Response to reviewer#1

We greatly appreciate the reviewer for providing very constructive comments which have helped us improve the paper. We have considered the comments carefully and revised the manuscript accordingly, as detailed below in our point-to-point responses to the specific comments.

Major comments

1. It looks like the whole source apportionment is centered on the regression analysis of VED (rBC) versus thickly coated particles, resulting in traffic related rBC particles of 150nm in size. This result is very central to the main findings of the study – source contribution of traffic related BC particles. However, no justification whatsoever is provided what defines thickly coated particle and, consequently, what impact it would have if criterion of thickly coated particle is varied (I believe the criterion is the ratio of equivalent diameters of the core and the particle). Overall, the method based on regression analysis is neglecting the fact that particles are rarely externally mixed, except very close to the source which in case of traffic is a car tailpipe. Further away from the source, spatially and temporarily, particles become internally mixed and sources combined (through coagulation, secondary processes and deposition) making it very difficult to justify whether 150 nm particle is indeed traffic related or some of them advected from a population of coal combustion particles (sub-population of smaller coal combustion particles). There is no firm justification that 150 nm particles are indeed originating from traffic only (why not e.g. 120 nm) and indirect evidence provided is not sufficient.

Response:

(1) The reviewer is concerned with the definition of 'thickly coated rBC-containing particles', and suspects the definition might have impact on the results presented in our manuscript. In our initial manuscript, we simply introduced the method to define the 'thickly coated rBC-containing particles' according to the delay time between SP2 detected incandescent and scattering signal peaks of individual

particle. Since this method was described in detail in literature (Schwarz et al., 2006; Moteki and Kondo, 2007) and has been widely used in SP2 related studies (e.g., Wang et al., 2014; Wu et al., 2016; …), there is no need for a detailed description in our study. We have added a short description in the revised manuscript to make the definition of 'thickly coated rBC-containing particles' clearer, which reads: "The rBC-containing particles were defined as either thickly coated or uncoated/thinly coated according to the distribution of detected lag times, which was bimodal and had a local minimum at 2 μs (Fig. S1 in the supplemental files). We defined the rBC particles as thickly coated if the lag times were longer than 2 μs" (Lines 162–166 in the revision). In addition, the method to distinguish the mixing status of rBC-containing particles used in this study is traditional and qualitative, which don't need the assumptions on the particle's physical and chemical properties (e.g., morphology and refractive indices). This method cannot give the exact diameter of the particles, which is different from the method according to the equivalent diameter of rBC core and optical size of the entire particle. The delay time method can only estimate whether the particle is thickly coated and cannot provide how thick the coating is. Although the definition of 'thickly coated' based on the delay time method is related to the ratio of equivalent diameters of the core and the particle, it is not entirely decided by the absolute ratio of the diameters. Moteki and Kondo (2007) indicated that at least a coating thickness of 70% was needed to reach the delay time threshold for 'thickly coated particles'. Laborde et al. (2012) also illustrated the delay time threshold was expected to occur somewhere in the range of ~70% coating volume fraction. The reviewer mentioned that particles are rarely externally mixed, except very close to the source which in case of traffic is a car tailpipe. We also illustrated that the rBC particles freshly emitted from traffic can be quickly coated (Line 70 in our initial manuscript). It took ~4.6 hours for the particles thickly coated by other component under the ambient conditions in Beijing (Peng et al., 2016). In this study, we are concerned about the sizes of rBC which are relatively stable in the atmosphere. The mixing states of rBC particles provide an auxiliary description in the discussion on

the sources of rBC. We don't focus on the mixing state of rBC particles and how thick the coating is. Thus, the qualitative method on the basis of delay time between incandescent and scattering signal peaks was employed.

(2) As the reviewer proposed, there is indeed no further firm justification to prove the typical mass equivalent diameter of rBC is ~150 nm for traffic source at current stage of our study. We tried to investigate the sizes of rBC directly measured using the similar method at typical sources, such as traffic, coal/biomass combustion from existing literatures. Unfortunately, to the best of our knowledge, we cannot find available supporting materials. However, the mass size distribution of elemental carbon (EC) from the size-segregated sample revealed a mode with peak at 150 nm in aerodynamic diameter for freshly emitted EC (Yu and Yu, 2009; Yu et al., 2010) in PRD region. Huang et al. (2006) reported a relatively smaller accumulate EC mode with peak at ~120 nm. However, in these studies, a much larger traffic-related EC size was also observed with peak diameter at ~400 nm, which was seldom observed in the urban area and tunnel in developed countries. Yu et al. (2010) considered this characteristic of EC size distributions is related to the result of high engine loads and low combustion efficiencies in Chinese vehicles. We don't know whether the size distribution of EC in Beijing is similar to that in PRD region as there were few studies measured the EC in such small sizes (i.e., with diameter < ~400 nm). Considering that the urban location of our site and the stringent fuel and vehicle emission standards implemented in urban Beijing, relatively higher combustion efficiencies can be expected, resulting in a smaller EC mode. On this basis, we considered the smaller EC mode with diameter of ~150 nm should be dominated at our site, although further direct measurement is needed. In the revised manuscript, we have added the citation of these relevant literatures (Lines 334–345 in the revision). In our study, this typical local traffic-related VED with diameter of ~150 nm was extrapolated from the linear regression of VED_{rBC} against NF_{coated}. The physical meaning can be expected from the extrapolation as the freshly traffic-emitted rBC are rarely thickly coated. During the analysis of experimental data, we also suspected the robustness of this linear regression and the deductive VED of

traffic-emitted rBC. Thus, we analyzed the data obtained in another independent campaign conducted in winter 2013. It was very interesting to find there was a similar linear relationship between VED_{rBC} and NF_{coated}. Meanwhile, the slope and y-intercept values of the linear regression in the two independent campaigns were almost the same (Fig. 4). On this basis, we considered that the similar linear regression might be commonly existed, although more observations are needed to further confirm this result. Meanwhile, the direct measurement of rBC sizes at the traffic emission source is also needed to give a more reliable evidence. At the current knowledge status, the assumption made in this study should be acceptable.

2. Second major problem is the absence of method validation. One obvious validation would be radiocarbon analysis if that was considered at the start of the study. As it stands, the authors should at least do a thorough analysis of the studies (primarily but not exclusively in China) where radiocarbon analysis has been done and BC has been isotopically apportioned. If the SP2 measurements were combined with radiocarbon analysis it would constitute a significant advancement.

Response: This comment proposed by the reviewer is meaningful and farsighted. It provides a direction for our further studies on BC sizes and apportionment. Unfortunately, we didn't perform the radiocarbon analysis in this study. Although the aerosol samples were collected in the campaign, there were not enough carbon amount for radiocarbon analysis in the laboratory as a low-volume sampler operated at a nominal flow rate of 16.7 L/min was utilized. According to the reviewer's suggestion, we have reviewed literature associated with BC apportionment based on radiocarbon analysis. The ^{14}C analysis was usually used to distinguish the fossil-fuel combustion and biomass burning elemental carbon (EC). Zhang et al. (2015) revealed 76% EC was attributed to fossil-fuel combustion in urban Beijing in the extreme winter haze episode of 2013 on the basis of ^{14}C analysis. The ^{14}C analysis for the samplers collected at a suburban site of Beijing before/during/after the Asia-Pacific Economic Cooperation (APEC) summit held in November 2014 revealed a relatively higher contribution of biomass burning to EC (36% / 46% / 33%). The significant decrease in the contribution

of fossil-fuel combustion during APEC was related to the control of industry and traffic emissions (Liu et al., 2016). However, it is difficult to distinguish the traffic-related source from the fossil-fuel combustion based on the ^{14}C analysis. Stable carbon isotopes of traffic source showed a distinguished range from coal combustion (Widory, 2006; Cao et al., 2011), it was also very difficult to identify the exact contribution of traffic to EC due to the wide range of stable carbon isotopes. Generally, the radiocarbon analysis is advantage to distinguish the fossil-fuel and biomass burning source, but incapable of separating traffic-related sources from the fossil-fuel combustion. On the basis of SP2 measurement, the contribution of fossil-fuel combustion (traffic and coal burning) contributed ~80% of rBC in Xi'an (Wang et al., 2016), close to the apportionment result based on the ^{14}C analysis (78%, Zhang et al., 2015). The apportionment results were comparable, even the completely different approaches were employed. The traffic related rBC was determined in Wang et al. (2016), with a mean contribution of 46%. It was not much different from our result where the local traffic contributed 59% to rBC on average. We will try to combine the two methods (i.e., SP2 and radiocarbon analysis) in future studies to give a more specific and reliable apportionment of BC.

Minor comments

1. Line 32. Why exactly VED would vary little once rBC is emitted into atmosphere when the time scale of secondary processes is many hours or as long as the particle is airborne and particles undergo cloud processing and dry/wet deposition?

Response: We meant that the VED of an individual rBC particle varied little during its lifetime in the atmosphere because the rBC is chemically inert under ambient condition. Although cloud processing will change the physical/optical size of the rBC-containing particle through coating of other components (e.g., organic matters, sulfate, …), the mass-size (i.e., the VED) of the rBC core varies little. Moreover, the typical lifetime of BC is ~1 week in the atmosphere (Bond et al., 2013), and ultimately removed from the atmosphere through wet (e.g., in precipitation) and dry deposition to the Earth's surface. Because there is no industrial rBC emission in urban Beijing, traffic should be one of the most important local sources of rBC. The emission intensity of vehicles is relative

stable, resulting a constant VED of rBC measured in our study if other sources effect little. Thus, the variation in VED of rBC should be greatly interpreted by the alteration in rBC sources.

2. Line 129. Introduce assumption(s) briefly here.

Response: We have illustrated the assumptions in our revised manuscript according the comment, which reads: "a novel approach was employed to evaluate the contribution of local traffic to the rBC concentration based on the measured rBC sizes and reasonable assumptions including a deductive mean diameter of rBC from local traffic and relatively stable rBC sizes in the air masses transported over certain regions." (Lines 129–133 in the revision)

3. Line 162. Provide a number for defining thickly-coated rBC particles. What constitutes "thickly"?

Response: As we mention in the response to the first major comment, the 'thickly coated rBC particle' defined here was a qualitative conception. It was distinguished using the delay time between SP2 detected incandescent and scattering signal peaks of an individual particle, instead of directly characterize the size of rBC and its coating. This method is relatively easy to operate and doesn't rely on the assumptions of particle physical/chemical properties, which has been widely used in SP2-related studies (e.g., Moteki and Kondo, 2007; Wang et al., 2016). Previous studies revealed that at least a coating thickness of 70% was needed to reach the delay time threshold for 'thickly coated particles' (Moteki and Kondo, 2007; Laborde et al., 2012). As the observation site is not close to the emission sources (e.g., traffic road), naked rBC without coating should be seldom observed. Due to the quick coating processes of freshly emitted rBC from traffic, there should be a great part of thinly coated rBC under traffic dominant condition. These thinly coated rBC particles were classified together with the naked ones, significantly distinguished from the thickly coated ones which were underwent sufficient coating processes in the atmosphere or from sources such as coal combustion/biomass burning. Once the regional transport dominated, a great fraction

of thickly coated rBC should be observed because the rBC particles were initially thickly coated from coal combustion/biomass burning sources and suffered from coating processes during their transport to the observation site. We don't concern about how thick the coating is in this study.

4. Line 167. "were" instead of "was".

Response: Corrected.

5. Line 180. When something mentioned for the first time, spell it out. PRD = Pearl River Delta?

Response: Corrected. We have also checked throughout the manuscript for other acronyms.

6. Line 188. What was the reason of choosing particular density?

Response: The rBC density with value of 1.8 g/cm^3 utilized in this study is referred to relevant literature (Bond and Bergstrom, 2006). This density was also widely used in SP2-related studies (e.g., Schwarz et al., 2013; Gong et al., 2016). There are also many studies chose the value of 2 g/cm^3 for the rBC density (e.g., Wang et al., 2016). We have considered the difference in rBC density when compared to the size distributions shown in other studies.

7. Line 195. The relatively similar…

Response: We have modified the statement there in the revision according to the comment.

8. Line 207. This is clearly the most likely reason for different VED values. Consider also cloud processing (~15min time scale) initiating wet deposition.

Response: Actually, we also consider the dry/wet deposition of large rBC particles result in the small VED values of rBC measured at the remote regions where local emissions are rare. In the manuscript, we just cited the initial interpretation for the small

rBC presented in the corresponding reference in which they considered the small rBC was result from the source. Please note that we are referring to the rBC core inside an aerosol particle while the reviewer frequently referred to the ambient aerosol. The rBC cores can be coated by other components through aging processes in the atmosphere regardless of the initial size of rBC cores. Coating alters the physical/chemical of the initial rBC particle, including the geometric/optical size and the hydrophilicity of the particle in which the rBC core is embedded. Thus, the coated rBC particles should all undergo the cloud processing no matter the initial rBC cores are large or small.

9. Line 214. It is not much smaller, only smaller by 10%.

Response: The size distribution of rBC cores was presented in this study rather than the ambient aerosol particle. In this sense, 10% is significant. Aging processing changed the size of rBC-containing particles and had less impact on the mass equivalent size of rBC cores. The difference in peak diameter of SP2 derived rBC during polluted and clean days was significant, although the relative deviation was ~10% (221 nm on polluted day vs. 199 nm on clean day).Wang et al. (2016) also showed a significant difference in rBC peak diameter on coal combustion (215 nm) and traffic (189 nm) dominant days. In the revised the manuscript, we have used 'obviously' instead of the initial 'much' to make the statement here more rigorous.

10. Line 230. Generally, VED(rBC) were positively correlating with AS/EC and AN/EC ratios....

Response: We have modified the statement there in the revision according to the comment.

11. Line 242. Availability of ammonia is most likely responsible for such patter, because sulphuric acid is neutralized first and only then nitric acid (acid strength effect) if there is enough ammonia. Neutralisation with ammonia is a passive process. Try looking at differences in the degree of neutralisation.

Response: Generally, there was enough ammonia to neutralize sulphuric acid and

nitiric acid in most samples except in several severely polluted samples (Figure R1). Even in the severely polluted samples, the amount of ammonia was enough to neutralize sulphuric acid. In this study, we simply assumed there was enough ammonia to neutralize both sulphuric acid and nitiric acid. The mass concentrations of ammonia sulfate were calculated from those of sulfate multiplying by a factor of 1.375, and those of ammonia nitrate were from nitrate multiplying by a factor of 1.29, according to the molecular weight. The AS/EC ratios should be constant even the neutralization was considered because there was enough ammonia to neutralize sulphuric acid first. Although the AN/EC ratios in severely samples might decrease because there was not enough residual ammonia to neutralize nitric acid entirely, it had little effect on the results and conclusion there (Figure 2b and 2d).

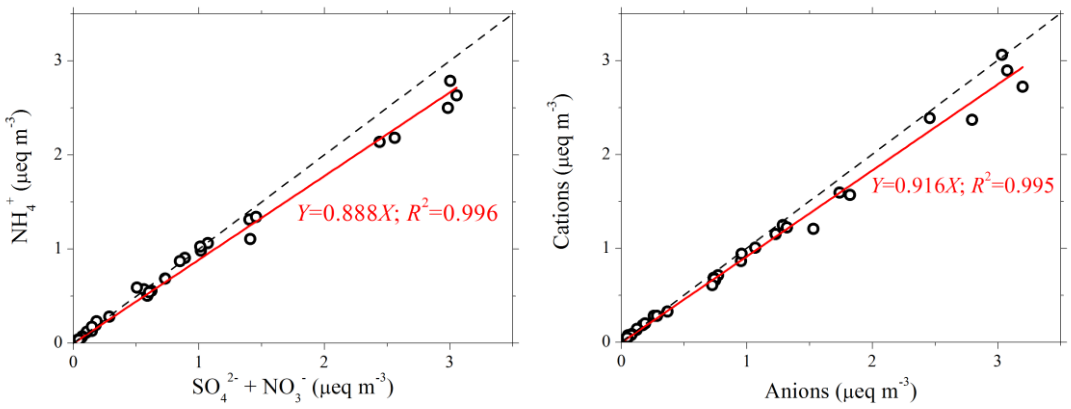

Figure R1 Correlations between cations and anions: (a) NH_4^+ versus SO_4^{2-}+NO_3^-; (b) Cations versus Anions

12. Line 252. How could secondary AN have any effect on the core size of rBC when formation processes of the two are completely different?

Response: The statement in the initial manuscript was indeed confusing. Actually, we intended to express that the secondary formation of AN played an important role in the coating processes of rBC while had negligible effect on the core size of rBC. The positive correlation between VED values of rBC and AN/EC ratios was resulted from the simultaneous effect of source alteration. Regional transport brought larger rBC particles as well as higher AN/EC. Secondary formation itself should not affect the core sizes of rBC. We have revised in the revised manuscript to this: “The secondary

formation of AN might play an important role in the coating processes of rBC but have a negligible effect on the core size of the rBC."

13. Line 274. Reference London study.

Response: We have added the reference in the revision.

14. Line 315. "which has little coating…"

Response: Revised.

15. Line 316. Why is this surprising as large VED(rBC) would be formed in the presence of copious amounts of gaseous precursors contributing to thick coating during atmospheric processing (secondary formation)?

Response: The VED of rBC presented in this study indicated the mass equivalent size of rBC cores. Thus, even coating can increase the size of an entire particle in which rBC core was embedded, the mass size of rBC core should not vary. If only the coating processing had effect, the VED_{rBC} should vary little while NF_{coated} gradually increase. The linear relationship between VED_{rBC} and NF_{coated} should relate to the rBC source alteration. We are surprised that almost the same linear relationship was observed in another winter campaign, having similar slope and *y*-intercept values. Thus, we suspected the linear relationship between VED_{rBC} and NF_{coated} might be a common result at our observation site.

16. Line 351. The method ignores the fact that local traffic VED is including contribution of other sources unless the authors have access to specific experiments proving the traffic VED. Considering contribution of other sources to VED makes local traffic contribution biased high. The method works for the estimating the upper limit, but the real contribution can be very different without proper measurement of traffic emitted VED (rBC).

Response: We quite agree with the reviewer's comments here. Actually, the VED of rBC from local traffic was inferred from the observed linear relationship between

VED_{rBC} and NF_{coated}, by assuming that the VED_{rBC} of non/thickly coated (i.e., non or thinly coated) rBC particles was from local traffic. As the freshly emitted rBC was gradually coated through aging processes in the atmosphere, the completely non/thinly coated rBC was seldom observed at an ambient site. The observed minimum NF_{coated} with value of ~10% at 5 minutes resolution (Figure 4) also indicated that there was no absolutely non/thinly coated rBC unless measured close to the traffic source (i.e., car tailpipe). This VED presented in this study is an inferred value and cannot be directly proved at this stage because of the limitation in the direct measurement of traffic VED. As mentioned in the response to the first major comment, size-segregated EC distributions revealed a typical traffic emitted EC mode with mass aerodynamic diameter of ~150 nm in China, although another traffic emitted EC mode with diameter of ~400 nm was also reported which was seldom observed in urban areas of developed countries (Kleeman et al., 2000; Allen et al., 2001; Huang et al., 2006, 2008; Yu and Yu, 2009; Yu et al., 2010). Further direct measurement to the VED of rBC from certain source is needed. However, the interpretation in our study is scientifically sound. Coal combustion, biomass burning and traffic exhaust should be the most major sources of the airborne rBC. Due to the combustion condition and fuel type, the rBC particles from coal combustion and biomass burning are most thickly coated by organic or inorganic components. In contrast, rBC particles freshly emitted from traffic source are usually naked and become thinly coated in a short time after emitted to the atmosphere. They should take several hours or longer to get thick coating. Thus, on this basis, we considered the VED of completely non/thinly coated rBC corresponded to traffic induced rBC. It was further confirmed by a very similar result observed in another independent campaign. As we illustrated in the conclusion section in our revised manuscript, “despite potential large uncertainties in the estimated contribution from the local traffic to rBC, due to the many assumptions employed, its relative variation is clearly demonstrated.” Further research measuring sizes of rBC directly from various sources, including coal combustion, biomass burning and traffic exhaust, is needed to validate the findings presented in this study.

17. Line 357. This is a very bold assumption when BC sources are not localized, but instead present in every region. Differences in VED in different regions depend on relative contribution of sources, but never fixed. Also consider heterogeneity of traffic sources as car fleet in major cities is very different from rural ones.

Response: Indeed, the assumption here is very bold. However, it is very difficult to identify the rBC sources when they are not localized. Carbon isotope method is suitable to identify whether rBC from fossil fuel or biomass burning, however, it is also difficult to distinguish the traffic source from coal or other fossil oil combustion. A simple method based on SP2 measurement was thus proposed in this study, although with uncertainties. We considered that the contribution of different rBC sources (coal combustion/biomass burning) in air masses from a certain direction should vary little since the emission factors should be spatially and temporally stable during a short period (e.g., several days). We didn't focus on how much the coal combustion/biomass burning contributed. As there were no sources of local coal combustion/biomass burning in urban Beijing, we treated the coal combustion/biomass burning as an ensemble source from regional transport which was distinguishable from local traffic according the rBC sizes. The rBC sizes from such ensemble source were mainly determined by where these rBC particles were from. Thus, the assumption here is reasonable to some degree. We presented the analysis of local traffic contribution as a discussion section, indicating there were inevitable uncertainties during the analysis. We cannot give a definite conclusion at current stage. In addition, considering the urban location of our observation site, the local traffic source referred in particular to the traffic emissions on the roads in urban Beijing in this study.

18. Line 370. Five typical VEDs were identified in VED range of 5% only? This is unreasonable.

Response: Considering the relative difference of rBC peak diameter on polluted and clean days is only 10%, the VED range of 5% is acceptable. The sizes of rBC core are generally small and relative stable. Due to their chemical inertia, the rBC sizes are mainly determined by sources and depositions. The five typical VEDs estimated in this

study represent the rBC sizes from sources other than local traffic. The rBC sizes from these sources should be relatively stable and influenced by the contribution of coal combustion/biomass burning as well as the deposition processing. We cannot distinguish the contribution of coal combustion and biomass burning from these sources other than local traffic. During our twenty days campaign, the emission inventory should vary little and significant wet scavenging wasn't observed. Thus, the difference with relative value of 5% can be expected.

19. Line 435. Those values must correlate, because they are methodologically related.

Response: Although the size and mass of rBC are methodologically related, the negative correlation between them is not inevitably. If the increase in mass concentration of rBC only induced by the meteorological condition (e.g., decrease in mixing layer height), the relative contribution of traffic to rBC should varied little. Change a way of thinking, if we used the mass concentration of $PM_{2.5}$ measured using a real-time $PM_{2.5}$ monitor instead of rBC, the contribution of traffic should also negatively correlated with the mass concentration of $PM_{2.5}$ because the mass concentrations of $PM_{2.5}$ and rBC are well positively correlated (Wu et al., 2016).

20. Why there is a gap in the spectrum?

Response: The gap is related to the methodology. The SP2 used in this study is revision C*. It has eight channels. The incandescence signals are simultaneously captured at high and low gain channels. The high gain channel provides a much sensitive measurement of small rBC particles while the low gain extend the up limitation of SP2. There is a merging of dataset recorded by the two channels, resulting in abnormal values at the junction. The gap in the spectrum is resulted from the artificial elimination of those abnormal values before curve fitting.

21. Fig.5 (and respective text). Sources are poorly separated, because of high traffic contribution around midnight. That is unreasonable and points at overestimated traffic contribution.

Response: The high rBC concentration of traffic in night time is greatly induced by the depressing of mixing height and suppressing of turbulence. Besides, although the vehicle number on the road decreases in night time, heavy-duty diesel vehicles are permitted to travel in the urban area of Beijing during the period of 23:00 to 06:00 (local time) under Beijing's traffic regulation (Song et al., 2012). They have much higher emission factors than light-duty gasoline vehicles, also resulting in the high traffic BC concentration around midnight (Song et al., 2013).

References:

Allen, J. O., Mayo, P. R., Hughes, L. S., Salmon, L. G., and Cass, G. R.: Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel, Environ. Sci. Technol., 35, 4189–4197, 2001.

Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, Aerosol Sci. Technol., 40, 27–67, 2006.

Bond, T. C., Doherty, S. J., Fahey, D. W., et al.: Bounding the role of black carbon in the climate system: A scientific assessment, J. Geophys. Res. Atmos., 118, 5380–5552, 2013.

Cao, J. J., Chow, J. C., Tao, J.: Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels, Atmos. Environ., 45, 1359–1363, 2011.

Gong, X. D., Zhang, C., Chen, H., Nizkorodov, S. A., Chen, J. M., and Yang, X.: Size distribution and mixing state of black carbon particles during a heavy air pollution episode in Shanghai, Atmos. Chem. Phys., 16, 5399–5411, 2016.

Huang, X. F., Yu, J. Z., He, L. Y., and Hu, M.: Size distribution characteristics of elemental carbon emitted from Chinese vehicles: results of a tunnel study and atmospheric implications, Environ. Sci. Technol., 40, 5355–5360, 2006.

Huang, X. F., and Yu, J. Z.: Size distributions of elemental carbon in the atmosphere of a coastal urban area in South China: characteristics, evolution processes, and implications for the mixing state, Atmos. Chem. Phys., 8, 5843–5853, 2008.

Kleeman, M.J., Schauer, J. J., and Cass, G. R.: Size and composition distribution of fine particulate matter emitted from motor vehicles, Environ. Sci. Technol. 34(7), 1132–1142, 2000.

Laborde, M., Mertes, P., Zieger, P., Dommen, J., Baltensperger, U., and Gysel, M.: Sensitivity of the

single particle soot photometer to different black carbon types, Atmos. Meas. Tech., 5, 1031–1043, 2012.

Liu, J. W., Mo, Y. Z., Li, J.: Radiocarbon-derived source apportionment of fine carbonaceous aerosols before, during, and after the 2014 Asia-Pacific Economic Cooperation (APEC) summit in Beijing, China, J. Geophys. Res. Atmos., 121, 4177–4187, 2016.

Moteki, N., and Kondo, Y.: Effects of mixing state on black carbon measurements by laser-induced incandescence, Aerosol Sci. Technol., 41, 398–417, 2007.

Schwarz, J. P., Gao, R. S., Perring, A. E., Spackman, J. R., and Fahey, D. W.: Black carbon aerosol size in snow, Sci. Rep., 3, 1356, doi:10.1038/srep01356, 2013.

Song, S., Wu, Y., Jiang, J., et al.: Chemical characteristics of size-resolved $PM_{2.5}$ at a roadside environment in Beijing, China, Environ. Pollut., 161, 215–221, 2012.

Song, S., Wu, Y., Xu, J., et al.: Black carbon at a roadside site in Beijing: Temporal variations and relationships with carbon monoxide and particle number size distribution, Atmos. Environ., 77, 213–221, 2013.

Wang, Q. Y., Huang, R. J., Zhao, Z. Z., Cao, J. J., Ni, H. Y., Tie, X. X., Zhao, S. Y., Su, X. L., Han, Y. M., Shen, Z. X., Wang, Y. C., Zhang, N. N., Zhou, Y. Q., and Corbin, J. C.: Physicochemical characteristics of black carbon aerosol and its radiative impact in a polluted urban area of China, J. Geophys. Res. Atmos., 121, doi:10.1002/2016JD024748, 2016.

Widory, D.: Combustibles, fuels and their combustion products: A view through carbon isotopes, Combust. Theor. Model., 10, 831–841, 2006.

Wu, Y. F., Zhang, R. J., Tian, P., et al..: Effect of ambient humidity on the light absorption amplification of black carbon in Beijing during January 2013, Atmos. Environ., 124, 217–223, 2016.

Yu, H., and Yu, J. Z.: Modal characteristics of elemental and organic carbon in an urban location in Guangzhou, China, Aerosol Sci. Technol., 43, 1108–1118, 2009.

Yu, H., Wu, C., Wu, D., and Yu, J. Z.: Size distributions of elemental carbon and its contribution to light extinction in urban and rural locations in the Pearl River Delta region, China, Atmos. Chem. Phys., 10, 5107–5119, 2010.

Zhang, Y. L., Huang, R. J., El Haddad, I., et al.: Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013, Atmos. Chem.

Phys., 15, 1299–1312, 2015.

Response to reviewer#2

We appreciate the criticisms from the reviewer, although we cannot agree completely as explained below. We also appreciate the several useful comments which helped us improve the paper.

1. The reviewer felt that the scientific novelty value of our results was poor and mentioned that there was a similar dataset published by Wang et al. (2016). Moreover, the reviewer pointed out that there had been already several other articles containing SP2 measurement results published from Beijing and urban areas in Asia with longer data time series and much larger set of instruments, and results from these relevant studies have include the main results of our work. A longer dataset with data collected during different seasons and a larger set of instruments was recommended.

Response:

We are fully aware of the article by Wang et al. (2016a) in the preparation of our manuscript. Wang et al. (2016a) presented the SP2-rBC measurement that was collected right before our campaign in Beijing. The study only revealed the mass concentration of rBC derived from the SP2 measurement, and focused on the contribution of regional transport to the BC mass concentration in Beijing on the basis of WRF-BC model analysis combined with the SP2 measurement. The size distribution and mixing state of rBC particles, which are important knowledge gaps on rBC related sciences, were discussed in our study but not mentioned in their study. Thus, our study and their study have completely different focuses, although both focused on the same city. We'd also like to mention that there are two common coauthors in both papers whose contribution to our work was to provide guidance on instrument operation and data analysis. Our study is independent of that presented by Wang et al. (2016a) and we present more specific and advanced information of rBC that SP2 can provide, including size distribution and mixing state.

We have reviewed many published SP2-related studies made in the urban areas in

Asia, especially those in China. Studies on the size distribution of rBC, are relatively limited in China, e.g., Pearl River Delta Region (Huang et al., 2011, 2012), Yangtze River Delta (Gong et al., 2016), Xi'an in West China (Wang et al., 2015), Qinghai-Tibetan Plateau (Wang et al., 2014), and no similar study using SP2 was available in urban Beijing, or the whole North China Plain (NCP) where Beijing is located. Since rBC size distribution varied substantially from region to region, as reviewed in Huang et al. (2012), conducting such a study as presented in our manuscript is needed and filled the knowledge gap on this important scientific topic.

As for the length of the campaign the reviewer concerned, we'd like to mention that measuring the rBC for a lengthy period with SP2 is challenging mainly due to its high cost, as well as complexity in operation and maintenance. Most in-situ SP2 measurements were performed in a period shorter than one-month (e.g., Liu et al., 2014; Huang et al., 2011; Wang et al., 2014; Gong et al., 2016; …). Sometimes a number of instruments were operated accompanied with SP2 to show richer aerosol characteristics. One of our previous work used a photoacoustic extinctiometer (PAX, DMT, USA) operating parallel to the SP2 to investigate the effect of mixing state on the mass absorption efficiency of rBC (Wu et al., 2016). The related in-situ experiment of the previous work was made at the same site in January 2013 when the heavy haze events occurred frequently in Beijing. However, our current research aimed to reveal the rBC size characteristic of rBC in urban Beijing. The following discussion on the sources of rBC in this study was mainly based on the measured rBC sizes. Actually, the size distributions of rBC is very similar in our two campaigns (the previous one was in the winter of 2013 and the current one was in the winter of 2014), because both measurements were made at the same site. They have been presented in Fig. S2 in the revised supplemental files. The slightly larger rBC sizes in the winter of 2013 is likely to relate with the higher rBC concentrations, which indicate more influence of larger rBC from sources other than local traffic, e.g., regional transport. In order to reveal the size distribution of rBC in urban Beijing and the causes of its variation, we focus on the campaign in the winter of 2014 in our current manuscript, during which the $PM_{2.5}$ samples were collected twice per day and chemical compositions of each sample

(including water-soluble ions, metal elements, carbonaceous matters) were comprehensively analyzed. In the discussion section of our current manuscript (Fig.4), we had already employed the dataset acquired in the winter of 2013 to verify the relationship between the number fraction of thickly coated rBC (NF_{coated}) and the average volume equivalent diameter of rBC (VED_{rBC}). Since the severe air pollution in Beijing is mainly occurred in wintertime, the rBC characteristics based on SP2 measurement in other seasons were seldom paid attention in our previous work. We will certainly consider the reviewer's suggestion in our future studies.

2. The reviewers mentioned that the develop method for analyzing the contribution of local traffic is poorly described and verified. Meanwhile, it is hard to estimate if it works. Proving the developed method works by comparing results of our method to other independent measurement data is recommended. The reviewer also suggests that it is necessary to estimate uncertainty and validate the method. Moreover, the reviewer is also concerned with universality of this developed method.

Response:

We have described the method in more detail in the revised manuscript, according to the review's comments (Lines 398–400 in the revision). Generally, the method employed in our study is based on the extrapolative size of local traffic source from the linear relationship between the number fraction of thickly coated rBC (NF_{coated}) and the average volume equivalent diameter of rBC (VED_{rBC}). This diameter cannot be verified at current stage, because the directly measurement to rBC size of certain rBC source, e.g., traffic exhaust, is still lacking. However, as mentioned in section 4.1, through the analysis of the data acquired at the same site in the winter of 2013, we found that this relationship between NF_{coated} and VED_{rBC} and the inferred traffic-rBC diameter could be repeated. Moreover, several references associated with size-segregated aerosol samples were added in the revised manuscript (Lines 334–345 in the revision), because a similar BC size with diameter of ~150 nm was also presented in these studies (Yu and Yu, 2009; Yu et al., 2010). Thus, we considered that this diameter actually existed in urban Beijing. Of cause, further work should be done to verify this result, especially

the measurement nearby the emission sources and in other seasons. Actually, it is very difficult to distinguish the source of ambient rBC, as the rBC was easily to be internally mixed with other components during a short period in the ambient (Peng et al., 2016). Considering the chemical inertness of BC and invariance of the mass-equivalent size of the individual rBC particle in ambient atmosphere, we developed this simple method to estimate the contribution of local traffic to rBC. A more accurate source apportionment of rBC was presented by Liu et al. (2014) also using the difference in the size distribution of traffic-related rBC and solid fuel-related rBC. Their method is much more complicated. Based on the combination of PMF analysis, Wang et al. (2016b) developed a method to distinguish the rBC from traffic, coal combustion and biomass burning sources. A large amount of trace elements should be analyzed if the method was employed. Moreover, large uncertainties should also be related in their method. The method developed in our study is relatively simple and requires only the SP2 measurement itself. We admit that large uncertainties existed in the resolved contribution of different sources to BC on the basis of our method, as explained in the revised manuscript.

Several other methods, such as radiocarbon analysis, are generally used to determine the source of BC. However, the ^{14}C analysis is mainly used to distinguish the contribution of biomass burning and fossil-fuel combustion to BC (Zhang et al., 2015; Liu et al., 2016). It is difficult to distinguish the traffic-related source from the fossil-fuel combustion based on the ^{14}C analysis (see the response to the second major comment in RC1 for detail). Actually, the method developed in our study to resolve the rBC sources is more qualitative than quantitative, as several rough assumptions were employed in this method. However, results from this method should well reflect the variation in the traffic contribution. According to the results resolved from this method, it was much clearer that a significant increase in the contribution of sources other than local traffic, e.g., regional transport, was observed during the haze period. Based on many assumptions, uncertainty in the resolved traffic contribution should be very large and cannon be simply quantized here.

As the sources of rBC are discrepant in different regions, we are not very sure this

method is suitable in other studies. However, considering the rBC freshly emitted from the local traffic source is mostly non/thinly coated, the extrapolation of local traffic-rBC size by assuming it equal to the VED_{rBC} of totally non/thinly coated rBC should be tried in the typical urban regions at least. The rBC source apportionment method developed in our study can also be tried in the local traffic dominated urban areas where other rBC sources, e.g., coal combustion and biomass burning, are rare.

3. Why the diurnal cycles of the BC from both traffic and other sources are highest during nighttime?

Response:

As mention in section 4.2 in the initial manuscript, the higher BC concentrations during nighttime were likely to be attributed to the lower mixing layer height. Obvious decrease in the mixing layer height suppressed the diffusion of air pollutants, resulting the higher BC from both traffic and other sources during nighttime. Another important cause of the higher traffic-BC during nighttime might be the increase in the flow of heavy-duty diesel vehicles. These vehicles have much higher emission factors of BC and are permitted to travel in urban Beijing only during the night time from 23:00 to 06:00 Local Time (Song et al., 2013). We have added such information in the revised manuscript with relevant references (Lines 432–436 in the revision).

4. Uncertainty estimation for BC results and especially for the larger mode would be important addition. The large BC mode (with maximum at around 500nm) is very small and very close to the upper particle size limit of the instrument, so it would be important to estimate how real this BC mode is.

Response:

Thanks for this recommendation. As mentioned in the methodology section, the overall uncertainty in the rBC mass determination was ~25%, including the uncertainties inherented in the mass calibration, flow measurement and estimation of BC masses beyond the SP2 detection range. Indeed, the large BC mode is very small and very close to the upper size limit of the SP2. At the initial stage of analyzing this

dataset, we also suspected the reliability of the large rBC mode. We then first consulted a large amount of relevant references and found that the large mode was also observed in several previous studies as mentioned in the first paragraph of section 3.1 in our manuscript (Huang et al., 2011; Wang et al., 2014). We still make reservations on whether the large rBC mode (only accounting for ~6% of the SP2-determined rBC masses) was related to the inherent measurement bias, as it is close to the upper size limit of the SP2. Thus, we chose not to focus on the large mode in our manuscript discussion, and leave this to future more accurate measurements. Since there is no explicit interpretation to this large mode in literature, we simply present the observational facts from the dataset without much discussions.

5. The title and aim of this article are slightly conflicting. Title suggest that this article focuses on BC size distributions and sources, whereas the aim states that the aim was to develop a novel approach to evaluate the contribution of local traffic to the rBC concentration. Might be useful to include the method development to the title, if that is the main goal.

Response:

Actually, the major goal of this study is to reveal the size distribution of rBC and analyze its variation in urban Beijing based on the SP2 measurement. The source of rBC is a second goal of the study. We have modified the last paragraph of the introduction section to make the subject of this study clearer according to the suggestion (Lines 125–133 in the revision).

References:

Gong, X. D., Zhang, C., Chen, H., Nizkorodov, S. A., Chen, J. M., and Yang, X.: Size distribution and mixing state of black carbon particles during a heavy air pollution episode in Shanghai, Atmos. Chem. Phys., 16, 5399–5411, 2016.

Huang, X. F., Gao, R. S., Schwarz, J. P., He, L. Y., Fahey, D. W., Watts, L. A., McComiskey, A., Cooper, O. R., Sun, T. L., Zeng, L. W., Hu, M., and Zhang, Y. H.: Black carbon measurements in the Pearl River Delta region of China, J. Geophys. Res., 116, D12208,

doi:10.1029/2010JD014933, 2011.

Huang, X. F., Sun, T. L., Zeng, L. W., Yu, G. H., and Luan, S. J.: Black carbon aerosol characterization in a coastal city in South China using a single particle soot photometer, Atmos. Environ., 51, 21–28, 2012.

Liu, D., Allan, J. D., Young, D. E., Coe, H., Beddows, D., Fleming, Z. L., Flynn, M. J., Gallagher, M. W., Harrison, R. M., Lee, J., Prevot, A. S. H., Taylor, J. W., Yin, J., Williams, P. I., and Zotter, P.: Size distribution, mixing state and source apportionment of black carbon aerosol in London during wintertime, Atmos. Chem. Phys., 14, 10061–10084, 2014.

Liu, J. W., Mo, Y. Z., Li, J.: Radiocarbon-derived source apportionment of fine carbonaceous aerosols before, during, and after the 2014 Asia-Pacific Economic Cooperation (APEC) summit in Beijing, China, J. Geophys. Res. Atmos., 121, 4177–4187, 2016.

Peng, J. F., Hu, M., Guo, S., Du, Z. F., Zheng, J., Shang, D. J., Zamora, M. L., Zeng, L. M., Shao, M., Wu, Y.-S., Zheng, J., Wang, Y., Glen, C. R., Collins, D. R., Molina, M. J., and Zhang, R. Y.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proc. Natl. Acad. Sci. U.S.A., 113, 4266–4271, 2016.

Song, S., Wu, Y., Xu, J., et al.: Black carbon at a roadside site in Beijing: Temporal variations and relationships with carbon monoxide and particle number size distribution, Atmos. Environ., 77, 213–221, 2013.

Wang, Q. Y., Schwarz, J. P., Cao, J. J., Gao, R. S., Fahey, D. W., Hu, T. F., Huang, R. J., Han, Y. M., and Shen, Z. X.: Black carbon aerosol characterization in a remote area of Qinghai–Tibetan Plateau, western China, Sci. Total Environ., 479–480, 151–158, 2014.

Wang, Q. Y., Liu, S. X., Zhou, Y. Q., Cao, J. J., Han, Y. M., Ni, H. Y., Zhang, N. N., and Huang, R. J.: Characteristics of Black Carbon Aerosol during the Chinese Lunar Year and Weekdays in Xi'an, China, Atmosphere, 6, 195–208, 2015.

Wang, Q. Y., Huang, R. J., Cao, J. J., et al.: Contribution of regional transport to the black carbon aerosol during winter haze period in Beijing, Atmos. Environ., 132, 11–18, 2016a.

Wang, Q. Y., Huang, R. J., Zhao, Z. Z., Cao, J. J., Ni, H. Y., Tie, X. X., Zhao, S. Y., Su, X. L., Han, Y. M., Shen, Z. X., Wang, Y. C., Zhang, N. N., Zhou, Y. Q., and Corbin, J. C.: Physicochemical characteristics of black carbon aerosol and its radiative impact in a polluted urban area of China, J. Geophys. Res. Atmos., 121, doi:10.1002/2016JD024748, 2016b.

Wu, Y. F., Zhang, R. J., Tian, P., et al..: Effect of ambient humidity on the light absorption amplification of black carbon in Beijing during January 2013, Atmos. Environ., 124, 217–223, 2016.

Yu, H., and Yu, J. Z.: Modal characteristics of elemental and organic carbon in an urban location in Guangzhou, China, Aerosol Sci. Technol., 43, 1108–1118, 2009.

Yu, H., Wu, C., Wu, D., and Yu, J. Z.: Size distributions of elemental carbon and its contribution to light extinction in urban and rural locations in the Pearl River Delta region, China, Atmos. Chem. Phys., 10, 5107–5119, 2010.

Zhang, Y. L., Huang, R. J., El Haddad, I., et al.: Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013, Atmos. Chem. Phys., 15, 1299–1312, 2015.

Marked-up manuscript version (with blue color)

Size distribution and source of black carbon aerosol in urban Beijing during winter haze episodes

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Abstract

Black carbon (BC) has important impact on climate and environment due to its light absorption ability, which greatly depends on its physicochemical properties including morphology, size and mixing state. The size distribution of the refractory BC (rBC) was investigated in urban Beijing during the late winter of 2014 with frequent haze events, through analysis of measurements obtained using a single particle soot photometer (SP2). By assuming void-free rBC with a density of 1.8 g cm^{-3}, the mass of the rBC showed an approximately lognormal distribution as a function of the volume-equivalent diameter (*VED*), with a peak diameter of 213 nm. Larger *VED* values of the rBC were observed during polluted periods than clean days, implying an alteration in the rBC sources, as the size distribution of the rBC from a certain source was relative stable and *VED* of an individual rBC varied little once it was emitted into the atmosphere. The potential source contribution function analysis showed that air masses from the south to east of the observation site brought higher rBC loadings with more thick coatings and larger core sizes. The mean *VED* of the rBC presented a significant linear correlation with the number fraction of thickly coated rBC, extrapolating to be ~150 nm for the completely thinly/non coated rBC. It was considered as the typical mean *VED* of the rBC from local traffic sources in this study. Local traffic was estimated to contribute 35% to 100% of the hourly rBC mass concentration with a mean of 59% during the campaign. Lower local traffic contributions were observed during polluted periods, suggesting increasing contributions of other sources (e.g., coal combustion/biomass burning) to the rBC. Thus, the heavy pollution in Beijing was greatly influenced by other sources in addition to the local traffic.

Keywords: black carbon aerosol, size distribution, source, haze

1 Introduction

Black carbon (BC), the major light-absorbing chemical component in atmospheric aerosols, plays an important role in the radiative balance of the earth system through its direct effect of heating the lower atmosphere and indirect effect of affecting cloud properties (Ramanathan and Carmichael, 2008). Although BC is hydrophobic, it can still act as cloud condensation nucleus when internally mixed with hydrophilic chemical compounds (Zhang et al., 2008a), and thus indirectly affect cloud properties and associated radiative budget (Ramanathan et al., 2001). BC aerosols thus have a great impact on regional and global climate and weather (Menon et al., 2002; Ramanathan and Carmichael, 2008; Ding et al., 2013; Liao et al., 2015; Huang et al., 2016). BC can also increase atmospheric stability by its heating effect in the lower troposphere and cooling role at the surface (Wang et al., 2013), which in turn suppresses the diffusion of pollutants, deteriorates air quality, and enhances haze weather intensity (Ding et al., 2016). However, quantifying BC's impact on radiative forcing and environment is challenging and has large uncertainties because of the large variations in its concentration and physicochemical properties (IPCC, 2013). The light absorption of BC highly depends on its size distribution and morphology. Mie calculations for hypothetical BC spheres show that the mass absorption cross-sections reach their peaks at a diameter of ~150 nm and then decrease sharply with further increases in size (see Fig. 4 in Bond and Bergstrom, 2006). However, atmospheric BC particles apparently consist of aggregates of small primary spherules ~15 to 60 nm in diameter (Alexander et al., 2008; Zhang et al., 2008a). They are chain agglomerates when freshly emitted from the combustion sources resulting in increasing mass normalized absorption with the particle mobility size (Khalizov et al., 2009). These fresh BC particles are quickly coated by other aerosol components in the atmosphere, leading to the collapse of the chain agglomerates into more compact BC cores (Zhang et al., 2008a). An alteration in the morphology of BC due to a thin coating causes competition between light absorption enhancement and decline, resulting in little variation in the absorption efficiency (Wang et al., 2013; Peng et al., 2016). Subsequently, the thickened coating of the scattering shell enwrapping the compact BC cores enhances the light absorption

of BC by the lensing effect, although the upper limit of the enhanced amplitude varied among different studies (e.g., Schnaiter et al., 2005; Shiraiwa et al., 2010; Khalizov et al., 2009; Peng et al., 2016).

With its rapid economic development, China has been suffering from heavy air pollution (Yin and Wang, 2016). Annual BC emissions to the atmosphere in China are very high, accounting for approximately half of the total emissions in Asia and one-fifth globally (Qin and Xie, 2012). Existing studies on ambient BC mostly focused on its mass concentrations (e.g., Cao et al., 2007; Zhang et al., 2008b), and little is known about its physicochemical properties, including size, morphology, and mixing state (e.g., Huang and Yu, 2008; Cheng et al., 2012), mainly due to the limitations of the measurement methodology. A traditional approach determining BC size distribution is through analyzing the BC mass of size-segregated aerosol samples (Huang and Yu, 2008; Yu et al., 2010), which provides size information of BC-containing particles because BC particles are frequently internally mixed with other aerosol components in the atmosphere (Shiraiwa et al., 2007; Schwarz et al., 2008).The time resolution in this approach was typically from hours to days. In the most recent decade, a novel analyzer, single particle soot photometer (SP2), has been developed, which can measure mass and size of the refractory BC (rBC) in high time resolution (Stephens et al., 2003; Schwarz et al., 2006). The mixing state of rBC particles can also be derived from the measurement of SP2 (Gao et al., 2007; Moteki and Kondo, 2007, 2008; Laborde et al., 2012). Measurements of the sizes and mixing states of rBC based on this technology has been limited to a few regions in China (e.g., Huang et al., 2012; Wang et al., 2014a, 2015a; Wu et al., 2016; Gong et al., 2016), as the SP2 is very expensive and its performance is limited (Gysel et al., 2012; Liggio et al., 2012). It should be noted that the sizes of rBC reported by SP2 are generally mass-equivalent diameters rather than mobility- or aerodynamic-based ones, which are determined on the basis of the mass measurements of individual rBC-containing particles. Thus, they are independent of the morphology or mixing.

Although the physicochemical properties of BC in the atmosphere are greatly diverse, its mass-equivalent sizes should vary little during their typical lifetime in the

atmosphere (~1 week) since BC itself is chemically inert under ambient conditions. In other words, the mass-size of a BC particle is independent of its morphology and mixing state, although coating with other components will reduce its mobility diameter and enlarge the size of the mixed particle in which the BC is embedded. As it is a byproduct of the incomplete combustion of fossil fuels and biomass, the BC size should be highly dependent on the emission sources, including fuel type and combustion condition. Based on the measurement of SP2, Liu et al. (2014) showed smaller sizes of the rBC cores from traffic than those from solid fuel sources and attributed the rBC concentrations from the two dominant sources accordingly. The rBC sizes measured at rural or remote sites were considerably larger than those measured at urban sites (Huang et al., 2012; Schwarz et al., 2013), implying that smaller sizes of rBC are emitted from traffic sources. Combining the measurement of SP2 and the chemical source apportionment of daily $PM_{2.5}$ samples, Wang et al. (2016) showed that the rBC from biomass burning and coal combustion had larger mass-equivalent diameter than that from traffic.

Influenced by the local emissions (e.g., traffic exhaust) as well as regional transport of air pollutants from the surrounding heavily polluted areas, the physicochemical properties of ambient BC aerosols in urban Beijing are highly varied. In this study, the mass-equivalent size distributions of rBC were first revealed in urban Beijing based on the SP2 measurement during a wintertime in 2014 when haze occurred frequently. The variations in the rBC size were also investigated, accompanied by an analysis of its relation with aerosol chemical composition and its potential source contributions. In the present study, a novel approach was employed to evaluate the contribution of local traffic to the rBC concentration based on the measured rBC sizes and reasonable assumptions including a deductive mean diameter of rBC from local traffic and relatively stable rBC sizes in the air masses transported over certain regions.

2 Methodology

In situ measurements of rBC were conducted using a SP2 (Droplet Measurement Technology, Inc., Boulder, CO, USA) on the rooftop (approximately 8 m above ground

level) of an experimental building at the Tower Division of the Institute of Atmospheric Physics, Chinese Academy of Sciences (39°58'N, 116°22'E), during a late winter period from 24 February to 15 March 2014 before the residential heating season ended. The SP2 directly detects the incandescent intensity of an individual rBC-containing particle when it passes through an intra-cavity Nd:YAG laser beam with a Gaussian distribution (Schwarz et al., 2006). The incandescent intensity is converted to the mass of rBC based on the calibration of incandescent signals of size-selected soot standards performed pre/post-sampling. In this study, the Aquadag (Acheson, Inc., USA) was used as a reference rBC and size-selected by a scanning mobility particle sizer spectrometer (SMPS; TSI, Inc., Shoreview, MN, USA) for calibration. Compared to the ambient rBC, it is more sensitive to the incandescence signal. Thus, a scaling factor of 0.75 is employed with the calibration curve to induce more reliable rBC mass determinations (Baumgardner et al., 2012; Laborde et al., 2012). Moreover, an approximately 10% underestimation of the SP2-derived bulk rBC mass concentration due to the detection limitations outside the rBC mass range of ~0.3–120 fg was considered (Wang et al., 2014a, 2015a). The total uncertainty in the rBC mass determination was ~25%, including the uncertainties inherent in the mass calibration, flow measurement and estimation of BC masses beyond the SP2 detection range (Wu et al., 2016). The scattering signal is synchronously detected by the SP2 and used to determine the optical size of a single particle (Gao et al., 2007; Laborde et al., 2012). In this study, the scattering signal was employed to distinguish the mixing state of rBC-containing particles. A traditional method based on the delay time between the incandescent and scattering peaks was utilized to distinguish the rBC cores with and without a thick coating (Schwarz et al., 2006; Moteki and Kondo, 2007; Wang et al., 2014a; Wu et al., 2016). The rBC-containing particles were defined as either thickly coated or uncoated/thinly coated according to the distribution of detected lag times, which was bimodal and had a local minimum at 2 μs (Fig. S1 in the supplemental files). We defined the rBC particles as thickly coated if the lag times were longer than 2 μs. On this basis, the number fraction of thickly coated rBC (NF_{coated}), defined as the ratio of the number of thickly-coated rBC particles to that of all detectable rBC particles, was

calculated to characterize the relative mixing extent of the BC aerosols in different ambient samples. A similar measurement was conducted in January 2013, and more details of the experimental setup and data process can be found in Wu et al. (2016).

Samples of $PM_{2.5}$ were collected twice a day during this campaign, each lasting for twelve hours. The chemical contents including organic carbon (OC), elemental carbon (EC), water-soluble ions (e.g., SO_4^{2-}, NO_3^-, and NH_4^+) and trace elements were analyzed in the laboratory, as presented in detail by Lin et al. (2016).

3 Results and Discussion

3.1 Size distribution of rBC and its variation

As shown in Fig. 1, the mass of rBC ($dM/d\log D_p$) exhibited an approximately lognormal distribution as a function of the volume-equivalent diameter (*VED*) of void-free rBC, as has been commonly observed (e.g., Schwarz et al., 2006; Huang et al., 2012; Wang et al., 2016). The similar size distribution was also observed in our previous campaign in January 2013 (Fig. S2 in the supplemental files). A minor mode was also captured at large sizes (peaked at ~600 nm), only accounting for ~6% of the SP2-determined rBC masses. An analogous minor mode was previously observed at other sites in China. Huang et al. (2011) reported a minor peak with a diameter of ~690 nm at Kaiping, a rural site in the Pearl River Delta (PRD) region of China. Wang et al. (2014b) found a minor peak with a diameter of ~470–500 nm in a remote area of the Qinghai–Tibetan Plateau and considered it a likely feature of the rBC distribution of biofuel/open fire burning sources, which needs further verification using measurements of the size distributions at the emission sources. The peak diameter of the primary mode, with a value of 213 nm, during the campaign is well within the range (~150–230 nm) presented by previous studies conducted in different regions (Huang et al., 2012 and references therein). It should be noted that the density of the assumed void-free rBC was set to 1.8 g cm^{-3} in calculating the *VED* from the rBC masses measured in this study, which should result in larger *VED* values compared to those based on the density of 2.0 g cm^{-3} used in previous studies. If the density of 2.0 g cm^{-3} was employed, the peak diameter of the primary mode would be ~206 nm in this study. This value is very

close to those observed in urban areas throughout China, e.g., 210 nm in Shenzhen in South China (Huang et al., 2012), 205 nm in Xi'an in West China (Wang et al., 2015b), and ~200 nm in Shanghai in East China (Gong et al., 2016). The relatively similar mass-size distributions of rBC suggest that there were similar dominant emission sources in different urban regions in China, where vehicle exhaust was one of the important sources emitting rBC particles. Compared to those measured at rural sites in the PRD region in South China (e.g., 220–222 nm, Huang et al., 2011, 2012), the peak diameters of rBC in urban areas are significantly smaller. This might be related to the greater amounts of coal combustion and biomass burning around the rural sites (Huang et al., 2012). In contrast, the sizes of the rBC were much smaller in remote regions, e.g., with a peak diameter of ~175–188 nm in the Qinghai–Tibetan Plateau area (Wang et al., 2014b, 2015a). Wang et al. (2015a) attributed this smaller peak diameter value to the source and considered that biomass burning generated a small rBC with peak *VED* values in the range of ~187–193 nm. Another important reason for the smaller rBC measured in remote regions, in our opinion, is that more large rBC particles are deposited during their long-range transport to the observation site. Further research on the sizes of rBC from different sources is needed.

The mass-size distributions of rBC during a polluted day (25 February) and a clean one (4 March) are also compared in Fig. 1. The average mass concentrations of rBC (MC_{rBC}) were 7.6 μg m^{-3} and 0.4 μg m^{-3}, respectively, on the polluted and clean days. The size distribution of rBC during the polluted day is similar to that during the entire observation period, although a larger peak diameter was observed, with a value of 221 nm. In contrast, the peak diameter on the clean day is obviously smaller, with a value of 199 nm. The secondary mode cannot be well characterized on the clean day. As mentioned above, the mass-sizes of rBC emitted from a certain source change little during their lifetime in the atmosphere. Thus, the considerable discrepancy of the rBC sizes illustrates significant source alteration during the polluted period compared to that on a clean day. Sun et al. (2014) used the measurements of ACSM at an urban site in Beijing to show that the regional contribution to the BC exceeded 50% during heavily polluted periods in January 2013. Model simulation also revealed that regional transport

contributed an average of 56% to the $PM_{2.5}$ in Beijing in January 2013 when the hazes occurred frequently, and even higher during polluted periods (Li and Han, 2016). Accordingly, regional transport might play an important role in the increase in rBC sizes during polluted periods in urban Beijing. By comparison, traffic emissions should be the dominant source of rBC on the clean day, contributing to smaller rBC sizes.

The variation in the *VED* of the rBC is further investigated by comparing the mean *VED* value of rBC (VED_{rBC}) with the mass ratios of secondary inorganic components (i.e., ammonium sulfate, AS; ammonium nitrite, AN) to EC, a representation of the aerosol aging degree. Generally, the average VED_{rBC} positively correlated with AS/EC and AN/EC ratios with correlation coefficients of 0.63 ($p<0.01$) and 0.61 ($p<0.01$), respectively (Fig. 2a and 2b). Higher AS/EC and AN/EC ratios were observed in polluted samples, corresponding to higher VED_{rBC} during these periods.

It is interesting to note that the VED_{rBC} correlated more closely with AS/EC ratio than AN/EC, especially under a clean condition. The correlation coefficient between VED_{rBC} and AS/EC is 0.88 ($p<0.01$) during clean periods with $PM_{2.5}$ mass concentrations lower than 35 $\mu g\ m^{-3}$ (blue dots in Fig. 2), much higher than that between VED_{rBC} and AN/EC. By contrast, the NF_{coated} varied less with AS/EC during these periods (Fig. 2c). This means that a higher AS/EC had less effect on the fraction of thickly coated rBC during these clean periods but was related to larger rBC sizes, which were highly dependent on the emission sources. In other words, higher AS/EC values might indicate an increasing contribution of sources producing larger rBC other than traffic, as sulfur is one of the major trace elements of coal combustion but not of traffic (Zhang et al., 2013; Wang et al., 2016). On the other hand, NF_{coated} was highly related to AN/EC, with a correlation coefficient of 0.81 ($p<0.01$) during the clean periods (Fig. 2d). Even considering the entire samples, the correlation coefficient between NF_{coated} and AN/EC was as high as 0.81 ($p<0.01$), much higher than that (0.65, $p<0.01$) between NF_{coated} and AS/EC. This implies that the mixing state of rBC is much sensitive to AN/EC in urban Beijing, especially during the clean periods. The secondary formation of AN might play an important role in the coating processes of rBC but have a negligible effect on the core size of the rBC.

3.2 Potential source contribution to rBC mass and size

The potential source contribution function (PSCF) analysis based on hourly resolved 48-h backward trajectories arriving at the observation site 100 m above ground level was performed using TrajStat software (Wang et al., 2009). The threshold of the PSCF analysis was set to the mean value of each variable. A weight function on the gridded PSCF values was employed on those cells having few trajectory endpoints (Wang et al., 2006). Generally, the areas east and south of the observation site had the largest number of potential source regions of high rBC concentrations, with weighted PSCF (WPSCF) values of MC_{rBC} larger than 0.7 (Fig. 3a). Previous studies showed that Hebei province, on the southern and eastern borders of Beijing, was a major contributor to pollutants in Beijing, as its industrial activities are intense (Zhang et al., 2013). The high coal consumption associated with the heavy industrial activities and residential heating in the cold season should be an important source of high atmospheric rBC loading in these areas. Similarly, the distribution of the WPSCF values of VED_{rBC} shows that the eastern and southern regions are also correlated with large VED_{rBC} values (Fig. 3b). This implies that the pollution sources in these regions, e.g. heavy industrial activities and residential heating, tend to produce highly concentrated rBC-containing particles with large rBC core sizes. The source apportionment of rBC aerosols in London based on in situ SP2 measurements showed that rBC-containing particles from solid fuel sources (coal combustion and biomass burning) had significantly larger rBC cores than those from traffic (Liu et al., 2014). Thus, the high WPSCF values of MC_{rBC} and VED_{rBC} in the east and south might highly correlate to anthropogenic coal/biomass combustion in these regions.

The spatial distribution of the WPSCF values of NF_{coated} is shown in Fig. 3c. Associated with the aging processes that increase the thickly coating states of rBC-containing particles through heterogeneous reactions, the WPSCF values of NF_{coated} are generally high in the areas surrounding the observation site. It should be noted that higher WPSCF values of NF_{coated} (> 0.7) dominate in the east to south. In addition to the transport of thickly coated BC particles from these regions, aging processes of

locally emitted BC particles (e.g., from traffic sources) under the southerly winds dominant condition, in which the relative humidity (RH) is high (Zhang et al., 2015; Zheng et al., 2015), also increase the fraction of thickly coated rBC (Wu et al., 2016). Although northerly/northwesterly winds also blow aged rBC-containing particles with thick coatings, the larger amounts of non-/thinly coated BC particles from local sources during these periods diminished the WPSCF values of NF_{coated} in the north to west regions of the observation site. The low RH and strong winds from these directions are unfavorable to the coating processes of locally emitted fresh rBC particles.

The VED_{coated}, defined as the *VED* of those thickly coated rBC cores, shows a dispersive WPSCF distribution (Fig. 3d). Compared to the distribution of VED_{rBC} with high WPSCF values that dominate in the east to south, high WPSCF values of VED_{coated} are located in the northern pathway of air masses being transported to the observation site as well. This implies that the regional transport of air masses brings large rBC, no matter which direction it comes from. Dominated by the locally emitted small rBC, the WPSCF values of VED_{rBC} are low in the northern region. It further illuminates that local sources such as traffic emit small rBC, while regional transport brings in large rBC. On the basis of the large discrepancy in rBC sizes between local traffic and regional transport generated particles, it is possible to extract the contribution of local traffic emissions from the mixed rBC sources.

4 Discussion

4.1 Relationship between rBC size and mixing state

As large rBC sizes are usually accompanied by significant contributions of regional transport, which also lead to a high fraction of thickly coated rBC, the VED_{rBC} is directly compared with the NF_{coated} as shown in Fig. 4. The two-dimensional histogram of the 5-min average VED_{rBC} and NF_{coated} presents a significant linear correlation between the two variables. It is characterized more clearly by the variation in the mean VED_{rBC} values averaged in increased NF_{coated} bins with a resolution of 2% (magenta circles in Fig. 4). The observed minimum value of the 5-min NF_{coated} is ~10%, representing that there is little pure external mixing of rBC in the atmosphere, even for

short periods. However, an assumed mean *VED* of completely non/thinly coated rBC is extrapolated from the linear curve to NF_{coated} with a value of 0% (i.e., the *y*-intercept value). This inferred *VED*, with a value of ~150 nm, might be considered as the typical mean *VED* of freshly emitted rBC from vehicle exhaust, which has little coating (Zhang et al., 2008a; Peng et al., 2016). We are surprised to find that the linear relationship between VED_{rBC} and NF_{coated} seems to be common, as was also found in another campaign conducted in January 2013 (Wu et al., 2016) (gray circles in Fig. 4). More observations are needed to further verify this relationship. According to the results presented in this study, a mean *VED* of ~150 nm is legitimately accepted as the typical SP2-determined mean *VED* of fresh rBC from local traffic sources. Size-segregated aerosol samples also revealed a mode peaked at ~150 nm in aerodynamic diameter for elemental carbon (EC) in urban Guangzhou, a megacity in PRD region, attributing to the traffic emissions (Yu and Yu, 2009; Yu et al., 2010). A second mode at diameter of ~400 nm was also observed and was also thought to be associated to the traffic emission (Yu and Yu, 2009). In contrast, only the smaller EC mode with peak diameter in the range of 100–200 nm was observed from traffic sources in urban areas of developed counties (Allen et al., 2001; Kleeman et al., 2000). To date, no literature is available for comparison with the case in Beijing because of the limitation in characterizing the size distribution of EC at the small mode (e.g., < 400 nm). Considering the stringent fuel and vehicle emission standards implemented in Beijing, the *VED* of ~150 nm for local traffic source is reasonable, although further measurement studies are still needed to verify this. As mentioned above, the *VED* of certain rBC varies little once it is emitted to the atmosphere. Thus, the mean *VED* with a value of ~150 nm was employed in this study as the representative of the rBC size from local traffic.

The variation in VED_{coated} with NF_{coated} is also shown (magenta triangles in Fig. 4). It is interesting to find that, compared to VED_{rBC}, VED_{coated} presents a fluctuant variation as NF_{coated} increases. The larger VED_{coated} at lower NF_{coated} is comprehensible because regionally transported large rBC dominates in the thickly coated rBC particles, and the small rBC from local traffic is mainly externally mixed with other aerosol components at this stage. As the NF_{coated} increases from 10–20% to 30–40%, the mean

VED_{coated} gradually decreases from ~200 nm to ~190 nm. This implies that some small rBC (e.g., rBC from local traffic) contributes a considerable portion of the thickly coated rBC particles at this stage. In addition to the influence of the emission sources on the rBC size, this decrease in VED_{coated} can also be explained by the contamination of the local traffic emitted small rBC into the thickly coated rBC particles through atmospheric aging processes (i.e., coating with other components). It should be noted that the VED_{rBC} sustained increases at this stage, implying that other sources besides the local traffic also brought large rBC at the same time. This is because if the increase in NF_{coated} only results from the coating processes of the local traffic emitted rBC, the *VED* of the entire rBC (i.e., VED_{rBC}) should vary little. The VED_{coated} increases significantly when NF_{coated} exceeds 40%, suggesting that regional transport dominates at this stage, bringing a large amount of thickly coated rBC particles with a large rBC core. Meanwhile, the mean MC_{rBC} increases dramatically from 1.3 μg m^{-3} to 5.0 μg m^{-3} when NF_{coated} increases from 30% to 50%, further confirming the great contribution of regional transport to the rBC at this stage. By comparison, the mean rBC concentration varies in a small range of 0.8–1.4 μg m^{-3} when NF_{coated} is lower than 30%. The observation from the campaign of 2013 showed a similar variation in VED_{coated} against NF_{coated} (gray triangles in Fig. 4).

4.2 Extracting the local traffic contribution to rBC

As VED_{rBC} with a value of ~150 nm is expected to be the typical mean *VED* of the local traffic emitted rBC and varies little in the atmosphere, it provides the possibility of extracting the contribution of the local traffic to the rBC from the total rBC mass concentration according to the variation in VED_{rBC}. However, the typical mean *VED* of rBC from other sources, such as coal combustion and biomass burning, is difficult to identify. It depends on many factors including fuel type and combustion condition. In this study, a simple assumption was employed to identify the typical mean *VED* of rBC from other sources besides local traffic according to where the air masses came from. During a short period when the source emissions were relatively stable, the rBC from a certain direction was assumed to have a certain mean *VED*, no matter from which

source it is emitted. Thus, a cluster analysis was performed on the 48-h backward trajectories that arrived at the observation site. Five clusters were identified using TrajStat software according to the total spatial variation in the cluster numbers (as shown in Fig. S3). As the rBC tends to be thickly coated in the regionally transported air masses, the mean *VED* of the rBC from sources other than local traffic was derived from the values of VED_{coated}. The local traffic emitted small rBC can also become thickly coated through aging processes in the atmosphere, so a further assumption is employed to consider the *VED* of rBC from other sources equal to the mean value of the upper 5% percentile of VED_{coated} in each cluster. Five typical mean *VED*s of rBC from sources other than local traffic were identified, with values in the range of 195.5–208.3 nm (Fig. S3). Such simple assumptions might induce large uncertainties in the absolute contribution of the local traffic to the rBC, but it should well reflect the variation in the traffic contribution.

Using a multiple linear regression to VED_{rBC}, the hourly-resolved traffic contribution to the rBC was extracted on the basis of the derived *VED* of the rBC from local traffic and other sources. The mass fraction of the traffic-induced rBC ($MF_{traffic}$) is shown in Fig. 5a (red line). During this campaign, approximately 35% to 100% of the hourly MC_{rBC} is attributed to local traffic emissions, with a mean of 59%. Based on a multiple linear regression analysis of the contributions of the three dominant factors (i.e., traffic, coal combustion and biomass burning) to the rBC derived from the chemical source apportionment of the daily $PM_{2.5}$ samples, Wang et al. (2016) showed a slightly lower contribution of the traffic to the rBC in urban Xi'an, with a mean of 46% and a daily contribution in the range of 0.8 to 77.2%. Since entirely different methods were employed in addition to the different locations, the resolved traffic contribution to the rBC should not be compared absolutely. However, the relatively lower MC_{rBC} in this study (with a mean of 2.8 μg m^{-3} compared to 8.0 μg m^{-3}) might partly interpret the slightly higher contribution of traffic, as a lower MC_{rBC} is usually accompanied by a higher contribution of the local traffic. It is clear that $MF_{traffic}$ is negatively correlated with MC_{rBC}, with the correlation coefficient as high as -0.84 ($p<0.01$) between the daily moving averaged $MF_{traffic}$ and MC_{rBC} (Fig. 5a). This means

that the traffic contribution to the rBC decreased significantly during the polluted periods when the rBC loading increased. In other words, the rBC from other sources such as coal combustion and biomass burning played an increased role in these polluted periods. This implies that the high MC_{rBC} in urban Beijing was not only due to the accumulation of the local traffic emissions during stable synoptic conditions but also attributed to the overlaying pollution from other sources.

The diurnal variations of the decomposed MC_{rBC} from local traffic and other sources are shown in Fig. 5b and 5c, respectively. A common diurnal variation in MC_{rBC} with high values during the nighttime and low ones in the daytime is shown for both the traffic and other sources produced rBC, suggesting the important impact of the mixing layer height on the surface MC_{rBC}. A high mixing layer in the daytime, especially in the afternoon, favors the diffusion of the pollutants, leading to a low value of MC_{rBC}. A low mixing layer in the nighttime suppresses the diffusion of pollutants, resulting in a high value of MC_{rBC}. It is noted that a significant peak MC_{rBC} of local traffic was observed in the early morning (05:00–06:00 local time). Moreover, the increase in the local traffic related MC_{rBC} occurs earlier than that of other sources in the evening. It corresponds well to the increased traffic contribution in the morning and evening rush hours. Although the traffic flow showed a significant decrease in the nighttime, a dramatic increase in the flow of heavy-duty diesel vehicles was observed due to Beijing's traffic regulation (Song et al., 2013). These vehicles have much higher emission factors of BC (~15–30 times) than light-duty gasoline ones, and thus play a non-negligible role in the high MC_{rBC} values around midnight. Generally, the diurnal variation of MC_{rBC} verifies to some degree the rationality of the method we employed to distinguish the contribution of the local traffic emission from that of other sources.

5 Summary and Concluding Remarks

An approximate lognormal size distribution of the rBC in volume-equivalent diameter was observed in urban Beijing during a polluted winter in 2014 based on measurements using a SP2. The peak diameter was 213 nm, assuming void-free rBC with a density of 1.8 g cm^{-3}, which is close to the values observed in other urban areas

in China. The measured sizes of the rBC were considerably larger during the polluted period than clean period, implying a source variation of the rBC. The mean VED_{rBC} positively correlated with the ratios of secondary inorganic aerosols (including AS and AN) to EC, especially the ratio of AS/EC under a clean condition. This implies that the rBC sizes are highly related to the emission sources because sulfur is one of the major trace elements in coal combustion, while little is emitted from traffic. By comparison, the mean NF_{coated} correlated more with AN/EC, implying the important effect of the secondary formation of nitrate on the rBC mixing state. The PSCF analysis showed that regional transport from the east to south of Beijing was a major source of high rBC loading in Beijing and accompanied by a large VED_{rBC} and high NF_{coated}.

A significant positive correlation existed between VED_{rBC} and NF_{coated}, inferring the typical mean *VED* of the rBC from local traffic, with a value of 150 nm. Based on the inferred *VED* and further reasonable assumptions, the local traffic contribution to the rBC was extracted. Local traffic emissions played an important role in the rBC loading in urban Beijing and contributed 59% of the MC_{rBC} on campaign average. However, its contribution decreased significantly in the polluted period compared to the clean period. A significant negative correlation is found between the daily moving average MC_{rBC} and $MF_{traffic}$ with a coefficient of -0.87. A similar diurnal variation in the decomposed MC_{rBC} associated with local traffic and other sources was observed with high values in the nighttime and low in the daytime. However, a significant increase in traffic MC_{rBC} was observed in the early morning and evening, indicating the increased contribution of local traffic emissions. Despite potential large uncertainties in the estimated contribution from the local traffic to rBC, due to the many assumptions employed, its relative variation is clearly demonstrated. Further research measuring sizes of rBC directly from various sources, including coal combustion, biomass burning and traffic exhaust, is needed to validate the findings presented in this study. This work provides a relatively simple but novel method to extract the contribution of the local traffic to the rBC on the basis of the size measurement of the rBC in atmosphere, which could enhance source apportionment research in urban Beijing and elsewhere air pollution is severe.

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References:

Alexander, D. T. L., Crozier, P. A., and Anderson, J. R.: Brown carbon spheres in East Asian outflow and their optical properties, Sciences, 321, 833–836, 2008.

Allen, J. O., Mayo, P. R., Hughes, L. S., Salmon, L. G., and Cass, G. R.: Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel, Environ. Sci. Technol., 35, 4189–4197, 2001.

Baumgardner, D., Popovicheva, O., Allan, J., Bernardoni, V., Cao, J., Cavalli, F., Cozic, J., Diapouli, E., Eleftheiadis, K., Genberg, P. J., Gonzalez, C., Gysel, M., John, A., Kirchstetter, T. W., Kuhlbusch, T. A. J., Laborde, M., Lack, D., Müller, T., Niessner, R., Petzold, A., Piazzalunga, A., Putaud, J. P., Schwarz, J., Sheridan, P., Surramanian, R., Swietlicki, E., Valli, G., Vecchi, R., and Viana, M.: Soot reference materials for instrument calibration and intercomparisons: a workshop summary with recommendations, Atmos. Meas. Tech., 5, 1869–1887, 2012.

Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, Aerosol Sci. Technol., 40, 27–67, 2006.

Cao, J. J., Lee, S. C., Chow, J. C., Watson, J. G., Ho, K. F., Zhang, R. J., Jin, Z. D., Shen, Z. X., Chen, G. C., Kang, Y. M., Zou, S. C., Zhang, L. Z., Qi, S. H., Dai, M. H., Cheng, Y., and Hu, K.: Spatial and seasonal distributions of carbonaceous aerosols over China, J. Geophys. Res., 112, D22S11, doi:10.1029/2006JD008205, 2007.

Cheng, Y. F., Su, H., Rose, D., Gunthe, S. S., Berghof, M., Wehner, B., Achtert, P., Nowak, A., Takegawa, N., Kondo, Y., Shiraiwa, M., Gong, Y. G., Shao, M., Hu, M., Zhu, T., Zhang, Y. H., Carmichael, G. R., Wiedensohler, A., Andreae, M. O., and Pöschl, U.: Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization, Atmos. Chem. Phys., 12, 4477–4491, 2012.

Ding, A. J., Fu, C. B., Yang, X. Q., Sun, J. N., Petäjä, T., Kerminen, V., Wang, T., Xie, Y. N., Herrmann, E., Zheng, L., Nie, W., Liu, Q., Wei X., and Kulmala, M.: Intense atmospheric pollution modifies weather: a case of mixed biomass burning wither fossil fuel combustion pollution in the eastern China, Atmos. Chem. Phys., 13, 10545-10554, 2013.

Ding, A. J., Huang, X., Nie, W., Sun, J. N., Kerminen, V.-M., Petäjä, T., Su, H., Cheng, Y. F., Yang, X.-Q., Wang, M. H., Chi, X. G., Wang, J. P., Virkkula, A., Guo, W. D., Yuan, J., Wang, S. Y., Zhang, R. J., Wu, Y. F., Song, Y., Zhu, T., Zilitinkevich, S., Kulmala, M., and Fu, C. B.: Enhanced haze pollution by black carbon in megacities in China, Geophys. Res. Lett., 43, 2873–2879, 2016.

Gao, R. S., Schwarz, J. P., Kelly, K. K., Fahey, D. W., Watts, L. A., Thompson, T. L., Spackman, J. R., Slowik, J. G., Cross, E. S., Han, J.-H., Davidovits, P., Onasch, T. B., and Worsnop, D. R.: A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer, Aerosol Sci. Technol., 41, 125–135, 2007.

Gong, X. D., Zhang, C., Chen, H., Nizkorodov, S. A., Chen, J. M., and Yang, X.: Size distribution and mixing state of black carbon particles during a heavy air pollution episode in Shanghai, Atmos. Chem. Phys., 16, 5399–5411, 2016.

Gysel, M., Laborde, M., Mensah, A., Corbin, J., Keller, A., Kim, J., Petzold, A., and Sierau, B.: Technical note: The single particle soot photometer fails to reliably detect PALAS soot nanoparticles, Atmos. Meas. Tech., 5, 3099–3107, 2012.

Huang, X., Ding, A. J., Liu, L. X., Liu, Q., Ding, K., Niu, X. R., Nie, W., Xu, Z., Chi, X. G., Wang, M. H., Sun, J. N., Guo, W. D., and Fu, C. B.: Effects of aerosol-radiation interaction on

precipitation during biomass-burning season in East China, Atmos. Chem. Phys., 16, 10063–10082, 2016.

Huang, X. F., and Yu, J. Z.: Size distributions of elemental carbon in the atmosphere of a coastal urban area in South China: characteristics, evolution processes, and implications for the mixing state, Atmos. Chem. Phys., 8, 5843–5853, 2008.

Huang, X. F., Gao, R. S., Schwarz, J. P., He, L. Y., Fahey, D. W., Watts, L. A., McComiskey, A., Cooper, O. R., Sun, T. L., Zeng, L. W., Hu, M., and Zhang, Y. H.: Black carbon measurements in the Pearl River Delta region of China, J. Geophys. Res., 116, D12208, doi:10.1029/2010JD014933, 2011.

Huang, X. F., Sun, T. L., Zeng, L. W., Yu, G. H., and Luan, S. J.: Black carbon aerosol characterization in a coastal city in South China using a single particle soot photometer, Atmos. Environ., 51, 21–28, 2012.

IPCC, 2013. Summary for policymakers. In: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Khalizov, A. F., Xue, H. X., Wang, L., Zheng, J., and Zhang, R. Y.: Enhanced light absorption and scattering by carbon soot aerosol internally mixed with sulfuric acid, J. Phys. Chem. A, 113, 1066–1074, 2009.

Kleeman, M.J., Schauer, J. J., and Cass, G. R.: Size and composition distribution of fine particulate matter emitted from motor vehicles, Environ. Sci. Technol. 34(7), 1132–1142, 2000.

Laborde, M., Mertes, P., Zieger, P., Dommen, J., Baltensperger, U., and Gysel, M.: Sensitivity of the single particle soot photometer to different black carbon types, Atmos. Meas. Tech., 5, 1031–1043, 2012.

Li, J. W., and Han, Z. W.: A modeling study of severe winter haze events in Beijing and its neighboring regions, Atmos. Res., 170, 87–97, 2016.

Liao, H., and Shang, J. J.: Regional warming by black carbon and tropospheric ozone: a review of progresses and research challenges in China, J. Meteor. Res., 29, 525–545, 2015.

Liggio, J. Gordon, M., Smallwood, G., Li, S.-M., Stroud, C., Staebler, R., Lu, G., Lee, P., Taylor, B., and Brook, J. R.: Are emissions of black carbon from gasoline vehicles underestimated? Insights from near and on-road measurements, Environ. Sci. Technol., 46, 4819–4828, 2012.

Lin, Y.-C., Hsu, S.-C., Chou, C.-C.-K., Zhang, R. J., Wu, Y. F., Kao, S.-J., Luo, L., Huang, C.-H., Lin, S.-H., and Huang, Y.-T.: Wintertime haze deterioration in Beijing by industrial pollution deduced from trace metal fingerprints and enhanced health risk by heavy metals, Environ. Pollut., 208, 284–293, 2016.

Liu, D., Allan, J. D., Young, D. E., Coe, H., Beddows, D., Fleming, Z. L., Flynn, M. J., Gallagher, M. W., Harrison, R. M., Lee, J., Prevot, A. S. H., Taylor, J. W., Yin, J., Williams, P. I., and Zotter, P.: Size distribution, mixing state and source apportionment of black carbon aerosol in London during wintertime, Atmos. Chem. Phys., 14, 10061–10084, 2014.

Menon, S., Hansen, J., Nazarenko, L., and Luo, Y. F.: Climate effects of black carbon aerosols in China and India, Science, 297, 2250–2253, 2002.

Moteki, N., and Kondo, Y.: Effects of mixing state on black carbon measurements by laser-induced incandescence, Aerosol Sci. Technol., 41, 398–417, 2007.

Moteki, N., and Kondo, Y.: Method to measure time-dependent scattering cross sections of particles evaporating in a laser beam, J. Aerosol Sci., 39, 348–364, 2008.

Peng, J. F., Hu, M., Guo, S., Du, Z. F., Zheng, J., Shang, D. J., Zamora, M. L., Zeng, L. M., Shao, M., Wu, Y.-S., Zheng, J., Wang, Y., Glen, C. R., Collins, D. R., Molina, M. J., and Zhang, R. Y.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proc. Natl. Acad. Sci. U.S.A., 113, 4266–4271, 2016.

Qin, Y., and Xie, S. D.: Spatial and temporal variation of anthropogenic black carbon emissions in China for the period 1980–2009, Atmos. Chem. Phys., 12, 4825–4841, 2012.

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Aerosols, climate, and the hydrological cycle, Science, 294, 2119–2125, 2001.

Ramanathan, V., and Carmichael, G.: Global and regional climate changes due to black carbon, Nature Geosci., 1, 221–227, 2008.

Schnaiter, M., Linke, C., Möhler, O., Naumann, K. H., Saathoff, H., Wagner, R., Schurath, U., and Wehner, B.: Absorption amplification of black carbon internally mixed with secondary organic aerosol, J. Geophys. Res., 110, D19204, doi:10.1029/2005JD006046, 2005.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Darbeheshti, M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. Q., Loewenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, J. Geophys. Res., 111, D16207, doi:10.1029/2006JD007076, 2006.

Schwarz, J. P., Gao, R. S., Spackman, J. R., Watts, L. A., Thomson, D. S., Fahey, D. W., Ryerson, T. B., Peischl, J., Holloway, J. S., Trainer, M., Frost, G. J., Baynard, T., Lack, D. A., de Gouw, J. A., Warneke, C., and Del Negro, L. A.: Measurement of the mixing state, mass, and optical size of individual black carbon particles in urban and biomass burning emissions, Geophys. Res. Lett., 35, L13810, doi:10.1029/2008GL033968, 2008.

Schwarz, J. P., Gao, R. S., Perring, A. E., Spackman, J. R., and Fahey, D. W.: Black carbon aerosol size in snow, Sci. Rep., 3, 1356, doi:10.1038/srep01356, 2013.

Shiraiwa, M., Kondo, Y., Moteki, N., Takegawa, N., Miyazaki, Y., and Blake, D. R.: Evolution of mixing state of black carbon in polluted air from Tokyo, Geophys. Res. Lett., 34, L16803, doi:10.1029/2007GL029819, 2007.

Shiraiwa, M., Kondo, Y. Iwamoto, T., Kita, K.: Amplification of light absorption of black carbon by organic coating, Aerosol Sci. Technol., 44, 46–54, 2010.

Song, S., Wu, Y., Xu, J., Ohara, T., Hasegawa, S., Li. J., Yang, L., and Hao, J.: Black carbon at a roadside site in Beijing: Temporal variations and relationships with carbon monoxide and particle number size distribution, Atmos. Environ., 77, 213–221, 2013.

Stephens, M., Turner, N., and Sandberg, J.: Particle identification by laser-induced incandescence in a solid-state laser cavity, Appl. Opt., 42, 3726–3736, 2003.

Sun, Y. L., Jiang, Q., Wang, Z. F., Fu, P. Q., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, J. Geophys. Res. Atmos., 119, 4380–4398, 2014.

Wang, Q. Y., Huang, R. J., Cao, J. J., Han, Y. M., Wang, G. H., Li, G. H., Wang, Y. C., Dai, W. T., Zhang, R. J., and Zhou, Y. Q.: Mixing state of black carbon aerosol in a heavily polluted urban area of China: implications for light absorption enhancement, Aerosol Sci. Technol., 48, 689–

697, 2014a.

Wang, Q. Y., Schwarz, J. P., Cao, J. J., Gao, R. S., Fahey, D. W., Hu, T. F., Huang, R. J., Han, Y. M., and Shen, Z. X.: Black carbon aerosol characterization in a remote area of Qinghai–Tibetan Plateau, western China, Sci. Total Environ., 479–480, 151–158, 2014b.

Wang, Q. Y., Huang, R. J., Cao, J. J., Tie, X. X., Ni, H. Y., Zhou, Y. Q., Han, Y. M., Hu, T. F., Zhu, C. S., Feng, T., Li, N., and Li, J. D.: Black carbon aerosol in winter northeastern Qinghai–Tibetan Plateau, China: the source, mixing state and optical property, Atmos. Chem. Phys., 15, 13059–13069, 2015a.

Wang, Q. Y., Liu, S. X., Zhou, Y. Q., Cao, J. J., Han, Y. M., Ni, H. Y., Zhang, N. N., and Huang, R. J.: Characteristics of Black Carbon Aerosol during the Chinese Lunar Year and Weekdays in Xi'an, China, Atmosphere, 6, 195–208, 2015b.

Wang, Q. Y., Huang, R. J., Zhao, Z. Z., Cao, J. J., Ni, H. Y., Tie, X. X., Zhao, S. Y., Su, X. L., Han, Y. M., Shen, Z. X., Wang, Y. C., Zhang, N. N., Zhou, Y. Q., and Corbin, J. C.: Physicochemical characteristics of black carbon aerosol and its radiative impact in a polluted urban area of China, J. Geophys. Res. Atmos., 121, doi:10.1002/2016JD024748, 2016.

Wang, Y., Khalizov, A., Levy, M., and Zhang, R. Y.: New direction: light absorbing aerosols and their atmospheric impacts, Atmos. Environ., 81, 713–715, 2013.

Wang, Y. Q., Zhang, X. Y., and Arimoto, R.: The contribution from distant dust sources to the atmospheric particulate matter loadings at Xi'an, China during spring, Sci. Total Environ., 368, 875–883, 2006.

Wang, Y. Q., Zhang, X. Y., and Draxler, R. R.: TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environ. Modell. Softw., 24, 938–939, 2009.

Wu, Y. F., Zhang, R. J., Tian, P., Tao, J., Hsu, S.-C., Yan, P., Wang, Q. Y., Cao, J. J., Zhang, X. L., and Xia, X. A.: Effect of ambient humidity on the light absorption amplification of black carbon in Beijing during January 2013, Atmos. Environ., 124, 217–223, 2016.

Yin, Z. C., and Wang, H. J.: Seasonal prediction of winter haze days in the north central North China Plain, Atmos. Chem. Phys., 16, 14843–14852, 2016.

Yu, H., and Yu, J. Z.: Modal characteristics of elemental and organic carbon in an urban location in Guangzhou, China, Aerosol Sci. Technol., 43, 1108–1118, 2009.

Yu, H., Wu, C., Wu, D., and Yu, J. Z.: Size distributions of elemental carbon and its contribution to light extinction in urban and rural locations in the Pearl River Delta region, China, Atmos. Chem. Phys., 10, 5107–5119, 2010.

Zhang, Q., Quan, J. N., Tie, X. X., Li, X., Liu, Q., Gao, Y., and Zhao, D. L.: Effects of meteorology and secondary particle formation on visibility during heavy haze events in Beijing, China, Sci. Total Environ., 502, 578–584, 2015.

Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C.S.L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053–7074, 2013.

Zhang, R. Y., Khalizov, A. F., Pagels, J. Zhang, D., Xue, H. X., and McMurry, P. H.: Variability in morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing, Proc. Natl. Acad. Sci. U.S.A., 105, 10291–10296, 2008a.

Zhang, X. Y., Wang, Y. Q., Zhang, X., Guo, W., Gong, S. L.: Carbonaceous aerosol composition over various regions of China during 2006, J. Geophys. Res., 113, D14111,

doi:10.1029/2007JD009525, 2008b.

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl., U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos. Chem. Phys., 15, 2969–2983, 2015.

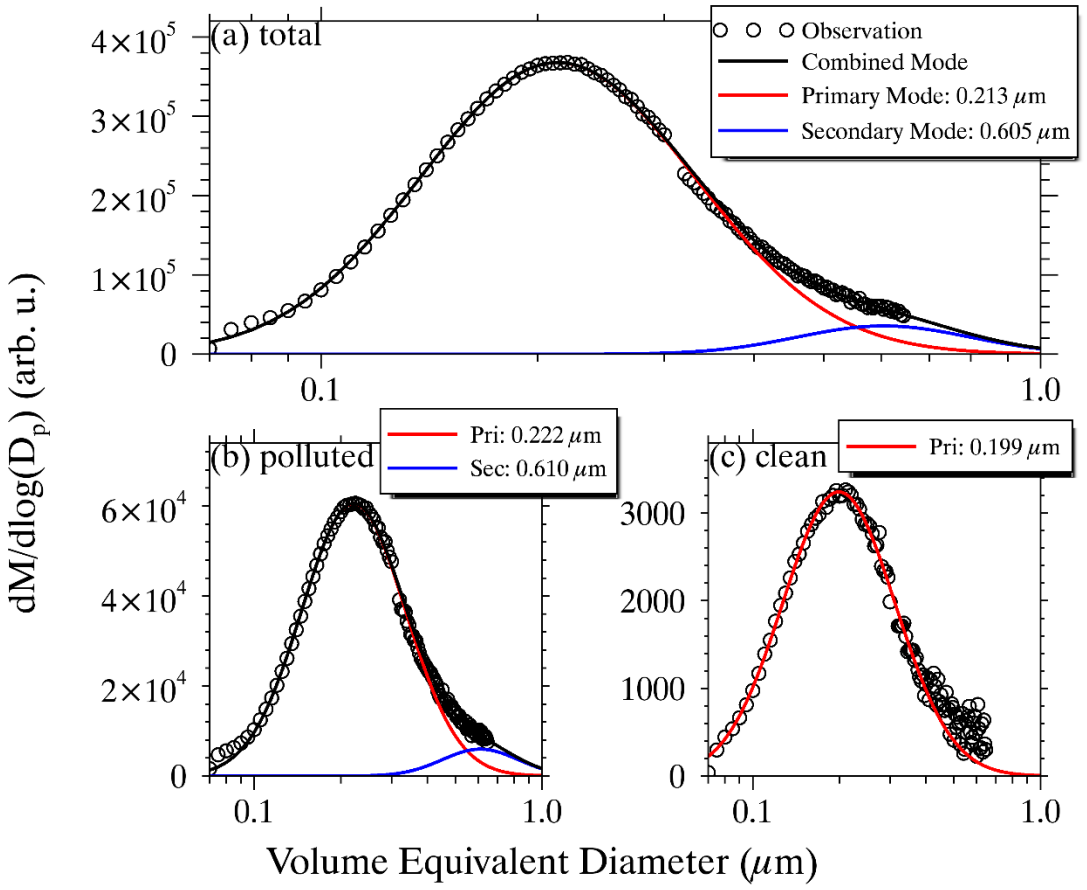

Fig. 1. Size distributions of rBC in volume-equivalent diameter during a campaign from 24 February to 15 March, 2014. The red and blue lines are the lognormal fittings to the primary and secondary modes, respectively, and the black ones correspond to the combined mode.

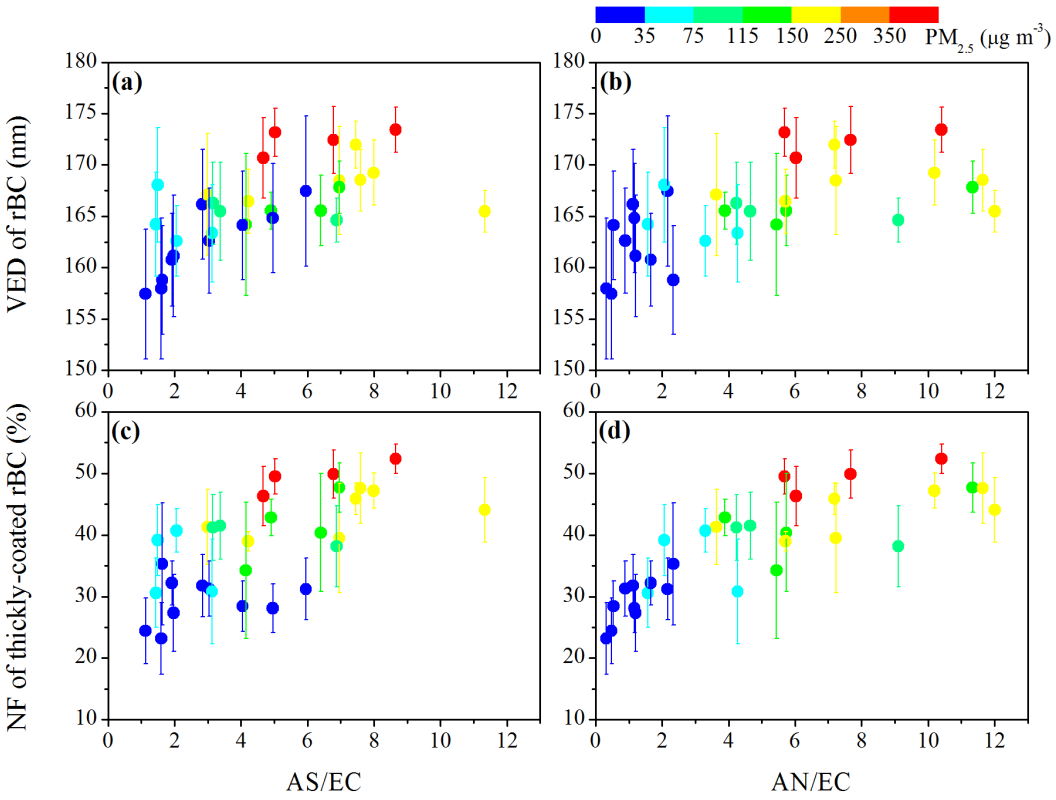

Fig. 2. Variation in the average volume-equivalent diameters of rBC (VED_{rBC}) as a function of the mass ratios of (a) ammonium sulfate (AS) and (b) ammonium nitrite (AN) to elemental carbon (EC). The same apply for (c) and (d), but for the number fraction of thickly coated rBC (NF_{coated}). The vertical bar denotes one standard deviation. The color scale represents the pollution levels defined as the $PM_{2.5}$ mass concentration according to the AQI standard of MEP of China.

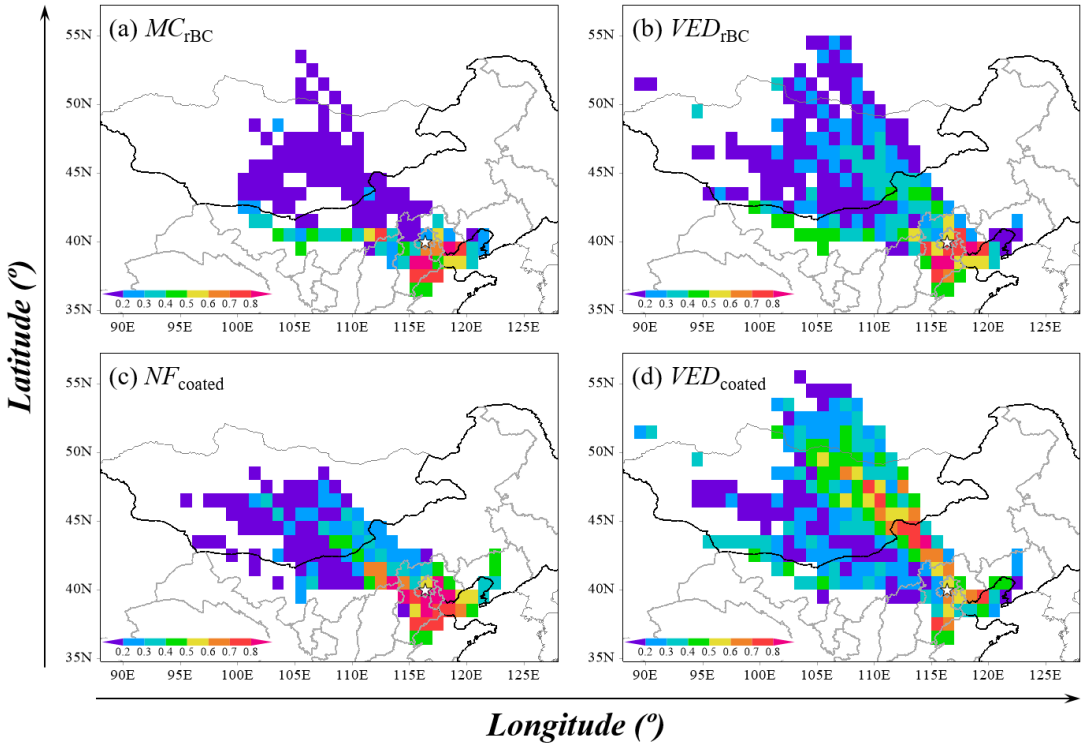

Fig. 3. Distributions of gridded (1°×1°) potential source contribution functions of (a) mass concentration (*MC*) and (b) volume equivalent diameter (*VED*) of rBC, and (c) number fraction (*NF*) and (d) *VED* of thickly coated rBC. The overlaid star symbol represents the geographical location of the observation site.

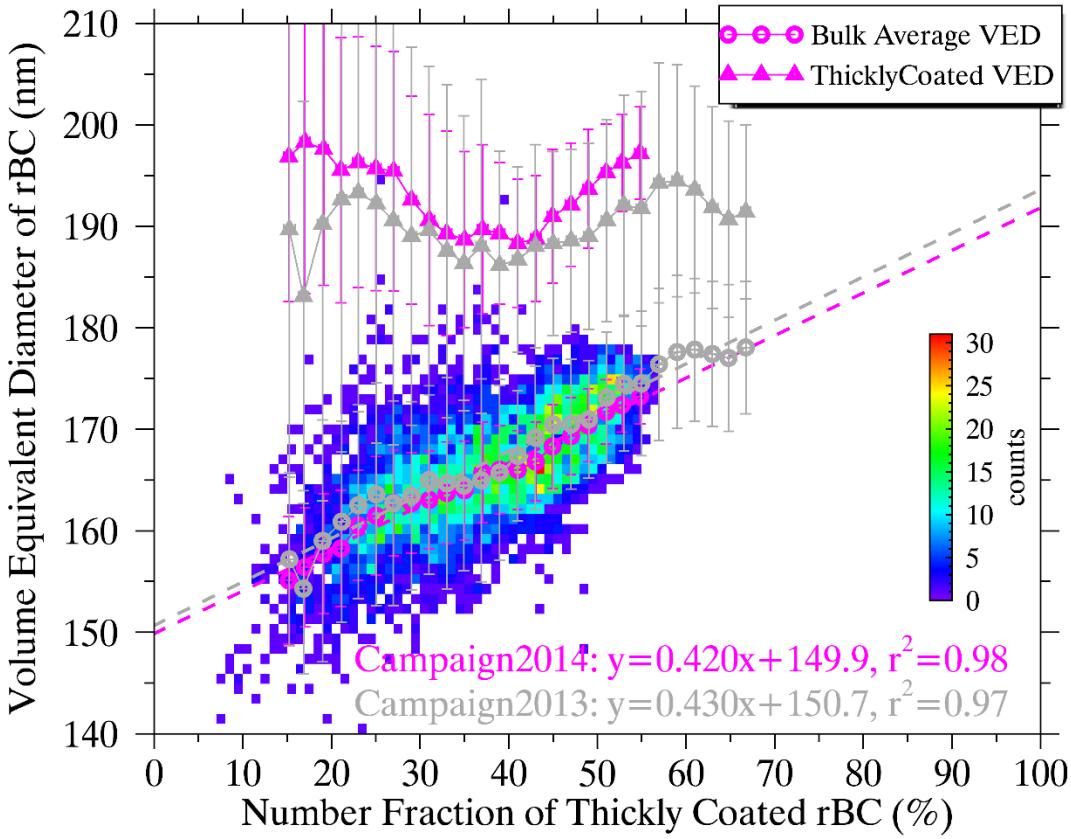

Fig. 4. Two-dimensional histogram of the 5-min average volume equivalent diameter of rBC (VED_{rBC}) against number fraction of thickly coated rBC (NF_{coated}) during the campaign in the late winter in 2014. The magenta circles and triangles with error bars represent the mean VED_{rBC} and VED of thickly-coated rBC (VED_{coated}) averaged in each NF_{coated} bin with a resolution of 2%, respectively. The dashed magenta line denotes the linear regression of VED_{rBC} against NF_{coated}. The relationship between VED_{rBC} and NF_{coated} during another campaign in January 2013 (Wu et al., 2016) is comparatively overlapped in gray.

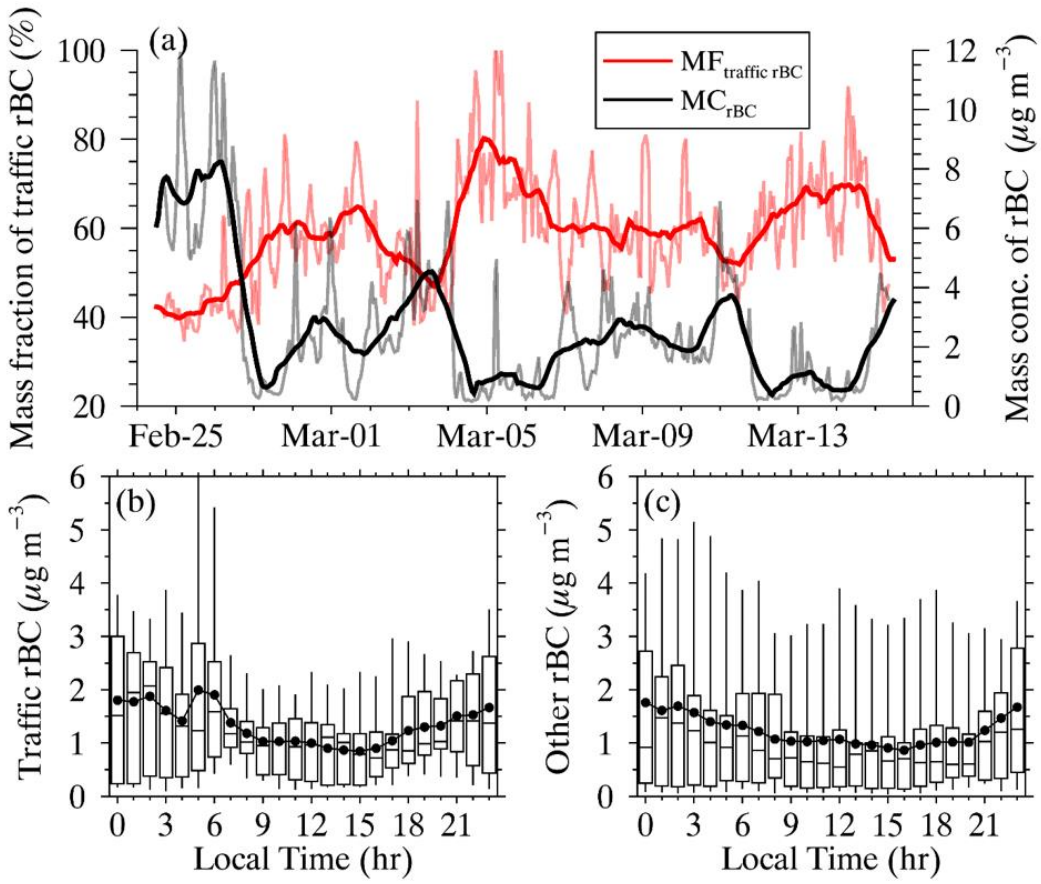

Fig. 5. (a) Time series of hourly mass concentration of rBC (MC_{rBC}) and mass fraction of local traffic related rBC ($MF_{traffic}$). The bold lines represent the variations of the daily moving averaged MC_{rBC} and $MF_{traffic}$. (b) and (c) show the diurnal variations in the decomposed rBC from local traffic emission and other sources, respectively.