Supplementary Information (SI) for Environmental Science: Atmospheres.
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Supporting Information for:

Optimizing Vocus proton-transfer-reaction mass spectrometry for detecting trace atmospheric amines

Yiqi Zhao[1], Zhaojin An[1,*], Yuyang Li[1], Rujing Yin[2], Dandan Li[1], Dongbin Wang[1], Xuan Zheng[3], Jun Zheng[4], Hong He[5,6,7], Jincai Zhao[6,8], Kebin He[1], Douglas R. Worsnop[9,10], Jingkun Jiang[1,*]

[1]State Key Joint Laboratory of Regional Environment and Sustainability, School of Environment, Tsinghua University, 100084, Beijing, China

[2]Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, 116024, Dalian, China

[3]College of Chemistry and Environmental Engineering, Shenzhen University, 518060, Shenzhen, China

[3]NUIST Reading Academy, Nanjing University of Information Science & Technology, 210044, Nanjing, China

[5]State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 100085, Beijing, China

[6]University of Chinese Academy of Sciences, 100049, Beijing, China

[7]Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, 361021, Xiamen, China

[8]Key Laboratory of Photochemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, China

[9]Institute for Atmospheric and earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00014, Finland

[10]Aerodyne Research, Inc., Billerica, Massachusetts 01821, USA

*Corresponding author: Jingkun Jiang (email: jiangjk@tsinghua.edu.cn), Zhaojin An (email: azj@tsinghua.edu.cn)

Figure S1. The map of the measurement site (© Google Maps). The measurement site is marked with a yellow star, located in the central part of Tsinghua University, Beijing. The main traffic roads are all outside the school area.

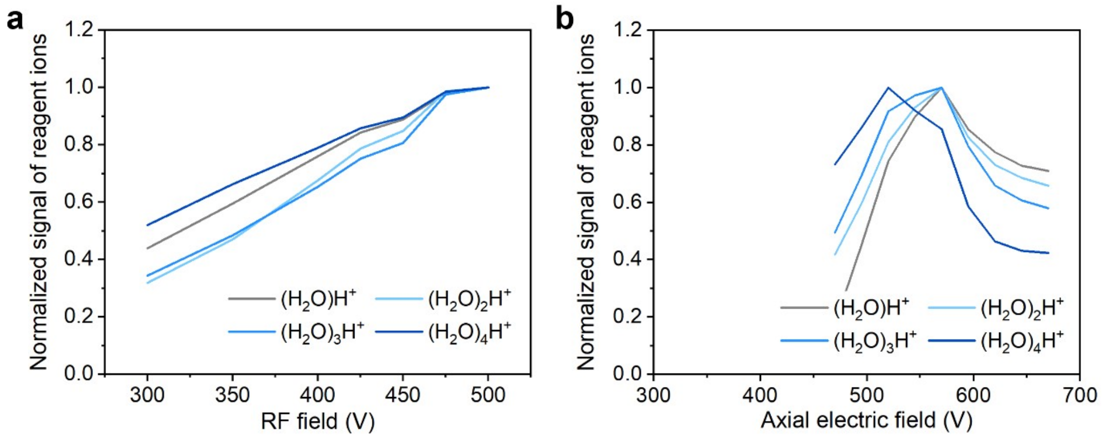

Figure S2. Dependence of normalized reagent ion signals on FIMR electric field parameters. (a) RF field; (b) Axial electric field.

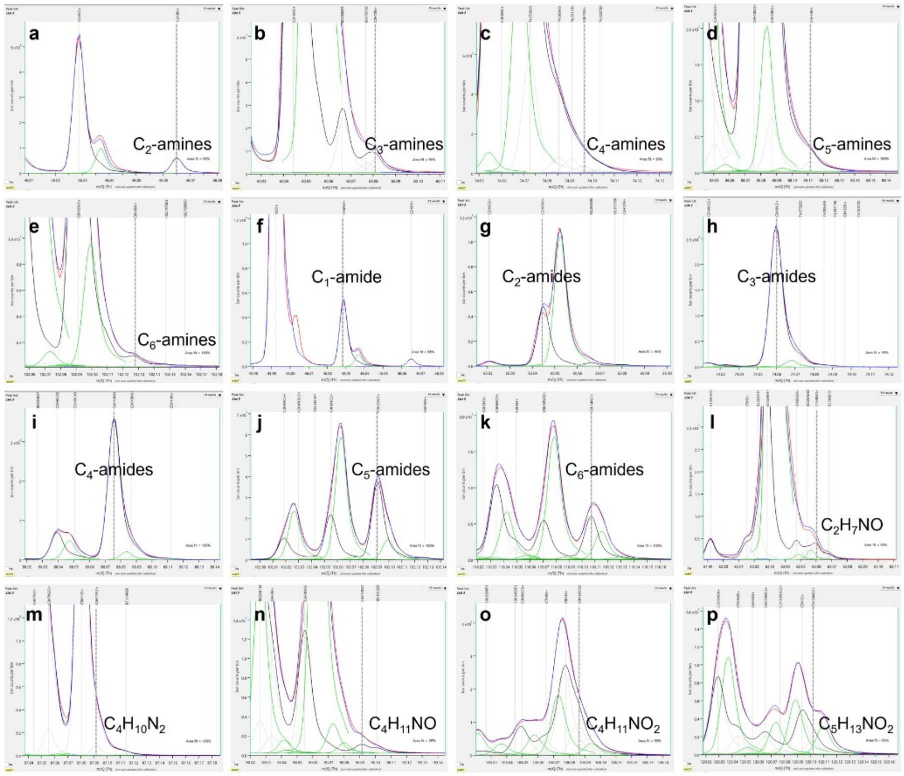

Figure S3. Mass spectra of identified atmospheric amines in urban Beijing in 2024. a-e correspond to $C_{2\text{-}6}$-amines, f-k to $C_{1\text{-}6}$-amides, and l-p to emerging amines.

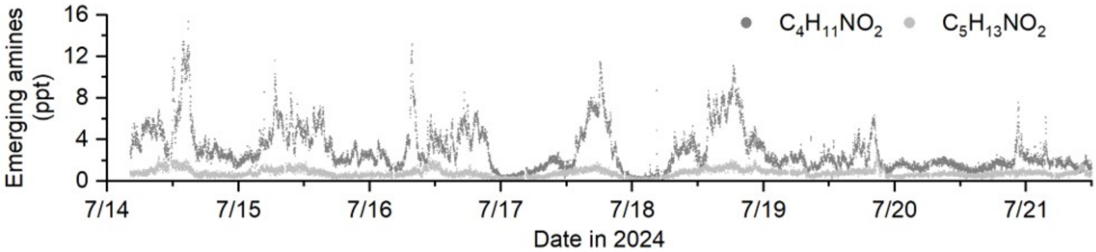

Figure S4. Time series of emerging amines ($C_4H_{11}NO_2$ and $C_5H_{13}NO_2$) in urban Beijing during measurement period.

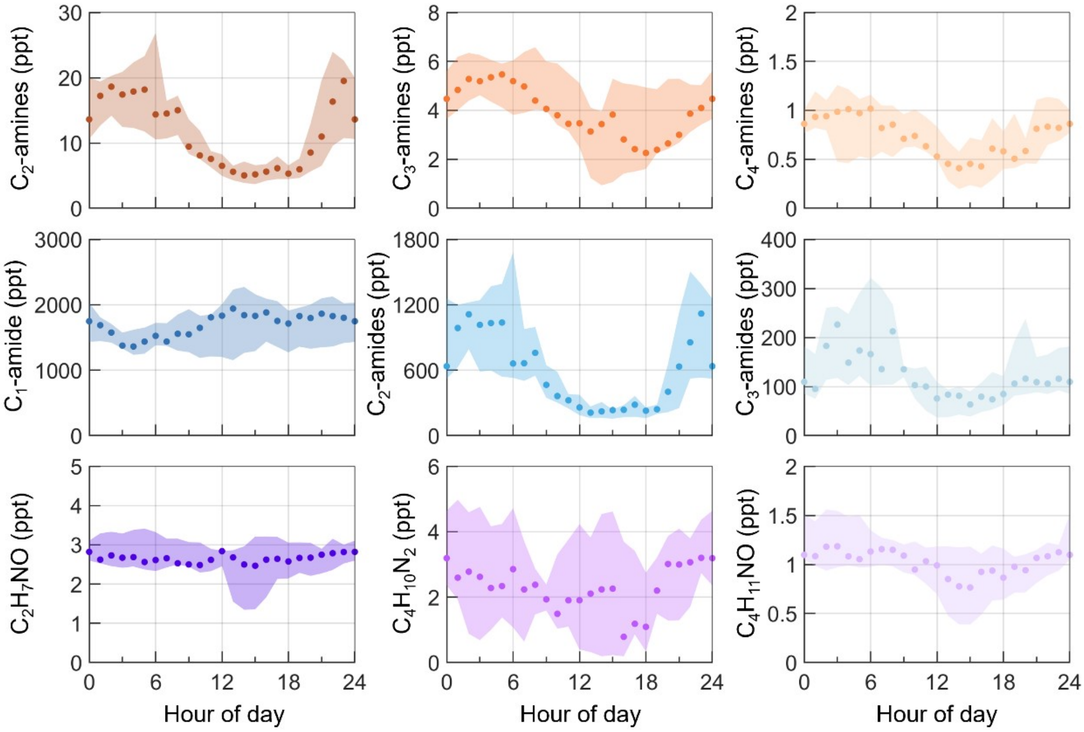

Figure S5. Median diurnal variations of typical alkylamines, amides, and emerging amines in urban Beijing. The shaded areas represent the 25th and 75th percentiles.

Table S1. Sensitivity and LOD of instruments for C_2-amines measurement

Instrument	Sensitivity (cps/ppbv)	LOD (pptv)	Ref.
CIMS	--	32.4	Sellegri et al. (2005)
AmPMS	--	Sub-pptv	Hanson et al. (2011)
Protonated ethanol CIMS	7200	7	Yu and Lee (2012)
Protonated acetone CIMS	2000	36	Yu and Lee (2012)
Protonated ethanol CIMS	--	0.5	You et al. (2014)
PTR-MS	40423	0.5	Zheng et al. (2015)
Nitrate CIMS	--	0.7	Simon et al. (2016)
Protonated ethanol CIMS	5600	0.5	Yao et al. (2016)
Vocus PTR-TOF	2680	1.44	Wang et al. (2020)
Vocus PTR-TOF-MS	1226	1.5	Chang et al. (2022)
Water cluster CIMS	31260	0.25	Zhu et al. (2022)
Vocus-PTR	6291	0.55	This work

Table S2. Improvement of atmospheric amine signal intensities

Amines	Response signal with optimization (cps)	Response signal without optimization (cps)	Fold increase
C_2-amines	106.1	116.1	0.91
C_3-amines	12.8	14.9	0.86
C_4-amines	4.8	3	1.60
C_5-amines	9.2	1.4	6.57
C_6-amines	3.1	1.4	2.21
C_1-amide	843.5	517	1.63
C_2-amides	842.8	377.7	2.23
C_3-amides	7262.8	2926.9	2.48
C_4-amides	1720.8	756.4	2.27
C_5-amides	67.1	32.1	2.09
C_6-amides	21.1	9.3	2.27
C_2H_7NO	7.6	3.2	2.38
$C_4H_{10}N_2$	16.4	4.1	4.00
$C_4H_{11}NO$	23.8	--	--
$C_4H_{11}NO_2$	52.6	16.5	3.19
$C_5H_{13}NO_2$	4.5	0.9	5.00

Text S1. Method for fragment and water cluster correction in Vocus-PTR.

The correction process mainly involves two steps: fragment/water cluster identification and signal correction. First, we referred to the fragment and water cluster lists in Jensen, et al. (2023),[1] Pfannerstill, et al. (2023),[2] and Coggon, et al. (2023).[3] Ions with a pearson correlation coefficient $r > 0.96$ were considered fragments or water clusters of the parent ion. We also attempted to exclude contributions from unknown fragments and water clusters based on time-series correlations (Ions exhibiting a correlation $r^2 > 0.96$ (if chemically reasonable) were examined for potential water clustering or fragmentation effects). Subsequently, the signals of ions identified as fragments or water clusters were aggregated with the parent ion signal after transmission efficiency adjustment, thereby completing the signal correction.

Text S2. The relationship between k_{PTR} and sensitivity, as well as the transmission efficiency in Vocus-PTR.

$$Normalized\ sensitivity\ to\ toluene = (1.35 \pm 0.39) \cdot k_{PTR} - (1.94 \pm 0.84)$$

$$Transmission\ efficiency = 1/(1 + exp((-0.18 \pm 0.02) \cdot m/z + (9.91 \pm 0.85)))$$

The sensitivity for toluene is 4683.9 cps/ppbv. k_{PTR} is in units of 10^{-9} $cm^3 molecue^{-1} s^{-1}$, taken from theoretical values when available and otherwise set to a default of 2.5×10^{-9} $cm^3 molecue^{-1} s^{-1}$. m/z is the mass-to-charge ratio.

References:

[1] Jensen, A. R.; Koss, A. R.; Hales, R. B.; de Gouw, J. A. Measurements of volatile organic compounds in ambient air by gas-chromatography and real-time Vocus PTR-TOF-MS: calibrations, instrument background corrections, and introducing a PTR Data Toolkit. Atmospheric Measurement Techniques 2023, 16 (21), 5261-5285. DOI: 10.5194/amt-16-5261-2023.

[2] Pfannerstill, E. Y.; Arata, C.; Zhu, Q.; Schulze, B. C.; Woods, R.; Seinfeld, J. H.; Bucholtz, A.; Cohen, R. C.; Goldstein, A. H. Volatile organic compound fluxes in the agricultural San Joaquin Valley – spatial distribution, source attribution, and inventory comparison. Atmos. Chem. Phys. 2023, 23 (19), 12753-12780. DOI: 10.5194/acp-23-12753-2023.

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