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The VOC Emission Rates of Boreal Deciduous Trees

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Introduction

The VOC emission rates of the most common deciduous trees in the boreal forests were measured during the summers 1996 and 1997. The species studied were silver birch (*Betula pendula*), downy birch (*Betula pubescens*), European aspen (*Populus tremula*), grey alder (*Alnus incana*) and tea-leafed willow *(Salix phylicifolia*). The emission rates were measured for the first time soon after budbreak and the measurements were continued throughout the growing season until the leaves were turning yellow.

The measurements were conducted at the research station of the Finnish Forest Research Institute 20 km north of Helsinki (60.4°N, 25.0°E). The measured tree was different each time, because their biomasses were weighted after the cuvette measurements. Ambient air was pumped through the Teflon chamber at a rate of 27 l/min. The Tenax samples and canister samples were taken from the outlet and inlet ports. The canister samples were analyzed using GC/FID and Tenax samples with GC/MS. A more detailed description of the analytical system is given in Hakola et al. (1998).

European aspen and tea-leafed willow

European aspen and tea-leafed willow emitted monoterpenes soon after the budbreak, but the emissions decreased rapidly as the leaves were growing. High monoterpene emissions in spring from balsam poplar have been measured by Isidorov et al., (1985). Also these emissions stopped completely in summer. In the beginning of the growing season willow emitted also 1-butene, ethene and propene, these emissions declined concomitant with the monoterpene emissions. At that time the willow was also blooming and the blossoms could be the source as well. About two weeks after the leaves had opened aspen and willow started to emit isoprene. The delayed isoprene emission has been noticed earlier by Grinspoon et al., (1991) and Guenther et al., (1991). Their studies showed that the isoprene emissions initiated

several days after the photosynthetic competence develops. Isoprene emissions of both aspen and willow remained high until September, the maximum emission rate of aspen was 50 μg $g(dw)^{-1}$ h^{-1} (T=29°C) and of willow 76 μg $g(dw)^{-1}$ h^{-1} (T=34°C).

Silver birch

The emission rates of silver birch were measured during two growing seasons 1996 and 1997. The daily average emission rates (2-4 daily measurements) are shown in Figures 1 (terpenoids) and 2 (light hydrocarbons). During both summers the monoterpene emission rates were higher in the first measurements days and they declined soon being very low in June. The buds may contain a small monoterpene pool that is evaporated soon after budbreak. At the end of June, when the leaves had reached their full size, the emission rates increased considerably and they remained high until September, when the growing season was ending. Also the monoterpene emission pattern changed; in the beginning of the growing season the emissions consisted mainly of α-pinene, β-pinene, carene or camphene, but after the leaves were fully expanded the emissions were almost only sabinene, *cis*-ocimene and *trans*-ocimene.

Downy birch

The monoterpene emission rates of downy birch were even smaller than those of silver birch during June. On the last day of June the emissions suddenly increased being 12 $\mu g*g^{-1}(dw)*h^{-1}$. The following day the different downy birch was measured, but instead of terpenes it emitted linalool and sesquiterpenes; *cis*-caryophyllene, *trans*-caryophyllene and α-farnesene. *Cis*-caryophyllene and α-farnesene are tentatively identified according to mass spectra, but without authentic standard. The emissions of downy birch varied more than the emissions of silver birch. When downy birch was measured in August for the first time it emitted only small amounts of terpenes, but the following day large sabinene emissions were detected. One explanation could be that the trees are not exactly at the same developing level. The daily average (consisting of 2-4 daily measurements) emission rates of downy birch are shown in Figures 1 and 2. At the end of May and in the beginning of June the monoterpenes emitted were α-pinene, β-pinene and sabinene, but later in June linalool was dominating. At the time of high emission rates the compounds emitting were sabinene, ocimenes, linalool and caryophyllenes.

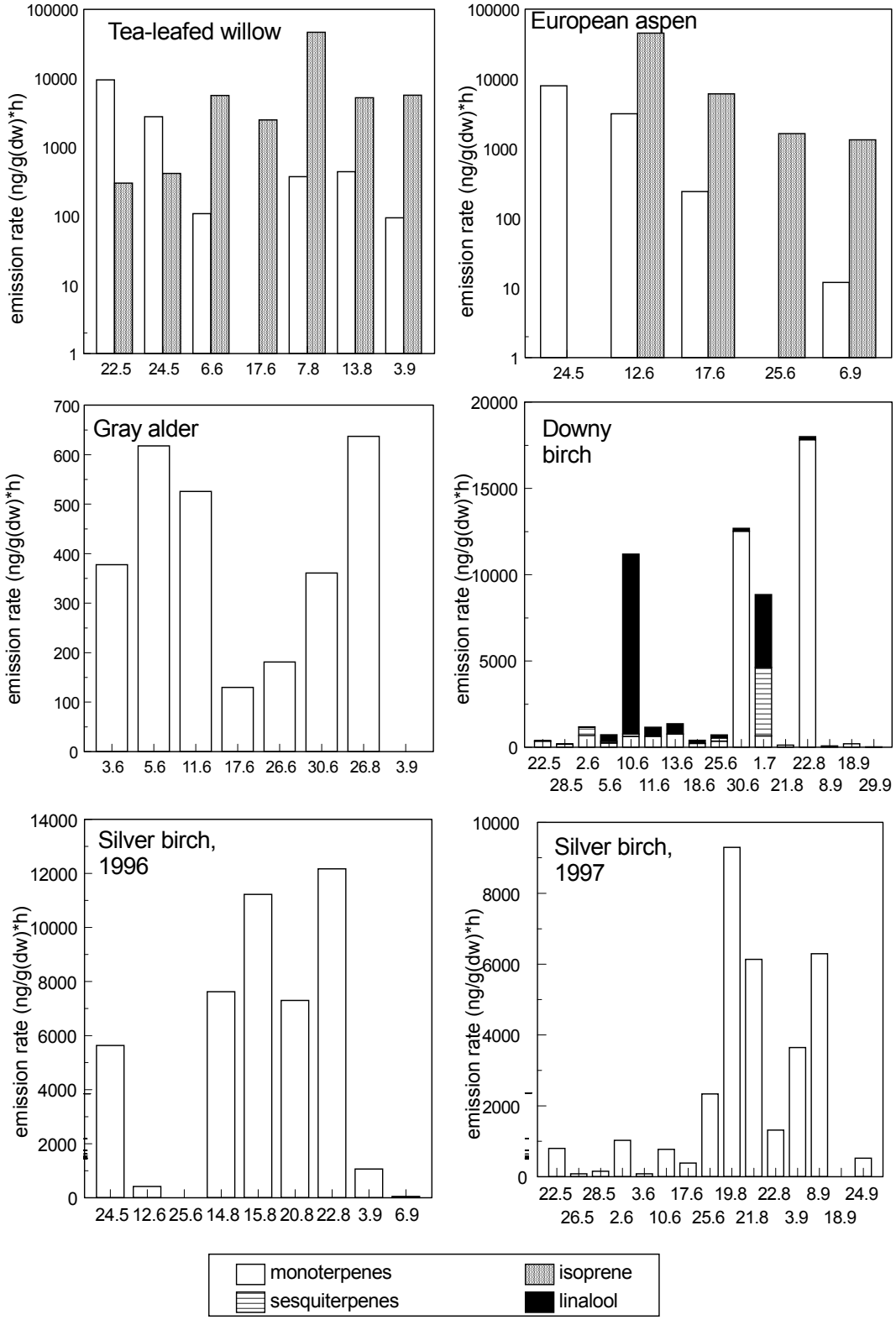

Figure 1. *The daily average (2-4 measurements) emission rates of terpenoid compounds from tea-leafed willow, European aspen, grey alder, downy birch, and silver birch.*

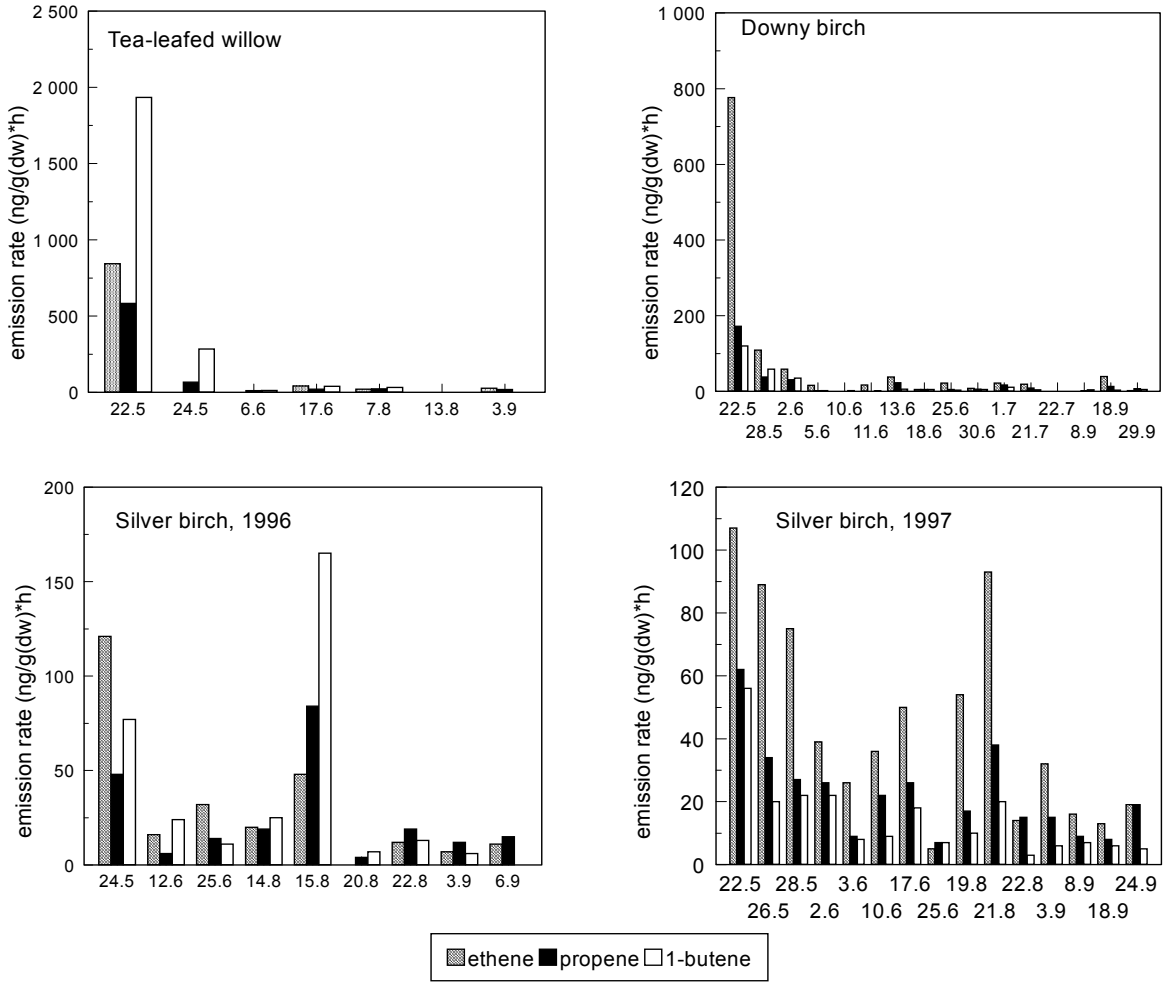

Figure 2. *The daily average emission rates (2-4 measurements) of light hydrocarbons from tea-leafed willow, downy birch, and silver birch.*

As early as the 10th June very high linalool emission rate (~10 $\mu g*g^{-1}(dw)*h^{-1}$) of downy birch was measured. Two measurements were made and they did not deviate much. Another high linalool emission rate was seen on the first July (~4 $\mu g*g^{-1}(dw)*h^{-1}$). On that day also high sesquiterpene emission rates were measured. Silver birch emitted some linalool too, but much less than downy birch. High linalool emissions have been detected earlier in the Valencia orange blossoms in California (Arey et al., 1991).

The terpenoid emissions of downy birch show the same kind of seasonal variation as silver birch. The time when leaves are growing is a period with low emissions, but after the leaves have reached their full size higher monoterpene/sesquiterpene emissions initiate. The leaves of

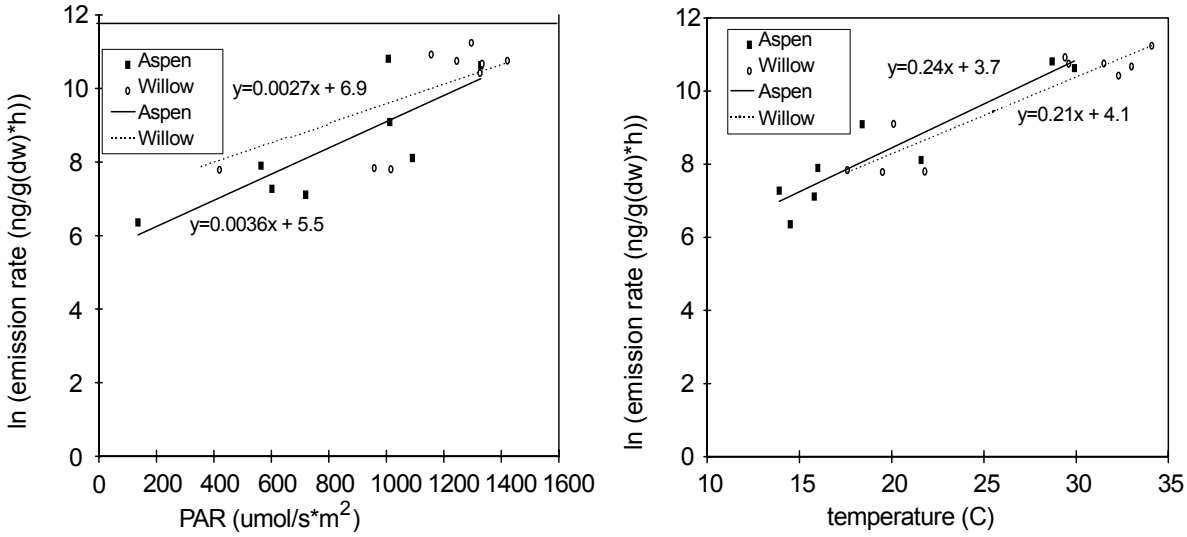

Figure 3. *Isoprene emission rates of willow and aspen as a function of PAR (left frame) and temperature (right frame).*

downy birch remain smaller than the leaves of silver birch and they reach their full size earlier in June than the leaves of silver birch. During the low emission period the main compounds emitting are linalool, α-pinene, β-pinene, and sabinene and in the period with higher emissions the main terpenoid compound are α-pinene, sabinene and trans-ocimene, although there are days with high linalool and caryophyllene emissions.

Grey alder

The emission rates of grey alder were low during the whole growing season. Small leaves emitted again more monoterpenes, and the emissions declined being less than 200 $ng*g^{-1}(dw)*h^{-1}$ during June. After the leaves had reached their full size the emission rates increased a little. Grey alder emitted only monoterpenes, mainly α-pinene, β-pinene and limonene. No isoprene emissions were detected. The highest total monoterpene emission rate was 0.6 $\mu g*g^{-1}(dw)*h^{-1}$.

Temperature dependence of the emission rates

Several laboratory studies have shown that the isoprene emission rates are temperature dependent (Monson and Fall, 1989; Guenther et al., 1991). This was shown also in the present study. Figure 3 shows the isoprene emission rates of willow and aspen as a function of

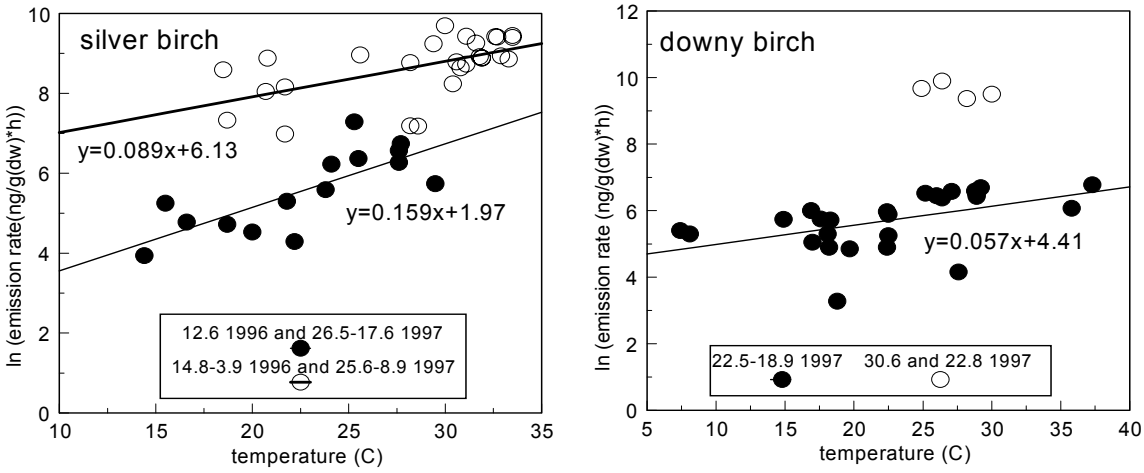

Figure 4. *Monoterpene emission rates of birches as a function of temperature.*

temperature and PAR (photosynthetically active radiation). In May willow emitted small amounts of isoprene together with other light hydrocarbons. This data has been excluded from the least-square analysis since it clearly differs from the rest of the data suggesting it could have a different source or mechanism.

The monoterpene emission rates are also strongly dependent on temperature as shown at least by Guenther et al., (1993) and Juuti et al., (1991). In the present study the temperature dependence of silver birch emission rates was found to be different at a time of leaf expansion and after the leaves were in their full size. The first measurement days of silver birch are plotted separately, because both years these first days had unexpectedly high emission rates indicating terpene pool in newly developed leaves. According to Kesselmeier et al. (1997), the high monoterpene emissions in young leaves could be do to defense mechanisms, young leaves may be more sensitive to attacks by injects and herbivores than mature leaves. The same kind of deviation to early and late growing season is not possible for downy birch, since the emissions are not only monoterpenes, but consist of sesquiterpenes and linalool as well. Two days with high monoterpene emission rates (30.6 and 21.8) clearly differ from the rest of data and they have been excluded from the least-squares analysis plotted in Figure 4. Very low terpene emissions of grey alder did not seem to depend on the temperature. Data points are more sparse than those of birches, and they do not allow to make any conclusions about the temperature dependence.

***Table 1**: The average monoterpene and isoprene emission rates (μg/g(dw)*h) normalized to 30℃ according to Guenther et al., (1991).*

		Monoterpene	Isoprene
European aspen:	May	11.29	0
	June	1.34	30.35
Tea-leafed willow:	May	8.61	0.52
	June, August	0.33	34.66
Downy birch:	early summer	0.76	
	late summer	6.08	
Silver birch:	early summer	1.12	
	late summer	6.93	
Grey alder:		0.80	

Conclusions

The measurements conducted on deciduous boreal trees clearly show the importance of long-term seasonal emission rate measurements and including seasonal variations in the biogenic emission inventories.

- European aspen and tea-leafed willow emitted monoterpenes only soon after budbreak, and initiated isoprene emissions in about two weeks. Willow emitted also ethene, propene and 1-butene.
- The monoterpene emissions of silver birch increased substantially after the leaves were fully expanded.
- The emissions of downy birch consisted of monoterpenes, linalool and sesquiterpenes. They varied more than the emission rates of silver birch. Generally the emissions were higher later in summer.

Acknowledgments

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References

Arey J., Corchnoy S.B., and Atkinson R., 1991. Emissions of linalool from the Valencia orange blossoms and its observations in the ambient air. Atmospheric Environment 25A, 1377-1381.

Grinspoon J., Bowman W. D., and Fall R., 1991. Delayed onset of isoprene emission in developing velvet bean (*Mucuna* sp.) leaves. Plant Physiology 97, 170-174.

Guenther A. B., Monson R. K. and Fall R., 1991. Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. Journal of Geophysical Research 96, 10799-10808.

Guenther A.B. Zimmerman P.R., Harley P.C., Monson R.K. and Fall R., 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. Journal of Geophysical Research 98, 12609-12617.

Hakola H., Rinne J., and Laurila T., 1998. The hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*). Atmospheric Environment 32,1825-1933.

Isidorov V.A., Zenkevich I.G. and Ioffe B.V., 1985. Volatile organic compounds in the atmosphere of forests. Atmospheric Environment 19, 1-8.

Juuti S., Arey J., and Atkinson R., 1990. Monoterpene emission rate measurements from a Monterey Pine. Journal of Geophysical Research 95, 7515-7519.

Kesselmeier J., Bode K., Schjorring J.K. and Conrad R., 1997. Biological mechanisms involved in the exchange of trace gases, in Sjaak Slanina (editor), Biosphere-Atmosphere Exchange of Pollutants and Trace Substances, pp. 117-133, Springer-Verlag, Berlin, Heidelberg, New York.

Monson R. K. and Fall R., 1989. Isoprene emission from aspen leaves. Plant Physiology 90, 267-274.