

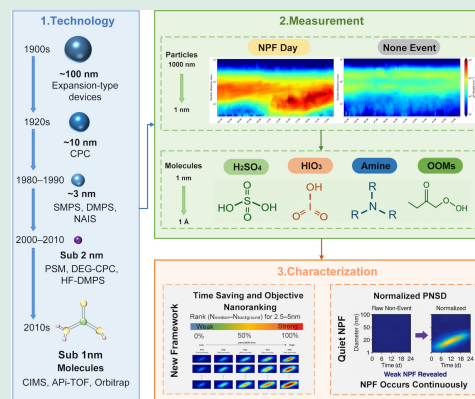
Atmospheric new particle formation: molecular-level understanding across diverse environments. Part I: measurement advances and characterization frameworks

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HIGHLIGHTS

- Part I of a two-part review on post-2019 advances in atmospheric NPF.
- Integrates the NPF measurement chain from sub-2 nm sizing to molecular precursors.
- Detection size frontier pushed from ~10 to ~1.5 nm, closing the cluster gap.
- CIMS techniques organized along the oxygen-number axis from VOCs to ULVOCs.
- Nanoparticle ranking and quiet NPF reveal continuous, pervasive particle formation.



ABSTRACT: Atmospheric new particle formation (NPF)—the conversion of condensable vapors into new aerosol particles—is the dominant source of particle number in the global troposphere, supplying more than half of all cloud condensation nuclei and profoundly influencing Earth’s radiative balance and air quality. This paper is Part I of a two-part review synthesizing recent advances in atmospheric NPF. Part I focuses on the measurement and characterization dimensions of this progress. We trace the evolution of NPF measurement from sub-2 nm particle size distribution instruments through molecular precursor mass spectrometry—covering sulfuric acid, iodic acid, amines, and oxygenated organic molecules—to emerging size-resolved particle composition techniques. We review new characterization frameworks, including the nanoparticle ranking method and the emerging concept of quiet NPF, which reveal that particle formation is far more pervasive and continuous than classical event-based statistics suggested. The molecular mechanisms of NPF across diverse atmospheric environments, and multi-scale modelling from box models to global Earth System Models, are addressed in the companion paper (Part II).

KEYWORDS: New particle formation, Particle size distribution, Chemical ionization mass spectrometry, Nanoparticle ranking, Quiet NPF

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1 Introduction

Atmospheric aerosol particles exert a profound influence on Earth's climate and human health. Through aerosol-radiation interactions, particles scatter and absorb incoming solar radiation, and through aerosol-cloud interactions, they modify the micro-physical properties, lifetime, and albedo of clouds by serving as cloud condensation nuclei (CCN). The latter effect represents the largest single source of uncertainty in estimates of anthropogenic radiative forcing (IPCC, 2021). Beyond climate, fine aerosol particles are among the leading environmental risk factors for human health, responsible for more than seven million premature deaths annually (World Health Organization, 2021). Ultrafine particles, smaller than 100 nm in diameter, are of particular concern because their small size permits deep penetration into the pulmonary alveoli and translocation into the bloodstream, with growing epidemiological evidence linking their exposure to adverse cardiovascular and neurological health outcomes. New particle formation (NPF)—the conversion of condensable atmospheric vapors into new aerosol particles—is the single largest source of particle number in the global troposphere, contributing approximately 50% of CCN concentrations globally (Merikanto et al., 2009; Gordon et al., 2017). In polluted megacities, NPF events can dominate the particle number budget during haze episodes (Kulmala et al., 2021), making NPF simultaneously a climate and an air quality problem of global significance.

NPF is a two-stage process. It begins with nucleation, i.e., the formation of thermodynamically stable molecular clusters from supersaturated gas-phase precursors. The principal nucleating agents identified to date include various acids (e.g., sulfuric acid (H_2SO_4) and iodic acid (HIO_3)), base molecules as stabilizers (e.g., ammonia and amines), and low-volatility organic oxidation products. The embryonic clusters they form, typically 1–2 nm in diameter, must then grow by condensation of low-volatility vapors through the nucleation mode to CCN-relevant sizes (~50–100 nm). Whether a nucleation event ultimately produces CCN depends on the balance between particle growth and coagulative loss to the pre-existing aerosol population, quantified by the condensation sink (CS). Understanding this balance requires knowledge of the vapors driving growth. The nucleation and growth processes are schematically illustrated in Fig. 1.

Over the past two decades, three parallel developments have fundamentally advanced our understanding of NPF. First, a continuous effort to reduce the lower cut-off size of particle size distribution

instruments—from approximately 3 nm in the early 2000s to the sub-2 nm regime now accessible with multiple instruments—has allowed observation of newly formed particles at sizes closer to their nucleating size, bridging the gap between cluster chemistry and particle population dynamics (reviewed in Section 2.1). Second, the deployment of chemical ionization atmospheric pressure interface time-of-flight mass spectrometers (CI-API-TOF) and complementary mass spectrometric techniques has made it possible to directly measure the molecular precursors of NPF at sub-pptv concentrations in real time, transforming NPF research from a macroscopic into a molecular-level discipline (reviewed in Sections 2.2 and 2.3). Third, systematic experiments at the CERN CLOUD (Cosmics Leaving Outdoor Droplets) chamber have established a controlled laboratory framework for individual nucleation mechanisms, quantifying their rates across a matrix of atmospheric conditions, and providing mechanistic parameterizations for models; the findings and impact of this experimental program is recently summarized by Kirkby et al. (2023). This Part I focuses on the first two advances—measurement and characterization—which together form the experimental foundation for molecular-level NPF science. The third advance, the CLOUD-anchored mechanistic understanding and its integration into multi-scale models, is treated in the companion paper (Part II).

Several major reviews of atmospheric NPF have

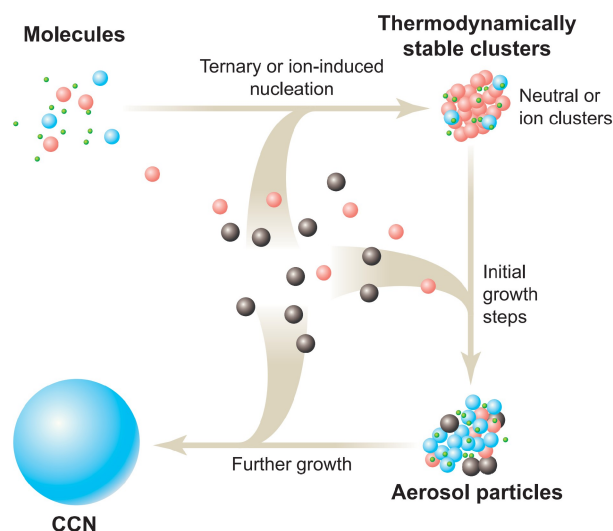


Fig. 1 From precursor molecules to cloud condensation nuclei. Atmospheric precursor molecules form thermodynamically stable neutral or ion clusters through nucleation. The clusters then undergo initial and further growth to form aerosol particles, some of which may reach sizes relevant to cloud condensation nuclei (CCN). Reproduced from Kulmala (2003) with permission of the author.

appeared in recent years, each addressing a distinct aspect of this rapidly developing field. Kerminen et al. (2018) synthesized field observations of NPF occurrence, formation rates, growth rates, and environmental variability. More recently, Stolzenburg et al. (2023) provided a physics-based treatment of atmospheric nanoparticle growth, whereas Shang et al. (2026) reviewed the chemical and physical pathways governing new particle growth and their consequences for particulate matter and cloud condensation nuclei. From a measurement perspective, Zhang et al. (2022) reviewed online techniques for determining the composition of atmospheric clusters and sub-20 nm particles, encompassing both direct mass-spectrometric measurements and indirect constraints derived from particle volatility and hygroscopicity. Li et al. (2023) focused more specifically on mass-spectrometry-based detection of airborne nanoparticle composition, highlighting recent analytical advances and remaining challenges in obtaining real-time molecular information. Lehtipalo et al. (2025) further traced how advances in measurement and analysis methods have shaped the evolution of NPF research.

Building on these complementary reviews, Part I of the present work integrates the measurement chain required to characterize NPF as a continuous process—from sub-2 nm particle size distributions and molecular precursor measurements to size-resolved particle composition and physicochemical properties. It also connects these instrumental advances with emerging characterization frameworks, including nanoparticle ranking and quiet NPF, which extend the detection and quantification of particle formation beyond the classical event/non-event paradigm. The molecular mechanisms operating across different atmospheric environments and their representation in models are addressed separately in Part II.

2 Critical measurements for NPF studies

2.1 Measurement of particle size distribution

The historical development of instruments designed to measure particle number size distributions has been driven primarily by the need to understand the fundamental mechanisms of NPF. For decades, the inability to observe the very smallest molecular clusters and track their rapid growth in real-time hindered a complete mechanistic understanding of how gaseous precursors convert into aerosol particles.

The pursuit of a lower cut-off size (the minimum

particle diameter an instrument can reliably detect) has been a century-long endeavor. The earliest quantitative atmospheric aerosol measurements date back to John Aitken in 1900, who utilized expansion-type devices to measure total particle concentrations without size-segregated distribution capabilities (Aitken, 1900). It was not until the 1960s and 1970s that electrical mobility principles, rooted in theories from the 1920s (Flagan, 1998), were successfully applied to aerosol analyzers, such as the Whitby aerosol analyzer and the electrical aerosol analyzer, which reached lower detection limits of approximately 15 and 10 nm, respectively (Whitby and Clark, 1966; Liu et al., 1974). The next major leap occurred with the refinement of optical particle counters into modern condensation particle counters (CPCs) (Metnieks and Pollak, 1959; Stolzenburg and McMurry, 1991). By integrating these advanced counters with electrical sizing techniques, researchers developed the differential mobility particle sizer (DMPS) and the scanning mobility particle sizer (SMPS) in the 1980s and 1990s (Keady et al., 1983; Wang and Flagan, 1990). For nearly two decades, the standard lower detection limit for these mobility particle size spectrometers remained around 3 nm.

While the 3 nm threshold provided a wealth of data regarding particle growth, it was insufficient for observing the actual nucleation process, which occurs at the molecular cluster level near 1 nm. This limitation created a significant observational gap. Because particles took hours to grow from their ~1 nm formation size to the 3 nm detection limit, researchers observed an artificial time delay between the increase in atmospheric precursor vapors, like sulfuric acid, and the appearance of newly formed particles. The breakthrough required to bridge this gap occurred in the late 2000s and early 2010s (Kulmala et al., 2007; Sipilä et al., 2008), catalyzed by the discovery that working fluids with low saturation vapor pressure and high surface tension could achieve higher supersaturations without triggering homogeneous nucleation of the fluid itself (Iida et al., 2009). This innovation led to the development of diethylene glycol CPCs (DEG-CPCs) and specialized water-CPCs capable of detecting particles down to 1 nm (Jiang et al., 2011; Vanhanen et al., 2011; Kuang et al., 2012; Hering et al., 2017). This breakthrough paved the way for other specialized sizing instruments, such as the DMA-train (Stolzenburg et al., 2017) and, more recently, the CPC FARM (Cheng et al., 2025), both of which achieve high time resolution by operating multiple detection channels in parallel at fixed cut-points; the high flow differential mobility particle sizer (HF-DMPS) (Kangasluoma et al., 2018, 2020), the nSEMS (Kong et al., 2021), and

alternative supersaturation scanning methods like the Particle Size Magnifier (PSM) (Lehtipalo et al., 2014; Chen et al., 2023a; Sulo et al., 2024). By breaking the 3 nm barrier, scientists eliminated the temporal lag, allowing for the direct observation of molecular clusters at their moment of genesis and enabling accurate, real-time comparisons with short-lived, gas-phase chemical precursors (Kulmala et al., 2013).

Simultaneous to the quest for smaller cut-off sizes, a second technological revolution occurred regarding the time resolution of particle measurements. Atmospheric aerosol populations are highly dynamic, changing rapidly within minutes or hours due to varying emission sources, atmospheric mixing, and photochemical processes. Early measurement techniques required extensive manual labor (Barus, 1902), resulting in fragmented data that provided mere snapshots of the atmosphere rather than a continuous narrative. The introduction of the automated DMPS and SMPS systems in the 1980s and 1990s transformed this landscape. These instruments could rapidly scan through a range of electrical mobilities, providing continuous size distribution measurements. This automated scanning made it possible to conduct long-term, high-resolution observations (Temnitschka et al., 1989), leading to the discovery in the mid-1990s that NPF was not a rare anomaly, but a frequent regional phenomenon characterized by the distinct “banana curve” of particle growth over time.

As the demand for capturing sudden, intense bursts of newly formed molecular clusters grew, researchers realized that even the rapid sequential scanning of an SMPS could introduce temporal smearing. This limitation drove the development of air ion mobility spectrometers, which prioritize absolute time resolution. Instruments such as the Electrical Aerosol Spectrometer (EAS) (Tamm et al., 2002) and the Neutral cluster and Air Ion Spectrometer (NAIS) (Mirme et al., 2007; Manninen et al., 2009; Mirme and Mirme, 2013) utilize parallel arrays of electrometers to measure the concentration of particles across multiple size fractions simultaneously. By eliminating the time required to scan across a voltage range, these spectrometers offer unparalleled temporal resolution. The analytical impact of high-time-resolution data has been profound. Continuous, second-by-second tracking of particle populations enabled the development of standardized criteria for classifying NPF events (Dal Maso et al., 2005) and allowed scientists to mathematically derive critical metrics such as formation and growth rates. The size ranges accessible to different particle size distribution instruments currently in use are summarized in Fig. 2.

2.2 Measurement of key precursors of NPF

Section 2.1 describes the macroscopic outcome of NPF through particle size distribution measurements, but understanding the underlying mechanisms requires direct molecular-level measurement of the precursor vapors that drive nucleation and growth. This presents some of the most demanding analytical challenges in atmospheric chemistry, because target species, including sulfuric acid (H_2SO_4), iodic acid (HIO_3), ammonia (NH_3), amines, and oxygenated organic molecules with varying oxidation degree (HOMs/OOMs), have concentrations ranging from 10^4 to 10^8 molecules cm^{-3} , equivalent to sub- to low parts-per-trillion (ppt) mixing ratios. This requires specialized instrumentation with much greater sensitivity and mass resolving power than conventional trace gas analyzers. Advanced chemical ionization mass spectrometry (CIMS), coupled to high-resolution time-of-flight (ToF) or Orbitrap mass analyzers, has made real-time molecular measurement possible, and its deployment over the past decade has fundamentally transformed our mechanistic understanding of NPF. In Section 2.2, we focus on the measurement of various gaseous species relevant to NPF, particularly based on mass spectrometry techniques.

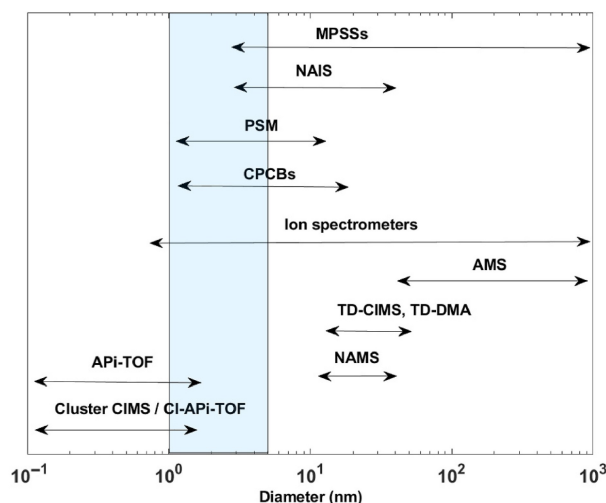


Fig. 2 Approximate size coverage of NPF instruments. The diagram compares instruments used to measure particle size distributions and chemical composition, spanning approximately 1 nm clusters to accumulation-mode particles. Mobility particle size spectrometers (MPSSs) include scanning mobility particle sizers (SMPSs) and differential mobility particle sizers (DMPSs). Other techniques, such as TD-CIMS, TD-DMA, API-TOF and CI-API-TOF will be extensively reviewed in the following sections. The size limits shown are indicative and vary with instrument model and configuration. Reproduced from Lehtipalo et al. (2025) under CC BY 4.0.

2.2.1 Inorganic precursors

Sulfuric acid and iodic acid. H_2SO_4 is the most important nucleating precursor in the atmosphere, and its measurement by chemical ionization was pioneered by Eisele and coworkers in 1990s, who developed the nitrate-ion inlet and demonstrated its application to ambient H_2SO_4 detection (Eisele and Berresheim, 1992; Eisele and Tanner, 1993). Jokinen et al. (2012) later connected this inlet to an atmospheric pressure interface time-of-flight mass spectrometer (CI-API-TOF), achieving a detection limit of $\sim 3.6 \times 10^4$ molecules cm^{-3} at 15-min averaging. The technique exploits strong clustering between NO_3^- reagent ions and H_2SO_4 , enabling near-kinetic-limit sensitivity, and simultaneously detects H_2SO_4 clusters up to the tetramer, which are direct indicators of the earliest nucleation steps. The same nitrate CI-API-TOF also detects HIO_3 , a key nucleating agent in coastal and polar environments; HIO_3 detection was established in CLOUD chamber experiments and subsequently confirmed in long-term ambient measurements in Beijing and Nanjing (Zhang et al., 2024b).

Ammonia and amines. NH_3 and amines can both stabilize H_2SO_4 -containing clusters through acid–base interactions, but their stabilization efficiencies and atmospherically relevant concentration regimes differ substantially. Quantum-chemical calculations show that H_2SO_4 –dimethylamine (DMA) clusters are considerably more stable against evaporation than the corresponding H_2SO_4 – NH_3 clusters (Ortega et al., 2012). In CLOUD experiments, 100 pptv NH_3 increased sulfuric-acid nucleation rates by factors of approximately 100–1000, although this enhancement remained insufficient to explain most boundary-layer nucleation rates (Kirkby et al., 2011). By comparison, DMA concentrations above approximately 3 pptv enhanced particle formation rates by more than three orders of magnitude relative to NH_3 because the resulting acid–base clusters evaporate much more slowly (Almeida et al., 2013). Field observations have subsequently identified H_2SO_4 –DMA clusters during intense urban NPF (Yao et al., 2018; Cai et al., 2021b; Yan et al., 2021) and ion-induced H_2SO_4 – NH_3 nucleation in coastal Antarctica (Jokinen et al., 2018), demonstrating that both pathways operate in the atmosphere, but under different chemical and environmental regimes. These pronounced differences make sensitive and compound-specific measurements of NH_3 and amines essential for interpreting NPF processes.

Several complementary techniques have been developed for this purpose. A water cluster CI-API-

TOF, using protonated water clusters ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$) as reagent ions, selectively measures high-proton-affinity compounds and achieves detection limits of ~ 0.5 pptv for NH_3 and below 0.2 pptv for dimethylamine (DMA) (Zheng et al., 2015; Pfeifer et al., 2020). A protonated ethanol CIMS takes a different approach, simultaneously detecting C1–C6 amines and amides with detection limits of 0.1–0.5 pptv at one-minute averaging, and has been applied to urban measurements in Shanghai (Yao et al., 2016). The Vocus PTR-TOF (Proton Transfer Reaction Time-of-Flight mass spectrometer) provides complementary amine measurements at pptv levels with sub-second time resolution alongside simultaneous VOC detection (Wang et al., 2020b). In addition, detection of DMA with a nitrate CI-API-TOF was also reported (Simon et al., 2016), though this approach has seen limited field application compared to other instruments. For longer-term monitoring, online ion chromatography systems simultaneously measure gas-phase NH_3 and amines alongside their particulate counterparts at hourly resolution (Hemmilä et al., 2018; Chen et al., 2022). Optical techniques, including cavity ring-down spectroscopy (PICARRO CRDS) and quantum cascade tunable infrared laser direct absorption spectrometry (QC-TILDAS), offer calibration-free NH_3 measurement at detection limits of ~ 100 –400 pptv and ~ 180 pptv, respectively, and are well-suited to long-term unattended deployment (Sun et al., 2023).

2.2.2 Organic precursors

The organic precursors of NPF span an enormous range in oxygenation state, from the parent hydrocarbons that serve as raw material for atmospheric oxidation to the highly oxygenated molecules that drive nucleation and condensational growth. Two terms are used to describe these species. Highly oxygenated organic molecules (HOM) are defined as gas-phase products of rapid multi-step RO_2 autoxidation of VOCs, characterized by an effective oxygen number $n\text{O} \geq 6$ (Ehn et al., 2014; Bianchi et al., 2019). HOM formation is most efficient in biogenic environments where monoterpene and sesquiterpene emissions sustain long autoxidation chains. In the urban atmosphere, multi-generation OH oxidation of anthropogenic VOCs under high- NO_x conditions yields oxidized organic products that are important for NPF but generally do not reach the HOM oxygen threshold. The broader term oxygenated organic molecules (OOM) captures this full spectrum—encompassing all oxygenated organics relevant to NPF across the complete range of oxygen content (Yan et al., 2021; Nie et al., 2022). HOMs are therefore a high-oxygen subset within the broader OOM category.

No single instrument detects the entire range of OOM. The sensitivity of each measurement technique is best understood as an optimum in oxygen-number space rather than an exclusive detection window: instruments show highest sensitivity in their characteristic range but retain measurable response outside it, and their deployment is therefore most powerful in combination.

Low-oxygen organic compounds ($O = 0-3$). Proton transfer reaction mass spectrometry (PTR-MS) has been the primary technique for real-time VOC measurement in the atmosphere for over two decades, using H_3O^+ to selectively protonate compounds with proton affinities exceeding that of water (De Gouw and Warneke, 2007; Yuan et al., 2017). Aromatic hydrocarbons are among the most sensitively detected species in PTR-TOF, as their proton affinities are well above the water threshold. Later instrument generations have further extended capability: the Vocus PTR-TOF, incorporating a focusing ion-molecule reactor with a radiofrequency field, increases sensitivity by about one order of magnitude and reduces humidity dependence (Krechmer et al., 2018; Li et al., 2024). The Vocus AIM (Adduct Ionization Mechanism) platform additionally supports benzene cation ($C_6H_6^+$) reagent ion chemistry, which is complementary to H_3O^+ for compounds with proton affinities near or below the water threshold, thereby further extending the detectable VOC range (Riva et al., 2024). For speciated isomer-resolved measurements, which online mass spectrometers cannot provide, GC-MS (Gas Chromatography–Mass Spectrometry) remains the reference approach, and the GC-Vocus instrument combines chromatographic separation with PTR and EI (Electron Ionization) detection, achieving pptv-level sensitivity for individual isomers (Claflin et al., 2021).

Moderately oxygenated organic compounds ($O = 2-5$). Iodide CIMS (I^- -CIMS) shows optimal sensitivity for molecules with two to five oxygen atoms, including organic acids, hydroperoxides, and organic nitrates, where sensitivity is governed by the binding enthalpy between I^- and the analyte (Lee et al., 2014). It also detects HNO_3 with high sensitivity, providing constraints on nitrate-driven particle growth (Wang et al., 2020a). NH_4^+ -CIMS takes a complementary approach, ionizing organic compounds via ligand-switching reactions with ammonium-water clusters; it covers compounds with $O \geq 1$ and shows highest sensitivity for carbonyl and hydroxyl-containing species including ketones, aldehydes, and alcohols, thereby bridging the range between PTR and I^- -CIMS (Zaytsev et al., 2019; Xu et al., 2022). In urban environments, NH_4^+ -CIMS has characterized a broad range of oxygenated compounds from volatile chemical

products and other anthropogenic sources (Khare et al., 2022). The amine CI-API-TOF shown in Fig. 3 uses protonated alkylamines as reagent ions and is distinct from NH_4^+ -CIMS. By forming clusters with oxygenated analytes, this approach can detect moderately oxygenated closed-shell products as well as some RO_2 radicals. For example, flow-tube measurements of isoprene oxidation detected early-generation products including $C_5H_8O_3$ using methyl-, ethyl-, and propylammonium reagent ions (Berndt et al., 2018). In the α -pinene chamber comparison represented in Fig. 3, protonated-butylamine ionization provided broader coverage of oxygenated products, although substantial reagent-ion depletion caused nonlinear responses for many monomers. While I^- -CIMS is better suited to acidic multifunctional species, NH_4^+ -CIMS and amine CI-API-TOF are better suited to less acidic, carbonyl-rich compounds, so the two instruments are largely complementary rather than redundant.

Highly oxygenated organic compounds ($O \geq 6$). HOMs, formed by autoxidation of VOCs and containing six or more oxygen atoms, were identified as a major source of low-volatility secondary organic aerosol (Ehn et al., 2014) and shown to drive pure biogenic nucleation without H_2SO_4 in CLOUD experiments (Kirkby et al., 2016), establishing nitrate CI-API-TOF as the primary tool for detecting participants of NPF. The technique exploits the strong affinity of NO_3^- for oxygenated functional groups, enabling detection of HOM monomers and dimers from monoterpene oxidation. In anthropogenic environments under high- NO_x conditions, autoxidation is less progressed and organic products generally reach lower oxygen numbers than in biogenic systems; however, nitrate CI-API-TOF retains good sensitivity to the organic nitrates that form abundantly under such conditions, since the nitrate group itself contributes to the high oxygen count needed for efficient NO_3^- clustering (Nie et al., 2022). Overall, multi-instrument comparisons confirm that nitrate CI-API-TOF, I^- -CIMS, and Vocus PTR-TOF together span the full OOM spectrum, with each instrument showing sensitivity optimized in its characteristic oxygen-number range, as summarized by Riva et al. (2019b) and shown in Fig. 3.

2.2.3 Multi-scheme ionization and Orbitrap developments

The growing recognition that no single reagent ion provides comprehensive OOM coverage has driven two parallel developments that are increasingly shaping how field campaigns approach precursor measurement. The

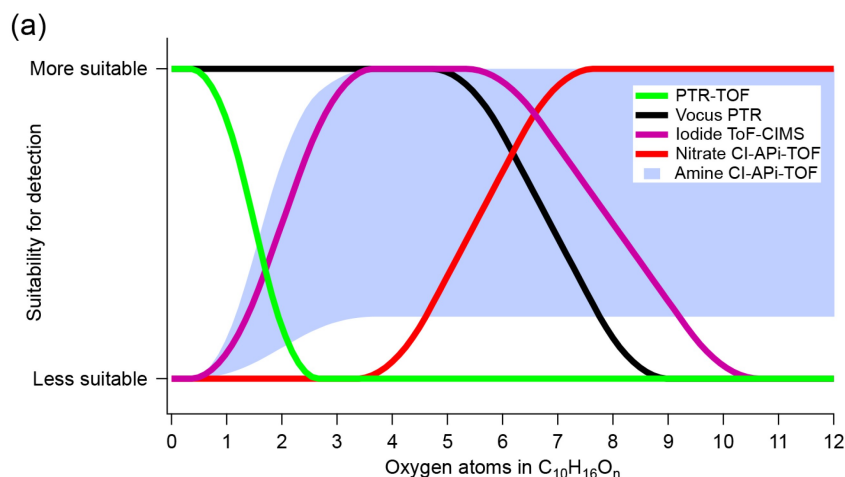


Fig. 3 Detection suitability across α -pinene oxidation products. The shaded ranges indicate the estimated suitability of conventional PTR-TOF, Vocus PTR-TOF, iodide TOF-CIMS, amine CI-API-TOF, and nitrate CI-API-TOF as a function of molecular oxygen number. Amine CI-API-TOF uses protonated amine reagent ions and is distinct from NH_4^+ -CIMS. Its shaded range is particularly dependent on measurement conditions. All ranges are indicative because sensitivity also depends on molecular functionality, analyte loading, and reagent-ion depletion. Reproduced from Fig. 6(a) of Riva et al. (2019b) under CC BY 4.0.

first is multi-scheme chemical ionization inlets, which allow rapid switching between different reagent ions within a single instrument, thereby avoiding the resource burden of deploying multiple CIMS in parallel. The MION inlet switches between NO_3^- and Br^- on a timescale of seconds, enabling near-simultaneous coverage from parent VOCs to ELVOCs (Rissanen et al., 2019; He et al., 2023). Similarly, the Vocus AIM reactor extends this to both positive and negative polarity schemes including NH_4^+ , I^- , and C_6H_6^+ within a single platform (Riva et al., 2024).

The second development is the coupling of chemical ionization inlets to Orbitrap Fourier transform mass spectrometers, which offer mass resolving powers more than an order of magnitude higher than ToF-based instruments, enabling unambiguous separation of isobaric peaks (Riva et al., 2019a). This resolving power is particularly valuable in urban environments, where nitrogen-containing OOMs from anthropogenic VOC oxidation produce dense, complex spectra that challenge ToF instruments, and year-long deployment in urban Beijing identified 2403 distinct OOM compounds using this approach (Yuan et al., 2024). It should be clarified that, both platforms (ToF and Orbitrap) have distinct and complementary strengths: ToF instruments offer lower detection limits ($\sim 10^4$ molecules cm^{-3}) and linear response across a wide concentration range, whereas Orbitrap provides superior mass resolution but has higher practical detection limits ($\sim 10^5$ molecules cm^{-3}) and non-linear response at very low signal levels (Cai et al., 2022).

2.2.4 Calibration

Calibration of CIMS instruments for NPF-relevant species faces a fundamental constraint: certified reference standards are absent for nearly all atmospherically relevant OOMs, and different instrument classes have consequently developed distinct approaches to address this gap, each carrying its own uncertainty characteristics.

For the nitrate CI-API-TOF, H_2SO_4 is calibrated using a photochemical H_2SO_4 source (Kürten et al., 2012). The combined uncertainty from this procedure alone is approximately $\pm 50\%$, arising from inlet wall losses and flow uncertainties. For most OOMs, no direct standards exist, so the accepted practice is to apply the H_2SO_4 calibration factor uniformly to all detected organic species and treat the result as a lower-bound concentration estimate. However, this can underestimate individual compound concentrations by orders of magnitude, as actual sensitivity depends on the specific binding enthalpy of each HOM with NO_3^- . Additionally, the mass-dependent transmission efficiency of the instrument across the detectable mass range must be characterized and applied, which is particularly important for organics with large mass-to-charge span (Heinritzi et al., 2016).

For I^- -CIMS, the sensitivity ceiling is determined using N_2O_5 , which reacts with I^- at the collision limit and provides an absolute upper bound on instrument sensitivity (Lopez-Hilfiker et al., 2016). Voltage scanning method has been developed specifically for I^- -CIMS and extended to NH_4^+ -CIMS (Lopez-Hilfiker

et al., 2016; Zaytsev et al., 2019), which characterize the stability of ion-molecule adducts via systematic variation of the declustering voltage. This method further constrains relative sensitivities among detected species without the need for standards.

Comparatively, calibration of PTR-based instruments is more tractable, because certified standards exist for most target VOCs and proton-transfer rate constants can be estimated from molecular properties, enabling calibration-free quantification of unstandardized compounds. Across all CIMS techniques, rigorous background subtraction and zero-air measurement protocols remain essential, particularly for sticky low-volatility OOMs for which surface desorption from instrument walls can introduce systematic positive artefacts if inlet conditioning is not properly characterized.

2.3 Measurement of nanoparticle composition

Understanding the chemical composition of atmospheric particles at the nanometer scale is indispensable for elucidating NPF and early growth mechanisms. Conventional bulk aerosol composition instruments—most notably the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and the Aerosol Chemical Speciation Monitor (ACSM)—provide real-time quantitative measurements of non-refractory aerosol components, including organics, sulfate, nitrate, ammonium, and chloride. However, their application to freshly formed particles is limited primarily by the strongly size-dependent transmission and focusing efficiency of the aerodynamic lens, which decreases rapidly toward the lower end of the ultrafine-particle size range. Consequently, particles in the 1–50 nm range central to NPF studies are transmitted inefficiently or not at all, and the very small particulate mass that reaches the detector further limits compositional sensitivity. The AMS can retrieve aerodynamic-diameter-resolved composition for particles that are efficiently transmitted by using particle time-of-flight measurements, whereas conventional ACSM measurements generally provide bulk non-refractory aerosol composition without equivalent size-resolved information. This section therefore focuses on specialized approaches capable of extending chemical characterization toward molecular clusters and newly formed nanoparticles: (1) direct molecular-level characterization of ion clusters using the APi-TOF; (2) online direct techniques for nanoparticle composition in the > 3 nm range; and (3) indirect methods using particle volatility and hygroscopicity to constrain composition and connect

NPF with subsequent growth toward CCN-relevant sizes.

2.3.1 Ion cluster composition: the APi-TOF mass spectrometer

The Atmospheric Pressure interface Time-of-Flight mass spectrometer (APi-TOF) directly samples naturally charged atmospheric ions at ambient pressure without any chemical ionization inlet, detecting ion cluster composition across ~100–2000 Th (Junninen et al., 2010). Because the smallest stable clusters formed during nucleation carry a natural charge fraction, the APi-TOF provides a direct molecular-level window into the very first steps of particle formation – effectively bridging the gas and condensed phases. This makes it uniquely complementary to the NAIS (Section 2.1), which measures the size distribution of charged particles, by revealing their chemical identity.

Early boreal forest deployments established the foundational picture of ion chemistry during NPF: negative ions during nucleation events are dominated by a sulfuric acid cluster series (H_2SO_4)_{0–3}·HSO₄[–], with tetramer and ammonia-stabilized clusters at peak intensity, while positive ions are dominated by amines and alkylated nitrogen bases (Ehn et al., 2010). At the high-altitude Jungfraujoch station, nine months of APi-TOF measurements identified two chemically distinct NPF cluster regimes—one driven by H_2SO_4 –NH₃ clustering and another by highly oxygenated organic molecules (HOMs)—with HOM-type events predominating when air masses had processed biogenic VOC emissions for longer (Frege et al., 2017). In urban Beijing, combined APi-TOF and CI-APi-TOF measurements of both neutral and charged acid-base clusters revealed that sulfuric acid–amine clusters dominate ion composition, and that the dimethylamine (DMA) fraction decreases with cluster size as NH₃ becomes increasingly important—consistent with insufficient DMA to fully stabilize larger clusters under urban conditions (Yin et al., 2021).

CLOUD chamber studies using paired APi-TOFs in positive and negative mode demonstrated that cluster growth in H_2SO_4 –base systems proceeds via sequential one-to-one acid-base addition independent of charge state, directly validating atmospheric cluster growth theory (Bianchi et al., 2014). Temperature-dependent APi-TOF measurements of pure biogenic (HOM) nucleation at CLOUD showed that lower temperatures shift cluster O:C ratios and allow HOM monomers to contribute to positive cluster nucleation (Frege et al., 2018).

2.3.2 Direct online techniques for nanoparticle composition (> 3 nm)

Thermal desorption CIMS family: TDCIMS, TD-DMA, and NPCIMS

The three instruments reviewed in this subsection—the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) (Smith et al., 2004), the Thermal Desorption Differential Mobility Analyzer coupled to a CI-API-TOF (TD-DMA) (Wagner et al., 2018), and the Nanoparticle Chemical Ionization Mass Spectrometer (NPCIMS) (Wang et al., 2022)—are technically near-identical in their working principle and can be considered the same instrument family. In all three, particles are first size-selected by a differential mobility analyzer, charged by either a radioactive source or a non-radioactive soft X-ray ionizer, and deposited by electrostatic precipitation onto a metal filament through a collection cycle of typically 15–30 min. The filament is then rapidly heated to thermally desorb particle-phase material into a flow of reagent ions for chemical ionization and downstream mass spectrometric detection. In TDCIMS and NPCIMS, the collection filament reaches an estimated maximum temperature of approximately 600 °C, whereas TD-DMA uses temperatures up to approximately 350 °C for sample evaporation and subsequently heats the filament to 600 °C for cleaning. The technique is inherently semicontinuous, alternating between collection and desorption phases, and supports both positive and negative ion modes by switching reagent ion chemistry. The three instruments differ primarily in the reagent ion scheme employed (proton-transfer and superoxide reagents in TDCIMS; nitrate ions in TD-DMA, targeting HOMs; mixed ionization in NPCIMS), and the DMA design optimized for the target size range.

This instrument family has been deployed across a wide range of environments. In laboratory and chamber settings, early TDCIMS work provided the first online molecular-level characterization of nanoparticle composition in the 6–20 nm range (Smith et al., 2004), and subsequent lab studies revealed size-dependent acid-base composition gradients in H₂SO₄-DMA and H₂SO₄-NH₃ clusters that deviate from bulk thermodynamic predictions (Chen et al., 2018). The TD-DMA was developed for and extensively applied at the CERN CLOUD chamber, where it enabled direct comparison of particle-phase HOM composition with simultaneously measured gas-phase HOM concentrations (Wagner et al., 2018; Caudillo et al., 2023). In ambient boreal forest environments, TDCIMS deployments at Hyytiälä and other sites demonstrated

the prevalence of aminium salts in nucleation-mode particles (Smith et al., 2010) and the contribution of terpene oxidation products to early growth (Lawler et al., 2018). In urban environments, the modified TDCIMS and NPCIMS have both been deployed in Beijing, revealing that organics (~80%) and sulfate (~13%) dominate the 8–40 nm composition during NPF events, with nitrate playing a minor role below 25 nm (Li et al., 2021; Chen et al., 2023b).

Despite their differences in detector and ionization design, all three instruments face a common set of analytical challenges. The most significant one is thermal decomposition during the desorption step. When the filament is rapidly heated to several hundred degrees Celsius, thermally labile compounds, particularly organonitrates, organosulfates, and HOM dimers, may fragment before detection, generating daughter ions whose signals cannot be unambiguously assigned to intact parent molecules.

These limitations have motivated the development of two novel continuous-flow inlet designs that attempt to minimize thermal decomposition while maintaining high time resolution. The Vaporization Inlet for Aerosols (VIA) coupled to NO₃-CIMS (Zhao et al., 2023, 2024; Häkkinen et al., 2023) evaporates particles in a continuous flow, featured by an extremely short residence time (~0.1 s) and much lower temperatures (150–300 °C) in the heated region, compared to the prolonged contact in filament-based systems. These features help preserve thermally labile species such as peroxides that are destroyed in TDCIMS and TD-DMA, enabling detection of intact HOM monomers and dimers in the particle phase. The more recently introduced WALL-E (Wall-free particle evaporator, Gao et al., 2025) takes the approach further by eliminating contact with heated walls entirely through an innovative wall-free evaporation geometry coupled to Br-CIMS, demonstrating minimal thermal decomposition and enabling quantitative concentration measurements of individual SOA components, including fragile HOM dimers, at sub-μg/m³ total SOA loadings (Gao et al., 2025).

The EESI-TOF (Extractive Electrospray Ionization TOF) (Lopez-Hilfiker et al., 2019) addresses the overheating problem from a fundamentally different angle: aerosol particles are continuously sampled into a charged electrospray plume where soluble components are directly extracted and ionized without any heating step, eliminating thermal decomposition entirely. This soft ionization approach yields mass spectra closely reflecting actual molecular distributions in the particle phase, with detection limits of ~1–10 ng/m³ in 5 s, and has been used to track real-time HOM condensation and

particle-phase reactions in chamber studies (Pospisilova et al., 2020). However, the extraction process introduces its own uncertainties: incomplete extraction of insoluble or low-polarity compounds, compound-dependent sensitivity that can vary by over an order of magnitude, and matrix effects from the aerosol chemical complexity (Lopez-Hilfiker et al., 2019; Lee et al., 2021). Notably, EESI-TOF sensitivity increases by 1–3 orders of magnitude as particle size decreases from 300 to 30 nm (Lee et al., 2021), making it inherently well-suited for NPF growth studies. All three techniques currently lack intrinsic size selection, but each has the potential to be coupled with an upstream DMA or impactor to enable size-resolved ambient measurements, representing an important frontier for future development in nanoparticle composition measurement.

2.3.3 Indirect physicochemical constraints from hygroscopicity and volatility measurements

Tandem differential mobility analyser (TDMA) techniques provide an indirect route to nanoparticle composition when the particle mass is too low for conventional aerosol mass spectrometry. In a hygroscopicity TDMA (H-TDMA), particles with a selected dry mobility diameter are exposed to a controlled relative humidity and the resulting hygroscopic growth-factor distribution is measured. In a volatility TDMA (V-TDMA), size-selected particles are passed through a thermodenuder at one or more temperatures, and the shrink factor or remaining volume fraction is derived from the post-heating size distribution. Combined VH-TDMA configurations additionally determine the hygroscopicity of the residual particle after partial volatilization, thereby separating the responses of volatile coatings and less-volatile cores and revealing whether the sampled population is internally or externally mixed (Villani et al., 2008; Hakala et al., 2017).

For NPF studies, the selected diameter in VH-TDMA must overlap the evolving growth-mode peak. Measurements below approximately 50 nm are therefore particularly informative, but this is a practical rather than absolute threshold: primary ultrafine particles must be excluded using the temporal evolution of the particle number size distribution, air-mass and source information, and the continuity of particle growth. The lower measurable size is also constrained by bipolar charging efficiency, diffusion losses through two DMAs, and the possibility that highly volatile particles shrink below the detection limit. Modern VH-TDMA systems have demonstrated hygroscopicity

measurements down to about 10 nm and volatility measurements down to about 20 nm, whereas reliable sub-10 nm measurements generally require exceptionally high particle concentrations and careful loss corrections (Sakurai et al., 2005; Hakala et al., 2017).

The joint response to heating and humidification can substantially narrow the plausible composition of growing particles. Highly hygroscopic particles with thermal behavior resembling laboratory ammonium sulfate or ammonium bisulfate standards point to a major contribution from ammoniated sulfate, whereas weak hygroscopic growth is consistent with a larger organic or otherwise poorly water-soluble fraction. A non-volatile residual at high temperature rules out a particle composed solely of sulfuric acid, ammonium sulfate, and water, while multimodal shrink-factor or growth-factor distributions indicate distinct volatility or hygroscopicity classes and hence an external mixture. Field applications illustrate these constraints across several size regimes: 4–10 nm particles formed in Atlanta were highly hygroscopic and relatively non-volatile, consistent with parallel TDCIMS detection of ammonium and sulfate; 15 nm particles in a boreal forest retained non-volatile residuals at 280 °C; 17–22.5 nm coastal particles were inferred from their combined VH-TDMA signatures to contain internally mixed sulfate and organic material; and the temporal evolution of hygroscopicity for 25–45 nm particles constrained changes in the relative contributions of inorganic and organic vapors during growth (Sakurai et al., 2005; Ehn et al., 2007; Modini et al., 2009; Wu et al., 2013).

These interpretations remain non-unique because evaporation depends not only on saturation vapor pressure but also on particle size, residence time, heating rate, decomposition, phase state, mixing state, and mass-transfer limitations; hygroscopic growth is likewise affected by the Kelvin effect, solute dissociation, surface tension, and organic–inorganic interactions. H/V-TDMA should therefore be treated as a source of physicochemical fingerprints rather than direct molecular identification. A more rigorous strategy is to test closure with simultaneous molecular measurements. Gas-phase CIMS composition can be converted into a volatility distribution, used in a condensational-growth and kinetic-evaporation model, and evaluated against both the observed particle growth and the temperature-dependent V-TDMA volume fraction remaining. Alternatively, particle-phase FIGAERO-CIMS thermograms and molecular formulas can be used to predict evaporation in the V-TDMA. Agreement among molecular composition, modeled growth or evaporation, and measured H/V distributions

provides a stronger constraint on the compounds driving NPF growth than any technique alone (Mohr et al., 2019; Graham et al., 2023).

3 Characterization of NPF

3.1 Classification of NPF events

3.1.1 Traditional NPF classification methods

A standardized and rigorous definition of NPF events is the prerequisite for ensuring the consistency and comparability of global observational datasets. The methodology for identifying these events has evolved from simple numerical thresholds to complex frameworks. Early identification efforts were primarily quantitative, relying on the calculated ratios of nucleation-mode particle concentrations to those of the Aitken-mode or the total particle population (Covert et al., 1992; Mäkelä et al., 1997). While these ratio-based methods provided a preliminary screening tool, they struggled to account for the dynamic evolution and full characteristics of particle number size distributions (PNSD) over time.

The classification scheme proposed by Dal Maso et al. (2005) represented a landmark in the field, establishing a standardized cornerstone for the statistical analysis of NPF frequency and characteristics. This framework categorizes observation days into three primary types based on the temporal persistence and subsequent growth of the sub-20 nm modal particles: Event days, Non-event days, and Undefined days. Crucially, the “Event” category is further subdivided to reflect the clarity and suitability of the data for further analysis. Class I events (comprising Class Ia and Class Ib) represent days with distinct appearance of newly formed particles and clear, continuous growth, whereas Class II events exhibit less clarity in their growth patterns. While the NPF frequency is calculated as the total number of Class I and II events over all observation days, Dal Maso et al. (2005) recommended that only these well-defined Event days be utilized for the precise calculation of NPF intensity parameters, such as formation and growth rates. Details of particle formation rate and growth rate calculations will be summarized in later sections.

Despite its widespread adoption, this system remains inherently reliant on manual, expert-based visual inspection of “banana plots”. This reliance introduces significant subjectivity, as the distinction between a Class Ib event and an Undefined day can vary between

researchers, and the process becomes prohibitively labor-intensive for multi-year or multi-site datasets. To address the ambiguity of the “Undefined” category, Buenrostro Mazon et al. (2009) refined the scheme by subclassifying these days into events including: failed particle growth, pollution-related concentration peaks, ultrafine mode concentration peaks, unclassified events, and missing data. Furthermore, studies utilizing ion spectrometers, which typically feature a lower size cutoff than conventional DMPS/SMPS systems, have employed modified classification schemes to account for ion-induced nucleation phenomena observable at sub-1 nm (Manninen et al., 2010; Dada et al., 2018). However, due to the simplicity and low requirement for instrument cut-off size, most studies continue to employ the original Dal Maso scheme or a slightly modified version, notwithstanding its limitations.

3.1.2 A new automated nanoparticle ranking method

The inherent subjectivity and labor-intensive nature of manual classification (as discussed in Section 3.1.1) have spurred the development of more objective, automated methods. Heintzenberg et al. (2007) pioneered an automated search algorithm based on integral parameters derived from size distributions. More recently, Aliaga et al. (2023) introduced a fully automated nanoparticle ranking method, which assesses NPF probability based on the concentration difference of 2.5–5 nm particles between nucleation-active and background periods within each day. The daily variation in nanoparticle concentration is then quantified and used to assign a rank: the larger the concentration increase, the higher the rank, indicating a greater likelihood of NPF and stronger particle formation rates. For quantitative analysis, the ranked days within a defined analysis period are divided into 20 rank bins, and particle number size distributions from the days assigned to each bin are combined to construct a representative diurnal size-distribution pattern. Growth trajectories remain identifiable in most of these bin-level distributions, allowing a rank-specific *GR* to be determined directly using mode-fitting or appearance-time methods, rather than being inferred from condensable-vapour proxies or assigned from a median *GR*. The temporal representativeness of the resulting *GR* values depends on the period included in the ranking analysis; for example, ranking multiple years of springtime observations yields representative springtime *GR* estimates for the different rank bins. Kulmala et al. (2024) articulated this as a “paradigm shift”, moving from the traditional manual classification (Event vs. Non-event) toward a

continuous, objective, and automated framework, which is particularly suitable for analyzing long-term datasets. The contrast between the traditional binary classification and the new continuous paradigm is illustrated schematically in Fig. 4.

This new classification method has been applied in several follow-up studies. Lampilahti et al. (2025) applied nanoparticle ranking analysis to measurements from a Siberian boreal forest during 2019–2021. The method captured continuous day-to-day variations in NPF intensity ($\Delta N_{2.5-5}$), including weak formation signatures at intermediate ranks that are not represented by annual event-frequency statistics. The method's versatility extends to polluted megacities (Kulmala et al., 2025), hemi-boreal forest (Ke et al., 2025), pristine Arctic regions (Heslin-Rees et al., 2026), and mountainous areas (Aliaga et al., 2025). Overall, these studies demonstrate that the nanoparticle ranking method is potentially a powerful tool for quantifying the contribution of NPF to regional particle number budgets.

It should be noted that, however, the method is not a universal replacement for manual classification. Particularly, it faces challenges when applied to short-

term field campaigns (typically lasting 2–4 weeks), where the statistical power required for robust ranking and clustering is often insufficient, as a few anomalous days (e.g., influenced by unique meteorological events or local plumes) can disproportionately skew the ranking distribution. In these instances, manual, expert-led classification remains a more reliable method, as it allows for the nuanced consideration of auxiliary data (e.g., trace gas spikes, wind direction changes) that automated algorithms might not yet fully integrate.

3.1.3 Machine learning-based method for NPF classification and characterization

Almost in parallel with the development of nanoparticle ranking method, machine learning algorithms have also been applied for NPF classification. Early efforts, such as those by Zaidan et al. (2018), utilized Bayesian classification and shallow Neural Networks to process time-series features (e.g., condensation sink, particle formation rates, and gas-phase precursor concentrations). This model aims to predict the occurrence of NPF based on environmental variables.

Later, computer vision-based approaches have been

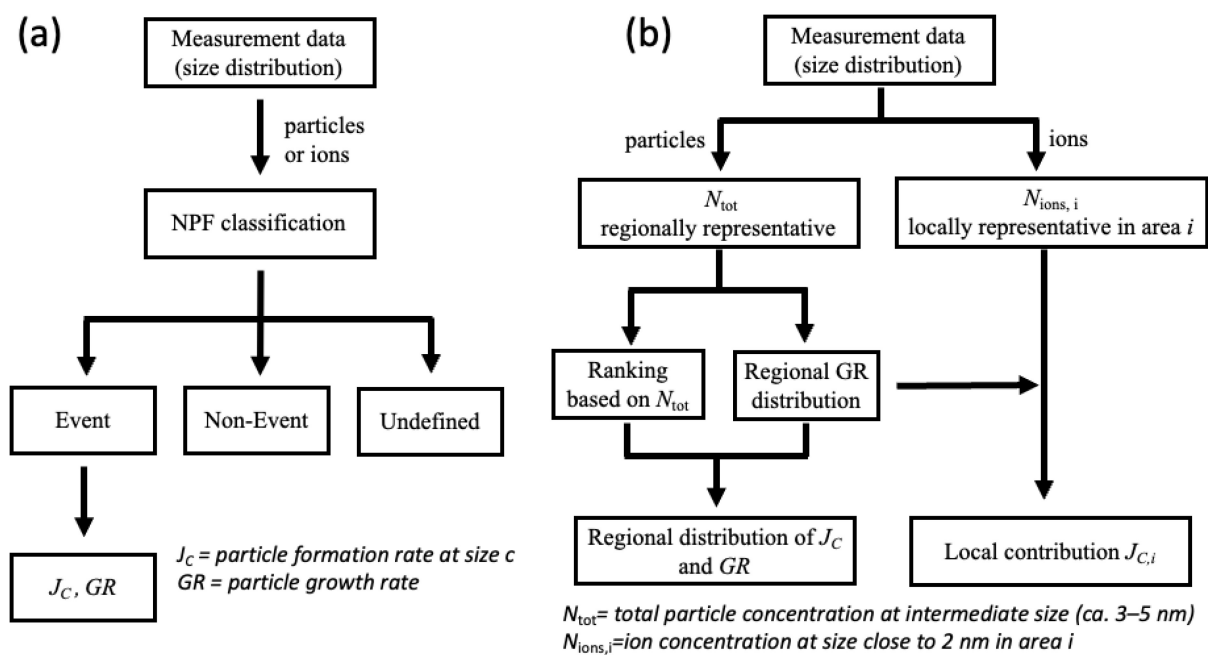


Fig. 4 From event classification to continuous NPF characterization. (a) Traditional classification separates event, non-event, and undefined days. Particle formation rates (J) and growth rates (GR) are typically derived only from clear events, leaving quiet NPF largely unquantified. (b) The ranking-based framework uses intermediate ions near 2 nm and total particle concentrations at 2.5–5 nm to characterize local and regional NPF, respectively. Rank-bin-specific growth rates are fitted directly from growth patterns in the corresponding particle number size distributions. These rates support probability distributions of J across measurement days, including days with quiet NPF. Adapted from Figs. 1 and 2 of Kulmala et al. (2024) under CC BY 4.0.

developed, which treat the “banana plot” as an image detection task. Differently from the study by Zaidan et al. (2018), these approaches are directly trained on particle size distribution data, and their working principles of “looking for banana” are the same as the manual classification method. Joutsensaari et al. (2018) pioneered this approach by employing Convolutional Neural Networks (CNN) to classify particle size distribution images, achieving an accuracy of approximately 90% in replicating expert-labeled datasets at the Hyytiälä station. Building upon this, Su et al. (2022) implemented the Mask R-CNN algorithm, which not only identifies the occurrence of NPF but also precisely defines its growth trajectory, with an appreciable mean average precision of 0.76. Furthermore, Zhang et al. (2024a) compared the performance of EfficientNet model, Swin Transformer model, and ConvNeXt model in replicating NPF classifications amount nine European sites, and suggest that deep learning can effectively standardize NPF identification across disparate observation networks. Most recently, Bhandari et al. (2025) introduced the YOLO (You Only Look Once) algorithm, a real-time detection framework. By training on data sets from 14 sites covering diverse environments, this model demonstrated high computational efficiency and classification accuracy (> 85%), even when transferred to environmentally distinct regions like the Arctic or polluted urban centers in India.

Differently from the nanoparticle ranking method, these machine-learning-based approaches usually do not require high statistical power and are therefore, not limited to long-term data. They are particularly suitable for a standardized NPF classification across disparate observation data sets. Although the current prediction accuracy is around 80%–90%, higher accuracy and adaptability can be expected with enlarged training data in future works.

3.1.4 Identification and impact of the “quiet NPF”

The traditional classification frameworks discussed in previous sections (Sections 3.1.1–3.1.3), either based on manual visual inspection or automated machine learning algorithms, primarily focus on “visible” NPF events. These events are characterized by a distinct “banana-shaped” growth pattern in the particle size distribution plots, typically requiring a particle formation rate high enough to overcome the coagulation loss and a sustained growth to reach detectable sizes (Dal Maso et al., 2005; Kulmala et al., 2012). However, a significant portion of “undefined” or “non-event” days may actually have weak but persistent

particle formation that remains below the detection limit of standard instrumentation or are obscured by high background aerosol concentrations.

The conceptual foundation of Quiet NPF stems from early observations of atmospheric air ions by Tammet et al. (2013), who identified “quiet periods” characterized by a steady-state population of nano-particles (1.5–7.5 nm) in the absence of macroscopic growth bursts. Kulmala et al. (2022) subsequently formalized “Quiet NPF”. By normalizing the particle concentration values in each size bin to a range of 0 to 1, which eliminates the influence of absolute concentration differences and preserves only the diurnal variation in the shape of the size distribution, the authors uncovered the previously invisible “banana shape” and demonstrated that weak but persistent particle formation occurs ubiquitously across diverse environments.

Quantitatively, the formation rate of sub-3 nm particles (J_3), during quiet periods is commonly in the range of 0.01–0.1 $\text{cm}^{-3} \text{s}^{-1}$, approximately one to two orders of magnitude lower than during traditional NPF events (Kulmala et al., 2022). By contrast, growth rates between 6 and 25 nm on quiet-NPF days can be similar to, or only slightly lower than, those observed on traditional event days. Quiet NPF is therefore characterized primarily by weak particle formation and limited survival, rather than by exceptionally slow particle growth.

These observations do not necessarily indicate that quiet NPF is governed by a distinct nucleation mechanism. Instead, quiet NPF may represent the lower-intensity part of a continuous distribution of atmospheric particle formation. In clean environments, this low-intensity regime may result mainly from low concentrations of precursor vapours, which produce intrinsically low nucleation rates. In polluted environments, the same underlying nucleation chemistry may operate, but the resulting signal can be strongly suppressed by pre-existing aerosols. The condensation sink reduces the concentrations of condensable precursor vapours and may limit subsequent growth, whereas the coagulation sink directly removes newly formed clusters and particles before they reach detectable sizes. High aerosol sinks can therefore mask ongoing particle formation even when precursor concentrations are not exceptionally low. This suppression is implicit in the population balance governing the observed formation rate at a specified particle diameter and should be distinguished from changes in the intrinsic molecular nucleation mechanism.

Although only a limited number of studies have quantified quiet NPF, its cumulative contribution to

atmospheric particle populations may be substantial. Kulmala et al. (2022) estimated that quiet NPF accounts for approximately 20% of the total particle number concentration in the clean boreal forest environment of Hyytiälä and may produce twice as many particles as traditional NPF events in urban Budapest. More recently, Meller et al. (2026) identified quiet NPF as a primary particle source in the Amazonian boundary layer, where its regional contribution to particle number concentrations was comparable to that of distinct NPF events. These results demonstrate that individually weak but frequently occurring formation periods can make an appreciable cumulative contribution, although their global importance and eventual contribution to the CCN population remain unquantified.

3.2 Determination of particle formation rates

Particle formation rate (J) and growth rate (GR ; Section 3.3) are the principal quantitative descriptors used to compare NPF across instruments, environments, and classification frameworks. A concise methodological basis is therefore retained here so that this review can be read independently, while detailed derivations and historical developments are available in established protocols and recent reviews (Kulmala et al., 2012; Kerminen et al., 2018; Stolzenburg et al., 2023).

3.2.1 Definitions and size-dependent formation rates

The nucleation rate (J^*) is, in strict thermodynamic terms, the rate at which critical clusters are produced. Because the critical size is generally below the detection limit of field instruments, ambient studies usually report a particle formation rate J_{dp} : the flux of particles growing past a specified mobility diameter d_p . Newly formed clusters are progressively removed by coagulation as they grow, so J_{dp} decreases with increasing detection diameter and cannot be interpreted independently of the coagulation sink ($CoagS$) and GR . Conversion between two detection sizes is possible using survival-probability expressions, most commonly the revised Kerminen–Kulmala formulation, but becomes uncertain below 3 nm where GR and detection efficiency may both be strongly size dependent (Lehtinen et al., 2007; Kulmala et al., 2012; Kerminen et al., 2018; Stolzenburg et al., 2023).

Common reporting diameters reflect instrument capability rather than different physical definitions: $J_{1.5}-J_{1.7}$ is obtained with sub-3 nm condensation particle counters and is closest to nucleation size; J_3 remains the most widely comparable long-term metric; and J_7-J_{10} is used when the particle size distribution begins in the upper nucleation mode. A formation rate

should therefore always be reported together with its detection diameter, directly measured size interval, temporal resolution, treatment of coagulation and transport, and whether it was measured directly or converted from another size (Lehtinen et al., 2007; Kulmala et al., 2012, 2013; Wimmer et al., 2013; Kerminen et al., 2018).

3.2.2 Estimation from particle number size distributions

Formation rates are derived from a number balance over a measured interval $[k, u]$. The general balance separates the temporal change in particle concentration, coagulation losses, external sources such as emissions and transport, and the flux of particles growing through the upper boundary:

$$\frac{dN_{[k,u]}}{dt} = J_k + E_{[k,u]} - S_{[k,u]} - J_u, \quad (1)$$

where $N_{[k,u]}$ is the particle concentration in the interval, J_k is the formation rate at the lower boundary, $S_{[k,u]}$ is the net coagulation loss, $E_{[k,u]}$ represents external sources or transport, and J_u is the growth flux through u . During spatially homogeneous NPF events, $E_{[k,u]}$ is often assumed negligible and the expression is commonly simplified to:

$$J_k \approx \frac{dN_{[k,u]}}{dt} + CoagS \cdot N_{[k,u]} + n_u \cdot GR_u, \quad (2)$$

where $CoagS$ is evaluated at a representative diameter, n_u is the particle size distribution at u , and GR_u is the growth rate at u . The upper boundary is normally selected between about 6 and 25 nm: it should be high enough to reduce uncertainty in the growth-flux term, but low enough to limit contamination from primary particles. This trade-off is environment dependent. In polluted conditions, coagulation may dominate the balance and must be calculated size-resolved rather than approximated as a single loss term; the resulting correction can substantially increase sub-3 nm formation rates (Kulmala et al., 2012; Cai and Jiang, 2017; Deng et al., 2021).

The main limitation is that fixed-site measurements are Eulerian. Changes in boundary-layer height, primary emissions, or the history of an advected air mass can alter $N_{[k,u]}$ without representing local particle formation. The external-source term may be small during intense regional events but can be important on weak, non-event, or traffic-influenced days. Formation rates derived outside clear event periods should therefore be interpreted as apparent local rates unless transport and emission contributions have been constrained with auxiliary observations (Rönkkö et al., 2017; Stolzenburg et al., 2023).

3.2.3 Charged-particle formation and ion-induced nucleation

Charged-particle formation rates provide an observational constraint on ion-induced nucleation (IIN). They are calculated from positive and negative ion size distributions measured by instruments such as the NAIS or AIS, using the same population balance as for total particles but including ion–ion recombination and ion–aerosol attachment (Kulmala et al., 2012; Mirme and Mirme, 2013):

$$J_k^\pm = \frac{dN_{[k,u]}^\pm}{dt} + \sum_{i=k}^u \sum_{j=u}^{\max} K_{i,j} N_i^\pm N_j + n_u^\pm \cdot GR_u + \alpha N_{[k,u]}^\pm N_{<k}^\mp - \chi N_{[k,u]} N_{<k}^\pm, \quad (3)$$

where $K_{i,j}$ is the coagulation coefficient between particles of sizes i and j , and N_j is the concentration of particles in size bin j , N_i is the concentration of charged particles in size bin i , $N_{\pm[k,u]}$ is the concentration of charged particles in the evaluated interval; α is the ion–ion recombination coefficient; and χ is the ion–aerosol attachment coefficient. Recombination removes charged clusters, whereas attachment transfers charge from smaller ions to pre-existing neutral particles and therefore acts as a source within the tracked interval (Tamm et al., 2005; Franchin et al., 2015).

The positive and negative formation rates are summed to estimate J_{IIN} , and the apparent IIN fraction is $J_{\text{IIN}}/J_{\text{total}}$. This fraction is size dependent because clusters formed on ions can neutralize before reaching the measurement diameter; estimates at 2–3 nm may therefore be lower than the contribution at nucleation size. Recent comparisons further show that apparent ion and total-particle GR can differ even under the same atmospheric conditions, because the evolving balance between ion-induced and neutral nucleation changes the measured particle populations (Tamm et al., 2005; Manninen et al., 2009, 2010; Leppä et al., 2013; Franchin et al., 2015; Gonzalez Carracedo et al., 2022).

3.3 Methods for growth-rate estimation

Growth rate describes the change in particle diameter with time and links molecular-scale formation to survival toward climatically and societally relevant sizes. In field studies, however, GR is inferred from the evolution of a particle population rather than from repeated observations of an individual particle. The retrieved value is therefore an apparent GR that may contain contributions from condensation, coagulation,

evaporation, emissions, and transport (Leppä et al., 2011; Kerminen et al., 2018; Cai et al., 2021a; Stolzenburg et al., 2023).

3.3.1 Population-tracking methods

Mode fitting and appearance-time analysis are the most widely used population-tracking approaches. In mode fitting, lognormal functions are fitted to successive particle number size distributions and GR is obtained from the change in the geometric mean diameter d_g of the nucleation mode (Whitby, 1978; Kulmala et al., 2012; Kerminen et al., 2018):

$$GR_{\text{mode}} = \frac{d_{g2} - d_{g1}}{t_2 - t_1}. \quad (4)$$

Mode fitting is robust when a distinct, continuously growing mode is visible, commonly above approximately 10 nm, but becomes ambiguous when modes overlap, the distribution is non-lognormal, or growth is interrupted. The appearance-time method instead identifies a representative time t_{app} —often the time at which a size-bin concentration reaches 50% or 100% of its event maximum—and derives GR from the progression between adjacent diameters (Kulmala et al., 2013; Dada et al., 2020; He et al., 2021; Deng et al., 2022):

$$GR_{\text{app}} = \frac{d_{p2} - d_{p1}}{t_{\text{app}2} - t_{\text{app}1}}. \quad (5)$$

Appearance-time analysis can be applied over a restricted size range and is therefore useful at cluster sizes where no stable modal peak exists. Its result depends on the selected threshold and can be biased by size-dependent coagulation, changing air masses, and primary particle sources. Corrections based on aerosol dynamics can separate part of the coagulation contribution, but neither population-tracking method should automatically be interpreted as a pure condensational growth rate (Leppä et al., 2011; Cai et al., 2021a; Stolzenburg et al., 2023).

3.3.2 General-dynamic-equation and inverse methods

GDE-based methods infer size- and time-resolved GR by fitting the observed evolution of the particle size distribution while explicitly representing condensation, coagulation, dilution, wall loss, or other known processes. Deterministic inverse methods attribute the difference between modeled and observed distributions to condensational growth, whereas Bayesian and Kalman-smoothing approaches retrieve J and GR together with their uncertainty. These approaches

provide more process information than trajectory methods and avoid imposing a single *GR* over a broad size range, but their solutions depend on the assumed process model and are best constrained in chambers or exceptionally well-characterized field measurements (Verheggen and Mozurkewich, 2006; Kuang et al., 2012; Pichelstorfer et al., 2018; Ozon et al., 2021; Stolzenburg et al., 2023).

3.3.3 Interpretation and method selection

Method selection should follow the observable structure in the data. Mode fitting is preferred for a clear growing mode; appearance-time methods are useful for a limited or sub-3 nm size range; and GDE-based inversion is appropriate when size-resolved process attribution and uncertainty estimates are required. For quiet or weak NPF days without a distinct banana trajectory, *GR* generally cannot be determined independently for every day. Analyses should instead state whether *GR* was obtained from normalized size-distribution evolution, constrained by a regional or seasonal distribution, or adopted from a representative subset of event days.

Particular caution is required when interpreting *GR* derived from fixed-site measurements. The apparent *GR* contains both the true diameter-change rate experienced by individual particles and a transport-related contribution arising from differences between consecutively sampled air masses. Transport may therefore bias the magnitude of an apparently positive *GR* even when no decreasing modal diameter is observed, with apparent shrinkage representing only an extreme and readily identifiable case. A practical assessment should examine whether air-mass histories remain consistent throughout the complete *GR*-fitting period, rather than only around an identifiable transition time. Hourly back trajectories, preferably ensemble retroplumes, can be used to compare source footprints, transport heights, and residence times for the particle populations sampled at different stages of an event. These footprints should be evaluated together with regional precursor distributions, source proxies, boundary-layer evolution, and wind fields. *GR* can then be recalculated within periods having relatively stable transport histories and compared with the value obtained over the complete event. A strong sensitivity to this segmentation indicates that the reported value should be interpreted as a transport-sensitive apparent *GR*. When sufficient aerosol-dynamic information is available, the transport contribution may also be estimated as a residual term in the particle population balance.

4 Summary and outlook

4.1 Summary

This Part I has examined recent advances in atmospheric NPF along two interconnected dimensions: measurement and characterization. On the measurement side, the detection size frontier has been pushed from ~10 nm in early electrical mobility analyzers to around 1.5 nm with particle size magnifiers and nano-scanning spectrometers, progressively closing the observational gap between molecular cluster chemistry and particle population dynamics. Equally transformative has been the deployment of chemical ionization mass spectrometers capable of resolving nucleating precursor vapors at sub-pptv concentrations, with organic precursor measurements organized along the oxygen-number axis from parent VOCs through to ultra-low-volatility organic oxidation products. On the characterization side, new analytical frameworks, including the nanoparticle ranking method and the concept of quiet NPF, have revealed that particle formation is far more pervasive and continuous than classical event-based statistics suggested. The molecular mechanisms of NPF across diverse atmospheric environments and multi-scale modelling from box models to global Earth System Models are reviewed in the companion paper (Part II).

4.2 Outlook

The advances reviewed in this Part I have transformed the measurement and characterization of atmospheric NPF from a macroscopic statistical exercise into a molecularly resolved discipline. Yet precisely because the field now operates at molecular resolution, the remaining gaps in measurement and characterization are more clearly defined than ever before. In the following subsections we outline what we consider the highest priorities for advancing the experimental foundation of NPF science along three lines: improving the accuracy of sub-10 nm particle size distribution measurements, improving the absolute calibration of chemical ionization mass spectrometers, and systematically evaluating quiet NPF across the full diversity of atmospheric environments.

4.2.1 Reducing uncertainties in sub-10 nm particle size distribution measurements

Although sub-2 nm particle size distribution measurement has matured considerably, substantial scientific work remains to improve sub-10 nm PSD

accuracy, especially in the low nanometer regime (Kangasluoma et al., 2020). The dominant source of uncertainty for mobility-based instruments is the poorly constrained sub-3 nm charging efficiency, which can introduce $\pm 50\%$ uncertainty at 2 nm, while for Kelvin-based instruments the dominant uncertainty comes from the CPC cut-off, which depends sensitively on particle composition near the activation threshold. Liu et al. (2025) recently demonstrated the magnitude of the calibration problem: applying a standard tungsten-particle calibration to a Particle Size Magnifier 2.0 deployed in Hyytiälä caused particles between 3 and 10 nm to be misattributed into the sub-3 nm size range, biasing inferred particle formation rates. Looking forward, we see three complementary measurement priorities.

First, traceable composition-independent calibration. The ideal sizing mechanism would be independent of particle composition (Kangasluoma et al., 2020), but until such a mechanism is realised, the practical path forward is *in-situ* calibration using ambient particles, paired with reference infrastructure such as the planned ACTRIS sub-10 nm calibration facility, and recurring inter-laboratory intercomparison exercises.

Second, atmospheric closure between co-located instruments. The integrated 1–10 nm concentration measured by mobility-based, Kelvin-based, and CPC-battery-based instruments should agree under steady-state conditions; persistent disagreement, often by a factor of 2–4 (Kangasluoma et al., 2020), points to systematic errors that propagate into formation- and growth-rate estimates and ultimately into NPF parameterizations. Coordinated multi-instrument deployments accompanied by simulations of each instrument's response would identify the dominant sources of residual disagreement and guide the next generation of instrument design.

Third, high-time-resolution PSD instruments that simultaneously cover a wide size range. Fast-time-resolution measurements are essential for capturing rapidly evolving NPF—for example, on board research aircraft where the air mass is sampled only briefly, or in highly polluted urban environments where sub-3 nm particle lifetimes can be on the order of seconds. Three complementary instrument strategies have emerged, each with different trade-offs (Section 2.1). The DMA-train uses parallel DMA–CPC pairs at fixed mobility voltages and reaches second-scale time resolution up to ~ 10 nm. The CPC FARM provides 1 Hz size-resolved measurements but is currently limited to the sub-3 nm range. The NAIS nominally extends to 40 nm via parallel electrometer arrays, but its reliability is

compromised by corona-charger artifacts in the sub-2 nm regime and by known systematic concentration overestimation above ~ 20 nm. None of these instruments currently delivers the ideal combination of fast time resolution and a size range spanning from sub-2 nm clusters up to several hundred nanometers—the size range needed to simultaneously capture cluster formation, the subsequent growth chain, and the eventual contribution to CCN-relevant sizes. Developing such a wide-range, high-time-resolution instrument—together with broader deployment of existing fast-PSD techniques at long-term observation sites and direct multi-instrument intercomparison campaigns—would substantially expand the range of NPF conditions and environments that can be reliably characterized.

4.2.2 Calibration of chemical ionization mass spectrometers

Equally pressing is the improvement of absolute calibration of chemical ionization mass spectrometers used for NPF precursor measurement. As reviewed in Section 2.2.4, the calibration uncertainty of nitrate CI-API-TOF for H_2SO_4 alone is approximately $\pm 50\%$ arising from inlet wall losses and flow uncertainties, and the situation is considerably worse for OOMs, for which no traceable vapor-phase standards exist. The accepted practice of applying the H_2SO_4 calibration factor uniformly to all detected organic species can underestimate individual compound concentrations by orders of magnitude. This systematic underestimation propagates directly into growth rate predictions and nucleation rate parameterizations, since CIMS measurements almost certainly underestimate total condensable organic concentrations to an unquantified degree. Developing traceable calibration standards and systematic protocols for OOM quantification—analogue to the established H_2SO_4 photochemical source calibration—is therefore a prerequisite for closing the gap between predicted and observed nanoparticle growth rates. A more comprehensive treatment of growth-rate closure across diverse environments, including the role of the recently identified nanoparticle concentration gradient mechanism, is given in the companion paper (Part II).

4.2.3 Systematic evaluation of quiet NPF across diverse environments

A major priority is to determine how frequently quiet

NPF occurs and quantify its cumulative contribution across clean continental, polluted urban, marine, polar, and high-altitude environments. The normalized particle size distribution framework of Kulmala et al. (2022) and the nanoparticle ranking method described in Section 3.1.2 provide a practical foundation for such an assessment. Applying these methods to long-term observations would extend the analysis beyond the highest-ranked 10%–20% of days and include moderate- and lower-ranking conditions that are commonly categorized as non-event or undefined days. Coordinated reanalysis of datasets from global observation networks could therefore establish whether quiet NPF is a widespread atmospheric phenomenon and identify the precursor and aerosol-sink conditions controlling its occurrence and intensity.

More importantly, the resulting probability distributions of J could provide a new observational constraint for global aerosol models. Current evaluations based on event frequency or formation rates from selected strong events primarily constrain the upper tail of the atmospheric J distribution. They provide much less information about the frequency and cumulative contribution of persistent low- J conditions. Models should therefore be evaluated against the complete observed distribution of formation rates, encompassing strong, moderate, and quiet particle formation, rather than against a binary event/non-event classification.

The required model development may differ between atmospheric environments. In clean environments, where quiet NPF may primarily reflect low precursor concentrations, existing precursor-based nucleation parameterizations should in principle reproduce the low- J regime. The key requirement is to evaluate whether models capture the frequency and cumulative particle production of these low-intensity periods. In polluted environments, models must additionally represent how pre-existing aerosol surfaces influence precursor availability and the survival of newly formed particles. This does not necessarily require inserting the condensation sink directly into parameterizations of the intrinsic nucleation rate. Instead, precursor-based nucleation should be coupled with sink-dependent particle growth and survival to calculate the effective formation rate at model-resolved sizes. Laboratory experiments that systematically vary both precursor concentrations and pre-existing aerosol sinks would be particularly valuable for developing and evaluating such representations. Together, these observational and experimental advances would provide a foundation for representing continuous, all-weather NPF and evaluating its contribution to regional and global particle number and CCN budgets.

Abbreviations

Abbreviation	Full term
ACSM	Aerosol Chemical Speciation Monitor
AIM	Adduct Ionization Mechanism
AIS	Air Ion Spectrometer
APi-TOF	Atmospheric Pressure interface Time-of-Flight mass spectrometer
CCN	Cloud condensation nuclei
CERN	European Organization for Nuclear Research
CI-API-TOF	Chemical ionization atmospheric pressure interface time-of-flight mass spectrometer
CIMS	Chemical ionization mass spectrometer
CLOUD	Cosmics Leaving OUTdoor Droplets
CN	Condensation nuclei
CNN	Convolutional Neural Network
CoagS	Coagulation sink
CPC	Condensation particle counter
CPC FARM	Condensation Particle Counters For Atmospheric Rapid Measurements
CS	Condensation sink
DEG	Diethylene glycol
DEG-CPC	Diethylene Glycol Condensation Particle Counter
DMA	Dimethylamine; also Differential Mobility Analyzer
DMPS	Differential Mobility Particle Sizer
EAS	Electrical Aerosol Spectrometer
EESI-TOF	Extractive Electrospray Ionization Time-of-Flight
ELVOC	Extremely low volatile organic compound
FIGAERO	Filter Inlet for Gases and AEROSols
GDE	General Dynamic Equation
GR	Growth rate
HF-DMPS	High Flow Differential Mobility Particle Sizer
H-TDMA	Hygroscopicity Tandem Differential Mobility Analyzer
HNO_3	Nitric Acid
HOM	Highly oxygenated organic molecule
HR-ToF-AMS	High-Resolution Time-of-Flight Aerosol Mass Spectrometer
IIN	Ion-induced nucleation
I-CIMS	Iodide Chemical Ionization Mass Spectrometry
J	Particle formation rate
LVOC	Low volatile organic compound
NAIS	Neutral cluster and Air Ion Spectrometer
NH_4^+ -CIMS	Ammonium Chemical Ionization Mass Spectrometry
NPCIMS	Nanoparticle Chemical Ionization Mass Spectrometer
NPF	New particle formation

OOM	Oxygenated organic molecule
Orbitrap	Orbitrap Fourier Transform Mass Spectrometer
PNSD	Particle Number Size Distribution
PSM	Particle size magnifier
PTR-MS	Proton Transfer Reaction Mass Spectrometry
PTR-TOF	Proton Transfer Reaction Time-of-Flight mass spectrometer
SMPS	Scanning mobility particle sizer
SOA	Secondary organic aerosol
TD-DMA	Thermal Desorption–Differential Mobility Analyzer
TDCIMS	Thermal Desorption Chemical Ionization Mass Spectrometer
TDMA	Tandem Differential Mobility Analyzer
VIA	Vaporization Inlet for Aerosols
VOC	Volatile organic compound
V-TDMA	Volatility Tandem Differential Mobility Analyzer
VH-TDMA	Volatility-Hygroscopicity Tandem Differential Mobility Analyzer
WALL-E	Wall-free Particle Evaporator
YOLO	You Only Look Once

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References

- Aitken J (1900). III. On some nuclei of cloudy condensation. *Transactions of the Royal Society of Edinburgh*, 39(3): 15–25
- Aliaga D, Sinclair V A, Krejci R, Andrade M, Artaxo P, Blacutt L, Cai R L, Carbone S, Gramlich Y, Heikkinen L, et al. (2025). New particle formation dynamics in the central Andes: contrasting urban and mountaintop environments. *Aerosol Research*, 3(1): 15–44
- Aliaga D, Tuovinen S, Zhang T H, Lampilahti J, Li X Y, Ahonen L, Kokkonen T, Nieminen T, Hakala S, Paasonen P, et al. (2023). Nanoparticle ranking analysis: determining new particle formation (NPF) event occurrence and intensity based on the concentration spectrum of formed (sub-5 nm) particles. *Aerosol Research*, 1(1): 81–92
- Almeida J, Schobesberger S, Kürten A, Ortega I K, Kupiainen-Määttä O, Praplan A P, Adamov A, Amorim A, Bianchi F, Breitenlechner M, et al. (2013). Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere. *Nature*, 502(7471): 359–363
- Barus C (1902). Preliminary results on the changes of atmospheric nucleation. *Science*, 16(415): 948–952
- Berndt T, Scholz W, Mentler B, Fischer L, Herrmann H, Kulmala M, Hansel A (2018). Accretion product formation from self- and cross-reactions of RO₂ radicals in the atmosphere. *Angewandte Chemie International Edition*, 57(14): 3820–3824
- Bhandari R, Sarangi C, Sebastian M, Hooda R K, Hyvärinen A P, Asmi E, Vakkari V, Pandithurai G, Singh S, Soni V K, et al. (2025). Identification of new particle formation events using a you only look once (YOLO) deep learning algorithm. *ACS ES&T Air*, 2(7): 1202–1213
- Bianchi F, Kurtén T, Riva M, Mohr C, Rissanen M P, Roldin P, Berndt T, Crounse J D, Wennberg P O, Mentel T F, et al. (2019). Highly oxygenated organic molecules (HOM) from gas-phase autoxidation involving peroxy radicals: a key contributor to atmospheric aerosol. *Chemical Reviews*, 119(6): 3472–3509
- Bianchi F, Praplan A P, Sarnela N, Dommen J, Kürten A, Ortega I K, Schobesberger S, Junninen H, Simon M, Tröstl J, et al. (2014). Insight into acid–base nucleation experiments by comparison of the chemical composition of positive, negative, and neutral clusters. *Environmental Science & Technology*, 48(23): 13675–13684
- Buenrostro Mazon S, Riipinen I, Schultz D M, Valtanen M, Dal Maso M, Sogacheva L, Junninen H, Nieminen T, Kerminen V M, Kulmala M (2009). Classifying previously undefined days from eleven years of aerosol-particle-size distribution data from the SMEAR II station, Hyytiälä, Finland. *Atmospheric Chemistry and Physics*, 9(2): 667–676
- Cai R L, Huang W, Meder M, Bourgain F, Aizikov K, Riva M, Bianchi F, Ehn M (2022). Improving the sensitivity of Fourier transform mass spectrometer (orbitrap) for online measurements of atmospheric vapors. *Analytical Chemistry*, 94(45): 15746–15753
- Cai R L, Jiang J K (2017). A new balance formula to estimate new particle formation rate: reevaluating the effect of coagulation scavenging. *Atmospheric Chemistry and Physics*, 17(20): 12659–12675
- Cai R L, Li C X, He X C, Deng C J, Lu Y Q, Yin R J, Yan C, Wang L, Jiang J K, Kulmala M, et al. (2021a). Impacts of coagulation

- on the appearance time method for new particle growth rate evaluation and their corrections. *Atmospheric Chemistry and Physics*, 21(3): 2287–2304
- Cai R L, Yan C, Yang D S, Yin R J, Lu Y Q, Deng C J, Fu Y Y, Ruan J X, Li X X, Kontkanen J, et al. (2021b). Sulfuric acid–amine nucleation in urban Beijing. *Atmospheric Chemistry and Physics*, 21(4): 2457–2468
- Caudillo L, Surdu M, Lopez B, Wang M Y, Thoma M, Bräkling S, Buchholz A, Simon M, Wagner A C, Müller T, et al. (2023). An intercomparison study of four different techniques for measuring the chemical composition of nanoparticles. *Atmospheric Chemistry and Physics*, 23(11): 6613–6631
- Chen D H, Yao X H, Chan C K, Tian X M, Chu Y X, Clegg S L, Shen Y J, Gao Y, Gao H W (2022). Competitive uptake of dimethylamine and trimethylamine against ammonia on acidic particles in marine atmospheres. *Environmental Science & Technology*, 56(9): 5430–5439
- Chen H H, Chee S, Lawler M J, Barsanti K C, Wong B M, Smith J N (2018). Size resolved chemical composition of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine. *Aerosol Science and Technology*, 52(10): 1120–1133
- Chen L D, Qi X M, Niu G D, Li Y Y, Liu C, Lai S Y, Liu Y L, Nie W, Yan C, Wang J P, et al. (2023a). High concentration of atmospheric sub-3 nm particles in polluted environment of eastern China: new particle formation and traffic emission. *Journal of Geophysical Research: Atmospheres*, 128(22): e2023JD039669
- Chen Y, Deng C J, Lei T, Li J L, Lian C F, Li Y R, Zheng J, Zhao J, Wang D B, Wu Z J, et al. (2023b). Size-dependent chemical composition of atmospheric nanoparticles in urban Beijing during springtime. *Atmospheric Environment*, 310: 119970
- Cheng D, Amanatidis S, Lewis G S, Jen C N (2025). Fast and sensitive measurements of sub-3 nm particles using condensation particle counters for atmospheric rapid measurements (CPC FARM). *Atmospheric Measurement Techniques*, 18(1): 197–210
- Claffin M S, Pagonis D, Finewax Z, Handschy A V, Day D A, Brown W L, Jayne J T, Worsnop D R, Jimenez J L, Ziemann P J, et al. (2021). An *in situ* gas chromatograph with automatic detector switching between PTR- and EI-TOF-MS: isomer-resolved measurements of indoor air. *Atmospheric Measurement Techniques*, 14(1): 133–152
- Covert D S, Kapustin V N, Quinn P K, Bates T S (1992). New particle formation in the marine boundary layer. *Journal of Geophysical Research: Atmospheres*, 97(D18): 20581–20589
- Dada L, Chellapermal R, Buenrostro Mazon S, Paasonen P, Lampilahti J, Manninen H E, Junninen H, Petäjä T, Kerminen V M, Kulmala M (2018). Refined classification and characterization of atmospheric new-particle formation events using air ions. *Atmospheric Chemistry and Physics*, 18(24): 17883–17893
- Dada L, Lehtipalo K, Kontkanen J, Nieminen T, Baalbaki R, Ahonen L, Duplissy J, Yan C, Chu B W, Petäjä T, et al. (2020). Formation and growth of sub-3-nm aerosol particles in experimental chambers. *Nature Protocols*, 15(3): 1013–1040
- Dal Maso M, Kulmala M, Riipinen I, Wagner R, Hussein T, Aalto P P, Lehtinen K E J (2005). Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland. *Boreal Environment Research*, 10(5): 323–336
- De Gouw J, Warneke C (2007). Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews*, 26(2): 223–257
- Deng C J, Cai R L, Yan C, Zheng J, Jiang J K (2021). Formation and growth of sub-3 nm particles in megacities: impact of background aerosols. *Faraday Discussions*, 226: 348–363
- Deng C J, Li Y R, Yan C, Wu J, Cai R L, Wang D B, Liu Y C, Kangasluoma J, Kerminen V M, Kulmala M, et al. (2022). Measurement report: size distributions of urban aerosols down to 1 nm from long-term measurements. *Atmospheric Chemistry and Physics*, 22(20): 13569–13580
- Ehn M, Junninen H, Petäjä T, Kurtén T, Kerminen V M, Schobesberger S, Manninen H E, Ortega I K, Vehkamäki H, Kulmala M, et al. (2010). Composition and temporal behavior of ambient ions in the boreal forest. *Atmospheric Chemistry and Physics*, 10(17): 8513–8530
- Ehn M, Petäjä T, Birmili W, Junninen H, Aalto P, Kulmala M (2007). Non-volatile residuals of newly formed atmospheric particles in the boreal forest. *Atmospheric Chemistry and Physics*, 7(3): 677–684
- Ehn M, Thornton J A, Kleist E, Sipilä M, Junninen H, Pullinen I, Springer M, Rubach F, Tillmann R, Lee B, et al. (2014). A large source of low-volatility secondary organic aerosol. *Nature*, 506(7489): 476–479
- Eisele F L, Berresheim H (1992). High-pressure chemical ionization flow reactor for real-time mass spectrometric detection of sulfur gases and unsaturated hydrocarbons in air. *Analytical Chemistry*, 64(3): 283–288
- Eisele F L, Tanner D J (1993). Measurement of the gas phase concentration of H₂SO₄ and methane sulfonic acid and estimates of H₂SO₄ production and loss in the atmosphere. *Journal of Geophysical Research: Atmospheres*, 98(D5): 9001–9010
- Flagan R C (1998). History of electrical aerosol measurements. *Aerosol Science and Technology*, 28(4): 301–380
- Franchin A, Ehrhart S, Leppä J, Nieminen T, Gagné S, Schobesberger S, Wimmer D, Duplissy J, Riccobono F, Dunne E M, et al. (2015). Experimental investigation of ion–ion recombination under atmospheric conditions. *Atmospheric Chemistry and Physics*, 15(13): 7203–7216
- Frege C, Bianchi F, Molteni U, Tröstl J, Junninen H, Henne S, Sipilä M, Herrmann E, Rossi M J, Kulmala M, et al. (2017). Chemical characterization of atmospheric ions at the high altitude research station Jungfraujoch (Switzerland). *Atmospheric Chemistry and Physics*, 17(4): 2613–2629
- Frege C, Ortega I K, Rissanen M P, Praplan A P, Steiner G, Heinritzi M, Ahonen L, Amorim A, Bernhammer A K, Bianchi F, et al.

- (2018). Influence of temperature on the molecular composition of ions and charged clusters during pure biogenic nucleation. *Atmospheric Chemistry and Physics*, 18(1): 65–79
- Gao L Y, Zgheib I, Stergiou E, Carstens C, Sari Doré F, Dupanloup M, Bourgain F, Perrier S, Riva M (2025). Characterization of the newly designed wall-free particle evaporator (WALL-E) for online measurements of atmospheric particles. *Atmospheric Measurement Techniques*, 18(19): 5087–5101
- Gonzalez Carracedo L, Lehtipalo K, Ahonen L R, Sarnela N, Holm S, Kangasluoma J, Kulmala M, Winkler P M, Stolzenburg D (2022). On the relation between apparent ion and total particle growth rates in the boreal forest and related chamber experiments. *Atmospheric Chemistry and Physics*, 22(19): 13153–13166
- Gordon H, Kirkby J, Baltensperger U, Bianchi F, Breitenlechner M, Curtius J, Dias A, Dommen J, Donahue N M, Dunne E M, et al. (2017). Causes and importance of new particle formation in the present-day and preindustrial atmospheres. *Journal of Geophysical Research: Atmospheres*, 122(16): 8739–8760
- Graham E L, Wu C, Bell D M, Bertrand A, Haslett S L, Baltensperger U, El Haddad I, Krejci R, Riipinen I, Mohr C (2023). Volatility of aerosol particles from NO₃ oxidation of various biogenic organic precursors. *Atmospheric Chemistry and Physics*, 23(13): 7347–7362
- Hakala J, Mikkilä J, Hong J, Ehn M, Petäjä T (2017). VH-TDMA: a description and verification of an instrument to measure aerosol particle hygroscopicity and volatility. *Aerosol Science and Technology*, 51(1): 97–107
- Häkkinen E, Zhao J, Graeffe F, Fauré N, Krechmer J E, Worsnop D, Timonen H, Ehn M, Kangasluoma J (2023). Online measurement of highly oxygenated compounds from organic aerosol. *Atmospheric Measurement Techniques*, 16(6): 1705–1721
- He X C, Iyer S, Sipilä M, Ylisirniö A, Peltola M, Kontkanen J, Baalbaki R, Simon M, Kürten A, Tham Y J, et al. (2021). Determination of the collision rate coefficient between charged iodic acid clusters and iodic acid using the appearance time method. *Aerosol Science and Technology*, 55(2): 231–242
- He X C, Shen J L, Iyer S, Juuti P, Zhang J Y, Koirala M, Kytökari M M, Worsnop D R, Rissanen M, Kulmala M, et al. (2023). Characterisation of gaseous iodine species detection using the multi-scheme chemical ionisation inlet 2 with bromide and nitrate chemical ionisation methods. *Atmospheric Measurement Techniques*, 16(19): 4461–4487
- Heinritzi M, Simon M, Steiner G, Wagner A C, Kürten A, Hansel A, Curtius J (2016). Characterization of the mass-dependent transmission efficiency of a CIMS. *Atmospheric Measurement Techniques*, 9(4): 1449–1460
- Heintzenberg J, Wehner B, Birmili W (2007). ‘How to find bananas in the atmospheric aerosol’: new approach for analyzing atmospheric nucleation and growth events. *Tellus B: Chemical and Physical Meteorology*, 59(2): 273–282
- Hemmilä M, Hellén H, Virkkula A, Makkonen U, Praplan A P, Kontkanen J, Ahonen L, Kulmala M, Hakola H (2018). Amines in boreal forest air at SMEAR II station in Finland. *Atmospheric Chemistry and Physics*, 18(9): 6367–6380
- Hering S V, Lewis G S, Spielman S R, Eiguen-Fernandez A, Kreisberg N M, Kuang C, Attoui M (2017). Detection near 1-nm with a laminar-flow, water-based condensation particle counter. *Aerosol Science and Technology*, 51(3): 354–362
- Heslin-Rees D, Tunved P, Aliaga D, Lampilahti J, Riipinen I, Ekman A M L, Park K T, Mazzini M, Gilardoni S, Thakur R, et al. (2026). Drivers governing the seasonality of new particle formation in the Arctic. *Aerosol Research*, 4(2): 457–483
- Iida K, Stolzenburg M R, McMurry P H (2009). Effect of working fluid on sub-2 nm particle detection with a laminar flow ultrafine condensation particle counter. *Aerosol Science and Technology*, 43(1): 81–96
- IPCC (2021). *Climate Change 2021: the Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge: Cambridge University Press
- Jiang J K, Chen M D, Kuang C, Attoui M, McMurry P H (2011). Electrical mobility spectrometer using a diethylene glycol condensation particle counter for measurement of aerosol size distributions down to 1 nm. *Aerosol Science and Technology*, 45(4): 510–521
- Jokinen T, Sipilä M, Junninen H, Ehn M, Lönn G, Hakala J, Petäjä T, Mauldin III R L, Kulmala M, Worsnop D R (2012). Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF. *Atmospheric Chemistry and Physics*, 12(9): 4117–4125
- Jokinen T, Sipilä M, Kontkanen J, Vakkari V, Tisler P, Duplissy E M, Junninen H, Kangasluoma J, Manninen H E, Petäjä T, et al. (2018). Ion-induced sulfuric acid–ammonia nucleation drives particle formation in coastal antarctica. *Science Advances*, 4(11): eaat9744
- Joutsensaari J, Ozon M, Nieminen T, Mikkonen S, Lähivaara T, Decesari S, Facchini M C, Laaksonen A, Lehtinen K E J (2018). Identification of new particle formation events with deep learning. *Atmospheric Chemistry and Physics*, 18(13): 9597–9615
- Junninen H, Ehn M, Petäjä T, Luosujärvi L, Kotiaho T, Kostianen R, Rohner U, Gonin M, Fuhrer K, Kulmala M, et al. (2010). A high-resolution mass spectrometer to measure atmospheric ion composition. *Atmospheric Measurement Techniques*, 3(4): 1039–1053
- Kangasluoma J, Ahonen L R, Laurila T M, Cai R L, Enroth J, Buenrostro Mazon S, Korhonen F, Aalto P P, Kulmala M, Attoui M, et al. (2018). Laboratory verification of a new high flow differential mobility particle sizer, and field measurements in Hyytiälä. *Journal of Aerosol Science*, 124: 1–9
- Kangasluoma J, Cai R L, Jiang J K, Deng C J, Stolzenburg D, Ahonen L R, Chan T, Fu Y Y, Kim C, Laurila T M, et al. (2020). Overview of measurements and current instrumentation for 1–10 nm aerosol particle number size distributions. *Journal of Aerosol Science*, 148: 105584

- Ke P P, Lintunen A, Kolari P, Lohila A, Tuovinen S, Lampilahti J, Thakur R, Peltola M, Peräkylä O, Nieminen T, et al. (2025). Potential of carbon uptake and local aerosol production in boreal and hemi-boreal ecosystems across Finland and in Estonia. *Biogeosciences*, 22(13): 3235–3251
- Keady P B, Quant F R, Sem G S (1983). Differential mobility particle sizer: a new instrument for high resolution aerosol size distribution measurements below 1 μm . *TSI Quarterly*, 9: 3–11
- Kerminen V M, Chen X M, Vakkari V, Petäjä T, Kulmala M, Bianchi F (2018). Atmospheric new particle formation and growth: review of field observations. *Environmental Research Letters*, 13(10): 103003
- Khare P, Krechmer J E, Machesky J E, Hass-Mitchell T, Cao C, Wang J Q, Majluf F, Lopez-Hilfiker F, Malek S, Wang W, et al. (2022). Ammonium adduct chemical ionization to investigate anthropogenic oxygenated gas-phase organic compounds in urban air. *Atmospheric Chemistry and Physics*, 22(21): 14377–14399
- Kirkby J, Amorim A, Baltensperger U, Carslaw K S, Christoudias T, Curtius J, Donahue N M, Haddad I E, Flagan R C, Gordon H, et al. (2023). Atmospheric new particle formation from the CERN CLOUD experiment. *Nature Geoscience*, 16(11): 948–957
- Kirkby J, Curtius J, Almeida J, Dunne E, Duplissy J, Ehrhart S, Franchin A, Gagné S, Ickes L, Kürten A, et al. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476(7361): 429–433
- Kirkby J, Duplissy J, Sengupta K, Frege C, Gordon H, Williamson C, Heinritzi M, Simon M, Yan C, Almeida J, et al. (2016). Ion-induced nucleation of pure biogenic particles. *Nature*, 533(7604): 521–526
- Kong W M, Amanatidis S, Mai H, Kim C, Schulze B C, Huang Y L, Lewis G S, Hering S V, Seinfeld J H, Flagan R C (2021). The nano-scanning electrical mobility spectrometer (nSEMS) and its application to size distribution measurements of 1.5–25 nm particles. *Atmospheric Measurement Techniques*, 14(8): 5429–5445
- Krechmer J, Lopez-Hilfiker F, Koss A, Hutterli M, Stoermer C, Deming B, Kimmel J, Warneke C, Holzinger R, Jayne J, et al. (2018). Evaluation of a new reagent-ion source and focusing ion–molecule reactor for use in proton-transfer-reaction mass spectrometry. *Analytical Chemistry*, 90(20): 12011–12018
- Kuang C, Chen M, Zhao J, Smith J, McMurry P H, Wang J (2012). Size and time-resolved growth rate measurements of 1 to 5 nm freshly formed atmospheric nuclei. *Atmospheric Chemistry and Physics*, 12(7): 3573–3589
- Kulmala M (2003). How particles nucleate and grow. *Science*, 302(5647): 1000–1001
- Kulmala M, Aliaga D, Tuovinen S, Cai R L, Junninen H, Yan C, Bianchi F, Cheng Y F, Ding A J, Worsnop D R, et al. (2024). Opinion: a paradigm shift in investigating the general characteristics of atmospheric new particle formation using field observations. *Aerosol Research*, 2(1): 49–58
- Kulmala M, Dada L, Daellenbach K R, Yan C, Stolzenburg D, Kontkanen J, Ezhova E, Hakala S, Tuovinen S, Kokkonen T V, et al. (2021). Is reducing new particle formation a plausible solution to mitigate particulate air pollution in Beijing and other Chinese megacities?. *Faraday Discussions*, 226: 334–347
- Kulmala M, Junninen H, Dada L, Salma I, Weidinger T, Thén W, Vörösmarty M, Komsaare K, Stolzenburg D, Cai R L, et al. (2022). Quiet new particle formation in the atmosphere. *Frontiers in Environmental Science*, 10: 912385
- Kulmala M, Kontkanen J, Junninen H, Lehtipalo K, Manninen H E, Nieminen T, Petäjä T, Sipilä M, Schobesberger S, Rantala P, et al. (2013). Direct observations of atmospheric aerosol nucleation. *Science*, 339(6122): 943–946
- Kulmala M, Petäjä T, Nieminen T, Sipilä M, Manninen H E, Lehtipalo K, Dal Maso M, Aalto P P, Junninen H, Paasonen P, et al. (2012). Measurement of the nucleation of atmospheric aerosol particles. *Nature Protocols*, 7(9): 1651–1667
- Kulmala M, Riipinen I, Sipilä M, Manninen H E, Petäjä T, Junninen H, Dal Maso M, Mordas G, Mirme A, Vana M, et al. (2007). Toward direct measurement of atmospheric nucleation. *Science*, 318(5847): 89–92
- Kulmala M, Wei D, Zhang X R, Zhang T H, Xia M, Wang Y Z, Zou Z H, Zheng F X, Zhang Y S, Yang C, et al. (2025). Understanding atmospheric processes: insights from the comparison between Beijing and Hyytiälä. *npj Clean Air*, 1(1): 26–46
- Kürten A, Rondo L, Ehrhart S, Curtius J (2012). Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid. *The Journal of Physical Chemistry A*, 116(24): 6375–6386
- Lampilahti A, Garmash O, Aliaga D, Arshinov M, Davydov D, Belan B, Lampilahti J, Kerminen V M, Petäjä T, Kulmala M, et al. (2025). Insights into new particle formation in a Siberian boreal forest from nanoparticle ranking analysis. *Aerosol Research*, 3(2): 441–459
- Lawler M J, Rissanen M P, Ehn M, Mauldin R L, Sarnela N, Sipilä M, Smith J N (2018). Evidence for diverse biogeochemical drivers of boreal forest new particle formation. *Geophysical Research Letters*, 45(4): 2038–2046
- Lee B H, Lopez-Hilfiker F D, Mohr C, Kurtén T, Worsnop D R, Thornton J A (2014). An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: application to atmospheric inorganic and organic compounds. *Environmental Science & Technology*, 48(11): 6309–6317
- Lee C P, Surdu M, Bell D M, Lamkaddam H, Wang M Y, Ataei F, Hofbauer V, Lopez B, Donahue N M, Dommen J, et al. (2021). Effects of aerosol size and coating thickness on the molecular detection using extractive electrospray ionization. *Atmospheric Measurement Techniques*, 14(9): 5913–5923
- Lehtinen K E J, Dal Maso M, Kulmala M, Kerminen V M (2007). Estimating nucleation rates from apparent particle formation rates and vice versa: revised formulation of the Kerminen–Kulmala equation. *Journal of Aerosol Science*, 38(9): 988–994
- Lehtipalo K, Leppä J, Kontkanen J, Kangasluoma J, Franchin A,

- Wimmer D, Schobesberger S, Junninen H, Petäjä T, Sipilä M, et al. (2014). Methods for determining particle size distribution and growth rates between 1 and 3 nm using the particle size magnifier. *Boreal Environment Research*, 19(SB): 215–236
- Lehtipalo K, Nieminen T, Schobesberger S, Ehn M, Kulmala M, Kerminen V M (2025). How the understanding of atmospheric new particle formation has evolved along with the development of measurement and analysis methods. *Journal of Aerosol Science*, 184: 106494
- Leppä J, Anttila T, Kerminen V M, Kulmala M, Lehtinen K E J (2011). Atmospheric new particle formation: real and apparent growth of neutral and charged particles. *Atmospheric Chemistry and Physics*, 11(10): 4939–4955
- Leppä J, Gagné S, Laakso L, Manninen H E, Lehtinen K E J, Kulmala M, Kerminen V M (2013). Using measurements of the aerosol charging state in determination of the particle growth rate and the proportion of ion-induced nucleation. *Atmospheric Chemistry and Physics*, 13(1): 463–486
- Li F B, Huang D D, Tian L H, Yuan B, Tan W, Zhu L, Ye P L, Worsnop D, Hoi K I, Mok K M, et al. (2024). Response of protonated, adduct, and fragmented ions in Vocus proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS). *Atmospheric Measurement Techniques*, 17(8): 2415–2427
- Li X X, Cai R L, Hao J M, Smith J N, Jiang J K (2023). Online detection of airborne nanoparticle composition with mass spectrometry: recent advances, challenges, and opportunities. *TrAC Trends in Analytical Chemistry*, 166: 117195
- Li X X, Li Y Y, Lawler M J, Hao J M, Smith J N, Jiang J K (2021). Composition of ultrafine particles in urban Beijing: measurement using a thermal desorption chemical ionization mass spectrometer. *Environmental Science & Technology*, 55(5): 2859–2868
- Liu B Y H, Whitby K T, Pui D Y H (1974). A portable electrical analyzer for size distribution measurement of submicron aerosols. *Journal of the Air Pollution Control Association*, 24: 1067–1072
- Liu Y L, Yli-Kujala A, Schmidt-Ott F, Holm S, Ahonen L, Chan T, Enroth J, Vanhanen J, Cai R L, Petäjä T, et al. (2025). Direct calibration using atmospheric particles and performance evaluation of particle size magnifier (PSM) 2.0 for sub-10 nm particle measurements. *Atmospheric Measurement Techniques*, 18(2): 431–442
- Lopez-Hilfiker F D, Iyer S, Mohr C, Lee B H, D'Ambro E L, Kurtén T, Thornton J A (2016). Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts. *Atmospheric Measurement Techniques*, 9(4): 1505–1512
- Lopez-Hilfiker F D, Pospisilova V, Huang W, Kalberer M, Mohr C, Stefenelli G, Thornton J A, Baltensperger U, Prevot A S H, Slowik J G (2019). An extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) for online measurement of atmospheric aerosol particles. *Atmospheric Measurement Techniques*, 12(9): 4867–4886
- Mäkelä J M, Aalto P, Jokinen V, Pohja T, Nissinen A, Palmroth S, Markkanen T, Seitsonen K, Lihavainen H, Kulmala M (1997). Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophysical Research Letters*, 24(10): 1219–1222
- Manninen H E, Nieminen T, Asmi E, Gagné S, Häkkinen S, Lehtipalo K, Aalto P, Vana M, Mirme A, Mirme S, et al. (2010). EUCAARI ion spectrometer measurements at 12 European sites: analysis of new particle formation events. *Atmospheric Chemistry and Physics*, 10(16): 7907–7927
- Manninen H E, Nieminen T, Riipinen I, Yli-Juuti T, Gagné S, Asmi E, Aalto P P, Petäjä T, Kerminen V M, Kulmala M (2009). Charged and total particle formation and growth rates during EUCAARI 2007 campaign in Hyytiälä. *Atmospheric Chemistry and Physics*, 9(12): 4077–4089
- Meller B B, Franco M A, Valiati R, Pöhlker C, Machado L A T, Ditas F, Krempel L A, Raj S S, Dias-Júnior C Q, D'Oliveira F A F, et al. (2026). Quiet new particle formation is a significant aerosol source in the Amazon boundary layer. *Atmospheric Chemistry and Physics*, 26(7): 4885–4899
- Merikanto J, Spracklen D V, Mann G W, Pickering S J, Carslaw K S (2009). Impact of nucleation on global CCN. *Atmospheric Chemistry and Physics*, 9(21): 8601–8616
- Metnieks A L, Pollak L W (1959). Instruction for Use of Photo-Electric Condensation Nucleus Counters. Dublin: School of Cosmic Physics, Dublin Institute for Advanced Studies (DIAS)
- Mirme A, Tamm E, Mordas G, Vana M, Uin J, Mirme S, Bernotas T, Laakso L, Hirsikko A, Kulmala M (2007). A wide-range multi-channel air ion spectrometer. *Boreal Environment Research*, 12: 247–264
- Mirme S, Mirme A (2013). The mathematical principles and design of the NAIS: a spectrometer for the measurement of cluster ion and nanometer aerosol size distributions. *Atmospheric Measurement Techniques*, 6(4): 1061–1071
- Modini R L, Ristovski Z D, Johnson G R, He C, Surawski N, Morawska L, Suni T, Kulmala M (2009). New particle formation and growth at a remote, sub-tropical coastal location. *Atmospheric Chemistry and Physics*, 9(19): 7607–7621
- Mohr C, Thornton J A, Heitto A, Lopez-Hilfiker F D, Lutz A, Riipinen I, Hong J, Donahue N M, Hallquist M, Petäjä T, et al. (2019). Molecular identification of organic vapors driving atmospheric nanoparticle growth. *Nature Communications*, 10(1): 4442
- Nie W, Yan C, Huang D D, Wang Z, Liu Y L, Qiao X H, Guo Y S, Tian L H, Zheng P G, Xu Z N, et al. (2022). Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities. *Nature Geoscience*, 15(4): 255–261
- Ortega I K, Kupiainen O, Kurtén T, Olenius T, Wilkman O, Mcgrath M J, Loukonen V, Vehkamäki H (2012). From quantum chemical formation free energies to evaporation rates. *Atmospheric Chemistry and Physics*, 12(1): 225–235
- Ozon M, Seppänen A, Kaipio J P, Lehtinen K E J (2021). Retrieval of process rate parameters in the general dynamic equation for aerosols using Bayesian state estimation: BAYROSOL1.0. *Geoscientific Model Development*, 14(6): 3715–3739

- Pfeifer J, Simon M, Heinritzi M, Piel F, Weitz L, Wang D Y, Granzin M, Müller T, Bräkling S, Kirkby J, et al. (2020). Measurement of ammonia, amines and iodine compounds using protonated water cluster chemical ionization mass spectrometry. *Atmospheric Measurement Techniques*, 13(5): 2501–2522
- Pichelstorfer L, Stolzenburg D, Ortega J, Karl T, Kokkola H, Laakso A, Lehtinen K E J, Smith J N, McMurry P H, Winkler P M (2018). Resolving nanoparticle growth mechanisms from size- and time-dependent growth rate analysis. *Atmospheric Chemistry and Physics*, 18(2): 1307–1323
- Pospisilova V, Lopez-Hilfiker F D, Bell D M, El Haddad I, Mohr C, Huang W, Heikkinen L, Xiao M, Dommen J, Prevot A S H, et al. (2020). On the fate of oxygenated organic molecules in atmospheric aerosol particles. *Science Advances*, 6(11): eaax8922
- Rissanen M P, Mikkilä J, Iyer S, Hakala J (2019). Multi-scheme chemical ionization inlet (MION) for fast switching of reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications. *Atmospheric Measurement Techniques*, 12(12): 6635–6646
- Riva M, Ehn M, Li D, Tomaz S, Bourgain F, Perrier S, George C (2019a). CI-orbitrap: an analytical instrument to study atmospheric reactive organic species. *Analytical Chemistry*, 91(15): 9419–9423
- Riva M, Pospisilova V, Frege C, Perrier S, Bansal P, Jorga S, Sturm P, Thornton J A, Rohner U, Lopez-Hilfiker F (2024). Evaluation of a reduced-pressure chemical ion reactor utilizing adduct ionization for the detection of gaseous organic and inorganic species. *Atmospheric Measurement Techniques*, 17(19): 5887–5901
- Riva M, Rantala P, Krechmer J E, Peräkylä O, Zhang Y J, Heikkinen L, Garmash O, Yan C, Kulmala M, Worsnop D, et al. (2019b). Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species. *Atmospheric Measurement Techniques*, 12(4): 2403–2421
- Rönkkö T, Kuuluvainen H, Karjalainen P, Keskinen J, Hillamo R, Niemi J V, Pirjola L, Timonen H J, Saarikoski S, Saukko E, et al. (2017). Traffic is a major source of atmospheric nanocluster aerosol. *Proceedings of the National Academy of Sciences of the United States of America*, 114(29): 7549–7554
- Sakurai H, Fink M A, McMurry P H, Mauldin L, Moore K F, Smith J N, Eisele F L (2005). Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban Atlanta. *Journal of Geophysical Research: Atmospheres*, 110(D22): 2005JD005918
- Shang D J, Hu M, Guo J L, Liu X, Feng Z Y, Chang H N, Guo S, Peng J F, Wu Z J, Wiedensohler A (2026). The current understanding of atmospheric new particle growth. *ENGINEERING Environment*, 20(5): 78
- Simon M, Heinritzi M, Herzog S, Leiminger M, Bianchi F, Praplan A, Dommen J, Curtius J, Kürten A (2016). Detection of dimethylamine in the low pptv range using nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometry. *Atmospheric Measurement Techniques*, 9(5): 2135–2145
- Sipilä M, Lehtipalo K, Kulmala M, Petäjä T, Junninen H, Aalto P P, Manninen H E, Kyrö E M, Asmi E, Riipinen I, et al. (2008). Applicability of condensation particle counters to measure atmospheric clusters. *Atmospheric Chemistry and Physics*, 8(14): 4049–4060
- Smith J N, Barsanti K C, Friedli H R, Ehn M, Kulmala M, Collins D R, Scheckman J H, Williams B J, McMurry P H (2010). Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proceedings of the National Academy of Sciences of the United States of America*, 107(15): 6634–6639
- Smith J N, Moore K F, McMurry P H, Eisele F L (2004). Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry. *Aerosol Science and Technology*, 38(2): 100–110
- Stolzenburg D, Cai R L, Blichner S M, Kontkanen J, Zhou P T, Makkonen R, Kerminen V M, Kulmala M, Riipinen I, Kangasluoma J (2023). Atmospheric nanoparticle growth. *Reviews of Modern Physics*, 95(4): 045002
- Stolzenburg D, Steiner G, Winkler P M (2017). A DMA-train for precision measurement of sub-10 nm aerosol dynamics. *Atmospheric Measurement Techniques*, 10(4): 1639–1651
- Stolzenburg M R, McMurry P H (1991). An ultrafine aerosol condensation nucleus counter. *Aerosol Science and Technology*, 14(1): 48–65
- Su P F, Joutsensaari J, Dada L, Zaidan M A, Nieminen T, Li X Y, Wu Y S, Decesari S, Tarkoma S, Petäjä T, et al. (2022). New particle formation event detection with mask R-CNN. *Atmospheric Chemistry and Physics*, 22(2): 1293–1309
- Sulo J, Enroth J, Pajunoja A, Vanhanen J, Lehtipalo K, Petäjä T, Kulmala M (2024). Pushing nano-aerosol measurements towards a new decade – technical note on the Airmodus particle size magnifier 2.0. *Aerosol Research*, 2(1): 13–20
- Sun Q, Gu M N, Wu D M, Yang T, Wang H L, Pan Y P (2023). Concurrent measurements of atmospheric ammonia concentrations in the megacities of Beijing and Shanghai by using cavity ring-down spectroscopy. *Atmospheric Environment*, 307: 119848
- Tammet H, Komsaare K, Hörrak U (2013). Estimating neutral nanoparticle steady-state size distribution and growth according to measurements of intermediate air ions. *Atmospheric Chemistry and Physics*, 13(18): 9597–9603
- Tammet H, Kulmala M (2005). Simulation tool for atmospheric aerosol nucleation bursts. *Journal of Aerosol Science*, 36(2): 173–196
- Tammet H, Mirme A, Tamm E (2002). Electrical aerosol spectrometer of Tartu university. *Atmospheric Research*, 62(3–4): 315–324
- Temnitschka G, Winklmayr W, Reischl G P (1989). Analysis of fine particle dynamics using a relational database system. *Journal of Aerosol Science*, 20(8): 1173–1176

- Vanhanen J, Mikkilä J, Lehtipalo K, Sipilä M, Manninen H E, Siivola E, Petäjä T, Kulmala M (2011). Particle size magnifier for nano-CN detection. *Aerosol Science and Technology*, 45(4): 533–542
- Verheggen B, Mozurkewich M (2006). An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions. *Atmospheric Chemistry and Physics*, 6(10): 2927–2942
- Villani P, Picard D, Michaud V, Laj P, Wiedensohler A (2008). Design and validation of a volatility hygroscopic tandem differential mobility analyzer (VH-TDMA) to characterize the relationships between the thermal and hygroscopic properties of atmospheric aerosol particles. *Aerosol Science and Technology*, 42(9): 729–741
- Wagner A C, Bergen A, Brilke S, Fuchs C, Ernst M, Hoker J, Heinritzi M, Simon M, Böhner B, Curtius J, et al. (2018). Size-resolved online chemical analysis of nanoaerosol particles: a thermal desorption differential mobility analyzer coupled to a chemical ionization time-of-flight mass spectrometer. *Atmospheric Measurement Techniques*, 11(10): 5489–5506
- Wang M Y, Kong W M, Marten R, He X C, Chen D X, Pfeifer J, Heitto A, Kontkanen J, Dada L, Kürten A, et al. (2020a). Rapid growth of new atmospheric particles by nitric acid and ammonia condensation. *Nature*, 581(7807): 184–189
- Wang S C, Flagan R C (1990). Scanning electrical mobility spectrometer. *Aerosol Science and Technology*, 13(2): 230–240
- Wang W G, Chen Y, Li L, Zhou L, Du X B, Liu M Y, Ge M F (2022). Chemical composition of different size ultrafine particulate matter measured by nanoparticle chemical ionization mass spectrometer. *Journal of Environmental Sciences*, 114: 434–443
- Wang Y W, Yang G, Lu Y Q, Liu Y L, Chen J M, Wang L (2020b). Detection of gaseous dimethylamine using Vocus proton-transfer-reaction time-of-flight mass spectrometry. *Atmospheric Environment*, 243: 117875
- Whitby K T (1978). The physical characteristics of sulfur aerosols. *Atmospheric Environment* (1967), 12(1–3): 135–159
- Whitby K T, Clark W E (1966). Electric aerosol particle counting and size distribution measuring system for the 0.015 to 1 μ size range. *Tellus*, 18(2–3): 573–586
- Wimmer D, Lehtipalo K, Franchin A, Kangasluoma J, Kreissl F, Kürten A, Kupc A, Metzger A, Mikkilä J, Petäjä T, et al. (2013). Performance of diethylene glycol-based particle counters in the sub-3 nm size range. *Atmospheric Measurement Techniques*, 6(7): 1793–1804
- World Health Organization (2021). WHO Global Air Quality Guidelines: Particulate Matter (PM_{2.5} and PM₁₀), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide. Geneva: World Health Organization
- Wu Z, Birmili W, Poulain L, Wang Z, Merkel M, Fahlbusch B, Van Pinxteren D, Herrmann H, Wiedensohler A (2013). Particle hygroscopicity during atmospheric new particle formation events: implications for the chemical species contributing to particle growth. *Atmospheric Chemistry and Physics*, 13(13): 6637–6646
- Xu L, Coggon M M, Stockwell C E, Gilman J B, Robinson M A, Breitenlechner M, Lamplugh A, Crounse J D, Wennberg P O, Neuman J A, et al. (2022). Chemical ionization mass spectrometry utilizing ammonium ions (NH₄⁺ CIMS) for measurements of organic compounds in the atmosphere. *Atmospheric Measurement Techniques*, 15(24): 7353–7373
- Yan C, Yin R J, Lu Y Q, Dada L, Yang D S, Fu Y Y, Kontkanen J, Deng C J, Garmash O, Ruan J X, et al. (2021). The synergistic role of sulfuric acid, bases, and oxidized organics governing new-particle formation in Beijing. *Geophysical Research Letters*, 48(7): e2020GL091944
- Yao L, Garmash O, Bianchi F, Zheng J, Yan C, Kontkanen J, Junninen H, Mazon S B, Ehn M, Paasonen P, et al. (2018). Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. *Science*, 361(6399): 278–281
- 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, et al. (2016). 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(22): 14527–14543
- Yin R J, Yan C, Cai R L, Li X X, Shen J W, Lu Y Q, Schobesberger S, Fu Y Y, Deng C J, Wang L, et al. (2021). Acid–base clusters during atmospheric new particle formation in urban Beijing. *Environmental Science & Technology*, 55(16): 10994–11005
- Yuan B, Koss A R, Warneke C, Coggon M, Sekimoto K, De Gouw J A (2017). Proton-transfer-reaction mass spectrometry: applications in atmospheric sciences. *Chemical Reviews*, 117(21): 13187–13229
- Yuan Y, Chen X, Cai R L, Li X X, Li Y Y, Yin R J, Li D D, Yan C, Liu Y C, He K B, et al. (2024). Resolving atmospheric oxygenated organic molecules in urban Beijing using online ultrahigh-resolution chemical ionization mass spectrometry. *Environmental Science & Technology*, 58(40): 17777–17785
- Zaidan M A, Haapasilta V, Relan R, Junninen H, Aalto P P, Kulmala M, Laurson L, Foster A S (2018). Predicting atmospheric particle formation days by Bayesian classification of the time series features. *Tellus B: Chemical and Physical Meteorology*, 70(1): 1530031
- Zaytsev A, Breitenlechner M, Koss A R, Lim C Y, Rowe J C, Kroll J H, Keutsch F N (2019). Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH₄⁺ CIMS) to oxygenated volatile organic compounds. *Atmospheric Measurement Techniques*, 12(3): 1861–1870
- Zhang K W, Xu Z N, Gao J, Xu Z H, Wang Z B (2022). Review of online measurement techniques for chemical composition of atmospheric clusters and sub-20 nm particles. *Frontiers in Environmental Science*, 10: 937006
- Zhang X, Wu L J, Liu X S, Wang T, Monge M, Garcia-Marlès M, Savadkoobi M, Salma I, Bastian S, Merkel M, et al. (2024a). New particle formation event detection with convolutional neural

- networks. *Atmospheric Environment*, 327: 120487
- Zhang Y, Li D Z T, He X C, Nie W, Deng C J, Cai R L, Liu Y L, Guo Y S, Liu C, Li Y R, et al. (2024b). Iodine oxoacids and their roles in sub-3 nm particle growth in polluted urban environments. *Atmospheric Chemistry and Physics*, 24(3): 1873–1893
- Zhao J, Häkkinen E, Graeffe F, Krechmer J E, Canagaratna M R, Worsnop D R, Kangasluoma J, Ehn M (2023). A combined gas- and particle-phase analysis of highly oxygenated organic molecules (HOMs) from α -pinene ozonolysis. *Atmospheric Chemistry and Physics*, 23(6): 3707–3730
- Zhao J, Mickwitz V, Luo Y Y, Häkkinen E, Graeffe F, Zhang J Y, Timonen H, Canagaratna M, Krechmer J E, Zhang Q, et al. (2024). Characterization of the vaporization inlet for aerosols (VIA) for online measurements of particulate highly oxygenated organic molecules (HOMs). *Atmospheric Measurement Techniques*, 17(5): 1527–1543
- Zheng J, Ma Y, Chen M D, Zhang Q, Wang L, Khalizov A F, Yao L, Wang Z, Wang X, Chen L X (2015). Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry. *Atmospheric Environment*, 102: 249–259