Contributions and source identification of biogenic and anthropogenic hydrocarbons to secondary organic aerosols at Mt. Tai in 2014[☆]

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ABSTRACT

Ambient fine particulate matter ($PM_{2.5}$) and volatile organic compounds (VOCs) collected at Mt. Tai in summer 2014 were analysed and the data were used to identify the contribution of biogenic and anthropogenic hydrocarbons to secondary organic aerosols (SOA) and their sources and potential source areas in high mountain regions. Compared with those in 2006, the 2014 anthropogenic SOA tracers in $PM_{2.5}$ aerosols and VOC species related to vehicular emissions exhibited higher concentrations, whereas the levels of biogenic SOA tracers were lower, possibly due to decreased biomass burning. Using the SOA tracer and parameterisation method, we estimated the contributions from biogenic and anthropogenic VOCs, respectively. The results showed that the average concentration of biogenic SOA was 1.08 ± 0.51 µg m^{-3}, among which isoprene SOA tracers were dominant. The anthropogenic VOC-derived SOA were 7.03 ± 1.21 µg m^{-3} and 1.92 ± 1.34 µg m^{-3} under low- and high-NO_x conditions, respectively, and aromatics made the greatest contribution. However, the sum of biogenic and anthropogenic SOA only contributed 18.1–49.1% of the total SOA. Source apportionment by positive matrix factorisation (PMF) revealed that secondary oxidation and biomass burning were the major sources of biogenic SOA tracers. Anthropogenic aromatics mainly came from solvent use, fuel and plastics combustion and vehicular emissions. However, for > C6 alkanes and cycloalkanes, vehicular emissions and fuel and plastics combustion were the most important contributors. The potential source contribution function (PSCF) identified the Bohai Sea Region (BSR) as the major source area for organic aerosol compounds and VOC species at Mt. Tai.

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1. Introduction

Secondary organic aerosols (SOA) are an important component of atmospheric particulate matter (PM) that can lead to visibility degradation, adversely affect human health and influence climate change (Tabazadeh, 2005; Seagrave et al., 2006; De Gouw and Jimenez, 2009). SOA can be formed by both biogenic and anthropogenic precursors, such as volatile organic compounds (VOCs).

Isoprene, monoterpenes and sesquiterpenes are considered to be the most important biogenic VOCs (Williams et al., 2013), whereas volatile alkanes and aromatic compounds are important anthropogenic VOC precursors for SOA formation (Chen et al., 2010). On global and continental scales, it is suggested that the amount of biogenic VOC emissions is more than an order of magnitude larger than the amount from anthropogenic sources (Farina et al., 2010; Ashworth et al., 2013). However, in some highly industrialised and densely populated regions, anthropogenic VOC contributions to SOA play a dominant role (Ding et al., 2012; Huang et al., 2015; Sun et al., 2016). Moreover, anthropogenic VOC emissions in these areas might promote biogenic VOC oxidation and SOA formation (Carlton et al., 2010; Hoyle et al., 2011). Given that

anthropogenic SOA are easier to mitigate than biogenic SOA, understanding their relative contributions and sources facilitates the development of an effective control strategy.

Some methods for measuring the contribution of SOA have been developed, including the EC-tracer method (Wang et al., 2012), carbon isotopic analysis (Lewis et al., 2004) and aerosol mass spectrometer (AMS) measurements (Zhang et al., 2007). However, these methods cannot determine the contributions of individual precursors to measured SOA.

In this study, we use the secondary organic tracer approach developed by Kleindienst and coworkers (Kleindienst et al., 2007) to evaluate contributions from biogenic SOA. Despite significant uncertainties due to the limited number of identified tracers and chamber parameters, the method is a valuable and convincing method for biogenic SOA estimation (Kleindienst et al., 2007). The contributions of anthropogenic VOCs were estimated by a parameterisation method based on photochemical age that has been applied in urban and rural locations (De Gouw et al., 2005; Yuan et al., 2012, 2013; Yao et al., 2016). The sources of biogenic and anthropogenic SOA were examined using a positive matrix factorisation (PMF) model, a developed receptor model that limits all of the elements in the factor score. Possible source areas were identified by potential source contribution function (PSCF) analysis using trajectory ensembles (Hopke et al., 1995). Both the PMF model and PSCF analysis have been widely applied to assess source categories and their locations on a regional scale (Heo et al., 2009; Cherian et al., 2010; Cheng et al., 2011; Yao et al., 2016).

Mt. Tai, as the highest mountain on the North China Plain (NCP), is frequently influenced by pollutants transported from the latter, which is one of the most developed regions in China and has abundant anthropogenic VOCs and NO_x emissions (Zhang et al., 2009). Therefore, Mt. Tai's location makes it a unique place to study SOA formation. In this study, fine particulate matter ($PM_{2.5}$) organic aerosol and VOC samples were collected at Mt. Tai in 2014 during the summer with the following objectives: (1) to investigate the molecular compositions of organic aerosol and VOC concentrations over Mt. Tai and compare the results with those obtained in 2006 to investigate concentration variations. In 2006, organic aerosol compounds in total suspended particulate (TSP) were collected between 28 May and 28 June at the balcony of the second floor of observatory (~10 m above ground level) at Mt. Tai (36.25 N, 117.10 E, 1534 m a.s.l) (Fu et al., 2008); (2) to estimate biogenic and anthropogenic hydrocarbons' contributions to SOA formation; and (3) to identify the sources and source areas of biogenic and anthropogenic SOA using the PMF model and PSCF analysis, respectively.

2. Experimental methods

2.1. Site description

The sampling site was located in the air force hotel on the summit of Mt. Tai (36.25 N, 117.10 E, ~1532.7 m a.s.l.) in Shandong province on the NCP, in the Houshiwu area, where there were less frequent tourists. Intensive measurements were conducted from 4 June to 4 July 2014. The meteorological data were measured by an automatic meteorological station (Kestrel 4500). During sample collection, ambient temperatures varied between 10 and 25 °C with an average of 17 °C; relative humidity ranged from 58 to 100% with an average of 87%; winds covered a range of 1–7 m/s, and the prevailing winds came from the northwest. The weather conditions at Mt. Tai were characterised as cloudy and occasionally foggy. Samples were collected only on no-rain days.

2.2. $PM_{2.5}$ sampling, extraction, derivatisation and GC/MS determination

Thirty-two daytime (06:00–18:00 local time) and twenty-seven night time (18:00–06:00 local time) $PM_{2.5}$ samples were collected using a TH-16A Intelligent $PM_{2.5}$ sampler at a flow rate of 100 L min^{-1} (Wuhan Tianhong Corporation, China). Two daytime blank and two night time blank samples were collected using the same method, but without power. Before and after collection, the sampler's airflow rate was calibrated. All of the samples were collected using pre-combusted (600 °C for 4 h) quartz fibre filters. After sampling, the loaded filter was recovered into plastic petri dishes, transported to the laboratory and stored at −20 °C before chemical analysis.

The samples were extracted with dichloromethane/methanol (2:1, v/v), concentrated and underwent derivatisation with 50 μL of N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h. Before GC/MS analysis, the derivatives were diluted with 140 μL of *n*-hexane, which contained 1.43 ng μL^{-1} of internal standard (C_{13} n-alkane). Blank samples were treated in the same manner as the samples. The sample analyses were performed with a Hewlett-Packard Model 6890 GC equipped with a mass-selective detector (Hewlett-Packard model 5973). A DB-5MS fused silica capillary column (30 m × 0.25 mm i. d., 0.25 μm film thickness) was used. The mass spectrometer was conducted by the electron impact (EI) mode at 70 eV and the mass fragment scan was from 50 to 650 Da. Individual compounds were determined based on authentic standards or literature data. No major contaminations were detected in the blanks and the mean recoveries were better than 80% for the organic aerosol compounds reported here. The data reported here were corrected by the field blanks.

2.3. VOC sampling and analysis

VOC samples were collected using pre-cleaned, evacuated stainless steel canisters provided by the University of California, Irvine (UCI). VOC samples were collected three times each day at 8:00, 14:00 and 0:00. A total of 70 canister samples were collected during this campaign. After sampling, the canisters were shipped to UCI's laboratory for chemical analysis.

The details on the chemical analysis, quality assurance and other aspects of each species are described elsewhere (Blake et al., 1994; Simpson et al., 2010). Briefly, for each sample, a 1520-cm^3 sample aliquot was introduced into the analytical system's manifold and split into 5 streams. Then, each stream was separated on an individual column by chromatographer and sensed by a single detector. VOC samples were quantified by gas chromatography-flame ionisation detector (FID) and mass spectrometer detector (MSD). In Table 2, the gases from ethane to benzene were quantified on the FID while the heavier gases were quantified on the MS. The identification of VOC species was based on the retention times and mass spectra. The National Bureau of Standards, Scott Specialty Gases and UCI-made standards were used as external standards. Multiple standards were also used in sample analysis for quality control (working standards − analysed every four samples; absolute standards − analysed twice daily). The detection limits for VOCs were 3 pptv.

2.4. Positive matrix factorisation (PMF)

The USEPA PMF 3.0 model was used to analyse the organic aerosol components and VOC data obtained at Mt. Tai, and to explore and quantify the sources of ambient air pollution. A detailed description of this method can be found in the user manual

(USEPA, 2008) and related references (Paatero and Tapper, 1994; Paatero, 1997). Two input files are required to initiate the model: one for concentration values and one for uncertainty values for each species. For concentration values less than the detection limit (MDL), the data were replaced by a half value of MDL. Missing data were substituted by median concentrations of that species (Brown et al., 2007). Uncertainties (Unc) were treated (Polissar et al., 1998; Reff et al., 2007) as follows: (1) if the concentration values were below or equal to the MDL, their uncertainty was calculated using the following equation: $Unc = 5/6 \times MDL$; (2) if the concentration values were greater than the MDL, the calculation used was: $Unc = [(Error\ fraction \times concentration)^2 + (MDL)^2]^{1/2}$.

Not all of the particulate organic compounds and VOC species were used in the PMF model. The principles for species choice were as follows: (1) species with more than 25% of their concentration values missing or that fell below the MDLs were excluded; (2) species with short atmospheric lifetimes were rejected; and (3) species with a low concentration and a-typical tracers of emission sources were not included. Eventually, 30 particulate organic compounds and 28 VOC species were selected for the source apportionment analysis. Q values are an assessment of how well the model fit the input data. Q_{robust} is the goodness-of-fit parameter excluding outliers. In this study the Q_{robust} value (4149.5) was close to the Q_{theory} value (4056), which indicated PMF results can reasonable explain potential sources of organic aerosol and VOC components.

2.5. Potential source contribution function (PSCF)

The PSCF (Hopke et al., 1995) was used to calculate the probability that air parcels had a higher source concentration than a certain criterion during transport to the sampling site. The PSCF value in the ij-th grid cell is calculated using the following equation:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}},$$

where n_{ij} is the total number of endpoints falling in the ij-th cell, and m_{ij} is the number of endpoints in the same cell where a source concentration exceeded a criterion value. In this study, the 75th percentile of a source concentration was set as the criterion value. Using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, 5-day back trajectories at a height of 1500 m a.s.l. were calculated for the sampling period every 2 h. The geophysical domain ($80°E–130°E$, $15°N-65°N$) was divided into 2500 grid cells with a $1 \times 1°$ resolution. The average number of endpoints per cell was 11. To minimise the uncertainties due to the limited amount of available data (Polissar et al., 2001), the $PSCF_{ij}$ value was weighted by a factor W_{ij}, as follows:

$$W_{ij} = \begin{cases} 1.0 & 33 < n_{ij} \\ 0.7 & 11 < n_{ij} \leq 33 \\ 0.4 & 7 < n_{ij} \leq 11 \\ 0.2 & 0 < n_{ij} \leq 7 \end{cases}$$

2.6. Parameterisation method

The detailed calculated procedure is described elsewhere (Yuan et al., 2013; Yao et al., 2016). Briefly, the method is provided below:

$$\Delta t = \frac{1}{[OH](k_T - k_B)} \times \left(ln\frac{[T]}{[B]}|t = 0 - ln\frac{[T]}{[B]} \right) \quad (1)$$

$$[NMHC_i] = ER_i \times ([CO] - [CO]bg) \times exp[\\ -(k_i, OH - kCO)[OH]\Delta t] \quad (2)$$

$$NMHC_i, consumed = ER_i \times (1 - exp(-k_i, OH[OH]\Delta t)) \quad (3)$$

$$SOA_{cal} = \sum_i NMHC_i, consumed \times Y_i \quad (4)$$

In Eq. (1), Δt is photochemical age. [OH] is the average concentration of OH radicals. In this study, the average OH radical concentration was 7.2×10^5 molecule cm^{-3} (Yuan et al., 2013). k_T and k_B are the OH rate constants of toluene and benzene (Atkinson and Arey, 2003). $\frac{[T]}{[B]}| t = 0$ and $\frac{[T]}{[B]}$ are the initial emission ratios and concentration ratio of toluene and benzene, respectively. $\frac{[T]}{[B]}| t = 0$ is calculated using the 97.5 percentile of the T/B ratio. In Eq. (2), [NMHC_i] and [CO] are the NMHC and CO concentrations, respectively. [CO]bg is the background concentration, which is the intercept of the scatter plot between CO and benzene. ER_i is the emission ratio of NMHC to CO. $k_{i,OH}$ and k_{CO} are the OH rate coefficients of NMHC and CO. It is noted that the $k_{i,OH}$ values lower than m/p-xylene are obtained from Atkinson and Arey (2003) and used to calculate ER_i. However, the $k_{i,OH}$ values higher than m/p-xylene are not used in this study, and ER_i values are obtained from Yuan et al. (2013). In Eq. (3), NMHC_{i, consumed} is the ratio of consumed NMHC concentration to CO (in $\mu g\ m^{-3}\ ppm^{-1}$ CO). In Eq. (4), SOA_{cal} is the SOA produced from VOC oxidation. Y_i is the SOA yield of NMHCs determined from chamber studies. The Y_i of alkanes and cyclic alkanes were obtained from Lim and Ziemann (2009). The Y_i value of Cyclopentane was equal to Cyclohexane value. The Y_i of benzene, toluene and m/p-xylene were from Ng et al. (2007), who estimated SOA formation under low-NO_x (<1 ppb) and high-NO_x (~1 ppm) conditions. The Y_i value of other aromatics species were the same with m/p-xylene. Given that the NO_x concentration at Mt. Tai covered a range of 0.9–21.5 ppb (average 8.3 ± 2.4 ppb), we separately calculated anthropogenic SOA concentrations under low- and high-NO_x conditions. Although used SOA yield in a large NO_x concentration range, the obtained result can be regarded as the upper and lower limits of SOA from anthropogenic sources at Mt. Tai.

3. Results

3.1. Data overview and comparison with 2006 results

A statistical summary of the concentrations of identified major organic aerosol compounds at Mt. Tai is presented in Table 1. Eight organic compound classes were detected in the Mt. Tai aerosol samples: n-alkanes, fatty acids, sugars, phthalate esters, hydroxy-/polyacids, aromatic acids, lignin and resin products and biogenic SOA tracers. The concentrations of total identified organic aerosol compounds ranged from 17.9 to 1740 ng m^{-3} with an average of 384 ± 197 ng m^{-3}. The biogenic SOA tracers, sugar compounds and hydroxy-/polyacids were the dominant compound classes, accounting for approximately 64.6% of the total mass concentrations of identified organics.

Thirty-seven VOC species were measured at Mt. Tai in summer 2014, including alkanes, alkenes, alkynes and aromatics. The concentrations of VOC species are listed in Table 2. The mixing ratio of total VOCs was 8040 ± 1530 pptv. Alkanes (55.5%) provided the largest contribution to total VOCs, followed by alkynes (17.4%), aromatics (14.7%) and alkenes (12.4%). Ethane, ethyne, propane, benzene and ethene were the most abundant compounds.

Owing to in 2006, TSP samples were collected for organic

Table 1
Concentrations of organic compounds in PM$_{2.5}$ aerosols collected at Mt. Tai in summer 2014 (unit: ng m^{-3}).

Compounds	Min	Max	Mean	Std[a]
I. n-Alkanes				
C$_{25}$	nd[b]	10.3	3.25	2.76
C$_{26}$	nd	9.40	2.78	3.42
C$_{27}$	nd	9.54	2.42	3.01
C$_{28}$	nd	10.9	2.69	2.60
C$_{29}$	nd	14.6	3.45	3.94
C$_{31}$	nd	16.8	4.06	2.24
subtotal	nd	60.1	18.7	10.2
II. Fatty Acids				
C$_{12:0}$	nd	9.85	1.32	2.16
C$_{14:0}$	nd	11.7	3.10	2.74
C$_{16:0}$	nd	132	14.4	28.4
C$_{18:0}$	nd	24.1	5.43	6.72
subtotal	nd	165	24.3	14.6
III. Sugars				
levoglucosan	1.22	843	70.4	39.8
arabitol	0.07	20.9	2.09	1.50
mannitol	0.09	55.7	3.97	3.57
fructose	0.12	11.1	1.62	2.29
glucose	0.26	22.9	3.40	4.02
inositol	0.04	0.75	0.22	0.15
sucrose	nd	14.6	2.11	1.24
trehalose	nd	5.90	1.02	1.55
erythritol	0.09	24.4	1.65	1.41
subtotal	1.37	907	86.5	29.0
IV. Phthalate Esters				
dimethyl	0.48	104	10.1	9.15
di-iso-butyl	2.74	117	12.5	11.3
di-n-butyl	1.11	42.3	7.03	6.43
di-(2-ethylhexyl)	0.79	94.0	7.26	11.4
subtotal	2.74	254	36.9	38.7
V. Hydroxy-/Polyacids				
tartaric acid	nd	14.6	4.72	3.16
malic acid	0.47	95.9	30.2	18.1
glycerol	0.25	52.6	18.9	10.7
glyceric acid	1.65	144	17.2	20.5
subtotal	0.25	182	71.0	36.9
VI. Aromatic Acids				
benzoic acid	0.63	8.05	8.01	1.94
phthalic acid	0.39	432	42.9	14.7
subtotal	0.25	428	50.9	19.8
VII. Lignin and Resin Products				
4-hydroxybenzoic acid	0.24	12.4	2.41	1.66
dehydroabietic acid	0.11	4.88	1.26	1.47
syringic acid	nd	1.51	0.86	0.57
vanillic acid	0.06	1.36	0.62	0.46
subtotal	0.11	20.2	5.15	4.89
VIII. Biogenic SOA Tracers				
2-methylglyceric acid	0.07	68.9	17.6	13.2
C$_5$-alkene triols[c]	0.58	83.8	22.8	21.7
2-methyltetrols	0.15	57.2	15.9	13.7
pinonic acid	nd	34.0	4.51	5.49
pinic acid	nd	30.5	4.01	5.71
3-HGA	0.78	78.5	25.9	17.4
subtotal	0.45	195	90.8	35.4
Σ isoprene SOA tracers	0.34	150	56.4	45.6
Σ α/β-pinene SOA tracers	0.59	83.7	34.4	28.4
Total measured organics	17.9	1740	384	197
OC (μgC m^{-3})	4.02	32.9	11.6	6.76

[a] Std: standard deviation.
[b] nd: not detected.
[c] C$_5$-alkene triols: cis-2-methyl-1,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene.

Table 2
Detected VOC compound mixing ratios from 4 June to 4 July 2014 at Mt.Tai (units: pptv).

VOC species	Average	Std[a]	Minimum	Maximum
Ethane	2295	615	1216	3900
Ethene	586	394	56	1918
Ethyne	1398	753	244	3412
Propane	824	461	282	3024
Propene	80	129	10	1068
i-Butane	322	479	47	3998
n-Butane	414	457	63	3398
1-Butene	23	29	4	218
i-Butene	59	45	15	276
i-Pentane	227	258	18	2082
n-Pentane	131	91	22	556
1-Pentene	8	12	nd[b]	84
Isoprene	150	180	nd	853
n-Hexane	61	43	8	200
n-Heptane	20	21	nd	150
n-Octane	9	13	nd	52
n-Nonane	17	22	nd	143
2,3-Dimethylbutane	10	13	nd	96
2-Methylpentane	54	43	5	201
3-Methylpentane	31	23	nd	110
Cyclopentane	18	20	nd	96
Cyclohexane	31	37	nd	205
Benzene	596	311	87	1754
Toluene	240	133	29	660
Ethylbenzene	73	64	11	351
m/p-Xylene	91	172	13	1345
o-Xylene	32	67	4	539
i-Propylbenzene	3	6	nd	40
n-Propylbenzene	9	21	nd	161
3-Ethyltoluene	26	103	nd	835
4-Ethyltoluene	13	48	nd	388
2-Ethyltoluene	12	47	nd	379
1,3,5-Trimethylbenzene	14	66	nd	534
1,2,4-Trimethylbenzene	50	236	nd	1938
1,2,3-Trimethylbenzene	20	84	nd	677
α-Pinene	76	48	10	309
β-Pinene	18	10	nd	40
Total	8040	1530	2670	20 592

[a] Std: standard deviation.
[b] nd: not detected.

same VOC species in 2014 and in 2006 (Suthawaree et al., 2010) to study the changes.

The comparison result is shown in Fig. 1. The total concentration of the same VOC species was similar in 2014 (mean 7589 ± 789 pptv) and in 2006 (mean 7781 ± 816 pptv). In 2014, the compound concentrations related to combustion sources (ethane, ethyne, ethene and propene) were lower than those in 2006, whereas those related to vehicular emissions (propane, i-butane, n-butane, i-pentane, n-pentane, 1-butene and m,p-xylene) were higher in 2014. The concentrations of other species — such as those related to solvent use (benzene, toluene and ethylbenzene) and biogenic emission (isoprene) compounds — were similar in 2014 and 2006.

The concentration of total organic aerosol compounds in PM$_{2.5}$ in 2014 (mean 384 ± 197 ng m^{-3}) was about four times lower than that in 2006 (mean 1529 ± 972 ng m^{-3}) (Fu et al., 2008; Deng et al., 2011). It is noted that concentrations of biomass burning tracers (levoglucosan, lignin and resin products) in 2014 were lower than those in 2006, especially for levoglucosan (approximately five times lower than that in 2006). The result confirmed the Chinese government's serious regulatory control of biomass burning. The concentrations of plastic consumption/combustion (phthalate esters) tracers were also significantly reduced from 2006 to 2014, possibly due to recycling plastic bags and bottles. However, anthropogenic secondary oxidation tracers (aromatic acids) had higher concentrations in 2014 than in 2006. The level of biogenic
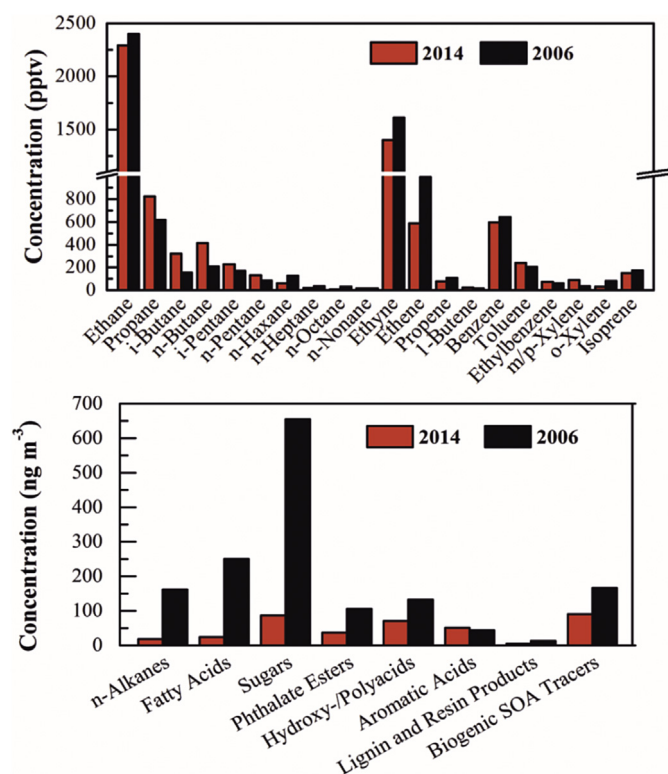
aerosol compounds analyse. To compare the concentrations of organic aerosol compounds in 2014 and 2006 at Mt. Tai, we used the ratio of PM$_{2.5}$ and TSP (PM$_{2.5}$/TSP = 0.91) obtained at Mt. Tai in June 2006 (Deng et al., 2011) to estimate the concentrations of organic aerosol compounds in PM$_{2.5}$ in 2006 at Mt. Tai. For a better comparison of VOC concentrations in 2014 and 2006, we chose the

Fig. 1. Concentrations of VOC (above) and organic compounds in PM$_{2.5}$ (below) in 2014 and 2006 at Mt. Tai.

SOA tracers and hydroxy-/polyacids in 2014 were lower than in 2006, which may be related to the decrease in biomass burning around Mt. Tai (Fu et al., 2012).

3.2. Biogenic and anthropogenic hydrocarbons' contributions to SOA

3.2.1. Estimation of SOA concentrations

The average concentration of organic carbon (OC) in PM$_{2.5}$ was 11.6 ± 6.76 μgC m^{-3} at Mt. Tai in summer 2014. Based on the ratio of organic matter (OM) and OC at the rural site (OM/OC = 2.07) (Yao et al., 2016), we estimated the OM concentration at Mt. Tai (24.4 ± 10.9 μg m^{-3}).

The elemental carbon (EC)-tracer method, which was used to calculate secondary organic carbon (SOC) concentrations, has been described in detail elsewhere (Zhou et al., 2012; Wang et al., 2012). The key parameter of the primary OC/EC ratio was estimated using a linear regression of the observed lowest 15% OC/EC concentration ratios, and the obtained primary OC/EC ratio was 2.44 (R^2 = 0.81) at Mt. Tai in summer 2014. The calculated SOC average concentration was 7.87 μgC m^{-3}, and the corresponding SOA concentration was 16.5 ± 10.2 μg m^{-3}. The contribution of SOA to the total OM ranged from 19.5 to 84.2% with an average of 67.7%.

3.2.2. Contribution of biogenic VOC oxidation to SOA formation

Six compounds were identified as isoprene-SOA tracers in the Mt. Tai aerosols, including 2-methylglyceric acid (2-MGA) (Claeys et al., 2004), three C$_5$-alkene triols (Wang et al., 2005) and two diastereoisomeric 2-methyltetrols (2-methylthreitol and 2-methylerythritol). The average concentration of 2-MGA was 17.6 ± 13.2 ng m^{-3}. This acid is produced by the oxidation of isoprene under high-NO$_x$ conditions (Surratt et al., 2006, 2010). The average concentration of 2-methyltetrols was 15.9 ± 13.7 ng m^{-3}

with 2-methylerythritol being approximately twice as high as 2-methylthreitol. The average concentration of C$_5$-alkene triols, which were unique photooxidation products of isoprene under low-NO$_x$ conditions (Wang et al., 2005), was 22.8 ± 21.7 ng m^{-3}.

We also detected α/β-pinene oxidation products, including pinonic acid, pinic acid and 3-hydroxyglutaric acid (3-HGA). These acids are formed by the photooxidation of α/β-pinene with O$_3$ and OH radicals (Glasius et al., 2000; Iinuma et al., 2004). Their total concentration was 34.4 ± 28.4 ng m^{-3}.

The contributions of organic aerosols from primary and secondary biogenic sources to OM were estimated using tracer-based methods. For primary biogenic sources, mannitol concentrations were used to estimate fungal spore-derived OC (Bauer et al., 2008; Holden et al., 2011), and then the OM/OC ratio was used to calculate the fungal spore-derived OM. The average mass percent ratio (8.14%) of levoglucosan to OC was then used to estimate the biomass burning-derived OC (Graham et al., 2002; Andreae and Merlet, 2001). Then, the OM/OC ratio was used to obtain the biomass burning-derived OM. Biogenic SOA from the isoprene and α/β-pinene oxidation were assessed by a tracer-based method reported by Kleindienst et al. (2007). A series of individual component hydrocarbon/NO$_x$ irradiations in the smog chamber was used to calculate the mass fraction of tracer compounds in SOA (f$_{SOA}$) with the following formula:

$$\text{fSOA} = \frac{\sum_i [tri]}{[SOA]},$$

where [tr$_i$] is the concentration of tracer i in μg m^{-3} and [SOA] is the SOA concentration in μg m^{-3}. The f$_{SOA}$ values for isoprene and α/β-pinene were 0.063 ± 0.016 and 0.168 ± 0.081, respectively (Kleindienst et al., 2007). Although the smog chamber experiments used in this method were conducted under relatively high NO$_x$ conditions, Kleindienst have shown that the mass fractions of isoprene were similar with those in the absence of NO$_x$. The result suggested that a tracer-based method could be applied to low-NO$_x$ levels for high mountain aerosols.

As Table 3 shows, biomass-burning-derived OM ranged from 0.03 to 21.8 μg m^{-3} (average 1.82 ± 2.37 μg m^{-3}), and accounted for 7.5% of the OM in Mt. Tai's aerosols. The concentration of fungal-spore-derived OM ($0.00-0.89$ μg m^{-3}, average 0.06 ± 0.08 μg m^{-3}) was lower than that of biomass-burning-derived OM. The concentrations of total biogenic SOA ($0.01-2.64$ μg m^{-3}, average 1.08 ± 0.51 μg m^{-3}) were much lower than those of total primary emission OM, among which isoprene-SOA was dominant. The result was higher than that at Mt. Fuji in Japan (Fu et al., 2014). The contribution of α/β-pinene SOA to OM (0.8%) was 4.5 times lower than that of isoprene-produced OM. In total, these biogenic primary and secondary sources accounted for 12.1% of OM, among which biomass burning was the largest contributor, followed by isoprene SOA.

Table 3
Concentrations of biogenic primary emission OM and secondary emission SOAs and their contributions to OM (%) in the Mt. Tai aerosol samples (unit: μg m^{-3}).

Component	Range	Mean	Std[a]	% in OM
OM	8.44–69.1	24.4	10.9	
Biomass burning OM	0.03–21.8	1.82	2.37	7.5
Fungal spore OM	0.00–0.89	0.06	0.08	0.3
α/β-pinene SOA	0.00–0.50	0.19	0.13	0.8
Isoprene SOA	0.01–2.38	0.89	0.38	3.6
Σ biogenic SOA	0.01–2.64	1.08	0.51	4.4
Subtotal	0.04–22.6	2.96	1.56	12.1

[a] Std: standard deviation.

3.2.3. Contribution of anthropogenic VOC oxidation to SOA formation

The average concentrations of alkanes, alkenes, alkynes and aromatics at Mt. Tai in summer 2014 were 4460 ± 1070, 1000 ± 465, 1400 ± 553 and 1180 ± 1020 pptv, respectively. The anthropogenic VOC species in this study selected aromatics, $> C6$ alkanes and cycloalkanes at concentrations of 1180 ± 1020, 46 ± 34 and 49 ± 22 pptv, respectively. A parameterisation method was used to calculate SOA formation from anthropogenic VOC oxidation.

The results of the parameterisation methods are presented in Table 4. The total SOA concentrations produced from detected anthropogenic VOC species were 12.04 ± 3.29 and 3.28 ± 0.73 $\mu g\ m^{-3}\ ppm^{-1}$ CO under the low- and high-NO_x conditions, respectively. The result is higher than that in Changdao (Yuan et al., 2013) and Yucheng (Yao et al., 2016) rural site in the North China Plain. Aromatics provided the largest contribution to the total SOA concentration, accounting for 98.3 and 93.6% under low- and high-NO_x conditions, respectively. Benzene, toluene, m/p-xylene, o-xylene, 3-ethyltoluene, 4-ethyltoluene and ethylbenzene were the dominant compounds under both low- and high-NO_x conditions.

According to CO concentration (average 584 ± 321 ppb), we obtained total SOA concentration in unit $\mu g\ m^{-3}$ (7.03 ± 1.21 and 1.92 ± 1.34 $\mu g\ m^{-3}$ in low- and high-NO_x conditions, respectively). Therefore, anthropogenic SOA contributed to 42.6 and 11.6% of the total SOA under low- and high-NO_x conditions, respectively. Biogenic SOA accounted for 6.5% of the total SOA concentration. It is clear that a large percentage of the SOA was not identified, and may be related to (1) missing SOA precursors, such as semi-volatile organic compounds (SVOCs); (2) only considered reactions between VOCs and OH radicals when calculating the SOA concentration (Yuan et al., 2013); or (3) the photochemical aging of primary organic aerosols (POAs). Many studies have found that POA aging (such as fossil combustion and biomass burning) can contribute large amounts of SOA (Hennigan et al., 2011; Jathar et al., 2011; Spracklen et al., 2011).

3.3. Source attribution by PMF

The PMF simulated concentrations matched the measured concentrations very well, with slopes (reconstructed to observe) in the range of 0.88–0.99 and R^2 of 0.86–0.97 for the whole dataset.

Fig. 2 shows the factor profiles for the identified sources. Probable source regions from the PSCF analysis for PMF identified sources are shown in Fig. 3. Five emission sources − vehicular emissions, secondary oxidation, biomass burning, solvent use and fuel and plastics combustion − were identified.

Source 1 was considered to be vehicular emission-related sources with a dominance of C_3-C_6 alkanes, propene, i-butene and BTEX (Benzene, Toluene, Ethylbenzene, Xylene), which are typical tracers of vehicular emissions (Guo et al., 2004; Song et al., 2007; Brown et al., 2007; Guo et al., 2007). The PSCF results for vehicular emissions identified the northwest portion of the sampling site as the major source region, including Hebei province, Beijing and Tianjin city and part of Inner Mongolia, Shanxi province. The total vehicle possession in these areas contributed about 18% to the national vehicle possession in 2014.

Source 2 largely featured aromatic acid species, hydroxy/polyacids and biogenic SOA tracers, indicating its relation to secondary oxidation (Simoneit et al., 2004; Fu et al., 2010). The PSCF results for secondary sources near Mt. Tai exhibited similar high values with other source regions, indicating that both long-range transport and local sources were important contributors to secondary sources.

Source 3 was associated with biomass burning, which is characterised by high levoglucosan, lignin and resin products (Simoneit, 2002; Simoneit et al., 1993) and a median concentration of ethene, ethyne and i-butene (Andreae and Merlet, 2001). Southwest Henan province, northwest Inner Mongolia and Jiangsu province, Southeast Hebei and Shanxi province, western Shandong province and northeast Anhui province, with significantly high PSCF values, were identified as the important regions for biomass burning sources. Hotspots (http://hjj.mep.gov.cn/index_726_5.htm) also revealed that these areas had highly active hotspot disturbances.

Source 4 was identified as solvent use by a significant presence of aromatics species (Chan et al., 2006; Guo et al., 2004). The PSCF results showed that solvent use had an almost parallel source area distribution: northwest Inner Mongolia, Beijing and Tianjin city, Hebei province, northern Anhui province and southeast Henan province were the most important source regions.

Source 5 was heavily correlated with C_2 VOCs species, phthalate esters and n-alkanes, which were related to fuel and plastics combustion (Liu et al., 2008; Fu et al., 2008). The PSCF results showed that the source generally had similar source areas to coal-fired power plants in North China, such as southern Hebei province,

Table 4
Concentrations and emission ratios of VOC species, and the SOA formed from VOC oxidation at Mt. Tai in summer 2014.

| Species	Concentration $\mu g\ m^{-3}$	ERi $\mu g\ m^{-3}\ ppm^{-1}$ CO	SOA formed, $\mu g\ m^{-3}\ ppm^{-1}$ CO	
			Low- NO_x	High- NO_x
n-Heptane	0.09	1.08	0.007	0.007
n-Octane	0.05	0.75	0.023	0.023
n-Nonane	0.10	1.96	0.126	0.126
Cyclopentane	0.06	0.53	0.012	0.012
Cyclohexane	0.12	1.49	0.041	0.041
Benzene	2.08	9.90	0.675	0.480
Toluene	0.99	9.84	1.799	0.720
Ethylbenzene	0.35	4.37	1.085	0.217
m/p-Xylene	0.43	6.18	2.130	0.426
o-Xylene	0.15	5.64	1.822	0.364
i-Propylbenzene	0.01	0.11	0.026	0.005
n-Propylbenzene	0.05	0.51	0.114	0.023
3-Ethyltoluene	0.14	3.90	1.341	0.268
4-Ethyltoluene	0.07	6.07	1.881	0.376
2-Ethyltoluene	0.06	1.70	0.528	0.106
1,3,5-Trimethylbenzene	0.08	0.24	0.086	0.017
1,2,4-Trimethylbenzene	0.27	0.71	0.254	0.051
1,2,3-Trimethylbenzene	0.11	0.24	0.086	0.017
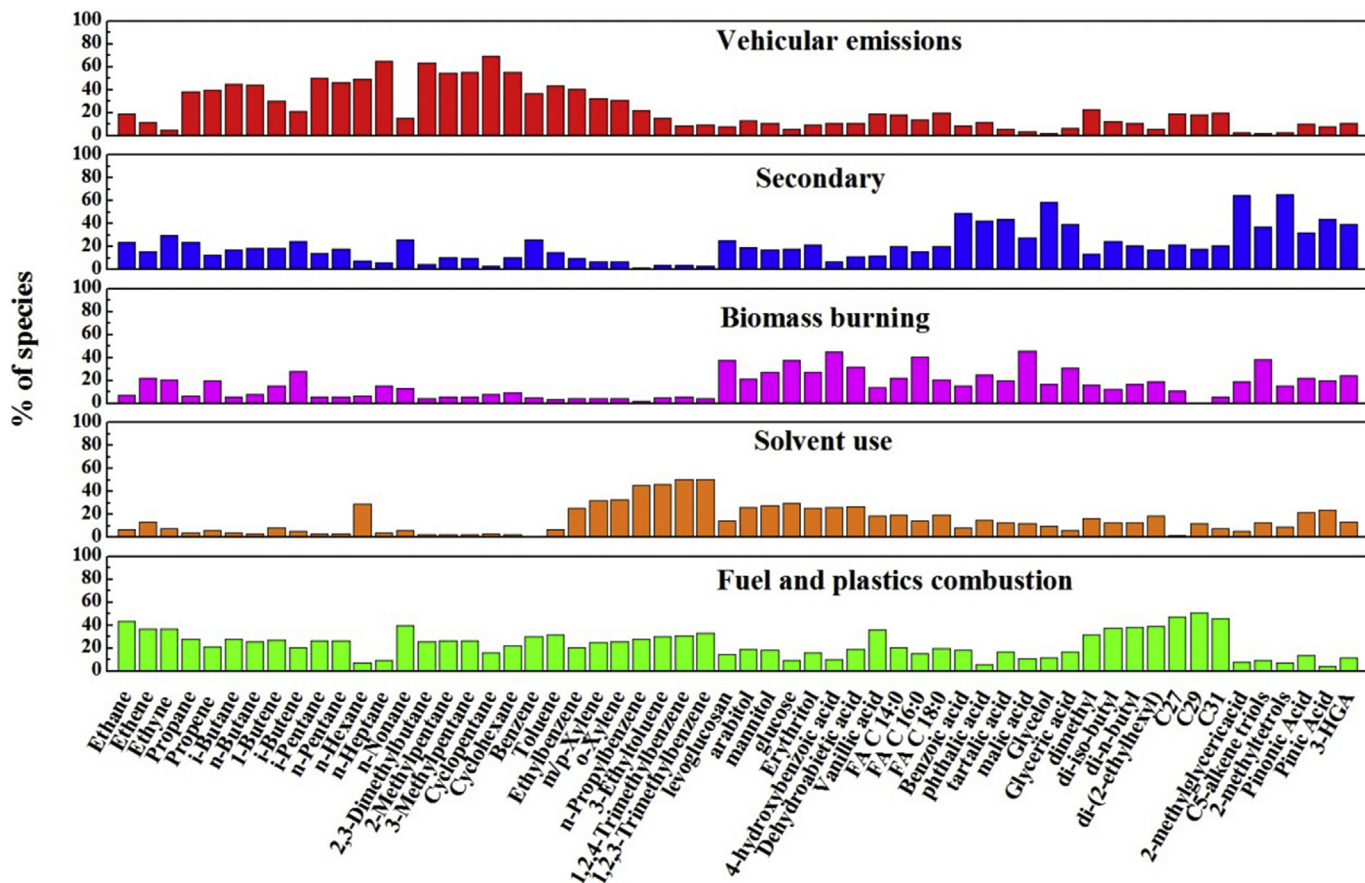
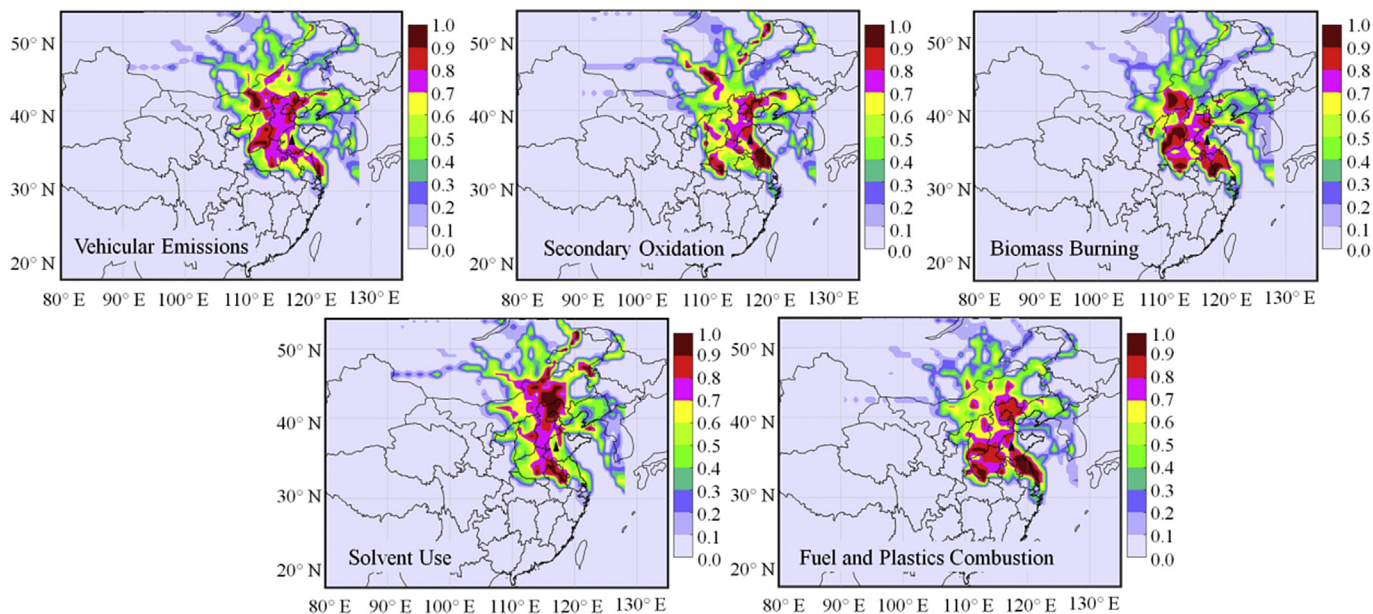**Fig. 2.** Factor profiles (% of species) for aerosol organic compounds and VOC species.

Fig. 3. Probable source regions deduced from PMF model analysis of the five identified sources at Mt. Tai during the observation period.

Beijing and Tianjin city, northwest Shandong province, Jiangsu and Henan province and northern Anhui province.

Fig. 4 shows the contributions of different sources to biogenic SOA tracers and anthropogenic VOC species based on the PMF results. Secondary oxidation, biomass burning and solvent use were the three major sources that collectively contributed more than 80% of biogenic SOA tracers. Secondary oxidation topped the sources of biogenic SOA tracers with a share of 55.9%, followed by 38.5% for
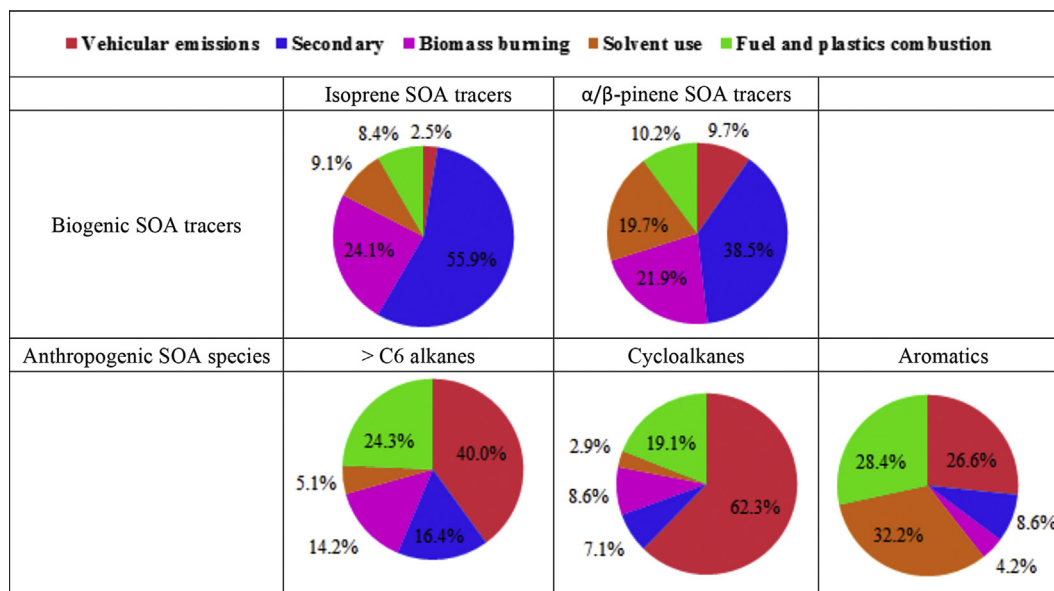
Fig. 4. Source contributions to biogenic SOA tracers and anthropogenic VOC species at Mt. Tai in summer 2014.

isoprene-SOA and α/β-pinene-SOA tracers. Biomass burning was the second-most abundant contributor, accounting for 24.1%, followed by 21.9% of total isoprene-SOA and α/β-pinene-SOA tracers. This result is consistent with the higher average concentration of levoglucosan at Mt. Tai in summer 2014 (70.4 ± 39.8 ng m^{-3}), especially during the first half of the campaign (134 ± 81.8 ng m^{-3}). Solvent use, however, accounted for a larger share of α/β-pinene-SOA tracers (19.7%). The vehicular emissions and fuel and plastics combustion also accounted for higher percentages of α/β-pinene-SOA tracers (9.7%, 10.2%) than isoprene-SOA tracers (2.5%, 8.4%).

Anthropogenic aromatic species mainly came from solvent use, with a share of 32.2%, and fuel and plastic combustion and vehicular emissions ranked second and third with similar contributions of 28.4% and 26.6%, respectively. The sum of secondary oxidation and biomass burning contributed only 12.8% to aromatics. Unlike aromatics, vehicular emissions were the major contributors of > C6 alkanes (40.0%) and cycloalkanes (62.3%). Fuel and plastics combustion was the second source of > C6 alkanes and cycloalkanes, contributing 24.3% and 19.1%, respectively, followed by secondary oxidation and biomass burning, which contributed more to > C6 alkanes (16.4%, 14.2%) than to cycloalkanes (7.1%, 8.6%). Solvent use made minor contributions to > C6 alkanes (5.1%) and cycloalkanes (2.9%).

4. Conclusions

Field measurements of organic compounds in PM$_{2.5}$ and VOCs were conducted at Mt. Tai in summer 2014. The concentration of total organic aerosol compounds was 384 ± 197 ng m^{-3}, and total VOC mixing ratio was 8040 ± 1530 pptv. Comparison of the results with those in 2006 showed that biomass burning tracer (levoglucosan) concentrations in 2014 were about five times lower than in 2006. However, anthropogenic secondary oxidation tracers had higher concentrations in 2014 than in 2006. Moreover, the concentrations of VOC species related to vehicular emissions were also higher in 2014. Using a tracer-based method, we estimated the concentrations of SOA derived from isoprene and α/β-pinenes to be 0.89 ± 0.38 μg m^{-3} and 0.19 ± 0.13 μg m^{-3}, respectively. And the two biogenic SOA corresponded to 3.6 and 0.8% of the OM, respectively. The parameterisation method revealed that aromatic-

derived SOA were much higher than those of > C6 alkanes and cycloalkanes. However, anthropogenic VOC oxidation can only explain 42.6% of SOA formation under low-NO$_x$ conditions, whereas 11.6% of SOA formation is explainable under high-NO$_x$ conditions. The PMF model identified secondary oxidation and biomass burning were the two major sources of biogenic SOA. For anthropogenic SOA produced by aromatics, solvent uses, fuel and plastics combustion and vehicular emissions were the most important contributors. The PSCF results suggested that secondary oxidation was mainly involved with long-range transport and local emissions, and vehicular emissions mainly came from the northwest region of the sampling site.

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