Online Supplementary Material

The regional nature of nitrate-dominant haze pollution during autumn over the Pearl River Delta area

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This file includes: Supplementary Text S1, Table S1, and Figures S1–S3

Text S1. Chemical analysis

Inorganic water-soluble ions in the samples were detected using an ion chromatograph (Dionex ICS-90, Sunnyvale, US). The anions, including F^- , Cl^- , NO_3^- , and SO_4^{2-} , were analyzed using an AS14A Column with an AMMS 300 Suppresser and were eluted with 3.5 mmol L^{-1} Na₂CO₃-

1.0 mmol L^{-1} NaHCO₃. The cations Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ were analyzed using a CS12A Column with a CSRS Ultra II Suppresser and were eluted with 20 mmol L^{-1} methanesulfonic acid.

A thermal-optical carbon aerosol analyzer (DRI Model 2001, Atmoslytic Inc., CA, USA) based on the thermal-optical transmittance method was used to determine the abundance of OC and EC. Full details of this instrument and analysis method can be found in Cheng et al (2009).

Teflon-membrane filters were analyzed by high-sensitivity X-ray fluorescence for Na, Mg, Al, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sb, Ba, Pb, etc (Cao et al. 2008).

Two typical anhydrosugars, levoglucosan (LG) and mannosan (MN), were measured by high-performance anion exchange chromatography with pulsed amperometric detection. Full details can be found in Zhang et al. (2010), but a brief description is provided here, as follows: A small punch from each quartz filter was extracted using 2.0 ml deionized water ($\Omega > 18.2$ M) under ultrasonic agitation for 1 h. The filter extracts were filtered to remove insoluble materials through Teflon syringe filters (pore size: 0.25 µm; PTFE, Whatman, USA) and were subsequently analyzed on a Dionex ICS-3000 system with a Dionex Carbopac MA1 analytical column (250 × 4 mm) using aqueous sodium hydroxide (NaOH) as eluent. The eluent was mixed in-line from 1000 mM NaOH and deionized water. A typical separation was carried out at eluent flow rate of 0.4 ml min⁻¹ for 60 min, including a 15 min equilibrium period (480 mM NaOH) before sample injection, a 30 min isocratic elution (from 480 to 650 mM NaOH). The limit of detection (LOD) for LG and MN was estimated to be 0.008 mg m⁻³ and 0.004 mg m⁻³, respectively, based on a signal-to-noise ratio of 3. The anhydrosugar contents in all field blanks

were lower than the LOD. The analytical errors of LG and MN were less than 10% (one relative standard deviation), based on analysis of replicate filter samples (n = 8).

References

- Cao, J. J., Chow, J. C., Watson, J. G., Wu, F., Han, Y. M., Jin, Z. D., Shen, Z. X., and An, Z. S.
 2008. Size-differentiated source profiles for fugitive dust in the Chinese Loess Plateau,
 Atmospheric Environment, 42, 2261-2275,
 http://dx.doi.org/10.1016/j.atmosenv.2007.12.041.
- Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., and Tan, J. H. 2009. Positive sampling artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC, Atmos. Chem. Phys., 9, 7243-7256, 10.5194/acp-9-7243-2009.
- Draxler, R. R. and Rolph, G. D. 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY, http://ready.arl.noaa.gov/HYSPLIT.php (last access: 1 May 2014), NOAA Air Resources Laboratory, Silver Spring, MD.
- Zhang, Z., Engling, G., Lin, C.-Y., Chou, C. C. K., Lung, S.-C. C., Chang, S.-Y., Fan, S., Chan, C.-Y., and Zhang, Y.-H. 2010. Chemical speciation, transport and contribution of biomass burning smoke to ambient aerosol in Guangzhou, a mega city of China, Atmospheric Environment, 44, 3187-3195, 10.1016/j.atmosenv.2010.05.024.

	NH	HS	SD
$PM_{2.5}/\mu g\ m^{-3}$	67.9 ± 27.6	68.3 ± 32.2	56.6 ± 20.4
$SO_4^{2-}/\mu g \ m^{-3}$	18.9 ± 6.7	16.9 ± 6.9	16.1 ± 6.6
$NO_3^{-}/\mu g \ m^{-3}$	6.5 ± 6.7	7.6 ± 9.1	5.5 ± 4.3
$Cl^{-}/\mu g m^{-3}$	1.9 ± 1.6	1.3 ± 1.0	1.0 ± 0.6
$NH_4^+/\mu g m^{-3}$	8.4 ± 3.6	8.1 ± 4.1	7.0 ± 2.8
$Na^+/\mu g m^{-3}$	0.9 ± 0.4	0.6 ± 0.6	0.5 ± 0.2
$K^{+}\!/\mu g \ m^{-3}$	1.5 ± 0.5	1.0 ± 0.4	0.9 ± 0.3
$Mg^{2+}\!/\mu g\ m^{-3}$	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
$Ca^{2+}/\mu g m^{-3}$	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
$OC/\mu g m^{-3}$	16.9 ± 6.7	13.2 ± 5.9	12.4 ± 4.3
$EC/\mu g m^{-3}$	2.8 ± 1.2	2.1 ± 0.9	1.7 ± 0.7
LG/ng m ⁻³	339.0 ± 183.9	202.2 ± 125.6	178.6 ± 103.5
MN/ng m ⁻³	20.7 ± 12.2	14.0 ± 9.6	11.7 ± 7.8
Al/ng m ⁻³	373.9 ± 125.7	464.1 ± 191.6	317.0 ± 155.9
Si/ng m ⁻³	700.1 ± 255.4	904.1 ± 293.1	525.3 ± 208.4
Ti/ng m ⁻³	33.7 ± 12.3	39.3 ± 14.7	26.3 ± 12.1
$V/ng m^{-3}$	5.6 ± 4.1	8.0 ± 5.1	6.7 ± 6.5
Cr/ng m ⁻³	13.2 ± 9.3	10.5 ± 8.1	11.8 ± 17.1
$Mn/ng m^{-3}$	56.3 ± 37.8	33.6 ± 13.2	25.9 ± 12.7
Fe/ng m ⁻³	392.7 ± 115.3	418.0 ± 120.0	339.3 ± 113.2
Co/ng m ⁻³	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Ni/ng m ⁻³	3.0 ± 2.6	3.1 ± 3.0	2.4 ± 2.0
$Cu/ng m^{-3}$	72.0 ± 30.2	31.7 ± 19.7	32.6 ± 17.8
Zn/ng m ⁻³	548.8 ± 249.6	344.5 ± 116.4	286.7 ± 108.8
Rb/ng m ⁻³	4.4 ± 3.7	4.9 ± 3.8	2.8 ± 3.4
$Sb/ng m^{-3}$	7.0 ± 8.4	17.2 ± 12.1	19.2 ± 21.0
Ba/ng m ⁻³	60.9 ± 30.3	20.3 ± 21.7	30.4 ± 86.8
Pb/ng m ⁻³	116.6 ± 52.0	92.5 ± 38.3	87.9 ± 34.8

Table S1. Average values and standard deviations of the major components in $PM_{2.5}$.



Figure S1. SOC concentrations and SOC/OC ratios at the three sites.



 Figure S2. Synoptic weather conditions at (a) 0800 (local time) on 13 October, (b) 0800 on 17

 October, (c) 0800 on 22 October, and (d) 0800 on 26 October. Red circles represent the PRD

 region.
 Weather
 charts
 were
 obtained
 from
 HKUST

 (http://envf.ust.hk/dataview/metplot/current/).



Figure S3. HYSPLIT 72-h backward trajectories ending at the three sites for normal days, EP1 and EP2 (Draxler and Rolph 2013). Color scales are the heights of air masses. Fire spot data were obtained by Moderate Resolution Imaging Spectroradiometer (MODIS), available at: https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms/active-fire-data.