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Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer

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Abstract

Biogenic volatile organic compounds (BVOCs) were measured on tethered balloon platforms in 11 deployments between 1985 and 1996. A series of balloon sampling packages have been used to describe boundary layer dynamics, BVOC distribution, chemical transformations of BVOCs, and to estimate BVOC emission rates from terrestrial vegetation. Measurements indicated a slow decrease of concentration for BVOCs with altitude in the mixed layer when sampling times were greater than average convective turnover time; surface layer concentrations were more variable because of proximity to various emission sources in the smaller surface layer footprint. Mixed layer concentrations of isoprene remained fairly constant in the middle of the day, in contrast to canopy-level isoprene concentrations, which continued to increase until early evening. Daytime emissions, which increase with temperature and light, appear to be balanced by changes in entrainment and oxidation. Daytime measurements of methacrolein and methyl vinyl ketone, reaction products of the atmospheric oxidation of isoprene, showed fairly constant ratio to each other with altitude throughout the mixed layer. BVOC emission flux estimates using balloon measurements and from the extrapolation of leaf level emissions to the landscape scale were in good agreement. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Biogenic emissions; Isoprene; Terpenes; Tethered balloon; Atmospheric boundary layer

1. Introduction

The composition of the Earth's atmosphere is largely a product of biological activity at the surface (Brasseur

et al., 1998). Over 90% of the total volatile organic compounds (VOCs) entering the atmosphere are biogenic. A balance in the chemical composition has been maintained, at least until recently, by interactions between the biosphere and the atmosphere.

Many BVOCs, especially isoprene and terpenes from terrestrial vegetation, are relatively reactive in the atmosphere. The initial atmospheric reaction products of these

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BVOCs are also very reactive. Most measurements of primary and secondary BVOCs have been made at the surface and may be biased by nearby emission and deposition processes.

The estimation of biogenic emissions from terrestrial vegetation has followed several approaches. Direct measurements of emissions from leaves or branches have been used to establish emission factors for individual species, which are later extrapolated using species distribution data to estimate area emissions (Geron et al., 1994; Guenther et al., 1996b). Tower-based measurements using gradient or eddy covariance techniques have provided flux estimates on scales of several hundreds of meters from the tower (e.g. Guenther et al., 1996b). While good success has been achieved at the leaf level in understanding the environmental factors which control those emissions, the extrapolation of leaf level measurements to landscapes requires exhausting detail in landscape characterization and monitoring of environmental variables. This is achievable in some landscapes where species diversity is small, but it is extremely difficult in areas not well characterized or where species diversity is high (e.g. tropical forests). Also, while tower flux measurement techniques have been successful, the extrapolation of tower emission fluxes to landscapes is difficult for some of the same reasons. Tethered balloon measurements have a footprint on the landscape scale and integrate the contributions from the variety of emitting species in the footprint. Detailed characterization of the landscape is not necessary for emissions estimates.

This paper describes a series of experiments using tethered balloon sampling systems to measure BVOCs in the atmospheric boundary layer. These experiments began with the NASA Amazon Boundary Layer Experiment in 1985 and continued at various US landscapes through 1996. During this time there has been adaptation and refinement of tethered balloon sampling techniques to more adequately investigate biogenic emissions, their distribution in the atmospheric boundary layer, the chemistry of BVOCs, and boundary layer meteorology.

2. Experimental

2.1. Balloon sampling systems

The development of the tethered balloon sampling platform is summarized in Table 1. The initial tethered balloon sampler (TS1), deployed in the 1985 Amazon Boundary Layer Experiment (ABLE 2a), consisted of a single package which collected samples into four Teflon bags by way of separate sampling pumps. The sampler was attached to the tether line several meters below the balloon. The balloon was raised or lowered to the

Table 1
History of tethered balloon deployments described in this manuscript

| Experiment | Tethered sampler revision no. | Sample container | Sampling sequence | Sampling period (min.) | Samplers in profile | BVOCs ^a | Balloon (m ³) | Samples/package | Weight (kg) | Flow control | Sequence control |
|---------------------|-------------------------------|------------------|-------------------|------------------------|---------------------|---------------------------|---------------------------|-----------------|-------------|--------------|------------------|
| Amazon (1985) | TS1 | Bag | Sequential | 2 | 4 | I, MT | 26 | 4 | 5 | No | Radio |
| Scotia (1988) | TS2 | Bag | Sequential | 3 | 4 | I, MT | 7 | 4 | 3 | No | Radio |
| ROSE (1990) | TS3 | Bag | Simultaneous | 15 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| Metter (1991) | TS3 | Bag | Simultaneous | 15 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| Oak Ridge (1992) | TS3 | Bag | Simultaneous | 30 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| Coweeta (1993) | TS3 | Bag | Simultaneous | 30 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| Temple Ridge (1993) | TS3 | Bag | Simultaneous | 30 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| Rhinelander (1993) | TS3 | Bag | Simultaneous | 30 | 3–5 | I, MT | 7 | 1 | 0.5 | No | Timer |
| La Copita (1994) | TS3 | Bag | Simultaneous | 30 | 3–5 | I, MT | 3&7 | 1 | 0.5 | No | Timer |
| Oak Ridge (1995) | TS4 | Bag or Cartridge | Simultaneous | 30 | 3–5 | I, MT, OVOCs ^b | 100 | 1 | 0.6 | Yes | Timer |
| Pittsboro (1996) | TS5 | Cartridge | Simultaneous | 30 | 4–7 | I, MT, OVOCs | 100 | 4 | 2.5 | Yes | Micro-computer |

^a I: isoprene; MT: monoterpenes.

^b OVOCs: oxygenated VOCs produced from the atmospheric oxidation of isoprene.

sampling level, a 2-min sample was collected, then the balloon was raised or lowered to the next sampling level. The package was attached to the tether line by a mechanism that allowed it to rotate freely to orient into the wind (subsequent revisions of the attachment system also allowed the packages to rotate freely). The sampling sequence (bag selection, pump on/off) was radio controlled. The sampling package weighed approximately 5 kg and was deployed with a 26 m³ balloon. Bag samples were pumped into electropolished stainless-steel canisters and returned to the laboratory for analysis.

A revised sampler (TS2) was used in 1988. The weight of the package was reduced to approximately 3 kg by using one sampling pump and a stream selection valve to direct the sample flow to one of four Teflon sample bags. The lighter sampler allowed the use of a smaller balloon (7 m³). The sampler was attached to the tether line several meters below the balloon. Samples were collected sequentially in a radio-controlled sequence.

A completely revised sampler (TS3) was used in 1990. Individual bag samplers were deployed at various altitudes along the tether line to allow for the simultaneous sampling of the VOC profile. Each package consisted of a timer (for sample on/off control), pump and sample bag. Individual packages weighed approximately 500 g and up to 4 were deployed simultaneously. Sampling times were extended to 15 min. This sampler configuration was used in campaigns through 1994.

The tethered balloon sampler (TS4) was modified in 1994. A flow-controlling pump was installed. This enabled sampling onto solid adsorbent cartridges, which increased the number of VOCs which could be measured. Some samplers were used to collect samples into Teflon bags, so that comparisons with cartridge samples could be made.

The sampling package was completely revised (TS5) for the 1996 experiment. An on-board datalogger-micro-computer was used to control sampling sequence for four cartridges manifolded on each sampler. A flow sensor was installed downstream of the sample cartridges to measure preset flows. A pressure sensor was included to record the true sampling altitude. (Previously, packages had been placed at selected positions along the tether line, which was marked every 50 m. Wind speed, turbulence, free lift, etc., often affected the shape of the tether line, leading to large uncertainties in the sampling altitude.) Additional sensors on TS5 recorded temperature and humidity continuously during sampling. The four-cartridge samplers greatly increased the number of profiles that could be collected, since balloon ascents to and descents from 1 km require approximately 30 min.

2.2. Trace gas collection

Most balloon samples have been collected in Teflon bags (Zimmerman et al., 1988; Andronache et al., 1994;

Guenther et al., 1996a, b). The bags are lightweight and inexpensive. Precise measurement of sampling volumes is not necessary, since an accurately determined volume of an aliquot of the sample collected (10–20 ℓ) is analyzed later. Sample bags have several negative qualities: they are difficult to clean, prone to leaks, and contribute some sampling artifacts. Sampling onto solid adsorbents offers a few advantages: collection and recovery of isoprene, terpenes, and isoprene oxidation products, such as methacrolein (MACR) and methyl vinyl ketone (MVK), are quantitative; adsorbents are easily cleaned; the adsorbent cartridges are more durable and smaller than bags. Samples may be stored on the cartridge, whereas samples from Teflon bags must be analyzed immediately or transferred to a storage medium (canister, cartridge).

On several flights during the 1995 Oak Ridge deployment, we compared, by simple linear regression analysis, bags and cartridge samples collected simultaneously at the same altitude (15 sample pairs). For isoprene, the correlation between cartridge and bag samples collected simultaneously was very good ($r^2 = 0.91$; $[\text{isoprene}]_{\text{bag}} = 0.94 * [\text{isoprene}]_{\text{cartridge}}$). The comparison of bag and cartridge results for α -pinene was fair ($r^2 = 0.58$; $[\alpha\text{-pinene}]_{\text{bag}} = 0.66 * [\alpha\text{-pinene}]_{\text{cartridge}}$) and may indicate incomplete recovery of terpenes from the teflon bag. This may imply that concentrations (and fluxes) for terpenes previously reported for bags may be underestimates. However, this comparison should be repeated more carefully.

The results for MACR and MVK were poor: ($[\text{MACR}]_{\text{bag}} = 0.22 * [\text{MACR}]_{\text{cartridge}}$, intercept 0.6 ppb, $r^2 = 0.22$ and $[\text{MVK}]_{\text{bag}} = 0.71 * [\text{MVK}]_{\text{cartridge}}$, intercept 1.0 ppb, $r^2 = 0.71$). The slope may indicate that MACR and MVK were not completely recovered from bag samples, whereas the intercept may also indicate that MACR and MVK were not completely resolved chromatographically from bag artifacts.

2.3. Trace gas analysis

Analytical details and techniques used for the analysis of BVOCs Teflon bag air samples have been described previously (Greenberg and Zimmerman, 1984; Zimmerman et al., 1988; Greenberg et al., 1993). The introduction of solid adsorbent sampling in 1995 required the development of additional techniques for sample collection and analysis.

Cartridge samples were introduced onto the chromatographic columns using an automated inlet system (Greenberg et al., 1994; Helmig and Greenberg, 1994). In the 1995 experiment (Helmig et al., 1998), cartridges were purged in the forward (sampling) direction 5 min with ultra-high purity helium at 30 ml min⁻¹ to remove adsorbed water (which may cause analytical problems, such as cryo-focusing trap or column freeze-up or flameout on the FID). The purge time was reduced to 2 min for

analyses in the 1996 experiment. The sample cartridge was heated rapidly from room temperature to 275°C and the adsorbed BVOCs were transferred to a cryo-focusing trap (−175°C) by a flow of helium at 20–30 ml min^{−1} for about 20 min. The cryo-focusing trap was rapidly heated to 150°C to transfer focused VOCs onto the chromatographic column.

Sample cartridges were analyzed by GC-MS (Hewlett Packard model HP5972 mass selective detector) for identification and GC-FID or GC-AED (atomic emission detector, Hewlett-Packard model HP5921A) for quantitation. GC-FID and GC-MS used 30 m × 0.32 mm ID, 1 μm film DB-1 column (J and W Scientific, Folsom, CA), temperature-programmed from −50 to 200°C at 4°C min^{−1} after an initial hold of 2 min; GC-AED used 100 m × 0.25 mm ID, 0.5 μm film DB-petro 100 column (J and W Scientific, Folsom, CA), programmed from −50 to 250°C at 8°C min^{−1} after a 4 min initial hold.

Identification information from GC-MS analyses was transferred to the GC-AED and GC-FID chromatograms by retention index comparisons. Retention indices for all peaks were computed with reference to C₂–C₁₁ n-alkanes, included in a mixture of NMHCs (alkanes, aromatics, and alkenes in N₂, Scott-Marrin, San Bernardino, CA). The retention indices of peaks identified by GC-MS were matched with those detected by GC-FID and GC-AED. Quantitation of GC-FID and GC-AED results were made with respect to a standard of n-butane (10.53 ppb) in nitrogen (Scott-Marrin, San Bernardino, CA). Oxygenated VOCs (O-VOCs) were quantified on the GC-AED with respect to the n-butane standard, since the AED gives an elemental response to carbon (Quimby et al., 1992). O-VOC relative response factors for GC-FID were determined by comparing O-VOC concentrations to those determined by GC-AED. The relative response of MACR and MVK using FID was determined to be approximately 90% of the response of a four carbon hydrocarbon.

Detection limits for the BVOCs for the 1995 and 1996 experiments were approximately 1 ppt (air was sampled through balloon cartridges for 30 min at approximately 200 standard milliliters per minute, giving a typical sample size of about 6000 ml). However, ambient concentrations of isoprene, MACR and MVK were of the order of 1 ppb (α -pinene concentrations were typically 100–500 ppt). Measurement precision for isoprene at 1 ppb was approximately 0.05 ppb; for α -pinene, the precision at 200 ppt was approximately 20 ppt. For MACR and especially MVK, the precision was less because of smaller, incompletely resolved chromatographic peaks (estimated to be as much as 30% of the area of the MVK peak). The uncertainty of MACR and MVK measurements at 1 ppb was estimated at approximately 0.25 ppb. Precision and detection limits for analytical techniques used in the earlier experiments were similar.

In the Oak Ridge 1995 experiment, a three-stage adsorbent cartridge (Carbotrap 300[®], Supelco Inc., Bellefonte, PA) consisting of (in order of increasing adsorbent strength) Carbotrap C[®] (300 mg), Carbotrap B[®] (200 mg) and Carbosieve S-III[®] (125 mg) was used. In the Pittsboro 1996 experiment, a three-stage adsorbent cartridge (Carbotrap 200[®], Supelco Inc., Bellefonte, PA) consisting of glass beads (80 mg), Carbotrap B[®] (170 mg), and Carbosieve III[®] (350 mg) was used. Both formulations were inefficient in trapping C₂ NMHCs at typical sampling volumes, but trapped and desorbed quantitatively most NMHCs in the C₃–C₁₂ range.

Several cartridge artifacts were observed. Benzene was the largest artifact in blanks (equivalent to approximately 50 ppt for a 6 l sample). Other blank artifact levels were much smaller; blank levels for isoprene, terpenes, MACR and MVK were negligible. In laboratory tests of terpene mixtures, Carbotrap 300[®] interconverted several terpenes (α -pinene, β -pinene, camphene, limonene). Carbotrap 200 performed better for terpenes; approximately 20% of β -pinene was converted to other terpenes, however (mostly α -pinene). α -Pinene concentrations reported for 1996 were not corrected for interconversion, since the contribution from the much lower concentration of β -pinene was negligible.

Storage experiments were performed using the NMHC mixture and laboratory prepared standards of terpenes and O-VOCs. VOCs in the C₆–C₁₂ range could be stored at room temperature for periods of up to 4 weeks without significant losses (<5%). Lower molecular weight VOCs, however, showed decreasing recovery after 10 days of storage at room temperature. Refrigeration at 0°C gave improved storage results, with losses <10% for the lower molecular weight VOCs after 4 weeks. Refrigeration at <−40°C eliminated losses for VOCs tested for storage up to 5 weeks.

2.4. Site descriptions

Ten sites were visited for tethered balloon profiling from 1985 to 1996. One site (Oak Ridge, TN) was visited twice. Details describing these sites and experiments are given in Table 2.

3. Results and discussion

3.1. General description of the atmospheric boundary layer

The daytime atmospheric boundary layer typically extends from the surface to a capping potential temperature inversion. It is subdivided into the surface layer and mixed layer. In the surface layer (ground level to several hundred meters), mechanical turbulence (provided by surface friction) is the most important transport

Table 2
Descriptions for the various tethered balloon sites

| Site | Latitude-Longitude | Dates of deployment | (No. of profiles/ (No. of samples) | Landscape characterization (dominant genera) | Temperature (°C) | PAR ^a | Additional references |
|---------------------------|--------------------|-----------------------|---------------------------------------|---|------------------|---------------------|--------------------------|
| Amazon forest, Brazil | 2 S, 60 W | 25 July–5 August 1985 | 25 (81) | tropical forest, diverse and uncharacterized flora | 29 | > 1000 | [1,2,5] |
| Scotia, PA | 41 N, 78 W | 11–28 August 1988 | 32 (102) | deciduous forest (Quercus) 28 18–23 Aug | 33 11–17 Aug. | > 1000 | [3] |
| ROSE, Kinterbush, AL | 32 N, 88 W | 29 June–19 July 1990 | 37 (137) | Southern mixed deciduous, coniferous forest | | | |
| Metter, GA | 33 N, 82 W | 2–13 August 1991 | 17 (36) | (Pinus, Quercus, Liquidambar) Oak-pine savanna, forest (Quercus, Pinus) | 28–34 32–38 | > 1000 1000–1800 | [4,5] [4] |
| Oak Ridge, Tennessee | 36 N, 84 W | 23 July–5 August 1992 | 29 (110) | Southern mixed deciduous, coniferous forest (Quercus) | 26 | 1150 | [6] |
| Coweeta, NC | 35 N, 84 W | 16–20 June 1993 | 12 (39) | Southern mixed deciduous, coniferous forest (Pinus, Quercus) | 28–29 | 1000–1500 | [7] |
| Rhinelandet, Wisconsin | 45 N, 90 W | 15–22 June 1993 | 14 (42) | Northern mixed deciduous, coniferous forest (Populus, Quercus, Pinus) | 23–24 | 1100–1300 | [8] |
| Temple Ridge, CO | 41N, 108 W | 24–25 August 1993 | 8 (29) | shrubland (Quercus) | 26–27 | 1200–1300 | [7] |
| La Copita, TX | 27 N, 98 W | 20–24 June 1994 | 15 (48) | crop and rangeland | 32–33 | 1600–1700 | [9] |
| Oak Ridge, Tennessee | 36 N, 84 W | 15–20 July 1995 | 12 (48) | Southern mixed deciduous, coniferous forest (Quercus) | 29–31 | 1100–1600 | |
| Pittsboro, NC | 36 N, 79 W | 20–23 June 1996 | 15 (65) | Southern mixed deciduous, coniferous forest (Pinus, Quercus) | 31–33 | 1300–1600 | |

[1] Fitzjarrald et al. (1988); [2] Zimmerman et al. (1988); [3] Parrish et al. (1993); [4] Guenther et al. (1996a); [5] Davis et al. (1994); [6] Guenther et al. (1996b); [7] Guenther et al. (1996c); [8] Isebrands et al. (1998); [9] Guenther et al. (1998).

^a $\mu\text{moles m}^{-2} \text{s}^{-1}$; clear sky PAR was usually in the range 1000–2000 $\mu\text{moles m}^{-2} \text{s}^{-1}$.

mechanism. In the mixed layer, which extends from the top of the surface layer to the height of the capping inversion, convective turbulence (thermally derived) is most important. At the top of the boundary layer during most of the daytime is an entrainment zone, where exchanges between the atmospheric boundary layer and the free atmosphere above take place.

The terrestrial atmospheric boundary layer undergoes diurnal variations. During the night, radiative cooling creates a stable layer near the surface (50–200 m in depth). About a half hour after sunrise, mixed layer growth begins as a result of solar surface heating and warm thermals rising from the surface. The mixed layer reaches the residual capping inversion by mid-afternoon and growth slows substantially. The mixed layer grows by entraining free tropospheric air. Convective clouds may also transport air between the mixed layer and the free troposphere. Near sunset, solar surface heating and thermally driven convection stops and a stable nighttime boundary layer reforms.

If an inert tracer with no source aloft is released from a homogeneous surface source, the mean mixing-ratio profile of the tracer is expected to decrease slowly with altitude in the mixed layer. The concentration will decrease more rapidly near the surface (close to the source) and at the top of the atmospheric boundary layer (where tracer-poor air is entrained into the atmospheric boundary layer). In most landscapes, the BVOC emission source is not homogeneous and the mean profile may differ from the ideal. In convective conditions, turbulent eddies will rapidly mix out such local variations in the mean profile as they are advected downwind.

Deviations from an idealized mean profile may also exist if the BVOC sampling time does not integrate over several advected convective eddies, since individual downdrafts and updrafts may contain substantially different BVOC mixing ratios. Some convective eddies are as large as the mixed layer depth (1–2 km). With typical wind speeds of about 5 m s^{-1} , minimum sample times of 15–30 min are needed to integrate over a few convective eddies (Lenschow et al., 1980).

The sampling footprints (the footprint is defined as that area of the surface encompassing the surface fluxes which create the vertical mean mixing ratio differences in the atmospheric boundary layer at a given observation point) generally increases with altitude. Near the surface, the strongest contribution is just upwind of the sampling point. Tethered balloons are launched from clearings, tens of meters in diameter, which usually have lower BVOC emissions. In light to moderate wind conditions, the clearing may impact mixing ratios up to tens of meters.

3.2. Atmospheric boundary layer concentrations of BVOCs

3.2.1. Median atmospheric boundary layer mixing ratios

The median and interquartile range of midday

(1000–1700 local standard time) concentrations of isoprene are shown in Fig. 1. Median concentrations are given for the surface or canopy level, surface layer and mixed layer. The surface layer was assumed to extend to approximately 200 m above ground; the height of the mixed layer, when not measured (with surface sounding systems, release-sondes or balloon-borne sondes), was estimated from climatological averages. The median profiles show a slow decrease in concentration of isoprene with altitude. Individual profiles showed more variability.

3.2.2. Spatial variations

Difference in atmospheric concentrations of BVOCs among the sites is, in some cases, due to differences in species composition and total biomass at the different sites. The La Copita launch site was within a small reserve, which had a moderate isoprene emission, surrounded by crop and rangeland. The footprint of balloon measurements included the much larger areas of crop and rangeland and suggested very low emissions of isoprene from those areas. The sites with the highest mixing ratios (Coweeta and Oak Ridge) are forests dominated by several species of oaks, which are strong isoprene emitters.

In desert and arid areas, where very high surface temperatures occur during summer, mixed layer heights tend to be higher than in more humid areas. Consequently, at La Copita and Temple Ridge, the greater mixed layer depth resulted in relatively low concentrations of BVOCs emitted from the landscape.

Differences in surface concentrations within a site were also observed. During the Scotia 1988 experiment, simultaneous measurements (25 measurement periods) at 5.3 m in a forested area (above canopy) and in a clearing, isoprene concentrations were in the range of 4.5–7 ppb above the forest, while the clearing measurements were in the range of 1.5–3.5 ppb.

3.2.3. Temporal variations

3.2.3.1. *Variations with temperature.* The beginning of the Scotia measurement period (11–17 August) was characterized by a stagnant high-pressure period, with high temperatures and low winds, high concentrations of NMHCs, NO_x and ozone. The latter part of the measurement period (18–28 August) followed the passage of a cold front. Isoprene concentrations were much lower than in the preceding hotter ($+3^\circ\text{C}$) high-pressure period. Average daytime temperatures during the 1992 Oak Ridge experiment were significantly lower than in 1995 (26 and 33°C , respectively). Isoprene emissions are predicted to be lower by approximately 50% with a 5°C decrease in temperature (Guenther et al., 1993).

3.2.3.2. *Daytime variations.* Fig. 2 gives median mixed layer concentrations for several midday time periods for

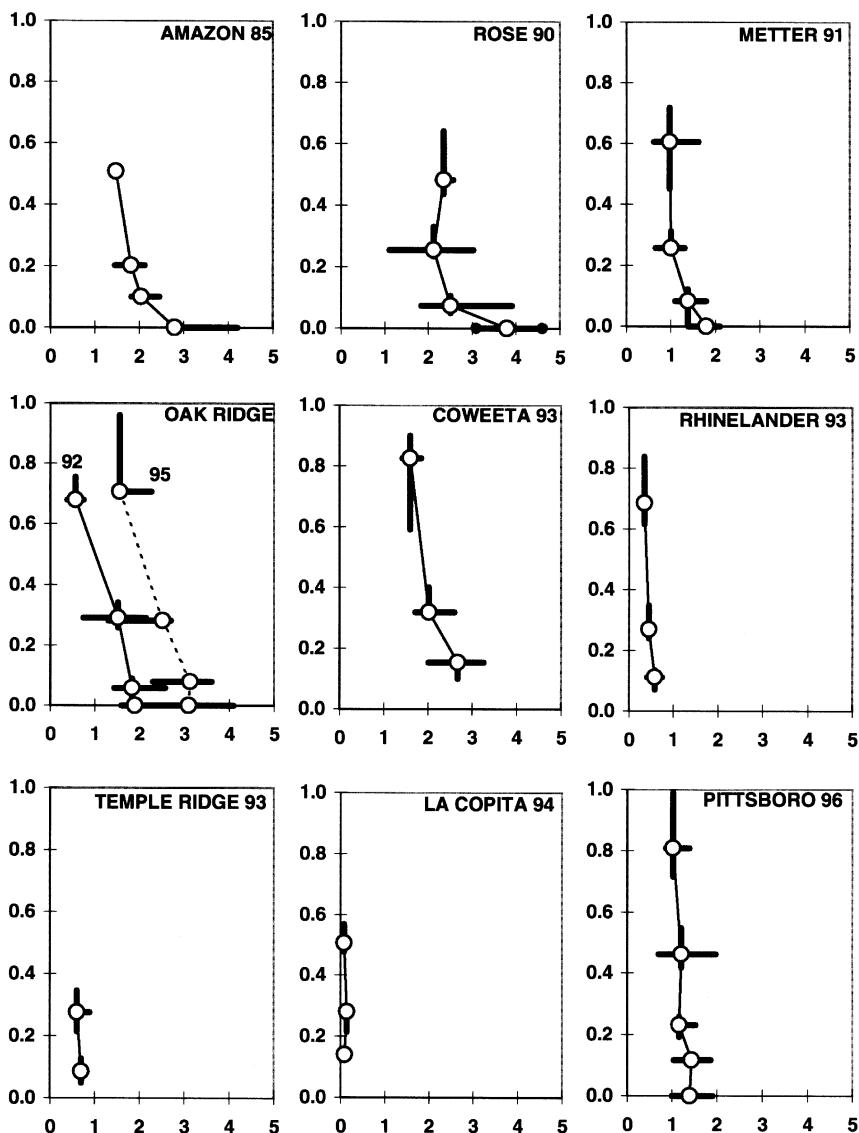


Fig. 1. Median mixed layer concentration (ppb, horizontal axis) profiles of isoprene from ten experimental sites (midday periods: 1000–1500 LST). Altitudes of sampling (vertical axis) were converted to the dimensionless altitude Z/Z_i , where Z is the sampling altitude and Z_i is the height of the mixed layer (estimated where actual height was not observed). The solid horizontal and vertical bars indicate the interquartile ranges of sampling altitude and mixing ratio, respectively, for the median values depicted. The average profiles show for most sites a slow decrease in concentration of isoprene with increasing altitude in the mixed layer.

the sites visited. Results from Scotia 1988 are not included, since measurements were only made in surface layer. In general, the resulting mixed layer concentrations of BVOCs increased only slowly from approximately 10:00 local standard time to mid-afternoon.

Midday mixed layer BVOC concentrations may differ from the daytime pattern of canopy level concentrations. Fig. 3 compares the average mixed layer and canopy level isoprene concentrations from the 1995 Oak Ridge experi-

ment. Canopy level measurements showed steady increases of isoprene concentrations from early morning through early evening period (also seen at canopy level at Scotia by Martin et al. (1991) and at ROSE by Goldan et al. (1995)), while mixed layer concentrations remained fairly constant.

3.2.3.3. *Variations with sampling time.* In early deployments, samples were collected over 2–5 min, shorter than

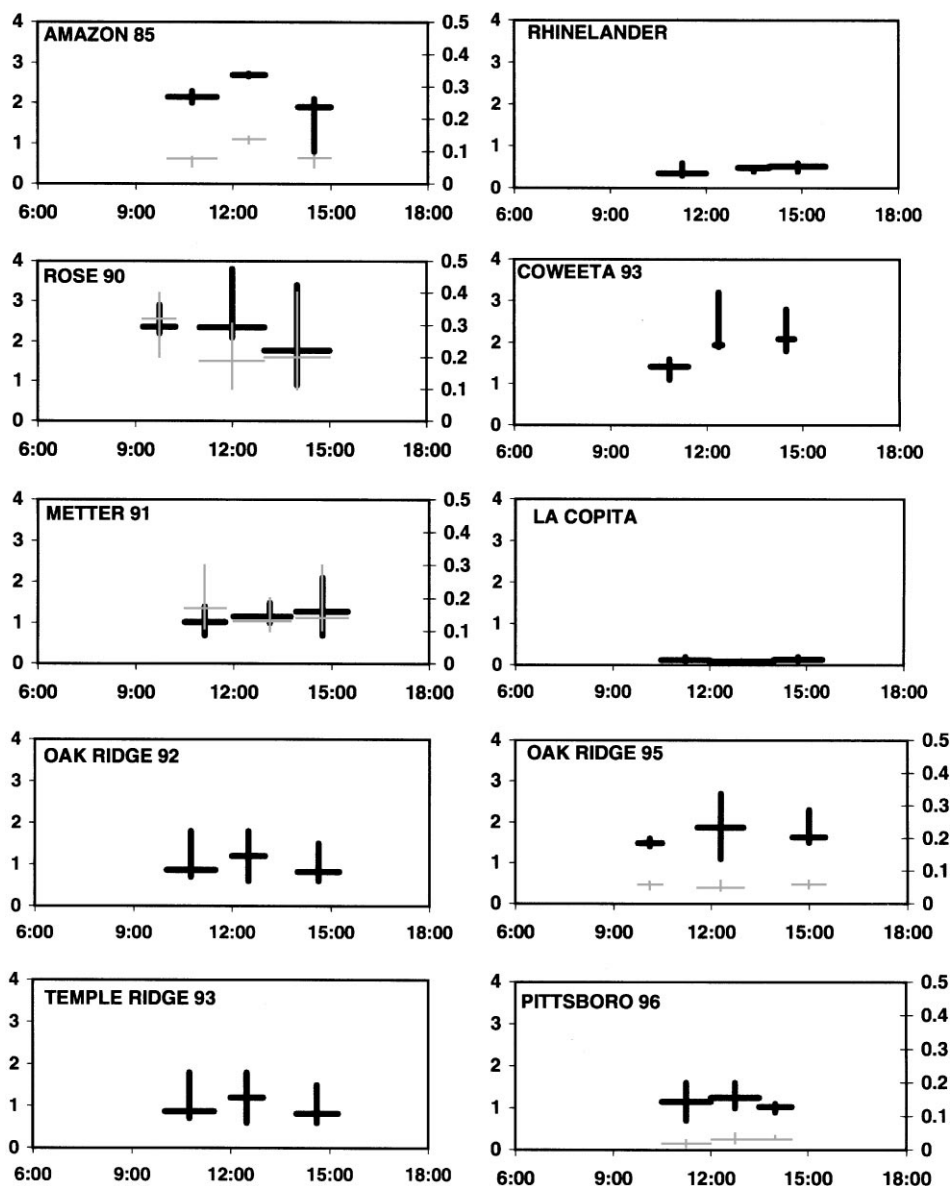


Fig. 2. Median mixed layer concentrations (ppb, vertical axis) for isoprene (bold lines, left axis) and α -pinene (narrow lines, right axis) at several mid-day time periods (horizontal axis). Ranges of concentrations and altitudes are also indicated. BVOC mixing ratios remained fairly constant in the middle of the day at most sites.

the scale of convective eddies (5–15 min). In these cases, incomplete sampling of the spectrum of eddies probably occurred, which may be responsible for profiles where the uniform decrease of concentrations with altitude in the mixed layer was not always observed (Zimmerman et al., 1988; Andronache et al., 1994). Sampling was integrated over longer time periods in later deployments and most subsequent profiles have shown the expected monotonic decrease of concentrations with altitude.

3.2.4. Isoprene and its initial oxidation products

The major initial oxidation products of isoprene are MACR and MVK. These are produced both by reaction of isoprene with OH radical and with ozone (Paulson et al., 1992). Montzka et al. (1993) observed, in above-canopy measurements, diurnal variability in the ratio of MACR and MVK concentrations, with MACR : MVK of approximately 0.5 midday, increasing to approximately 1 during the night. Similar ratios at the surface were

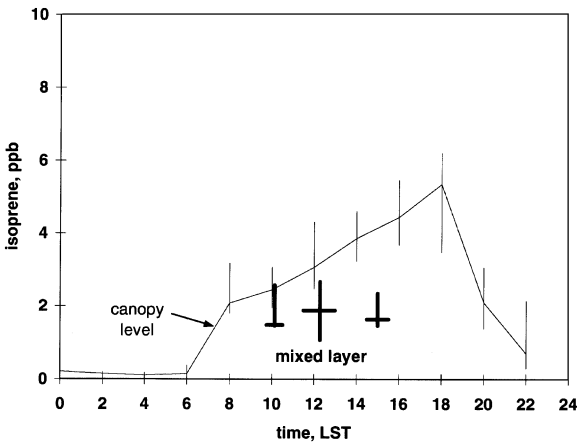


Fig. 3. Comparison of isoprene concentrations at the canopy level and in the mixed layer from the Oak Ridge 1995 experiment. Canopy level concentrations increased through late afternoon, while mixed layer concentrations remained fairly constant.

observed by other investigators (Martin et al., 1991; Yokouchi, 1994; Lewis et al., 1995).

Tethered balloon measurements from Oak Ridge and Pittsboro indicated a median daytime MACR: MVK ratio of approximately 0.5–0.6 at all altitudes (Fig. 4). The MACR:isoprene and MVK:isoprene ratios are lower near the surface, presumably because of proximity to recent, non-oxidized isoprene emissions.

3.3. Landscape biogenic emissions fluxes

Tethered balloon measurements of BVOCs have been used to estimate landscape level emission fluxes by way of mass balance (MB) and mixed layer gradient (MLG) calculation techniques. The MB approach is based upon mass conservation; with several assumptions, the surface flux is equated with the chemical loss of the BVOC in the atmospheric boundary layer. In the MLG approach, an emission flux is adjusted to reproduce the observed BVOC concentration profile from meteorological observations. A detailed discussion and evaluation of assumptions and uncertainties of these techniques has been

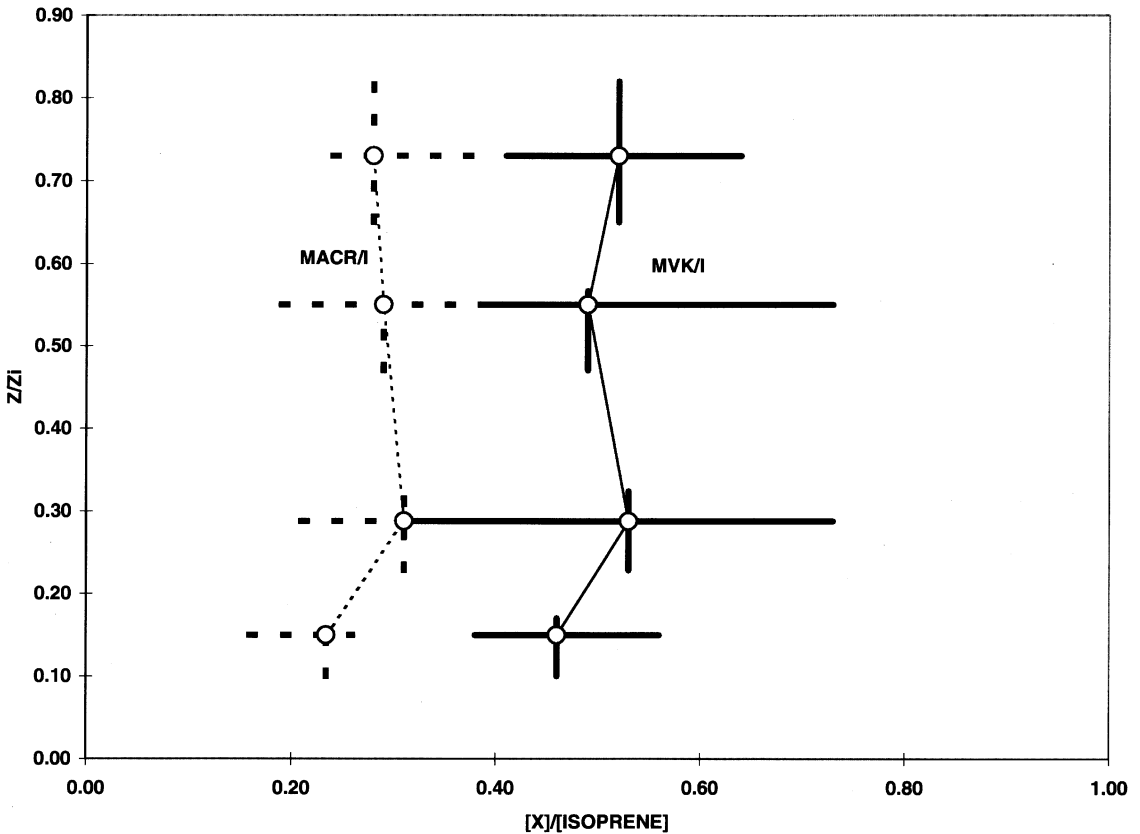


Fig. 4. Profiles of MACR and MVK (normalized to the simultaneously determined concentration of isoprene) from the Pittsboro 1996 experiment. The ratio of MACR and MVK to isoprene is lowest at the 100 m level because of the strong isoprene surface emissions. The ratio of MACR to MVK concentrations is in the range of 0.5–0.6 at all altitudes.

presented previously (Davis et al., 1994; Guenther et al., 1996a).

MB emission fluxes for the tethered balloon experiments (Fig. 5) were estimated for several mid-day time intervals. Median mixed layer concentrations were used in the MB estimation of surface fluxes. Surface layer concentrations were often influenced by the balloon launch clearing and not used in the MB calculation. When not directly measured, the mixing depth was assumed to increase at a rate of 5 cm s^{-1} from a level of 100 m at 0800 until a maximum mixing depth was reached, according to climatological averages (Holzworth, 1964).

The chemical loss of isoprene and α -pinene during the daytime is mostly through reaction with OH radical and O_3 . $[\text{OH}]$ and $[\text{O}_3]$ concentrations were set at values reported in the literature for similar regions (0.83×10^6 molecules cm^{-3} OH and 20 ppb O_3 for the Amazon study, Jacob and Wofsy, 1988; 4×10^6 molecules cm^{-3} OH and 40 ppb O_3 for sites in the SE US, Chameides et al., 1992; and 2.3×10^6 molecules cm^{-3} and 40 ppb O_3 for Temple Ridge, Eisele et al., 1994, 1997). The concentration of OH was adjusted hourly, assuming peak concentrations in the early afternoon, approximately 20% less 2 h earlier or later. Rate constants used for reactions with OH were 100 and $53 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and for reactions with O_3 were 1.17 and $8.5 \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for isoprene and α -pinene, respectively (Atkinson, 1990).

Isoprene and terpene fluxes estimated (Fig. 5) increase through the mid-day period, when both temperature and PAR also increase. Emission rates of BVOCs are expected to increase with temperature (isoprene and terpenes) and light (isoprene), according to the empirical relationships given by Guenther et al. (1993). In contrast to the relatively constant concentrations of isoprene observed in the mixed layer in the middle of the day, the emission rate increased sharply during the morning, reaching a maximum in the afternoon. The effect of increasing emissions is diluted by oxidation and by the entrainment of BVOC-depleted air as the atmospheric boundary layer grows during the same time period.

The area emission rates calculated for the Temple Ridge, CO site are similar to those estimated for some regions of the southeastern US, whereas ambient concentrations were much lower. The Temple Ridge landscape is dominated by Gambell's oak, whose isoprene emission rate is high and typical of oaks prevalent in other areas. The density of Gambell's oak at Temple Ridge was estimated at 70 g m^{-2} ground, compared to oak foliar densities of approximately $60\text{--}80 \text{ g m}^{-2}$ reported for the ROSE, Oak Ridge and Metter, GA sites (Guenther et al., 1996a, b). The much deeper mixed layer ($\sim 3.5 \text{ km}$ at mid-afternoon) at the Temple Ridge, CO experiment are typical for the dry climate and resulted in low average mixing ratios. In more humid regions, such as the south-

east US and Amazon, the mid-afternoon mixed layer height is 1–1.5 km.

MLG and MB flux estimates for isoprene and α -pinene from balloon profiles were compared with emission estimates for the landscape area derived from extrapolating leaf level emissions to the landscape level, using the Biogenic Emission Inventory model (BEIS-2, Geron et al., 1994) in Table 3. The MB and MLG emission flux estimates were not normalized to standard conditions. However, since profiles were measured under clear sky conditions, actual PAR during profile sampling would have similar effect on emissions. Temperature differences ($\pm 3^\circ\text{C}$) from standard conditions may result in up to 25% difference in MB and MLG flux estimates.

An analysis of the uncertainties in the MB and MLG estimations is given in Guenther et al. (1996a). The MB estimations introduce a random error of approximately 25% due to uncertainties in concentration determinations and the mixed layer height. A larger uncertainty is associated with the concentration of OH radical used in the calculation. We estimate this uncertainty to be about 50%. Since the MB calculation neglects entrainment, the calculated flux probably underestimates BVOC emission. We estimate the uncertainty of MB estimates at approximately 60%.

The MLG method includes random errors on the order of 25% from measurement precision of the concentrations and altitude and another 25% from uncertainties in the estimates of convective velocity scale, mixed layer height, chemical reactivity, and displacement height. We estimated the uncertainty of the MLG estimates at approximately 40%.

Guenther et al. (1996a) point out that an additional large source of uncertainty in MB and MLG estimates was attributable to heterogeneity in surface fluxes on the scale of several kilometers. They postulated that the variability in the observed profiles caused by heterogeneous emissions was random according to wind direction and that the average result over all profiles should provide meaningful landscape average emission fluxes.

4. Conclusions

Tethered balloon sampling platforms, deployed between 1985 and 1996 in nine US landscapes and a primary forest in the Brazilian Amazon, characterized the BVOC mixing ratios and their distributions in the atmospheric boundary layer and have allowed for the estimation of BVOC emission fluxes from those landscapes.

Average mixed layer concentrations of BVOCs showed a slow decrease of concentration with altitude for measurements made at midday under mostly clear skies. Surface and surface layer concentrations were more sensitive to the heterogeneous distribution of emitting vegetation species in the much smaller measurement

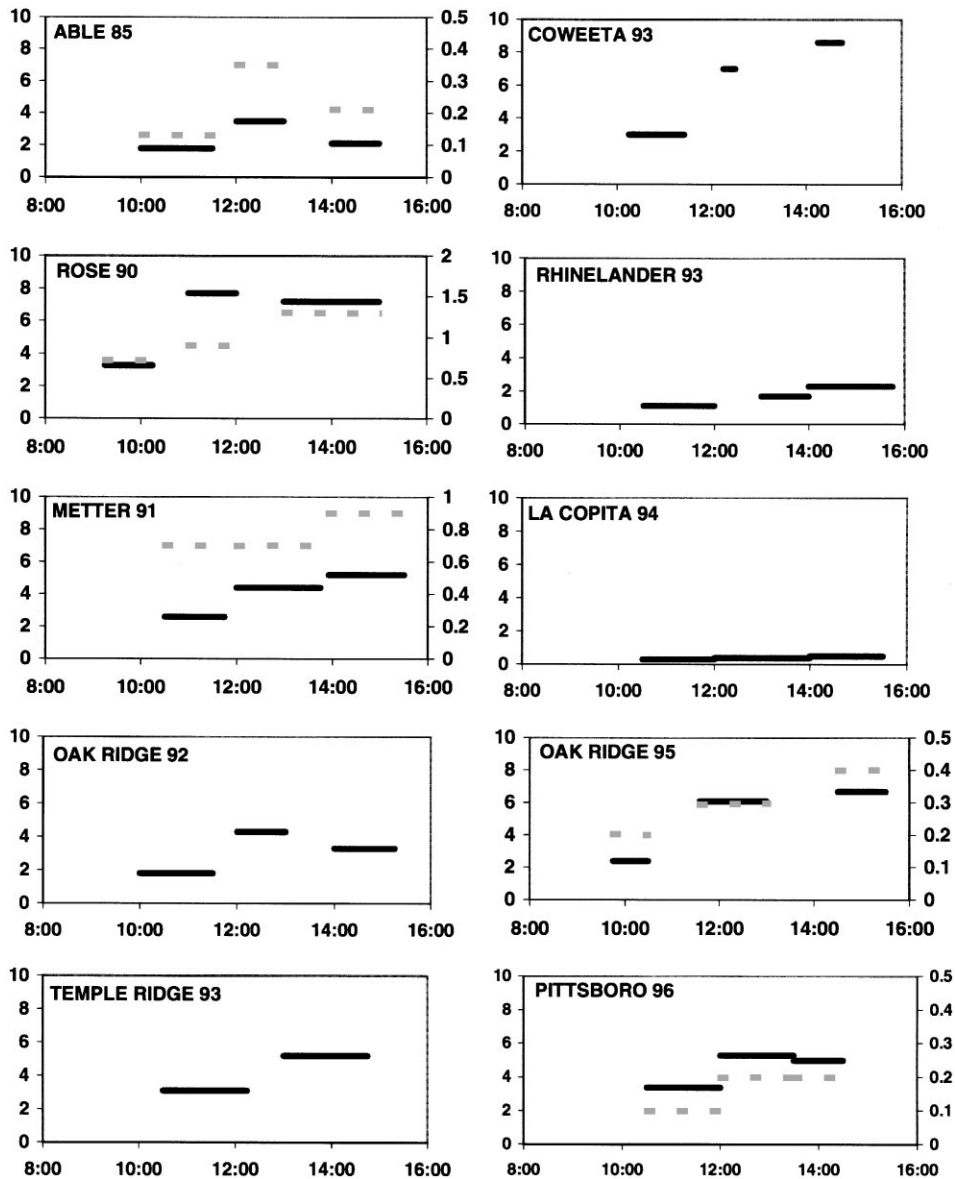


Fig. 5. Estimates of isoprene (solid black lines) and α -pinene (dashed grey lines) emission fluxes at several midday times from mass balance calculations. In most sites, emissions increase through the morning and early afternoon, as temperature and PAR are also increasing.

footprint. The observed ratio of MACR to MVK (both isoprene reaction products) was approximately 0.5–0.6 throughout the mixed layer.

The atmospheric boundary layer grows until early afternoon by entraining air with very low concentrations of BVOCs. Increasing air (and leaf) temperatures and PAR during the same period, however, result in higher emissions. Oxidation and the dilution effect of entrainment largely balance the increased emissions, so that mixed layer concentrations observed varied only slowly

from mid-morning to afternoon. This contrasted with canopy level and surface measurements, which showed increasing mixing ratios of isoprene until early evening.

MB and MLG techniques used to estimate landscape emissions from balloon profiles agree well with each other and with an independent inventory technique. This agreement gives confidence for applying balloon emission flux estimation techniques to other landscapes, especially those where landscape characterization is unavailable or difficult to obtain. Of particular interest are

Table 3

Isoprene and α -pinene emission rates estimated for the sites from mass balance (MB), mixed layer gradient (MLG) and biogenic emission inventory system (BEIS-2) models

| Study | | MB | | MLG | | BEIS | | Reference |
|--------------|------------------|------|-----------|------|-----------|-----------|-----------|-----------|
| | | AVE. | (\pm) | AVE. | (\pm) | AVE. | (\pm) | |
| Amazon | | 3.1 | 1.6 | 3.6 | 1.4 | | | 3, 4 |
| Rose | Isoprene | 6.6 | 1.1 | 6.7 | 3.9 | 2.1–4.8 | | 1 |
| | MT* | 1.8 | 0.2 | 2.3 | 1.1 | 0.29–0.85 | | 1 |
| Metter | Isoprene | 3.2 | 0.7 | 1.5 | 1.2 | 2.4–3.7 | | 1 |
| | MT | 1.4 | 0.2 | 2 | 1.7 | 0.36–0.93 | | 1 |
| Oak Ridge 92 | Isoprene | 2.8 | 0.7 | 5 | 1.7 | 1.73 | 0.25 | 2 |
| | MT | | | | | | | |
| Temple Ridge | Isoprene | 3.3 | 1.8 | | | 1.3 | 0.2 | 2 |
| Rhineland | Isoprene | 1.9 | 0.9 | | | 1.3 | 0.1 | 2 |
| Coweeta | Isoprene | 6.5 | 4.4 | | | 5.4 | 1 | |
| La Copita | Isoprene | 0.56 | 0.08 | | | 0.72 | | |
| Oak Ridge 95 | Isoprene | 3.1 | 2.7–5.8 | | | 4.5 | | |
| | α -Pinene | 0.15 | 0.10–0.22 | | | 0.9 | | |
| Pittsboro | Isoprene | 5.3 | 1.3 | 4 | 2.1 | 5.3 | | |
| | α -Pinene | 0.12 | 0.04 | 0.12 | 0.2 | < 1 | | |

[1] Guenther et al. (1996a); [2] Guenther et al. (1996b); [3] Davis et al. (1994); [4] Zimmerman et al. (1988).

* MT: monoterpene.

tropical forest and savanna landscapes, which contain approximately 60% of the terrestrial biomass.

The different modeling techniques for estimating landscape level emissions described here complement and constrain each other. However, they are indirect flux estimates. Direct flux measurement techniques may require eddy covariance or relaxed eddy accumulation techniques.

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