



Supplement of

Simultaneous measurements of gas- and aerosol-phase water-soluble organic nitrogen in the winter urban atmosphere of Chengdu, China

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Text S1. Detailed description of the online measurement by the IGAC and method accuracy test.

Ambient air is sampled through a PM_{2.5} sharp-cut cyclone at a flow rate of 16.7 L min⁻¹, and then passes sequentially through a wet annular denuder (WAD) where gaseous compounds are absorbed into pure water, and a scrub and impactor aerosol collector (SIC) where PM_{2.5} are collected and transformed into liquid samples. The collected gas and aerosol samples, after removal of insoluble species and bubbles, are injected into an ion chromatography system (ICS-5000+) for determination of water-soluble inorganic ions and small molecular amines (e.g., methylamine (MA), dimethylamine (DMA)), while the remaining portions are simultaneously analyzed by a TOC/TN analyzer (TOC-L CPH).

WSOC is determined by difference: total carbon (TC) is measured via high-temperature (680°C) Pt-catalyzed combustion converting all carbon to CO₂ detected by non-dispersive infrared (NDIR), yielding water-soluble total carbon (WSTC); inorganic carbon (IC) is measured after acidification with 25% H₃PO₄ converting inorganic carbonates to CO₂ detected by NDIR, yielding water-soluble inorganic carbon (WSIC); WSOC is calculated as WSTC minus WSIC. Similarly, WSON is obtained as the difference between water-soluble total nitrogen (WSTN) measured by combustion and water-soluble inorganic nitrogen (WSIN, mainly ammonium, nitrate, and nitrite) determined by ion chromatography. Calibration curves for TC and IC are established using standard solutions of NaHCO₃, Na₂CO₃, and potassium hydrogen phthalate. The calibration curve for total nitrogen was created using a KNO₃ standard solution.

Text S2. Calculation of the contributions of the major components of PM_{2.5} to ALWC.

Inorganic ALWC was simulated using the ISORROPIA-II thermodynamic model, constrained by ambient meteorological parameters and measured concentrations of

38 inorganic ions. The contribution of $(\text{NH}_4)_2\text{SO}_4$ to total ALWC was isolated by
 39 calculating the difference between the full model prediction and a simulation excluding
 40 $(\text{NH}_4)_2\text{SO}_4$ input (i.e., setting $(\text{NH}_4)_2\text{SO}_4 = 0$). Similarly, the contribution of NH_4NO_3
 41 was derived from the difference in ALWC between simulations performed with and
 42 without NH_4NO_3 (i.e., setting $\text{NH}_4\text{NO}_3 = 0$). The equation for ALWC_{org} is as follows
 43 (Lv et al., 2022a; Lv et al., 2022b):

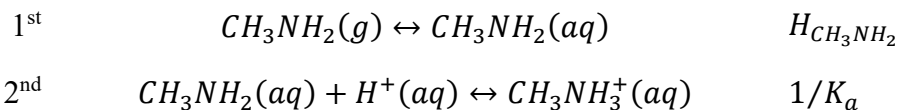
$$\text{ALWC}_{\text{org}} = \frac{[\text{OM}]\rho_w}{\rho_{\text{org}}} \frac{\kappa_{\text{org}}}{\frac{1}{\text{RH}} - 1} \quad (\text{S1})$$

44 Where $[\text{OM}]$ is the concentration of fine particulate organic matter ($\text{OM} = \text{OC} \times 1.6$);
 45 ρ_w and ρ_{org} are the density of water ($\rho_w = 1.0 \text{ g cm}^{-3}$) and OM ($\rho_{\text{org}} = 1.4 \text{ g cm}^{-3}$),
 46 respectively; and κ_{org} is the hygroscopicity parameter for organic aerosol
 47 composition ($\kappa_{\text{org}} = 0.06$).

48 **Text S3. The dependencies of amines on pH, ALWC, and T (S-curve** 49 **equation derivations)**

50 **3.1 CH_3NH_2 – CH_3NH_3^+ partitioning**

51 Here, we show the detailed derivation of equation (4) in that paper. The
 52 equilibrium between gaseous CH_3NH_2 and particle-phase CH_3NH_3^+ involves two
 53 processes: First, CH_3NH_2 dissolves into the aqueous phase (assuming the particles are
 54 liquids). Second, dissolved CH_3NH_2 undergoes hydrogenation (H^+) to form CH_3NH_3^+ .
 55 The two processes are reversible and often reach thermodynamic equilibria at
 56 ambient conditions (RH, T) for fine particles.

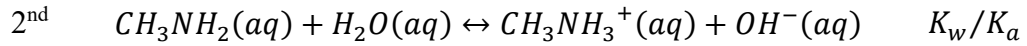


57 for which reaction equilibria are expressed as follows,

$$H_{\text{CH}_3\text{NH}_2} = \gamma_{\text{CH}_3\text{NH}_2} [\text{CH}_3\text{NH}_2] / p_{\text{CH}_3\text{NH}_2} \quad (\text{S2})$$

$$1/K_a = \frac{\gamma_{CH_3NH_3^+} [CH_3NH_3^+]}{\gamma_{CH_3NH_2} [CH_3NH_2] \gamma_{H^+} [H^+]} \quad (S3)$$

58 where, $H_{CH_3NH_2}$ is CH_3NH_2 Henry's law constant ($H_{CH_3NH_2} =$
59 $90.179 \text{ mol atm}^{-1} \text{ kg}^{-1}$, 298.15 K) (Sander, 2023), K_a is $CH_3NH_3^+$ acid
60 dissociation constant ($K_a = 2.1878 \times 10^{-11} \text{ mole L}^{-1}$, 298.15 K) (Ge et al., 2011a),
61 γ_i represents activity coefficient , $p_{CH_3NH_2}$ is partial pressure of CH_3NH_2 in
62 atmosphere, and $[x]$ represents aqueous concentrations (mole L^{-1}). Please note that
63 methylamine is an organic amine classified as a weak base. When methylamine comes
64 into contact with water, a reaction similar to that between ammonia and water occurs
65 (Fountoukis and Nenes, 2007). Methylamine can accept a proton (H^+) from water. In
66 this reaction, methylamine acts as a base, causing water to dissociate and produce
67 hydroxide ions (OH^-). The reaction is represented by the equation:



68 where K_w is water dissociation constant. Equations (S2) and (S3) give the total
69 dissolved CH_3NH_2 or total particle-phase methylammonium ion ($[CH_3NH_3^T]$) as

$$[CH_3NH_3^T] = [CH_3NH_2] + [CH_3NH_3^+] = H_{CH_3NH_2} p_{CH_3NH_2} \left(\frac{1}{\gamma_{CH_3NH_2}} + \frac{\gamma_{H^+} [H^+]}{\gamma_{CH_3NH_3^+} K_a} \right) \quad (S4)$$

70 Combining with ideal gas law, that is

$$c[CH_3NH_2] = \frac{p_{CH_3NH_2}}{RT} \quad (S5)$$

71 Where $c[x]$ is concentration per volume of air , R is the gas constant, and T is the
72 temperature. Therefore, the particle-phase fraction of the methylammonium ion is:

$$\varepsilon(CH_3NH_3^+) = \frac{c(CH_3NH_3^T)}{c(CH_3NH_2) + c(CH_3NH_3^T)} = \frac{[CH_3NH_3^T] W_i}{c(CH_3NH_2) + [CH_3NH_3^T] W_i} \quad (S6)$$

73 where W_i is the liquid water content of the particles ($\mu\text{g m}^{-3}$; mass per volume of air).

74 Taking equations (S4) and (S5) into (S6), we get $\varepsilon(CH_3NH_3^T)$ as

$$\varepsilon(CH_3NH_3^+) = \frac{\left(\frac{\gamma_{H^+}[H^+]}{\gamma_{CH_3NH_3^+}} + \frac{K_a}{\gamma_{CH_3NH_2}} \right) \frac{H_{CH_3NH_2}}{K_a} W_i RT}{1 + \left(\frac{\gamma_{H^+}[H^+]}{\gamma_{CH_3NH_3^+}} + \frac{K_a}{\gamma_{CH_3NH_2}} \right) \frac{H_{CH_3NH_2}}{K_a} W_i RT} \quad (S7)$$

75 To be consistent with the SI units and substitute $[H^+] = 10^{-pH}$, equation (S7) is
 76 presented as:

$$\varepsilon(CH_3NH_3^+) = \frac{\left(\frac{\gamma_{H^+}}{\gamma_{CH_3NH_3^+}} 10^{-pH} + \frac{K_a}{\gamma_{CH_3NH_2}} \right) \frac{H_{CH_3NH_2}}{K_a} W_i RT \times 0.987 \times 10^{-14}}{1 + \left(\frac{\gamma_{H^+}}{\gamma_{CH_3NH_3^+}} 10^{-pH} + \frac{K_a}{\gamma_{CH_3NH_2}} \right) \frac{H_{CH_3NH_2}}{K_a} W_i RT \times 0.987 \times 10^{-14}} \quad (S8)$$

77 Please note that 0.987×10^{-14} is derived from the use of $R =$
 78 $8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mole}^{-1}$, so 1 atm and 1 L must be converted to 1 Pa and 1 μg ,
 79 respectively.

80 **3.2 (CH₃)₂NH –(CH₃)₂NH₂⁺ partitioning**

81 Following the same derivation procedure as CH₃NH₂ –CH₃NH₃⁺ partitioning, we
 82 have $\varepsilon((CH_3)_2NH_2^+)$ as

$$\varepsilon((CH_3)_2NH_2^+) = \frac{\left(\frac{\gamma_{H^+}}{\gamma_{(CH_3)_2NH_2^+}} 10^{-pH} + \frac{K_a}{\gamma_{(CH_3)_2NH}} \right) \frac{H_{(CH_3)_2NH}}{K_a} W_i RT \times 0.987 \times 10^{-14}}{1 + \left(\frac{\gamma_{H^+}}{\gamma_{(CH_3)_2NH_2^+}} 10^{-pH} + \frac{K_a}{\gamma_{(CH_3)_2NH}} \right) \frac{H_{(CH_3)_2NH}}{K_a} W_i RT \times 0.987 \times 10^{-14}} \quad (S9)$$

83 where, $H_{(CH_3)_2NH}$ is (CH₃)₂NH Henry's law constant ($H_{(CH_3)_2NH} = 56.742 \text{ mol atm}^{-1}$
 84 kg^{-1} , 298.15 K) (Sander, 2023), K_a is (CH₃)₂NH₂⁺ acid dissociation constant ($K_a =$
 85 $1.8621 \times 10^{-11} \text{ mole L}^{-1}$, 298.15 K) (Ge et al., 2011a), γ_i represents activity
 86 coefficient.

87 **Table S1.** Interannual statistics of PM_{2.5} and its chemical components in the SCB during
88 winter ($\mu\text{g m}^{-3}$).

Year	PM _{2.5}	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Cl ⁻	OM ^a	References
2012	108	22	19	16	—	—	(Chen et al., 2019)
2015	115.41 ± 65.28	25.0	22.7	15.1	—	45.2	(Kong et al., 2020)
2016	195.8 ± 91.0	17.5	25.5	15.8	4.9	60	(Zhang et al., 2024a)
2017	153.9 ± 63.1	11.3	23	12.5	3.9	48	(Zhang et al., 2024a)
2018	119.8 ± 32.0	8.8	17.5	10.8	1.4	35	(Zhang et al., 2024a)
2020	96.1 ± 39.3	7.5	18.5	8.2	1.7	29	(Zhang et al., 2024a)
2021	98.5 ± 38.7	10 ± 4.2	29 ± 14	15.1 ± 6.4	5.2 ± 4.1	39.2 ± 3.9 ^b	(Bao et al., 2023)
2023	95.6 ± 28.7	8.8	21.0	7.5	1.7	33.7	(Zhang et al., 2024b)
2024	76 ± 38	4.9 ± 2.0	16.7 ± 8.3	7.2 ± 3.0	1.3 ± 1.0	21.1 ± 9.6	this study

89 ^aOM = OC × 1.6. ^bObtained via ToF-ACSM.

90 **Table S2.** Atmospheric physicochemical properties of different alkaline nitrogen-
91 containing compounds (25 °C).

	Ammonia	Methylamine	Dimethylamine
CAS	7664-41-7	74-89-5	124-40-3
Molecular weight	17	31	45
pKa (Huang, 2022)	9.25	10.66	10.73
Vapor pressure (kPa)	1003 (Youn et al., 2015)	350.6 (He et al., 2026)	203 (Youn et al., 2015)
Henry's law constant (mol atm ⁻¹ kg ⁻¹) (Sander, 2023)	59.96	90.179	56.742
Reaction rate of •OH (cm ³ molecule ⁻¹ s ⁻¹)	1.6 × 10 ⁻¹³	(2.20 ± 0.22) × 10 ⁻¹¹	(6.54 ± 0.66) × 10 ⁻¹¹
[half-life] (Ge et al., 2011b)	[72.3 d]	[12.6 h]	[4.3 h]

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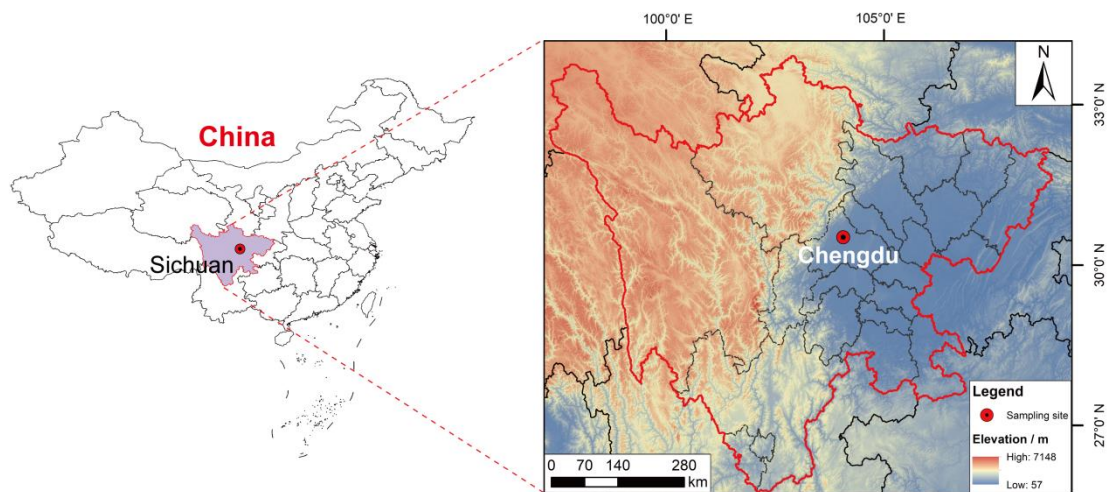


Figure S1. Geographic location of the sampling site in Chengdu (CD), China.

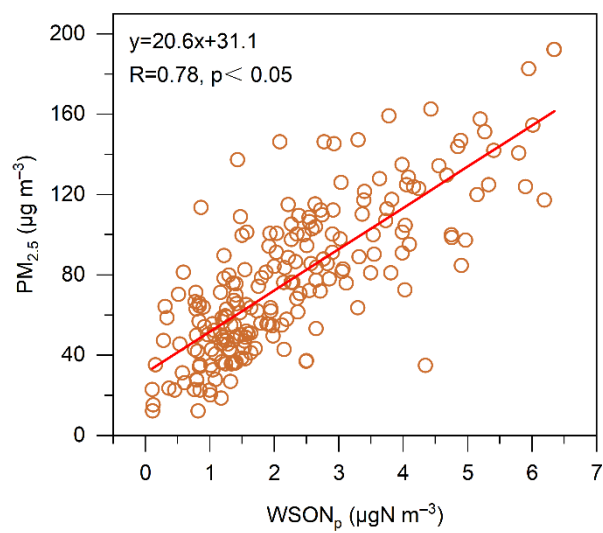


Figure S2. Correlation Scatter Plot Between WSON_p and PM_{2.5}.

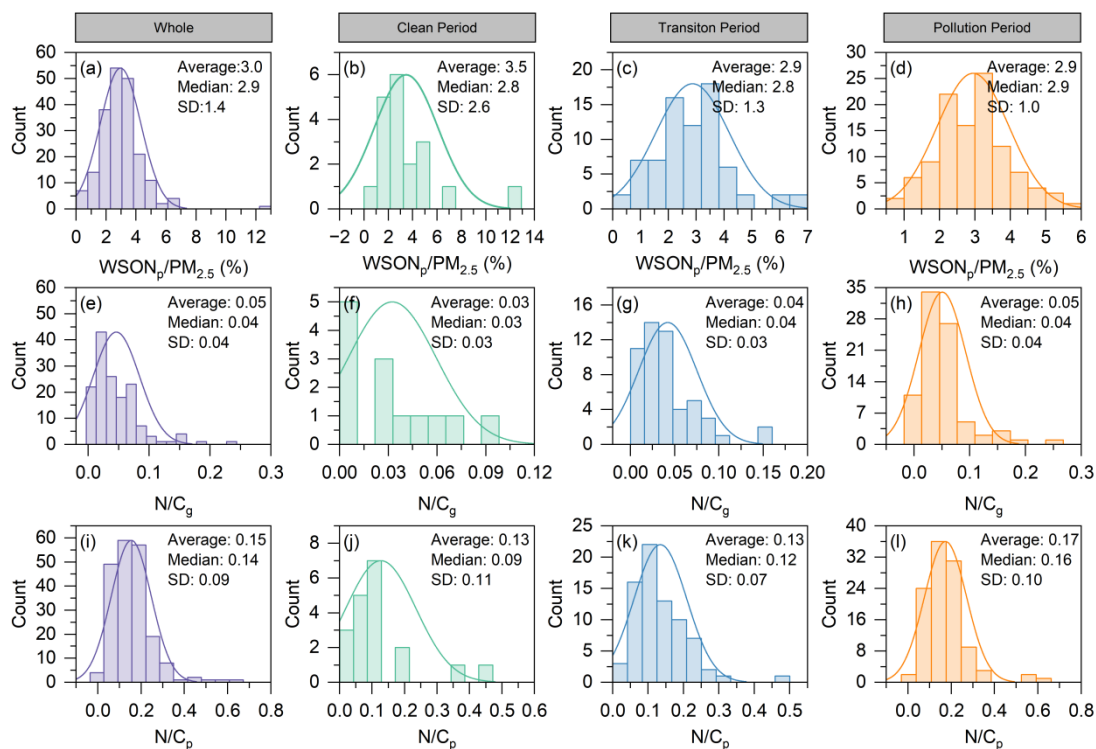
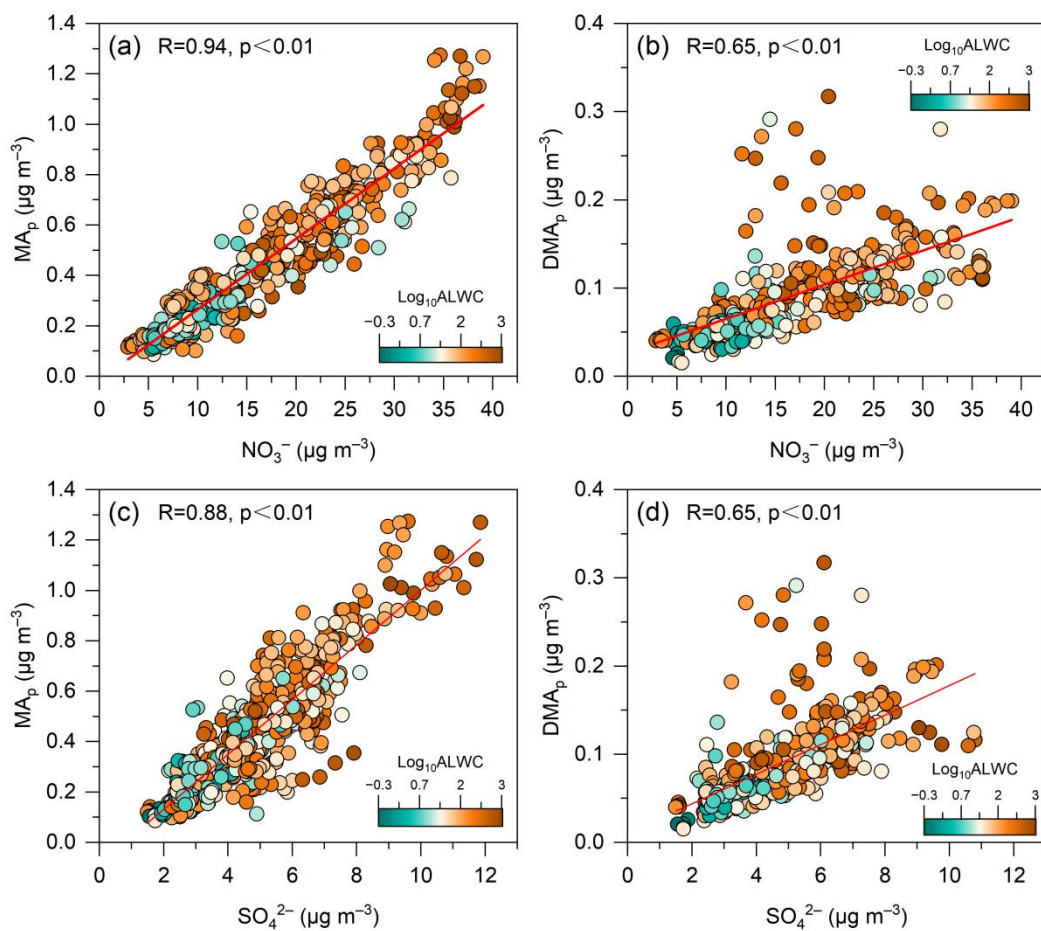


Figure S3. Frequency distribution characteristics of WSON contribution and nitrogen to carbon (WSON/WSOC) ratios in PM_{2.5} during different periods. (a–d) Mass percentage of water-soluble organic nitrogen in PM_{2.5} (WSON_p/PM_{2.5}, %); (e–h) Molar ratio of nitrogen to carbon in the gas phase (WSON/WSOC_g); (i–l) Molar ratio of nitrogen to carbon in the particle phase (WSON/WSOC_p). The solid lines represent Gaussian distribution fits to the data. The average, median and standard deviation (SD) for each dataset are indicated in the panels.



Figure S4. Pearson correlation matrix of gaseous and particulate methylamine (MA) and dimethylamine (DMA) with NH₃, CO, and NO₂ during the wintertime observation in CD. Pearson (linear).



109

110 **Figure S5.** Linear regression analysis for the amines with inorganic salts.

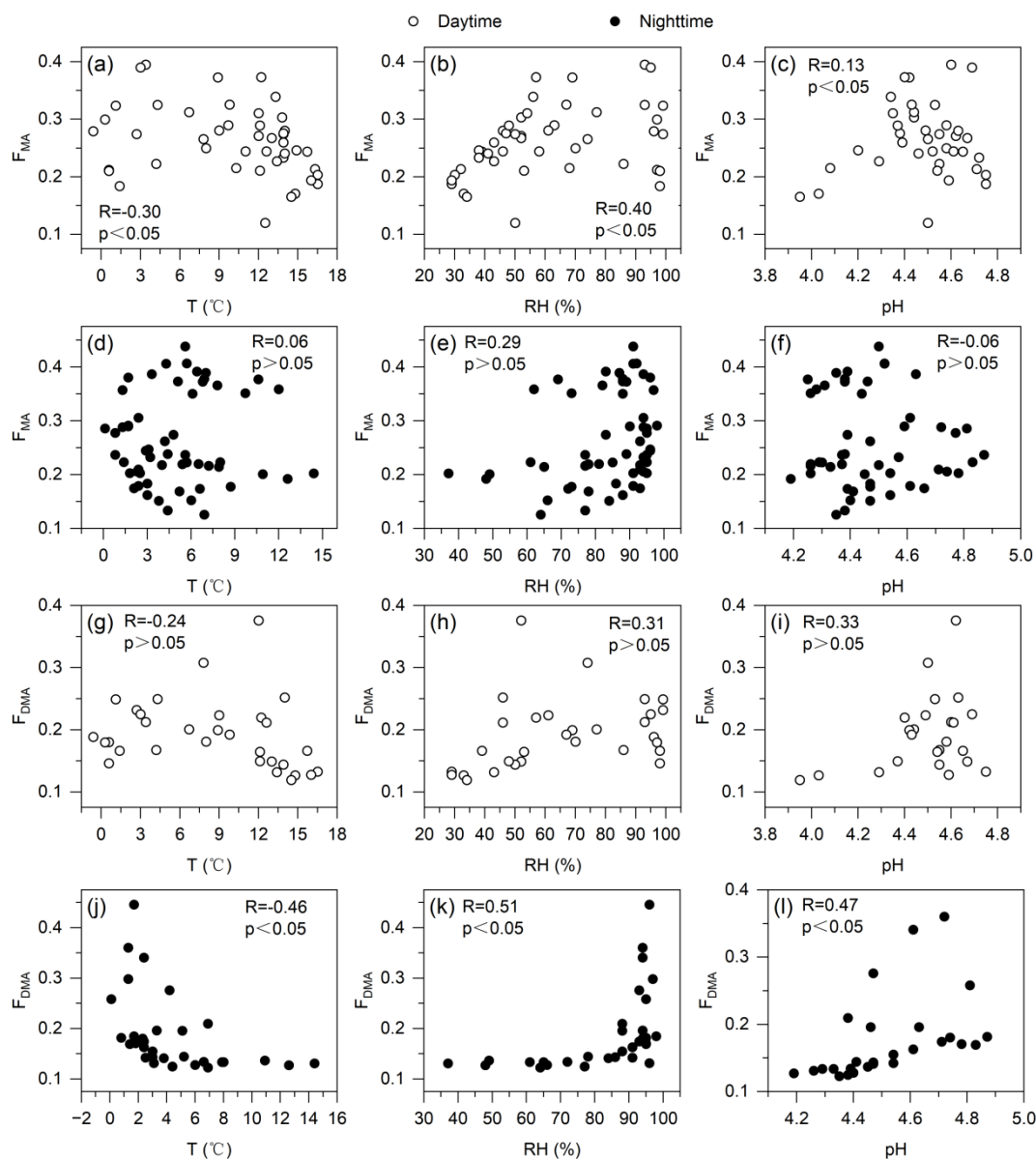


Figure S6. Factors affecting the gas-to-aerosol phase-partitioning coefficients of methylamine (F_{MA}) and dimethylamine (F_{DMA}) in Chengdu (CD) under the daytime and nighttime during the pollution period (2025.1.2—2025.1.6).

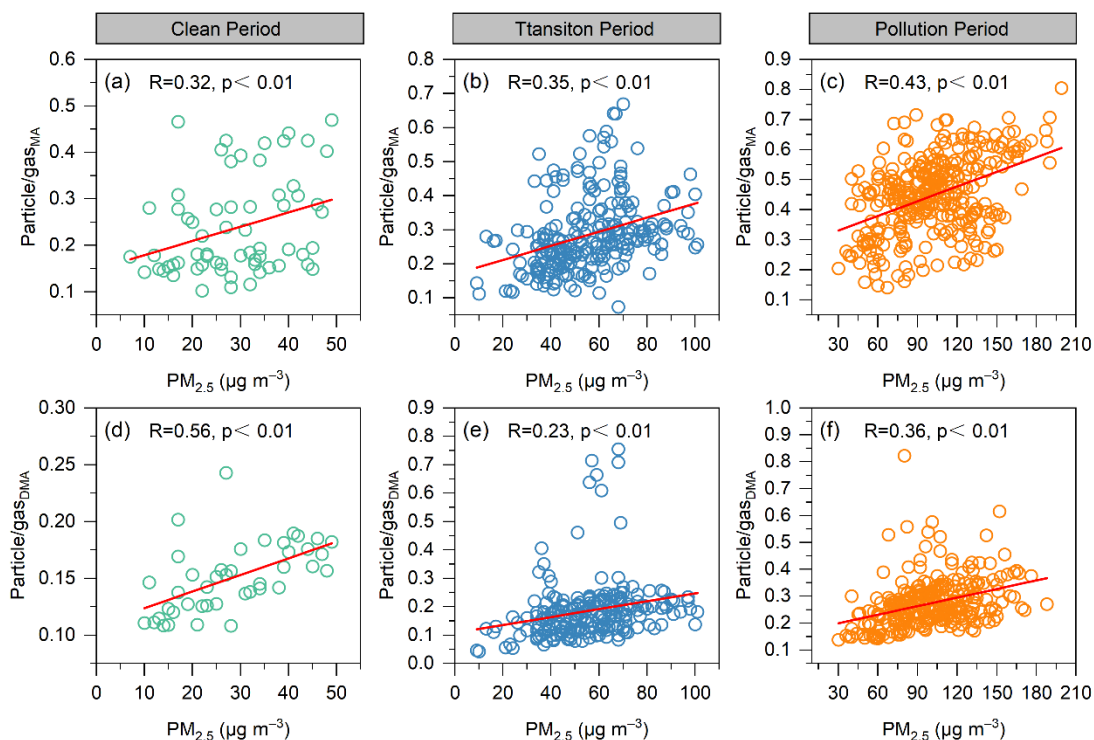


Figure S7. Ratio in particle and gas phase signal of the methylamine (MA) and dimethylamine (DMA)–versus total $PM_{2.5}$ concentration ($\mu g m^{-3}$) for all observations during the campaign. According to equation (10), the slope of a linear fit will provide K_i for the selected constituent.

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