Electronic Supplementary Material (ESI) for Faraday Discussions.
This journal is © The Royal Society of Chemistry 2020

Supporting Information for

Molecular Characterization of Size-Segregated Organic Aerosols in the Urban Boundary Layer in Wintertime Beijing by FT-ICR MS

Qiaorong Xie [a,e], Sihui Su [b], Shuang Chen [b], Qiang Zhang [b], Siyao Yue [a,e], Wanyu Zhao [a,e], Huiyun Du [a], Hong Ren [b], Lianfang Wei [a], Dong Cao [c], Yisheng Xu [d], Yele Sun [a], Zifa Wang [a], and Pingqing Fu [b,a,e*]

[a] State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

[b] Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, China

[c] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing, China

[d] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China

[e] College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing, China

*Corresponding author: Pingqing Fu (fupingqing@tju.edu.cn)

This supplementary information document contains 17 pages including 3 tables, 12 figures, and references.

Table S1. Sampling record for the size-segregated aerosol samples. Blank samples were collected before the sampling period. Except for pumping, the procedure for collecting blank samples was the same as for the real samples.

No.	Start	End	Duration (h)
Size-8-blk	2018/01/13 07:20		1min
Size-260-blk	2018/01/13 07:20		1min
Size-8-H*	2018/01/13 08:20	2018/01/16 08:20	72
Size-260-H	2018/01/13 08:20	2018/01/16 08:20	72
Size-8-C	2018/01/22 08:20	2018/01/25 08:20	72
Size-260-C	2018/01/22 08:20	2018/01/25 08:20	72

* Size-8-H: the size-segregated aerosol samples collecting at 8m during the pollution periods

Table S2. The average carbon oxidation state (OS_C) values for compounds in both 8 m and 260 m aerosols.

Particle size	Hazy days			Clean days		
	8 m	260 m	$R_{260m/8m}$	8 m	260 m	$R_{260m/8m}$
$PM_{1.1}$	-0.39	-0.36	1.09	-0.43	-0.39	1.10
$PM_{1.1-3.3}$	-0.47	-0.46	1.02	-0.64	-0.62	1.03
$PM_{3.3-9}$	-0.65	-0.62	1.05	-0.69	-0.76	0.91

Table S3. The stoichiometric classification ranges of VK classes.[1, 2]

Class	H/C	O/C
Lipids-like	1.5<H/C≤2.0	0≤O/C≤0.3
Aliphatic/peptides-like	1.5<H/C≤2.2	0.3<O/C≤0.67
CRAMs-like / lignin-like	0.67<H/C≤1.5	0.1≤O/C<0.67
Carbohydrates-like	1.5<H/C≤2.5	0.67<O/C<1.2
Unsaturated hydrocarbons	0.67<H/C≤1.5	O/C<0.1
Aromatic structures	0.2≤H/C≤0.67	O/C<0.67
tannins-like / HOC	0.6<H/C≤1.5	0.67≤O/C≤1.2

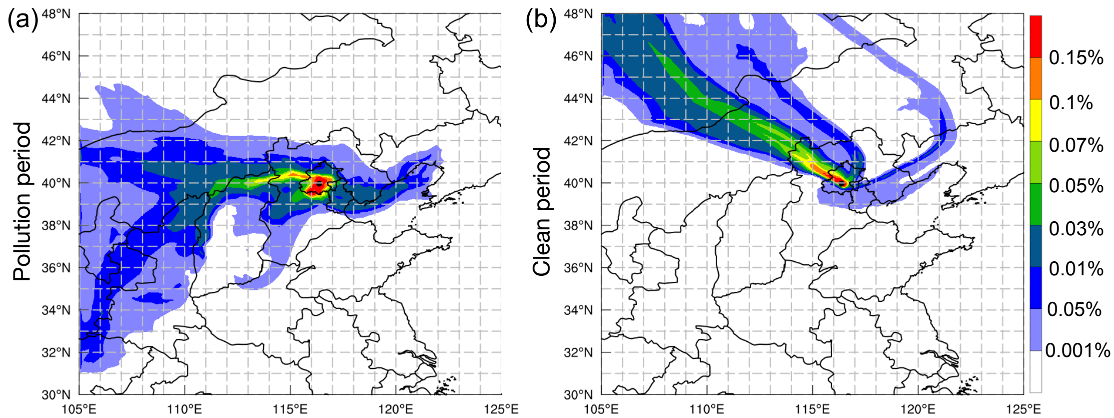

Figure S1. Footprint regions of (a) pollution (13th – 16th January) and (b) clean period (22nd – 25th January) at 8 m in the urban troposphere. The color bar indicates the relative residence time of tracer particles. The black dot represents the location of the sampling site in urban Beijing.

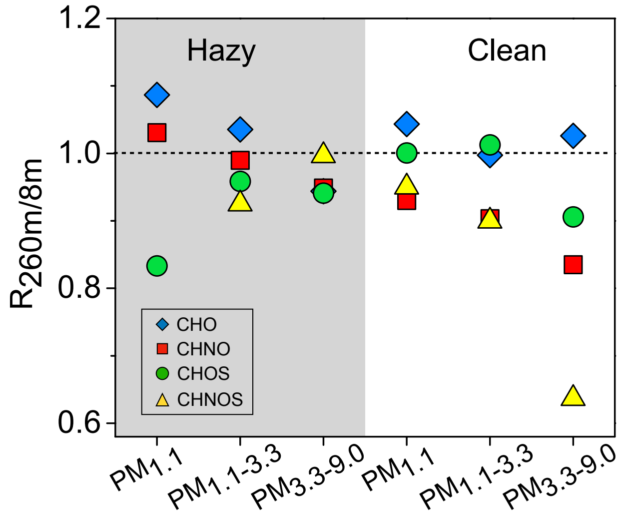

Figure S2. The ratios of the total number compounds ($R_{260m/8m}$) in size-segregated aerosols.

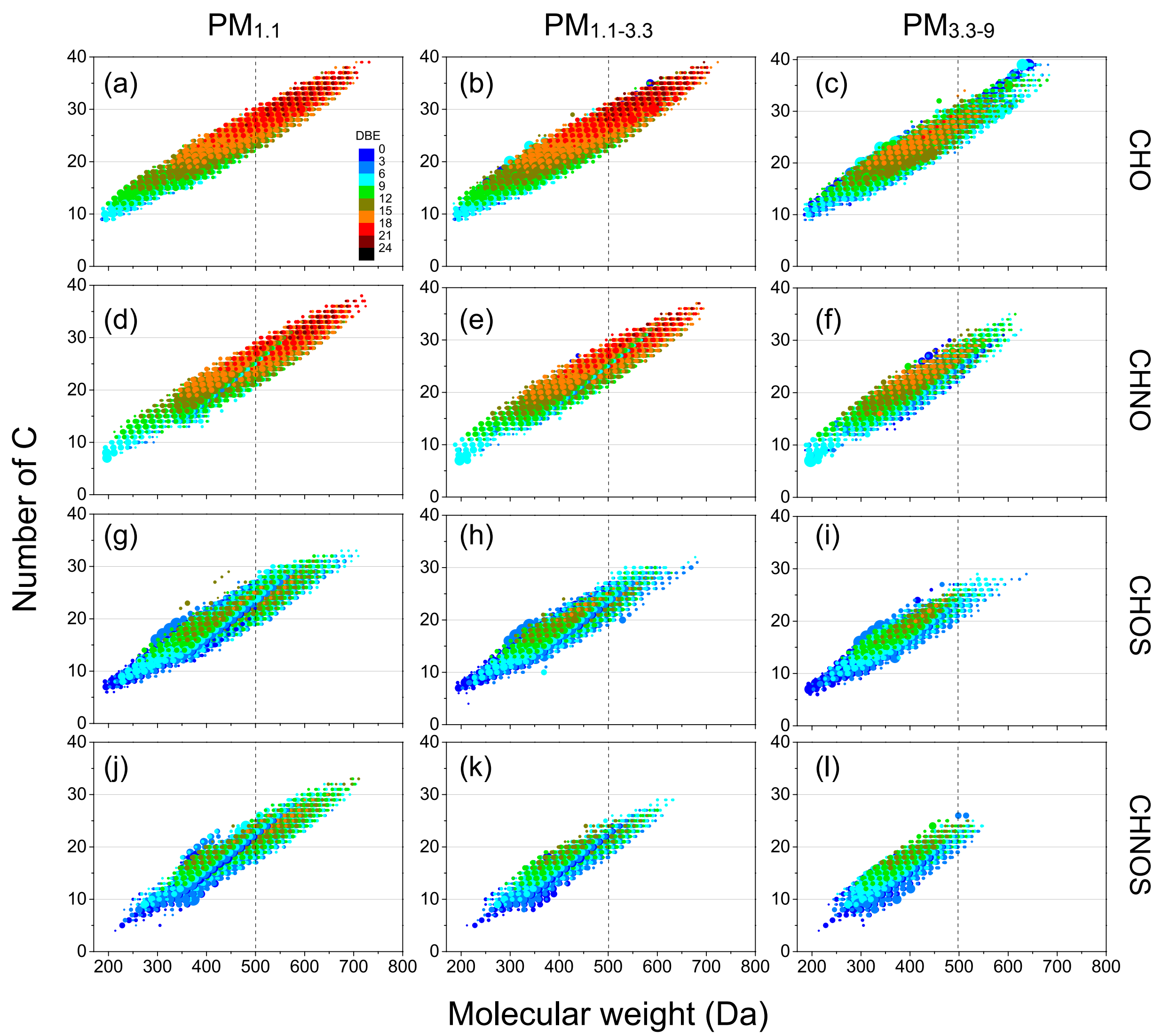

Figure S3. The molecular weight distributions of compounds during the pollution periods. The color bar in denotes the number of DBE. The size of the symbols reflects the relative peak intensities of molecular formulae on a logarithmic scale.

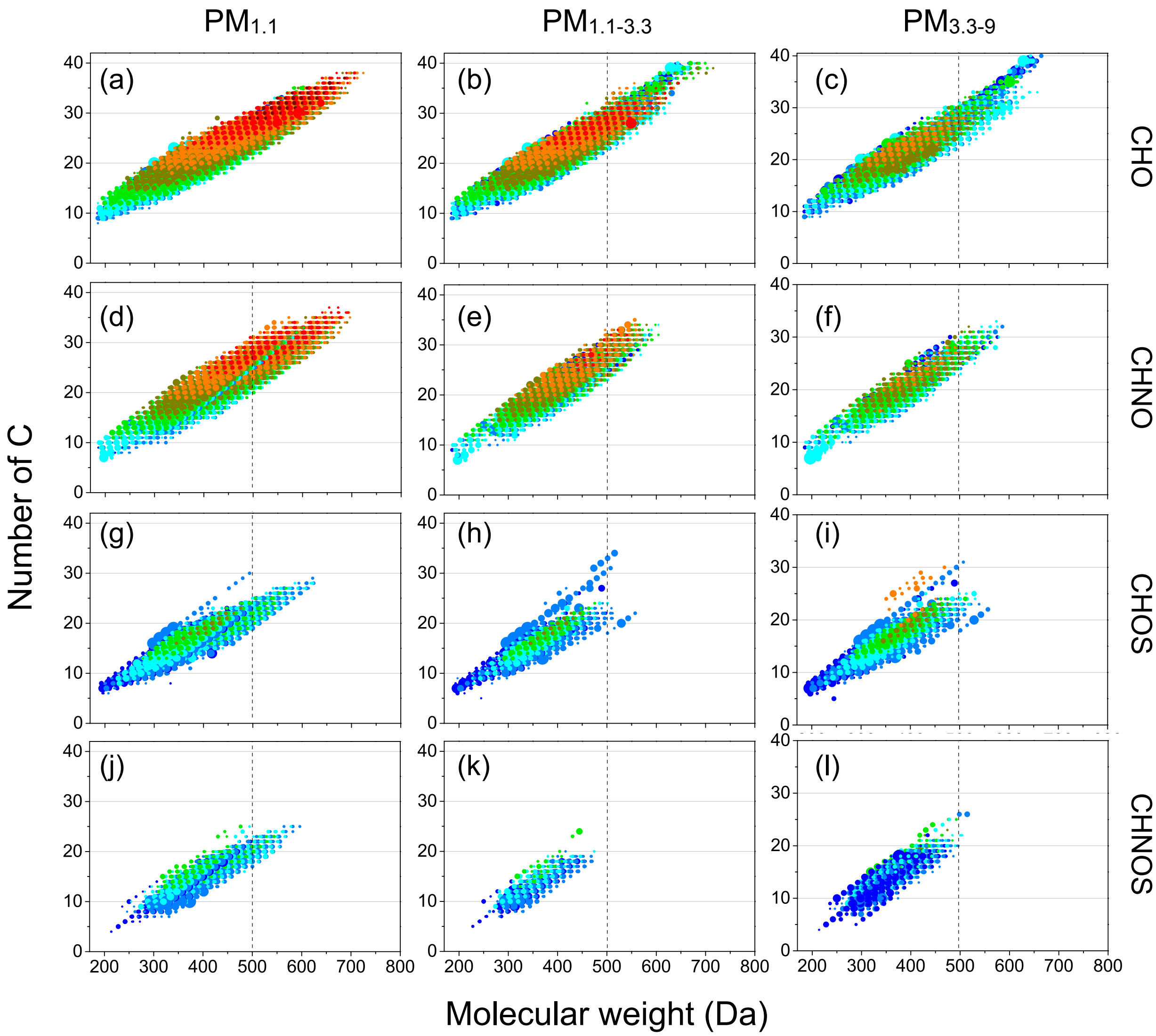

Figure S4. The molecular weight distributions of compounds during the clean periods. The color bar in denotes the number of DBE. The size of the symbols reflects the relative peak intensities of molecular formulae on a logarithmic scale.

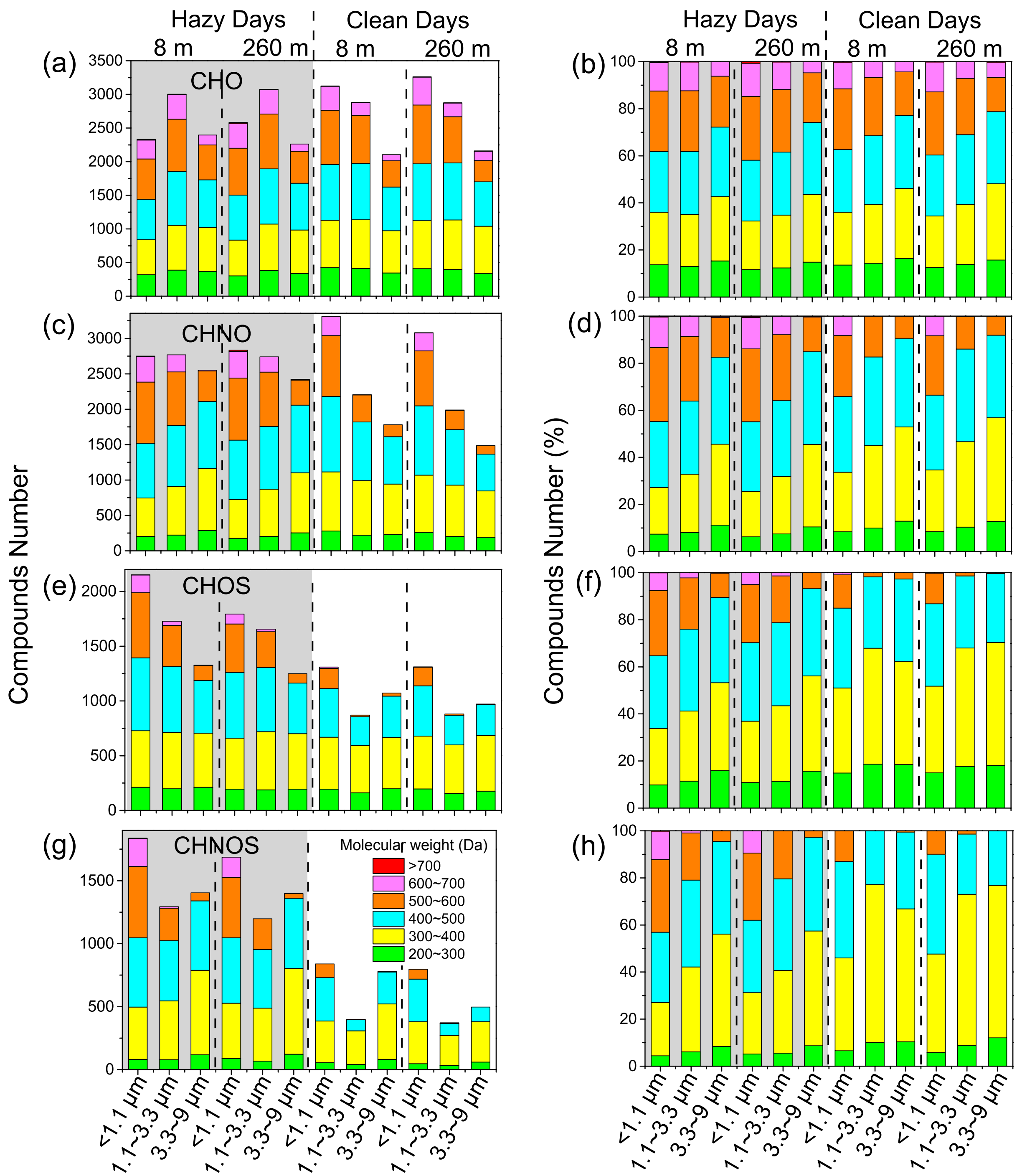

Figure S5. Molecular weight distributions of the number for CHO, CHNO, CHOS and CHNOS compounds in different particle sizes during pollution and clean periods at two heights (8 m and 260 m). The color bar denotes various molecular weight ranges.

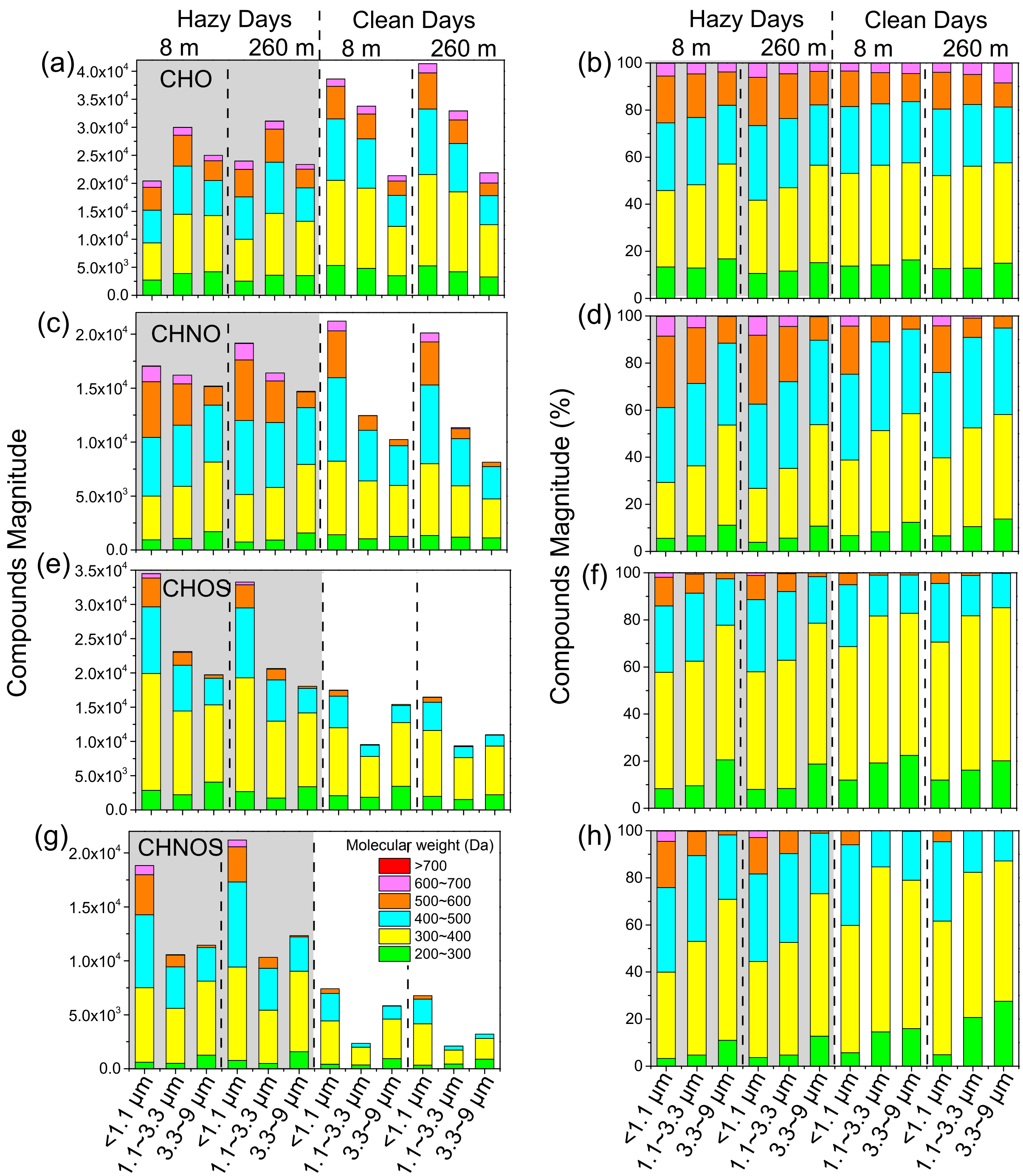

Figure S6. Molecular weight distributions of the magnitudes for CHO, CHNO, CHOS and CHNOS compounds in different particle sizes during pollution and clean periods at different height. The color bar denotes various molecular weight ranges.

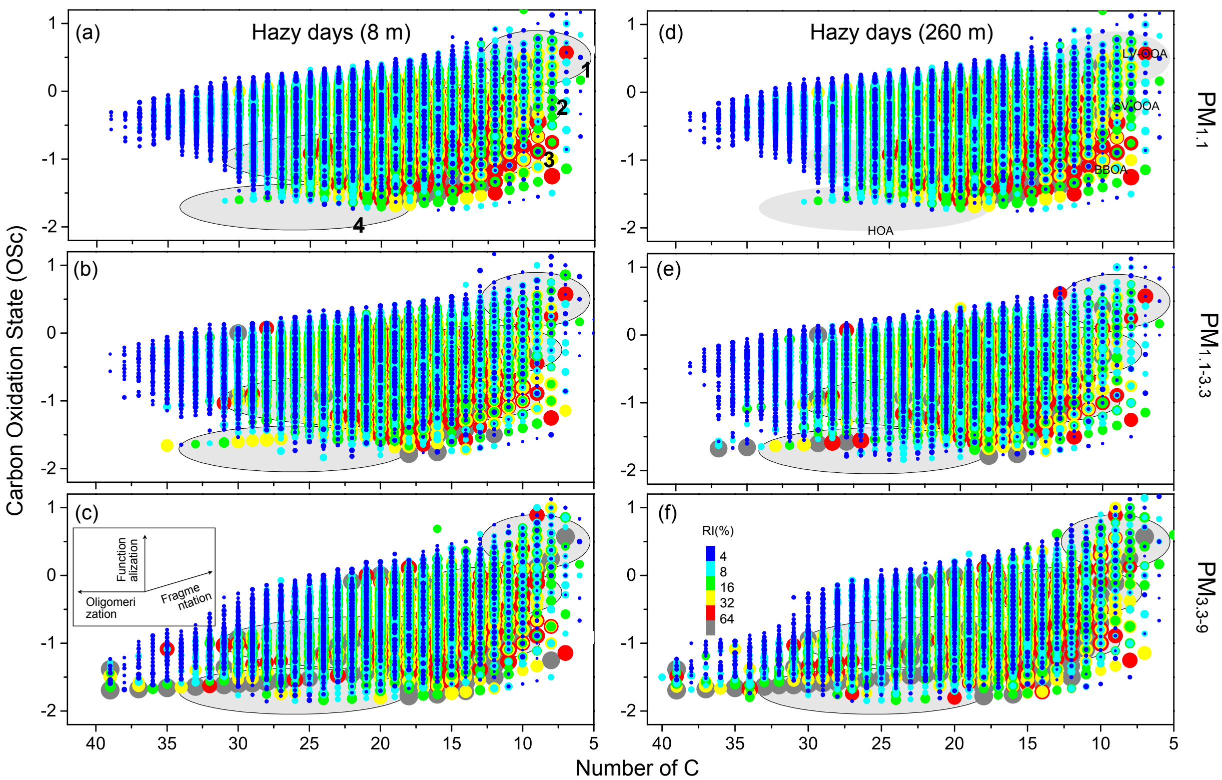

Figure S7. The carbon oxidation state (OS_C) symbols for compounds between 8 m and 260 m. The size and color bar of the markers reflects the relative peak intensities of compounds on a logarithmic scale. The gray areas were marked as SV-OOA (1, semi-volatile oxidized organic aerosol), LV-OOA (2, low-volatility oxidized organic aerosol), BBOA (3, biomass burning organic aerosol) and HOA (4, hydrocarbon-like organic aerosol).[3, 4]

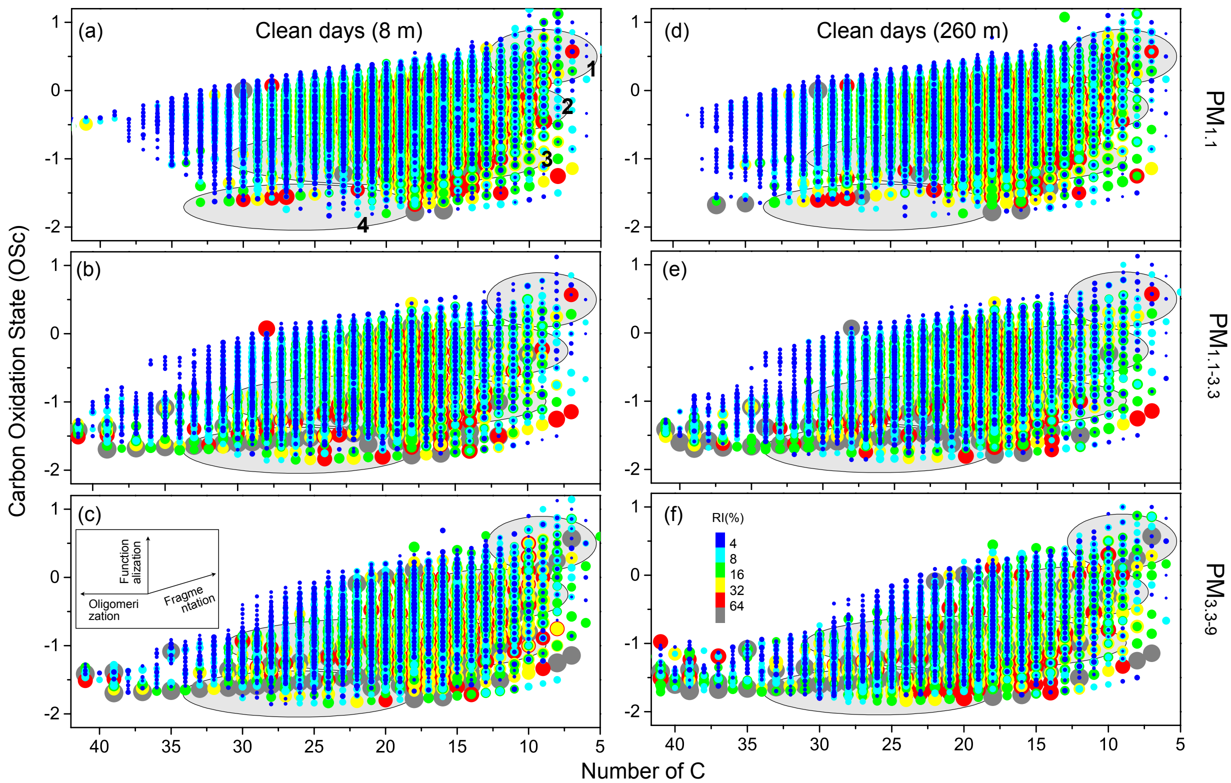

Figure S8. The carbon oxidation state (OS_C) symbols for compounds between 8 m and 260 m. The size and color bar of the markers reflects the relative peak intensities of compounds on a logarithmic scale. The gray areas were marked as SV-OOA (1, semi-volatile oxidized organic aerosol), LV-OOA (2, low-volatility oxidized organic aerosol), BBOA (3, biomass burning organic aerosol) and HOA (4, hydrocarbon-like organic aerosol).[3, 4]

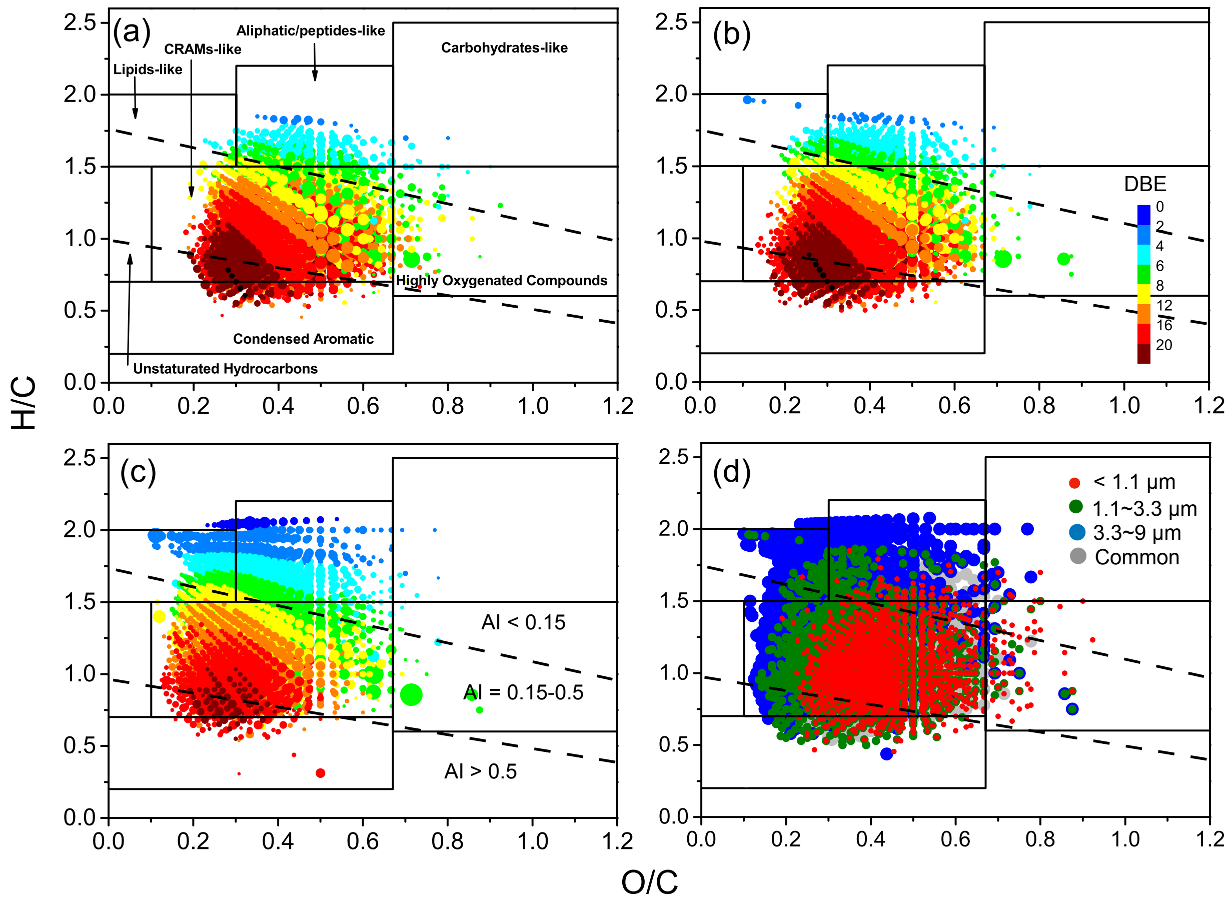

Figure S9. Typical Van Krevelen plots for CHNO compounds in (a) $PM_{1.1}$, (b)$PM_{1.1\text{-}3.3}$ and (c) $PM_{3.3\text{-}9}$ with separation by AI value ranges in black dotted lines. The color bar in (a) – (c) denotes the number of DBE. Black lines show class identification. The stoichiometric ranges set as boundaries of the classifications are showed in Table S3. The size of the symbols reflects the relative peak intensities of molecular formulae on a logarithmic scale. The diagram (d) presents the common and unique compounds among the size-segregated aerosols.

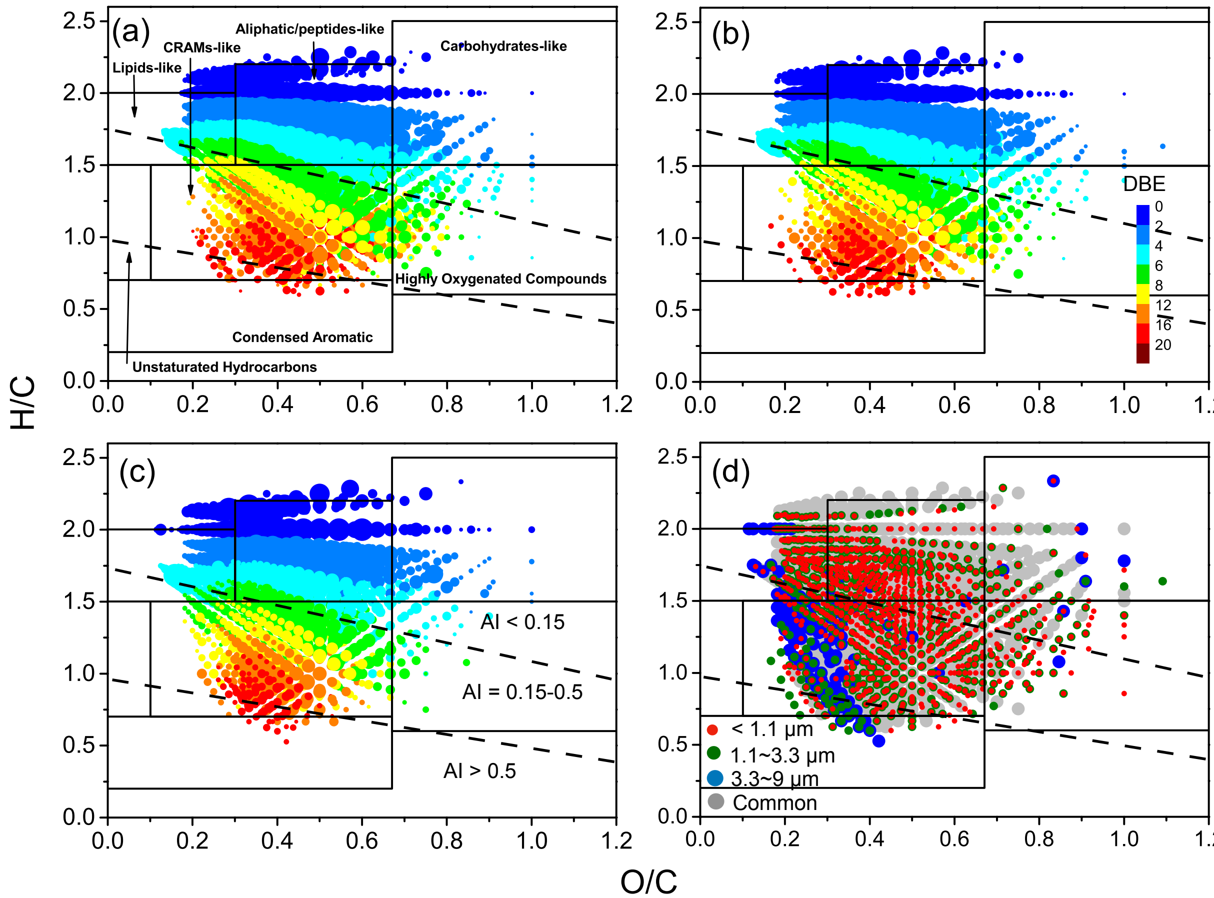

Figure S10. Typical Van Krevelen plots for CHOS compounds in (a) $PM_{1.1}$, (b)$PM_{1.1\text{-}3.3}$ and (c) $PM_{3.3\text{-}9}$ with separation by AI value ranges in black dotted lines. The color bar in (a) – (c) denotes the number of DBE. Black lines show class identification. The stoichiometric ranges set as boundaries of the classifications are showed in Table S3. The size of the symbols reflects the relative peak intensities of molecular formulae on a logarithmic scale. The diagram (d) presents the common and unique compounds among the size-segregated aerosols.

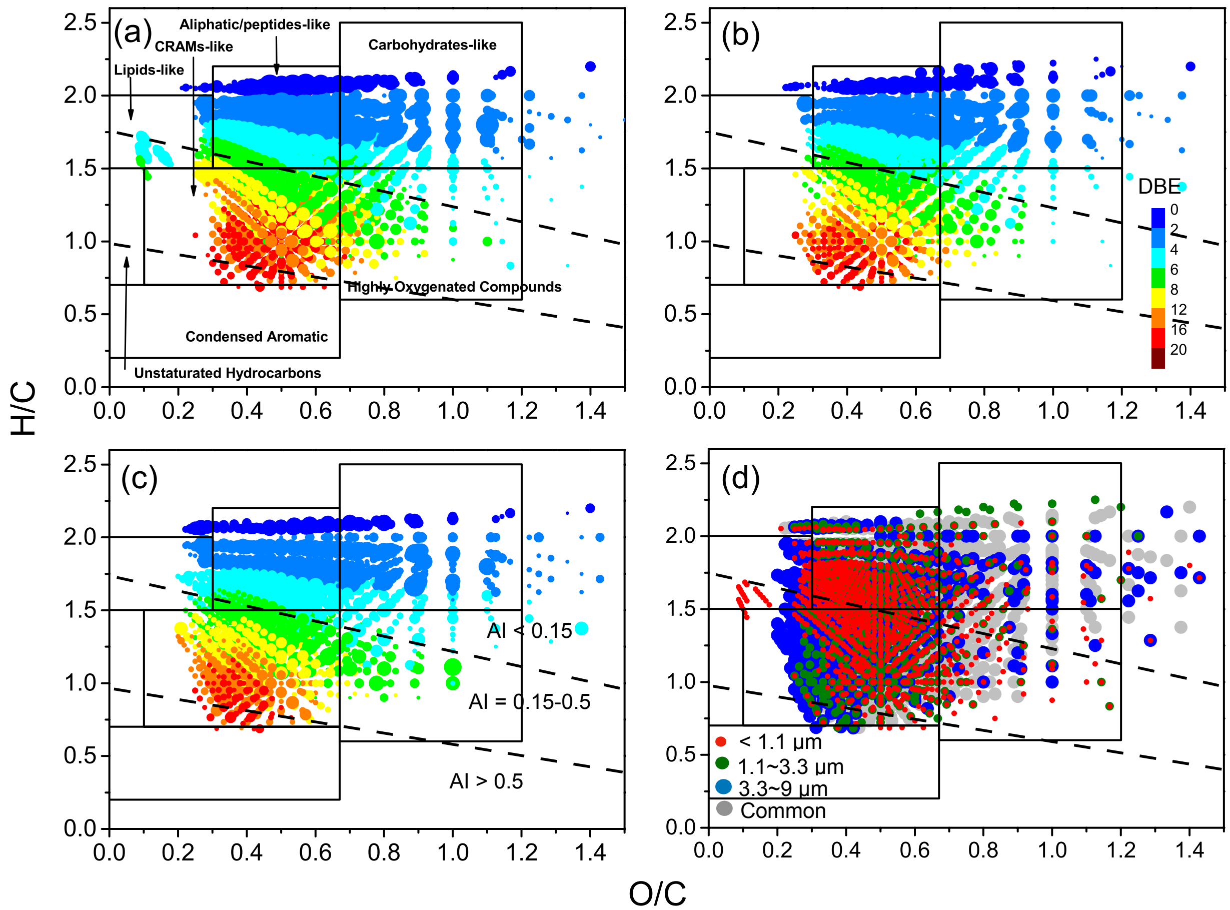

Figure S11. Typical Van Krevelen plots for CHNOS compounds in (a) $PM_{1.1}$, (b)$PM_{1.1\text{-}3.3}$ and (c) $PM_{3.3\text{-}9}$ with separation by AI value ranges in black dotted lines. The color bar in (a) – (c) denotes the number of DBE. Black lines show class identification. The stoichiometric ranges set as boundaries of the classifications are showed in Table S3. The size of the symbols reflects the relative peak intensities of molecular formulae on a logarithmic scale. The diagram (d) presents the common and unique compounds among the size-segregated aerosols.

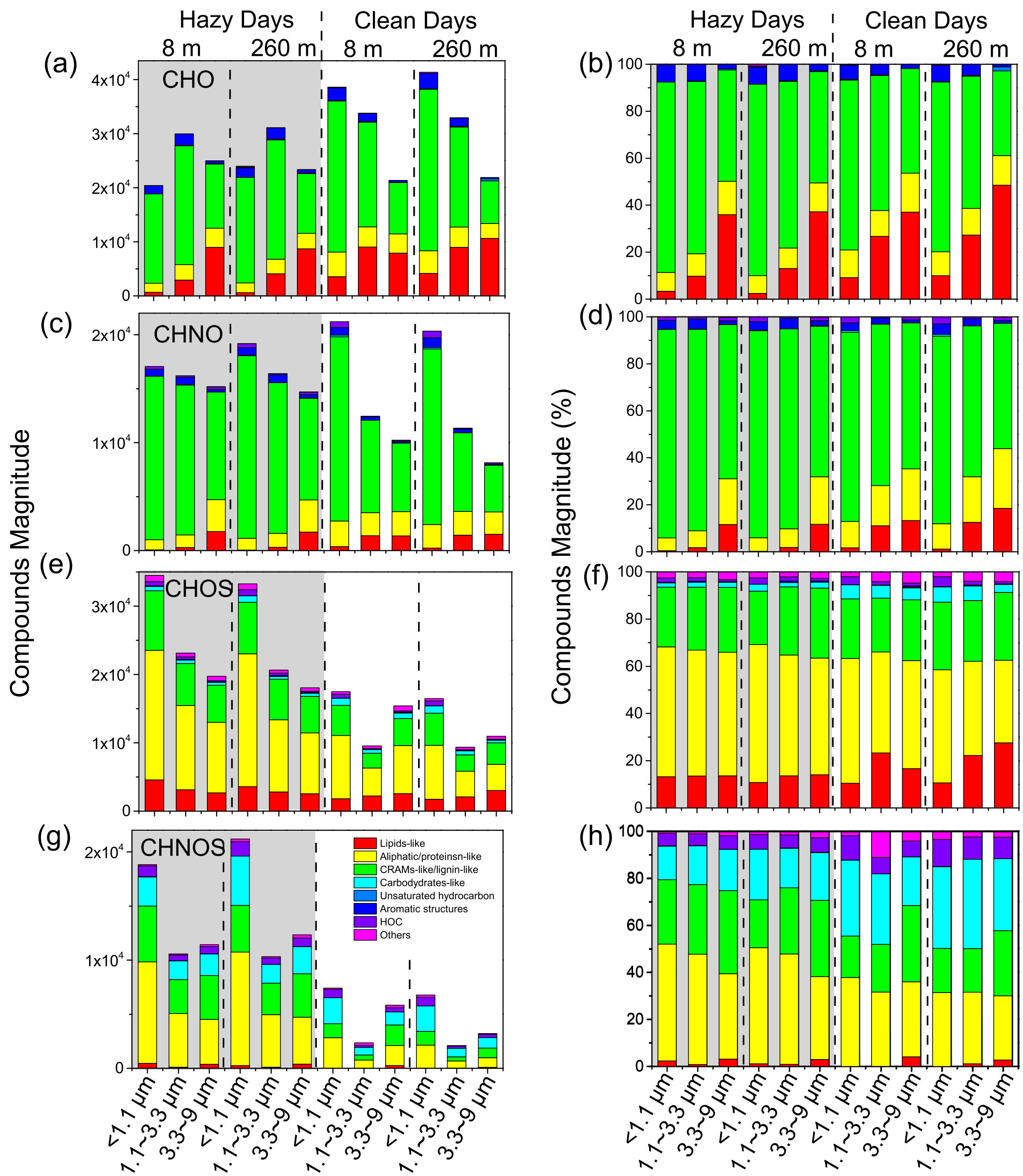

Figure S12. The magnitudes contribution of seven categories in VK classes. The color bar denotes various categories of potential sources.

REFERENCES

1. A. Bianco, L. Deguillaume, M. Vaïtilingom, E. Nicol, J. L. Baray, N. Chaumerliac and M. C. Bridoux, *Environ. Sci. Technol.*, 2018, acs.est.8b01964.
2. A. S. Wozniak, J. E. Bauer, R. L. Sleighter, R. M. Dickhut and P. G. Hatcher, *Atmos. Chem. Phys.*, 2008, **8**, 5099-5111.
3. I. Kourtchev, R. H. M. Godoi, S. Connors, J. G. Levine, A. T. Archibald, A. F. L. Godoi, S. L. Paralovo, C. G. G. Barbosa, R. A. F. Souza, A. O. Manzi, R. Seco, S. Sjostedt, J. H. Park, A. Guenther, S. Kim, J. Smith, S. T. Martin and M. Kalberer, *Atmos. Chem. Phys.*, 2016, **16**, 11899-11913.
4. J. H. Kroll, N. M. Donahue, J. L. Jimenez, S. H. Kessler, M. R. Canagaratna, K. R. Wilson, K. E. Altieri, L. R. Mazzoleni, A. S. Wozniak and H. Bluhm, *Nature Chem.*, 2011, **3**, 133-139.