Supplemental Information
Emission regulations altered the concentrations, origin, and formation of carbonaceous aerosols in the Tokyo metropolitan area

Takuma Miyakawa[1 2]*, Yugo Kanaya[1 2], Yuichi Komazaki[1], Takao Miyoshi[3], Hideki Nara[3], Akinori Takami[3], Nobuhiro Moteki[4], Makoto Koike[4], and Yutaka Kondo[5]

[1]Department of Environmental Geochemical Cycle Research, Japanese Agency for Marine-Earth Science and Technology, 3173-25, Showa-machi, Kanazawa-ku, Yokohama-city, Kanagawa 236-0001, Japan
[2]Institute of Arctic Climate and Environment Research, Japanese Agency for Marine-Earth Science and Technology, 3173-25, Showa-machi, Kanazawa-ku, Yokohama-city, Kanagawa 236-0001, Japan
[3]Center for Regional Environmental Research, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba-city, Ibaraki 305-8506, Japan
[4]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8654, Japan
[5]National Institute of Polar Research, 10-3, Midori-cho, Tachikawa-city, Tokyo 190-8518, Japan

*Corresponding author: Tel: 81-45-778-5726; Fax: 81-45-778-5706
E-*mail address*: miyakawat@jamstec.go.jp

S1. *Positive matrix factorization analysis of organic aerosol measured using an Aerodyne Aerosol Mass Spectrometer*

We performed the positive matrix factorization (PMF) analyses of the temporal variations of mass spectra (MS) of organic aerosol (OA) derived from Aerodyne AMS (Lanz *et al.*, 2007; Ulbrich *et al.*, 2009). The purpose of the use of the PMF is to analyze the secondary fraction of OA (i.e., SOA) and compare them with ozone (O_3) in the Tokyo Metropolitan Area (TMA) in the summers of 2004 and 2014. Note that a strong correlation of O_3 with oxygenated organic aerosol (OOA), which is calculated using a custom principal component analysis (CPCA; Zhang *et al.*, 2005), was found in daytime in the summer of 2004 (Takegawa *et al.*, 2006; Kondo *et al.*, 2008). We conducted, for the consistency to such previous studies, the extraction of two factors based on the PMF and comparison between PMF-derived OOA and O_3. In this study, factors were

extracted using the PMF analysis software (PMF Evaluation Tool, PET; Ulbrich *et al.*, 2009) with an FPEAK value of 0 for both years. We compared mass concentrations of CPCA-based OOA (Kondo *et al.*, 2008) with PMF-based OOA (this study) in the summer of 2004 (**Fig S1**). It is found that they are almost same and compatible. We therefore used the PMF method to derive OOA from MS data in this study.

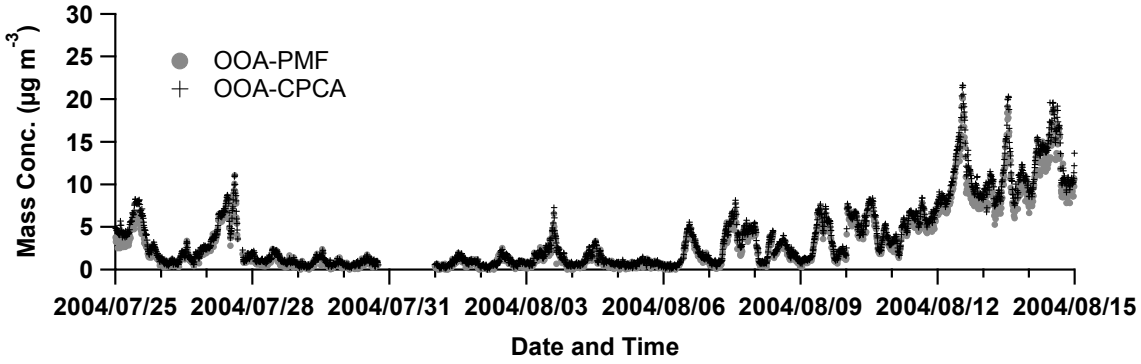

Fig S1. Temporal variations of OOA derived from CPCA (crosses) and PMF (gray circles) methods in the summer of 2004.

Fig S2 depicts the extracted mass spectra of OOA and hydrocarbon-like organic aerosol (HOA) in the summers of 2004 and 2014. MS of OOA and HOA in the summer of 2004 are similar to those in the summer of 2014 (r^2 = 0.94 and 0.95, respectively). The ratio of mass spectral signal at mass-to-charge (m/z) 44 to total (f44) for OOA is higher in 2014 than in 2004, indicating possible differences in the compositions of OOA in summer between 2004 and 2014.

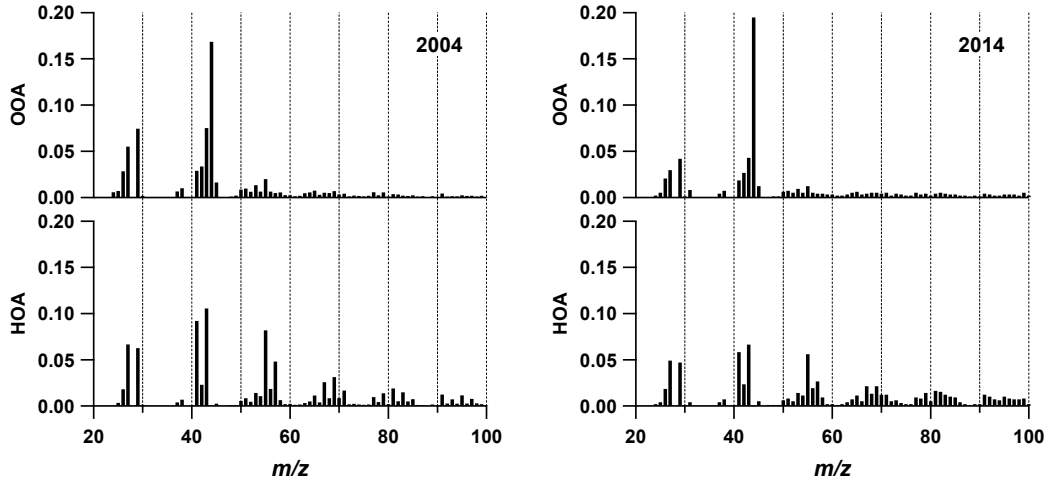

Fig S2. Extracted mass spectra of OOA and HOA (upper and bottom, respectively) in the summers of 2004 and 2014 (left and right panels, respectively).

Temporal variations of mass concentrations of OA, OOA, and HOA in the summers of 2004 and 2014 are shown in **Fig S3**. It is clearly found that reconstructed OA (i.e., sum of OOA and HOA) can well account for the temporal variations of measured OA. During both observations periods, the enhancements of the contribution of OOA to OA were observed when mass concentrations of OA increased. As discussed in the section "*SOA formation processes in terms of the relationship with O_3*", enhancements of OOA were generally associated with increases in O_3. This suggests the secondary formation of OOA through the photochemical reactions in the daytime. The capability to use OOA as a proxy of SOA in the TMA has been validated by Kondo *et al.* (2007).

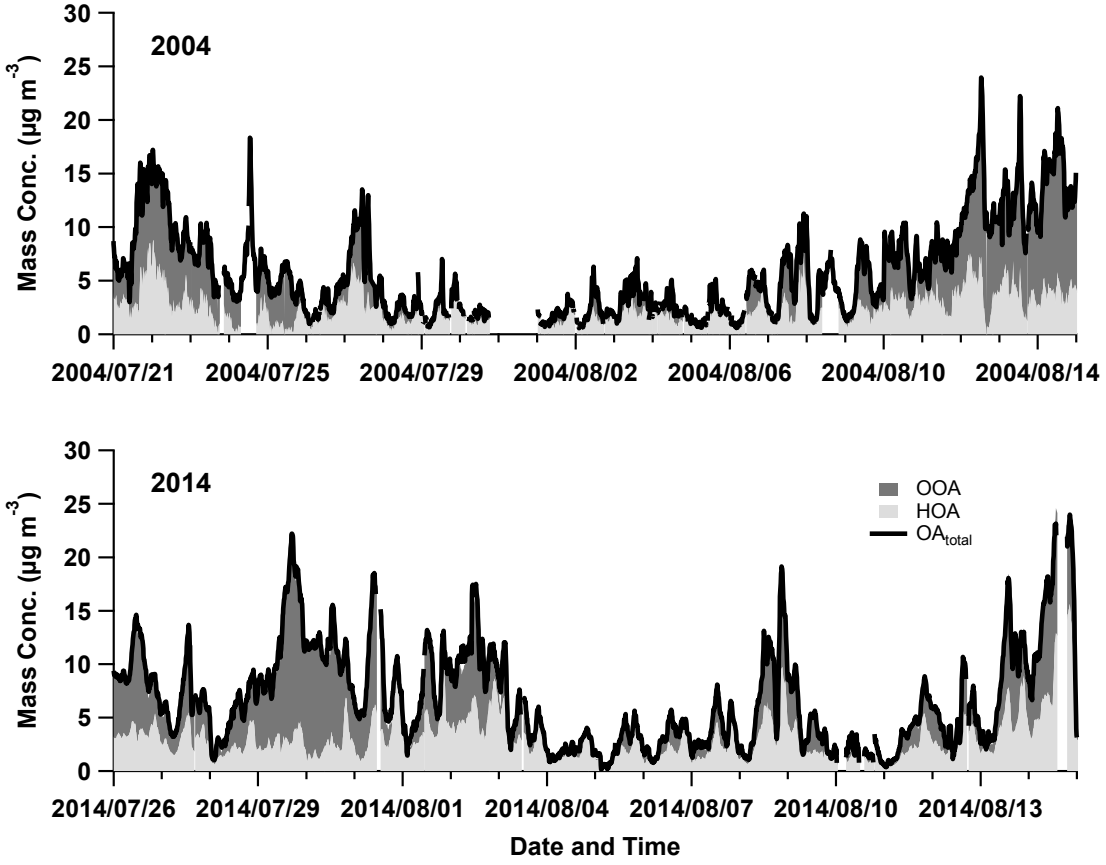

Fig S3. Time series of mass concentrations of OA (black lines), OOA (dark gray areas), and HOA (light gray areas) in the summers of 2004 and 2014 (upper and lower panels, respectively). OOA and HOA are cumulative.

S2. *Examining effects of biomass burning to the source of carbonaceous aerosols in the TMA*

Cubison *et al.* (2011) proposed a diagram that can be used to diagnose the impact of

biomass burning (BB) on OA using the signals at m/z 44 and 60 (m44 and m60, respectively) derived from the OA mass spectra (**Fig S4**). Their study suggests that ambient and laboratory-generated BB-OA have different mass spectra to those of non-BB-OA (representing urban and biogenic OA), and the combination of f44 and m60/total (f60) for BB-OA falls within the triangular region in the diagram. The sets of f44 and f60 observed in the TMA during the high $F^{14}C_{TC}$ period (see the text for details) were overlaid on the diagram (**Fig S4**). These data points are out of the triangular region and correspond to the f44 – f60 combination of urban/biogenic OA, indicating that such the enhancement of modern carbon contributions in summer was likely caused by the formation of biogenic SOA.

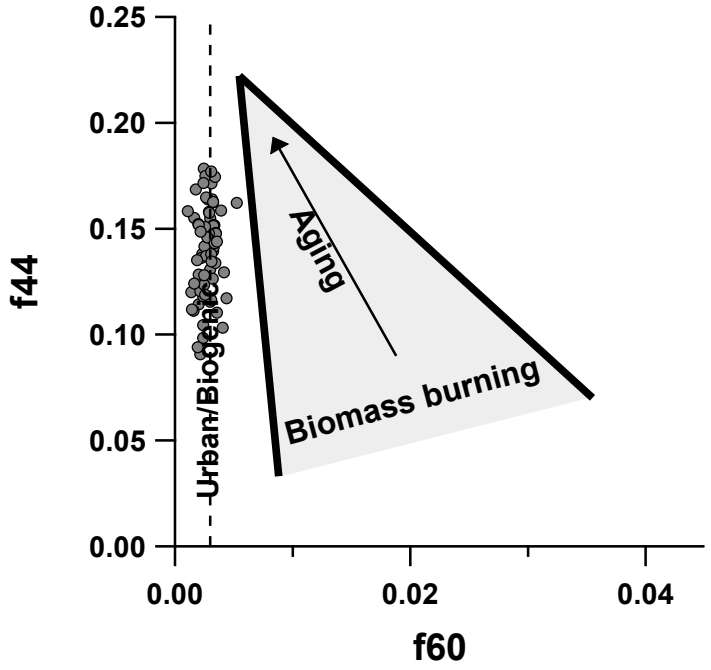

Fig S4. Diagram for diagnosis of the impacts of BB on OA, measured using an Aerodyne AMS. f44 - f60 observed during the high $F^{14}C_{TC}$ period are plotted as shaded circles.

References

Cubison, M. J. *et al.* (2011). Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. *Atmos. Chem. Phys.* 11: 12049-12064.

Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and Worsnop, D. R. (2007). Oxygenated and water-soluble organic aerosols in Tokyo. J. Geophys. Res. 112. D01203. doi:10.1029/2006JD007056.

Kondo, Y., *et al.* (2008). Formation and transport of oxidized reactive nitrogen, ozone, and secondary organic aerosol in Tokyo. *J. Geophys. Res.* 113. D21310. doi:10.1029/2008JD010134.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H. (2007). Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra. *Atmos. Chem. Phys.* 7: 1503-1522.

Takegawa, N., *et al.* (2006). Evolution of submicron organic aerosol in polluted air exported from Tokyo, *Geophys. Res. Lett.* 33. L15814. doi:10.1029/ 2006GL025815.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L. (2009). Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. *Atmos. Chem., Phys.* 9: 2891-2918.

Zhang, Q., Alfarra, R., Worsnop, D., Allan, J., Coe, H., Canagaratna, M., and Jimenez, J. (2005). Deconvolution and Quantification of Hydrocarbon-like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry. *Environ. Sci. Technol.* 39(13). 4938-4952. doi:10.1021/es048568l