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Quantitative and qualitative sensing techniques for biogenic volatile organic compounds and their oxidation products

Saewung Kim,^{*a} Alex Guenther^b and Eric Apel^b

The physiological production mechanisms of some of the organics in plants, commonly known as biogenic volatile organic compounds (BVOCs), have been known for more than a century. Some BVOCs are emitted to the atmosphere and play a significant role in tropospheric photochemistry especially in ozone and secondary organic aerosol (SOA) productions as a result of interplays between BVOCs and atmospheric radicals such as hydroxyl radical (OH), ozone (O₃) and NO_x (NO + NO₂). These findings have been drawn from comprehensive analysis of numerous field and laboratory studies that have characterized the ambient distribution of BVOCs and their oxidation products, and reaction kinetics between BVOCs and atmospheric oxidants. These investigations are limited by the capacity for identifying and quantifying these compounds. This review highlights the major analytical techniques that have been used to observe BVOCs and their oxidation products such as gas chromatography, mass spectrometry with hard and soft ionization methods, and optical techniques from laser induced fluorescence (LIF) to remote sensing. In addition, we discuss how new analytical techniques can advance our understanding of BVOC photochemical processes. The principles, advantages, and drawbacks of the analytical techniques are discussed along with specific examples of how the techniques were applied in field and laboratory measurements. Since a number of thorough review papers for each specific analytical technique are available, readers are referred to these publications rather than providing thorough descriptions of each technique. Therefore, the aim of this review is for readers to grasp the advantages and disadvantages of various sensing techniques for BVOCs and their oxidation products and to provide guidance for choosing the optimal technique for a specific research task.

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The role of biogenic volatile organic compounds (BVOCs) in controlling oxidation capacity and aerosol formation has been highlighted over the past five decades. Many breakthroughs on quantitative and qualitative analytical techniques have provided important clues to understand how the minor chemical constituents in the atmosphere drive atmospheric photochemistry governing ozone and secondary aerosol formation. Gas chromatography techniques have served as a main analytical tool for BVOC quantification since the early stage of BVOC quantification research. In addition, many different techniques such as mass spectrometry and spectroscopic methods have emerged. New insights from the emerging techniques have revealed new perspectives on BVOCs photochemistry to regional and global air quality. This critical review concisely summarizes the current understanding of BVOC emissions and their atmospheric photooxidation processes along with discussion about their impacts on air quality and climate. The discussion shows how new emerging techniques provide important clues in understanding BVOC photochemistry in the troposphere. In addition, principles, advantages and disadvantages of a wide variety of analytical techniques are discussed in the manuscript. Therefore, we believe that this critical review will serve as important guidance especially for emerging scientists who are just starting their career in biosphere–atmosphere interaction research and a useful guide for established scientists who would like to review the overall development of analytical techniques for BVOC observations.

1 Introduction and scope of this review

Atmospheric chemistry research in the past several decades reveals that (1) in the global perspective, the emissions of

biogenic volatile organic compounds (BVOCs) are around an order of magnitude higher than the VOC emissions from anthropogenic activities,^{1,2} (2) photochemical oxidation processes of BVOCs directly affect ozone and aerosol productions and thus they have significant implications for regional air quality and global climate,^{3,4} (3) BVOCs play a significant role in air quality even in some urban areas with high anthropogenic VOC and NO_x (NO + NO₂) emissions,⁵ and (4) in very remote areas with little influence of anthropogenic pollution, BVOC

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photochemistry amplifies concentrations of the hydroxyl radical (OH),^{6,7} which is a universal tropospheric oxidant and determines the lifetime of most trace gases including methane – an important greenhouse gas. These expansions of our understanding have been achieved through the development and application of analytical techniques for BVOCs and their oxidation products in field and laboratory studies.

Technical breakthroughs in air sampling and quantification techniques indeed have expanded the horizon of our understanding of the atmospheric chemistry of volatile organic compounds. For example, cartridge-sampling techniques using solid sorbents (*i.e.* Tenax TA) allowed us to monitor VOC distributions in a wide spatial range so that BVOC measurements could be conducted in widespread geographical environments. The extensive observational results have served as an important basis in constructing BVOC emission inventories and emission models.¹ In addition, the development of a Proton Transfer Reaction-Mass Spectrometry (PTR-MS[®]) technique, which can monitor a wide range of volatile organic compounds with high sensitivity in real time at a high sampling frequency, has enabled quantification of very reactive and low volatility compounds in the atmosphere, which have significant implications for understanding tropospheric ozone and secondary aerosol formation processes.

In this review, we first provide an overview of BVOCs and their photochemistry in the troposphere and discuss their implications in regional air quality and global climate. In the following sections, we review measurement techniques used for quantifying BVOCs and their oxidation products and discuss how the new observational dataset could expand our horizon in tropospheric BVOC photochemistry. We review most of the measurement techniques that have been used to quantify emission rates and ambient distributions of BVOCs and their oxidation products since 1960 when Went⁹ first suggested the importance of BVOCs in aerosol formation in remote forest regions. Since then, there have been a number of reviews on sensing techniques such as gas chromatography, chemical ionization mass spectrometry, and optical spectroscopy. Therefore the aim of this review is to succinctly introduce the currently available sensing techniques for BVOCs and their oxidation products, so that readers are fully informed about the advantages and disadvantages of each analytical technique and can choose the appropriate sensing techniques for their own research.

2 BVOCs in the regional air quality and the global climate system

Haagen-Smit¹⁰ first presented a tropospheric photochemical reaction mechanism in an attempt to explain secondary photochemical product formations (ozone and aerosols) from anthropogenic precursors such as NO_x (NO + NO₂), VOCs, and SO₂. Due to a lack of understanding of the central role of the hydroxyl radical (OH) in tropospheric photochemistry, the proposed photochemical mechanisms speculated that molecular oxygen was the main oxidant in the troposphere although the mechanisms correctly contained the precursors (NO_x and

VOCs) and the products (ozone and organic aerosols) of photochemical smog. In 1960, Went speculated that BVOCs are a main source for the “blue haze” that had been observed since the sixteenth century (*e.g.* by Leonardo da Vinci) near forest areas especially during the summer season. This speculation was also supported by John Tyndall's (1820–1893) empirical finding that aerosol formation inside of a glass jar filled with organic vapor (alkene compounds) could be triggered by light and ozone. Went⁹ argued that BVOCs, especially monoterpenes (C₁₀H₁₆; MTs) with their multiple carbon–carbon double bonds in their chemical structure, are a major source of aerosols. MTs were widely known as important plant constituents long before 1960.¹¹ However, their existence in the atmosphere as an important gas phase component was controversial. Went⁹ argued that the similarities between the ambient air smell near forest areas and smell from crushed pine needles were proof of MT's presence in the ambient air.

Quantification of BVOCs in various forest environments was first reported by Rasmussen and Went.¹² They deployed a GC system coupled with a packed column (Diatoport S 60–80 mesh) and a hydrogen flame ionization detector in a mobile trailer. They drove the trailer around rural U.S. regions to quantify terpenoid species in the ambient air. The results showed that VOCs are present at up to a few ppbv in the summer season. In the following studies, Went *et al.*¹³ demonstrated that BVOCs, especially terpenes, can be a significant source for atmospheric particulate matter (Aitken condensation nuclei). The emissions of terpenoids from plants were confirmed by Rasmussen¹⁴ from static leaf chamber measurements of five different tree species (oak, cottonwood, sweetgum, eucalyptus and white spruce). In the study, the author used three different analytical methods (GC-FID, infrared spectrometry, and mass spectrometry) to confirm the presence of isoprene in complex organic vapor mixtures in the static chamber air.

In 1971, Levy¹⁵ postulated that tropospheric OH present at very low levels (usually less than 10⁷ molecules per cm³ out of 2.5 × 10¹⁹ molecules per cm³ at standard temperature and pressure) governs tropospheric photochemistry. This finding triggered a series of laboratory studies to characterize the reaction kinetics of atmospheric oxidants (*e.g.* OH and ozone) and BVOCs (*e.g.* Westberg and Rasmussen¹⁶). In addition, comprehensive research was conducted in the 1970s to characterize ambient distributions of natural hydrocarbons, especially terpenoid species (isoprene, hemiterpenoid and monoterpene, monoterpenoids) to assess their fate in the atmosphere and impacts on regional and global air quality. Graedel¹⁷ reviewed the understanding of BVOCs and their photochemistry in the atmosphere that had been accumulated by the late 1970s. At that time, the consensus of the scientific community was that isoprene and a few monoterpenes are the most dominant BVOCs in the atmosphere among the 20 organic compounds that had been confirmed as vegetation emissions. The unit of μg g⁻¹ h⁻¹ was typically used to express emission rates of those compounds at that time.^{17,18} The laboratory characterization of oxidation reaction rates of selected BVOCs with atmospheric oxidants was first conducted by Winer *et al.*¹⁹ In addition, several laboratory smog chamber and theoretical

studies elucidated reaction mechanisms, products and aerosol yields from BVOC oxidation.^{16,20–24} Those results showed that as oxidation proceeds, the vapor pressure of reaction products tends to be significantly decreased. Those less volatile oxidation products, therefore, are more partitioned into the particle phase. Estimation by Duce²⁵ based on those laboratory observations indicated that global secondary organic aerosol mass burden (60–140 MT OC per year) is much higher than the estimated burden from the anthropogenic source (~20 MT OC per year). However, Weiss *et al.*²⁶ reported contradictory aerosol composition observations that indicated sulfate compositions, mostly from anthropogenic activities, dominated in several rural locations in the U.S. where one would expect high BVOC emissions to trigger organic aerosol formation. These contradicting results urged more comprehensive research including inter-phase partitioning characterizations. Another controversy, caused by insufficient understanding of gas phase oxidation mechanisms of BVOCs in the late 1970s, was the contribution of BVOCs to regional and global photochemistry, specifically ozone formation. For example, Gay *et al.*²⁷ and Lonneman *et al.*²⁸ concluded that BVOCs are not important for local and regional photochemistry even in forest areas. In contrast, Zimmerman *et al.*²⁹ speculated that BVOCs were a significant source of global CO and H₂, by-products of BVOC oxidation processes, and thus important for atmospheric photochemistry.

The first comprehensive discussion about the impacts of BVOCs on regional air quality was presented by Altshuller.³⁰ Previously, Arnsts and Meeks³¹ concluded that BVOCs were a minor contribution to total VOCs even in rural places (*e.g.* Rio Blanco County Colorado and the Smoky Mountain Region in the U.S.) based on a relatively small measurement dataset. Lonneman *et al.*²⁸ also claimed that BVOCs did not contribute to ozone formation in Florida based on VOC measurements in multiple locations (*e.g.* St. Petersburg/Tampa and Miami, FL). The analysis by Altshuller³⁰ was conducted using BVOC and AVOC emission inventories in the United States. In addition, Altshuller³⁰ comprehensively reviewed a number of field VOC measurement and laboratory (smog chamber) experiment results to assess the ozone and aerosol formation potential from the oxidation of major AVOCs and BVOCs. The emission inventories introduced in the early 1980s were mostly constructed using datasets from branch enclosure measurements.^{17,18} Based on the small number of experimental points, emission rates from regional scales were estimated. Those bottom-up emission inventories were tested several times by top-down estimations from field observations of chemical and micrometeorological parameters. The results indicated some general agreement but in some cases there was a major discrepancy between top-down and bottom-up BVOC emission estimations (–19% to 400%^{32,33}). Ambient measurements of both biogenic and anthropogenic VOCs in rural areas were also used to evaluate emission inventories of BVOCs and AVOCs. The analysis showed a higher degree of underestimated reactive AVOC (*e.g.* propene) emissions up to 100 times^{28,31,34–36} compared to underestimated reactive BVOC emissions such as isoprene and α -pinene. Altshuller,³⁰ therefore, suggested the two possibilities – either underestimated AVOC or

overestimated BVOC emissions could cause these discrepancies although anecdotal evidence for unmeasured BVOCs especially oxygenated compounds was reported.^{17,18,37} From the assessments of emissions and oxidation processes using the best available knowledge at that time, Altshuller³⁰ concluded that BVOC photochemistry contribution to ozone and aerosol levels in the U.S. was insignificant compared to contributions from AVOC photochemistry.

These conclusions, however, were not confirmed by follow up mechanistic photochemical modelling studies constrained by field observations. Trainer *et al.*³⁸ interpreted a field measurement data suite of NO_x, VOCs both anthropogenic and biogenic, and ozone observations from a rural research site in summer (Scotia, Pennsylvania) using a one-dimensional photochemical model. The study presented three different model runs using the following ozone precursors: (1) NO_x only, (2) NO_x and BVOCs and (3) NO_x, BVOCs and AVOCs and compared the model results to the observed ozone levels. The results indicated that most of the photochemical ozone formation was from BVOC photochemistry, which enhances HO₂ levels and other organic peroxy radicals (RO₂). This conclusion is quite contradictory to the previous several studies and the authors explained that non-linearity of photochemistry which has not been considered in the previous studies led to this new conclusion. In the following year, Chameides *et al.*⁵ demonstrated that ozone formation in the urban area of Atlanta, Georgia U.S.A. was controlled by BVOC photochemistry. With detailed photochemical model calculations, the authors demonstrated that policy implementation for photochemical ozone pollution control should consider BVOC photochemistry. For example, a photochemical model scenario without BVOCs indicated that 30% reduction of AVOCs in the Atlanta area could reduce ozone to the EPA compliance level, 120 ppbv in one hour average but once BVOC photochemistry was taken into consideration then a 70% reduction was required to achieve the same goal. In addition, Chameides *et al.*³⁹ demonstrated that the concentration-based evaluations of impacts on tropospheric photochemistry from VOCs in the previous studies could be misleading because of a wide range of photochemical VOC reactivities. Chameides *et al.*,³⁹ therefore, developed the concept of “propylene-equivalent concentration”, which is a normalized concentration scale with respect to the propylene reactivity towards OH. The analysis of measurement datasets in various urban and remote locations using the propylene-equivalent concentration scale indicates that BVOC contributions, especially isoprene and MT, to photochemistry had been significantly underestimated not only in forested rural areas but also in urban/suburban areas, where the importance of BVOCs in photochemistry had been ignored. In addition, Chameides *et al.*³⁹ also speculated about the possibility that there were significant unmeasured VOCs, especially oxygenated compounds, that may play a significant role in photochemistry.

As Went first hypothesized, important roles of MT in aerosol formation have been confirmed by laboratory and field experiments since 70s. However, the isoprene contributions to global aerosol formation had been ignored because most of the first generation isoprene oxidation products (methyl vinyl ketone,

methacrolein, and formaldehyde) are highly volatile and early aerosol chamber experiments observed no secondary aerosol formation. This assumption, however, has been overturned by recent field^{44–46} studies and laboratory^{40–43} experiments with more realistic chamber experimental conditions. Considering the dominance of isoprene in BVOC emissions (about half of the global total¹),² a few percent of aerosol yields from isoprene is still significant in the global scale. Based on the latest research results, Hallquist *et al.*⁴ estimated the amount of secondary organic aerosol loading from BVOCs including isoprene and MT to be 88 TgC per year, which is significantly higher than that from AVOCs (10 TgC per year).

A comprehensive isoprene photooxidation process was presented by Paulson and Seinfeld.⁴⁷ Atkinson and Arey⁴⁸ reviewed oxidation mechanisms and reaction rate constants of other BVOCs including monoterpenes for atmospheric oxidants such as OH, ozone and NO₃. In the past few years, new findings on the isoprene photo-oxidation mechanisms revealed isoprene oxidation products that previously have not been known or observed. For example, Paulot *et al.*^{42,49} detected a number of new first generation oxidation products of isoprene oxidation by OH such as C5- and C4-hydroxycarbonyl compounds, hydroxy acetone, glyoxal and methylglyoxal. Wolfe *et al.*⁵⁰ and Taraborrelli *et al.*⁵¹ presented critical reviews on recent breakthroughs on isoprene oxidation mechanisms and products. These new findings on isoprene oxidation chemistry suggest that further research is necessary for other relatively less studied BVOCs such as monoterpenes and sesquiterpenes.

Early research (1970s) probing BVOC photochemistry was mostly dependent on traditional GC techniques. As new techniques became available, including advanced GC techniques, chemical ionization mass spectrometry (CIMS), and optical techniques, new experimental findings expanded our understanding of BVOC tropospheric photochemistry. In addition, calibration methods have been advanced to quantify semi-volatile and very reactive compounds that have significant implications for photochemistry and aerosol formations. In the following sections, we will review technical advances that have taken place during the past several decades for quantifying BVOCs and their oxidation products and how those advances have expanded our understanding of BVOC photochemistry in regional and global air quality and climate.

3 Sensing techniques for BVOCs and their oxidation products

3.1 Sensing techniques before 1990

The most commonly used analytical technique for BVOC measurements has been GC. Two early qualification and quantification studies of isoprene and monoterpenes^{12,14} used a GC system with a packed column. This was coupled with a sampling loop for sample injections to the GC system. In these early studies, the big challenge in applying a GC method to BVOC sensing was identifying BVOC peaks from chromatograms. The challenge was addressed by applying analytical tools such as mass spectrometry and FT-IR spectroscopy. As shown in Fig. 1, the major peaks from branch enclosure samples were identified by the multiple

qualitative analytical tools. Interestingly, the olfactory sense was useful for identifying BVOCs in these early studies. Rasmussen and Went¹² noted that “Some terpenes, commonly formed in plants, were tested to determine their retention times on the chromatographic columns used, making it possible to identify the odors found in free air, at least tentatively.” Similarly, Rasmussen¹⁴ wrote “Some of observations from smelling these accumulated foliage volatiles at concentrations of a few ppm are of note. ----- The description given most often was “smells like an oak forest.” The response for smelling nonisoprene releasing foliages like maples, ash, birch, and alders was “smells like fresh leaves.””

These studies used the Flame Ionization Detector (FID), which is still commonly used for VOC quantifications. The sensitivity of the FID (in a standard configuration) to molecules of the light alkanes (C₁ to C₈) shows a nearly proportional response to the number of C atoms per mole.^{52–55} The response for alkenes may be slightly altered but proportional to the carbon number within 10%. The response for alkynes may be dramatically different and dependent on the flame conditions.^{54,56} Also there is a reduced response to oxidized groups such as carbonyl or carboxyl groups,⁵⁷ and the response to carbons attached to hydroxyl groups or halogens is reduced. Many investigators have taken advantage of the proportional response and simply report concentrations of a myriad of hydrocarbons referenced to a particular standard hydrocarbon (*e.g.*, propane from the National Institute of Standards and

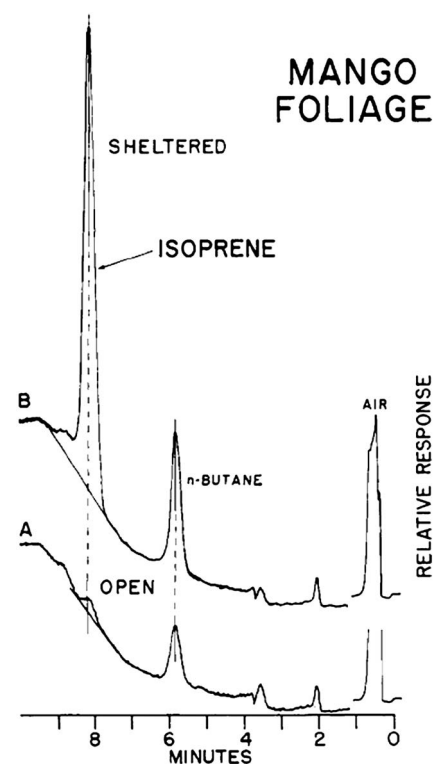


Fig. 1 A chromatogram of sample air next to *Mangifera indica* foliage presented by Rasmussen.¹⁴ The top chromatogram (noted as “SHELTERED”) shown is a chromatogram from branch enclosure air and the bottom chromatogram (noted as “OPEN”) shown is a chromatogram from the ambient air. Reproduced with permission from Ref. 14. Copyright 1970 American Chemical Society.

Technology (NIST)). Other laboratories do not rely on this proportional response of the FID. These laboratories generate a standard for each compound that they wish to analyze, and calibrate their instruments accordingly.

Whitby and Coffey⁵⁸ reported ambient concentrations of speciated monoterpeneoids (α -pinene, β -pinene, and *p*-cymene) in ambient air of the Adirondack Mountain region, New York USA. The GC instrumentation for this study was equipped with two nearly identical columns for back-flushing and a liquid nitrogen (LN₂) cryogenic concentrator. The sample concentration technique could provide more sensitivity so that relatively small amounts of MTs in the range of ~64 pptv in the morning and ~1.7 ppbv during the afternoon were quantified.

However, single-stage cryogenic concentrating methods have drawbacks of water condensation and aerosol formation.⁵⁹ The concentrated water in the trap can significantly interfere with the FID signals. Therefore, multi-stage preconcentrating methods or solid sorbent concentration techniques that do not have the water interference issue have gained a wide interest in the VOC measurement community. An early study by Pellizzari *et al.*⁵⁹ tested several candidate sorbent materials (polymer beads, activated carbons, and liquid phases) and reported that Tenax GC (2,6-dimethyl-*p*-phenylene oxide) and Chromosorb 101 (styrene-divinyl benzene) showed good adsorption efficiencies for a wide range of compounds (NMHCs and oxygenated compounds) and flow rates (up to 9 slm). The study concluded that Tenax GC and Chromosorb are adequate substances for cartridge sampling. It was noted that Tenax GC has an advantage over other materials because of its stability at high temperature and relative insensitivity to water vapor. Brown and Purnell⁶⁰ investigated necessary sampling volumes as a function of sampling flow-rate, sample concentration, temperature, and relative humidity for a wide range of analytes (hydrocarbons, chlorinated hydrocarbons, other halogenated hydrocarbons, esters, aldehydes and ketones, alcohols, acids and anhydrides, and amines). The results indicated that optimal sampling volumes are a strong function of flow-rates, concentrations of VOCs, and sample temperatures. Helmig *et al.*⁶¹ explored additional materials and confirmed again that Tenax shows the most ideal performance in terms of the desorption efficiency, the adsorption capacity, and minimized blanks. Since then there have been major advances in sorbent sampling technology. Sorbents having a wide range of characteristics including temperature stability, hydrophobicity/hydrophilicity, and retention strength are now available. These may be used singly but are often used in combinations in modern applications and can be tailored for specific measurement applications, *e.g.*, OVOC, low, midrange, and semivolatiles NMHC measurements, *etc.* For a comprehensive review of the subject and additional details see Woolfenden^{62,63} and references therein.

Another important aspect to be considered for accurate VOC measurements using cartridge sampling is chemical transformation of the trapped and sorbent molecules while sampling is conducted. The reason is that the molecules adsorbed to the sorbent bed are exposed to the ambient airstream for a significant time period so oxidants in ambient

air can transform reactive VOCs to their oxidation products. Pellizzari and Krost⁶⁴ and Pellizzari *et al.*⁶⁵ reported laboratory experiment results of those surface reactions between oxidant and adsorbed molecules. The results indicated that a measurable amount of benzaldehyde, acetophenone, and phenol were detected from sorbent material oxidation by ozone and adsorbed analytes can be significantly transformed to oxidized compounds by ozone. The degree of transformation was highly dependent on the reactivity of the analytes (*e.g.* alkenes showed more loss compared with alkanes). To inhibit those unintended reactions, Pellizzari *et al.*⁶⁵ tested several filter options and suggested that filters for oxidants should be carefully selected because the filter material may interfere with atmospheric VOCs to be sampled.

Canister samplers (whole air samplers) have also been used for BVOC sampling.⁶⁶ The canister sampling method has several advantages over the sorbent sampling method such as (1) sampling without breakthrough, and (2) no interactions with the sorbent material.⁶⁷ However, more care is required for canister preparations (*e.g.* samplings and canister clean up) than that for the sorbent sampling method. In addition, some compounds are not stable in some sampling canisters and should be carefully assessed by laboratory experiments. A major disadvantage is the much larger volume required to transport samples. In general, the canister sampling method has been used for compounds below C₁₁, which include hemiterpenoid (isoprene and 2-methyl-3-buten-2-ol) and monoterpeneoid BVOCs.⁶⁸ Although some studies extend the compound list up to C₁₃,⁶⁹⁻⁷¹ Zielinska *et al.*⁶⁸ presented intercomparison results between canister and sorbent samplings that indicated significant sampling losses in the compound ranges C₁₁ and higher when canister sampling was applied. Apel *et al.*⁷² used electropolished SS canisters as the basis for their Non-Methane Hydrocarbon Intercomparison Experiment (NOMHICE). Individual canisters containing an ambient air sample were prepared and analyzed and then sent to participants for analysis and then reanalyzed upon return to the reference laboratory at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado U.S.A. Compounds were found to be stable through C₈ over a period of months but >C₈ species tended to show some losses. Since that time, there have been advances in electropolishing technology (Don Blake, personal communication) and in deactivating the surface of the canisters with proprietary ceramic coatings to reduce the potential for chemical adsorption. Bags (mostly Tedlar or Teflon) have also been used for whole air sampling but Wang *et al.*⁷³ reported the possibility of significant sampling losses within 24 hours which must be considered when using this technique.

3.2 Sensing techniques after 1990

As important roles of BVOCs in regional photochemical pollution were elucidated in the late 1980s, several intensive measurement campaigns to understand the roles of BVOCs in regional air-quality were conducted in the 1990s (*e.g.* Southern Oxidants Study (SOS)). Although GC-FID and GC-FID-MS techniques were used as the main tools to identify and quantify

BVOCs in the atmosphere, growing interest in quantifying oxygenated compounds required new analytical techniques. GC-based techniques for oxygenated compounds are challenging due to their low volatility and surface reactivity. In addition, importance of constraining semi-volatile BVOCs such as sesquiterpenoids ($C_{15}H_{24}$) grew as they have significant implications for secondary organic aerosol formation.⁷⁴ To quantify those compounds, sensing techniques should meet several conditions such as (1) minimal contact of samples with the sampling and analysis interface to minimize wall loss, (2) real time measurement to avoid any chemical transformation, and (3) fast response for applications such as eddy-covariance flux observations and airborne observations.

3.2.1 Advanced GC techniques. Quantification of oxygenated compounds using a GC technique was well described by Goldan *et al.*⁷⁵ The main technical details that they adapted were:

A Teflon sampling inlet to prevent the loss of hydrophilic and reactive compounds.

In-line removal of ozone to prevent sample loss during the cryo-trap process, especially, alkene compounds.

An in-line water trap to prevent the loss of water soluble compounds on the column (polar compounds especially oxygenated compounds).

A water trap to remove potential interferences was installed as 1/4" o.d. Teflon tubing (50 cm), and maintained at $-50\text{ }^{\circ}\text{C}$ with dry ice as shown in Fig. 2. Goldan *et al.*⁷⁵ reported the possible sample loss for more polar compounds such as light alcohols could be up to 15% due to the water trap. Other water removal techniques such as using a Nafion dryer have also been used but those techniques potentially cause the significant chemical structure rearrangement of analytes.⁷⁶ Goldan *et al.*⁷⁵ also investigated the possible sample loss for BVOCs by ozonolysis reactions. The test results indicated that reactive BVOCs such as isoprene (~ 500 pptv) and alpha-pinene (~ 500 pptv) can be completely scrubbed away by ozonolysis with one liter of ambient air that contains 100 ppbv of ozone. To prevent sample

loss from ozone, Goldan *et al.*⁷⁵ used a Na_2SO_3 filter to remove ozone. Detailed description of various alternative ozone scrubbing methods can also be found in Helmig.⁷⁷

Singh *et al.*^{78,79} developed an aircraft-based gas chromatographic technique to measure acetone, ethanol, methanol, methyl ethyl ketone, acetonitrile, hydrogen cyanide, acetaldehyde and propanal. These species were measured on a column coupled with a photoionization detector (PID) and a reduction gas detector (RGD) placed in series. Typically, a 200 mL aliquot of air was cryogenically trapped at $-140\text{ }^{\circ}\text{C}$ prior to analysis. Moisture was greatly reduced by passing air through a water trap held at $-40\text{ }^{\circ}\text{C}$ during sampling and $-50\text{ }^{\circ}\text{C}$ between samples. Laboratory tests were performed to ensure the integrity of oxygenates during this drying process. The calibration standards were added to the ambient air stream in the main manifold and were analyzed in a manner that was identical to normal ambient sampling. This procedure was designed to compensate for any line losses. An on-board dilution system allowed varied concentrations to be prepared. The limit of detection of reactive nitrogen species was estimated to be 1 ppt, while that of other oxygenates was 5–20 ppt. There was an indication of artifact OVOC formation under high ozone concentrations in the stratosphere.

Apel *et al.*⁷² developed a fast GC-MS technique to measure oxygenated organic compounds for deployments on aircraft platforms. The system used a cryogenic water trap, an enrichment trap and a cryofocusing trap to effectively concentrate the analytes. The key for fast analysis is to synchronize the sample preparation time (cryotrapping, water removal, cryofocusing) with the analysis time, which includes GC run-time and cool down time. A custom-built cryogenic system and low thermal mass GC were developed to accomplish the instrument objectives. For the GC cycle, the authors adopted a temperature program starting at $30\text{ }^{\circ}\text{C}$ for 10 seconds and ramping up to $120\text{ }^{\circ}\text{C}$ at the rate of $100\text{ }^{\circ}\text{C min}^{-1}$ followed by a fast cool down procedure. Possible interferences for light oxygenated hydrocarbon compounds were thoroughly investigated. The investigators set up a glass manifold system and generated a number of light oxygenated compounds using a dynamic dilution system between a compressed standard mixture and zero air. In the length of ~ 2 m manifolds, Apel *et al.* (2003) added a number of possible chemical interferences such as ozone, NO_x , SO_2 and water vapor. The series of tests indicated that the Teflon diaphragm in some pumps can be a source for ethanol from degassing. This problem was easily addressed by replacing the pump with a metal bellows pump. In addition, this study reported significant interferences from ozone for acetaldehyde, propanal, acetone and butanal quantifications. On the other hand, alcohols and methyl ethyl ketone were not interfered by ozone. The source of the interferences appeared to be the rotor material in the VICI valves and they found that the Teflon (PTFE) composite material was most inert. The degree of the interferences was a strong function of ozone concentrations so concurrent ozone measurement data were used to correct the ambient OVOC observational dataset. Second and third generation instruments were subsequently developed by Apel *et al.*⁸⁰ resulting in a technique that is able to provide full GC-MS analyses of over 45 trace species every 2 minutes at near or

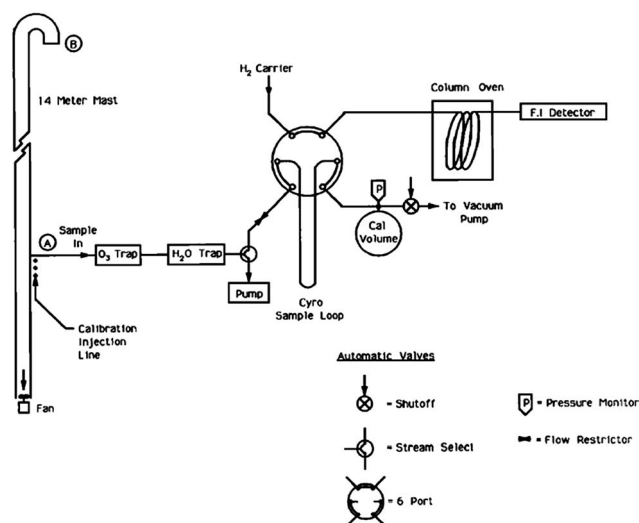


Fig. 2 A schematic diagram of a field deployable GC system (Goldan *et al.*⁷⁵). Copyright 1995 American Geophysical Union.

sub-pptv levels. Measurements include C₂ to C₉ carbonyl compounds, alcohols, and additional 25 or more compounds such as NMHCs, nitriles and halogenated compounds.⁸⁰ The system has been deployed in a series of aircraft field campaigns to characterize distributions of VOC species in the troposphere and chemical transformation of VOCs on regional and global scales.^{72,80} Recently, the system has been deployed at a ground-based site measuring primarily biogenic species including terpenoids that can vary considerably over short time periods.⁸¹

A critical aspect for quantifying reactive and semi-volatile organic compounds is the preparation of accurate reference calibration gases. In general, for oxygenated compounds, compressed gas mixtures have been used for calibration standards. Goldan *et al.*⁷⁵ tested 30 VOCs of different classes (alkanes, oxygenated hydrocarbons, aromatics, alkenes, monoterpenes, and cyclic hydrocarbons), which were gravimetrically prepared in an Aculife™ treated aluminum cylinder with a batch of 4–6 compounds. They were prepared at 10 ppmv levels and a dynamic dilution system allowed multi-point calibration in the range of 0.2 to 2 ppbv. Apel *et al.*⁸² described the preparation of OVOC standards in high-pressure cylinders in the ppmv range and their subsequent validation. Another popular way to prepare standards is using diffusion sources. To generate commercially unavailable compounds using pure liquids, Helmig *et al.*⁸³ developed a capillary diffusion calibration system. They built a constant temperature housing for multi-channel diffusion sources for a number of sesquiterpene and oxygenated-sesquiterpene compounds. Those compounds were kept in glass vials connected to glass capillaries. Since diffusion rates from the vials is a function of pressure and temperature, one can expect constant diffusion rates under the constant temperature and pressure environment. A nitrogen dilution flow swept the diffused flow to the outlet, branched to an online GC system monitoring the concentrations of the generated standard samples. The calibration system was used to evaluate analytical characteristics and potential interferences by ozone in sesquiterpene sampling of sorbent cartridges.⁸⁴ Results from the study clearly indicated that with proper ozone removal, sesquiterpenoid compounds can be quantified by conventional sorbent cartridge sampling techniques and a number of studies have clearly demonstrated sesquiterpenoid quantifications with GC techniques especially for branch enclosure samples.⁸⁵ Finally, Bouvier-Brown *et al.*⁸⁶ presented a field deployable GC system for ambient sesquiterpenoid measurement. The whole analytical system is kept in a temperature controlled container (~50 °C) to prevent the wall loss of semi-volatile compounds. The system was also equipped with an ozone removal filter and an on-line ozone monitor to prevent chemical loss. Bouvier-Brown *et al.*⁸⁶ used a micro-syringe injection method for the on-site sensitivity calibration of sesquiterpenoid compounds. A small amount of liquid (0.25–1 microliter) was injected upstream of the zero air to produce calibration standard samples in mixing ratios of 2–100 pptv.

The potential of GC × GC technology for the measurement of VOCs in ambient air was first demonstrated by Lewis *et al.*⁸⁷ showing that a large number of atmospheric species go undetected by conventional chromatographic methods; more than 500 individual components were separated in an urban air

sample. GC × GC instrumentation consists of an injector, primary column, modulator, secondary column, detector and data processor. In essence the GC × GC separation is a normal GC separation (primary) followed by a steady repetition of secondary GC separations. The selectivity of the primary and secondary stationary phases is chosen to be different and the timescale of the secondary separations (the modulation period) is small enough to only minimally diminish the primary separation resolution. Thus, a consistent portion of each peak emerging from the primary stationary phase is transferred to the secondary phase (column) so that the total area of the secondary phase is representative of the component concentration. The resulting 2-D chromatogram has peaks scattered about a plane rather than along a line. Good modulation, which is critical to the performance of GC × GC systems, is achieved through the precise control of flow. A great deal of effort has been devoted to developing precise, reliable and robust modulators which have come to fruition and are key components in recently introduced GC × GC products from a variety of vendors. Xu *et al.*⁸⁸ applied the technique to the measurement of C7–C14 organic compounds including monoterpenes. To aid in peak identification, the GC × GC system was coupled with a time-of-flight (ToF) mass spectrometer: approximately 650 peaks were identified. Recently, the technique has also been used to analyze the organic composition of aerosols.^{89,90} Bartenbach *et al.*⁹¹ recently deployed a GC × GC-FID technique in a rural agricultural and forested area in southern Germany and found good quantitative agreement with a conventional GC-MS technique in the measurement of both anthropogenic and biogenic VOCs. In addition, for light oxygenated-VOC (OVOC) quantifications in the ambient air, a high-performance liquid chromatography (HPLC) technique has also been utilized.⁹² This application requires stripping light OVOCs into a solvent stream that is analyzed by HPLC for its ion contents.⁹³

3.2.2 Chemical ionization mass spectrometry (CIMS). CIMS techniques have been popular for a wide range of pure and applied chemical research such as ion chemistry, biochemistry, medical and environmental applications. Chemical ionization is a representative low-energy ionization technique (soft ionization) with no or mild fragmentation. This analytical characteristic can provide clearer molecular information and precise quantification.⁹⁴ Although the technique was introduced in 1966,⁹⁵ the application in atmospheric chemistry started in the late 1970s.^{96,97} Since then, a number of ion chemistry and ion-neutral reaction chamber configurations have been developed to measure inorganic (such as nitric acid, OH/HO₂, and H₂SO₄) and organic (such as alkenes, aromatic compounds, peroxy radicals, acetonitrile, and more) compounds in the atmosphere with very low detection limits (tens of pptv or lower) and a very fast time response (~1 s or less).⁹⁸ Protons Transfer Reaction-Mass Spectrometry (PTR-MS) is one of the most widely used CIMS techniques for VOC quantifications. This technique utilizes proton transfer reaction by applying an excess amount of protonated water ions (reagent ion; H₃O⁺).⁹⁹ A very comprehensive review of the PTR-MS technique including principles of the technique and various applications can be found in Blake *et al.*¹⁰⁰ In addition, a critical

review on atmospheric chemistry applications is given by de Gouw and Warneke.⁸

From an ion thermochemistry perspective, the PTR method is applicable for any gas molecules with a higher proton affinity than water (691 kJ mol^{-1}). Most VOCs except alkanes have a higher proton affinity than water. This universal detecting ability gives PTR technology a great advantage over other selective CIMS techniques. From a reaction kinetics perspective, the sensitivity of VOCs depends on proton transfer reaction rates between volatile organic compounds and hydronium ions. The reaction rate constants of some of the stable compounds can be assessed by empirical methods using standard samples such as standard gas mixtures or diffusion sources. However, the growing interest in the quantification of very reactive or semi-volatile compounds, which are difficult to prepare as conventional standard samples, has resulted in the use of an alternative theoretical method to calculate reaction rate constants. The average dipole moment (ADO) theory is the most widely used method. This method estimates reaction rates by considering ion induced dipole interactions with both polar and non-polar molecules.¹⁰¹ Several studies have assessed the sensitivity of molecules towards PTR-MS and other CIMS techniques using the ADO theory.¹⁰²⁻¹⁰⁴ Notably, Zhao and Zhang¹⁰⁵ and Paulot *et al.*⁴² presented comprehensive intercomparison results between theoretical and empirical values of polarizability (α) and permanent dipole moment (μ_D) for the molecules, particularly relevant with tropospheric photochemistry.

Quadrupole-Secondary Electron Multiplier (SEM) has been used as a detection method for the protonated ions (PTR-QMS; Fig. 3a). The ion-throughputs of the detection unit decrease significantly towards higher mass ions. The nature and the mathematical description of the mass discrimination were well established in the 1970s^{106,107} and several studies have characterized the mass discrimination behavior of PTR-MS using empirical methods. Early publications^{108,109} monitored the ratios between H_3O^+ and $\text{VOC}\cdot\text{H}^+$ signals by standard sample additions to characterize the mass discrimination behavior. However, several recent studies^{103,110} demonstrated a method obtaining a transmission curve for the mass range (m/z) 70^+ to 205^+ using aromatic compound standard gas mixtures. Those compounds show no pronounced fragmentation and have uniform proton transfer reaction rate constants. Therefore, normalized signal

distributions over the mass range can be directly interpreted as sensitivity differences from mass discrimination.

In addition, since mass-spectrometry techniques using a quadrupole mass filter detect compounds only as a function of molecular mass, significant overlaps may occur if there are multiple compounds corresponding to one given nominal mass. In addition, potential fragmentation of high mass compounds (m/z >100 and higher) could hinder the identifications of molecules. For this reason, a number of studies have explored the possible interference from isobaric compounds or fragments for the conventionally monitored masses. One way to address this issue is by interfacing a GC upstream of the PTR-QMS system.¹¹¹⁻¹¹⁴ These GC-PTR-MS studies explored common masses that were routinely monitored in urban and rural areas for anthropogenic and biogenic VOCs and their oxidation products. The results indicate that users should take extra care in interpretation of the datasets due to interferences from isobaric compounds. Comprehensive information about the potential interferences is provided by de Gouw and Warneke.⁸ Also, several recent studies have reported fragmentation of high mass compounds and their possible interferences on other masses. For example, Lee *et al.*¹¹⁵ presented aerosol chamber observation results of monoterpene and sesquiterpene compounds by PTR-QMS. Fragmentation patterns of the terpene compounds and their oxidation products are described and they discussed possible implications for ambient measurements to identify unknown peaks in ambient air. Kim *et al.*¹¹⁶ presented laboratory experiment results about fragmentation patterns of seven different sesquiterpene species and their possible interferences on other masses as a function of analytical parameters such as relative humidity and energy level in the ion reactor (drift tube).

Recently, a new PTR application was introduced using a Time-of-Flight (ToF) detector.^{117,118} This adaptation could overcome most of the drawbacks of the quadrupole-SEM detector unit by taking advantage of greatly enhanced mass resolution ($m/\Delta m = 6000$) and no mass discrimination towards higher mass ions of the ToF detector (Fig. 3b). These significant advantages were demonstrated in eddy covariance (EC) flux measurements for BVOCs and their oxidation products (17 compounds) in a mass range of 33 to 205 (m/z) over a grass land.^{112,119} This emerging analytical technique, however, requires significant data mining efforts to deduce ambient

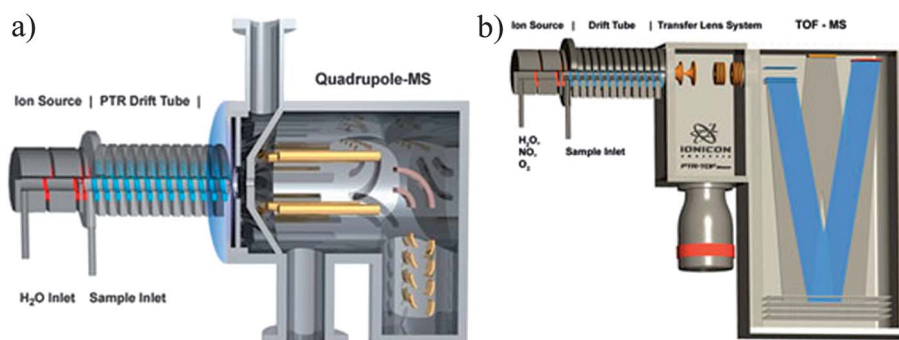
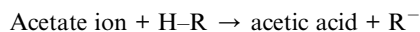


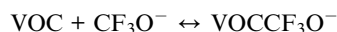
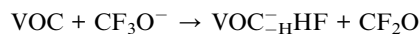
Fig. 3 Schematic diagrams of the PTR-MS system with (a) a quadrupole detector unit and (b) a Time-of-Flight detector unit (from the company website of IONICON Analytik GmbH). Copyright 2013 Ionicon Analytik GmbH.

concentrations from raw data. Cappellin *et al.*^{120,121} described physical and mathematical descriptions of each step for data mining from raw datasets.

Other ionization methods with different reagent ions have also been used for sensing BVOCs in the atmosphere. Slusher *et al.*¹²² demonstrated that the I^- ion is a suitable reagent ion to detect peroxyacyl nitrates (PANs) such as peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and peroxyethoxyacetyl nitrate (MPAN). Recently Veres *et al.*¹²³ developed negative-ion proton-transfer chemical ionization mass spectrometry (NI-PT-CIMS) to analyze organic acids in the atmosphere. The ion chemistry uses an acetate ion to take hydrogen away from organic acids as follows



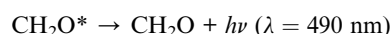
Thermochemically, any acids with a lower acidity than acetic acid can be quantified by the technique. Considering the high acidity of acetic acid, the ion chemistry can be applicable to many different organic acids and an application for inorganic acids was recently presented.¹²⁴ Paulot *et al.*⁴² presented a CIMS technique using CF_3O^- . CF_3O^- is a relatively non-selective reagent ion, previously used for peroxide analysis.^{125,126} The authors characterized two different ion-neutral reaction pathways for isoprene oxidation product detections:



Paulot *et al.*⁴² identified 38 oxidation products of isoprene that have not been routinely quantified by other techniques from laboratory isoprene oxidation experiments, which have significant implications to SOA formation in the background atmosphere⁴⁹ and oxidation capacity.

3.2.3 Optical techniques. Optical techniques such as chemiluminescence, fourier transform infrared spectroscopy (FT-IR), cavity ring-down laser absorption spectroscopy (CRLAS), tunable diode laser spectroscopy (TDLS), differential optical absorption spectrometry (DOAS) and laser induced fluorescence (LIF) have been used mostly to quantify relatively small oxygenated VOCs that are not easily detected by GC or mass spectrometry techniques.

Zimmerman and Hills¹²⁷ demonstrated a fast isoprene sensing technique using chemiluminescence reactions:



An instrument with a sampling frequency of ~ 2 Hz was developed to quantify the photons from relaxation of excited

formaldehyde (CH_2O^*) and glyoxal (HCOCHO^*).¹²⁷ This fast response system was utilized for canopy scale flux measurements (EC).¹²⁸

FT-IR is a multiplex instrument that is a single channel instrument with an ability to simultaneously scan over a wide wavelength range. This technique has advantages over IR spectroscopy such as higher throughput and wavelength accuracy (Skoog and Leary, 1992 (ref. 129)). The applications of the FT-IR technique in atmospheric chemistry are thoroughly reviewed by Tuazon *et al.*,^{130,131} Marshall *et al.*,¹³² and Hanst and Hanst.¹³³ Recent applications of the FT-IR technique are mostly in controlled environment such as reaction chambers or combustion facilities due to inferences of common atmospheric constituents (*e.g.* water vapor, CO_2 and CH_4). For example, Yokelson *et al.*^{134,135} demonstrated simultaneous measurements of CH_2O , CH_3OH , CH_3OOH , C_2H_4 , C_2H_2 , C_3H_6 , $\text{C}_6\text{H}_5\text{OH}$ by FT-IR in a combustion laboratory facility. A series of publications about chamber experiments to characterize oxidation product yields (*e.g.* by OH and O_3) and reaction rates of BVOCs can be found in Orlando *et al.*¹³⁶⁻¹³⁸ The references contain specific information about chamber preparations and quantifications of product yields and reaction rates. The compilations of the laboratory experiment results on BVOC oxidation reaction rates and products can be found in Atkinson *et al.*⁴⁸

TDLS uses a laser light source that can be tunable over a small wavenumber range with a very narrow line width. One of the representative TDLS applications for BVOC related research is the quantification of formaldehyde (CH_2O). Fried *et al.*¹³⁹ presented TDLS instrumentation for CH_2O measurement utilizing two wavenumber absorption in $2912.0918 \text{ cm}^{-1}$ and $2914.4598 \text{ cm}^{-1}$. The path length was achieved at ~ 100 m and interferences from atmospheric water vapors were carefully characterized. The method has been successfully deployed in both ground and aircraft measurements.¹⁴⁰⁻¹⁴²

Recently, CH_2O quantification by LIF was applied for the canopy scale flux observations by the EC technique.¹⁴³ The technique demonstrated an excellent lower detection limit (~ 300 pptv in 1 second average). A laser induced phosphorescence (LIP) instrument was developed by Huisman *et al.*¹⁴⁴ for atmospheric glyoxal observations. They used the laser induced phosphorescence (LIP) instrument to achieve a limit of detection of below 10 pptv (1 min average, $S/N = 3$). The method has been deployed in chamber and field studies to characterize aerosol formation¹⁴⁵ from BVOCs and explore photochemistry inside of forest canopies.¹⁴⁶

The DOAS technique adopts broadband light sources such as a high-pressure Xe, incandescent quartz-iodine lamp, a broadband laser, the sun, and the moon. Spectral radiation through the path length is monitored to calculate mixing ratios of atmospheric constituents using the Beer-Lambert law. The instrumentation and its application for atmospheric chemistry are thoroughly reviewed by Platt¹⁴⁷ and Plane and Smith.¹⁴⁸ From the 1990s, the technique has been used to report ambient concentrations of CH_2O . Recently, Volkamer *et al.*¹⁴⁹ developed a method to quantify ambient glyoxal (CHOCHO) using long path DOAS (LP-DOAS). Glyoxal is a primary oxidation product of many different VOCs and the direct measurement of glyoxal can

constrain photochemical models to assess regional and global photochemical O₃ and SOA formations from VOCs. Indeed, ambient glyoxal observational results in Mexico City clearly indicated that our current understanding of SOA formation in the urban area significantly underestimated the observed aerosol loading.¹⁵⁰ A global modeling study¹⁵¹ demonstrated that almost half of the glyoxal is coming from biogenic VOC oxidation processes on the global scale and urged more observations in various environments.

CRLAS quantifies spectral absorptions from specific analytes. It improves the sensitivity of a conventional infrared spectrometer by trapping a laser pulse in a highly reflective detection cavity resulting in an effective path length of many kilometers. CRLAS techniques^{152,153} have been used to quantify small BVOC molecules such as ethene, formaldehyde, and glyoxal at the levels typically observed in BVOC emission enclosure systems and at the high end of the range of ambient levels. This can be accomplished using CRLAS without any preconcentration. However, further improvements in sensitivity are needed to make this technique more widely applicable for BVOC applications. In addition, LIF and CRDS NO₂ (ref. 154 and 155) quantification techniques have been utilized to quantify peroxy radicals¹⁵⁶ and alkyl nitrates¹⁵⁷ in the ambient air by applying chemical conversions up-stream of the sample air.

Optical sensors deployed in space-based platforms are providing an important constraint for global distributions of some important BVOCs. Satellite derived formaldehyde column data have been used in a number of studies¹⁵⁸ to infer emissions of isoprene, the globally dominant BVOC. Formaldehyde is a high yield product of isoprene and variations in formaldehyde in many regions are dominated by isoprene oxidation. Satellite observations of glyoxal, an oxidation product of many VOCs, also have a considerable potential for constraining BVOC emissions and distributions.¹⁴⁹ Global methanol distributions have recently been derived from the Tropospheric Emission Spectrometer on the EOS Aura satellite.¹⁵⁹ These satellite based spectrometers are greatly improving the information available for constraining emissions and concentrations of certain BVOCs although it should be noted that considerable uncertainties are associated with these estimates and more *in situ* observations are needed to assess these data.

3.2.4 Undetected compounds. Finally, the possibility that conventional analytical techniques may not detect all non-methane organic compounds has long been speculated.^{39,160} Indeed, several experiments^{87,161,162} to quantify total non-methane hydrocarbons in the atmosphere have shown that as air masses are more photochemically oxidized, the ratio of total NMHCs and sum of speciated NMHCs could reach up to a factor of 2–3. The methodology used for those studies was a conversion of total NMHCs to CO₂ (ref. 161 and 162) or a 2D GC technique.⁸⁷ Total OH reactivity, the reciprocal of OH chemical lifetime (s⁻¹), provides quantitative information about the total amount of atmospheric constituents in the reactivity scale. Therefore, the comparison between measured OH reactivity and calculated OH reactivity from an observational dataset such as CO, CH₄, NO₂, and VOCs can provide a unique opportunity to assess our ability to measure all reactive atmospheric

constituents. Several ambient total OH reactivity measurement results have consistently indicated significant “missing OH reactivity”, which cannot be explained by observational datasets of known trace gases. The degree of discrepancies tends to be higher in BVOC dominant environments.¹⁶³ The cause of missing OH reactivity has been speculated: unknown/unmeasured BVOC emissions¹⁶⁴ or sources of unknown/unmeasured oxidation products of known BVOCs.¹⁶⁵ A similar approach can be used to quantify the total VOC reactivity with ozone and other oxidants and measurement systems are being developed to accomplish this.

4 Summary and outlook

We extensively reviewed analytical techniques that have been widely used to characterize emissions and ambient distributions of BVOCs and their oxidation products. For the past five decades, GC techniques have served as the main analytical methods for most BVOCs and their oxidation products. These applications have been expanded to oxygenated and semi-volatile organic compounds, which were not routinely measured by GC techniques but have tremendous implications for SOA formation and tropospheric photochemistry. In addition, some cryofocusing techniques have become available to expedite GC analysis times on the order of a few minutes. This technology makes GC techniques suitable for fast time response applications such as airborne measurements. CIMS techniques have provided very selective and fast response measurements for BVOCs and their oxygenated products. Since mass spectrometry with a soft ionization interface can provide molecular mass information of analytes, it has been effectively used for identification of unknown compounds. Also, optical techniques have been and are being developed for light oxygenated compounds, such as glyoxal and methyl glyoxal, that cannot be measured by conventional techniques.

Although the development of new sensing techniques provided new insights on BVOC emission and oxidation processes in the atmosphere, relatively few intercomparison efforts have been reported among different analytical techniques and for identical techniques with different configurations. Apel *et al.*¹⁶⁶ reported extensive instrument intercomparison results among 15 groups with some overlaps of analytical techniques (*e.g.* GC, HPLC, DOAS and PTR-MS). The campaign was mostly focused on oxygenated VOCs. The results indicate that the reported concentrations from each group of the tested compounds, especially low volatility compounds, vary significantly and the authors concluded reliable measurements require “a high-quality instrument, and experience with the instrument including strict attention to analytical procedures such as zeroing the instrument and calibration”. This statement should be noted by all investigators. As Kim *et al.*¹¹⁶ discussed, significant uncertainty associated with the measurement of known compounds such as isoprene can cause issues in constraining total reactive BVOCs in the atmosphere because a few dominant BVOC species contribute most of the reactivity towards oxidants in many instances. Therefore, we as a community should concentrate on both new technique

development and promote assessment, intercomparison, and characterization of the existing sensing techniques (e.g. Kaser *et al.*⁸¹). As the past decades of history indicates, new perspectives from well characterized and reliable measurements can expand our understanding of the importance of BVOCs and their oxidation processes in regional and global air quality and climate.

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