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Biogenic volatile organic compound emissions and their impact on urban air quality: Lessons learned, current understanding and future challenges

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Biogenic volatile organic compound emissions and their impact on urban air quality: Lessons learned, current understanding and future challenges

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ABSTRACT

Biogenic volatile organic compounds (BVOCs) can have a significant impact on atmospheric composition, impacting both air quality and climate. This review provides a comprehensive examination of BVOC emissions including their measurement techniques, modelling approaches, current estimates and uncertainties, as well as BVOC emission impacts on ozone and particles and the implications for air pollution management. The historical context is described from the first emission calculations to the current numerical computer models. The review also addresses the challenges including limited observations and the complexity of the factors controlling BVOC emissions. The methodologies for BVOC flux measurements and modelling are described and their effectiveness is discussed. Additionally, strategies for controlling BVOC impacts on air quality are considered including both direct emission reduction and indirect approaches through anthropogenic pollution control. The limitations and knowledge gaps in current BVOC research are identified, along with future challenges and opportunities to improve the predictive capability of BVOC emission models.

KEYWORDS

Biogenic Volatile Organic Compounds (BVOCs), emissions, concentrations, air quality, measurements, modelling, MEGAN

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1. INTRODUCTION

More than a gigaton of volatile organic compounds (VOCs) are emitted into the atmosphere each year. Methane and isoprene each comprise about a third of the total and hundreds of other VOC make up the remainder (Guenther et al. 2012). Although the non-methane VOC (NMVOC) are about two thirds of the total VOC emission, they are less than 0.1% of the total VOC in the atmosphere. This discrepancy is due to their relatively short atmospheric lifetimes, ranging from minutes to days, while methane remains in the atmosphere for about a decade. While some NMVOCs can directly impact radiative forcing or human health, their atmospheric concentrations are too low to have a significant impact, except in highly polluted areas. Instead, NMVOC's primarily influence the environment through the production of secondary pollutants such as ozone and particles and by removing oxidants like OH, significantly affecting climate and air quality.

Over 80% of annual global NMVOC emissions have biogenic VOC (BVOC) sources, predominately foliar (vegetation leaves) emissions (Guenther et al. 2012). Historically, urban and industrial landscapes were dominated by anthropogenic volatile organic compound (AVOC) emissions from fossil fuels and industrial processes with AVOC to BVOC ratios of 20 or more (e.g., Chameides et al. 1988). Developments in the regulations controlling air pollutant emissions have substantially reduced AVOC emissions. At the same time, urban greening and global warming have been increasing vegetation emissions, thus BVOCs are becoming the dominant reactive VOC emission source, even in urban areas (Ren et al. 2017, Gu et al. 2021, Pfannerstill et al. 2024).

Seminal studies conducted over 50 years ago suggested that BVOC could significantly impact climate and air quality (e.g., Went 1960, Rasmussen and Went 1965, Rasmussen 1972). The conclusions of these studies were initially rejected due to the conflicting evidence of BVOC concentrations that were much lower than AVOCs (Dimitriades 1981, Altshuller 1983). Understanding BVOC magnitude and role was at that time essential for managing ozone since it could determine whether agencies should prescribe anthropogenic VOC emissions reduction as an optimal strategy for reducing ozone. By the early 1990s, scientists recognized that the existing pollution control strategies were ineffective for reducing urban and regional ozone pollution leading to a call for "rethinking the ozone problem in urban and regional air pollution" (National Research Council, 1991). The National Research Council panel concluded that *"the combination of biogenic VOCs with anthropogenic NOx can have a significant effect on photochemical ozone formation in urban and rural regions of the United States"* and recommended that "*emissions of biogenic VOCs must be more adequately assessed to provide a baseline from which the effectiveness of ozone control strategies can be estimated before such strategies are applied for a specific urban core or larger regions*".

BVOC emission measurement studies have primarily focused on terrestrial vegetation foliage and most BVOC emission models do not consider any other sources (Rassmussen 1972, Duan et al. 2021). While uncertainties remain regarding the contributions of other plant organs, such as flowers and roots, and other organisms, such as microbes, these other sources may be important for at least some locations and conditions and should be assessed. BVOC studies are also complicated by the thousands of BVOC chemical species (Cagliero et al. 2021) although a relatively small number of compounds dominate the total global emission predicted by models (e.g., Guenther et al 2012, Sindelarova et al. 2022). However, these BVOC have varying impacts on atmospheric composition, so that a compound with relatively small emissions can significantly impact atmospheric chemistry due

to its higher ozone formation potential (OFP) or secondary organic aerosol production (SOAP). In addition, a compound that may be a minor component of global annual emissions could be important in a specific location and time.

Prior to the 1990s, VOC emissions from vegetation were typically referred to as "natural emissions", a problematic term since plant volatile emissions from a cropland or urban forest are not "natural". The term "biogenic" VOC is used in this manuscript which excludes natural abiotic emissions of VOC such as geogenic which makes only a small contribution to global total VOC emissions. Describing the impact of BVOC on secondary pollutants is also challenging since the impact is highly dependent on the chemical regime, especially the presence of NOx, SO_x and other pollutants. In a pristine environment, BVOCs produce little secondary pollution but the yields are much higher in a polluted environment. One approach that could be used for secondary organic aerosol (SOA), a major pollution issue, is to consider any carbon in the aerosol coming from BVOC as biogenic SOA. However, Carlton et al. (2008) recognized that labeling biogenic SOA as natural could hinder effective air quality management if it led to considering this portion of atmospheric SOA to be uncontrollable. They introduced the term "controllable" biogenic secondary organic aerosol (SOA) to refer to the fraction of SOA from BVOCs that could be reduced by controlling anthropogenic emissions of NOx, SOx and particles in urban and industrial landscapes. Building on this concept, "controllable BVOC" is used here to refer to BVOC emissions from landscapes where the amount, type and environmental conditions of BVOC emission sources are actively managed, such as in urban and agricultural areas.

This article summarizes the current state of BVOC concentration and flux measurements (**section 2**) and modeling (**section 3**) capabilities, describes existing BVOC emission model estimates (**section 4**), and summarizes regional efforts to study BVOC emissions in **section 5**. The current understanding of BVOC impacts on air pollution and the potential for controlling BVOC emissions in managed landscapes is given (**section 6**). Uncertainties, knowledge gaps and existing limitations are assessed in **section 7** and future challenges, research priorities and air quality management implications are presented in **section 8**.

2. BVOC COMPOUNDS

Living organisms produce an extensive variety of over 200,000 different chemical compounds (Christianson 2017). These natural products include essential compounds like peptides, proteins and carbohydrates, that play vital roles in an organism's function, and secondary compounds like alkaloids, flavonoids, benzenoids, and terpenoids, found in some but not all organisms. Some of these compounds are volatile, meaning they readily evaporate into the air, creating the scents of flowers, spices, citrus fruits and other familiar fragrances. The volatility of these compounds varies significantly, with some primarily existing as gases under ambient conditions while others are primarily liquids or solids but still emit a small fraction into the atmosphere.

The terpenoids in vegetation are an especially large and diverse class of natural products, with about 60,000 different chemical species (Köksal et al. 2011). Terpenes serve various functions, including acting as hormones, biotic defense (e.g., toxins, repellants, attract predators), protection from abiotic stress (e.g., antioxidants, membrane stabilizers, stress defense inducers), and attracting mutualistic organisms (e.g., pollinators, seed dispersers). This vast diversity occurs not only between species but also within species (Gershenson and Dudareva 2007). This diversity complicates the task of quantifying and representing BVOC emissions in chemistry and transport models. The need to accurately represent this diversity must be balanced with requirements to minimize computational costs and complexity.

BVOC emission inventories initially included just two compounds, isoprene and a-pinene, and a third category comprised of all other BVOCs (e.g., Rasmussen 1972, Zimmerman et al. 1979). Later inventories expanded to include total monoterpenes, other reactive VOCs and other VOCs (Winer et al. 1982, Guenther et al. 1995, and Pierce et al. 1998). MEGAN2.1 (Guenther et al. 2012) introduced greater chemical diversity by including ~150 BVOC chemical species. This was accomplished by lumping the 150 BVOC species into just 18 BVOC categories to minimize complexity and computational cost. The scheme for mapping the 18 categories into 150 chemical species provided flexibility for mapping BVOC emissions into the schemes of the various chemical mechanisms used in regional air quality models and global chemistry and transport models. More detailed chemical speciation in BVOC emissions schemes may not significantly improve air quality simulations if the atmospheric chemistry schemes used for air pollution studies do not include detailed speciation. Many of the atmospheric chemistry schemes commonly used for air quality modeling include only isoprene and a single lumped category for all monoterpenes but some comprehensive schemes now include a suite of terpenoid categories similar to those used for MEGAN. However, these schemes typically have different chemistry only for the initial terpenoid surrogate while the first- and second- generation products are shared to reduce computational cost.

The MEGAN2.1 results identified three BVOC with an annual global emission rate exceeding 50 Tg: isoprene, methanol, and a-pinene and another four compounds with rates between 20 and 50 Tg yr^{-1}: acetone, ethanol and acetaldehyde, and ethene (Guenther et al. 2012). Together these 7 compounds contribute about 75% of the total annual flux while the remaining hundreds of BVOC make up the remainder. In addition to a-pinene, there are more than 1000 other monoterpenes that have been observed in plants. They can be grouped into four main categories based on their structure: acyclic trienes (e.g., ocimene and myrcene), monocyclic (e.g. limonene and terpinolene), bicyclic (e.g., b-pinene and carene) and oxygenated or aromatic (e.g., linalool and p-cymene). Another terpenoid group, the

sesquiterpenes, can be grouped into two categories: highly reactive (e.g., b-caryophyllene) and less reactive (e.g., longifolene). The remaining BVOC together comprise only about 5% of the total flux. They include organic acids (e.g., acetic acid) which have been reported as major primary or secondary products (Stavrakou et al. 2012), leaf surface oxidation products (e.g., formaldehyde and oxopentanal) have been described by Jud et al. 2016) and light hydrocarbons (e.g., ethane, ethene, propane, propene, and hexane) described by Rhew et al. (2017). Vegetation stress-induced BVOC compounds can also be considered as a separate category because of their common sensitivity to stress conditions which may not be a large global annual flux but could still be a major source at a specific time and location.

Since total BVOC emission is dominated by less than 20 compounds, most BVOC emission models include fewer compounds than MEGAN. However, some studies suggest that minor compounds are important in some locations under some conditions and there may be compounds that have not yet been identified because they are difficult to measure. One example is diterpenes that may be a significant source of biogenic SOA but have only recently been observed as a canopy scale flux into the atmosphere (Vettikkat et al. 2022). Other examples include the stress induced compounds that can dominate BVOC emissions, especially in urban areas experiencing heat waves and droughts which correspond with periods of high ozone and particle concentrations (Ghirardo et al. 2016).

3. BVOC MEASUREMENTS

3.1. ANALYTICAL DETECTORS

Analytical systems that can identify and quantify BVOC are essential tools for measuring the magnitude and variability of BVOC emission rates, which form the basis for algorithms and parameterizations necessary for numerical simulations of biogenic emissions and their atmospheric impact. These measurements are challenging due to the vast number of BVOC chemical species, some of which require substantially different analytical approaches. While significant advancements have enabled the measurement of both known and unknown compounds (Yang et al. 2016), no single sample collection, preparation and analysis approach can measure all BVOCs. Comprehensive BVOC analysis requires a suite of instruments that often involves different stakeholder collaborations and advanced instrumentation that is expensive and requires considerable expertise.

Otto Wallach (1887) demonstrated that essential oils, which at that time were thought to be distinct chemical substances, are complex mixtures of BVOC and was awarded the 1910 Nobel Prize for Chemistry for this research. Measuring BVOC in ambient air posed a greater challenge due to the much lower concentrations. Rasmussen and Went (1965) reported the first ambient BVOC concentration measurement using gas chromatography with a hydrogen flame ionization detector (GC-FID) with a detection limit of about 0.1 ppb. GC-FID was the primary tool for BVOC measurements prior to the 1990s and had limitations such as potential interferences leading to overestimations of BVOC emissions (Dimitriades, 1981). This early research underscored the need for robust analytical tools for BVOC emission studies.

BVOC measurement advances from 1990 to 2010, reviewed by Kim et al. (2013), include improved sensitivity and specificity from widespread use of mass spectrometry (MS) methods, techniques for measuring oxygenated BVOC including ketones (Konig et al. 1995), methanol (Fall 1996), and organic acids (Kesselmeier et al. 1998). The development of approaches for low-cost, fast response, real-time (no preconcentration) sensors enabled fast surveys to identify high emitters (e.g., Klinger et al. 1998). Fast response BVOC analyzers with higher sensitivity and specificity enabled biochemical and physiological process studies and landscape-scale direct eddy flux measurements, first for isoprene using an optical technique with a fast isoprene sensor (FIS) developed by Hills et al. (1992) and then for other BVOC using Chemical Ionization Mass Spectrometers (CIMS) as described by Hansel et al. (1995), Karl et al. (2001), and Graus et al. (2010). Although a range of optical sensors have been used for BVOC research including fourier transform infrared spectroscopy, cavity ring-down laser absorption spectroscopy, tunable diode laser spectroscopy, differential optical absorption spectrometry and laser induced florescence (Kim et al. 2013), there is still significant potential for further advancing these tools as BVOC sensors. The major impact of optical approaches for BVOC measurements has been their use for satellite remote sensing which started with quantifying atmospheric distributions of formaldehyde concentrations and using this to estimate isoprene emissions (Palmer et al. 2003).

Major analytical advances since 2010 include techniques for measuring highly oxygenated VOC species (Tiusanen et al. 2023) and low volatility compounds such as diterpenes (Vettikkat et al. 2023). There have also been significant advances in analytical approaches for detecting total BVOC, including compounds that are not detected by other approaches, which enables the identification and quantification of unknown “missing” compounds. The approaches include measurements of total

OH reactivity (Yang et al. 2016), total ozone reactivity (Helmig et al. 2022) and potential aerosol mass (Zhang et al. 2024) and are especially useful because they specifically target the precursors of ozone and particles. These techniques have extended BVOC emission studies to new compounds and facilitated investigations of BVOC atmospheric oxidation and their role in air pollution (e.g., Breitenlechner et al. 2017).

3.2. SAMPLING PLATFORMS

To effectively study the processes controlling biogenic emissions, a variety of measurement platforms are required to probe the multitude of BVOC emission sources and their variability across the different spatial and temporal scales illustrated in **Figure 1**. The short lifetime of reactive VOC requires sampling spatial heterogeneity in heterogeneous terrestrial landscapes at scales of hundreds of meters to tens of kilometers (Ye et al. 2021).

Above-canopy surface-layer tower platforms equipped with instruments that continuously measure BVOC can provide long-term observations without disturbing an ecosystem but are limited in spatial coverage of ~1 km for fluxes and tens of km for concentrations. Tall towers (> 300 m) have a larger footprint and have been used to study BVOC in remote (e.g., Andrea et al. 2015) and urban (e.g., Park et al. 2010) locations. Tethered balloon platforms have been used for sampling in the mixed layer, which limits the influence of a few dominant sources near the sampling point (e.g., Greenberg et al. 2010), but are now being replaced with unmanned aerial vehicles (UAV) which can be used for both vertical and horizontal sampling gradients (e.g., McKinney et al. 2018).

Mobile platforms, including motor vehicles, river boats, ocean ships and aircraft, are used to characterize spatial heterogeneity and link observations to the scales used by chemistry and transport models (e.g., Ferracci et al. 2024, Zhao et al. 2021, Pfannerstill et al. 2023a, Yu et al. 2023, Wang et al. 2020). Satellite measurement coverage ranges from regional to global including areas where there are no other BVOC measurements. BVOC investigated using satellite data include formaldehyde (Mueller et al. 2024), methanol (Stavrakou et al. 2011), formic acid (Stavrakou et al. 2012), isoprene (Fu et al. 2019), acetone (Franco et al. 2019) and acetic acid (Franco et al. 2020). Satellite data is expected to be even more widely used with future improvements in spatial and temporal resolution, precision and accuracy.

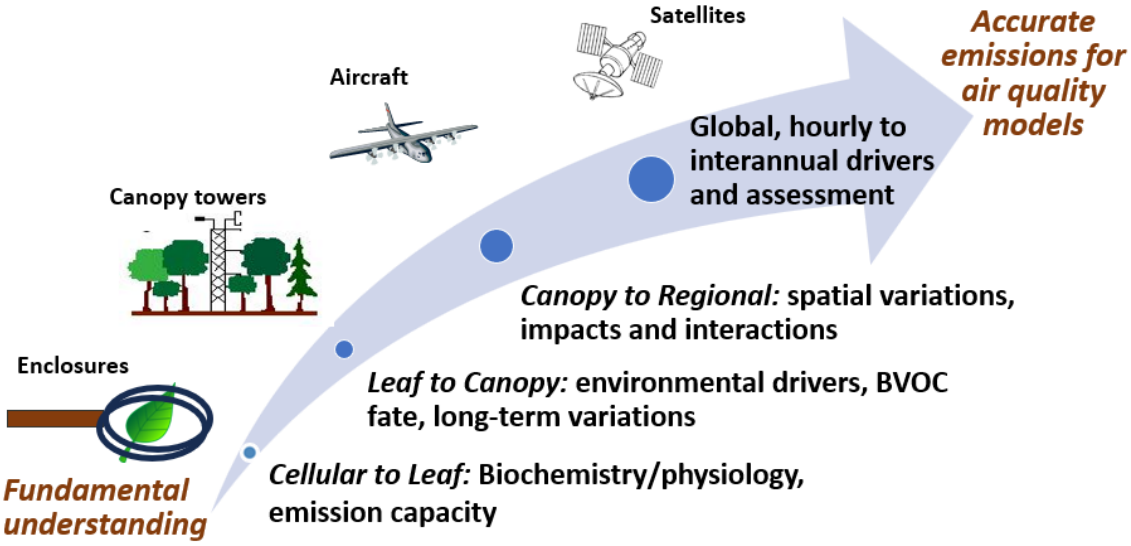


Figure 1 Schematic of BVOC processes operating across different scales and the sampling platforms suitable for investigating them

3.3. FLUX MEASUREMENT TECHNIQUES

Investigating all of the processes controlling BVOC fluxes requires techniques capable of spanning a wide range of spatial and temporal scales (**Figure 1**). The approaches shown in **Figure 1** are complementary with each technique providing an important contribution to the overall task of accurately estimating BVOC emissions. Early attempts to measure BVOC emissions began in the 1920s-30s in the former Soviet Union and included estimates based on both enclosures and ambient concentrations (Isidorov 1993). The three main approaches that are used to characterize fluxes are vegetation enclosures (e.g., Niinemets et al. 2012), micrometeorological techniques (e.g., Rinne et al. 2021), and inverse modeling (e.g., Kittitananuvong et al. 2024).

Enclosure measurement techniques use a mass balance approach to calculate emissions based either on the time rate of BVOC change within a static enclosure or the difference in BVOCs transported into and out of the enclosure in a dynamic enclosure. Both approaches need to account for BVOC wall losses and outgassing from enclosure materials using an enclosure calibration system (e.g., Pompe et al. 2000). The dynamic approach is preferred because it minimizes disturbances and provides the ability to control and manipulate environmental conditions, but the static approach can be useful for screening studies with high sensitivity. Enclosure measurement techniques are ideal for investigating species-specific emission factors and emission activity responses. Disadvantages are the physical disturbances that can occur when enclosing a plant and the potential for high temperature and humidity and low CO_2 if the enclosure system does not have environmental control. Niinemets et al. (2011) recommend suitable measurement systems, data processing, quality assurance and data measurement protocols and emphasize the importance of characterizing the quality of measurement data when synthesizing values reported in the literature.

Tower-based micrometeorological flux measurements average over hundreds of meters to kilometers, depending on the height of the tower and environmental conditions, while aircraft eddy flux systems can extend these measurements over

hundreds of kilometers. The most accurate and direct micrometeorological approach is the eddy covariance (EC) technique which is a direct flux measurement based on the high frequency fluctuations of vertical wind velocity and BVOC concentration. The covariance of the deviations (the difference between the instantaneous value and the mean for the time period) of these two variables represents the net vertical flux at a given location. The fast (<0.1 s) sampling frequency required for EC flux measurements can be accomplished for vertical wind speed using commercial sonic anemometers that are available with relatively low cost, power and maintenance requirements. The first BVOC EC flux measurements were made with a chemiluminescence analyzer for isoprene (Guenther and Hills 1998) and with Proton Transfer Reaction with Quadrupole Mass Spectrometer (PTR-QMS) for isoprene, total monoterpenes and several light oxygenated BVOC (Karl et al. 2001). Recent advances such as PTR with Time-Of-Flight Mass Spectrometer (PTR-TOFMS) have enabled systems that quantify the flux of hundreds of BVOC masses (e.g., Park et al. 2013) with recent advances adding fluxes of more compounds such as diterpenes (e.g. Vettikkat et al. 2023).

The disadvantages of the fast-response analytical instruments required for BVOC EC measurements are that they are relatively expensive, have high power requirements and are bulky and difficult to maintain, which limits the sites where they can be deployed, and require specialized expertise. Alternative eddy flux micrometeorological techniques include gradient flux, relaxed eddy accumulation, and disjunct eddy accumulation. These methods have higher uncertainties than the EC technique, particularly when their key assumptions are not met, but their lower cost, power, maintenance and expertise requirements allow them to be more widely applied. The samples can be transported to a laboratory for analysis, instead of being analyzed in the field, which further simplifies their use, but the disadvantage of this offline approach is that those measurements typically result in fewer data and are often operated only for a short period of time. The EC approach is ideal for long-term, continuous BVOC measurements while alternative eddy flux measurements are optimal for low-cost surveys of many different landscapes.

The gradient flux micrometeorological approach was used to measure BVOC fluxes in the 1980s and 1990s Arnts et al. 1982). It requires only concentration measurements at two height and an approach for estimating eddy diffusivity. This approach was widely used in the past but has since been replaced by other techniques, described below, with fewer assumptions and lower uncertainties because they are a more direct measurement (Rinne et al. 2021). For example, the true eddy accumulation technique is based on eddy covariance concept but does not require fast response sensors (Emad, A., and Siebicke, 2023). Instead, air samples are collected into an upward and downward reservoir, at a sampling rate proportional to the vertical wind speed fluctuation, over a sampling period (e.g., 30 minutes). However, sampling proportional to the fast (10 Hz) fluctuations in vertical wind speed is challenging, leading investigators to use disjunct eddy accumulation which does not require continuous sampling (Turnipseed et al. 2009) but have uncertainties that are about a factor of 2 higher than direct eddy covariance (Rinne4 et al. 2021). Another simplification, referred to as relaxed eddy accumulation, involves sampling at a constant flow rate and requires an empirical parameter, beta. This parameter can be derived from measurements of the standard deviation of vertical wind speed and sensible heat flux measured using a sonic anemometer (Sarkar et al. 2020).

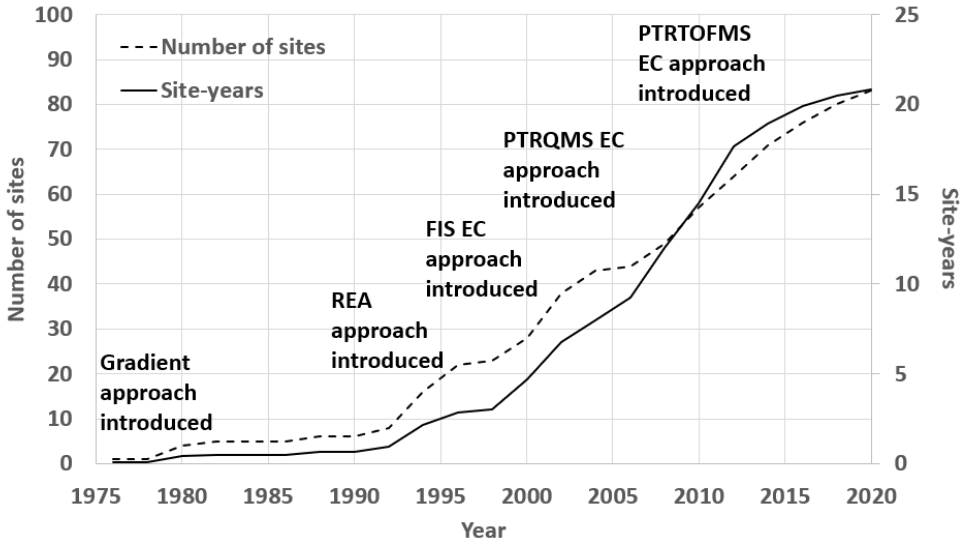


Figure 2 Global BVOC flux tower cumulative number of sites (dashed line) and site-years of measurements (solid line) from 1975 to 2020

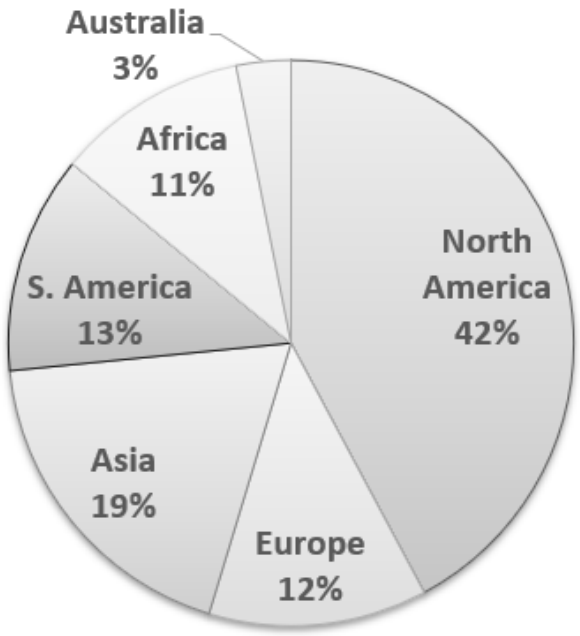


Figure 3 Global BVOC flux tower sites distribution across six continents for studies conducted from 1975 to 2020

The progressive adoption of new micrometeorological BVOC flux measurement techniques from 1975 to 2020 is illustrated in **Figure 2** alongside the increase in the number of investigated sites globally and the duration of these measurements. Over this 45-year period, measurements were made at about 80 flux tower sites, contributing to a total of about 20 site-years. **Figure 3** shows that ~40% of the measurements were in North America, mostly in the U.S. during 1975 to 2010. The

measurements conducted from 2000 to 2020 have been primarily in Africa, Europe and South America (~12% each each) and Asia (~20%). The BVOC flux measurements at most of these sites were conducted for less than 6 weeks. The longest-term measurements at any BVOC flux sites include five years of summertime isoprene flux measurements at a mixed temperate forest in the University of Michigan Biological Station in the U.S. (Pressley et al. 2006) and four years of methanol flux measurements covering most of each year in a temperate grassland in Austria. A few other sites have measurements for multiple years, but most cover just a portion of the growing season in each year. In contrast, carbon, water and energy (CWE) flux measurements had surpassed 500 sites and accumulated 2000 site-years by 2015 (Pastorello et al. 2020). The extensive CWE flux data have demonstrated that developing and deploying robust, low-cost instruments for long-term land-atmosphere flux measurements can lead to significant scientific advancements (Baldocchi et al. 2001, Pastorello et al. 2020). Rinne et al. (2016) advocate for extending these measurements to include long-term BVOC flux measurements at representative sites for all major global ecosystems. However, they note current systems are not optimal. For widespread use, BVOC flux measurement systems need to be lower in cost, power and maintenance requirements. An ideal BVOC flux measurement system would resemble the long-term CWE flux measurement systems that have successfully operated in global networks (Pastorello et al. 2020).

The inverse modeling approach can be applied with a simple mass balance technique that requires only observed ambient BVOC concentrations, estimates of daytime atmospheric mixed layer height and BVOC chemical lifetime. This method can be implemented using aircraft, drones, tethered balloons or tall tower sampling platforms to access the atmospheric mixed layer, which is typically located between about 100 and 1000 meters above ground level (e.g., Greenberg et al. 2014). Vertical gradients of BVOC concentrations within the mixed layer can constrain these estimates and account for entrainment of BVOC from above the mixed layer (Guenther et al. 1996). More accurate estimates can be derived using chemistry and transport models that comprehensively represent all relevant emission, transport and dispersion, and chemical processes. However, significant uncertainties remain in model simulations of these processes, especially in the surface layer where large horizontal and vertical gradients exist (McKinney et al. 2019). These gradients are often not captured by the coarse spatial resolution of most current chemistry and transport models.

4. BVOC EMISSION MODELING

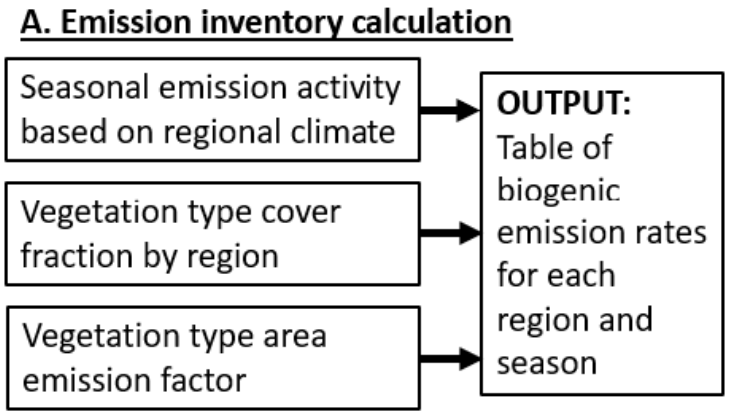
4.1. EMISSION MODEL APPROACHES

Emission models typically have three main components: source distributions, emission capacities, and emission activities. For BVOC emissions, the three components can be represented as:

$$\text{Emission} = Q \times \varepsilon \times \gamma$$

where Q is the amount of foliage or fraction of area covered by a vegetation type, ε is the emission capacity at a certain set of conditions, and γ is an emission activity response to driving variables like light and temperature. Vegetation foliage is the dominant BVOC source but there are other sources. The first BVOC models used foliar density (grams of dry weight foliage per m^2) because values were available in the literature for representative ecosystems and tree species (e.g., Zimmerman 1979, Winer et al. 1982). Emission capacities were reported with units of BVOC carbon mass per gram dry weight leaf biomass per hour. The mass of carbon was used, rather than mass of compound, because the FID detectors used at that time measured the mass of carbon in a compound. Leaf mass was also convenient to use because it was relatively easy to measure. However, when satellite-based foliage estimates became available, leaf area index (LAI, m^2/m^2) was used which meant that foliar mass emission rates needed to be converted to area-based emission rates.

The three main approaches for estimating BVOC emissions are illustrated in **Figure 4**. The simplest is the inventory method used in the 1970s and 80s that can be calculated by hand. The availability of computers introduced the capability of offline computer models that integrate high resolution output from weather models with detailed land cover data and complex algorithms to simulate the major processes controlling BVOC emissions. This enabled the generation of gridded, time dependent emission inputs for numerical air quality models. Finally, online models integrate a BVOC emission model into a larger Earth System model framework. This allows for simulations where climate, chemistry, vegetation and BVOC emissions can interact and influence each other. Online BVOC models can be based on an offline model but modified to adapt to the data developed for a specific Earth System model.



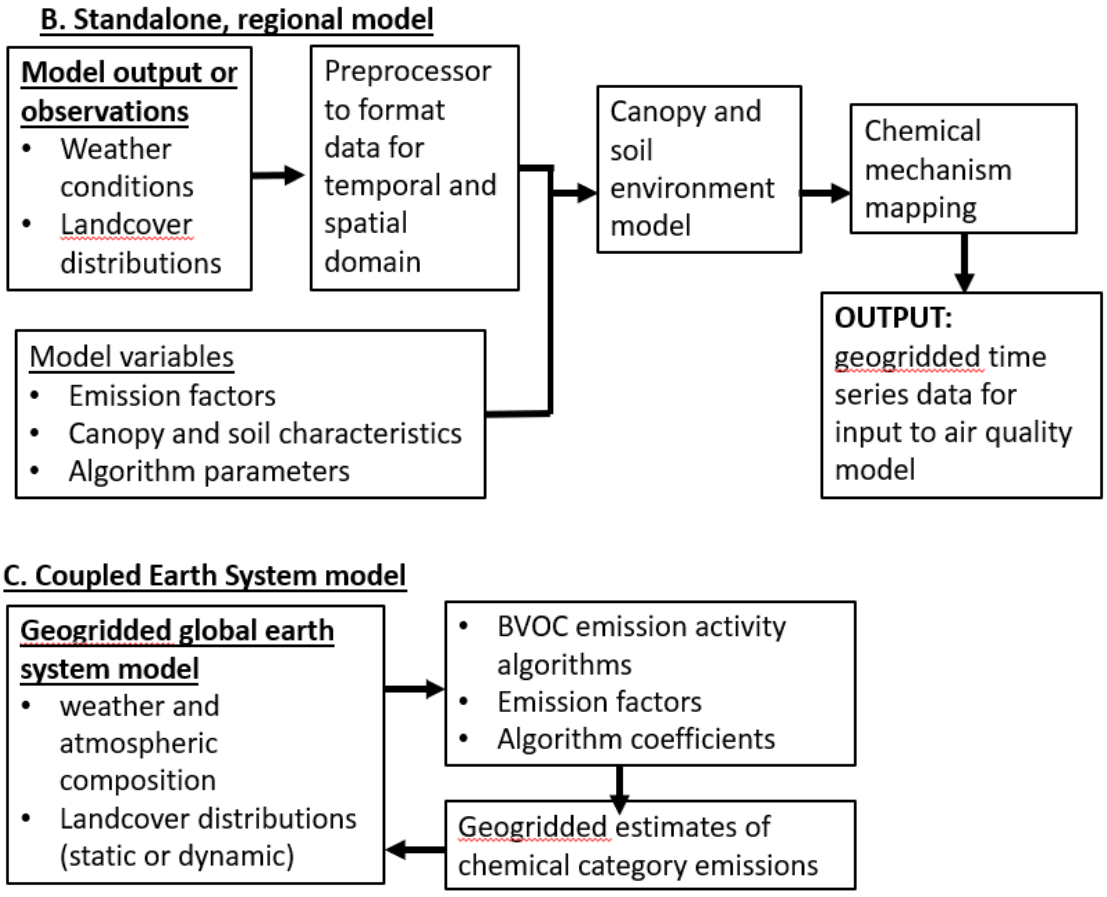


Figure 4 Schematic of BVOC emission estimation approaches including a simple emission inventory calculation (e.g., Rasmussen 1972), standalone offline models that generate input for air quality models (e.g., Lamb et al. 1987), and coupled models for online emission estimations and that enable interactions between BVOC emissions and Earth System responses (e.g., Levis et al. 2003)

BVOC emission estimates were initially based on simple emission inventory approaches (**Figure 4A**). The first applications include Z.I. Briantseva's regional estimates for the former Soviet Union in the 1950s (described by Isidorov, 1993), and Went's (1960) global annual emission estimate. Emission inventories continued to be used in the 1970s and 80s and were successfully used to demonstrate the potential contribution of BVOCs at urban to regional scales (e.g., Zimmerman 1979, Winer et al. 1983).

The Biogenic Emission Inventory System (BEIS) approach replaced inventory calculations in the late 1980s with a computer system designed to compile inputs for regional U.S. air quality models (**Figure 4B**). The original BEIS was based on BVOC emission data from twelve studies that were extrapolated using a database of U.S. landcover and climate and simple emission algorithms (Lamb et al. 1987, Pierce and Waldruff 1991). Later studies suggested that BEIS isoprene emissions were underestimated, primarily due to sampling from shaded lower branches, and monoterpene emissions were overestimated, due to disturbance (Guenther et al. 1994). The emission factors updated for BEIS2 predicted significantly higher isoprene and lower monoterpene emission estimates (Pierce et al. 1998). The third

generation BEIS3 model was integrated into the US Environmental Protection Agency's (USEPA) SMOKE emissions modeling system (Bash et al. 2016). Regional models developed for Europe (e.g., Luebkert and Schoepp 1989, Simpson et al. 1999, Poupkou et al. 2011, Liora et al. 2015), Asia (e.g., Bai and Duhl 2021), Africa (e.g., Otter et al. 2003), and South America (e.g., Li et al. 2020) used a similar approach with regionally relevant emissions data. Guenther et al. (1995) expanded this regional approach by creating a global model to support the Global Emissions Inventory Activity (GEIA) mission to provide consistent, high-quality emission inventories for global atmospheric chemistry modeling (Graedel et al. 1994). This model was further developed as the Model of Emissions of Gases and Aerosol from Nature (MEGAN) (Guenther et al. 2006, 2012) that synthesized regionally specific data within a global modeling framework.

Levis et al. (2003) integrated the offline Guenther et al. (1995) global BVOC emission model into the global Community Land Model (CLM) of the Community Earth System Model (CESM) to create the first coupled BVOC emission model (**Figure 4C**). This coupled modeling framework provided online weather and landcover inputs to drive BVOC emissions that were then passed to CESM's atmospheric chemistry and transport model component to determine changes in atmospheric constituents that affect air quality and climate. This enabled two-way interactions where the BVOC emissions could impact atmospheric constituents and climate which then affect BVOC emissions in the next model time step. Other global models now include coupled BVOC emission models, but other models continue to use static inventories output from offline global models (Turnock et a. 2020).

4.2. EMISSION SOURCES

4.2.1. Source density

BVOC emission models require estimates of the amount and type of each biogenic emission source. Most models consider only plant foliage and use LAI or foliar density to characterize source variations. The three approaches that are typically used to estimate foliage distributions are satellite imagery, dynamic vegetation models, and assigning a constant value based on the vegetation type.

Satellite LAI estimates are derived indirectly, based on measurements of light reflection and models of solar radiation interaction with plant canopies. Challenges with this method include uncertain inversion procedures that are sensitive to a priori assumptions, inclusion of stems and trunks along with foliage, the requirement for specifying leaf orientation and clumping, measurement of effective rather than actual LAI, lack of distinction between overstory and understory canopies, signal saturation in dense canopies, and interference from clouds, ice, snow. Despite these issues, satellite LAI is widely used for BVOC emission modeling due to its ability to provide global data with high spatial (10 m to 1 km) and temporal (2 to 10 days) resolution data.

Dynamic vegetation models estimate LAI using empirical relationships with climate or process-based simulations of physiological processes governing leaf growth and senescence. These models simulate photosynthesis, respiration, carbon allocation, responses to stress and other factors. They can capture complex interactions and responses to changing conditions, such as climate change, but require extensive data on plant physiology, biochemistry, and environmental variables are not well known on regional to global scales, potentially leading to errors due to model complexity and limitations.

The BEIS model assigns representative peak LAI values to different vegetation types and tree species (Geron et al. 1994). For example, LAI was set to 3 for all pine trees, 5 for all deciduous broadleaf trees, and 7 for some conifers (fir, spruce and douglas-fir). The decrease in foliage for deciduous plants was simulated by decreasing LAI to 0 outside of the growing season.

4.2.2. Vegetation type

BVOC foliar emission rates of different vegetation types differ both in total emission magnitude and chemical speciation profile (Purser et al. 2020). For example, for the same environmental conditions, BVOC emission rates are less than 30 nmol m^{-2} s^{-1} for Lagerstroemia (Crepe myrtle) species and exceed 30000 nmol m^{-2} s^{-1} for some Quercus (oak) species. With nearly 400,000 plant species on Earth, prioritizing sampling of dominant species and categorizing vegetation types is essential. Examples of representations of emission types in the first BVOC emission models include Lamb et al. (1987) with 15 emission types for U.S. regional ecosystems and Guenther et al. (1995) with 57 global emission types. Earth System models have vegetation categories prescribed by their land model component, which are typically limited to around 15 landscape types (e.g., deciduous forest, grassland, barren desert) or plant functional types (e.g., broadleaf tropical trees, cool C3 grass, cropland). BVOC emission models embedded in Earth System models usually adopt the vegetation type scheme used in the land model component of the modeling framework. The limited number of vegetation types in these models is insufficient for accurately characterizing BVOC diversity.

The global MEGAN model (Guenther et al. 2012) uses detailed species information where available (e.g., U.S., Australia, Europe, China, Japan) and general landscape types where detailed inventories are not available. Satellite observations of the major growth forms (tree, shrub, grass, crop) are used to quantify the vegetation source types within a landscape. Luttkus et al. (2022) simulations of air quality in Germany demonstrated that using species specific BVOC emissions, rather than general vegetation types, changed ozone by 2.5% and SOA by 60%.

4.2.3. Plant age

BVOC emissions vary with the age of an individual plant. Street et al. (1997) compared emissions from a young (first-year sapling) and an older (~ 7 years) *Eucalyptus globulus* tree and found that the younger tree emitted isoprene at a rate about 5 times higher than the older tree and monoterpene emissions at about nine times higher than the older tree. This finding was supported by Winters et al. (2009) and He et al. (2000), who reported isoprene emissions about four times lower in mature Eucalyptus species compared to two-year-old trees. However, they also observed that mature trees had monoterpene emissions four times higher, contrasting with Street et al. (1997). The higher monoterpene and lower isoprene emission rates for mature trees aligned better with ambient isoprene and monoterpene concentrations measured at several field sites in Australia (Emmerson et al. 2016).

It should be noted that leaves of young and old trees can differ. For example, the leaves of young Eucalyptus trees tend to have a round shape while leaves of mature trees have the long, hanging leaves typically associated with Eucalyptus. Madronich (2003) found monoterpene emissions to be twice as high and methylbutenol emission 60% higher, in young *Pinus ponderosa* trees compared to mature trees. In contrast, Kim et al. (2005) observed higher BVOC emissions from mature *Cryptomeria japonica* and *Pinus koraiensis* trees than from young ones. Another study found no significant difference in isoprene emission rates of young and mature

individuals (Niinemets et al. 2021). Including plant age in BVOC emission models will require species-specific measurements and distributions of tree age. These data are not available on a global scale and have not yet been included in regional or global models, but could be developed for the dominant vegetation in a specific region.

4.2.4. Non-foliar sources

BVOC models typically consider only emissions from plant foliage. To include other sources, MEGAN2.1 simulated the net (emission and deposition) BVOC flux of the entire terrestrial ecosystem, inherently including all BVOC sources and sinks. When above canopy flux measurements are used to assign the canopy scale emission capacities, this approach accounts for all emissions but there are few reported whole ecosystem BVOC flux measurements, so most emission factors are based on foliage enclosure measurements.

Floral emissions can significantly contribute to agricultural (Arey et al. 1991) and urban (Baghi et al. 2012) BVOC emissions. For example, urban tree floral emissions were estimated to contribute 11% of the total summertime monoterpene emissions in Boulder, Colorado (Baghi et al. 2012). The investigators noted that urban tree flowers make an even greater contribution to some non-terpenoid BVOC such as benzenoid compounds. The study did not consider floral emission from ground cover (flowers and shrubs) which are an additional source of BVOC.

Other non-foliar components that could make a significant contribution to total ecosystem BVOC emissions include tree trunks (Steinbrecher and Ziegler, 1997), plant stems and sap balls (Harley et al. 2014), buds (Macdonald and Fall 1993), soil microbes (Greenberg et al. 2012) and leaf litter (Warneke et al. 1999). Yang et al. (2024) found that leaf litter and roots primarily emit terpene, benzenoid, and alcohol BVOCs, while bare soil and microbial activity are sources of alkane, ester, and alcohol BVOCs. They also noted that soils are crucial sinks for VOCs which can alter the dynamics of the net flux of BVOCs from an ecosystem. An extensive analysis of essential oils showed that while sesquiterpenes are usually lower than monoterpenes in foliage, they are often more abundant than monoterpenes in roots, bark and woody material (Kumari et al. 2014) indicating the need to investigate sesquiterpene emissions from these sources. Additionally, an entire growing season of foliar emissions can be less than the intense burst that occurs during ecosystem management activities not considered in BVOC emission models, including resin tapping (Pio and Valente 1998), thinning (Goldstein et al. 2004), and harvesting (Haapanala et al. 2012).

4.3. EMISSION CAPACITIES

Emission capacities are the BVOC emissions of a vegetation type under standard conditions and are used in both empirical and mechanistic emission models. For example, the Niinemets et al. (1999) process-based isoprene emission model has a parameter, ε, representing the fraction of electrons available for isoprene synthesis. Due to the lack of direct measurements of this parameter, its value in BVOC emission models has been derived from measured emission capacities (e.g., Unger et al. 2013). Ideally, emission measurements should be conducted under standard conditions, which can be done using an enclosure with environmental control. The plant should be allowed to adjust to these conditions before taking measurements. Studies using enclosures without environmental controls typically measure emissions at ambient conditions and then use model algorithms to estimate the corresponding emission capacity. Niinemets et al. (2010) describe detailed

protocols for emission capacity measurement, but most studies do not follow these recommendations.

The two most important factors driving emission variations of most BVOC are light and temperature. A standard leaf temperature condition of 30°C was established by Zimmerman (1979) for studies of temperate vegetation on hot summer days using enclosures without environmental control. While 30°C is a suitable standard for some vegetation, it is not appropriate for cooler climates where leaves never or rarely achieve these temperatures. Instead, the standard condition should be representative of typical midday conditions in the peak growing season. BVOC emissions also vary with the temperature and light of the past several days (Petron et al. 2001), and this information should be reported with any emission capacity measurement, although few studies do this. A standard light condition of a Photosynthetic Photon Flux Density (PPFD) of 1000 ¤mol m^{-2} s^{-1}, about half of full sunlight, was established by Evans et al. (1982). BVOC field measurement emissions data may be biased towards shaded conditions, since lower branches are easier to access, but it is difficult to know for many studies since they do not measure or report the light conditions. This may have led to the low isoprene emissions reported in earlier field studies (Guenther et al. 1994). Emissions are also sensitive to other factors, as described in **section 3.4**, but these factors are typically not controlled or measured, contributing to the large differences in emission capacities reported for a given plant species by different researchers.

Zimmerman (1979) defined a foliar BVOC emission capacity that was expressed as the mass of carbon emitted per dry leaf mass per hour. Since most BVOC emission models now use foliage area, which can be obtained from satellite observations, the mass-based emission capacities reported in the literature must be converted to area-based emission capacities using an estimate of specific leaf area (SLA), defined as the one-sided projected leaf area per leaf mass. However, this SLA varies widely, from < 40 cm^2 g^{-1} for some needleleaf species to >200 cm^2 g^{-1} for some broadleaf species. SLA within a single tree can also vary considerably, with sun leaves at the top of a canopy having more than double the SLA of shade leaves in the lower canopy. In addition, the SLA of young saplings in potted plants are 41% to 74% higher than the SLA of mature trees (He et al. 2000; Winer et al. 2009). Uncertainties in SLA are a substantial component of total emission capacity uncertainty for values converted without accurate specific leaf area data.

Some leaves of a given plant species have BVOC emission rates that are an order of magnitude higher than most other leaves of that species, particularly for terpenes and stress compounds, even in the absence of visible stress or obvious differences (e.g., Farmer and Riches 2020, Yu et al. 2024). These outliers could be due to measurement artifacts (e.g., Juuti et al. 1990, Guenther et al. 1994), stress-induced elevated emissions (e.g., Sulaiman et al. 2023) or genetic variability (e.g., Bäck et al. 2012). Some investigators may exclude these super emitters from their reported species-average emission capacities, assuming undetected past stress or unintended disturbance from their enclosure measurement approach. However, excluding these measurements could significantly underestimate the assigned emission capacities if these higher emissions are representative of realistic environmental conditions.

Measuring the emission factors of all plant species may be impractical, especially in regions with high biodiversity. Alternative approaches include landscape-scale measurements, described in **section 2.3**, or relating emission capacities to measurable factors like climate variables. This approach could also improve predictions of future BVOC emission trends. For example, the fraction of isoprene emitters in a landscape might relate to temperature, though it is likely more

complex than a simple correlation with mean annual temperature. Interactions with precipitation are also likely to be important, given the integral role of water availability in determining plant responses to high temperatures (Potosnak et al. 2014). Sharkey and Monson (2017) hypothesized that isoprene may be most useful for surviving extreme heat and drought events that occur infrequently, such as once in several generations, allowing non-emitters to outcompete isoprene emitters in most years but die off under extreme stress. Several studies provide evidence that the fraction of high isoprene emitters in a landscape is related to temperature. Taylor et al. (2018) combined leaf-level isoprene enclosure surveys and plot-scale tree inventories at sites throughout Amazonia to show that the fraction of isoprene emitters in a landscape significantly increased with higher mean annual temperature and following drought. In addition, a long-term warming manipulation study in the Scandinavian Arctic found a similar increase in the fraction of high isoprene emitters for plots exposed to elevated temperatures for more than a decade (Tang et al. 2018).

4.4. EMISSION ACTIVITY

Emission activity algorithms simulate BVOC responses to changing conditions. The time scales associated with the controlling factors include diurnal (up to a day), seasonal (one day to a year), interannual (more than a year), and periodic stress events. These emission responses can vary over orders of magnitude, necessitating accurate representations in models to reliably simulate BVOC emissions.

4.4.1. Diurnal variations

Isoprene emissions increase with increasing light and exponentially with temperature, peaking around 40ºC, while a-pinene emission from pine trees increases exponentially with temperature, with no limit, and are insensitive to light (Tingey et al. 1991). These short-term BVOC emission behaviors have been categorized as light-dependent versus light-independent emissions. Guenther et al. (1991, 1993) integrated the light and temperature behaviors into a single algorithm for light-dependent emissions, based on enzyme activity and electron transport behavior. Later studies showed that monoterpene and sesquiterpene emissions from some plant species are also light-dependent (Kesselmeier 1996). These terpene emissions can have both light-dependent and light-independent fractions for a single terpene in an individual plant (Schuh et al. 1997, Ghirardo et al. 2010).

Some models, like BEIS, assume that a specific BVOC is either light-dependent, such as isoprene, or light-independent, such as a-pinene. Other models, like MEGAN, recognize that a given monoterpene or sesquiterpene can be produced by both light-dependent and light-independent pathways, even for a specific plant. Furthermore, the fraction associated with each pathway, referred to as the light dependent fraction (LDF), can vary among plant species and so models should include both emission capacities and LDF for each plant species and compound type. However, most studies do not report LDF fractions, resulting in limited LDF data and high uncertainty in assigning LDF fractions.

While light and temperature are the most important drivers of diurnal behavior, they are not the only ones. Some plants have a 24-hour internal clock, referred to as circadian cycle, which anticipates daily environmental changes and optimizes physiological processes accordingly. Funk et al. (2003) reported that isoprene emission and the isoprene synthase activity that produces it, has a circadian rhythm in some plants. This was shown by exposing plants to a regular light-dark cycle and then shifting to constant light conditions to isolate the effects of the circadian clock from other light-dependent processes. Hewitt et al. (2011) found that the isoprene

circadian effect was large enough to impact the timing of daily ozone concentrations peaks.

Changes in ambient humidity can also influence BVOC emissions by altering stomatal resistance, which affects leaf temperature and controls the emission of some BVOCs, like methanol (Fall and Benson 1996). Croteau (1977) found that monoterpene emissions from mint plants increased with humidity, attributing this to an increased cuticle permeability. Canopy-scale monoterpene emissions from a pine plantation showed increased emissions at high humidity and dramatically decreased emissions at relative humidity below 40% (Schade et al. 1999). Emissions from wet Douglas fir branches were an order of magnitude higher in comparison to dry branches, but changes in ambient humidity had no detectable influence on emissions (Lamb et al. 1985). Janson (1993) observed a large increase in monoterpene emissions with condensation from relative humidity > 90% but otherwise saw no humidity influence. Other studies have observed negligible monoterpene emissions responses to changes in humidity (Guenther et al. 1991, Loreto et al. 1996). Li et al. (2024) found that BVOC concentrations above vegetation under drought conditions decreased with decreasing humidity and that the degree of change was more important than the absolute value.

4.4.2. Seasonal variations

Many terrestrial ecosystems experience seasonal cycles in temperature, sunlight and precipitation leading to phenological variations in plant growth and physiology that influence BVOC emissions including flowering, seed production and changes in foliage age and amounts. In addition, the weather of the past few days can affect the production and storage of BVOC substrates impacting emissions over time scales of days to months.

Isoprene emission can increase by several orders of magnitude within a few weeks of leaf emergence (Kuzma and Fall 1993) with the specific pattern dependent on the temperatures to which young leaves are exposed (Monson et al. 1994). In contrast, methanol emission is much higher for young leaves (Harley et al. 2007), following the expected pattern for methanol production as a byproduct of pectin demethylation during leaf expansion. Monoterpene production and storage tend to decrease as foliage ages, although monoterpene emissions do not necessarily follow the production and storage trends (Vanhatalo et al. 2018). Guenther et al. (2012) synthesized BVOC emission observations for different leaf ages (e.g., new, young, mature, old leaves) to develop an algorithm to predict BVOC emission variations with changes in leaf age for each BVOC chemical species category. The MEGAN model (Guenther et al. 2012) applies a numerical approach to estimate the fraction of new, young, mature and old leaves in a canopy based on the temporal change in LAI derived from global satellite data. For example, a canopy with increasing LAI is assumed to have more young leaves, while decreasing LAI indicates more old leaves and an unchanging LAI indicates that there are mostly mature leaves.

Plants exposed to warmer or sunnier conditions for a few days can acclimate their physiological processes by increasing the availability of the substrates and enzymes required for isoprene and some other BVOC emissions. This acclimation can substantially elevate emissions above what would be expected from the short-term diurnal behavior during a few days of warm, sunny weather (Wang et al. 2024). Conversely, cool or cloudy conditions suppress emissions.

In addition to seasonal variations in canopy foliage, other plant organs, such as flowers, fruits, cones, buds, have distinct seasonal cycles. Some of these organs have strong BVOC emission capacities that could contribute a large fraction of total

emissions in certain seasons. For example, Arey et al. 1991 reported that floral emissions of linalool dominate local BVOC emissions in orange groves during blooming.

4.4.3. Stress events

Plant stress occurs when conditions exceed a plant's optimal range for an extended period, disrupting vital processes like photosynthesis, growth, reproduction, and other functions. This can lead to reduced yield, permanent damage or even death. BVOC emissions are highly sensitive to plant stress, including abiotic (e.g., extreme temperatures, water availabilities, light, air pollution, salinity, and severe storms) and biotic (e.g., herbivores, boring insects, pathogens) stresses that can occur over time scales ranging from minutes to years. Types of stresses and the general behavior of BVOC emission responses are described in detail by Niinemets et al. (2013). Acute stress can elevate the emissions of BVOCs involved in plant defense, while chronic stress reduces photosynthesis, ultimately decreasing BVOC substrate production and emissions. There is tremendous variability in the responses of different BVOCs and plant species, making it difficult to develop robust quantitative algorithms for modeling. Some conditions associated with plant stress, such as droughts and heat waves, are associated with both climate change and air pollution events (DeMetillo et al. 2019). This makes understanding the BVOC responses to these stress conditions essential for predicting impact of BVOC on future air quality.

Insect herbivory can suppress BVOC emissions by reducing the amount of foliage and elevate BVOC emissions by dramatically increasing the emission capacity of the remaining foliage. Faiola and Taipale (2020) synthesized results of studies reporting quantitative measurements from tree BVOC response to insect herbivory. The observations demonstrate that insect pests can change the quantity and composition of BVOC emission depending on the type of insect damage and the tree species under attack. Their synthesis provides insights into how insect herbivory alters BVOC emissions from trees, but additional field observations are needed to develop numerical algorithms for emission models.

Mild drought can increase isoprene emissions through increased leaf temperature, while severe drought will ultimately decrease emissions if photosynthesis shuts down and carbon substrates are no longer available (**Figure 5**). This has been demonstrated with potted plants under controlled conditions, enabling the development of numerical algorithms (e.g., Tingey et al. 1981, Pegoraro et al. 2004), and later confirmed with whole ecosystem flux measurements (Potosnak et al. 2014, Seco et al. 2015). Remote sensing observations of BVOC oxidation products confirm this general behavior for regional-scale isoprene emissions (e.g., Opacka et al. 2021, Wang et al. 2022). Bonn et al. (2019) reviewed the available literature on BVOC drought response and concluded that monoterpene and sesquiterpene responses to drought are more complex and variable. They found that terpene emissions generally decrease with mild drought and increase with severe drought, in contrast to isoprene emissions. The increase in terpene emissions, especially sesquiterpenes, can be modulated by gene expression (Caser et al. 2019). Additionally, BVOC emissions may respond to drought in some seasons but not others (Saunier et al. 2017). Natural tracer measurements, such as enantiomer monoterpenes, can enable investigators to distinguish between different sources and show the individual responses of different plants (Byron et al. 2022).

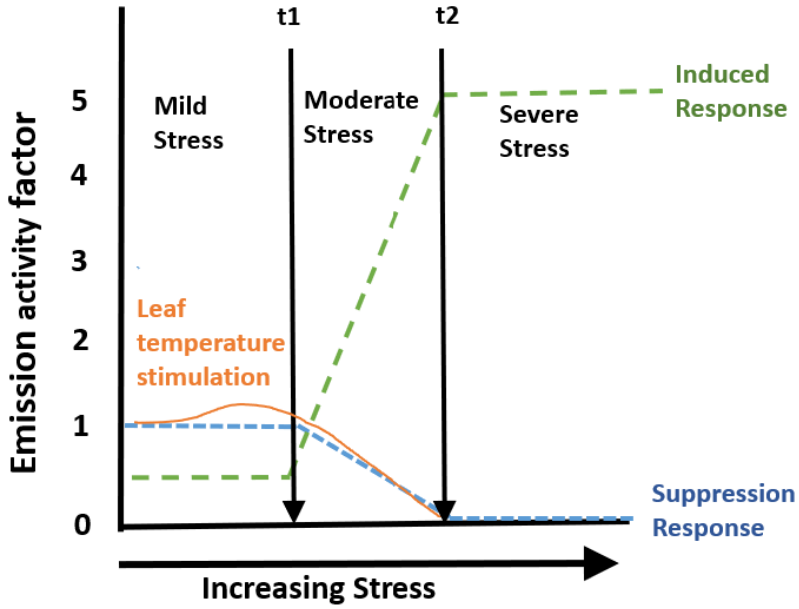


Figure 5 Illustration of approaches for representing BVOC stress response in numerical algorithms: drought and CO_2 suppression response (short-dash blue line), induced emission response for ozone, heat, cold and severe storm stress (long-dash green line), and leaf temperature stimulation during drought (solid orange line). Point t1 represents the level where stress response can be detected and t2 represents the maximum response point

BVOC emissions can be stimulated by mechanical wounding, as can be experienced from the burst of odor that occurs when crushing the leaf or stem of a plant with essential oil storage structures. Juuti et al. (1990) found that rough handling during enclosure emission measurements could increase monoterpene emissions by more than a factor of 10 for some species, and Guenther et al. (1994) suggested that mechanical disturbances occurring with some enclosure measurement approaches were responsible for large overestimates in monoterpene emissions reported for some studies. However, elevated BVOC emissions from mechanical wounding do occur naturally (Panthee et al. 2022). Kaser et al. (2013) concluded that these emissions can be significant, as in the case of a severe wind and hailstorm that caused a 40% increase in monthly total monoterpene emissions from a western U.S. pine plantation. This behavior can be included in existing models, using the approach shown in **Figure 5**, as a function of wind speed or other indicators of a severe storm. In addition to the release of BVOCs associated with damaged terpene storage structures, stress volatiles such as methanol and C5/C6 oxygenated VOCs are released within minutes of leaf wounding (Portillo-Estrada et al. 2021).

Wang et al. (2020) synthesized observations of BVOC emission responses to ozone exposure, conducted between 1990 and 2018, and found that most studies show chronic high ozone influences BVOC emissions by decreasing photosynthesis and inducing defense mechanisms. They developed a response function that simulates a decrease in isoprene emission with increasing chronic ozone. They noted large discrepancies for different plant species and developed an algorithm recommended only for deciduous broadleaf trees. This behavior can be simulated using the simple approach shown in **Figure 5**. Ghirardo et al. (2016) found that several categories of BVOC emissions (benzenoids, sesquiterpenes, green leaf volatiles) increased in

response to ozone stress in laboratory studies and found that trees growing in urban Beijing, exposed to various urban stresses, had higher emissions of these compounds. They estimated that BVOC emissions induced by ozone and other air pollution stresses increased total BVOC emissions in the Beijing region by about 65% (Ghirardo et al. 2016) but more studies are needed to determine if this behavior is typical for urban areas. Hoshika et al. (2020) found that elevated ozone increases isoprene emission in the middle of the growing season but later decreases emissions, suggesting an initial activation of isoprene with O_3 stress followed by a decline due to ozone inhibition of photosynthesis. Other recent studies found no change or just decreased emissions (e.g., Vo and Faiola 2023). An additional source of VOC emissions in response to elevated ozone is reactions with organics on leaf surfaces that release VOCs into the atmosphere (Jud et al. 2016).

Studies with trees and herbaceous plants have demonstrated that isoprene emission rates are positively correlated with nitrogen availability (Harley et al. 1994 and Litvak et al. 1996). Hoshika et al. (2020) found that isoprene emissions are also positively correlated with phosphorus, and Ndah et al. (2022) reported that increased nutrient availability could also increase monoterpene and sesquiterpene emission rates and alter the BVOC emission profiles of plants. These results indicate that plants experiencing stress from a lack of nutrients may have suppressed emissions. Monson et al. (2004) suggest that this relationship also plays a role in seasonal variations, with the late season decline in emission determined by the depletion of leaf nitrogen during senescence.

Both chilling and heat stress can induce BVOC emissions (Ding et al. 2002, Emmerson et al. 2016, Karl et al. 2008). Many plants have a temperature optimum for photosynthesis around 25°C and are not stressed by temperatures within about 5 to 10°C of this optimum. Lower (e.g., <10 °C) or higher (e.g., >40 °C) temperatures may induce stress BVOC emissions, including monoterpenes and methyl salicylate, with responses more related to temperature changes than absolute temperatures (Karl et al. 2008). Warm climate plants tend to be more susceptible to cold temperature stress, while cool climate plants are more susceptible to high temperatures (Kleist et al. 2012). BVOCs like isoprene may improve heat tolerance during short, high-temperature episodes (Sharkey and Monson 2017). Isoprene and other light-dependent emissions typically increase with temperature up to a maximum level, then decline as the enzymes producing the BVOCs begin to denature (Guenther et al. 1993). The increase to the maximum emission is reproducible, but the behavior at higher temperatures is variable and highly time dependent. The temperature of maximum emission is around 42°C for plants that have been exposed to typical temperate weather conditions but is higher (lower) if the plants have recently been exposed to warmer (cooler) temperatures. Emissions of BVOCs from storage structures can continue to increase with temperature until the compounds are depleted.

Guenther et al. (2006) introduced a simple framework to represent BVOC emission activity responses to drought stress. The approach assigns an initial stress threshold value, where stress begins to influence BVOC emission, and a maximum threshold value, where further stress has no additional impact. Soil moisture was used as the drought indicator, with the initial threshold set at a value 0.06 m^3/m^3 below the wilting point for a given soil type. The maximum threshold was assumed to be equal to the wilting point. Potosnak et al. (2012) noted that mild drought can indirectly stimulate isoprene emissions through higher leaf temperature, which can be simulated using a leaf energy balance model for calculating leaf temperature. The MEGAN stress-induced emission activity framework was extended to assess the potential importance of other stresses. For example, threshold temperatures of 10°C for chilling stress and 40°C for heat stress were set, with increased emission

activity factors implemented for compound categories sensitive to stress, including some monoterpenes (e.g., ocimene), sesquiterpenes (e.g., farnesene, longifolene), and stress compounds (e.g., linalool). Additional research is required to determine if BVOC emission responses to chilling or heating stress can significantly contribute to total BVOC emissions. If so, the emission response algorithms and parameters need further development. Additional stresses included in the MEGAN framework are severe storms (Kaser et al. 2013), mechanical damage, and biotic stress (Ameye et al. 2018).

4.4.4. Interannual variations

The processes controlling diurnal to seasonal variations and stress events combine with additional processes, such as responses to carbon dioxide and vegetation succession, to control long-term interannual BVOC emission trends. Elevated CO_2 enhances photosynthesis, increasing the availability of carbon within a leaf, which can lead to higher LAI and foliar density, thus increasing foliar BVOC emissions. Conversely, elevated CO_2 can also suppress emissions of isoprene and possibly other BVOCs (Sharkey and Loreto, 1999). Estimates of the impact of CO_2 suppression on global isoprene emission range from about 3% per decade (Heald et al. 2009) to 6% per decade (Young et al. 2009) depending on the observations that are used to develop the response curve algorithm. Niinemets et al. (2021) has shown that the CO_2 inhibition of isoprene varies by more than a factor of two among different tree species. Recent studies have also shown that higher temperatures reduce the isoprene inhibition, with a 5°C increase reducing the effect by ~50% (Sahu et al. 2023) which could eliminate all or most of the inhibition. The relative impact of these processes on past and future emission trends is discussed in **section 4.5.2**.

4.5. EMISSION ESTIMATES

4.5.1. Global rates and regional distributions

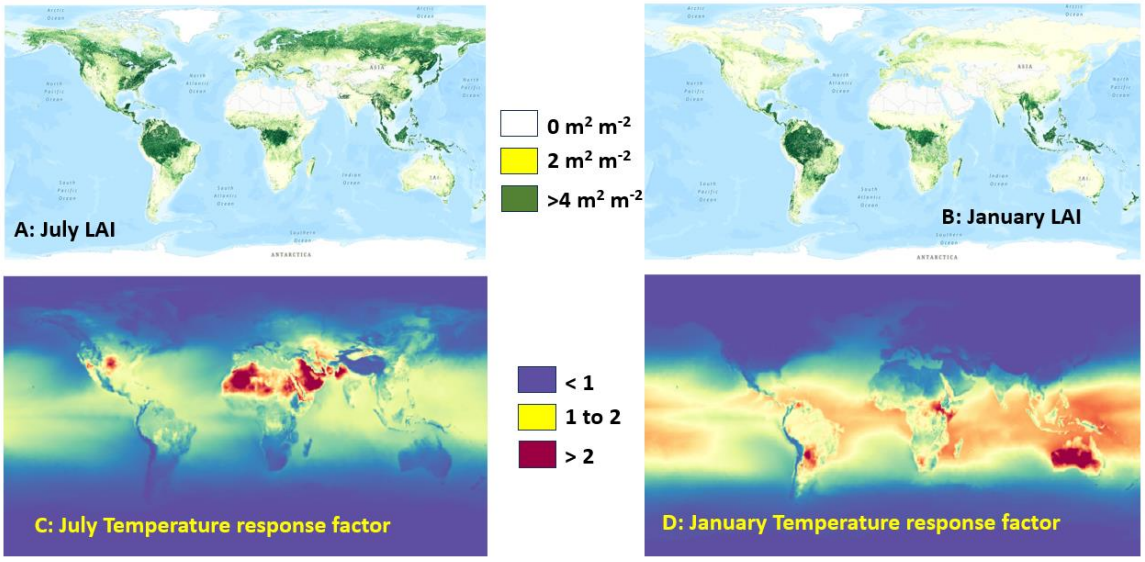
The first estimates of global annual monoterpene emissions (Went, 1960; Rasmussen and Went, 1965) were about 150 Teragrams (Tg = 10^{12} g), which is remarkably similar to current estimates. As additional BVOC emissions were discovered and added to this total, especially around 500 Tg of isoprene and 100 Tg of methanol (Guenther et al. 1995), the estimated global total BVOC emission increased to ~1000 Tg (Guenther et al. 2012). This corresponds to an annual BVOC emission rate of approximately 10 g m^{-2} averaged over all terrestrial surfaces.

Guenther et al. (1995) estimates of annual BVOC emissions for 57 global biomes ranged from less than 1 g m^{-2} for sparsely vegetated landscapes to >30 g m^{-2} for ecosystems with dense vegetation cover and year-round growing seasons. Cool climate biomes were about a factor of three to four lower than similar ecosystems with warm climates. **Figure 6** shows that the highest annual BVOC emission rates occur with high LAI and emission capacities, ample light and temperature, and long growing seasons. Increasing LAI above 3 or 4 does not substantially increase isoprene and other light-dependent emissions, which are about half of the global total, due to self-shading of leaves in a canopy. Guenther (2002) estimated maximum hourly total BVOC emissions of about 25 mg m^{-2} h^{-1} and maximum annual emissions of around 100 g m^{-2} for landscapes where emissions are sustained throughout the year. Regional emission estimates shown in **Table 1** show that about two thirds of global BVOC emissions are from Latin America and Africa, primarily in their large tropical forest regions. Asia, North America and the European Union (EU) contribute about 13%, 3% and 1%, respectively.

Estimates of annual global anthropogenic VOC emissions range from 110 to 163 Tg (Huang et al. 2017, Duan et al. 2023) which indicates that BVOC are more than 85% of the global total. **Table 1** shows that this percentage varies for different regions with BVOC contributing about 45% in China and the EU, around 75% in North America, India and the rest of Asia and about 90% or more in the rest of the world. These differences are primarily driven by fossil fuel combustion but are also influenced by BVOC emission distributions illustrated in **Figure 6**. Regional scale BVOC and AVOC emissions are compared in **Table 1**.

Table 1 Annual emissions (Tg) for 2012 from Huang et al. 2017 for AVOC and Guenther et al 2012 for BVOC. BVOC percentage of total (BVOC+AVOC) VOC emissions is also shown

Region	BVOC emission	AVOC Emission	BVOC % of TVOC
European Union	8.7	10	46%
North America	33	11	75%
Latin America	388	20	95%
Africa	265	34	89%
Russia	20	9	91%
China	24	30	44%
India	24	7	78%
Rest of Asia	68	19	78%
Rest of the world	164	12	93%



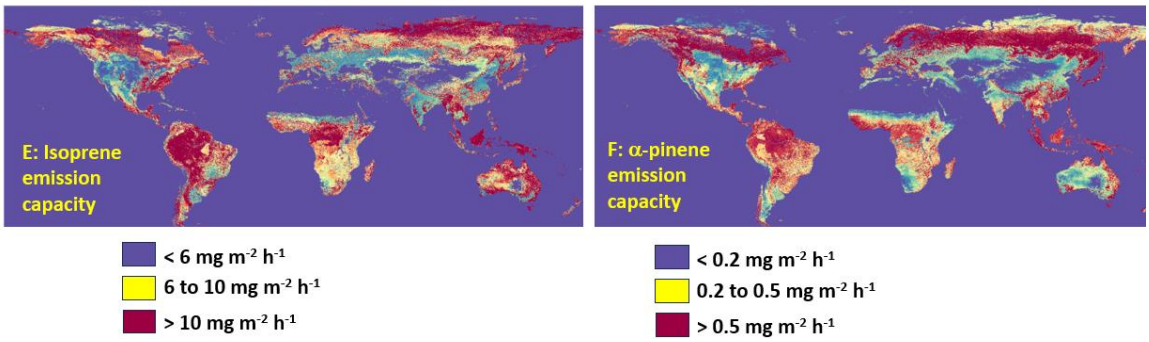


Figure 6 Global distributions of the main drivers of BVOC spatial distributions: LAI (A: July, B: January), temperature response activity (C: July, D: January) and emission capacity (E: isoprene emission capacity, F: ¤-pinene emission capacity)

4.5.2. Emission trends

Annual global BVOC emission estimates vary in response to global scale changes in land cover and environmental conditions, as shown in **Figure 7**. Land use and land cover changes influence both LAI and vegetation type, which determine the average BVOC emission capacities. Environmental conditions, including temperature and carbon dioxide, determine emission activity levels. Vegetation type changes can result directly from land-use changes and indirectly from CO_2 and climate change. Interannual BVOC emission variations may include large local changes that have little impact on global emissions due to offsetting increases and decreases in different areas. In contrast, global scale phenomena like climate warming and expanding agriculture can result in substantial global emission trends. The current understanding of global BVOC emission trends for the distant past (interglacial), recent past (pre-industrial), present, and future are discussed below.

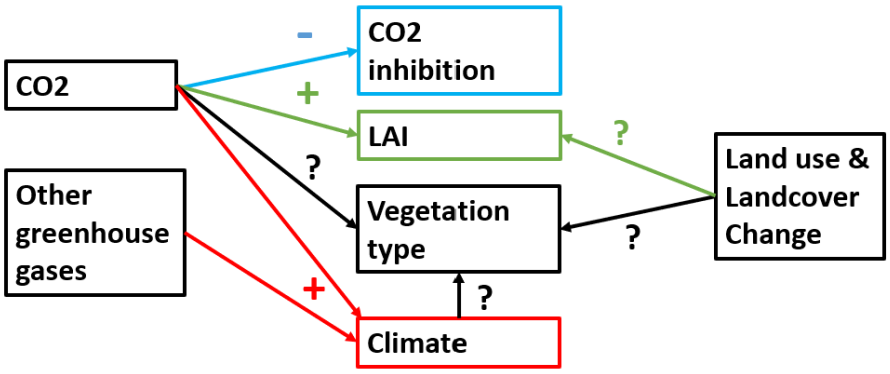


Figure 7 Schematic showing the expected trends of "-" decrease, "+" increase, and unknown, "?" associated with drivers of future BVOC emission trends

Past BVOC emission trends have been investigated using climate and dynamic vegetation models over periods of centuries to millennia. Adams et al. (2001) investigated BVOC changes since the last glacial period, approximately 20,000 years ago, and estimated that current BVOC emissions are about 40% higher due to more global forest cover and an additional ~60% increase due to warmer temperatures. Kaplan et al. (2006) also estimated that BVOC emissions doubled from the last

glacial maximum to the current time and suggested that the lower BVOC emissions during the glacial period increased methane lifetime and concentrations, since the hydroxyl radical is a dominant sink for both BVOC and methane, and could have significantly impacted the climate during this period. However, Arneth et al. (2007) concluded that the inhibition of isoprene emission by rising CO_2 concentrations means that isoprene had only a minimal impact on glacial-interglacial methane changes. However, the change in isoprene emission is highly uncertain due to the limited understanding of isoprene suppression and because the global dynamic vegetation models used in these studies are designed to simulate changes in major plant functional types, such as tropical forest changing to grassland, and do not consider specific plant species, which can have very different emission capacities.

Martin and Guenther (1995) coupled a BVOC emission model to a climate model with a gap-phase forest dynamics model that simulated changes in tree species in northcentral U.S. They found that climate-driven changes in tree species composition over a 100-year period could change BVOC emissions by a factor of 2 to 5, depending on the local forest type. One case study simulated a temperate needleleaf evergreen forest dominated by spruce trees transitioning to a temperate broadleaf deciduous forest dominated by maple trees. PFT-based models would estimate a large increase in isoprene emission for this case, since broadleaf trees tend to have higher isoprene emissions than needleleaf trees. However, this is inaccurate since spruce has much higher isoprene emissions than maple. As discussed in **section 3.3**, if the fraction of isoprene emitters in a landscape increases with higher temperatures, this could lead to an overall increase in isoprene emissions through higher landscape-average emission capacities. Large-scale changes in plant species composition in Earth's past could have dramatically increased BVOC emissions if the dominant species were isoprene emitters. For example, during the Eocene epoch approximately 50 million years ago, a massive bloom of Azolla, a water fern, is hypothesized to have occurred in the Arctic Ocean, which might have significantly reduced atmospheric CO_2 and influenced global climate conditions. If those Azolla emitted isoprene, as modern Azolla species do (Silver and Fall 1995), the resulting increase in isoprene emissions could have substantially impacted the atmospheric oxidation capacity and methane lifetime.

Unger (2013) estimated a 16% decrease in isoprene emissions during the past century, from 1880 to 2000. The estimated direct CO_2 inhibition of isoprene was offset by a stimulation of LAI, resulting in an overall increase of 7% due to the emissions of CO_2. Anthropogenic land cover change was associated with a 22% decrease in isoprene, while climate change increased isoprene emissions by only 3% (Hantson et al. 2017). Much higher changes occur on regional scales. For example, Schaab et al. (2000) estimated that vegetation changes in southern France over 34 years, as farmlands were abandoned and replaced by regrowing forests, led to an isoprene and monoterpene increase of 100% per decade. Additional studies report large impacts from deforestation and afforestation (e.g., Wiedinmyer et al. 2006).

Turner et al. (1991) made the first estimates of how isoprene emissions will change in the future by considering climate change impacts on short-term temperature response, LAI and vegetation type. They concluded that there would be an increase in isoprene emissions due to an expansion of tropical humid forests that they assumed had relatively high isoprene emission. Weaver et al. (2009) summarized future predictions of U.S. BVOC emissions and their impacts on air quality using five different modeling approaches with different assumptions about changes due to long-term temperature acclimation, solar radiation, plant species composition, and CO_2 inhibition of BVOC emission. All the models predicted a large overall increase in BVOC emissions, but the regional estimates differed by a factor of five, and in some cases did not even agree on the sign of the change. In contrast to these

studies, Hantson et al. (2017) concluded that a future global increase in BVOC emissions is improbable.

The main global drivers of BVOC emission change, illustrated in **Figure 7**, are increasing greenhouse gases and land use/land cover change. BVOC emission trends are primarily driven by changes in CO_2, climate, LAI and vegetation type. Additional impacts include changes in light and water availability and air pollution, but their estimates are highly uncertain. The range of future emission changes estimated for individual processes and the combined total are illustrated in **Figure 8**. One of the processes, the suppression of isoprene emission in response to increasing CO_2, is expected to decrease future BVOC emissions (Arneth et al. 2007, Heald et al. 2009). In contrast, two other processes, CO_2 stimulation of LAI (Heald et al. 2009) and temperature increases (Guenther et al. 2012), are expected to increase future BVOC emissions per decade. Land cover change could either increase or decrease emissions, depending on future trends of afforestation and deforestation. Combining the estimates for these four processes suggests future changes in annual isoprene emissions of about 5% per decade with a range of a decrease of a few percent per decade to an increase of about 14% per decade.

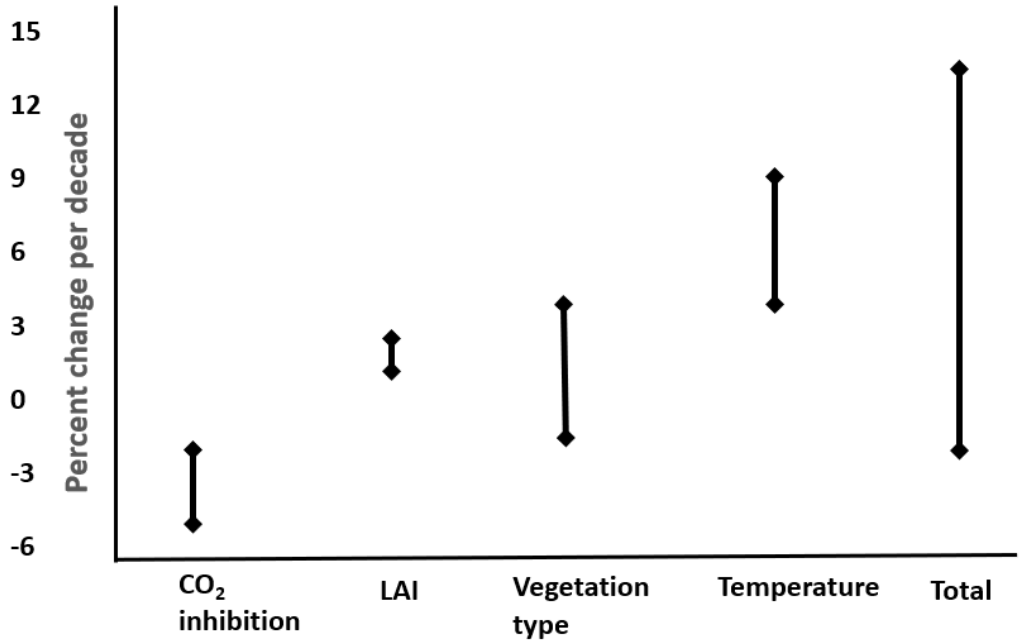


Figure 8 Schematic showing the range of estimates for changes (percent per decade) in annual global isoprene emission trends

The accurate prediction of future emissions, which are needed to develop regulatory control strategies that will be effective in reducing pollution and maintaining clean air in the future, are one of the greatest challenges for BVOC emission modeling. This will require representative estimates of future land cover and climate conditions including the frequency of extreme events, like heat waves and droughts, and the plant species composition of future urban forests and agricultural lands. The expected increasing frequency of extreme weather events (IPCC 2022) elevates the need for accurately simulating BVOC emission responses to drought, flooding, severe storms, heat waves, and other events. These efforts require collaboration with the scientific community focused on simulating agriculture and urban vegetation responses to future climate, land use and

management. This includes studies characterizing urban heat islands and carbon sequestration. The need for predicting BVOC emission response to future extreme events is also an opportunity for atmospheric scientists to work more closely with plant physiologists and ecologists to quantitatively understand the mechanisms driving BVOC emission responses to stress and develop algorithms with measurable parameters that can be integrated into BVOC emission models.

4.6. BIOGENIC CONTRIBUTION TO URBAN EMISSIONS

Chameides et al. (1988) presented a case study for Atlanta, GA, USA, demonstrating the significant role of BVOCs in ozone production near this urban area. They showed that the estimated BVOC emissions in the forests surrounding Atlanta were about twice as high as the anthropogenic emissions in the 11-county ozone non-attainment region (~9000 km^2). BVOCs, interacting with anthropogenic NOx, were responsible for ozone production in the region. However, since AVOC emissions were about 20 times higher in the Atlanta urban core area (~100 km^2), BVOC emissions contributed less than 5% of the total VOCs in this smaller region. Because BVOCs made only a small contribution to urban total VOC emissions and due to the complexity of estimating BVOC emissions in urban areas, regional to global BVOC emissions models may neglect to assign BVOC emissions in urban areas or simply assign a constant low value to all urban areas.

The steady decrease of anthropogenic VOC emissions, accomplished through emissions controls, along with an increase in biogenic VOC emissions from tree planting efforts and a warming environment, is leading to the dominance of BVOC emissions in some urban areas. Ren et al. (2017) estimated annual BVOC emissions ranging from 6.7 to 11.6 g C m^{-2} for Beijing urban green spaces. In comparison, the estimated emission rate for the natural forests surrounding Beijing was 6.5 g C m^{-2}. They suggested that actual emissions from the urban green spaces were even higher due to the urban heat island effect, increased light availability from a more open canopy, and a greater fraction of high BVOC-emitting trees. Ren et al. also estimated that although urban BVOCs were only 15% of the total BVOCs in the Beijing administrative district, they were responsible for 62% of the total human health impacts due to the higher population density and the higher ozone production in the urban area. They predicted that by 2050, this would increase to 23% of the total BVOC emissions and 74% of the total health impacts due to increasing urbanization and urban greening.

Studies in other cities have shown that BVOC emissions can comprise an even larger fraction of total VOCs. Gu et al. (2021) estimated a BVOC emission rate of ~7 g m^{-2} for Los Angeles County, including both urban and surrounding areas, which is higher than the US average emission rate. This is partly due to the warm climate and higher than average BVOC emission capacities. BVOCs accounted for about 41% of the total VOC emissions and were responsible for 63% of the total ozone formation potential (OFP), primarily due to the relatively high OFP of isoprene, which is the dominant BVOC. A recent aircraft flux measurement study confirmed that BVOC emissions are important contributors to total VOC mass, and they dominate the total OH reactivity flux, indicating a strong influence on ozone production. The aircraft flux measurements also indicated that BVOCs, especially monoterpenes and sesquiterpenes, dominate total SOA formation potential.

PTRMS eddy flux measurements of VOCs in the city center of Helsinki, Finland in 2013 and 2014 by Rantala et al. (2016) indicate that the wintertime VOC fluxes are primarily methanol, ethanol, acetone, benzene, toluene and monoterpenes, all of which have both biogenic and anthropogenic sources but presumably are dominated by anthropogenic sources in winter. Summertime fluxes of isoprene, monoterpenes,

methanol, acetone and acetaldehyde were higher than the wintertime values. If this increase is assumed to be biogenic then the summertime BVOC flux is about 25% of the total VOC by mass and is more than a third if weighted by OH reactivity. Peron et al. (2024) report direct VOC flux measurements from an urban (Innsbruck, Austria) location demonstrate that isoprene, methanol and monoterpenes have both biogenic and anthropogenic sources with the biogenic sources dominating in summer and the anthropogenic sources dominating in winter. The total midday summer terpenoid fluxes were ~ 300 mg m^{-2} h^{-1} which is about a factor of four higher than the measured sum of benzene plus toluene fluxes, which are primarily from anthropogenic sources. Since the terpenoid compounds are more reactive, they have an even greater contribution to total reactivity and ozone formation potential.

While BVOC contributions to total urban VOC are becoming dominant in at least some U.S. and European cities, urban areas in developing countries continue to have much smaller BVOC contributions. For example, Cui et al. (2023) estimated annual BVOC emission rates of ~2 g m-2 for the Shenzhen urban area and reported that this was 5.2% of the total VOC emissions in Shenzhen in 2019. This is likely to change in urban areas with active tree planting programs and efforts to reduce anthropogenic VOC emissions.

5. BVOC AND AIR POLLUTION

5.1. AIR QUALITY MODELING

Numerical air quality models simulate atmospheric distributions of pollutants and other constituents by representing the processes that control emission, deposition, chemical production and loss, and transport and dispersion. They are essential tools for investigating the processes that control atmospheric composition and finding effective management strategies for improving air quality. Recent improvements in modeling approaches have been driven by advances such as multi-scale, online-coupling frameworks, machine learning methods, and multi-platform data assimilation and bias correction techniques. Innovative machine learning technologies, including deep neural networks for air quality index forecasting (e.g., Le et al. 2022), machine learning methods to downscale and enhance air quality model predictions (e.g., Dinkelacker et al. 2023, 2024) and group-aware graph neural networks, are being utilized to improve air quality predictions. Enhanced data assimilation capabilities, further improved by higher spatial and temporal resolution of geostationary satellites, provide more accurate and comprehensive coverage of relevant measurement wavelengths (Kim et al. 2020). Dense networks of low-cost VOC sensors also offer significant potential data sources (e.g., Kolarik et al. 2023).

Air quality modeling tools include zero-dimensional “box” chemistry models, one-dimensional (1D) chemistry and vertical transport models, and three-dimensional (3D) chemistry and transport models. These models include the emission and deposition fluxes of VOCs and other compounds that drive atmospheric composition. Box models, used with complex chemical schemes, can assess the simpler schemes used in 3D models. Similarly, 1D models with complex chemistry and vertical transport schemes can investigate chemistry-transport interactions and the performance of simpler schemes. 3D chemistry and transport models (CTMs) are the primary tool for regulatory air quality predictions of regional ozone and fine particles. Examples include the CMAQ, WRF-Chem, CAMx, and NAQPMS regional air quality models, described and compared by Gao and Zhou (2024), and global models described and compared by Arneth et al. (2011). Some models use online coupling of chemical and meteorological components, allowing calculated chemical composition to impact atmospheric dynamics, which can then modify BVOC and other emissions, simulating interactions including feedbacks. Other models are offline, running weather models, BVOC emission models, and atmospheric chemistry models sequentially, using the outputs of one as inputs to the other. Grid resolution is another consideration, with resolutions ranging from fine grids of a kilometer or less to coarse grids of several hundred kilometers or more. Modeling across scales allows global-scale models like MUSICA (Tang et al. 2023) to achieve spatial resolutions of a few kilometers within portions of their domain, suitable for investigating local to global air pollution issues.

Chemical mechanism schemes are a fundamental component of a CTM. Some air quality modeling frameworks offer multiple choices, depending on the simulation objectives. The number of chemical species and reactions varies considerably depending on the scheme, but most regional air quality simulations use schemes with tens (e.g., CB4 with 33 species and 81 reactions) to hundreds (e.g., SAPRC11 with 174 chemical species and 478 chemical reactions) species. Box models can use more explicit schemes (e.g., GECKO-A, MCM) with millions of chemical species and reactions. For example, Camille Mouchel-Vallon et al. (2020) investigated oxidant and SOA formation downwind of the Manaus urban area in the Amazon by simulating the oxidation of 12 biogenic and 53 anthropogenic VOCs present in the atmosphere.

They reduced the number of chemical species represented in their explicit scheme by assuming low vapor pressure compounds immediately partition into the aerosol phase and by lumping lower-yield, long-chain species with chemically similar compounds based on molecular structure. The resulting scheme contained 23 million chemical reactions involving 4.4 million chemical species. Most chemical schemes include isoprene as a specific species and may include one or a few monoterpenes and sesquiterpenes. Sesquiterpenes are often much more reactive than monoterpenes, e.g., the common sesquiterpene, β-caryophyllene, is much more reactive than the common monoterpene, β-pinene, but there is a wide range of reactivity within both groups, with some sesquiterpenes being less reactive than some monoterpenes. Monoterpenes with similar structures can have ozone formation potentials that differ by a factor of 2 or more (e.g., Gu et al. 2021, Thomsen et al. 2021).

Model approaches for estimating SOA formation from BVOCs range from simply assigning empirical SOA yields to applying mechanistic models with detailed reactions (Mouchel-Vallon et al. 2020). An example of an approach that balances complexity and computational feasibility is the 2-D Volatility Basis Set approach (Donahue et al. 2011) that determines the SOA formation of organic compounds based on their volatility and other chemical properties.

A robust atmospheric dynamics model is also an essential component of a regional air quality model, and needs to accurately predict the dispersion, and transport of pollutants within the atmosphere by simulating the physical processes describing atmospheric motion, including wind patterns, temperature variations, pressure changes, and other meteorological factors. These processes are crucial for controlling BVOC emissions and the deposition processes responsible for removing BVOC and their products from the atmosphere. A key aspect of this is a solar radiation transfer model that simulates solar radiation penetration down to the earth's surface, driving atmospheric dynamics, photochemistry, and the biological production of BVOCs.

5.2. OZONE AND PARTICLES

Photochemical smog is a persistent regional air pollution problem that poses significant human health risks, morbidity and mortality especially in many urban areas and causes negative impacts on the surrounding agricultural and natural ecosystems. Surface-level ozone and fine particles, along with other air pollutants, are a contributing cause of over 6 million deaths annually and exposure to air pollution is considered the third highest risk factor, after high blood pressure and smoking (Azimi and Rahman 2024). Controlling these secondary pollutants is challenging because they are not directly emitted but produced in the atmosphere through precursor emissions and photochemical reactions. Both biogenic and anthropogenic VOCs feed the photochemical formation of ozone and secondary organic aerosol in the presence of nitrogen oxides, sulfur dioxide, and other air pollutants. Reducing photochemically induced secondary pollution is further complicated by the non-linearity of the controlling processes, which can result in regulatory actions that reduce precursor emissions (like AVOC) in one region but have little effect or even cause increases in others, e.g., ozone formation. Net ozone production is highly sensitive to the VOC:NOx ratio. NOx reductions can reduce ozone in regions with a high VOC:NOx ratio (NOx-limited) but increase ozone in regions, such as urban environments, with a low VOC:NOx ratio (VOC-limited). The reduction of anthropogenic NOx emissions in many U.S. cities has decreased ozone sensitivity to VOCs and increased sensitivity to NOx i.e., being NOx-limited (Geddes et al. 2022). Another complication is that since ozone production is dependent on solar radiation, with little ozone produced in the absence of strong

sunlight, the scattering and absorbing of incoming sunlight by high levels of particles can suppress ozone levels.

The scientific community's understanding of the importance of BVOCs for ozone and secondary particle pollution has evolved over decades. Speculation in the 1960s and 1970s (Went 1960, Rasmussen 1972) led to controversy in the 1980s (Altshuller 1983), and eventually to acknowledgement and acceptance in the 1990s (NRC 1991). Including BVOC emissions in regional photochemical model simulations significantly changed ozone pollution management strategies, emphasizing the effectiveness of NOx control (e.g., Russell and Dennis 2000). Integrated regional aircraft, ground observations, and modeling studies, such as the Southeastern Atmospheric Study in 2013 (Carlton et al. 2018) and GOAMAZON from 2014 to 2015 (Martin et al. 2015), confirmed the role of BVOCs in regional ozone and secondary fine particle production and their impacts on air pollution and climate. Cao et al. (2022) conducted long-term simulations from 1981–2018 and found that BVOC emission increase over this period, primarily due to increased leaf biomass, resulted in a 7.4% in ozone and a 39% increase in SOA. Reductions in anthropogenic air pollutants from 1990 to 2010 were estimated to decrease SOA from on-road transport sources by more than a factor of three while SOA from biogenic sources was estimated to increase by 23% due to the combination of increased BVOC emissions and higher SOA formation yields due to lower NOx levels (Skyllakou et al. 2021, Dinkelacker et al. 2023).

Integrated observational and modeling studies of BVOC and air pollution impacts have primarily focused on regional scales, with relatively few efforts investigating urban-scale interactions. The importance of urban tree BVOCs has been recognized for nearly three decades, including the possibility that large-scale urban tree planting could either improve or degrade air quality depending on the BVOC emission capacities of the tree species planted (Benjamin et al. 1996) but at that time BVOC were considered a small contributor to urban scale VOC even though they were significant contributors to regional scale VOC (Chameides et al. 1988). Calfapietra et al. (2013) reviewed 33 studies of urban BVOC impacts on air quality that were primarily located in Europe, U.S. and Asia, and concluded that there were substantial uncertainties regarding both the impact of BVOC emissions on ozone and the effects of ozone on BVOC emissions. They did not find any clear differences associated with the results from the different regions. The importance of urban BVOC for ozone pollution was clarified by the work of Ren et al. (2017) that showed that the urban core of Beijing can be a hotspot of BVOC emissions and that urban BVOCs could be more important than rural BVOCs for overall health impacts since the ozone is formed in densely populated areas. Fitzky et al. (2019) continued this reevaluation of the importance of urban BVOC with a review of interactions between ozone and urban vegetation in Europe and other regions that emphasized the need to develop ozone pollution control strategies that consider the physiological status of trees, including stress and species composition, to determine BVOC emissions and ozone deposition. The steady decrease of anthropogenic VOCs and the increase of urban forests has resulted in some cities having more biogenic VOC than anthropogenic VOC, especially when weighted by reactivity or ozone formation potential (e.g., Gu et al. 2021, Pfannerstill et al. 2024).

Jiang et al. 2019 investigated the effects of two different biogenic emission models, with BVOC emissions that differed by about a factor of three, on modelled summertime ozone and aerosol concentrations in Europe. They found that simulated ozone differed by <10% (about 7 ppb) while the estimated SOA changed by 110%. A study focused on BVOC emissions in Paris found that urban trees typically resulted in a 1% increase in ozone and 5% increase in particle organic matter but during heatwaves there was a 2.4% increase in ozone and a 14% increase in organic matter

(Maison et al. 2024). They note that the organic matter was especially sensitive to monoterpene emissions. Air quality model simulations have also shown that a reduction in isoprene emissions could increase SOA more in Northern Europe, compared to southern Europe, and suggested this could be due to the impact of isoprene on the availability of radicals for monoterpene oxidation (Ciarelli et al. 2024). Liora et al. (2016) investigated European air quality using model simulations and found that removing summertime biogenic emissions from their model decreased SOA by more than 90% while at the same time increasing PM2.5 in central Europe and Eastern Mediterranean due to the BVOC interaction with anthropogenic pollution. Biogenic emissions decrease PM2.5 in central Europe, and other areas with a low contribution of BVOC to total VOC, due to the corresponding decrease in nitrates when biogenic emissions are included. Aksoyoglu et al. (2017) found that a doubling of BVOC in Europe resulted in a doubling of SOA along with a 35% decrease in particulate inorganic nitrate and a smaller decrease in sulfate concentrations. The overall impact will depend on the relative contribution of organics and inorganics to total secondary aerosol. Bartik et al. (2024) used a particle source apportionment approach to show that stationary combustion was the main wintertime $PM_{2.5}$ source in Central Europe while biogenic VOC emissions contributed the most to summertime $PM_{2.5}$.

5.3. OTHER AIR POLLUTION ISSUES

In addition to their impact on urban and regional ozone and fine particle pollution, BVOC have been of interest for other air pollution issues. Some early efforts to develop BVOC emission inventories for regional modeling (e.g., Lamb et al. 1987) were supported by U.S. National Acid Precipitation Assessment Program (NAPAP) efforts to investigate the sources of acid rain. This includes the direct emission of organic acids (acetic acid, formic acid, etc.) and their atmospheric production from oxidation of other VOC.

Unger (2014) summarized the climate impacts of the reduction in BVOC emissions associated with the conversion of forests to cropland from 1850 to 2000. This conversion led to cooling from a reduction in two greenhouse gases, ozone and methane, and warming from a reduction in biogenic SOA. The net impact was a radiative forcing (cooling) of about -0.1 W m^{-2}, which is of the same order as the estimated radiative forcing from changes in albedo and CO_2 concentration due to agricultural expansion (Unger 2014). This implies that future increases in BVOC emissions due to reforestation could result in warming that might offset the cooling from CO_2 uptake. Predicting the magnitude and even the sign of the net radiative forcing is challenging due to the complex interactions between reforestation, atmospheric chemistry, and climate feedback mechanisms. However, it could result in cooling if the radiative forcing from biogenic SOA cooling outweighs the warming from methane and ozone (Weber et al. 2024).

6. CONTROLLABLE BVOC EMISSIONS

Recognition that BVOCs can interact with anthropogenic pollutants, especially nitrogen oxides, to enhance ozone and SOA formation has driven interest in the impact of BVOCs on air pollution. BVOC influenced ozone and SOA are referred to here as biogenic ozone and biogenic SOA (BSOA). BSOA can be directly associated with BVOCs since the carbon in BSOA can be directly traced to the carbon in BVOC. BVOCs do not directly produce ozone but by impacting ozone sinks they can change ambient ozone concentrations. However, BVOC influence on ozone is complex since they can both increase ozone loss, by reacting with ozone, and decrease ozone loss, by removing ozone sinks, depending on the level of NOx and VOC in the atmosphere.

BVOC impacts on air pollution can be directly and indirectly controlled. Since biogenic ozone and BSOA production are higher in polluted environments compared to pristine conditions, reducing anthropogenic pollution can serve as an indirect control of biogenic ozone and BSOA. The direct control approach involves reducing BVOC emissions into the atmosphere. These approaches are discussed below along with potential strategies for managing BVOC impacts on air pollution.

6.1. INDIRECT CONTROL

Radiocarbon C14 measurements (Lewis et al. 2004) and molecular tracers of BVOC oxidation products (e.g., Kleindienst et al. 2007) in aerosols have shown that the BSOA contribution to total SOA can exceed 50%, especially in summertime, even in urban areas. If all biogenic SOA and ozone are considered natural constituents of the atmosphere, they might be viewed as background components that cannot be regulated. However, Carlton et al. (2010) argue that this assumption can hinder effective air quality management since BVOCs do not increase ozone and SOA production to the same degree in a clean environment. While a fraction can be considered a natural background level, the remainder can be mitigated by controlling anthropogenic emissions.

Although the controllable fraction of biogenic ozone and SOA cannot be directly measured, regional air quality model simulations can estimate this quantity. Carlton et al. (2010) showed this with a series of model simulations in the eastern U.S. and found that more than half of the BSOA can be removed when controllable anthropogenic emissions are eliminated. They reported that this indirectly controllable BSOA was most sensitive to reductions in primary carbonaceous particulates and oxides of nitrogen. Primary particulate matter provides organic material for condensable semi-volatile species, while oxides of nitrogen increase oxidant levels.

While the indirect control of biogenic ozone and BSOA may not be explicitly implemented into regulatory frameworks, it is inherently considered by air quality management efforts that use 3D numerical air quality models, which include accurate estimates of biogenic VOC emissions. This approach involves developing effective air pollution mitigation strategies to meet required ozone and SOA target levels by reducing anthropogenic emissions while accounting for the representative ambient level of BVOCs.

6.2. DIRECT CONTROL

While indirect control of BVOC emissions occurs through air quality management strategies based on the results of numerical models that include BVOC emissions, direct control is not considered as a regulatory strategy. Direct control would be

the active reduction of total BVOC emissions in a region by either reducing the amount of vegetation, replacing high-emitting species with low-emitting ones, or decreasing the emission activity of existing vegetation. Reducing the amount of vegetation is unnecessary and could be counterproductive since vegetation uptake of air pollutants reduces pollution. However, replacing vegetation or modifying emission activity could be considered in managed landscapes, although this approach may be controversial due to the perception that BVOC emissions are natural components of the Earth System and should not be controlled. While this is a valid argument for natural ecosystems, BVOC emissions are already being managed in landscapes in urban and agricultural areas, though not specifically for air quality.

Mature cannabis plants have high BVOC emissions, especially terpenes, and their cultivation has been rapidly expanding, including in some areas that exceed allowable limits of ambient ozone or SOA (Wang et al. 2019, Samburova et al. 2019, MetroVancouver 2023). For example, Wang et al. (2019) showed that the expansion of cannabis cultivation around Denver, Colorado, could increase daytime ozone pollution. These results led air quality agencies to consider the possibility of directly controlling BVOC emissions for air quality purposes (e.g., Public Health Ontario, 2018; Denver Public Health and Environment, 2018; MetroVancouver 2023) and fund studies to quantify cannabis emissions (e.g., Urso et al. 2023). de Ferreyro Monticelli et al. (2022) describe the best available technology, such as carbon scrubbers, that can be used to effectively remove BVOCs from the air within indoor greenhouse cannabis production facilities, but this would not be a solution for outdoor cultivation. An example of efforts to directly control BVOC emissions is the incorporation of BVOC emission characteristics into tree selection guides that describe the benefits and disadvantages of various tree traits (e.g., https://selectree.calpoly.edu/). These traits include pollen allergens, which have been the focus of longstanding efforts to control air quality by managing tree characteristics. Other tree selection considerations include other health concerns, such as falling branches and toxic compounds, as well as infrastructure impacts such as power and water lines and sidewalks. In addition to these considerations of BVOC regulation in North America, there is also a growing interest in BVOC emission regulation by the scientific community in Europe (e.g., Rosenkratz et al. 2015) and Asia (e.g., Zhang et al. 2024a).

Sawers (2019) indicates that increasing awareness has had little impact on pollen emissions, and it is unlikely that merely providing information will significantly reduce urban BVOC emissions. Increasing prices through taxes, fees, or cap-and-trade systems is an approach used to regulate CO_2 emissions (e.g., Rickels et al. 2021). However, Sawers (2019) argues that this would not be the best approach for managing BVOC emissions since tree selection is unlikely to be very price sensitive. Instead, Sawers (2019) concludes that a mandate banning high BVOC-emitting trees is the most appropriate approach. Since governments already restrict the planting of certain tree species based on other undesirable traits, restricting high-emitting trees would be an extension of this practice.

Opportunities for direct control of BVOC emissions also exist in managed landscapes outside of urban areas (e.g., Trail et al. 2015). Liu et al. 2024 demonstrate that, in addition to selecting plant species, management practices can modify BVOC emissions from agricultural landscapes. Since ozone management is complex, with BVOCs potentially increasing ozone in NOx-saturated regions but decreasing ozone in NOx-limited regions, any direct control of BVOC emissions would need to consider the environment where the BVOCs are emitted. Any efforts to control BVOC emissions should also consider the differing abilities of plants to take up pollutants and so reduce air pollution. While BVOC impacts on biogenic SOA are more

straightforward, they are still dependent on characterizing and understanding the current atmospheric composition.

Any efforts to directly control BVOC emissions should based on systematic, high-quality measurements of BVOC emission capacities and needs to consider both emissions at standard conditions and under stress. These measurements should be guided by standard operating protocols and quality control and assurance analogous to procedures used for anthropogenic VOC measurements (Simon et al. 2010).

7. UNCERTAINTIES

A quantitative understanding of the uncertainties associated with BVOC emission estimates and their impacts on air quality is necessary for developing optimal air pollution control strategies. This section assesses the uncertainties associated with existing emission model components and discusses efforts to investigate these uncertainties through model intercomparisons. Insights into overall model performance evaluations are provided through comparisons with direct flux measurements and indirect methods using ambient concentrations and inverse models. The impact of these uncertainties on air pollutants are considered through model sensitivity studies. While the focus of this section is on BVOC emission uncertainties, it should be recognized that uncertainties in modeling atmospheric dynamics and chemistry also contribute significantly to overall uncertainties of the impact of BVOCs on air pollution.

7.1. MODEL INTERCOMPARISONS

The differences in BVOC emission model parameters, algorithms, and inputs can provide valuable insights when examining their variations and the resulting impact on emission estimates. For instance, there is nearly a twofold difference between BEIS3.61 and MEGAN2.1 predictions of isoprene emission rates, even though their isoprene emission capacities are based on nearly the same data, and their canopy environment models, and emission activity algorithms are similar. An inspection of each model component showed that the major difference lies in the specific leaf area (SLA) used to convert reported leaf mass emission capacity factors to leaf area emission capacities. MEGAN2.1 used a broadleaf tree SLA of 80 cm^2/g compared to the BEIS3 broadleaf tree SLA of 133 cm^2/g. After accounting for this 66% difference in SLA, the MEGAN2.1 and BEIS3 isoprene emission factors agree within 13%. SLA varies by more than 60% for different North American broadleaf isoprene-emitting genera (Berner and Law, 2016; Geron et al., 2001; He et al., 2000; Winters et al., 2009; Harley et al., 1996, 1997; Eller et al., 2012; Ortega et al., 2010; Wang et al., 2024). These studies indicate that Quercus, Eucalyptus, and Salix tend to have lower SLA, similar to the MEGAN2.1 value, while other isoprene-emitting genera tend to have higher SLA values, similar to the BEIS3 values. Also, the MEGAN2.1 SLA are more representative of the sun leaf values at the top of the canopy while the BEIS3 values are more representative of shade leaf values in the lower canopy (Harley et al., 1996, 1997). By reconciling area-based and mass-based emissions data MEGAN and BEIS isoprene emission estimates tend to be within about 20%.

Arneth et al. (2011) designed a study to investigate the variation within and between isoprene emission models by comparing results from three different global BVOC emission models (LPJ, MEGAN, and BVOCEM), using three different climate data sets (CRU for LPJ, NCEP for MEGAN, UM for BVOCEM) and three different vegetation cover data sets (LPJV for LPJ, MEGANV for MEGAN, and SDGVM for BVOCEM). The annual global isoprene emissions estimated by the three models, when each used their own set of climate and vegetation variables, was 446 Tg with a standard deviation of 61 Tg (13%). The impact of swapping climate and vegetation data varied for the different models and was sensitive to the combination of climate and land cover. For example, replacing CRU with NCEP climate in LPJ increased emissions by 28% when vegetation was fixed but only by 3% when using LPJ dynamic vegetation. In contrast, replacing CRU with NCEP decreased MEGAN isoprene emissions by 11% when used with MEGAN vegetation but increased isoprene emissions by 8% when used with LPJ vegetation. Swapping LPJ fixed vegetation for MEGAN vegetation increased isoprene emissions by 67% for LPJ with NCEP climate and 26% for MEGAN with NCEP climate. The change resulting from switching from

NCEP to CRU climate ranged from a 30% increase to a 10% decrease, depending on the model and land cover data used. The different responses to changing climate and vegetation data appear to be due to interactions between emission capacity distributions and the regional patterns of vegetation and climate. Arneth et al. (2011) also found that changes in climate and land cover inputs modified seasonal latitudinal patterns in unexpected ways and concluded that incorporating isoprene emission modules into coupled chemistry-climate models requires careful checking of annual totals, spatial patterns, and seasonal emission patterns. **Figure 9** shows that the Arneth et al. (2011) key finding, that the emission estimate differences associated with input datasets are similar or greater than the differences from the model used, can be extended to other global models and to other compounds including total monoterpenes, acetone, methanol. This means that it is necessary to indicate not only what model was used to estimate BVOC emissions but also what input datasets were used.

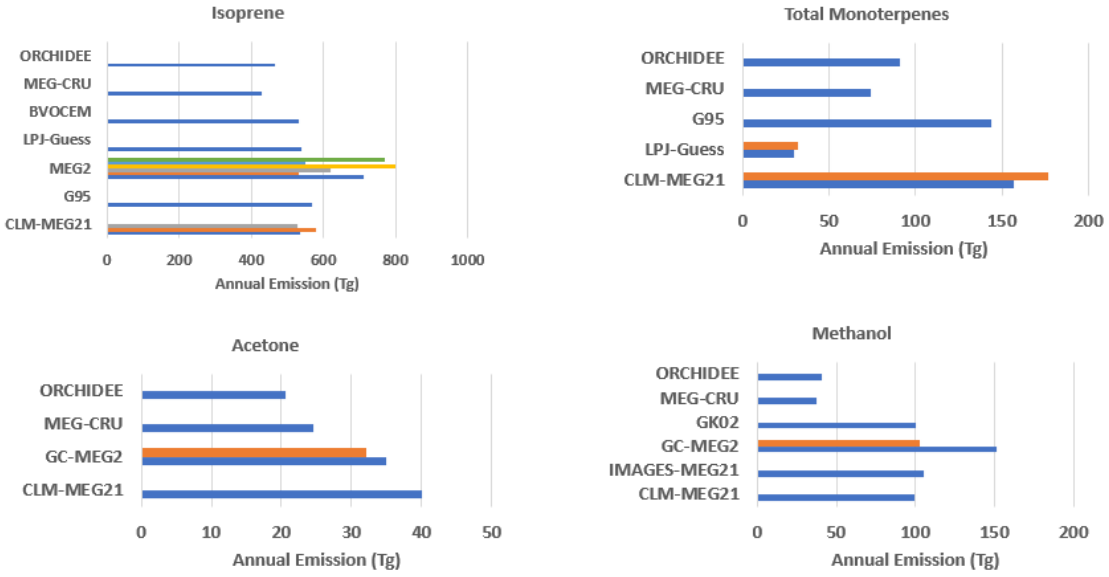


Figure 9 Annual global emissions of isoprene, total monoterpenes, acetone and methanol estimated by various global models and input variables. The different colored bars illustrate results reported by different investigators using the same model but different input data

Most BVOC emission models have a time step of around an hour, but some have much longer ones. Ashworth et al. (2010) demonstrated the need to use hourly time resolution due to the non-linearity of BVOC temperature and light response. Their estimated total global annual emission of isoprene was increased to 766 Tg y^{-1} when using hourly input data compared to 746 Tg y^{-1} for daily average input data and 711 Tg y^{-1} for monthly average input data. They also showed that the impact on a local scale can be more significant, with increases of up to 55% at some locations when using hourly average data compared with monthly data. In comparison to daily and monthly average temperature data used without the imposition of a diurnal cycle, global emission estimates based on hourly data are 43% higher and local annual emissions by up to 56%. These results demonstrate that BVOC emission models should be driven by temperature and solar radiation data resolved to one hour or less.

The choice of canopy environment model can significantly impact estimated BVOC emissions due to BVOC emission responses to light and temperature, which can deviate from ambient values. Guenther et al. (1994) compared leaf-level and branch-level isoprene emissions for the same environmental conditions and found branch-level emissions were 43% lower due to self-shading, which results in lower light and temperature on shaded leaves. Canopy environment models estimate leaf light and temperature conditions for sun and shade leaves at various canopy depths. For example, the MEGAN2.1 canopy environment model predicts canopy average isoprene emissions that are 64% lower than the emissions expected for above-canopy conditions. This result is based on a weighted average of 28.2% sun leaves, which are 20% lower than for above canopy conditions, and 71.8% shade leaves, which are 81.5% lower than for above canopy conditions. The average sun leaf emission is lower than a leaf perpendicular to direct beam sunlight because it is assumed that they are at an average angle of 60° to the sun's direct beam. In comparison to MEGAN2.1, the CLM4 and BEIS4 canopy environment models calculate light and temperature conditions that result in isoprene emissions that are 16% higher for CLM4 and 16% lower for BEIS4. Bash et al. (2016) compared the MEGAN2.1 and BEIS3.61 leaf temperature estimates with observations and found that the canopy top temperature estimated by BEIS3.61 and MEGAN2.1 compared well with observations.

Considering the significant uncertainties associated with isoprene emission estimates, Arneth et al. (2008) highlighted a notable consistency among 15 annual global isoprene emission estimates published from 1995 to 2007, with a standard deviation of only 11% of the mean value. They concluded that this convergence was not the result of an accurate understanding of isoprene emissions but indicated that emission capacities are unknown for most global biomes, and these global modeling studies all followed the same approach by assigning the emission capacities reported by Guenther et al. (1995). However, if the models all used the same emission capacities, then the emissions should differ due to different climate and land cover data as shown by Arneth et al. (2011). The consistency in estimated annual global emissions indicates that emission capacities may have been adjusted to get the same annual global total.

7.2. EMISSION MODEL UNCERTAINTIES

Lamb et al. (1987) used propagation of uncertainties from individual model components to estimate the total uncertainty of their U.S. annual BVOC emission estimate. The individual components included emission rate measurements, the emission activity algorithm used to account for variations in environmental conditions throughout the year, and the biomass densities and land use distributions used to extrapolate the emissions. They concluded that the dominant error was associated with the emission activity model, which only considered temperature and had a scatter of about a factor of three. The other individual uncertainties were smaller, resulting in a total uncertainty of about a factor of three, which corresponds with a total uncertainty range of about an order of magnitude. Other regional BVOC emission modelers have suggested uncertainties of a factor of four for Great Britain (Stewart et al. 2003) and a factor of three to five for Europe (Simpson et al. 1999). Guenther et al. (1995) assessed the uncertainties of relatively well-studied BVOCs, such as isoprene and monoterpenes, in well-studied landscapes like temperate forests in the U.S. and Europe, to be at least a factor of three, but higher for other BVOCs and landscapes like tropical forests. Guenther et al. (1999) estimated BVOC emission uncertainties of a factor of two for regions where ground measurements of model inputs are available and more than a factor of five for locations without available ground measurements.

Most assessments of BVOC emission model uncertainties are qualitative estimates, generally falling in the range of a factor of three to five for regional totals. Several studies have conducted more quantitative assessments using Monte Carlo approaches, which quantify the uncertainties related to each model parameter and then propagate them while running the model. For example, Smiatek and Bogacki (2005) assessed BVOC emission model estimates driven by land cover, temperature, light intensity, foliar biomass, LAI, and plant-specific emission factors. They created a probability distribution function for each of these driving variables. They estimated BVOC emission uncertainties of −71% to +73% for isoprene, −57% to +140% for monoterpenes, and −55% to +57% for other VOCs when averaged over the entire domain and modeling period. Uncertainties were higher for specific locations and times, such as for daily estimates, due to the lack of averaging. They found that the largest individual uncertainty was associated with emission factors, followed by individual uncertainties for temperature and foliar biomass. They pointed out that these are only the known uncertainties and do not include all possible variables and factors, thus underestimating the total uncertainty. Hanna et al. (2005) used a similar Monte Carlo probabilistic approach and determined uncertainties of a factor of three for isoprene, but only ±20% for monoterpenes and other VOCs. The lower uncertainty estimates for monoterpenes and other VOCs are unexpected given the greater certainty of isoprene emissions compared to monoterpenes and other VOCs but can be understood as the result of a lack of robust estimates of uncertainty associated with each model component. The results are a reminder that this uncertainty estimation approach can only account for uncertainties in the known driving variables. A large part of the total uncertainty is associated with knowledge gaps that cannot be quantified since they are still unknown.

7.3. MODEL PERFORMANCE

Model intercomparisons and sensitivity studies are valuable for their insights into BVOC emission model uncertainties, but model performance assessments require observations to determine the accuracy of landscape-scale BVOC emission estimates. The flux measurement techniques described in **section 2.3** provide a means of directly quantifying the accuracy of BVOC emission estimates. Since these measurements are available for relatively few locations, assessing BVOC emission models for most of the world requires the use of indirect approaches that use measurements of the distributions of atmospheric concentrations of BVOC or the products of BVOC oxidation. These ambient concentrations are related to BVOC emissions through inverse modeling approaches that require a quantitative understanding of atmospheric chemistry and dynamics processes.

These observations demonstrate that there is a large amount of variability that cannot be explained but it tends to balance out and averages tend to agree. In this section we summarize efforts that have been made to assess BVOC emission estimates using these approaches.

7.3.1. Eddy flux measurements

The eddy flux sampling platforms described in **section 2.2** include tower and aircraft-based systems. Aircraft flux systems have characterized BVOC fluxes along flight paths that together total tens of thousands of kilometers while tower flux systems have monitored canopy-scale BVOC emission variations over tens of thousands of hours. The techniques are described in **section 2.3** and the results, and their application for quantifying model performance, are summarized in this section.

Eight airborne BVOC eddy flux measurement studies have been conducted in Africa, Europe and North America in urban, agricultural and rural landscapes and the results are summarized in **Table 2**. Two studies were completed in 1996 using the REA approach and six studies were conducted from 2011 to 2021, using the PTRMS eddy covariance technique. The eight studies were conducted using seven different research aircraft including four from the US and one each from Canada, France and the UK. This demonstrates that BVOC eddy flux measurements can be made on a wide range of research aircraft (De Havilland Twin Otter, Fokker 27, Douglas DC 8, Lockheed C-130, Dornier 228, Gulfstream 1) but also shows that the successful demonstration of a BVOC eddy flux measurement capability does not ensure that a research aircraft will continue to take advantage of the new capability since only one aircraft was used for two studies and the rest were used for only one study. Five of the aircraft flux efforts were part of integrated regional studies (BOREAS, EXPRESSO, SAS, GOAMAZON) that combined multi-scale measurements and modeling by international teams of investigators targeting a wide range of scientific questions. In each case, the BVOC eddy flux aircraft was a facility funded by the agency that also funded the integrated regional study. The other three studies were conducted for the purpose of assessing landscape scale VOC and NOx emissions. Both integrated regional studies and targeted emission assessment studies have the potential to extend the currently limited amount of aircraft flux data available for evaluating BVOC emission model performance. While earlier studies could only measure isoprene fluxes, and in some cases total monoterpenes, Pfannerstill et al. (2023a) demonstrated that the latest generation of PTRMS systems can measure airborne fluxes of a wide range of biogenic and anthropogenic VOC which greatly expands the utility of these measurements. In addition, the utilization of these data for model performance evaluation would be greatly enhanced if these data were more easily accessible by the BVOC emission modeling community.

Table 2 Airborne BVOC flux measurements

Continent	Ecosystem	Compounds	Flux (mg m^{-2} h^{-1})	Approach	Reference
N. America	Boreal aspen forest	isoprene	3.3	REA	Zhu et al. 1999
N. America	Boreal black spruce forest	isoprene	1.3	REA	Zhu et al. 1999
Africa	Tropical semideciduous forest	isoprene	0.89	REA	Greenberg et al. 1999
Africa	Tropical degraded woodland	isoprene	0.57	REA	Greenberg et al. 1999
N. America	30 Temperate and Medit. ecosystems	isoprene	< 1 to 15	PTRMS eddy covariance	Misztal et al. 2014, 2016
N. America	Temperate deciduous forest	Isoprene	8	PTRMS eddy covariance	Wolfe et al. 2015
N. America	14 Temperate forest and agricultural landscapes	Isoprene	2.3 to 7.9	PTRMS eddy covariance	Yu et al. 2017

N. America	14 Temperate forest and agricultural landscapes	Total monoterpenes	0.45 to 1.3	PTRMS eddy covariance	Yu et al. 2017
S. America	Tropical forest	Isoprene	6.2 to 12.9	PTRMS eddy covariance	Gu et al. 2017
Europe	Urban forest	Isoprene	0.48 to 0.74	PTRMS eddy covariance	Vaughn et al. 2017
Europe	Urban forest	Total monoterpenes	0.12 to 0.16	PTRMS eddy covariance	Vaughn et al. 2017
N. America	Urban	isoprene	0.7	PTRTOFMS eddy covariance	Pfannerstill et al. 2023a
N. America	Oak woodlands	Isoprene	0.73	PTRTOFMS eddy covariance	Pfannerstill et al. 2023b
N. America	Urban	Total monoterpene	0.8	PTRTOFMS eddy covariance	Pfannerstill et al. 2023a
N. America	Oak woodlands	Total monoterpene	0.24	PTRTOFMS eddy covariance	Pfannerstill et al. 2023a

Zhu et al. (1999) results for two Canadian Boreal Forest ecosystems are within a factor of two of MEGAN2.1 estimates for these locations, and they confirmed the model predictions that aspen stands have higher isoprene emissions than black spruce. Aircraft REA flux measurements in two African landscapes (Greenberg et al. 1999) were also within about a factor of two agreement with an earlier version of MEGAN (Guenther et al. 1999). Misztal et al. (2014, 2016) measured isoprene fluxes over about 30 different Californian ecosystems along ~10,000 km of flight paths and found the observed fluxes were within ~20% of MEGAN2.1 predictions in most ecosystems but the differences for some landscapes were much higher. Isoprene fluxes measured over a U.S. temperate deciduous forest by Wolfe et al. (2015) were ~40% lower than the predictions of the GEOS-Chem-MEGAN BVOC emission model. Yu et al. (2017) used PTRMS eddy covariance to measure isoprene and total monoterpene fluxes from fourteen forest and agricultural landscapes in the Southeastern U.S. and found that the observed isoprene emissions were within 20% of MEGAN2.1 for the high isoprene landscapes dominated by oaks but were about a factor of two lower for pine plantations where the isoprene emitting species are in the shaded understory. Their observed monoterpene emissions agreed with MEGAN2.1 in landscapes dominated by pine plantations, which are relatively high monoterpene emitters, but were more than a factor of three higher than model estimates for landscapes dominated by oaks and other broadleaf trees that are considered relatively low monoterpene emitting trees. Gu et al. 2017 aircraft isoprene fluxes measured over Amazonian tropical forest landscapes were about a factor of two higher in the dry season than in the wet season and were also about a factor of two higher for upland forests compared to lowland forests. The observed emissions were about 35% higher than MEGAN2.1 model predictions. Airborne PTRMS eddy covariance measurements conducted over an urban forest near London confirmed that isoprene and total monoterpene emissions were lower with cooler and cloudier conditions (Vaughn et al. 2017). They also compared their measurements with predictions of the UK regional application of the European Monitoring and Evaluation Programme model (EMEP4UK) and found that the model underpredicted the observed emissions by about 50%. Pfannerstill et al. (2023a, b) measured fluxes of a much wider range of VOC emitted from woodlands, croplands and urban landscapes. They compared BVOC fluxes with BEIS and MEGAN, using

updated landcover, and found that the isoprene emissions from oak woodlands were similar to the estimates of BEIS and MEGAN, in agreement with the previous aircraft flux study by Misztal et al. (2014, 2016). Both models overestimated isoprene and sesquiterpenes from croplands by a factor of three or more. Modeled monoterpene emissions were within a factor of 2 but were overestimated for croplands and underestimated for citrus plantations. Both models overestimated isoprene by less than a factor of two in the urban area and underestimated monoterpene and sesquiterpene emissions by a factor of three or more. Overall, these eight regional aircraft BVOC flux studies suggest that emission models can estimate isoprene fluxes within a factor of two but uncertainties in monoterpenes and sesquiterpenes are a factor of three or more.

Tower-based eddy covariance systems have been used to assess model simulations of diurnal (e.g., Loubet et al. 2022), daily (e.g., Fares et al. 2013), seasonal (e.g., Seco et al. 2022) and interannual (Presseley et al. 2006, Seco et al. 2015) BVOC emission variations. Most of these studies show that the model short-term light and temperature response algorithms can simulate diurnal variations in isoprene and monoterpene emissions although there is some evidence that circadian rhythms should also be accounted for (Hewitt et al. 2012). Daily variations are typically better simulated when longer-term (one to 10 days) light and temperature response algorithms are included in the model (e.g., Fares et al. 2013). Seasonal variations are not fully captured by light and temperature algorithms and other factors, such as phenology, need to be considered and likely differ among biomes (Alves et al. 2023). The limited observations of interannual variations indicate that there are long-term processes that are not represented in BVOC emission models (e.g., Presseley et al. 2006, Seco et al. 2013).

Tower flux studies using eddy covariance and REA have also been used to measure ecosystem average emissions of isoprene, monoterpenes, methanol and other BVOC and used to assess bottom-up emission model estimates, based on leaf enclosure surveys and landcover distributions, including both regional to global model default values and estimates using site specific observations (e.g., Wohlfahrt et al. 2015, Sarkar et al. 2020). These tower flux data have also been used to parameterize the emission capacities used in models (e.g., Unger et al. 2013, Langford et al. 2017)

7.3.2. In situ concentration measurements of BVOC and their products

Ambient concentration measurements of BVOC and their oxidation products are useful for constraining BVOC emission estimates, but it is important to recognize that they are a function of all the relevant controlling processes including emissions and deposition, chemical production and losses, transport and dispersion. They can be used to assess the BVOC emissions only if the chemical and dynamical processes are relatively well constrained. This is often not the case and these studies are limited to placing total constraints on an emission, chemistry and transport model that is still useful for identifying overall discrepancies and providing insights into the sum of all the controlling factors. The concept that ambient BVOC concentrations can be used to characterize BVOC emissions and impacts on air pollution was presented by Dimitriades (1981) more than four decades ago. At that time, discrepancies between high emissions data and low ambient concentration measurements led some researchers to conclude that BVOC emission estimates are inaccurate, and these emissions were too low to contribute significantly to photochemical air pollution. However, comparisons of model and observed surface layer BVOC concentrations are difficult to interpret because of subgrid scale emission heterogeneity and because models may not accurately simulate transport from the surface to the above atmosphere resulting in high uncertainties in surface layer concentrations (Wiedinmyer et al. 2005). Mixed layer BVOC concentrations,

sampled from tall towers, tethered balloons, drones and aircraft at hundreds of meters above the surface, are less susceptible to errors in dynamical processes and source heterogeneity (Guenther et al. 1996).

Global budget studies can be used to estimate emissions of longer-lived BVOC such as methanol and acetone. Sensitivity studies can be used to identify the factors that contribute the most to the uncertainties in global BVOC budgets and determine whether emissions are the dominant uncertainty. For example, Brewer et al (2017) found that the uncertainty associated with direct emissions of acetone from the terrestrial biosphere is the most important factor in the global acetone budget and Tsigaridis and Kanakidou (2007) identified BVOC emissions uncertainties as a major contributor to the overall uncertainty in the global SOA production budget. These sensitivity studies of budgets can identify major uncertainties and target sources, sinks and processes that need further investigation.

Yu et al. (2023) compared CMAQ/MEGAN simulated BVOC concentrations with ground and NASA DC8 aircraft observations for S. Korea and found that while the results appeared reasonable for isoprene, monoterpenes were underestimated by about a factor of four. They also noted that the first generation isoprene products were underestimated even though isoprene concentrations were reasonably well simulated, suggesting uncertainties in the chemical mechanism.

7.3.3. Satellite measurements of BVOC concentration distributions and products

Space-based measurements of formaldehyde column distributions, which began more than twenty years ago with the Global Ozone Monitoring Experiment (GOME) satellite sensor, enabled an important new capability for mapping seasonal to interannual variations in isoprene emissions (Abbot et al. 2003). Formaldehyde is a major product of isoprene oxidation and can serve as a proxy for isoprene emission in regions dominated by isoprene by estimating the emission required to produce the observed formaldehyde concentration (Mueller et al. 2024). Initial studies (e.g., Palmer et al. 2003) suggested that the GOME isoprene estimates were about 20% lower than the Guenther et al. (1995) model estimates and about 35% higher than BEIS isoprene emission model estimates. Other studies using GOME to constrain isoprene emissions reported varying results that were due largely to the differences in the retrieval approaches (Mueller et al. 2024). The next generation, and higher resolution, Ozone Monitoring Instrument (OMI) formaldehyde data produced more consistent and accurate results for characterizing regional isoprene emission spatial distributions (e.g., Gu et al. 2017) and responses to landcover (e.g., Opacka et al. 2021b), drought (e.g., Opacka et al. 2021a, Wang et al. 2022) and temperature trends (e.g., Bauwens et al. 2016) in regions where there are few or no other available measurements. The recent synthesis of the Ozone Monitoring Instrument formaldehyde data with aircraft and ground based FTIR measurements has now produced a more reliable bias-corrected dataset that differs considerably from earlier versions and is now more in agreement with MEGAN and other BVOC emission model estimates (Mueller et al. 2024). In addition to assessing model output, satellite data are also being used to optimize isoprene emission model parameters (e.g., DiMaria et al. 2023). Fu et al. (2019) describe a more direct approach for quantifying isoprene emissions with satellite-based sensors by using the CrIS infrared sensor for direct retrieval of isoprene columns. Improvements in the spatial and temporal resolution and retrieval accuracy of the CrIS isoprene indicate that these data can provide valuable constraints on daily isoprene emission estimates (Wells et al. 2022). The combination of isoprene data with space-based formaldehyde, ozone and oxides of nitrogen estimate, that are now available at higher spatial resolution from the TROPOMI satellite platform (Oomen et al. 2023),

could be especially effective at characterizing isoprene emission. These capabilities are poised to improve even further with the hourly, <10 km spatial resolution of geostationary satellites monitoring atmospheric composition over Asia, North America and Europe (e.g., Lee et al. 2024).

Stavrakou et al. (2011) extended satellite BVOC measurements to methanol, the second largest BVOC emissions with a flux of about 25% of isoprene, which can be directly measured using the Tropospheric Emission Spectrometer (TES) sensor. Comparisons with MEGAN2.1 suggest the model underpredicts methanol emissions by about 40% (Wells et al. 2013). The production of large quantities of another BVOC, formic acid, from boreal and tropical forests was discovered by Stavrakou et al. (2012) using IASI satellite measurements but it is difficult to determine the relative contributions of direct emissions and secondary production from the atmospheric oxidation of BVOC. Franco et al. (2020) used IASI satellite data to demonstrate that forests are also a source of acetic acid, which is also both a primary emission from vegetation and has a secondary source from atmospheric oxidation.

7.4. MODEL SENSITIVITY STUDIES

Model sensitivity analyses show the impact of uncertainties associated with individual model inputs by examining how changes in inputs impact model outputs. This can be done by increasing or decreasing an input variable by a specified amount or by using alternative sets of inputs. For example, Guenther et al. (2012) compiled a table of global annual emissions for selected BVOC classes (isoprene, total monoterpenes, ß-pinene, methanol, acetaldehyde, and acetone) estimated using combinations of 10 different models, 10 weather datasets, 13 LAI datasets, 11 vegetation type datasets, and 7 emission factor datasets. The results demonstrate that the choice of input data can lead to variations in emissions of about ±50% for land cover data and ±35% for weather data, which is similar or more than the variations associated with the choice of the model.

The highly sensitive light and temperature responses of BVOC emissions require accurate estimates of light and temperature, starting with above-canopy conditions. Weather model predictions often have temperature biases of a few degrees Celsius, which result in a ~30% or more BVOC emission error. While weather model temperatures can be biased high or low, sunlight tends to be biased high due to a lack of accounting for clouds and aerosols. Isoprene and other light-dependent BVOC emissions are sensitive to biases in sunlight conditions but only at low light levels since the isoprene emission increase with light is linear at low light levels but saturates, and stops increasing, at high light levels.

BVOC emissions are also highly sensitive to land cover. Messina et al. (2016) found that global average LAI in the ORCHIDEE dynamic vegetation model is 1.5-2 m^2/m^2 higher than MODIS LAI measurements, which is a difference of about a factor of 2. While the global averages followed a similar seasonal pattern, there were regional differences. They found a 50% decrease in LAI resulted in a 21% decrease in isoprene and a 43% decrease in monoterpenes for ORCHIDEE, while a 50% LAI increase resulted in an 8% increase in isoprene and a 40% increase in monoterpenes. This non-linear response is because sun leaves have much higher emissions than shade leaves so adding more shade leaves to a canopy has only a small impact on emissions. Ma et al. (2023) investigated the impacts of LAI and vegetation in China and found that changing land cover inputs had a larger impact on BVOC emission estimates than using different LAI datasets. Another land cover sensitivity study by Yu et al. (2023) examined the results from three different vegetation cover

distributions for South Korea and found an emission difference of about a factor of two for isoprene and only ~20% for monoterpenes.

The model uncertainty and sensitivity studies described in this section provide insights on the level of accuracy needed for BVOC emission inputs to air quality model simulations under various conditions. The results show that, while there are also significant uncertainties associated with the chemistry and transport processes, BVOC emission estimate uncertainty is a major contributor to overall air quality model uncertainties and this uncertainty must be significantly reduced, especially in regions where ozone is VOC-sensitive, in order to improve the accuracy of air quality model predictions. Air quality model performance evaluations also highlight the difficulties in simulating trends in ozone and particles, including their responses to changes in VOC and NOx emissions (Wu et al. 2023). This underscores the importance of improving quantitative BVOC emission estimates at the scales and locations required for air quality model simulations. Comparisons of different landcover and emission factors for estimating BVOC emissions in Europe have shown that there are differences of about a factor of three difference in emission estimates (e.g., Luttkus et al. 2022).

7.5. KNOWLEDGE GAPS AND LIMITATIONS

More than fifty years after Rei Rasmussen asked, “What do the hydrocarbons from trees contribute to air pollution?” (Rasmussen 1972), over 3000 peer-reviewed journal articles on BVOC emissions research have been published (see Cai et al. 2021). Yet, persistent knowledge gaps and limitations continue to impede progress toward accurate predictions of BVOC emissions and the development of effective photochemical air pollution control strategies. These knowledge gaps include a lack of quantitative understanding of some BVOC emission-controlling processes and their driving variables, as well as potential unknown compounds, sources, and controlling processes. Significant limitations include barriers to obtaining essential observations and the inherent complexity of BVOC sources, compounds, and processes.

While short-term (tens of minutes to hours) responses to light and temperature, which are major factors controlling BVOC emission variations, can often be accurately simulated, other emission activity processes are difficult to represent in models due to high variability among and within plant species. Some of these processes, including longer-term responses (days to years) to light, temperature, soil moisture, CO_2, and leaf age, are included in some BVOC emission models. However, they are based on limited measurements, and substantial differences are seen by various studies. Major knowledge gaps are associated with processes, including many stress responses, which have been demonstrated to be important contributors to BVOC emissions in specific locations and times. The current limited knowledge prevents the development of algorithms that can be applied in a global model. Additionally, unknown knowledge gaps may exist related to sources, compounds, and processes that have not yet been identified as important.

Model comparison and sensitivity studies suggest that differences in model inputs, primarily land cover and weather data, influence BVOC emission model results more than differences in model algorithms and parameters (e.g., emission factors and algorithm coefficients). This is at least partly because BVOC emission models use similar algorithms and parameters. Characterizing land cover and weather conditions is crucial for many Earth System modeling efforts (e.g., biogeochemistry, climate, carbon, energy, and water cycles), but BVOC emissions are even more sensitive to these inputs. For example, temperature sensitivities can result in more than a 15% change per degree K, and emission amount and diversity can vary over

orders of magnitude for different species within the same genus, which is more variable than for other biogeochemical cycles.

BVOC emission capacity measurements, which form the foundation of BVOC emission models, are often not representative of the typical conditions assumed for emission capacities, and there is no robust approach for assessing and synthesizing existing data. This limitation for BVOC emission model development could be mitigated by implementing standardized protocols and quality assurance (e.g., Niinemets et al. 2011), but this will not improve the quality of the existing available data. In recent years, there have been relatively few emission factor studies so most available data is from past decades.

Quantifying BVOC emissions is further complicated by the vast diversity of hundreds of thousands of plant species, thousands of BVOC chemical compounds, and dozens of emission source components (e.g., foliage, stems, roots, microbes) within an ecosystem, each with its own controlling processes. BVOC emission models must balance the explicit representation of each organism, compound, and mechanistic process with necessary simplifications. These simplifications involve lumping chemical species, averaging vegetation (e.g., species, genera, and even broad vegetation types), applying empirical or semi-empirical emission response algorithms, and omitting factors that are either non-essential or lack existing inputs or parameters. Studies have shown that these simplifications can result in large model errors and biases at specific times and locations. Other studies have shown good model performance for specific times and locations, but this does not ensure that the model always performs accurately everywhere and at all times.

All BVOC emission model uncertainties, simplifications, and missing processes need to be rigorously assessed to determine their impact on total mass emission, and more importantly, the total ozone formation potential and SOA production. This can be accomplished through approaches that constrain their total impact, such as landscape-scale tower and aircraft direct eddy flux measurements (see **section 2.3**). These measurements serve as overall constraints on the sum of individual sources (e.g., foliage, flowers, stems, trunks, roots, soil and leaf microbes, minor vegetation species, etc.) that comprise the total flux, including any missing sources. Total OH reactivity, ozone reactivity, and potential aerosol mass measurement techniques (see **section 2.1**) can also be used to assess whether there are missing (unidentified) BVOC compounds or sources that could significantly impact ozone or fine particle production. This could be accomplished through a systematic approach that integrates satellite observations and VOC flux sites, building on the FLUXNET network for the carbon, water, and energy flux research community. This network requires the development of simple, stable, and affordable BVOC landscape-scale flux capabilities as advocated by Rinne et al. (2016) and NASEM (2016).

8. CONCLUSIONS

8.1. BVOC EMISSION ESTIMATES

- Current global annual BVOC emissions are estimated to be about 1000 ± 500 Tg. Isoprene is about half of the total emission and, along with monoterpenes and sesquiterpenes, terpenoids contribute about two thirds of the total emission. The remaining third is dominated by methanol and other light oxygenated VOC (organic acids, aldehydes, alcohols) and stress compounds that can dominate local BVOC emissions at specific locations and times.

- Biogenic sources dominate globally comprising over 85% of total VOC emissions with regional contributions ranging from about 45% in China and Europe to about 90% in Africa and South America. The relative contribution of biogenic sources to total VOC in many urban areas has increased from a few percent in the 1990s to about half of the total at present. BVOC emissions now dominate the OH reactivity, ozone formation potential and SOA yield in some European and North American cities.

- BVOC emission future trends are uncertain, but the current evidence suggests that global isoprene emissions will increase by about 5% per decade and even more in some locations.

8.2. BVOC IMPACTS ON AIR POLLUTION

- Under polluted conditions, model simulations predict increased BVOC emissions can increase ozone by 1 to 10% and fine particles by 5 to 110% can increase ozone and fine particles.

- Given the potential impact of BVOC emissions on air pollution, enhancing the accuracy of BVOC emission simulations is crucial for refining air quality model predictions.

8.3. FUTURE CHALLENGES

- Global input data are not suitable for modeling urban BVOC emissions. Representative inputs require locally specific inputs based on data and tools that are widely available.

- Accurate representation of BVOC emission responses to extreme climate events and land use change are needed to account for expected future changes in emissions. This requires a more mechanistic understanding of BVOC emissions.

- A quantitative understanding of the factors controlling BVOC emissions, including disturbance and other stresses, is needed to characterize BVOC emission factors

8.4. OPPORTUNITIES

- Advances in satellite observations and aircraft eddy -flux techniques provide exceptional capabilities for investigating regional to global and long-term variations.

- Improved methods for measuring total OH reactivity, ozone reactivity, and potential aerosol may enable constraints for identifying missing BVOC and lower cost approaches for widespread comprehensive VOC characterization.

- BVOC emission reductions in managed landscapes could be a component of air quality management strategies. This should be accomplished by maintaining or increasing the total vegetation cover fraction while reducing the average emission rate.

- Regulatory agency interest in reliable BVOC emission factors and algorithms could initiate high quality, systematic measurements using standard operating procedures and quality control.

- The existing global flux tower network for carbon, water and energy fluxes could be extended to include long-term BVOC emission measurements.

9. ACRONYMS

ε is the emission capacity at a certain set of conditions

γ is the emission activity factor

ATTO: Amazon Tall Tower Observatory

AVOC: anthropogenic volatile organic compound

BEIS: Biogenic Emission Inventory System

BEIS3.61: Biogenic Emission Inventory System version 3.61

BOREAS: Boreal Ecosystem-Atmosphere Study

BSOA: Biogenic secondary organic aerosol

BVOC: biogenic volatile organic compound

BVOCEM: biogenic volatile organic compound emission model

C2: hydrocarbon with 2 carbons

C3: hydrocarbon with 3 carbons

C4: hydrocarbon with 4 carbons

C14: radioactive carbon isotope

CAMx: comprehensive air quality model with extensions

CARB: California Air Resources Board

CB4: Carbon bond mechanism version 4

CB05: Carbon bond mechanism version 5

CB6: Carbon bond mechanism version 6

CESM: Community Earth System Model

CGLS: Copernicus Global Land Service

CIMS: Chemical Ionization Mass Spectrometer

CLM4: Community Land Model version 4

CMAQ: Community Multiscale Air quality modeling system

CO_2: carbon dioxide

CrIS: Cross-track Infrared Sounder

CRU: climatic research unit

CTM: chemistry and transport models

CWE: carbon, water and energy

DC8: Douglas DC-8 aircraft

EC: eddy covariance

EMEP4UK: European Monitoring and Evaluation Programme model applied to the UK

ESAWC: European Space Agency World Cover

EXPRESSO: Experiment for regional sources and sinks of oxidants

FID: flame ionization detector

FIS: Fast isoprene sensor

FLUXNET: Flux tower network

FT-IR: Fourier transform infrared spectroscopy

GC: gas chromatograph

GECKO-A: Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere

GEIA: Global Emissions Inventory Activity

GEMS: Global Environmental Monitoring System

GEOS-Chem: Goddard Earth Observing System chemistry model

GOAMAZON: Green Ocean Amazon field study

GOME: Global Ozone Monitoring Experiment

LAI: leaf area index, m^2 m^{-2}

LPJ: Lund-Potsdam-Jena model

LPJV: Lund-Potsdam-Jena model vegetation

MCM: Master Chemical Mechanism

MEGAN2.1: Model of Emissions of Gases and Aerosol from Nature version 2.1

MEGANV: Model of Emissions of Gases and Aerosol from Nature version 2.1 vegetation

MODIS: Moderate Resolution Imaging Spectroradiometer

MS: Mass spectrometry

MUSICA: Multi-Scale Infrastructure for Chemistry Modeling

NAPAP: National Acid Precipitation Assessment Program

NAQPMS: Nested Air Quality Prediction Modeling System

NASA: National Aeronautics and Space Administration

NCEP: National centers for environmental prediction

NOx: Oxides of nitrogen (NO plus NO2)

NRC: National Research Council

OFP: ozone formation potential

OH: hydroxyl radical

OMI: Ozone Monitoring Instrument

ORCHIDEE: Organising Carbon and Hydrology In Dynamic Ecosystems model

PFT: Plant Functional Type

PhD: Doctor of Philosophy

PID: photo ionization detector

ppb: parts per billion

PTRMS: Proton Transfer Reaction Mass Spectrometer

PTR-QMS: Proton Transfer Reaction- Quadrupole Mass Spectrometer

PTR-TOFMS: Proton Transfer Reaction -Time of Flight Mass Spectrometer

Q: Amount of foliage

RACM: regional atmospheric chemistry mechanism

REA: relaxed eddy accumulation

SAPRC07: California Statewide Air Pollution Research Center mechanism version 2007

SAPRC11: California Statewide Air Pollution Research Center mechanism version 2011

SDGVM: Sheffield Dynamic Global Vegetation Model

seBVOC: semi empirical biogenic volatile organic compound

SLA: specific leaf area

SOA: secondary organic aerosol

SOAP: secondary organic aerosol production

TOFMS: Time-of-flight mass spectrometry

TROPOMI: TROPOspheric Monitoring Instrument

UAV: unmanned aerial vehicles

UM: Unified Model

USEPA: United States Environmental Protection Agency

VOC: volatile organic compound

WRF-chem: Weather research and forecasting with chemistry

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