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

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Abstract

New particle formation (NPF) is a major source of aerosol particles and cloud condensation nuclei in the troposphere, playing an important role in both air quality and climate. Frequent NPF events have been observed in heavily polluted urban environments, contributing to the aerosol number concentration by a significant amount. The Po Valley region in northern Italy has been characterized as a hotspot for high aerosol loadings and frequent NPF events in Southern Europe. However, the mechanisms of NPF and growth in this region are not completely understood. In this study, we conducted a continuous 2-month measurement campaign with state-of-the-art instruments to elucidate the NPF and the growth mechanisms in Northern Italy. Our results show that abundant sulfuric acid, ammonia and amines from agricultural activities may be the dominant components driving the frequent NPF events (66% of all days during the measurement campaign) in this area. In contrast, oxygenated organic vapors seem to...
have a smaller role in cluster formation but contribute to the consecutive growth process. According to ion cluster measurements and kinetic model results, dimethylamine is not sufficient to stabilize all of the sulfuric acid during springtime in the Po Valley, suggesting that other amines and ammonia can also be involved. Generally, the high formation rates of sub-2 nm particles (87 cm⁻³ s⁻¹) and nucleation mode growth rates (5.1 nm h⁻¹) together with the relatively low condensational sink (8.9×10⁻³ s⁻¹) will result in a high survival probability of newly formed particles, making NPF crucial for the springtime aerosol number budget in the Po Valley region.

1. Introduction

New particle formation (NPF) occurs ubiquitously in the troposphere and affects the global climate (Dunne et al., 2016) and local or regional air quality (Kulmala et al., 2021). NPF and further growth of the newly formed particles dominate aerosol number concentrations and are the major contributor to the ultrafine (<100 nm) aerosol budget, which poses a significant health threat to the population in polluted areas (Schraufnagel, 2020). While air pollution mitigation strategies mostly focus on reducing particulate mass (particulate matter below 2.5 µm (PM₂.₅)), ultrafine particle number concentrations might not be affected by such policies (De Jesus et al., 2019). It is therefore essential that we understand the mechanisms leading to NPF in polluted environments to design better targeted air quality strategies for polluted European regions, where PM₂.₅ reduction measures are already implemented.

In theoretical calculations, it is generally assumed that NPF events are more favorable to occur in clean conditions due to lower concentrations of preexisting aerosols, which act as condensational sink (CS), capable of scavenging the gaseous precursors (Kulmala et al., 2017). However, frequent NPF events have also been observed in heavily polluted urban environments (Kulmala et al., 2017; Du et al., 2022), including megacities in China (Chu et al., 2019; Yao et al., 2018) and India (Sebastian et al., 2022). This phenomenon might be associated with the overestimations of CS (Du et al., 2022) and the involvement of multiple precursors in the complex polluted environment (Cai et al., 2023b). Various studies have reported NPF precursors in strongly anthropogenically impacted environments. For instance, in Shanghai and Beijing, China, sulfuric acid (SA, H₂SO₄) and amines were identified as key contributors (Yao et al., 2018; Cai et al., 2021; Yan et al., 2021). In Barcelona, Spain, NPF was reported to be associated with SA along with highly oxygenated organic molecules (HOMs) (Brean et al., 2020). Meanwhile, some studies also address the importance of photooxidation products of vehicle emitted organic vapors to NPF in Chinese megacities (Guo et al., 2020). Generally, NPF in the polluted regions exhibits comparable growth rates and higher formation rates (J) compared to clean environment, making it the dominant contributor to the number concentration of PM₂.₅ in urban environment (Kulmala et al., 2021).

The Po Valley region is one of the most important industrial and agricultural areas in Southern Europe with dense population (>17 million/70,000 km²). It is located in northern Italy, surrounded by the Alps (in the north), the Apennine mountains (in the south), and the Adriatic Sea (in the east). High primary anthropogenic emissions, a mixture of numerous pollutants from industrial, urban and agricultural sources, together with frequently occurring stagnant meteorological conditions in winter make the Po Valley region a hotspot in Europe for high aerosol loadings (Saarikoski et al., 2012; Li et al., 2014; Finzi and Tebaldi, 1982; Daellenbach et al., 2023). At the same time, NPF occurs frequently in the Po Valley (Hamed et al., 2007; Manninen et al., 2010). For example, Shen et al. (2021) observed that NPF events took place on approximately 70% of the days during spring and summer. Similarly, Kontkanen et al. (2017) discovered that during summer, NPF occurred on 89% of the days. During NPF event days, high formation rates of sub-2nm neutral particles (J₂, ~10⁷ to 10² cm⁻³ s⁻¹, (Kontkanen et al., 2017)) and SA concentrations (~1×10² cm⁻³) were observed in the Po Valley (Paasonen et al., 2010; Kontkanen et al., 2017). These levels were among the highest recorded in a study conducted at nine sites across the Northern Hemisphere (Kontkanen et al., 2017).
The aforementioned studies mainly characterized the NPF process in the Po Valley based on particle size distribution observations in terms of NPF frequency, nucleation and growth rates. Detailed knowledge on the mechanisms of NPF and further growth in the Po Valley is still limited. In this study, with a 2-month field campaign in the months of March – April 2022, we 1) identified the chemical composition of atmospheric neutral and ion clusters by a set of state-of-the-art mass spectrometers, 2) characterized the initial NPF and further growth rates using particle number size distribution measurement down to 1 nm, and 3) compared the field measurement results with the recent Cosmics Leaving Outdoor Droplets (CLOUD) chamber experiments to investigate the mechanism of NPF events in the Po Valley region. This allowed us to elucidate the NPF and growth mechanisms at a severely polluted Southern European site, and to give insights in best mitigation strategies for ultrafine particle pollution in the context of already implemented PM$_{2.5}$ reduction strategies.

2. Method

2.1 Measurement site

Our measurement was part of the Fog and Aerosol InterAction Research Italy (FAIRARI) field campaign in San Pietro Capofiume (SPC, 44.65°N, 11.62°E, 5 m a.s.l.), located in the Po Valley region in Northern Italy. The measurement site is part of the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS)-Italy network and operated by the Italian National Research Council-Institute of Atmospheric Sciences and Climate (CNR-ISAC). The SPC site is approximately 30 km northeast of Bologna (~400, 000 residents) and 20 km south of Ferrara (~130, 000 residents), the two major cities in the area. The distance from the measurement site to the Adriatic Sea (to the east) is about 50 km. The area around the sampling site consists of agricultural fields and a smaller town (<2, 000 inhabitants, within 5 km) and smaller settlements in the proximity. Given its location, the SPC rural station is considered to be representative of the regional background of the Po Valley (Paglione et al., 2021; Paasonen et al., 2010; Hamed et al., 2007; Saarikoski et al., 2012; Deecesari et al., 2014; Paglione et al., 2020). The instruments for the NPF measurement were operated in a temperature controlled (~20 °C) container from March 1 to April 30, 2022.

During the sampling period, the daily average temperature ranged from 1 °C to 17 °C. The average wind speed (WS) was approximately 2.4±1.5 m/s (Fig. 1b). The average WS in the daytime was 3.5 m/s from the east, which was significantly higher than at night (1.5 m/s) from the west. Strong diurnal variations of wind direction were observed, which was typically from the west at night and shifted to the east during the day (Fig. 1a). This pattern was potentially influenced by the sea-land breeze from the Adriatic Sea. Accordingly, the daily average relative humidity (RH) varied from 41% to 98%, with values as high as 85% at night, which sharply decreased to around 40% at noon caused by the strong temperature variation.

2.2 Instruments

2.2.1 Chemical composition measurements

The chemical composition of cluster ions was measured using a high-resolution atmospheric-pressure-interface time-of-flight mass spectrometer (API-TOF, Aerodyne Research Inc. & Tofwerk AG). The API-TOF measures naturally charged ions present in the ambient environment. A detailed description of the instrument can be found in Junninen et al. (2010). In this study, ambient air was sampled through a 0.57-meter stainless steel tube with a flow rate of ~10 liters per minute (LPM), with 0.8 LPM of the sample flow entering the API-TOF.

The concentration of SA was measured using a nitrate ion (NO$_3^-$)-based chemical-ionization (CI) atmospheric-pressure-interface time-of-flight mass spectrometer (CI-API-TOF, Aerodyne Research Inc. & Tofwerk AG (Jokinen et al., 2012)). The CI-API-TOF is an API-TOF coupled with a CI-unit, equipped with a soft X-ray source (L9490, Hamamatsu’s 9.5 kV) to produce the primary ions. The sampling flow went into the instrument through a ~0.6-meter ¾ inch stainless steel tube. The sampling flow was 10 LPM and the sheath flow was set to 20 LPM. Data acquisitions for CI-API-TOF was
performed with a time resolution of 10 s. A calibration factor of $1.0 \times 10^{10} \text{ cm}^{-3}$ for SA was determined with sampling loss corrections before the campaign according to the method proposed by Kurten et al. (2012).

Dimethylamine (DMA) measurements were performed using a Vocus CI-ToF (time-of-flight) mass spectrometer (hereafter Vocus, Aerodyne Research Inc. & Tofwerk AG) using $\text{H}_2\text{O}^+$ as a reagent ion. The Vocus has been described in detail in Krecmer et al. (2018) and the study by Wang et al. (2020) utilized Vocus for DMA observations. In this study, the Focusing Ion-Molecular Reactor (FIMR) of Vocus operated at a pressure of 2.0 mbar and a temperature of 100 °C with the radio frequency amplitude of 350 V and frequency of $1.4 \times 10^8 \text{ Hz}$. Data acquisition was performed with a time resolution of 10 s in the mass range 0–1000 amu.

### 2.2.2 Particle size distribution measurements

#### Particle Size Magnifier

The Airmodus A11 nano-CNC-system (nano-Condensation Nucleus Counter), colloquially known as the Particle Size Magnifier (PSM), is a two-step condensation particle counter (CPC) capable of measuring particle size distributions of sub-3 nm particles (Vanhanen et al., 2011). The system consists of two parts, in which the PSM (Airmodus A10) acts as a preconditioner where particles are grown first before being funneled to the CPC (Airmodus A20) for further growth and optical detection. In the PSM the sample flow is turbulent mixed with a heated flow saturated with diethylene glycol (DEG) in the mixing section and the DEG then condenses on the particles in the growth tube. By scanning the flow rate through the DEG saturator, the smallest activated particle size is altered which can be converted into a sub-3 nm particle size distribution. Further particle growth is achieved by butanol in the CPC such that the particles reach optically detectable sizes.

The PSM was calibrated according to the standard operation procedure for PSM (Lehtipalo et al., 2022) using a known aerosol population from a glowing tungsten wire generator. The detection efficiency for different particle sizes was determined by comparing the concentration of size selected particles to a reference instrument, in this case a Faraday cup electrometer (FEC).

The system was set up with an Airmodus Nanoparticle Diluter (AND) inlet (Lampimäki et al., 2023) for sample dilution and automatic background measurement to make sure that the CPC stays within a single counting range during the campaign. The inlet was set up at around 2 meters above the ground and the background was measured roughly every 8 hours and subtracted from the signal during the inversion process.

#### HFDMPS and DMPS

The high-flow differential mobility particle sizer (HFDMPS) system utilizes a half-mini differential mobility analyzer (DMA) to size-select particles that are then grown and detected by an A11 nano Condensation Nucleus Counter system (Airmodus Ltd., A11 nano-CNC) (Kangasluoma et al., 2018).

The HFDMPS significantly improves sub-10 nm particle measurements compared to a typical differential mobility particle sizer (DMPS) system, allowing us to better characterize the sub-10 nm particle size distribution when combined with the PSM measurements. The A11 nano-CNC system was size-calibrated with electro sprayed positively charged monomer ions of tetraheptylammonium bromide (THA+) (Ude and De La Mora, 2005).

The HFDMPS inlet was set up at a height of 1 m and used a 50 cm long 10 mm outer diameter tube with a core sampling system to minimize losses. A home-built Soft X-Ray ionization source (similar to the TSI Inc. Model 3087) was used to charge particles. The HFDMPS measured the particle size-distribution from 2–15 nm for both polarities at 15 predefined size-steps within 10 minutes (Fernández De La Mora and Kozlowski, 2013).
Sampling from the same inlet and using the same charging device, a conventional DMPS system equipped with a Hauke-type DMA (aerosol flow 1 LPM, sheath flow 5 LPM) and a TSI Inc. CPC (Model 3772) was measuring the particle size-distribution from 10–800 nm at 16 predefined size-steps within 10 minutes. In addition, a DMPS measuring from 15–800 nm was available in another measurement container at the same field site. The total particle number concentrations measured routinely with the CPCs after a size-scanning cycle of each DMPS system was compared with a reference CPC (TSI Inc. Model 3025A) operated at the same site during the first weeks of the campaign. It revealed on average a factor of 2 lower concentrations measured by the Hauke-type DMPS which was confirmed to be rather size-independent by a comparison of the measured size-distributions and their overlap with the Halfmini-DMPS system and was thus subsequently corrected for.

2.2.3 Co-located measurements

Additional co-located measurements of auxiliary data from CNR-ISAC network (www.isac.cnr.it/en) and from the routine monitoring program of the Regional environmental protection agency of Emilia Romagna (ARPAE, https://www.arpac.it/it) were used in this study. Trace gases were also measured with 1 minute time resolution: O₃ (Thermo Scientific, model TEI-49i), NOₓ (Teledyne-API, model 200A), NH₃ (Teledyne-API, model 201E), and SO₂ (Thermo Scientific, Model 43i Trace Level-Enhanced). Moreover, meteorological parameters (e.g., RH, temperature, wind direction and wind speed) were measured by a meteorology station (VAISALA Ltd, model wxt536).

2.3 Data processing

2.3.1 New particle formation classification

We classified each day according to whether a growing mode appeared in the particle size distribution or not. This classification was done separately for both the DMPS and the PSM size distributions. A growing mode was defined as a new particle mode that appeared in the particle size distribution and continued to grow to larger sizes for at least two hours. If there was a growing mode visible in both the PSM and DMPS size distributions, the day was defined as “NPF with growth”. If there was no growth or the growth was unclear in the DMPS size distribution but there was a growing mode in the PSM size distribution, then the day was classified as “NPF with no growth”. If there was no growing mode in either size distribution, then the day was marked as “no NPF events”. The definition is similar to Dada et al. (2018) who used naturally charged ions to separate between NPF days with clustering only and clustering plus visible growth. If there was a growing or an undefined new mode visible in the combined size distribution but there was no clustering detected by the PSM, this day was marked as “unclear”. Days that lacked data from one of the instruments were marked as “no data”.

2.3.2 Condensation sink, nucleation and growth rate calculations

The condensation sink and coagulation sink were calculated according to Dal Maso et al. (2005) from the DMPS size distribution without any correction of aerosol hygroscopic behavior. Growth rates were calculated using the maximum concentration method, in which we fit a Gaussian distribution to the particle concentration evolution at a fixed size to determine the time of maximum concentration for a given size channel in the HFDMPS. From these, the growth rate was calculated as the slope of a linear least squares fit to the time-points of maximum concentration and their corresponding particle diameters. The formation rates were calculated for several sizes by using the balance equation in which we fit a Gaussian distribution to

2.3.3 Mass spectrometer data analysis

The APi-TOF and CI-APi-TOF data were analyzed using the Tofware package (v.3.1.0, Tofwerk, Switzerland, and Aerodyne, USA) in the Igor Pro software (v.7.08, WaveMetrics, USA). The mass accuracy is within 10 ppm (APi-TOF) and 5 ppm (CI-APi-TOF), and the mass resolutions were ~4500 (APi-TOF) and ~5000 (CI-APi-TOF) for ions >200 Th. Detailed information on the mass spectrometer
data analysis methods can be found in previous studies (Cai et al., 2022a; Cai et al., 2023a; Zha et al., 2018; Zha et al., 2023; Fan et al., 2021).

2.3.4 Kinetic model Simulations

In order to evaluate the contribution of SA-amine clustering to cluster formation in the Po Valley, we applied a kinetic model to simulate SA dimer concentrations. We simulated the cluster concentrations and particle formation rates under different amine levels based on the model. The simulation was performed with a temperature of 283 K, atmospheric pressure of 1.01x10^5 Pa, and the condensation sink (CS) of 0.01 s^{-1} based on our measurement during the sampling period. In the model, the formation rate of SA tetramer was regarded as the simulated particle formation rate. The standard molar Gibbs free energy of formation and the corresponding evaporation of SA-amine clusters was based on quantum chemistry with corrections from the experimental data. The detailed settings of the kinetic model can be found in Cai et al. (2021).

3. Results and discussions

3.1 NPF event frequency in Po Valley

During the measurement period, frequent NPF events occurred in Po Valley (Fig. 2, Fig. S1). On 27% of the days, we observed new particle formation with growth at the site, while on 39% of the days we observed new particle formation without growth (Fig. S1). In total we observed new sub-3 nm clusters forming on 66% of the days. Even though we applied the similar definition of NPF events as previous study, we can only compare our NPF events with growth type with the reported NPF event frequency due to the lack of capacity to measure the sub-3nm particles in previous literature. Our results were similar to those by Hamed et al. (2007) who observed NPF events on 36% of the time in March and April of 2002 at the same site. Manninen et al. (2010) observed NPF events during more than half of all days from March to Oct in 2008 and Kontkanen et al. (2016) observed NPF during 89% of the days in July at the same site, which is higher than our observations. Hamed et al. (2007) also observed that NPF with growth events on 60% of the days during summer, which suggests that summertime NPF frequency at SPC is typically higher than our observation in springtime 2022. This difference in the observed NPF was likely due to the different season with favorable conditions for NPF such as potential lower CS (due to higher boundary layer mixing and less stagnant meteorological conditions) and higher basic and organic molecule concentrations in summer. In addition, the abundant solar radiation and low aerosol water content (limiting surface area and heterogenous reactions (Du et al., 2022)), likely create favorable conditions for NPF to occur.

The median average particle formation rates at 1.7 nm, 3 nm and 7 nm for all sampling days with NPF with growth events were 87 cm^{-3} s^{-1} (32 – 133 cm^{-3} s^{-1}), 3.2 cm^{-3} s^{-1} (1.4 cm^{-3} s^{-1} – 7.0 cm^{-3} s^{-1}) and 1.4 cm^{-3} s^{-1} (0.3 cm^{-3} s^{-1} – 3.0 cm^{-3} s^{-1}), respectively. The formation rate at 1.7 nm during NPF with growth days (NPF with growth, 87 cm^{-3} s^{-1}) is similar to that observed previously at the same site by Kontkanen et al. (2016) in summer. The high formation rate, which is comparable with heavily polluted urban environments such as Beijing and Shanghai, China (59 cm^{-3} s^{-1} – 225 cm^{-3} s^{-1} (Deng et al., 2020; Yao et al., 2018)), will be further discussed in section 3.4. The average formation rate (J_{SA}) on NPF days without growth (24 cm^{-3} s^{-1}) is much lower. During the noontime, the formation rate of particles for NPF events with no growth was less than half of J_{SA} for NPF with growth (Fig. S2). It suggests that for particles to grow in a polluted environment such as the Po Valley, there needs to be abundant clustering to overcome losses to the existing condensation sink so that at least some of the particles survive to grow into larger sizes.

3.2 Nucleation mechanism

Previous studies have demonstrated that SA is the most important gaseous precursor for NPF in continental environments due to its extremely low volatility (Kirkby et al., 2011; Kulmala et al., 2013). During the sampling period, high SA concentration was measured in the Po Valley, concurrent with the frequent NPF events. The daily average concentration of SA was 4.6x10^6 cm^{-3} (10:00 – 14:00 LT),
similar to those in polluted megacities in China (5×10^6 cm^-3 – 7×10^6 cm^-3). During the NPF with growth
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days, the SA concentration was as high as 8.5×10^6 cm^-3. The generally high concentrations were
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consistent with a previous study conducted at the same site (1.6×10^7 cm^-3 during NPF in summer of
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2009, (Paasonen et al., 2010)). For the entire sampling period, SA was moderately correlated with the
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calculated J_{1,7} (r = 0.49, Spearman correlation coefficient, for the logarithmic values) but varied among
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different days. This suggests that in addition to SA, other components, such as basic molecules and
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oxygenated organic molecules (OOMs), may also play a crucial role in driving NPF events and further
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growth in the Po Valley.
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To investigate the NPF mechanism in the Po Valley, in this study we firstly compared the
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simultaneously measured J_{1,7} and SA with recent Cosmos Leaving Outdoor Droplets (CLOUD)
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chamber experiments that simulated NPF under polluted boundary layer conditions with anthropogenic
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emissions (Xiao et al., 2021). In those experiments, amines, ammonia, as well as aromatics were added
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to reflect a heavily anthropogenic emission-influenced environment. Certain basic molecules, including
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amines (e.g., dimethylamine (DMA)) and ammonia (NH_3) have been shown to substantially enhance
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nucleation and reduce evaporation by stabilizing atmospheric SA in chamber studies (Almeida et al.,
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2013). Besides, OOMs can also contribute to NPF and subsequent particle growth, even without the
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inclusion of SA (Kirkby et al., 2016; Xiao et al., 2021). As shown in Fig. 3a, most of the measurements
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were above the SA-NH_3 system at 278K from the CLOUD chamber, suggesting the SA-NH_3 mechanism
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itself cannot solely explain the measured J_{1,7} and that other species are most likely participating to NPF
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in the Po Valley. For instance, amines, such as DMA or TMA, with higher basicity may contribute to
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NPF, consistent with not negligible concentrations of amines in previous studies in the aerosol at SPC
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(Paglione et al., 2014; Decesari et al., 2014). For the whole sampling period, the median SA and J_{1,7}
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values in Po Valley follows the SA-DMA-NH_3 (4 ppt DMA and 1ppb NH_3) and SA-DMA-NH_3-Org
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(adding additional oxidized aromatic organics (Xiao et al., 2021)) lines from the CLOUD chamber at
293K even though during most of the NPF days the average noontime temperature was around 285K
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(Fig. 3a).
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The SA dimer measured by CI-API-TOF is typically used as an indicator for the initial step for the
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cluster formation in NPF events (Yan et al., 2021). According to a previous study (Yan et al., 2021),
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the source and sink terms of the SA dimer can be determined by calculating the formation rate from SA
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monomer collisions and the loss rate from the SA dimer through coagulation onto pre-existing particles
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(Fig. 2b). In general, the correlation coefficient between SA dimer and its source to sink term ratios (r
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= 0.80, Spearman correlation coefficient) indicated that similar to Chinese urban areas, SA dimer was
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in a pseudo steady-state between the formation of SA monomer collision and the loss onto CS by
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coagulation.
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To further assess the influence of DMA, one of the most common and efficient base molecules for NPF
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in urban environments (Yao et al., 2018), we compared the measured SA dimer concentrations with the
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simulated ones under different DMA levels (from 0.1 ppt to reaching kinetic limit) by the kinetic model
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(Fig. 3b). From our cluster kinetics simulations, during the peak hours of NPF, DMA concentrations
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are expected to be in the range of 0.1 ppt to 5 ppt, which is lower than the need for reaching the kinetic
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limit (Figs. 3b and S3). It implies that other factors, for example, the abundant ambient NH_3
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concentrations (~10 ppb) or trimethylamine (TMA) during our study period may also participate in
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cluster formation. It is consistent with the Vocus measurement, which suggests the ambient DMA
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signals were close to the background levels (Fig. S4) even though it was difficult to quantify during the
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campaign due to the absence of a suitable calibration method. The reason for not reaching SA-DMA
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limit during the campaign could be 1) the relatively low emissions such as vehicle flows near our
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sampling site that are reported to be the main sources for DMA in Chinese urban areas (Ge et al., 2011;
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Zhu et al., 2022), 2) the nighttime high RH (85%) and daytime photolysis process quickly scavenge
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gaseous DMA by wet deposition, heterogeneous reaction and photolysis (Leng et al., 2015; Yao et al.,
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Therefore, both of the abundant ambient NH₃ concentrations (~10 ppb) and amines likely participated in cluster formation during our study period.

Median particle growth rates (GR) during NPF events for 1.5 – 3 nm, 3 – 7 nm, 7 – 15 nm were 1.3 (1.0 – 2.4) nm h⁻¹, 4.6 (2.9 – 5.8) nm h⁻¹, and 5.1 (3.8 – 8.8) nm h⁻¹, respectively. The values in brackets represent the 25th and the 75th percentile of data (Fig. 3c). Growth rates increase with particle diameters, a phenomenon observed in other campaigns around the world as well (Kontkanen et al., 2017, Kulmala et al., 2013)) typically indicative of an increasing organic vapors contribution with size (e.g., Stolzenburg et al. (2018)). The growth rates observed here were similar to those observed by Kontkanen et al. (2016) at SPC in summer (7.2 nm h⁻¹ for 7 – 20 nm) and our 1.5 – 3 nm growth rate matches well with Manninen et al. (2010) (1.5 nm h⁻¹) during spring in the Po Valley. A comparison to predicted growth rates from sulfuric acid condensation without organics, which was calculated based on kinetic collisions of the measured SA concentrations and the effect of van-der-Waals forces on the collision frequency ((Stolzenburg et al., 2020), Fig. 3c), suggests that sulfuric acid condensation may be on average sufficient for the growth of the smallest clusters (below 3 nm). It supports the argument that in the initial steps of NPF and growth in Po Valley sulfuric acid and its stabilizing molecules (likely the bases NH₃ and amines) were controlling particle formation. However, for particles to grow beyond 3 nm in size other vapors were needed, which was suggested by the significantly lower contribution of growth by SA (indicated by the green line) than the measured GR for 3 – 7 nm and 7 – 15 nm (Fig. 3c).

Those vapors were likely a mixture of organics of anthropogenic and biogenic origin (with the latter emitted at higher rates during summer, which could cause the slightly higher values in Kontkanen et al. (2017)). We compared the GR during NPF with and without growth events using the method proposed in Kulmala et al. (2022) where the signal was averaged for all classified non-event days and then an appearance time fit was performed for each size channel independently, revealing also a growth pattern.

We found no significant difference for the GR in 7 – 15 nm size range (GR=5.1 nm h⁻¹ in NPF with growth days and average GR=6.1 nm h⁻¹ in NPF without growth days). Considering the similar CS and GR levels for NPF with and without growth days, the higher formation rates at 1.7 nm (87 cm⁻³ s⁻¹) may be the decisive factor to overcome the CS and determine if a growing mode can be observed leading to a classification of the day as an NPF with growth day.

### 3.3 Ion and neutral clusters and further particle growth

During the campaign, we observed and identified different types of ion clusters with cluster ion measurements using the API-TOF, including SA-NH₃, SA-Amine, SA-NH₁-Amine, SA-NH₁-Org during NPF. In Fig. 4a, we presented the mass defect plot of the naturally charged ion clusters on April 20th, when strong NPF events were observed (J₆: 83 cm⁻³ s⁻¹). The presence of these clusters was usually in conjunction with SA tetramers (SA₄), pentamers (SA₅), and hexamers (SA₆), which potentially contribute to the NPF events. Acid-base clusters were not observed in monomer (SA₁), dimer (SA₂), or trimers (SA₃), likely due to declustering effects in the API-TOF instrument (Cai et al., 2022b; Zha et al., 2023; Alfaouri et al., 2022).

Among all SA-base (SA-B) clusters, the most abundant SA-NH₁ clusters were from SA₂-B to SA₆-B (Fig. 4a), even though they are reported to more easily escape than DMA clusters due to collision-induced dissociation (Passananti et al., 2019). Pure SA-Amine clusters were only found in the SA₆-B clusters with different types of amines, including methylamine (C₁-amine), DMA (C₂-amine), trimethylamine (C₃-amine), and Butylamine (C₄-amine). The detection of other SA-B than SA-DMA clusters indicates that other candidate bases could also play a crucial role in the complex atmosphere for nucleation. For example, a recent study conducted in Beijing highlights the importance of TMA that can accelerate the SA-DMA formation by 50% – 100% (Cai et al., 2023b). In the Po Valley, the signal intensity of SA₃-NH₃ was significantly higher than that of the pure SA₃-amine clusters (~2 times) even though amines (e.g., DMA) were proven to be more efficient (~3 orders of magnitude) than NH₃ in clustering (Almeida et al., 2013). It is different from Chinese cities such as Shanghai (Yao et al., 2018),
where high signals of SA$_2$-DMA clusters were found even with CI-API-TOF which is more easy for
declustering.

SA-NH$_3$-Amine clusters could be found along with SA-NH$_3$ clusters in SA$_3$-B and SA$_6$-B. Similar
patterns of the high fractions of SA-NH$_3$ and SA-NH$_3$-Amine clusters were also reported in the CLOUD
chamber studies under relatively low DMA and high NH$_3$ conditions (Schobesberger et al., 2013).
Therefore, it can be concluded that a large amount of NH$_3$ also participates in NPF in the Po Valley
region. Meanwhile, with a much lower amount, amines may also play a crucial role in the formation of
small clusters (SA$_3$-B) due to their high stabilization efficiencies.

Moreover, some SA-NH$_3$-Org and I-containing ion clusters were also observed on NPF days, but to a
much lower extent than clusters involving NH$_3$ or DMA. It has been shown in previous CLOUD
chamber studies that the oxidation products of anthropogenic volatile organic compounds (AVOCs, e.g.,
naphthalene, trimethylbenzene and toluene) can largely promote the formation rate of particles (Xiao
et al., 2021). The I-containing ions (mainly IO$_3^-$) likely originated from the Adriatic Sea during the
daytime, which was indicated by the easterly wind. Since no large iodine clusters were identified in the
API-TOF (e.g., (HO$_2$I)$_2$-(IO$_3$I)$_2$, IO$_3^-$, (He et al., 2021)), iodine-induced new particle formation in the
Po Valley may not be as important as the pristine marine environment (Sipila et al., 2016). During NPF
without growth days, the formation mechanism was similar to the NPF days regarding the ion cluster
measurement (Fig. S5).

Similar to polluted cities such as Beijing or Shanghai (Yan et al., 2021; Yao et al., 2018), the SA
monomer in the Po Valley can be observed during the peak hours (10:00 – 14:00 LT) in both NPF and
non-NPF days, but much lower SA dimer or trimers were found in the non-NPF days (Figs. 4b, and S6).
In the nighttime, the SA concentrations were close to zero due to the scavenging effect of hydrated
aerosol and hygroscopic growth of particles, as indicated by the high RH (Fig. 1). During our sampling
period, large amounts of organics were identified by the CI-API-TOF. They were typically smaller than
400 Th with carbon numbers $< 8$ and oxygen numbers $< 6$ (Fig. S7). Due to the relatively high NO$_x$
levels (13 ppb) that can terminate the dimerization reactions (Yan et al., 2020), no OOM dimers were
found, which is different from clean and biogenically dominated environments such as Hyytiälä
(Lehtipalo et al., 2018). The compositions of OOMs were similar between NPF and non-NPF days but
with different abundance. Extremely high abundances of nitrophenols and their homologous
compounds were found on non-NPF days (~8 times higher than on NPF days), likely caused by both of
the enhanced primary (e.g., biomass burning (Mohr et al., 2013) and pesticide usage (Harrison et al.,
2005)) and secondary (e.g., photochemical and/or aqueous-phase secondary formation) sources (Zheng
et al., 2021; Gilaroniti et al., 2016). C$_{2}$-C$_{5}$N$_{n}$O$_{m}$ compounds were found to be 50% higher (Fig. S7)
due to the higher RH during the non-NPF days and the enhanced heterogeneous reactions that form
smaller organics such as carboxylic acids. Previous studies also reported aqueous-phase organic aerosol
processing at high RH (Gilaroniti et al., 2016) and high concentrations of carboxylic acids such as
formic, oxalic, and malonic acids in the springtime in the Po Valley (Saarikoski et al., 2012). In general,
the fraction of the abundance of nitrogen-containing OOMs (CHON) of total identified OOMs were 60%–
70%, which is close to the levels reported in polluted cities such as Nanjing (Nie et al., 2022) and
Beijing (Guo et al., 2022). A slightly higher fraction of CHON compounds (73 %) was found during
non-NPF days than NPF days (67 %), consistent with higher NOx and fine particulate matter levels
(Fig. S8). It is likely associated with the stagnant meteorological conditions and accumulation of
pollutants during the non-NPF days. However, the overall high amounts of CHON compounds and the
lack of organic dimers make it unlikely that OOMs drive the NPF process in the sub-3nm range (both
clustering and initial growth as no organic molecules of extremely- or ultra-low volatility were formed,
see e.g., Simon et al. (2020)). Their similar abundance on non-NPF and NPF days was also in line with
the similar estimated GR for both types of days.
3.4 Comparison between Po Valley and other environments

Even though the measured \( J_{27} \) in Po Valley was at the same level of the values found in Chinese polluted megacities, it was much higher than in clean environments, such as the boreal forest of Hyytiälä in Finland, mountain sites Jungfraujoch in Switzerland, and Chacaltaya in Bolivia (1.5 \( \text{cm}^{-3} \text{s}^{-1} \) – 2.0 \( \text{cm}^{-3} \text{s}^{-1} \), Fig. 5a). Similarly, the overall SA concentrations were similar to those in polluted megacities in China (Fig. 5c), but much higher than those from the remote areas such as Hyytiälä (9×10^5 \( \text{cm}^{-3} \)) and the Jungfraujoch (5×10^5 \( \text{cm}^{-3} \)). Compared to other remote sites, Chacaltaya has a higher SA concentration (2.3×10^6 \( \text{cm}^{-3} \)) due to active volcanic degassing in the Andes (Zha et al., 2023). The SA concentrations on NPF days (8.6×10^5 \( \text{cm}^{-3} \)) were twice as high as those during the non-NPF days (4×10^5 \( \text{cm}^{-3} \)), potentially associated with the higher RH and CS loss during the non-NPF days. This is different from the findings from Beijing, where similar or even higher levels of SA during the non-NPF days were found (Yan et al., 2021).

The overall CS in spring (median: 8.9×10^3 \( \text{s}^{-1} \)) in the Po Valley was lower than that in other polluted cities (1.5×10^3 – 2.0 \( \text{s}^{-1} \)), but significantly higher than that in clean environments (2.0×10^4 \( \text{s}^{-1} \) (Hyytiälä and Jungfraujoch) – 3.0×10^3 \( \text{s}^{-1} \) (Chacaltaya with the influence of volcanoes), Fig. 5e). Contrary to Beijing or Shanghai where CS levels and efficiencies are the dominant factors for the NPF process (Du et al., 2022), no strong influence of CS was found between NPF and non-NPF days in the Po Valley, and only slightly higher CS was found during the nighttime of non-NPF days (median: 9.4×10^3 \( \text{s}^{-1} \)) than NPF days (median: 8.6×10^3 \( \text{s}^{-1} \)). It is likely associated with the general lower CS than the Chinese megacities. The observed growth rate for 7 – 15 nm particles in the Po Valley was about 5.1 nm h\(^{-1}\), comparable to other urban and remote sites (2.9 – 9.1 nm h\(^{-1}\), Fig. 5f). The general similar growth rates among different types of environments were also reported in previous studies (Deng et al., 2020), which needs further investigation in future research.

For the basic gaseous precursors, the average concentration of NH\(_3\) was ~10 ppb, which was in the same range as that found in the Chinese megacities (10 – 30 ppb) and much higher than that at remote sites (<0.1 ppb, Table S1). The high NH\(_3\) can be attributed to agricultural activities such as fertilization, which were widely applied during springtime in the region. The strong interference of ammonia emitted from fertilization to NPF was also observed in Qvidja, an agricultural site in Southern Finland (Olin et al., 2022). During our sampling period, measured DMA were too close to the detection limit of the Vocus (Fig. S2), and lower than those observed in the Chinese megacities (10 – 40 ppt, Fig. 5d). In the spring season, DMA in the Po Valley cannot fully stabilize all atmospheric SA clusters and hence NPF is very sensitive to variations in the concentrations of the different stabilizers (NH\(_3\), DMA, and as shown by our analysis likely only to a lower extent organics). This could explain the scattered correlation between the formation rate and SA concentrations on different days (Fig. 3).

Therefore, it can be concluded that the high sulfuric acid concentrations, basic molecules and formation rates may be the reason for the high frequency of NPF events in the Po Valley region. The abundant organics led to a comparable GR to Chinese megacities such as Beijing and Shanghai. Due to the relatively lower CS than these megacities, the newly formed particles may however have a higher survival probability compared to the megacities and provide more long-term surviving particles in the Po Valley, indicating a decisive role of NPF for Po-Valley aerosol and PM\(_{2.5}\) concentrations.

4. Conclusions

In this study, we conducted a continuous two-month measurement campaign of the chemical composition and physical properties of newly formed particles and clusters in the Italian Po Valley during springtime. The Po Valley experienced frequent NPF events during the sampling period, occurring on approximately 66% of the days. We observed high concentrations of sulfuric acid during the NPF events, comparable to those found in Chinese megacities. The correlation between the formation rate of particles and sulfuric acid concentrations, together with the information from dimethylamine simulations and CLOUD chamber experiments, suggest that gaseous DMA might have
been insufficient to stabilize all atmospheric sulfuric acid during our sampling period. Except for DMA, other amines and NH$_3$ were also involved in NPF in the Po Valley, which was supported by the high abundance of SA-NH$_3$ and SA-amine-NH$_3$ clusters measured by the API-TOF on NPF days. Generally, the NPF mechanism is therefore very sensitive to the abundance of amines (e.g., DMA) with high levels of NH$_3$, resulting in a more scattered correlation between H$_2$SO$_4$ concentrations and measured formation rate. At the same time, OOMs do not seem to be decisive for the sub-3 nm formation process due to the lack of ultra-low volatility organics (highly oxygenated CHO compounds and dimers), however low volatility organics were abundant enough to induce fast growth processes above 3 nm. The comparable GR and formation rate, but lower CS compared to other polluted environments, indicate a high survival probability for the newly formed particles. Therefore, NPF is likely to play an important role in the fine particle concentrations and pollution levels in the Po Valley region.

Data availability

Data are available from the authors upon request.

Competing interests

At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics

Author contributions

JC, DS, FB, and MK designed the research. JC, JS, YFG, SH, MP, AN, FM, SD, MR, NZ and CM collected the data at the SPC site. JC, JS, YG, ST, RY, DA, QZ, DS and FB interpreted the data. MP, WH, YL, GC, LQ, KL, YG, CW, WN, CM, QZ, DS, FB helped to improve the manuscript. JC, JS, DS, and FB wrote the manuscript with contributions from all co-authors. All authors have given approval to the final version of this manuscript.

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Figure 1. The diurnal variations of (a) average wind vectors, (b) wind speed, (c) relative humidity (RH), and (d) temperature.

Figure 2. (a) The frequency of NPF events with and without growth, of days without NPF, and days with unclear classification or no data during this study, (b) calculated formation rates at 1.7 nm, 3 nm and 7 nm from this study and values reported by Kontkanen et al. 2016 (yellow squares). The red lines are the median values of the maximum formation rates measured during an NPF event, the blue boxes show the values between 25th and 75th percentiles and the black whiskers mark the 5th and 95th percentiles. Red dots are outliers, and the width of the box is proportional to the square root of the number of the J values.
Figure 3. (a) The formation rate of 1.7 nm particles ($J_{1.7}$) versus SA concentrations in during springtime in the Po Valley (shown as circles) and experimental results from CLOUD chamber experiments (shown as solid diamonds). The solid lines are from fitted results of CLOUD chamber experiments and the black hexagon represented the mean values under different SA levels. (b) The relationship between sulfuric acid dimer concentration (SA dimer), the square of monomer concentration ($SA$)$^2$, and the CS. The lines are from the kinetic model simulations under different DMA levels and the dots are from the measurement. In (a) and (b), the results from the field measurements are from the daytime (10:00 – 14:00 LT) and color-coded by the temperature at the site. The $J_{1.7}$ and corresponding SA concentrations of CLOUD chamber results are from previous literature (Xiao et al., 2021). (c) Calculated growth rates for 1.5 – 3 nm, 3 – 7 nm, and 7 – 15 nm from this study and values reported by Kontkanen et al. (2016, yellow squares). The red horizontal lines are the median values, the blue boxes show the values between 25th and 75th percentiles and the black whiskers mark the 5th and 95th percentiles. The green solid line represents predicted growth rates from pure sulfuric acid without organics condensation (Stolzenburg et al., 2020). The width of the box is proportional to the square root of the number of the GR values.
Figure 4. Mass defect plots, which represent the difference between compounds’ exact mass and nominal mass, for (a) ion clusters and (b) neutral clusters during the NPF period (10:00 – 14:00 LT) of April 20. The size of the dots is proportional to the logarithm of the signal intensity of each cluster.
Figure 5. Parameters and gaseous precursors of NPF in the Po Valley and other environments. (a) formation rate of sub-2 nm particles, (b) the atmospheric NH$_3$ concentrations, (c) SA concentrations, (d) DMA concentrations, (e) CS levels, and (f) growth rate in different environments. The diamond dots represent the median values, and the error bars represent the 25th and 75th percentiles. For the Po Valley data, the formation rates, growth rates, SA concentrations and CS data were selected for 10:00 – 14:00 LT. The formation rates, growth rates, SA concentrations and CS during NPF in Beijing, Shanghai, Hyytiälä, Jungfraujoch and Chacaltaya are from Deng et al. (2020). The GR calculation range varies for different sites. Beijing (GR$_{7-15}$, (Deng et al., 2020)), Shanghai (GR$_{7-15}$, (Yao et al., 2018)), Nanjing (GR$_{7-20}$, (Yu et al., 2016)), Hyytiälä (GR$_{7-20}$, (Vana et al., 2016)), Jungfraujoch (GR$_{7-20}$, (Boulon et al., 2010)), Chacaltaya (GR$_{7-20}$, (Rose et al., 2015)), and Po Valley (GR$_{7-15}$, this study) are used for comparison. The NH$_3$ and DMA concentrations are from literature, which is listed in the Table S1. Half of the limit of detection (LOD) of DMA concentrations in Hyytiälä was applied in panel d. DMA concentrations in Po Valley was not presented since it is not quantified in this study.