

## EDITORIAL

### 1. Introduction

Biogenic hydrocarbons produced by vegetation at the surface of the earth play an important role in the atmosphere as oxidant precursors and indirectly as absorbers and emitters of radiation. Through the intervening atmospheric boundary layer, biogenic hydrocarbons released at the surface can be transported into the deeper atmosphere. During the past two decades substantial interest in emissions, transport, and chemistry of biogenic hydrocarbons has resulted in both field and laboratory research together with new analytical developments and photochemical modeling activities. In August 1997 the need to review the progress in the field was recognized by the convening of a workshop devoted to characterizing and understanding of biogenic hydrocarbons in the atmospheric boundary layer.

The workshop was organized upon the premise that although nonmethane hydrocarbons exist in trace amounts in the atmosphere, they play key roles in the oxidation capacity of the atmosphere, the earth's climate system, and the global carbon budget. Because they rapidly react with hydroxyl radicals (HO), ozone ( $O_3$ ), and nitrate radicals ( $NO_3$ ), nonmethane hydrocarbons can generate undesirable secondary chemical species. For example, the reaction of nonmethane hydrocarbons with HO produces carbon monoxide and carbonyl compounds that once in environments rich in nitrogen oxides can produce  $O_3$  and other oxidants such as peroxyacetyl nitrate (PAN) and hydrogen peroxide ( $H_2O_2$ ) (Chameides et al. 1988; Fehsenfeld et al. 1992; Singh and Zimmerman 1992). By reacting with HO, hydrocarbons contribute to increased lifetimes of greenhouse gases such as methane, thereby indirectly contributing to the earth's greenhouse effect. Additionally, photooxidation processes convert hydrocarbons to oxygenated species whose vapor pressure is lower than gaseous hydrocarbons. Such oxygenated compounds can undergo a phase transition and lead to the formation of aerosols (Hoffman et al. 1997; Leaitch et al. 1998) whose impacts may include feedback mechanisms in the earth's radiation balance. Because phytogenic hydrocarbons such as isoprene are linked to photosynthesis (Monson and Fall 1989; Sharkey et al. 1991), they also constitute a source of atmospheric carbon and can thus play a key role in the global carbon budget and cycling. Thus, given the functions hydrocarbons play in the oxidizing capacity of the atmosphere and the earth's climate system, it is essential to understand the dynamics and strength of their sources, their atmospheric transport processes, and their reaction rates and pathways in the troposphere.

Not all hydrocarbons are equally important in atmospheric chemistry, and neither are their sources. The most important sources of anthropogenic hydrocarbons include fossil fuel combustion, direct release from industry, and industrial processing of chemicals and waste. The global estimated anthropogenic hydrocarbon flux is approximately  $10^{14}$  g C yr<sup>-1</sup> (Singh and Zimmerman 1992). Biological processes in both marine and terrestrial environments contribute to biogenic hydrocarbon sources. For the terrestrial biosphere, the principal hydrocarbon source comes from vegetation. At the global scale it is estimated that vegetation emits approximately  $1.2 \times 10^{15}$  g C yr<sup>-1</sup> (Guenther et al. 1995). Plants produce a variety of hydrocarbons (Isodorov et al. 1985; Arey et al. 1991; Winer et al. 1992; Guenther et al. 1994), including isoprene ( $C_5H_8$ ), the class of compounds known as monoterpenes ( $C_{10}H_{18}$ ), and oxygenated ( $C_xH_yO_z$ ) species. Because isoprene is the most reactive and abundantly plant-produced hydrocarbon, with an estimated global flux of  $5.1 \times 10^{14}$  g C yr<sup>-1</sup> (Guenther et al. 1995), considerable knowledge exists concerning its biosynthesis, environmental controls on emissions, and

its atmospheric chemistry. In this overview paper, emphasis is placed on the measurement and modeling of isoprene emissions from forest ecosystems.

Isoprene is principally released by deciduous trees (Fehsenfeld et al. 1992; Guenther et al. 1994) and is instantaneously produced in chloroplasts from photosynthetically fixed carbon (Monson and Fall 1989; Delwiche and Sharkey 1993). It is not stored in the leaf tissue; instead isoprene is released immediately after its biosynthesis. Foliage temperature and intercepted photosynthetically active radiation (PAR) exert the greatest environmental influence on its release from vegetation. Temperature regulates the enzymatic (isoprene synthase) activity responsible for isoprene biosynthesis (Silver and Fall 1991), whereas PAR mediates the increased metabolite substrates required to form isoprene (Loreto and Sharkey 1993). Although we still do not know why plants release isoprene, circumstantial evidence indicates that many plants emit isoprene as a mechanism to cope with thermal stress (Sharkey and Singsaas 1995).

The workshop included topics on 1) biological controls of phytogenic hydrocarbons, 2) micrometeorology of biogenic hydrocarbon emissions—measurements and modeling, 3) atmospheric observations, 4) chemical mechanisms, and 5) modeling of the photochemical role of biogenic hydrocarbons. New findings presented at the workshop were assembled and submitted as manuscripts for publication. Manuscripts focusing on biological controls over hydrocarbon emissions will appear in a special issue of *Ecological Applications* (Sharkey et al. 1998), while papers addressing topics 3, 4, and 5 will be published in a special issue of the *Journal of Geophysical Research* (Bottenheim et al. 1998). This special issue of the *Journal of Applied Meteorology* includes manuscripts with emphasis on measurements and modeling of hydrocarbon emissions from forests. Given the important role of micrometeorology in the transport and diffusion of biogenic hydrocarbon emissions into the atmosphere and also given our reliance upon current micrometeorological tools for measuring the flux of gases from forests, it is appropriate to present a special issue of the *Journal of Applied Meteorology* dedicated to the measurement and modeling of forest emissions to the atmosphere.

## 2. Overview

A summary of the principal findings of six manuscripts that constitute the special issue follows. Hydrocarbon emissions from five different forest ecosystems, ranging from boreal deciduous and coniferous forests in Canada, to a broad-leaved (oak–hickory) temperate forest in Tennessee, and to an oak–pine forest in Germany are reported. Leaf-based hydrocarbon emission rates, combined with hydrocarbon active biomass and environmental forcing variables, are employed to scale hydrocarbon flux densities to the plant canopy dimension. A common feature in all the papers is that they evaluate the role of temperature and radiation in determining hydrocarbon emissions at the forest ecosystem level. The required foliage temperature and light levels inside plant canopies are estimated following approaches ranging from random-walk models, the localized near-field diffusion method, and the transilient approach coupled with radiative transfer theory.

To some extent, the source strength of biogenic hydrocarbons at the ecosystem level depends on plant species and the amount of biomass distribution. During the 1994 growing season, Fuentes et al. (1999) studied the seasonal isoprene fluxes from a deciduous, boreal aspen forest whose isoprene source came from trees of the same species and age. Approximately 12 field studies conducted only for selected periods of the growing season are reported in the literature (for a review, see Seufert et al. 1997; Baldocchi et al. 1999). Thus, the seasonal flux dataset reported by Fuentes et al. can be valuable for model testing and establishing annual isoprene budgets. Their field studies confirmed laboratory findings that isoprene emissions change substantially with growing season. In the boreal aspen forest the onset of isoprene emissions occurred two weeks after the forest attained its maximum leaf area. When canopy fluxes were scaled to the foliage level and normalized to 25°C and photosynthetically active radiation of 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , springtime averaged isoprene emissions approached  $0.6 \pm 0.3 \mu\text{g C m}^{-2} \text{s}^{-1}$  ( $10 \pm 5 \text{ nmol of isoprene m}^{-2} \text{s}^{-1}$ ). During the middle of the growing season averaged isoprene emissions amounted to  $1.7 \pm 0.2 \mu\text{g C m}^{-2} \text{s}^{-1}$ , whereas

autumnal values reached  $1.0 \pm 0.1 \mu\text{g C m}^{-2} \text{ s}^{-1}$ . One objective of their study was to establish the annual budget of isoprene emitted from a remote boreal forest. To meet such a goal, they applied a one-dimensional multilayered model to estimate the forcing variables (i.e., light levels) influencing isoprene emissions. For the aspen forest having an active biomass of  $144 \text{ g m}^{-2}$ , the estimated annual isoprene emission was  $32 \text{ mmol m}^{-2}$  ( $\sim 2 \text{ g C m}^{-2}$ ). Such isoprene emissions accounted for approximately 1% of the carbon photosynthetically fixed by the aspen forest. Fuentes et al. also demonstrated that isoprene inventory modeling systems can introduce uncertainties exceeding 65% (models overestimating emissions) if constant, midgrowing season emission rates are incorporated in models as opposed to seasonally adjusted emission factors. In addition to the seasonal controls dictated by the inherent plant metabolic activity, they found that low temperatures ( $<10^\circ\text{C}$ ) strongly modulated the amplitude of diurnal isoprene emissions. Given that low temperatures can frequently occur in mid- and high-latitude regions during the growing season, additional long-term measurements are required to discern whether other forest ecosystems exhibit similar responses to low temperatures.

Isoprene fluxes from coniferous forests are rare as only selected conifer plant species emit isoprene. During the 1994 growing season Pattey et al. (1999) applied the relaxed eddy-accumulation (REA) and the flux–gradient techniques to obtain diel cycles of canopy isoprene fluxes from a boreal black spruce forest. Both techniques yielded similar diurnal trends in isoprene fluxes, but on average the fluxes determined with the gradient diffusion approach were 19% lower than those obtained using REA. The authors ascribed the discrepancies in isoprene fluxes to the inherent limitation of similarity theory. Despite the limited dataset obtained in 1994, the isoprene fluxes changed substantially with growing season. For example, at the end of July the mean isoprene flux amounted to  $2.3 \text{ mg C (m}^2 \text{ h)}^{-1}$  and decreased to  $0.54 \text{ mg C (m}^2 \text{ h)}^{-1}$  in early September. Senescent black spruce leaves and lower ambient air temperature probably accounted for the lower isoprene emission during the later part of the growing season. Using canopy isoprene fluxes, Pattey et al. derived foliage-based isoprene emission rates ( $E_s$ ) defined at  $30^\circ\text{C}$  and photosynthetically active radiation of  $1000 \mu\text{mol}^{-2} \text{ s}^{-1}$ . The estimated  $E_s$  values ranged from 4 to  $9 \mu\text{g (g h)}^{-1}$ , with an overall average of  $6 \mu\text{g (g h)}^{-1}$ . This new  $E_s$  estimate is substantially lower than previously assumed emission rates [ $6$  to  $18 \mu\text{g (g h)}^{-1}$ ], which have been incorporated in biogenic hydrocarbon inventory modeling systems.

Interpretation of hydrocarbon fluxes from mixed forests is rather complex because not all tree species release hydrocarbons. Another confounding quandary is that hydrocarbon emitting species exhibit different emission rates. To address the issue of heterogeneous hydrocarbon sources, Kaharabata et al. (1999) conducted a source footprint analysis for a mixed deciduous forest (Camp Borden in southern Ontario). They applied the advection–diffusion equations coupled with the local hydrocarbon source distribution to examine how sampling of hydrocarbon concentrations and fluxes made above the forest varied depending on the “sampled” upwind source areas. They assumed that the hydrocarbon source was distributed in clumps of trees; each clump was assumed randomly but uniformly distributed throughout the landscape. Clumps of four to six trees were considered with each clump occupying a diameter of about 10 m. Ambient hydrocarbon concentration data obtained at 1.4 and 1.9 canopy heights were included in the analysis. Because of the heterogeneity of the hydrocarbon source, Kaharabata et al. found that under similar temperature and light levels canopy fluxes derived from the gradient diffusion approach varied by 27%. Their analysis demonstrated that the variability observed in measured hydrocarbon fluxes could be accounted for by varying numbers of heterogeneously distributed clumps of emitter species within a varying footprint. Also, they confirmed previous analysis (Lamb et al. 1996) in that the heterogeneous source distribution of hydrocarbons has to be explicitly considered when estimating and comparing emissions based on above-canopy measurements.

To a large extent, the research agenda on biogenic hydrocarbons is driven by the need to derive accurate emission inventories so that assessments can be made on the contribution of hydrocarbons upon regional and global atmospheric chemistry. This special issue includes three modeling studies to integrate hydrocarbon emissions from foliage to the forest ecosystem level and thus assess uncertainties associated with current

inventory modeling systems. A common feature in all studies is the use of the same emission algorithms (Guenther et al. 1993) to derive hydrocarbon inventories. The principal differences in the three studies are the manner in which the environmental forcing variables are described inside plant canopies of each forest ecosystems.

Baldocchi et al. (1999) conducted a comparative study to discern whether the reported errors in canopy-scale and process-level isoprene emission models are due to inadequacies in leaf-to-canopy integration theory or the imperfect assessment of the isoprene emitting biomass in the flux footprint. To address this issue, they tested a mechanistic model over the aspen boreal forest (Fuentes et al. 1999) and a temperate mixed-species, broad-leaved forest whose isoprene active biomass was known. Their model computed leaf and soil energy exchange, turbulent diffusion, scalar concentration profiles, and radiative transfer through the canopy. The ability of the model to describe the forest microclimate was tested by comparing its energy balance outputs with measured quantities. Acceptable agreement between measured and modeled energy balance components was achieved for the two forests. With the computed forcing variables of foliage temperature and light levels, rates of isoprene emission were determined at several depths in the canopy and integrated to the ecosystem level. Modeled and measured diurnal isoprene emission rates closely agreed over the boreal aspen stand. In contrast, the fidelity of modeled isoprene emission rates over the mixed temperate forest depended upon the isoprene emitting biomass. When information on the spatial distribution of isoprene active biomass and the flux footprint probability distribution function were included, modeled isoprene emissions compared well with flux measurements. They concluded that their mechanistic model can reliably integrate leaf-scale, isoprene emissions to the canopy dimension over dissimilar vegetation types as long as the hydrocarbon active biomass can be appropriately characterized. The modeling studies reported by Baldocchi et al. did not consider the influences of water stress or low temperature influences in carbon flow into isoprene biosynthesis.

Making use of localized near-field diffusion theory, Huber et al. (1999) applied a model to establish uncertainties associated with isoprene emission inventories due to the inadequacy of microclimate characteristics. Their modeling study was conducted over a mixed deciduous (red maple–aspen) temperate forest where seasonal canopy isoprene fluxes were measured during 1995. For unstable conditions, modeled and measured temperature closely agreed, with the model overestimating measured temperature by less than 2°C. Model results deteriorated during periods of atmospheric stability when estimated temperature exceeded measurements by as much as 4°C, particularly in the lower region of the forest canopy. Compared to measurements made above the forest floor, radiation levels inside the canopy were reliably estimated. The uncertainties associated with the estimation of isoprene forcing variables overestimated isoprene emissions by 30% compared to measurements made during the middle of the growing season. However, such uncertainties became larger (~45%) if sunlit and shaded leaves were not explicitly considered. Using a constant emission rate, their model results gave uncertainties within a factor of 2 compared to gradient–diffusion-derived fluxes during the early part of the growing season. Once applied to the entire growing season, the estimated isoprene emissions were within 20% of measured quantities when seasonally adjusted emission rates were included in the flux calculations.

Based on transilient turbulent theory, Inclán et al. (1999) employed a microclimate model coupled with hydrocarbon emissions algorithms to estimate fluxes of isoprene,  $\alpha$ -pinene, and  $\beta$ -pinene from a mixed (oak–pine) forest in Germany. The forest height was 12 m and had a leaf area index of 4. The canopy crown was divided into five layers of equal leaf area increment. The algorithms developed by Guenther et al. (1993) were applied to predict the monoterpene emission from leaves in each canopy layer. The value of photosynthetic active radiation and foliage temperature required by these algorithms were provided by the model. The base emission factors were derived from chamber measurements. A distinct feature of this modeling study was that different emission rates were included in the model to represent emissions from shaded and sunlit leaves. Their estimated hydrocarbon emissions were underestimated by 40% compared to experimentally derived fluxes. These workers also proposed to simplify the method

of determining hydrocarbon emissions by introducing a function in which emissions are exponentially related to the difference between canopy temperature and 30°C.

### 3. Concluding remarks

The findings presented here and elsewhere (Seufert et al. 1998; Bottenheim et al. 1998; Sharkey et al. 1998) show that substantial advances have been made with regard to measuring and modeling emissions of biogenic hydrocarbons from forest ecosystems. The common conclusion in the studies reported in this issue is that modeling systems can realistically integrate leaf-based hydrocarbon emissions to the forest ecosystem level provided that 1) active biomass distributions are adequately represented in the modeling system, and 2) the environmental forcing variables driving emissions as they vary with plant canopy depth are reliably prescribed. Despite such progress, further model development is required to incorporate in emission algorithms the influences of drought events, low temperature episodes observed during the middle of the growing season, nutrient (nitrogen) status, and seasonal perturbations on emissions.

Measurements of biogenic hydrocarbon fluxes are still too labor intensive and require development of automatic in situ flux measurement systems. Such new systems will permit continuous and long-term field measurements to be made. The data reported here (Fuentes et al. 1999; Pattey et al. 1999) show that hydrocarbon fluxes change dynamically with growing season. Therefore, there is a need for more long-term measurements of hydrocarbon fluxes from other types of forest ecosystems to quantify variations in hydrocarbon fluxes due to changes in temperature and canopy structure, and biotic (i.e., onset of emissions and leaf senescence effects) and abiotic (drought and temperature) influences on emissions. Most studies reported to date pertain to mid- and high-latitude forest ecosystems. There is a dearth of information on the hydrocarbon source strength from tropical systems. Because tropical forest ecosystems are physiologically active year round, it is crucial to determine their contribution to the total atmospheric load of biogenic hydrocarbons.

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