

Emissions of Biogenic VOCs from Boreal Ecosystems

R. Janson and C. De Serves

*Institute for Applied Environmental Chemistry: Air Pollution Laboratory
Stockholm University, Sweden*

Summary

Emission measurements of monoterpenes, isoprene, other light hydrocarbons, and light aldehydes and ketones were made with the chamber technique on Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), pine and spruce forest floors, and *Sphagnum* wetlands in Sweden and Finland. It was found that both Scots pine and Norway spruce emit significant amounts of acetone and some acetaldehyde to the atmosphere. The variability in the composition of monoterpene emissions from Scots pine is larger than hitherto thought. Notably a specimen of Scots pine in northern Finland was found to emit large amounts of beta-myrcene and very little Δ^3 -carene. A Scots pine in southeastern Finland also emitted only small amounts of Δ^3 -carene. It is confirmed that Scots pine is a low or insignificant isoprene emitter, while Norway spruce is a high isoprene emitter. While the floors of both Scots pine and Norway spruce forests emit terpenes and some light hydrocarbons, the flux is small in comparison to the flux from the tree needles. Low and wet parts of the *Sphagnum* fen have been found to emit significant amounts of isoprene and small amounts of terpenes and other light hydrocarbons. The raised and drier parts of the fen emit 20 to 30 times less isoprene. The areal emission of isoprene from wetlands can be as large or larger than the areal emission from spruce forests and thus contribute a significant amount of isoprene to the boreal atmosphere.

Introduction

The main ecosystems of the Scandinavian boreal zone are the coniferous forest and wetlands. Two species dominate the coniferous forest, Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). The general rule of thumb has been that conifers emit mainly monoterpenes while deciduous species emit mainly isoprene. The boreal zone being a coniferous zone, its contribution to atmospheric chemistry has been thought to be mainly by the emission of monoterpenes, and the few studies to date have also concerned monoterpenes [1;2;3]. A

number of recent works have demonstrated, however, that some conifers, in particular Norway spruce and Sitka spruce, emit significant amounts of isoprene [4;5]. The work of *Kesselmeir et al.* [6] has also shown that carbonyl compounds are emitted at significant rates by some conifers. Indeed, recent model calculations of regional BVOC fluxes by *Simpson et al.* [7] have estimated the oxygenated species, primarily aldehydes, ketones, organic acids, and alcohols, to be a considerable part of the total flux, although there exist very little experimental data. As for the boreal zone, no measurements of isoprene or carbonyl compound emissions from Norway spruce or Scots pine have previously been done.

The forest floor, i.e. soil and/or field vegetation, is also known to emit VOC to the atmosphere, although the few measurements to date are not conclusive as to the significance or sources of these fluxes [2;3;5]. Typical ground and field vegetation in the pine forest are mosses, lichens, blueberry (*Vaccinium myrtillus*), lingonberry (*Vaccinium vitis-idaea*), and heather (*Calluna vulgaris*), whereas the dense spruce forest usually does not have ground vegetation, but is covered only with spruce needles.

Peatlands are a prominent feature of the boreal environment covering on the order of 1 million km². Carbon dioxide and CH₄ fluxes in these environments have been the subject of interest for many years, primarily for peat accumulation, carbon budget, and climate considerations. Very little work has been done on the flux of other reactive biogenic hydrocarbons, compounds which are important to the chemistry and oxidation capacity of the troposphere. As *Klinger et al.* [8] pointed out, boreal ecosystems can be particularly sensitive to future climate changes. In a study of the carbon fluxes from the Hudson Bay lowlands, they reported isoprene fluxes as high as several hundred $\mu\text{gC m}^{-2} \text{h}^{-1}$.

The goals of this study have been to determine the emission patterns of biogenic volatile organic compounds (monoterpenes, isoprene, other C₁–C₅ hydrocarbons, C₁–C₅ aldehydes and ketones) from the major ecosystems of the boreal environment in Scandinavia, coniferous forests and wetlands, and to determine ambient air concentrations of the light aldehydes and ketones at background sites in northern and southern Finland.

Experimental

Measurement campaigns were conducted in mixed Scots pine and Norway spruce forests at the Pallas Research Station in northern Finland (July, 1996), the NOPEX site in Björklinge at the

northern extent of the boreonemoral zone in Sweden (June and August, 1996), the Asa Research Station in southern Sweden (May-June, 1997), and in a Scots pine forest at the Mekrijärvi Research Station in southeastern Finland (August, 1997). Wetland emission measurements were made at the NOPEX site during the summer of 1997 and at the Mekrijärvi site in August, 1997.

Branch emission measurements were made at all forest sites with the dynamic chamber technique using an all Teflon chamber. The chamber was a 17 liter Teflon bag, 25 cm diameter, tied over approximately 25 cm pine or spruce branch. The bag was held inflated, the walls kept away from the needles of the sample branch, and leakage of ambient air into the chamber was avoided by maintaining a slight overpressure inside the bag. A fan ensured mixing but not excess wind over the branch. The chamber was continuously flushed with 10 L min⁻¹ ambient air, purified of ozone with a KI scrubber. The water content of the input air was decreased with a Peltier cooling element so that the relative humidity, with branch transpiration, would be similar to ambient humidity. The BVOC emissions were determined from the difference between their air concentrations at the inlet and outlet of the chamber, normalized to the branch needle dry weight. To investigate the influence of environmental factors on the BVOC emission rates, temperature and relative humidity were continuously recorded from the inlet air flow and the chamber air, and Photosynthetic Active Radiation (PAR) recorded from just above the chamber. The responses from the temperature and relative humidity sensors were compared regularly.

Forest floor measurements and the wetland measurements were made with a 252 L (empty) all Teflon chamber. A frame of stainless steel (60x60x20 cm), lined on the inside with Teflon film, was placed on the ground/wetland site at the beginning of the season or campaign. The frame was carefully pressed into the ground just far enough to avoid gaps between it and the ground, care being taken to avoid excess damage to roots and bushes. To make a measurement, the chamber was placed on the frame, enclosing the air space over the sample site, and air samples taken over a period of 20 to 30 minutes. For the carbonyls, which need a long sampling time, ambient and chamber air samples were taken simultaneously for one hour. Chamber air temperature and relative humidity, ground temperature at 5 and 15 cm, and PAR were recorded.

Monoterpenes were collected on Tenax absorption tubes (200 mg Tenax TA), light carbonyl compounds on Sep-Pak ® DNPH-Silica cartridges (360 mg 2,4-Dinitrophenylhydrazine) and light hydrocarbons in whole air samples collected in 3 L electro-polished stainless steel cylinders.

Analysis was done at the ITM Air Pollution Laboratory: monoterpenes by GC-MS, light hydrocarbons by GC-FID and carbonyls by HPLC. Identification and quantification were done with authentic standards. Chamber blank values were determined for both chambers and all compounds by taking samples in the normal way from empty chambers. In the case of the ground chamber, the bottom of the chamber was closed with Teflon film for the blank value experiment. Laboratory experiments were also conducted to ascertain the stability of isoprene in the branch cuvette and in the sampling canisters.

Ambient air samples were taken twice a week from May to September, 1996 and 1997, at the Pallas Research Station in northern Finland and Mekrijärvi in southeastern Finland with DNPH absorption cartridges for the determination of ambient air light carbonyl concentrations. Four hour samples were taken with battery operated pumps, and the total sample volume recorded with gas meters. Ozone scrubbers, potassium iodide in Cu tubing, were used for all sampling.

Results

Ambient concentrations of light aldehydes and ketones

Acetone accounted for 30 to 80% of the light carbonyls in the ambient air at both the Pallas and Mekrijärvi sites in northern and southeastern Finland, respectively, during the May to September sampling period, Figure 1. Formaldehyde was the second most abundant carbonyl, while the acetaldehyde mixing ratios were always below 500 pptv. The total carbonyl mixing ratio ranged from 500 to 2000 pptv. At Mekrijärvi, the concentrations showed a slightly larger day-to-day variation, and the concentration of formaldehyde would sometimes surpass that of acetone.

Scots pine emissions

The composition of the monoterpene emission from Scots pine was found to vary from one site to the next (Table 1). At Pallas in northern Finland, the predominant monoterpene in July, 1966, was β -myrcene, accounting for $71\pm 8\%$ of the total monoterpene emission. Alpha-pinene accounted for only 12% and Δ^3 -carene was not observed. Delta-3-carene was not either observed in the emission of Scots pine at Mekrijärvi in August, 1997. There, α -pinene accounted for 64% of the terpene emission. At the NOPEX and Asa sites in Sweden, the

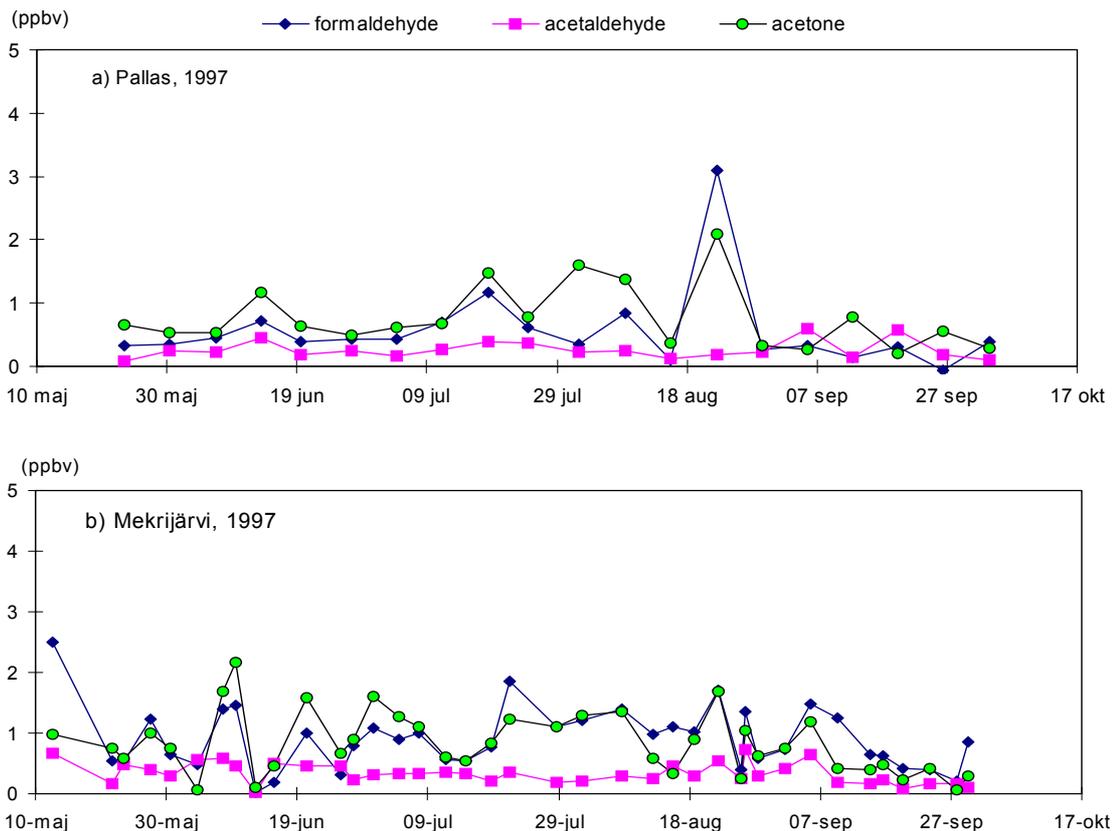


Figure 1. Light carbonyl daytime mixing ratios (ppbv) in a) northern Finland (Pallas) and b) southeastern Finland (Mekrijärvi), 1997.

monoterpene flux was dominated by α -pinene and Δ^3 -carene with 30% and 57%, respectively, at the NOPEX site (July, 1996) and 35% and 30%, respectively, in Asa (June, 1997).

In Pallas, the total monoterpene emission varied around several hundred $\text{ngC gdw}^{-1} \text{h}^{-1}$ and did not correlate to temperature. Temperatures were between 8 and 18°C and current needles were not developed. At Mekrijärvi (July-August, 1997), monoterpene emissions reached up to 600 $\text{ng gdw}^{-1} \text{h}^{-1}$ (Figure 2) and the correlation to temperature was good, $R^2=0.8542$, but with a steeper slope than the $\beta=0.09$ used by *Guenther et al.* [9]. Standard emission factors (30°C, 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$) derived from the observed temperature correlation and the Guenther et al. algorithm were 0.60 and 0.37 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, respectively. At Asa, the temperature correlation was also good and the standard emission factors derived by the two methods were in good agreement, 0.33 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ by the temperature correlation and 0.34 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ using the Guenther et al. β factor.

Table 1. *Relative composition of monoterpene emission from Scots pine.*

	<u>Pallas</u>		<u>NOPEX</u>		<u>Asa</u>		<u>Mekrijärvi</u>	
	July, 1996		July, 1996		June, 1997		August, 1997	
	avg	std	avg	std	avg	std	avg	std
a-pinene	12%	3%	30%	9%	35%	4%	64%	4%
Camphene	0%	4%	3%	2%	13%	6%	11%	3%
Sabinene	1%	1%	5%	4%	0%	0%	1%	0%
b-pinene	2%	1%	-2%	5%	2%	3%	4%	1%
myrcene	71%	8%	5%	6%	4%	3%	3%	1%
3-carene	0%	1%	57%	6%	30%	8%	0%	2%
limonene	13%	6%	1%	2%	9%	6%	13%	4%

Because of high and variable blank values of the Sep-Pak ® DNPH cartridges, emission rates of the light aldehydes and acetones were often below their detection limits. Nevertheless, daytime emission rates similar to and higher than monoterpene emission rates were observed from Scots pine at NOPEX, Asa and Mekrijärvi. The results from Mekrijärvi are seen in Figure 2. Maximum rates observed reached $0.8 \mu\text{gC gdw}^{-1}\text{h}^{-1}$. The emission was dominated by acetone, accounting for 80 to more than 90% of the total carbonyl flux, and followed by acetaldehyde, at all sites. The rates were highest at noon/early afternoon, and decreased at night.

Measurements on Scots pine at all sites have confirmed that it is a low to insignificant emitter of isoprene. Small emissions were sometimes observed at all sites, but always lower than $0.025 \mu\text{gC gdw}^{-1}\text{h}^{-1}$.

Norway spruce emissions

The monoterpene emission from Norway spruce also varied somewhat from site to site. At the NOPEX and Pallas sites, α -pinene accounted for 34% and 42% of the emission, respectively, while at Asa a rapid change in the relative composition was observed in the springtime. Spring was late and the weather cold at the beginning of the measurement period, and new growth was not observed on the branch until the last day of the period. On May 20, 41% of the emission was α -pinene, while on May 28-29 it accounted for 53% of the emission and on June 1-2, it was 82%. The β factor suggested by Guenther et al. describes the temperature cor-

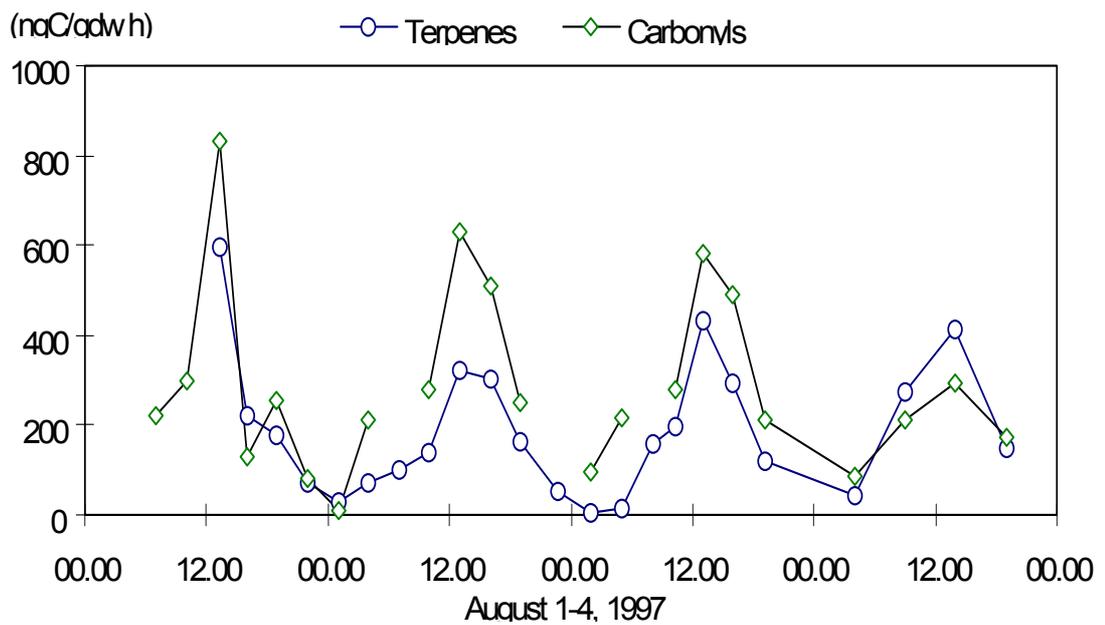


Figure 2. Monoterpene and carbonyl emissions from Scots pine, Mekrijärvi, 1997.

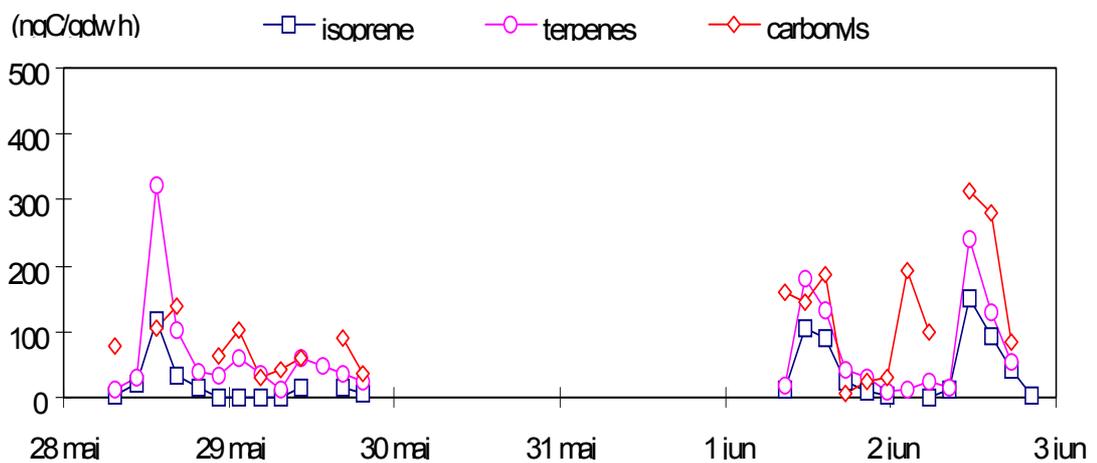


Figure 3. Emission of isoprene, monoterpenes, and light aldehydes and ketones ($\text{ngC}/\text{gdw h}$) from Norway spruce, Asa Research Park, 1997.

relation observed at Asa well. The standard emission rate (total terpene emission) calculated by the observed temperature correlation and the Guenther et al. algorithm are $0.24 \mu\text{gC gdw}^{-1}\text{h}^{-1}$ and $0.26 \mu\text{gC gdw}^{-1}\text{h}^{-1}$, respectively.

Of the light aldehydes and ketones emitted by Norway spruce, acetone was the most abundant, as with Scots pine, accounting for 80 to 90% of the carbonyl flux. On a carbon basis, the daytime flux was similar to that of the monoterpenes, Figure 3, while on a molecular basis, the carbonyl flux dominates.

Isoprene is also emitted by Norway spruce at rates comparable to that of the monoterpenes, Figure 3, although the isoprene season is probably shorter. Measurements at Asa were made during and after a cold spell and prior to visible new growth. It is therefore not surprising that the emission rate was so low. The mean standard emission rate factor by the Guenther et al. model was only $0.38 \pm 0.20 \mu\text{gC gdw}^{-1}\text{h}^{-1}$ for the Asa measurements. At the NOPEX and Pallas sites, average standard emission rates of 1.2 and $0.64 \mu\text{gC gdw}^{-1}\text{h}^{-1}$, respectively, have been determined.

Forest floor emissions

Both pine and spruce forest floors were found to emit small amounts of terpenes and light hydrocarbons, but no emission of light carbonyls was seen in this study. The pine forest floor at Mekrijärvi consisted of mosses (90% coverage), heather (75%), and a few small blueberry bushes and emitted only tens of $\mu\text{gC m}^{-2}\text{h}^{-1}$ monoterpenes, Figure 4, where 54% was α -pinene and 16% Δ^3 -carene. The flux of light hydrocarbons was less than $1 \mu\text{gC m}^{-2}\text{h}^{-1}$ and dominated by ethene with 33%, propene with 18% and propane with 11%. At Asa, the floor was covered with mosses and a few small blueberry and lingonberry bushes. Here the terpene emission reached $100 \mu\text{gC m}^{-2}\text{h}^{-1}$, consisting of α -pinene (43%) and Δ^3 -carene (46%). The fluxes of hydrocarbons from the spruce forest in Asa were similar to those of the pine forest, tens of $\mu\text{gC m}^{-2}\text{h}^{-1}$ terpenes and a few $\mu\text{gC m}^{-2}\text{h}^{-1}$ light hydrocarbons. The composition of the terpene emission was different however, consisting of α -pinene (22%), camphene (26%), β -pinene, myrcene, and limonene (24%).

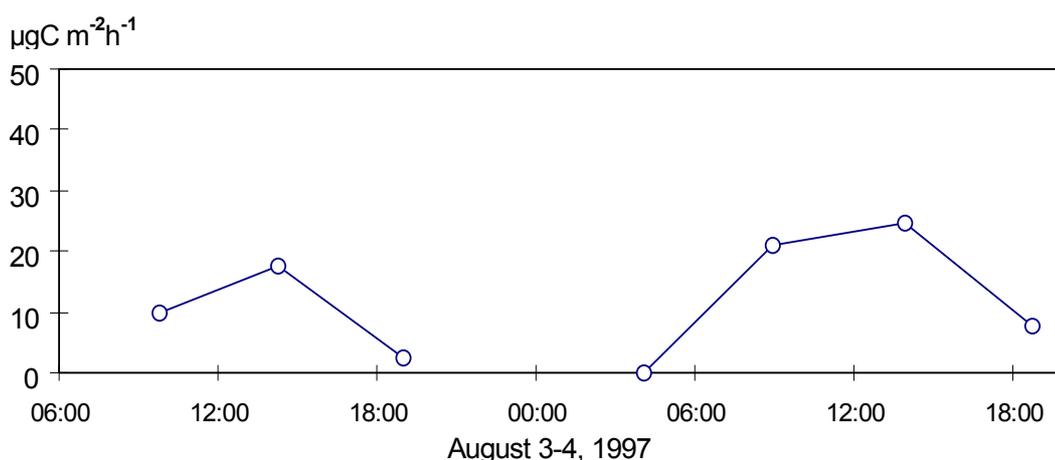


Figure 4. Flux of monoterpenes ($\mu\text{g m}^{-2}\text{h}^{-1}$) from the forest floor of a Scots pine forest at Mekrijärvi, August, 1997.

Sphagnum moss peatland emissions

Seasonal emissions of isoprene and other light hydrocarbons were measured from both an elevated, dry site (hummock) and low, wet site (flark) on a *Sphagnum* fen in Sweden, and diurnal emissions from a wet site on a *Sphagnum* fen in Finland, Figure 5. Both fens are in the southern boreal zone. Isoprene clearly dominated the flux of light hydrocarbons while ethene, propene, and 2-butene, as well as traces of n-butane and propane were also observed.

The isoprene emission season extended from the spring thaw to the occurrence of ground frost in the fall. The highest fluxes of isoprene were observed from wetter sites (flarks), and reached up to $2000 \mu\text{gC m}^{-2} \text{h}^{-1}$, while the fluxes from the hummocks did not exceed $70 \mu\text{gC m}^{-2} \text{h}^{-1}$. The fluxes of ethene and propene did not exceed $15 \mu\text{gC m}^{-2} \text{h}^{-1}$. All emissions showed strong diurnal variations with zero or near-zero values at night. Much of the data can be explained by temperature and light, as is the case for isoprene emitting trees, but other factors are important. The mean normalized emission rate for the wet *Sphagnum* environments was $624 \pm 357 \mu\text{gC m}^{-2} \text{h}^{-1}$ ($1000 \mu\text{mol m}^{-2}\text{s}^{-1}$, 30°C). Our data indicate that, in comparison with emissions from forests, the flux of isoprene from *Sphagnum* peatlands is a significant source of volatile organic compounds to the atmosphere in boreal regions [10].

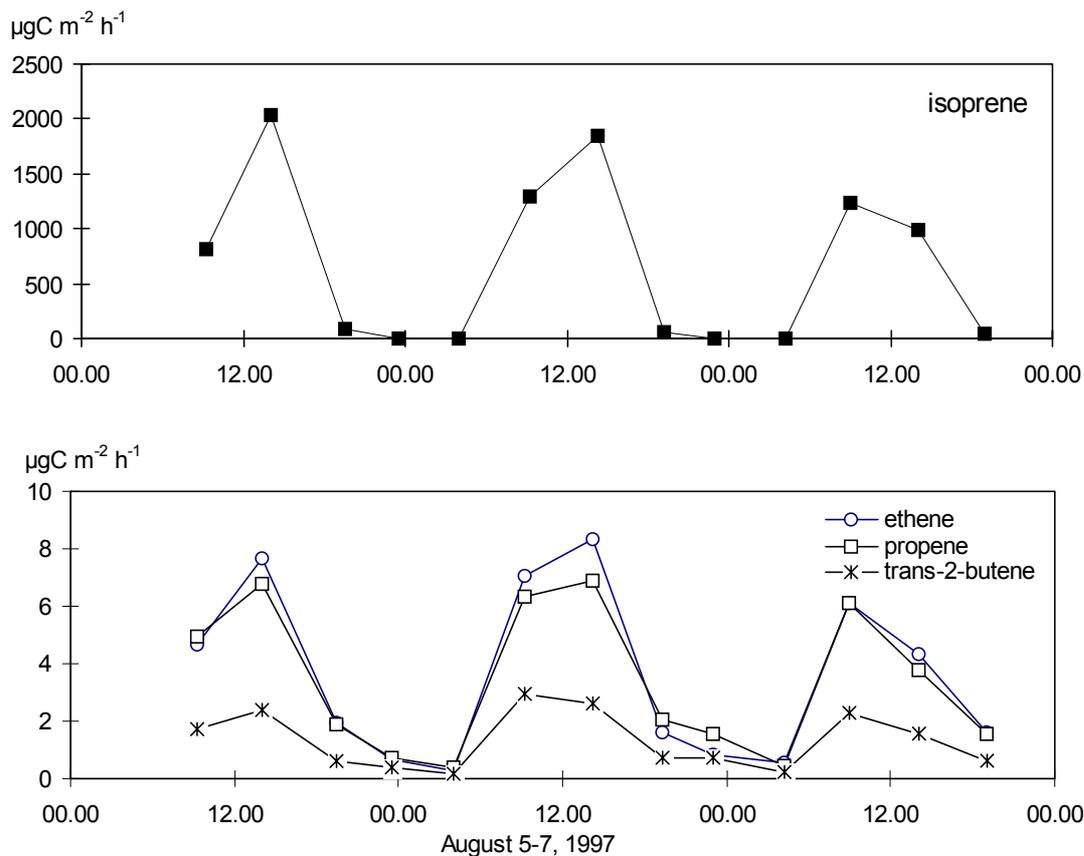


Figure 5. Flux of isoprene, ethene, propene, and trans-2-butene from a wet Sphagnum site on Salmisuo, a wetland in southeastern Finland, 1997.

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References

- [1] Janson, R., 1992. Monoterpene concentrations in and above a forest of Scots pine. *Journal of Atmospheric Chemistry* 14, 385-394.
- [2] Janson, R., 1993. Monoterpene emissions from Scots pine and Norwegian spruce. *Journal of Geophysical Research* 98, 2839-2850.
- [3] Isidorov, V., Zenkevich, I. and Ioffe, B., 1985. Volatile organic compounds in the atmosphere of forests, *Atmospheric Environment* 19, 1-8.
- [4] Street, R.A., Duckham, S.C. and Hewitt, C.N., 1996. Laboratory and field studies of biogenic volatile organic compounds from Sitka spruce (*Picea sitchensis* Bong.) in the United Kingdom. *Journal of Geophysical Research* 101, 22799-22806.
- [5] Steinbrecher, R., Ziegler, H., Eichstädter, G., Fehsenfeld, U., Gabriel, R., Kolb, Ch., Rabong, R., Schönwitz, R. and Schürmann, W., 1997. Monoterpene and isoprene emission in Norway spruce forests. In S. Slanina (Ed.), *Biosphere-atmosphere exchange of pollutants and trace substances*, Springer-Verlag, Berlin, pp352-365.
- [6] Kesselmeier, J., Bode, K., Hofmann, U., Müller, H., Schäfer, L., Wolf, A., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Ferrari, C., Jacob, V., Fugit, J.L., Dutaur, L., Simon, V. and Torres, L., 1997. Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms. *Atmospheric Environment* 31, 119-133.
- [7] Simpson, D., Guenther, A., Hewitt, C.N. and Steinbrecher, R., 1995. Biogenic emissions in Europe 1: Estimates and uncertainties. *Journal of Geophysical Research* 100, 22875-22890.
- [8] Klinger, L.F., P.R. Zimmerman, J.P. Greenberg, L.E. Heidt, and A. B. Guenther, Carbon trace gas fluxes along a successional gradient in the Hudson Bay lowland, *Journal of Geophysical Research* 99, 1469-1494, 1994.
- [9] Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. *Journal of Geophysical Research* 100, 8873-8892.
- [10] Janson, R. and De Serves, C., 1998. Isoprene Emissions from Boreal Wetlands in Scandinavia. *Journal of Geophysical Research* (in press).

