

Elucidating the mechanisms of atmospheric new particle formation in the highly polluted Po Valley, Italy

Jing Cai¹, Juha Sulo¹, Yifang Gu¹, Sebastian Holm¹, Runlong Cai¹, Steven Thomas¹, Almuth Neuberger², Fredrik Mattsson², Marco Paglione³, Stefano Decesari³, Matteo Rinaldi³, Rujing Yin¹, Diego Aliaga¹, Wei Huang¹, Yuanyuan Li^{1,4}, Yvette Gramlich², Giancarlo Ciarelli¹, Lauriane Quéléver¹, Nina Sarnela¹, Katrianne Lehtipalo^{1,5}, Nora Zannoni³, Cheng Wu⁶, Wei Nie⁴, Claudia Mohr^{7,8}, Markku Kulmala^{1,4,9}, Qiaozhi Zha^{1,4}, Dominik Stolzenburg^{1,10*}, Federico Bianchi^{1*}

¹ Institute for Atmospheric and Earth System Research, Faculty of Science, University of Helsinki, Helsinki 00014, Finland

² Department of Environmental Science, Stockholm University, Stockholm 11418, Sweden

³ Italian National Research Council-Institute of Atmospheric Sciences and Climate (CNR-ISAC), Bologna, 40129, Italy

⁴ School of Atmospheric Sciences, Nanjing University, Nanjing, 210023, China

⁵ Finnish Meteorological Institute, Helsinki, 00560, Finland

⁶ Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, Gothenburg 41296, Sweden

⁷ Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, 5232, Switzerland

⁸ Department of Environmental System Science, ETH Zurich, Villigen, 5232, Switzerland

⁹ Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

¹⁰ Institute for Materials Chemistry, TU Wien, Vienna 1060, Austria

Correspondence to: federico.bianchi@helsinki.fi and dominik.stolzenburg@tuwien.ac.at

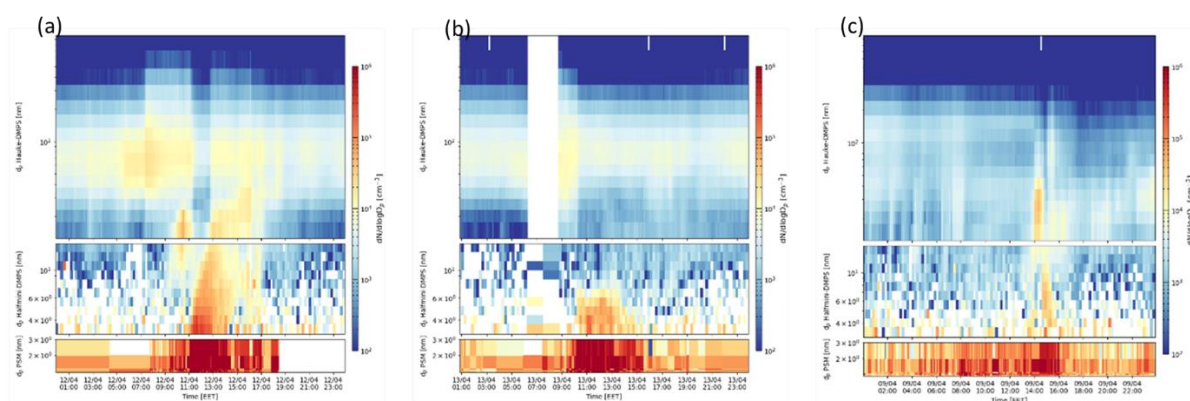


Figure S1. Particle size distributions (x-axis time, y-axis size in nm and color code is number concentration in $dN/d\log D_p$) from 1.3 – 800 nm as measured by three different instruments (upper panel Hauke-DMPS, middle panel Halfmini-DMPS and lower panel PSM) for (a) an NPF with growth event (12th of April), (b) an NPF with growth event, and (c) a non-NPF day.

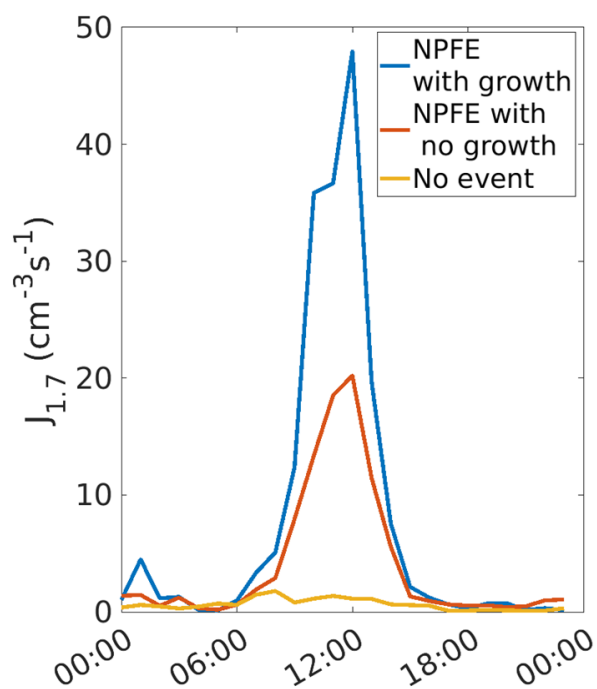


Figure S2. The average formation rate of 1.7 nm particles ($J_{1.7}$) during NPF with growth, NPF without growth and no NPF events during our sampling period.

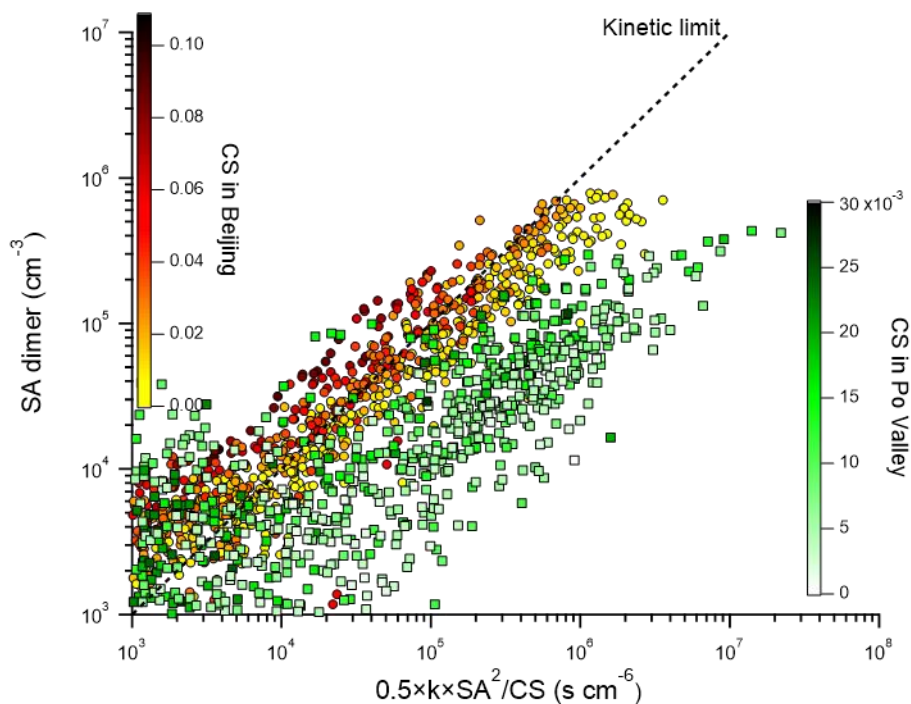


Figure S3. The relationship between sulfuric acid dimer concentration (SA dimer), monomer concentration (SA), and the CS in the Po Valley region. The theoretical molecular collision rate constant (k) was set as $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Stolzenburg et al., 2020).

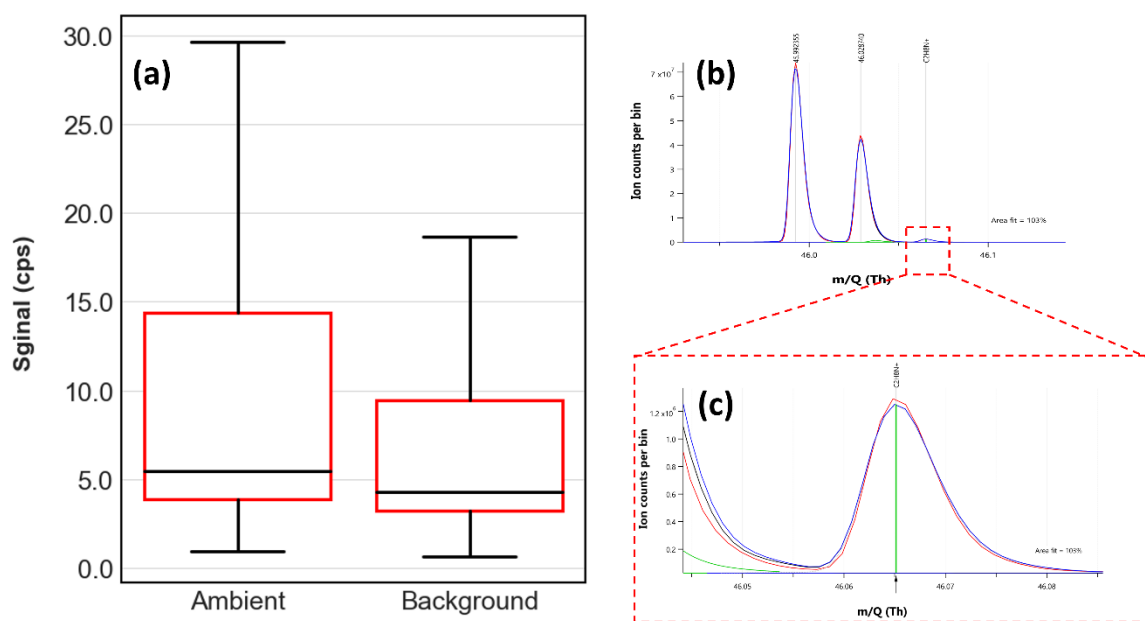


Figure S4. (a) $\text{C}_2\text{H}_7\text{N}$ signal observed from March to April (excluding outliers). (b) Peak fitting at m/z 46. (c) Zoomed-in view of $\text{C}_2\text{H}_8\text{N}^+$ (DMA) peak fitting.

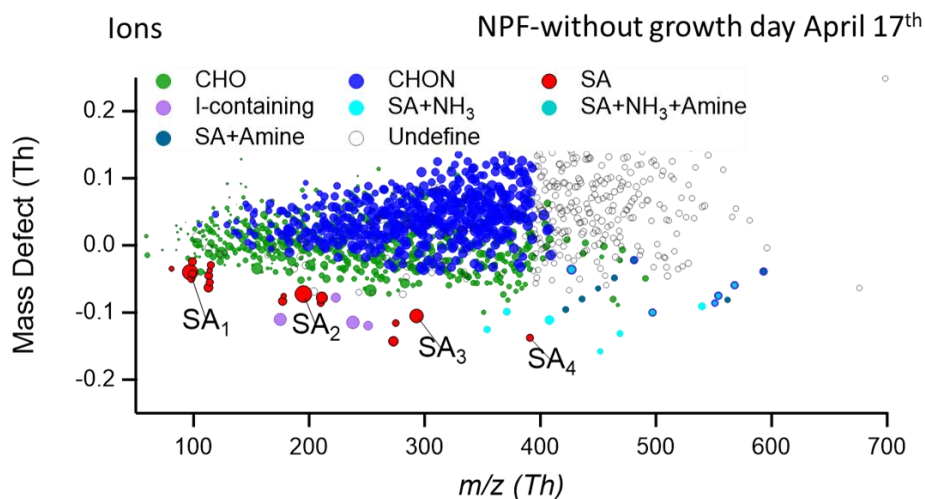


Figure S5. Mass defect plots for ion clusters during the NPF without growth day (10:00 – 14:00 LT of April 17th). The size of the dots is proportional to the logarithm of the signal intensity of each cluster.

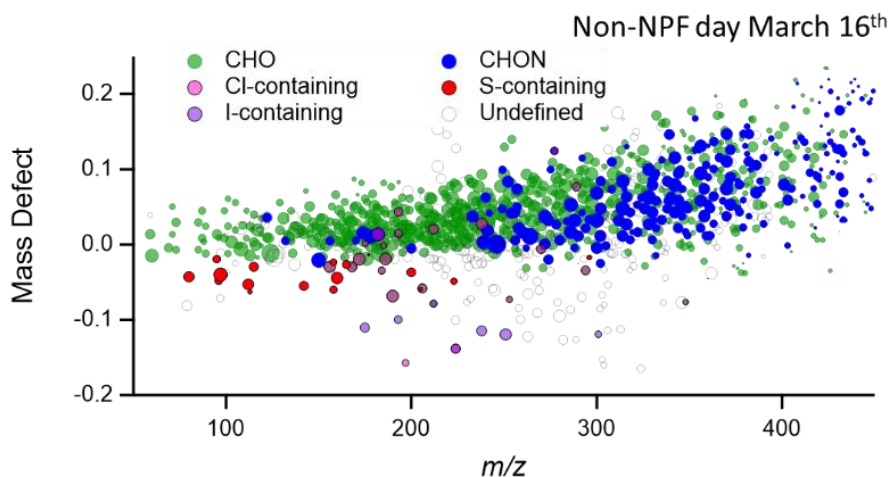


Figure S6. Mass defect plots for neutral clusters during the non NPF period (10:00 – 14:00 LT of March 16th). The size of the dots is proportional to the logarithm of the signal intensity of each cluster.

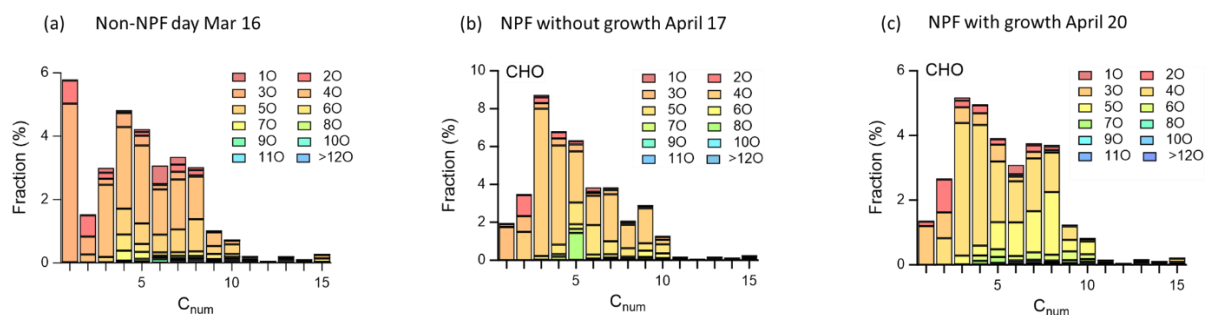


Figure S7. Signal fractions to total identified organic molecules with different numbers of oxygen and carbon atoms of CHO compounds in the (a) non-NPF day (March 16), (b) NPF with no growth day (April 17) and NPF with growth day (April 20) during peak hours (10:00 – 14:00 LT).

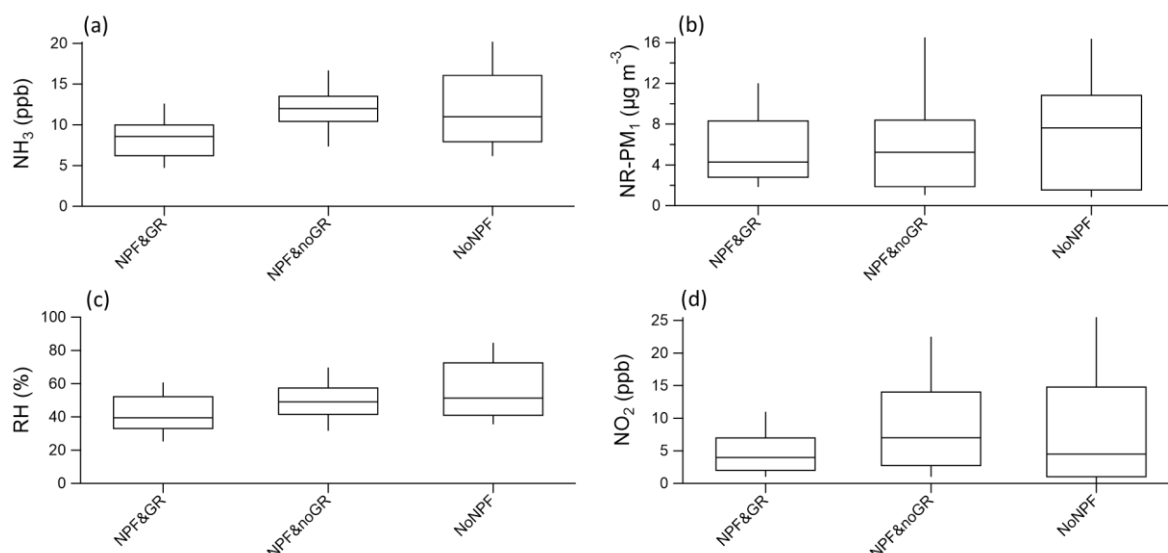


Figure S8. (a) the NH_3 , (b) NR-PM_{10} , (c) RH, and (d) NO_2 for NPF with growth (NPF&GR), NPF without growth (NPF&noGR) and no NPF event (NoNPF) days. In each box plot, the median (middle horizontal line), 25th and 75th percentiles (bottom and top ends of the box, respectively), and 10th and 90th percentiles (bottom and top whiskers, respectively) are presented. The NR-PM_{10} is from a co-located aerosol mass spectrometer measurement (Paglione et al., 2020).

Table S1. Ambient NH_3 and DMA concentrations from different measurement sites

Site	Sampling period	DMA (ppt)	NH_3 (ppb)	Instrument	Ref
Beijing	Oct 2018-Nov 2018	7.3	20.8	H_3O^+ -tof-CIMS (both DMA and NH_3)	(Cai et al., 2021)
Wangdu	Dec 2018-Jan 2019	14.6	31.2	Vocus (DMA), DOAS (NH_3)	(Wang et al., 2020; Liu et al., 2023)
Shanghai	Jul 2015-Aug 2015	40	6.2	Protonated ethanol-CIMS (DMA), DOAS (NH_3)	(Yao et al., 2016; Wang et al., 2015)
Nanjing	Sep 2022-Oct 2022	20.8	13.1	Vocus (DMA), Picarro (NH_3)	unpublished data
Hyytiälä	Mar-Dec 2015	< LOD	0.066	MARGA (both DMA and NH_3)	(Hemmilä et al., 2018)
Po Valley	Mar 2022-May 2022	Not quantified	10.6	Vocus (DMA), Teledyne-API (NH_3)	this study

Note: The Limit of Detection (LOD) for DMA with instrument for Measuring AeRosols and Gases in Ambient Air (MARGA) is 1.7 ppt and the LOD for DMA with Vocus is ~2 ppt.

DOAS is short for differential optical absorption spectroscopy.

Reference

- Cai, R., Yan, C., Yang, D., Yin, R., Lu, Y., Deng, C., Fu, Y., Ruan, J., Li, X., Kontkanen, J., Zhang, Q., Kangasluoma, J., Ma, Y., Hao, J., Worsnop, D. R., Bianchi, F., Paasonen, P., Kerminen, V. M., Liu, Y., Wang, L., Zheng, J., Kulmala, M., and Jiang, J.: Sulfuric acid–amine nucleation in urban Beijing, *Atmos. Chem. Phys.*, 21, 2457–2468, 10.5194/acp-21-2457-2021, 2021.
- Hemmilä, M., Hellén, H., Virkkula, A., Makkonen, U., Praplan, A. P., Kontkanen, J., Ahonen, L., Kulmala, M., and Hakola, H.: Amines in boreal forest air at SMEAR II station in Finland, *Atmospheric Chemistry and Physics*, 18, 6367–6380, 10.5194/acp-18-6367-2018, 2018.
- Liu, P., Chen, H., Song, Y., Xue, C., Ye, C., Zhao, X., Zhang, C., Liu, J., and Mu, Y.: Atmospheric ammonia in the rural North China Plain during wintertime: Variations, sources, and implications for HONO heterogeneous formation, *Sci Total Environ*, 861, 160768, 10.1016/j.scitotenv.2022.160768, 2023.
- Paglione, M., Gilardoni, S., Rinaldi, M., Decesari, S., Zanca, N., Sandrini, S., Giulianelli, L., Bacco, D., Ferrari, S., Poluzzi, V., Scotto, F., Trentini, A., Poulain, L., Herrmann, H., Wiedensohler, A., Canonaco, F., Prévôt, A. S. H., Massoli, P., Carbone, C., Facchini, M. C., and Fuzzi, S.: The impact of biomass burning and aqueous-phase processing on air quality: a multi-year source apportionment study in the Po Valley, Italy, *Atmospheric Chemistry and Physics*, 20, 1233–1254, 10.5194/acp-20-1233-2020, 2020.
- Stolzenburg, D., Simon, M., Ranjithkumar, A., Kürten, A., Lehtipalo, K., Gordon, H., Ehrhart, S., Finkenzeller, H., Pichelstorfer, L., Nieminen, T., He, X.-C., Brilke, S., Xiao, M., Amorim, A., Baalbaki, R., Baccarini, A., Beck, L., Bräkling, S., Caudillo Murillo, L., Chen, D., Chu, B., Dada, L., Dias, A., Dommen, J., Duplissy, J., El Haddad, I., Fischer, L., Gonzalez Carracedo, L., Heinritzi, M., Kim, C., Koenig, T. K., Kong, W., Lamkaddam, H., Lee, C. P., Leiminger, M., Li, Z., Makhmutov, V., Manninen, H. E., Marie, G., Marten, R., Müller, T., Nie, W., Partoll, E., Petäjä, T., Pfeifer, J., Philippov, M., Rissanen, M. P., Rörup, B., Schobesberger, S., Schuchmann, S., Shen, J., Sipilä, M., Steiner, G., Stozhkov, Y., Tauber, C., Tham, Y. J., Tomé, A., Vazquez-Pufleau, M., Wagner, A. C., Wang, M., Wang, Y., Weber, S. K., Wimmer, D., Wlasits, P. J., Wu, Y., Ye, Q., Zauner-Wieczorek, M., Baltensperger, U., Carslaw, K. S., Curtius, J., Donahue, N. M., Flagan, R. C., Hansel, A., Kulmala, M., Lelieveld, J., Volkamer, R., Kirkby, J., and Winkler, P. M.: Enhanced growth rate of atmospheric particles from sulfuric acid, *Atmospheric Chemistry and Physics*, 20, 7359–7372, 10.5194/acp-20-7359-2020, 2020.
- Wang, S., Nan, J., Shi, C., Fu, Q., Gao, S., Wang, D., Cui, H., Saiz-Lopez, A., and Zhou, B.: Atmospheric ammonia and its impacts on regional air quality over the megacity of Shanghai, China, *Scientific Reports*, 5, 10.1038/srep15842, 2015.
- Wang, Y., Yang, G., Lu, Y., Liu, Y., Chen, J., and Wang, L.: Detection of gaseous dimethylamine using vocus proton-transfer-reaction time-of-flight mass spectrometry, *Atmospheric Environment*, 243, 10.1016/j.atmosenv.2020.117875, 2020.
- Yao, L., Wang, M.-Y., Wang, X.-K., Liu, Y.-J., Chen, H.-F., Zheng, J., Nie, W., Ding, A.-J., Geng, F.-H., Wang, D.-F., Chen, J.-M., Worsnop, D. R., and Wang, L.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, *Atmospheric Chemistry and Physics*, 16, 14527–14543, 10.5194/acp-16-14527-2016, 2016.