Measuring Biogenic Volatile Organic Compounds (BVOCs) from Vegetation in Terms of Ozone Reactivity

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ABSTRACT

A new system that uses the total reactivity with ozone ($R_{O3}$) was developed for measuring biogenic volatile organic compounds (BVOCs) emitted from vegetation into the atmosphere. The decrease in ozone caused by the reaction with VOCs was monitored at the ppbv level by dual chemiluminescence detectors (CLDs) based on the NO–O$_3$ reaction. Ozone was monitored by the dual CLDs before and after the reactor to correct for fluctuations in the ozone concentration. Such dual detectors can remove the interference caused by water vapor. A glass double-tube was adopted as the reactor. The loss rate of ozone to the wall was typically $(6 \pm 3) \times 10^{-4}$ s$^{-1}$. Gaseous cyclohexane was also added to the sample before it was introduced into the reactor to scavenge secondary OH radicals. From the characterization of the $R_{O3}$ analyzer using the standard VOC sample, the dependence of ozone reduction on the reaction time and reactivity were shown to agree with theoretical predictions. A calibration procedure for determining the reaction time was also established. Consequently, the detection limit for $R_{O3}$ in a 57-s reaction was determined to be $1.4 \times 10^{-4}$ s$^{-1}$ ($S/N = 3$), which corresponded to 27 ppbv of limonene. It was confirmed that the $R_{O3}$ analyzer was capable of measuring BVOC levels. Finally, a practical trial was conducted in which BVOCs emitted from a real needle-leaf tree were monitored. BVOC emissions from the tree were detected and a significant increase in $R_{O3}$ was observed when the tree was irradiated with light.

Keywords: Air quality; Precursors; Secondary organic aerosol; Photochemical oxidants; Development of an analyzer.

INTRODUCTION

Volatile organic compounds (VOCs) have been focused on in atmospheric chemistry as critical precursors of photochemical oxidants and secondary organic aerosols (SOAs) (Atkinson, 2000; Donahue et al., 2009). VOCs are emitted into the atmosphere from biogenic sources such as vegetation and plants, as well as from anthropogenic sources. It has been estimated that the annual global VOC flux is 1150 TgC, consisting of 44% isoprene and 11% monoterpenes, both of which are biogenic VOCs (BVOCs) (Guenther et al., 1995). To investigate the impact of BVOCs on air quality and pollution, atmospheric BVOCs have been one of the most discussed topics in atmospheric chemistry in recent decades. Contributions of BVOCs to photochemical oxidants (Papiez et al., 2009) and SOAs (Henze and Seinfeld, 2006), observations and estimation of emission factors of BVOCs such as isoprene and monoterpenes (Guenther et al., 1995, 1996; Tani et al., 2002; Guenther et al., 2006), and laboratory experiments to establish the mechanisms of SOA formation from BVOCs (Claeys et al., 2004; Perraud et al., 2010; Surratt et al., 2010) have all been investigated.

When VOCs are emitted into the atmosphere, they react with atmospheric radicals such as the hydroxyl radical (OH), ozone (O$_3$), and the nitrate radical (NO$_3$). The OH radical is significant only during daytime and NO$_3$ only at night, whereas O$_3$ can be abundant during both daytime and nighttime (Atkinson and Arey, 2003). The initial reactions of VOCs with atmospheric radicals are important for both the atmospheric degradation of VOCs and production of oxidants and SOAs. VOCs can react with radical X to form peroxy radicals such as HO$_2$ and RO$_2$, where R represents an organic functional group. Then, peroxy radicals oxidize NO to form NO$_2$, which can be photolyzed to produce ozone. Thus, VOCs are important as precursors of photochemical oxidants such as ozone. Semi-volatile organic compounds, SVOCs, are also formed as secondary products of reactions of VOCs with atmospheric radicals. Condensation of SVOCs with low vapor pressures is critical for the formation of SOAs because of the following reaction.

\[
\text{VOC} + X \rightarrow \text{SVOC} \rightarrow \text{SOA} \quad \text{(R1)}
\]

The atmospheric lifetimes of VOCs, $\tau_{VOC}$, are determined as the inverse of the VOC loss rate in the initial reaction.
with X:
\[ \tau_{VOC} = (k_0 [X])^{-1} \]  
(1)

where \( k \) is the reaction rate coefficient for VOC + X, and [X] is the number density of X. The lifetimes of many VOCs are dominated by the reaction with daytime OH radicals because of the high reaction rate coefficients (Atkinson and Arey, 2003). For some VOCs such as alkenes, reactions with \( O_3 \) are also significant (Calvert and Yarwood, 2000). It is known that the first step of the ozonolysis of alkenes is the addition of \( O_3 \) to \( C = C \) double bonds. BVOCs originating from plants, such as isoprene and terpenes, contain \( C = C \) double bonds, and thus, ozonolysis is an important reaction for these compounds. The following are examples of “highly ozone-reactive BVOCs” with \( k_0 \) directly monitored by a chemiluminescence detector (CLD) at 298 K given in parentheses: (monoterpenes, \( C_{10}H_{16} \)): α-pinene (1.6), α-terpinene (58), 2-carene (2.9), α-phellandrene (9.6); (sesquiterpenes, \( C_{15}H_{24} \)): α-humulene (40) and β-caryophyllene (59) (Atkinson and Arey, 2003; Calvert and Yarwood, 2000). Other “less ozone-reactive” BVOCs are limonene (0.13) and β-pinene (0.21).

From the standpoint of air pollution and air quality, it is important to investigate detailed emission characteristics of BVOCs from plants. It has been reported that these emissions depend on meteorological conditions (e.g., air temperature, intensity of solar radiation, wind speed, relative humidity) and canopy environment (e.g., broadleaf trees and needle trees, leaf temperature) (Guenther et al., 1993, 1996, 2006; Donahue et al., 2009). Thus, to study the emission of BVOCs from plants in detail, it is essential to observe the emission flux based on sensitive and fast-response measurements of various BVOC compounds. Gas chromatography (GC) is widely used to analyze gaseous VOCs. GC-based analyzers can quantify concentrations of multiple VOC compounds simultaneously. However, monitoring of VOCs by GC is based on batch analysis and is unsuitable for fast-response, continuous, real-time analysis. Proton transfer reaction-mass spectrometry (PTR-MS) has been developed as a real-time analyzer of VOCs (Lindinger et al., 1993, 1998). PTR-MS is powerful enough to capture short-term variations and the emission flux of specific BVOCs. Several examples of the measurement of BVOC emissions from plants have been reported in recent years (Fall et al., 2001; Tani and Kawawata, 2008). However, it must be noted that isomers of monoterpenes cannot be separated and that PTR-MS cannot characterize certain reactive alkenes. Furthermore, VOCs and BVOCs include a vast number of compounds and it is difficult to measure all of these by individual analyses. As a comprehensive method for detecting various VOCs, measurement of the total OH reactivity has been proposed (Kovacs and Brune, 2001; Sadanaga et al., 2004). This method monitors a VOC mixture using the loss rate of the OH radicals resulting from the reaction with VOCs, which corresponds to the sum of the OH reactivity of individual VOCs. The total reactivity of the VOC mixture for X is described as follows.

\[ R_x = \sum k_i [VOC_i] \]  
(2)

where \([VOC_i]\) is the number density of the individual VOC compound (VOC\(_i\)) and \( k_i \) is the reaction rate coefficient for the reaction \( VOC_i + X \). Previous studies of OH reactivity indicated that the comprehensive measurement of the total radical reactivity, \( R_x \), is useful for evaluating the impact of VOCs on the atmosphere.

This study focuses on the high reactivity of BVOCs with ozone, and a new tool employing this ozone reactivity (\( R_{O_3} \)) for BVOC measurements is proposed. The \( R_{O_3} \) measurement system is based on the determination method of reaction rate coefficients of VOCs with ozone (Matsumoto, 2011). A gaseous sample of VOCs is introduced into a flow-tube reactor, through which a flow of ozone is then fed. \( R_{O_3} \) was determined as the ozone loss rate in the reactor, which was directly monitored by a chemiluminescence detector (CLD) based on the NO-O\(_3\) reaction. The system was calibrated and further improved to detect BVOCs from real plants. By combining the enclosure method with the analyzer, BVOCs emitted from a needle-leaf tree were measured as a practical test of the new method.

**METHODS**

**Principles for the Determination of the Total Ozone Reactivity (\( R_{O_3} \))**

When a given amount of ozone is generated and mixed with the VOC sample, the ozone is reduced by the following reaction.

\[ VOC_i + O_3 \rightarrow \text{products} \]  
(R2)

In the case where VOC is in large excess of ozone (pseudo-first-order reaction), the rate of ozone reduction can be expressed as follows.

\[ [O_3(t_{R_{O_3}}, \text{VOC})]/[O_3(0)] = \exp (-\tau_{R_{O_3}}) \]  
(3)

where \( \tau_{R_{O_3}} \) is the reaction time in the reactor, \( k_w \) is the rate of wall loss of ozone, \([O_3(0)]\) is the initial number density of ozone in the inlet of the reactor, and \([O_3(t_{R_{O_3}}, \text{VOC})]\) is the number density of ozone after reaction with the VOC sample in the reactor. Meanwhile, when ozone is mixed with clean air without VOCs (zero gas, ZG), the rate of ozone reduction can be described as follows.

\[ [O_3(t_{R_{O_3}}, \text{ZG})]/[O_3(0)] = \exp (-k_w \tau_{R_{O_3}}) \]  
(4)

where \([O_3(t_{R_{O_3}}, \text{ZG})]\) is the number density of ozone after the \( O_3/ZG \) gas passes through the reactor. By dividing Eq. (3) by Eq. (4), the contribution of \( k_w \) can be cancelled out as follows.

\[ [O_3(t_{R_{O_3}}, \text{VOC})]/[O_3(t_{R_{O_3}}, \text{ZG})] = \exp (-\tau_{R_{O_3}}) \]  
(5)

where \( R_{O_3} = (\sum k_i [VOC_i]) \) is the ozone loss rate through the reaction with the VOCs, corresponding to the total ozone.
reactivity of the VOC mixture. Eq. (5) can be rewritten as

\[ R_{O3} = \ln \left( \frac{[O_3(t_R, VOC)]}{[O_3(t_R, ZG)]} \right) / (-t_R) \]  

(6).

Therefore, the ozone reactivity of the VOC sample can be determined by the measurement of ozone reduction in the reactor. The ozone reduction by the VOC reaction is measured by monitoring ozone levels in the zero air and VOC samples. Standard VOC samples were initially adopted to characterize the \( R_{O3} \) measurement system. Then, as a practical application of the system, BVOC samples emitted from real plants were analyzed using the enclosure method. It should be noted that when compounds other than VOCs react with ozone, their contribution to the ozone reduction rate can cause potentially critical interference. In this study, both standard and real samples were prepared by supplying ZG to the standard gas generator or the enclosure. Even if there were residual contaminants in the ZG, the ozone reduction of such contaminants is cancelled out in Eq. (6). If such contaminants are emitted from real plants, the \( R_{O3} \) value determined from the ozone reduction may be overestimated. In particular, NO reacts rapidly with ozone \((k = 2.0 \times 10^{-14}\text{ cm}^3/\text{molecule/s} \text{ at } 298 \text{ K})\), and therefore, it can cause significant interference in the measured \( R_{O3} \) values.

To determine \( R_{O3} \) in Eq. (6) precisely, it is necessary to minimize uncertainties in the measurement of ozone reduction. To this end, temporal variations in ozone levels from the ozone generator must be reduced and/or corrected for. In this study, in addition to monitoring \([O_3(t_R)]\) exiting the reactor using the main detector (CLD1), variations in \([O_3(0)]\) entering the reactor were also monitored by another detector (CLD2). Thus, by employing “dual” CLDs, the ozone concentration exiting the reactor was corrected as follows.

\[ [O_3(t_R)]_{\text{corrected}} = [O_3(t_R)]_{\text{CLD1}} \times \left( [O_3(0)]_{\text{CLD2}} / [O_3(0)]_{\text{CLD2init}} \right)^{-1} \]  

(7)

where \([O_3(t_R)]_{\text{CLD1}}, [O_3(0)]_{\text{CLD2}}, \) and \([O_3(0)]_{\text{CLD2init}}\) were the observed ozone levels exiting and entering the reactor, and the initial ozone concentration entering the reactor, respectively. The term in parenthesis represents the relative temporal variation of ozone. CLDs are capable of sensitive and real-time monitoring of gaseous ozone. Note that when CLDs are utilized to quantify ozone concentrations in humid samples, the reduction in the chemiluminescence signal due to the quenching effect of water vapor can be important (Matteu et al., 1977; Lenschow et al., 1981; Ridley et al., 1992). In this study, however, the use of dual CLDs is expected to reduce/remove the interference of water vapor. Even when the sample contains water vapor, its quenching effect on the CLDs can be cancelled out in Eq. (7) if the two CLDs are similarly affected by water vapor. Uncertainties in the reaction time, \( t_R \), are also important in Eq. (6). The reaction time is determined primarily through the reaction volume, \( V \), and flow rate, \( F \), by \( t_R = V/F \). Errors associated with \( V \) and \( F \) cause uncertainties in \( t_R \). In this study, standard VOC samples were introduced, and the analyzer response dependencies on the reaction time and ozone reactivity were examined to validate the accuracy of the calculated reaction time.

**Overview of \( R_{O3} \) Analyzer**

Fig. 1 is a schematic diagram of the experimental apparatus and gas flow system for measuring the total ozone reactivity of VOCs. The ZG without VOCs was continuously supplied by a zero air generator (TECO Model 111). Flow rates were controlled by mass flow controllers (MFC; KOFLOC Model 8500MC). The precision of the flow rate was ±1.5% of the full scale of the MFCs. To characterize and calibrate the \( R_{O3} \) analyzer, standard VOC samples were prepared by a gas-diffusion tube technique (Gastec Corp., PD-1B). The concentration of the standard VOC sample was determined from the reduction rate of reagent mass in the PD-1B and the flow rate of the sample gas (Matsumoto et al., 2009; Matsumoto, 2011). The uncertainty in the VOC concentration in the standard sample was typically ±10%. To measure the \( R_{O3} \) value of BVOCs emitted from vegetation, a plant was enclosed in a 10-L Teflon bag, and the bag was connected to the \( R_{O3} \) analyzer. Sample gas was introduced into the reactor after the pressure was reduced to atmospheric pressure using the “vent” line, as shown in the figure (“VOC” mode). To monitor the ozone concentration without reaction with VOCs, \([O_3(t_R, ZG)]\), ZG was introduced directly into the reactor without any VOC sources (“ZG” mode). To measure the reduction of \( O_3 \) by VOCs in Eq. (6), the flows of VOC and ZG were switched using 3-way valves.

One of the ZG flows was irradiated with UV light from a low-pressure mercury lamp (Sen Light Corp., SP-5-2H), and \( O_3 \) was generated from the photolysis of oxygen in the ZG. To achieve the required ozone concentrations, ozone generation was reduced by light shielding of the UV lamp. Additionally, not all of the ozone was introduced into the reactor. The ozone flow was mixed with flows of ZG or VOC just before the reactor. The initial ozone mixing ratio in the reactor was typically 30 ppbv (ppbv = 10^-9 mol/mol). The temporal variation of ozone was monitored and corrected by use of the dual CLDs.

A glass double-tube flow reactor was constructed. The inner tube (Pyrex, O.D. 10 mm, I.D. 8 mm) was for the main flow (sample + \( O_3 \)), and the outer (Pyrex, O.D. 50 mm, I.D. 46 mm, length 700 mm) was for the additional ZG flow to reduce the wall loss of ozone at the edges of reactor. The \( O_3 \) concentration at the reactor exit was continuously monitored at a temporal resolution of 1 s by CLD1. Overflow from the reactor was controlled by an MFC and vented by a pump. The reaction time, \( t_R \), in the reactor was preliminarily set by the position of the inner tube in the reactor and/or the sample flow rate, \( F \), by \( t_R = V/F = \pi r^2 L/F \), where \( r \) and \( L \) are the inner radius of the outer tube and the distance between the two inner tubes, respectively. To reduce the loss of ozone onto the tube wall, 1/4 inch PFA tubing was used, except for in the glass reactor. The air temperature of the laboratory was maintained at 295 K.

When certain BVOCs react with ozone, the OH radical can be formed as a secondary product (Calvert and Yarwood, 2000). Secondary OH radicals can react with BVOCs and ozone in the reactor. When OH reacts with BVOCs, the reduction of BVOCs by OH can result in underestimation of
**Fig. 1.** Schematic diagram of measurement system for total ozone reactivity of VOCs. MFC: mass flow controller; CLD: chemiluminescence ozone analyzer based on NO-O₃ reaction; OH scav.: OH scavenger; ZG: zero gas.

$R_{O₃}$. The reaction of OH with ozone can cause additional ozone reduction and lead to the overestimation of $R_{O₃}$. To reduce such potential interference by secondary OH, an appropriate OH scavenger is usually added. In this study, cyclohexane was vaporized at room temperature and mixed with the sample before introducing it into the reactor to act as an OH scavenger. Cyclohexane was typically at levels of 400 ppmv in the reactor, which was sufficient for secondary OH to be rapidly scavenged ($OH$ lifetime = 15 ms for $k = 7.0 \times 10^{-15} \text{ cm}^3/\text{molecule/s}$ at 295 K). The artifacts due to the OH scavenger are negligible in this study for the following reasons: (1) $R_{O₃}$ of the scavenger is insignificant (estimated to be $< 1.0 \times 10^{-7} \text{ s}^{-1}$ for $k < 1.0 \times 10^{-23} \text{ cm}^3/\text{molecule/s}$, Atkinson and Arey, 2003); (2) cyclohexane (Wako Pure Chemical Industries, Ltd., “Special Grade”) contains $< 0.05\%$ cyclohexene as an impurity, which corresponds to $R_{O₃} = 0.0004 \text{ s}^{-1}$. Nevertheless, the scavenger was introduced in both the “VOC” mode and the “ZG” mode and any O₃ reduction induced by the scavenger was cancelled out in Eq. (6).

**Ozone Monitor**

To quantify the ozone reactivity ($R_{O₃}$) of the VOC sample, it is necessary to measure rapid ppbv-level variations in ozone before and after the gas passes through the reactor. This is accomplished using an ozone detector (CLD), which is sensitive enough to continuously measure ozone at the ppbv level. Interference of VOCs on the CLD is insignificant. Here, the CLD was based on a modified commercial chemiluminescence NO analyzer (ECO PHYSICS, CLD770). The chemiluminescence detector relies on the reaction of NO and O₃, which produces excited NO₂ molecules that emit chemiluminescence. For NO detection, an excess of ozone is added to the sample air. To measure ozone, an excess of NO is added (Pearson Jr. and Stedman, 1980; Ritter et al., 1994; Matsumoto et al., 2006). NO/N₂ standard gas (4% v/v, 0.06 SLM; SLM = standard L/min) was supplied to the CLD and mixed with the sample flow (0.7 SLM). The absolute ozone concentration was determined using a UV-O₃ analyzer (Dylec Inc., Model 1100) as a secondary standard. The sensitivity and detection limit of the CLD were 150 cps/ppbv and 0.10 ppbv ($S/N = 3$; 60-s average), respectively. The correlation coefficient, $R^2$, of the regression line between the standard ozone mixing ratio (0–150 ppbv) and the analyzer signal was 0.998, and within the given ozone range, it was confirmed to be highly linear.

As can be seen in Eq. (6), for an accurate $R_{O₃}$ analysis, both a stable supply of ozone and precise measurements of the ratio $[O₃(τ_R, VOC)]/[O₃(τ_R, ZG)]$ are critical. In this study, when ozone was supplied and mixed with zero air and the ozone mixing ratio was monitored by CLD (“ZG” mode in Fig. 1), the observed O₃ concentration reached a stable level within 20 minutes of the ozone generator being switched on. After that, the stability of the ozone level was typically $30 \pm 0.30 \text{ ppbv}$, as shown in Fig. 2 ($S/N = 3$, 60-s average of observed ozone). When the dual CLDs were employed, the stability of the ozone concentration corrected using Eq. (7) was typically $30 \pm 0.23 \text{ ppbv}$, owing to the correction of long-term fluctuations in the ozone concentration and the reduction in error propagation in Eq. (7). Therefore, the total deviation of $[O₃(τ_R,ZG)]$ was $\pm 0.8\%$. For the ratio $[O₃(τ_R,VOC)]/[O₃(τ_R,ZG)]$, which is an important factor in the quantification of $R_{O₃}$, an upper limit of 0.992 was obtained, which was the highest measured value that differed significantly from unity. When the ozone concentration was 30 ppbv, a lower limit for the ratio of 0.09 was obtained ($S/N = 3$; 60-s average), which was determined as the lowest measured value that significantly differed from zero.
Fig. 2. Example of observed ozone variation, before and after isoprene \((2.1 \times 10^4\ \text{ppbv})\) was mixed. Small points represent 1-sec data of ozone mixing ratio. Solid circles are 60-sec averages of the 1-sec data.

**Reaction Tube**

As shown in Eq. (4), the ozone loss rate onto the wall surface, \(k_w\), is important for the determination of the ozone baseline in the \(R_{O3}\) measurement, and it is desirable that \(k_w\) be reduced as much as possible. To characterize the \(R_{O3}\) analyzer, the value of \(k_w\) must be determined. To accomplish this, the stable \(O_3/ZG\) sample (“ZG” mode) was introduced into a glass double-tube reactor, and the distance between the two inner tubes, \(L\), and the sample flow rate, \(F\), were varied. Then, the ozone concentration exiting the reactor was monitored. When the reaction time, \(\tau_R\), was changed from 35 s \((L = 35\ \text{cm})\) to 62 s \((L = 62\ \text{cm})\), yielding a net difference in reaction time of 27 s, the ozone concentration decreased from 52.6 ppbv to 51.7 ppbv. As a result, the ozone loss rate was determined to be \(k_w = (6 \pm 3) \times 10^{-4}\ \text{s}^{-1}\).

Samples were periodically alternated between “ZG” and “VOC” to cancel out the contribution of such wall loss, according to Eq. (6). The value of \(R_{O3}\) determined by Eq. (6) was the ozone reactivity of the VOC sample “in the reactor.” To determine \(R_{O3}\) for the original sample, a correction is needed to account for the dilution of the sample flow by the ozone and scavenger flows. The flow rates of ozone, the scavenger, and sample were 0.02, 0.03, and 1.0 SLM, respectively. Thus, the reductions in the VOC concentration and \(R_{O3}\) due to dilution by ozone and scavenger addition were 2 and 3%, respectively. In the following, corrected values are shown.

**RESULTS AND DISCUSSION**

**Characterization of the \(R_{O3}\) Analyzer**

All modules such as the reactor and ozone monitor were fabricated, and the ozone reactivity \((R_{O3})\) analyzer was constructed as in Fig. 1. The entire \(R_{O3}\) analysis system was characterized. Fig. 2 shows an example of the observed variation in the corrected ozone concentration with 1-s and 60-s temporal resolutions, before and after the sample was changed from ZG to VOC. In this case, an isoprene standard sample \((2.1 \times 10^4\ \text{ppbv})\) was prepared. The reaction time was 57 s. A significant reduction in ozone was observed when VOC was introduced. The average concentration of ozone before and after the addition of the VOC sample were defined as \([O_3(\tau_R, ZG)]\) and \([O_3(\tau_R, VOC)]\), respectively, and used to determine \(R_{O3}\) in Eq. (6). For example, in Fig. 2, the ozone level decreased from 30.5 to 21.4 ppbv, and the ozone reactivity of the sample was determined to be \(R_{O3} = 6.2 \times 10^{-3}\ \text{s}^{-1}\).

Next, the quantitative accuracy of the \(R_{O3}\) analyzer was evaluated. When the reaction time was varied in the range 16–62 s \((L = 16–62\ \text{cm})\) and ozone reduction was measured for standard isoprene \((2.3 \times 10^4\ \text{ppbv})\), the dependence of the ozone reduction ratio on reaction time was determined as shown in Fig. 3(a). The ozone reactivity of the isoprene standard sample was theoretically estimated to be \(7.2 \times 10^{-3}\ \text{s}^{-1}\) for \(k = 1.2 \times 10^{-17}\ \text{cm}^3/\text{molecule/s}\) \((295\ \text{K})\) using the Arrhenius equation (Atkinson and Arey, 2003). The theoretically predicted ozone reduction on the right side of Eq. (5) is also shown in the figure. The experiment agreed well with the theoretical prediction. Furthermore, by taking the natural logarithm of Eq. (6), the following equation is obtained.

\[
\ln \frac{[O_3(\tau_R, VOC)]}{[O_3(\tau_R, ZG)]} = R_{O3} \tau_R
\]  

(8)

Thus, \(R_{O3}\) can be determined as the slope of the regression line of a correlation plot between the reaction time and the left side of Eq. (8). Fig. 3(b) shows such a correlation plot for the experimental data in Fig. 3(a). A strong correlation was observed (correlation coefficient \(R^2 = 0.997\)). All uncertainties in this study are presented as 3\(\sigma\). The intercept of the regression line was \((-1 \pm 2) \times 10^{-2}\), and thus, there is no significant deviation between the intercept and zero. The slope of the regression line was \((7.3 \pm 0.6) \times 10^{-3}\ \text{s}^{-1}\), which agreed with the theoretical reactivity \((7.2 \times 10^{-3}\ \text{s}^{-1})\) within the experimental uncertainties. This demonstrates that the observed dependence of ozone reduction on reaction time was reasonable.

Subsequently, the response of the analyzer to ozone reactivity was explored. When the reaction time was fixed at 57 s and the ozone reactivity of the VOC samples (isoprene
Fig. 3. (a) Dependence of ozone reduction ratio on the reaction time at the reactor. (b) Similar to (a), except for the y-axis (natural logarithmic). Regression line slope corresponds to ozone reactivity (Eq. (8)).

and limonene) were varied in the range $4.3 \times 10^{-4} - 1.5 \times 10^{-2}$ s$^{-1}$, the dependence of the ozone reduction ratio on ozone reactivity was resolved as shown in Fig. 4(a). The reaction rate coefficient of limonene with ozone was calculated to be $k = 2.1 \times 10^{-16}$ cm$^3$/molecule/s at 295 K (Atkinson and Arey, 2003). The experiment agreed well with the theoretical prediction. Furthermore, in Eq. (8), the reaction time is given by the slope of the regression line of the correlation plot between the ozone reactivity and the left side of Eq. (8). Fig. 4(b) shows such a correlation plot for the experimental data in Fig. 4(a). A strong correlation is observed ($R^2 = 0.999$). The intercept of the regression line is $(2 \pm 7) \times 10^{-3}$. The slope of the regression is $56.9 \pm 1.2$ s, which agrees with the preliminary value derived from $\tau_R = V/F$ (57 s). Thus, the observed dependence of ozone reduction on ozone reactivity was considered to be reasonable. Note that Fig. 4(b) is a plot of the standard values of the measurement target and the analyzer response, and hence, it corresponds to the standard calibration curve for the $R_{O3}$ analyzer. The analyzer reaction time can be calibrated through this procedure.

To validate the performance of the $R_{O3}$ analyzer, the dependence of the observed $R_{O3}$ on concentrations of BVOCs is shown in Fig. 5: (a) isoprene (10–52 ppmv) and (b) limonene (85–620 ppbv). In these ranges, the linearity between the concentrations of olefins and observed $R_{O3}$ was confirmed ($R^2 = 0.999$ for isoprene and 0.988 for limonene). The slopes of the regression lines agreed with the reaction rate coefficients $k(O_3 + VOC)$. For example, the slope for isoprene ($2.9 \times 10^{-7}$ s/ppbv) can be converted to $1.2 \times 10^{-17}$ cm$^3$/molecule/s, which corresponds to $k(295$ K). It was confirmed that the response of the $R_{O3}$ analyzer was quantitatively correct for standard samples of isoprene and limonene. The $R_{O3}$ analyzer is based on the assumption of a pseudo-first-order reaction, i.e., $[O_3] << [VOC]$. When $[VOC]$ is of a comparable magnitude to $[O_3]$, the errors in the $R_{O3}$ measurement are possibly more significant due to variations in the VOC concentrations in the reactor. To consider such errors, a box model calculation was performed for the $O_3$-limonene reaction. When the “observed $R_{O3}$” was estimated from the calculated ratio $[O_3/(r_k = 57 s)][O_3(0)]$ for $[limonene(0)] = 0.1 - 1000$ ppbv and $[O_3(0)] = 30$ ppbv, the observed $R_{O3}$ was underestimated by 0.4% at most. Consequently, even when the limonene level is as low as the ozone level, the underestimation of the $R_{O3}$ measurement is negligible for the present experimental parameters. (Note that, when the reaction time is much longer, this underestimation could be more significant.)
The responses of the $R_{O_3}$ analyzer reasonably reflect the principle on which the measurement is based (Eq. (5) and Eq. (8)). The ozone reactivity of the VOC sample could be quantitatively determined by measuring ozone reduction, and the dependency of the reaction time and reactivity represents fundamental characteristics of the $R_{O_3}$ analyzer. When settings such as the shape and volume of the reactor or the sample flow rate are changed, it is necessary to conduct calibration experiments to determine these characteristics. As a routine calibration procedure, the following method is proposed for the simple determination of the reaction time: (P1) the positions of the inner tubes of the reactor are set such that the preliminary reaction time is close to the desired value; (P2) a standard VOC sample is prepared and the ozone reduction is measured, and the reaction time is accurately determined as in Fig. 4(b); (P3) the ozone reactivity of the target sample, $R_{O_3}(\text{VOC})$, is determined using the following equation.

$$R_{O_3}(\text{VOC}) = R_{O_3}(\text{cal})\left[\ln\left(O_3(t_{\text{R,voc}})/O_3(t_{\text{R,ZG}})\right)/\ln\left(O_3(t_{\text{R,voc}})/O_3(t_{\text{ZG,cal}})\right)\right]$$  \hspace{1cm} (9)

where $R_{O_3}(\text{cal})$ and $[O_3(t_{\text{R,voc}})/O_3(t_{\text{ZG,cal}})]$ are the ozone reactivity and ozone reduction, respectively, for calibration with a standard VOC sample.

**Interference from Water Vapor**

For CLD analyzers, water vapor in the sample gas has a quenching effect and can reduce the sensitivity of the ozone detector (Matthews et al., 1977; Lenschow et al., 1981; Ridley et al., 1992). When a CLD is adopted for the $R_{O_3}$ measurement of a humid sample such as emissions from a plant, the reduction in the ozone signal due to water vapor can cause potential interference in Eq. (6). In this study, however, such effects of water vapor can be cancelled out by use of the “dual CLD” set-up. The ozone signals of CLD1 and CLD2 decreased by 12% when the relative humidity of the sample was 98%. It was experimentally confirmed that the response characteristics of CLD1 to water vapor agreed well with those of CLD2. Thus, the interference of water vapor can be reduced when the correction shown in Eq. (7) is adopted.

**Specifications of the $R_{O_3}$ Analyzer**

The $R_{O_3}$ analyzer ($S/N = 3; 60 \text{s average}$) could measure ozone reactivity across the range of $1.4 \times 10^{-4} - 4.2 \times 10^{-2} \text{s}^{-1}$ for a reaction time of 57 s and the range of the ozone reduction ratio was 0.992-0.09. The lower limit of the $R_{O_3}$ range, $1.4 \times 10^{-4} \text{s}^{-1}$, corresponds to 27 ppbv limonene equivalent. The total uncertainty of the $R_{O_3}$ measurement was estimated to be ±11% from the propagation of errors (e.g., standard gas: ± 10%, reaction time: ± 2%). To ensure that there was a sufficiently long interval for changes between “ZG” and “VOC” modes, a measurement cycle was typically 12 minutes long.

**Measurement test of BVOCs Emitted from Vegetation**

Finally, to verify the applicability of the $R_{O_3}$ analyzer, a test was conducted to monitor BVOCs emitted from real vegetation. The analyzer was combined with an enclosure method to determine the plant’s VOC emission factor. A plant was placed in a Teflon bag (10 L), into which clean air (ZG) was supplied. From the exit of the bag, the sample air was fed into the reactor and CLD1. O$_3$ was added before the reactor and CLD2 monitored variations in the ozone concentration. The $R_{O_3}$ value of the sample gas was continuously monitored (“Sample” mode in Fig. 1). The reaction time and total sample flow rate in the reactor were set to 57 s and 1.0 SLM, respectively. We used “Cryptomeria japonica,” a kind of needle leaf tree, as the sample plant. The tree height was about 50 cm, and it was covered by the Teflon bag from stem to top. To keep the sample pressure at atmospheric pressure, a “vent” tube was inserted into the bag, from which the excess gas was vented. For the light irradiation experimentation, two fluorescent lamps ($2 \times 30 \text{ W}$) were placed about 20 cm above the tree. The flow rate of zero air into the enclosure, $F_{ec}$, was typically 4.9 SLM. The time constant of air exchange in the bag was estimated to be 2 minutes for the volume of 10 L. $R_{O_3}$ increased significantly 10 minutes after irradiation started, and it reached a maximum of $1.4 \times 10^{-3} \text{s}^{-1}$, as shown in Fig. 6(a). It has been reported that BVOC emission from plants can be increased by irradiation (Guenther et al., 1993; Tani and Kawawata, 2008). In this study, these increased emissions from the tree were well captured by the $R_{O_3}$ analyzer. The time constant of air exchange in the enclosure (2 minutes) is comparatively short, and the 10-minute delay in the $R_{O_3}$ increase can probably be attributed to the delayed response of the tree to the irradiation. The delay in the BVOC emission from the plant was well captured.

After a sufficient interval in the enclosure through which the zero air was continuously passed, the emissions stabilized in line with the inflow/outflow flux, and the VOC concentrations in the enclosure reached steady-state values (Matsumoto et al., 2009). In the steady state, the emission rate of individual VOC compounds, $ER(VOC_{i,SS})$, can be described as follows.

$$ER(VOC_{i, SS}) = F_{ec} \cdot [VOC_{i}]_{SS}$$  \hspace{1cm} (10)

where $F_{ec}$ and $[VOC_{i}]_{SS}$ are the flow rate into the enclosure and the steady-state number density of VOC, respectively. When the sum of the products of the reaction rate coefficients of VOC with ozone ($k_i$) and both sides of Eq. (10) are calculated, the equation can be rewritten as follows.

$$\sum k_i ER(VOC_{i, SS}) = \sum k_i F_{ec} \cdot [VOC_{i}]_{SS} = F_{ec} R_{O_3}(SS)$$  \hspace{1cm} (11)

where $R_{O_3}(SS)$ is the steady-state ozone reactivity observed at the bag exit. $R_{O_3}(SS)$ can be expressed as follows.

$$R_{O_3}(SS) = F_{ec}^{-1} ER(R_{O_3}, SS)$$  \hspace{1cm} (12)

where $ER(R_{O_3}, SS)$ is defined as $\sum k_i ER(VOC_{i, SS})$, which corresponds to the emission rate of VOCs in terms of ozone reactivity. The emission rate of all BVOCs in terms of $R_{O_3}$, $ER(R_{O_3}, SS)$, can be obtained from the slope of the regression line between the inverse of $F_{ec}$ and the observed
emission rate of \((5.4 \pm 0.5) \times 10^{14}\) molecule/s. A trace level of \(R_{O_3}\) was detected for the “dark” condition before irradiation began (Figs. 6(a) and 6(b)). Without irradiation, \(ER(R_{O_3}, SS)\) was determined to be \((1.0 \pm 0.1) \times 10^{-7}\) (cm³/s)s⁻¹, corresponding to a limonene-equivalent emission rate of \((4.5 \pm 0.4) \times 10^{15}\) molecule/s. In this study, the emission factor of BVOCs from the irradiated plant was about 12 times larger than that for the dark condition.

The influence of NO on the \(R_{O_3}\) measurement in the real-tree test was also explored. After the measurement of \(R_{O_3}\), the NO concentration in the enclosure was checked using another CLD NO analyzer (modified TECO 42S, detection limit = 0.1 ppbv). Significant concentrations of NO were not detected when the same settings as for the \(R_{O_3}\) experiment were used. When the NO concentration was assumed to be at the detection limit (0.1 ppbv), \(R_{O_3}\) was overestimated by \(5 \times 10^{-5}\) s⁻¹, which was less than the detection limit for \(R_{O_3}\) \((1.4 \times 10^{-4}\) s⁻¹). Thus, the potential interference due to coexisting NO was insignificant.

In this study, the BVOC emission from a real tree was successfully captured using the ozone reactivity measured by the \(R_{O_3}\) analyzer. The \(R_{O_3}\) values of “clean” BVOC samples that did not contain significant amounts of NO were successfully determined. In order to use this analyzer for samples with significant NO contents, reduction of and/or correction for interference from NO would be necessary. Although this interference remains an issue, the \(R_{O_3}\) analyzer has the potential to be a useful tool in the analysis of BVOCs.

**CONCLUSIONS**

A measurement system for the total reactivity with ozone \((R_{O_3})\) was developed as a new tool for measuring biogenic volatile organic compounds (BVOCs) emitted from vegetation into the atmosphere. The system consisted of an ozone generator, reactor, and ozone detectors. To ensure the pseudo-first-order reaction of VOCs and ozone in the reactor, initial ozone levels were set to 30 ppbv. The decrease in ozone due to the reaction with VOC was monitored by sensitive, precise, real-time ozone detectors, based on the chemiluminescence reaction between NO and \(O_3\). By use of dual detectors before and after the reactor, temporal variations in the generated ozone concentration and interference from water vapor were corrected for. The upper limit of the measurable ozone reduction ratio was 0.992 \((S/N = 3; 60\ s\ average)\. A glass double-tube flow reactor was adopted. The reaction time was controlled through the positions of the inner tube and the sample flow rate. The loss rate of ozone onto the reactor wall was typically \((6 \pm 3) \times 10^{-4}\) s⁻¹. Characterization of the \(R_{O_3}\) analyzer using the standard VOC samples (isoprene and limonene) demonstrated that the dependence of ozone reduction on the reaction time and reactivity agreed with theoretical prediction. Consequently, the detection limit of \(R_{O_3}\) for a 57-s reaction was found to be \(1.4 \times 10^{-4}\) s⁻¹, which corresponds to 27 ppbv of limonene. It was confirmed that the \(R_{O_3}\) analyzer is capable of measuring standard samples.
Finally, to verify the applicability of the $R_{O_3}$ analyzer, an $R_{O_3}$ measurement test was conducted for BVOCs emitted from a real needle-leaf tree. A significant increase in $R_{O_3}$ was observed, especially when the tree was irradiated by lamps. Using the enclosure method, the BVOC emission rate was found to be $(1.2 \pm 0.1) \times 10^{-1}$ (cm$^3$/s)$^{-1}$ from the real tree. The practical utility of the $R_{O_3}$ analyzer was confirmed in this preliminary test, and the newly developed analyzer represents a promising new measurement tool in the analysis of BVOC emissions.

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