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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 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.

**Abstract**
Total OH reactivity was measured during the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H₂O, 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 s⁻¹, smaller than that measured in urban (33.4 s⁻¹, Yoshino et al., 2012) and suburban (27.7 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 traces species such as CO, NO, NOy, O₃ and SO₂ 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.

**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, O₃, NO₃, 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...
and chemical characterization of biogenic VOCs, the clarification of the reaction mechanism for the formation of HO$_2$ 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 (Leelaveld et al., 2008), Peeters et al. (2009) have proposed a different chemical process for the formation of OH during isoprene oxidation under low NO$_x$ condition. They have suggested that isomerization of a peroxy radical generated by the reaction of isoprene with OH under low NO$_x$ is caused, so called the 1, 5 and 1, 6-H shifts, resulting of the production of HO$_2$ and unsaturated hydroperoxo-aldehydes (HPALDs) and OH forms through the photolysis of HPALDs. To estimate the formation of photochemical oxidants and the amount of HO$_x$, it is essential to clarify the loss and production processes of HO$_x$, 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$_2$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 the 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 monoterpene (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$_2$, O$_3$, NO and NO$_2$, 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$_2$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$_3$ and successive reaction of generated oxygen atom and water vapor as follows,

\[
O_3 + h\nu(266 \text{ nm}) \rightarrow O_2 + O(^1D) \quad (R1)
\]

\[
O(^1D) + H_2O \rightarrow 2OH \quad (R2)
\]

Ambient O$_3$ was employed in the formation of OH and no further O$_3$ 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$_4$ laser (YP40-532, 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-SBQ, 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$_3$, SO$_2$ 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$_x$) were monitored by chemiluminescence (Model CLD-88Y, Ecophysics) combined with a molybdenum converter. It is necessary to know the concentration of nitrogen dioxide (NO$_2$) 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$_2$ was almost the same as that
of NOx. In other words, the maximum of the OH reactivity for NOx 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 mm length, 0.53 mm diameter and 1.5 μm film thickness) and HP-1 (60 mm 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, O3, SO2, NO and NO2 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 SO2 on the other hand, regular diurnal variation for the concentration was observed. The concentration of SO2 rapidly increased at noon or evening time and decreased within the day. No strong correlation for the diurnal variation between SO2 and CO, NO or NO2 was found. This result implies that there may be some special anthropogenic sources of SO2 around MEF. However, the contribution of SO2 on OH reactivity was quite low due to its low reactivity, so that the effect of the special source of SO2 was thought to be negligible. Clear diurnal variation was observed for O3 and NO2. The maximum concentration of O3 was ca. 60 ppbv in daytime and about 10–20 ppbv of O3 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 O3 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

| No. | Species                        | Conc. (unit: ppbv) | kOH–N |
|-----|--------------------------------|--------------------|--------|
| CO  |                                | 168 ± 27           | 1.36 × 10^13 |
| O3  |                                | 35 ± 14            | 8.12 × 10^14  |
| NO  |                                | 0.23 ± 0.44        | 1.04 × 10^11  |
| NO2 |                                | 2.3 ± 1^10         | 1.30 × 10^11  |
| SO2 |                                | 0.14 ± 0.16        | 1.26 × 10^12  |
| CH4 |                                | 1780 (assumed)     | 6.41 × 10^14  |

### Alkenes (unit: pptv)

| No. | Species                        | Conc. (unit: pptv) |
|-----|--------------------------------|--------------------|
| 1   | Ethene                         | 2462 ± 739         |
| 2   | Propane                        | 1098 ± 436         |
| 3   | Isobutane                      | 138 ± 68           |
| 4   | n-Butane                       | 277 ± 131          |
| 5   | Isopentane                     | 163 ± 93           |
| 6   | n-Pentane                      | 80 ± 61            |
| 7   | Cyclopentane                   | 37 ± 24            |
| 8   | 2,2-Dimethylbutane             | 3 ± 2              |
| 9   | 2,3-Dimethylbutane             | 6 ± 5              |
| 10  | 2-Methylpentane                | 33 ± 23            |
| 11  | 3-Methylpentane                | 13 ± 12            |
| 12  | n-Hexane                       | 22 ± 18            |
| 13  | Methylcyclopentane             | 14 ± 10            |
| 14  | Cyclohexane                    | 10 ± 7             |
| 15  | 2,4-Dimethylpentane            | 2 ± 2              |
| 16  | 2-Methylhexane                 | 43 ± 59            |
| 17  | 2,3-Dimethylhexane             | 7 ± 5              |
| 18  | 3-Methylhexane                 | 36 ± 14            |
| 19  | n-Heptane                      | 11 ± 7             |
| 20  | Methylcyclohexane              | 9 ± 8              |
| 21  | 2,2,4-Trimethylpentane         | 7 ± 5              |
| 22  | 2,3,4-Trimethylpentane         | 12 ± 8             |
| 23  | 2-Methylheptane                | 3 ± 2              |
| 24  | 3-Methylheptane                | 15 ± 8             |
| 25  | n-Octane                       | 6 ± 4              |
| 26  | n-Nonane                       | 6 ± 5              |

### Alkanes and acetylene (unit: pptv)

| No. | Species                        | Conc. (unit: pptv) |
|-----|--------------------------------|--------------------|
| 1   | Ethylene                       | 203 ± 119          |
| 2   | Acetylene                      | 114 ± 45           |
| 3   | Propylene                      | 168 ± 197          |
| 4   | 1-Butene                       | 16 ± 15            |
| 5   | Butadiene                      | 4 ± 5              |
| 6   | trans-2-Butene                 | 4 ± 4              |
| 7   | cis-2-Butene                   | 4 ± 4              |
| 8   | 3-Methyl-1-Butene              | 2 ± 2              |
| 9   | 1-Pentene                      | 1 ± 1              |
| 10  | trans-2-Pentene                | 1 ± 1              |
| 11  | cis-2-Pentene                  | 1 ± 1              |
| 12  | 2-Methyl-2-butene              | 2 ± 2              |
| 13  | Cyclopentene                   | 32 ± 28            |
| 14  | 4-Methyl-1-pentene             | 1 ± 3              |
| 15  | 2-Methyl-1-pentene             | 2 ± 2              |
| 16  | trans-2-Hexene                 | 1 ± 1              |
| 17  | cis-2-Hexene                   | 1 ± 1              |

### Aromatics (unit: pptv)

| No. | Species                        | Conc. (unit: pptv) |
|-----|--------------------------------|--------------------|
| 18  | Benzenes                       | 67 ± 30            |
| 19  | Toluene                        | 93 ± 57            |
| 20  | Ethylbenzene                   | 12 ± 7             |
| 21  | p.m-Xylene                     | 26 ± 18            |
| 22  | Styrene                        | 10 ± 10            |
| 23  | o-Xylene                       | 62 ± 70            |
| 24  | iso-Propylbenzene              | 1 ± 1              |
| 25  | n-Propylbenzene                | 2 ± 1              |
| 26  | 1,3,5-Trimethylbenzene         | 2 ± 3              |
| 27  | 2,4,6-Trimethylbenzene         | 1 ± 2              |

### Biogenics (unit: pptv)

| No. | Species                        | Conc. (unit: pptv) |
|-----|--------------------------------|--------------------|
| 28  | Isoprene                       | 68 ± 69            |
| 29  | a-Pinene                       | 157 ± 244          |
| 30  | Camphene                       | 35 ± 50            |
| 31  | b-Pinene                       | 112 ± 184          |
| 32  | Limonene                       | 56 ± 13            |
| 33  | Carene                         | 137 ± 267          |
| 34  | 2-methyl-3-buten-2-ol (MBD)     | 1346 ± 777         |
| 35  | Sesquiterpenes (SQTs)          | 41 ± 21            |

(continued on next page)
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 s⁻¹. On Aug. 23rd, OH reactivity in the afternoon rapidly increased and values were occasionally above the range of our instrument (over 40 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,

\[
k_{\text{calc}} = \sum_i k_{\text{OH}+N_i}[N_i].
\]  

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 NO₂, the concentration of NO₂ was assumed to be the same as that of NOₓ. 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, NOₓ, O₃, SO₂ 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 s⁻¹) and suburban (27.7 s⁻¹) areas in Tokyo in the same summer season (Yoshino et al., 2006, 2012) using techniques that
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 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 NO$_y$ were the highest contribution to OH reactivity and that for methane was about one third of that for CO or 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 β-pinene when the missing OH was related to the concentration of β-pinene.

Table 2 shows the examples of the total OH reactivity measurement in various environments. The maximum OH reactivity in...
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 (HMPr), glycolaldehyde and some unidentified oxygenated monoterpenes

| Publication | Measurement site | Measurement period | Range of OH reactivity | Fraction of missing OH sink |
|-------------|------------------|--------------------|------------------------|-----------------------------|
| 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 work | South Rockey Mountain, pine forest | April, 2008 | 7–84 | 48% |
| 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% |

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

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), anthropogenic (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.
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 HOx 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 HOx has been reported under low NOx condition (Lei 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 HOx. 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 HOx.

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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.

References

Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. Science 276, 1052–1058.
Atkinson, R., 1994. Gas-phase tropospheric chemistry of organic compounds. J. Phys. Chem. Ref. Data Monogr. 2, 1–216.
Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. alkanes and alkenes. J. Phys. Chem. Ref. Data. 26, 215–290.
Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, J.R., Kerr, J.A., Rossi, M.J., Troe, T., 1997. Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VI. J. Phys. Chem. Ref. Data. 26, 1329–1449.
Baker, M., Guenther, A., Greenberg, J., Fall, R., 2001. Canopy level fluxes of 1-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system. Environ. Sci. Technol. 35, 1701–1708.
Calvert, J.G., Atkinson, R., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J., Yarwood, G., 2000. Reaction of alkenes with OH radical. In: The Mechanisms of Atmospheric Oxidation of the Alkenes. Oxford Univ. Press, New York.
Di Carlo, P., Brune, W.H., Martines, M., Harder, H., Lesher, R., Ren, X.R., Thornberry, T., Carroll, M.A., Young, V., Shepson, P.B., Riemer, D., Apel, E., Campbell, C., 2004. Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs. Science 304 (5671), 722–725.
Edwards, P.M., Evans, M.J., Fruenbe, K.L., Hopkins, J., Ingham, T., Jones, C., Lee, J.D., Lewis, A.C., Moller, S.J., Stone, D., Whalley, L.K., Heard, D.E., 2013. OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project. Atmos. Chem. Phys. 13, 9497–9514.
Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Theory, Experiment and Application. Academic Press.
Fuentes, J.D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J.W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T.D., Stockwell, W., 2000. Biogenic hydrocarbons in the atmospheric boundary layer: a review. Bull. Am. Meteorol. Soc. 81, 1537–1575.
Goldstein, A.H., 2007. Known and unexplored organic constituents in the earth’s atmosphere. Environ. Sci. Technol. 41, 1514–1521.
Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P.A., 1995. Global-model of natural volatile organic compound emissions. J. Geophys. Res. 100 (DS), 8873–8882.
Ingham, T., Goddard, A., Whalley, L.K., Fruenbe, K.L., Edwards, P.M., Seal, C.P., Self, D.E., Johnson, G.P., Read, K.A., Lee, J.D., Heard, D.E., 2009. A flow-tube based laser-induced fluorescence instrument to measure OH reactivity in the troposphere. Atmos. Meas. Tech. 2, 465–477.
Kato, S., Pochanart, P., Kajii, Y., 2001. Measurements of ozone and non methane hydrocarbons at Chichijima island, a remote island in western Pacific: long-
range transport of polluted air from the Pacific rim region. Atmos. Environ. 35, 6021–6029.
Kim, S., Karl, T., Guenther, A., Tyndall, G., Orland, J., Harley, P., Rasmussen, R., Apel, E., 2010. Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in ponderosa pine ecosystem: interpretation of PTR-MS mass spectra. Atmos. Chem. Phys. 10, 1759–1771.
Kim, S., Guenther, A., Karl, T., Greenberg, J., 2011. Contributions of primary and secondary biogenic VOC to total OH reactivity during the CABINEX (Community Atmosphere-Biosphere Interactions Experiments)-09 field campaign. Atmos. Chem. Phys. 11, 8613–8623.
Kim, S., Wolfe, G.M., Maalidin, I., Cantrell, C., Guenther, A., Karl, T., Turnipseed, A., Greenberg, J.R., Hall, S., Ullmann, K., Apel, E., Hornbrook, R., Kajii, Y., Nakashima, Y., Keutsch, F.N., DiGangi, J.P., Henry, S.B., Kaser, L., Schnitzhofer, R., Graus, M., Hansel, A., Zheng, W., Flocke, F.F., 2013. Evaluation of HOx sources and cycling using measurement-constrained model calculations in a 2-methyl-3-butene-2-ol (MB0) and monoterpenes (MT) dominated ecosystem. Atmos. Chem. Phys. 13, 2031–2044.
Lee, J.D., Young, J.C., Read, K.A., Hamilton, J.F., Hopkins, J.R., Lewis, A.C., Bandy, B.J., James Davey, J., Edwards, P., Ingham, T., Self, D.E., Smith, S.C., Pilling, M.J., Heard, D.E., 2009. Measurement and calculation of OH reactivity at a United Kingdom coastal site. J. Atmos. Chem. 64, 53–76.
Leileveld, J., Butler, T.M., Crowley, J.N., Dillon, T.J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.G., Martinez, M., Arabolrelli, D., Williams, J., 2008. Atmospheric oxidation capacity sustained by a tropical forest. Nature 452, 737–740.
Mao, J., Ren, X., Brune, W.H., Olson, J.R., Crawford, J.H., Fried, A., Huey, L.G., Cohen, R.C., Heikes, B., Singh, H.B., Blake, D.R., Sachse, G.W., Diskin, G.S., Hall, S.R., Shetter, R.E., 2009. Airborne measurement of OH reactivity during INTEX-B. Atmos. Chem. Phys. 9, 163–173.
Nakashima, Y., Kamei, N., Kohayashi, S., Kajii, Y., 2010. Total OH reactivity and VOC analyses for gasoline vehicular exhaust with a chassis dynamometer. Atmos. Environ. 44, 468–475.
Nakashima, Y., Tsurumaru, H., Imamura, T., Bejan, I., Wenger, J., 2012. Measurements of total OH reactivity and reactive trace species in the urban atmosphere of central Tokyo. Atmos. Environ. 46, 242–247.
Nölscher, A.C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A.M., Axinte, R., Bozern, H., Fischer, H., Poulwiss, N., Phillips, G., Crowley, J.N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H.G., Vilà-Guerau de Arellano, J., Leileveld, J., 2012. Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010. Atmos. Chem. Phys. 12, 8257–8270.
Peeters, J., Nguyen, T.L., Vereecken, L., 2009. HOx radical regeneration in the oxidation of isoprene. Phys. Chem. Chem. Phys. 11, 5935–5939.
Sander, S.P., Fried, R.R., DeMore, W.B., Golden, D.M., Kurylo, M.J., Huie, R.E., Orkin, V.L., Moortgat, G.K., Pavulnarkara, A.R., Kolb, C.E., Molina, M.J., Flayson-Pitts, B.J., 2002. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 14. JPL Publication, pp. 2–25.
Sadana, Y., Yoshino, A., Watanabe, K., Yoshioka, A., Wakisano, Y., Kanaya, Y., Kajii, Y., 2004. Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique. Rev. Sci. Instrum. 75, 2648–2655.
Sadana, Y., Yoshino, A., Kato, S., Kajii, Y., 2005a. Measurements of OH reactivity and photochemical ozone production in the urban atmosphere. Environ. Sci. Technol. 39, 8847–8852.
Sadana, Y., Kondo, S., Hashimoto, K., Kajii, Y., 2005b. Measurement of the rate coefficient for OH + NO2 reaction under the atmospheric pressure: its humidity dependence. Chem. Phys. Lett. 419, 474–478.
Shinha, V., Williams, J., Crowley, J.N., Leileveld, J., 2008. The comparative reactivity method – a new tool to measure total OH reactivity in ambient air. Atmos. Chem. Phys. 8, 2213–2227.
Shinha, V., Williams, J., Leileveld, J., Ruuskane, T.M., Kajos, M.K., Patokoski, J., Heil, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., Kulmala, M., 2010. OH reactivity measurements within a boreal forest: evidence for unknown reactive emissions. Environ. Sci. Technol. 44, 6614–6620.
Shu, Y., Atkinson, R., 1995. Atmospheric lifetimes and fates of a series of sesquiterpenes. J. Geophys. Res. 100, 7275–7281.
Wiedinmyer, C., Guenther, A., Harley, P., Hewitt, N., Ceron, G., Artaxo, P., Steinbrecher, R., Rasmussen, R., 2004. Global organic emissions from vegetation. In: Emissions of Atmospheric Trace Compounds. Academic Publishers, pp. 115–170.
Yoshino, A., Sadana, Y., Watanabe, K., Kato, S.Y., Miyakawa, Y., Matsumoto, J., Kajii, Y., 2006. Measurements of total OH reactivity by laser-induced pump and probe technique – comprehensive observations in the urban atmosphere of Tokyo. Atmos. Environ. 40, 7869–7881.
Yoshino, A., Nakashima, Y., Miyazaki, K., Kato, S., Suthawaree, J., Shimo, N., Matsuana, S., Chatani, S., Apel, E., Greenberg, J., Guenther, A., Ueno, H., Sasaki, H., Hoshi, J., Yokota, H., Ishi, K., Kajii, Y., 2012. Air quality diagnosis from comprehensive observations of total OH reactivity and reactive trace species in urban central Tokyo. Atmos. Environ. 49, 51–59.