PERGAMON

Atmospheric Environment 33 (1999) 2527–2536

ATMOSPHERIC ENVIRONMENT

Volatile organic compound emission rates from mixed deciduous and coniferous forests in Northern Wisconsin, USA

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Received 13 January 1998; accepted 23 June 1998

Abstract

Biogenic emissions of volatile organic compounds (VOC) from forests play an important role in regulating the atmospheric trace gas composition including global tropospheric ozone concentrations. However, more information is needed on VOC emission rates from different forest regions of the world to understand regional and global impacts and to implement possible mitigation strategies. The mixed deciduous and coniferous forests of northern Wisconsin, USA, were predicted to have significant VOC emission rates because they are comprised of many genera (i.e. *Picea, Populus, Quercus, Salix*) known to be high VOC emitters. In July 1993, a study was conducted on the Chequamegon National Forest near Rhinelander, WI, to identify and quantify VOC emitted from major trees, shrubs, and understory herbs in the mixed northern forests of this region. Emission rates were measured at various scales – at the leaf level with cuvettes, the branch level with branch enclosures, the canopy level with a tower based system, and the landscape level with a tethered balloon air sampling system. Area-average emission rates were estimated by scaling, using biomass densities and species composition along transects representative of the study site. Isoprene (C_5H_8) was the primary VOC emitted, although significant quantities of monoterpenes ($C_{10}H_{16}$) were also emitted. The highest emission rates of isoprene (at 30°C and photosynthetically active radiation of 1000 $\mu mol\,m^{-2}\,s^{-1}$) were from northern red oak (*Quercus rubra*, $>110\ \mu g(C)\,g^{-1}\,h^{-1}$); aspen (*Populus tremuloides*, >77); willow (*Salix spp.*, >54); and black spruce (*Picea mariana*, >10). Emission rates of hybrid poplar clones ranged from 40 to 90 $\mu g(C)\,g^{-1}\,h^{-1}$ at 25°C; those of *Picea* provenances were generally <10, and emission rates of a hybrid between North American and European spruces were intermediate to parental rates. More than 30 species of plants were surveyed from the sites, including several from previously unstudied genera such as *Alnus, Chamaedaphne, Ledum, Tilia, Rubus*, and *Sphagnum*. Based on the measured isoprene concentrations in the daytime atmospheric surface layer and mixed layer, area-averaged fluxes of isoprene were estimated to be about 1 $mg(C)\,m^{-2}\,h^{-1}$. This estimate agrees reasonably well with model predictions. Our results indicate that mixed

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1352-2310/99/$ - see front matter
PII: S1352-2310(98)00250-7

forests in the Lake States region of the USA are a significant source of reactive VOC to the atmosphere. Accurate estimates of these emissions are required for determining appropriate regulatory air pollution control strategies. Future studies are needed to extrapolate these estimates to other landscapes and to better understand the factors controlling observed variations in VOC emissions.

Keywords: Tropospheric ozone; *Quercus*; *Populus*; *Picea*; *Salix*; Isoprene; Monoterpene, VOC

1. Introduction

Tropospheric ozone (O_3) concentrations are increasing globally as a result of increasing urban population, fossil fuel burning, and transportation (Firor, 1990), and they will increase further if rising anthropogenic atmospheric pollutants are not abated (Chameides et al., 1994, 1997). These increases may greatly influence future forest health because O_3 is a widespread phytotoxin known to decrease productivity in crops and forests (MacKenzie and El-Ashry, 1989).

Natural emissions of volatile organic compounds (VOC) such as isoprene from forests are known to play an important role in influencing atmospheric chemistry related to regional O_3 concentrations (Lamb et al., 1987; Guenther et al., 1994, 1996a). However, more information on VOC identities and emission rates from trees and forests is needed to estimate regional biogenic VOC concentrations (Geron et al., 1994). Such information will help us to better understand atmosphere-biosphere interactions (Taylor et al., 1994) and global change scenarios, and to implement possible mitigation strategies (Guenther et al., 1994).

The mixed deciduous and coniferous forests of northern Wisconsin are comprised of numerous genera which exhibit high VOC emission rates (Guenther et al., 1994) including *Picea* (5% of basal area), *Populus*(14%), *Quercus* (3%), and *Salix* ($< 1\%$) (Hansen, 1984). These forests also contain a number of important plant genera that had not been previously studied for VOC emissions such as *Alnus*, *Tilia*, *Rubus*, and *Sphagnum*. In addition, the arboretum of the Forestry Sciences Laboratory, Rhinelander, WI contains numerous genetic sources of high isoprene emitting genera such as *Picea*, *Populus*, and *Quercus* planted in common garden experiments, providing access for the field study of genetic variation of isoprene emission rates reported to occur in tree genera (Tingey et al., 1991).

The objectives of our study were to: (1) survey VOC emission rates of important northern Wisconsin forest species in the field across different scales (i.e. leaf, branch, canopy, and landscape) with qualitative and quantitative methods, and (2) quantify genetic variation of isoprene emission rates among selected genotypes of *Picea* and *Populus* not previously studied.

2. Materials and methods

In July 1993, measurements of VOC emissions were made in common garden plantations of *Picea* and *Populus* in the arboretum at the Forestry Sciences Laboratory, Rhinelander, WI, and on mixed deciduous and conifer forests of the Chequamegon National Forest nearby. Measurements were made at leaf, branch, canopy, and landscape scales. Some measurements were made on-site with portable equipment, and other samples were collected in stainless-steel canisters and subsequently analyzed in the laboratory. Details of methods are given by Guenther et al. (1996a, b). Preliminary isoprene emission measurements were made on selected poplar clones and *Quercus rubra* trees, both known high isoprene emitters (Guenther et al., 1994), to assess possible effects of leaf position and temperature on isoprene emission in the field for the purposes of establishing sampling protocol. Position and temperature effects on isoprene emission rates have been reported for other species (Guenther et al., 1991, 1996a, b; Kuzma and Fall, 1993) and for *Populus* and *Quercus* by Sharkey et al. (1991b).

2.1. Enclosure flux systems

To assess isoprene emission rates at the leaf and branch level for a variety of species, three different sampling schemes were used: two for assessing isoprene fluxes from individual leaves, and one for measuring branch level emissions. Emission rates for the poplar clones were measured with an open-path gas exchange system (MPH-1000, Campbell Scientific, Logan, UT) consisting of a temperature-controlled, fan-stirred cuvette, with an internal measurement and control system. Artificial light was also provided. Branches were cut from trees and then recut immediately under water before measurement. Details are provided by Harley et al. (1996).

A second leaf cuvette system, used for all leaf measurements except those on *Populus*, provided no control over leaf temperature. A portion of a leaf was enclosed in the 0.25 ℓ cuvette of a commercially available portable photosynthesis system (Model 6200, Li-Cor, Inc., Lincoln, NE), operated in the open, flow-through mode. Leaf temperature and incident photosynthetically active radiation (PAR) were measured using the thermocouple and

PAR sensor supplied with the system. Immediately after isoprene was determined, the system was converted to the closed, recirculating mode, and CO_2 uptake and water loss were measured. For both leaf cuvette systems, that portion of a leaf inside the cuvette was excised and its area measured with a leaf area meter (Model 3000A, Li-Cor, Inc, Lincoln, NE). All leaves were then oven-dried (60°C) for 48 h and weighed.

Isoprene concentration in the air entering and leaving both leaf cuvette systems was measured using a chemiluminescence detector (Hills and Zimmerman, 1990) which was calibrated hourly against a known isoprene standard.

Branch level emission rates of *Picea* were measured with a 24 ℓ flow-through branch enclosure consisting of 5 mm Teflon film over a stainless-steel support frame. Ambient air was pumped through the enclosure at a known rate of approximately 9 ℓ min^{-1}. Leaf temperature and air temperature inside the enclosure were measured with shielded thermistors (YSI, Yellow Springs, OH), and incident PAR was measured with a Li-190SA quantum sensor (Li-Cor, Lincoln, NE) mounted adjacent to the enclosure. Replicate samples of air entering and leaving the enclosures were collected with 10 ml glass syringes, and the isoprene concentration was determined using gas chromatography with a reduction gas detector (RGD2; Trace Analytical, Menlo Park, CA). Details of this analytical system may be found in Greenberg et al. (1993). This system was also calibrated several times daily against a 71 ppbv isoprene standard. All leaves within each branch enclosure were removed, oven-dried at 60°C for 48 h, and weighed.

2.2. Above canopy flux systems

For the canopy and landscape level portions of the study on the Chequamegon National Forest, estimation procedures were used for scaling isoprene emission rates from the leaf level to a ground area basis. These estimates require detailed information on species composition and leaf biomass (Guenther et al., 1994). Specifically, two sites were chosen for study—one was a bog site dominated by *Picea mariana*, *Larix laricina*, and *Sphagnum*, and the other a mixed deciduous forest dominated by *Acer saccharum*, *Fraxinus americana*, and *Quercus rubra*. On both sites, transects were used to characterize the composition, successional status, and environment of vegetation communities. For a general overall estimate of the composition of the major vegetation communities of the surrounding forests (50 km) on the Chequamegon, the Eastwide forest inventory data base was used (Hansen et al., 1992). Geron et al. (1994) have successfully used this approach for estimating regional VOC emissions.

Vertical gradients of isoprene concentration were measured in the surface layer above the canopy at the bog site on the Chequamegon National Forest. An 8 m tower provided access above the canopy. Isoprene fluxes (F) in the surface layer were estimated as follows:

$$F = K\,\mathrm{d}C/\mathrm{d}z \tag{1}$$

where dz is the difference in height, dC is the difference in isoprene concentration at different heights, and K is eddy diffusivity ($m^{-2}\,s^{-1}$). Estimates of eddy diffusivity were calculated using the Bowen ratio-energy balance technique (Guenther et al., 1996a, b). The Bowen ratio estimates of K were based on data from net radiometers (REBS Q6, Seattle, WA) and two temperature and humidity sensors positioned at the same heights as the air sampling systems. In addition, soil heat flux was estimated from heat flow transducers (REBS HFT-3, Seattle, WA) at a soil depth of 10 cm. Wind direction and speed were measured with a prop-vane anemometer (R.M. Young 05305-5, Traverse City, MI). PAR above and within the canopy was measured with quantum sensors (Li-190SA, Li-Cor, Inc., Lincoln, NE).

Estimates of dC were obtained from ambient air samples pumped into Teflon bags during a 30 min sampling period at heights of 2.4 and 9 m above the mean canopy height. Eight vertical gradient replicates were measured. Samples were transferred into stainless steel canisters and stored for up to 3 weeks. Then they were analyzed for isoprene and monoterpenes by gas chromatography with cryogenic preconcentration using a flame ionization detector (GC-FID) to quantify concentrations (Greenberg and Zimmerman, 1984).

Isoprene fluxes, F, were estimated from mixed layer measurements over the mixed hardwood site as follows:

$$F = z_i L C \tag{2}$$

where z_i is the height (m) of the mixed layer, L is the estimated isoprene loss rate (s^{-1}) due to oxidation by OH and ozone, and C is the mixed layer average isoprene concentration ($mg(C)\,m^{-3}$). The calculated flux is typically representative of the region within 10–15 km upwind of the sampling site. The assumptions used to develop Eq. (2) are described by Guenther et al. (1996a, b). Guenther et al. (1996c) have shown that midday (1100–1400) isoprene concentrations in the mixed layer change very slowly with time. The isoprene emission rate increases considerably during this time but is offset by the increasing mixed layer height so that isoprene concentrations are nearly steady state. The estimates of z_i were obtained from a LORAN atmospheric sounding system that used airsondes to measure temperature and humidity profiles up to 5 km above the ground. The mixed layer height was identified by an inversion layer that appears as a region of increasing temperature with height. To estimate the lifetime of isoprene, L, we used the OH and ozone reaction rate coefficients reported by Atkinson (1990) and an estimated midday ozone concentration of 40 ppb (variations in O_3

concentration result in relatively small changes in L) and OH concentration of 4×10^6 molecules cm^{-3}. Uncertainties in L are about $\pm 50\%$ and comprise the largest component of the overall uncertainty in the flux estimate (Guenther et al., 1996a, b).

Our estimate of the mean isoprene concentration, C, was determined from ambient air samples collected in Teflon bags, using timer controlled, whole air samplers attached to the tether line of a helium-filled balloon. Samples were collected simultaneously over a 30 min sampling period at 2–4 heights between 10 m and 1 km above ground level. Fourteen balloon flights were made, but at times heavy winds made sampling difficult. Samples were transferred into stainless-steel canisters and analyzed for isoprene by the GC-FID method described above.

2.3. Emission model

Emission model estimates of isoprene fluxes, F, for the bog and mixed hardwood sites were obtained as follows:

$$F = \varepsilon \gamma D \quad (3)$$

where ε is a landscape average isoprene emission factor, γ is a temperature and PAR adjustment factor, and D is the total foliar density ($g\,m^{-2}$) of isoprene emitting species. The foliar density estimation techniques described by Geron et al. (1994) were used to calculate regional estimates of D for comparison with mixed layer measurements. Estimates of D around the tower, used for comparison with the surface layer measurements, were based on the field measurements described above. Temperature and PAR were measured at the field sites, and the algorithms developed by Guenther et al. (1993) were used to estimate γ. Landscape level estimates of isoprene emission rates from observed measurements at the bog and mixed hardwood sites were then compared to the model estimates for model verification.

3. Results and discussion

3.1. VOC compounds

Biogenic VOC are frequently classified into three categories – isoprene, monoterpenes, and others, which contribute about 45, 10 and 45%, respectively, of the total annual global biogenic VOC emission (Guenther et al., 1995). Isoprene is categorized as a secondary metabolite (Fall, 1991) and is the basic chemical unit of monoterpenes and other terpenoid compounds (Lerdau, 1991). Secondary metabolites are known to play a role in allelopathy, thermal protection, chemical defense, attractants for pollination, and as phytopathic agents although no causal role has been found for isoprene per se (Fall, 1991). Secondary metabolites also commonly accumulate with stress and there are indications that some stresses enhance isoprene emissions (Sharkey et al., 1991a).

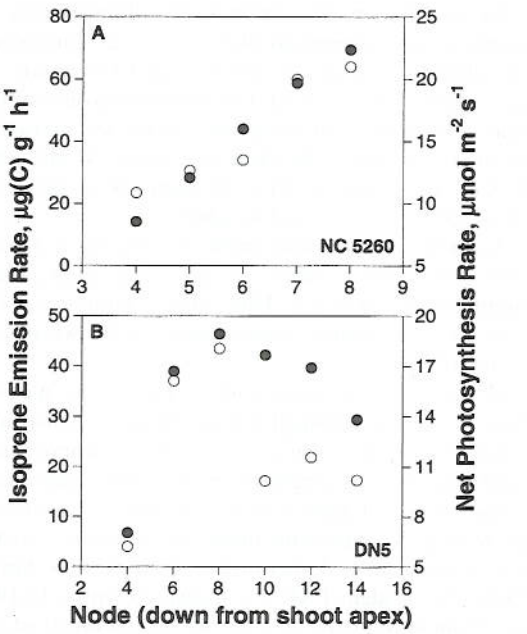

Fig. 1. Leaf position effects on isoprene emission rates (filled symbols) and net photosynthesis rates (open symbols) in two hybrid poplar clones: (A) NC- 5260, (B) DN5 growing in Rhinelander, WI. Clone parentage is given in Table 1. Notes are leaf insertion points, starting with Node 1 (youngest leaf) at tip of shoot.

3.2. VOC emission rates

3.2.1. Leaf position effects

Isoprene emission rates are known to vary with leaf developmental stage and position (Guenther et al., 1991; Sharkey et al., 1991b; Kuzma and Fall, 1993). Our survey of leaf developmental series of two hybrid poplar clones (Fig. 1) showed the importance of sampling the same leaf developmental stage in the field. In a developing shoot of clone NC5260, isoprene emission rates (measured at 25°C and PAR = 1000 $\mu mol\,m^{-2}\,s^{-1}$) were measured on a series of successively older leaves, as indicated by their nodal position (i.e. leaf insertion point). Counting down from the newest leaf at the branch tip (Node 1), isoprene emission rates increased with leaf developmental age from Node 4 up to Node 8, a recently mature leaf (Fig. 1A). In an older shoot of clone DN5, isoprene emission rates increased with leaf development stage up to Node 8 and then decreased in older leaves (Fig. 1B). Isoprene emission rates of recently mature leaves were high in both poplar clones, peaking at 70 and 45 $\mu g(C)\,g^{-1}\,h^{-1}$ in NC5260 and DN5, respectively. Isoprene emission rates and net photosynthetic rates in

each of the two poplars were highly correlated as shown previously in *Populus* and *Quercus* by Sharkey et al. (1991b). Our results prompted us to select recently mature leaves as our sampling position for the remainder of the field study.

3.2.2. Temperature effects

The effects of temperature on isoprene emission rates in plants are well known (Sharkey et al., 1991b; Tingey et al., 1991; Guenther et al., 1991). Isoprene emission rates of recently mature leaves of field-grown trees of two hybrid poplar clones (DN34, DN182) and two northern red oak trees (*Quercus rubra*) growing in the field in northern Wisconsin increased dramatically with increasing leaf temperature (Fig. 2). As expected, isoprene emission rates were very high (i.e., poplar > 150 $\mu g(C)\,g^{-1}\,h^{-1}$, oak > 175 $\mu g(C)\,g^{-1}\,h^{-1}$), especially at temperatures above 30°C. While isoprene emission rates increased exponentially up to 35°C, net photosynthesis rates were flat or declined over the temperature range studied. As a result, the percentage of photosynthetically fixed carbon which is re-emitted as isoprene increases dramatically as temperature increases.

3.2.3. Genetic effects

Populus. Eleven poplar clones which are widely planted in the North Central region of the USA (Hansen et al., 1994), and whose parentage is given in Table 1, were surveyed to assess genetic variation of isoprene emission rates in *Populus*. The selected clones represented a range of hybrid parentages among the *Aegerios* and *Tacamahaca* sections of the genus *Populus*. They included five frequently planted *P. deltoides x P. nigra* clones and six other clones that have performed well in the field under short rotation culture (Hansen et al., 1994). Isoprene emission rates measured at PAR of 1000 $\mu mol\,m^{-2}\,s^{-1}$ and 25°C were all high (clonal means ranging from 46 to 91 $\mu g(C)\,g^{-1}\,h^{-1}$; Fig. 3A) with a clonal average of 68 $\mu g(C)\,g^{-1}\,h^{-1}$. Using the

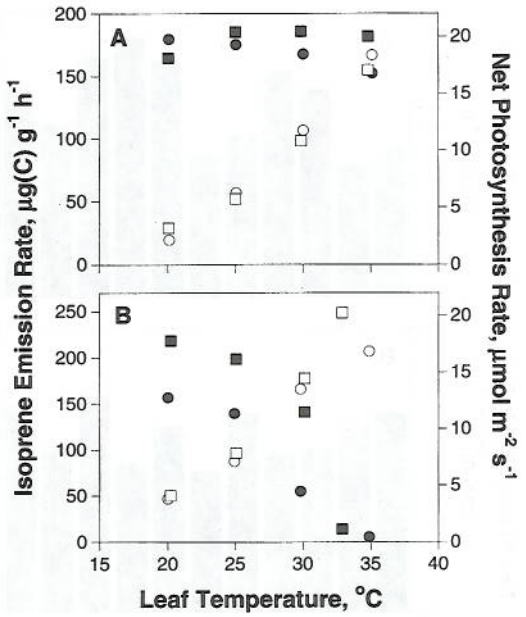

Fig. 2. Leaf temperature effects on isoprene emission rates and net photosynthetic rates in (A) two hybrid poplar clones, DN34 and DN182; and B) two *Quercus rubra* trees growing in Rhinelander, WI. Open symbols are isoprene emission; filled symbols are net photosynthesis. Circles in A are DN182; squares are DN34. Poplar clone parentage is given in Table 1.

temperature response data shown in Fig. 2A, emission rates at 30°C can be predicted using the algorithms of Guenther et al. (1993), in which case the clonal average is 129 $\mu g(C)\,g^{-1}\,h^{-1}$, a very high rate. There was no apparent trend in isoprene emission rates associated with the intersectional crosses. Notably three of the most widely planted clones—DN34, DN182, and NE308—had some of the highest isoprene emission rates. We found no significant correlation between isoprene emission rates and net photosynthetic rates for the clones (Fig. 3) as we

Table 1
List of *Populus* clones surveyed for isoprene emission rates in an arboretum at Rhinelander, WI, in July 1993 (see Fig. 3)

Fig. 3#	Clone #	Parentage (lone name)	*Populus* section
1	DN5	*P. deltoides* × *P. nigra*	*Aegeiros* × *Aegeiros*
2	DN17	*P. deltoides* × *P. nigra* (Robusta)	*Aegeiros* × *Aegeiros*
3	DN34	*P. deltoides* × *P. nigra* (Eugenei)	*Aegeiros* × *Aegeiros*
4	DN182	*P. deltoides* × *P. nigra* (Raverdeau)	*Aegeiros* × *Aegeiros*
5	DN	*P. deltoides* × *P. nigra* (Siouxland)	*Aegeiros* × *Aegeiros*
6	NE252	*P. angulata* × *P. trichocarpa*	*Aegeiros* × *Tacamahaca*
7	NE19	*P. charkowiensis* × *P. candina*	*Aegeiros* × *Aegeiros*
8	NE308	*P. charkowiensis* × *P. incrassata*	*Aegeiros* × *Aegeiros*
9	NM6	*P. nigra* × *P. maximowicizii*	*Aegeiros* × *Tacamahaca*
10	CH15	*P. trichocarpa*	*Tacamahaca*
11	NC5260	*P. tristis* × *P. balsamifera* (Tristis)	*Tacamahaca* × *Tacamahaca*

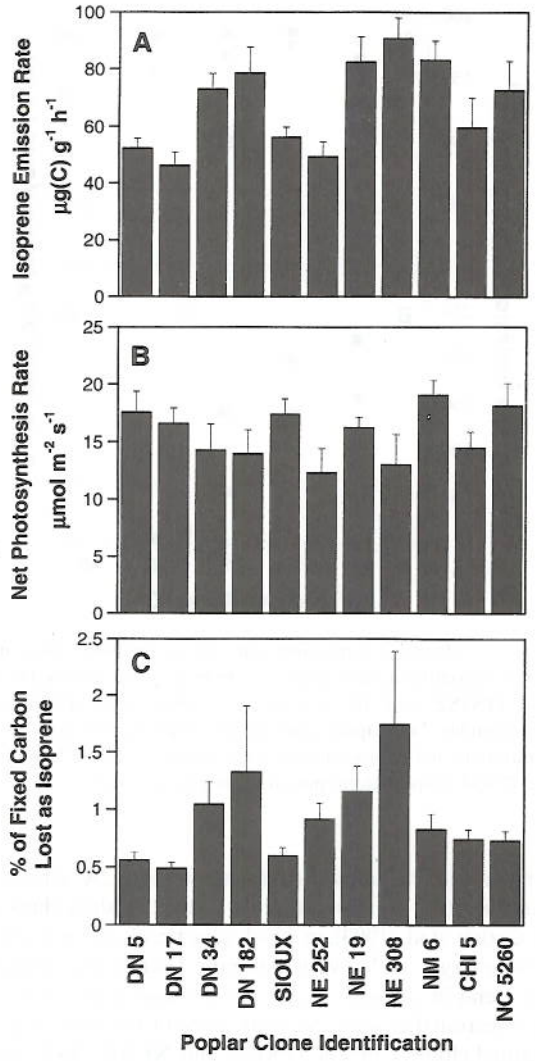

Fig. 3. Mean values (±S.E.; $n = 6$) for (A) isoprene emission rates, (B) net photosynthesis rates, and (C) percentage of fixed carbon lost as isoprene, for recently mature leaves of 11 hybrid poplar clones growing in an arboretum in Rhinelander, WI in July 1993. Clone parentage is given in Table 1.

had expected (Monson et al., 1991); their correlation coefficient was very low ($r^2 = 0.04$).

VOC emissions can make up a significant portion of the carbon budget from trees (Gower et al., 1995). The percent of carbon (C) lost as isoprene at 25°C in these clones ranged from 0.5 to 1.75% with a mean of 0.9% (Fig. 3C), and these values would nearly double at 30°C (Harley et al., 1996). This range of percent C lost agrees with the 1–2% of photosynthetically fixed carbon lost as isoprene reported by Sharkey et al. (1991b). Again, three of the most widely planted poplar clones – DN34, DN182, and DN308 – had the highest percent C lost as isoprene. Our results suggest that poplar clones are very high isoprene emitters and that there is significant clonal variation in the emission rates (i.e. two fold in our clones). In our study, specific causal genetic effects of isoprene emission rates could not be discerned. To detect a causal relationship between isoprene emission rates and heritability will require collaborative studies with molecular geneticists using pedigreed clonal material (Haissig et al., 1992).

Picea. Twelve *Picea* provenances of wide geographic origin were selected for survey of isoprene emission rates (Table 2). The provenances included 11 Asian, European, and North American provenances and one hybrid between a European and Chinese seed source produced at Rhinelander, WI (Nienstaedt and Teich, 1971). The spruce provenances had much lower isoprene emission rates, when normalized to 30°C and 1000 $\mu mol\, m^{-2} s^{-1}$, than the poplar clones. The range for branch level emissions was from 0.01 $\mu g(C)\, g^{-1} h^{-1}$ for *Picea abies* from Europe to 14.0 $\mu g(C)\, g^{-1} h^{-1}$ for *Picea asperata* from China. It should be noted that the hybrid between *P. abies* and *P. asperata* had an intermediate isoprene emission rate (2.6 $\mu g(C)\, g^{-1} h^{-1}$). These findings suggest that isoprene emission rates may be subject to genetic manipulation in breeding programs.

The mean emission rate for the spruce species was 4.2 $\mu g(C)\, g^{-1} h^{-1}$, which is in the "low" category for isoprene emission rates. The most common spruces in North America, *Picea glauca* (white spruce) and *Picea mariana* (black spruce), had branch level emission rates of 9.5 and 5.8 $\mu g(C)\, g^{-1} h^{-1}$, respectively. *Picea mariana* on a landscape scale is an important overall contributor to total VOC emissions from forests in the region because it makes up a large biomass component of the extensive boreal ecosystems in North America (Vitt et al., 1994).

3.2.4. VOC emission rates-leaf and branch level

Most of the uncertainties about existing isoprene emission rate inventories are associated with knowledge gaps in leaf level emission rates and leaf biomass estimates (Fall, 1991; Geron et al., 1994). Isoprene emission rates are classified as "high" when they exceed 40 $\mu g(C)\, g^{-1} h^{-1}$, "medium" when they are between 10 and 40 $\mu g(C)\, g^{-1} h^{-1}$, "low" when they are between 1 and 10 $\mu g(C)\, g^{-1} h^{-1}$, and "negligible" when less than 1 $\mu g(C)\, g^{-1} h^{-1}$(Guenther et al., 1996a). Monoterpene emission rates are classified as "high" when they exceed 3 $\mu g(C)\, g^{-1} h^{-1}$, "medium" when they are between 1 and 3 $\mu g(C)\, g^{-1} h^{-1}$, "low" when they are between 0.2 and 1 $\mu g(C)\, g^{-1} h^{-1}$, and "negligible" when less than 0.2 $\mu g(C)\, g^{-1} h^{-1}$. Summaries of isoprene and monoterpene emissions from trees and other plants in the forest are given in Tables 3–5. Emissions of other VOC from this Wisconsin-based study are summarized by Helmig et al. (1998).

Table 2
Isoprene emission rates (mean ± standard error) from selected *Picea* provenances in an arboretum at Rhinelander, WI, in July 1993. Rates normalized to 30°C and PAR = 1000 μml $m^{-2} s^{-1}$

Provenance	Origin	Isoprene emission rate μg(C) $g^{-1} h^{-1}$ ± S.E.
Picea abies	Europe	0.01 ± 0.01
P. abies × *asperata*	Europe × China	2.63 ± 0.45
P. asperata	China	14.00 ± 6.85
P. bicolor	Japan	0.36 ± 0.26
P. glauca	North America	9.47 ± 5.64
P. glehnii	Japan	0.05 ± 0.05
P. koraiensis	Korea	0.06 ± 0.04
P. koyamai	Japan, Korea	3.97 ± 0.52
P. mariana	North America (spruce bog)	5.79 ± 0.76
P. montigena	China	6.75 ± ---
P. omorika	Europe	6.74 ± 0.66

Table 3
Qualitative evaluation of isoprene emission rates of tree species from northern Wisconsin forests screened in the field near Rhinelander, WI in July 1993. Emission rates are compared to data base previously measured in other regions (Guenther et al., 1994). Symbols: "=" = similar to data base; "↓" = lower than data base; "↑" = higher than data base; "—" = not measured

Previously measured species	Comparison to existing database	
	Isoprene emission rates	Monoterpene emission rates
Abies balsamea	=	↓
Acer rubrum	=	↓
Acer saccharum	=	↓
Betula allegheniensis	=	↓
Betula papynifera	=	=
Cornus alternifolia	=	↓
Fraxinus americana	=	=
Fraxinus nigra	=	=
Picea mariana	=	↓
Pinus resinosa	=	↓
Pinus strobus	=	=
Populus grandidentata	=	↑
Populus tremuloides	=	=
Prunus pennsylvanica	=	=
Prunus serotina	=	↑
Quercus rubra	=	↓
Salix discolor	↑	—
Salix humulis	=	—
Salix petiolaris	↑	—
Salix subsericea	↑	—
Thuja occidentalis	=	↑
Tsuga canadensis	=	↑

3.2.5. Field surveys

In the mixed deciduous and coniferous forests of the Chequamegon National Forest, we conducted a qualitative evaluation of isoprene emission rates of 21 tree species that had been previously measured in other regions (Guenther et al., 1994, 1996a, b). Our qualitative evaluation, done to validate the present data base, involved

Table 4
Isoprene emission rates of previously unstudied plant species from northern Wisconsin forests screened in the field in July 1993. Isoprene emission rates in μg(C) $g^{-1} h^{-1}$: H: > 40; M: 10–40; L: 1–10; and N: < 1. Monoterpene emission rates in μg(C) $g^{-1} h^{-1}$: H: > 3; M: 1–2, L: 0.2–1, and N: < 0.2. H = high; M = medium; L = low; N = negligible

Species	Isoprene emission rates	Monoterprene emission rates
Alnus rugosa	N	M
Amelanchier arborea	N	N
Chamaedaphne calyculata	N	H
Larix laricina	N	M
Ledum groenlandicum	N	H
Ostrya virginiana	N	N
Rubus sp.	N	H
Sphagnum spp.	L	L
Tilia americana	N	N

Table 5
Isoprene emission rates (mean ± standard error) for known isoprene emitting species growing in the field at Rhinelander, WI, in July 1993. Emission rates normalized to 30°C and 1000 μmol $m^{-2} s^{-1}$ PAR (Guenther et al., 1981). *n* = number of measurements

Species	Normalized isoprene emission rates (μg(C) $g^{-1} h^{-1}$)	
	n	Mean ± S.E.
Picea glauca	7	24.4 ± 3.5
Populus euramericana (DN34)	43	153 ± 9.6
Populus tremuloides	20	77.5 ± 9.8
Quercus rubra	78	111.6 ± 6.6
Salix discolor	2	90.7 ± 2.8
Salix humulis	2	40.5 ± 1.4
Salix petiolaris	2	101.5 ± 6.1
Salix subsericea	13	56.8 ± 9.5
Salix spp (average)	19	54.7 ± 8.7

screening two plants per species. Our results on isoprene and monoterpene emission rates in northern Wisconsin are compared to the existing database in Table 3. All species surveyed were within the range of expected isoprene emission rates, except for the *Salix* (willow) species where limited previous data were available. Three of the willow species were higher emitters than expected. As expected, our qualitative study showed that *Picea*, *Populus*, *Quercus*,and *Salix* were high emitters. These results prompted us to single out these species for further quantitative study of isoprene emission rates (reported below).

The estimates of monoterpene emission rates were less consistent with the data base. For example, *Abies*, *Acer*, *Betula*, *Cornus*, *Pinus*, and *Quercus* species had lower emission rates than expected, while *Populus*, *Prunus*, *Thuja*, and *Tsuga* species had higher monoterpene emissions than expected (Table 3). The inconsistencies with the monoterpene emission rates are probably related to the difficulties in field methodology. However, our results suggest that the aforementioned species deserve further study.

We also surveyed a number of plant species from the forest that have not previously been studied for isoprene and monoterpene emission rates (Table 4). Isoprene emission rates for all the species were negligible except for *Sphagnum*, which was within the "low" category (i.e. 1–10 $\mu g(C)\,g^{-1}\,h^{-1}$). Even though *Sphagnum* is a low emitter, it makes up a large portion of the overall biomass (Vitt et al., 1994) of the over 500 million hectares of boreal forest in North America. From a global perspective, it could be a significant contributor to overall biogenic VOC emissions and deserves further study. Monoterpene emission rates ranged in these species from "negligible" to "high". *Amelanchier*, *Ostrya*, and *Tilia* had "negligible" rates; *Sphagnum* was "low"; *Alnus* and *Larix* were "medium" emitters; and *Chamaedaphne*, *Ledum*, and *Rubus* were "high" emitters (Table 4). These findings are significant from the standpoint of total regional VOC emissions in northern Wisconsin because the "medium" and "high" emitters make up a very large portion of the biomass in northern Wisconsin forests (Hansen, 1984) and other northern North American forest ecosystems (Whitney, 1986; Vitt et al., 1994). *Chamaedaphne* (leather leaf), *Ledum* (Laborador tea), and *Rubus* spp (raspberry) are important bog and understory plant species in northern Wisconsin, and *Alnus* and *Larix* are important riparian and bog tree species in the region.

Based upon the results of the qualitative survey summarized in Table 3, we made a more intensive quantitative study of the prominent "high" isoprene emitters, *Picea*, *Populus*, *Quercus*, and *Salix* spp., from the forest (Table 5). *Quercus rubra* had a high isoprene emission rate (112 $\mu g(C)\,g^{-1}\,h^{-1}$) as found in other regions of the USA (Sharkey et al., 1991b; Geron et al., 1994; Guenther et al., 1994). Other high emitters were *Salix petiolaris* and *Salix dicolor* with 102 and 91 $\mu g(C)\,g^{-1}\,h^{-1}$, respectively. The *Populus* species were also "very high". *Populus euramericana* (DN34), probably the most widely planted clone in the North Central region of the US (Hansen et al., 1994), emitted over 84 $\mu g(C)\,g^{-1}\,h^{-1}$of isoprene (>150 $\mu g(C)\,g^{-1}\,h^{-1}$ at 30°C); and *Populus tremuloides* (trembling aspen), which occupies over 15 million hectares of forest land in the northern USA, had isoprene emission rates of over 77 $\mu g(C)\,g^{-1}\,h^{-1}$. Aspen with its "high" isoprene emission rates is also a very sensitive species to ambient levels of tropospheric ozone (Coleman et al., 1995). The only *Picea* that we studied intensively was the native American white spruce that emitted isoprene in the "medium" category (i.e. 24 $g(C)\,g^{-1}\,h^{-1}$). These results confirmed our hypothesis that numerous tree species comprising our northern Wisconsin forest are "high" emitters of isoprene and that these forests are playing an important biogenic role in influencing tropospheric chemistry in the region (Geron et al., 1994).

3.2.6. VOC emission rates – landscape level

Landscape estimates of biogenic VOC are needed as inputs into regional models of atmospheric chemistry used by policy makers (Geron et al., 1994; Guenther et al., 1995). However, more information is needed about VOC emission rates for forested regions of the northern Lake States of the US for model inputs and model validations. The results of our surface layer (tower) estimates of isoprene emissions from the black spruce bog on the Chequamegon National Forest and mixed layer (tethered balloon) estimates from the mixed hardwood forest are given in Table 6. The observed mean value of isoprene flux from the spruce bog was 1.25 ± 0.48 $mg(C)\,m^{-2}\,h^{-1}$ compared to a model estimate of 0.82 ± 0.25 $mg(C)\,m^{-2}\,h^{-1}$. The model estimate was derived by multiplying the isoprene emission factor for *Picea* (i.e., 14 $\mu g(C)\,g^{-1}\,h^{-1}$) from Guenther et al. (1994) by the measured *Picea* foliar mass (i.e. 136 $g\,m^{-2}$) times a temperature and PAR

Table 6
Landscape level estimates of isoprene emission rates (mean ± standard error) for forest types of the Chequamegon National Forest in northern Wisconsin in July 1993. n = number of replicates

Forest type	Measurement method n	Isoprene emission rates ± S.E. ($mg(C)\,m^{-2}\,h^{-1}$)
Black spruce bog	Tower	Observed 1.25 ± 0.48
	($n = 8$)	Model 0.82 ± 0.25
Mixed hardwood forest	Tethered balloon	Observed 1.89 ± 0.24
	($n = 14$)	Model 1.27 ± 0.10

adjustment factor from Guenther et al. (1996a) (i.e., 0.43 for 24°C at PAR = 1300 μmol $m^{-2} s^{-1}$, the mean conditions during data collection). The model deviation was 0.43 mg(C) $m^{-2} h^{-1}$, which means the predicted isoprene emission rates were within the limits of the standard error of the observed values. Our observed values were also within the range of 0–2 mg(C) $m^{-2} h^{-1}$ reported by Geron et al. (1994) for the county-wide average of isoprene emission in northern Wisconsin. The observed mean value of the mixed layer estimates of the mixed hardwood site from the 14 tethered balloon flights was 1.89 ± 0.24 mg(C) $m^{-2} h^{-1}$, which compared to the 1.27 ± 0.10 mg(C) $m^{-2} h^{-1}$model estimate. The model estimate assumed a regional species composition of three "high" isoprene emitters – 12.5% *Picea*, 11.3% *Populus*, and 2% *Quercus* from Hansen et al. (1992), and average isoprene emission rates of 14 μg(C) $g^{-1} h^{-1}$for *Picea* and 70 μg(C) $g^{-1} h^{-1}$ for *Populus* and *Quercus* (Guenther et al., 1994) with a mean temperature and PAR adjustment factor of 0.39 for 23°C and 1150 μmol $m^{-2} s^{-1}$ for PAR (Guenther et al., 1996a). Although the model deviation was 0.61 mg(C) $m^{-2} h^{-1}$, both the observed and model estimates agree reasonably well with county-wide estimates for isoprene emission given by Geron et al. (1994). Based upon the results of both our extensive and intensive studies (Tables 2–5), it is not surprising that the observed isoprene emissions were higher than predictions based upon just the high three emitters and the existing emissions database. Based on our measurements, many northern Wisconsin plant species with significant biomass in the tethered balloon footprint emitted isoprene at levels higher than found in the data base, e.g. *Quercus rubra* (112 μg(C) $g^{-1} h^{-1}$), *Populus tremuloides* (78 μg(C) $g^{-1} h^{-1}$), and the *Salix* spp. (55 μg(C) $g^{-1} h^{-1}$).

In summary, numerous northern Wisconsin forest plant species emit high concentrations of isoprene and other VOC, and the mixed deciduous and coniferous forests of northern Wisconsin are a significant source of VOC in the atmosphere. The highest isoprene emitters are species of *Populus*, *Quercus*, and *Salix*, with a lesser contribution from *Picea*. Genetic variation in isoprene emission was observed in *Populus* and *Picea*, but molecular genetic studies with pedigree material are needed to determine causal genetic relationships. Landscape level estimates of isoprene emission were between 1 and 2 mg(C) $m^{-2} h^{-1}$, which agrees reasonably well with regional model predictions. Future studies are needed to extrapolate these estimates to other landscapes and to better understand the factors controlling observed variation in VOC emissions from forests.

Acknowledgements

Excerpts of this research were presented at the International Union of Forestry Research Workshop entitled "Interactive Environmental Effects on Forest Stands", Christchurch, New Zealand, 28 January–7 February 1995. The authors gratefully acknowledge the technical assistance of Edmund Bauer on the graphics as well as the clerical assistance of Kathryn Heise. The National Center for Atmospheric Research (NCAR) is sponsored by the National Science Foundation. This work was partially funded by the US Environmental Protection Agency, under Interagency Agreement Grant #DW49934973-01-0 to NCAR. Mention of trade names or companies is for reader information only and does not indicate endorsement by the USDA, Forest Service, or NCAR.

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