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Effects of Anthropogenic Pollutants on Biogenic Secondary Organic Aerosol Formation in the Atmosphere of Mt. Hua, China

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Abstract: Anthropogenic effects on biogenic secondary organic aerosol (BSOA) formation in the upper boundary layer are still not fully understood. Here, A synchronized 4-hourly monitoring of three typical BSOA tracers from isoprene, monoterpenes, β-caryophyllene and other particulate pollutants was conducted at the mountain foot (MF, 400 m a.s.l.) and mountainside (MS, 1120 m a.s.l.) of Mt. Hua, China, to investigate the chemical evolution of BSOA in air mass lifting. Our findings revealed that BSOA was the predominant source of organic matter (OM) at MS site, with an average fraction of ~43% being ~7-fold of that at MF site. As the prevalent BSOA tracer, isoprene-derived SOA tracers ($BSOA_I$) maintained comparable level at MF site (182.5±81 ng/m^3) and MS site (197.3±127 ng/m^3), yet exhibited an inverse diurnal pattern between both sites. And the $BSOA_I$ fraction in OM aloft moderately decreased during the daytime, and correlated positively with 2-methyltetrols/2-methylglyceric acid ratio but negatively with NOx transported from ground level, indicating that anthropogenic NOx would significantly affect the daytime BSOA formation aloft by inhibiting the HO_2·-pathway products. Additionally, the further formation of sulfate in lifting air mass would significantly enhance aerosol water content aloft, which suppressed the reactive uptake of isoprene epoxydiol and ultimately diminished the $BSOA_I$ yields during the daytime. These findings provide more insight into the intricate anthropogenic−biogenic interactions affecting BSOA formation in the upper boundary layer atmosphere.

Keywords: Biogenic Secondary Organic Aerosol; Isoprene; Anthropogenic pollutants; Vertical distribution

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1. Introduction

Volatile organic compounds (VOCs) play a crucial role in atmospheric chemistry (Mcfiggans et al., 2019; Coggon et al., 2021), exerting profound influences on the atmospheric oxidizing capacity, tropospheric ozone burden and regional climate (Mellouki et al., 2015; Wu et al., 2020). Among the diverse VOCs, biogenic VOCs (BVOCs) primarily emitted by terrestrial vegetation predominate the global VOC flux at 1Pg/yr (Guenther et al., 2012), exceeding anthropogenic sources by an order of magnitude. The high reactivity of dominant BVOCs (particularly, isoprene, monoterpene, and sesquiterpenes) towards O_3, OH· and NO_3· would drive rapid formation of secondary organic aerosol (SOA) (Zhang et al., 2018; Ng et al., 2017). Consequently, these biogenically-derived SOA (BSOA) would represent a prominent contribution to global SOA budget (Kelly et al., 2018; Hodzic et al., 2016), although the models remain highly uncertain in BSOA prediction owning to the complexity of physicochemical processes involved (Hallquist et al., 2009). Given the significant climate interactions and public health implications of BSOA (Scott et al., 2014; Shrivastava et al., 2017), advancing the understanding of BSOA, including its precursors, formation processes, is urgently needed.

Over past two decades, mounting evidences indicate that anthropogenic pollutants (e.g., SO_2, NOx) critically regulate the BSOA formation through altering oxidation pathways and gas-to-particle partitioning processes (Xu et al., 2015; Zheng et al., 2023; Xu et al., 2016). For example, sulfate aerosol formed by heterogeneous reactions of SO_2 would influence particle acidy and water content (Wang et al., 2016;

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Wang et al., 2025), which accelerates SOA formation by the "salting-in" effect and corresponding acid-catalyzed reactions (Offenberg et al., 2009; Xu et al., 2016). NOx as an important driver for BSOA formation could modulate the fate of peroxy radicals (RO_2·), and subsequently affect the yield and chemical composition of BVOC-oxidized products (Lin et al., 2013; Pye et al., 2010). Abundant O_3 could also significantly promote BSOA formation via enhancing BVOCs ozonolysis. Thus, the changes of anthropogenic emissions would potentially perturb the BSOA formation. As modeling studies demonstrated, anthropogenic emission controls substantially decreased the BSOA formation in the United States during 1990-2012 (Ridley et al., 2018), and ~ a further 35% of isoprene-derived SOA (SOA_I) would be reduced in 2025 if ongoing the similar emission regulations (Marais et al., 2016). The parallel effects also emerged in China, where the effective control on SO_2 emissions drove a significant decline of SOA_I at −8.0%/yr over 2007−2015, even being two-fold that of SO_4^{2-} (Dong et al., 2022).

Numerous studies have comprehensively characterized the surface BSOA, yet the vertical distribution of BSOA remains insufficiently understood, which is a critical driver of uncertainties in the global climate models (Nazarenko et al., 2017; Hodnebrog et al., 2014). The mountain-based observations revealed that BSOA constitutes a substantial fraction (30–60%) of aerosols in free troposphere (Fu et al., 2014; Ren et al., 2019; Yi et al., 2021); And these elevated BSOA are significantly influenced by the valley breeze that would transport the surface pollutants to upper boundary layer, indicating a potential effect of surface pollutant emissions on BSOA

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formation aloft. In addition, airborne pollutants likely undergo aging in the vertical transport process (Wu et al., 2022), causing increasingly complex compositions and changes in oxidizing capacity and aerosol properties compared with that at ground level. Consequently, more observations studies are necessary to obtain an improved understanding of the anthropogenic−biogenic interactions driving BSOA formation aloft.

Guanzhong Basin of inland China is a typical semiarid region in East Asia, suffering serious particle pollution due to the large anthropogenic emissions (Wang et al., 2016). In our previous studies (Li et al., 2013; Wang et al., 2012), the molecular distribution, evolutionary mechanism and sources of BSOA have been investigated; Whereas, the anthropogenic emissions experienced dramatical changes recently in this region (Zhang et al., 2019a), thereby, the primary factors currently driving the BSOA formation are probably distinct from those that prevailed previously. To elucidate the formation mechanism of biogenic SOA aloft in this region, synchronous observations were conducted on the mountainside and the mountain foot of Mt. Hua, adjoined the Guanzhong basin. In this study, we firstly investigate chemical molecular compositions and diurnal variation of the of BSOA over Mt. Hua, then explored the impacts of anthropogenic pollutants on BSOA formation during the vertical transport, and finally quantified its source contributions.

2 Experiment

2.1 Sample collection

From 27 August to 17 September 2016, aerosol sampling with 4-hr interval were

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synchronously conducted at two locations in Mt. Hua region, employing the high-volume air samplers with a flow rate of 1.13 m^3/min. One sampling site (34°32′N, 110°5′E, 400 m a.s.l; MF) is situated at the mountain foot of Mt. Hua, enveloped by several traffic arteries, residential and commercial buildings. Another site is located on mountainside (34°29′N, 110°3′E, 1120 m a.s.l; MS), approximately 8 km away from MF site in horizontal distance; This site is adjacent to one of the larger valleys of Mt. Hua, characterized by precipitous terrain and less anthropogenic activities. The surface-level pollutants can be transported to here by the prevailing valley breeze, which has been validated by the organic tracers and meteorological field simulated by WRF-Chem model in our previous studies (Wu et al., 2022; Wu et al., 2024). All the aerosol samples were collected on pre-combusted quartz filters (450 ℃ for 6 hr), and stored in a freezer (< −18 ℃) prior to chemical analysis.

Additionally, the hourly concentration of the pollutants, including $PM_{2.5}$, O_3, NO_2, were also monitored at MS site by corresponding online equipment; While, those data for MF site were mainly acquired through Weinan Ecological Environment Bureau (http://sthjj.weinan.gov.cn/, last access: 8 July 2021). All meteorological data were downloaded from the Shaanxi Meteorological Bureau website (http://sn.cma.gov.cn/, last access:8 July 2021). The comprehensive details regarding the sampling sites and instrumentation were delineated in our previous studies (Wu et al., 2022; Wu et al., 2024).

2.2 Chemical analysis

The details of organic matter extraction, derivatization, and gas

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chromatography/mass spectrometry (GC/MS) analyses can refer to elsewhere (Wang and Kawamura, 2005). Briefly, for the analytical procedure of organic tracers in the aerosol, one-quarter of $PM_{2.5}$ sample was cut into pieces and then ultrasonically extracted with a mixture of dichloromethane and methanol (2: 1, v/v) three times (each for 15 min). The extracts were filtered through a pasteur pipette plugged with quartz wool into a pear-shaped bottle. The filtrates were concentrated by a rotary evaporator under vacuum state and then dried by pure nitrogen. After reaction with 60 Ml derivatization reagent (a mixture of 50 Ml of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and 1 % trimethylsilyl chloride and 10 Ml of pyridine) for 3 h at 70 °C in order to convert COOH and OH groups to the corresponding trimethylsilyl esters and ethers. After cooling down to room temperature, an aliquot of 40 Ml internal standard (C_{13} n-alkene) was added into the derivative solution prior to GC/MS analyses. The blank filters were also analyzed following the same analytical procedure for the ambient samples.

Furthermore, partial filters were cut into pieces, and then extracted three times under sonication with 15ml Milli-Q pure water (18.2 MΩ). Ten ions such as SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, and K^+ were determined using ion chromatography (Dionex, ICS-1100). A DRI model 2001 thermal–optical carbon analyzer was used to measure the organic carbon (OC) and element carbon (EC) in each $PM_{2.5}$ filter samples, of which water-soluble organic carbon (WSOC) was extracted into Mill-Q pure water (18.2 MΩ) and ultimately quantified by a total organic carbon (TOC) analyzer (Model TOC-L CPH, Shimadzu, Japan).

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2.3 Aerosol liquid water content (ALWC) and in situ pH

The thermodynamic model (ISORROPIA-II) can provide robust predictions of the aerosol liquid water content (ALWC) and in situ pH in $PM_{2.5}$ samples. By combining the actual temperature (T) and relative humidity (RH) in the atmosphere and the composition, the ALWC and H^+ loads can be simulated, which are used for calculating the situ pH.

2.4 Positive matrix factorization (PMF) source apportionment

As a receptor model, PMF is a mathematical approach to quantify the contribution of sources to samples, and has been widely used in the source apportionment of air pollutant. More details of model can be found on the EPA website (https://www.epa.gov/air-research/epa-positive-matrix-factorization-50-fundamentals-and-user-guide). In this work, the organic matter (OM), EC WSOC, secondary inorganic ions, biogenic SOA of all the samples served as the fingerprint species to identify potential sources of the BSOA at Mt. Hua. After numerous tests, the model would output an optimal solution according to the minor difference between Q_{True} and Q_{Robust}; This is indicative of the robust model performance, as confirmed by the high correlation coefficients between input and estimated values. Furthermore, as revealed in our pervious study (Wu et al., 2022), the change of the main emission sources was insignificant in air mass lifting process on Mt. Hua. Thus, the samples from both sites were added together as one data matrix. Based on the Q values and interpretability, five factors were obtained as the optimal solution after numerous testes, and the input species matched well with simulated ones with significant correlations (R^2>0.92).

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3.1 Overview of OM during the campaign

The bulk chemical compositions of $PM_{2.5}$ during the campaign have been reported in our previous work (Wu et al., 2022), and strongly substantiate that organic matter (OM) is the principal component of $PM_{2.5}$ at the surface and high elevation, with a mass fraction of 32%~46%. For a deeper insight into the relative abundances, vertical variability and sources of OM among two sampling sites, a comprehensive comparison was given in Figure 1. The OM concentration was 30.0±10.4 μg/m^3 at MF site, approximately three-fold of that at MS site. Such abundant OM at surface was apparently driven by fresh emissions from nearby roads and residences, as evidenced by its strong correlation with hopanes (Figure S1(a), R^2=0.46, p<0.05) being a known tracer for combustion sources; Whereas, a weak correlation between OM and hopanes was found at MF site, indicating the different sources for the OM aloft. Moreover, subaerial OM was characterized by a higher nocturnal load, and exhibited a decreased trend before midafternoon, which was thermally driven boundary layer growth. Nonetheless, an inverse diel pattern was observed at high elevation site with a daily OM peak at the moment (12:00~16:00) of strong photochemical activity, suggesting that OM components aloft was probably driven by photochemistry.

To determine the sources of OM at both sites, we performed a positive matrix factorization (PMF) analysis, and identified five types of sources for OM (Figure S2). Among these sources, biomass burning (BB) and fossil fuel combustion were believed to the primary sources for OM at MF site, accounting for 52% and ~18% of OM

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(Figure 1c), respectively. This coincided with that in Xi'an (~ 43% for BB) and Lin Village (30%~40% for BB) located on Guanzhong plain (Elser et al., 2016; Li et al., 2022). Whereas, merely ~24% of OM was explained by above anthropogenic sources at MS site; and most of OM aloft was dominated by biogenic secondary organic aerosol (BSOA, Figure 1d), with a fractional contribution of ~43% being septuple of that for subaerial OM. This elucidated a significant influence of biogenic primary and secondary sources on OM aloft.

3.2 Abundance and spatiotemporal variations of BSOA tracers

To characterize the spatiotemporal variations of biogenic SOA among two sites, a plenty of BSOA tracers including isoprene, monoterpene and sesquiterpene were quantified as summarized in Table1. The sum of detected BSOA tracers ranged 31 ng/m^3 to 459 ng/m^3 at MF site (269.4±1107.6 ng/m^3, Figure S3), which was slightly lower than that at MS site (276.5±159.0 ng/m^3); Such spatial pattern was also observed at Mt. Tai on North Chian Plain (Yi et al., 2021), further underscoring the significance of biogenic sources in mountainous OM formation aloft. Specifically, isoprene SOA tracers ($BSOA_I$) as the dominant species accounted for ~70% of the identified BSOA tracers, with average of 197.3±126.8 ng/m^3 at MS site and 182.5±81.0 ng/m^3 at MF site, respectively; These were comparable to that in the Kathmandu Valley of India (182.5±81.0 ng/m^3) (Wan et al., 2019) and a mid-latitudinal forest zone (~240 ng/m^3) (Zhu et al., 2016), but ~2 orders of magnitude higher than those measured over the North Pacific (3.6 ng/m^3) (Fu et al., 2011). As for total monoterpene SOA tracers ($BSOA_M$) and sesquiterpene tracers ($BSOA_S$), their

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abundances were lower by a factor of approximately 4~6 than $BSOA_I$, probably due to a less emissions of monoterpene and sesquiterpene from the vegetation in this region. Noteworthily, $BSOA_M$ exhibited a converse spatial pattern, with a high load at surface (MF: 52.4±23.1 ng/m^3 vs. MS: 32.3±19.9 ng/m^3). The coniferous plants, as primary emitter of monoterpene (Gagan et al., 2023), may be less densely distributed at the ground level relative to that on Mt. Hua; Thus, relatively abundant $BSOA_M$ at MF site likely affect by intensive BB activities that can also release numerous monoterpenes, thereby potentially augmenting the surface $BSOA_M$ levels. This can be manifested by that $BSOA_M$ strongly correlated with levoglucosan being known as BB tracer, but weakly with C_{29}-alkane that mainly derived from vegetation emissions (Figure S4).

3.2.1 Isoprene SOA tracers

A total of eight isoprene tracers formed by oxidated reactions of isoprene with NOx and OH_2· were identified in this study, namely C_5-alkene triols (cis-2-MTB, trans-2-MTB and 3-MTB), 2-MGA, 2-methyltetrols (2-MT and 2-ME) and 3-MeTHF-3,4-diols (trans-3-Methyltetrahydrofuran-3,4-diol and cis-3-Methyltetrahydrofuran-3,4-diol). The $BSOA_I$ at MF site exhibited a pronounced diurnal cycle, characterized by a higher daytime load with an afternoon peak of 210.4±96.0 ng/m^3 (Figure 2(a)). This pattern aligns with temperature-driven characteristic of isoprene emission; and a positive correlation between $BSOA_I$ and temperature (R^2=0.63) implied that a substantial part of surface $BSOA_I$ was expected to be formed locally (Figure S5 (a)), given the short atmospheric lifetime of isoprene. Whereas, $BSOA_I$ aloft was

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characterized by an inverse diurnal variation, with a moderate enhancement in the nocturnal load. As revealed by a high-elevation CWT analysis of $BSOA_1$ (Figure 3), relatively high nocturnal loading distributed over Mt. Hua and adjacent regions, indicating that these SOA tracers aloft were significantly influenced by regional/super-regional transport, especially during the nighttime.

2-methyltetrols (2-MTLs), as the predominant species at both sites, was more abundant at high-elevation site (98.6±68.5 ng/m^3) relative to surface site (73.8±32.1 ng/m^3). This pattern was akin to the level observed at Mt. Tai (98 ng/m^3) (Yi et al., 2021) and Mt. Changbai (22~282 ng/m^3) (Wang et al., 2008). As the oxidation products of isoprene under low/free-NOx condition, 2-MTLs at MF site was significantly formed during the daytime, and peaked at 12:00~16:00 LT (local time, 85.2 ng/m^3, Figure 2(b)), corresponding to the period of reduced NOx loads, high temperature and intense solar radiation. Conversely, the concentration of 2-MTLs aloft decreased progressively during the daytime, bottoming out until 16:00~20:00 LT; This inverse diurnal pattern was probably due to the influx of the surface NOx that was transported aloft by the prevailing valley breeze, which subsequently inhibited the 2-MTLs formation at MS site. Meanwhile, such relatively abundant NOx condition during the daytime would promote the formation of 2-MGA aloft (culminating at 12:00~16:00 LT), as corroborated by a positive correlation between 2-MGA and NO_2 (Figure S5 (c)). This finding was consistent with the laboratory measurements of 2-MGA being derived from oxidization of isoprene with high NOx load (Wang et al., 2008). Moreover, surface 2-MGA also exhibited a similar diurnal

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pattern with average of 28.6±14.7 ng/m^3 being 1.8-fold of that aloft, albeit a weak relationship between 2-MGA and NO_2; This appreciably suggested that, beyond NOx, other factors also drove the 2-MGA formation at MF site.

C_5-alkene triols and 3-MeTHF-3,4-diols were another prevalent isoprene tracers, of which concentration were comparable among two sites (Table 1). As the photooxidation products under low/free-NOx level, above two tracers exhibited a diurnal cycle paralleled to that of 2-MTLs at two sites, and were characterized by higher loads during nighttime. Despite that, the correlation between C_5-alkene triols and 3-MeTHF-3,4-diols (R^2>0.74) was more robust than that involving 2-MTLs. This was probably owing to that C_5-alkene triols and 3-MeTHF-3,4-diols were mainly formed via acid-catalyzed intermolecular rearrangement reactions of epoxy-diols, whereas 2-MTLs are likely to the result from nucleophilic addition of water to the ring opening of epoxy-diols.

3.2.2 Monoterpene SOA tracers

The detected monoterpene tracers, including pinic acid (PA), cis-pinonic acid (PNA), 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), are mainly derived from photooxidation of α/β pinene initiated by ·OH and O_3; Therefore, those four tracers exhibited a similar diurnal pattern, peaking at 12:00~16:00 LT when ·OH and O_3 concentrations remained at highest daily level. Based on the chamber measurements, PA and PNA are the early-generation products of α/β pinene (Liu et al., 2022; Jaoui et al., 2005), merely accounting for ~10% and ~12%-17% of the $BSOA_M$, respectively. Strikingly, PNA at two sampling sites was

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more abundant by a factor of ~1.5 than PA, consistent with the observations at Mt. Tai, Mt. Huang and in Duke Forest, North Carolina (Wang et al., 2023; Bhat and Fraser, 2007; Yi et al., 2021). The saturation vapor pressure of PNA is ~7.2 × 10^{-5} Pa (at 298 K, estimated by E-AIM model) is lower than that of PA (~2.0× 10^{-4} Pa), thus, PNA can be readily nucleated and saturated in the atmosphere. Given that, PNA was expected to have a higher abundance in aerosol than PA.

During the campaign, MBTCA was the most abundant $BSOA_M$ tracer, explaining more than half of the surface $BSOA_M$ tracers at both sites, and followed by 3-HGA with fractional contributions of ~20% to total $BSOA_M$. MBTCA and 3-HGA are regarded as the later-generation products of α/β-pinene, and can be derived from further photodegradation of PNA or PA; Thus, MBTCA/(PA+PNA) ratio (abbreviated as M/P hereafter) is commonly used to estimate the α/β-pinene-derived SOA aging, of which a higher value is indicative of more aged α/β-pinene SOA. As depicted in Figure S6, the M/P value (2.6±1.3) at MS site was ~1.4-fold of that at MF site, reflecting that the $BSOA_M$ tracers aloft were more aged compare to that at surface; This finding was coincided with the variation of oxidation state of carbon (OSc) measured by the aerosol mass spectrometer. Additionally, a clear diurnal pattern of M/P ratio was found at MF site, with a daily peak at 16:00~20:00 lagged that of MBTCA by ~4 hr. However, the diurnal cycle of M/P ratio at MS site exhibited a bimodal pattern, with two nearly equivalent peaks during the daytime (16:00~20:00) and nighttime (4:00~8:00). Relatively high M/P ratios during nighttime indicated a more aged state of nocturnal α/β-pinene SOA at upper atmosphere, markedly differing

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from the ground-based observations. This was partially due to that the nocturnal pollutants at MS site were mostly driven by regional or long-range transport (Figure 3), in which α/β-pinene SOA aloft would undergo a deeper aging, and leading to the high M/P ratio.

3.2.3 Sesquiterpene SOA tracers

As a typical and abundant sesquiterpene, β-caryophyllene has been widely studied due to its high reactivity and significant aerosol formation potential; and it can be oxidated into β-caryophyllinic acid for via ozonolysis/photooxidation. In this study, β-caryophyllinic acid was found to exhibit a relatively high concentration among the detected BSOA tracers (Table 1), with average of 34.5±19.1 ng/m^3 at MF site and 56.0±41.0 ng/m^3 at MS site, respectively; These loads were comparative to Mt. Wuyi (7.6-54 ng/m^3) (Ren et al., 2019) and Mt. Tai (0.05-48 ng/m^3) (Fu et al., 2012). As expected, β-caryophyllinic acid robustly correlated with $BSOA_M$ (R^2>0.60, p<0.05) at both sampling sites, indicating similar formation pathways for these species. Additionally, the significant relationship between β-caryophyllinic acid and levoglucosan at MF site could be a result of intensive biomass burning as indicated in section 3.1; This observation aligns with previous findings that sesquiterpenes accumulated in leaves and wood can be released in the biomass burning process, subsequently oxidized to form β-caryophyllinic acid (Zhang et al., 2019b). Notably, β-caryophyllene SOA tracers aloft in this study showed clearly enhanced concentrations during the daytime from 10:00 to 16:00; whereas, the diurnal cycle of β-caryophyllinic acid at MF site was less pronounced, despite significant diurnal

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differences in Ox load and temperature that are known to influence heterogeneous reactions of β-caryophyllene.

3.3 Influencing factors of BSOA formation in upper troposphere

A comparison of diurnal cycles of mass fraction of BSOA to OM ($F_{BSOA/OM}$) among both sampling sites is illustrated in Figure 4. At MF site, a spike in $F_{BSOA/OM}$ was observed at around 12:00-16:00 (Figure 4(a)), demonstrating that the surface BSOA formation was strongly enhanced in the presence of abundant O_3/OH radical load and high biogenic emissions, especially for isoprene SOA; Such diurnal variation was in good agreement with the measurements at other sites (Zhang et al., 2019b; Zhu et al., 2016; Lee et al., 2016). Whereas, $F_{BSOA/OM}$ for isoprene aloft exhibited a decreasing pattern during photochemically active period (Figure 4(b)), reaching a minimum at 12:00-16:00. Although oxidant levels remained relatively high at this time, the $F_{BSOA/OM}$-isoprene was only 75% of that for the prior moment. Our previous observational evidences have corroborated that surface-level anthropogenic pollutants can be transported to upper atmosphere by the prevailing valley breeze (Wu et al., 2022; Wu et al., 2024). Those anthropogenic pollutants (e.g., SO_2, NOx) likely modulated BSOA formation aloft, leading to above unusual diurnal cycles $F_{BSOA/OM}$-isoprene. To elucidate the above hypothesis, the mantel test and random forest analysis were applied for daytime BSOA aloft.

3.3.1 Effects of meteorological factors on BSOA

As shown in Figure 6(a), the BOSA positively correlated with ambient temperature for daytime samples aloft, consistent with the temperature-dependent characteristic of

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isoprene and monoterpene emissions from terrestrial vegetation; Thus, the relatively high temperature was expected to enhance biogenic SOA yields rom the photooxidation of isoprene and monoterpenes, which also found at other mountainous studies, e.g., Mt. Tai, Mt. Huang and Mt. Wuyi (Ren et al., 2019; Wang et al., 2023; Yi et al., 2021). Additionally, the strong temperature-dependence of BSOA also indicated a significant part of BSOA tracers aloft undergo rapid in-situ formation once the oxidants concentrations built up during the daytime, contrasting with those during nighttime. An insignificant correlation was observed between relative humidity and BSOA tracers. However, the moist weather frequently occurred at MS site, even at the daytime with average RH of 62.3±19.0% (Wu et al., 2022); Thus, the less pronounced variation can explain the insensitivity of BSOA formation to RH. Even so, the high RH during daytime could indirectly influence BSOA formation aloft by modulating aerosol water content (ALWC), aerosol acidity, gas–particle partitioning of BSOA precursors.

3.3.2 Effects of anthropogenic pollutants on BSOA

Evidences from field and modeling studies indicates that biogenic SOA yield is enhanced in presence of elevated NOx level (Xu et al., 2015; Shrivastava et al., 2017). However, the BSOA tracers aloft, especially isoprene-derived SOA, negatively correlated with NO_2 (r=0.36, P<0.05) (Figure 6(a)). Additionally, the 2-MTLs/2-MGA ratio, which is indicative of NOx influence on SOA formation, followed a similar diurnal pattern to that of the $F_{BSOA/OM\text{-}isoprene}$ (Figure 6(b)). All those findings indicated that the NO_2 transported from the surface to high altitude may limit the formation of

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391 SOA_I in the daytime. As is well known, isoprene oxidization primarily follows two
392 pathways, i.e., HO_2 pathway forming 2-MTLs in NOx-limited conditions and
393 NO/NO_2 channel yielding 2-MGA in high-NOx scenarios. Thereby, we hypothesized
394 that the increasing NOx at MS site may perturb BSOA formation by competing with
395 HO_2 pathway, diminishing the net SOA yield relative to NOx-limited conditions. This
396 was consistent with experimental finding conducted by Thornton et al. (2020), who
397 demonstrated that a nonlinear dependence of BSOA yield on NOx level and a steep
398 decrease in isoprene-derived SOA formation beyond a certain NOx threshold; Notably,
399 they also found that, at high NOx level (NO~500 ppt) that is akin to our daytime
400 observations at MS site, the maximum BSOA yield is 10% lower than that at low
401 NOx.

402 As shown in Figure 5(c), the sulfate presented a statistically significant positive
403 relationship with $BSOA_I$. This feature appeared to be common for other similar filed
404 studies (Wang et al., 2008; Xu et al., 2015; Liu et al., 2017), underscoring the
405 significant role of sulfate in the isoprene-derived SOA formation. According to
406 laboratory studies (Eddingsaas et al., 2010), the sulfate can act as nucleophiles to
407 facilitate the ring-opening reaction of epoxydiols (IEPOX), which is pivotal oxidation
408 product of isoprene when organic peroxy radicals mainly react with HO_2 radicals.
409 While, the sulfate level was moderately enhanced, with a daily maximum at 12:00-
410 16:00 LT (Figure 5(c)); This is indicative of the further formation in air mass lifting
411 process (Wu et al., 2022). An increase in sulfate would boost the ion strength and
412 salting-in effect of aerosol, thereby enhancing IEPOX reactive uptake and inhibiting

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its reversible partitioning back to the gas phase. Furthermore, sulfate can modulate the H^+ level, acting as a more efficient proton donor to catalyze IEPOX ring opening and isoprene ozonolysis; Thus, H^+ concentration predicted by thermodynamic model ISORROPIA II positively correlates with $BSOA_I$, as indicated in Figure 5(a).

Additionally, the further formation of sulfate in lifting air mass can also promote an enhancement in ALWC aloft (Figure 5(c)), with a daytime maximum at 12:00-16:00 LT, which temporally coincided with a significant decrease in $F_{BSOA\text{-}isoprene/OM}$. This pattern suggested an inhibited effect of aerosol water on BSOA formation, consistent with laboratory observation by Gaston et al. (2014), who found a 50% reduction in IEPOX reactive uptake on NH_4HSO_4 particles as RH increases from 30% to 70%. As evidenced by previous studies (Xu et al., 2015; Riedel et al., 2015), the abundant aerosol water can moderate BSOA formation by affecting ionic strength, proton donor/nucleophilic activity, and consequently altering the reactive uptake (e.g., IEPOX) and subsequent reactions. To quantitatively evaluate the effects of ALWC, the pseudo-first-order heterogeneous reaction rate constant for IEPOX reactive uptake (k_{het}) was calculated for the samples at MS site following the method of Gaston et al. (2014) (Text S1). The simulated uptake coefficient of IEPOX (γ_{IEPOX}) during the daytime was 4.3×10^{-4} being in the range of field and laboratory observations ($0.1–6.5\times10^{-4}$) (Zhang et al., 2017; Gaston et al., 2014). As shown in Figure 6, the high ALWC commonly corresponds to low γ_{IEPOX} during the daytime, characterized by weak ionic strength and low $H^+_{(aq)}$ concentration. This indicates that enhanced ALWC at MS likely impeded the IEPOX uptake onto particle surface. Consequently, the

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average k_{het} at 12:00-16:00 L was merely 9.8×10^{-8} 1/s, which was an order of magnitude lower than that in the rest of daytime. These results underscore that enhanced ALWC during the daytime would lead to an insufficiently rapid heterogeneous reaction of IEPOX, and finally diminished the $BSOA_I$ formation.

To elucidate the key factors that affect BSOA formation aloft, a RF analysis was conducted for the daytime samples at MS site. The RF model commendably highlighted the significance of the factors contributing to $BSOA_I$ formation, as evidenced by the robust correlations between the predicted and observed data for both the training and testing datasets (R^2>0.8, Table S1), along with minimal error metrics. As shown in Figure 5(d), the daytime $BSOA_I$ concentration was largely affected by the ozone (~29%), with a robust positive correlation between them (Figure 5(a)); This indicated that enhanced O_3 is likely to augment isoprene oxidation products aloft. Additionally, NO_2 and ALWC also play pivotal roles in $BSOA_I$ formation, with the importance of ~19% and 13.3%, respectively; These findings further corroborated that the enhanced NOx may lead an impedimental effect on the daytime BSOA formation in the upper boundary layer of Mt. Hua. Such limiting effect on isoprene-derived SOA formation under high NOx scenario was also found in Eastern China and Amazon (Zhang et al., 2017; De Sa et al., 2017).

4 Summary and conclusion

The $PM_{2.5}$ samples with 4 h intervals were synchronously collected at mountain foot and mountainside of Mt. Hua, to elucidate the chemical evolution and spatiotemporal differences of the organic matter among two sites. At the MF site, the

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anthropogenic emissions, such as biomass burning and fossil fuel combustion, were identified as substantial contributors to the OM, accounting for more than 70% of total OM. Whereas, only ~24% of OM aloft was derived from anthropogenic emissions, with biogenic secondary organic aerosol (43%) emerging as the predominant OM source aloft.

Three distinct types of BSOA tracers were identified, predominantly featuring isoprene-derived species. At MF site, most of the BSOA tracers were more abundant during the daytime and peaked at 12:00~16:00 LT, indicative of photochemical oxidation as the primary formation pathway. Whereas, there is a marked decrease in the absolute concentration and relative abundance of daytime isoprene-derived tracers in the upper atmosphere. This decline can be attributed to the intrusion of ground-level NOx, which significantly modifies BSOAI formation at higher altitudes by inhibiting the $HO_2\cdot$ oxidative pathway. Additionally, a further formation of sulfate in lifting air mass moderately enhanced ALWC aloft, leading to a low IEPOX reactive uptake on the particle surface, which would also limit the daytime $BSOA_I$ formation aloft. Unfortunately, our limited data does not allow us to peer into the fundamental mechanistic and kinetic details of this process. All these findings highlighted the complex and regional variability of the influences of NOx on BSOA formation. Over the past decade, atmospheric environment in China has undergone substantial change unevenly implemented emission controls, resulting in much higher levels of NO_2 compared with SO_2 (Zheng et al., 2018). These alterations in pollutant emissions could substantially affect BSOA formation; Thus, there is an urgent need for long-

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term characterization of BSOA to better assess its potential impacts on radiative forcing, human health, and to fully understand the anthropogenic–biogenic interactions.

Data availability. The data used in this study are freely available at https://doi.org/10.5281/zenodo.15164940 (Wu, 2025). And Meteorological data and hourly $PM_{2.5}$, NO_2, O_3 concentrations can be obtained from https://doi.org/10.5281/zenodo.7413640 (Wu, 2022).

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Competing interests. The authors declare no competing interest.

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Table 1 Summary of the average BSOA tracers at the two sampling sites during the whole campaign.

Compounds	Mountain foot			Mountainside		
	Average	Daytime	nighttime	Average	Daytime	nighttime
Isoprene derived SOA tracers						
2-MGA[a]	28.6±14.7	35.7±16.8	21.7±7.4	16.2±8.4	19.5±9.4	12.9±5.6
2-methyltetrols						
2-Methylthreitol	24.0±10.1	24.7±10.4	23.3±9.8	32.1±22.6	28.6±20.9	35.6±23.7
2-Methylerythritol	49.7±22.4	51.9±23.2	47.7±21.3	66.6±46.4	57.3±41.8	76.0±48.9
subtotal	73.8±32.1	76.6±33.1	71.0±30.7	98.6±68.4	85.9±62.4	111.6±71.8
C_5-alkene triolsb						
cis-2-Me-1,3,4-THB[b]	20.1±12.8	20.1±12.7	20.1±12.9	21.8±17.9	19.2±15.4	24.4±19.8
3-Me-2,3,4-THB[c]	22.6±14.7	22.2±13.6	23.0±15.6	23.2±19.2	20.7±16.9	25.8±21.0
trans-2-Me-1,3,4-THB[d]	30.9±19.1	30.3±18.9	31.2±19.4	29.6±22.3	26.0±18.7	33.0±24.8
subtotal	73.5±46.4	72.6±44.9	74.3±47.7	74.5±59.2	65.9±50.8	83.2±65.5
3-MeTHF-3,4-diols						
trans-3-Me-THF-diol[e]	3.0±1.4	2.9±1.3	3.0±1.4	3.2±1.9	3.1±1.8	3.3±2.0
cis-3-Me-THF-diol[f]	3.8±1.5	3.7±1.5	3.8±1.5	4.7±3.7	4.4±3.4	5.0±4.0
subtotal	6.7±2.8	6.6±2.8	6.8±2.9	7.9±5.5	7.5±5.0	8.3±5.8
Total	182±81	191±83	173±77	197±126	178±114	216±135
α/β-pinene derived SOA tracers						
cis-pinonic acid	8.9±3.5	9.3±3.8	8.5±±3.0	4.0±2.4	4.4±2.3	3.6±2.5
pinic acid	5.1±2.2	5.8±2.2	4.5±2.1	3.3±2.0	3.6±2.0	3.1±1.9
MBTCA[g]	26.3±14.1	30.1±13.6	22.7±13.6	19.4±12.9	21.2±13.7	17.6±11.8
3-HGA[h]	12.1±6.4	13.7±6.2	10.6±6.2	5.5±4.0	6.9±4.5	4.1±2.8
Total	52.4±23.1	59.0±22.4	46.2±22.0	32.3±20.0	36.1±21.0	28.4±18.0
β-caryophyllene derived SOA tracer						
β-Caryophyllinic acid	34.5±19.1	35.2±17.6	33.7±20.4	56.0±40.1	70.2±46.2	41.6±28.4

[a]2-MGA: 2-methylglyceric acid;
[b]cis-2-Me-1,3,4-THB: cis-2-Methyl-1,3,4-trihydroxy-1-butene;
[c]3-Me-2,3,4-THB: 3-Methyl-2,3,4-trihydroxy-1-butene;
[d]trans-2-Me-1,3,4-THB: trans-2-Methyl-1,3,4-trihydroxy-1-butene;
[e]trans-3-Me-TH-diol: trans-3-Methyltetrahydrofuran-3,4-diol;
[f]cis-3-Me-TH-diol: cis-3-Methyltetrahydrofuran-3,4-diol;
[g]MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid;
[h]3-HGA: 3-Hydorxyglutaric acid

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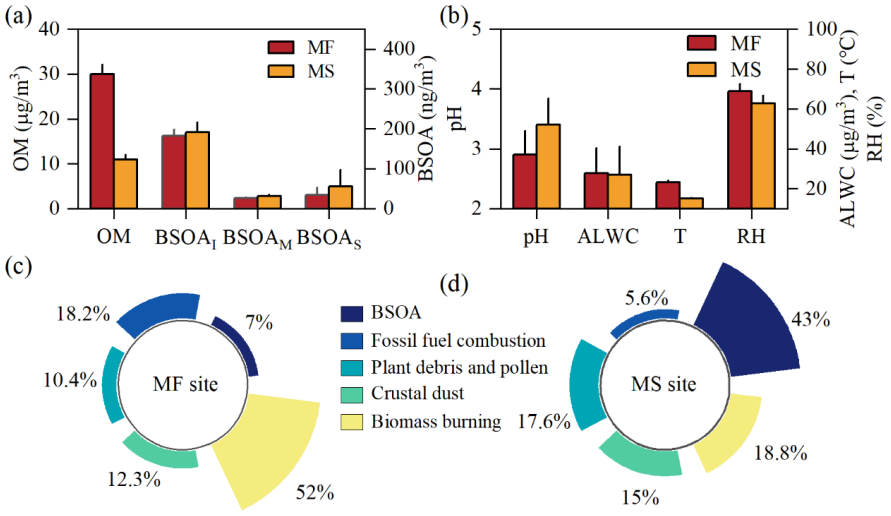

Figure 1 Comparisons upon chemical composition **(a)**, meteorological conditions **(b)**, and sources for OM **(c and d)** among two sampling sites. (OM concentration is converted by the OM/OC ratio measured in our previous (Wu et al., 2024))

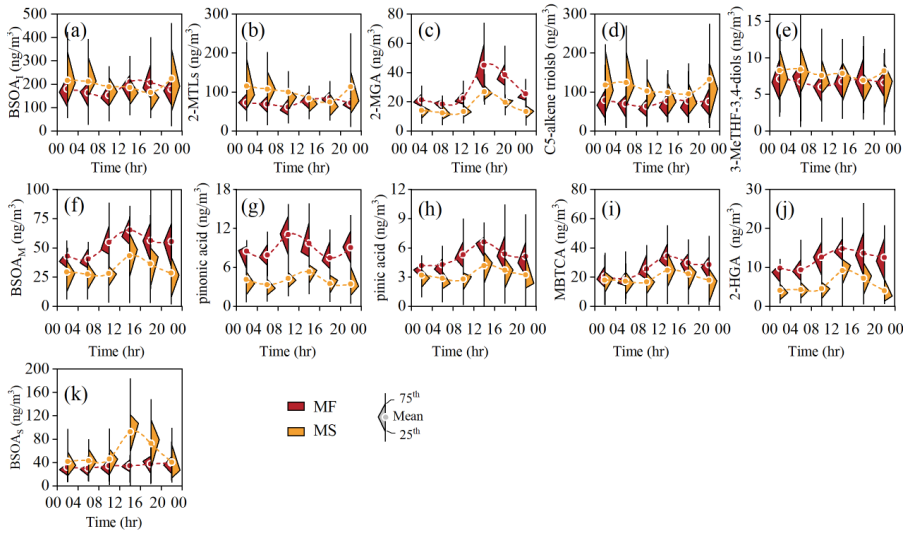

Figure 2 Diurnal variations in BOSA tracers among both sites. **(a-e)** isoprene-derived SOA tracer; **(f-j)** monoterpenes-derived SOA tracer; **(k)** β-caryophyllene -derived SOA tracer.

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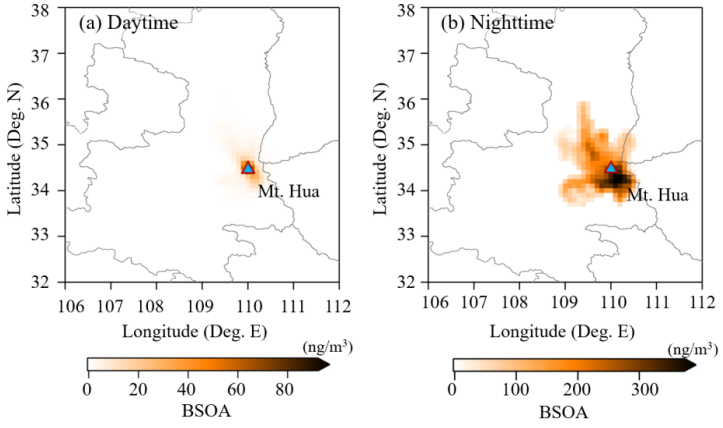

Figure 3 A concentration-weighted trajectory (CWT) analysis for $BSOA_I$ at MS site.

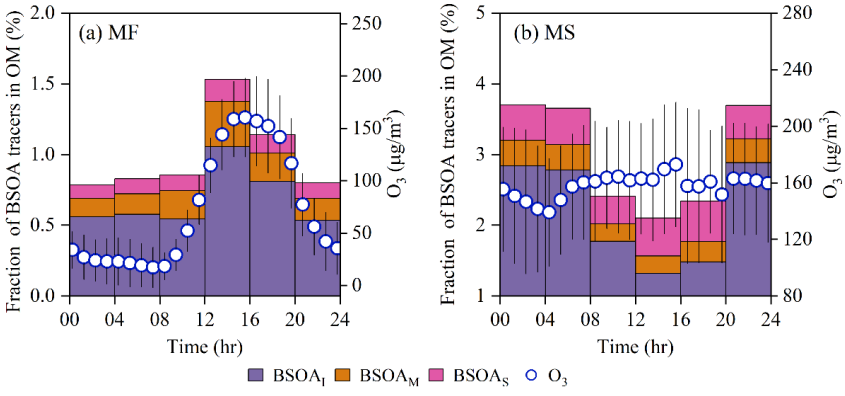

Figure 4 Diurnal cycles of mass fraction of BSOA tracers in OM and O_3 at both sampling sites.

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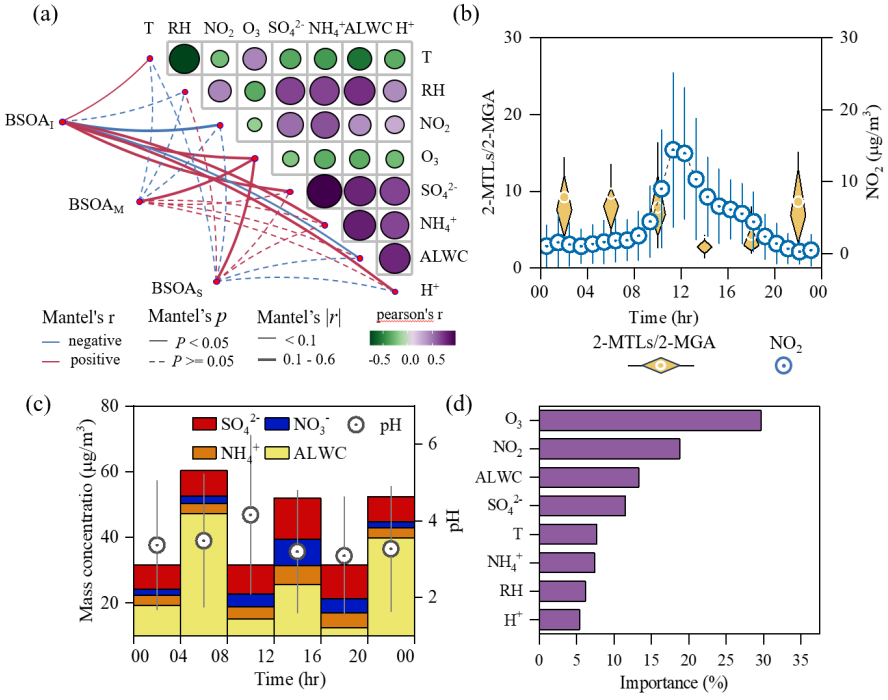

Figure 5 Formation of daytime isoprene-derived SOA in upper troposphere. **(a)** Mantel test between BSOA tracers and potential influencing factors at MS site; **(b and c)** Diurnal variations 2-MTLs/2-MGA ratio, pH, and the concentration of NO_2, SNA, ALWC at MS site; **(d)** Importance assessment for the key factors affecting the daytime isoprene-derived SOA at the MS site.

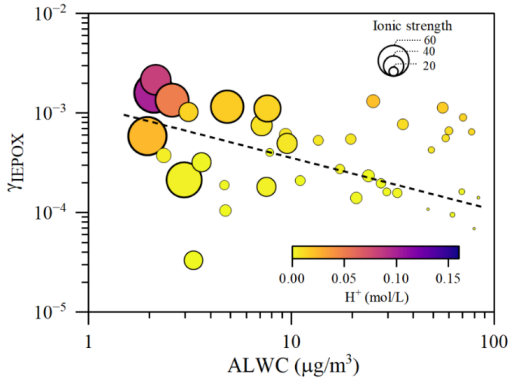

Figure 6 Reactive uptake (γ_{IEPOX}) as a function of ALWC during the daytime at MS site.