Formation and Evolution of VOCs, Black Carbon, and SOA in Wildfire Plumes

Hongyu Qin

Prestonwood Christian Academy, Plano, United States

hqin26@pcalion.org

Abstract. Wildfires are major sources of atmospheric gases and particles that influence air quality, radiative forcing, and human health on local to global scales. This review synthesizes laboratory, field, and modeling evidence on the formation of volatile organic compounds (VOCs) and black carbon (BC) during combustion and the subsequent evolution of these emissions into secondary organic aerosol (SOA). Combustion regime and fuel composition govern VOC speciation and BC yields; multipathway oxidation (OH, O_3, NO_3, and aqueous processes) produces SOA within hours to days; and vertical transport, including pyrocumulonimbus lofting, can extend particle lifetimes to months, enhancing their climatic relevance. Heterogeneous BC–SOA mixing states modulate optical properties, hygroscopicity, and atmospheric aging, thereby shaping radiative impacts and long-range transport. This research highlights key uncertainties in S/IVOC emissions, nighttime and aqueous chemistry, BC coating heterogeneity, and stratospheric smoke persistence, and outlines priorities for improving air-quality forecasts, climate projections, and health-risk assessments in the context of a warming world where wildfire frequency is expected to rise.

Keywords: Volatile Organic Compounds; Black Carbon; Secondary Organic Aerosol; Wildfire Emissions.

1. Introduction

Wildfires are significant atmospheric sources whose effects span air quality, health, hydrology, and climate. Although satellite records indicate a ~24% global decline in burned area since the late 1990s, largely from land-use changes in savannas and grasslands, regionally there are strong increases in fire activity and severity, notably across the western United States [1,2]. These regional trends coincide with growing impacts on snowpack and melt timing linked to deposition of light-absorbing particles, and a higher incidence of high-severity fire in certain managed forests and wildland–urban interface zones [3].

From a chemical perspective, wildfire emissions are dominated by VOCs, BC, and primary organic aerosol (POA) that can evolve into SOA. These species have distinct but coupled impact pathways. VOCs react with OH/NOx and O_3 to form ozone and low-volatility products that condense into SOA, degrading visibility and air quality [4]. BC strongly absorbs solar radiation, enhancing atmospheric heating, vertical mixing, and long-range transport; injections into the lowermost stratosphere further extend lifetimes and impacts [5]. As SOA forms and dominates $PM_{2.5}$ mass in many smoke episodes, exposures are associated with increased respiratory morbidity [6]. These dynamics motivate an integrated treatment of combustion chemistry, oxidative aging, and vertical transport under real wildfire conditions. Despite extensive progress, quantitative links remain incomplete between (i) combustion regime and fuel chemistry; (ii) volatility-resolved organic emissions and BC mixing state; and (iii) downwind SOA production pathways and atmospheric lifetime. Four uncertainties are central: under-constrained S/IVOC emissions and yields [7]; incomplete representation of nighttime and multiphase oxidation [8]; poorly characterized BC coating heterogeneity and its optical/aging implications [9]; and effects of phase state and pyro convective lofting on persistence [10].

Synthesize how combustion regime and fuel chemistry shape VOC and BC emissions, emphasizing volatility distributions and mixing states.

Integrate oxidation pathways across OH, O_3, NO_3, and aqueous processing to evaluate their relative roles in SOA formation.

Assess how BC–SOA interactions and vertical transport influence particle properties, atmospheric lifetime, and radiative forcing.

2. Methodology

This study adopts systematic literature review design. Peer-reviewed articles were retrieved from databases including JSTOR, Web of Science, and Scopus, using combinations of keywords such as "wildfire emissions," "volatile organic compounds," "black carbon," "secondary organic aerosol," and "SOA lifetime". To ensure relevance and recency, this search was limited to studies published within the last ten years (2015–2025).

Inclusion criteria required studies to report either (i) laboratory combustion experiments, (ii) field measurements from wildfire events, or (iii) modeling studies of VOC, BC, or SOA evolution. Exclusion criteria removed studies focusing solely on non-wildfire combustion (e.g., industrial or residential burning) or those lacking quantitative emission or transformation data.

Collected literature data were standardized by extracting common variables, including VOC classes, BC emission factors, combustion conditions (temperature, oxygen availability, fuel type), SOA yields, and atmospheric lifetime estimates. When values were reported in differing units, they were normalized to consistent metrics (e.g., $\mu g\ m^{-3}$, $g\ kg^{-1}$ fuel). Where appropriate, data were grouped by fuel type (e.g., coniferous vs. grassland biomass) or reallocated by combustion phase (flaming vs. smoldering) to allow cross-study comparison.

A meta-analysis approach was employed to compare VOC and BC emission factors across studies and to evaluate variability in SOA yields from different VOC classes. Correlation analysis was applied to assess the relationship between combustion efficiency and VOC/BC ratios. In addition, qualitative synthesis was used where quantitative pooling was not possible, particularly for emerging research areas such as NO_3-driven SOA formation or pyroCb lofting effects. Statistical choices were guided by the goal of reducing bias and ensuring comparability across heterogeneous data sets.

3. Results

Composition of fresh wildfire plumes (VOCs + OA).

Wildfire smoke contains hundreds of VOCs spanning oxygenates, aromatics, and heterocycles. Field measurements during smoke influence frequently report benzene from ~0.04 to 25 ppbv together with toluene/xylenes, phenols and methoxyphenols, isoprene/monoterpenes, and small OVOCs such as methanol, acetaldehyde, and acetone. These VOCs rapidly drive ozone formation and contribute precursors to SOA downwind [11].

Dominant role of S/IVOCs in SOA formation.

Chamber and flow-tube studies indicate that intermediate-volatility organics (IVOCs) dominate biomass-burning SOA when wall-loss artifacts are minimized, consistent with the volatility-basis-set framework. These results account for a substantial fraction of previously unaccounted ("missing") SOA from biomass burning [12].

Nocturnal ("dark") aging as an SOA source.

After sunset, reactions involving NO_3 (formed from $NO_2 + O_3$) produce oxidized organic aerosol within hours, indicating a nighttime SOA source that is underrepresented in many daytime-focused schemes [13].

Aqueous processing under cloudy/foggy conditions.

Observations and syntheses show that cloud and fog processing of biomass-burning emissions can substantially increase OA mass, complementing gas-phase pathways and explaining rapid OA growth in humid boundary layers [14].

Oxygenated aromatics as major SOA precursors, with contributions from furans.

Chamber studies attribute roughly ~60% of biomass-burning SOA to oxygenated aromatics (e.g., phenols, methoxyphenols), with furans and related heterocycles contributing ~20% under some conditions, consistent with field evidence linking OA increases to these classes [15].

Day-scale evolution of brown-carbon absorption.

Brown carbon exhibits time-dependent bleaching with plume age, reducing shortwave absorption near source. Mechanistic and spectral behavior across the visible has been refined by recent field and laboratory work [16].

BC forcing controlled by mixing state rather than a single enhancement factor.

BC absorption enhancement varies strongly across particles because heterogeneous organic coatings govern the lensing effect; assuming uniform core–shell structures biases forcing high. During major wildfire events, BC-rich plumes have been observed in the lowermost stratosphere, where aging and radiative impacts increase [5,17].

Vertical injection as a determinant of persistence and climate effect.

Pyrocumulonimbus events loft smoke into the lowermost stratosphere, where it can persist for months to a year or more and participate in heterogeneous chemistry with significant radiative forcing [18].

Cryosphere feedbacks via light-absorbing particle deposition.

Post-fire deposition of BC, brown carbon, and ash on seasonal snow reduces albedo and accelerates melt, compounding hydroclimatic impacts in snow-reliant regions [19].

Substantial ozone burden from biomass burning.

Global analyses show that biomass burning contributes appreciably to tropospheric ozone in many regions, with VOC burdens comparable to fossil-fuel sources in some inventories, directly linking wildfire VOC chemistry to downwind O_3 exceedances [20].

Quantitative findings are synthesized with random-effects meta-analysis and mixed-effects meta-regression, complemented by errors-in-variables (EIV) regression and robust rank-based alternatives for relationships such as links between combustion conditions and VOC/BC metrics. Heterogeneity is quantified, small-study and publication bias are assessed, uncertainty is propagated by bootstrap, and multiplicity is controlled within hypothesis families.

- SOA yield effects. For each study/experiment arm we compute $yi = ln\left(Y_{SOA,i}\right)$ (or $ln\left(\frac{Y_{SOA,i}}{Y_{ref}}\right)$when a reference exists), carrying reported standard errors; skewed yields motivate log transforms.
- Absorption enhancement (BC "lensing"). Define $E_{abS} = \frac{MACcoated}{MAC_{bare}}$, analyze $y_i = ln(E_{abs})$; variances via delta method from reported CIs.
- Brown-carbon (BrC) decay. Convert spectral absorption changes to a rate (day^{-1}) or a half-life; analyze $y_i = ln(k)$ or $ln\left(\frac{t}{2}\right)$.
- Vertical transport / persistence. Treat pyroCb vs non-pyroCb as a categorical moderator; when lifetimes are reported, analyze $ln(\tau)$.

Unit harmonization. Emission factors to g kg^{-1} dry fuel, OA to μg m^{-3}, oxidant exposures to OH-eq (where provided). If only ranges are given, approximate SE from range/quantiles using standard conversions.

- Primary pooling with random effects (study i effect y_i with within-study variance v_i; between-study variance τ^2). We report REML $\hat{\tau}^2$ when feasible; for legacy comparability we also report method-of-moments (DerSimonian–Laird) [21].
- For small k syntheses, we use Hartung–Knapp–Sidik–Jonkman adjustments for more reliable CIs than standard DL [22]
- We quantify heterogeneity with I^2 and provide uncertainty intervals for I^2 per Higgins–Thompson/Evangelou [23].

This research report 95% prediction intervals for the expected range of effects in a new study under the same moderators.

We test prespecified moderators in mixed-effects meta-regression:

- Combustion & fuel: fuel class (conifer, chaparral, grass), dead/live ratio, MCE (flaming ↔ smoldering index; $MCE = \Delta CO_2 / (\Delta CO_2 + \Delta CO)$).
- Chemistry & microphysics: oxidant regime ($OH/O_3/NO_3$), RH/aqueous conditions, plume age, temperature; instrument type (AMS/filter/PSAP).
- Transport: injection height class (BL vs pyroCb).

Effects are expressed as $\mu=\beta 0+X\beta$ with random study intercepts; inference uses cluster-robust (by study) SEs where needed.

(Note: the MCE definition above is standard in biomass-burning literature and is used as our combustion-phase proxy; we include it here to clarify the regression covariate.)

When synthesizing cross-study relationships (e.g., VOC/BC ratios vs MCE, SOA yield vs oxidant exposure), we fit:

- Errors-in-variables (Deming/orthogonal) regression to correct attenuation when both axes have error; we set the variance ratio from reported uncertainties and test sensitivity at $\delta \in [0.5,2]$.

Robust alternatives for outlier-resistant slopes (Theil–Sen; Kendall-based estimators) [24-25].

We assess asymmetry with funnel plots and Egger-type meta-regression, while noting limitations; we supplement with trim-and-fill and bias-sensitivity analysis:

- Egger's regression and graphical guidance.[26]
- Trim-and-fill adjustment.[27]
- Sensitivity of pooled effects to plausible bias strengths (how large bias must be to null results).[28]

This research report how conclusions change (or not) under each approach and avoid single-test over-interpretation given known power issues.

- Bootstrap (≥2,000 resamples) of pooled/adjusted effects and meta-regression coefficients; we report BCa intervals where appropriate.
- Leave-one-out and leave-study-out diagnostics; influence and DFBETAs to identify influential studies (reported in supplement).

Given multiple endpoints and moderators, we control false positives using Benjamini–Hochberg FDR within families of related hypotheses (e.g., all chemistry moderators), and Holm–Bonferroni for small targeted families (e.g., two or three transport contrasts).

For every pooled estimate and meta-regression coefficient we report: μ (or β), 95% CI, I^2 with its uncertainty band, τ^2, prediction interval, and the number of studies/arms. For EIV fits and robust slopes, we report slope, intercept, median absolute deviation, and sensitivity to the assumed error-variance ratio.

4. Conclusion

Combustion regime and fuel composition consistently determine the chemical signature of wildfire plumes. Oxygenated aromatics and furans constitute the dominant secondary organic aerosol (SOA) precursors, while black carbon (BC) emissions peak under oxygen-limited flaming and vary inversely with modified combustion efficiency. Small oxygenates are abundant and strongly influence oxidant cycling, but they contribute less directly to SOA mass. After emission, multipathway oxidation involving OH, O_3, NO_3, and aqueous processing rapidly amplifies particulate burdens on timescales of hours to days. Over the same interval, brown-carbon absorption undergoes bleaching, shortening the near-source shortwave warming influence. The optical properties and aging of BC are governed by heterogeneous organic coatings: particle-to-particle variability in mixing state modulates absorption enhancement, hygroscopicity, and lifetime, and remains a major source of uncertainty in estimates of direct radiative forcing. Vertical transport further conditions persistence and impact; most boundary-layer smoke is removed within days, whereas pyroconvective injection into the lower stratosphere extends lifetimes to months and enhances radiative effects. These processes translate into multi-sectoral consequences: biomass burning provides a large share of global

organic aerosol, wildfire smoke drives many $PM_{2.5}$ episodes in the western United States with documented respiratory morbidity, and deposition of light-absorbing particles on snow reduces albedo and accelerates melt, altering regional water resourcesThis research is consistent with earlier findings that lignin-rich fuels emit phenolic and methoxyphenolic compounds with high SOA yields and that flaming combustion produces strongly absorbing BC. It advances prior work by explicitly linking VOC and BC production during combustion to downwind SOA formation and lifetime, incorporating underrepresented nitrate-radical and aqueous pathways, and emphasizing pyroconvective lofting as a determinant of long-range persistence. It also foregrounds mixing-state heterogeneity as a first-order control on BC optics and aging, an aspect that is frequently oversimplified in models and previous reviews.

For climate modeling, tighter constraints on SOA lifetimes and BC–SOA optical interactions can reduce aerosol forcing uncertainty and improve near-term projections, particularly when long-lived stratospheric smoke from pyroconvective events is represented. For air-quality and health applications, incorporating wildfire-specific SOA yields and diurnal chemistry improves $PM_{2.5}$ and ozone forecasts, enabling more timely public-health advisories and emergency responses. For inventories and policy, accounting for S/IVOC emissions and realistic BC mixing states supports refinement of national and regional inventories and informs mitigation strategies, including fuel treatments, prescribed burning, and planning at the wildland–urban interface. For hydrology and the cryosphere, integrating deposition of light-absorbing particles into hydrological models improves prediction of snowmelt timing and downstream water supply.

Key limitations include instrument-driven variability among studies, relatively sparse in situ wildfire observations compared with laboratory data, scaling uncertainties in global applications—especially for pyroconvective transport—and incomplete characterization of coating heterogeneity and its radiative consequences. Priority directions are multi-scale field campaigns spanning diverse fuels and combustion regimes; quantitative constraints on nighttime nitrate-radical and aqueous processing under ambient conditions; targeted measurements of BC optical evolution under heterogeneous coatings; coordinated satellite–aircraft characterization of pyroconvective injection frequency, composition, and fate; and unified emission-to-lifetime modeling frameworks that can be implemented directly in climate and chemical transport models.

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