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A source-orientated approach for estimating daytime concentrations of biogenic volatile organic compounds in an upper layer of a boreal forest canopy

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Biologically justified statistical models for daytime atmospheric concentrations of methanol, acetaldehyde, acetone, isoprene and monoterpene were tested using measurements at a boreal forest stand in southern Finland in 2006–2007 and in summer 2008. The canopy-scale concentrations of all compounds except monotepene were closely correlated with shoot-scale concentrations indicating a strong link to biological emission source. All the models were based on the exponential relationship between air temperature and atmospheric concentration of biogenic volatile organic compounds (BVOCs). The first model — an exponential function of air temperature (T model) — could explain 27%–64% of the variation in BVOC daytime concentrations in the test data. The second model — a Temperature-State of Development model (T-S model) having two explaining variables (air temperature and seasonal photosynthetic efficiency) — was derived from an empirical adjustment of seasonality. This model slightly increased the fraction of explained variation but it still could not explain the high concentration peaks, which accounted for most of the unexplained variation. To better analyse these peaks we tested the Trigger model including two potential environmental triggers, a PAR index (high photosynthetically active photon flux density (PAR) and high ozone concentration, that could increase the concentrations momentarily. However, the Trigger model described the peak concentrations only somewhat better than the T or T-S model. It seems that it is very difficult to explain more than 32%–67% of variation in BVOC concentrations by a straightforward source-oriented modelling without deep understanding of biological and physical processes. In order to improve the models profound studies on specific stress factors and events inducing BVOC emissions are needed.

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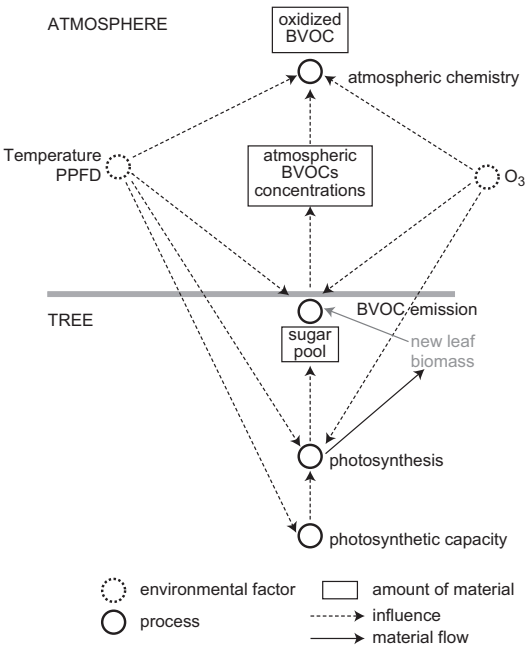

Fig. 1. Conceptual scheme of the factors [temperature, photosynthetically active radiation (PPFD), ozone (O_3)] affecting BVOC emission source physiological state (photosynthesis, photosynthetic capacity), emissions and air concentrations in a boreal forest.

Introduction

Atmospheric concentrations of biogenic volatile organic compounds (BVOCs) are an important parameter in aerosol and climate models (Peñuelas and Staudt 2010). Globally the biosphere is emitting annually over 1150 Tg carbon as reactive volatile compounds, mostly isoprene, monoterpenes and methanol (Guenther *et al*. 1995, Galbally and Kirsten 2002). In the atmosphere, BVOCs participate in several focal processes related to atmospheric chemistry. For example, they take part in aerosol growth processes and regulate the OH radical concentrations in the troposphere and affect the amount of atmospheric ozone and methane, and contribute to the secondary organic aerosol (SOA) growth (Kulmala *et al*. 2004, Di Carlo *et al*. 2004, Noziere and Esteve 2005, Tunved *et al*. 2006).

Estimates of the atmospheric VOC budget are needed for atmospheric chemistry and climate models, but due to the complexity of the involved processes, it seems to be a very difficult task to develop reliable and robust models. Measured BVOC concentrations at the boundary layer vary with time and space by a factor of 100 even within one biome, and are dependent on the properties of the emitted compound as well as on the vegetation surrounding the measurement point. They are affected by e.g. chemical reactions in the canopy space and the boundary layer, transport phenomena and the strength of the biogenic emission source (Forkel *et al*. 2006, Boy *et al*. 2011). The biogenic emission processes act at many different time scales, as they are related to both vegetation dynamics (seasonal time scale) and incident plant physiological activity (daily or hourly time scale) (e.g. Niinemets *et al*. 2010). Therefore, both empirical and process-based models have been developed to describe the biogenic influence on atmospheric composition. The most commonly used one is the semi-empirical Guenther algorithm (Guenther *et al*. 1993, 1995) describing the dependency of isoprene and monoterpene emissions on instantaneous temperature and light. Critics towards this approach has been expressed e.g. by Niinemets *et al*. (2010). Current atmospheric chemistry models get easily heavily parameterized, and therefore their applicability is not as good as it would be desired (*see* Stockwell *et al*. 1997, Forkel *et al*. 2006).

An alternative method of estimating atmospheric BVOC concentrations could be a simplified source-based model. We can assume that atmospheric BVOCs in a rural environment originate mainly from biogenic sources, and that the environmental factors affecting the production intensity and the emission pathway are the same factors that control the atmospheric BVOC forming from the emissions (Peñuelas *et al*. 2001) (Fig. 1). All biogenic VOCs are formed from carbon originating from photosynthetic carbon assimilation, and thus a close link to plant activity can be assumed at least at the seasonal scale. Photosynthetic reactions are strongly temperature-driven. Temperature also affects physical properties of VOCs such as gas vapour pressure and the resistance in the emission pathway in the plant tissues (Niinemets *et al*. 2004). Thus the whole BVOC process and emission chain starting from short term responses of photosynthesis, emission pathway and concentrations in a forest

may follow similar function shapes (Niinemets *et al*. 2004, Laothawornkitkul *et al*. 2009).

To some extent, the same factors controlling the instant (minutes to hours) photosynthetic activity also drive the long-term seasonal photosynthetic capacity. In a boreal forest, the seasonal variation, especially the spring recovery of photosynthetic capacity, has been correlated with temperature of the previous several days (Mäkelä *et al*. 2004). This temperature-based proxy of photosynthetic capacity can be linked to the canopy-layer BVOC concentrations, provided that the main source of BVOCs are photosynthesis-related processes, and that the atmospheric lifetime of the substances is long enough compared with measurement frequency (Lappalainen *et al*. 2009).

The most relevant air molecules affecting the atmospheric lifetimes of the BVOC compounds are ozone, OH and nitrate radicals. The atmospheric lifetimes of the most common BVOC compounds vary from less than an hour to several days (Atkinson and Arey 2003a, 2003b). In a boreal forest, methanol reacts with OH and has a chemical lifetime of a few days. The estimated lifetime of acetone is even longer, 8 days. Daytime concentrations of acetone are reduced by OH and photolysis. Compounds having long lifetimes, such as methanol and acetone, result in higher and more stable background concentrations (Rinne *et al*. 2007). Instead, terpenoids are removed soon after emission, i.e. within few hours. As opposed to substances with longer lifetimes, terpenoids, due to their short atmospheric lifetimes, may be connected to the temperature (Rinne *et al*. 2007).

However, in our earlier analysis, in particular the peak concentrations of all compounds were found to occur mostly simultaneously (Lappalainen *et al*. 2009). This suggests that despite the differences in lifetimes of the compounds due to atmospheric chemistry, variations in concentrations at the canopy scale can be related to the changes in their sources, i.e. emission variation driven by plant activity.

In this study, we tested how well empirical algorithms based on a biologically-relevant temperature proxy could be used to describe the variations in atmospheric daytime concentrations of BVOC compounds in a boreal coniferous forest at a daily and seasonal time scales. Here, we focused on methanol, acetone, acetaldehyde, isoprene and monoterpenes, since their emission rates are high and they seem to be most crucial in terms of their amount in the atmosphere and/or their role in atmospheric chemistry (Kesselmeier and Staudt 1999, Fuentes *et al*. 2000, Atkinson and Arey 2003a, 2003b). Our aims were to test whether the canopy-layer concentrations of BVOCs predicted by air temperature (T) alone could be improved by a model including a parameter describing the seasonally changing photosynthetic capacity (S) of the trees. We also studied whether occasional high BVOC concentrations could be predicted by a trigger-type model that includes environmental stress for vegetation. We tested the model results using BVOC concentrations measured in the open air in the upper layer of the forest canopy, and the concentrations close to the emission source, pine shoot.

Material and methods

VOC and environmental datasets

Concentrations of methanol, acetaldehyde, acetone, isoprene, and monoterpenes were measured at the SMEAR-II station (Station for Measuring Forest Ecosystem–Atmosphere Relations), which is located in a boreal forest in Hyytiälä (61°51´N, 24°17´E, 181 m a.s.l.), southern Finland (*see* Hari and Kulmala 2005). The methanol, acetone, isoprene and monoterpene concentrations [ppbv] (volume mixing rations) were measured at the upper-canopy level (14-m height) using a proton transfer reaction mass spectrometer (PTR-MS, Ionicon GmbH, Austria). Methanol was detected at 33 protonated mass [amu] (M33), acetaldehyde at 45 amu (M45), acetone at 59 amu (M59), isoprene at 69 amu (M69), and monoterpenes at 137 amu (M137) (Taipale *et al*. 2008). The samples were taken every second or third hour and the ambient BVOC concentration was measured by taking 15–25 samples per hour. We used time windows specified for each season representing the time when the sun is high enough to cause atmospheric mixing (Rinne *et al*. 2005): March–May 09:00–17:00, June–

August 07:00–19:00, September 09:00–16:00, December–February 11:00–16:00 (Lappalainen *et al*. 2009, 2010).

The forest around the measurements site is a homogeneous, 16-m tall, Scots pine (*Pinus sylvestris*) stand grown from seeds in 1962. Norway spruce and deciduous tree species are scarce at the observation site (only few percent), but are growing in larger proportions in the vicinity (Ilvesniemi *et al*. 2009). Continuous VOC concentration measurements above the canopy were made between June 2006 and September 2007. The winter observations (December, January, February) were omitted from this analysis. Measurements were continued during 1 June–31 August 2008.

To ensure that the main potential source of transported BVOCs, the Korkeakoski sawmill, would not affect our analysis, the concentrations measured during the SE wind were omitted (*see* also Lappalainen *et al*. 2009).

We also measured the air in the close vicinity of Scots-pine shoots for a shoot-scale model parameterization and to study how well the concentrations measured in the upper layer of the forest canopy were correlated with concentrations inside the canopy. These measurements were carried out between 23 March and 23 May 2007, and between 13 and 26 June 2007. Two chambers were placed near the top of the tree crowns, on one-year-old shoots of two Scots pines. The chambers had been installed in the trees several months before the BVOC measurements started. The measurement setup was similar to that described in Ruuskanen *et al*. (2005) with some exceptions: The chambers were cylindrical with the volume of 3.5 dm^3 each, and the sample air was drawn from each chamber to PTR-MS through a separate Teflon PTFE tube of 50 m length and 4 mm internal diameter. The chambers were normally open and intermittently closed for three minutes, five times every third hour. Hereafter, the shoot-scale concentrations refer to concentration in the open chamber immediately before the chamber closure. For environmental datasets, *see* Hari and Kulmala (2005) and Lappalainen *et al*. (2010).

BVOC daytime concentration models

The fit of the models to daytime BVOC concentrations was tested by using the cross-validation (CV) technique. A joined BVOC dataset from the years 2006–2007 and summer 2008 was used. We used 60% of the data for model fitting (training data) and 40% for testing (test data). Discrepancies between the data and the model results were quantified by the coefficient of determination (r^2) and norm of residuals. The norm of the residuals was calculated as the sum of the squares of the differences between the predicted values and the observed values, i.e. the sum of the squares of the residuals. The random division to training data and testing data was repeated 100 times. The parameter estimation was done by minimizing the norm of residuals. The mean value of the 100 fitted parameter values was set as the best parameter value (Table 1).

The first model was an exponential temperature model (T model) where the daytime median BVOC concentration, y (ppbv), was presented as an exponential function of daytime median air temperature:

$$y = ae^{bT} \quad (1)$$

Table 1. The mean parameter values for the T model ($y = ae^{bT}$), T-S model ($y = ae^{bT} + ce^{fS}$) and Trigger model. Parameter values determined for the upper canopy scale.

Compound	T model		T-S Model				Trigger model	
	a	*b*	*a*	*b*	*c*	*f*	*A*	*B*
Methanol	0.45	0.09	0.53	0.09	–0.02	–0.04	0.28	–0.06
Acetaldehyde	0.14	0.05	0.06	0.09	0.15	–0.08	0.17	–0.10
Acetone	0.44	0.07	0.26	0.09	0.29	–0.02	0.16	–0.10
Isoprene	0.04	0.08	0.01	0.14	0.04	–0.06	–0.12	–0.05
Monoterpene	0.07	0.07	0.04	0.09	0.02	0.10	0.03	–0.14

The exponential relationship fitting and the preliminary testing for a number of compounds were shown by Lappalainen *et al*. (2009, 2010).

In the second model (T-S model), we combined the direct effect of air temperature (T) on atmospheric BVOC concentrations with the longer-term effect of the tree photosynthetic activity on the BVOC biosynthesis. The parameter S describing photosynthetic efficiency of trees was, hence, added to the T model (Eq. 1) in an exponential term e^{fS} (*see* also Mäkelä *et al*. 2004, Lappalainen *et al*. 2010):

$$y = ae^{bT} + ce^{fS} \quad (2)$$

All the parameter values (a, b, c and f) were fitted simultaneously.

The photosynthetic efficiency is associated with the maximum rate of light-saturated carbon fixation in the photosynthesis dark reaction. Mäkelä *et al*. (2004) found a linear relationship between the seasonal course of photosynthetic efficiency and air-temperature history. In a boreal forest, photosynthetic efficiency of trees (S) follows ambient temperature (T, °C) in a delayed manner with the time constant (τ) 200 h (Kolari *et al*. 2007, *see* also Fig. 2):

$$dS/dt = (T - S)/\tau \quad (3)$$

Our third approach in testing was a Trigger model, aimed at improving the performance of the T-S model at times of occasional peaks in VOC concentrations. Here, the new BVOC concentration (q) during high concentration peaks was obtained by multiplying the result of Eq. 2 (y) by a factor whose value was determined by finding the best fit with the dataset of 2006–2007 (Lappalainen *et al*. 2010).

$$q = (1 + A + B)y \quad (4)$$

The parameters A and B refer to the O_3 trigger and days of relatively high PAR, respectively, the multipliers associated with two environmental triggers stimulating an extra-high BVOC concentration. The selection of the triggers was based on literature (Peñuelas and Staudt 2010). Before the trigger testing, we checked that atmospheric boundary layer (ABL) height would not have an effect on the BVOC concentrations and found that atmospheric boundary layer (ABL) height (day time mean, median and maximum values) did not correlate with BVOCs. The ABL heights for the study period were based on calculations done using the meteorological boundary layer model, the submodel of SOSA (the model to simulate the concentration of organic vapours and sulphuric acid) (Boy *et al*. 2011).

Ozone was chosen because the value of 40 ppbv has been considered to be a threshold concentration for its deleterious long-term effects on vegetation (e.g. Fuhrer *et al*. 1997, Karlsson *et al*. 2004). High PAR could accelerate photosynthesis and production of BVOCs or their release from storage. This was postulated to be true especially for monoterpenes. PAR and temperature are the most commonly used parameters in the isoprene emission models (Guenther *et al*. 1995, Arneth *et al*. 2007, Grote and Niinemets 2008, Niinemets *et al*. 2010). Also for ox-VOCs (short-chained oxygenated compounds, here methanol, acetone, acetaldehyde) light-dependent emissions have been reported from orange (*Citrus sinensis*) foliage (Staudt *et al*. 2000). However, high light availability, especially during the dormancy period, is involved in severe stress to photosynthetic light capturing pigments, and may lead to photoinhibition and irreversible damage (Huner *et al*. 1998), and also potentially result in increased VOC emissions due to this damage. Since high-incident PAR values could be masked by seasonally changing available irradiation, we hypothesized that such high emissions leading to high concentrations of BVOCs could occur when the irradiation level was high as compared with potentially available seasonal irradiation. Available irradiation was estimated from the solar elevation (radians) multiplied by the solar constant (1360 W m^{-2}). A relative PAR index was calculated by dividing the daytime mean PAR by the potential available irradiation.

We studied the effect of a single trigger and the combinations of chosen triggers in improving the T-S model for days with the high concentration peaks. For other days, we ran the T-S model alone. We determined the A and B parameters first independently keeping one of them

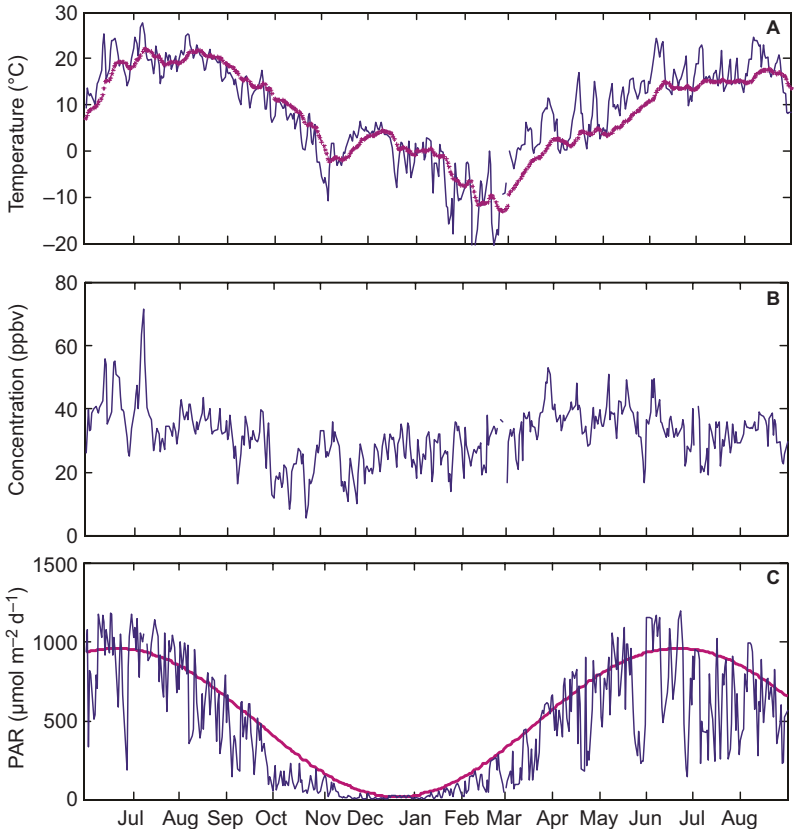

Fig. 2. (**A**) Mean daytime temperature (blue line) and state of development (*S*) (red crosses), (**B**) mean daytime ozone concentration, and (**C**) mean daytime PAR (photosynthetically active radiation, 400–700 nm; blue line) and seasonal average (red line) during 2006–2007 (figure originally published in Lappalainen *et al.* 2010).

at zero. Then we tested for the combined effect of the selected triggers and different threshold values by minimizing the residual sum of squares (RSS). This trigger model resembles a "broken-stick" model, in which standard nonlinear models are fitted, but the model has certain breakpoints (Toms and Lesperance 2003).

Results

Modelling daytime concentrations in a upper canopy scale

We examined the histograms of the r^2 values and norm of residuals of the training data to estimate the best parameter values for the studied models (Fig. 3). The model fit to randomly-selected training and test data was repeated 100 times. The histograms of the r^2 values and norm of residuals showed that majority of the iterated parameter values concentrated around their means for all studied compounds except for acetaldehyde. In case of acetaldehyde, it seems that one exceptionally high concentration had a major impact on the parameter estimation and model fitting. This high concentration can either be a measurement error or a real observation. The more likely option is that it reflects the actual high concentrations triggered by environmental factors related to the drought period in the summer of 2006 (*see* also Fig. 4 and Lappalainen *et al*. 2009). The distributions of the r^2 values and norm of residuals of the training data indicated that that we could consider the mean value of a model parameter (n = 100) as the final parametrization and as a starting point of a modelling approach. The mean values of all parameter values are presented in Table 1.

The T model fitted to the training data described 23%–64% of the variation in concentrations of all measured compounds (Fig. 3 and Table 2). The T model worked especially well for early spring (March–April 2007). Although

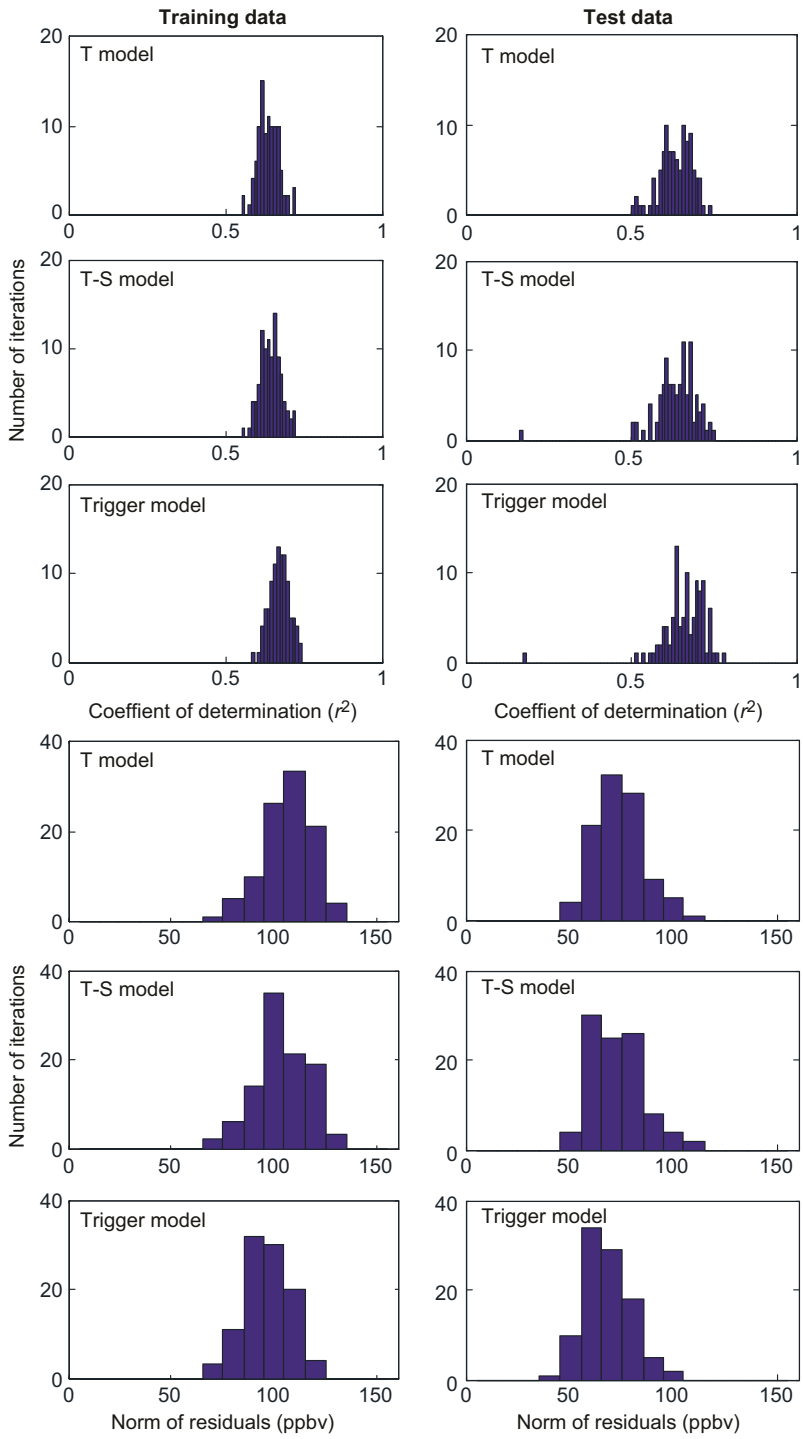

Fig. 3. Distributions of r^2 (three top rows) and norm of residuals (three bottom rows) for methanol produced by the T, T-S and Trigger models. The model runs were repeated 100 times.

in general the T model was able to describe concentration variation well, it underestimated the high concentrations of acetaldehyde and acetone in the end of March. Another period for which the model did not reproduce the concentrations well — especially for acetaldehyde, isoprene and monoterpenes — was the summer drought in July and August 2006. At that time,

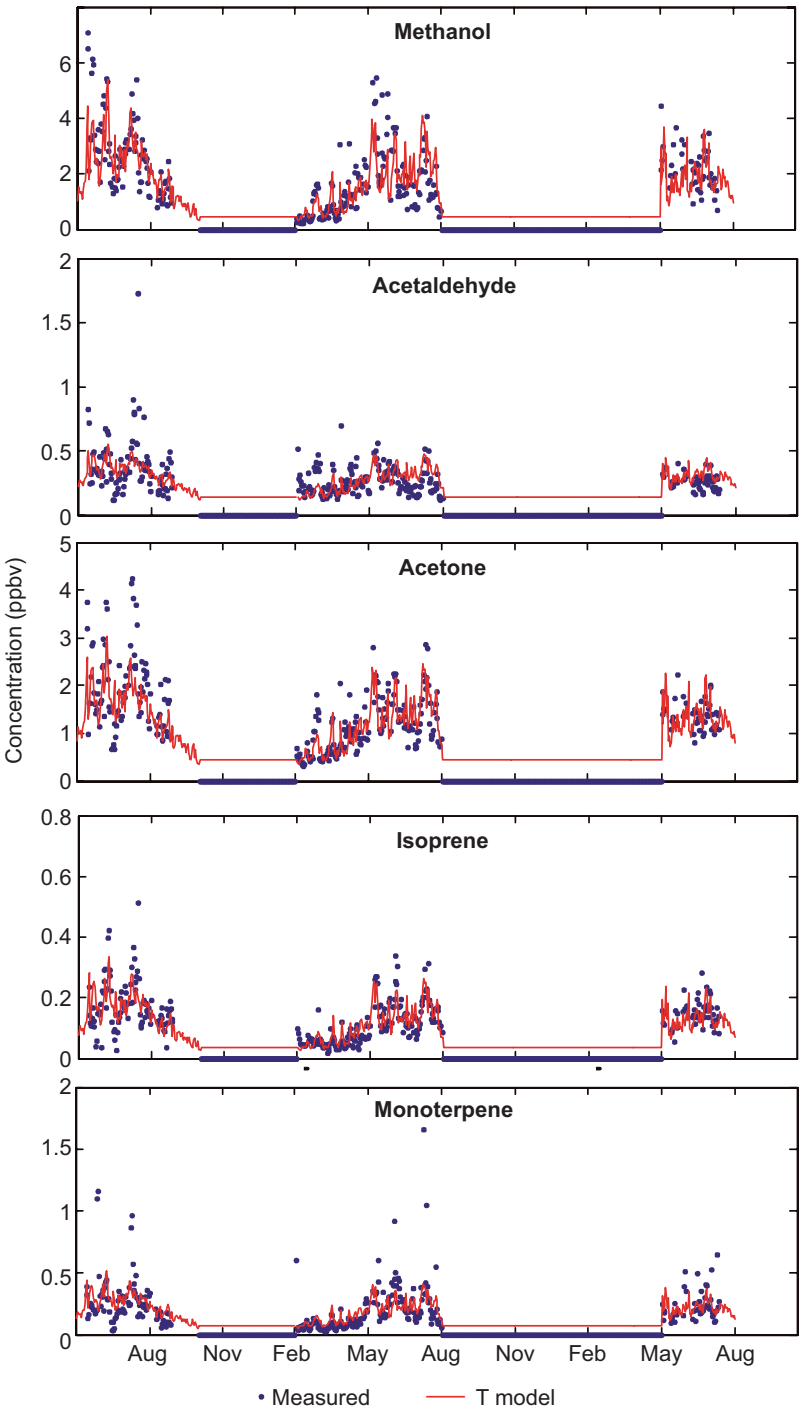

Fig. 4. The measured and modelled daytime BVOC concentrations at the 14-m height between 1 June 2006 and 31 Aug. 2008 at the SMEAR-II station.

the BVOC concentrations also varied more than during other times, and high peak concentrations were frequently observed (Fig. 3). In general, the T model underestimated the highest mesured values of all studied compounds.

By comparing the r^2 values of the training data with those of the test data it was shown that the T model captured the general variation in test (27%–64%) as well as during the training. The norm of residual cannot be compared because

the training and testing data numbers were not equal (training data 60%, test data 40% of observations).

In order to include the effect of changing plant activity, we added the photosynthetic efficiency of trees (S) to the T model (*see* Eq. 2 and section 'BVOC daytime concentration models'). As compared with the T model, the T-S model explained slightly more of the variation (29%–65%) in the training data for all compounds. However, the improvement was not statistically significant (Table 2). The r^2 values of the T-S model for the test data remained at the same level as those of the T model (Table 1).

Since S describes a seasonal-scale variation of the photosynthesis (a long-term effect), its influence on the daily-scale BVOC emissions (a short-term effect), and consequently on the emitted concentrations, seems to be overridden by some stronger, instant factors. To better capture instant short-term (daily) variations in BVOC concentrations, we developed a Trigger model. It was postulated that relatively high PAR and/or O_3 could stimulate high BVOC concentrations. We tested these two factors separately and simultaneously. The PAR trigger alone did not improve our predictions, not even when days of high relative PAR were taken into account. Also the ozone trigger improved the predictions only very little (results not shown here) but combining O_3 together with PAR improved the Trigger model fit more than the trigger effect of either factor alone. When compared with that of the T and T-S models, the explanation power of the Trigger model with the training data was the highest for all studied compounds (32%–67%), and the norm of residuals was the lowest as compared with that of the T and T-S models (Table 2). For the test data, however, the Trigger model fit was only slightly better as compared with the fits of the T and T-S models for all studied compounds (Table 2).

For the summer of 2006, the measured methanol, acetaldehyde and acetone concentrations were clearly higher than the values produced by the T model (*see* Fig. 4). Also some high concentrations of monoterpene and isoprene were registered. The differences between the T and T-S models as compared with the Trigger model grew larger with groving compound concentrations (*see* Fig. 5).

Concentration variation near the top of the tree crowns

One of the key questions in this study was, how well the atmospheric concentrations detected at the upper canopy represented the BVOCs freshly emitted from the upper shoots of a pine tree. The atmospheric concentrations at the 14-m height (canopy scale) were compared with those from the open-chamber measurements of pine shoots near the top of the tree crowns (shoot scale). The shoot- and canopy-scale concentrations were highly correlated (r = 0.82–0.95; Table 3) for all studied compounds except for monoterpenes (r = 0.19) (Fig. 6 and Table 4), but only methanol and acetone concentrations were similar in both measurements (slope close to 1 in Fig. 6). For acetaldehyde and isoprene, the shoot-scale concentrations exceeded the canopy-scale ones by approximately a factor of 2, and for monoterpenes, the canopy-scale concentrations were two orders of magnitude lower than the shoot-scale concentrations. Also the correlation was weakest for monoterpenes. The measured monoterpene mass in PTR-MS (M137) includes several compounds with the same m/z ratio, which makes

Table 2. Average values (100 rounds) of norm of residuals and r^2 of the models fitted to the upper-canopy data: training (= 60% of the data) and test (= 40% of the data).

Model/ Compound	Residuals		r^2	
	Training	Test	Training	Test
T model				
Methanol	106.28	73.31	0.64	0.64
Acetaldehyde	3.49	2.07	0.26	0.28
Acetone	33.92	23.22	0.63	0.63
Isoprene	0.38	0.26	0.63	0.62
Monoterpene	4.48	3.12	0.23	0.27
T-S model				
Methanol	104.06	73.81	0.65	0.64
Acetaldehyde	3.13	1.85	0.34	0.36
Acetone	33.43	23.20	0.64	0.63
Isoprene	0.36	0.25	0.64	0.63
Monoterpene	4.34	3.12	0.29	0.27
Trigger model				
Methanol	96.23	68.85	0.67	0.66
Acetaldehyde	2.99	1.79	0.38	0.38
Acetone	0.63	21.73	0.67	0.65
Isoprene	0.35	0.26	0.66	0.63
Monoterpene	4.23	3.12	0.32	0.27

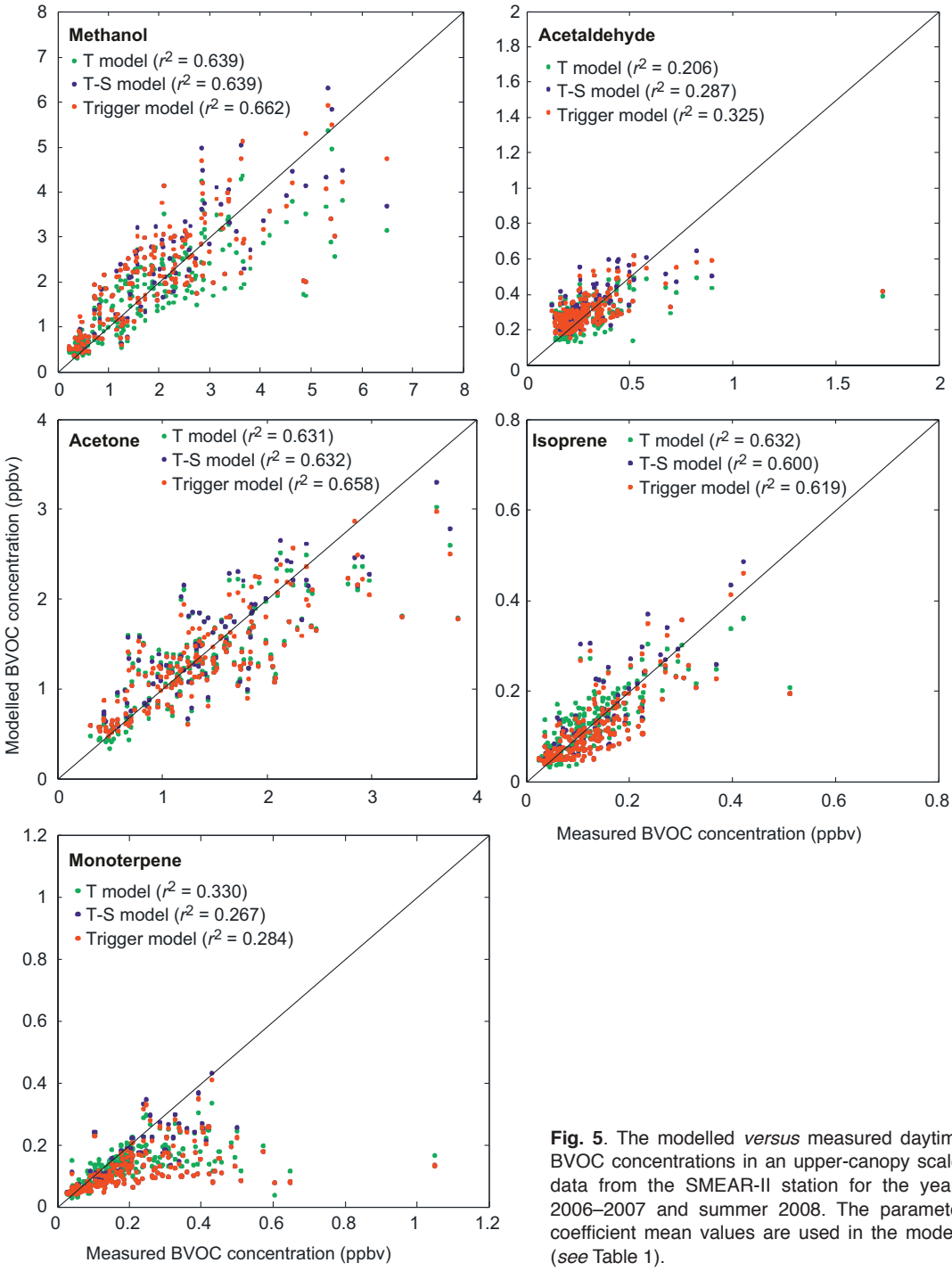

Fig. 5. The modelled *versus* measured daytime BVOC concentrations in an upper-canopy scale, data from the SMEAR-II station for the years 2006–2007 and summer 2008. The parameter coefficient mean values are used in the models (*see* Table 1).

the use of these measurements very difficult for simplified models in atmospheric chemistry. Apart from that, the high correlations of the other studied compounds suggest that the upper-canopy measurements follow closely the emissions, although these measurements represent different footprint. The shoot-scale concentrations were 17%–58% higher for the studied compounds,

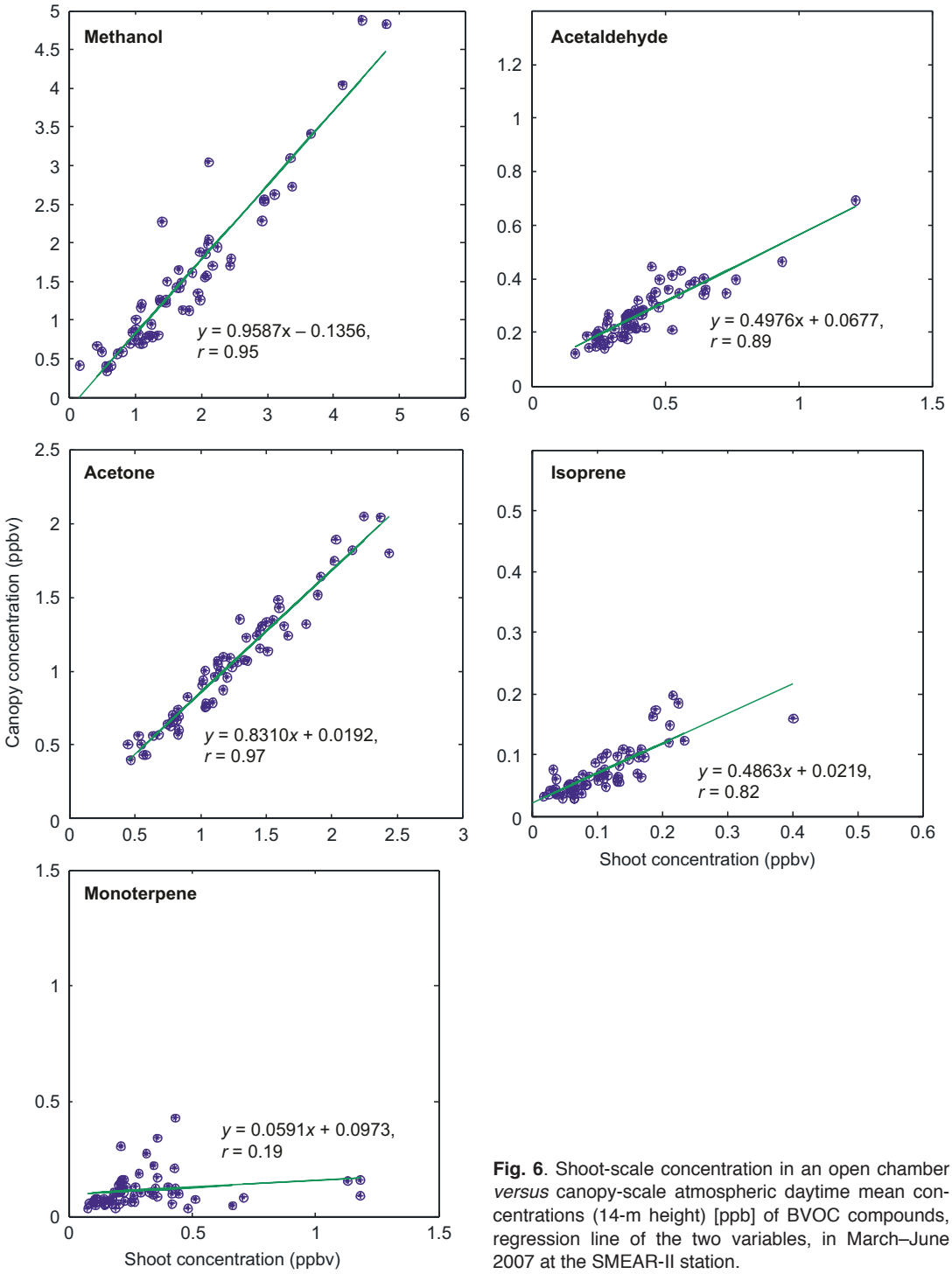

Fig. 6. Shoot-scale concentration in an open chamber *versus* canopy-scale atmospheric daytime mean concentrations (14-m height) [ppb] of BVOC compounds, regression line of the two variables, in March–June 2007 at the SMEAR-II station.

indicating a compound loss (chemical reactions or deposition) before the canopy-scale measurement (*see* Table 4). The compound loss seemed to be more distinct in early spring (April and March), and was especially evident for acetaldehyde and monoterpene (Fig. 7).

Table 3. Correlation coefficients (r) between the measured concentrations and the shoot-scale data for March–June 2007 (n = 122).

	Acetaldehyde	Acetone	Isoprene	Monoterpene
Methanol	0.34	0.82	0.64	0.08
Acetaldehyde	–	0.76	0.73	0.37
Acetone	–	–	0.84	0.20
Isoprene	–	–	–	0.28

Discussion

Above- *versus* inside-canopy concentrations

In this study, we analyzed the daytime canopy-level methanol, acetaldehyde, acetone, isoprene and monoterpene concentrations with a simple, source-based approach, assuming they have mainly biogenic sources. This was shown to be a valid approach for compounds that are not very reactive and thus will not be destroyed between the source and the measurement point, but problems arise with compounds with high reactivity with O_3 or OH radicals. Our earlier finding that the daytime canopy-level concentrations were highly intercorrelated (*see* Lappalainen *et al*. 2009) was taken to indicate a similar regulating environmental factors among the biogenic emission processes of these compounds (Schade and Goldstein 2006). In-canopy concentrations are highest during nighttime due to slow mixing, even though the emission rates of most compounds are much lower in the absence of light and at low nighttime temperatures (Rinne *et al*. 2005).

For the purposes of regional air quality and climate models, an escape efficiency (the ratio of the mass flux out of the canopy to the mass flux emitted within the canopy) has been developed in order to account for the canopy-scale photochemical loss and transport of compounds to the boundary layer (Stroud *et al*. 2005). The combination of a strong emission profile and stagnant conditions caused by forest canopy, results in large BVOC mixing ratios in the canopy. In turn, the rates of gas-phase photochemical reactions between BVOCs and radicals and oxidants in the canopy layer depend on mixing ratios of oxidants and BVOCs, and environmental conditions. For isoprene and monoterpenes the escape efficiency in an evergreen forest was 0.9 and 0.93, implying that close-to-canopy chemical reactions played only a small role in isoprene and monoterpene mixing ratios at canopy top level (Stroud *et al*. 2005). In our study, the canopy-scale concentrations were linked to the shoot-scale concentrations especially for acetone and methanol, and the concentration fluctuations were similar at both shoot and canopy scales. This is rather expected since the oxygen-containing biogenic volatiles have low reactivities and thus are not prone to undergo chemical destruction in such a limited space between the emission source and the measurement site on top of the canopy. However, for other compounds the in-canopy chemistry may be important at this site, which is reflected in their lower escape-efficiency values (*see* Fig. 6). The mean concentrations of acetaldehyde and monoterpenes measured at these two locations were almost identical in summer, but were higher at the shoot scale in spring, when rapid changes due to shoot elongation influence the source strength.

Table 4. Correlations between daytime mean concentrations at the shoot (S) and canopy scales (F), and mean concentrations for April–June 2007.

Compound	r	Mean (F) (ppb)	Mean (S) (ppb)
Methanol	0.95	1.46	1.76
Acetaldehyde	0.89	0.27	0.42
Acetone	0.97	0.99	1.23
Isoprene	0.82	0.08	0.11
Monoterpene	0.19	0.13	0.31

T model

One way of overcoming the complexity in VOC

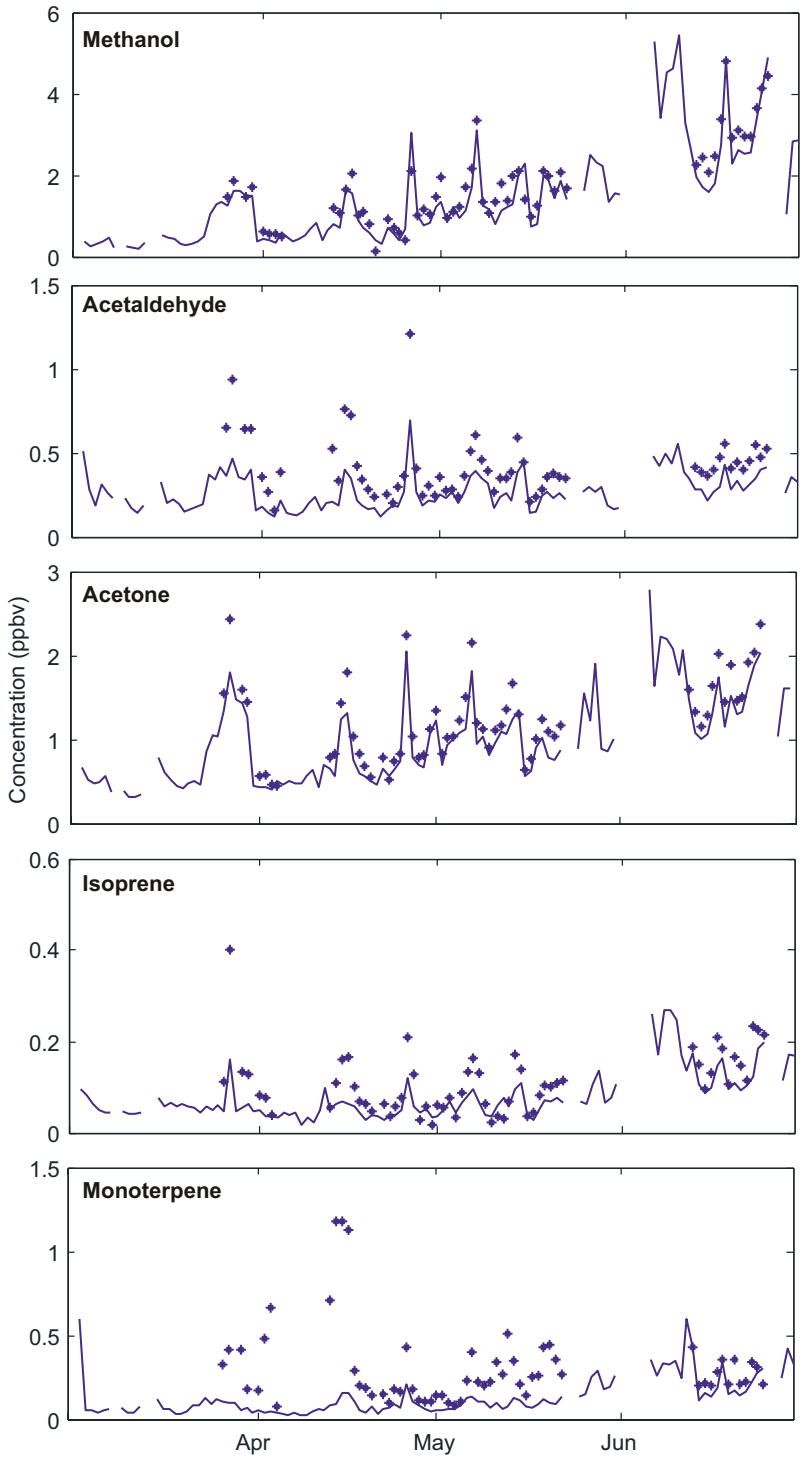

Fig. 7. Shoot (crosses) and canopy (lines) scale daytime mean concentrations [ppb] of BVOC compounds in March–June 2007 at the SMEAR-II station.

concentration modelling is to try to simplify the response functions so that they take into account most of the processes in such a manner that the residual variation is minimized. Temperature is clearly one of the most important regulating factors for both biosynthesis of VOCs and their

diffusion from the source to the atmosphere (e.g. Guenther *et al*. 1993, Niinemets and Reichstein 2002), and thus it can be used as a simple proxy for describing leaf-scale processes leading to emissions. In line with the earlier studies (Schade and Goldstein 2006), our T-model approach showed that the canopy-level air concentrations of methanol, acetone and acetaldehyde can rather reliably be reproduced using a simple exponential relationship between temperature and concentrations, whereas the acetaldehyde and monoterpene concentrations proved to be more difficult to predict with a simple temperature function. The reasons for this can lie in the different source dynamics of isoprenoids, for example in large storage pools (monoterpenes) or in the strong linkage to incident light levels (isoprene). Another reason could be related to the fact that the monoterpene (M137) is covering several compounds which makes the mass 137 too complex to be described by simplified models (Noe *et al*. 2006). High acetaldehyde concentrations measured just after snow melt, in March 2007, and the end of the growing season, in September 2006, may be associated with emissions from soil processes or litter fall (Bäck *et al*. 2010, Aaltonen *et al*. 2011).

T-S Model

The explanation level of the model improved slightly by adding a biological factor *S*, based on the temperature dependent recovery of photosynthesis, which was considered to represent the seasonal capacity of a tree to produce and emit volatiles. This T-S model predicted the general level of daily and seasonal variation of the daytime concentrations somewhat better than the T model for all compounds. This is in line with the result of Gray *et al*. (2006) who showed that the methylbutenol (MBO) basal emission rate was regulated by the temperature history and that the emission rate was not constant during the annual cycle. This model, however, could not explain the high concentration peaks measured especially during the summer of 2006, and it also failed to explain the difference in the background concentration levels among the summers of 2006–2007 and 2008, which indicates that the difference was not due to different inherent emission capacity among the years. During the drought in 2006, photosynthetic production decreased dramatically which may have also reduced BVOC synthesis. In such conditions *S* did not work as a proxy for photosynthetic capacity.

The T or T-S model predicted the general level of the daily and seasonal variation of the canopy-level concentrations quite well, but they were unable to capture the range, i.e. the very high or very low concentrations. In our upper-canopy scale dataset, high concentration peaks were most common in the late summer of 2006 and during the late spring of 2007. The model residuals were high especially during the drought in the summer of 2006 and in the early spring and summer of 2007. Unfortunately, we did not have shoot-scale emission measurements during the drought period in the summer of 2006, and therefore cannot analyze the shoot-level responses to this event more carefully.

Trigger model

In order to analyze potential other factors triggering high emissions and leading to concentration peaks, we selected two factors capable of inducing emission peaks from the pine shoots. The reason for selecting the relative PAR as a trigger was twofold. First, high light would stimulate incident BVOC emissions by enhancing photosynthetic electron transport rate, and thus amplify the source for VOC biosynthesis. Since isoprenoids are produced in a common pathway with photosynthetic pigments, their emission capacity is linked to the photosynthetic pigment metabolism and thus is responsive to changes in irradiation levels (Owen and Peñuelas 2005, Porcar-Castell *et al*. 2008, Porcar-Castell *et al*. 2009). Second, high irradiation is potentially harmful to vegetation, in particular on occasions when carbohydrate sink strength does not match the available energy gain (e.g. Demmig-Adams and Adams 1996), and it can potentially induce VOC production due to strong stress and photoinhibition. Therefore, high relative PAR values indicate potentially harmful levels of irradiation, especially in springtime. However, the result was negative: the effect of the PAR trigger alone

was clearly weaker than that of the O_3 trigger. The effect of PAR together with O_3 was negative for all studied compounds (coefficient $B < 0$). The intercorrelation between PAR and O_3 could explain why the Trigger model performed best when both factors were taken into account.

Ozone is a potent plant stress-agent, which has been shown to reduce photosynthesis, influence carbon allocation and induce production of detoxifying compounds (Kangasjärvi *et al*. 1994). One potential group of protective agents for the plant is the reactive compounds, such as isoprenoids, capable of destroying O_3 before it inflicts damage to tissues. Beech and poplar trees exposed to elevated O_3 emitted isoprene, acetaldehyde and acetone at enhanced rates (Cojocariu *et al*. 2005, Fares *et al*. 2006), suggesting that a larger proportion of assimilates is used for VOC production under ozone stress. An exposure index (AOT 40) based on accumulated exposure over a threshold 40 ppb has been created to describe the plant responses to chronic ozone stress (e.g. Lee *et al*. 1998). Based on our dataset and the subsequent model analysis, exposure over the 40 ppb threshold seems to correlate with high emissions of methanol, acetone and acetaldehyde, and seems to corroborate the earlier findings from experimental studies. As a whole, the effect of ozone was positive for all studied compounds (coefficient $A > 0$), except isoprene. However, isoprene and monoterpene peaks were poorly explained by high ozone concentrations. This is in line with the result by Peñuelas *et al*. (1999), who also did not find any significant effect of ozone on VOCs and terpene emission by *Pinus halepensis*. With our model approach, we cannot analyze the role of chemical reactions in the air, which can influence the isoprene and monoterpene concentrations (Atkinson and Arey 2003).

The remaining discrepancy between the models and observed BVOC concentrations might be explained by other sources besides the shoot emissions for the measured VOCs. Although the agreement between the shoot-scale and canopy-scale concentrations was good, it is still very likely that also other sources affect the measured canopy scale concentrations. The unexplained variation in concentrations may also be related to the dynamically changing physiological and phenological status of the trees. In principle, the parameter S, describing the seasonally varying photosynthetic capacity should take the physiological status into account. However, it does not account for the changes in leaf or needle area. The growing leaf biomass influences the amount of synthesized BVOCs, and bud burst may also provoke emission peaks especially for methanol in spring (Schade *et al*. 2006). This was noticed also earlier, and a fixed temperature sum was used to predict the onset of isoprene and monoterpene emissions from *Betula pendula* (Hakola *et al*. 2000).

In addition to the challenge of modelling sporadic BVOC concentration peaks, the whole concentration dynamics may change under stress conditions. We were not able to capture the high concentration variation by the Trigger model during the drought-stress period in the summer of 2006. The measured low monoterpene concentrations detected in July 2006 were in line with earlier result by Lavoir *et al*. (2009), who showed that persistent drought significantly reduced the monoterpene fluxes into the atmosphere due to a sustained inhibition of photosynthetic carbon assimilation in *Quercus ilex* forest. In our case, in addition to drought stress, fast changes could have been even more triggered by simultaneous ozone stress (*see* Staudt *et al*. 2008, Niinemets 2009).

Furthermore high atmospheric concentration variation could not only be linked to atmospheric chemistry but also originate from the biogenic source, from the storage pools. For example monoterpenes are emitted from the needle resin canals in coniferous species (Persson *et al*. 1996, Peñuelas *et al*. 2001). Similarly to non-stored emissions, emissions from storage could be triggered by short-term changes in environmental drivers such as drought and ozone (Niinemets *et al*. 2010). The rapid and transient fluctuations in measured VOC data that occur typically in both emission (Grote and Niinemets 2008) and concentration measurements (Lappalainen *et al*. 2009) are poorly explained by the models (Rinne *et al*. 2009).

Conclusions

Our results show that a temperature model provides a relevant backbone for further devel-

opment of a BVOC concentration model for boreal forests. Seasonal variation in photosynthetic capacity (*S*) improved the model prediction. However, in order to capture large variations in concentrations, a trigger effect needs to be incorporated into the model in a more detailed manner. In our case, we tested two triggers: relatively high PAR and ozone. Although we attained better fit for the training data, we were not able to improve the model predictability with the test data. Detecting the trigger effect from the air concentrations is challenging and separating the fundamental stress factor is difficult due to various relations between environmental factors and BVOC concentrations and inter-correlation between factors. Despite these shortcomings, a temperature-based model explained the BVOC concentrations relatively well for methanol, acetone and isoprene. In order to improve the trigger aspect in the model, specific stress-induced concentrations events should be analysed in more detail, especially for drought episodes. Furthermore, we need to take into account and analyze delayed-stress effects. In this study, we used the average daytime values in the analysis. Finding correct time intervals for each process may also be a crucial task in future studies.

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