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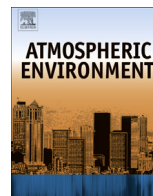
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# Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign



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## HIGHLIGHTS

- The averaged total OH reactivity for ambient pine forest air in Colorado was  $6.8 \text{ s}^{-1}$ .
- 2-methyl-3-buten-2-ol was the most prominent contribution to OH reactivity.
- About 30% of total OH reactivity was not assigned, implying the existence of missing OH sinks.
- One of the candidates of missing OH is thought to be the oxidation products of biogenic species.

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## ABSTRACT

Total OH reactivity was measured during the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H<sub>2</sub>O, Organics and Nitrogen-Southern Rocky Mountain 2008 field campaign (BEACHON-SRM08) held at Manitou Experimental Forest (MEF) in Colorado USA in August, 2008. The averaged total OH reactivity was  $6.7 \text{ s}^{-1}$ , smaller than that measured in urban ( $33.4 \text{ s}^{-1}$ , Yoshino et al., 2012) and suburban ( $27.7 \text{ s}^{-1}$ , Yoshino et al., 2006) areas in Tokyo in the same season, while sporadically high OH reactivity was also observed during some evenings. The total OH reactivity measurements were accompanied by observations of trace species such as CO, NO, NO<sub>y</sub>, O<sub>3</sub> and SO<sub>2</sub> and Volatile Organic Compounds (VOCs). From the calculation of OH reactivity based on the analysis of these trace species, 46.3% of OH reactivity for VOCs came from biogenic species that are dominated by 2-methyl-3-buten-2-ol (MBO), and monoterpenes. MBO was the most prominent contribution to OH reactivity of all trace species. A comparison of observed and calculated OH reactivity shows that the calculated OH reactivity is 29.5% less than the observed value, implying the existence of missing OH sinks. One of the candidates of missing OH is thought to be the oxidation products of biogenic species.

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## 1. Introduction

Volatile organic compounds (VOCs) play an important role in the formation of photochemical oxidants and secondary organic aerosol resulting from reactions with OH, O<sub>3</sub>, NO<sub>3</sub>, etc. (Finlayson-Pitts and Pitts, 2000). VOC emission sources are typically

categorized as either anthropogenic or biogenic activities. The estimations of the emission rate for the total anthropogenic and biogenic VOCs have been reported to be 142 and 1150 Tg per year, respectively (Goldstein, 2007), so that the biogenic activity is thought to be the largest VOC emission source on a global basis (Guenther et al., 1995). Therefore, intensive studies have been conducted to investigate biogenic VOC emissions and oxidation processes (Kim et al., 2010, 2013; Wiedinmyer et al., 2004; Guenther et al., 1995; Fuentes et al., 2000; Andreae and Crutzen, 1997). In addition to the research focused on the identification

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and chemical characterization of biogenic VOCs, the clarification of the reaction mechanism for the formation of HO<sub>x</sub> in tropical forest air has been an important research topic. Recently, higher concentrations of OH in ambient air have been observed than are estimated with models (Leileveld et al., 2008). Peeters et al. (2009) have proposed a different chemical process for the formation of OH during isoprene oxidation under low NO<sub>x</sub> condition. They have suggested that isomerization of a peroxy radical generated by the reaction of isoprene with OH under low NO<sub>x</sub> is caused, so called the 1, 5 and 1, 6-H shifts, resulting of the production of HO<sub>2</sub> and unsaturated hydroxyperoxide-aldehydes (HPALDs) and OH forms through the photolysis of HPALDs. To estimate the formation of photochemical oxidants and the amount of HO<sub>x</sub>, it is essential to clarify the loss and production processes of HO<sub>x</sub>, identify the oxidation products of the photochemical reaction of BVOCs, and determine their chemical properties.

OH is a strong oxidizer and reacts with any gaseous trace species in the troposphere except for some extremely unreactive species such as halocarbons, N<sub>2</sub>O and so on. Using the chemical property of OH, techniques for measuring total OH reactivity, the reciprocal of the lifetime of OH, have been developed (Sadanaga et al., 2004; Sinha et al., 2008; Ingham et al., 2009). By comparing observed and calculated OH reactivity, derived from the traditional chemical analysis, we can determine whether all of the trace species related to the formation of photochemical oxidants have been quantified. Recently, OH reactivity has been recognized as a useful index for the observation of trace species in ambient air. The results of the measurements of OH reactivity and comparison with the trace species analysis have been reported for some environmental conditions (Sadanaga et al., 2004; Yoshino et al., 2006, 2012; Ingham et al., 2009; Mao et al., 2009; Lee et al., 2009; Sinha et al., 2008, 2010; Kim et al., 2011, Nakashima et al., 2010). OH reactivity measurements have been reported for several forests which the concentration of isoprene (Di Carlo et al., 2004; Ingham et al., 2009; Sinha et al., 2008; Edwards et al., 2013) and that of monoterpenes (Sinha et al., 2010; Nölscher et al., 2012) is predominant.

In the present study, the measurement of total OH reactivity at a temperate coniferous forest site was carried out during summer 2008. Together with the measurement of OH reactivity, trace species analysis including inorganic species like CO, SO<sub>2</sub>, O<sub>3</sub>, NO and NO<sub>2</sub>, and VOCs were performed simultaneously. Comparison between observed and calculated OH reactivity allows investigation of the existence, amount, and origin of any missing OH sink. These observations were carried out during the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H<sub>2</sub>O, Organics & Nitrogen – South Rocky Mountain 2008 (BEACHON-SRM08) field campaign in August 2008 (Kim et al., 2010).

## 2. Experiments

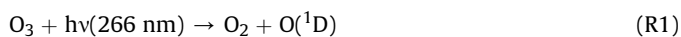
### 2.1. Measurement site

Measurements of the total OH reactivity in ambient air in a coniferous pine forest were conducted in summer, Aug. 22nd–28th in 2008, at the Manitou Experimental Forest (MEF), maintained and operated by the U.S. Forest Service. MEF (39°06′02″ N, 105°06′05″ W, 2286 m altitude) is located in the southern part of the Rocky Mountains and is about 40 km northwest of Colorado Springs, and about 70 km southwest of Denver. In the vicinity of the site, there is a road (route-67) but the traffic density is very low. Since MEF is far from big cities like Denver or Colorado Springs. MEF is mainly covered with ponderosa pine (*Pinus ponderosa*) with a canopy height of about 18.5 m. An especially heavy thunderstorm occurred near noon on Aug. 23rd resulting in severe

hail and a tornado was generated around 2 mile northeast of the measurement site.

### 2.2. Total OH reactivity

The measurement technique of the total OH reactivity was the same as reported previously (Sadanaga et al., 2004, 2005; Nakashima et al., 2010). Briefly, the conditions for measuring the total OH reactivity are explained. The sampling inlet (1/2″ ID, made from PFA) was placed at a height of approximately 4 m above the ground. Ambient air was introduced into a reaction tube (1.4 m length, 40 mm inner diameter, made from aluminum with a quartz window set at the end of the tube) in which the total flow rate was kept at 20 SLM. Pressure in the reaction cell was approximately 760 hPa. In the reaction cell, OH was supplied by the photolysis of O<sub>3</sub> and successive reaction of generated oxygen atom and water vapor as follows,



Ambient O<sub>3</sub> was employed in the formation of OH and no further O<sub>3</sub> or water vapor was added to the sample. A 266 nm light source was supplied by the fourth harmonic of a flash lamp–pumped Nd:YAG laser (Tempest 300, New Wave Research). The energy of the laser was set to around 20 mJ per pulse and the repetition rate was 2 Hz. Laser Induced Fluorescence (LIF) technique was employed to detect OH. At 0.8 m downstream from the inlet of the reaction tube, the mixture of ambient air and OH was collected through a 0.5-mm orifice and introduced into the LIF cell. The LIF cell was pumped by an oil rotary pump (D-950, ULVAC), and the pressure was kept at approximately 2 torr. The second harmonic of a pulsed dye laser (Sirah Precision, Spectra Physics) pumped by the second harmonic of a Nd:YVO<sub>4</sub> laser (YHP40-532Q, Spectra Physics) was used and the wavelength of the dye laser was set to the maximum intensity of a rotational transition of OH (308 nm). The laser power was adjusted to about 2–3 mW and the repetition rate was 10 kHz. The fluorescence signal was detected by a photomultiplier tube (R2256P, Hamamatsu Photonics). The output signals of the photomultiplier tube were recorded by the photon counting method. Together with the measurement of the LIF signal, the dye laser power was monitored by a photodiode (R1226-5BQ, Hamamatsu Photonics) to normalize the LIF signal. The decay curve of OH was typically integrated 240 times and analyzed by the non-linear least square fit to single exponential function to derive the OH reactivity. Uncertainty of the OH reactivity was estimated to be about 10% of the measurement value.

### 2.3. Analysis of trace species

Together with the measurements of OH reactivity, trace gas species in ambient air were measured simultaneously. O<sub>3</sub>, SO<sub>2</sub> and CO were measured by UV absorption (Model 205 dual beam, 2B Technology), pulsed fluorescence (Model 43C-TLE, Thermo Environmental) and non-dispersed infrared absorption spectrometer (Model 48, Thermo Environmental), respectively. NO and the sum of reactive nitrogen compounds (NO<sub>y</sub>) were monitored by chemiluminescence (Model CLD-88Y, Ecophysics) combined with a molybdenum converter. It is necessary to know the concentration of nitrogen dioxide (NO<sub>2</sub>) because it has a higher concentration and OH reactivity than any other reactive nitrogen compound except for NO. For the calculated OH reactivity estimated for this study, it is assumed that the concentration of NO<sub>2</sub> was almost the same as that

of NO<sub>y</sub>. In other words, the maximum of the OH reactivity for NO<sub>y</sub> can be derived.

Canister sampling of ambient air for subsequent analysis by Gas Chromatograph with Flame Ionization Detection (GC–FID) was carried out for the analysis of some non-methane hydrocarbons (NMHCs) summarized in Table 1. Canister sampling was carried out every 2 h between 900 and 2300 local time. The method of analysis by GC–FID was the same as that reported by Kato et al. (2001). A three-stage pre-concentrator (Model 7000, Entech) was used to concentrate 0.5 L of the sample gas, which was injected into the GC–FID. Plot (50 m length, 0.53 mm diameter and 1.5 μm film thickness) and HP-1 (60 m length, 0.32 mm diameter and 1.0 μm film thickness) columns were employed to analyze the lighter (2–3 carbon number) and other hydrocarbons, respectively. Standard gases containing 54 species at 1 ppmv (Matheson, Enviro-Mat) were measured for identification and quantification of each hydrocarbon. Detection limit was about 6 and 2 pptv for ethane and hexane, respectively.

Biogenic and oxygenated VOCs were measured by Proton-Transfer Mass Spectrometry (PTR-MS, IONICON Analytik, Innsbruck, Austria) simultaneously. Detailed methods of the measurements and results were already reported by Kim et al. (2010).

### 3. Results and discussions

#### 3.1. Observations of trace species

Fig. 1 shows the results of the measurements of CO, O<sub>3</sub>, SO<sub>2</sub>, NO and NO<sub>2</sub> together with the average concentration and standard deviation in Table 1. For CO and NO, diurnal variation of the concentrations was small and averaged concentration was low compared with that measured in urban areas. Low concentrations of CO and NO support the small contribution of anthropogenic sources. For SO<sub>2</sub>, on the other hand, regular diurnal variation for the concentration was observed. The concentration of SO<sub>2</sub> rapidly increased at noon or evening time and decreased within the day. No strong correlation for the diurnal variation between SO<sub>2</sub> and CO, NO or NO<sub>y</sub> was found. This result implies that there may be some special anthropogenic sources of SO<sub>2</sub> around MEF. However, the contribution of SO<sub>2</sub> on OH reactivity was quite low due to its low reactivity, so that the effect of the special source of SO<sub>2</sub> was thought to be negligible. Clear diurnal variation was observed for O<sub>3</sub> and NO<sub>y</sub>. The maximum concentration of O<sub>3</sub> was ca. 60 ppbv in daytime and about 10–20 ppbv of O<sub>3</sub> was observed in nighttime. Since the concentration of NO is always low around the measurement point, ozone can still exist in the nighttime. Diurnal variation of O<sub>3</sub> and the high concentration indicates that ozone formation process undergoes in MEF by the reaction of ambient OH and VOCs.

Unfortunately, the measurements of NMHCs could not be obtained because of accidental contamination of canisters. Then, the data for them measured in the same place during Aug. 7th–11th, 2008 were employed. Canister sampling was carried out every 2 h between 900 and 2300 local time. The averaged concentrations and standard deviation of NMHCs are summarized in Table 1. Averaged concentration of biogenic species, isoprene and monoterpenes, were higher than that of heavy alkanes, alkenes and aromatics. These results indicate that biogenic species are predominant in MEF and the contribution of anthropogenic species is small. The same measurements in MEF were performed in Aug. 12th–15th, 2009 and the obtained results were shown in Fig. 2 together with those in 2008. Comparing the two results, there were no differences for the averaged concentration except for 3 alkenes, 3-methyl-1-butene, 1-pentene and trans-2-pentene. Since the concentration of 3 species is quite low, the big differences for each averaged concentration were observed. From the results, it is

**Table 1**

Lists of the average concentrations, standard deviations and reaction rate constant at 298 K in atmospheric pressure for measured trace species.

No.	Species	Conc.	k <sub>OH+N</sub>
<i>Inorganics</i> (unit: ppbv)			
CO		168 ± 27	1.36 × 10 <sup>-13</sup>
O <sub>3</sub>		35 ± 14	8.12 × 10 <sup>-14</sup>
NO		0.23 ± 0.44	1.04 × 10 <sup>-11</sup>
NO <sub>y</sub>		2.3 ± 1.3 <sup>a</sup>	1.30 × 10 <sup>-11</sup>
SO <sub>2</sub>		0.14 ± 0.16	1.26 × 10 <sup>-12</sup>
CH <sub>4</sub>		1780 (assumed)	6.41 × 10 <sup>-14</sup>
<i>Alkanes</i> (unit: pptv)			
1	Ethane	2462 ± 739	2.52 × 10 <sup>-13</sup>
2	Propane	1098 ± 436	1.12 × 10 <sup>-12</sup>
3	Isobutane	138 ± 68	2.13 × 10 <sup>-12</sup>
4	n-Butane	277 ± 131	2.37 × 10 <sup>-12</sup>
5	Isopentane	163 ± 93	7.98 × 10 <sup>-12</sup>
6	n-Pentane	80 ± 61	3.70 × 10 <sup>-12</sup>
7	Cyclopentane	37 ± 24	4.85 × 10 <sup>-12</sup>
8	2,2-Dimethylbutane	3 ± 2	2.24 × 10 <sup>-12</sup>
9	2,3-Dimethylbutane	6 ± 5	6.04 × 10 <sup>-12</sup>
10	2-Methylpentane	33 ± 23	5.44 × 10 <sup>-12</sup>
11	3-Methylpentane	13 ± 12	5.87 × 10 <sup>-12</sup>
12	n-Hexane	22 ± 18	5.23 × 10 <sup>-12</sup>
13	Methylcyclopentane	14 ± 10	8.60 × 10 <sup>-12</sup>
14	Cyclohexane	10 ± 7	6.71 × 10 <sup>-12</sup>
15	2,4-Dimethylpentane	2 ± 2	5.65 × 10 <sup>-12</sup>
16	2-Methylhexane	43 ± 59	6.80 × 10 <sup>-12</sup>
17	2,3-Dimethylpentane	7 ± 5	6.46 × 10 <sup>-12</sup>
18	3-Methylhexane	36 ± 14	7.20 × 10 <sup>-12</sup>
19	n-Heptane	11 ± 7	6.40 × 10 <sup>-12</sup>
20	Methylcyclohexane	9 ± 8	9.40 × 10 <sup>-12</sup>
21	2,2,4-Trimethylpentane	7 ± 5	3.65 × 10 <sup>-12</sup>
22	2,3,4-Trimethylpentane	12 ± 8	6.50 × 10 <sup>-12</sup>
23	2-Methylheptane	3 ± 2	8.20 × 10 <sup>-12</sup>
24	3-Methylheptane	15 ± 8	8.60 × 10 <sup>-12</sup>
25	n-Octane	6 ± 4	7.46 × 10 <sup>-12</sup>
26	n-Nonane	6 ± 5	1.02 × 10 <sup>-11</sup>
<i>Alkenes and acetylene</i> (unit: pptv)			
1	Ethylene	203 ± 119	7.98 × 10 <sup>-12</sup>
2	Acetylene	114 ± 45	6.73 × 10 <sup>-13</sup>
3	Propylene	168 ± 197	2.52 × 10 <sup>-11</sup>
4	1-Butene	16 ± 15	3.65 × 10 <sup>-11</sup>
5	Butadiene	4 ± 5	6.12 × 10 <sup>-11</sup>
6	trans-2-Butene	4 ± 4	7.04 × 10 <sup>-11</sup>
7	cis-2-Butene	4 ± 4	5.34 × 10 <sup>-11</sup>
8	3-Methyl-1-Butene	2 ± 2	3.12 × 10 <sup>-11</sup>
9	1-Pentene	1 ± 1	3.12 × 10 <sup>-11</sup>
10	trans-2-Pentene	1 ± 1	6.86 × 10 <sup>-11</sup>
11	cis-2-Pentene	1 ± 1	6.38 × 10 <sup>-11</sup>
12	2-Methyl-2-butene	2 ± 2	7.68 × 10 <sup>-11</sup>
13	Cyclopentene	32 ± 28	5.71 × 10 <sup>-11</sup>
14	4-Methyl-1-pentene	1 ± 3	3.80 × 10 <sup>-11</sup>
15	2-Methyl-1-pentene	2 ± 2	6.23 × 10 <sup>-11</sup>
16	trans-2-Hexene	1 ± 1	6.02 × 10 <sup>-11</sup>
17	cis-2-Hexene	1 ± 1	6.19 × 10 <sup>-11</sup>
<i>Aromatics</i> (unit: pptv)			
18	Benzene	67 ± 30	1.19 × 10 <sup>-12</sup>
19	Toluene	93 ± 57	5.66 × 10 <sup>-12</sup>
20	Ethylbenzene	12 ± 7	6.07 × 10 <sup>-12</sup>
21	p,m-Xylene	26 ± 18	1.72 × 10 <sup>-11</sup>
22	Styrene	10 ± 10	5.86 × 10 <sup>-11</sup>
23	o-Xylene	62 ± 70	1.14 × 10 <sup>-11</sup>
24	iso-Propylbenzene	1 ± 1	6.61 × 10 <sup>-12</sup>
25	n-Propylbenzene	2 ± 1	6.94 × 10 <sup>-12</sup>
26	1,3,5-Trimethylbenzene	2 ± 3	5.41 × 10 <sup>-11</sup>
27	1,2,4-Trimethylbenzene	1 ± 2	3.32 × 10 <sup>-11</sup>
<i>Biogenics</i> (unit: pptv)			
Isoprene		68 ± 69	9.29 × 10 <sup>-11</sup>
a-Pinene		157 ± 244	5.05 × 10 <sup>-11</sup>
Camphene		35 ± 50	1.69 × 10 <sup>-10</sup>
b-Pinene		112 ± 184	5.33 × 10 <sup>-11</sup>
Limonene		56 ± 113	7.02 × 10 <sup>-11</sup>
3-Carene		137 ± 267	8.70 × 10 <sup>-11</sup>
2-methyl-3-buten-2-ol (MBO)		1346 ± 777	5.60 × 10 <sup>-11</sup>
Sesquiterpenes (SQTs)		41 ± 21	2.91 × 10 <sup>-10b</sup>

(continued on next page)

**Table 1** (continued)

No.	Species	Conc.	$k_{\text{OH}+\text{N}}$
Oxygenated (unit: pptv)			
	Methanol	3776 ± 1391	$8.98 \times 10^{-13}$
	Acetaldehyde	472 ± 399	$1.23 \times 10^{-11}$
	Acetone + Propanal	1575 ± 534	$1.95 \times 10^{-13\text{c}}$
	Glycolaldehyde + acetic acid	1227 ± 734	$7.36 \times 10^{-13\text{d}}$
Other (unit: pptv)			
	Acetonitrile	122 ± 28	$4.04 \times 10^{-12}$

<sup>a</sup> The reaction rate constant for NO<sub>2</sub> with OH was employed.

<sup>b</sup> The reaction rate constant for humulene with OH was employed.

<sup>c</sup> The reaction rate constant for acetone with OH was employed.

<sup>d</sup> The reaction rate constant for glycolaldehyde with OH was employed.

predictable that the averaged concentration of NMHCs in MEF is almost constant for the same season.

### 3.2. OH reactivity measurements

Fig. 3 shows the results of the measured total OH reactivity. Diurnal variation of OH reactivity was observed unambiguously for Aug. 27th and 28th. The value of OH reactivity in daytime was quite low, while that in evening and nighttime reached over  $10 \text{ s}^{-1}$ . On Aug. 23rd, OH reactivity in the afternoon rapidly increased and values were occasionally above the range of our instrument (over  $40 \text{ s}^{-1}$ ). During this time, a strong thunderstorm with hail and a tornado devastated an area around 2 mile northeast direction of the sampling site. The strong wind disturbed trees and damaged plants around MEF resulting in a burst of BVOC causing a large increase in OH reactivity. After the end of the thunderstorm, OH reactivity still increased and then rapidly decreased in evening time. In the following section, data for the afternoon in Aug. 23rd are excluded due to the exceptional event mentioned above.

### 3.3. Comparison to the calculated OH reactivity

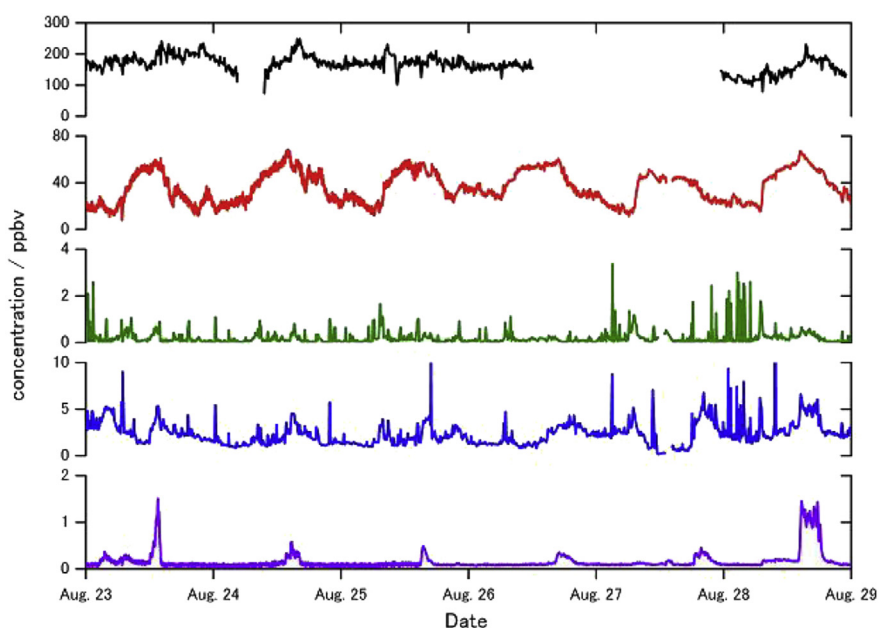
Calculation of OH reactivity ( $k_{\text{calc}}$ ) was derived from number concentration of trace gas species  $N_i$  and their OH reaction rate constant as follows,

$$k_{\text{calc}} = \sum_i k_{\text{OH}+\text{N}_i} [N_i]. \quad (1)$$

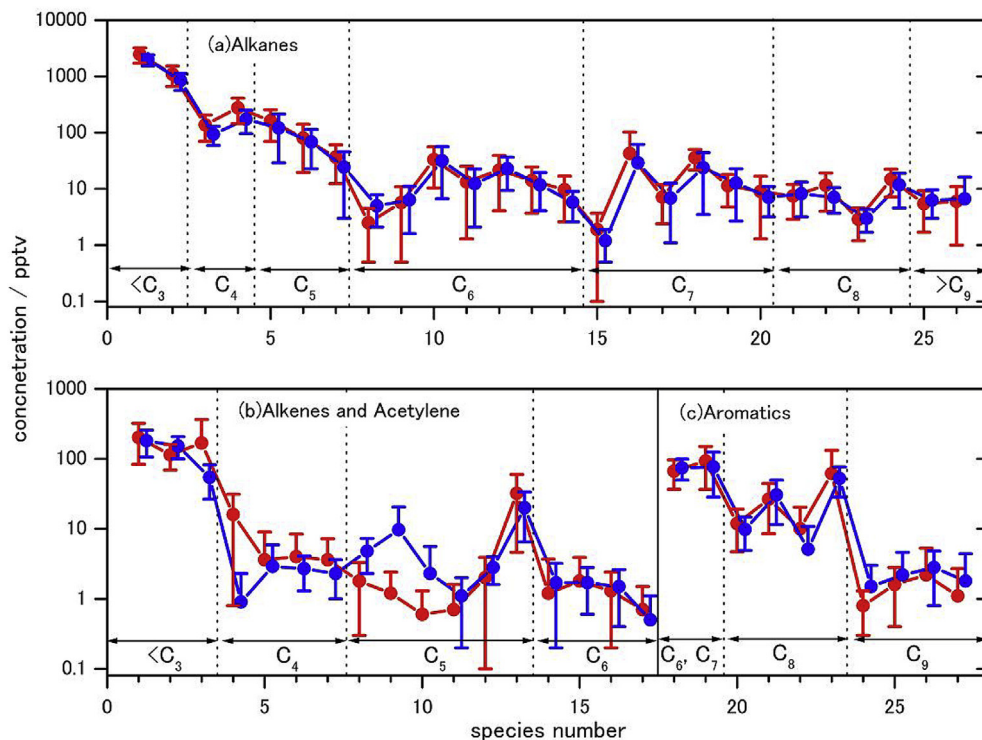
Reaction rate constants of OH for the species quantified in the present study were taken from the literature (e.g., Atkinson, 1994, 1997; Atkinson et al., 1997; Calvert et al., 2000; Sander et al., 2002; Sadanaga et al., 2005a,b) as summarized in Table 1. To know the maximum value of the OH reactivity for NO<sub>2</sub>, the concentration of NO<sub>2</sub> was assumed to be the same as that of NO<sub>y</sub>. For sesquiterpenes, Kim et al. reported that the measured SQT were mostly identified as isolongifolene (Kim et al., 2010). However, the reaction rate coefficient for OH with isolongifolene has not been derived. Thus, the rate constant for isolongifolene was assumed to be the same as that for humulene (Shu and Atkinson, 1995). Averaged concentrations of NMHCs derived from the GC–FID analysis were employed except for the biogenic species. For both periods, a value of 1780 ppbv of methane was assumed for the OH reactivity calculations. Calculated OH reactivity is shown in Fig. 3. During midday, there was good agreement between the two OH reactivities. Observation of the good agreement between the two OH reactivities is presumably related to the detailed dataset of measured trace species. However, there were still differences between measured and calculated OH reactivities. Correlation diagram between observed and calculated OH reactivity was shown in Fig. 4 together with the 1:1 line described by dot. It is clear that the value of the measured OH reactivity is larger than that of the calculated one. These results indicate the existence of some missing OH sink in ambient air in MEF.

### 3.4. Contribution to the OH reactivity

Averaged total OH reactivity for each period is shown in Fig. 5 together with the contribution of each species. OH reactivity for the sum of CO, NO, NO<sub>y</sub>, O<sub>3</sub>, SO<sub>2</sub> and methane is assigned as “inorganics” and that for NMHCs except for biogenic species (isoprene and monoterpenes) is assigned as “anthropogenic”. Averaged total OH reactivity at MEF is much lower than that measured in urban ( $33.4 \text{ s}^{-1}$ ) and suburban ( $27.7 \text{ s}^{-1}$ ) areas in Tokyo in the same summer season (Yoshino et al., 2006, 2012) using techniques that



**Fig. 1.** Diurnal profiles of the concentration of CO (black), O<sub>3</sub> (red), NO (green), NO<sub>y</sub> (blue) and SO<sub>2</sub> (purple) measured in Period II. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

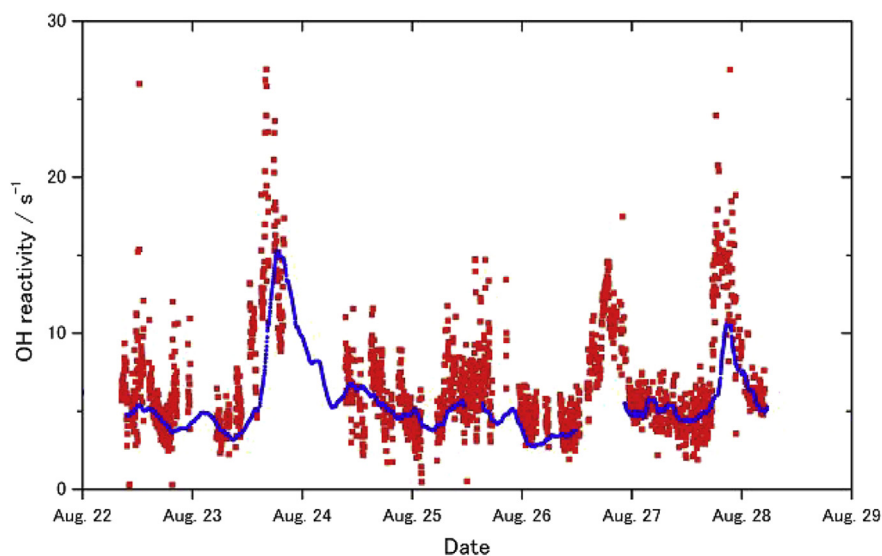


**Fig. 2.** Plots of the average concentration of (a) alkanes, (b) alkenes and acetylene and (c) aromatics in 2008 (red) and 2009 (blue). For horizontal axis, each number corresponds to species listed in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are the same as that used at MEF for this study. Measurements of OH reactivity in the boreal forest in summer have been reported (Sinha et al., 2010) and the averaged total OH reactivity ( $9 \text{ s}^{-1}$ ) was similar to that derived from the present study. Biogenic species, isoprene, monoterpenes, 2-methyl-3-buten-2-ol (MBO) and SQT, were the most prominent contribution to total OH reactivity. It has been reported that MBO is one of the famous biogenic species emitted from ponderosa pine (Baker et al., 2001). For inorganic species, CO and  $\text{NO}_y$  were the highest contribution to OH reactivity and that for methane was about one third of that for CO or  $\text{NO}_y$ . For

anthropogenic species, the concentrations of light NMHCs were higher than that of any biogenic species, but the contribution of OH reactivity for anthropogenic species was smaller due to the low reactivity of OH. During the measurements, about 29.5% of total OH reactivity could not be identified in the present study, corresponding to the existence of some missing OH sink. These values correspond to about 2 ppbv of  $\beta$ -pinene when the missing OH was related to the concentration of  $\beta$ -pinene.

Table 2 shows the examples of the total OH reactivity measurement in various environments. The maximum OH reactivity in



**Fig. 3.** Overall observed (red) and calculated (blue) OH reactivity during the BEACHON-SRM08 campaign in Period I (a) and II (b), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

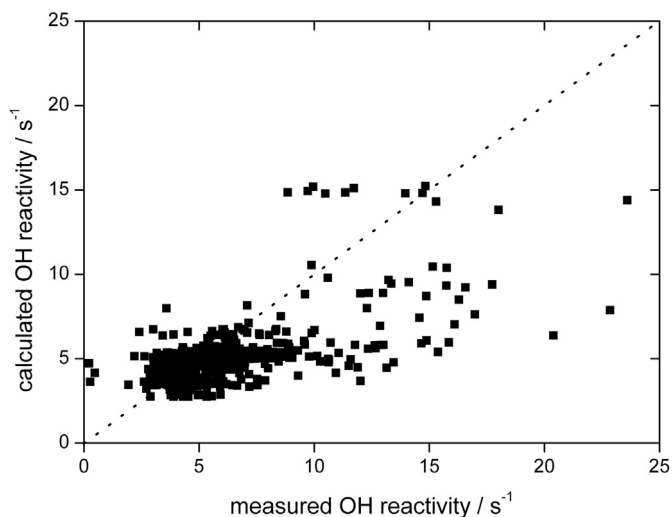


Fig. 4. Averaged total OH reactivity and its contribution for each trace species.

Table 2

Summary of the total OH reactivity measurements in various environments.

Publication	Measurement site	Measurement period	Range of OH reactivity	Fraction of missing OH sink
<b>Forest</b>				
Sinha et al. (2008)	Surinam, tropical forest	October, 2005	28–72	70%
Sinha et al. (2010)	Finland, boreal forest	August, 2008	5–12	50.60%
Nölscher et al. (2012)	Finland, boreal forest	July, 2010	3–76	89%
Edwards et al. (2013)	Boreo, tropical forest	August, 2010	3–30	58%
This works	South Rockey Mountain, pine forest	April, 2008	7–84	48%
<b>Other place</b>				
Lee et al. (2009)	UK, North Norfolk coast	May, 2004	1.3–9.7	40%
Yoshino et al. (2006)	Suburban area, Tokyo	July–August, 2006	10–80	30%
Yoshino et al. (2012)	Urban area, Tokyo	August, 2007	15–70	27%

the present measurements is smaller than that measured in tropical forest, and comparable with that in boreal forest due to may be the low concentration of isoprene, which possess the high reactivity for OH. Since there is a little emission source around coast area, the maximum OH reactivity is small. The fraction of the missing OH sink in the present measurements is smaller than any measurement in forest. Since about 70 kinds of trace species including inorganic, NMHCs, biogenic VOCs and oxygenated VOCs were measured, fraction of missing OH sink can be reduced. However, the missing OH sink is still left.

Averaged diurnal variation of OH reactivity and its breakdown are shown in Fig. 6. It is clear that the OH reactivity gradually increases at nighttime. Contribution of MBO was prominent in daytime, while that of monoterpenes dominated in nighttime or morning time. Since the concentration of SQT was low and OH reactivity for oxygenated species was low, clear diurnal dependence was not observed. Missing OH sink was observed for all time periods. Averaged missing OH sink in nighttime (18–5 o'clock) was about 1.4 times higher than that in daytime (6–17 o'clock). The ratio of each biogenic species to total OH reactivity is shown in Fig. 7(a). Diurnal variation of the ratio of monoterpenes and MBO to total OH reactivity,  $k_{MTs}/k_{meas}$  and  $k_{MBO}/k_{meas}$  in Fig. 7(a) expressed

the similar trend with that of their concentration (Kim et al., 2010). The trend of the ratio of SQT, on the other hand, was different from that of its concentration due to its small concentration. The ratio of total biogenic species and missing OH to total OH reactivity,  $k_{Biogenics}/k_{meas}$  and  $k_{missing}/k_{meas}$  are shown in Fig. 7(b). It seemed that diurnal variation of  $k_{Biogenics}/k_{meas}$  and  $k_{missing}/k_{meas}$  had an inverse correlation. This result implies that the candidates of missing OH sink may be (1) some secondary species generated by the oxidation of biogenic species, or (2) some species for which variation of the concentration is the inverse of that for biogenic species. However, the variation of the concentration for monoterpenes is the inverse of that for MBO, and there were no correlation with missing OH sink with the concentration of monoterpenes or MBO. Therefore, it is more suitable that the one of the candidate of missing OH sink may be some species generated by the oxidation of biogenic species. Some oxidation products of monoterpenes have been reported. For example, 2-hydroxy-2-methylpropanal (HMPPr), glycolaldehyde and some unidentified oxygenated monoterpenes

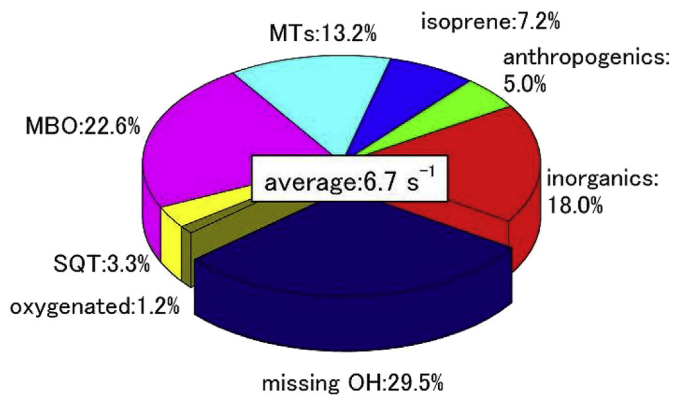


Fig. 5. Diurnal variation of the averaged total OH reactivity and contribution of trace species in Period II. Each color stands for the contribution of inorganics (red), anthropogenics (green), isoprene (blue), monoterpenes (pale blue), MBO (pink), sesquiterpene (yellow), oxygenated VOCs (dark yellow) and missing OH (navy).

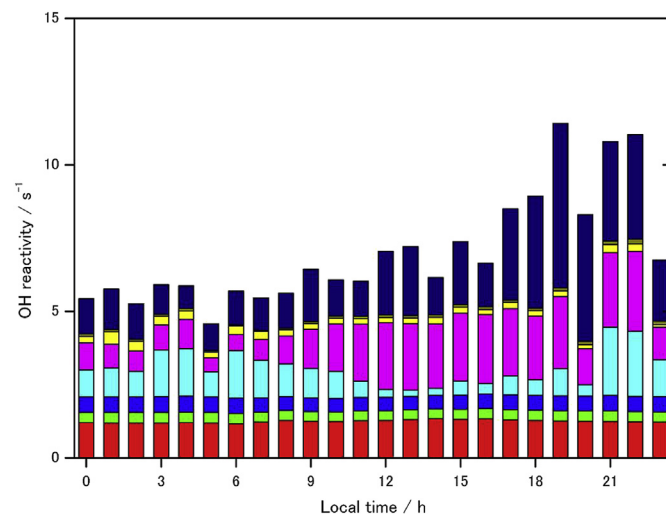


Fig. 6. Averaged diurnal variation of (a) ratio of each biogenic species to total OH reactivity, and (b) ratio of total biogenic species and missing OH reactivity to total OH reactivity.

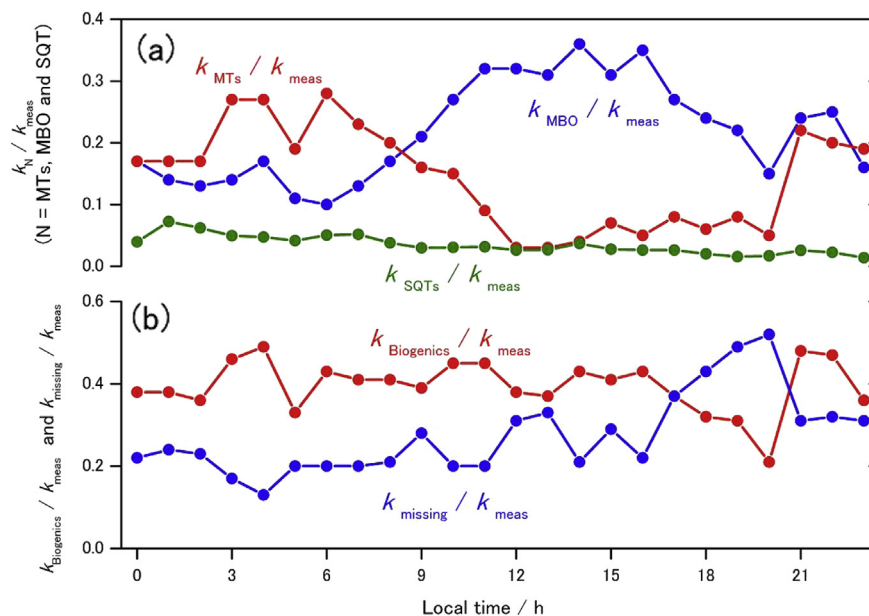


Fig. 7. Averaged diurnal variation of (a) ratio of each biogenic species to total OH reactivity, and (b) ratio of total biogenic species and missing OH reactivity to total OH reactivity.

were detected by the environmental chamber experiments (Kim et al., 2010). Unfortunately, these species were not measured in the present study. A better explanation of the missing OH required additional measurements and identification of oxidation species for biogenic species.

#### 4. Conclusion

Total OH reactivity was measured in a southern Rocky mountain forest consisting mainly of ponderosa pine trees in summer 2008. The value of OH reactivity was low and the effect of the anthropogenic sources was small. Comparison of the measured and calculated OH reactivity derived from the analysis of trace species shows that about 29.5% of total OH reactivity is associated with the missing sink. The candidates of missing OH sink are thought to be some oxidation products of biogenic species. Compared with the examples of the previous measurement of OH reactivity in forest, the fraction of missing OH sink can be reduced due to the expansion of the measurements for the trace species. The present study demonstrates that it is essential to identify and quantify additional atmospheric oxidation products. In addition, fundamental data for the reaction of OH with oxidation products are necessary to evaluate the loss and formation process of  $\text{HO}_x$  in forest air. For example, the total OH reactivity for photooxidation products by the photochemical smog chamber has been carried out (Nakashima et al., 2012). It is well known that forest is one of the huge emission sources of NMHCs (Goldstein, 2007). In addition, unknown production process of  $\text{HO}_x$  has been reported under low  $\text{NO}_x$  condition (Leivelveld et al., 2008). Secondary species produced by the photochemical reaction of isoprene is thought to be the key of the understanding of the additional process of  $\text{HO}_x$ . Developments of the additional techniques for measuring of trace species, especially secondary species generated by photochemical reaction of VOCs, will be required to reveal for both the OH loss process and production of  $\text{HO}_x$ .

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