

Characterizing emissions, chemistry, and health impacts of aged wildfire smoke in a western US city

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Abstract. We report hourly surface observations of PM_{2.5}, CO, NO_x, O₃, and 75 speciated VOCs in Missoula, Montana, during a strong smoke event in 2020. This study tests our current understanding of wildfire emissions, chemistry, and health effects as implemented in the GEOS-Chem chemical transport model. Three-or-more-day-old smoke transported from California and the Pacific Northwest increased CO, PM_{2.5}, and total measured VOCs by factors of 2–8, with hourly maxima of 800 ppb, 120 µg m⁻³, and 85 ppb, respectively. In contrast, NO_x levels were not elevated compared to the urban background. O₃ showed a non-monotonic response to wildfire smoke: MDA8 O₃ increased under light smoke but flattened or declined when PM_{2.5} exceeded ~30–40 µg m⁻³, a feature that GEOS-Chem failed to reproduce. A 2020-style wildfire season recurring annually would yield an excess lifetime cancer risk of 100-in-1 million or approximately 7 times the non-smoke baseline. The noncancer hazard index (HI) would reach 3.0, meaning substantially elevated acute risks during high-smoke periods. About 90% of cancer risks are from PM_{2.5}, whereas non-cancer risks are dominated by formaldehyde, benzene, acrolein, and acetaldehyde. GEOS-Chem captured major smoke intrusions but underestimated CO, PM_{2.5}, and VOCs by 30–90%. These model biases propagate to health metrics, with GEOS-Chem underestimating smoke-attributable cancer risk by ~40% and chronic HI by ~10 times. We attribute the model errors to underpredicted fire emissions and unrepresented VOC chemistry, which together led to an overestimation of OH and insufficient secondary production.

1 Introduction

Wildfires are the second largest source of volatile organic compounds (VOCs) in the western US (Hoesly et al., 2018; Jin et al., 2023). Some VOCs are designated hazardous air pollutants (HAPs) due to their carcinogenicity and potential for acute or chronic health effects (Naeher et al., 2007; Reid et al., 2016). Lengthening and intensified fire seasons in recent decades have posed direct air quality risks to rural populations and the inhabitants of ~50 million U.S. homes that already lie within the fire-prone wildland–urban interface (WUI), a figure expected to grow by one million every three years (Burke et al., 2021). Moreover, recent years have shown that western US and Canadian biomass burning (BB) smoke frequently impacts cities in

western North America and can reach population centers thousands of kilometers downwind on the East Coast (Yu et al., 2024). Despite the growing threat of more frequent and intense wildfires, the health effects of HAPs emitted from wildfires are not well documented, and residents often lack chemically resolved data on the pollutants to which they are exposed, because of limited ground-level measurements. Here, we combine hourly ground-based observations of VOCs and criteria
35 pollutants with the GEOS-Chem chemical transport model (CTM) to characterize the composition, chemical evolution, and health implications of aged wildfire smoke.

Past observational efforts have provided valuable yet incomplete insights into the health risks associated with wildfire smoke exposure (Gould et al., 2024). For example, some studies have targeted near-source fireline PM (Navarro et al., 2021), CO
40 (Semmens et al., 2021), or high-altitude plumes sampled by aircraft (O'Dell et al., 2020), and others have examined speciated VOCs and/or aerosol composition (Akagi et al., 2014; Fiddler et al., 2024; Joo et al., 2024; Liang et al., 2022). Speciated, near-surface data where the majority of human exposure to fresh and aged smoke actually occurs are still seriously under sampled. The lack of sufficient measurements also limits the evaluation of CTMs, which are widely used for smoke forecasting and health-risk assessments. Recent aircraft observations show that GEOS-Chem (a commonly used
45 CTM) underestimates BB CO and key HAPs such as formaldehyde by a factor of three or more (Jin et al., 2023). However, analogous ground-based validation remains absent. Because near-surface chemistry differs fundamentally from lofted plumes (e.g., ambient temperature, nighttime oxidants, boundary layer mixing) (Decker et al., 2019; Pagonis et al., 2023), ground observations are urgently needed to improve model validation and exposure assessments.

50 The western U.S. fire season of 2020 produced some of the most extreme smoke levels on record in OR, WA, and CA (Albores et al., 2023; Reilly et al., 2022), with September standing out as the peak month (Abatzoglou et al., 2021; Mass et al., 2021). More than 4 million acres burned in California alone, releasing an estimated ~ 127 Tg CO_2 -equivalent, nearly twice the state's cumulative 2003–2019 greenhouse-gas reductions (Jerrett et al., 2022). These BB events provide an ideal natural laboratory for quantifying the composition of aged smoke, and testing CTM capabilities for representing regional
55 smoke and assessing the continental-scale impacts of wildfires.

In this study, we present hourly ground-based measurements of 75 VOCs (including 15 HAPs), $\text{PM}_{2.5}$, CO, NO_x , and O_3 collected during aged (> 3 days) regional ~~BB events~~wildfire smoke in September 2020 in Missoula, Montana—a representative northwestern U.S. city frequently impacted by regional wildfire smoke. Leveraging this comprehensive
60 dataset, we (i) characterize the temporal evolution of VOCs and criteria pollutants (Sect. 4), (ii) quantify species-specific BB enhancements (Sect. 5), (iii) investigate O_3 – $\text{PM}_{2.5}$ relationships (Sect. 6), (iv) assess public health risks using regulatory exposure metrics for $\text{PM}_{2.5}$ and HAPs (Sect. 7), and (v) evaluate GEOS-Chem simulations against observations to diagnose model biases in BB emissions and chemistry, and their implications for health-risk estimates (Sect. 8).

2 Methods

65 2.1 Missoula Science Observatory

Missoula, MT (46.8721°N, 113.9940°W) lies in a mountain valley in the northern Rocky Mountains with a population of approximately 120,000. Missoula has been studied in the past for its frequent impacts from both local (Montana and Idaho) and regional wildfires, including long-range smoke transport from the West Coast and the Pacific Northwest, such as California, Oregon, Washington, and British Columbia (Selimovic et al., 2019, 2020). Its frequent exposure to surface smoke
70 makes it a representative site for evaluating human exposure and air quality under real-world wildfire conditions.

Long-term air quality monitoring at the Missoula Science Observatory (MSO) began in 2017 with measurements including four criteria pollutants (PM_{2.5}, CO, NO₂, and O₃) and aerosol optical properties (Selimovic et al., 2019, 2020). In 2020, the monitoring scope expanded to include 75 individual VOCs, of which 15 are classified as HAPs by the US EPA. The
75 University of Montana (UM) campus serves as the primary site for CO, NO, NO₂, O₃, and VOC measurements. The NO, NO₂, and O₃ inlet was located 12.5 m above ground at the Charles H. Clapp Building; the CO and VOCs inlet was initially located 109 m above ground on the Chemistry Building, ~70 m away.

Measurements of PM_{2.5} were obtained from the Montana Department of Environmental Quality site at Boyd Park, roughly 3
80 km southwest of the UM campus. Despite the spatial separation between measurement sites, previous studies have validated the temporal and spatial agreement in pollutant concentrations between the two sites for 2017–2019 summers (Selimovic et al., 2019, 2020); we confirm similar agreement among PM_{2.5} measured at the Boyd Park and other tracers measured at the UM campus for this study ($R^2 > 0.9$), supporting the use of combined datasets in this analysis.

85 Hourly meteorological data were obtained from the MesoWest database and accessed via the Synoptic Data API (<https://synopticdata.com/>). Incoming shortwave radiation (W m^{-2}) was obtained from the Blue Mountain site (station ID: BLMM8; 46.73° N, 114.09° W), while air temperature (°C), relative humidity (percent), and precipitation accumulation (mm) were obtained from the Missoula Valley site (station ID: E0591; 46.86° N, 114.02° W). These stations were selected as the closest available meteorological observations to the MSO (10 km and 5 km away, respectively). We used broadband
90 shortwave (SW) as a first-order proxy for actinic flux and photolysis as they were not measured; We note that the SW (200–4000 nm) can diverge from the near-UV range relevant to $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$ (~300–420 nm) under smoke. Planetary boundary layer (PBL) mixing height (m) was obtained from the High-Resolution Rapid Refresh (HRRR, 3km), an operational forecast and analysis system developed by NOAA with hourly updates at 3-km horizontal resolution (Dowell et al., 2022). We also obtained the mixing height data from the NASA Goddard Earth Observing System Forward Processing
95 system (GEOS-FP, $0.25^\circ \times 0.3125^\circ$, hourly) as it serves as one of the inputs for GEOS-Chem.

Figure 1 illustrates the climatology of PM_{2.5}, defined here as the multi-year statistical distribution of daily-mean PM_{2.5} during the wildfire season (June–October) over 2010–2024 in Missoula~~climatological distribution of daily PM_{2.5} during the wildfire season (June–October) for 2010–2024 in Missoula.~~ Despite large interannual variability, a clear seasonal progression is evident. The multi-year daily ~~Daily~~ average PM_{2.5} concentrations remain below 15 $\mu\text{g m}^{-3}$ throughout June, increase steadily during July, and peak from mid-August to occasionally mid-September, coincident with increases in wildfire smoke episodes. ~~During the month-long peak periods, the multi-year daily mean PM_{2.5} concentrations exceed the WHO 24 h guideline (15 $\mu\text{g m}^{-3}$) on 18 days and the US EPA standard (35 $\mu\text{g m}^{-3}$) on 6 days based on the climatology.~~ Peak hourly PM_{2.5} even reached $\sim 470 \mu\text{g m}^{-3}$ in 2017. Reflecting this chronic smoke burden, in 2024, Missoula ranks 14th among 223 U.S. metropolitan areas for 24-hour particle pollution, measured by the weighted annual average number of unhealthy 24-hour PM_{2.5}, and 29th for annual particle pollution, measured by the annual average PM_{2.5} concentration ~~Reflecting this chronic smoke burden, Missoula ranks 14th among 223 U.S. metropolitan areas for 24 hour particle pollution and 29th for annual particle pollution~~ (American Lung Association, 2024). In this study, we focus specifically on September 2020, when regional smoke transport led to one of the most prolonged and chemically distinct episodes of aged wildfire smoke observed at the surface (blue line in Fig. 1; Sect. 4).

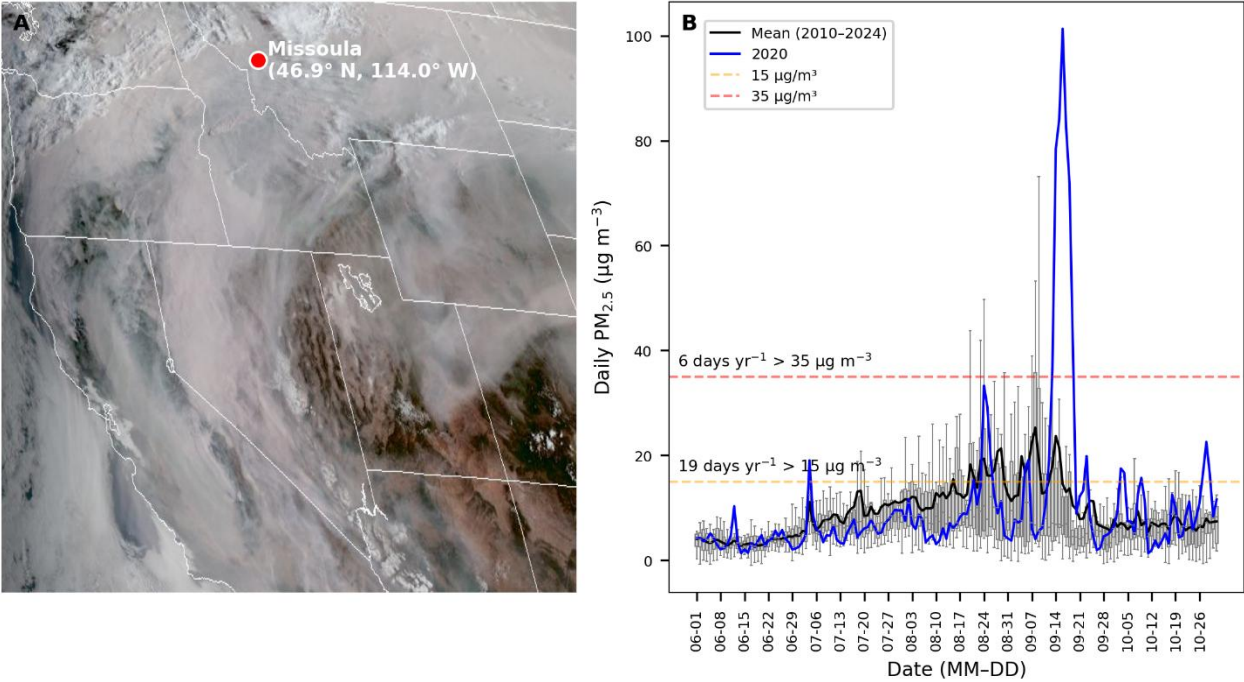


Figure 1. Wildfire smoke over the western US and climatological PM_{2.5} in Missoula, Montana. (A) Cropped GOES-17 GeoColor satellite image (15 September 2020) over the Western United States, with the location of Missoula, Montana indicated by the red dot. (B) Daily-mean PM_{2.5} concentrations at Missoula during the 2020 fire season (blue) compared with the 2010–2024 climatology (black line; grey box plots give the interquartile range and whisker range ($\pm 1.5 \times \text{IQR}$; vertical lines) for each calendar day). Dashed horizontal lines indicate 15 and 35 $\mu\text{g m}^{-3}$, as the WHO 24-hour guideline and the US EPA 24-hour standard.

2.2 VOC measurements

Ambient mixing ratios of 75 VOCs were measured ~~every-as 2--minute~~ averagess using a custom-built Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS; PTR-ToF-4000, Ionicon Analytik GmbH, Innsbruck, Austria). Instrument operation followed protocols developed in our previous campaigns (Cope et al., 2024; Permar et al., 2021; Selimovic et al., 2022), with drift tube conditions set to E/N = 130 Td, 3.00 mbar, 60 °C, and 800 V.

Air was continuously sampled from an inlet ~10 m above ground through ~10 m of heated (60 °C) 6.35 mm (1/4 inch) outer diameter (O.D.) PTFE tubing. The PTR-ToF-MS then subsampled via ~1 m of 1.59 mm (1/16 inch) O.D. PEEK tubing, also maintained at 60°C. The sampling inlet featured a 2-μm PTFE filter to prevent particle intrusion. Filters were replaced every two weeks, or more frequently during high pollution periods. Instrument backgrounds were quantified every 2.5 hours by sampling VOC-free air generated via a heated platinum catalyst (375 °C; Sigma-Aldrich, 1 wt%).

In this work, we included 75 VOC species measured by PTR-ToF-MS in the analysis. Calibrations were conducted every other day using two compressed gas standard cylinders for 25 individual VOCs (±5% at ~1 ppmv; Apel-Riemer Environmental, Inc.). Among them, isomers calibrated at the same m/z (i.e., methyl vinyl ketone and methacrolein at m/z 71.049; ethylbenzene and o-xylene at m/z 107.086; 1,2,4- and 1,3,5-trimethylbenzene at m/z 121.101), which used a weighted average sensitivity based on the corresponding isomeric contributions (Permar et al., 2021). A third standard gas cylinder containing 10 species was calibrated after the campaign (±5% at ~1 ppmv; Apel-Riemer Environmental, Inc.). The overall measurement uncertainty for these species is estimated to be less than 15%. Formaldehyde was calibrated after the campaign using a gas standard cylinder (stated accuracy 5% at ~2 ppm; Airgas USA LLC, Plumsteadville, PA, USA). Gases were mixed in a Liquid Calibration Unit (LCU, Ionicon Analytik GmbH, Innsbruck, Austria) to derive the dependence of instrument sensitivity on changing humidity. Formic and acetic acids were calibrated after campaign using LCU, which also applied humidity dependence. Uncertainty for these species is estimated at ~30% (Permar et al., 2021). For 40 uncalibrated species, instrument sensitivities were estimated using theoretical methods (Sekimoto et al., 2017) refined by field comparisons (Permar et al., 2021), yielding overall uncertainties of ~50%. Sensitivity of all compounds used in this study ranges from 0.9 to 14 ncps ppbv⁻¹, where ncps denotes normalized counts per second. The background signal of all compounds ranges from 0.05 to 10.1 ncps.

~~Calibrations were conducted every other day using dynamically diluted standard gas mixtures for 26 36 of the 75 VOCs (±5% at ~1 ppmv; Apel-Riemer Environmental, Inc.). The overall measurement uncertainty for these species is estimated to be less than 15%. Formic and acetic acids were calibrated using permeation tubes, with estimated uncertainties of ~30% . For 57 37 uncalibrated species, instrument sensitivities were estimated using theoretical methods refined by field comparisons Click or tap here to enter text., yielding overall uncertainties of ~50%. Sensitivity of all compounds used in this study ranges from 0.9 to 14 ncps ppbv⁻¹.~~

150 **2.3 Measurements of CO, NO_x, O₃, and PM_{2.5}**

CO was measured every ~3 minutes using a Reducing Compound Photometer (Peak Performer 1, PEAK Laboratories, Mountain View, CA, USA), which separates CO by gas chromatography and detects it via photometric absorption of mercury vapor produced from CO reduction of HgO. The instrument was calibrated weekly via CO standard in a compressed standard gas cylinder, with a detection limit of 0.3 ppb. The instrument shared the inlet with PTR-ToF-MS and sampled
155 ambient air at 40 sccm through 5 m of 3.175 mm (1/8 inch) O.D. PTFE tubing.

NO₂ and NO were measured every 1 minute using a model 405 nm NO_x monitor (2B Technologies, Boulder, CO, USA), which directly quantifies NO₂ by measuring optical extinction at 405 nm, where NO₂ strongly absorbs. NO is measured by adding excess ozone into the optical cell, which quantitatively converts NO to NO₂. The instrument was calibrated by the manufacturer with a detection limit of 1 ppb for NO and NO₂. Ambient air was drawn at ~1.5 L min⁻¹ through ~1 m of 6.35
160 mm (1/4 inch) O.D. tubing and passed through a 47 mm, 5 µm PTFE filter (Savillelex), which was replaced biweekly or upon visible loading.

PM_{2.5} and O₃ were obtained from the hourly measurements at the Montana DEQ site at Boyd Park. PM_{2.5} measurements were conducted using a Met One BAM-1020 with VSCC inlet (Volumetric Size-Selective Cyclone), which determines particle mass by measuring the attenuation of beta radiation through the filter tape as particles accumulate. The instrument has a
165 detection limit of 5 µg m⁻³ for hourly measurements. O₃ was measured using an ultraviolet photometric analyzer (Thermo Scientific Model 49i UV photometric O₃ analyzer), which quantifies absorption of UV radiation at 254 nm, and with a detection limit of 5 ppb. We note that the Thermo 49i instrument can exhibit positive interferences in wildfire smoke between the two measurements. This -interference would not affect our conclusion and would, if anything, make the inferred O₃ suppression and model ozone biases more conservative.

170 **2.4 GEOS-Chem chemical transport model**

We use the nested-grid GEOS-Chem CTM over North America (version 13.3.0; 10-70 °N, and 140-60 °W) to interpret Missoula ground-based measurements. The model is driven by the NASA GEOS-FP meteorological data, with 0.25° × 0.3125° horizontal resolution (~25 km × 30 km; latitude × longitude) and 47 vertical layers extending up to 0.01 hPa (Kim et al., 2015; Wang et al., 2004). Boundary conditions were updated every 3 hours from a 4° × 5° global simulation. Transport
175 and convection time steps were 5 minutes; emission and chemistry time steps were 10 minutes. Model spin-up included a 1-year global simulation followed by a 1-week nested simulation to ~~remove-reduce~~ the influence of initial conditions prior to September 1, 2020.

The chemical mechanism included detailed HO_x-NO_x-VOC-ozone-halogen-aerosol chemistry with fully coupled troposphere and stratosphere (Eastham et al., 2014; Mao et al., 2010; Park, 2004; Schmidt et al., 2016). Dry deposition used a resistance-
180 in-series approach (Wesley and Wesely, 1989), and wet deposition included scavenging of soluble tracers in convective

updrafts, as well as rainout and washout of soluble tracers (Liu et al., 2001). GEOS-Chem uses the non-local scheme for PBL mixing (Lin and McElroy, 2010). As a sensitivity test, we also conducted simulations using the “full mixing” scheme, assuming instantaneous vertical mixing of tracers evenly through the mixing depth, which did not affect the conclusions we derived.

185 Emissions were computed using the HEMCO module (Keller et al., 2014). These include biogenic VOC emissions from MEGANv2.1 (Guenther et al., 2012) as implemented in GEOS-Chem (Hu et al., 2015). Anthropogenic emissions are from the CEDS global emission inventory, overwritten with the 2011 EPA NEI inventory for the US (Hoesly et al., 2018). Daily BB emissions were taken from the Global Fire Assimilation System (GFAS) version 1.2, chosen for its relatively better VOC performance when compared to other commonly used BB inventories over the western US (Jin et al., 2023; van der Werf et al., 2017). Following previous work (Jin et al., 2023), we expanded the default GFAS VOC speciation by adding lumped
190 $\geq C_3$ aldehydes (RCHO), MEK, formic acid, and acetic acid by scaling CO BB emissions with corresponding emission ratios reported from temperate forest burns (1.01, 0.73, 9.5, and 8.61 ppb ppm⁻¹, respectively) (Permar et al., 2021). All fire emissions followed a climatological diurnal profile, which allocates ~85 % of daily fire emissions to the afternoon (local time) (Western Regional Air Partnership, 2005).

195 Biomass burning injection heights are prescribed with the daily $0.1^\circ \times 0.1^\circ$ mean altitude of maximum injection (“mami”) product derived from a satellite-constrained plume rise model (Freitas et al., 2007; Latham, 1994; Rémy et al., 2017). For each GEOS-Chem grid cell, we computed emission-flux-weighted “mami” values to correct the grid-dependence inherent in the standard model (Jin et al., 2023). BB emissions were then distributed evenly from the surface up to this “mami”.

Overall, four nested simulations were conducted for September 2020: (i) a base run using default GFAS emissions and non-
200 local PBL mixing scheme, (ii) a sensitivity run as the base but without fire emissions (noBB), (iii) a second sensitivity run as the base but with GFAS VOC and CO emissions tripled ($3 \times BB$), and (iv) a third sensitivity run using GFAS and the full instantaneous mixing within the PBL mixing height.

3 Identification of smoke-impacted events

Wildfire smoke at ground level is often detected using particle-based diagnostics, for example: (i) satellite-derived aerosol
205 products such as the overhead information from the NOAA Hazard Mapping System (HMS) (Jaffe et al., 2022; O’Dell et al., 2021), (ii) column-integrated aerosol optical depth from AERONET, (iii) sustained elevations in surface PM_{2.5} relative to the general urban background (Selimovic et al., 2019, 2020), and (iv) combinations of these metrics (Kaulfus et al., 2017; McClure and Jaffe, 2018). ~~Some~~ Many studies also incorporate gas-phase tracers—initially CO, hydrogen cyanide (HCN), acetonitrile (ACN), and more recently, furan, maleic anhydride (MA) (Coggon et al., 2019; de Gouw et al., 2003, 2006; Li et
210 al., 2000). Among these VOCs, furan is a sensitive indicator of fresh BB smoke due to its short lifetime and smaller emission

amount from anthropogenic sources. In addition, MA is an oxidation product of furan and its derivatives, with a longer lifetime; thus, it has been proposed as a tracer of aged smoke (Coggon et al., 2019).

Here, we evaluate some current BB-impacted identification metrics in the context of our MSO case study and examine whether our VOC measurements provide additional value in identifying BB events in the urban setting. We first derive the hourly median diurnal urban background for BB tracers and other species using HMS “no-fire” days for September 2020. Any enhancement (ΔX) > 1.5 times the background is considered BB-impacted, and a provisional smoke day is defined when at least six such hours occur. We also tested the $PM_{2.5}/CO$ criterion ($> 30 \mu g m^{-3} ppm^{-1}$) proposed for urban smoke identification (Jaffe et al., 2022). However, at MSO this threshold classified nearly all days as smoke-impacted, consistent with the limitation that $PM_{2.5}/CO$ becomes non-discriminating when background $PM_{2.5}$ and CO are low (Jaffe et al., 2022). We therefore do not use $\Delta PM_{2.5}/\Delta CO$ as a standalone classifier for this site.

Figure 2 summarizes the various daily BB classifications for September 2020 in Missoula. HMS alone identifies 20 smoke days (the greatest number among the diagnostics), but it can flag a day as smoke-impacted even when surface concentrations remain low if smoke is primarily aloft. For example, HMS triggers on 2 September and 30 September (daily average $PM_{2.5}$ is 8.5 and 5.5 $\mu g m^{-3}$, respectively), which likely reflect elevated plumes that were not mixed down to the surface (Liu et al., 2024). By comparison, the $\Delta PM_{2.5}$ criterion identifies 16 days. Its diagnostic power depends strongly on aerosol loading at the surface.

When daily mean $PM_{2.5}$ exceeded 35 $\mu g m^{-3}$ ($n = 7$; 13–19 September), the $\Delta PM_{2.5}$ approach aligned with HMS and with all gas-phase tracers considered here (i.e., CO, ACN, furan, and MA), indicating concentrated smoke that coupled large aerosol mass with gaseous enhancements. A k-means clustering analysis ($k = 3$: smoke, no-smoke, uncertain) applied to pairwise combinations of CO, $PM_{2.5}$, and each tracer corroborated this classification, reinforcing that at extreme-high aerosol loadings, routine ground-level $PM_{2.5}$ alone can reliably identify smoke during summer in Missoula. We therefore classify these seven days as a high-confidence BB period.

At intermediate daily mean $PM_{2.5}$ between 20 and 35 $\mu g m^{-3}$ ($n = 5$; 5–6, 11–12, and 23 September), $\Delta PM_{2.5}$ still overlaps at least two gas-phase tracers but not all, signaling moderately aged or dispersed smoke and therefore medium diagnostic confidence. When the daily-mean $PM_{2.5}$ falls below 20 $\mu g m^{-3}$ ($n = 4$; 7, 21–22, and 24), $PM_{2.5}$ overlaps with at most one gas tracer, and HMS does not indicate smoke on 24 September, so these low-load cases warrant only low-to-medium confidence. One additional case (21 September) meets the $PM_{2.5}$ threshold but lacks corroboration from the gas-phase tracers, suggesting a potential false positive, although HMS indicates overhead smoke. Across September (a total of 30 days), the remaining 14 days do not meet the $\Delta PM_{2.5}$ criterion and are classified as non-smoke by this approach.

Gas-phase tracers extend the detectability of wildfire smoke beyond what is captured by HMS and PM_{2.5} alone, particularly during precipitation events. For example, on 20 September, CO and furan enhancements were observed in the absence of corroborating HMS smoke or elevated PM_{2.5}. A rain event from the preceding day into the afternoon of 20 September efficiently scavenged aerosol mass, resulting in a sharp decrease of ~30 $\mu\text{g m}^{-3}$ in PM_{2.5}, whereas gas-phase species were less affected and their enhancements persisted in the boundary layer.

Because no single tracer is definitive, we adopt a balanced multi-indicator rule: an hour is classified as smoke-impacted when at least three independent smoke indicators support smoke influence, based on HMS smoke detection and/or BB-associated species exceeding $1.5 \times$ their background values for at least six hours on that day~~when at least three independent tracers exceed their thresholds, and a day is smoke-impacted if it contains six or more such hours~~. Applied to September 2020, this criterion identified 14 smoke days (5–7, 11–19, and 22–23 September). For subsequent sections, we describe the three smoke events ~~as an overview, while and~~ we focus on the high-confidence BB period of 13–19 September to analyze its enhancement ratios, thereby minimizing uncertainties from marginal or non-BB sources.

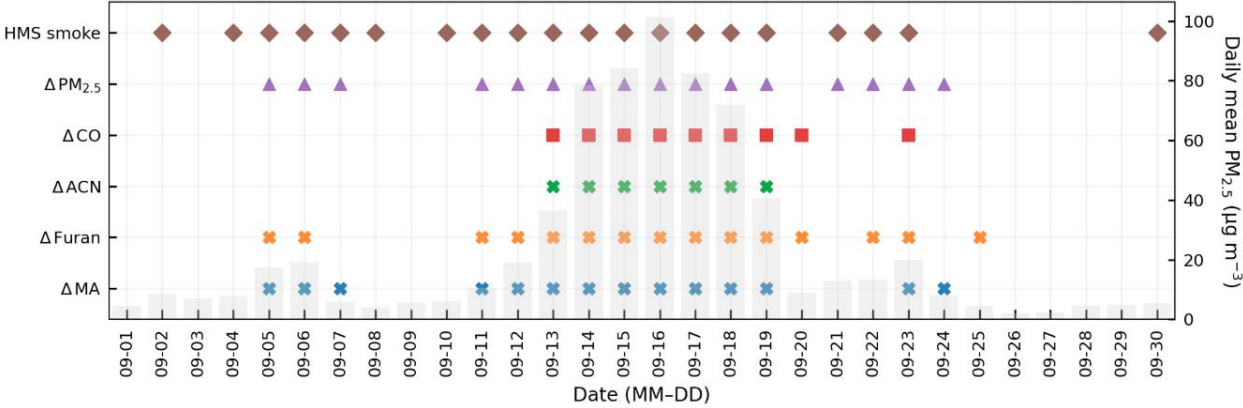


Figure 2. Wildfire smoke identification in Missoula, Montana, during September 2020. Rows show the six individual smoke metrics evaluated in this study. A filled marker indicates that HMS smoke was detected, or that the enhancement of a biomass burning (BB) ~~tracer indicator~~ (ΔX) exceeded ~~both~~ $1.5 \times$ its diurnal background ~~and the metric-specific threshold~~ for at least six hours on that calendar day. Gray bars (right axis) show the daily mean PM_{2.5} concentration.

4 Overview of BB smoke in September 2020

Wildfires across the Pacific Northwest and northern California were exceptionally active in 2020 (Albores et al., 2023; Higuera and Abatzoglou, 2021; Neyra-Nazarrett et al., 2025; Reilly et al., 2022), and September delivered strong smoke signatures in Missoula. ~~According to the U.S. EPA AirNow data, air quality index (AQI) values failed to reach the "Good" category on 19 out of 30 days. Specifically, 12 days were classified as "Moderate" and 7 days fell into "Unhealthy" or "Unhealthy for Sensitive Groups", due to wildfire emissions~~ Applying the three-tracer classification described in Section

3, we identified 16 smoke-impacted days across confidence levels. Applying the three-tracer classification of Section 3, smoke affected 16 days (or 384 hrs) of our measurements in September.

Figures 3 and S1 show three distinct multi-day smoke episodes affecting Missoula identified using the criteria described in Sect. 3, including 5–7 September (Event 1), 11–20 September (Event 2), and 22–24 September (Event 3). Because each episode involved multiple overlapping plumes from different fires with varying transport times, we refer to them as “events” rather than discrete “plumes”. Analysis of GOES-17 and VIIRS satellite imagery, and synoptic meteorological conditions indicate that these events were predominantly driven by southwesterly transport of wildfire smoke from Oregon, Idaho, and California, with likely influence from local smaller fires.

Event 1 (5-7 September) resulted from the California Creek Fire (United States Forest Service, 2025), which started on 4 September mixing with a localized, narrow plume moving east-northeast over the Bitterroot Mountains toward Missoula, as captured by GOES-17 imagery. Correspondingly, hourly $\text{PM}_{2.5}$ increased rapidly from <10 to $30 \mu\text{g m}^{-3}$ by 06:00 Mountain Daylight Time (MDT, UTC-6) on 6 September and CO from 100 to ~ 300 ppb by 09:00 MDT the same day, with brief spikes (≤ 50 ppt) of the fresh-smoke tracer furan at 01:00 MDT. Pollutant concentrations returned to the urban background within 24 h after a post-frontal north-westerly wind flushed the valley.

Event 2 (11–20 September) was the longest and strongest impact on Missoula from the Oregon–California “megafire” complex that ignited in August and erupted on 7 September (Abatzoglou et al., 2021). Intense smoke on 8 September was advected westward offshore, where it became entrained into a cut-off low over the NE Pacific (around 42°N , 135°W), and subsequently advected eastward inland, mixing with smoke freshly emitted by the megafire complex and fires in Idaho. By 11 September, dense smoke formed a clearly visible “smoke river” that stretched across Washington, Oregon, and Idaho into western Montana. Back-trajectory analyses indicate that air parcels reaching Missoula had aged for at least two days. Consistently, smoke-impacted hours during this event exhibited pollutant enhancements of four- to fifteen-fold for CO, $\text{PM}_{2.5}$, acetonitrile, and total measured VOCs (TVOCs), reaching peak values of 800 ppb CO, $120 \mu\text{g m}^{-3}$ $\text{PM}_{2.5}$, 2 ppb acetonitrile, and 85 ppb TVOCs in mid-September. Strong correlation ($r^2=0.9$; Fig. S2) among $\text{PM}_{2.5}$ measured at the Boyd Park and other tracers measured at the UM campus indicates thorough smoke mixing, spatially coherent smoke influence across Missoula at the surface. Brief furan spikes (≤ 0.7 ppb) on 12–13 and 18–19 September suggest additional influence from local fires. Overall, this event accounts for ~ 80 % of smoke hours in this month and is the focus of the enhancement ratio analysis (Sect. 5).

Event 3 (22–24 September) was a weaker resurgence of smoke from the same Oregon–California fires in Event 2. A preceding rain event on 20 September coincided with a rapid decrease in the 24-h mean $\text{PM}_{2.5}$ from 40 to $10 \mu\text{g m}^{-3}$, whereas most gas-phase species decreased less, with CO declining from 500 to 350 ppb. 24-h mean removed a substantial amount of

aerosol mass, as indicated by the sharp drop in $\text{PM}_{2.5}$ in Fig. from 40 to $10 \mu\text{g m}^{-3}$, whereas most gas-phase species persisted remain relatively less decreased, with CO declining from 500 ppb to 350 for CO and total VOCs from 50 to 30 ppb. This pattern suggests preferential removal of particle particles removal by precipitation scavenging and may provide a physical explanation for “smoke-present but low- $\text{PM}_{2.5}$ ” days. It also highlights that smoke identification based on column indicators (e.g., HMS) may not always reflect surface PM exposure when precipitation occurs. Subsequent south-westerly flow reintroduced the residual, aged smoke into the region. As a result, 24-h $\text{PM}_{2.5}$ concentrations reached $40 \mu\text{g m}^{-3}$ and hourly CO peaked at 350 ppb before a front cleared the valley, which is especially evident for $\text{PM}_{2.5}$ but still leaving fire influences for trace gases.

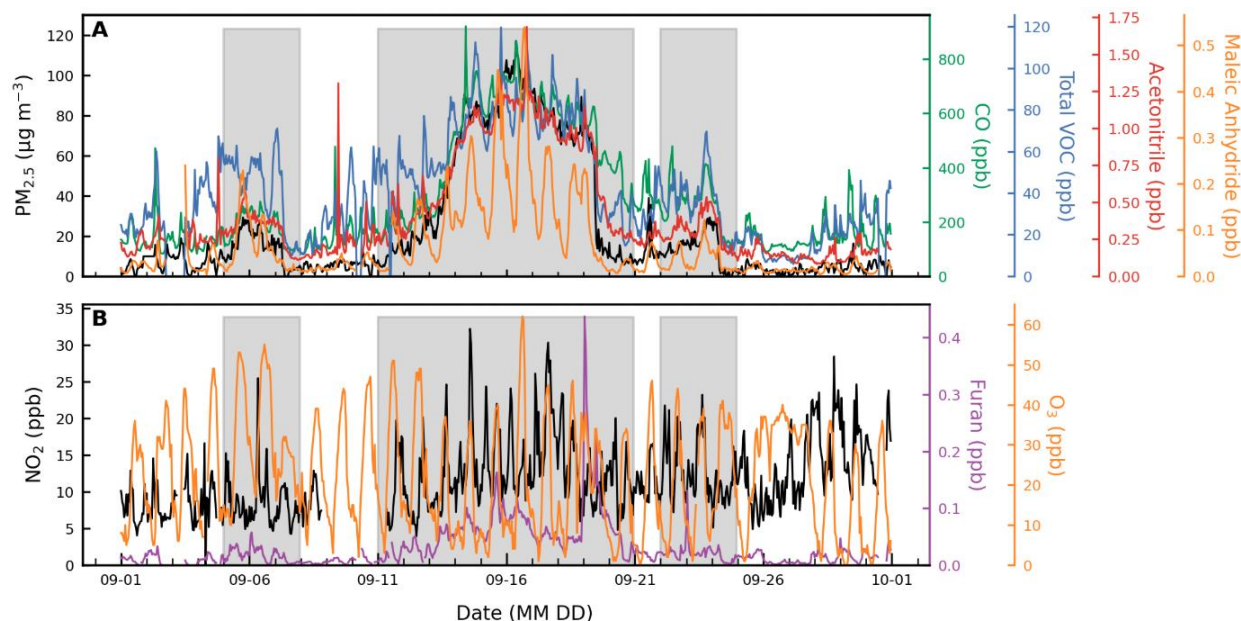
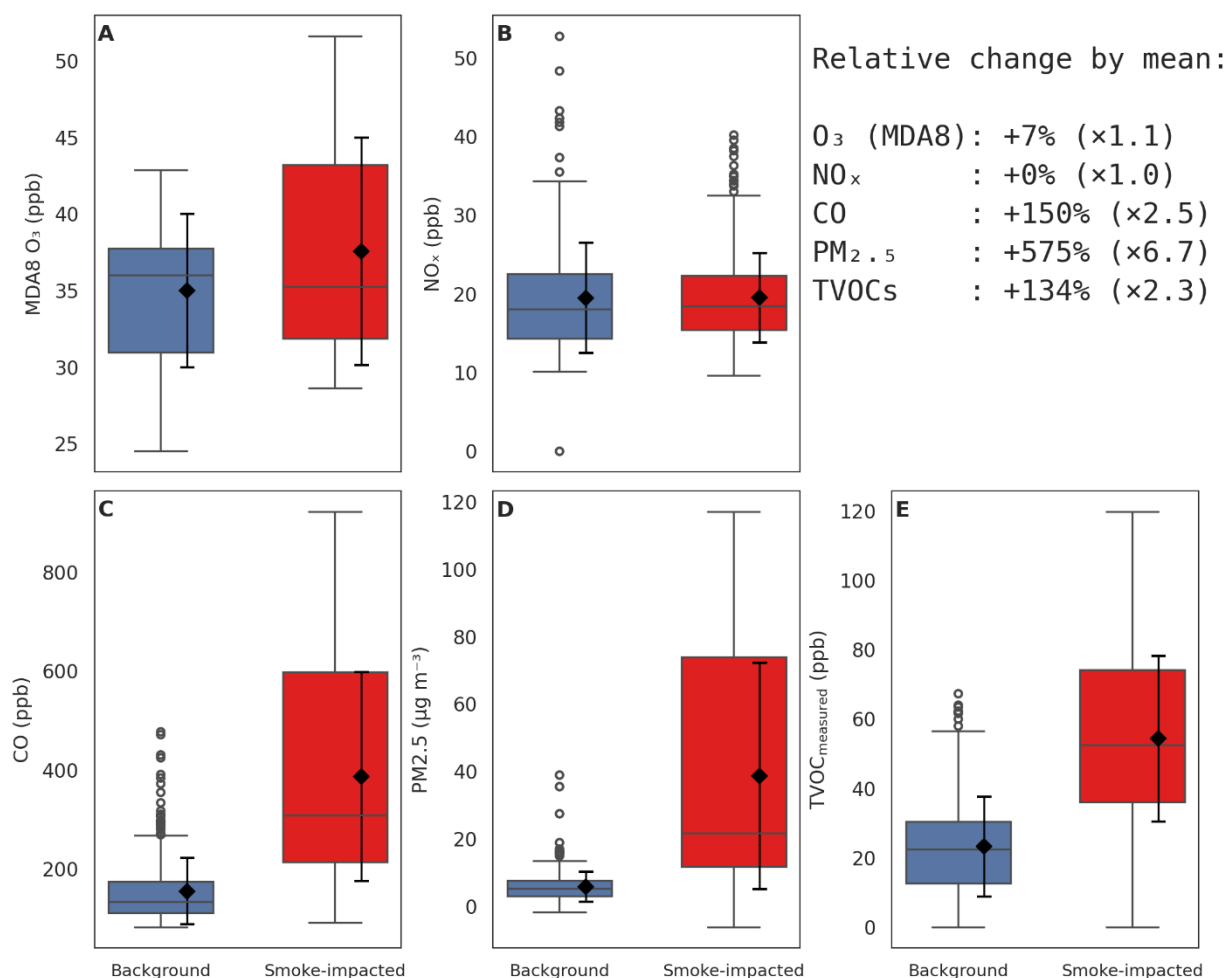


Figure 3. Time series of selected VOCs and criteria pollutants in Missoula, Montana, during September 2020. Time is shown in local time (MDT, UTC-6). (A) Hourly measurements of $\text{PM}_{2.5}$ (black; left axis), carbon monoxide (CO; green, right axis), total measured VOCs (blue, right axis), acetonitrile (red, right axis), and maleic anhydride (orange, right axis). (B) Concurrent hourly NO_2 (black; left axis), furan (purple; right axis), and ozone (orange, right axis). Gray shading indicates smoke days based on the criteria in Sect. 3.

Figure 4 compares pollutant concentrations during smoke-impacted and background periods in September 2020. On average, MDA8 ozone increased by 3 ppb (7%) during smoke episodes, while NO_x showed no visible change. In contrast, CO, $\text{PM}_{2.5}$, and TVOCs were significantly elevated, with hourly concentrations increasing by a factor of 3 – 8 compared to urban background. Average hourly CO concentrations increased from 160 ± 80 ppb (mean $\pm$ SD of hourly data) to 420 ± 205 ppb on smoke days. $\text{PM}_{2.5}$ showed even larger enhancements, rising from $6.1 \pm 4.5 \mu\text{g m}^{-3}$ to $43 \pm 34 \mu\text{g m}^{-3}$. The background CO and $\text{PM}_{2.5}$ concentrations agree with typical western US urban levels (150 – 200 ppb and 5 – $10 \mu\text{g m}^{-3}$) (Cope et al., 2024; Lill et al., 2022; Lopez-Coto et al., 2020; Pfister et al., 2011).

Measured hourly TVOCs tripled from 23 ± 15 ppb to 55 ± 24 ppb, with individual species enhancements summarized in Table S2. Ten VOCs increased by factors of ~ 4 –7, five of which were furanoids or their derivatives. These species included furfural, methylfurfural, 2-furanmethanol, 2-furanone, 5-hydroxy-2-furfural/2-furoic acid, maleic anhydride, acrylonitrile, methyl benzoic acid, methyl methacrylate, and anisole. Forty-eight VOCs increased by a factor of 2–4, while 16 species increased by a factor of 1–2. Fifteen of the 75 measured VOCs are on the EPA's list of HAPs, and they collectively represented 51% of TVOCs by average molar mixing ratio. During smoke events, total HAPs (THAPs) increased threefold relative to background periods (28 ± 13 ppb vs. 11 ± 7 ppb), with individual species exhibiting enhancements ranging from 40% (dichlorobenzene) to nearly fivefold (acrylonitrile and maleic anhydride). Figure S3 shows that OH reactivity (OHR) from CO and TVOCs is doubled during smoke-impacted days compared to background (14.2 s^{-1} vs. 7.1 s^{-1}). During background periods, the OHR was dominated by the biogenic tracer isoprene (0.89 s^{-1} ; 12.5 % of total OHR), followed by monoterpenes (9.6%), formaldehyde (8.3 %), CO (8.1 %), and other individual VOCs. During smoke-impacted days, CO became the largest contributor (1.4 s^{-1} ; 10 %), and the relative importance of monoterpenes fell to 5.6 %, consistent with previous urban smoke OHR analyses in Boise, ID (Permar et al., 2023). Other VOC groups show similar contributions to OHR in both periods. Together, these enhancements underscore the strong influence of regional wildfire smoke on western US air quality and motivate continued monitoring of smoke exposure in communities such as Missoula.



340 **Figure 4. Enhanced surface-level pollutant concentrations during smoke-impacted days/periods.** Boxplots ~~show of hourly surface~~
 345 ~~concentrations of~~ (A) ~~m~~Maximum daily 8-hour average ozone (MDA8 O₃), ~~and hourly concentrations of~~ (B) nitrogen oxides (NO_x), (C)
 carbon monoxide (CO), (D) fine particulate matter (PM_{2.5}), and (E) total measured volatile organic compounds (TVOCs) during smoke-
 impacted (red) and background (blue) periods ~~observed~~ in Missoula, Montana, during September 2020. Boxes represent interquartile
 ranges (25th–75th percentiles) with medians shown as center lines; whiskers extend to 1.5× the interquartile range. Black diamonds and
 error bars indicate mean ± standard deviation for each group. The right-hand summary block lists mean enhancement factors (smoke-
 impacted ÷ background) for each pollutant.

5 Smoke enhancement ratios (EnRs) and emission ratios (ERs)

We further apply a photochemical-age framework to determine whether VOC enhancement ratios (EnRs) measured in aged
 smoke reaching Missoula still preserve interpretable source information after multi-day transport and mixing (Figure 5).
 350 We provide corresponding methodological details in the Sect. S1. Originally developed for urban plumes, this framework
 provides a useful diagnostic for separating direct emissions, chemical removal and formation (de Gouw et al., 2017). [Here,](#)

photochemical age is an oxidation-based metric inferred from the VOC ratio clock and should not be interpreted as the exact physical time since emission, with some negative values reflecting clock uncertainty, background variability, or mixing with fresher air. For primary VOCs, linear fits of $\ln(\text{EnR})$ versus photochemical age yield back-extrapolated time-zero emission ratios (ERs) and effective OH rate constants (k_{OH}) under the assumptions of plume-integrated aging. For oxygenated VOCs (OVOCs), the same relationships are interpreted qualitatively because secondary formation can offset chemical loss. We provide methodological details in the Sect. S1. ~~We provide corresponding methodological details in the Sect. S1. We here combine enhancement ratios (EnRs) with a photochemical clock to extract chemical processing information from fixed site observations of aged smoke at Missoula~~

~~with a photochemical clock to assess smoke aging for all measured VOCs. Figure 5 illustrates the $\ln(\text{EnR})$ age framework used to retrieve infer approximate time zero emission ratios (ERs) and effective OH rate constants (k_{OH}) for representative primary aromatics, where the regression intercept and slope correspond to ER and k_{OH} , respectively (method in Sect. S1).~~

For relatively long-lived primary aromatics, the framework-inferred ERs are physically reasonable, indicating that aged smoke arriving at Missoula still retains measurable source signatures for these species. ~~From the photochemical clock analysis of aged smoke reaching Missoula, we~~ We infer initial ERs of 2.05 ± 0.02 ppb ppm⁻¹ for benzene and 1.42 ± 0.02 ppb ppm⁻¹ for toluene, and 1.20 ± 0.05 ppb ppm⁻¹ for C₈-aromatics. These values agree with near-source ranges reported from the WE-CAN and FIREX-AQ campaigns within ~20% (benzene: 1.8–2.3 ppb ppm⁻¹; toluene: 1.2–1.5 ppb ppm⁻¹) (Gkatzelis et al., 2024; Permar et al., 2021), indicating that the framework can recover plausible source-like ERs for relatively unreactive primary species even after multi-day transport. However, inferred ERs for C₈–C₁₀ aromatics are higher than published near-source wildfire values by roughly a factor of 2–3, suggesting that these species were substantially influenced by non-fire sources during transport. Urban mixing is a likely contributor, consistent with city-based measurements showing elevated aromatics relative to CO during wildfire-smoke periods (Cope et al., 2024).

~~We also infer ERs of 0.41 ± 0.03 ppb ppm⁻¹ for C₉-aromatics and 0.18 ± 0.01 ppb ppm⁻¹ for C₁₀-aromatics. For C₃–C₅ alkenes (propene, butenes, and pentenes/methylbutenes) and 1,3-cyclopentadiene, inferred ERs are 1.19 ± 0.04 , 1.45 ± 0.05 , 0.17 ± 0.01 , and 0.10 ± 0.01 ppb ppm⁻¹, respectively.~~

Beyond ER derivation, the $\ln(\text{EnR})$ -age framework also provides insight into the net photochemical evolution of VOCs. For primary VOCs, EnRs decreased significantly with photochemical age ($p \ll 0.01$), and the relative decay rates broadly tracked their OH rate constants (k_{OH})

~~The inferred benzene and toluene ERs agree with near-source ranges reported from the WE-CAN and FIREX-AQ campaigns within ~20% (benzene: 1.8–2.3; toluene: 1.2–1.5 ppb ppm⁻¹). For~~

385 ~~The relative decay rates also broadly followed their OH rate constants (k_{OH}). For example, benzene exhibited only modest decay over one week of photochemical aging, whereas toluene and C₈ aromatics decayed more rapidly, consistent with their higher reactivitywith higher k_{OH} ~~decayed more rapidly~~. The inferred k_{OH} values ~~inferred from the photochemical clock~~ were $(9.8 \pm 1.6) \times 10^{-13}$ and $(5.6 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for benzene and toluene, respectively. These values, agreeing with literature within ~10–20%, although this agreement is partly expected because photochemical age is derived from the~~

390 toluene-to-benzene clock. For C₈ aromatics, the inferred k_{OH} (7.9×10^{-12} cm³ molecule⁻¹ s⁻¹) lies between those of ethylbenzene and the xylene isomers, as expected for a lumped mixture, consistent with expectations for a lumped mixture.

The framework becomes less robust for more reactive hydrocarbons and OVOCs. Effective k_{OH} values inferred for C₉–C₁₀ aromatics and small alkenes are lower than literature values by factors of 3 or more, indicating that simple plume-integrated first-order loss does not adequately describe these compounds in aged smoke.

In contrast, effective k_{OH} inferred for several more reactive hydrocarbons (e.g., C₉–C₁₀ aromatics and small alkenes) are lower by factors of 3 or more than literature.A likely reason is that the most reactive species were already preferentially removed during the earliest, OH-rich stage of plume evolution, before the smoke reached Missoula. Additional uncertainty

400 likely arises from dilution, urban mixing, background correction, and species lumping. OVOCs such as methanol, formaldehyde, and acetaldehyde, exhibited weaker and often statistically insignificant ln(EnR)-age trends ($p \approx 0.02$ – 0.21), and in several cases the relationships flattened with age. Such behavior is consistent with secondary production partially offsetting chemical loss.This low bias is consistent with ground-based sampling of aged wildfire smoke and likely reflects preferential loss of highly reactive VOCs during the first few hours after emission, when OH concentrations are highest;

405 thus, the plume sampled at MSO represents the surviving fraction of the original emissions. Additional contributions may arise from dilution and mixing with urban air, as well as uncertainties associated with background correction and species lumping.

We find that EnRs of primary VOCs decrease significantly with photochemical age ($p \ll 0.01$), consistent with OH-driven oxidation. In contrast, oxygenated VOCs (OVOCs) such as methanol, formaldehyde, and acetaldehyde exhibit weaker and often statistically insignificant ln(EnR)–age trends ($p \approx 0.02$ – 0.21), and in several cases the relationships flatten with age, consistent with secondary production partially offsetting chemical loss during plume evolution., while additional contributions from non-fire sources such as biogenic emissions may further obscure the relationships

410 Other non-fire sources such as biogenic emissions could also affect the analyses for OVOCs. Together, these results show that the ln(EnR)-age framework remains informative for relatively long-lived primary VOCs, but becomes progressively less diagnostic for reactive hydrocarbons and especially OVOCs in regionally aged smoke. As a result, the photochemical clock framework is well suited for constraining estimating ERs (and effective k_{OH}) for primary VOCs, though it could be subject to large uncertainty due to the influence of the urban general background, but This approachit cannot be directly used to derive ERs

415

for OVOCs because net production violates the assumption of purely first-order decay (Sect. S1). Overall, photochemical
clocks provide useful constraints on ERs for many primary VOCs in aged smoke but can overestimate BB contributions for
species with strong non-fire sources.

To complement the age-framework analysis, we also calculated event-integrated EnRs of PM_{2.5} and 27 VOCs relative to CO
as bulk descriptors of the aged-smoke event. These values provide an observational reference for VOC-to-CO relationships
in regionally aged smoke and are also used for model evaluation in Sect. 8. Species-level values and literature comparisons
are provided in Table S3 and Fig. S4.

Additionally, we report the event-integrated EnRs of PM_{2.5} and VOCs relative to CO. The PM_{2.5} EnR in several-day aged
smoke was $0.11 \pm 0.01 \text{ g g}^{-1}$ at Missoula, consistent with previous surface measurements ($0.11\text{--}0.13 \text{ g g}^{-1}$) but about half of
high-elevation/aircraft value. We derived event-integrated EnRs for 27 VOCs, excluding species weakly correlated with CO
($R^2 < 0.4$); corresponding species-level EnRs and literature comparisons are summarized in Table S3 and Fig. S4.

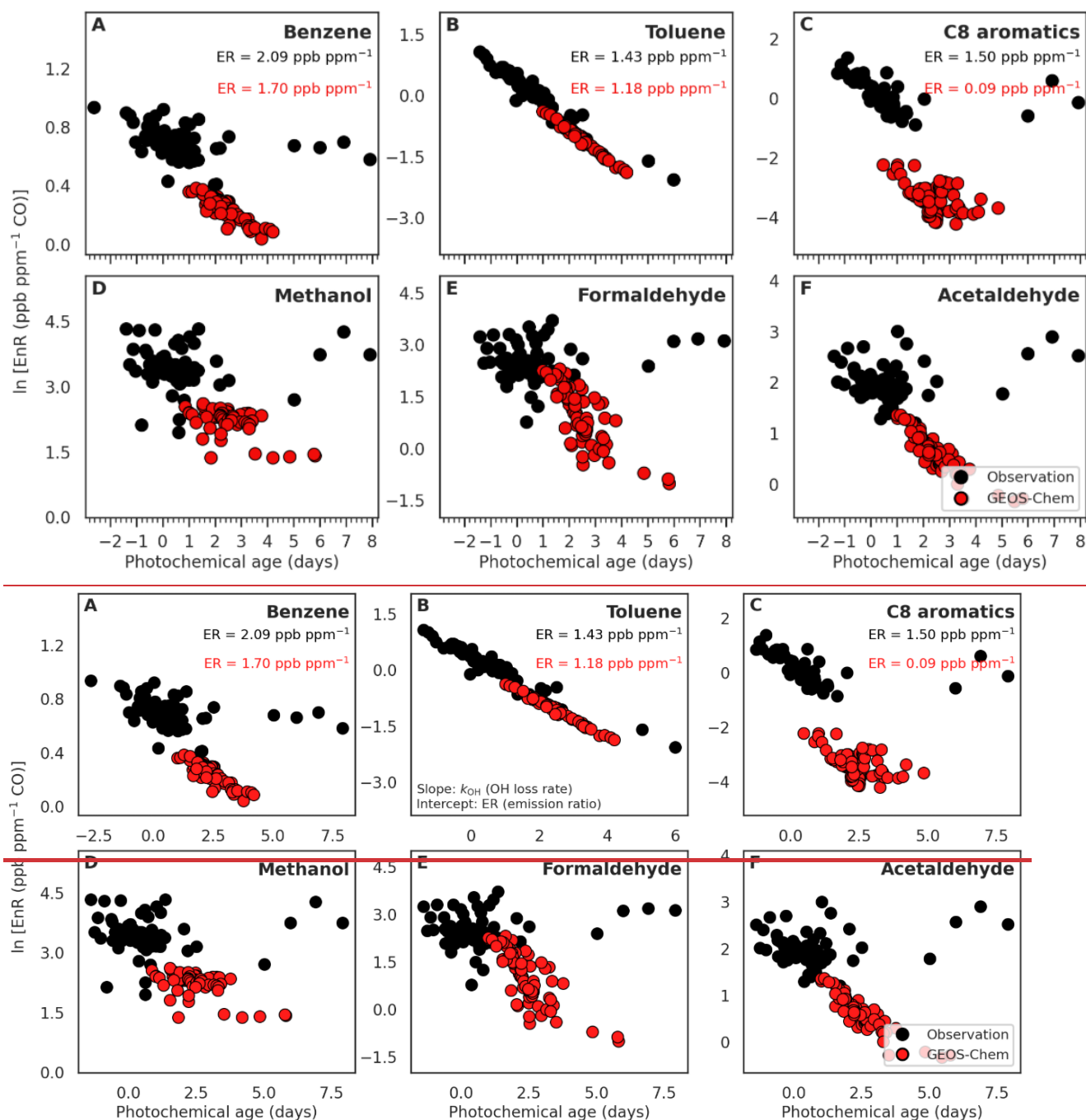


Figure 5. Observed and modeled enhancement ratios (EnR) of key volatile organic compounds (VOCs) versus photochemical age. Panels show $\ln(\text{EnR})$ versus photochemical age for (A) benzene, (B) toluene, (C) C₈ aromatics, (D) methanol, (E) formaldehyde, (F) acetaldehyde, where EnR is defined as $\Delta\text{VOC}/\Delta\text{CO}$ (ppb ppm⁻¹ CO). Observations are shown as black circles and results from GEOS-

Chem driven by GFAS fire emissions are shown as red circles. ~~Points represent consecutive 3 h binned data during the main aged-smoke event. Photochemical age is derived from the toluene-to-benzene ratio clock (Sect. S1).~~ ~~Points represent 3 h binned data.~~

6 Non-monotonic O₃–PM_{2.5} relationship

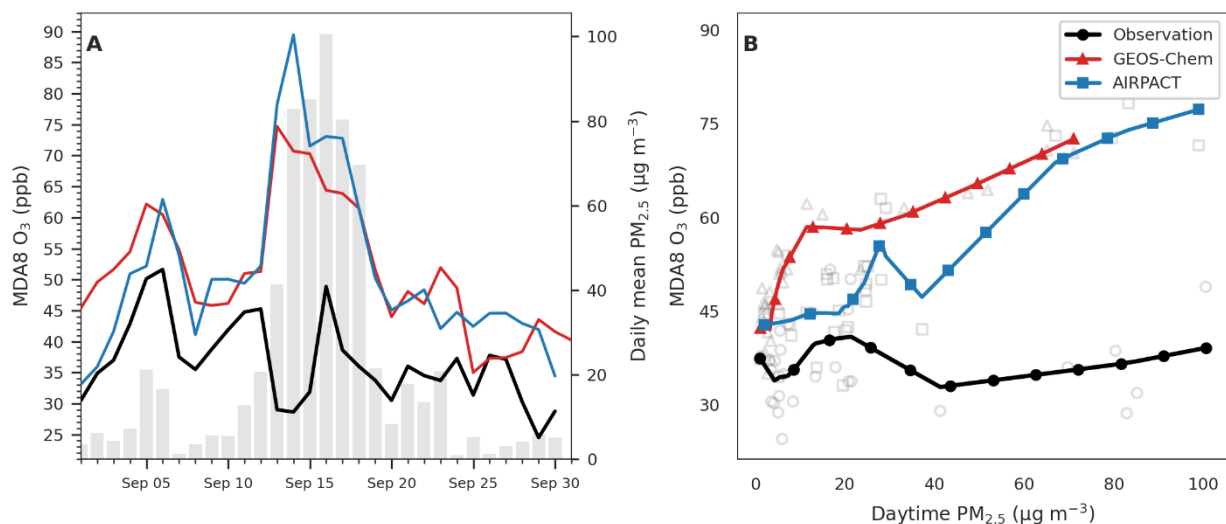
440 Figure 6 shows the relationship between maximum daily 8-hour average (MDA8) O₃ and daytime mean PM_{2.5} at Missoula during September 2020. During the strongest smoke episodes, observed MDA8 O₃ was suppressed by up to ~15 ppb (e.g., 6–7 September; Fig. 6A). These decreases coincide with ~50% reductions in downwelling shortwave radiation (SW) (Fig. S5A), a first-order proxy for actinic flux and photolysis $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$, indicating attenuated photolysis reduces radical production and suppresses in-situ ozone formation. NO_x levels were not substantially different from the urban background.

445 In addition, heavy smoke was associated with lower observed daytime maximum temperature and a shallower planetary boundary layer height (PBLH) (Fig. S5B–S5C), which may further reduce surface ozone by slowing reaction rates and weakening entrainment of O₃-rich air aloft.

Across BB days, the relationship between MDA8 O₃ and daytime mean PM_{2.5} is non-monotonic (Fig. 6B). A locally weighted scatterplot smoothing (LOWESS) curve suggests that MDA8 O₃ increases at low PM_{2.5} (< ~20 μg m⁻³), ~~but decreases at moderate PM_{2.5} (~20–60 μg m⁻³), and may increase again at higher PM_{2.5} (>60 μg m⁻³) despite only four daily points exist.~~ The non-monotonic relationship likely reflects a transition from precursor-driven O₃ production under light smoke (< ~20 μg m⁻³) to aerosol-dominated suppression of net O₃ production at moderate aerosol loadings (>~20–60 μg m⁻³).

455 The non-monotonic behavior is not unique to Missoula but is also evident across other northwestern sites during the same September 2020 period. At Cheeka Peak (WA) and Eugene (OR), ~~both of which were where they were near the BB sources during that month, and~~ daily PM_{2.5} reached up to 250 and 450 μg m⁻³, respectively. O₃ similarly increased ~~s~~ with PM_{2.5} under low smoke but leveled ~~ed~~s off or declines at higher aerosol loadings (Fig. S6). ~~Such Similar~~ nonlinear O₃–PM_{2.5} relationships

460 have been reported ~~aeross-in multi-year, multi-site analyses across the western U.S., smoke observations, with reflecting similar controlling factors that affect the~~ O₃ ~~increasing with PM_{2.5} under light-to-moderate smoke and decreasing under heavier smoke~~ (Buysse et al., 2019; McClure and Jaffe, 2018). ~~smoke interaction.~~



465 **Figure 6. Temporal evolution and PM_{2.5} dependence of maximum daily 8-hour average ozone during September 2020.** (A) Time series of daily maximum 8-hour average ozone (MDA8 O₃, ppb) from surface observations (black), GEOS-Chem driven by GFAS fire emissions (red), and the AIRPACT forecast system (blue). Shaded bars (right axis) show observed daily mean PM_{2.5} (µg m⁻³), providing context for smoke influence. (B) Relationship between MDA8 O₃ and daytime PM_{2.5} for observations (circles), GEOS-Chem (triangles), and AIRPACT (squares). Open gray symbols show individual daily values for observation and model simulations. Solid curves denote locally weighted regression (LOWESS) fits applied consistently across datasets (smoothing fraction = 0.5; robust iteration = 3).
 470 ~~AIRPACT outputs are sampled in space and time at the monitoring locations and~~ were obtained from the Washington State University AIRPACT data portal (<https://airpact.wsu.edu/>).

7 Chronic and acute health risks

Figure 7 summarizes the upper-limit chronic inhalation risks from wildfire smoke, assuming that a 2020-style wildfire season were to recur annually over the next century. We do not seek to estimate the total public-health burden of wildfire smoke, but instead use several well-defined screening metrics for PM_{2.5} and HAPs with available toxicity values as a transparent basis for comparison. Methodological details are described in Supplement Sect. S2. Over lifetime exposure (70 yr), the total excess cancer risk attributable to wildfire smoke is 100 cases per million people. Roughly 90 % of this smoke-driven risk is attributed to PM_{2.5}, with the remaining 10 % arising from HAPs combined. Among HAPs, the major contributors are formaldehyde (42 % of HAP cancer risk), benzene (34 %), acetaldehyde (8 %), acrylonitrile (9 %), and naphthalene (6 %). These relative contributions agree with recent aircraft observations of lofted plumes and confirm that PM_{2.5} dominates cancer risk both aloft and at ground level (Pye et al., 2024).

For context, the climatological annual-mean of non-smoke background PM_{2.5} is ~6 µg m⁻³ in Missoula. If the same BB-impacted days had instead experienced typical non-smoke background concentrations~~As an assumed counterfactual baseline, if the same set of BB-impacted days had instead experienced typical non smoke background concentrations~~~~If the BB-impacted days instead experienced typical non smoke conditions,~~ the corresponding PM_{2.5}-attributable excess cancer risk

would be ~15 cases per million people~~the excess cancer risk would be ~15 cases per million people~~. Thus, the 2020-style wildfire season increases the PM_{2.5}-attributable cancer risk by ~7× relative to the PM-related baseline. Even using a 10-fold lower PM_{2.5} unit-risk estimate ($4.8 \times 10^{-5} \mu\text{g}^{-1} \cdot \text{m}^3$), PM_{2.5} still accounts for ~50% of the total cancer risk, ~~and with~~ the total risk remain~~ings~~ ~20 cases per million people (i.e., ~30% higher than the baseline). Thus, even when the community's exposure to wildfire smoke is annualized and using a lower-bound PM_{2.5} unit-risk estimate, aged wildfire smoke ~~as at~~ the level experienced in September 2020 in Missoula still shows a quantifiable carcinogenic burden.

Non-cancer chronic risk is expressed as a hazard index (HI), with the dominant effects in this study associated with respiratory and cardiopulmonary systems. The full calculation framework is provided in Supplement Sect. S2. The calculated HI = 3 indicates appreciable potential for adverse effects. HAPs account for ~90 % of this index, driven by acrolein (60 % of HAP non-cancer risk), formaldehyde (24 %), acetaldehyde (3 %), and all other species (< 1 % each). PM_{2.5} contributes to the remaining ~10 %. The result contrasts with aircraft-based assessments, in which PM_{2.5} dominated non-cancer risk (O'Dell et al., 2020; Pye et al., 2024). The lower relative contribution of PM_{2.5} observed here likely reflects the evaporation of semi-volatile particulate mass as plumes descend from aloft to the surface (Pagonis et al., 2023; Selimovic et al., 2019, 2020). If PM_{2.5} were assumed 10-times more toxic (~~RfC = $0.5 \mu\text{g} \cdot \text{m}^{-3}$, comparable to acrolein~~), it would instead contribute ~70 % of the HI.

No acute reference exposure levels (RELs) are available for PM_{2.5}, so the acute HI analysis was restricted to HAPs. During September 2020, 719 of 720 one-hour windows exhibited HI < 1, implying negligible acute non-cancer concern. A single exceedance (19 September, HI = 1.05) was apportioned to acrolein (52 %), formaldehyde (32 %), benzene (12 %), and other HAPs (< 5 %). Expanding to eight-hour windows (Fig. S7), 49 % of periods remained below the HI = 1 threshold, whereas 51 % exceeded it, aligned with smoke incursions. Of the exceedances, 30 % fell within HI = 1–2 and 21 % reached up to HI = 5. The eight-hour hazards were driven by formaldehyde (38 %), acrolein (31 %), and benzene (29 %), with all other HAPs contributing < 2 %.

The recurrence of the same three drivers across acute and chronic metrics highlights two practical needs. First, smoke-impacted communities would benefit from continuous, high-time-resolution monitoring of formaldehyde, acrolein, and benzene to track rapidly evolving exposures and guide advisories. Second, because particle-only strategies do not address these gases, indoor interventions should pair particle filtration (HEPA or MERV 13+ for PM_{2.5}) with sorbent media (e.g., activated carbon) when using indoor air cleaners during smoke events (Maximoff et al., 2022; May et al., 2021).

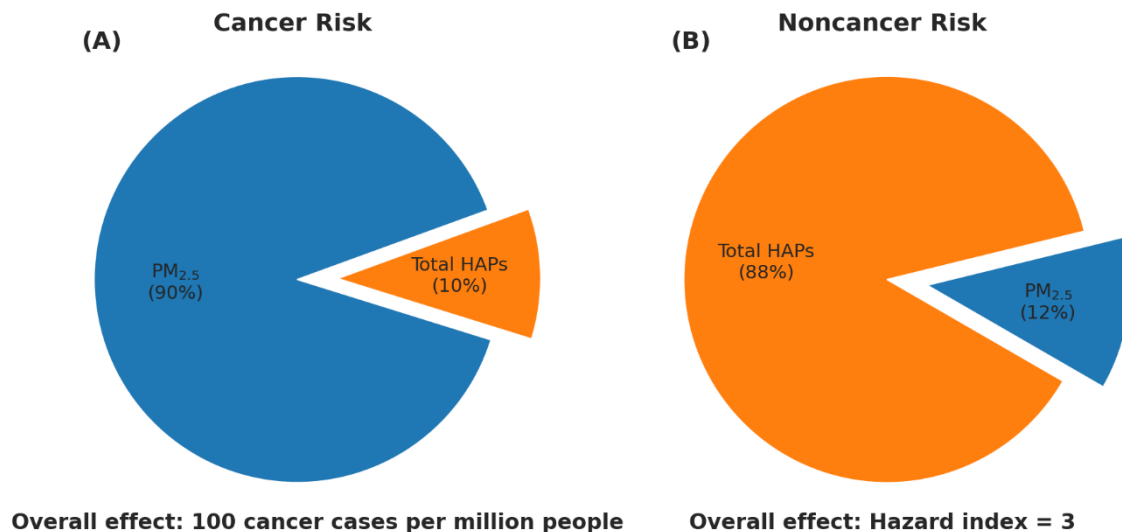


Figure 7. Chronic health-risk from fine particulate matter (PM_{2.5}) and hazardous air pollutants (HAPs). (A) Estimated excess cancer risk (cases per million people) attributed to ambient PM_{2.5} versus all combined HAPs. (B) Noncancer hazard index (HI) attributed to ambient PM_{2.5} versus combined HAPs. In each panel, slices are exploded for clarity, and labels show the percentage of total risk contributed by each component. The bottom annotation reports the overall risk magnitude: total cancer cases per million for panel A and HI for panel B.

8 Model evaluation

8.1 Model uncertainties in fire emissions and OH exposure

Figure 8 compares hourly observations of CO, PM_{2.5}, and four representative VOCs with model simulations; additional VOC comparisons are shown in Fig. S8. The default GEOS-Chem simulation captures the timing of smoke-impacted enhancements of CO, PM_{2.5}, and VOCs during the first two events (5–7 September and 11–20 September), with high correlations ($R^2 = 0.8$ – 0.9 for hourly measurements). The agreement indicates that the model generally captures the timing, transport, and location of fire smoke. However, the model fails to reproduce the observed enhancements during Event 3 (22–24 September), likely reflecting overly efficient modeled wet scavenging during the 21 September rainout and/or unresolved smoke transport pathways discussed in Sect. 4.

Even during Events 1–2, GEOS-Chem underestimates the magnitude of fire impacts, with low biases of 30–40% for CO and PM_{2.5}, 60–80% for primary aromatics, and 50–90% for most OVOCs. Model performance during background periods is notably better, suggesting BB-related emissions and/or chemistry drive the majority of these underestimations under smoky conditions. MEK is the only exception, showing an average high bias of ~20%, reflecting overestimated anthropogenic or biogenic emissions, as pointed out in earlier studies (Chen et al., 2019; Jin et al., 2023).

540 GEOS-Chem systematically underestimates event-integrated VOC EnRs by 35% for benzene and 60–80% for other VOCs (Fig. S9), despite ERs being reproduced within ~20–40% in Fig. 5 and other work (Jin et al., 2023). This ER–EnR decoupling points to chemistry-related biases: the model overpredicts plume photochemical age (Fig. 5) and OH exposure (by ~100%; Fig. S10), which over-oxidizes VOCs relative to CO and depresses EnRs. For OVOCs, the negative bias of EnRs likely also reflects missing secondary production, particularly for methanol, formaldehyde, and acetone, which exhibit multi-day growth in aged smoke in Fig. 5 and previous work (Alvarado et al., 2020; Bates et al., 2021; Holzinger et al., 2005; Jin et al., 2023). By contrast, GEOS-Chem overestimates the event-integrated PM_{2.5} EnR by ~33%, implying excessive PM_{2.5} produced (or retained) per unit CO, consistent with the reported biases in the simplified GEOS-Chem SOA scheme used here (Oak et al., 2022; Pai et al., 2019).

550 ~~An~~Our previous ~~earlier~~ study using airborne observations to constrain total western wildfire emissions showed that GFAS likely underestimates the fuel consumed in these fires by a factor of three. Motivated by aircraft constraints that standard inventories underpredict BB emissions by ~3× (Jin et al., 2023). Thus, we conducted a 3×BB sensitivity test, which improved overall model agreement with 2020 MSO measurements and reduced modeled OH by ~2×. This ~~and~~ lowered the OH-exposure positive bias from ~100% to ~30% during Missoula smoke episodes. The remaining modeled OH positive bias likely reflects missing OH reactivity from unrepresented compounds such as furanoids (Coggon et al., 2019; Jin et al., 2026; Permar et al., 2023). Correspondingly, gas-phase NMBs improve on average across smoke-impacted periods ~~improve~~ (CO: –40% to +20%; benzene: –70% to –10%; toluene: –80% to –50%), although CO appears to be overcorrected during some periods, especially Event 2. Several OVOCs remain substantially underestimated (e.g., methanol –80% to –50%; formaldehyde –70% to –40%; acetaldehyde –75% to –35%; acetic acid –80% to –45%; acetone –60% to –40%), consistent with missing secondary production ~~as a likely cause as the cause~~ of the persistent OVOC low bias. Meanwhile, PM_{2.5} shifts from a –30% bias to a +80% bias, indicating that a uniform BB scaling cannot reconcile gases and aerosol. It also points to limitations in the default GEOS-Chem “simple SOA” fire treatment, where the SOA precursor tracer (SOAP) is parameterized proportional to BB CO; scaling fire CO therefore scales SOAP and can over-amplify OA and PM_{2.5} during smoke events.

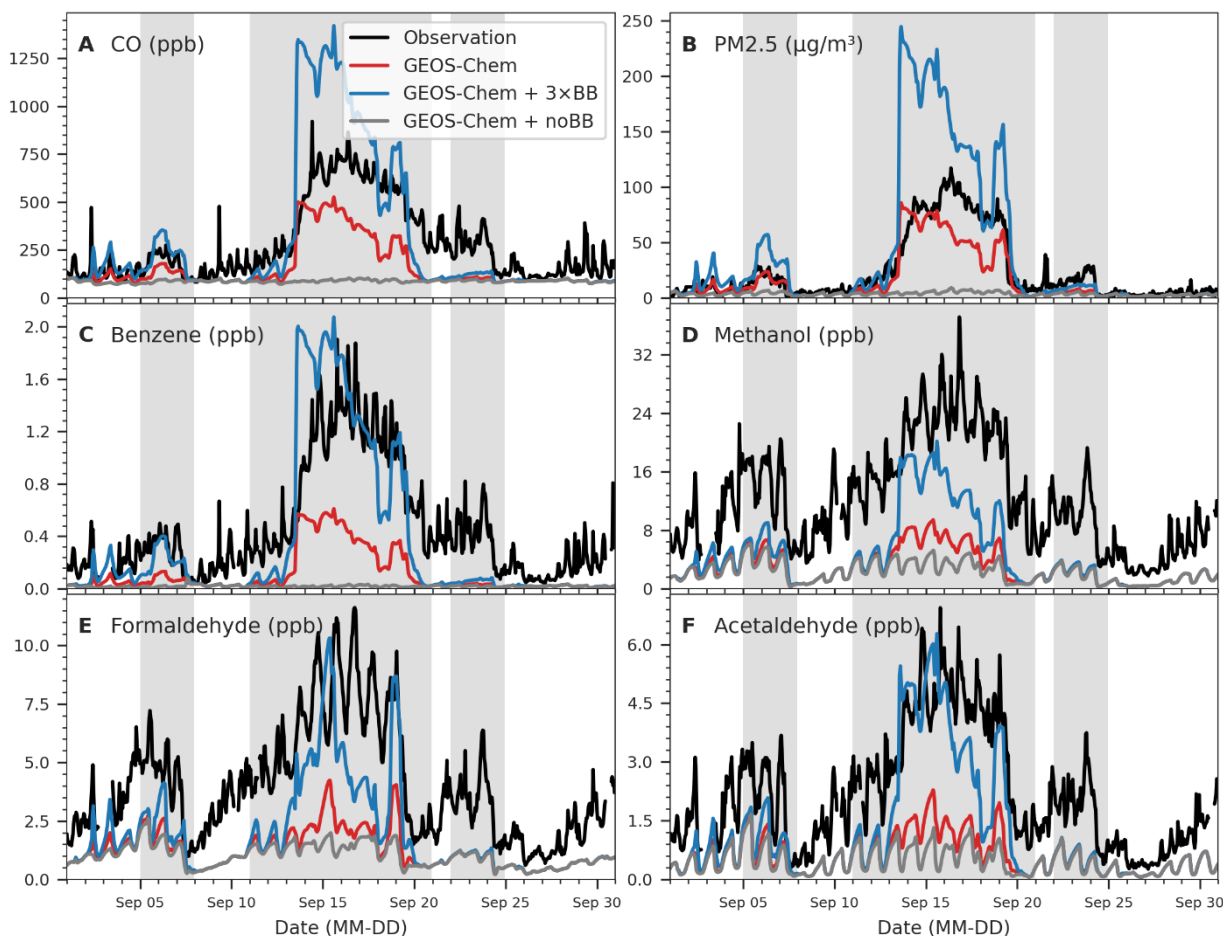


Figure 8. Time series of observed and modeled concentrations for key pollutants during September 2020 in Missoula, Montana. Observations (black lines) are compared with the base GEOS-Chem simulation (red). Also shown are two model sensitivity tests: one with tripled biomass burning emissions (GEOS-Chem + 3×BB; blue) and one with biomass burning emission turned off (GEOS-Chem + noBB; gray). Panels show hourly averaged concentrations of (A) carbon monoxide (CO), (B) fine particulate matter (PM_{2.5}), (C) benzene, (D) methanol, (E) formaldehyde, and (F) acetaldehyde. Model outputs are sampled at the observational location and time. Gray shading indicates smoke-impacted days based on the criteria in Sect. 3. The modeled PM_{2.5} is calculated offline from the SpeciesConc diagnostic as the sum of inorganic ions ($1.10 \times [\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}]$), black carbon (BCPI + BCPO), organic matter ($(\text{OCPO} + 1.05 \times \text{OCPI}) \times \text{OM:OC}$), fine dust ($\text{DST1} + 0.30 \times \text{DST2}$), sea salt ($1.86 \times \text{SALA}$), and secondary organic aerosol ($1.05 \times (\text{SOAS} + \text{SOAP} + \text{SOAIE} + \text{SOAGX})$).

8.2 Model uncertainties in ozone formation under high PM_{2.5}

GEOS-Chem overestimates MDA8 O₃ in September of 2020 by ~15 ppb on average and fails to capture the observed day-to-day variability (Fig. S11), regardless of the BB emission scenario (noBB, base, or 3×BB). The persistent positive bias in the noBB simulation suggests an overestimate of background MDA8 O₃. Biases further increase on smoke days, reaching up to ~70 ppb at Missoula and scaling with observed daytime PM_{2.5} in the base model ($r \approx 0.7$) (Fig. S12). Similar smoke-amplified positive ozone biases have been reported in other CTMs (e.g., CMAQ-based simulations; Fig. 6A) and in prior

580 ~~GEOS-Chem~~CTM work (Baker et al., 2016, 2018; Zhang et al., 2014), suggesting that regional-to-global CTMs may systematically overestimate background O₃ and/or net O₃ production under BB influence.

However, the main value of this analysis is not simply to document another case of positive O₃ bias in smoke. Rather,
Figure 6B shows that GEOS-Chem does not reproduce the observed non-monotonic O₃–PM_{2.5} relationship. At Missoula, the
585 model captures the initial O₃ increase when PM_{2.5} is below ~30–40 µg m⁻³, but it predicts increasing O₃ at higher PM_{2.5},
whereas observations flatten or decline beyond this threshold. A similar failure is evident in AIRPACT, a publicly available
regional air quality forecasting system (Chen et al., 2008; Vaughan et al., 2004). Across Missoula and other western U.S.
sites (e.g., Eugene, OR; Yreka, CA; Cheeka Peak, WA; Fig. S6), observations show strong O₃ suppression under heavy
smoke, while AIRPACT predicts a monotonic increase of O₃ with PM_{2.5}. Together, these consistent biases across two
590 independent CTM frameworks point to a shared model limitation in representing the nonlinear ozone response under intense
BB smoke, which may partly explain the positive O₃ bias commonly seen in CTMs under wildfire influence.

Part of the positive model bias may reflect errors in meteorological processes under smoke conditions. First, GEOS-Chem
captures the relative reduction in broadband shortwave radiation on smoke days, suggesting reduced photolysis (i.e., $J(\text{O}^1\text{D})$
595 and $J(\text{NO}_2)$), but it still overestimates the absolute downwelling shortwave flux by ~25% during smoke-impacted periods
(versus ~20% on non-BB periods) (Fig. S5). These “over-sunny” conditions likely result in excessive radical production,
although we lack observed J values for a direct photolysis evaluation. Second, model temperature is biased high by +1.13 °C
on smoke days (implying ~20% faster PAN thermal loss at ~289 K) ~~and biased low by -1.5 °C during non-BB periods,~~
which could favor enhanced NO_x recycling and ~~sustained contribute to higher in situ modeled~~ O₃ formation. Third, ~~model~~
600 PBLH tracks the temporal variability of assimilated products (e.g., HRRR, 3 km) but is higher by ~500 m (33%) during
smoke ~~and slightly lower (-20 m, -1%) during non-BB periods.~~ The elevated PBLH can increase entrainment of O₃-rich air
from aloft and ~~thereby contribute to higher modeled background strengthen the influence of transported (upwind)~~
~~background~~ O₃. In addition, heterogeneous NO₃/N₂O₅ loss in BB plumes may be too weak (Decker et al., 2019, 2021), which
could prolong NO_x lifetime and contribute to overproduction of O₃ under smoke (Shen et al., 2025). We cannot attribute the
605 discrepancy to a single process, but collectively these factors provide a plausible explanation for the spurious modeled
MDA8 O₃ increases during heavy smoke and the growth of the O₃ error with PM_{2.5}.

8.3 Model uncertainties in health-risk estimates

GEOS-Chem captures the order of magnitude of the smoke-attributable excess lifetime cancer risk but still underestimates it
by ~40% (63 vs 100 per million), primarily due to its low bias in PM_{2.5}. Because cancer risk is dominated by PM_{2.5} whereas
610 HI is driven by a small number of high-potency HAPs, model errors in HAP composition have a much larger impact on HI
than on cancer risk. Accordingly, the base simulation substantially underestimates chronic non-cancer risk ($\text{HI} \approx 0.3$, $\sim 10\times$

lower than observed). For acute risk, GEOS-Chem predicts no 1-h HI exceedances (max 1-h HI = 0.2) and only limited 8-h exceedances (15 hours with HI > 1; max 8-h HI = 1.2), far fewer and weaker than observed (476 hours; max 8-h HI = 6.3).

615

In the 3×BB sensitivity run, the modeled cancer risk increases to 155 per million (exceeding the observation-based estimate), highlighting the uncertainty in modeled PM_{2.5} under smoke conditions. Acute non-cancer risk increases in the 3×BB run (135 hours with 8-h HI > 1; max 8-h HI = 3.4), but the model still predicts no 1-h exceedances (max 1-h HI = 0.5). This low bias in HI is driven by incomplete BB VOC representation, including underestimated BB VOC burdens (by ~3×), missing secondary sources, and missing high-potency HAPs (e.g., acrolein, which accounts for >50% of the observed HI). Overall, CTMs such as GEOS-Chem can provide a first-order estimate of PM_{2.5}-driven cancer burden, but the predicted HI is much less reliable without improved HAP speciation, secondary production, and inclusion of high-potency compounds.

620

9 Conclusion

Missoula, Montana (46.9 °N, 114.0 °W). ~~Missoula~~ experienced persistent and chemically complex wildfire smoke during September 2020, reflecting the widespread influence of wildfires across California and the Pacific Northwest. We report hourly surface observations of PM_{2.5}, CO, NO_x, O₃, and 75 speciated VOCs in ~~Missoula, Montana (46.9 °N, 114.0 °W)~~, during the wildfire-smoke-impacted month of September 2020. Of the 75 measured VOCs, 15 were classified as HAPs by the EPA. Leveraging comprehensive measurements, we quantified EnRs of PM_{2.5} and VOCs relative to CO in smoke aged for several days, and characterized the temporal evolution of criteria pollutants and VOCs under smoke-impacted and no-/low-smoke conditions. We performed nested GEOS-Chem simulations and compared them with observations to constrain BB emissions and photochemistry in the model. Finally, we assessed public health risks based on regulatory exposure metrics for PM_{2.5} and HAPs.

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We find that combining gas-phase tracers with conventional particle-based diagnostics improves the identification of surface-level wildfire smoke in urban environments. While traditional aerosol-based smoke diagnostics (HMS, AERONET, and PM_{2.5}) remain useful for detecting dense, optically thick plumes, they often misclassify events when plumes are aloft, optically thin, or when rainfall removes aerosols. In contrast, VOC tracers, especially furan and maleic anhydride (MA), provide complementary value: furan identifies fresh smoke, while MA captures more aged plumes. We thus develop a balanced multi-indicator rule that requires concurrent enhancements in at least three independent tracers, thereby capturing smoke episodes with higher confidence. Three major smoke events driven by long-range transport resulted in multi-day elevations of CO and total VOC abundances by factors of 2–3, while ozone increased only modestly and NO_x showed little to no change. In addition, PM_{2.5} and total HAPs (which comprised approximately ~half of the measured TVOCs by molar fraction) increased by factors of ~3–8 during smoke periods. Concurrently, the total OH reactivity doubled (14.2 vs 7.1 s⁻¹),

640

shifting the dominant OHR contributor from biogenic tracers in background conditions to CO and BB VOCs during smoke.

645 These results highlight the strong influence of regional wildfire smoke on air quality in the western U.S.

Photochemical-clock analysis constrains ERs for a wide range of primary VOCs in aged BB smoke, yielding values consistent with those reported for western U.S. wildfires. The observed decay patterns of primary VOCs broadly follow their known OH rate constants (k_{OH}). Some underestimation of k_{OH} (by factors of ≈ 3) for reactive VOCs likely arises from rapid
650 depletion, dilution, or background contamination. OVOCs such as methanol, formaldehyde, and acetaldehyde also decrease with age, but their shallow slopes indicate substantial secondary production offsetting primary decay.

Intense smoke episodes in Missoula suppressed surface ozone, with MDA8 O_3 declining by up to ~ 15 ppb (6–7 September), coincident with 50 % reductions in solar radiation and lower planetary boundary layer heights (PBLH), confirming that
655 reduced photolysis and weaker mixing limit in-situ ozone formation. Across smoke-impacted days, the MDA8 O_3 – $PM_{2.5}$ relationship was non-monotonic: ozone increased under light smoke ($PM_{2.5} < \sim 20 \mu g m^{-3}$) but tended to flatten or decrease at higher smoke loadings ($> \sim 20 \mu g m^{-3}$).

Chronic and acute health assessments indicate that prolonged exposure to 2020-level wildfire smoke in Missoula poses
660 quantifiable health risks. If a season of similar intensity were to recur annually, the smoke-attributable excess lifetime cancer risk would be ~ 100 cases per million people ($\approx 7\times$ the non-smoke baseline of ~ 15 per million for the same days), with $PM_{2.5}$ accounting for ~ 90 % of the cancer burden. The chronic non-cancer hazard index (HI) is ~ 3 , with $\sim 90\%$ attributable to HAPs (driven primarily by acrolein and formaldehyde) and the remaining $\sim 10\%$ to $PM_{2.5}$. For acute non-cancer risk, 1-hour HI exceedances are rare, but 8-hour averaging reveals frequent smoke-aligned exceedances ($\sim 51\%$ of periods with $HI > 1$).
665 Across both chronic and acute metrics, the repeated importance of the same few HAP drivers (notably acrolein, formaldehyde, and benzene) indicates that mitigating wildfire-related health impacts should extend beyond particle-only strategies to include gas-phase toxics.

The GEOS-Chem simulation reproduces the timing and transport of major smoke plumes ($R^2 = 0.8$ – 0.9) but underestimates
670 the magnitude of smoke enhancements, with model low biases of ~ 30 – 40% for CO and $PM_{2.5}$ and ~ 60 – 90% for most VOCs. The model overestimates OH exposure by roughly 100 %, leading to excessive chemical loss and artificially low EnRs for reactive VOCs. Persistent low EnRs for oxygenated VOCs further suggest missing secondary production during multi-day aging, whereas the $+33\%$ bias in $PM_{2.5}$ EnR points to overly efficient secondary aerosol formation and/or retention in the GEOS-Chem simplified “simple SOA” treatment. Tripling BB emissions ($3\times$ BB) largely improves the modelled ~~CO and~~
675 ~~primary VOCs-primary compounds~~ (e.g., ~~the model CO bias is changed from -40% to $+20\%$;~~ benzene from -70% to -10%) and reduces the model bias of OH exposure to ~ 30 % within smoke-impacted periods, but the modeled $PM_{2.5}$ is worse (from -30% to $+80\%$), demonstrating that uniform emission scaling cannot reconcile errors in both gases and aerosol. Together,

these results highlight that reducing model biases in smoky environments requires not only better fire emission magnitudes but also improved representation of missing OH reactivity (e.g., furanoids), secondary OVOC formation, and smoke SOA parameterizations.

GEOS-Chem exhibits a persistent positive bias in September MDA8 O₃ in Missoula (+15 ppb on average) and fails to reproduce observed day-to-day variability, regardless of the BB emissions scenario (base, 3×BB, or noBB). This is in part due to the modeled O₃ being too high for urban general background, and the model bias further amplifies on smoke days, reaching +70 ppb and increasing with observed daytime PM_{2.5} ($r \approx 0.7$). More importantly, the model fails to reproduce the observed non-monotonic O₃–PM_{2.5} response, where observations flatten or decline beyond ~30–40 μg m⁻³. Instead, GEOS-Chem continues to increase O₃ with PM_{2.5}. The same monotonic behavior is also present in the independent CMAQ-based AIRPACT forecast system across Missoula and other western U.S. sites, pointing to a shared CTM limitation in representing nonlinear ozone responses under intense BB smoke. These model biases are likely related to overestimated radiation, warm temperature biases, PBLH/entrainment errors, and potentially too-weak heterogeneous NO₃/N₂O₅ loss in CTMs, although isolating the dominant drivers will require additional observational constraints.

GEOS-Chem underpredicts the smoke-attributable lifetime excess cancer risk by 40% (63 vs 100 cases per million), due to the underestimated PM_{2.5}. The model's capability to predict non-cancer HI is even worse (~0.3 in GEOS-Chem vs 3 in observations). The model also underrepresents acute hazards, predicting limited 8-h exceedances (15 h with 8-h HI > 1; max 8-h HI = 1.2), far fewer and weaker than observed (476 h; max 8-h HI = 6). Overall, these results indicate that GEOS-Chem can provide a defensible screening-level estimate of PM_{2.5}-dominated cancer burden, whereas HI estimates remain unreliable without improved BB VOC speciation, secondary production pathways, and inclusion of high-potency toxics such as acrolein.

Code and data availability

The data and analysis code supporting this study are publicly available and enable full reproduction of the figures and results presented here. [The processed data archive is available at Zenodo \(doi: 10.5281/zenodo.18209324\).](https://zenodo.org/doi/10.5281/zenodo.18209324) [The analysis code is available on GitHub at https://github.com/jinlx/Aged-wildfire-smoke-emission-chemistry-health](https://github.com/jinlx/Aged-wildfire-smoke-emission-chemistry-health) (last access: 24 March 2026). Raw air-quality observations were obtained from the Montana Department of Environmental Quality and are included in the Zenodo archive. [Meteorological and ancillary datasets were obtained from publicly available sources cited in the manuscript.](#) ~~The data and analysis code used in this study will be made publicly available upon final publication. During the review process, the full analysis code and processed datasets have been made available to reviewers through the Copernicus review system with access restricted to reviewers only. The archived materials allow full reproduction of all figures and results presented in this paper. Raw air quality observations were obtained from the Montana Department of Environmental~~

710 ~~Quality and are subject to the agency's data-use policies. Meteorological and ancillary datasets were obtained from publicly available sources cited in the manuscript.~~

Author contributions

715 LJ: investigation; conceptualization; methodology; simulations; formal analysis; visualization; writing (original draft); data
curation. LT: investigation; data curation. DK: investigation; data curation. KN: investigation; data curation. VS:
investigation; writing (review and editing). BY: supervision; conceptualization; writing (review and editing). LH:
supervision; conceptualization; writing (review and editing); funding acquisition. All authors reviewed and approved the
final manuscript.

Competing interests

720 A declaration of all potential conflicts of interest is required by Copernicus Publications as this is an integral aspect of a
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Disclaimer

The contact author has declared that none of the authors has any competing interests.

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