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Modelling day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy

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Abstract

Three different models for day-time atmospheric methanol, acetaldehyde, acetone, isoprene and monoterpene concentrations were developed using measurements above a boreal forest stand in Southern Finland in 2006–2007 and tested against an independent dataset from the same forest measured in summer 2008. The models were based on the exponential relationship between air temperature and the concentration of biogenic volatile organic compounds (BVOC). Our first model for BVOC concentrations was a simple exponential function of air temperature (T-model). The T-model could explain 27–66% of the variation of all the compounds, but it failed to catch the extremely high concentration peaks observed in summer. To improve the temperature model we developed two other models. The second model, a Temperature-State of Development- model (T-S model), included two explaining variables: air temperature and the seasonal photosynthetic efficiency. This model performed slightly better compared to the T-model for both datasets and increased the fraction of variation explained to 29–69%, but it still could not explain the high concentration peaks. To explain those we modified the T-S model to include environmental triggers that could increase the concentrations momentarily. The triggers that improved the model most were high photosynthetically active photon flux density (PPDF) compared to the seasonally available radiation and high ozone concentration. The Trigger model described the peak concentrations somewhat better than T or T-S model, thus the level of explanation was improved and was 30–71%. This study shows the importance to include seasonal variations in photosynthetic efficiency when modeling BVOC concentrations and presents the idea of a trigger model for explaining high peak concentrations of BVOCs. Our study suggests that when developing a trigger type modelfurther the model and the triggers should be more compounds-specific.

1 Introduction

Biogenic volatile organic compounds (BVOCs) are an important part of aerosol and climate research. The number of BVOC compounds emitted by plants is diverse. However, the group consisting of methanol, acetone, acetaldehyde, isoprene and monoterpenes seems to be most crucial in terms of their amount in the atmosphere and/or their role in atmospheric chemistry (Atkinson and Arey, 2003; Kesselmeier and Staudt, 1999; Fuentes et al., 2000). In the atmosphere BVOCs participate in several focal processes related to atmospheric chemistry. They affect the amount of atmospheric ozone and methane, contribute to the secondary organic aerosol (SOA) growth (Tunved et al., 2006; Kulmala et al., 2004), and take part in aerosol growth processes by affecting the light absorption properties of sulfate aerosols (Noziere and Esteve, 2005). They also participate the regulation of OH radical concentrations in the troposphere (Di Carlo et al., 2004). Therefore, integrated studies of measurements and modelling of atmospheric BVOC concentrations and BVOC emissions in different temporal scales are an important part of our attempts to understand biosphere-atmosphere interactions and atmospheric chemistry in the lower atmosphere (Rinne et al., 2009).

Modelling of atmospheric BVOCs is currently based on emission studies in which data is usually obtained by chamber measurements or other enclosure techniques (Guenther et al., 2006). The enclosure techniques, however, often have technical difficulties and shoot measurements need to be upscaled in order to represent a forest or ecosystem scale BVOC emissions inventory. A number of compound specific emission algorithms for isoprenoids have been developed and applied to many ecosystems during recent years (Tingey et al., 1980; Guenther et al.,1993; Zimmer et al., 2003; Tarvainen et al., 2005). The uncertainties related to oxygenated VOCs are still very high, and thus the algorithms for other volatile compounds are poorly available (Schnitzler et al., 2002).

As a whole, atmospheric BVOC emissions and concentrations are affected by a great and complex number of controlling factors, which makes modeling them challenging (Penuelas and Llusia, 2001). Temperature- and light-based functions can describe BVOC emissions in a scale of minutes to days relatively well. Guenther algorithms (after Guenther et al., 1993, 1995, 1997, 2000) have been proved to be useful tools for estimating monoterpene and isoprene emissions. However, fast changes in BVOC observations, especially emissions from monoterpene pools, resulting in unexpectedly high concentrations, occur typically in both BVOC emission (Grote and Niinemets, 2008) and concentration data (Lappalainen et al., 2009) and these are poorly explained by the models (Rinne et al., 2009).

In BVOC emission models a constant parameter, the “basal emission rate”, typically represents the inherent capacity of a plant to produce a particular VOC. Gray et al. (2006) showed, however, that the temperature history regulates for example the methylbutenol (MBO) basal emission rate, and that the rate is not constant during the annual cycle. Therefore, the quantity of BVOC emissions seems to depend on the instant response of trees to the environmental conditions, but the level of emissions is constrained by the physiological capacity, here called “seasonal effect” (see Monson et al., 1995). The analogous type of connection between biological activity and temperature has been described between seasonal capacity of photosynthesis and a temperature history. In a boreal forest, photosynthetic efficiency or “state of development” is strongly correlated with the temperature history with a time constant of 200 h (Mäkelä et al., 2004). Furthermore, the seasonal variation of biogenic volatile organic compounds concentrations seems to co-vary with the seasonal photosynthetic capacity (Lappalainen et al., 2009; Kolari et al., 2007).

In principle the same environmental factors, temperature and light, could control both the instant (minutes to hours) and long term emissions (days to months) via affecting photosynthetic reactions both in short and long time scale. Photosynthetic reactions are the main biological processes synthesizing most of the precursors of isoprenoid compounds (Laothawornkitkul et al., 2009) and temperature also affects the physical properties of BVOC (monoterpenes) such as gas vapour pressure and the resistance in the emission pathway in the tree tissues (Staudt and Bertin, 1998). In a longer time scale, BVOC emissions are also related to seasonal variation of the same environmental factors and their longer-term effect on biological processes. In coniferous species the BVOC emissions may also include emissions from the storage pools such as monoterpenes from e.g. the needle resin canals (Persson et al., 1996; Penuelas and Llusia, 2001). Similarly to non-stored emissions, emissions from storage could be triggered by fast changes in environmental drivers. Although cuvette measurements are prone to measurement errors, the abundance of high emission peaks indicates that a real biological response, triggered by environmental conditions, is behind them. The high instantaneous peak concentrations (Lappalainen et al., 2009) could be related to a real biological response triggered by either short time-scale or seasonal changes in the environmental conditions such as bud and leaf development, flowering, fruiting or senescence (Penuelas and Llusia, 2001; Llusia and Penuelas, 2000; Tingley et al., 1991; Penuelas and Staudt, 2010).

At the moment, measurements of atmospheric BVOC concentrations made by proton transfer reaction mass spectrometry offer the longest datasets of BVOCs and the only data available for studying seasonal variation in BVOCs. The measurement setup can be installed directly to represent the forest scale concentrations (Lappalainen et al., 2009; Ruuskanen et al., 2009, Taipale et al., 2008) but the ambient BVOC concentrations above a forest present a situation where the emitted BVOCs of local biota are affected by atmospheric chemistry (Fig. 1). As long as atmospheric mixing is high (measurements done at the top canopy level, Rinne et al., 2009) and anthropogenic sources can be excluded, understanding the behavior of day-time BVOC concentrations is based on the understanding of the BVOC emission biology.

In this study we modelled daytime BVOC concentrations in a seasonal time scale using three different approaches. Our aims were to test whether: 1) atmospheric concentrations of BVOCs can be modelled using air temperature (T), 2) adding a parameter describing the seasonality changing emission capacity of the canopy would improve the T-model and 3) occasional high BVOC concentrations could be explained either by direct environmental triggers or environmental triggers changing the internal response of the plant.

The atmospheric lifetime of the most common BVOC compounds varies from hours to several days (Atkinson and Arey, 2003). In a boreal forest, methanol has a chemical lifetime of a few days during its daytime reaction with OH. Acetone is slowly removed by OH and photolysis during days and has an estimated lifetime of 8 days. The long lifetimes of methanol and acetone result in higher background concentrations whereas terpenoids are removed a few hours after emission (Rinne et al., 2007). Despite the differences in the atmospheric lifetimes, the daytime atmospheric concentrations of BVOC compounds are highly correlated with each other (Lappalainen et al., 2009). The intercorrelation is strong even though the lifetimes and biological processes synthesizing the compounds are not connected. In particular, the peak concentrations occur mostly simultaneously (Lappalainen et al., 2009). This convergent behaviour of these compounds suggests that a Guenther-type emission algorithm approach could also be applied to concentrations modelling if the air concentration peaks triggered by fast changes in environmental factors are also included in the model (see Niinemets, 2009).

2 Material and methods

2.1 BVOC datasets

The concentrations of methanol (detected at 33 amu, M33), acetaldehyde (M45), acetone (M59), isoprene and methylbutenol (M69), and monoterpenes (M137) 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 (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). The forest around the measurements site is a homogeneous, currently 16 m tall, Scots pine (*Pinus sylvestris* L.) stand originally planted from seed in 1962. Deciduous tree species are represented in minority, only 1% at the observation site but are growing in larger proportions in the vicinity (Ilvesniemi and Liu, 2001). Continuous measurements were made between June 2006 and September 2007(Ruuskanen et al., 2009). The winter month observations (December, January, February) were omitted in the analysis. Measurements were continued during period of 1 June–31 August 2008.

To make the dataset representative of maximum emissions and to exclude possible night time deposition of BVOCs on the foliage, we used day-time medians of the BVOC concentrations. The day time windows specified for each season represented the time when the sun is high enough to cause atmospheric mixing (Lappalainen et al., 2009). To ensure that the main potential source of transported BVOCs, the Korkeakoski the sawmill, would not affect our analysis, concentrations measured during the South-East wind were omitted.

2.2 Environmental factors datasets

Meteorological data was obtained from standard half-hourly micrometeorological measurements at the SMEAR-II station. Air temperature was measured using a ventilated and shielded Pt-100 sensor at 8.4 m height inside the canopy. Photosynthetically active photon flux density (PPFD, 400–700 nm) was detected by a quantum sensor (LI-190SZ quantum sensor, LiCor, Lincoln, NE, USA) above the canopy. The ozone concentrations was measured with one ultraviolet light absorption analyser (TEI 49, Thermo Environmental, Franklin, MA, USA). A more detailed description of the environmental measurements can be obtained from Hari and Kulmala (2005).

2.3 BVOC day-time concentration models

We tested three different approaches to model daily day-time BVOC concentrations. For each model and compound we first used the data set of 2006–2007 to determine the model parameters and then tested how well the model performed to the independent dataset of summer 2008. The parameters were fitted by minimizing the sum of residuals squared and the model performance was evaluated using the coefficient of determination (R^2).

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

$$y = ae^{bT} \tag{1}$$

Here a and b are the parameters fitted using the 2006–2007 data set. The model was recently presented by Lappalainen et al. (2009).

The second model (T-S-model) aimed at improving the performance of the T-model by including the seasonal variation in the photosynthetic efficiency of trees represented by the state-of development parameter, S, (Mäkelä et al., 2004) (Fig. 2). Here we follow the approach of Gray et al. (2006), where the basal emission rate depends on the temperature history. In this model the temperature part was identical to the temperature model (Eq. 1) and the state of development (S) was included in the model as an additional exponential term, $ce^{(fS)}$.

$$y = ae^{bT} + ce^{fS} \tag{2}$$

Model coefficients a, b, c and f were determined simultaneously.

Parameter S, state of development, formulated by Mäkelä et al. (2004), follows ambient temperature (T, °C) in a delayed manner with the time constant (tau) 200 h in a boreal forest (Kolari et al., 2007, see also Fig. 2) as:

$$dS/dt = (T - S)/\tau \tag{3}$$

The Eq. (2) performed best of all two-variable models we tested. We tested a standard stepwise linear regression for any two factors (air temperature (T)+photosynthetic active light (PAR) or state development (S) or photosynthesis (GPP), soil temperature (Tsoil), total ecosystem respiration (TER)) and a linear function of these added to the exponential temperature function but none of these models performed better than the T-model alone (see also Lappalainen et al., 2009).

The third model was a trigger model, which responded to relatively high ozone and or PAR and aimed at improving the performance of the T-S model (Eq. 2) for peak concentrations. Now, during certain environmental conditions or biologically active times the new BVOC concentration (q) was obtained by multiplying the output of Eq. (2) (y) by a factor, the value of which was determined by finding the best fit with the dataset of 2006–2007.

$$q = (1 + A + B)\cdot y \tag{4}$$

The parameters A and B refer to the multipliers associated with two environmental triggers stimulating extra high BVOC concentration: 1) relatively high PAR and 2) ozone >40 ppb (Fig. 2). The selection of a trigger were based on models residual analysis and literature. The explaining factors for the moments where the T model failed to predict the BVOC concentrations were studied by analysing the model residuals against five factors: relative humidity, precipitation, photosynthesis (GPP), total ecosystem respiration (TER) and radiation (PAR, relative PAR) (see also Lappalainen et al., 2009). Limits for an unexplained peak were set when the residuals were >1.5 ppmv for methanol, >0.05 ppmv for acetaldehyde, >0.5 ppmv for acetone, >0.007 ppmv for isoprene and >0.02 ppmv for monoterpene. Peaks, which could not be modelled by the T-S model, were associated most often with high values of radiation or relatively low values of air humidity.

Based on this we postulated that high PAR would accelerated photosynthesis and especially biosynthesis of isoprene and monoterpenes. PAR together with temperature is most commonly used factor in the isoprene emission models (Guenther et al., 1995;

Arneth et al., 2007). Also ox-VOCs have shown light-trigger emissions (Staudt et al., 2000). Since high PAR values could be masked by the seasonally changing available light, we hypothesized that high emissions leading to high concentrations of BVOCs could occur when the light level was high compared to the seasonally potentially available light. Available light was estimated from the solar elevation (in radians) multiplied by the solar constant (1360 W/m^2). A relative PAR index was calculated by dividing the day time mean PAR by the available potential light. A threshold value of 0.015 (arbitrary units) was used as a limit value for the relatively high daily PAR.

We also added ozone to trigger analysis, since the value of 40 ppb(v) has been considered to be a threshold concentration for deleterious long term effects on vegetation (e.g. Fuhrer et al., 1997; Karlsson et al., 2004).

We studied a single trigger and the combinations of chosen triggers, which could improve the T-S model in days of the high concentration peaks. During other days we run the T-S model. We determined the coefficients *A* and *B* first independently keeping one of them at zero. Then we tested for the combined effect of the selected triggers. This trigger model resembles a "broken-stick" model, where standard nonlinear models are fitted, but the model has certain breakpoints (Toms and Lesperance, 2003).

2.4 Model evaluation

The discrepancy between the data and a model and the model comparison were quantified by the sum of squares of residuals (RSS) and correlation coefficients. A small RSS indicates a close fit of the model to the data. To obtain the result in concentrations, RSS was calculated as:

$$\mathrm{RSS} = \sum_{n=1}^{n} ((y_i - x_i)^2 \qquad (5)$$

where *y* is a model concentrations and *x* is a measured concentration.

3 Results

3.1 Temperature model

The simple T-model fitted in the 2006–2007 data described 27–66 per cent of variations ($N = 257$) in BVOC concentrations (Fig. 3, Table 1). The T model worked especially well during early spring (March–April 2007) and was able to describe concentration variation well in general but in the end of March T-model underestimated the high concentrations of acetaldehyde and acetone. The model performed weakest for all compounds in July and August 2006. At that time the BVOC concentrations varied also more than at other times and high peak concentrations were observed frequently (Fig. 3). In general the T-model underestimated the highest observations in all studied compounds. In June–August 2006 the daily variation of observed BVOCs was large and temperature function was not able to capture the high peaks and the lowest concentrations especially in acetaldehyde, isoprene and monterpenes.

Tests with the independent dataset from summer 2008 showed that the T-model captured the general variation in methanol, acetaldehyde, acetone, isoprene but the level of explanation was lower than for the dependent data (Table 1). This was due to that the background level of BVOC concentrations measured at 2008 was lower than in the 2006–2007 data set (Fig. 4). The temperature dependence itself was unchanged. The summer 2008 day-time medians (methanol 2.09 ppbv, acetaldehyde 0.27 ppbv, acetone 1.36 ppbv, isoprene 0.14 ppbv, monoterpene 0.20 ppbv) were lower compared to summers 2006 and 2007 (Lappalainen et al., 2009). The T model was able to predict 19–34% of the variation in all compounds except monoterpene. For monoterpenes the level of explanation was especially poor for the independent data. The response of ox-VOC compounds (short-chained oxygenated compounds, here methanol, acetone, acetaldehyde) to T model differed from the isoprene and monoterpenes. In general the T-model overestimated concentrations of methanol, acetaldehyde and acetone while it underestimated the isoprene and monoterpene concentrations (Fig. 4). This was some what similar result compared to model fit in 2006–2007 data, however the independent dataset was clearly less representative in terms of number of measurement. The summer 2008 data also lacked the constitutive peak concentrations which were measured in summer 2006.

3.2 Temperature-state-of-development model

When compared to T-model, the T-S model improved slightly the explanation of variation (29–69 per cent) and for all compounds for 2006–2007 (Table 1). However, adding the S to T model did not improve the isoprene and monoterpene predictions in a test with the independent data from 2008 (Figs. 7, 8). The monoterpene peaks in summer 2006 were relatively high compared to the other compounds and dominated the statistical analysis. If the concentrations >0.6 ppbv would have been omitted the T-S model (2006–2007 data: R^2=0.52 ressum=1.75) would fit to data sightly better compared to the T-model (2006–2007 data: R^2=0.51, ressum=1.80).

3.3 Trigger model

The PAR-trigger alone did not correlated with BVOCs, not even if days of a relative high PAR were considered (Fig. 7). However O_3 together with PAR improved the Trigger model fit more compared to Trigger effect of ozone or PAR alone. When compared to the T and TS-S model the coefficients were the highest in all studied compounds and the residual sum of squares were the smallest. When compared to the 2008 data the Trigger model performed best for all studied compounds except isoprene (Table 3).

A general agreed threshold value of 40 ppbv for O_3 was detected from the relationship between O_3 and BVOC concentrations in Hyytiälä forest stand: below 40 ppbv there is hardly any relationship between O_3 and BVOC, but above 40 ppbv indication of a positive correlation can be observed (Fig. 7).

Major part of the highest BVOC concentration variation was observed in summer 2006 (Fig. 3). The summer 2006 was characterized by a exceptional drought episode starting from 20 July until 31 August (see Lappalainen et al., 2009). In the initial stage of the drought, mid of July, the BVOC concentrations were dropped and while the drought continued increased concentrations were measured in the begin of August. The trigger model could not grab only part of this variation. During the drought episode especially methanol concentrations were well described by the trigger model.

The recovery of biological activity in spring 2007 can also be considered an other specific time window. During the spring recovery of photosynthesis and, later in May, the springtime phenological development could be linked to occasionally high peak concentrations (see also Lappalainen et al., 2009). In end of March days of elevated concentrations were measured. This short episode was described by the models for all compounds except for acetaldehyde and acetone. None of the three models captures this short period of elevated concentrations for acetone and acetaldehyde, thus the trigger effect of O_3 nor PAR could not explain this.

The *A* coefficients of the Trigger model describing the effect of O_3 were positive in all studied compounds indicating the positive correlation between BVOCs and O_3 concentration over 40 ppb (Table 3, Fig. 7). The coefficient *B* referring to relatively high PAR during the days of high O_3 concentrations was negatively correlated to BVOC concentrations (Table 3).

4 Discussion

In principle, the BVOC air concentrations in a boreal forest stand for the BVOC emission but are affected by atmospheric chemistry. In this study we considered and modelled the atmospheric BVOC concentrations from the perspective of biogenic sources. This approach was justified by the fact that daytime concentrations were highly intercorrelated (see Lappalainen et al., 2009) and indicated a strong link between their biogenic emission sources (Schade and Goldstein, 2005). First we described the BVOC concentrations by temperature, which is the main driving factor for photosynthesis, and consequently BVOC biosynthesis and evaporation. In line with earlier studies (Schade and Goldstein, 2005) the atmospheric BVOC concentrations were described relatively well by only air temperature (T model) assuming an exponential relationship. In our case the temperature model explained 27–66 per cent of day time concentrations.

We improved the level of explanation by adding a new biological factor S, representing the seasonal capacity of a tree to emit BVOCs, to our T model. This T-S- model predicted the general level of daily and seasonal variation of the day-time concentrations somewhat better when compared to the T-model. This is in line with the result of Gray et al. (2006) who showed that the methylbutenol (MBO) basal emission rate is regulated by the temperature history and that the rate is not constant during the annual cycle.

In our dataset, periods of high peaks were most common in the late summer 2006 and during the late spring of 2007. In summer 2006 the model residuals were high especially during the summer drought and in 2007 in early spring and summer. The T or T-S-model predicted the general level of daily and seasonal variation of the day-time concentrations quite well. However, the T-model was unable to capture very high or very low concentrations. This indicates that there might exist some other prevailing factors, which trigger high emission and concentration peaks. Basically high peaks could have been related to measurement error or represent a real biological response triggered by environmental conditions. These type of fast changes are typical for BVOC emissions and could be related to several kind of environmental changes (temperature, light, drought) and different plant physiological processes or ontogenic structures. For example high monoterpene (Noe et al., 2006) bursts are released from storage pools. Also phenological stages may create emission peaks that are not directly explained by environmental triggers. The growing leaf biomass increases the amount of synthesized BVOCs, and bud burst may also provoke emission peaks, especially for methanol in spring (Schade and Goldstein, 2006).

Our baseline assumption for the PAR trigger was that it would stimulate constitutive BVOC emissions, especially in monoterpenes by exciting photosynthesis light reactions. We postulated that high PAR would enhance short term photosynthesis (minutes, hours) and initiate the exceptionally high BVOC emissions and concentrations. This hypothesis was supported by the tree physiological observation that the monoterpene emission capacity is affected by the photosynthetic pigment metabolism for which the main driver is radiation (Porcar-Castell et al., 2008, 2009). Furthermore, the biosynthesis of volatiles is dependent on the energy gain from solar light, as well as from the substrates which are more or less closely linked to photosynthesis. On the other hand, high light is potentially dangerous to vegetation, in particular on occasions when carbohydrate production does not match the energy gain (e.g. Demmig-Adams and Adams, 1996), and it can potentially induce VOC production from photo-damaged tissues. Therefore, high relative PAR values indicate potentially harmful levels of light, and can be used as trigger in the modeling approach. However, the effect of PAR trigger alone was clearly weaker when compared to the O_3 trigger. This could imply that the biological effect of the PAR trigger is hidden by the loss processes related to atmospheric chemistry. In the atmosphere high PAR values indicate a high rate of hydroxyl radical production, which accelerates the degradation of monoterpene, isoprene and acetaldehyde. Using PAR improved the trigger effect, when it was used together with the O_3 trigger. The effect of PAR together with O_3 was negative for all studied compounds (coefficient $B < 0$).

We also tested another biological stress factor, ozone. It has been found that 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 was 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., 1988). Based on our dataset and the subsequent model analysis, exposure over the 40 ppb threshold seems to correlate surprisingly well with high emissions of methanol, acetone and acetaldehyde, and seems to corroborate the earlier findings from experimental studies. However, the high isoprene and monoterpene peaks are poorly explained by high ozone concentrations, and obviously the regulation of isoprenoid concentrations at the boundary layer above Scots pine forest includes some yet unattributed factors. As a whole the effect of ozone was positive for all studied compounds (coefficient $A > 0$). It is the first time when a positive relationship between ozone and high VOC concentrations has been shown in natural conditions. This indicates that the effect of ozone stress on trees is more dominant process compared to the atmospheric chemistry. This is supported by the knowledge on the oxidising chemical processes of methanol, acetaldehyde, acetone, which are hardly reacting with O_3. Isoprene (life time 1.6 d) and monoterpene alpha -pinene (4.7 h for example) have shorter atmospheric lifetime at the presence of O_3 (Atkinson and Arey, 2003).

The remaining discrepancy between the models and observed BVOC might be explained by compound specific (bio)synthesis, specific stress periods and/or atmospheric chemistry processes. High acetaldehyde concentrations measured just after snow melt, in early spring in March 2007, and the end of the growing season, in September 2006, could be associated with the synthesis process. Acetaldehyde is synthesised via the processes related to soil (oxygen deficiency in the soil - soil flooding) or during senescence (Fall, 2003). However, current knowledge of the soil emissions is weak. The unexplained concentration variation could also be related to the physiological and phenological status of the trees. There is an indication that seasonal and phenological stages may create emission peaks that are not directly explained by standard environmental light and temperature algorithms (Penueals and Lusia, 2001). The growing leaf biomass increases the amount of synthesized BVOCs, and bud burst may also provoke emission peaks especially for methanol in spring (Schade and Goldstein, 2006). Certain developmental stages entail changes in VOC concentrations and composition and in permeability of the cuticle and thus effect the VOC vapour pressure and cuticle diffusive resistance (Penuelas and Llusia, 2001). Some attempts have been made to relate the bud burst via the corresponding effective temperature sum to a single emission peak. For example a fixed temperature sum has been use to predict the initiation of isoprene emission and terpene emissions from *Betula pendula* (Hakola et al., 2000).

In summer 2006, during the drought stress episode large concentration variations were detected. Low monoterpene concentrations were detected during mid-July. This observation is in line with earlier result by Lavoir et al. (2009), who showed that persistent drought had 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 due to simultaneous ozone stress (see Niinemets, 2009).

The significant intercorrelation between the studied compounds (see also Lappalainen et al., 2009) also draws attention to the possibility that the BVOC concentrations are controlled by the oxidation processes or produced by oxidation of other VOCs. Our test with the summer 2008 data indicated that a trigger type high emissions could be confused by the atmospheric processes. In a boreal forest the effect of OH destruction is strongest during summer months, when the seasonal OH concentrations are high (Hakola et al., 2003). Of the compounds studied here, isoprene, monoterpene and acetaldehyde have fairly short atmospheric lifetimes, and therefore their concentrations at the measurement site are potentially controlled by chemical loss as well as sources and transport. Methanol and acetone have comparably long chemical lifetimes. Methanol is also part of the oxidation chain of acetone, but the effect is likely to to be minor. Acetaldehyde is produced by photo-oxidation of non-methane hydrocarbons, such as alkenes and alkanes and partly also from the oxidation of isoprene. The atmospheric photochemical source is globally considered to be the main source for acetaldehyde (Millet et al., 2010). Isoprene and monoterpene are mainly emitted directly from vegetation. Globally, a large fraction of acetone is produced by the oxidation of hydrocarbons, however this source is likely to be minor of clean background air as in our case.

5 Conclusions

According to our results, a temperature based function approach could serve as a core for the further development of a seasonal BVOC concentration model for the boreal forest. Although temperature and photosynthetic capacity seem to be the main driving factors on a daily scale, some other processes seem to replace them occasionally and be temporary main contributor(s) to BVOC emissions from a forest stand. The T-S model was not able to capture extreme concentration variation and the trigger effect needed to be incorporated into the model. In our case we tested two triggers: relatively high PAR and ozone. Although we attained better fit for the 2006–2007 data we were not able to improve the model predictability with the independent dataset 2008. Detecting the trigger effect from the air concentrations is a tricky task. The triggers may be over driven by fast atmospheric chemistry reactions. Also, separating the fundamental stress factor is difficult due to the complex relation between environmental factors and BVOC concentrations and inter correlation between factors. This study presented the first idea of a trigger type model. In the future model development should focus more compound-specific approach. In order to keep the number of modelling parameters limited, other temperature based processes such as phenological development could be linked to BVOC modelling more closely.

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Table 1. T-model ($y = ae^{(bt)}$) and T-S-model ($y = ae^{(bt)} + ce^{(fS)}$), correlation coefficients (r^2), T-model coefficients a, b. (D)=dependent dataset 2006–2007 (N=257), (I)=independent dataset summer 2008 (N=49). Compounds: met=methanol, act=acetaldehyde, ace=acetone, iso=isoprene, mon=monoterpene.

Comp.	$r^2(D)$	$r^2(I)$	$r^2(D)$	$r^2(I)$	a	b
met	0.66	0.34	0.69	0.38	0.42	0.095
act	0.27	0.30	0.34	0.33	0.15	0.048
ace	0.66	0.19	0.66	0.20	0.43	0.075
iso	0.65	0.27	0.66	0.27	0.03	0.084
mon	0.27	0.07	0.29	0.09	0.06	0.076

Table 2. T-S-model ($y = ae^{(bT)} + ce^{(fS)}$) coefficients a, b, c, f. Model was fitted to dependent dataset 2006–2007, Compounds: met=methanol, act=acetaldehyde, ace=acetone, iso=isoprene, mon=monoterpene.

Comp.	a	b	c	f
met	0.505	0.095	−0.004	0.303
act	0.060	0.086	0.147	−0.079
ace	0.311	0.087	0.215	−0.031
iso	0.034	0.081	0.000	1.000
mon	0.041	0.079	0.009	0.143

Table 3. Trigger-model: correlation coefficient (r^2) and model coefficients A, B (see Eq. 3) where O_3 is a trigger for A and PAR for B, (D)=dependent dataset 2006–2007, (I)=independent dataset summer 2008. Compounds:met=methanol, ace=acetone, iso=isoprene, mon=monoterpene.

Comp.	$r^2(D)$	$r^2(I)$	A	B
met	0.71	0.46	0.242	−0.059
act	0.38	0.35	0.196	−0.104
ace	0.69	0.28	0.150	−0.096
iso	0.67	0.23	0.154	−0.039
mon	0.30	0.12	0.077	−0.134

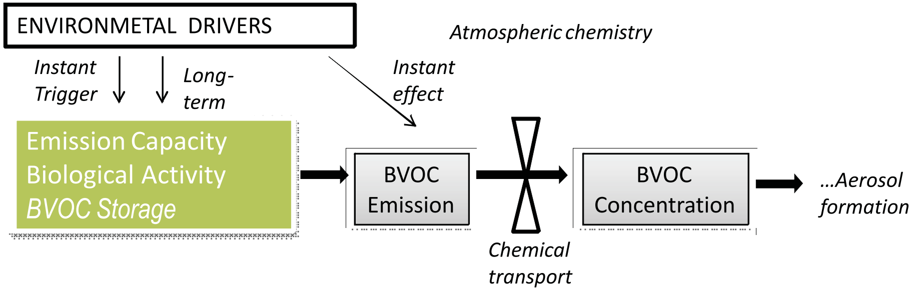

Fig. 1. Conceptual scheme of factors effecting BVOC emission and air concentrations in a boreal forest stand.

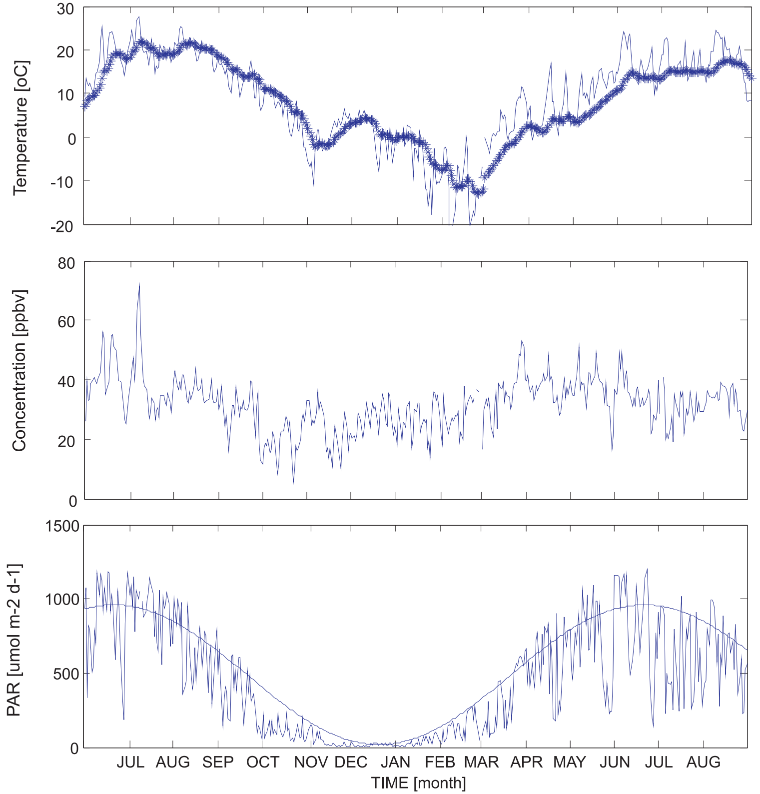

Fig. 2. Mean day-time temperature (thin line) and state of development (*S*) (thick line) (top), ozone day-time mean concentration (middle), mean day-time PAR and seasonal average (sine curve) (lowest) in a period 2006–2007.

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Modelling of BVOC concentrations in a boreal forest

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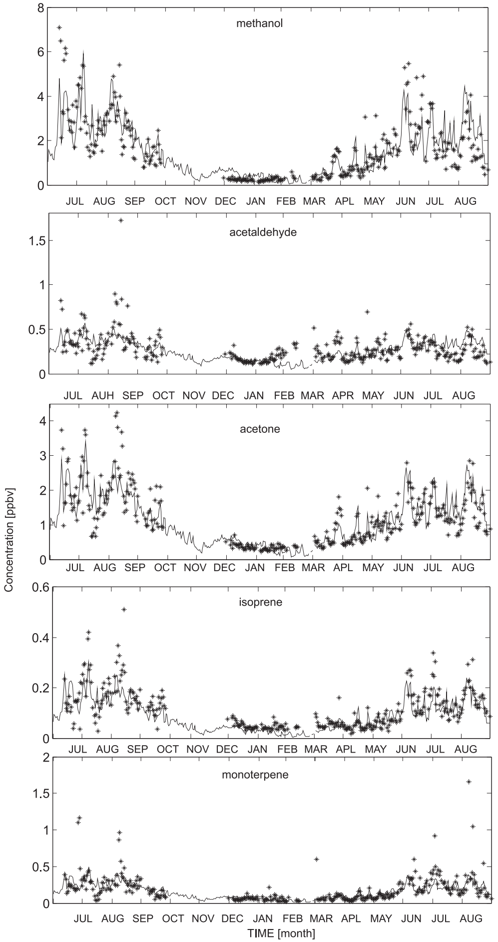

Fig. 3. The modelled (T-model, $y = ae^{(bt)}$, black line) and observed (crosses) daytime BVOC concentrations in 1 June 2006–31 August 2007 at the SMEAR-II station.

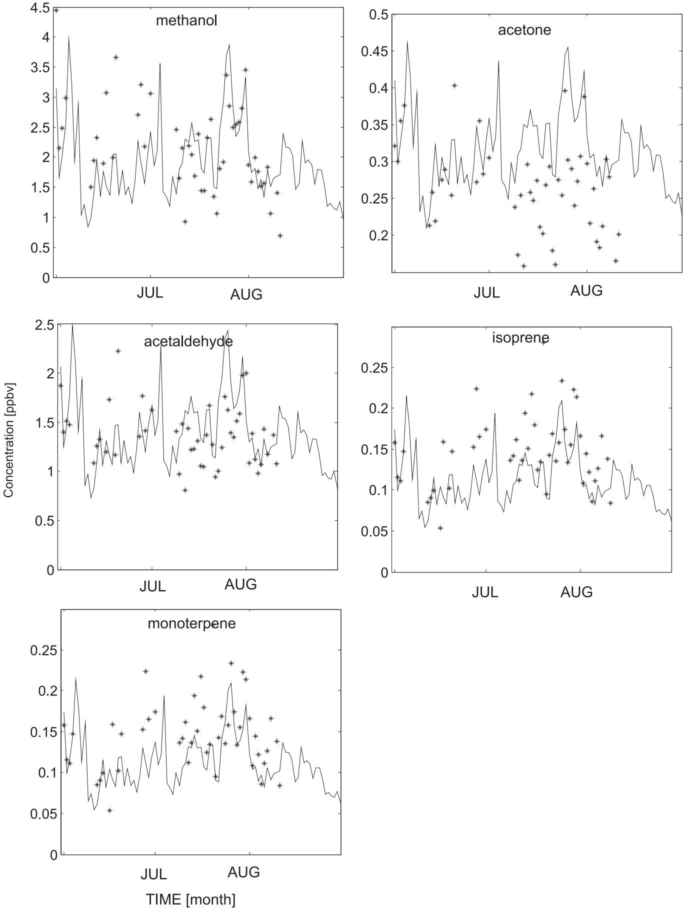

Fig. 4. The modelled (T-model, $y = ae^{(bt)}$, black line) and observed (crosses) daytime BVOC concentrations in 1 June–31 August 2008 at the SMEAR-II station.

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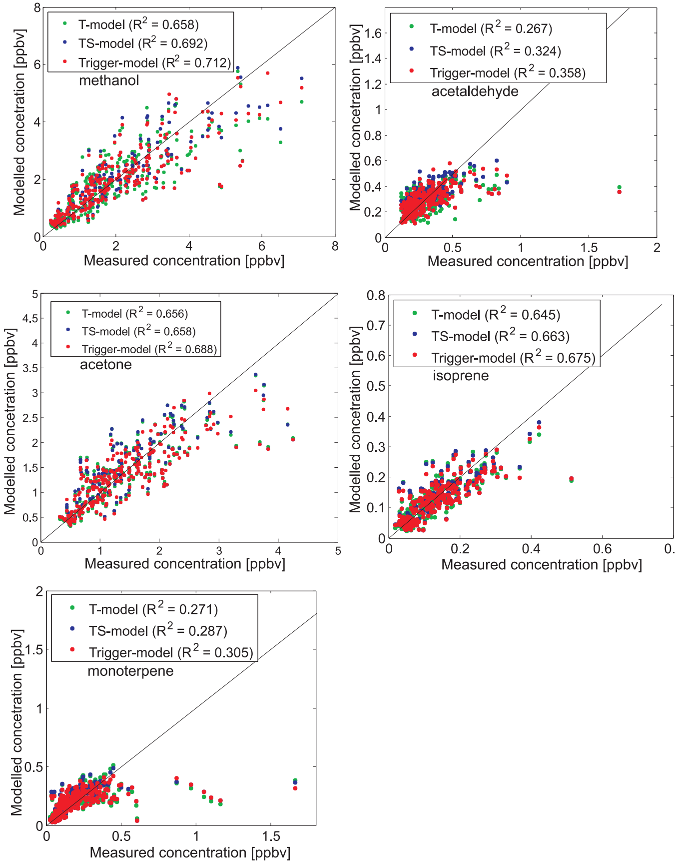

Fig. 5. The modelled (T-model $y = ae^{(bt)}$ green, TS-model $y = ae^{bT} + ce^{fS}$ blue, Trigger model red) versus observed daytime BVOC concentrations dependent dataset 2006–2007 at the SMEAR-II station.

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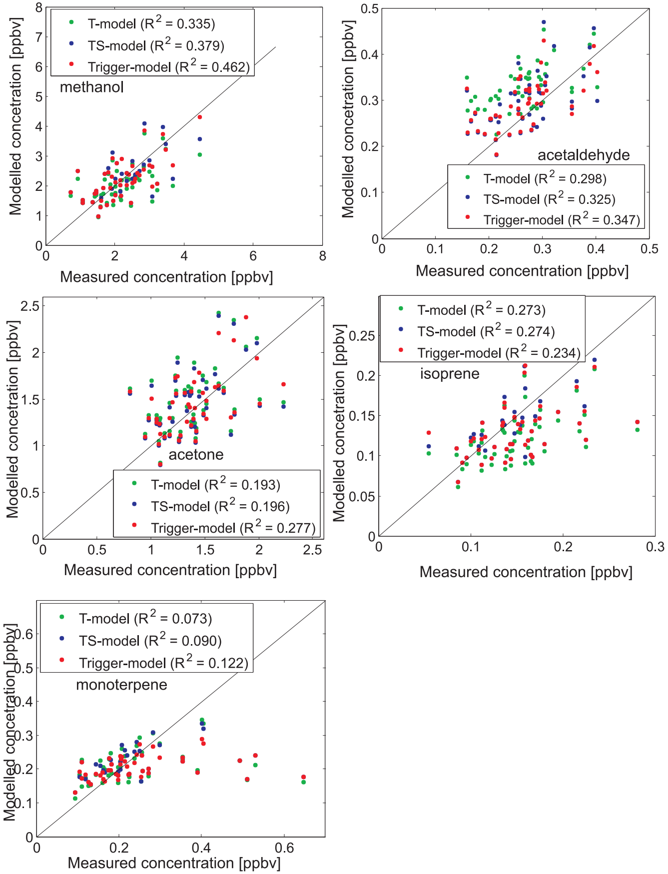

Fig. 6. The modelled (T-model $y = ae^{(bt)}$ green, TS-model $y = ae^{bT} + ce^{fS}$ blue, Trigger model red) versus observed daytime BVOC concentrations independent dataset 2008 at the SMEAR-II station.

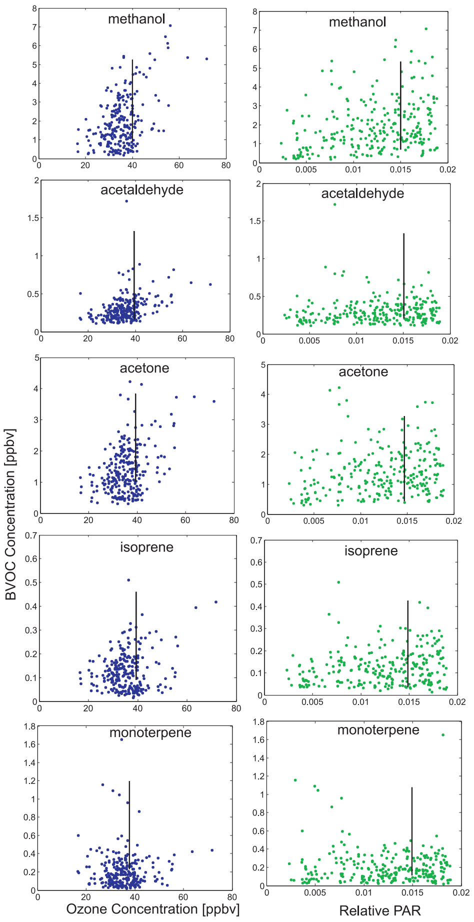

Fig. 7. Day-time mean ozone concentrations versus BVOC concentrations (left), Daytime relative PAR versus BVOC concentrations (right) during the period 2006–2007 at the SMEAR II station.

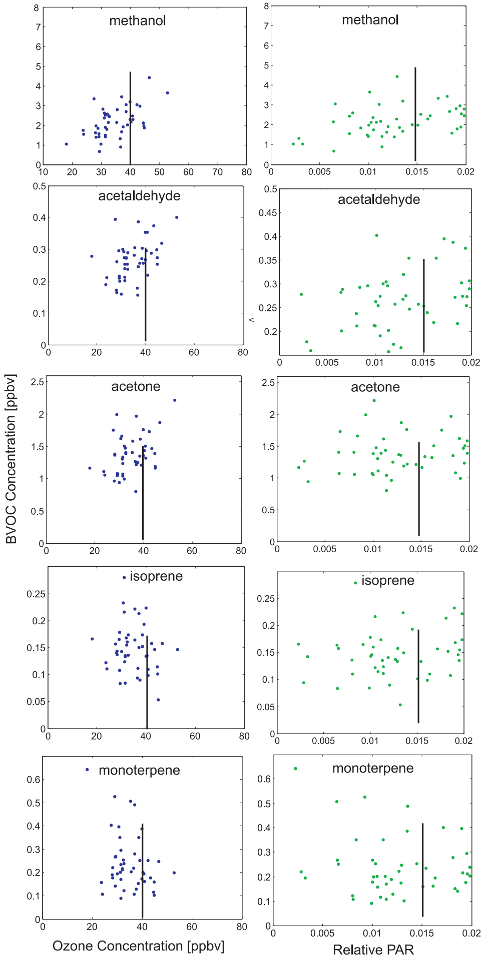

Fig. 8. Day-time mean ozone concentrations versus BVOC concentrations (left), Daytime relative PAR versus BVOC concentrations (right)in summer 2008 at the SMEAR II station.

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