Supplement of

Measurement report: Source characteristics of water-soluble organic carbon in PM$_{2.5}$ at two sites in Japan, as assessed by long-term observation and stable carbon isotope ratio

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**Figure S1.** Sampling locations at the Japan Automobile Research Institute (Tsukuba, Ibaraki) and Akita Prefectural University (Yurihonjo, Akita). This map plots the sampling locations on a standard map provided by the Geospatial Information Authority of Japan.
| Sampling site          | Site type | Particle size | Sampling period | n  | Analytical method          | δ^{13}C_{WSOC} (%) | Reference                  |
|------------------------|-----------|---------------|-----------------|----|-----------------------------|-------------------|----------------------------|
| Tsukuba, Japan         | Suburban  | PM_{2.5}      | Jul 2017–Jul 2019 | 62 | Wet oxidation/IRMS          | −25.2 ± 1.1       | This study                 |
| Yurihonjo, Japan       | Rural     | PM_{2.5}      | Aug 2017–Jul 2019 | 45 | Wet oxidation/IRMS          | −24.6 ± 2.4       | This study                 |
| Delhi, India           | Urban     | PM_{2.5}      | Jan–Mar 2016    | 7  | Combustion-EA/IRMS          | −25.4 ± 1.0       | Dasari et al. (2019)       |
| Bhola, Bangladesh      | Rural     | PM_{2.5}      | Jan–Mar 2016    | 12 | Combustion-EA/IRMS          | −24.2 ± 0.6       | Dasari et al. (2019)       |
| Hanimaadhoo, Maldives  | Rural     | PM_{1.0}      | Jan–Mar 2016    | 15 | Combustion-EA/IRMS          | −20.9 ± 0.6       | Dasari et al. (2019)       |
| Seoul, Korea           | Urban     | TSP           | Mar 2015–Jan 2016 | 78 | TOC analyzer/IRMS          | −24.0 ± 1.5       | Han et al. (2020)          |
| Nanjing, China         | Suburban  | PM_{2.5}      | Jan 2015        | 7  | GasBench/IRMS              | −26.24 to −23.35  | Zhang et al. (2019)        |
| Beijing, China         | Urban     | PM_{2.5}      | Jan, Jun, 2013  | 10 | Combustion-EA/IRMS          | −25.40 ± 0.46     | Yan et al. (2017)          |
| Hanimaadhoo, Maldives  | Rural     | PM_{2.5}      | Feb–Mar 2012    | 14 | Combustion-EA/IRMS          | −20.8 ± 0.7       | Bosch et al. (2014)        |
| Jeju, Korea            | Rural     | TSP/PM_{2.5}  | Mar 2011        | 10 | Combustion-EA/IRMS          | −25.1 ± 0.49      | Kirillova et al. (2014a)   |
| New Delhi, India       | Urban     | PM_{2.5}      | Oct 2010–Mar 2011 | 20 | Combustion-EA/IRMS          | −24.1 ± 0.9       | Kirillova et al. (2014b)   |
| Sapporo, Japan         | Rural     | TSP           | Sep 2009–Oct 2010 | 21 | Combustion-EA/IRMS          | −24.2 ± 1.59      | Pavuluri and Kawamura (2017) |
| Sapporo, Japan         | Forest    | TSP           | Jun 2009–Dec 2010 | 15 | Combustion-EA/IRMS          | −26.0 to −23.9    | Miyazaki et al. (2012)     |
| Stockholm, Sweden      | Forest    | TSP           | Aug–Oct 2009    | 3  | Combustion-EA/IRMS          | −25.6 to −25.1    | Kirillova et al. (2010)    |
| Hanimaadhoo, Maldives  | Rural     | TSP           | Jan 2008–Apr 2009 | 12 | Combustion-EA/IRMS          | −18.4 ± 0.5       | Kirillova et al. (2013)    |
| Sinhagad, India        | Rural     | TSP           | Jan 2008–Apr 2009 | 12 | Combustion-EA/IRMS          | −20.4 ± 0.5       | Kirillova et al. (2013)    |
| Millbrook, USA         | Rural     | TSP           | Mar, May, Aug 2007 | 3  | Combustion-EA/IRMS          | −24.7             | Wozniak et al. (2012b)     |
| Harcum, USA            | Rural     | TSP           | Feb, Apr, Aug 2007 | 3  | Combustion-EA/IRMS          | −25.4             | Wozniak et al. (2012b)     |
| Millbrook, USA         | Rural     | TSP           | May 2006–May 2007 | 9  | Combustion-EA/IRMS          | −25.2 ± 0.2       | Wozniak et al. (2012a)     |
| Harcum, USA            | Rural     | TSP           | Jun 2006–Jun 2007 | 10 | Combustion-EA/IRMS          | −25.3 ± 0.6       | Wozniak et al. (2012a)     |
Supplement S1 Water-soluble ion analysis

A portion of each quartz fiber filter (1.44 cm²) was extracted in 3 mL of Milli-Q water under ultrasonic agitation for 15 min. The extract was filtered through a syringe filter (Chromatodisc Type A 0.45 μm, GL Sciences, Japan) to remove insoluble materials. Anion concentrations were determined in the filtrate using an IonPac AS17-C column and IonPac AG17-C guard column (Thermo Fisher Scientific Inc.), with a 1–40 mM gradient of potassium hydroxide as the eluent. Cation concentrations were determined using a CS12A column and CG12A guard column (Thermo Fisher Scientific Inc.), with 20 mM methanesulfonic acid as the eluent. Calibration curves were prepared using cation mixed standard solution 2 and anion mixed standard solution 4 (Kanto Chemical Co., Inc., Tokyo, Japan).

The coefficient of determination was >0.999 for all compounds, and the detection limits were 4 ppb (Cl⁻), 5 ppb (NO₂⁻), 12 ppb (NO₃⁻), 8 ppb (SO₄²⁻), 8 ppb (Na⁺), 5 ppb (NH₄⁺), 15 ppb (K⁺), 15 ppb (Mg²⁺), and 20 ppb (Ca²⁺). These values were comparable to those used in other research (Shen et al., 2009).
References

Bosch, C., Andersson, A., Kirillova, E. N., Budhavant, K., Tiwari, S., Praveen, P. S., Russell, L. M., Beres, N. D., Ramanathan, V., and Gustafsson, Ö.: Source-diagnostic dual-isotope composition and optical properties of water-soluble organic carbon and elemental carbon in the South Asian outflow intercepted over the Indian Ocean, J. Geophys. Res., 119, 11743-11759, https://doi.org/10.1002/2014JD022127, 2014.

Dasari, S., Andersson, A., Bikkina, S., Holmstrand, H., Budhavant, K., Satheesh, S., Asmi, E., Kesti, J., Backman, J., Salam, A., Bisht, D. S., Tiwari, S., Hameed, Z., and Gustafsson, Ö.: Photochemical degradation affects the light absorption of water-soluble brown carbon in the South Asian outflow, Sci. Adv., 5, eaau8066, https://doi.org/10.1126/sciadv.aau8066, 2019.

Han, H., Kim, G., Seo, H., Shin, K.-H., and Lee, D.-H.: Significant seasonal changes in optical properties of brown carbon in the midlatitude atmosphere, Atmos. Chem. Phys., 20, 2709-2718, https://doi.org/10.5194/acp-20-2709-2020, 2020.

Kirillova, E. N., Sheesley, R. J., Andersson, A., and Gustafsson, Ö.: Natural Abundance $^{13}$C and $^{14}$C Analysis of Water-Soluble Organic Carbon in Atmospheric Aerosols, Anal. Chem., 82, 7973-7978, https://doi.org/10.1021/ac1014436, 2010.

Kirillova, E. N., Andersson, A., Sheesley, R. J., Kruså, M., Praveen, P. S., Budhavant, K., Safai, P. D., Rao, P. S. P., and Gustafsson, Ö.: $^{13}$C- and $^{14}$C-based study of sources and atmospheric processing of water-soluble organic carbon (WSOC) in South Asian aerosols, J. Geophys. Res., 118, 614-626, https://doi.org/10.1002/jgrd.50130, 2013.

Kirillova, E. N., Andersson, A., Han, J., Lee, M., and Gustafsson, Ö.: Sources and light absorption of water-soluble organic carbon aerosols in the outflow from northern China, Atmos. Chem. Phys., 14, 1413-1422, https://doi.org/10.5194/acp-14-1413-2014, 2014a.

Kirillova, E. N., Andersson, A., Tiwari, S., Srivastava, A. K., Bisht, D. S., and Gustafsson, Ö.: Water-soluble organic carbon aerosols during a full New Delhi winter: Isotope-based source apportionment and optical properties, J. Geophys. Res., 119, 3476-3485, https://doi.org/10.1002/2013jd020041, 2014b.

Miyazaki, Y., Fu, P. Q., Kawamura, K., Mizoguchi, Y., and Yamanoi, K.: Seasonal variations of stable carbon isotopic composition and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, Atmos. Chem. Phys., 12, 1367-1376, https://doi.org/10.5194/acp-12-1367-2012, 2012.

Pavuluri, C. M., and Kawamura, K.: Seasonal changes in TC and WSOC and their $^{13}$C isotope ratios in Northeast Asian aerosols: land surface–biosphere–atmosphere interactions, Acta Geochim., 36, 355-358, https://doi.org/10.1007/s11631-017-0157-3, 2017.

Shen, Z., Cao, J., Arimoto, R., Han, Z., Zhang, R., Han, Y., Liu, S., Okuda, T., Nakao, S., and Tanaka, S.: Ionic composition of TSP and PM$_{2.5}$ during dust storms and air pollution episodes at Xi'an, China, Atmos. Environ., 43, 2911-2918, https://doi.org/10.1016/j.atmosenv.2009.03.005, 2009.

Wozniak, A. S., Bauer, J. E., and Dickhut, R. M.: Characteristics of water-soluble organic carbon associated with aerosol particles in the eastern United States, Atmos. Environ., 46, 181-188, https://doi.org/10.1016/j.atmosenv.2011.10.001, 2012a.

Wozniak, A. S., Bauer, J. E., Dickhut, R. M., Xu, L., and McNichol, A. P.: Isotopic characterization of aerosol organic carbon components over the eastern United States, J. Geophys. Res., 117, D13303,
Yan, C., Zheng, M., Bosch, C., Andersson, A., Desyaterik, Y., Sullivan, A. P., Collett, J. L., Zhao, B., Wang, S., He, K., and Gustafsson, O.: Important fossil source contribution to brown carbon in Beijing during winter, Sci. Rep., 7, 43182, https://doi.org/10.1038/srep43182, 2017.

Zhang, W., Zhang, Y.-L., Cao, F., Xiang, Y., Zhang, Y., Bao, M., Liu, X., and Lin, Y.-C.: High time-resolved measurement of stable carbon isotope composition in water-soluble organic aerosols: method optimization and a case study during winter haze in eastern China, Atmos. Chem. Phys., 19, 11071-11087, https://doi.org/10.5194/acp-19-11071-2019, 2019.