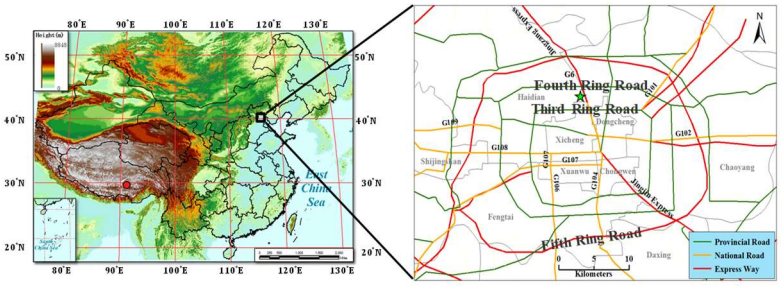
Response: We thank the reviewer for the constructive comments and suggestions. We have done our best to address all the comments and to improve our manuscript.

Specific comments

Comment 1

Figure 1. What is the "star" in the figure? Figure 1. Where is the first ring road? 4. Ring road? G6 highway? Please put these names on the map, so that reader can understand which roads you are referring to, or describe roads with notations on the map, such as, G108 etc.

Response: Thank you for pointing this out. The “star” denotes the study site. We have added the notations for the Third Ring Road, the Fourth Ring Road, the Fifth Ring Road, G6, G101, G102, G107, G108 and G109 in Fig. 1. The notations are provided near the roads and highways.



G6=Jingzang Expressway; G101=National Highway 101; G102= National Highway 102; G107= National Highway 107; G108= National Highway 108; G109= National Highway 109

Fig.1

Comment 2

Lines 210 - 214. Authors discuss that concentrations of EC, OC and PM2.5 decreased from 2013 towards 2017. They should provide statistical significance of this comment. The difference between 14.0±11.7 and 11.9±11.3 (OC concentrations in 2013 and 2016, respectively) may or may not be statistically significant and must be tested. This comment also holds for EC and PM2.5 concentrations.

Response: Thank you for pointing this out. In Table 1, it can be seen that the annual average concentrations of both OC and EC peaked in 2014 and then started to decline gradually during the remainder of the study period. Nonetheless, the annual average concentration of $PM_{2.5}$ was generally decreasing from 2013 to 2017 with a moderate peak in 2016. As advised by the reviewer, 2-tailed paired t-tests were applied for OC, EC and $PM_{2.5}$ using their monthly average concentrations in 2013 and 2016 as paired datasets. At a confidence level of 98%, from March to October, the paired data are statistically different, indicating that the concentrations of OC, EC and $PM_{2.5}$ declined during the above period from 2013 to 2016; however, the concentrations of OC, EC and $PM_{2.5}$ during November and February from 2013 to 2016 are not statistically different. This part has been modified in lines 219-232 in the revised manuscript.

Comment 3
For the same discussion.
It will be better if authors should also present median concentrations of EC, OC and $PM_{2.5}$ in table (maybe in parenthesis by the averages), which represent right-skewed data population better than average.

Response: Thank you for pointing this out. The median concentrations of EC, OC and $PM_{2.5}$ have been added in Table 1 of the revised manuscript; as the median are lower than the averages, it can be concluded that the data populations for OC, EC and $PM_{2.5}$ are right-skewed.

Comment 4
Line 230. "Compared to previous studies, the ratio of TC to $PM_{2.5}$ became smaller ...." Last column in Table 1 suggests that TC-to-$PM_{2.5}$ ratio did not change much between 2013 and 2018 in Beijing. Can the difference with "other" data be due to different characteristics of sampling locations, rather than time? Author's explanations with stringent measures make sense, but if that is the case shouldn't the TC/$PM_{2.5}$ ratio decrease in five years between 2013 and 2018 at their site as well?

Response: Thank you for pointing this out. The TC/$PM_{2.5}$ ratio is not only associated with emission sources and different environment of the sampling locations, but also depends on the formation of secondary aerosols. Following up on the reviewer's comments and suggestion, we revised the relevant discussion in lines 249-263 in the revised manuscript: "Compared to previous studies in Beijing (Table S4), the TC to $PM_{2.5}$ ratio became smaller, indicating a relatively lower contribution from carbonaceous aerosols to $PM_{2.5}$ in this study. The difference in the TC/$PM_{2.5}$ ratio could be

ascribed to two factors. One factor is the difference in characteristics of sampling locations between that in our study and those in the earlier studies. However, our site and those in the previous studies used for comparison are all located in urban areas of Beijing (Chaoyang and Haidian district, respectively). It is reasonable to assume that they are affected by common sources since the surrounding environments exhibit similar features. Besides, the annual average $PM_{2.5}$ concentrations in both districts published by the Ministry of Environmental Protection of China (http://106.37.208.233:20035/) were quite comparable to each other from 2013 to 2017 (y=0.99x, r^2=0.92), indicating that both areas had particle pollution of a similar degree. The second factor is that the contribution from secondary inorganic aerosols to the $PM_{2.5}$ became more important because of a stronger atmospheric oxidation capacity (the annual average O_3 concentrations were 102, 109, 116, 119, and 136 μg/m^3, respectively, from 2013 to 2017 in the Beijing-Tianjin-Hebei region; published by http://106.37.208.233:20035/), which could give rise to a lower TC to $PM_{2.5}$ ratio."

Comment 5
Line 237. Table you are referring to is Table 3 not Table 2.

Response: Our apologies for this error. We have corrected it.

Comment 6
Line 260 Authors should explanation the criteria they used to classify air quality as Excellent, good, LP, MP HP and SP

Response: Thank you for pointing this out. The criteria used to classify the air quality have been added in the revised manuscript. Air quality as Excellent, good, LP, MP, HP and SP were based on the daily average $PM_{2.5}$ concentration, i.e., excellent (0<$PM_{2.5}$≤35 μg/m^3), good (35<$PM_{2.5}$≤75 μg/m^3), lightly polluted (LP, 75<$PM_{2.5}$≤115 μg/m^3), moderately polluted (MP, 115<$PM_{2.5}$≤150 μg/m^3), heavily polluted (HP, 150<$PM_{2.5}$≤250 μg/m^3) and severely polluted (SP, $PM_{2.5}$>250 μg/m^3), respectively.

Comment 7
Line 271 - 305 Authors discussed long-term variation in concentrations of EC, OC, SO_2, NO_2 and tried to relate them with variations in fuel use and traffic intensity. The discussion is very speculative. Particularly, attempts to link the drop in EC concentrations in 2010 (not in OC, not in SO_2 and NO_2) to moving a steel factory to somewhere else is not convincing.

Response: Thanks for the constructive comment. For better clarity, the last paragraph of section 3.2 has been modified in lines 350-358 in the revised manuscript: "Similar to OC and EC, the annual mean SO_2 and NO_2 concentrations also showed a decreasing trend. As well-known, SO_2 originates from coal combustion and sulfur-containing oil (Seinfeld and Pandis, 1998). With the replacement of coal for industrial facilities, residential heating and cooking by clean energy (e.g., natural gases, electricity and lower sulfur content in oil), a clear decline in annual SO_2 concentrations was observed in the Beijing area starting from 2002. As compared to SO_2, the annual decreasing rate of NO_2 was relatively lower. Besides the power plants and other boilers, traffic emissions are another major source of NO_2. The rapid increase of vehicle population may partly offset the great effort in reducing coal consumption to lower the NO_2 level despite the transition to more stringent traffic emission standards."

Comment 8

More information should be provided about data they used from literature (2002-2012). Are these data from one study and from one measurement site, or are they from combination of various studies and various sites? This is important, because what you measure also depends on location of your sampling point. For example, can the drop they observed in EC concentrations in 2010 be an artifact due to different measurement point?

Response: Thank you for pointing this out. We have added the information for the data cited from literature (2002-2012, He et al., 2001; Zhao et al., 2013; Ji et al., 2016; Lang et al., 2017; Tao et al., 2017); information about the sampling sites is given in the references. A discussion on the decline in OC and EC concentrations has been added to substantiate its validity in lines 308-328 of the revised manuscript. Considering that measurements of OC and EC were rather scarce from 2002 to 2012, the comparison of OC and EC between multiple sites cannot be used to exclude the difference caused by location of the sampling points. However, the annual average $PM_{2.5}$ concentrations in the observation regions (Chaoyang and Haidian districts in Beijing) published by Ministry of Environmental protection, China (http://106.37.208.233:20035/) were very similar to each other from 2013 to 2017 (y=0.99x, r^2=0.92).

References:

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Zhao, P., Dong, F., and Yang, Y.: Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China, Atmos. Environ., 71, 389-398, 2013.

Comment 9

Authors should also explain why only EC concentration dropped but not SO_2 when a large steel industry stopped its operations in 2010.

Response: Thank you for pointing this out. As shown in Fig. 3, from 2010 to 2011, the concentrations of OC, EC and SO_2 have decreased. It is known that the clean air act was not started yet and the emission standards for most coal-intensive industries, including thermal power plants, had not been replaced yet by more stringent standards during that period. The significant decrease in coal consumption in 2011 compared to 2010 was to be ascribed to the relocation of Shougang Corporation and a few other highly polluting industrial facilities, which could lead to a decrease in OC, EC and SO_2 levels.

Comment 10

Line 315 Does "unfavorable meteorological conditions" mean lower mixing height, slower winds? Please state. (Unfavorable met conditions are later explained in the text. It will be better if they can bring that explanation here)

Response: Thank you for pointing this out. Unfavorable meteorological conditions included a lower mixing height and lower wind speeds (Ji et al., 2014), as indicated in line 370 in the revised manuscript.

Reference:

Ji, D., Li, L., Wang, Y., Zhang, J., Cheng, M., Sun, Y., Liu, Z. R., Wang, L. L., Tang, G. Q., Hu, B., Chao, N., Wen, T. X., and Miao, H. Y.: The heaviest particulate air-pollution episodes occurred in northern China in January, 2013: Insights gained from observation, Atmos. Environ., 92, 546-556, 2014.

Comment 11

Lines 318 - 326 Authors observed decreasing EC and OC concentrations in "warm" months, but no similar decreasing trend in "cold" months. This is confusing, because throughout the manuscript they mentioned about more stringent measures of coal use, switching to cleaner forms of energy production etc. These all affect EC and OC concentrations in cold season, but hey observed decreasing pattern in warm season. Please explain. Please, also state in the text, how you define cold and warm seasons.

Response: Thank you for pointing this out. For better clarity, the cold season extends from November to February next year when the centralized urban residential heating is provided, and the warm season starts in April and ends in October. In the warm season, lower OC and EC levels were observed, which could be attributed to the following factors: no extra energy consumed for domestic heating, strong wet scavenging by frequent precipitation occurring in these months, and more unstable atmospheric conditions favorable for pollutant dispersion; in addition, during this period, the monthly mean OC and EC concentrations generally decreased from year to year. In contrast, in the cold season, the monthly mean OC and EC concentrations did not show a clear decreasing trend from year to year. In addition to the more intensive energy consumption in the cold season, the EC and OC levels could also be enhanced strongly by regional transport and stagnant meteorology, leading to ground surface accumulation in the autumn and winter (Wang et al., 2019; Yi et al., 2019); this would have counteracted the efficacy of the energy structure change in the Beijing-Tianjin-Hebei region in the past few years. It is worth pointing out that, on a year to year basis, the monthly average OC and EC concentrations in the cold seasons of 2017 and 2018 were generally lower than those in 2016, demonstrating to some extent the effectiveness of the execution of the radical pollution control measures for cities on the air pollution in the Beijing-Tianjin-Hebei region. The modifications can be seen in lines 360-388 of the revised manuscript.

References:

Wang, C., An, X., Zhang, P., Sun, Z., Cui, M., and Ma, L.: Comparing the impact of strong and weak East Asian winter monsoon on $PM_{2.5}$ concentration in Beijing, Atmos. Res., 215, 165-177, 2019.

Yi, K., Liu, J. F., Wang, X. J., Ma, J. M., Hu, J. Y., Wan, Y., Xu, J. Y., Yang H. Z., Liu, H. Z., Xiang, S. L., and Tao, S.: A combined Arctic-tropical climate pattern controlling the inter-annual climate variability of wintertime $PM_{2.5}$ over the North China Plain. Environ. Pollut., 245, 607-615, 2019.

Comment 12

Line 323. What does "cyclic accumulation and scavenging process" mean?

Response: Thank you for pointing this out. The accumulation and scavenging processes occur in cycles because of changes in air mass origin and meteorological conditions. The concentration of particulate matter increases rapidly when the air mass back trajectories change from the northwest and north to the southwest and south over successive days in Beijing; in contrast, the concentration of particulate matter declines sharply when a cold front causes a shift of back trajectories from the southwest and south to the north and northwest (Ji et al., 2012). The accumulation processes are closely associated with unfavorable meteorological conditions, which give rise to higher OC and EC concentrations, while more scavenging of aerosols by cold fronts leads to lower levels. The modifications can be seen in lines 392-398 of the revised manuscript.

Reference:
Ji, D. S., Wang, Y. S., Wang, L. L., Chen, L. F., Hu, B., Tang, G. Q., Xin, J. Y., Song, T., Wen, T. X., Sun, Y., Pan, Y. P., and Liu, Z. R.: Analysis of heavy pollution episodes in selected cities of northern China, Atmos. Environ., 50, 338-348, 2012.

Comment 13
Line 371 "The amplitude of the diurnal variation in the EC concentrations was smaller in the last three years." Please support this with traffic counts.

Response: Thank you for pointing this out. It is a pity that no diurnal variations in traffic counts are available but the hourly average traffic counts in 2015, 2016 and 2017 could be found in (Beijing Transportation Annual Report, http://www.bjtrc.org.cn/JGJS.aspx?id=5.2&Menu=GZCG). The hourly average traffic counts in urban Beijing were 5969/hr, 5934/hr and 6049/hr in 2015, 2016 and 2017, respectively (Beijing Transportation Annual Report, http://www.bjtrc.org.cn/JGJS.aspx?id=5.2&Menu=GZCG). Supposedly, the small amplitude of the diurnal variation in the last three years might be related to local emission intensities; these might been significantly affected by the enforcement of a series of traffic emission control measures since 2015, including more strict restriction of emission from heavy-duty diesel vehicle public buses, wider usage of electric public buses, and scrappage of all the high-emitting (yellow-labelled) vehicles, etc. (Table S2). All these actions led to a decline in emissions of OC and EC and narrowed the amplitude of the diurnal variation in the EC concentration.

Comment 14

Line 393. "OC and EC exhibited higher concentrations on weekends than on weekdays" Statistical significance of the difference between 13.2 ± 1.8 (OC in WE) and 11.8 ± 1.8 (OC in WD) and between 3.9 ± 2.7 (EC in WE) and 3.6 ± 3.5 (EC in WD) must be tested. These numbers are close to each other.

Response: Thanks for the comment. The difference in OC and EC concentrations between weekends and weekdays was found to be statistically significant based on the analysis of the weekly data using *t*-test statistics. Hence, the above statement was modified in line 463 in the revised manuscript: OC and EC statistically (p<0.05) exhibited higher concentrations on weekends than on weekdays in this study.

Comment 15
Also, please check the standard deviations, given for OC in both WD and WE. They are too small to be real.

Response: Thanks for pointing this out. The standard deviations of OC in both WD and WE have been double checked and the correct average concentrations should be 13.2 ± 11.8 and 11.8 ± 10.8 μg/m^3 for WD and WE, respectively. The related parts have been changed in lines 464 and 466 in the revised manuscript.

Comment 16
Line 434 "This could be because vehicular emissions became the dominant pollution source and gradually replaced the industrial emissions in Beijing". Hand-waving. Must be removed.

Response: Thank you for pointing this out. This sentence is indeed very speculative and has been removed as suggested.

Comment 17
Line 489 ".... highlighting probable trans-boundary transport from highly industrialized regions upwind of the Hebei province of China ...", NWR is performed using surface meteorological data. How correct is it to infer long-distance transport with surface met data? Please explain in the text.

Response: Thank you for pointing this out. As the NWR analysis provides an allocation of local sources, we feel that it is inappropriate to infer the impact of long-range transport of air masses on the studied site. Hence, the trans-boundary transport inferred from the NWR results has been removed in the revised manuscript.

Comment 18

Line 493 "The joint probability data in Figs. 14 and 15 show...." There is only 10 figures in this paper.

Response: Our apologies for this error. We have modified them. All the joint probability data are shown in the right panels in Figs. 7 and 8.

Comment 19
Line 500 "Considering that the NWR analysis can only provide an allocation of local sources, the PSCF analysis is a helpful complement to investigate potential advection of pollution over larger geographical scales" How realistic is it to attempt to locate distant sources using PSCF in the middle of a huge source like Beijing? No matter where they are coming from, all trajectories will end up in Beijing and will pick up pollutants emitted in Beijing. If every single trajectory is effected emissions in Beijing, it will be very difficult (probably impossible) to differentiate information trajectories carry about distant sources. If you agree with me, please remove PSCF from manuscript. If you do not agree with me, please explain how you avoid this drawback in the text.

Response: Thanks for this comment, but we still believe that potential source contribution function (PSCF) is a useful tool to pinpoint non-nearby potential source areas, from which the air masses can affect the acceptor site via transboundary transport. It is extensively used in the literature for pinpointing non-nearby source areas; according to the Web of Science there are currently 465 publications in which “potential source contribution function” or PSCF was used. The detailed explanation of PSCF is as follows. PSCF is one type of residence time analysis of back trajectory endpoints within a fixed space, which provides the conditional probability that a given grid cell is within the source region of the pollutant species of interest if air mass trajectories passing through the cell give rise at the receptor site to measured levels of the pollutant above a pre-defined threshold value (Sofowote et al., 2011). Consequently, PSCF analysis is able to identify geographically-disperse source regions and the preferred pathways of contaminant species to a receptor site. In this study, we selected 48-h trajectories terminating at Beijing at a height of 100 m using the Trajstat software (Wang et al., 2009). 48-h trajectories with long pathways suggest that they have a rapid moving speed corresponding with relatively higher surface WS. When trajectories with long pathways are accompanied with a higher loading of the species of interest, it suggests that regional transport has an effect on the loading of species of interest at the receptor site. The PSCF calculations were performed on a longitude-latitude grid which covers the spatial domain of interest. We assume that a species emitted within a grid cell is swept into the air parcel and transported to the receptor

site without loss through diffusion, chemical transformation or atmospheric scavenging. Let n_{ij} be the total number of trajectory segment endpoints falling in the grid cell (i, j) over the period of study, and let m_{ij} be the number of endpoints in (i, j) corresponding to trajectories associated with concentration values at the receptor site exceeding a specified threshold. The ratio, multiplied with a weighing factor, is then the conditional probability PSCF(i, j) that an air parcel passing over the cell (i, j) on its way to the receptor site arrives at the site with a concentration value above the threshold. Hence, high values in the spatial distribution of PSCF(i, j) will pinpoint geographical regions that are likely to produce high concentration values at the receptor site. In order to identify the high PSCF values that might have arisen purely by chance, it is necessary to test these values against the null hypothesis that there is no association between concentrations and trajectories. The statistical significance of the spatial distribution of the PSCF values is examined by making use of a nonparametric bootstrap method. The method assumes that the concentration values are independent and identically distributed. We draw with replacement from the original concentration data set, $C=\{c_1, c_2, \ldots, cN\}$, B random subsamples of size equal to the length of the data set, $C^*=\{c_1^*, c_2^*, \ldots, c_N^*\}$. We then calculate for each bootstrapped sample k the corresponding PSCF spatial distribution, $W_k^*;ij$. Let $W_k^*;ij < \ldots < W_{(B)}^*;ij$ be the ordered values $\{W_k^*;ij\}$ $k=1, \ldots, B$, and let α be the chosen significance level. If $\{W_k^*;ij\} \geq W^*(B+1)(1-\alpha/2));ij$, the null hypothesis is rejected at the $(1-\alpha)$% confidence level. We decided to retain for our further analysis only the PSCF values satisfying the above relation. Note that if there is more than one trajectory assigned to a concentration value, the simple bootstrap on the concentration data set is equivalent to a blocked bootstrap on the trajectory set. In this study, a weighting function $w(n_{ij})$ was multiplied by the m_{ij}/n_{ij} value when n_{ij} was lower than three times of the average number of trajectory endpoints (n_{mean}) for each cell (Dimitriou and Kassomenos et al., 2015; Polissar et al., 2001). The weight function is as follows:

$$w(n_{ij}) = \begin{cases} 1.00, 3n_{mean} < n_{ij} \\ 0.70, 1.5n_{mean} < n_{ij} \leq 3n_{mean} \\ 0.40, n_{mean} < n_{ij} \leq 1.5n_{mean} \\ 0.20, n_{ij} \leq n_{mean} \end{cases}$$

The results of our PSCF analysis were consistent with the emission inventory data (Zhu et al., 2018), suggesting that our PSCF analysis is trustworthy.

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Dimitriou, K., and Kassomenos, P., 2015. Three year study of tropospheric ozone with back trajectories at a metropolitan and a medium scale urban area in Greece. Sci. Total Environ. 502, 493–501.

Petit, J. E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind and trajectory analyses. Environ. Modell. Softw., 88, 183-187, 2017.

Polissar, A.V., Hopke, P.K., Poirot, R.L.: Atmospheric aerosol over Vermont: chemical composition and sources. Environ. Sci. Technol. 35, 4604–4621, 2001.

Sofowote, U. M., Hung, H., Rastogi, A. K., Westgate, J. N., Deluca, P. F., Su, Y. S., and McCarry, B. E.: Assessing the long-range transport of path to a sub-arctic site using positive matrix factorization and potential source contribution function. Atmos. Environ., 45(4), 967-976, 2011.

Zhu, C., Tian, H., Hao, Y., Gao, J., Hao, J., Wang, Y., Hua, S., Wang, K., and Liu, H.: A high-resolution emission inventory of anthropogenic trace elements in Beijing-Tianjin-Hebei (BTH) region of China, Atmos. Environ., 191, 452-462, https://doi.org/10.1016/j.atmosenv.2018.08.035, 2018.

Impact of air pollution control measures and regional transport on carbonaceous aerosols in fine particulate matter in urban Beijing, China: Insights gained from long-term measurement

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Abstract As major chemical components of airborne fine particulate matter ($PM_{2.5}$), organic carbon (OC) and elemental carbon (EC) have vital impacts on air quality, climate change, and human health. Because OC and EC are closely associated with fuel combustion, it is helpful for the scientific community and policymakers assessing the efficacy of air pollution control measures to study on the impact of the control measures and regional transport on the OC and EC levels. In this study, hourly mass concentrations of OC and EC associated with $PM_{2.5}$ were semi-continuously measured from March 2013 to February 2018. The results showed that annual mean OC and EC concentrations declined from 14.0 to 7.7 μg/m^3 and from 4.0 to 2.6 μg/m^3, respectively, from March 2013 to February 2018. In combination with the data of OC and EC in previous studies, an obvious decreasing trend in OC and EC concentrations was found, which was caused by clean energy policies and effective air pollution control measures. However, no obvious change in the ratios of OC and EC to the $PM_{2.5}$ mass (on average, 0.164 and 0.049, respectively) was recorded, suggesting that inorganic ions still contributed a lot to $PM_{2.5}$. Based on the seasonal variations of OC and EC, it appeared that higher OC and EC concentrations were still observed in the winter months, with the exception of winter of 2017-2018. Traffic policies executed in Beijing resulted in nighttime peaks of OC and EC, caused by heavy-duty vehicles and heavy-duty diesel vehicles being permitted to operate from 0:00 to 6:00. In addition, the fact that there was no traffic restriction in weekends led to higher concentrations in weekends compared to weekdays. Significant correlations between OC and EC were observed throughout the study period, suggesting that OC and EC originated from common emission sources, such as exhaust of vehicles and fuel combustion. OC and EC levels increased with enhanced SO_2, CO and NO_x concentrations while the O_3 and OC levels enhanced simultaneously when O_3 concentrations were higher than 50 μg/m^3. Nonparametric wind regression analysis was performed to examine the sources of OC and EC in the Beijing area. It was found that there were distinct hot spots in the northeast wind sector at wind speeds of approximately 5 km/h, as well as diffuse signals in the southwestern wind sectors. Source areas further away from Beijing were assessed by potential source contribution function (PSCF) analysis. A high-potential source area was precisely pinpointed, which was located in the northwestern and southern areas of Beijing in 2017 instead of solely in the southern areas of Beijing in 2013. This work shows that improvement of the air quality in Beijing benefits from strict control measures; however, joint prevention and

control of regional air pollution in the regions is needed for further improving the air quality. The results provide a reference for controlling air pollution caused by rapid economic development in developing countries.

Key words air pollution control measures, regional transport, organic carbon, elemental carbon, Beijing

1 Introduction

Worldwide attention on atmospheric organic carbon (OC) and elemental carbon (EC) has been paid by the public and the scientific community because OC and EC have vital effects on air quality, atmospheric visibility, climate, and human health (Bond et al., 2013; Boucher et al., 2013; World Health Organization (WHO), 2012). OC is composed of thousands of organic compounds and occupies 10-50 % of the ambient $PM_{2.5}$ mass (Seinfeld and Pandis, 1998) while EC, which is emitted from fuel combustion, represents 1-13 % of the ambient $PM_{2.5}$ mass (Shah et al., 1986; Tao et al., 2017; Malm et al., 1994). Considering that OC and EC occupy high fractions of the $PM_{2.5}$, a decline in OC and EC concentrations will improve air quality. Due to the light scattering potential of OC and the light absorption ability of EC, high concentrations of OC and EC can impair the atmospheric visibility. In addition, OC and EC can affect the atmospheric energy balance through scattering and absorbing incoming and outgoing solar and terrestrial radiation (direct effect) and through modifying the microphysical properties of clouds, like influencing cloud condensation nuclei and/or ice nuclei (indirect effects). Direct and indirect effects of OC and EC remain one of the principal uncertainties in estimates of anthropogenic radiative forcing (Boucher et al., 2013). In particular, black carbon (BC also called EC) coated with secondary particles can enhance aerosol radiative forcing (Wang et al., 2013; Zhang et al., 2008). BC is found to aggravate haze pollution in megacities (Ding et al., 2016; Zhang et al., 2018). Most of all, OC and EC adversely affect human health. As important constituents of OC, polycyclic aromatic hydrocarbons (PAHs) are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health and the well-being of humans (Boström et al., 2002). Short-term epidemiological studies provide sufficient evidence of all-cause and cardiovascular mortality and cardiopulmonary hospital admissions associated with daily variations in BC concentrations; besides, cohort studies proved that all-cause and cardiopulmonary mortality are linked with long-term average BC exposure (WHO, 2012). Thus, long-term continuous observations of OC and EC are a prerequisite to further study air quality, atmospheric visibility, climate effects, and human health. However, long-term continuous observations of OC and EC in China are scarce.

In the world, China is considered as one of the regions of high emissions of OC and EC due to high energy consumption and increasing vehicle population, accompanying rapid economic

development and urbanization for decades (http://www.stats.gov.cn/tjsj/ndsj/2017/indexch.htm). As the capital of China, Beijing with a residential population of 21.7 million, domestic tourists of 2.9×10^2 million and foreign tourists of approximately 3.3 million in 2017 (http://tjj.beijing.gov.cn/English/AD/) faces severe air pollution problems, which have attracted worldwide attention. A series of studies on OC and EC have already been performed in Beijing. Lang et al. (2017) indicated that OC showed a downward trend and EC had almost no change before 2003, both increased from 2003 to 2007, but decreased after 2007. The decline in OC concentrations was associated with coal combustion and motor vehicle emission control measures, while that in EC was caused by the replacement of fossil fuel and control of biomass emissions. Tao et al. (2017) stated that the nearly 30 % reduction in total carbon (TC) in recent years in Beijing can be taken as a real trend. Lv et al. (2016) found that the concentrations of OC and EC remained unchanged from 2000 to 2010 in Beijing. Yang et al. (2011a) conducted a long-term study of carbonaceous aerosol from 2005 to 2008 in urban Beijing and found a decline in the ratio of carbonaceous species to the $PM_{2.5}$ mass in contrast to what was observed 10 years earlier, which indicated that the importance of carbonaceous species in $PM_{2.5}$ had decreased. In addition, pronounced seasonal variations were recorded with the highest concentrations occurring in winter and the lowest ones in summer. Overall, these previous researches seem somewhat inconsistent with each other and they seldom focused on studying the impact of air pollution control measures and regional transport on the carbonaceous aerosol levels in detail.

Notably, a series of the strictest measures on emission abatement and pollution control were implemented in China from September 2013 (Jin et al., 2016). Substantial manpower and material resources have been put into improving the air quality in the past five years and significant measures are being taken for the atmospheric environment and ecosystem (Gao et al., 2017). To evaluate the effectiveness of air pollution control measures, it is necessary to conduct a long-term continuous observation of OC and EC and to study their long-term variation. Most of the previous studies showed average information for certain periods based on filter sampling and laboratory analysis and did not reflect the dynamic evolution processes of OC and EC with hourly resolution, which can provide important and detailed information for the potential health risk in the area with frequent occurrence of air pollution episodes. In addition, long-term measurements in urban areas of China

with high population density were scarce (Yang et al., 2005, 2011a; Zhang et al., 2011; Li et al., 2015; Chang et al., 2017) and the knowledge on long-term continuous hourly observations is still lacking, which is yet important for recognizing the influence of source emissions on air quality.

Based on the-above mentioned background, it is necessary to perform a long-term continuous hourly observation to explore the characteristics of OC and EC, to examine the relationship between OC and EC and with major air pollutants and their sources so as to better assess the influence of emission control measures on the OC and EC levels. In this study, inter-annual, seasonal, weekly and diurnal variation of OC and EC were investigated. The influence of local and regional anthropogenic sources was evaluated using non-parametric wind regression (NWR) and potential contribution source function (PSCF) methods. This study will be helpful for improving the understanding of the variation and sources of OC and EC associated with $PM_{2.5}$ and assessing the effectiveness of local and national PM control measures and it provides a valuable dataset for atmospheric modelling study and assessing the health risk. It also is the first time that a continuous hourly measurement for a 5-year period based on the thermal-optical method is reported for urban Beijing.

2 Experimental

2.1 Description of the site

The study site (39°58'28'' N, 116°22'16'' E, 44 m above ground) was set up in the second floor in the campus of the State key laboratory of atmospheric boundary physics and atmospheric chemistry of the Institute of atmospheric Physics, Chinese Academy of Science (Fig. 1). The site is approximately 1 km south from the 3rd Ring Road (main road), 1.2 km north from the 4th Ring Road (main road), 200 m west of the G6 Highway (which runs north-south) and 50 m south of the Beitucheng West Road (which runs east-west), respectively. The annual average vehicular speeds in the morning and evening traffic peaks were approximately 27.8 and 24.6 km/h, respectively, in the past five years. During the whole study period the level of traffic congestion is mild based on the traffic performance index published by the Beijing Traffic Management Bureau (http://www.bjtrc.org.cn/), which indicated 1.5-1.8 times more time will be taken to publicly travel during traffic peaks than during smooth traffic. The study site is surrounded by residential zones, a street park and a building of ancient relics without industrial sources. The experimental campaign

was performed from March 1, 2013 to February 28, 2018. The periods of March 1, 2013 to February 28, 2014, March 1, 2014 to February 28, 2015, March 1, 2015 to February 28, 2016, March 1, 2016 to February 28, 2017 and March 1, 2017 to February 28, 2018 are, hereinafter, called for short 2013, 2014, 2015, 2016 and 2017, respectively.

2.2 Instrumentation

Concentrations of $PM_{2.5}$-associated OC and EC were hourly measured with semi-continuous thermal-optical transmittance method OC/EC analyzers (Model 4, Sunset Laboratory Inc. Oregon, Unite states of America (USA)). The operation and maintenance are strictly executed according to standard operating procedures (SOP, https://www3.epa.gov/ttnamti1/spesunset.html). Volatile organic gases are removed by an inline parallel carbon denuder installed upstream of the analyzer. A round 16-mm quartz filter is used to collect $PM_{2.5}$ with a sampling flow rate of 8 L/m. A modified NIOSH thermal protocol (RT-Quartz) is used to measure OC and EC. The sampling period is 30 min and the analysis process lasts for 15 min. Calibration is performed according to the SOP. An internal standard CH_4 mixture (5.0 %; ultra-high purity He) is automatically injected to calibrate the analyzer at the end of every analysis. In addition, off-line calibration was conducted with an external amount of sucrose standard (1.06 μg) every three months. The quartz fiber filters used for sample collection were replaced by new ones before the laser correction factor dropped below 0.90. After replacement, a blank measurement of the quartz fiber filters is carried out. The uncertainty of the TC measurement has been estimated to be approximately ±20 % (Peltier et al., 2007). The analyzers/monitors for O_3, CO, SO_2, NO_x and $PM_{2.5,}$ and their precision, detection limits and calibration methods have been described in detail elsewhere (Ji et al., 2014). Briefly, O_3 was measured using an ultraviolet photometric analyzer (model 49i, Thermo Fisher Scientific (Thermo), USA), CO with a gas filter correlation nondispersive infrared method analyzer (model 48i, Thermo, USA), SO_2 using a pulsed-fluorescence analyzer (model 43i, Thermo, USA), NO-NO_2-NO_x with a chemiluminescence analyzer (model 42, Thermo, USA) and $PM_{2.5}$ using a US Environmental Protection Agency Federal Equivalent Method analyzer of $PM_{2.5}$ (SHARP 5030, Thermo, USA). Meteorological data such as wind speed (WS), wind direction (WD), relative humidity (RH) and atmospheric temperature (*T*) were recorded via an automatic meteorological station (Model AWS310; Vaisala, Finland). The data were processed using an Igor-based software (Wu et al., 2018)

and the commercial software of Origin.

2.3 NWR and PSCF methods

2.3.1 NWR method

NWR is a source-to-receptor source identification model, which provides a meaningful allocation of local sources (Henry et al., 2009; Petit et al., 2017). Wind analysis results using NWR were obtained using a new Igor-based tool, named ZeFir, which can perform a comprehensive investigation of the geographical origins of the air pollutants (Petit et al., 2017). The principle of NWR is to smooth the data over a fine grid so that concentrations of air pollutants of interest can be estimated by any couple of wind direction (θ) and wind speed (u). The smoothing is based on a weighing average where the weighing coefficients are determined using a weighting function $K(\theta, u, \sigma, h) = K_1(\theta, \sigma) \times K_2(u, h)$ (i.e., Kernel functions). The estimated value (E) given θ and u is calculated by the following equations (1)-(3):

$$E(\theta|u) = \frac{\sum_{i=1}^{N} K1\left(\frac{\theta - Wi}{\sigma}\right) \times K2\left(\frac{u - Yi}{h}\right) \times Ci}{\sum_{i=1}^{N} K1\left(\frac{\theta - Wi}{\sigma}\right) \times K2\left(\frac{u - Yi}{h}\right)} \quad (1)$$

$$K_1(x) = \frac{1}{\sqrt{2\pi}} \times e^{-0.5x^2} \qquad -\infty < x < \infty \quad (2)$$

$$K_2(x) = 0.75 \times (1 - x^2) \qquad -1 < x < 1 \quad (3)$$

where σ and h were smoothing parameters, which can be suggested by clicking on the button of suggest estimate in the software of Zefir; *Ci*, *Wi*, and *Yi* are the observed concentration of a pollutant of interest, resultant wind speed and direction, respectively, for the *i*th observation in a time period starting at time t_i; N is the total number of observations.

After the calculation, graphs of the estimated concentration and the joint probability are generated. The NWR graph of the air pollutant of interest, acquired directly via the NWR calculation, represents an integrated picture of the relationship of estimated concentration of the specific pollutant, wind direction and wind speed. The graph of the joint probability for the wind data, equivalent to a wind rose, shows the occurrence probability distribution of the wind speed and wind direction.

2.3.2 PSCF method

The PSCF method is based on the residence time probability analysis of air pollutants of interest (Ashbaugh et al., 1985). Source locations and preferred transport pathways can be identified

(Poirot and Wishinski, 1986; Polissar et al., 2001; Lupu and Maenhaut, 2002). The potential locations of the emission sources are determined using backward trajectories. A detailed description can be found in Wang et al. (2009). In principle, the PSCF is expressed using equation (4):

$$PSCF(i,j) = w_{ij} \times (m_{ij}/n_{ij}) \quad (4)$$

where w_{ij} is an empirical weight function proposed to reduce the uncertainty of n_{ij} during the study period, m_{ij} is the total number of endpoints in (i, j) with concentration value at the receptor site exceeding a specified threshold value (the 75th percentiles for OC and EC each year were used as threshold values to calculate m_{ij}) and n_{ij} is the number of back-trajectory segment endpoints that fall into the grid cell (i, j) over the period of study. The National Oceanic and Atmospheric Administration Hybrid Single-Particle Lagrangian Integrated Trajectory model (https://ready.arl.noaa.gov/HYSPLIT.php) was used for calculating the 48-h backward trajectories terminating at the study site at a height of 100 m every 1 h from March 1 2013 to February 28 2018. In this study, the domain for the PSCF was set in the range of (30-70 °N, 65-150 °E) with the grid cell size of 0.25 × 0.25°.

3 Results and discussion

3.1 Levels of OC and EC

Statistics for the OC and EC concentrations from March 1, 2013 to February 28, 2018 are summarized in Table 1. Benefiting from the Air Pollution Prevention and Control Action Plan and increasing atmospheric self-purification capacity (ASC, shown in Table S1), a decline in annual average concentrations is on the whole recorded. In detail, the annual average concentrations of both OC and EC peaked in 2014 and then started to decline gradually during the remainder of the study period. Nonetheless, the annual average concentrations of $PM_{2.5}$ were generally decreasing from 2013 to 2017. To assess whether the decreases are statistically significant, 2-tailed paired t-tests were applied for OC, EC and $PM_{2.5}$ using their monthly average concentrations in 2013 and 2016 as paired datasets. At a confidence level of 98%, from March to October, the paired data are statistically different, indicating that the concentrations of OC, EC and $PM_{2.5}$ declined during the above period from 2013 to 2016; however, the concentrations of OC, EC and $PM_{2.5}$ during November and February from 2013 to 2016 are not statistically different. The decline in OC and EC concentrations is closely associated with decreasing coal consumption, increasing usage of natural

gases and the implementation of a stricter vehicular emission standard and increasing atmospheric self-purification capacity (Tables S1-S3). Knowledge of the relative contribution of OC and EC to $PM_{2.5}$ is important in formulating effective control measures for ambient PM (Wang et al., 2016a). The ratios of OC and EC to $PM_{2.5}$ varied little during the whole study period, suggesting that vehicular emission might be an important contributor of OC and EC although several other pollution sources also contributed to the OC and EC loadings. The ratios of OC to $PM_{2.5}$ ranged from 15.5 to 17.8 % with the average of 16.4 %, while those of EC to $PM_{2.5}$ ranged from 4.5 to 5.2 % with the average of 4.9 %. OC accounted, on average, for 77.0 ± 9.3 % of the total carbon (TC, the sum of OC and EC), while EC amounted for 23.0 ± 9.3 % of the TC. These results are consistent with those in previous studies (Wang et al., 2016a; Tao et al., 2017, Lang et al., 2017). The contribution of TC to $PM_{2.5}$, 21.3 ± 15.8 %, is also similar to those reported in previous studies, listed in Table S4, for example, at urban sites of Hongkong, China (23.5-23.6 % in 2013), Hasselt (23 %) and Mechelen (24 %) in northern Belgium, rural sites in Europe (19-20 %) and some sites in India (on average, 20 %, Bisht et al., 2015; Ram and Sarin, 2010; Ram and Sarin, 2012), but lower than those observed historically at multiple sites in China (on average 27 %, Wang et al., 2016a), with Beijing (27.6 %, from March 2005 to Feb 2006), Chongqing (28.3 %, from March 2005 to February 2006), Shanghai (34.5 %, from March 1999 to May 2000) and Guangzhou (26.4 %, December 2008 to February 2009), in Budapest (40 %), Istanbul (30 %), and many sites in the USA, like Fresno (43.2 %), Los Angeles (36.9 %) and Philadelphia (33.3 %) (Na et al., 2004). Compared to previous studies in Beijing (Table S4), the TC to $PM_{2.5}$ ratio became smaller in this study, indicating a relatively lower contribution from carbonaceous aerosols to $PM_{2.5}$ in this study. The difference in the TC/$PM_{2.5}$ ratio could be ascribed to two factors. One factor is the difference in characteristics of sampling locations between that in our study and those in the earlier studies. However, our site and those in the previous studies used for comparison are all located in urban areas of Beijing (Chaoyang and Haidian district, respectively). It is reasonable to assume that they are affected by common sources since the surrounding environments exhibit similar features. Besides, the annual average $PM_{2.5}$ concentrations in both districts published by the Ministry of Environmental Protection, China (http://106.37.208.233:20035/) were quite comparable to each other from 2013 to 2017 (y=0.99x, r^2=0.92), indicating that both areas had particle pollution of a similar degree. The other factor is that

the contribution from secondary inorganic ions to the $PM_{2.5}$ became more important because of a stronger atmospheric oxidation capacity (the annual average O_3 concentrations were 102, 109, 116, 119, and 136 μg/m^3, respectively, from 2013 to 2017 in the Beijing-Tianjin-Hebei region; published by http://106.37.208.233:20035/), which could give rise to a lower TC to $PM_{2.5}$ ratio. A higher TC to $PM_{2.5}$ ratio suggests that there is a lower contribution from secondary inorganic ions to $PM_{2.5}$, while a lower ratio may indicate a larger contribution from secondary inorganic ions to $PM_{2.5}$. The carbonaceous aerosol (the sum of multiplying the measured OC by a factor of 1.4 and EC) represented on average, 27.7 ± 16.7 % of the observed $PM_{2.5}$ concentration, making it a dominant contributor to $PM_{2.5}$.

Table 3 lists recently published results for OC and EC mass concentrations in major megacities. Although the observation periods were not same, a comparative analysis of OC and EC concentrations between different megacities could show the status of energy consumption for policymakers, drawing lessons and experience from other countries. It is obvious that the $PM_{2.5}$-associated OC and EC levels in the megacities in the developing countries were far higher than those in the developed countries. The $PM_{2.5}$-associated OC and EC concentrations in Beijing were higher than those in Athens, Greece (2.1 and 0.54 μg/m^3), Los Angeles (2.88 and 0.56 μg/m^3) and New York (2.88 and 0.63 μg/m^3), USA, Paris, France (3.0 and 1.4 μg/m^3), Soul, South Korea (4.1 and 1.6 μg/m^3), Tokyo, Japan (2.2 and 0.6 μg/m^3) and Toronto, Canada (3.39 and 0.5 μg/m^3). That is because clean energy has widely been used and strict control measures are taken to improve the air quality step by step in the developed countries. Of the megacities in the developing countries, OC and EC concentrations in Beijing were lower than those in most other megacities, like Mumbai and New Delhi, India, and Xi'an and Tianjin, China, but close to those in Shanghai and Hongkong, China, and higher than those in Lhasa, China. These differences/similarities indicate that OC and EC gradually declined in Beijing and that a series of measures had progressive effects. However, to further improve the air quality, more synergetic air pollution abatement measures of carbonaceous aerosols and volatile organic compounds (VOCs) emissions need to be performed.

Fig. 2 shows the mass fractions of carbonaceous aerosols in different $PM_{2.5}$ levels classified according to $PM_{2.5}$ concentrations during the whole study period. There were 571, 561, 310, 169, 142 and 74 days for excellent, good, slightly polluted, moderately polluted, heavily polluted and

severely polluted air quality levels during the whole period. It was obvious that OC and EC concentrations increased with the degradation of air quality. OC and EC concentrations were 6.3 and 1.7, 10.2 and 2.9, 13.7 and 4.1, 17.3 and 5.3, 24.6 and 7.9 and 35.5 and 11.3 μg/m^3 for excellent, good, slightly polluted (LP), moderately polluted (MP), heavily polluted (HP) and severely polluted (SP) air quality days, respectively (The criteria used to classify the air quality have been added in the revised manuscript. Air quality as Excellent, good, LP, MP, HP and SP were based on the daily average $PM_{2.5}$ concentration, i.e., excellent ($0<PM_{2.5}\leqslant 35$ μg/m^3), good ($35<PM_{2.5}\leqslant 75$ μg/m^3), lightly polluted (LP, $75<PM_{2.5}\leqslant 115$ μg/m^3), moderately polluted (MP, $115<PM_{2.5}\leqslant 150$ μg/m^3), heavily polluted (HP, $150<PM_{2.5}\leqslant 250$ μg/m^3) and severely polluted (SP, $PM_{2.5}>250$ μg/m^3), respectively.). However, the percentages of OC and EC accounting to $PM_{2.5}$ decreased with the deterioration of air quality. OC and EC made up for 31.5 % and 8.3 %, 18.9 % and 5.4 %, 14.7 % and 4.4 %, 13.4 % and 4.1 %, 12.9 % and 4.2 % and 11.4 % and 3.6 % during excellent, good, slightly polluted, moderately polluted, heavily polluted and severely polluted air quality days, respectively. The percentage for OC decrease from 31.4 to 11.4 % while that for EC decreased from 8.3 to 3.6 % with the deterioration of air quality, indicating that other $PM_{2.5}$ constituents than OC and EC contributed more to the increased $PM_{2.5}$ levels. This is consistent with previous studies showing that secondary inorganic ions play a more important role in the increase in $PM_{2.5}$ concentrations (Ji et al., 2014, 2018).

3.2 Inter-annual variation of OC and EC

To evaluate the effect of the clean air act over a prolonged period, our OC and EC data were combined with the data of previous studies for Beijing (He et al., 2011; Zhao et al., 2013; Ji et al., 2016; Tao et al., 2017; Lang et al., 2017). As shown in Fig. 3, a decreasing trend in OC and EC concentrations is on the whole observed. Table S2 summarizes a variety of policies and actions to reduce pollutant emissions in power plants, coal-fired boilers, residential heating and traffic areas in Beijing since 2002. Although the gross domestic product, population, energy consumption and vehicular population rapidly increased (Table S3), the general decreasing trends in OC and EC concentrations could be attributed to the combined effect of the more stringent traffic emission standards and traffic restriction, the energy structure evolving from intensive coal and diesel consumption to replacement with natural gas and electricity, and retrofitting with SO_2 and NO_2

removal facilities to meet the new emission standards applicable to different coal-fired facilities, etc. In particular, there is an obvious dividing line of OC and EC concentrations in 2010. After 2010, the OC and EC concentrations became substantially lower than those observed previously. In addition to the measures mentioned in Table S2, the relocation of Shougang Corporation, which is one of the China's largest steel companies, and other highly polluting factories out of Beijing might have helped to some extent; all the small coal mines in Beijing were shut down and plenty of yellow label (heavy-polluting) vehicles were forced off road. Note that the OC and EC levels in 2008 and 2009 were also somewhat lower, which was caused by a series of radical measures to improve the air quality for the Olympic Games in 2008 and a decline in industrial production because of China's exports crash in 2009, respectively. It suggests that a stringent clean air act and rectifying industry played important roles in the air quality improvement.

In this study, the fire spots were counted in the domain of (30-70° N, 65-150° E) using the MODIS Fire Information for Resource Management System (Giglio, 2013). Note also that the effective control of biomass burning might contribute to the decrease in OC and EC concentrations. In Fig. 3, it can be seen that the annual average EC concentration and fire spot counts exhibit a rather similar variation from 2004 to 2017, except in the year 2012, which suggests that the EC levels are somewhat correlated with the biomass burning; this might indicate that biomass burning contributed somewhat to the EC levels. The reduction in fire spot counts from 2014 to 2017, which resulted from efforts to control the agricultural field residue burning since 2013, helped to reduce the EC concentrations to some extent, but the low EC levels during 2014-2017 are likely mostly due to the implementation of the clean air act. With regard to the anomaly in the year 2012, based on the MODIS data for this year, a very non-uniform distribution of fire spots in the BTH region was observed, with a distinct decrease of fire spot counts in Beijing, but higher fire spot counts in the southern Hebei Province; this may be ascribed to the fact that the policy of Banning Straw Burning in Summer and Autumn was executed to different degrees in the whole region, with better implementation in Beijing area and worse action in the other parts. (http://www.beijing.gov.cn/zfxxgk/110029/qtwj22/2012-12/11/content_357114.shtml). In addition, for the years from 2002 to 2017, the highest precipitation volume in Beijing was recorded in 2012, i.e., 733.2 mm, and the rainy days mainly occurred in the intensive straw burning periods,

accounting for 76.4% of all rainy days in 2012. The frequent wet scavenging might have suppressed the EC concentrations during the intensive straw burning periods, so that the annual EC level for 2012 was comparable to those recorded from 2011 onward.

Similar to OC and EC, the annual mean SO_2 and NO_2 concentrations also showed a decreasing trend. As well-known, SO_2 originates from coal combustion and sulfur-containing oil (Seinfeld and Pandis, 1998). With the replacement of coal for industrial facilities, residential heating and cooking by clean energy (e.g., natural gases, electricity and lower sulfur content in oil), a clear decline in annual SO_2 concentrations was observed in the Beijing area starting from 2002. As compared to SO_2, the annual decreasing rate of NO_2 was relatively lower. Besides the power plants and other boilers, traffic emissions are another major source of NO_2. The rapid increase of vehicle population may partly offset the great effort in reducing coal consumption to lower the NO_2 level despite the transition to more stringent traffic emission standards.

3.3 Monthly and seasonal variations

Fig. S1 shows the monthly mean OC and EC concentrations at our study site for the whole 5-year period. Similar variations are observed with generally higher mean OC and EC levels in the cold season (from November to February next year when the centralized urban residential heating is provided) and lower ones in the warm season (from April to October). The highest average OC and EC concentrations were 24.1 ± 18.7 μg/m^3 in December 2016 and 9.3 ± 8.5 μg/m^3 in December 2015, respectively. However, the lowest OC and EC levels were not observed in the warm months; they were 5.0 ± 4.6 μg/m^3 in January, 2018 and 1.5 ± 1.7 μg/m^3 in December, 2017, respectively; this was associated with both frequent occurrence of cold air mass and the implementation of a winter radical pollution control action plan (Chen and Chen, 2019) in Beijing from November, 2017. Overall, the increased fuel consumption for domestic heating in addition to unfavorable meteorological conditions (lower mixing layer height, temperature inversion and calm wind) in the colder months is considered to lead to higher OC and EC levels (Ji et al., 2014). In addition, the lower air temperature in the cold months led to shifting the gas-particle equilibrium of semi-volatile organic compounds (SVOCs) into the particle phase, leading to the higher OC levels. In the cold months, the cold start of vehicles (5.64 million vehicles in Beijing at the end of 2017) also increased the emission of OC. In the warm season, lower OC and EC levels were observed, which could be

attributed to the following factors: no extra energy consumed for domestic heating, strong wet scavenging by frequent precipitation occurring in these months, and more unstable atmospheric conditions favorable for pollutant dispersion; in addition, during this period, the monthly mean OC and EC concentrations generally decreased from year to year. In contrast, for the cold season, the monthly mean OC and EC concentrations did not show a clear decreasing trend from year to year. In addition to the more intensive energy consumption in the cold season, the EC and OC levels could also be enhanced strongly by regional transport and stagnant meteorology leading to ground surface accumulation in the autumn and winter (Wang et al., 2019; Yi et al., 2019); this would have counteracted the efficacy of the energy structure change in the Beijing-Tianjin-Hebei region in the past few years. It is worth pointing out that, on a year to year basis, the monthly average OC and EC concentrations in the cold seasons of 2017 and 2018 were generally lower than those in 2016, demonstrating to some extent the effectiveness of the execution of the radical pollution control measures for cities on the air pollution in the Beijing-Tianjin-Hebei region. The interquartile ranges of OC and EC in the warm months were narrower than in the cold months, indicating that there was more substantial variation in concentration in the latter months. The larger variation in the colder months could be caused by the cyclic accumulation and scavenging processes. In this region, due to these processes, the concentration of particulate matter increases rapidly when the air mass back trajectories change from the northwest and north to the southwest and south over successive days in Beijing; in contrast, the concentration of particulate matter declines sharply when a cold front causes a shift of back trajectories from the southwest and south to the north and northwest (Ji et al., 2012). The accumulation processes are closely associated with unfavorable meteorological conditions, which give rise to higher OC and EC concentrations, while more scavenging of aerosols by cold fronts leads to lower levels.

As to the seasonality in OC and EC, similar seasonal variations are observed in the various years with generally higher mean concentrations in autumn and winter and lower levels in spring and summer (Fig. 4). Remarkably, the OC and EC concentrations in the autumn and winter of 2017 were lower than those in the previous years. This was due to the combined effect of controlling anthropogenic emissions strictly and favorable meteorological conditions. Since September 2017, a series of the most stringent measures within the Action Plan on Prevention and Control of Air

Pollution was implemented to improve the air quality; these measures included restricting industrial production by shutting down thousands of polluting plants, suspending the work of iron and steel plants in 28 major cities and limiting the use of vehicles and reducing coal consumption as a heating source in northern China. In addition, the air quality improvement in the autumn and winter of 2017 was closely tied to frequent cold fronts accompanied by strong winds, which was favorable for dispersing the pollutants. The average OC and EC concentrations in the winter were 1.69 and 1.14, 2.17 and 1.93, 1.49 and 2.14, 2.41 and 2.29 and 0.80 and 0.88 times higher than those in the summer for 2013, 2014, 2015, 2016 and 2017, respectively. The difference in the ratios for 2017 was due to the series of the most stringent measures taking effect and favorable meteorology. The Beijing municipal government in particular has made great efforts to replace coal by natural gases and electricity-powered facilities. Besides, new energy vehicles are increasingly used to replace the gasoline vehicles.

3.4 Diurnal variation and weekly pattern for OC and EC

As can be seen in Figs. S2 and S3, a clear diurnal variation is observed for both OC and EC in each year. This variation is closely tied to the combined effect of diurnal variation in emission strength and evolution of the PBL. The pattern for EC with higher concentrations in the nighttime (from 20:00 to 4:00) and lower levels in the daytime (from 9:00 to 16:00) is largely linked to the vehicular emissions. The EC concentrations increased starting from 17:00, corresponding with the evening rush hours, emission from nighttime heavy-duty diesel trucks (HDDT) and heavy-duty vehicles (HDV) and the formation of a nocturnal stable PBL. As regulated by the Beijing Traffic management Bureau (http://www.bjjtgl.gov.cn/zhuanti/10weihao/), HDV and HDDT are allowed to enter the urban area inside the 5th Ring Road from 0:00 to 06:00 (local Time). At other times, both the higher PBL height and lower traffic intensity resulted in lower EC concentrations. The amplitude of the diurnal variation in the EC concentrations was smaller in the last three years. The maximum peak concentration (22:00-7:00) was 1.68, 1.62, 1.43, 1.40 and 1.40 times higher than that observed in the valley period (13:00-15:00) for 2013, 2014, 2015, 2016 and 2017, respectively. Similar to EC, the diurnal pattern for OC was also characterized by higher concentrations in the nighttime (from 20:00 to 4:00) and lower levels in the daytime (from 14:00 to 16:00). However, the formation of secondary organic carbon from gas-phase oxidation of VOCs with increased solar radiation during

midday gave rise to a small additional peak of OC. Like for EC, the amplitude of the diurnal variation in the OC concentrations was smaller in the last three years. The maximum peak concentration (19:00-3:00) was 1.47, 1.47, 1.30, 1.34 and 1.26 times higher than that observed in the valley period (14:00-16:00) for 2013, 2014, 2015, 2016 and 2017, respectively. It was pity that no diurnal variation in traffic counts can be available but the hourly average traffic counts in 2015, 2016 and 2017 could be found in (Beijing Transportation Annual Report, http://www.bjtrc.org.cn/JGJS.aspx?id=5.2&Menu=GZCG). Considering that the hourly average traffic counts varied little in urban Beijing and they were 5969/hr, 5934/hr and 6049/hr in 2015, 2016 and 2017, respectively, the small amplitude of the diurnal variation in the last three years might be related to local emission intensities; these might have been significantly affected by the enforcement of a series of traffic emission control measures since 2015, including more strict restriction of emission from heavy-duty diesel vehicle public buses, wider usage of electric public buses, and scrappage of all the high-emitting (yellow-labelled) vehicles, etc. (Tab. S2). All these actions led to a decline in emissions of OC and EC and narrowed the amplitude of the diurnal variation in the EC concentration.

Separate diurnal variations of OC and EC for each season in each year are shown in Figs S4 and S5. Similar patterns are observed in in the four seasons but the difference between peak and valley levels is larger in the winter than in the other three seasons. The larger variation in the winter is due to the additional emission from residential heating and more unfavorable meteorological conditions (Ji et al., 2016).

The difference in diurnal pattern between weekdays and weekends was also examined, see Figs. S6 and S7. Similar diurnal variations are found on weekdays and weekend days. The maximum peak concentration for EC (22:00-7:00) was 1.55, 1.43, 1.55, 1.51, 1.51, 1.46 and 1.59 times higher than the valley concentration (13:00-15:00) for Monday, Tuesday, Wednesday, Thursday, Friday, Saturday and Sunday, respectively, while the maximum peak concentration for OC (19:00-3:00) was 1.41, 1.32, 1.38, 1.43, 1.37, 1.31 and 1.43 times higher than the valley concentration (14:00-16:00) for Monday, Tuesday, Wednesday, Thursday, Friday, Saturday and Sunday, respectively. In contrast to previous studies (Grivas et al., 2012; Jeong et al., 2017; Chang et al., 2017), OC and EC exhibited statistically significant higher concentrations on weekends than on weekdays in this study

(statistically significant based on the analysis of the weekly data using *t*-test statistics, $p<0.05$). The average OC and EC concentrations on Saturday and Sunday were 13.2 ± 11.8 μg/m^3 and 3.9 ± 2.7 μg/m^3 and 12.0 ± 10.4 μg/m^3 and 3.7 ± 3.6 μg/m^3, respectively, whereas the average OC and EC levels during the weekdays were 11.8 ± 10.8 μg/m^3 and 3.6 ± 3.5 μg/m^3, respectively. This indicates that there is no significant decline in anthropogenic activity in the weekends compared to weekdays. In fact, enhanced anthropogenic emissions could be caused by no limit on driving vehicles based on license plate on weekends. The larger OC and EC concentrations in the weekend are thus mainly attributed to enhanced traffic emissions, which is consistent with higher NO_2 and CO concentrations in the weekend (on average 56.6 ± 35.9 μg/m^3 for NO_2 and 1.16 ± 1.18 mg/m^3 for CO on weekdays (number of samples = 29492); 57.8 ± 37.0 μg/m^3 for NO_2 and 1.25 ±1.18 mg/m^3 for CO on weekends (number of samples = 11881)).

3.5 Relationship between OC and EC and with gaseous pollutants

The relationship between particulate OC and EC is an important indicator that can give information on the origin and chemical transformation of carbonaceous aerosols (Chow et al., 1996). Primary OC and EC are mainly derived from vehicular emissions, coal combustion, biomass burning, etc. in urban areas (Bond, et al., 2013). Primary OC and EC could correlate well with each other under the same meteorology. However, the correlation would become gradually less significant with the enhancement of secondary OC formation via complex chemical conversion of VOCs (gas-to-particle or heterogeneous conversion). In addition, it should be noted that EC is more stable than OC (Bond, et al., 2013). Hence, the relationship between OC and EC can to some extent be used as a parameter reflecting the source types and contributions (Blando and Turpin, 2000). Fig. 5 presents the regression between the OC and EC concentrations for the $PM_{2.5}$ samples of the separate years 2013 to 2017. Significant correlations (R^2 ranging from 0.87 to 0.66) were observed with the slopes declining from 3.6 to 2.9 throughout the study period. The significant correlations suggest that in most cases OC and EC originated from similar primary sources. The slopes are consistent with the OC/EC ratios ranging from 2.0 to 4.0 for urban Beijing in previous studies (He et al., 2001; Dan et al., 2004; Zhao et al., 2013; Ji et al., 2016). In addition, the average OC/EC ratios observed in this study are comparable to those observed at other urban sites with vehicular emission as a dominant source in China and foreign countries, but lower than those in cities where

coal is an important source of the energy needed (Table 3). The decline in the OC/EC ratio may be caused by decline in coal consumption and restriction in biomass burning. Coal combustion, biomass burning and secondary formation give rise to higher OC/EC ratios while vehicular emission result in lower ones (Cao et al., 2005).

EC and part of the OC originate from primary anthropogenic emissions, including fossil fuel combustion and biomass burning (Bond et al., 2013), and secondary OC is formed along with ozone formation. Hence, long-term and concurrent measurement of OC, EC, SO_2, NO_x, CO and O_3 is helpful for understanding the emission features or formation processes and for providing tests to current emission inventories. The variation in the OC and EC as a function of the SO_2, NO_x, CO and O_3 concentration is shown in Fig. 6. There is a clear increase in OC and EC with increasing SO_2, NO_x and CO, suggesting that the latter played a role in the enhancement of the former and that these various species shared common sources although they have a different lifetime. OC and EC increased, on average, by approximately 8.9 μg/m^3 and 5.7 μg/m^3, respectively, with an increase of 2 mg/m^3 in CO. Considering that CO has a long lifetime (Liang et al., 2004) and that its increase depends on source strength and meteorology, high CO concentrations usually occur in the heating season when unfavorable meteorological conditions prevail. At very high CO concentrations, the increase in OC becomes slower than that in EC. This can be explained by that local emissions became dominant because the unfavorable meteorological conditions corresponding with the high CO concentrations resulted in a weak exchange of air on the regional scale. The OC/EC ratio declined at very high CO concentrations. This could be because vehicular emissions played an important role in the OC and EC loadings (Ji et al., 2019). As documented by previous studies (Schauer et al., 2002, Na et al., 2004), emission of gasoline vehicles results in an OC/EC ratio varying from 3 to 5 while that of diesel vehicles is below 1. The above results are consistent with previous studies which showed that gasoline and diesel vehicles give rise to higher CO emissions (Wu et al., 2016).

Given that NO_x and CO have some common emission sources (Hassler et al., 2016), the OC and EC levels were also analyzed in different intervals of NO_x concentrations. Both OC and EC are enhanced with increasing NO_x concentrations. Their enhancements were 5.0 μg/m^3 and 2.1 μg/m^3, respectively, for an increase in NO_x concentration of 40 μg/m^3. Although NO_x are highly reactive

and have a short lifetime (Seinfeld and Pandis, 1998) in contrast to CO, the OC/EC ratio also declined at very high NO_x concentrations, be it to a lesser extent than was the case at very high CO concentrations. As was the case for high CO concentrations, more stable meteorological conditions and local emissions became prevailed when higher concentrations of NO_x were observed. In fact, 63.5 % of all NO_x emissions come from vehicular emissions based on the statistical data of air pollutant emissions in Beijing (http://www.bjepb.gov.cn/bjhrb/xxgk/ywdt/zlkz/hjtj37/827051/index.html).

Examining the variation of OC and EC for different intervals of SO_2 concentrations allows us to further study the impacts of industrial production or coal combustion on the OC and EC levels. Similar to the relationship between CO and the carbonaceous species, the OC and EC concentrations enhanced with increasing SO_2 concentrations. Their enhancements were 2.8 μg/m^3 and 0.7 μg/m^3, respectively, for an increase in SO_2 concentration of 10 μg/m^3. An increase in the OC/EC ratio occurred at large SO_2 concentrations, suggesting that coal consumption provided a substantial contribution to the OC and EC levels in Beijing. Because oil with a low sulfur content has been widely used in Beijing since 2008 and little coal was used in the urban areas of Beijing, the SO_2 mostly originated from industrial production in the surrounding areas of Beijing and from coal combustion for residential heating in the suburban and rural areas of Beijing. Previous studies also showed that a higher OC/EC ratio is due to coal consumption and not from vehicular emissions (Cao et al., 2005). Hence, coal combustion (for industrial production) on the regional scale led to the enhancement of both the OC/EC ratio and SO_2 concentrations in Beijing via long-range transport.

Emissions of primary air pollutants lead through multiple pathways to the formation of ozone and secondary organic carbon (SOC) (Seinfeld and Pandis, 1998), both of which are the principal components of photochemical smog. The relationship between OC and O_3 is of use for understanding their variation and formation. The OC concentrations were highest for an O_3 concentration of 50 μg/m^3, which is approximately the average O_3 concentration in Beijing in winter (Cheng et al., 2018). During the period of an O_3 concentration of 50 μg/m^3, low atmospheric temperature (9.4±9.9 ºC), relatively high RH (59.2±23.7 %), lower WS (1.1±0.8 m/s) and higher NO_x concentrations (72.7±57.5 ppb) were observed and a lower mixed layer height was recorded in winter (Tang et al., 2016), which were favorable for accumulation and formation of OC. A relatively

lower temperature is beneficial for condensation/absorption of SVOCs into existing particles (Ji et al., 2019), which would then experience further chemical reactions to generate secondary organic aerosol (SOA). Note that a low temperature does not significantly reduce SOA formation rates (Huang et al., 2014) in the winter. In addition, processes including aqueous-phase oxidation and NO_3-radical-initiated nocturnal chemistry may contribute to or even dominate SOA formation during winter (Hallquist et al., 2009; Rollins et al., 2012; Huang et al., 2014). Hence, the above factors gave rise to the higher OC concentration at an O_3 concentration of 50 μg/m^3 particularly in winter. In addition, scattering and absorbing effects of aerosols that were trapped in the lower mixed layer height led to less solar radiation reaching the ground and further restrained the O_3 formation in the cold season (Xing et al., 2017; Wang et al., 2016b). OC declined when O_3 concentrations increased from 50 to 100 μg/m^3. Usually moderate O_3 concentrations accompanying lower OC concentrations are caused by increasing *T* (19.5±8.3 ºC), increasing WS (2.0±1.3 m/s) and less titration of relatively lower observed NO concentrations (6.4±14.6 ppb). It can also be seen that there was a concurrent increasing trend of OC and ozone when the O_3 concentration was above 100 μg/m^3, which generally occurred in the warmer season. Besides the impact of meteorological conditions, such a trend might not be dominated by gas-to-particle partitioning of low-volatility organic compounds but by the oxidation of VOCs driven by hydroxyl radicals to generate both SOC and O_3 with relatively long lifetimes (>12 h; Wood et al., 2010).

3.6 Impact of atmospheric transport on the OC and EC concentrations

Figs. 7 and 8 show the results of the NWR analysis applied to 1-h $PM_{2.5}$-associated OC and EC concentrations measured from 2013 and 2017 in Beijing. Fig. S8 presents the gridded emissions of OC and BC for the Beijing-Tianjin-Hebei (BTH) region and China, based on emission inventory (Zheng et al., 2018). The NWR results exhibit distinct hot spots (higher concentrations) in the northeast wind sector at wind speeds of approximately 0-6 km/h, which were closely associated with local emissions under stagnant meteorological conditions (low wind speed), as well as diffuse signals in the southwestern wind sector. The joint probability data in Figs. 7 and 8 show prevailing winds were from N to E and from S to W with wind speeds of approximately 1-6 km/h and of approximately 4-9 km/h, respectively. Note further that the hot spots of OC are broader than those of EC in the graphs of estimated concentrations; this might be due to the fact that the VOCs (the

precursors of SOC) emitted from upwind areas at the relatively higher WS in contrast to EC, including the SW wind sector, led to an increase in OC concentrations at the receptor site while the EC concentrations slowly declined due to dilution and deposition.

Considering that the NWR analysis can only provide an allocation of local sources, the PSCF analysis is a helpful complement to investigate potential advection of pollution over larger geographical scales (Petit et al., 2017). Fig. 9 presents the PSCF results for OC and EC for the years 2013 to 2017. Similar to the NWR analysis, the PSCF results indicated that local emissions and regional transport from southerly areas were important contributors to the OC and EC loadings during the whole study period. Only slight differences in the potential source regions are observed between the different years. In 2013, a clear high potential source area was recorded for both OC and EC; it was located in the southern plain areas of Beijing, particularly in the adjacent areas of the Hebei, Henan, Shandong, Anhui and Jiangsu provinces. This was because there were intensified anthropogenic emissions from those in 2013. The high pollutant emissions were caused by rapid economic growth, urbanization and increase in vehicle population, energy consumption and industrial activity in the southern plain areas of Beijing (Zhu et al., 2018), which resulted in a high aerosol loading in the downwind areas. This result is consistent with previous studies (Ren et al., 2004; Wu et al., 2014; Ji et al., 2018). In contrast to 2013, in the years 2014 to 2017 the high potential source regions for OC and EC stretched to the juncture of Inner Mongolia and the Shaanxi and Shanxi provinces, and even to the juncture of Inner Mongolia and the Ningxia Hui Autonomous Region and of Inner Mongolia and the Gansu province. This is consistent with coal power plants being abundant in the above areas (Liu F. et al., 2015). As well known, coal power plants are also important emitters of SO_2, and those emissions were seen in satellite images (Li et al., 2017; Zhang et al., 2017), thus proving evidence for those sources. The potential source areas for OC and EC were similar in 2013 and 2014. Overall, the potential source areas were more intense for OC than for EC. The emission of OC precursors (i.e., volatile organic compounds) from the Hebei, Henan, Shandong, Anhui, Jiangsu, Shanxi and Shaanxi provinces led to OC concentrations downwind via chemical conversion during the atmospheric transport. The widest potential source areas for OC and EC were recorded in 2016 and they expanded into the eastern areas of Xinjiang Uyghur Autonomous Region. They are probably associated with the economic boom in the western areas of China. In

2015, the potential source areas were like in 2013 and 2014 also more intense for OC than for EC. Although the winter action plan was enforced in Beijing, Tianjin and 26 surrounding cities (the so-called "2+26 cities"), whereby the industrial output was curtailed, inspections of polluting factories were ramped up and small-scale coal burning was banned at the end of 2017, there was still a clear spatial difference in emission of air pollutants, with relatively higher $PM_{2.5}$ concentrations in the southern areas of Beijing. Hence, these areas still contributed substantially to OC and EC loading in Beijing.

As found in earlier studies (Ji et al., 2018; Zhu et al., 2018), the southern areas of Beijing were main source areas. Despite the ever-stringent air pollution control measures, which are enforced in key areas of China, the economic booming in the western areas of China gave rise to substantial air pollution in the adjacent areas of several provinces and the northwestern areas of China. To further improve the air quality in Beijing, strict emission restrictions should be launched in the above areas and joint control and prevention of air pollution should be enforced on the regional scale. It should be avoided that polluted enterprises, which are closed in key regions, are moved to the western areas of China or to areas where there is no supervision and control of the emission of air pollutants.

4 Conclusions

In this study, hourly mass concentrations of OC and EC in $PM_{2.5}$ were semi-continuously measured from March 1, 2013 to February 28, 2018 at a study site in Beijing. The inter-annual, monthly, seasonal and diurnal variations in OC and EC are presented, the relationship between the carbonaceous species and other pollutants was examined and the source regions were assessed using both NWR and PSCF analysis. The impact of the air pollution control measures and of the regional transport on carbonaceous species in the fine particulate matter was investigated. The following main conclusions can be drawn:

(1) OC and EC occupied a high fraction of the observed $PM_{2.5}$ concentrations, making it a dominant contributor of $PM_{2.5}$. Their concentrations increased with the degrading air quality whereas their percentage in $PM_{2.5}$ declined, which was consistent with previous studies showing that secondary inorganic ions played a relatively more important role in increasing $PM_{2.5}$ concentrations.

(2) A clear decline in OC and EC levels was observed after a series of energy policies for air pollution abatement and control had been implemented. To further improve air quality, more

synergistic air pollution abatement measures of carbonaceous aerosols and VOCs emissions are needed.

(3) OC and EC showed marked seasonal, monthly, weekly and diurnal variations. The seasonal patterns were characterized by higher concentrations in the colder months (from November to February) and lower ones in the warm months (from May to October) of the various years. Because of stringent measures for air pollution abatement, the difference between the winter and summer levels decreased. The EC diurnal pattern was characterized by higher concentrations in the nighttime (from 20:00 to 4:00) and lower ones in the daytime (from 9:00 to 16:00). The higher OC and EC levels during the weekend can be attributed to the traffic regulation in Beijing. The diurnal fluctuation in OC and EC was closely tied to a combined effect of change in emission sources and evolution of the PBL.

(4) Significant correlations between OC and EC were observed throughout the study period, suggesting that OC and EC originated from common sources, such as vehicle exhaust, coal combustion, etc. The contribution of coal combustion and biomass burning decreased and this resulted in lower OC/EC ratios. The OC and EC concentrations increased with higher SO_2, CO and NO_x levels, while the O_3 and OC concentrations increased simultaneously for O_3 levels above 50 $\mu g/m^3$.

(5) Local emissions and regional transport played an important role in the OC and EC concentrations. Higher concentrations were observed for winds from the northeast sector at wind speeds of approximately 5 km/h, but there were also diffuse signals in the southwestern wind sectors. The potential source regions of OC and EC stretched to the broader areas in northwestern and western regions where coal and coal power plants are abundant. Some slight differences in the potential source regions were observed from 2013 to 2017, which was closely associated with the economic boom in the western areas of China. In addition, the southern areas of Beijing still contributed a lot to OC and EC loading in Beijing.

In summary, this study will be helpful for improving the understanding the sources of OC and EC associated with $PM_{2.5}$ and for assessing the effectiveness of local and national PM control measures. In addition, it provides valuable datasets for modelling studies and for assessing the health risk.

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Author contributions

D.S., W.M. and Y.S. designed the research. D.S., W.M., J.H., Z.W., W. K., W.P., Y.S., J.Y., B.H. and Y.S. performed the research. D.S., Z.W., and W.M. analyzed the data. D.S., J.H., and W.M. wrote and edited the manuscript. All other authors commented on the manuscript.

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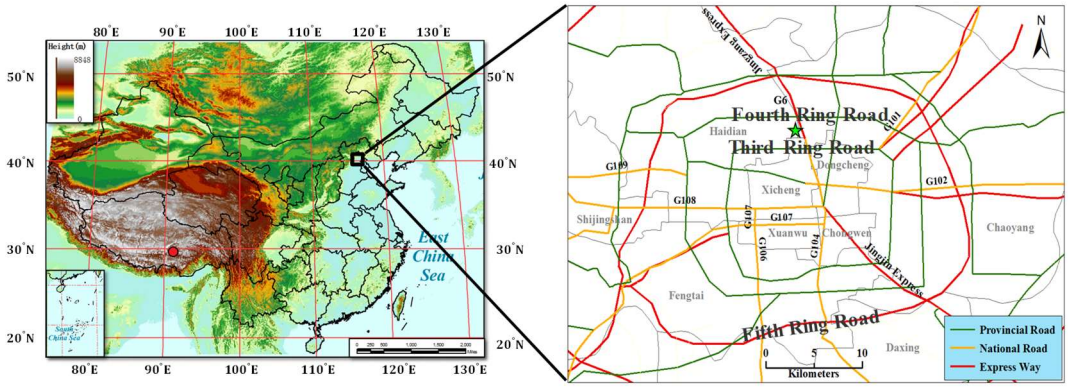

G6=Jingzang Expressway; G101=National Highway 101; G102= National Highway 102; G107= National Highway 107; G108= National Highway 108; G109= National Highway 109

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1013 Fig. 1. Map with location of the sampling site (the asterisk in the right figure indicates the sampling
1014 site).

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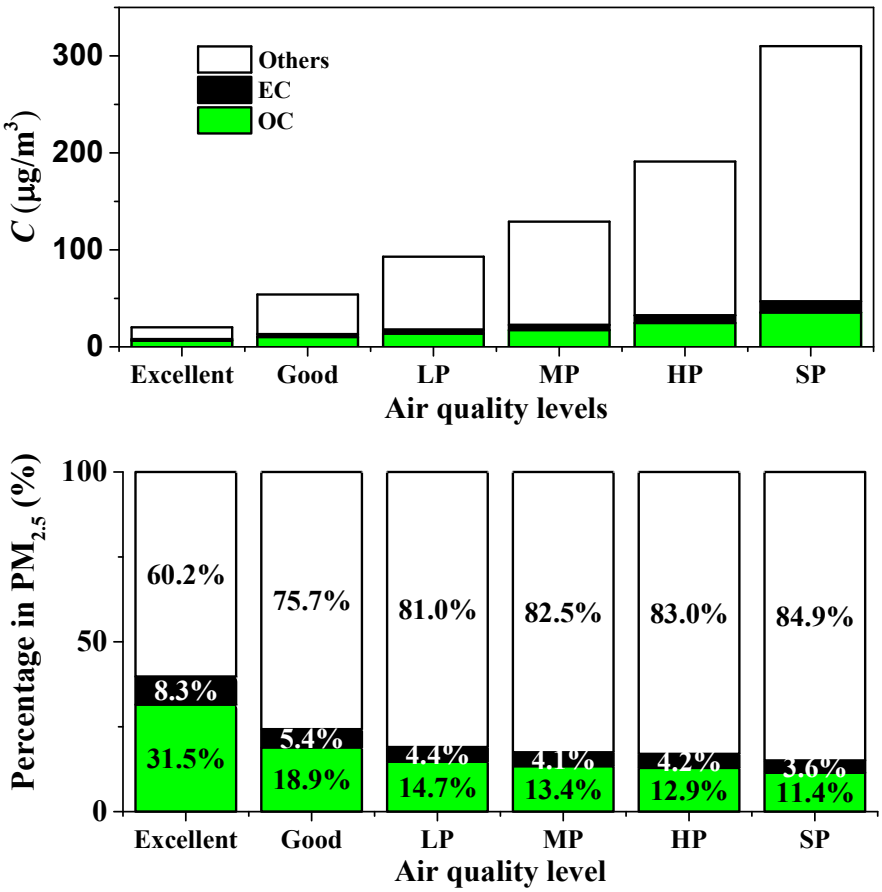

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1018 Fig. 2. Variation of average OC, EC and $PM_{2.5}$ concentrations (top) and of the percentages of OC,
1019 EC and other components in $PM_{2.5}$ (bottom) for different air quality levels.

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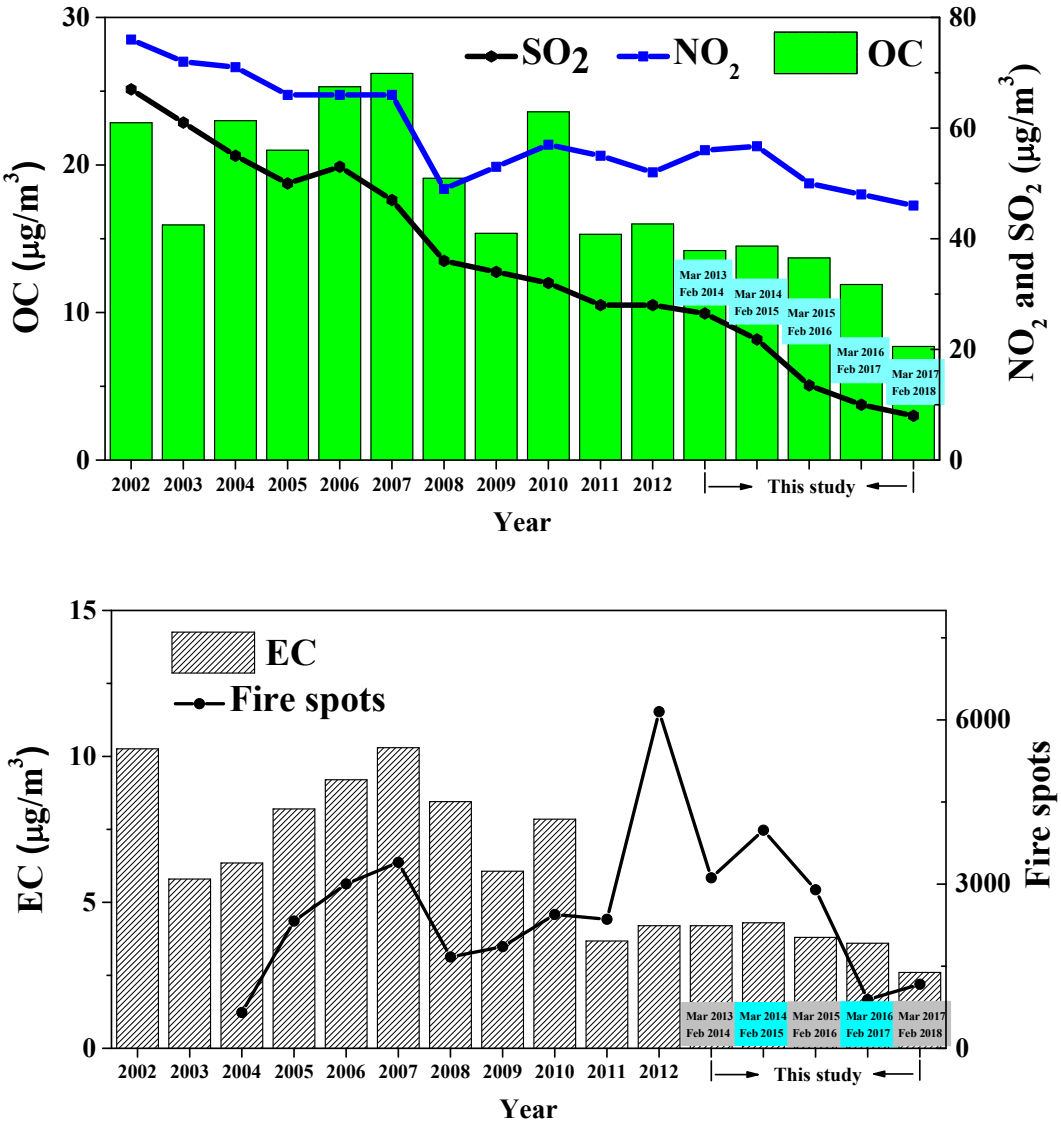


Fig. 3. Variation of the annual mean OC and EC concentrations in $PM_{2.5}$ from 2002 to 2018 in Beijing. The variation in NO_2 and SO_2 concentrations and in the number of fire spots counted for the domain of (30-70° N, 65-150° E) is also shown.

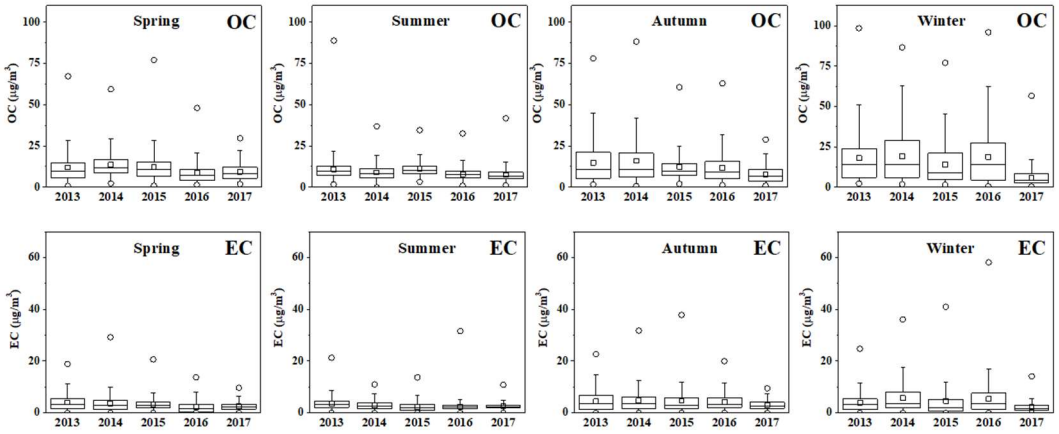
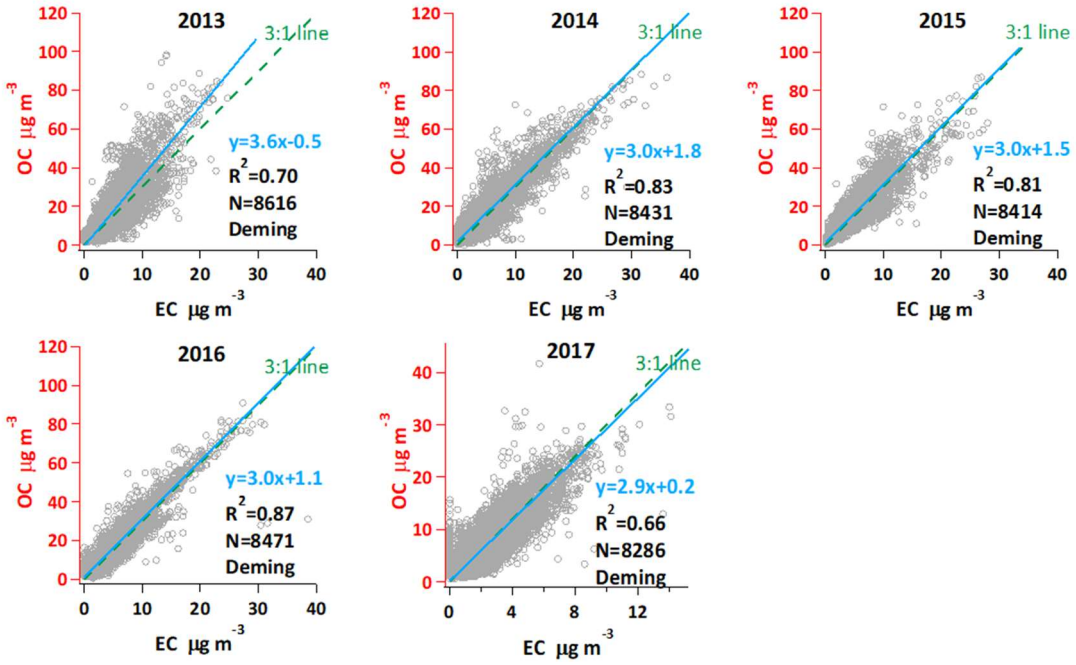


Fig. 4. Seasonal variations of OC and EC concentrations from March 2013 to February 2018.



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1033 Fig. 5. Relationship between OC and EC using the Deming regression method from 2013 to 2017
1034 (the dashed line indicates a OC/EC ratio of 3:1).

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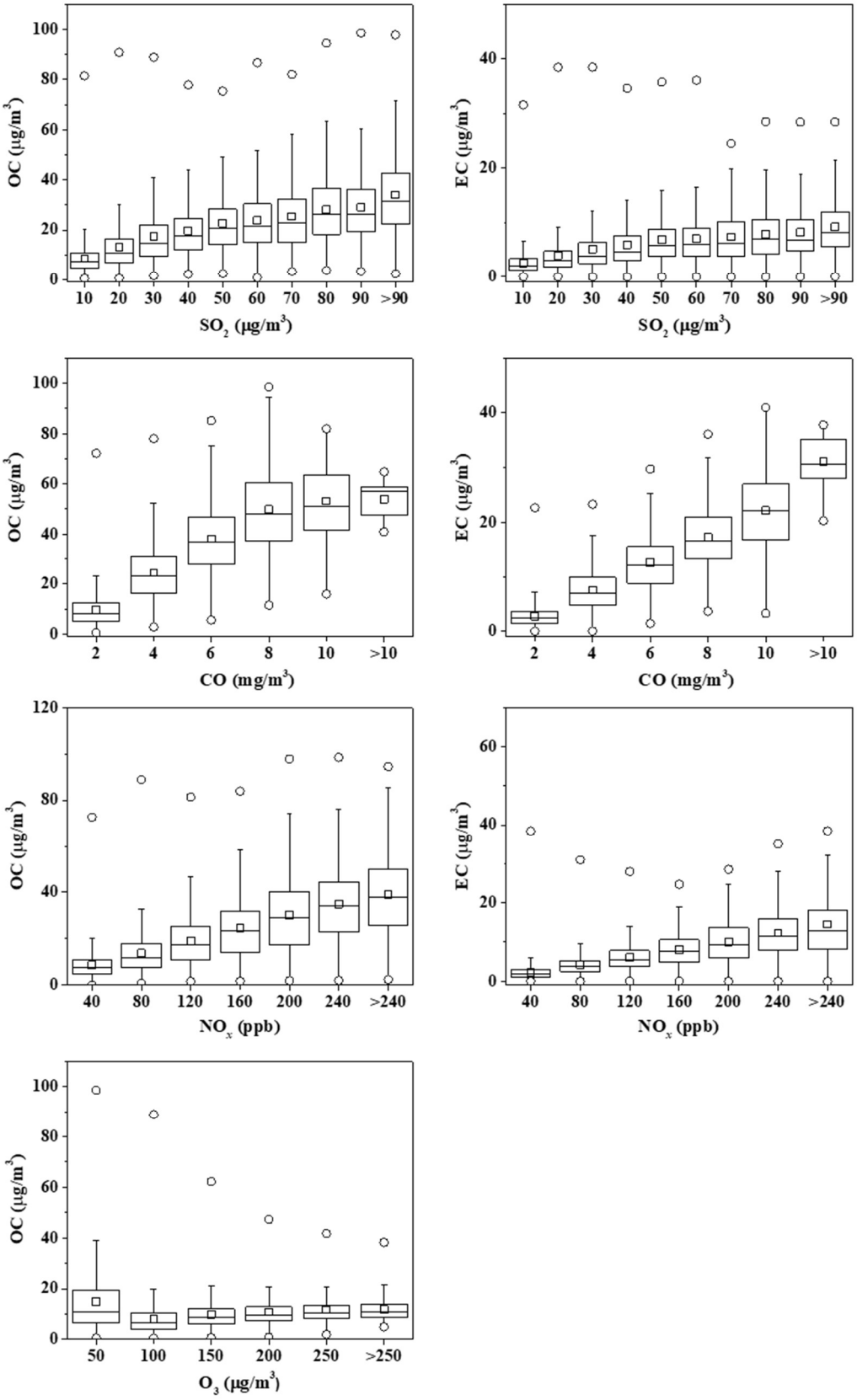

Fig. 6. OC and EC concentrations as a function of the SO_2, CO, NO_x and O_3 concentration.

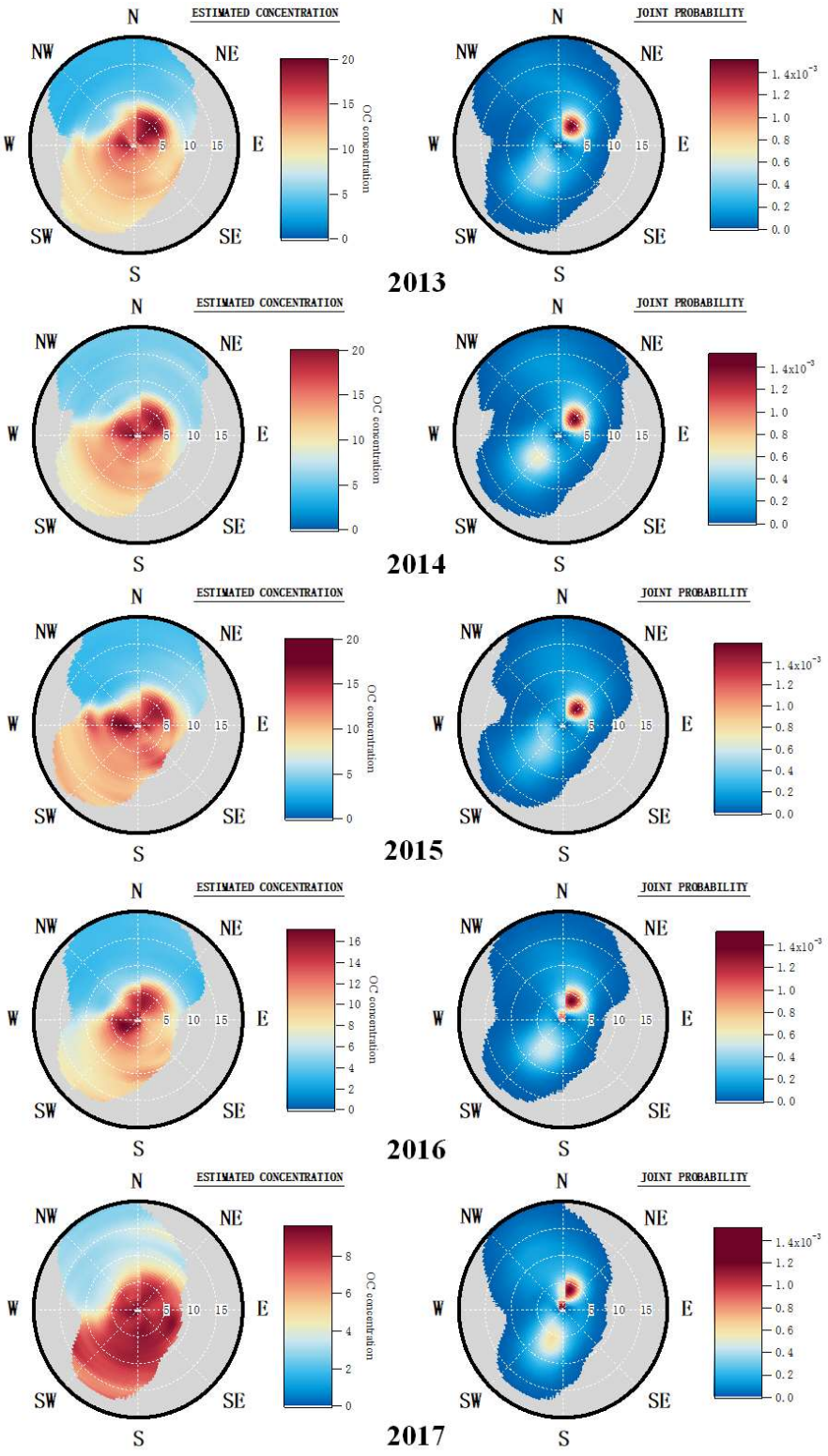

Fig. 7. Wind analysis results using NWR on 1-h OC concentrations measured in Beijing from 2013 to 2017 (Unit of wind speed: km/h).

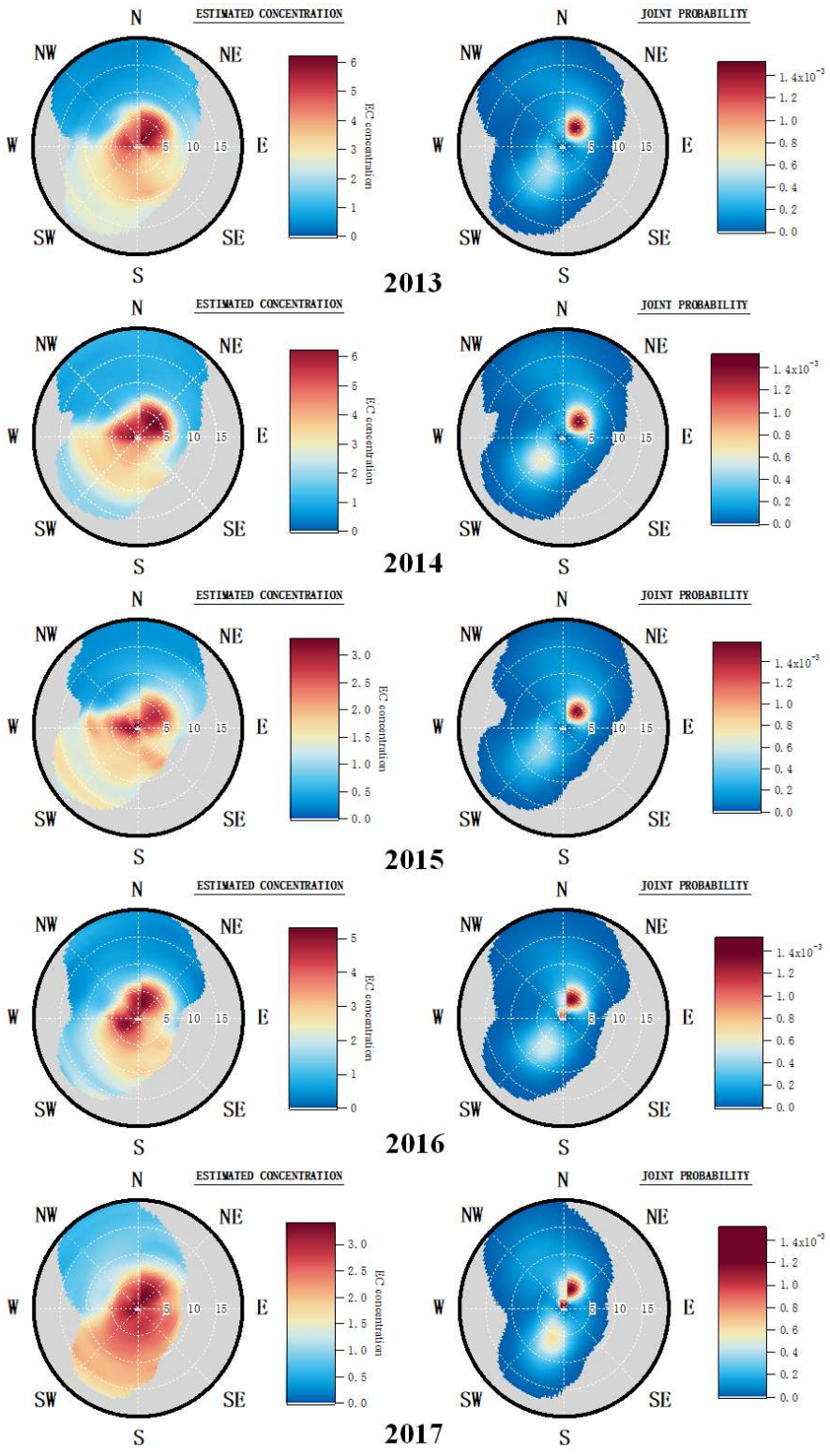

Fig. 8. Wind analysis results using NWR on 1-h EC concentrations measured in Beijing from 2013 to 2017.

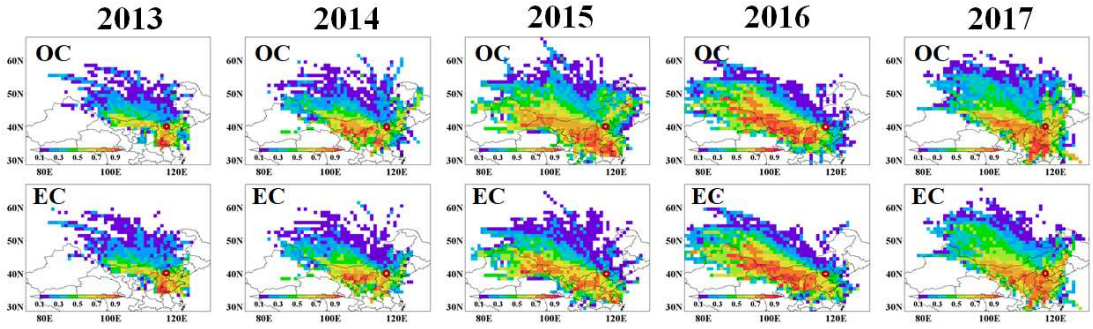

Fig. 9 Potential source areas for OC and EC in Beijing from 2013 to 2017. The color code denotes the PSCF probability. The measurement site is indicated with a ⭘. The identification of the provinces is given in Fig. S9.

Table 1. Medians, averages and associated standard deviations for the OC, EC and PM2.5 concentrations (in μg/m^3) and averages for the OC/$PM_{2.5}$, EC/$PM_{2.5}$ and TC/$PM_{2.5}$ ratios from March 2013 to February 2018.

	OC			EC			$PM_{2.5}$			OC/$PM_{2.5}$	EC/$PM_{2.5}$	TC/$PM_{2.5}$
	Median	Average	Stdev	Median	Average	Stdev	Median	Average	Stdev	Average	Average	Average
Mar-2013 − Feb-2014	10.6	14	11.7	3.2	4	3.3	66	89	82.9	0.157	0.045	0.203
Mar-2014 − Feb-2015	10.4	14.5	12.1	3	4.3	4	66	85.5	76.6	0.169	0.05	0.219
Mar-2015 − Feb-2016	9.1	13.7	9.2	1.3	3.8	4.4	48	76.9	85.6	0.178	0.049	0.228
Mar-2016 − Feb-2017	8.2	11.9	11.3	2.5	3.6	3.7	53	79.4	82.8	0.15	0.045	0.195
Mar-2017 − Feb-2018	6.8	7.7	4.7	2.3	2.6	1.6	35	49.4	48.6	0.155	0.052	0.208
whole study period	9.3	12.4	10.6	2.7	3.7	3.6	52	75.7	77.6	0.164	0.049	0.213

Table 2. Mean or median OC and EC mass concentrations (in μg/m^3) observed in major megacities of the world published in the literature and obtained in this study.

Megacities	Method	Period	Number or frequency of sampling	OC	EC	Literature
Athens	TOT	May 2008 to April 2013	Once everyday	2.1	0.54	Paraskevopoulou et al., 2014
Beijing	TOT	March 2017-Feburary 2018	Hourly	7.7	2.6	This study
Hongkong	TOR	from July to October 2014 and December 2014 to March 2015	N=161	7.8	2.2	Chen et al., 2018
Lhasa	TOR	May 2013 to March 2014	once each week	3.27	2.24	Li et al., 2016
Los Angele	TOT	March 2017-Feburary 2018	once every 3 days	2.88	0.56	US EPA*
Mexico	TOT	March 2006	Hourly	5.4-6.4	0.6-2.1	Yu et al., 2009
Mumbai	TOT	March-May 2007, October-November 2007 and December-January 2007-2008	15 days in a season	20.4-31.3	5.0-9.2	Villalobos et al., 2015
New Delhi	TOR	January 2013 -May 2014	N=95	17.7	10.3	Sharma and Mandal, 2017
New York	TOT	March 2017-Feburary 2018	Once every 3 days	2.88	0.63	US EPA*
Paris	TOT	from 11 September 2009 to 10 September 2010	Once everyday	3.0	1.4	Bressi et al., 2013
São Paulo	TOT	2014	Once each Tuesday	10.2	7	Pereira et al., 2017
Shanghai	TOT	from July 2013 to June 2014	Hourly	8.4	3.1	Xu et al., 2018
Soul	TOT	from January 2014 to December 2014	Hourly	4.1	1.6	Park et al., 2015
Tianjin	TOR	from Dec 23, 2013, to Jan 16, 2014	N=25	30.53	8.21	Wu et al., 2015
Tokyo	TOT	from July 27 to August 15, 2014	Once everyday	2.2	0.6	Miyakawa et al., 2016
Toronto	TOT	December 1, 2010-November 30, 2011	Hourly	3.39	0.5	Sofowote et al., 2014
Wuhan	TOT	From August 2012 to July 2013	Once every six days	16.9	2.0	Zhang et al., 2015
Xi'an	TOR	Four months of 2010	N=56	18.6	6.7	Wang et al., 2015

*https://aqs.epa.gov/api

TOR: thermal-optical reflectance; TOT: thermal-optical transmittance

1060 Table 3. OC/EC ratios in main domestic and foreign cities.

	Cities	Period	Method	OC/EC	References
Domestic cities	Beijing	1999-2000	TOR	2.7	He et al., 2001
		2000	TOT	7.0	Song et al., 2006
		2001-2002	EA	2.6	Duan et al., 2006
		2005-2006	TOT	3.0	Yang et al., 2011b
		2008	TOT	2.2	Yang et al., 2011a
		2008-2010	TOR	4.4	Hu et al., 2015
		2009-2010	TOR	2.9	Zhao et al., 2013
		2009-2010	TOT	3.4	Zhang et al., 2013
		2012-2013	TOT	7.0	Wang et al., 2016c
		2013	TOT	5.0	Ji et al., 2018
		2014	TOT	4.8	Ji et al., 2018
		2013	TOT	3.6	This study
		2014	TOT	3.0	This study

	2015	TOT	3.0	This study
	2016	TOT	3.0	This study
	2017	TOT	2.9	This study
Baoji	March 2012 - March 2013	TOR	5.3	Niu et al., 2016
Chengdu	2009-2010 annual	TOR	2.5	Tao et al., 2013
	2009–2013	TOR	4.4	Shi et al., 2016
	2011 annual	TOR	2.4	Tao et al., 2014
	2012-2013 annual	TOT	4.1	Chen et al., 2014
Chongqing	2005-2006 annual	TOR	4.7	Yang et al., 2011b
	2012-2013 annual	TOT	3.8	Chen et al., 2014
	May 2012-May 2013	TOT	3.6	Chen Y. et al., 2017
Ya‘an	June 2013 - June 2014	TOT	13.3	Li et al., 2018
Hangzhou	2004-2005 annual	EA	2.0	Liu G. et al., 2015
Hongkong	July - October 2014 and December 2014 - March 2015	TOR	3.5	Chen et al., 2018
Lhasa	May 2013 - March 2014	TOR	1.5	Li et al., 2016

Nanjing	2014 annual	TOT	1.8	Chen D. et al., 2017
	2011-2014 annual	TOR	2.6	Li et al., 2015
Ningbo	2009-2010 annual	TOR	2.8	Liu et al., 2013
Neijiang	2012-2013 annual	TOT	4.5	Chen et al., 2014
Qingling	March 2012 - March 2013	TOR	6.3	Niu et al., 2016
Shanghai	2009 annual	TOR	3.4	Zhao et al., 2015a
	2011	TOT	2.6	Chang et al., 2017
	2012	TOT	2.9	Chang et al., 2017
	2012 annual	TOR	5.4	Zhao et al., 2015b
	2013	TOT	3.4	Chang et al., 2017
Shijiazhuang	Four seasons (2009-2010)	TOR	2.7	Zhao et al., 2013
Tianjin	2009-2010	TOR	2.7	Zhao et al., 2013
Xi'an	2010 annual	TOR	2.7	Wang et al., 2015
	March 2012 - March 2013	TOR	4.0	Niu et al., 2016
	March 2012 - March 2013	TOR	4.0	Niu et al., 2016

		March 2012 - March 2013	TOR	3.8	Niu et al., 2016
		December 2014 - November 2015	TOT	10.4	Dai et al., 2018
	Weinan	March 2012 - March 2013	TOR	4.4	Niu et al., 2016
	Wuhan	From August 2012 - July 2013	TOT	8.5	Zhang et al., 2015
Foreign cities	Athens	May 2008 - April 2013	TOT	3.9	Paraskevopoulou et al. 2014
	Los Angeles	March 2017-Feburary 2018	TOT	5.1	US EPA*
	New Delhi	January 2013 -May 2014	TOR	1.7	Sharma and Mandal, 2017
	New York	March 2017-Feburary 2018	TOT	4.6	US EPA*
	Paris	September 11, 2009 - September 10, 2010	TOT	2.1	Bressi et al., 2013
	São Paulo	2014	TOT	1.5	Pereira et al., 2017
	Seoul	January 2014 - December 2014	TOT	2.6	Park et al., 2015
	Tokyo	July 27 - August 15, 2014	TOT	3.7	Miyakawa et al., 2016
	Toronto	December 1, 2010-November 30, 2011	TOT	6.8	Sofowote et al., 2014

*https://aqs.epa.gov/api

TOR: thermal-optical reflectance; TOT: thermal-optical transmittance; EA: elemental analysis