International Journal of Advanced Research and Multidisciplinary Trends (IJARMT)
An International Open Access, Peer-Reviewed Refereed Journal
Impact Factor: 6.4 Website: https://ijarmt.com ISSN No.: 3048-9458

The Formation of Secondary Organic Aerosol (SOA) And Effect Global Climate

Dr. Manoj Kumar
Associate Professor department of Chemistry
Government College Kota,Rajasthan, India
mjkrdhawan@gmail.com

Article Received: 19-05-2025, Revised: 11-06-2025, Accept: 16-06-2025
https://doi.org/10.65578/ijarmt.v2.i2.705

Abstract

Secondary Organic Aerosols (SOA) are a major component of atmospheric particulate matter and play a significant role in influencing global climate and air quality. SOA are formed through the atmospheric oxidation of volatile organic compounds originating from both natural and anthropogenic sources, followed by the partitioning of low-volatility products into the aerosol phase. These particles affect the Earth’s radiative balance directly by scattering and absorbing solar radiation and indirectly by altering cloud formation, cloud albedo, and precipitation processes through their activity as cloud condensation nuclei. The formation, composition, and climatic impacts of SOA are highly sensitive to environmental conditions such as temperature, humidity, oxidant availability, and emission patterns. Despite extensive research, large uncertainties remain in quantifying SOA formation pathways and their interactions with clouds and radiation in climate models. This study reviews the mechanisms of SOA formation and evaluates their direct and indirect effects on global climate, highlighting current challenges and future research needs.

Keywords: Secondary organic aerosols; Volatile organic compounds; Climate forcing; Aerosol–cloud interactions; Radiative effects

Introduction

Secondary Organic Aerosols (SOA) constitute a major fraction of atmospheric fine particulate matter and play a critical role in regulating Earth’s climate system and air quality. Unlike primary aerosols, which are directly emitted into the atmosphere, SOA are formed through complex chemical reactions involving gaseous precursor compounds, predominantly volatile organic compounds (VOCs) of both biogenic and anthropogenic origin. These precursors undergo oxidation processes initiated by atmospheric oxidants such as hydroxyl radicals, ozone, and nitrate radicals, leading to the formation of low-volatility products that partition into the particulate phase. The global abundance of SOA is substantial, with estimates suggesting that they account for a significant proportion of organic aerosols in the troposphere, particularly over forested and urban-influenced regions. The formation and evolution of SOA are highly sensitive to meteorological conditions, including temperature, humidity, and solar radiation, as well as to changes in land use and emission patterns driven by human activities. From a climate perspective, SOA influence the Earth’s radiative balance through both direct and indirect mechanisms. Directly, SOA scatter and, in some cases, absorb solar radiation, thereby altering the amount of energy reaching the Earth’s surface. Indirectly, SOA modify cloud microphysical properties by acting as cloud condensation nuclei, affecting cloud reflectivity, lifetime, and precipitation processes. These interactions introduce significant uncertainties into climate models, as the chemical composition, optical properties, and hygroscopic behavior of SOA vary widely depending on their sources and atmospheric processing. Moreover, climate change itself can influence SOA formation by altering biogenic VOC emissions, atmospheric oxidant levels, and aerosol–cloud interactions, creating feedback loops that further complicate climate projections. Despite advances in observational techniques and modeling approaches, substantial gaps remain in understanding the formation pathways, transformation processes, and climate impacts of SOA on regional and global scales. Consequently, investigating the formation of secondary organic aerosols and their effects on global climate is essential for improving climate predictions, developing effective air quality management strategies, and informing policy decisions aimed at mitigating the impacts of anthropogenic emissions on the Earth's atmosphere.

Background of Atmospheric Aerosols

Atmospheric aerosols are minute solid and liquid particles suspended in the Earth's atmosphere, originating from a diverse range of natural and anthropogenic sources and exerting profound influences on climate, weather, air quality, and human health. Natural aerosols include sea salt generated from oceanic wave action, mineral dust emitted from arid and semi-arid regions, volcanic ash released during eruptions, and biogenic particles derived from vegetation and marine ecosystems. Anthropogenic aerosols primarily result from fossil fuel combustion, industrial processes, vehicular emissions, agricultural activities, and biomass burning. Based on their origin, aerosols are classified into primary aerosols, which are directly emitted into the atmosphere, and secondary aerosols, which are formed through chemical and physical transformations of precursor gases such as sulfur dioxide, nitrogen oxides, ammonia, and volatile organic compounds. Aerosols exhibit wide variability in size, composition, and atmospheric lifetime, ranging from a few hours to several weeks, which determines their transport, transformation, and removal processes. From a climatic perspective, atmospheric aerosols influence the Earth's radiative balance by scattering and absorbing incoming solar radiation and outgoing terrestrial radiation, leading to either cooling or warming effects depending on their properties. Aerosols also play a critical role in cloud formation by acting as cloud condensation and ice nuclei, thereby modifying cloud reflectivity, lifetime, and precipitation patterns. Beyond climate impacts, aerosols are a major determinant of air quality and public health, as fine particulate matter can penetrate deep into the respiratory system and contribute to cardiovascular and respiratory diseases.

Significance of the Study

The significance of this study lies in its contribution to improving the understanding of Secondary Organic Aerosols (SOA) as a key component of atmospheric particulate matter and an important driver of climate variability. By examining the formation mechanisms and climatic effects of SOA, the study helps address major uncertainties in estimating aerosol radiative forcing and aerosol–cloud interactions in climate models. Enhanced knowledge of SOA processes is essential for refining global and regional climate predictions, particularly under changing emission scenarios and future climate conditions. Furthermore, the study provides valuable insights for air quality management by linking SOA formation to precursor emissions from both natural and anthropogenic sources. This understanding can support the development of effective mitigation strategies and evidence-based environmental policies aimed at reducing particulate pollution and its associated health risks. Overall, the study bridges gaps between atmospheric chemistry, climate science, and policy-making, reinforcing the importance of SOA research in addressing global environmental challenges.

Definition and Classification of Secondary Organic Aerosols (SOA)

Secondary Organic Aerosols (SOA) are a class of atmospheric particulate matter formed through the chemical transformation of gaseous organic precursor compounds rather than being emitted directly into the atmosphere. These precursors, primarily volatile organic compounds (VOCs), originate from both natural sources such as vegetation and marine environments and anthropogenic sources including fossil fuel combustion, industrial emissions, and biomass burning. Through atmospheric oxidation reactions initiated by oxidants such as hydroxyl radicals, ozone, and nitrate radicals, VOCs are converted into low- and semi-volatile organic products that subsequently condense onto existing particles or contribute to new particle formation, resulting in SOA. Based on their sources, SOA are broadly classified into biogenic SOA, derived from naturally emitted VOCs like isoprene and terpenes, and anthropogenic SOA, formed from human-related emissions such as aromatic hydrocarbons and other industrial VOCs. Another important classification distinguishes SOA according to their formation pathways, including gas-phase oxidation products that partition into the particulate phase and SOA formed through multiphase and heterogeneous reactions occurring within cloud droplets or aqueous aerosol particles. SOA can also be categorized by volatility into low-volatility, semi-volatile, and extremely low-volatility organic compounds, which influence their atmospheric persistence and climatic effects.

Importance of SOA in the Earth’s Climate System

Secondary Organic Aerosols (SOA) are a critical component of the Earth’s climate system due to their substantial contribution to atmospheric particulate matter and their complex interactions with radiation, clouds, and biogeochemical cycles. SOA influence the global energy balance primarily through their direct radiative effects, as organic aerosol particles scatter incoming solar radiation back to space, leading to a net cooling effect at the Earth’s surface, while certain light-absorbing organic components can contribute to atmospheric warming. Beyond these direct interactions with radiation, SOA exert significant indirect effects by acting as cloud condensation nuclei, thereby altering cloud microphysical properties such as droplet number concentration, size distribution, cloud albedo, and lifetime. These changes in cloud characteristics can modify precipitation patterns and regional climate systems, amplifying or dampening climatic responses. The climatic importance of SOA is further emphasized by their sensitivity to environmental conditions, including temperature, humidity, and oxidant availability, which makes their formation and evolution closely linked to both natural processes and anthropogenic activities. Climate-driven changes, such as rising temperatures and altered vegetation patterns, can enhance biogenic volatile organic compound emissions, leading to increased SOA formation and creating feedback mechanisms between the biosphere and climate. SOA play a role in atmospheric chemistry by interacting with other aerosol components and trace gases, influencing oxidative capacity and the lifetime of greenhouse gases. Despite their recognized importance, SOA remain one of the largest sources of uncertainty in climate modeling, largely due to their complex chemical composition, dynamic formation pathways, and variable optical and hygroscopic properties. Accurately representing SOA in climate models is therefore essential for reliable predictions of radiative forcing and future climate scenarios. Understanding the role of SOA in the Earth's climate system not only advances fundamental climate science but also supports the development of effective climate mitigation and adaptation strategies by improving assessments of aerosol-related climate forcing.

Mechanisms of SOA Formation

Secondary Organic Aerosol (SOA) formation involves a series of interconnected chemical and physical processes that transform gaseous organic precursors into particulate matter in the atmosphere.

- **Gas-Phase Oxidation Processes**

The primary mechanism of SOA formation begins with gas-phase oxidation of volatile organic compounds (VOCs), during which these compounds react with atmospheric oxidants to form oxygenated products with reduced volatility. These oxidation reactions increase molecular weight and introduce functional groups such as hydroxyl, carbonyl, and carboxyl groups, promoting the transfer of products from the gas phase to the particle phase.

- **Role of Oxidants (OH, O_3, NO_3 Radicals)**

Hydroxyl radicals dominate daytime oxidation processes and are responsible for initiating the majority of VOC transformations, while ozone plays a major role in oxidizing unsaturated hydrocarbons, particularly terpenes, even in the absence of sunlight. Nitrate radicals are especially important during nighttime, driving oxidation reactions in low-light conditions and contributing to SOA formation under high nitrogen oxide environments.

- **Multiphase and Heterogeneous Reactions**

In addition to gas-phase pathways, SOA can form through multiphase and heterogeneous reactions occurring within cloud droplets, fog, and aqueous aerosol particles. These processes enable further chemical transformations, leading to the formation of highly oxidized, low-volatility compounds that enhance SOA mass.

- **Nucleation, Condensation, and Aging Processes**

Newly formed low-volatility products may nucleate to form new particles or condense onto pre-existing aerosols. Over time, atmospheric aging through continued oxidation, oligomerization, and particle-phase reactions alters the chemical composition, size, and hygroscopicity of SOA.

- **Influence of Temperature, Humidity, and Solar Radiation**

Meteorological factors strongly regulate SOA formation, as higher temperatures influence precursor emissions and volatility, humidity affects aqueous-phase chemistry and particle growth, and solar radiation controls photochemical reaction rates. Together, these mechanisms determine the abundance, properties, and climatic impacts of SOA in the atmosphere.

Chemical Composition and Properties of SOA

The chemical composition and physicochemical properties of Secondary Organic Aerosols (SOA) are governed by the nature of precursor compounds, oxidation pathways, and subsequent atmospheric processing.

- **Molecular Composition and Functional Groups**

SOA are composed of a complex mixture of oxygenated organic molecules formed through oxidation of volatile organic compounds (VOCs). Typical reactions include the hydroxyl radical–initiated oxidation of VOCs ($VOC + OH \rightarrow RO_2 \rightarrow RO \rightarrow$ oxygenated products), ozonolysis of unsaturated hydrocarbons (terpene + $O_3 \rightarrow$ carbonyls + organic acids), and nitrate radical reactions at night ($VOC + NO_3 \rightarrow$ organic nitrates). These processes generate multifunctional compounds containing hydroxyl (–OH), carbonyl (–C=O), carboxyl (–COOH), peroxide (–OOH), and nitrate ($–ONO_2$) functional groups, which reduce vapor pressure and enhance particle-phase stability.

- **Volatility and Hygroscopic Properties**

SOA exhibit a wide volatility range, from semi-volatile organic compounds (SVOCs) to extremely low-volatility organic compounds (ELVOCs), formed through repeated oxidation and accretion reactions such as $RO_2 + RO_2 \rightarrow$ oligomers. Reduced volatility promotes condensation onto existing particles or new particle formation. The presence of polar functional groups enhances hygroscopicity, enabling SOA to uptake water vapor ($SOA + H_2O \rightleftharpoons$ hydrated SOA), thereby increasing particle size and cloud condensation nuclei efficiency under high relative humidity conditions.

- **Optical Properties (Light Scattering and Absorption)**

SOA primarily scatter solar radiation due to their fine size and organic composition, contributing to atmospheric cooling. However, certain nitrogen-containing and aromatic oxidation products form light-absorbing organic material known as brown carbon, which absorbs ultraviolet and visible radiation (brown carbon + hv → energy absorption), influencing atmospheric heating rates and photochemistry.

- **Atmospheric Lifetime and Transformation**

The atmospheric lifetime of SOA typically spans several days to weeks, during which particles undergo aging processes such as further oxidation ($SOA + OH \rightarrow$ more oxidized SOA), fragmentation, and heterogeneous reactions with acidic or aqueous aerosol components. These transformations continuously modify SOA chemical composition, hygroscopic behavior, and optical properties, ultimately affecting their transport, removal, and overall role in climate forcing and air quality.

Impact of SOA on Global Climate

Secondary Organic Aerosols (SOA) exert a significant influence on global climate through a combination of radiative, microphysical, and chemical interactions within the atmosphere.

- **Direct Radiative Effects of SOA**

SOA affect the Earth's radiative balance primarily by scattering incoming solar radiation, resulting in a net cooling effect, expressed conceptually as SOA + hν → scattered radiation → surface cooling. Certain SOA components, particularly light-absorbing organic compounds known as brown carbon, can absorb ultraviolet and visible radiation (brown carbon + hν → energy absorption), contributing to localized atmospheric warming.

- **Indirect Effects on Cloud Formation and Albedo**

SOA influence cloud properties by modifying cloud droplet number and size distributions, which enhances cloud reflectivity or albedo, represented by SOA ↑ → cloud droplet number ↑ → cloud albedo ↑ → radiative cooling. These indirect effects often produce stronger climate forcing than direct radiative interactions but remain a major source of uncertainty in climate models.

- **Role of SOA as Cloud Condensation Nuclei (CCN)**

Due to their hygroscopic nature, many SOA particles readily absorb water vapor and act as cloud condensation nuclei, described by SOA + H_2O → activated CCN → cloud droplets. This process increases cloud lifetime and suppresses precipitation in some regions, further influencing regional and global climate patterns.

SOA interact with greenhouse gases by altering atmospheric oxidative capacity and trace gas lifetimes. For example, reactions such as SOA + OH → aged SOA reduce available hydroxyl radicals, indirectly influencing the atmospheric persistence of greenhouse gases like methane. Climate change can modify SOA formation through temperature-driven increases in biogenic VOC emissions and changes in oxidant concentrations, expressed as temperature ↑ → BVOC emissions ↑ → SOA formation ↑. In turn, enhanced SOA levels can alter radiation and cloud properties, creating feedback loops that either amplify or mitigate climate change.

Regional and Global Distribution of SOA

The regional and global distribution of Secondary Organic Aerosols (SOA) exhibits strong spatial and temporal variability driven by differences in precursor emissions, atmospheric chemistry, and meteorological conditions.

- **Spatial and Temporal Variability**

SOA concentrations vary seasonally and geographically, with higher levels typically observed during warmer months when biogenic volatile organic compound emissions and photochemical activity are enhanced. This variability can be represented conceptually as temperature ↑ + solar radiation ↑ → VOC oxidation ↑ → SOA formation ↑. Tropical and temperate regions with dense vegetation show consistently elevated SOA levels, while polar regions generally experience lower concentrations due to limited precursor availability and reduced photochemistry. Diurnal variations are also pronounced, with daytime SOA formation dominated by hydroxyl radical–initiated reactions and nighttime formation influenced by nitrate radical chemistry (VOC + NO_3 → organic nitrates → SOA).

- **SOA Formation in Urban, Rural, and Forested Regions**

In urban environments, SOA formation is strongly influenced by anthropogenic VOCs and nitrogen oxides from traffic and industrial activities, as illustrated by aromatic VOC + OH + NO_x → oxygenated products → urban SOA. Rural regions often exhibit mixed influences, where transported anthropogenic pollutants interact with locally emitted biogenic VOCs, enhancing SOA yields. Forested regions are major global SOA hotspots due to high emissions of isoprene and terpenes, with reactions such as terpene + O_3 → ELVOCs → biogenic SOA dominating aerosol production.

- **Contribution of SOA to Global Aerosol Burden**

On a global scale, SOA contribute a substantial fraction of fine particulate matter, accounting for a significant portion of the organic aerosol mass in the troposphere. Biogenic SOA dominate the global aerosol burden, particularly over continental and forested areas, while anthropogenic SOA contribute prominently in densely populated and industrialized regions. Long-range transport processes allow SOA and their precursors to influence remote regions, linking local emissions to global aerosol distributions. Overall, understanding the regional and global distribution of SOA is essential for accurately assessing their role in atmospheric composition, climate forcing, and transboundary air pollution.

Methodology

A series of photochemical experiments were conducted using toluene (Peking Reagent, 99.5%), *m*-xylene (Sigma-Aldrich, 99.5%), 1,3,5-trimethylbenzene (TMB; Sigma-Aldrich, analytical standard), and isoprene (Sigma-Aldrich, 99%) in the presence of nitrogen oxides (NO_x). All experiments were performed in a 30 m^3 indoor smog chamber operated in batch mode, which has been described in detail in previous studies. Briefly, the chamber consists of a cuboid fluorinated ethylene propylene (FEP) reactor housed in a temperature-controlled room equipped with an air-conditioning system capable of maintaining the temperature with a precision of ±1 °C. A Teflon-coated fan installed at the bottom of the chamber ensured rapid and uniform mixing of reactants.

Photochemical reactions were initiated using 120 ultraviolet lamps (Philips, 365 nm), providing a NO_2 photolysis rate of $0.55\ min^{-1}$, comparable to noon-time solar radiation conditions in Beijing. Prior to each experiment, the chamber was flushed with purified, dry zero air for 24–36 h at a flow rate of $100\ L\ min^{-1}$ until concentrations of gas-phase species (e.g., NO_x, O_3, and VOCs) were below instrument detection limits and the particle number concentration was less than $10\ cm^{-3}$.

Known volumes of one or more liquid VOCs were then introduced into the chamber through a heated Teflon inlet system (~100 °C) using purified, dry zero air as a carrier gas. VOC concentrations were measured in real time using thermal desorption gas chromatography–mass spectrometry (TD-GC/MS; UNITY 2, Markes, UK; 7890B GC and 5977A MS, Agilent, USA). Nitric oxide (NO) was subsequently injected from a calibrated standard gas cylinder (1020 ppm NO in N_2, Beijing Huayuan) using a mass-flow controller; the cylinder contained a minor fraction of NO_2. NO_x concentrations were continuously monitored with a chemiluminescence analyzer (Model 42i-TL, Thermo Fisher Scientific, USA).

After stable mixing of VOCs and NO_x was achieved, experiments were initiated by switching on the UV lamps and were conducted for approximately 360 min at 26 ± 1 °C under dry conditions (relative humidity ~5%). Temperature and relative humidity were monitored continuously using a hydro-thermometer (Vaisala HMP110, Finland). Average hydroxyl radical (OH) concentrations during each experiment were estimated from the first-order decay rates of VOCs.

Gas-phase organic intermediates were measured using an iodide high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS; Tofwerk AG, Aerodyne Research Inc., USA). Ozone concentrations were monitored with a UV photometric analyzer (Model 49i, Thermo Fisher Scientific, USA), while secondary organic aerosol (SOA) size distributions and mass concentrations were measured using a scanning mobility particle sizer (SMPS; Model 3082 with Model 3776 CPC, TSI, USA). In addition, a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; Aerodyne Research Inc., USA) was employed to quantify SOA mass concentration and chemical composition. The AMS alternated between V-mode (3 min) and W-mode (2 min) during measurements. Ionization efficiency (IE) calibrations were routinely performed using 300 nm dried ammonium nitrate aerosols. AMS mass concentrations were corrected using SMPS-derived aerosol mass following the approach of Gordon et al., as detailed in our previous work.

Wall Loss Corrections

To account for wall losses of both gas- and particle-phase species to the Teflon chamber walls, all measured concentrations were carefully corrected. First-order wall loss rate constants for NO_2, NO, O_3, and VOCs were determined to be $(1.67 \pm 0.25) \times 10^{-4}$, $(1.32 \pm 0.32) \times 10^{-4}$, $(3.32 \pm 0.21) \times 10^{-4}$, and $(2.20 \pm 0.39) \times 10^{-4}$ min^{-1}, respectively. Aerosol wall loss was corrected using a size-dependent deposition rate constant (k_dep, h^{-1}), expressed as

$$k\_dep = 4.15 \times 10^{-7} \times Dp^{1.89} + 1.39 \times Dp^{-0.88},$$

where Dp is the particle diameter (nm). This relationship was derived using polydisperse ammonium sulfate aerosols and has been widely applied in previous chamber studies.

The effects of vapor wall loss on SOA formation were also evaluated and are discussed in detail in the Supplementary Methods.

Results and Discussion

- **Particle Size Distributions**

The mass spectra of incomplete combustion products sampled at 8, 10, and 14 mm above the flame were analyzed using HR-ToF-AMS under non-oxidized (0 ppm O_3) and oxidized (5 ppm O_3) conditions. Unit mass resolution (UMR) spectra in the 100–1100 m/z range show that the dominant signals are distributed between m/z 100 and 600, with several peaks attributable to polycyclic aromatic hydrocarbons (PAHs) and pure carbon clusters (C_x), particularly at H = 14 mm. Upon photo-oxidation, a pronounced decrease in PAH-related peaks is observed across all heights, especially in the m/z range 300–500, indicating their active participation in oxidative processes. At the highest sampling height, additional reductions in the 700–1000 m/z range suggest further degradation of large aromatic species. Simultaneously, total ion signals increase by 12%, 17%, and 18% at H = 8, 10, and 14 mm, respectively, implying enhanced particle formation or growth under oxidizing conditions.

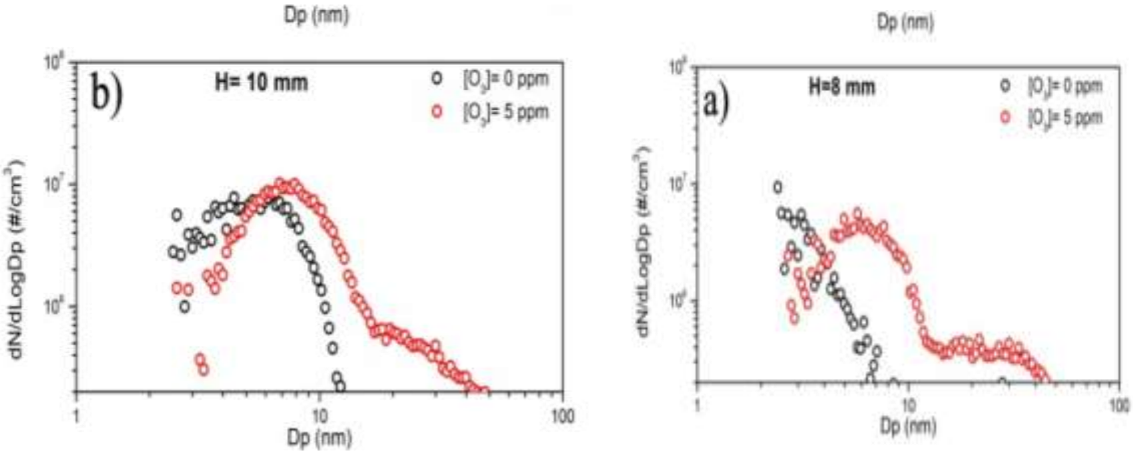


Fig. 1. Particle Size Distributions at Different Flame Heights with and without Ozone

High-resolution analysis in the lower m/z range (12–120) reveals that photo-oxidation leads to a systematic increase in oxygenated organic fragments (CHO and CHO>1 families), while hydrocarbon-like species (CH family) decrease. Strong enhancements at m/z 43–47 (e.g., $C_2H_3O^+$, CO_2^+, CHO_2^+) and concurrent reductions in hydrocarbon fragments (m/z 55–85) confirm the transformation of primary organic aerosol into more oxygenated secondary organic aerosol. These compositional changes are consistent with literature-reported SOA aging signatures.

These chemical transformations are reflected in the particle size distribution measured at H = 14 mm. Under ozonated conditions, the PSD shows a clear increase in particle number concentration and a shift toward larger diameters, particularly in the 20–60 nm range, indicating effective oxidative aging and condensational growth. In contrast, the non-oxidized case is characterized by smaller particles and narrower distributions. Together, AMS and PSD results demonstrate that ozone-driven photo-oxidation rapidly converts hydrocarbon-rich combustion emissions into oxygenated SOA, significantly altering both aerosol composition and microphysical properties within the DOFR™.

Figures 2a and 2b show the particle size distributions (PSDs) measured at flame sampling heights H = 8 mm and H = 10 mm, respectively, under non-oxidized (0 ppm O_3) and oxidized (5 ppm O_3) conditions, representing the early stages of aerosol evolution within the DOFR™. At H = 8 mm, the PSD without ozone is dominated by very small particles with low number concentrations and a rapidly declining tail toward larger diameters, typical of freshly emitted particles with minimal secondary processing. When ozone is introduced, a pronounced enhancement in particle number concentration is observed across a wider size range, together with the emergence of a distinct accumulation mode extending approximately from 10 to 40 nm. This behavior indicates that oxidative reactions promote particle growth even at short residence times, primarily through the condensation of low-volatility oxidation products onto existing particles rather than exclusively through new particle nucleation. At H = 10 mm, the influence of ozone becomes more evident, with substantially higher particle number concentrations and a clearer shift of the modal diameter toward larger sizes compared with the non-ozonated case. The accumulation mode is more developed than at 8 mm, reflecting increased oxidative exposure and enhanced secondary material formation, whereas the 0 ppm

O_3 condition remains characterized by a narrower distribution confined to the nucleation and small Aitken modes. The PSDs at 8 and 10 mm demonstrate a progressive evolution of aerosol particles along the reactor axis, confirming that oxidative aging initiates rapidly after particle formation and intensifies with increasing residence time, thereby promoting early secondary organic aerosol formation and condensational growth.

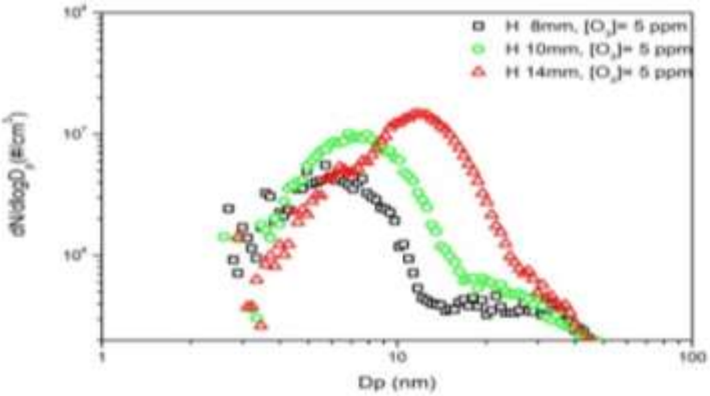


Fig. 2. Particle Size Distributions at Three Residence Times under 5 ppm Ozone

A distinct new particle mode is observed, most prominently at H = 14 mm. This mode is likely associated with fragmentation processes induced by oxidative aging of soot particles under ozone exposure. Such oxidation-driven fragmentation can generate smaller particles from larger soot aggregates, contributing to the emergence of this additional mode in the PSD. Further chemical characterization of particles within this size range would be valuable for clarifying their composition and formation mechanisms, thereby improving understanding of the processes governing particle transformation during oxidative aging.

Table 1. Summary of HOA Tracer Behavior under Photo-Oxidation

m/z	**Assigned Fragment**	**Aerosol Type**	**Trend with O_3 (5 ppm vs 0 ppm)**	**Interpretation**
57	$C_4H_9^+$	HOA (POA)	Decreases at all heights	Loss of short-chain hydrocarbon fragments due to oxidation
67	$C_5H_7^+$	HOA (POA)	Decreases	Oxidative degradation of unsaturated hydrocarbons
69	$C_5H_9^+$	HOA (POA)	Decreases	Consumption of alkyl fragments during aging
71	$C_5H_{11}^+$	HOA (POA)	Decreases	Breakdown of aliphatic chains
81	$C_6H_9^+$	HOA (POA)	Decreases	Oxidation of aromatic-related fragments
83	$C_6H_{11}^+$	HOA (POA)	Decreases	Progressive oxidation of hydrocarbon backbone
85	$C_6H_{13}^+$	HOA (POA)	Strong decrease	Highly oxidation-sensitive long-chain hydrocarbon tracer

95	$C_7H_{11}^+$	HOA (POA)	Decreases	Oxidative loss of larger hydrocarbon species
97	$C_7H_{13}^+$	HOA (POA)	Strong decrease	Marker of advanced oxidation of POA

Table 1 summarizes the behavior of the main hydrocarbon-like organic aerosol (HOA) tracers at three flame sampling heights (H = 8, 10, and 14 mm) under non-oxidized (0 ppm O_3) and oxidized (5 ppm O_3) conditions. For all heights, the HOA-related mass-to-charge ratios (m/z 57, 67, 69, 71, 81, 83, 85, 95, and 97), which are associated with alkyl and aromatic hydrocarbon fragments ($C_4H_9^+$ to $C_7H_{13}^+$), show a consistent decrease following ozone addition. This systematic reduction indicates progressive oxidation and degradation of hydrocarbon-rich primary organic aerosol during photo-oxidative aging. The magnitude of decrease becomes more pronounced at higher flame heights, reflecting longer residence times and enhanced oxidative exposure. Table 1 clearly demonstrates that ozone-driven oxidation efficiently reduces hydrocarbon-like aerosol components, marking the transformation of freshly emitted primary organic aerosol into more chemically aged material.

SOA Formation under Different Conditions

A series of photochemical experiments was conducted under various mixed VOC scenarios, including individual anthropogenic VOCs (AVOCs), mixed AVOC–biogenic VOC (BVOC) systems, and mixed AVOC systems, in the presence of NO_x (~20 ppb). The detailed experimental conditions are summarized in Table 1. The initial $HC_0/NO_{x,0}$ ratios ranged from 5.5 to 38.2 ppbC ppb^{-1}, covering conditions representative of severe haze episodes frequently observed in China. The temporal evolution of secondary organic aerosol (SOA) concentrations formed in these photo-oxidation systems is shown in Fig. 1. Under higher VOC concentration conditions (Fig. 1a), substantial SOA formation was observed in the toluene-only experiment (Exp. Tol01), with a maximum SOA concentration of 5.8 ± 0.12 μg m^{-3} and a calculated toluene SOA yield of 4.8%. This value is comparable to yields reported in previous chamber studies. However, the yield is significantly lower than those (~0.2–0.5) reported by Zhang et al., who conducted experiments in the presence of high concentrations of ammonium sulfate seed aerosols that strongly enhance gas–particle partitioning. In the mixed AVOC/BVOC system (Exp. Tol/Iso02), the presence of isoprene led to a pronounced suppression of SOA formation, reducing SOA mass by up to 61.7%, consistent with earlier studies demonstrating the inhibitory effect of isoprene on anthropogenic SOA formation. In contrast, the mixed AVOC system containing toluene, *m*-xylene, and 1,3,5-trimethylbenzene (Exp. Tol/mXy/TMB03) produced the highest SOA concentrations, reaching 10.8 ± 0.22 μg m^{-3}—an 85.6% increase relative to the toluene-only case—indicating a strong enhancement effect from coexisting aromatic VOCs. Similar trends in SOA production were also observed under lower VOC concentration conditions.

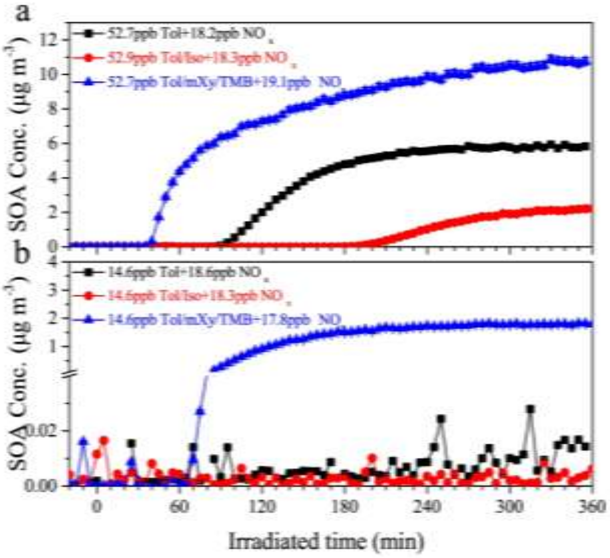


Fig. 3: Evolution of SOA Concentration during Photo-oxidation of Toluene and Aromatic Mixtures at High and Low NO_x Levels

Table 2 — SOA Yield Comparison Across VOC Scenarios

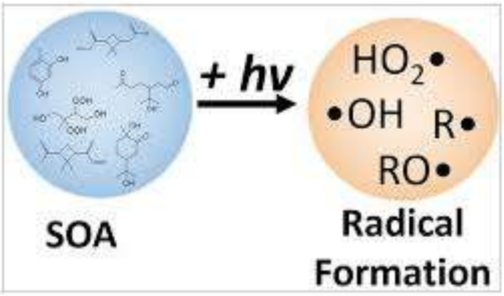
VOC Scenario	Key Condition	Relative SOA Yield (vs Toluene only)	Mechanistic Insight
Toluene only	Reference baseline	1.0 × (reference)	Standard anthropogenic SOA formation from toluene oxidation
Toluene + *m*-xylene + 1,3,5-TMB	Mixed AVOC	**+83.9 %**	Enhanced RO_2 cross-reaction chemistry forms more low-volatility products
Toluene + Isoprene	Mixed AVOC/BVOC	**−51.4 %**	OH scavenging by isoprene reduces condensable intermediates
Lower VOC conc. (all systems)	Reduced precursor load	Higher relative SOA yield	Formation of more LVOC/ELVOC intermediates enhances partitioning

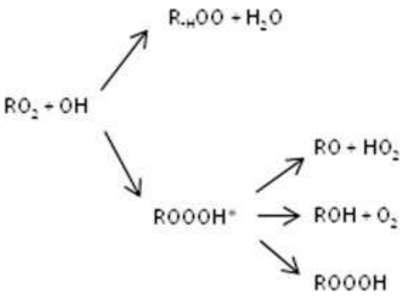
Table 2 highlights how VOC mixture composition strongly controls secondary organic aerosol (SOA) formation. The mixed anthropogenic VOC (AVOC) system containing toluene, *m*-xylene, and 1,3,5-trimethylbenzene shows the highest SOA yield, with an enhancement of nearly 84% compared to toluene alone. This enhancement reflects synergistic interactions among aromatic oxidation intermediates, particularly through RO_2 cross-reactions that generate low-volatility products. In contrast, the addition of isoprene (a biogenic VOC) to toluene leads to a pronounced reduction in SOA yield (~51%), demonstrating a suppression effect. This occurs because isoprene efficiently scavenges OH radicals and alters RO_2 chemistry, limiting the formation of condensable SOA precursors.

Table 3 RO₂ Cross-Reaction Contributions to SOA

RO₂ Interaction Type	Contribution to SOA (%)	Interpretation
RO₂ self-reactions (same VOC)	~20–30%	Standard peroxyl chemistry producing HOMs from individual VOC oxidation
RO₂ cross-reactions (different VOCs)	up to ~39%	Major driver in mixed AVOC systems, forming low-volatility dimers
Total RO₂ derived contribution	~40–65% (mixed systems)	Indicates organic peroxide dimers are central to SOA mass

Table 2 emphasizes the critical role of RO₂ radical chemistry in SOA formation, especially in mixed VOC systems. RO₂ self-reactions from a single precursor contribute moderately to SOA mass, but RO₂ cross-reactions between radicals derived from different AVOCs account for a substantially larger fraction, reaching up to ~39% of total SOA. These cross-reactions form organic peroxide dimers and highly oxygenated organic molecules (HOMs) with very low volatility, which efficiently partition into the particle phase. The combined contribution of RO₂-driven processes can explain up to 40–65% of SOA mass in mixed systems, underscoring that RO₂ cross-chemistry is a dominant pathway for enhanced SOA formation.





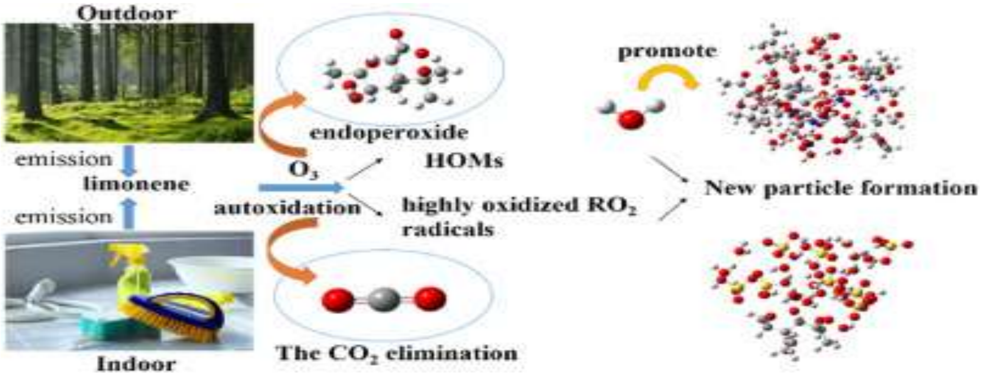


Fig 4 Limonene–Ozone Oxidation Pathways Leading to HOM Formation and New Particle Growth

Table 4 Effects of Precursor Concentration

Condition	Dominant Volatility Classes	SOA Yield Trend	Mechanistic Drivers
High VOC conc.	More SVOCs (semi-volatile)	Moderate to low	Larger reactant pools, but lower fraction of LVOC/ELVOC
Low VOC conc.	More LVOC/ELVOC	**Higher SOA yield**	Enhanced oxidation to lower-volatility products increases partitioning
High VOC w/ low [OH]	Less oxidation depth	Lower yield	OH competition limits deep oxidation
Low VOC w/ high [OH]	More oxidation products	Higher yield	Higher OH promotes deep oxidation cycles

Under high VOC concentrations, secondary organic aerosol (SOA) formation is dominated by semi-volatile organic compounds (SVOCs), resulting in moderate to low SOA yields. Although a larger pool of organic precursors is available, limited oxidation depth prevents efficient conversion into low-volatility species. In contrast, low VOC concentrations favor the formation of low-volatility and extremely low-volatility organic compounds (LVOC/ELVOC), leading to higher SOA yields as enhanced oxidation promotes effective gas-to-particle partitioning. When high VOC levels coincide with low hydroxyl radical (OH) concentrations, oxidation is shallow due to OH competition, suppressing SOA yield. Conversely, low VOC conditions with high OH availability promote deeper multi-generation oxidation, increasing production of low-volatility products and significantly enhancing SOA yield through repeated oxidation cycles.

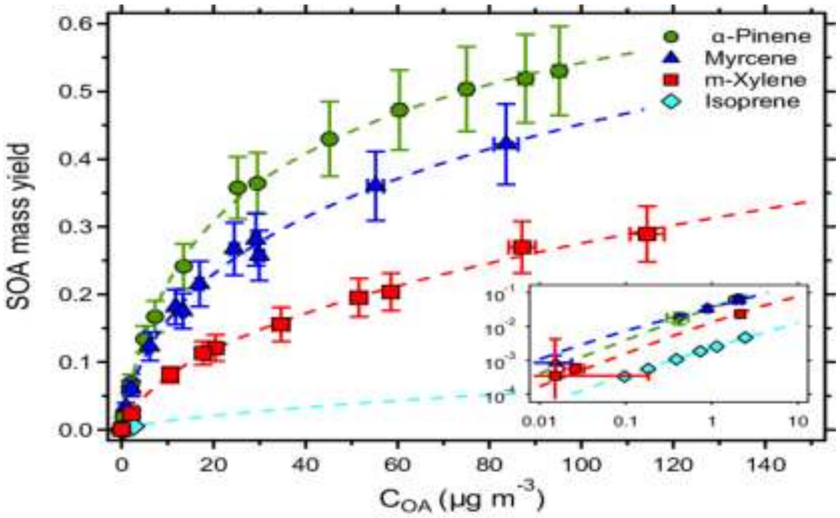


Fig 5 Synergistic Effects of Wildfire–Urban Aerosol Mixing on Organic Aerosol Composition

Figure 5 show how the interaction between wildfire emissions and urban air pollutants leads to synergistic changes in organic aerosol (OA) composition. When biomass-burning aerosols mix with urban emissions rich in nitrogen oxides and anthropogenic volatile organic compounds, enhanced atmospheric oxidation occurs. This process promotes the formation of more oxygenated and nitrogen-containing organic aerosols, increasing secondary organic aerosol (SOA) mass beyond what would be expected from simple additive effects. The figure highlights shifts toward higher oxidation states, altered chemical pathways, and increased aerosol aging, demonstrating that wildfire–urban mixing significantly modifies aerosol chemistry, with important implications for air quality, climate forcing, and human health.

Conclusion

The formation of Secondary Organic Aerosols (SOA) represents one of the most complex and influential processes in atmospheric chemistry, with profound implications for global climate regulation and air quality. SOA are produced through the oxidation of volatile organic compounds from both biogenic and anthropogenic sources, followed by gas–particle partitioning and continuous atmospheric aging that alters their chemical composition and physical properties. These aerosols play a critical role in the Earth's climate system by directly affecting the radiative balance through scattering and absorption of solar radiation and indirectly influencing cloud formation, cloud albedo, and precipitation dynamics by acting as cloud condensation nuclei. The interaction of SOA with greenhouse gases and atmospheric oxidants further highlights their importance in controlling atmospheric lifetimes of climate-relevant gases and overall oxidative capacity. Regional and global distributions of SOA are strongly governed by precursor availability, land-use patterns, and meteorological conditions, with forested regions contributing significantly to global SOA burdens and urban–industrial areas enhancing formation through complex chemical interactions. Despite substantial scientific advances, large uncertainties remain in quantifying SOA formation pathways, transformation processes, and climate impacts, particularly in representing aerosol–cloud interactions within climate models. Addressing these uncertainties is essential for improving the accuracy of climate projections and understanding feedback mechanisms between aerosols and climate change. Overall, this study emphasizes that a comprehensive understanding of SOA formation and its climatic effects is vital for advancing climate science, guiding air quality management, and supporting effective mitigation strategies aimed at reducing the impacts of anthropogenic emissions on the Earth's atmosphere.

References

1. Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., … Wildt, J. (2009). The formation, properties and impact of secondary organic aerosol: Current and emering issues. *Atmospheric Chemistry and Physics, 9*(14), 5155–5236.
2. Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., … Worsnop, D. R. (2009). Evolution of organic aerosols in the atmosphere. *Science, 326*(5959), 1525–1529.
3. Kroll, J. H., & Seinfeld, J. H. (2008). Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmospheric Environment, 42*(16), 3593–3624.
4. Shrivastava, M., Cappa, C. D., Fan, J., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., … Zaveri, R. A. (2017). Recent advances in understanding secondary organic

aerosol: Implications for global climate forcing. *Reviews of Geophysics, 55*(2), 509–559.

5. Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., … Wilson, J. (2005). Organic aerosol and global climate modelling: A review. *Atmospheric Chemistry and Physics, 5*(4), 1053–1123.
6. Donahue, N. M., Robinson, A. L., Stanier, C. O., & Pandis, S. N. (2006). Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environmental Science & Technology, 40*(8), 2635–2643.
7. Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., … Kulmala, M. (2014). A large source of low-volatility secondary organic aerosol. *Nature, 506*(7489), 476–479.
8. IPCC. (2021). *Climate Change 2021: The Physical Science Basis*. Cambridge University Press.
9. Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., … Worsnop, D. R. (2007). Ubiquity and dominance of oxygenated species in organic aerosols. *Geophysical Research Letters, 34*(13), L13801.
10. Goldstein, A. H., & Galbally, I. E. (2007). Known and unexplored organic constituents in the Earth's atmosphere. *Environmental Science & Technology, 41*(5), 1514–1521.
11. Andreae, M. O., & Crutzen, P. J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science, 276*(5315), 1052–1058.
12. Pöschl, U. (2005). Atmospheric aerosols: Composition, transformation, climate and health effects. *Angewandte Chemie International Edition, 44*(46), 7520–7540.
13. Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., … Seinfeld, J. H. (2008). Secondary organic aerosol formation from m-xylene, toluene, and benzene. *Atmospheric Chemistry and Physics, 8*(14), 4117–4140.
14. Tsigaridis, K., & Kanakidou, M. (2003). Global modelling of secondary organic aerosol in the troposphere. *Journal of Geophysical Research: Atmospheres, 108*(D3), 4009.
15. Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., & Donahue, N. M. (2012). The contribution of organics to atmospheric nanoparticle growth. *Nature Geoscience, 5*(7), 453–458.