

# Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions

Janne Rinne<sup>1)</sup>, Jaana Bäck<sup>2)</sup> and Hannele Hakola<sup>3)</sup>

<sup>1)</sup> Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland

<sup>2)</sup> Department of Forest Ecology, P.O. Box 27, FI-00014 University of Helsinki, Finland

<sup>3)</sup> Finnish Meteorological Institute, Air Quality Research, P.O. Box 503, FI-00101 Helsinki, Finland

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In this paper, the research conducted on the emissions of the biogenic volatile organic compounds (BVOCs) from the European boreal zone, or taiga, is reviewed. We highlight the main findings and the key gaps in our knowledge. Ecosystem scale BVOC emissions from the Eurasian taiga are observed to be relatively low as compared with those from some forest ecosystems in warmer climates. One of the distinctive features of the Eurasian taiga is the predominance of monoterpene emitting coniferous trees. Recent research indicates that in addition to evaporation from storage structures, part of the monoterpene emission of conifers originates directly from synthesis. Monoterpene emission from boreal deciduous trees originates mainly directly from synthesis. The boreal trees exhibit distinct intra-species variation in the monoterpene mixtures they emit. Important sources of isoprene in the Eurasian taiga include Norway spruce, open wetland ecosystems and some non-dominant woody species, such as European aspen and willows. Many boreal tree species also emit non-terpenoid compounds and highly reactive sesquiterpenes. The future challenges in the research on BVOC emissions from the Eurasian taiga include (i) quantification and understanding the non-terpenoid VOC emissions from the taiga ecosystems, (ii) bringing ecosystems in the eastern Eurasian taiga into the sphere of BVOC emission studies, (iii) establishing long-term ecosystem flux studies combined with plant physiological measurements, and (iv) integrating knowledge and research skills on BVOC synthesis, storages and emissions, land cover changes and atmospheric processes in different spatial and temporal scales in order to better understand the impact of biosphere on atmospheric chemistry and composition in changing climate.

## Introduction

Biogenic volatile organic compounds (BVOCs) play a central role in the tropospheric chemistry. Many BVOCs participate in aerosol growth and formation processes (Went 1960, Claeys *et al.* 2004, Tunved *et al.* 2006). As the volatile organic compounds (VOCs) react with ozone,

and OH and NO<sub>3</sub> radicals, the reaction products may have lower volatility and thus condense into aerosol particles. BVOCs also affect the production and destruction of tropospheric ozone (Atkinson and Arey 2003). As they compete with methane for OH, they may have an influence on the atmospheric lifetime and concentration of this powerful greenhouse gas (Kaplan *et al.*

2006). VOCs may also affect the optical properties of aerosol particles (Nozière and Esteve 2005). Even though in Europe the anthropogenic VOC emissions generally surpass the biogenic emissions, in northern Europe the biogenic emissions dominate (Simpson *et al.* 1999, Lindfors *et al.* 2000). Also on the global scale, the biogenic VOC emissions clearly dominate over the anthropogenic ones (Guenther *et al.* 1995).

Biogenic VOCs are a very heterogeneous group of compounds, which are naturally produced in many different plant organs and in a variety of physiological processes in all plant genera. A large variation among plant species exists in the emitted volatile mixture and their quantities. Globally the most significant compounds among the non-methane BVOCs are isoprene, mono- and sesquiterpenes, and some short-chained alcohols, ketones and aldehydes. A general phenomenon is that the warmer regions are dominated by isoprene emitting plant genera, while in the temperate and boreal areas, monoterpene emitters are more abundant.

The Eurasian boreal forest, or taiga, covers 10.5 million km<sup>2</sup> of land (FAO 2001). The climate of the area is characterized by cold snowy winters with temperatures ranging from 0 to -50 °C, and moderately warm but short summers, the growing season average temperature being above 10 °C for 1–3 months. Annual precipitation ranges from 300 up to 800 mm, and it exceeds the evaporation clearly due to low temperatures. Many taiga forests are characterized by low belowground temperatures, and permafrost frequently occurs in the more continental areas. Typical biomes in the region are evergreen or mixed evergreen-deciduous forests and peat forming wetlands. In comparison with other major ecosystems plant species diversity in taiga forests is rather low. In the Eurasian taiga the dominant evergreen tree species are Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). In the more eastern parts the deciduous larch species (e.g. *Larix sibirica*, *L. gmelinii* and *L. decidua*) form extensive monocultures. Mixed or early successional forests include several deciduous species and woody shrubs such as willows (*Salix* sp.), birches (*Betula* sp.), alders (*Alnus* sp.), and aspens (*Populus* sp.). The understory vegetation consists of several evergreen

or deciduous shrub species, belonging e.g. to genera *Vaccinium*, *Rubus* and *Erica*. Towards the north, the woody vegetation becomes smaller and more sparsely distributed, and eventually turns into subarctic and tundra vegetation. In Scandinavia, most of the boreal forest is under economic exploitation and management whereas in Canada and Russia there are large rather pristine forest areas (Metsäntutkimuslaitos 2007: <http://www.metla.fi/metinfo/tilasto/julkaisut/vsk/2007/>; Canadian Council of Forest Ministers: [http://nfde.ccfm.org/sivilculture/quick\\_facts\\_e.phn](http://nfde.ccfm.org/sivilculture/quick_facts_e.phn); Metsäntutkimuslaitos 2008: <http://www.idanmetsatiето.info/fi/cfmldocs/>).

First measurements of BVOC emissions from Eurasian boreal vegetation were reported by Isidorov *et al.* (1985). They qualitatively described emissions of various compounds from many plant species but the emission rates were not properly quantified. During the 1990s an EU funded research project BIPHOREP concentrated on the quantification of BVOC emission from North European boreal zone (Laurila and Lindfors 1999). The justification for BIPHOREP came primarily through the impact of BVOCs on tropospheric ozone formation. However, since BIOFOR project in the late 1990s (Kulmala *et al.* 2001) the BVOC emissions have been studied mainly as a part of various projects aimed at understanding the aerosol particle formation and growth.

In this paper, the research conducted on BVOCs in the Eurasian taiga during the past two decades is reviewed in order to give a picture of the current knowledge. Some of the main questions we try to find answers for are: (i) What VOC compounds are emitted by boreal ecosystems? (ii) What are the typical ranges of emissions from these ecosystems? (iii) What are the processes determining the emissions from these ecosystems? At the same time we point out emerging discrepancies and key gaps, which require further investigation.

## Emissions from ecosystems in the Eurasian taiga

Many dominant tree species in the Eurasian boreal landscape are predominantly monoter-

pene emitters (Table 1). Isoprene and sesquiterpenes are also emitted by a number of species and many plants emit also non-terpenoid compounds. Even though in the Eurasian taiga there are only few major tree species, as compared with e.g. tropical rainforests, there are still gaps in our knowledge on the VOCs emitted by many of major tree species. Especially non-terpenoid emissions are not well characterized. It is noteworthy that many Eurasian boreal tree species are divided into distinctive subspecies (e.g. *Betula pubescens* and *B. pubescens* subsp. *czerepanovii*; *Picea abies* and *P. abies* subsp. *obovata*) which are often adapted to different environmental conditions and may differ in their VOC emissions.

## Monoterpenes

Monoterpene emissions particularly from Scots pine forests have been measured extensively.

Since Scots pine is one of the dominant tree species in the Eurasian taiga, this is well justified. The measurements conducted at a branch scale by an enclosure technique, micrometeorological gradient and disjunct eddy covariance measurements tend to yield similar ecosystem-scale monoterpene emissions (e.g. Rinne *et al.* 2000a, Hakola *et al.* 2006). The diurnal cycle of monoterpene emission of Scots pine canopy is rather well described by the commonly utilized temperature dependent algorithm of Guenther *et al.* (1993). The published emission potentials for Scots pine and other monoterpene emitters, normalized to 30 °C using  $\beta = 0.09 \text{ °C}^{-1}$  are listed in Table 2. Many of the published summertime emission potentials for Scots pine are in the magnitude of  $1\text{--}2 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$ . However, many longer term studies show distinct seasonal variations in the emission potential.

The fact that the monoterpene emissions from Scots pine are often observed to depend only on temperature has been taken as indica-

**Table 1.** Common tree species in Eurasian boreal zone, taiga, with the VOC species emitted. ++ = major compounds emitted, + = considerable emission, 0 = low or no emission, – = no data.

Species	Isoprene	Monoterpenes	Sesquiterpenes	Methanol	Acetaldehyde	Acetone	Ref.
<i>Abies sibirica</i>	–	–	–	–	–	–	
<i>Picea abies</i>	+	++	+	0	+	+	J99, J01, Ha03, G06
<i>Larix sibirica</i>	0	++	+	–	–	–	Ru07
<i>Larix gmelinii</i>	–	–	–	–	–	–	
<i>Pinus sylvestris</i>	0	++	+	+	+	+	I85, J93, J99, J01, K02, T05, Ha06, Ho06, Ri07
<i>Pinus cembra</i>	–	++	–	–	–	–	I85
<i>Juniperus communis</i>	–	++	–	–	–	–	I85
<i>Betula pendula</i>	0	++	–	–	–	–	Ha98
<i>Betula pubescens</i>	0	++	+	–	–	–	Ha01
<i>Betula fructicosa</i>	–	–	–	–	–	–	
<i>Alnus glutinosa</i>	–	–	–	–	–	–	
<i>Alnus incana</i>	0	+	–	–	–	–	Ha99
<i>Alnus viridis</i>	–	–	–	–	–	–	
<i>Salix</i> sp.	++	0	–	–	–	–	I85, Ha98, O05
<i>Populus tremula</i>	++	0	–	–	–	–	I85, Ha98

References: I85: Isidorov *et al.* 1985; J93: Janson 1993; Ha98: Hakola *et al.* 1998; Ha99: Hakola *et al.* 1999; J99: Janson *et al.* 1999; Ha01: Hakola *et al.* 2001; J01: Janson and De Serves 2001; K02: Komenda and Koppmann 2002; Ha03: Hakola *et al.* 2003; O05: Olofsson *et al.* 2005; T05: Tarvainen *et al.* 2005; G06: Grabmer *et al.* 2006; Ha06: Hakola *et al.* 2006; Ho06: Holzke *et al.* 2006; Ri07: Rinne *et al.* 2007; Ru07: Ruuskanen *et al.* 2007.

**Table 2.** Normalized isoprene and monoterpene emission potentials from boreal tree species. Only those observed monoterpene emission potentials are presented which are derived using monoterpene emission algorithm of Guenther *et al.* (1993) with  $\beta = 0.09 \text{ }^\circ\text{C}^{-1}$  and standardized conditions of  $T = 30 \text{ }^\circ\text{C}$  for monoterpenes. For isoprene the emission potentials are based on isoprene emission algorithm of Guenther *et al.* (1993) and normalization conditions of  $T = 30^\circ\text{C}$  and  $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ . Emission potentials used in emission modelling studies are also shown. Some emission models calculate monoterpene emission using a hybrid algorithm in which the emission from storage pool is calculated using temperature dependent algorithm and emission directly from synthesis using light and temperature dependent isoprene algorithm. These are indicated as pool and synth., respectively.

Species	Reference	Emission potential range ( $\mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$ )	Emission potential, high summer ( $\mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$ )	Remarks
<b>Monoterpenes, observed values</b>				
<i>Picea abies</i>	Janson <i>et al.</i> (1999)	2.3–8.3	2.3	Seasonal variation
	Hakola <i>et al.</i> (2003)	0.2–1.4	0.4	Seasonal variation
<i>Pinus sylvestris</i>	Janson <i>et al.</i> (1999)	0.86	0.86	
	Rinne <i>et al.</i> (2000)	1.2	1.2	Derived from ecosystem scale flux data
	Ruuskanen <i>et al.</i> (2005)	2.1–4.4	2.1	Seasonal variation
	Hakola <i>et al.</i> (2006)	0.20–1.35	0.5–1.0	Average of two branches, seasonal variation
	Rinne <i>et al.</i> (2007)		2.0–2.5	Derived from ecosystem scale flux data
<i>Larix sibirica</i>	Ruuskanen <i>et al.</i> (2007)	5.2–21	7–21	Seasonal variation
<i>Betula pendula</i>	Hakola <i>et al.</i> (2001)	0.7–7.7	0.7	Seasonal variation
<i>Betula pubescens</i>	Hakola <i>et al.</i> (2001)	0.2–5.5	0.3–0.7	Seasonal and intraspecies variation
<b>Monoterpenes, values used in emission models</b>				
<i>Picea abies</i>	Simon <i>et al.</i> (2001)		2.1	
	Tarvainen <i>et al.</i> (2007)		0.81 (pool)	
			0.45 (synth)	
	Karl <i>et al.</i> (2008)		1.15 (pool)	
<i>Pinus sylvestris</i>			1.8 (synth)	
	Simon <i>et al.</i> (2001)		7.9	
	Tarvainen <i>et al.</i> (2007)		2.1	
<i>Betula pendula</i>	Karl <i>et al.</i> (2008)		2.25	
	Simon <i>et al.</i> (2001)		2.9	
	Tarvainen <i>et al.</i> (2007)		3.35	
<i>Betula pubescens</i>	Karl <i>et al.</i> (2008)		2.82 (synth)	
	Tarvainen <i>et al.</i> (2007)		3.35	
	Karl <i>et al.</i> (2008)		0.2 (pool)	
			1.45 (synth)	
<b>Isoprene, observed values</b>				
<i>Picea abies</i>	Janson <i>et al.</i> (1999)	1.1–2.2	1.5	Seasonal variation
	Janson and De Serves (2001)	0.45		
	Hakola <i>et al.</i> (2003)	0–1.3	0.2	Seasonal variation
<i>Populus tremula</i>	Hakola <i>et al.</i> (1998)	0–60	30	Seasonal variation
<i>Salix phylicifolia</i>	Hakola <i>et al.</i> (1998)	0–60	43	Seasonal variation
<b>Isoprene, values used in emission models</b>				
<i>Picea abies</i>	Simon <i>et al.</i> (2001)		1.1	
	Tarvainen <i>et al.</i> (2007)		0.22	
	Karl <i>et al.</i> (2008)		0.345	
<i>Populus tremula</i>	Simon <i>et al.</i> (2001)		51.0	
	Tarvainen <i>et al.</i> (2007)		34	
	Karl <i>et al.</i> (2008)		51	
<i>Salix alba</i>	Simon <i>et al.</i> (2001)		16.8	
	Karl <i>et al.</i> (2008)		37	
<i>Salix</i> spp.	Tarvainen <i>et al.</i> (2007)		34	
	Karl <i>et al.</i> (2008)		28	

tion that the emission would originate from large pools in specialized storage structures such as resin ducts (Guenther *et al.* 1991, 1993, Grote and Niinemets 2008). However, some indication of additional emission control exerted by light levels has been pointed out by e.g. Shao *et al.* (2001) and Tarvainen *et al.* (2005). Also, recent  $^{13}\text{CO}_2$  labelling experiment has shown a considerable fraction of the emitted monoterpenes to be labelled, indicating that a part of the emitted monoterpenes originate directly from synthesis (Ghirardo *et al.* 2009). According to Shao *et al.* (2001), 20%–30% of the monoterpene emission from Scots pine originates directly from synthesis. The reason why this has not been observed using field measurements may be in the relatively low light saturation of monoterpene emissions, which implies that at PAR levels above 200–300  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , the emissions are already saturated. Most of the emission measurements in field conditions were made during the long summer days, when light levels very seldom drop below the saturation level. For example, during 2008 there were only 8 days between 15 April and end of August, when the daily maximum light levels remained below 300  $\mu\text{mol m}^{-2} \text{s}^{-1}$  at the SMEAR II field station in southern Finland (61°51'N), where extensive emission measurements on Scots pine have been conducted. Further, even at the southern limits of the boreal region (around 60°N), the daylength during most of the growing period (between 15 April and 22 August) is more than 15 hours.

Scots pine populations can be divided into distinct chemotypes, containing and emitting a different mixture of monoterpenes (Hiltunen and Laakso 1995, Komenda and Koppmann 2002, Manninen *et al.* 2002, Tarvainen *et al.* 2005, Holzke *et al.* 2006). These have been referred to as  $\alpha$ -pinene and  $\Delta^3$ -carene types. Also monoterpene mixtures emitted by Norway spruce and downy birch exhibit tree to tree variations (Janson 1993, Hakola *et al.* 2001). To what extent other boreal monoterpene emitters show this kind of behaviour is unknown.

Contrary to Scots pine, there are only very few extensive emission measurements conducted on Norway spruce, despite its major importance in boreal ecosystems (Janson 1993, Hakola *et al.* 2003). According to Hakola *et al.* (2003),

monoterpenes were the only terpenoids emitted during winter from Norway spruce foliage. Also part of the monoterpene emissions from Norway spruce are expected to be emitted directly from synthesis in a light and temperature controlled manner (Steinbrecher *et al.* 1999, Ghirardo *et al.* 2009). Typically  $\alpha$ - and  $\beta$ -pinene, and  $\Delta^3$ -carene are the most abundant monoterpenes emitted by Norway spruce (Janson 1993, Christensen *et al.* 2000).

It is interesting to note that the emissions of monoterpenes from different plants vary in their enantiomeric compositions, as do the monoterpenes stored in needles of conifers (Hiltunen and Laakso 1995, Yassaa and Williams 2007). For example the  $\alpha$ -pinene emission from Scots pine is dominated by the (+)-enantiomer (ca. 70%) as compared with the (–)-enantiomer (ca. 30%) (Yassaa and Williams 2007). Also the atmospheric concentration of  $\alpha$ -pinene in the North European boreal region is dominated by the (+)-enantiomer (80%) over the (–)-enantiomer (20%), whereas in the tropical location in South America the opposite was observed [(+)- $\alpha$ -pinene 30%, (–)- $\alpha$ -pinene 70%] (Williams *et al.* 2007). Also other monoterpenes show similar differences in enantiomers between tropical and boreal sites (Williams *et al.* 2007). As the atmospheric chemistry of the different mirror-image monoterpenes is likely to follow the same reaction pathways, the differences in the atmospheric concentrations should closely reflect the differences in the landscape-scale emissions of the different enantiomers. Thus the division between enantiomers should not concern atmospheric chemists. However, the biosynthesis and complex interactions with herbivores can be different for different enantiomers (Fäldt *et al.* 2006). Therefore, in the plant–insect interaction studies, the monoterpenes should be identified down to the enantiomer level. Very little is known on the possible variation in the emission dynamics of the monoterpene enantiomers.

Of the broadleaved trees in the Eurasian taiga, birches (*Betula* sp.) have been reported to emit mainly monoterpenes (Hakola *et al.* 1998, 2001). Birches have very low monoterpene emission in early summer with sudden rise after the leaves are fully grown (Hakola *et*

al. 1998 and 2001), similarly to isoprene emission from many broadleaved trees (Hakola et al. 1998, Olofsson et al. 2006). In the  $^{13}\text{C}$  labeling studies very fast  $^{13}\text{C}$  incorporation into the monoterpenes emitted by birches indicate close relation between the emission and photosynthesis (Ghirardo et al. 2009).

## Isoprene

Globally, isoprene is the most abundantly emitted BVOC (Guenther et al. 1995). However, in the Eurasian taiga the BVOC emissions seem to be dominated by monoterpenes (Guenther et al. 1995, Simpson et al. 1999, Tarvainen et al. 2007, Karl et al. 2008). This is also reflected in the atmospheric concentrations as the total monoterpene concentrations tend to be higher than isoprene concentrations (Ruuskanen et al. 2009). There exists high-isoprene-emitting tree species in this region, such as willows (*Salix* sp.) and European aspen (*Populus tremula*) (Tables 1 and 2), but these do not appear as dominant species in the Eurasian boreal landscape. These broadleaved trees typically have a low isoprene emission in the early season with a sudden increase after the leaves are fully grown (Hakola et al. 1998, Olofsson et al. 2006). Since the isoprene emitters are predominantly deciduous, the annual emission pattern differs from that of monoterpenes, and the emission occurs mainly in summer months.

Of the mainly monoterpene emitting coniferous trees, Norway spruce also emits isoprene. The isoprene emission potential of Norway spruce is in the same range with its emission potential for monoterpenes. Its summertime emission potential for isoprene has been reported

to vary between 0.5 and  $2 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ , which is very small as compared with the isoprene emission potentials of broadleaved trees. Even though Norway spruce has relatively low isoprene emission potential, its large needle biomass density can make it an important contributor to the atmospheric isoprene concentrations (Tarvainen et al. 2007). However, as monoterpene emission continues through the night, contrary to the isoprene emissions which are restricted into daylight hours, its daily emission ends up being larger.

Of the Eurasian boreal ecosystems, only the open wetlands seem to be dominantly isoprene emitting systems (Janson and De Serves 1998, Janson et al. 1999, Rinnan et al. 2005, Haapanala et al. 2006, Hellén et al. 2006, Tiiva et al. 2007a, 2007b, Holst et al. 2008). The isoprene emission from wetland ecosystems per land area can be of the same order of magnitude than monoterpene emissions from boreal coniferous forests (Janson and De Serves 1998, Haapanala et al. 2006). The dynamics of the emission has been observed to follow the traditional isoprene emission model (Haapanala et al. 2006) with emission potentials between 0.2 and  $0.7 \text{ mg m}^{-2} \text{ h}^{-1}$  (Table 3). Of the plant species growing in these open wetland ecosystems, at least sedges *Eriophorum angustifolium* and *Carex rostrata* have been identified as isoprene emitters (Ekberg et al. 2008). However, our knowledge on the isoprene emitting species among wetland plants such as mosses is still incomplete. Most of the isoprene emission measurements at wetlands have been campaign-style measurements and no data covering a full growing season has been published. Therefore, we do not know whether the isoprene emissions from wetlands, where many species are evergreen, exhibit a similar seasonal cycle than isoprene

**Table 3.** Normalized isoprene emission potentials from wetland ecosystems. Only those emission potentials are presented which are derived using isoprene emission algorithm by Guenther et al. (1993) and normalization conditions of  $T = 30 \text{ }^\circ\text{C}$  and  $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ .

Reference	Method	Emission potential ( $\mu\text{g m}^{-2} \text{ h}^{-1}$ )
Janson and De Serves (1998)	Enclosure	700
Haapanala et al. (2006)	Relaxed eddy accumulation	680
Hellén et al. (2006)	Enclosure	224
<b>Values used in emission models</b>		
Tarvainen et al. (2007)		680

emissions from broadleaved deciduous trees. Thus long term studies at wetland ecosystems are needed in order to understand VOC emission dynamics in these environments.

Until recently, the isoprene emission from wetlands has been omitted from emission inventories. As the open wetlands are a typical feature of the landscape in the northern boreal region, the emission from wetlands may contribute up to 30% to the total isoprene emissions from these areas (Tarvainen *et al.* 2007). Bäckstrand *et al.* (2008) even estimated that the non-methane VOC emissions from wetlands are about 5% of the total carbon uptake thus being a significant part of the carbon budget. However, according to Aurela *et al.* (2007), the isoprene emission from a boreal fen was less than 1% of the total carbon budget and even the total hydrocarbon emission is unlikely to be significant for carbon budget. These slightly conflicting results imply that the factors regulating emissions from wetlands should be elucidated in further, long-term ecosystem studies and in different types of wetlands.

## Sesquiterpenes

Many boreal plant species have also been observed to emit significant quantities of sesquiterpenes, which are a group of very reactive hydrocarbons (Table 1; Hakola *et al.* 2001, 2003, 2006, Holzke *et al.* 2006, Ruuskanen *et al.* 2007). Emissions of these compounds have received attention due to their potential role in aerosol particle formation and growth (Bonn and Moortgat 2003). Relatively little is still known about their emissions from many boreal ecosystems and on the driving factors. Sesquiterpene emissions have traditionally been considered to follow external stimuli, such as herbivore attacks (Holopainen *et al.* 2004). For example, mountain birches have been observed to emit very high quantities of sesquiterpenes, which may be connected to occasional outbreaks of leaf herbivores (Haapanala *et al.* 2008). Also downy birches exhibit large tree to tree variations in their sesquiterpene emissions (Hakola *et al.* 2001). This could suggest sesquiterpene emissions being induced only when needed for defensive purposes. However, also under normal conditions at least pines, spruces,

larches and birches can emit significant quantities of sesquiterpenes, typically 5%–15% of the total monoterpene emission by mass (Hakola *et al.* 2001, 2003, 2006, Holzke *et al.* 2006, Ruuskanen *et al.* 2007). Their emissions from Scots pine and Norway spruce are highly seasonal, peaking in mid-summer (Hakola *et al.* 2003, 2006). In order to understand the emissions of highly reactive sesquiterpenes and their relation to the environmental stresses, laboratory experiments and longer term field observations are needed. However, as their reactivity makes the observation of these compounds challenging, advances in analytical tools would facilitate the more reliable measurements.

## Other BVOCs

Much of the research on biogenic VOC emissions has been directed towards understanding the role of terpenoids, mainly isoprene and monoterpenes. These are estimated to comprise about half of the VOCs emitted by the vegetation globally. Other VOCs emitted by vegetation include alcohols such as methanol, several carbonyl compounds (acetone, acetaldehyde) and C<sub>6</sub>–C<sub>8</sub> carbohydrates. As many of these compounds have longer lifetime in the atmosphere than terpenoids, the biogenic emissions have an effect also on upper tropospheric concentrations (Dufour *et al.* 2007). Methanol, acetone, acetaldehyde and formaldehyde seem to be the main light carbonyls emitted by many boreal plant species (e.g. Janson *et al.* 1999, Janson and De Serves 2001, Cojocariu *et al.* 2004). It is estimated that about half of the VOC emissions from Scots pine ecosystem can be comprised of methanol, acetone and acetaldehyde (Janson *et al.* 1999, Rinne *et al.* 2007, Taipale *et al.* 2009). Emission measurements of these compounds from other European boreal ecosystems have not been conducted. However, branch scale measurements show that also Norway spruce emits carbonyls (Janson *et al.* 1999). The 2-methyl-3-buten-2-ol (MBO) emission from Scots pine is very small (Tarvainen *et al.* 2005, Hakola *et al.* 2006) in contrast to many western-hemisphere pine species (Harley *et al.* 1998).

Recently methanol emissions have been

empirically related to temperature (Brunner *et al.* 2007, Custer and Schade 2007, Harley *et al.* 2007). However, there exist no reliable emission algorithms based on the biochemical and physical reasoning for emissions of non-terpenoid compounds to be used in emission inventory models. The emissions of methanol are considered to originate from metabolism related to plant cell wall elongation processes, and therefore the emissions tend to correlate with plant growth (Nemeck-Marshall *et al.* 1995, Galbally and Kirstine 2002, Hüve *et al.* 2007, Folkers *et al.* 2008). Biosynthetic pathways for acetone and acetaldehyde production have been described by Fall (2003). However, since they mainly are linked to stress or damage (e.g. herbivory, flooding, sunflecks), it is surprising that such huge quantities can be emitted from intact foliage. The diurnal pattern of acetone emissions suggests a connection with plant metabolic activity, most probably with xylem transport processes (Cojocariu *et al.* 2004, 2005), but future research may reveal some other processes involved in acetone emissions.

### From branch scale to ecosystems and regions

Most of the BVOC emission measurements have been conducted in branch scale by enclosure techniques. Only few ecosystem scale studies have been conducted and all of these in the western end of the Eurasian taiga (Table 4). Most of the measured BVOC fluxes were below  $1 \text{ mg m}^{-2} \text{ h}^{-1}$ . These fluxes are much lower than those sometimes observed in forest ecosystems in warmer climatic conditions (e.g. Spirig *et al.* 2005, Pressley *et al.* 2006, Karl *et al.* 2007). Only a couple of ecosystem scale experiments on non-terpenoid VOC fluxes has been conducted.

Atmospheric concentrations at any location are governed by the emissions from a much larger area than the immediate vicinity of the site. We can estimate the downwind distance a reactive compound is transported horizontally in the boundary layer,  $\delta$ , by multiplying the atmospheric lifetime of the compound  $\tau_c$  by mean wind velocity,  $U$ , yielding  $\delta = \tau_c U$ . As the lifetime and wind velocity both change with time, also

transport distance varies. By using atmospheric lifetimes for mid-July daytime in southern Finland given and wind velocity of  $5 \text{ m s}^{-1}$ , we can arrive to travel distances listed in the Table 5. The transport distances calculated for the very short lived compounds give unrealistically large values. This is due to the fact that the compounds are transported slower inside the plant canopy, from where they are emitted, before they enter the faster boundary layer flow. Therefore, we did not include the transport distances of compounds with chemical lifetime below 10 minutes. The transport times give an indication of the areal coverage we need to take into account when studying atmospheric concentrations of these compounds. Thus, to interpret the isoprene and monoterpene concentrations we should take into account the sources and sinks within about 50 km from the measurement site but to interpret the methanol and acetone concentrations we should consider the sources and sinks within continental to hemispheric scales. This emphasizes the need of regional emission modelling when interpreting the measured boundary layer VOC concentrations.

Thus, in order to understand how the biogenic emissions affect the atmospheric concentrations at our measurement sites, we need to know the emissions at larger landscape scale. These can be estimated using emission models of various complexities and by boundary layer profiling techniques (Spirig *et al.* 2004, Haapanala *et al.* 2007). As the boundary layer profiling techniques for VOCs are labor intensive and expensive to run, it is unlikely that they will be used routinely in long term experiments in near future. However, even shorter term experiments may be used to verify our up-scaling procedures. The boundary layer profiling may also give us insight on how the BVOC concentrations behave in the boundary layer above the surface layer. This may be crucial if we aim at understanding the chemistry and transformations of BVOCs in the lower atmosphere.

In addition to emissions, the concentrations are affected by atmospheric chemistry and mixing in the boundary layer. For example, the atmospheric concentrations of monoterpenes in boreal coniferous forests are generally highest during the night, even though the emissions



**Table 4.** Measurements of ecosystem scale VOC emissions from ecosystems in the European boreal zone by micrometeorological techniques. SLG = Surface layer gradient, DEC = Disjunct eddy covariance, REA = Relaxed eddy accumulation, MS = Mass spectrometry, GC = gas chromatography, FID = Flame ionization detector, PTR = Proton transfer reaction, n.a. = Not available or not reported in the paper, n.d. = Not detected.

Site	Ecosystem	References	Methods	Length of datasets	T (°C)	PPFD ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ )	Typical flux range ( $\text{mg m}^{-2} \text{h}^{-1}$ )				
							Isoprene	Monoterpenes	Methanol	Acetone	Acetaldehyde
<b>Hyytiälä</b> 61°51' N,	Scots pine forest	Rinne <i>et al.</i> (2000a)	SLG-GC-MS	Two days, Aug.	12–18	n.a.	n.a.	0–0.5	n.a.	n.a.	n.a.
		Spanke <i>et al.</i> (2001)	SLG-CG-MS	Few days, Apr., Aug.	n.a.	n.a.	n.a.	0–0.3	n.a.	n.a.	n.a.
24°17' E		Rinne <i>et al.</i> (2007)	DEC-PTR-MS	Few days, July	12–25	0–1500	n.a.	0–0.8	0–0.4	0–0.3	0–0.1
		Taipale <i>et al.</i> (2009)	DEC-PTR-MS	Two months, June–Aug.	n.a.	n.a.	n.a.	0–0.5	n.a.	n.a.	n.a.
<b>Huhus</b> 62°52' N, 30°49' E	Scots pine forest	Rinne <i>et al.</i> (1999), (2000a)	SLG-GC-MS	Few days, May–Aug.	6–24	n.a.	n.a.	0–0.4	n.a.	n.a.	n.a.
		Räisänen <i>et al.</i> (2009)	SLG-GC-MS	Several days, June–Sep.	6–30	n.a.	n.a.	0.04–1.5	n.a.	n.a.	n.a.
<b>Kenttäröva</b> 67°58' N, 24°14' E	Mixed Siberian spruce–mountain birch forest	Rinne <i>et al.</i> (2000b)	SLG-GC-FID/MS	Few days, July	6–16	n.a.	n.a.	0–0.2	n.a.	n.a.	n.a.
<b>Siikaneva</b> 61°50' N, 24°12' E	Boreal fen	Haapanala <i>et al.</i> (2006)	REA-GC-FID	Few days, Apr.–Oct.	?–27	?–1600	0–0.4	n.a.	n.a.	n.a.	n.a.
		Holst <i>et al.</i> (2008)	DEC-PTR-MS	Two months, Aug.–Sep.	0–23	0–1300	0–0.5	n.a.	<0.1	n.d.	n.d.
<b>Grästorps</b> 58°21' N, 12°34' E	Willow plantation	Olofsson <i>et al.</i> (2005)	REA-GC-MS	Few days, June, July, Sep.	7–19	0–900	0–0.7	n.a.	n.a.	n.a.	n.a.

are lowest at that time of the day (Hakola *et al.* 2000, Rinne *et al.* 2005, 2007). This is caused by the strong control exerted by the diurnal cycle of surface layer mixing on the concentrations. In an ecosystem where the monoterpene emissions originate directly from synthesis and therefore go to zero at night, a different diurnal concentration cycle is observed. In such ecosystems, as e.g. neo-tropical rainforests, the daytime surface concentrations of monoterpenes are higher than nighttime concentrations (Rinne *et al.* 2002).

While VOC emissions from ecosystems dominated by Scots pine have been studied quite intensively, the emissions of other ecosystems in the Eurasian taiga remain less studied. Especially ecosystem scale micrometeorological measurements have been conducted only in a few other boreal ecosystems, such as mixed spruce–birch forest (*Picea abies* subsp. *obovata*, *Betula pubescens* subsp. *czerepanovii*, Rinne *et al.* 2000b), willow plantation for energy production (Olofsson *et al.* 2005) and treeless wetland ecosystems (Haapanala *et al.* 2006, Holst *et al.* 2008). Many of these studies were short-term campaigns. Practically all studies, both at the branch and ecosystem scales, have been conducted in the western part of the Eurasian taiga, whereas there are no measurements conducted in eastern parts. Therefore, in order to understand the regional- and continental-scale BVOC emissions, vegetation species in the eastern part of the Eurasian taiga should receive more attention. Ecosystem-scale measurements are especially needed for Norway spruce (*Picea abies* and *P. abies* subsp. *obovata*) and larch (*Larix gmelinii* and *L. sibirica*) forests,

as these are the major ecosystems from which no data exists in the Eurasian taiga. Also ecosystem scale emission measurements on forests under forest management practices are needed, as there are indications that these practices may dramatically enhance the emissions of reactive BVOCs (Räsänen *et al.* 2008a).

## Emission inventories in boreal areas

In order to give best quantitative estimates of the total BVOC emissions at the regional scale, bottom-up emission inventory models have been commonly utilized (Lindfors and Laurila 2000, Lindfors *et al.* 2000, Simon *et al.* 2001, Tervainen *et al.* 2007, Karl *et al.* 2008). These can also be used to estimate the importance of various ecosystems to emissions of different compounds. These models employ the data obtained from emission measurements in the form of emission algorithms and their parameters. The terpenoid emission algorithms are typically those presented by Guenther *et al.* (1993). As data on emissions from new ecosystems, on the emissions of new compounds, and on seasonal changes in emissions, become available, these inventory models are updated to yield the latest information on the emissions. The regional emission inventory models are similar to the global emission inventory models, such as presented by Guenther *et al.* (1995, 2006) and Müller *et al.* (2008). However, the vegetation description in the regional models can be much more detailed than in the global models. The latter usually divide the vegetation into a few ecosystem types or plant functional types and assign emission parameters for each of these groups, whereas the regional models can utilize plant specific emission parameters and detailed vegetation maps, which make their results more reliable.

The global emission inventories tend to result in similar global emissions for isoprene, while for monoterpenes there is more variation (Arneth *et al.* 2008). At a regional scale, global emission inventories and regional ones can give very different results. In Table 6 we summarize available regional emission inventories for Finland together with data for Finland from some

**Table 5.** Typical transport distances for various BVOCs in mid-July with the wind speed of 5 m s<sup>-1</sup>. OH concentration is taken to be 1 × 10<sup>6</sup> molecules cm<sup>-3</sup> (0.04 ppt) and ozone 1 × 10<sup>12</sup> molecules cm<sup>-3</sup> (40 ppb). Rate coefficients are as in Atkinson (1994) and Atkinson *et al.* (1981).

	Daytime lifetime	Transport distance
Methanol	12 d	5300 km
Acetone	53 d	23 000 km
Acetaldehyde	18 h	320 km
Isoprene	2.4 h	44 km
α-pinene	2.0 h	36 km
Δ <sup>3</sup> -carene	2.2 h	40 km

global inventory models. We can see that the global models tend to overestimate the regional isoprene emissions as compared with regional models. Especially the benchmark inventory of Guenther *et al.* (1995) yields annual isoprene emission over ten times higher than the more recent regional inventories. For monoterpenes, sesquiterpenes and other BVOCs, fewer emission inventories are available. As the lifetime of isoprene and monoterpenes is short, and thus so is also the horizontal transport distance (Table 5), localized emission information should be utilized in the regional air chemistry models rather than more uncertain global model results.

A series of national emission inventories for Finland by Lindfors and Laurila (2000), Lindfors *et al.* (2000) and Tarvainen *et al.* (2007) have synthesized the empirical knowledge on the BVOC emissions from the western Eurasian taiga. The results indicate that the terpenoid emissions are dominated by monoterpenes, with emission of 330–470 kg km<sup>-2</sup> year<sup>-1</sup>. Isoprene emissions are 10%–15% of monoterpene emission in mass basis. The regional emission inventories also reflect the major shortcomings in the quantification of emissions. Below we list some of the most obvious ones.

### Intra-species variation

We know that the chemotypic differences in Scots pine monoterpene emission spectra can be significant even in a seemingly homogeneous forest (Komenda and Koppmann 2002, Tarvainen *et al.* 2005). The emission inventories may derive the regional BVOC emissions from branch-scale measurements conducted only on a few branches,

leading to high uncertainties in the regional scale emissions. For example, Tarvainen *et al.* (2007) assume  $\Delta^3$ -carene emission to comprise 75% of the total monoterpene emission from Scots pine, based on chamber measurements on a limited number of trees. However, the ecosystem-scale emission measurements in Scots pine forests indicate that  $\alpha$ -pinene is the dominant monoterpene emitted from these ecosystems (Rinne *et al.* 1999, 2000) or at least as important as  $\Delta^3$ -carene (Spanke *et al.* 2001). This is also reflected by the abundance of  $\alpha$ -pinene in the ambient air (Hakola *et al.* 2003). Furthermore, it is still very uncertain if the emission potential, dynamics and responses to various triggering factors can be combined between chemotypes. This points out to a need of ecosystem scale measurements of speciated monoterpene emissions and ambient concentrations.

Normally the branch-level emission measurements are performed using the well-lit upper canopy branches with mostly new needles, and upscaling to canopy level is just a multiplication with biomass. However, in many tree species emissions differ greatly depending on the canopy position (Bertin *et al.* 1997), and upscaling from the well-lit upper canopy branches may lead into considerable overestimation of emissions. Also the emission capacity of young and old needles is different, which produces additional sources of error in the canopy level estimates.

### Seasonal changes in emission parameters

In many emission studies, normalized emission potentials have been observed to change during

**Table 6.** BVOC emission inventory results for Finland.

Study	Isoprene (Gg yr <sup>-1</sup> )	Monoterpenes (Gg yr <sup>-1</sup> )	Sesquiterpenes (Gg yr <sup>-1</sup> )	Other VOCs (Gg yr <sup>-1</sup> )
Guenther <i>et al.</i> (1995)	240	400	n.a.	510
Simpson <i>et al.</i> (1999)	39	160	n.a.	140
Lindfors and Laurila (2000)	25	150	n.a.	170
Lindfors <i>et al.</i> (2000)	21	160	n.a.	340
Guenther <i>et al.</i> (2006)	160	n.a.	n.a.	n.a.
Tarvainen <i>et al.</i> (2007)	15	110	9.2	n.a.
Müller <i>et al.</i> (2008)	110	n.a.	n.a.	n.a.

the growing season. For example, isoprene emissions from broadleaved trees typically start only few weeks after leafing (Hakola *et al.* 1998). Not all the inventories have taken this into account which can lead to erroneous results.

### **CO<sub>2</sub> decrease in chamber during measurements**

Experimental evidence points out to significant interactions between isoprene emission and ambient CO<sub>2</sub> levels. Short-term exposures to elevated CO<sub>2</sub> are often shown to rapidly reduce leaf-level isoprene emissions (Monson and Fall 1989, Loreto and Sharkey 1990), whereas growth in subambient CO<sub>2</sub> levels tends to increase emissions (Possell *et al.* 2005). Photosynthetic CO<sub>2</sub> removal from the air in the chamber during emission measurement by chamber technique may in some cases lead to overestimation of isoprene emission.

### **Insufficient knowledge in emissions and biomass of non-dominant vegetation**

We have insufficient knowledge on the emission pattern of many ecosystems. This is partly due to the incomplete knowledge on emission patterns of many plant species and partly due to insufficient knowledge on the biomass densities of some highly emitting species. For example willows (*Salix* sp.) are known to be high isoprene emitters (Hakola *et al.* 1998, Olofsson *et al.* 2005). As they have no major economic value, they are not included in the national forestry inventories. Thus their contribution to the isoprene emission is highly uncertain. However, they are very common in forest edges, wetlands, lakeshores, etc. The abundance of the isoprene emitting shrub vegetation might explain some of the discrepancy between BVOC emission inventories and relative atmospheric concentrations of isoprene and monoterpenes. The national scale emission inventories for Finland generally estimate the isoprene emission in the summertime to be 10%–15% of the monoterpene emission (Lindfors *et al.* 2000, Tarvainen *et al.* 2007). However, the concentration measure-

ments commonly show the isoprene concentrations in the high summer to be about one half of the total monoterpene concentrations (Hakola *et al.* 2000). As the atmospheric chemical lifetimes of isoprene and major monoterpenes are approximately equal, the emission estimates of isoprene might be inadequate.

### **Lack of empirical emission data on sesquiterpenes and OxVOCs**

Only limited data sets on the emissions of sesquiterpenes and oxygenated VOCs (OxVOCs) are available for inventory purposes. This is reflected in the lack of emission algorithms and parameters for making such inventories. Although the emissions of oxygenated VOCs such as alcohols, aldehydes and ketones from many plant species including e.g. Scots pine have been recognized already for at least a decade (Nemecek-Marshall *et al.* 1995, Janson *et al.* 1999), the annual patterns and quantities of these emissions from many important plant species are not fully uncovered. The advent of new analytical methods such as proton transfer reaction-mass spectrometry (PTR-MS) has now enabled monitoring of these emissions in a more comprehensive manner, and thus new information will be expected in near future.

### **Dynamic process models**

Even though the algorithms describing the diurnal changes in isoprene and monoterpene emissions in inventory models are implicitly based on the physical and physiological processes controlling their emission (Guenther *et al.* 1991), the emission is described as a one-step process. The basal emission rates and their seasonal changes are taken into account as empirical parameters and no explicit description of e.g. changes in storage pools is included. The inventory models are basically up-scaling of the emissions from branch and ecosystem scales to regional or global scales using the abovementioned emission algorithms. These models can not be used in estimating the effect of e.g. climatic change to the BVOC emissions as the factors influenc-

ing the basal emission rates are not explicitly described. Instead, models based on process understanding of the VOC synthesis by the plants must be developed. As ecosystems in the Eurasian taiga are predominantly monoterpene emitters, process models including monoterpene synthesis, storage and emission are needed.

The origin of emissions can be investigated using isotope labeling, which can be used in order to separate the emissions from storage organs from those originating from *de novo* synthesis. Isoprene emitted from plants has been observed to be quickly almost completely labeled with  $^{13}\text{C}$ , when the plant is in the atmosphere in which all the  $\text{CO}_2$  is  $^{13}\text{CO}_2$  (Delwiche and Sharkey 1993), whereas  $\alpha$ -pinene labeling is incomplete and suggests significance of storage pools in leaves (Loreto *et al.* 2000). The nature and dynamical features of emission, such as filling up the storage or emissions from the storage pools, depend on the chemical properties of the compounds in question. In addition to the constituent storage pools in resin ducts and glands of some plant species, also non-specific storage influences the emission dynamics of many VOCs. Depending on their octanol/water partitioning coefficient and Henry's law constants, some compounds prefer lipid phase, while some others are preferentially stored in aqueous phase (Niinemets and Reichstein 2003, Copolovici and Niinemets 2005), and this has major implications to the emission route and temporal dynamics of their emissions (Niinemets and Reichstein 2003). Since plant species-specific differences in liquid volume to area ratio are marked, the partitioning of some VOCs into the structural compartments imposes a significant delay for emissions of those compounds. These effects can only be taken into account with proper process-based modeling approach, based on physico-chemical parameterization specifically for each compound.

Process understanding and more dynamic process models are needed in order to estimate the effect of the changing environment to the emissions. The physiological knowledge on biogenic VOC formation pathways has been used to construct several process-based models describing the biosynthesis and further diffusion of volatile compounds from leaves into atmosphere (e.g. Niinemets *et al.* 1999, Bäck *et al.* 2005, Arneth *et*

*al.* 2007). These models use the photosynthetic processes as the starting point, which provides both carbon and energy for the production of VOCs within tissues. They are useful tools when one analyses changes in emissions under changing climate and the connections between emissions and plant metabolic activity under varying environmental conditions. The present models are capable of reproducing short-term changes in isoprene emissions from leaves and needles with reasonable accuracy, although improvements e.g. in respect to seasonal plant activity in perennial evergreens are needed to be able to use the models on larger scale predictions. However, process-based models describing emissions of monoterpenes and sesquiterpenes are still under development, which hinders our understanding on the effects of climate change on BVOC emissions from the Eurasian taiga.

Most of the current emission inventory models assume that the emission of monoterpenes from boreal landscape can be described by temperature-dependent algorithm, implicitly meaning that the monoterpene emissions are assumed to result from vaporization from large storage pools inside the needles and leaves. Indeed, the monoterpene storage in the needles of Scots pine is at least five fold compared to the total monoterpene emission during a growing season (Kainulainen and Holopainen 2002, Räisänen *et al.* 2008c, 2009). These large monoterpene storages are assumed to uncouple most of the emission from synthesis (Grote and Niinemets 2008). However, as mentioned above, it is very likely that a variable part of the emission originates directly from biosynthesis (Steinbrecher *et al.* 1999, Shao *et al.* 2001, Ghirardo *et al.* 2009) and should be calculated by an algorithm describing this process.

Contrary to the conifers, no significant pools on monoterpenes in birch leaves, which also emit monoterpenes, have been reported (e.g. Klika *et al.* 2004, Başer and Bemirci 2007). Many of the broadleaved monoterpene-emitting trees, including birches, do not have resin ducts common to conifers. The significantly smaller monoterpene storage capacity of birch leaves suggest that the majority of mono- and sesquiterpene emissions from these species originates directly from biosynthesis and is likely be light

dependent. *Quercus ilex*, a Mediterranean species, which has insignificant monoterpene storage pool as compared to conifers, emits monoterpenes in a light dependent manner (Staudt and Seufert 1995, Alessio *et al.* 2008). Also most of the monoterpenes emitted by both *Betula pendula* and *Quercus ilex* are rapidly labelled when the plants are fed  $^{13}\text{C}_2$  which indicates the monoterpene emission originating directly from synthesis (Ghirardo *et al.* 2009).

## Climate change and boreal BVOC emissions

Changes in temperature, precipitation and  $\text{CO}_2$  concentration can have a large impact on the integrated annual BVOC emissions, and on their temporal and regional dynamics at stand and ecosystem level, in particular in boreal areas where the changes in temperatures have been predicted to be greatest (ACIA 2004). The effects can be manifested both at the process level and in a more integrated manner. Increased atmospheric  $\text{CO}_2$  concentration will enhance photosynthetic  $\text{CO}_2$  assimilation, and due to the close connections between photosynthesis and VOC biosynthesis suggested by the process-based models, also VOC emissions can be expected to change. However, isoprene emission has been observed to be inhibited at elevated  $\text{CO}_2$  concentrations (Rosenstiel *et al.* 2003, Arneth *et al.* 2007 and references therein). Emission reductions due to elevated  $\text{CO}_2$  have mainly been connected to down-regulation at biochemical and/or enzymatic level (e.g. Loreto *et al.* 2001, Rosenstiel *et al.* 2003). The isoprene emissions have often a broad maximum between 50 and 500 ppm  $\text{CO}_2$ , following a sharp decrease below the optimum concentration and a slow decline above the optimum concentration (Loreto and Sharkey 1990). Since many of the experimental results regarding  $\text{CO}_2$ -BVOC interaction originate from studies with model plants under laboratory conditions, the results are not necessarily applicable to natural conditions where several limiting factors may coexist. It is also unknown if the  $\text{CO}_2$  inhibition happens also when the plants have been acclimatized to higher  $\text{CO}_2$  concentration for longer periods. The effect of elevated  $\text{CO}_2$

on the monoterpene emission and biosynthesis has been studied much less and the results are less clear (Vuorinen *et al.* 2005, Räisänen *et al.* 2008b). However, the monoterpene content in the needles of Scots pine grown in high  $\text{CO}_2$  are reported to be lower than in those grown in ambient  $\text{CO}_2$  (Räisänen *et al.* 2008c) indicating that there may be a similar down-regulation than for isoprene synthesis. Carefully designed laboratory experiments using for example stable isotopes may also reveal dynamic patterns in the regulation of the less studied VOC emissions.

On a more integrated scale, rising  $\text{CO}_2$  concentrations will also increase the productivity and standing biomass of plants, and influence the emissions at the landscape level. However, it is not well known how VOC emissions develop if water or nutrient availability changes, if autumn and winter temperatures increase, or if the outbreaks of herbivores become more excessive or more frequent due to climate change in northern ecosystems.

One important climate feedback regarding BVOC emissions from northern regions comes through changes in the duration of favourable conditions for plant metabolism and in the length of the growing season. The growing-period length is related to geographic location, which is reflected in the accumulated temperature sum, and the timing of major phenological events (leafing, flowering and senescence) will be greatly affected by climate change (Häkkinen *et al.* 1998, Menzel and Fabian 1999, Taylor *et al.* 2008). The temperature-driven annual cycle of NPP (net primary production) is important in the northern boreal areas, whereas in warmer climatic zones with milder winters the role of temperature in the annual cycle of photosynthesis is not as dominating as in the boreal zone. The climate change influence on NPP may eventually be important regarding the cumulative annual BVOC emissions in the boreal areas.

One of the major effects of the climate change to the biogenic VOC emissions may be via its effect on land-use and natural land cover (Kellomäki *et al.* 2001). The northern forest treeline has changed due to changes in climatic condition during the Holocene and global warming is expected to drive the northern forest edge northwards thus transforming the current tundra into

monoterpene emitting forest ecosystems (Grace *et al.* 2002, Seppä and Hicks 2006, MacDonald *et al.* 2008). At the same time, the southern part of the taiga coniferous forest can be changed into hemiboreal mixed forests with oaks (e.g. *Quercus robur*), maples (e.g. *Acer platanoides*) and beech (*Fagus sylvatica*). This would lead to different emission dynamics as the evergreen monoterpene emitting conifers are replaced by broadleaves, of which some are isoprene emitters (Isidorov *et al.* 1985). The southern forest edge between the taiga and steppe in central Asia has been observed to be sensitive to changes in climate, especially precipitation, during Holocene (Rudaya *et al.* 2009). As anthropogenic climate change is likely to affect the precipitation patterns (Giorgi and Bi 2005) it may also cause a shift of border between forest and steppe ecosystems and thus change regional BVOC emissions.

In the western parts of the Eurasian taiga, the land cover is largely governed by human land use, i.e. agriculture and forestry. In the changing climate the economic viability of different sectors of agriculture and forestry may change and cause major shifts in the respective areas, and in the proportions and species of different agricultural plants and tree species cultivated (Kellomäki *et al.* 2008). It may even cause the introduction of previously alien tree species in large scale (Koca *et al.* 2006). Also the possible future production of biofuels in large scales may lead to shifts in land use. To explore the effects of these processes, inventory models utilizing different agricultural and forestry scenarios may be beneficial.

The emerging picture on the interactions of terpenoid emissions with the physical and biological environment is thus far more complex than the one presented by Kulmala *et al.* (2004). Especially the fact that there are both positive and negative forcings exerted by the physical climate on BVOC emissions, and also positive and negative feedbacks on climate makes predictions challenging.

## Concluding remarks

This review has given an overview on the research conducted on the biogenic VOC emissions from the Eurasian taiga ecosystems during

the past two decades. The research has revealed following key findings:

- Generally the ecosystem scale emissions of VOC from ecosystems in the Eurasian taiga have been observed to be relatively low as compared with those from some forest ecosystems in warmer climates.
- Monoterpene-emitting coniferous trees predominate over isoprene emitters in the Eurasian taiga.
- Monoterpene emission from coniferous trees originates partly as evaporation from large specialized storages and partly directly from synthesis.
- Monoterpene emission from boreal broad-leaved trees originates directly from synthesis as they do not have significant specialized storage structures such as resin ducts.
- Many boreal tree species exhibit intraspecies variation in the monoterpene mixture they emit.
- Important sources of isoprene in the Eurasian taiga include Norway spruce, open wetland ecosystems, and some non-dominant woody species such as European aspen and willows.
- Many boreal tree species also emit highly reactive sesquiterpenes, even without any observable stress.
- Seasonal changes in plant functioning influence especially the isoprene emissions, and they also have major impact on monoterpene and sesquiterpene emissions
- Physicochemical factors of the compounds, such as water or lipid solubility influence the emissions.

We have identified the following gaps in our knowledge on BVOC emission from the Eurasian taiga:

- Lack of knowledge on non-terpenoid VOC emission from most boreal tree species. This includes both the emission strength and dependencies on environmental variables.
- Lack of data on BVOC emissions from the eastern Eurasian taiga, as most of the measurements have been conducted in Sweden and Finland. Especially striking is the lack of data on larch species covering huge areas.

- Our knowledge on monoterpene synthesis, storage, and emission dynamics in seasonal time scale is insufficient for process modelling. This hinders the prediction on how the climate change will influence the BVOC emissions.
- Especially the effect of rising atmospheric CO<sub>2</sub> concentrations on other terpenoids than isoprene is not understood.
- Heterogeneity in vegetation, including chemotypic variations, is not understood well enough to be taken into account in emission models.

Future challenges in research of BVOC emissions from the Eurasian taiga include:

- Understanding the dynamics of monoterpene synthesis, storage, and emission from boreal coniferous trees.
- Quantification of non-terpenoid VOC emissions from the taiga ecosystems.
- Bringing ecosystems in the eastern Eurasian taiga into the sphere of BVOC emission studies.
- Long term ecosystem flux studies combined with plant physiological measurements.
- Integrating knowledge and research skills on BVOC synthesis, storages, and emissions, land cover changes, and atmospheric processes in different spatial and temporal scales.

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## References

- ACIA 2004. *Impacts of a warming Arctic: Arctic climate impact assessment*. Cambridge University Press, UK.
- Alessio G.A., Peñuelas J., De Lillis M. & Llusia J. 2008. Implications of foliar terpene content and hydration on leaf flammability of *Quercus ilex* and *Pinus halepensis*. *Plant Biol.* 10: 123–128.
- Arneth A., Niinemets Ü., Pressley S., Bäck J., Hari P., Karl T., Noe S., Prentice I.C., Serça D., Hickler T., Wolf A. & Smith B. 2007. Process-based estimates of terrestrial ecosystem isoprene emissions: incorporating the effects of a direct CO<sub>2</sub>-isoprene interaction. *Atmos. Chem. Phys.* 7: 31–53.
- Arneth A., Monson R.K., Schurgers G., Niinemets Ü. & Palmer P.I. 2008. Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)? *Atmos. Chem. Phys.* 8: 4605–4620.
- Atkinson R. 1994. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data Monogr.* 2: 1–216.
- Atkinson R., Aschmann S.M., Winer A.M. & Pitts J.N.Jr. 1981. Rate constants for the gas-phase reactions of O<sub>3</sub> with a series of carbonyls at 296 K. *Int. J. Chem. Kinet.* 13: 1133–1142.
- Atkinson R. & Arey J. 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos. Environ.* 37: S197–S219.
- Aurela M., Riutta T., Laurila T., Tuovinen J.-P., Vesala T., Tuittila E.-S., Rinne J., Haapanala S. & Laine J. 2007. CO<sub>2</sub> balance of a sedge fen in southern Finland – the influence of a drought period. *Tellus* 59B: 826–837.
- Başer K.H.C. & Demirci B. 2007. Studies on *Betula* essential oils. *ARKIVOC* vii: 335–348.
- Bertin N., Staudt M., Hansen U., Seufert G., Ciccioli P., Foster O., Fugit J.L. & Torres L. 1997. Diurnal and seasonal course of monoterpene emissions from *Quercus ilex* (L.) under natural conditions — application of light and temperature algorithms. *Atmos. Environ.* 31: 135–144.
- Bonn B. & Moortgat G.K. 2003. Sesquiterpene ozonolysis: origin of atmospheric new particle formation from biogenic hydrocarbons. *Geophys. Res. Lett.* 30, 1585, doi: 10.1029/2003GL017000.
- Brunner A., Ammann C., Neftel A. & Spirig C. 2007. Methanol exchange between grassland and the atmosphere. *Biogeosci.* 4: 395–410.
- Bäck J., Hari P., Hakola H., Juurola E. & Kulmala M. 2005. Dynamics of monoterpene emissions in *Pinus sylvestris* during early spring. *Boreal Env. Res.* 10: 409–424.
- Bäckstrand K., Crill P., Mastepanov M., Christensen T. & Bastviken D. 2008. Non-methane volatile organic compound flux from a subarctic mire in northern Sweden. *Tellus* 60B: 226–237.
- Christensen C.S., Hummelshøj P., Jensen N.O., Larsen B., Lohse C., Pilegaard K. & Skov H. 2000. Determination of the terpene flux from orange species and Norway spruce by relaxed eddy accumulation. *Atmos. Environ.* 34: 3057–3067.
- Claeys M., Grahon B., Vas G., Wang W., Vermeylen R., Pashynska V., Cafmeyer J., Guyon P., Andreae M.O., Artaxo P. & Maenhaut W. 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303: 1173–1176.
- Cojocariu C., Kreuzwieser J. & Rennenberg H. 2004. Correlation of short-chained carbonyls emitted from *Picea abies* with physiological and environmental parameters. *New Phytol.* 162: 717–727.
- Cojocariu C., Escher P., Haberle K.H., Matyssek R., Rennenberg H. & Kreuzwieser J. 2005. The effect of ozone on the emission of carbonyls from leaves of adult *Fagus*



- sylvatica*. *Plant Cell Environ.* 28: 603–611.
- Copolovici L.O. & Niinemets Ü. 2005. Temperature dependencies of Henry's law constants and octanol/water partition coefficients for key plant volatile monoterpenoids. *Chemosphere* 61: 1390–1400.
- Custer T. & Schade G. 2007. Methanol and acetaldehyde fluxes over ryegrass. *Tellus* 59B: 673–684.
- Delwiche C.F. & Sharkey T.D. 1993. Rapid appearance of  $^{13}\text{C}$  in isoprene when  $^{13}\text{CO}_2$  is fed to intact leaves. *Plant Cell Environ.* 16: 587–591.
- Dufour G., Szopa S., Hauglustaine D.A., Boone C.D., Rinsland C.P. & Bernath P.F. 2007. The influence of biogenic emissions on upper-tropospheric methanol as revealed from space. *Atmos. Chem. Phys.* 7: 6119–6129.
- Ekberg A., Arneth A., Hakola H., Hayward S. & Holst T. 2008. Leaf isoprene emission in a subarctic wetland sedge community. *Biogeosci.* 6: 601–613.
- Fäldt J., Solheim H., Långström B. & Borg-Karlson A.-K. 2006. Influence of fungal infection and wounding on contents and enantiomeric compositions of monoterpenes in phloem of *Pinus sylvestris*. *J. Chem. Ecol.* 32: 1779–1795.
- Fall R. 2003. Abundant oxygenates in the atmosphere: a biochemical perspective. *Chemical Reviews* 103: 4941–4951.
- FAO 2001. *Global forest resources assessment 2000*. FAO Forestry Paper 140.
- Folkers A., Huve K., Ammann C., Dindorf T., Kesselmeier J., Kleist E., Kuhn U., Uerlings R. & Wildt J. 2008. Methanol emissions from deciduous tree species: dependence on temperature and light intensity. *Plant Biol.* 10: 65–75.
- Galbally I.E. & Kirstine W. 2002. The production of methanol by flowering plants and the global cycle of methanol. *J. Atmos. Chem.* 43: 195–229.
- Ghirardo A., Koch K., Schnitzler J.P. & Rinne J. 2009.  $^{13}\text{CO}_2$  feeding experiment of four common European boreal tree species:  $^{13}\text{C}$  incorporation into monoterpenes. In: Hansel A. & Dunkl J. (eds.), *4th International Conference on Proton Transfer Reaction Mass Spectrometry and its applications – Contributions*, Innsbruck University Press, pp. 219–220.
- Giorgi F. & Bi X. 2005. Updated regional precipitation and temperature changes for the 21st century from ensembles of recent AOGCM simulations. *Geophys. Res. Lett.* 32, L21715, doi:10.1029/2005GL024288.
- Grabmer W., Kreuzwieser J., Wisthaler A., Cojocariu C., Graus M., Rennenberg H., Steigner D., Steinbrecher R. & Hansel A. 2006. VOC emissions from Norway spruce (*Picea abies* L. [Karst]) twigs in the field — results of a dynamic enclosure study. *Atmos. Environ.* 40 S1: 128–137.
- Grace J., Berninger F. & Nagy L. 2002. Impacts of climate change on the tree line. *Annals of Botany* 90: 537–544.
- Grote R. & Niinemets Ü. 2008. Modeling volatile isoprenoid emissions — a story with split ends. *Plant Biol.* 10: 8–28.
- Guenther A.B., Monson R.K. & Fall R. 1991. Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. *J. Geophys. Res.* 96: 10799–10808.
- Guenther A.B., Zimmermann P.R., Harley P.C., Monson R.K. & Fall R. 1993. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. *J. Geophys. Res.* 98: 12609–12617.
- 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. & Zimmerman P. 1995. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* 100: 8873–8892.
- Guenther A., Karl T., Harley P., Wiedinmyer C., Palmer P. & Geron C. 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* 6: 3181–3210.
- Haapanala S., Rinne J., Pystynen K.-H., Hellén H., Hakola H. & Riutta T. 2006. Measurements of biogenic hydrocarbon emissions from a boreal fen in the southern Finland with a REA system. *Biogeosci.* 3: 103–112.
- Haapanala S., Rinne J., Hakola H., Hellén H., Laakso L., Lihavainen H., Janson R., O'Dowd C. & Kulmala M. 2007. Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring. *Atmos. Chem. Phys.* 7: 1869–1878.
- Haapanala S., Ekberg A., Rinne J., Hakola H., Hellén H., Tarvainen V. & Arneth A. 2008. Emissions of volatile organic compounds from mountain birch. *Report Series in Aerosol Science* 92: 70–72.
- Hakola H., Rinne J. & Laurila T. 1998. Hydrocarbon emission rates of tea-leaved willow (*Salix phylicifolia*), Silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmos. Environ.* 32: 1825–1833.
- Hakola H., Rinne J. & Laurila T. 1999. The VOC emission rates of boreal deciduous trees. In: Laurila T. & Lindfors V. (eds.), *Biogenic VOC emissions and photochemistry in the boreal regions of Europe*, Air Pollution Research Report 70, Commission of European Communities, Luxembourg, pp. 21–28.
- Hakola H., Laurila T., Rinne J. & Puuto K. 2000. The ambient concentrations of biogenic hydrocarbons at a North-European site. *Atmos. Environ.* 34: 4971–4982.
- Hakola H., Laurila T., Lindfors V., Hellén H., Gaman A. & Rinne J. 2001. Variation of the VOC emission rates of birch species during the growing season. *Boreal Env. Res.* 6: 237–249.
- Hakola H., Tarvainen V., Laurila T., Hiltunen V., Hellén H. & Keronen P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* 37: 1623–1634.
- Hakola H., Tarvainen V., Bäck J., Ranta H., Bonn B., Rinne J. & Kulmala M. 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. *Biogeosci.* 3: 93–101.
- Harley P., Fridd-Stroud V., Greenberg J., Guenther A. & Vasconcellos P. 1998. Emission of 2-methyl-3-buten-2-ol by pines: a potentially large natural source of reactive carbon to the atmosphere. *J. Geophys. Res.* 103: 25479–25486.
- Harley P., Greenberg J., Niinemets Ü. & Guenther A. 2007. Environmental controls over methanol emission from

- leaves. *Biogeosci.* 4: 1083–1099.
- Hellén H., Hakola H., Pystynen K.-H., Rinne J. & Haapanala S. 2006. C<sub>2</sub>–C<sub>10</sub> hydrocarbon emissions from a boreal wetland and forest floor. *Biogeosci.* 3: 167–174.
- Hiltunen R. & Laakso I. 1995. Gas chromatographic analysis and biogenetic relationships of monoterpene enantiomers in Scots pine and Juniper needle oils. *Flavour and Fragrance Journal* 10: 203–210.
- Holopainen J.K. 2004. Multiple functions of inducible plant volatiles. *Trends in Plant Science* 9: 529–533.
- Holst T., Armeth A., Hayward S., Ekberg A., Mastepanov M., Jackowicz-Korczynski M., Friberg T., Crill P.M. & Bäckstrand K. 2008. BVOC ecosystem flux measurements at a high latitude wetland site. *Atmos. Chem. Phys. Discuss.* 8: 21129–21169.
- Holzke C., Hoffmann T., Jaeger L., Koppmann R. & Zimmer W. 2006. Diurnal and seasonal variation of monoterpene and sesquiterpene emission from Scots pine (*Pinus sylvestris* L.). *Atmos. Environ.* 40: 3174–3185.
- Hüve K., Christ M.M., Kleist E., Uerlings R., Niinemets Ü, Walter A. & Wildt J. 2007. Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata. *J. Exp. Bot.* 58: 1783–1793.
- Häkkinen R., Linkosalo T. & Hari P. 1998. Effects of dormancy and environmental factors on timing of bud burst in *Betula pendula*. *Tree Physiol.* 18: 707–712.
- Isidorov V.A., Zenkevich I.G. & Ioffe B.V. 1985. Volatile organic compounds in the atmosphere of forest. *Atmos. Environ.* 19: 1–8.
- Janson R. 1993. Monoterpene emissions from Scots pine and Norwegian spruce. *J. Geophys. Res.* 98: 2839–2850.
- Janson R.W. & De Serves C. 1998. Isoprene emissions from boreal wetlands in Scandinavia. *J. Geophys. Res.* 103: 25513–25517.
- Janson R., De Serves C. & Romero R. 1999. Emission of isoprene and carbonyl compounds from a boreal forest and wetland in Sweden. *Agric. For. Meteorol.* 98–99: 671–681.
- Janson R. & De Serves C. 2001. Acetone and monoterpene emissions from the boreal forest in northern Europe. *Atmos. Environ.* 35: 4629–4637.
- Kainulainen P. & Holopainen J.K. 2002. Concentrations of secondary compounds in Scots pine needles at different stages of decomposition. *Soil Biol. Biochem.* 34: 37–42.
- Kaplan J.O., Folberth G. & Hauglustaine D.A. 2006. Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations. *Global Biogeochem. Cycles* 20, GB2016, doi:10.1029/2005GB002590.
- Karl T., Guenther A., Yokelson R.J., Greenberg J., Potosnak M., Blake D.R. & Artaxo P. 2007. The tropical forest and fire emissions experiment: emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia. *J. Geophys. Res.* 112, D18302, doi:10.1029/2007JD008539.
- Karl M., Guenther A., Köble R. & Seufert G. 2008. A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models. *Biogeosci. Discuss.* 5: 4993–5059.
- Kellomäki S., Rouvinen I., Peltola H., Strandman H. & Steinbrecher R. 2001. Impact of global warming on the tree species composition of boreal forests in Finland and effects on emissions of isoprenoids. *Global Change Biology* 7: 531–544.
- Kellomäki S., Peltola H., Nuutinen T., Korhonen K.T. & Strandman H. 2008. Sensitivity of managed boreal forests in Finland to climate change, with implications for adaptive management. *Phil. Trans. R. Soc. B* 363: 2339–2349.
- Klika K.D., Demirci B., Salminen J.-P., Ovcharenko V.V., Vuorela S., Başer K.H.C. & Pihlaja K. 2004. New, sesquiterpene-type bicyclic compounds from the buds of *Betula pubescens* — ring-contracted products of  $\beta$ -caryophyllene? *Eur. J. Org. Chem.* 2004: 2627–2635.
- Koca D., Smith B. & Sykes M.T. 2006. Modelling regional climate change effects on potential natural ecosystems in Sweden. *Climatic Change* 78: 381–406.
- Komenda M. & Koppmann R. 2002. Monoterpene emissions from Scots pine (*Pinus sylvestris*): field studies of emission rate variabilities. *J. Geophys. Res.* 107, 4161, doi: 10.1029/2001JD000691.
- Kulmala M., Hämeri K., Aalto P.P., Mäkelä J.M., Pirjola L., Nilsson E.D., Buzorius G., Rannik Ü., Dal Maso M., Seidl W., Hoffmann T., Janson R., Hansson H.C., Viisanen Y., Laakkonen A. & O’Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.
- Kulmala M., Suni T., Lehtinen K.E.J., Dal Maso M., Boy M., Reissell A., Rannik Ü., Aalto P., Keronen P., Hakola H., Bäck J., Hoffmann T., Vesala T. & Hari P. 2004. A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* 4: 557–562.
- Laurila T. & Lindfors V. (eds.) 1999. *Biogenic VOC emissions and photochemistry in the boreal regions of Europe*. Air Pollution Research Report 70, Commission of the European Communities, Luxembourg.
- Lindfors V. & Laurila T. 2000. Biogenic VOC emissions from forests in Finland. *Boreal Env. Res.* 5: 95–113.
- Lindfors V., Laurila T., Hakola H., Steinbrecher R. & Rinne J. 2000. Modeling biogenic terpene emissions in the European boreal region. *Atmos. Environ.* 34: 4983–4996.
- Loreto F. & Sharkey T.D. 1990. A gas exchange study of photosynthesis and isoprene emission in *Quercus rubra* L. *Planta* 182: 523–531.
- Loreto F., Ciccioli P., Brancaleoni E., Frattoni M. & Delfino S. 2000. Incomplete <sup>13</sup>C labelling of  $\alpha$ -pinene content of *Quercus ilex* leaves and appearance of unlabelled C in  $\alpha$ -pinene emission in the dark. *Plant Cell Environ.* 23: 229–234.
- Loreto F., Fischbach R.J., Schnitzler J.P., Ciccioli P., Brancaleoni E., Calfapietra C. & Seufert G. 2001. Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak *Quercus ilex* L. grown at elevated CO<sub>2</sub> concentrations. *Global Change Biology* 7: 709–717.
- MacDonald G.M., Kremetski K.V. & Beilman D.W. 2008. Climate change and the northern Russian treeline zone. *Phil. Trans. R. Soc. B* 363: 2283–2299.
- Manninen A.-M., Tarhanen S., Vuorinen M. & Kainulainen

- P. 2002. Comparing the variation of needle and wood terpenoids in Scots pine provenances. *J. Chem. Ecol.* 28: 211–228.
- Menzel A. & Fabian P. 1999. Growing season extended in Europe. *Nature* 397: 659–659.
- Metsäntutkimuslaitos 2007: *Metsätilastollinen vuosikirja, Finnish Statistical Yearbook of Forestry 2007*. Metsäntutkimuslaitos, Vantaa.
- Monson R.K. & Fall R. 1989. Isoprene emission from aspen leaves — influence of environment and relation to photosynthesis and photorespiration. *Plant Physiol.* 90: 267–274.
- Müller J.-F., Stavrakou T., Wallens S., De Smedt I., Van Roozendael M., Potosnak M.J., Rinne J., Munger B., Goldstein A. & Guenther A.B. 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. *Atmos. Chem. Phys.* 8: 1329–1341.
- Nemecek-Marshall M., MacDonald R.C., Franzen J.J., Wojciechowski C.L. & Fall R. 1995. Methanol emission from leaves (enzymatic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development). *Plant Physiol.* 108: 1359–1368.
- Niinemets Ü. & Reichstein M. 2003. Controls on the emission of plant volatiles through stomata: a sensitivity analysis. *J. Geophys. Res.* 108, 4211. doi:10.1029/2002JD002626.
- Niinemets Ü., Tenhunen J.D., Harley P.C. & Steinbrecher R. 1999. A model of isoprene emission based on energetic requirements for isoprene synthesis and leaf photosynthetic properties for *Liquidambar* and *Quercus*. *Plant Cell Environ.* 22: 1319–1335.
- Nozière B. & Esteve W. 2005. Organic reactions increasing the adsorption index of atmospheric sulfuric acid aerosols. *Geophys. Res. Lett.* 32, doi:10.1029/2004GL021942.
- Olofsson M., Ek-Olausson B., Jensen N.O., Langer S. & Ljungström E. 2005. The flux of isoprene from a willow plantation and the effect on local air quality. *Atmos. Environ.* 39: 2061–2070.
- Possell M., Hewitt C.N. & Beerling D.J. 2005. The effects of glacial atmospheric CO<sub>2</sub> concentrations and climate on isoprene emissions by vascular plants. *Global Change Biology* 11: 60–69.
- Pressley S., Lamb B., Westberg H. & Vogel C. 2006. Relationships among canopy scale energy fluxes and isoprene flux derived from long-term, seasonal eddy covariance measurements over a hardwood forest. *Agric. For. Meteorol.* 136: 188–202.
- Räisänen T., Ryyppö A. & Kellomäki S. 2008a. Impact of timber felling on the ambient monoterpene concentration of a Scots pine (*Pinus sylvestris* L.) forest. *Atmos. Environ.* 42: 6759–6766.
- Räisänen T., Ryyppö A. & Kellomäki S. 2008b. Effects of elevated CO<sub>2</sub> and temperature on monoterpene emission of Scots pine (*Pinus sylvestris* L.). *Atmos. Environ.* 42: 4160–4171.
- Räisänen T., Ryyppö A., Julkunen-Tiitto R. & Kellomäki S. 2008c. Effects of elevated CO<sub>2</sub> and temperature on secondary compounds in the needles of Scots pine (*Pinus sylvestris* L.). *Trees — Structure and Function* 22: 121–135.
- Räisänen T., Ryyppö A. & Kellomäki S. 2009. Monoterpene emission of a boreal Scots pine (*Pinus sylvestris* L.) forest. *Agric. For. Meteorol.* 149: 808–819.
- Rinnan R., Rinnan A., Holopainen T., Holopainen J.K. & Pasanen P. 2005. Emission of non-methane volatile organic compounds (VOCs) from boreal peatland microcosms — effects of ozone exposure. *Atmos. Environ.* 39: 921–930.
- Rinne J., Hakola H. & Laurila T. 1999. Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone. *Phys. Chem. Earth B* 24: 711–715.
- Rinne J., Hakola H., Laurila T. & Rannik Ü. 2000a. Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests. *Atmos. Environ.* 34: 1099–1107.
- Rinne J., Tuovinen J.P., Laurila T., Hakola H., Aurela M. & Hypén H. 2000b. Measurements of isoprene and monoterpene fluxes by a gradient method above a northern boreal forest. *Agric. For. Meteorol.* 102: 25–37.
- Rinne H.J.I., Guenther A.B., Greenberg J.P. & Harley P.C. 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmos. Environ.* 36: 2421–2426.
- Rinne J., Ruuskanen T.M., Reissell A., Taipale R., Hakola H. & Kulmala M. 2005. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem. *Boreal Env. Res.* 10: 425–436.
- Rinne J., Taipale R., Markkanen T., Ruuskanen T.M., Hellén H., Kajos M.K., Vesala T. & Kulmala M. 2007. Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling. *Atmos. Chem. Phys.* 7: 3361–3372.
- Rosenstiel T.N., Potosnak M.J., Griffin K.L., Fall R. & Monson R.K. 2003. Increased CO<sub>2</sub> uncouples growth from isoprene emission in an agriforest ecosystem. *Nature* 421: 256–259.
- Rudaya N., Tarasov P., Dorofeyuk N., Solovieva N., Kalugin I., Andreev A., Daryin A., Diekmann B., Riedel F., Tserendash N. & Wagner M. 2009. Holocene environments and climate in the Mongolian Altai reconstructed from the Hotoon-Nur pollen and diatom records: a step towards better understanding climate dynamics in central Asia. *Quat. Sci. Rev.* 28: 540–554.
- Ruuskanen T.M., Kolari P., Bäck J., Kulmala M., Rinne J., Hakola H., Taipale R., Raivonen M., Altimir N. & Hari P. 2005. On-line field measurements of monoterpene emissions from Scots pine by proton transfer reaction — mass spectrometry. *Boreal Env. Res.* 10: 553–567.
- Ruuskanen T.M., Hakola H., Kajos M.K., Hellén H., Tarvainen V. & Rinne J. 2007. Volatile organic compound emissions from Siberian larch. *Atmos. Environ.* 41: 5807–5812.
- Ruuskanen T.M., Taipale R., Rinne J., Kajos M.K., Hakola H. & Kulmala M. 2009. Quantitative long-term measurements of VOC concentrations by PTR-MS: annual cycle at a boreal forest site. *Atmos. Chem. Phys. Discuss.* 9: 81–134.
- Seppä H. & Hicks S. 2006. Integration of modern and past pollen accumulation rate (PAR) records across the arctic tree-line: a method for more precise vegetation reconstructions. *Quat. Sci. Rev.* 25: 1501–1516.

- Shao M., Czapiewski K.V., Heiden A.C., Kobel K., Komenda M., Koppman R. & Wildt J. 2001. Volatile organic compound emissions from Scots pine: mechanisms and description by algorithms. *J. Geophys. Res.* 106: 20483–20491.
- Simon V., Luchetta L. & Torres L. 2001. Estimating emission of volatile organic compounds (VOC) from the French forest ecosystem. *Atmos. Environ.* 35, suppl. 1: S115–S126.
- Simpson D., Winiwarter W., Börjesson G., Cinderby S., Ferreira A., Guenther A., Hewitt N., Janson R., Khalil M.A.K., Owen S., Pierce T., Puxbaum H., Shearer M., Skiba U., Steinbrecher R., Tarrasón L. & Öquist M.G. 1999. Inventorying emissions from nature in Europe. *J. Geophys. Res.* 104: 8113–8152.
- Spanke J., Rannik Ü, Forkel R., Nigge W. & Hoffmann T. 2001. Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modelling. *Tellus B* 53: 406–422.
- Spirig C., Guenther A., Greenberg J.P., Calanca P. & Tarvainen V. 2004. Tethered balloon measurements of biogenic volatile organic compounds at a boreal forest site. *Atmos. Chem. Phys.* 4: 215–229.
- Spirig C., Neftel A., Ammann C., Dommen J., Grabmer W., Thielmann A., Schaub A., Beauchamp J., Wisthaler A. & Hansel A. 2005. Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry. *Atmos. Chem. Phys.* 5: 465–481.
- Staudt M. & Seufert G. 1995. Light-dependent emission of monoterpenes by Holm oak (*Quercus ilex* L.). *Naturwissenschaften* 82: 89–92.
- Steinbrecher R., Hauff K., Hakola H. & Rössler J. 1999. A revised parameterisation for emission modelling of isoprenoids for boreal plants. In: Laurila T. & Lindfors V. (eds.), *Biogenic VOC emissions and photochemistry in the boreal regions of Europe*. Air Pollution Research Report 70, Commission of European Communities, Luxembourg, pp. 29–43.
- Taipale R., Ruuskanen T.M., Kajos M.K., Patokoski J., Hakola H. & Rinne J. 2009. VOC emission from boreal forest — direct ecosystem scale measurements by PTR-MS in 2006–2008. In: Hansel A. & Dunkl J. (eds.), *4th International Conference on Proton Transfer Reaction Mass Spectrometry and its applications — Contributions*, Innsbruck University Press, pp. 299–302.
- Tarvainen V., Hakola H., Hellén H., Bäck J., Hari P. & Kulmala M. 2005. Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys.* 5: 989–998.
- Tarvainen V., Hakola H., Rinne J., Hellén H. & Haapanala S. 2007. Towards a comprehensive emission inventory of terpenoids from boreal ecosystems. *Tellus* 59B: 526–534.
- Taylor G., Tallis M.J., Giardina C.P., Percy K.E., Miglietta F., Gupta P.S., Gioli B., Calfapietra C., Gielen B., Kubiske M.E., Scarascia-Mugnozza G.E., Kets K., Long S.P. & Karnosky D.F. 2008. Future atmospheric CO<sub>2</sub> leads to delayed autumnal senescence *Global Change Biology* 14: 264–275.
- Tiiva P., Rinnan R., Holopainen T., Mörsky S.K. & Holopainen J.K. 2007a. Isoprene emissions from boreal peatland microcosms; effects of elevated ozone concentration in an open field experiment. *Atmos. Environ.* 41: 3819–3828.
- Tiiva P., Rinnan R., Faubert P., Räsänen J., Holopainen T., Kyrö E. & Holopainen J.K. 2007b. Isoprene emission from a subarctic peatland under enhanced UV-B radiation. *New Phytol.* 176: 346–355.
- Tunved P., Hansson H.-C., Kerminen V.-M., Ström J., Dal Maso M., Lihavainen H., Viisanen Y., Aalto P.P., Komppula M. & Kulmala M. 2006. High natural aerosol loading over Boreal forests. *Science* 312: 261–263.
- Vuorinen T., Nerg A.M., Vapaavuori E. & Holopainen J.K. 2005. Emission of volatile organic compounds from two silver birch (*Betula pendula* Roth.) clones grown under ambient and elevated CO<sub>2</sub> and different O<sub>3</sub> concentrations. *Atmos. Environ.* 39: 1185–1197.
- Went F.W. 1960. Blue hazes in the atmosphere. *Nature* 187: 641–643.
- Williams J., Yassaa N., Bartenbach S. & Lelieveld J. 2007. Mirror image hydrocarbons from tropical and boreal forests. *Atmos. Chem. Phys.* 7: 973–980.
- Yassaa N. & Williams J. 2007. Enantiomeric monoterpene emissions from natural and damaged Scots pine in a boreal coniferous forest measured using solid-phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr. A* 1141: 138–144.