

Towards a comprehensive emission inventory of terpenoids from boreal ecosystems

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ABSTRACT

The biogenic volatile organic compound emissions in the south boreal, middle boreal and north boreal vegetation zones in Finland were calculated utilizing satellite land cover information and actual meteorological data in a BEIS-type canopy emission model. The sesquiterpene emissions from the boreal forest were estimated for the first time, and the inventory was further complemented by the inclusion of wetland isoprene emissions from open fens. Recently published results from emission measurements carried out in various parts of the boreal region were utilized in the compilation of the standard emission potentials and monoterpene emission spectra for the deciduous and coniferous forest categories and wetlands. The average annual isoprene emission fluxes from forests were 73, 56 and 45, and those of monoterpenes 657, 567 and 342 kg per km² of forest area in the south boreal, middle boreal and north boreal vegetation zones, respectively. The average annual sesquiterpene fluxes were of the same order of magnitude as isoprene, being 54, 46 and 26 kg per km² of forest area in the south boreal, middle boreal and north boreal vegetation zones, respectively. The isoprene emissions from wetlands were significant, contributing 3%, 18% and 31% of the annual isoprene emissions in the south boreal, middle boreal and north boreal vegetation zones, respectively. Throughout the boreal region, the main emitted monoterpenes were α -pinene and Δ^3 -carene, with significant contributions from β -pinene and sabinene in summer and autumn. Due to the new seasonal emission potentials of the coniferous species introduced in this work, the overwhelming role of spruce as the main isoprene and monoterpene emitter in the boreal forest is subdued. The new emission inventory also accentuates the role of the boreal deciduous trees as terpenoid emitters in the late summer months.

1. Introduction

The biogenic volatile organic compounds (BVOCs) emitted by forest ecosystems are known to affect the local and regional photochemistry through their reactions with the hydroxyl and nitrate radicals and ozone, and their aerosol forming capacity (e.g. Chameides et al., 1992; Carter, 1996; Hoffmann et al., 1997; Calogirou et al., 1999; Griffin et al., 1999a,b; Bonn and Moortgat, 2003; Jaoui et al., 2003; Claeys et al., 2004). Especially in the rural and remote boreal regions, the biogenic compounds have been shown to be more important with respect to the ozone reactivity than the anthropogenic emissions (Laurila and Hakola, 1996; Hakola et al., 2000). Recently, the role of the BVOCs emitted by the boreal forest as a source of natural aerosols in the background regions of the northern hemisphere has become the focus of scientific attention, as the high

aerosol loading may have important implications also in the context of global climate change (e.g. Chung and Seinfeld, 2002; Kanakidou et al., 2005; Tunved et al., 2006).

Ever since the pioneering days of the BIPHOREP measurement campaign (Laurila and Lindfors, 1999), the volatile organic compound (VOC) emissions of the boreal region have been under intensive study. In addition to the terpenoid (monoterpene, isoprene and sesquiterpene) emissions and emission patterns of the main boreal trees Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and the birch species (*Betula pendula* and *Betula pubescens*) reported by various authors (Janson, 1993; Hakola et al., 1998, 2001, 2003, 2006; Rinne et al., 1999, 2000; Steinbrecher et al., 1999; Staudt et al., 2000; Janson and De Serves, 2001; Komenda and Koppman, 2002; Tarvainen et al., 2005), there is now also information available of the wetland isoprene emissions (Janson and De Serves, 1998; Janson et al., 1999; Haapanala et al., 2006; Hellén et al., 2006).

Terpenoid emission inventories for the boreal vegetation zones have previously been presented by Lindfors and Laurila (2000) and Lindfors et al. (2000). In this work, we have extended these

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inventories by updating the deciduous emission potentials and the monoterpene emission spectra, based on available new data (Hakola et al., 2001). As the seasonal variation of the coniferous emissions is now firmly established (Hakola et al., 2003, 2006; Tarvainen et al., 2005), we introduce separate emission potentials and monoterpene emission spectra for early and late growing season also for the coniferous species. In addition, we present the first estimate of the annual sesquiterpene emissions from the forests in the south boreal, middle boreal and north boreal vegetation zones in Finland. The emission inventory is further complemented by the inclusion of the isoprene emissions from the boreal wetlands outside the snow cover period.

2. Materials and methods

The biogenic emissions for the south boreal, middle boreal and north boreal vegetation zones were calculated for the period April 1–October 31 utilizing satellite land cover information and actual meteorological data in a BEIS-type canopy emission model, following the methodology described in detail in Lindfors and Laurila (2000) and Lindfors et al. (2000). The variation of the forest biomass within the boreal region (60°N–70°N) was taken into account and the seasonality of the deciduous foliage was included in the model through a simple boreal climatology parametrization using the method developed in Lindfors et al. (2000). In addition to the forest categories described in Lindfors and Laurila (2000) and Lindfors et al. (2000) we calculated emissions for the open wetland categories (i.e. fens not growing trees or used for peat production) included in the LANDSAT land use database. In accordance with the previous inventory, the model calculation was carried out regionally, on the basis of the *Nomenclature des Unités Territoriales Statistiques* (NUTS) Level 3 area classification of the European Union. The assignment of the NUTS Level 3 regions to the different boreal vegetation zones was adopted from Lindfors et al. (2000) where it was based on Ahti et al. (1968) and Solantie (1990). The model domain with the resulting zonal division is presented in Figure 1.

Based on the previous inventory and recent literature, isoprene, monoterpene and sesquiterpene emission potentials were put together for three different types of deciduous trees: high isoprene emitters (*Salix* and *Populus* sp.), low isoprene emitters (*Betula* sp.) and non-isoprene emitters (*Alnus* sp.), as well as for two types of conifers: Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) (Table 1). Whenever feasible, separate emission potentials were extracted from the available data for early growing season (up to the end of June in the Finnish environmental conditions) and for late growing season. The emission potentials of the deciduous trees were revised, based on Hakola et al. (1998, 2001) and Simpson et al. (1999). The emission potentials of the coniferous trees which were based on Janson (1993), Simpson et al. (1999) and Steinbrecher et al. (1999) were also revised, according to Hakola et al. (2003, 2006) and

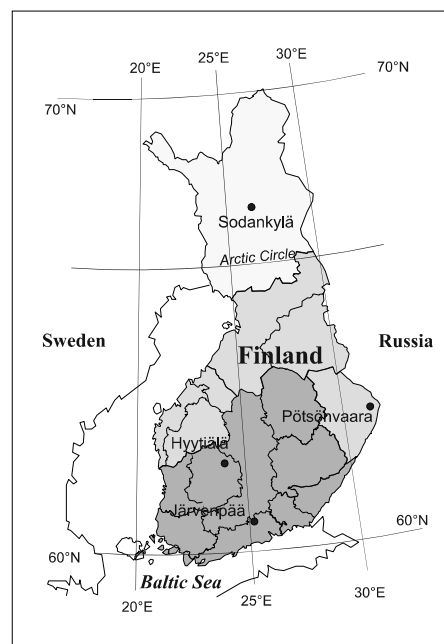


Fig. 1. The model domain with the assignment of the NUTS Level 3 regions of Finland to the south boreal, middle boreal and north boreal vegetation zones (Ahti et al., 1968; Solantie, 1990) indicated by the progressively lighter grey shading. The sites where the measurements utilised when compiling the new emission potentials and the monoterpene emission spectra have been carried out are indicated by black dots.

Tarvainen et al. (2005). In Table 1, the values that have been updated, compared to the work of Lindfors et al. (2000) are distinguished by bold lettering. The isoprene emission potentials used in the calculation for northern Finland, where Norway spruce is partly substituted by Siberian spruce (*Picea abies* ssp. *obovata*) are given in parenthesis. The isoprene emission potential for wetlands, $680 \mu\text{g m}^{-2} \text{h}^{-1}$, obtained from the measurements carried out by Haapanala et al. (2006), was applied throughout the modelling season. In the northern parts of Finland the snow cover period starts already in October and may extend all the way to May (long-term statistics of the Finnish Meteorological Institute). This was taken into account by setting the wetland emissions to zero during snow cover in the appropriate parts of the country.

The emission inventory of Lindfors et al. (2000) was based on 1997 as the model meteorological year. In this work we repeated the calculation for the year 1997 using our updated emission potentials in order to facilitate the comparison of our results with those of Lindfors et al. (2000). To reduce the uncertainty of our new emission estimate, we also did the calculation for the meteorological conditions of three additional years, 1999, 2000 and 2003. These years were chosen because, together with 1997, they correspond with the meteorological years of the Baseline Scenario of the Clean Air for Europe (CAFE) Programme launched

Table 1. The emission potentials (in $\mu\text{g g}^{-1} \text{h}^{-1}$) at standard conditions (303.15 K and $1000 \mu\text{mol photons m}^{-2} \text{s}^{-1}$), used in the model calculations for the boreal tree species in early (April–June) and late (July–October) growing season. The values updated compared to the previous emission inventory (Lindfors et al., 2000) are distinguished by bold lettering. The values used in the calculation for northern Finland are given in parenthesis, and the emission potentials assigned separately for pool (pool) and synthesis (synth) emissions are indicated

	Isoprene		Monoterpenes		Sesquiterpenes	
	Early	Late	Early	Late	Early	Late
Deciduous trees						
<i>Betula pendula</i> and <i>Betula pubescens</i>	0.1	0.1	0.84	3.35	0	2.69
<i>Populus</i> , <i>Salix</i> sp.	34	34	3	0.3	0	0
<i>Alnus</i> sp.	0	0	0.72	0.72	0	0
Coniferous trees						
<i>Pinus sylvestris</i>	0.1	0.1	2.39	1.46	0.05	0.13
<i>Picea abies</i>			0.81 pool	0.81 pool		
	0.90 (0.6)	0.22 (0.6)	0.45 synth	0.45 synth	0	0.16

by the European Union for the development of new air pollution control strategies (Amann et al., 2005). Unless stated otherwise, all model results reported here are given as averages of the 4 yr 1997, 1999, 2000 and 2003.

The FMI-BEIS emission model (Lindfors and Laurila 2000; Lindfors et al. 2000) used to calculate the monoterpene, isoprene and sesquiterpene emissions is based on the emission algorithms presented by Guenther et al. (1993) and Guenther (1997) for pool and synthesis emissions of forest foliage. FMI-BEIS has recently been validated by a comparison with tethered balloon isoprene and monoterpene flux measurements in a boreal forest environment (Spirig et al., 2004). In the present model version, isoprene is parametrized as a synthesis only emission for both deciduous and coniferous tree species, as usual. The sesquiterpenes are considered to be pool emissions (Tarvainen et al., 2005; Hakola et al., 2006). Monoterpenes from deciduous trees are also parametrized as pool emissions. The assumption of Lindfors et al. (2000) of pool and synthesis monoterpene emissions for coniferous trees has been retained for spruce, but in the case of pine, only pool emissions are considered (Tarvainen et al. 2005). The beta coefficients of the pool algorithm have been revised to reflect the newly published results of Tarvainen et al. (2005) and Hakola et al. (2006). Thus, the values $\beta = 0.10$ and 0.19 have been used to parametrize the temperature dependence of the pool monoterpene and sesquiterpene emissions, respectively. The wetland isoprene emissions are parametrized using the isoprene emission algorithm of Guenther (1997), as recommended by Haapanala et al. (2006).

The monoterpene emission profiles of the boreal tree species introduced in the work of Lindfors et al. (2000) have been revised according to the measurements reported by Hakola et al. (2001, 2003, 2006) and Tarvainen et al. (2005). Thus, the monoterpene profiles of the *Betula* species (Downy birch and Silver birch) have been updated, and early and late growing season profiles have also been extracted for spruce and pine. As there was no new information available about the monoterpene composition of the de novo synthesis emissions of the Norway spruce, the

profile of the synthesis emissions was adopted as such from the work of Lindfors et al. (2000), as well as the emission profiles of the *Populus* (aspen), *Salix* (willow) and *Alnus* (alder) species. The emission profiles used in this work are presented in Table 2. Of the oxidized species, 1,8-cineole is included in the total monoterpene profile while linalool is given separately, relative to the total monoterpenes.

3. Results and discussion

3.1. Seasonal variation of the emissions

According to our model results, the annual monoterpene, isoprene and sesquiterpene emissions (average and standard deviation of the years 1997, 1999, 2000 and 2003) from forests in Finland are 114 ± 5 , 12.5 ± 2.0 and 9.2 ± 2.3 kilotonnes, respectively. The average annual isoprene emission from wetlands is 2.4 ± 0.3 kilotonnes, which is 19% of the forest isoprene emissions. The seasonal variation of the average monoterpene, isoprene and sesquiterpene emissions in Finland is presented in Figure 2 as tonnes per month. The values in the figure are the averages and the error bars show the range of the emissions calculated for the four meteorological years. The monoterpene emissions are expectedly dominated by the coniferous species which carry the bulk of the boreal foliage biomass. At the annual level, 49% of the 114 kilotonnes of monoterpenes is emitted by spruce, 29% by pine and 22% by the deciduous species. However, the contribution of the deciduous species is more notable in late summer, after the leaves have matured and before senescence sets in. For instance in August the contributions to the monthly monoterpene emissions are 21%, 45% and 34% for pine, spruce and the deciduous trees, respectively.

The isoprene emissions are dominated by spruce in early summer, whereas in late summer the emissions are mostly due to deciduous species. At the annual level, the isoprene emissions are about 15 kilotonnes, of which 42% is emitted by spruce, 38% by deciduous trees, 16% by wetlands and 4% by pine. The wetland

Table 2. Early (April–June) and late (July–October) growing season monoterpene emission profiles (in % of total monoterpene emission) of the boreal tree species. Linalool is also given in the profile, relative to total monoterpenes. ‘Pub’ and ‘pend’ refer to *Betula pubescens* (Downy birch) and *Betula pendula* (Silver birch), respectively. For spruce, separate profiles are given for emissions arising from storage pools (pool) and de novo biosynthesis (synth) emissions

	Birch (pub)	Birch (pend)	Willow, aspen	Alder	Pine	Spruce (pool)	Spruce (synth)
Early growing season							
α -pinene	12.3	12.7	26.7	28.0	10.8	54.7	26.9
β -pinene (incl. myrcene)	9.6	24.5	13.3	24.8	2.7	15.5	40.0
Carene	3.9	4.7	0.4	8.0	74.6	3.3	5.4
Camphene	2.1	2.5	1.9	2.3	1.8	5.1	1.8
Limonene	6.0	5.1	17.5	18.0	0.6	9.1	12.6
Sabinene	13.2	27.1	5.0	6.0	2.9	7.3	3.7
Ocimenes	9.1	23.3	35.2	8.3	0	0	0
Terpinolene	41.2	0	0	0	1.6	0	0
1,8-cineole	2.5	0	0	5.0	2.2	5.1	9.6
Other monoterpenes	0	0	0	0	2.9	0	0
Linalool (relative to total monoterpenes)	213	0	0	0	0.2	0	0
Late growing season							
α -pinene	9.9	8.2	12.2	14.0	14.5	43.0	26.9
β -pinene (incl. myrcene)	6.4	5.8	4.8	19.3	3.1	20.0	40.0
Carene	0.7	0.5	13.2	5.7	69.8	4.2	5.4
Camphene	0.4	0.2	0.6	3.0	3.0	7.2	1.8
Limonene	1.9	3.7	19.9	27.7	0.8	13.3	12.6
Sabinene	72.9	42.4	6.3	9.7	2	4.4	3.7
Ocimenes	3.1	39.0	41.5	14.3	0	0.3	0
Terpinolene	3.9	0	0	0	1.6	0	0
1,8-cineole	0.8	0	0	6.3	3.8	4.0	9.6
Other monoterpenes	0	0	1.6	0	1.4	3.5	0
Linalool (relative to total monoterpenes)	2.8	0	0	0	2.0	9.3	0

isoprene emissions are thus quite important, especially during the high emission period in summer, with an approximate contribution of 13%, 19% and 18% to the total isoprene emission in June, July and August, respectively

Sesquiterpenes are mainly emitted in July and August, with the deciduous *Betula* species as the largest contributor. Of the annual total of 9.2 kilotonnes, 71% is emitted by deciduous trees, 23% by spruce and 6% by pine. The sharp increase of the emissions from June to July (Fig. 2), however, is probably an artefact produced by our modelling method and it is possible that there are sesquiterpene emissions from the *Betula* species already in June as indicated by the experimental results of Hakola et al. for *Betula pubescens* (fig. 1C in Hakola et al., 2001). This would mean that our present estimate should be regarded as a lower limit for the annual sesquiterpene emissions. Then again, Hakola et al. (2001) only obtained the higher emission potentials for one of the studied trees, and thus, in order to keep our emission estimate as conservative as possible, we have taken the average of the three reported values (table 1 in Hakola et al., 2001). Our adopted methodology also dictated the use of early and late growing season emission potentials in the model instead of, for example, monthly values, and lacking more detailed in-

formation we were not able to assign the sesquiterpene emission potentials for the *Betula* species for early growing season.

An added uncertainty in our sesquiterpene emission estimate arises from their parametrization in the model using the temperature dependent emission algorithm, albeit with an individually assigned beta coefficient. This simple approach was chosen because no clear light dependence was found in recent sesquiterpene emission measurements in the boreal region (Tarvainen et al., 2005; Hakola et al., 2006). Hakola et al. (2006) also showed that at least in late summer the temperature algorithm could reasonably well be applied to describe the variation of the sesquiterpene emissions in the boreal environmental conditions.

3.2. Emissions from boreal vegetation zones

The calculated monoterpene, isoprene and sesquiterpene emission fluxes (average of the years 1997, 1999, 2000 and 2003) from forests and wetlands (in kg per km² of either forest or wetland area, as appropriate) in Finland during the modelling period are shown in Figure 3 as a function of northern latitude. The latitudes are those of the synoptic stations from which meteorological data was extracted for the model for each region (Lindfors

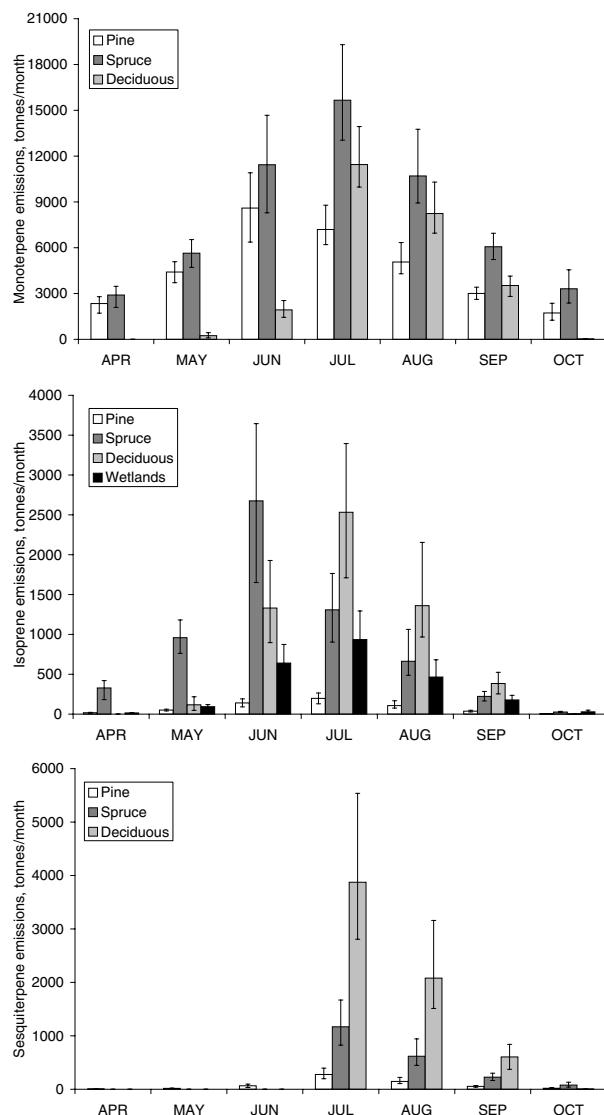


Fig. 2. The variation of the total monoterpene (top panel), isoprene (middle panel) and sesquiterpene (bottom panel) emissions (in tonnes per month) during the growing season (1 April–31 October) in Finland. The columns are the averages of the four meteorological years 1997, 1999, 2000 and 2003, and the error bars show the range of the calculated emissions in individual years.

and Laurila, 2000; Lindfors et al., 2000). Not surprisingly, the fluxes are highest in the south and steadily decrease towards the northern regions. In the case of the forests, this is due to both the latitudinal variability of the tree species distribution (i.e. emission potentials) and leaf biomass, which were taken into account in the model, and the variation of the climatological conditions between southern and northern Finland. For wetlands, the same isoprene emission potential was used throughout the country for the whole modelling period, and the south–north gradient of the emission flux is mostly due to the climatological variability.

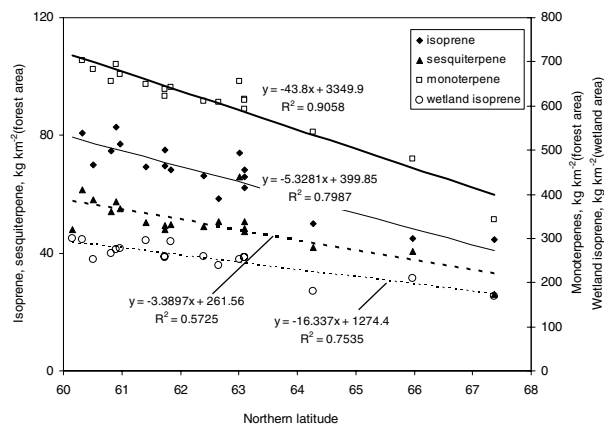


Fig. 3. The variation of the calculated annual isoprene (solid diamonds, left axis), sesquiterpene (solid triangles, left axis), monoterpene (open squares, right axis) and wetland isoprene (open circles, right axis) emission fluxes as a function of latitude. The fluxes (averages of the years 1997, 1999, 2000 and 2003) are given as kg per km² of forest or wetland area. The linear regression equation and R^2 are shown for each data set.

Also, the emission period in the northern parts of the country was shorter than in the south due to snow cover, which further reduces the wetland isoprene fluxes in the north.

The annual average monoterpene, isoprene and sesquiterpene emission fluxes for forests and the isoprene fluxes for wetlands in the south boreal, middle boreal and north boreal vegetation zones in Finland during the modelling period are presented in Table 3 in kg per km² forest or wetland area. A clear south to north decreasing trend is obtained for the emission fluxes of all studied compounds and ecosystems. While the relative contributions of the terpenoids in the forest emissions are almost the same in all vegetation zones (Table 3), the importance of the wetland contribution to the regional total isoprene emissions radically increases when moving towards the north. During the modelling period the contribution of wetlands (average of the years 1997, 1999, 2000 and 2003) to the total isoprene emissions was 3%, 18% and 31% in the south boreal, middle boreal and north boreal vegetation zones, respectively. This is due to both the larger proportion of wetlands and the smaller amount of isoprene emitting leaf biomass in the north which are typical features of the more remote boreal regions. Also, the majority of the wetlands in southern Finland have been drained for forestry during the 20th century, whereas a larger proportion of the wetlands of northern Finland remain intact (Minkinen et al., 2002).

3.3. Monoterpene speciation

The seasonal average compound distribution of monoterpenes emitted by forests in different parts of the boreal vegetation zone is presented in Table 4, and the seasonal average fluxes of the individual compounds, including also isoprene, sesquiterpenes

Table 3. The calculated forest and wetland emission fluxes (in kg per km² of forest area or wetland area, respectively) during the growing season (1 April–31 October) for the different boreal zones. The values are the average and standard deviation of years 1997, 1999, 2000 and 2003

	South boreal		Middle boreal		North boreal	
	kg km ⁻²	% of total	kg km ⁻²	% of total	kg km ⁻²	% of total
Forest emission fluxes (per km ² forest area)						
Monoterpenes	657 ± 41	84%	567 ± 24	85%	342 ± 15	83%
Isoprene	73 ± 13	9%	56 ± 11	8%	45 ± 7	11%
Sesquiterpenes	54 ± 14	7%	46 ± 12	7%	26 ± 6	6%
Total flux kg km ⁻² forest area	784 ± 64		669 ± 44		413 ± 27	
Wetland emission fluxes (per km ² wetland area)						
Isoprene	275 ± 39		228 ± 28		169 ± 27	

Table 4. Average compound distribution (in % of total monoterpene emission, averages of the years 1997, 1999, 2000 and 2003) of monoterpenes emitted by forests in different parts of the boreal vegetation zone in spring (April–May), summer (June–August), and autumn (September–October)

	South boreal			Middle boreal			North boreal		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
α -pinene	34.6	27.9	28.4	32.7	26.3	27.8	33.2	26.4	28.9
β -pinene*	11.5	13.3	13.5	10.5	12.2	12.9	10.5	12.2	13.2
Δ^3 -carene	32.3	20.2	19.6	36.3	22.1	22.4	36.0	21.4	23.0
Camphene	3.5	3.8	4.6	3.4	3.6	4.5	3.4	3.6	4.8
Limonene	5.8	7.2	8.0	5.3	6.5	7.5	5.3	6.5	7.8
Sabinene	5.5	16.7	15.5	5.2	20.2	16.5	5.2	21.5	14.6
Ocimenes	0.4	4.5	3.9	0.2	2.4	1.8	0.1	1.5	0.9
Terpinolene	1.1	1.4	0.9	1.1	2.0	1.1	0.9	2.1	1.1
1,8-cineole	4.1	3.5	3.4	3.9	3.3	3.4	3.9	3.3	3.5
Other	1.2	1.6	2.1	1.3	1.5	2.1	1.3	1.5	2.2

* Includes myrcene.

and linalool, are shown in Figure 4. The seasonal development of the monoterpene spectra is quite similar throughout the boreal region. In spring the monoterpenes are dominated by α -pinene and Δ^3 -carene, while in summer and autumn β -pinene and sabinene contribute significantly to the total (Table 4). The emission fluxes (Fig. 4) reflect the importance of α -pinene and Δ^3 -carene as the main emitted monoterpenes all through the growing season in all parts of the boreal vegetation zone. In addition to sabinene, also isoprene, sesquiterpene and linalool emissions are prominent in summer throughout the boreal region.

When compared with the earlier emission speciation (Lindfors et al. 2000), the role of Δ^3 -carene as one of the main compounds emitted by the boreal forest is now strongly enhanced. In spring its contribution has increased by more than 20% and in summer and autumn by more than 10%. This is in line with the observed high Δ^3 -carene concentrations in the boreal forest air (e.g. Hakola et al., 2003). Due to our revised emission potentials and monoterpene emission spectra, the contribution of sabinene is now also notably larger in summer and

autumn. Compared with earlier estimates, the dominance of α -pinene is reduced, especially in spring and in the northern parts of the boreal region. The relative importance of β -pinene has slightly increased throughout the growing season. This is partly due to the changes in the emission factors and monoterpene emission spectra, but also the fact that myrcene is now included in the β -pinene contribution (see e.g. Hakola et al. (2000) for a description of the analysis method) for all tree species, while in the earlier inventory a separate emission potential was assigned for myrcene from the coniferous species.

3.4. Comparison with the previous inventory

In 1997, the total annual emissions of isoprene, monoterpenes and sesquiterpenes in Finland were 146 kilotonnes, which is approximately 20% lower than the previous estimate of Lindfors et al. (2000). The annual total isoprene emissions obtained for 1997 were 17.7 kilotonnes, of which 15 kilotonnes were emitted by the forests. This is 32% lower than the earlier forest

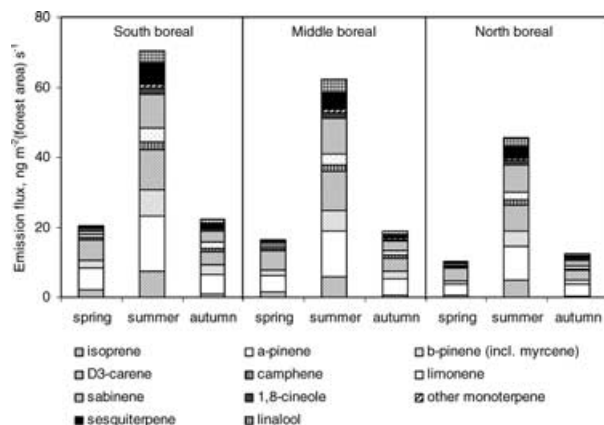


Fig. 4. Average terpenoid emission fluxes (in ng per m² of forest area per second) from forests in the different boreal vegetation zones in spring (April–May), summer (June–August), and autumn (September–October). The values are averages for the meteorological years 1997, 1999, 2000 and 2003.

emission estimate of Lindfors et al. (2000). Mostly, our lower annual emissions compared to the previous estimate are explained by the revised seasonal emission potentials used in this work for the main boreal tree species, based on new experimental results from measurements carried out in actual boreal forests. Especially for the conifers, Lindfors et al. (2000) were compelled to using the generic isoprene and monoterpene emission potentials of $1 \mu\text{g g}^{-1} \text{h}^{-1}$ (isoprene, spruce) and $1.5 \mu\text{g g}^{-1} \text{h}^{-1}$ (monoterpenes, spruce and pine), throughout the modelling period. As the boreal foliage biomass is mostly contributed by the conifers, we expect that our present inventory is more accurate than the previous one for both the isoprene and monoterpene emissions. In addition to the monoterpenes and isoprene, Lindfors et al. (2000) used the generic emission potential of $1.5 \mu\text{g g}^{-1} \text{h}^{-1}$ to calculate the annual emissions of the so called other VOCs (OVOC) which were 159 kilotonnes, bringing their total BVOC emission estimate to 342 kilotonnes per annum. As there is very little new information available on the OVOC emission potentials, this calculation was not repeated in our study. However, these OVOCs are estimated to make up to 50% of the total BVOC emissions, and development of emission algorithms and parameters for such compounds as methanol and acetone, commonly emitted by the vegetation (Janson et al., 1999; Warneke et al., 2002; Spirig et al., 2005), is called for.

Sesquiterpenes (caryophyllenes) were included in the emission inventory of Lindfors et al. (2000) only through their contribution to the total monoterpene emission spectra (despite the fact that they are not monoterpenes) of the deciduous (*Betula*) species while the conifers were assumed to emit no sesquiterpenes at all. According to the new experimental evidence, it is obvious that in addition to the birches, sesquiterpenes are also emitted by pine and spruce (Hakola et al., 2003, 2006; Tarvainen et al., 2005). The recent findings also suggest that the tempera-

ture dependence of the sesquiterpene emissions is stronger than that of monoterpenes, which has been taken into account in our revised model as explained above in Chapter 2.

Compared to the emission inventory of Lindfors et al. (2000), we find that the emissions of deciduous trees are relatively more important, contributing approximately 28% of the annual total forest emissions (average of the years 1997, 1999, 2000 and 2003), while their share in the previous inventory was 24%. Spruce now emits 47% of the annual total of the forests; thus it is not quite as dominant as in the previous inventory, where its share was 59%. The contribution of pine, on the other hand has increased to 25% from the previous 17%.

The most significant changes in the annual emission patterns, however, concern isoprene. While the forest isoprene emissions peaked in July in the previous inventory (Lindfors et al., 2000), their distribution has now markedly shifted towards early summer, with the highest emissions in June (Fig. 2). This is caused by the significantly lower isoprene emission factors of spruce in early and especially in late growing season. This also means that spruce and the deciduous trees are now equally important isoprene emitters, both contributing about 48% of the annual total of forest isoprene emissions in the boreal region in Finland. Our inventory is also complemented by the wetland isoprene emissions, which are an important contribution, especially in the more remote boreal areas. The seasonal pattern of the wetland emissions is similar to that of monoterpenes with the highest emissions in July. This is obviously due to the fact that the same emission potential was applied for the wetlands throughout the growing season and the emissions thus reflect the average course of the temperature and solar radiation. Even though the wetland emission potential used in this work is based on measurements carried out on one single fen, Siikanen, in the south boreal zone (Haapanala et al., 2006), unpublished data from the few measurements carried out at other mires in Finland by the same group support the data collected at the Siikanen site.

4. Conclusions

We present a significantly revised seasonal terpenoid emission inventory for the south boreal, middle boreal and north boreal vegetation zones in Finland. The emission potentials used in this work are compiled from measurements carried out in actual boreal forests and wetlands, and the recently published results also confirm that our modelling approach with the light and temperature and temperature dependent parametrization of the isoprene, monoterpene and sesquiterpene emissions is applicable in the boreal environmental conditions (Tarvainen et al., 2005; Haapanala et al., 2006; Hakola et al., 2006). The validity of our emission model has been further confirmed by a comparison of calculated isoprene and monoterpene fluxes with tethered balloon flux measurements of biogenic emissions carried out in boreal environmental conditions (Spirig et al., 2004).

At the annual level, 49% of the 114 kilotonnes of monoterpenes is emitted by spruce, 29% by pine and 22% by the deciduous species. The annual isoprene emissions are 15 kilotonnes, of which 42% is emitted by spruce, 38% by deciduous trees, 16% by wetlands and 4% by pine. Due to the new seasonal emission potentials of the coniferous species introduced in this work, the overwhelming role of spruce as the main isoprene and monoterpene emitter in the boreal forest is subdued. The new emission inventory especially accentuates the role of the deciduous trees as terpenoid emitters in the late summer months.

The wetlands contribute a considerable part of the total isoprene and their inclusion in the model calculations improves the isoprene emission inventory of the boreal vegetation zones. The importance of wetlands is especially pronounced in the north, both because of the larger proportion of wetland and the smaller amount of isoprene emitting leaf biomass, which are typical features of the remote boreal regions. Thus, our work is an important step towards a more comprehensive boreal terpenoid emission inventory.

The annual sesquiterpene emissions in Finland are 9.2 kilotonnes. 71% of this is emitted by deciduous trees, 23% by spruce and 6% by pine. The estimate obtained in this work should most probably be considered a lower limit for the actual emissions due to the fact that no emission potential could be assigned for the birches for early growing season. Further model calculations, preferably with more experimental data on the emissions and emission potentials with higher temporal resolution, and especially emission algorithm development, are expected to significantly improve the sesquiterpene emission inventory for the boreal forest. Furthermore, in this work we have only been able to include the birches as deciduous sesquiterpene emitters. Sesquiterpene emission data for the other deciduous trees prevalent in the boreal regions – even if their contribution to the total deciduous biomass is small compared to the birches – would nicely complement the present set of emission potentials.

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