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ROLE OF TEMPERATURE IN THE BIOLOGICAL ACTIVITY
OF A BOREAL FOREST

Hanna Lappalainen

Faculty of Biological and Environmental Sciences
University of Helsinki
Helsinki, Finland

Academic dissertation

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Author: Hanna Katriina Lappalainen

Thesis Supervisors:

Tapio Linkosalo

Finnish Forest Research Institute (Metla), Finland

Heikki Hänninen

Department of Biosciences, University of Helsinki, Finland

Pre-examiners:

Ülo Niinemets

Department of Plant Physiology, Estonian University of Life Sciences, Estonia

Risto Häkkinen

Finnish Forest Research Institute (Metla), Finland

Opponent:

Pekka Niemelä

Department of Biology, Section of Biodiversity

University of Turku, Finland

Custos:

Jaakko Kangasjärvi

Department of Biosciences, Faculty of Biological and Environmental Sciences

University of Helsinki, Finland

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Role of temperature in the biological activity of a boreal forest

Abstract

In northern latitudes, temperature is the key factor driving the temporal scales of biological activity, namely the length of the growing season and the seasonal efficiency of photosynthesis. The formation of atmospheric concentrations of biogenic volatile organic compounds (BVOCs) are linked to the intensity of biological activity. However, interdisciplinary knowledge of the role of temperature in the biological processes related to the annual cycle and photosynthesis and atmospheric chemistry is not fully understood. The aim of this study was to improve understanding of the role of temperature in these three interlinked areas: 1) onset of growing season, 2) photosynthetic efficiency and 3) BVOC air concentrations in a boreal forest.

The results present a cross-section of the role of temperature on different spatial (southern – northern boreal), structural (tree – forest stand - forest) and temporal (day-season- year) scales. The study was based on two data unities: phenological recordings from an area representing the southern and middle boreal forests in Finland, and measurements from Stations for Measuring the Forest Ecosystem – Atmosphere Relations (SMEAR). The phenological data were used to find the best temperature-based phenological model for predicting the onset of bud burst in a boreal forest, and to analyse the long-term trends in the spring recovery of biological activity. The SMEAR station measurements were used first to analyse the relationship between temperature and the seasonal pattern of photosynthesis in the southern and the northern boreal zone, and then to examine the relationship between temperature and the atmospheric concentrations of biogenic volatile organic compounds in a boreal forest stand.

The fundamental status of the Thermal Time model in predicting the onset of spring recovery was confirmed. However, it was recommended that sequential models would be more appropriate tools when the onset of the growing season is estimated under a warmer climate. A similar type of relationship between photosynthetic efficiency and temperature history was found in both southern and northern boreal forest stands. This result draws attention to the critical question of the seasonal efficiency of coniferous species to emit organic compounds under a warmer climate. New knowledge about the temperature dependence of the concentrations of biogenic volatile organic compounds in a boreal forest stand was obtained. The seasonal progress and the inter-correlation of BVOC concentrations in ambient air indicated a link to biological activity. Temperature was found to be the main driving factor for the concentrations. However, in addition to temperature, other factors may play a significant role here, especially when the peak concentrations are studied.

There is strong evidence that the spring recovery and phenological events of many plant species have already advanced in Europe. This study does not fully support this observation. In a boreal forest, changes in the annual cycle, especially the temperature requirement in winter, would have an impact on the atmospheric BVOC composition. According to this study, more joint phenological and BVOC field observations and laboratory experiments are still needed to improve these scenarios.

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Nimeke Lämpötilan merkitys boreaalisen metsän biologiseen aktiivisuuteen

Tiivistelmä

Lämpötila on keskeinen biologisista aktiivisuutta, kuten kasvukauden pituutta ja fotosynteesiä, säätelevä ympäristötekijä pohjoisella havumetsävyöhykkeellä. Ilmakehän säätelymekanismien kannalta keskeisten orgaanisia hiilivety-yhdisteiden muodostuminen on yhteydessä biologiseen aktiivisuuteen. Tämän tutkimuksen tavoitteena on lisätä ymmärrystä lämpötilan merkityksestä näillä kolmella toisiinsa liittyvillä alueilla: 1) kasvukauden alkaminen, 2) fotosynteesin tehokkuus sekä 3) ilmakehän orgaanisten hiilivetyjen pitoisuudet. Tutkimustuloksia tarkastellaan orgaanisten hiilivetyjen näkökulmasta ja pohditaan, mitä mahdollisia vaikutuksia ilman lämpötilan muutoksilla voisi olla boreaalisen metsän orgaanisiin hiilivety pitoisuuksiin.

Tutkimustulokset esittelevät lämpötilan vaikutusta eri aika (päivä – vuodenaika- vuosi) ja alueskaaloilla (etelä-pohjoisboreaalinen metsä). Tutkimus perustuu kahteen erityyppiseen mittausaineistoon: 1) fenologiset havainnot, jotka edustavat Etelä – ja Keski Suomen aluetta. 2) SMEAR (Stations for Measuring the Forest Ecosystem – Atmosphere Relations) -mittausasemaverkoston fotosynteesi ja ilmakehän orgaaniset hiilivetypitoisuus mittaukset Hyytiälän ja Värriön tutkimusasemilta. Fenologista aineistoa käytettiin lämpötilapohjaisten fenologisten mallien vertailututkimukseen. Fenologisten mallien avulla voidaan ennustaa lehtipuun silmunpukkeaminen keväällä, toisin sanoen kasvukauden alkamista. Lisäksi fenologista mittausaineiston pohjalta analysoitiin, onko kevään heräämisen ajankohdassa havaittavissa pitkän aikavälin muutoksia kuten aikaistumista. SMEAR mittausaineistoa käytettiin vahvistamaan jo aiemmissa tutkimuksissa havaittua käsitystä lämpötilan ja fotosynteesin tehokkuuden yhteydestä. Lisäksi tutkittiin Hyytiälän mittausaseman tiettyjen orgaanisten hiilivetyjen ilmapitoisuuksien aikasarjan yhteyttä lämpötilaan ja biologiseen aktiivisuuteen.

Tutkimuksen perusteella voidaan todeta, että ns. yksinkertaistettu lämpösomma-malli ennustaa parhaiten lehteentulon päivämäärän. Sen sijaan fenologinen malli, joka huomioi lepokauden aikaisen lämpötilavaatimuksen, on todennäköisesti tarkempi ilmaston muuttuessa. Laaja SMEAR mittausaineisto vahvistaa käsitystä, että fotosynteesitehokkuuden yhteys lämpötilaan on hyvin samantyyppinen niin etelä- kuin pohjoisborealisessa metsässä. Tätä tietoa voidaan hyödyntää arvioitaessa orgaanisten hiilivety päästöjä ja ilmakehäpitoisuuksia muuttuneissa ilmasto-olosuhteissa. Lämpötila ohjaa voimakkaasti ilmakehän orgaanisten hiilivety pitoisuuksia borealisessa metsässä, mutta hiilivedyille tyypillisten korkeiden pitoisuuspiikkien kuvaamisen tarvitaan lisätutkimusta.

Aikasarja-analyyseihin perusteella on havaittu, että kasvillisuuden keväänherääminen on keskimäärin aikaistunut Euroopassa. Tämä tutkimus ei suoraan vahvista tätä yleistä käsitystä. Erityispiirteinä borealisille puulajeille on lepokaudenaikainen lämpötilavaatimus, jolla voi olla tulevaisuudessa vaikutusta biologisen aktiivisuuden käynnistymisen ajankohtaan ja tätä kautta aina ilmakehän orgaanisten hiilivetyjen pitoisuuksiin asti. Tämän tutkimuksen perusteella tarvitsemme lisää samanaikaisia fenologisia ja BVOC yhdisteisiin liittyviä havaintoja ja mittauksia näiden arvioiden tueksi.

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Helsinki, November 2010

Hanna Lappalainen

NOMENCLATURE

Atmospheric lifetime	amount of time taken for a chemical compound to be converted into another chemical compound or to be removed from the atmosphere by chemical reactions or other sinks
Annual cycle of a tree	A cycle consisting of the ecophysiological phases of active period (growth), hardening for winter rest, winter dormancy, and de-hardening for the next active period, completed within one calendar year
Biological activity	biological processes related to the annual cycle and photosynthesis
Biogenic volatile organic compound (BVOC)	volatile organic atmospheric trace gases, other than CH ₄ , originating from biological processes, e.g., photosynthesis and growth
Biosynthesis	an enzyme-catalyzed process in cells consisting of several enzymatic steps in which the product of one step is used as substrate in the following step.
Dormancy	time period of inhibited growth, the rest phase
Effective temperature sum (T_{sum})	sum of the positive differences between diurnal mean temperatures and a commonly-used threshold of temperature +5 °C
Ontogenetic development	developmental change in an entity, for example from leaf bud to full leaf.
Phenology	visible biological events during the annual cycle, such as bud burst and flowering, and how these events are influenced by seasonal and inter-annual variations in climate
Photosynthetic efficiency	associated with the maximum rate of light-saturated carbon fixation in the dark reaction (Calvin cycle)
State of development (S) (°C)	a theoretical variable of temperature history corresponding to the temperature at which the photosynthetic apparatus is acclimated

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LIST OF ARTICLES

This thesis is based on the following articles (subject matter order), which are referred to in the text by their Roman numerals:

I Linkosalo, T., Lappalainen, H.K. and Hari, P. 2008. A comparison of phenological models of leaf bud burst and flowering of boreal trees using independent observations. *Tree Physiology* 28: 1873-1882.

II Kolari, P., Lappalainen, H.K., Hänninen, H. and Hari, P. 2007. Relationship between temperature and the seasonal course of photosynthesis in Scots pine at northern timberline and in southern boreal zone. *Tellus B* 59: 542–552.

III Lappalainen, H.K., Sevanto, S., Bäck J., Ruuskanen, T.M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M. and Hari, P. 2009. Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors. *Atmospheric Chemistry and Physics* 9: 5447-5459.

IV Lappalainen, H.K., Sevanto, S., Dal Maso M., Kajos, M.K., Taipale, R. and Bäck, J. 2010. Modelling day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy. Manuscript.

V Lappalainen, H.K., Linkosalo, T. and Venäläinen, A. 2008. Long-term trends in spring phenology in a boreal forest in central Finland. *Boreal Environment Research* 13: 303–318.

AUTHOR'S CONTRIBUTIONS

I Lappalainen took part in the planning and writing of the article. Linkosalo was mainly responsible for the data analysis and writing the manuscript. Hari commented on the manuscript.

II Lappalainen took part in the planning of the article, in the preliminary data analysis and in writing the article. Kolari was mainly responsible for writing the manuscript and carrying out the data analysis. Article II was also included in Kolari's PhD thesis. Hänninen and Hari commented on the manuscript.

III Lappalainen was responsible for planning the article together with Sevanto and Bäck. Lappalainen was mainly responsible for the data analysis, and for writing the paper. The computer codes (MatLab) were created by Sevanto and Lappalainen. Rinne, Ruuskanen and Taipale provided the BVOC concentration data and commented on the manuscript. Kulmala, Hari and Kolari commented on the manuscript.

IV Lappalainen was responsible for planning the article together with Sevanto and Bäck. Lappalainen was mainly responsible for the data analysis and for writing the article. Sevanto, Bäck and Dal Maso commented on the manuscript. Taipale and Kajos provided BVOC concentration data and also commented on the manuscript. Computer codes (MatLab) were created by Sevanto, Dal Maso and Lappalainen.

V Lappalainen was mainly responsible for planning the article, for the data analysis and for writing the article. Linkosalo and Venäläinen commented on the manuscript.

1 INTRODUCTION

According to the latest scenarios, the climate in Finland will become significantly warmer, more so in winter than in summer (Jylhä et al. 2009). Climate affects the temporal scales of biological activity, namely the length of the growing season and the seasonal efficiency of photosynthesis. Biosynthesis and the emissions of biogenic volatile organic compounds (BVOCs) are linked to the intensity of biological activity (Peñuelas et al. 2003, Peñuelas et al. 2009). In the atmosphere, BVOCs participate in several ways in various atmospheric processes related to O_3 , methane lifetime, aerosol formation and aerosol growth (Kulmala et al. 2004, Tunved et al. 2006, Peñuelas and Staud 2010), which makes them crucial components of the atmosphere. In order to understand the consequences of climate change, improved knowledge on the links between vegetation, BVOCs and the atmosphere on different time -scales is needed (Peñuelas and Llusia 2003, Peñuelas and Staudt 2010, Rinne et al. 2009) (Fig.1). The scope of this thesis lies within the framework of this scheme: the links between biological activity, BVOC air concentrations and temperature in a boreal forest.

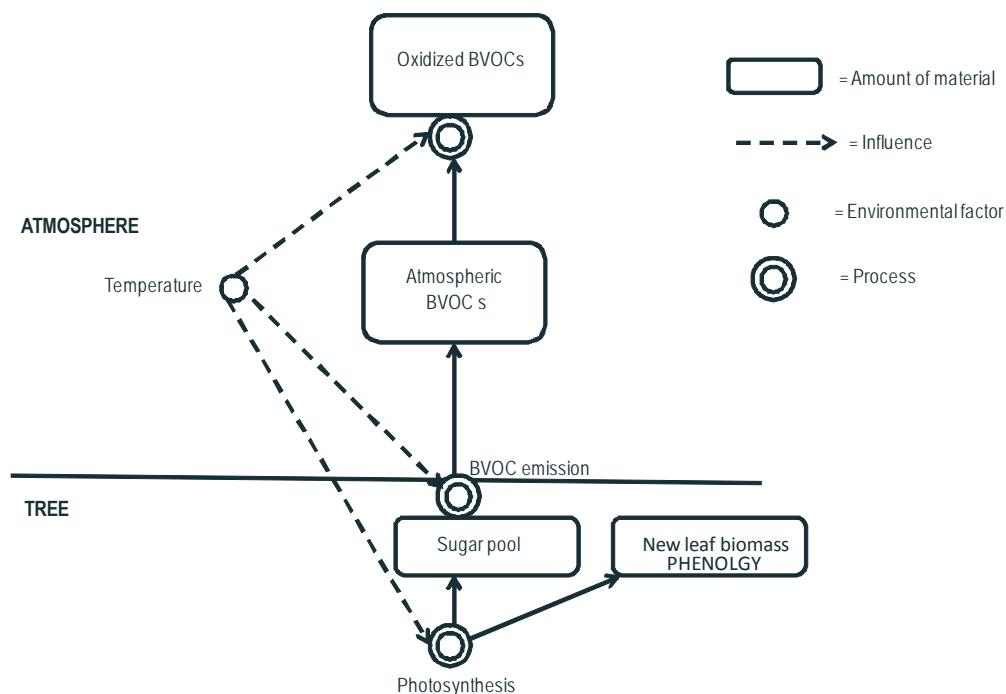


Figure 1. The scope of this thesis: to analyse the links between biological activity, BVOC air concentrations and temperature in a boreal forest (symbols adopted from Hari and Kulmala 2008).

1.1. Biological Activity

1.1.1. Annual cycle of boreal trees

In a boreal forest the annual cycle of biological activity can be divided into two main phases: the active period of photosynthesis and growth, and the passive period of rest. In spring, the recovery of biological activity can be observed as visible phenological development. Phenological observations, such as those of bud burst, shoot growth and flowering, indirectly reflect the underlying, internal plant physiological processes taking place during the active period of growth (Sarvas 1972, Lieth, 1974, Menzel 2002). Temperature is the main climate factor driving the progress of these underlying physiological processes and hence the phenological event.

During recent decades, the value of phenological datasets in reflecting trends of life history events or growth rhythm has been recognized, and phenological recordings have become an essential part of environmental monitoring, especially with regard to climate change (Sparks 1999, Sparks et al. 2000, Menzel 2002). To discover evidence of the phenological responses of biota to already-existing climate warming, is especially salient for species living near the northern limits of their distribution areas in the boreal forest. Proper timing of active growth and rest periods is essential for the survival of boreal trees, especially in spring due to the risk of frost damage. However, observations representing northern areas are scarce in number. Several studies have reported the advancement of phenological events in spring on a wider spatial scale. On a global scale the advancement of spring phenological events in general has been estimated to be of the order of 2.3 days per decade (Parmesan and Yohe 2003) and a similar order of magnitude is valid for Europe, with an average advance of phenological events in spring or summer of 2.5 days per decade (Menzel et al. 2006). Furthermore, 30 years of observations in Europe show that the average annual growing season can be estimated to have lengthened by 10.8 days since the early 1960s (Menzel and Fabian 1999).

In addition to long-term trend analysis in identifying already occurred changes, validation of phenological models is also needed to predict the length of the growing season. Model comparisons and validation studies are few in number; The lack of test data limits the testing of models in different environments. For example, phenological models are usually constructed by using a single dataset, which is used for the model parameterization. Often tests with a separate test dataset are totally omitted, or the same dataset is also used for testing by the method of leave-one-out cross-validation (Häkkinen 1999). This method uses a single observation from the original sample as the validation data with the remaining observations being the training data. This is repeated so that each observation in the sample is used once as validation data.

Traditionally, the recording of phenological events most often consists of observations of the bud burst dates of deciduous trees. Consequently, phenological models have been developed for predicting the spring phenology of deciduous trees. The main difference between the different models is how they take into account chilling and forcing (Fig 2.) (Hänninen 1987). Basically, deciduous trees fall into a dormancy phase in autumn, and need a certain amount of lower temperatures (chilling) to complete their dormancy. After dormancy release has occurred, higher temperatures (forcing) are needed for the ontogenetic development towards bud burst (Sarvas 1967) (Fig. 2). In addition to sufficient temperature conditions, an additional light signal from the changing light environment is also needed both for the onset

of the dormancy period in autumn and for the bud burst in spring (Heide 1993, Linkosalo and Lechowicz 2006).

Phenological models can be divided into phenological model subgroups solely based on the interplaying effect of chilling (cold) and forcing (warm) conditions on the timing of bud burst. Thermal time (TT) models assume that after a fixed calendar date the environmental conditions for dormancy release are met, and bud burst is predicted to take place when the temperature sum exceeds a certain pre-set threshold temperature (Sarvas 1972). However, in the future, in a warmer climate, also the climate conditions before dormancy release may play a more central role in the process of bud development. A period of chilling temperatures between -5 °C and +10 °C, are required for the budburst (Hänninen 1991). Sequential models describe the phases before and after dormancy release. The two “sub models” are run, one after another, i.e., first, a model describing the chilling requirement needed for the dormancy release and then a second model from the date of dormancy release towards bud burst (Sarvas 1974, Hänninen 1990). Parallel models are a synchronous description of the chilling and forcing conditions leading to bud burst (Landsberg 1974, Kramer 1994). For example, in a parallel model by Cannel and Smith (1983), each day after a specific starting date is classified as either a chill day or a forcing day. The critical temperature sum threshold for bud burst depends on the number of chill days: an increasing number of chill days decreases the required temperature sum for bud burst (Cannel and Smith 1983). Flexible models are a sophisticated mathematical description of how different processes interact or take turns. The Promoter-Inhibitor model by Schaber and Badeck (2003) describes two features that control bud development, one inhibiting and the other promoting it. The inhibiting process depends on the plant’s environment (temperature) and changes in the day length. The inhibiting factor starts at full strength; favourable environmental conditions then gradually turn the inhibiting feature off. The promoting process, on the other hand, also depends on the environment, but in addition it depends on the state of the inhibiting factor. The promoting factor starts in the totally-off state, and is gradually turned on until it reaches a threshold value, at which the bud burst is modelled as taking place. The Unified model, also classified as a flexible model, is a combination of sequential and parallel models. The basic model is a sequential model, but after dormancy release the forcing period can still be affected by a chill day, which affects the threshold for bud burst (Chuine 2000).

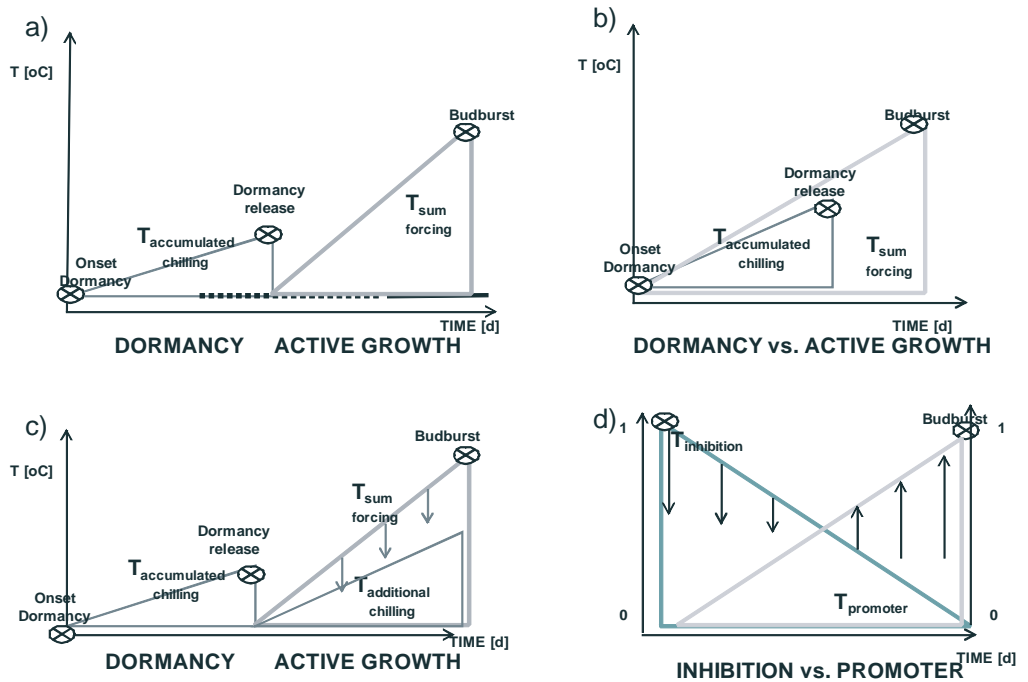


Figure 2. Schematic figure of the prototypes of phenological models. Phenological models can be divided into phenological model subgroups based on the interplaying effect of chilling ($T_{accumulated_chilling}$) and forcing temperatures ($T_{sum_forcing}$) on the timing of bud burst: a) Thermal Time model and Sequential models (Sarvas 1972, 1974; Hänninen 1987) b) Parallel models (Cannel and Smith 1983), c) Flexible-Unified model (Chuine 2000) and d) the Flexible - Promoter-Inhibitor model (Schaber and Badek 2003).

In conifers, the springtime development can also be detected as new shoot and needle growth. In Scots pine new shoot growth starts in May, followed by needle growth later in May and summer (Pietarinen et al. 1982). Secondary growth of the Scots pine stem can also be used as a growth measure (Sevanto et al. 2005). However the overwintering of conifer trees differs from that of deciduous trees. During the annual cycle, evergreen tree species maintain their ability for photosynthesis in the overwintering needles. In Scots pine the photosynthesis can take place even in winter time if favourable temperature conditions are met and the water needed for photosynthesis can be extracted either from the soil or from the stems (Sevanto et al. 2006). In spring, rising air temperatures revoke the frost hardness of the needles (Repo et al. 2006) and increase the photosynthetic efficiency. However, in spring, biological activity (photosynthesis) may decrease in temporary cold weather (Pelkonen and Hari 1980, Mäkelä et al. 2004).

1.1.2. Photosynthesis - Photosynthetic efficiency

The role of temperature in the seasonal metabolism of the photosynthesis of deciduous trees is indicated by phenological studies that predict phenological events on the basis of cumulative temperatures (Sarvas 1967, Heikinheimo and Lappalainen 1997, Linkosalo

2000). However, phenological models predict a single day when the event takes place, but are not able to describe the biological activity of the growing season as a whole. In conifers the metabolism of photosynthesis is related to gradual changes during the annual cycle.

The instantaneous response of photosynthesis to environmental factors is fairly well understood (Farquhar and von Caemmerer 1982, Hari and Mäkelä 2003); the actual driving forces and mechanisms behind the seasonal variation of photosynthetic activity are, however, less well known. Most of the daily variation in photosynthesis is attributed to the changes in the daily patterns of light level and temperature. Instant photosynthesis consists of two main reaction chains, i.e., the light reaction and the Calvin cycle. In the light reaction, visible light energy is transported via electron transport, and the energy is changed into chemical energy in the form of ATP and NADPH. The first part of the light reaction (light interception by chlorophyll molecules and charge separation) is temperature-independent. In the dark reaction, the chemical energy is used to synthesize photosynthates (sugars) from CO₂. The dark reaction is temperature-dependent and its rate is reduced in cold conditions (Sharpe 1983). The time-scale for these two reactions is less than seconds.

The question is, how does one understand the photosynthetic efficiency representing a longer-term physiological acclimation of photosynthesis in terms of the instant photosynthetic process? One solution is to use the optimal control of gas exchange model (hereafter referred to Optimal control model) and field measurements of gas exchange (Hari and Mäkelä 2003). According to the optimal control model, a tree tends to maximize the use of intercellular water (H₂O) and carbon dioxide CO₂ for photosynthesis by optimizing the leaf gas exchange (Cowan 1982, Hari et al. 1986) (Fig. 3). Atmospheric CO₂, diffused into the stomatal cavity, is the main source of carbon for photosynthesis. Carbon dioxide derived from respiration is an additional carbon source for photosynthesis in the stomatal cavity (Hari and Mäkelä 2003). Part of the incoming water is lost in transpiration and is thus never fully used for photosynthesis. The instant photosynthesis of a Scots pine needle is proportional to the intercellular CO₂ concentration and energy fixation in the light reactions (Hari and Mäkelä 2003). The light response of the biochemical reaction of photosynthesis can be described by the light response function $f(I)$:

$$f(I) = \frac{\beta I}{I + \gamma}$$

The photosynthetic efficiency (β) represents the carboxylation efficiency in an energy fixation in the light reactions of photosynthesis, and can be associated with the maximum rate of light-saturated carbon fixation in the dark reaction (Calvin cycle). The photosynthetic efficiency can be determined by fitting the optimal control model to measurements of needle CO₂ exchange. Later Mäkelä et al. (2004) found a linear relationship between the seasonal course of photosynthetic efficiency (β) and air temperature history (T). Due to this relationship with photosynthesis, temperature history was named the “state of development of photosynthesis” (S) or “state of acclimation of photosynthesis”, in short “state of development” or “state of acclimation”.

The possibility of using air temperature for predicting the photosynthetic efficiency from spring to autumn is a major step forward in the modelling of the seasonal pattern of photosynthesis. It may enable us, for example, to estimate photosynthesis more reliably in a changed climate, when it is especially important to take into account the limitation of photosynthetic capacity (Pelkonen and Hari 1980, Bergh et al. 1998, Mäkelä et al. 2004).

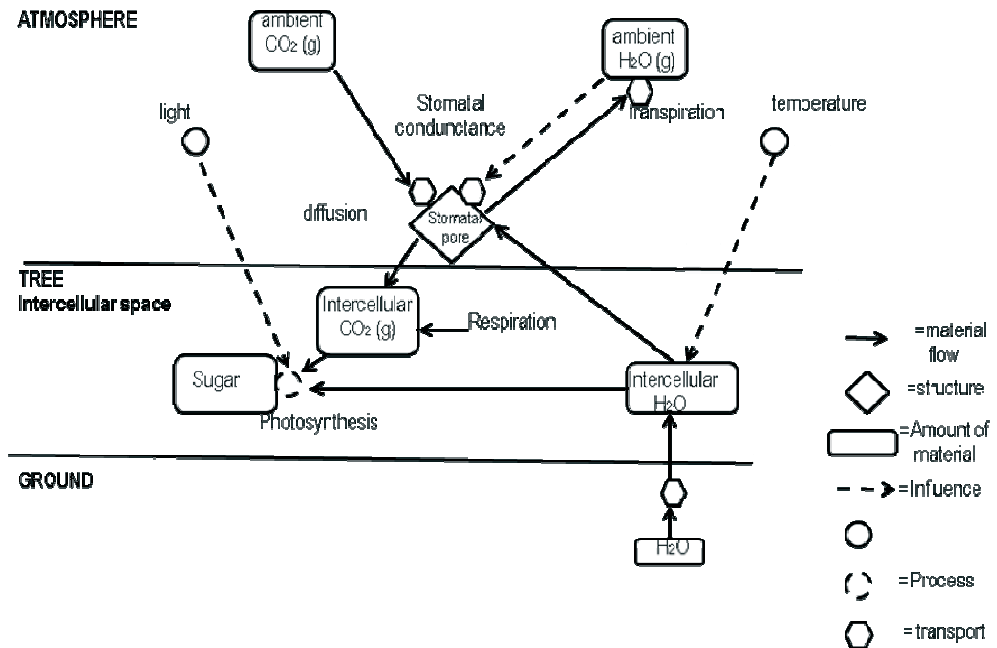


Figure 3. According to the optimal control of gas exchange theory, a tree aims to maximize the amount of carbohydrates (sugar) production per unit of water transpired (Cowan 1982). The degree of stomatal opening, affected by ambient water concentration and air temperature, controls the volume of gas exchange. The light response, which can be called as photosynthetic efficiency, is proportional to internal CO₂ concentration. In addition to the light response to intercellular CO₂, it can also be related to the air temperature history (S model) (Hari et al. 1986, Mäkelä et al. 2004).

1.2. Biogenic volatile organic compounds (BVOCs)

1.2.1. Seasonal cycle of BVOC concentrations in the atmosphere

Boreal forests are one of the major sources of BVOC emissions. Globally, emissions from boreal areas are less than those from temperate or tropical regions, but their contribution to the regional BVOC budget is significant (Guenther et al. 1995). In a boreal forest, a clear seasonal cycle of BVOCs can be detected, with high emission rates and air concentrations in early spring, a decrease in emissions in late spring and early summer, high emissions again in late summer, and a gradual decrease in autumn (Tarvainen et al. 2005, Hakola et al. 2006, Holzke et al. 2006, Ruuskanen et al. 2009). Observations of significant seasonal changes in the leaf and needle BVOC emissions have been associated with photosynthetic efficiency changes (Monson et al. 1994, Staudt et al. 1997, 1998, Yatagai et al. 1995, Yokouchi et al. 1984, Lerdau et al. 1995, Street et al. 1996). Since deciduous trees cannot maintain their photosynthesis ability during the dormancy period, the BVOC emission of deciduous trees is limited to the active period (Fig.4), while the emission from a coniferous forest is not as strictly controlled by the timing of spring phenology.

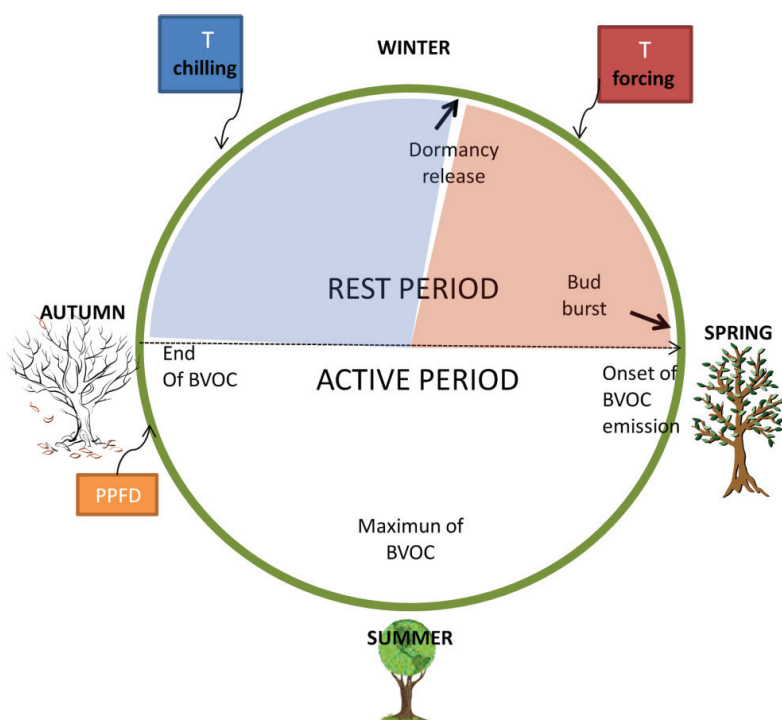


Figure 4. Schematic figure of the annual biological activity in deciduous trees. The annual cycle of biological activity is strongly driven by temperature. Dormancy is released after a critical amount of lower temperatures (chilling, blue), after which the development towards bud burst is controlled by higher temperatures (forcing, red). T = air temperature, PPFD = photosynthetically active radiation (400-700 nm).

Another aspect of the annual cycle is that the composition of emitted compounds differs between forest types. A boreal pine forest is a strong monoterpene source, but other compounds such as methanol, acetaldehyde and acetone may also show significant emission fluxes (Rinne et al. 2007). The most common tree species of boreal forests, such as *Pinus sylvestris*, *Picea abies* and *Betula pubescens*, *Betula pendula*, are strong monoterpene emitter species (Isidorov et al. 1985, Rinne et al. 2009). Norway spruce and Scots pine also emit acetone and acetaldehyde. While the deciduous tree species *Populus tremula* and *Salix* sp. are isoprene emitters (Rinne et al. 2008, Isidorov et al. 1985), *Betula pubescens* is mainly an monoterpene emitter (Janson et al. 2001, Hakola et al. 2000).

1.2.2. Biosynthesis, storage and emissions of BVOCs

The largest group of BVOCs are the isoprenoids, which are formed of five-carbon skeletons. The most simple isoprenoid is isoprene (C_5H_8). Other group of isoprenoids, e.g., monoterpenes are formed by condensation. Isoprene and the monoterpenes are synthesized in a complex processes closely related to photosynthesis (Fig. 5). The biosynthesis of terpenoids results from PEP (phosphoenolpyruvate) synthesis via glycolysis in the cytoplasm. PEP is

transported to chloroplast stroma, where further reactions with the GA-3-P (glyceraldehyde-3-phosphate) produced in the Calvin cycle take place; at the end of the biochemical reactions, the terpenoid precursors IPP (isopentenyl pyrophosphate) and DMAPP (dimethylallylpyrophosphate) are formed (Lichtenthaler 1999). Since the substrates involved in isoprene and monoterpene biosynthesis are derived from the Calvin cycle, a direct link to photosynthesis has been postulated in physiological models describing isoprene and monoterpene emissions (Niinemets et al. 1999, Niinemets et al. 2002, Bäck et al. 2005).

The BVOC emission can be either directly connected to synthesis, i.e., the so-called temporary emissions, or derives from permanent storage pools, i.e., the so-called induced emissions (Ghirardo et al. 2010). The defence-related monoterpene emissions are emitted from the resin canals of a conifer needle (Lerdau and Gray 2003) or from the glandular trichomes and epidermal glands in leaves. The monoterpene release from storage pools is induced by mechanical injury, such as timber logging (Haapanala et al. 2009 unpublished), or by herbivore attack (Gray 2008).

The short-chained oxygenated compounds (ox-VOCs) are synthesized along several different pathways. Methanol (CH_3OH) is synthesized in the ontogenic growth processes, and is mainly a by-product of pectin biosynthesis during cell-wall expansion (Fall and Benson 1996, Galbally and Kirstine 2002). Most plants emit methanol, especially during the early stages of leaf expansion (Fall and Benson 1996). Although the synthesis itself emerges from the growth processes, the driving reaction can be considered as photosynthesis. Acetaldehyde (CH_3CHO) synthesis is especially associated with different stress conditions and is produced during, e.g., light-dark transitions as a result of sunflecks, soil flooding due to anaerobic conditions, senescence and leaf wounding (Fall 2003, Graus et al. 2004). Stress factors may trigger more sporadic diurnal acetaldehyde concentration peaks throughout the annual cycle. Acetone (CH_3COCH_3) is produced in both light-dependent and -independent processes, which may be related to the decarboxylation of acetoacetate or to a cyanogenic pathway to deter herbivores (Fall 2003).

After biosynthesis, BVOC are emitted into the atmosphere in two ways: through stomatal pores and/or directly through the cuticle. The emission pathways into the air depend on the chemical character of the compound concerned. The non-water-soluble compounds, isoprene and the monoterpenes, are emitted in both ways (Guenther et al. 1991, Niinemets 2003). The ox-VOCs, methanol, acetone and acetaldehyde are more stomata-controlled, because the gas-phase concentration rises slowly and practically no emissions occur directly through the cuticle (Nemecek-Marshall et al. 1995, Niinemets 2003). Due to their water solubility, the ox-VOC emissions are primarily linked to transpiration, thus making the emissions sensitive to changes in stomatal conductance (Seco et al. 2007).

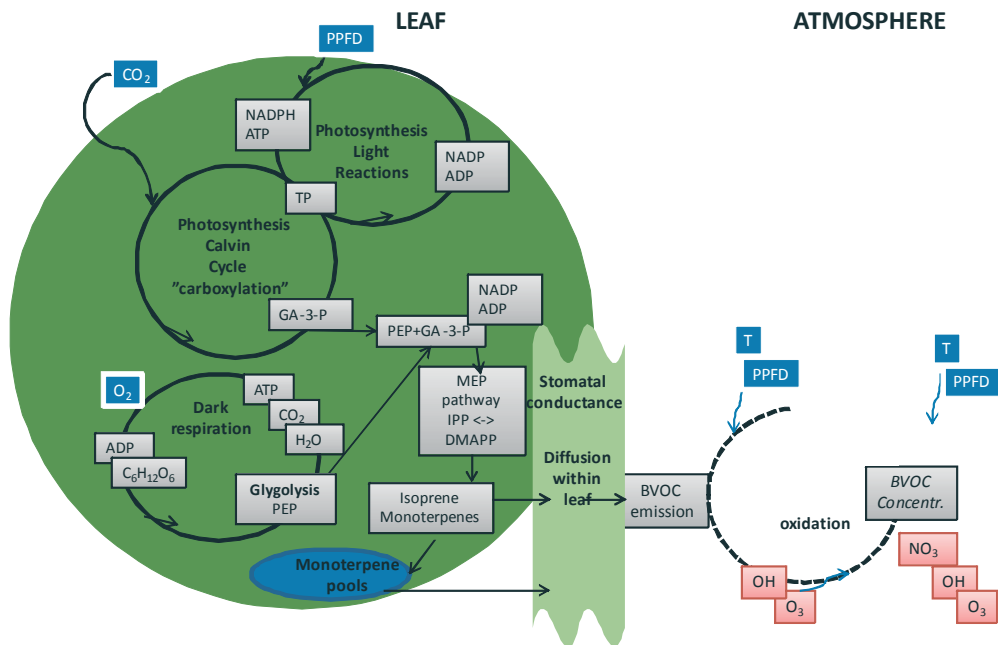


Figure 5. Schematic figure of links between photosynthesis, dark respiration, stomatal conductance and the biosynthesis of BVOCs (isoprenoids). Photosynthesis (the light reaction and the Calvin cycle in chloroplast stroma), dark respiration and stomatal conductance are the submodels of the optimum stomatal control model. (GA-3-P= glyseraldehyde-3-phosphahete, IPP= isopentenyl pyrophosphate, DMAPP = dimethylallylpyrophosphate, PEP= phosphoenolpyrvate). In the atmosphere BVOCs are oxidised by hydroxyl (OH), ozone (O₃) and nitrate radicals (NO₃). VOC are also removed from the atmosphere by deposition onto leaf surfaces, for example.

1.2.3. Atmospheric BVOC concentrations

Current knowledge about the factors determining ambient BVOC concentrations in the atmosphere is insufficient. This is partly due to the challenges met with in analytical and sampling techniques. The development of the proton transfer reaction mass spectrometer analyzer (PTR-MS) has enabled long-term measurements of VOC compounds, as well as holistic studies of the effects of changing climate and biological controls on VOC concentrations (Lindinger et al. 1998, Fall 2003). At the moment, air concentration measurements made by PTR-MS offer the longest BVOC datasets. Long-term in-situ measurements are especially important in areas like the boreal forests, which are characterized by potentially high BVOC emissions. In many cases BVOC emission measurements are made at the leaf and/or branch scale (shoot chamber technique) and then scaled up to represent canopy-emissions or atmospheric concentrations using canopy-scale models (Grote and Niinemets 2008). Long-term measurements in natural conditions are sparse in number.

Basically, the ambient BVOC concentrations inside a forest represent the emitted BVOCs of local biota affected by atmospheric chemistry and mixing. The same environmental factors drive the biosynthesis of BVOCs, their emissions and their concentrations in the atmosphere. The basic external controlling factors are temperature and light (Tingey et al. 1980, Gunther et al. 1991), but the short-term, diurnal and seasonal responses of BVOC emissions may deviate from the standard temperature and light relationship (Peñuelas and Llusia 2001). The seasonal variation of BVOC emissions, also projected to BVOC air concentrations, is regulated by the internal physiological state of the tree, such as its seasonal phenological development or photosynthetic efficiency. From the bud break to a fully-developed leaf, and later during their leaf-fall, deciduous trees undergo physiological changes. As a whole, a complex network of driving factors works in parallel to the biological source of BVOCs, as does also their atmospheric chemistry (Peñuelas and Llusia 2001).

In the atmosphere, the initial BVOC reactions in the troposphere are the chemical process of photolysis ($h\nu$) with the hydroxyl (OH) radical, nitrate (NO_3), and ozone (O_3) (Atkinson and Arey 2003). The reaction with the hydroxyl radical occurs typically during the daytime. The atmospheric lifetime of a BVOC is related to the tropospheric concentrations of OH, NO_3 , O_3 and ambient temperature (Atkinson and Arey 2003). Atmospheric lifetimes vary among BVOCs from minutes and hours (monoterpenes, isoprene) to several days (oxygenated VOCs). Due to their long atmospheric lifetime, oxygenated VOCs (methanol, acetone, acetaldehyde) may be transported long distances from the pollution sources (Atkinson 2000, Seco et al. 2007).

The long lifetimes of methanol and acetone result in a higher background concentration due to long-distance transport, whereas terpenoids are removed a few hours after their emission (Rinne et al. 2007). Methanol is a less reactive compound, with an estimated (daytime) lifetime of 69 hours in the atmosphere (Guenther et al. 1995, Fall and Benson 1996). In a boreal forest, methanol has a chemical lifetime of a few days while undergoing its daytime reaction with OH. The atmospheric lifetime of acetone is long, 8-15 days; it is lost by photolysis (45-64%) through reaction with OH (Sigh et al. 2004). The atmospheric lifetime of acetaldehyde is short, less than one day (Guenther et al. 1995). Secondary photochemical production from VOCs is thought to be the main atmospheric source of oxygenated VOCs; this is at its maximum at midday coincident with high biological activity (Seco et al. 2007). However, the low reactivity of ox-VOCs may in fact ensure that secondary photochemical production from VOCs would be of little importance (Seco et al. 2007).

Light triggers the photochemical destruction of isoprene, which reacts rapidly with OH radicals in the troposphere. The atmospheric lifetime of isoprene is only some hours (Fall and Benson 1996, Kesselmeier and Staudt 1999). The chemical lifetime of monoterpenes is from 5 minutes to 3 hrs (day) depending on the compound (Atkinson and Arey 2003).

Due to the complex emission dynamics and atmospheric chemistry involved, ambient BVOC concentrations in the atmosphere vary significantly. The biological processes and environmental triggers behind the high concentrations are hard to identify. However, presumably different internal (physiological) or external schemes (specific period of environmental conditions) could be identified. For example, short-term and prolonged drought stress periods induce different responses (Niinemets 2009). In the case of monoterpenes, BVOC emissions are even more elevated due to emissions from the storage pools (Bäck et al. 2005, Porcar-Castell et al. 2009, Ghirardo et al 2010). In a particular biological and phenological state, a tree could be especially prone to emit BVOCs. In the

atmosphere, a BVOC reacts with other compounds, resulting in an increased concentration of another BVOC. For example, Scots pine has been shown to emit methylbutenol (MBO) in mid-summer (Tarvainen et al. 2005), which could be an additional source of acetone. According to Goldstein and Scahade (2000), direct biogenic acetone emissions accounted for about 35% of acetone concentrations in *Pinus ponderosa* forest, whereas the oxidation of biogenic MBO contributed about twice as much to the acetone concentrations. The opposite process can also take place. Monoterpene concentrations, for example, can suddenly decrease in the atmosphere by chemical reactions with O₃, OH and NO₃ at high temperatures (Atkinson 2003).

The current BVOC models describe emissions and represent both empirical (Gunther et al. 2006, Niinemets et al. 2010) and process-type approaches (Zimmer et al. 2003, Bäck et al. 2005, Grote et al. 2006). Furthermore, the modelling work has so far been concentrated mainly on isoprene, whereas other biogenic emissions have received less attention.

2 AIMS OF THE STUDY

The aim of this thesis is to analyse the role of temperature in the biological activity of a boreal forest and discuss its consequences for biosphere – atmospheric interactions. The role of temperature is considered from several perspectives.

The specific aims of the thesis were:

- to determine the best temperature-based phenological model describing the onset of plant phenology events in a boreal forest (**I**)
- to analyse the relationship between temperature history and the seasonal pattern of photosynthesis on the shoot scale at two different sites, a Scots pine stand growing in the southern boreal zone and another at the timberline in the northern boreal zone (**II**)
- to analyse the relation between temperature and other environmental and biological factors on BVOC air concentrations in a boreal forest stand (**III**)
- to develop a temperature-based model predicting the air concentrations of biogenic volatile organic compounds (BVOCs) in a boreal forest stand and to study if an environmental trigger inducing BVOC emissions could also be detected in BVOC atmospheric concentrations (**IV**)
- to detect long-term trends in spring phenology in a boreal forest (**V**)

The study articles discuss the topics listed above with the different spatial, structural and temporal scales indicated below, but the emphasis is on the seasonal measurements from the southern boreal Scots pine stand (the SMEAR II station) (Table 1).

Table 1. The type of scales covered by Articles (A) **I-V**. The scales are adopted from Hari and Kulmala (2008), *x* = scale covered by the article.

A	TIME				STRUCTURE			SPATIAL		
	<hours	days	month	year	<organ	tree	stand	region	Southern boreal	Northern boreal
I		X		X	X			X	X	X
II		X	X	X			X	X	X	X
III		X	X	X			X	X	X	
IV		X	X	X			X	X	X	
V		X		X	X			X		X

3 MATERIAL AND METHODS

The data used for this work consisted of two exceptional extensive datasets: phenological recordings (**I**, **V**) and the standard and campaign measurements of SMEAR stations (Stations for measuring forest ecosystem – atmosphere relations) (**II**, **III**, **IV**) (Fig. 6) (Hari and Kulmala 2005). Articles **I** and **V** dealt with the long-term phenological datasets combined with air temperature data. Two datasets were used: the legacy Juhonsalo dataset (Articles **I**, **V**) and the phenological dataset coordinated by the Finnish Society of Sciences and Letters (Articles **I**). These two phenological datasets share a common observation method, defining the onset of each phenological event as an average observation for the site.

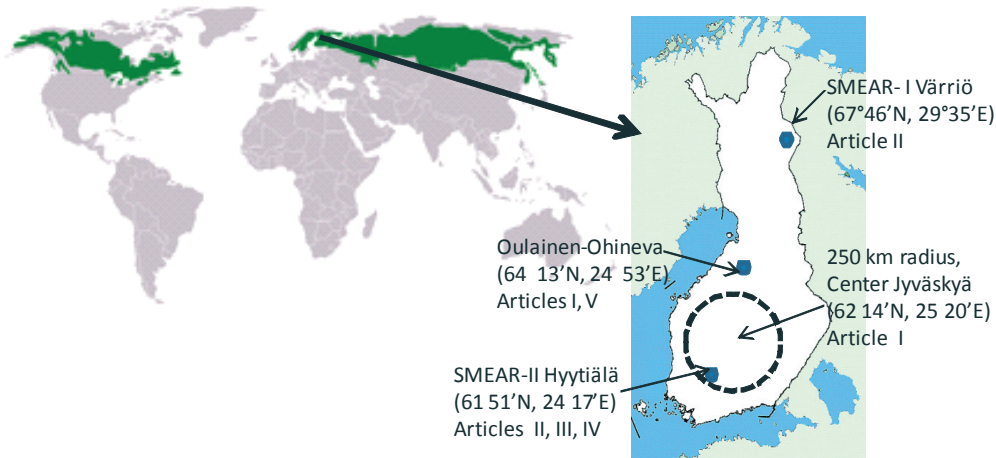


Figure 6. Locations of the datasets used in this study. The study area represents a boreal forest zone (<http://fi.wikipedia.org/wiki/>, left). Phenological data was obtained from Oulainen-Ohineva and from an area representing Central Finland. BVOC concentration measurements were obtained from the SMEAR-II (Station for Measuring Forest Ecosystem - Atmosphere Relations) at Hyttiälä, while the shoot photosynthesis data were from SMEAR-I at Värriö and SMEAR-II at Hyttiälä (map the right).

3.1. Phenological datasets and models

3.1.1. *The Juhonsalo legacy - dataset*

The Juhonsalo legacy - dataset was used for the phenological model parametrisation estimation (I). The analysis of long-term trends in spring phenology were based on this dataset (V). The Juhonsalo phenological observation site is at Oulainen-Ohineva (64°13'N, 24° 53' E, 78 m above sea level) in Northern Finland. The observation site is a 20 hectare field area surrounded by a spruce mire, representing the middle boreal vegetation zone. The Juhonsalo family started to make the spring phenological observations in 1952. The number of years of the species -specific time series varied from 4 up to 54 years. The total number of observed species was 31. The most representative time series were the onset date for the bud burst and flowering of birch (*Betula pendula*), rowan (*Sorbus aucuparia*) and bird cherry (*Prunus padus*).

3.1.2. *The Finnish Society of Sciences and Letters -dataset*

The recordings coordinated by the Finnish Society of Sciences and Letters produced phenological data for the period 1860 – 1962 on natural plant species. The observation were collected into annual year books by the society. Later, the dataset was digitized and filed into a database by the Finnish Meteorological Institute (Lappalainen and Heikinheimo 1992). Later observations of the Society, up to the year 2002 were collected and filed in co-operation with the Zoological Museum at the University of Helsinki (unpublished data); these data were used to test the models.

The dataset of the Finnish Society of Sciences and Letters represents the observations made by a number of volunteer nature observers, and the quality of the data cannot be considered as congruent as the Juhonsalo data. Changing observers affected the quality and temporal coverage of the observations. In order to improve the disjointed data, the method of calculating combined time series by Häkkinen et al. (1995) was applied for constructing the Jyväskylä time series in Article I.

3.1.3. *Phenological models*

Altogether ten temperature (T) based phenological models were tested and compared in Article I. All the models were first fitted to the Juhonsalo data and the parameter values were estimated, and then evaluated with the phenological data of the Finnish Society of Sciences and Letters. The ten studied models represented four different phenological model subgroups, as listed below A-D.

A Thermal Time models:

- Model No.1: The state of bud development is a cumulative temperature sum where the rate of bud development ($r(T)$) is described by Eq.1, and the state of bud development ($S(t)$) by Eq. 2. Parameters estimated (3):

- a critical temperature threshold for the effective temperature (T_{crit}) (Eq. 1)
- starting date of temperature sum accumulation (t_0) (Eq. 2)
- a critical temperature sum threshold for the phenological event (S_{crit}) (Eq. 2)

Rate of bud development $r(T)$ (Eq. 1):

$$r(T) = \begin{cases} T - T_{crit} & , T \geq T_{crit} \\ 0 & , T < T_{crit} \end{cases}$$

State of bud development $S(t)$ (Eq.2) :

$$S(t) = \int_{t_0}^t r(T) dt \approx \sum_{t_0}^t (r(T) \cdot \Delta t)$$

- Model No.2: The rate of ontogenetic development, $r(T)$, was based on empirically-determined values (Sarvas 1972). The state of ontogenic development was determined by Eq.2. Parameters estimated (2):
 - starting date of temperature sum accumulation (t_0) (Eq. 2)
 - critical temperature sum threshold for the phenological event (S_{crit}) (Eq. 2)
- Model No.3: Identical to Model No-2, except that a fixed starting date (January 1) was used. Parameters estimated (1):
 - critical temperature sum threshold for the phenological event (S_{crit})

B Sequential models:

- Model No.4: The rate of chill sum accumulation was based on tabulated values (Sarvas 1972, 1974). The onset of a “forcing” part of the sequential model is triggered after a sufficient accumulation of chilling temperatures (C_{crit}) has taken place. Also the rate of ontogenetic bud development ($r(T)$) in the “forcing” phase was based on an empirical function (Sarvas 1972) (same as for Model No-2). Parameters estimated (3):
 - chill sum accumulation starting date (t_0)
 - critical chill sum to trigger ontogenic development (C_{crit})
 - critical temperature sum threshold for the phenological event (S_{crit})
- Model No.5: Eq.3 was used for the rate of chilling and Eq.4 for the rate of ontogenic development (forcing) (Hänninen 1990, Kramer 1994a). The onset of a “forcing” part of the sequential model starts when a sufficient accumulation of chilling temperatures (C_{crit}) has taken place. The state of chilling and state of bud development was determined by Eq. 2. Parameters estimated (7):
 - chill sum accumulation starting date (t_0) (similar to Eq.2)
 - min., max., optimum temperature threshold for rate of chilling (T_{min}), (T_{max}), (T_{opt})
 - critical chill sum to trigger ontogenic development (C_{crit}) (similar to Eq. 2)
 - budburst threshold model constants b and c in Eq. 4
 - critical temperature sum threshold for the phenological event (S_{crit}) (Eq. 2)

Rate of chilling (inhibition) $r(T)$ (Eq.3):

$$r_{cs}(T) = \begin{cases} \frac{T-T_{Min}}{T_{Opt}-T_{Min}} & , T_{Min} \leq T < T_{Opt} \\ \frac{T_{Max}-T}{T_{Max}-T_{Opt}} & , T_{Opt} \leq T \leq T_{Max} \\ 0 & , T < T_{Min} \quad T > T_{Max} \end{cases}$$

Rate of temperature sum accumulation (forcing) $r_{ts}(T)$ (Eq. 4):

$$r_{ts}(T) = \frac{27}{1 + e^{-b*(T-c)}}$$

C Parallel models:

Model No.6: The critical temperature sum threshold for triggering budburst depends on the number of accumulated chilling days as formulated in Eq. 5 (Cannel and Smith 1983). Eq. 1 was used for the rate of ontogenetic bud development $r(T)$ and Eq. 2. for the state of development. Parameters estimated (5):

- starting date of chill sum accumulation (t_{c0})
- chill sum accumulation starting date model constants a, b, c (Eq.5)
- critical temperature sum threshold for the phenological event (S_{crit}) (Eq. 5)

The effect of the number of chilling days (n) on the critical temperature sum threshold required (S_{crit}) to trigger the bud burst (Eq. 5):

$$S_{crit}(t) = a + b \cdot e^{-n \cdot c(t)}$$

Model No.7: Identical to Model no.6 with fixed starting dates of chilling ($t_{c0} = \text{Nov 1}$) and forcing (Feb 1) . Parameters estimated (3):

- model parameters a, b, c (Eq.5)

D Flexible models:

Model No.8: A Promoter-Inhibitor model (Schaber and Badeck 2003) where the stage of inhibition (“chilling”) (Eq. 7) and the stage of promotion (“forcing”) (Eq. 8) depend on ambient temperature, day length and stage of inhibition. The rate of inhibition and promotion follows basically the same temperature function format as Eq. 3. Parameters estimated (10):

- rate of chilling: minimum temperature threshold for rate of chilling (T_{min}), rate of chilling (T_{opt}), maximum temperature threshold for rate of chilling (T_{max}) (similar to Eq. 3)
- rate of forcing: minimum temperature threshold for rate of forcing (T_{min}), rate of forcing (T_{opt}), maximum temperature threshold for rate of forcing (T_{max}) (similar to Eq. 3).
- rate constants: a_2, a_3, a_4 in Eq. 7, 8.
- phenological event (S_{crit}) takes place when the promotion (P) = 1

State of inhibition (I) (Eq. 7):

$$\Delta I = a_2 \cdot f_2(T) \cdot I$$

State of promotion (P) (Eq. 8):

$$\Delta P = a_3 \cdot f_3(T) \cdot (1 - I) - a_4 \cdot P \cdot \frac{24 - L}{24},$$

Model No.9: Unified model (Chuine 2000), where the state of chilling is described similar to Eq. 2., the rate of chilling as Eq.3 and the rate of forcing as Eq. 4 (using the value of "28.4" instead of "27" as Kramer used). The state where the critical date for bud burst is attained is described by Eq. 9, where the temperature sum threshold for budburst is affected by accumulated chilling (C_{tot}). Parameters estimated (10):

- chill sum starting date (t_0)
- critical threshold for dormancy release (C_{crit})
- max amount of chilling days for dormancy release (t)
- rate of dormancy release temperature parameters (c_c, a_c, b_c) (Eq. 3)
- budburst temperature parameters (B_f, C_f) of the forcing rate function (Eq. 4)
- model parameters (w, k) of the critical threshold for budburst (Eq. 9)

Critical threshold for budburst (F) (Eq. 9):

$$F^* = w e^{k C_{tot}}$$

Model No.10: Model No-9 with a fixed chill sum date (t_0). Parameters estimated (9): as in the list above, except t_0 .

The model comparisons and evaluation were based on the analysis of internal and external RMSEs (square root of the mean of the squared errors). The internal RSME refers to the RMSE analysis of the parameter estimation, where the data from the Oulainen Ohineva site were used (the Juhonsalo legacy - dataset).

The evaluation of how well the model can predict the phenological event was made by analysing the external RMSE of test data (the Finnish Society of Sciences and Letters dataset from Central Finland). In order to separate the error originating from the model structure in the external RMSE, the so-called systematic part of the external RMSE (hereafter referred to as the systematic RMSE) was calculated. The systematic RMSE was determined by fitting a phenological model to test data. The systematic RMSE represented the best fit to test data.

3.2. SMEAR stations' measurements

3.2.1. Description of the site

The measurements used in Articles **II**, **III** and **IV** were performed at two field stations with the acronym SMEAR “Station for Measuring Forest Ecosystem - Atmosphere Relations”. SMEAR -stations are designed to study material and energy flows in the atmosphere - vegetation - soil - continuum at different temporal and spatial scales. The stations can be characterized as versatile and automatic units operating in a continuous and long-term manner to solve cross-disciplinary environmental problems involving physics, chemistry and biology. SMEAR-I is located at Värriö (67°46'N, 29°35'E) in Finnish Lapland, near the timberline 400 metres above sea level. SMEAR-II is situated at Hyytiälä (61°51'N, 24°17'E), in Southern Finland, 180 metres above sea level. Both sites are dominated by homogeneous 40-50-year old Scots pine stands, but at Värriö the stand has a clearly arctic character (Hari et al. 1994). SMEAR-stations are state-of-the-art infrastructures making automatic measurements on the atmosphere, vegetation and soil (Hari et al. 1999, Hari and Kulmala 2005).

3.2.2. Measurements

This study utilized the existing dataset collected at the SMEAR I and II stations, where meteorological data were also obtained from standard half-hourly micrometeorological measurements (Table 2). For the purposes of this study (**III**, **IV**) the standard meteorological measurements were averaged to represent the daily and daytime averages and medians.

Table 2. List and description of the standard, continuous measurements used in the study. I= SMEAR I Värriö site, II= SMEAR II Hyytiälä site.

variable	measurement method of raw data	I	II	articles
Temperature [°C]	<ul style="list-style-type: none"> standard half-hourly meteorological measurements measured at 8.4 m, soil 	x	x	III, IV
wind speed [m/s] direction [degree]	<ul style="list-style-type: none"> ultrasonic anemometer ref. Vesala et al. 1998 		x	III
precipitation [mm]	<ul style="list-style-type: none"> sampled with bottles and buckets 			
photosynthetically active photon flux density (PPFD 400-700 nm) [$\mu\text{mol m}^{-2} \text{d}^{-1}$]	<ul style="list-style-type: none"> thermistor and quantum sensor 	x	x	II, III, IV
O ₃ air concentr.[ppbv]	<ul style="list-style-type: none"> ultraviolet light absorption analyser 		x	IV
Net Ecosystem Exchange (NEE) [$\mu\text{mol m}^{-2} \text{d}^{-1}$]	<ul style="list-style-type: none"> eddy covariance method (sonic anemometer with gas analyzer Solent) average data over 30 min. 		x	III
Gross Primary Production	<ul style="list-style-type: none"> obtained from the equation: TER-NEE=GPP when the measured night-time net ecosystem exchange of CO₂ 		X	III

(GPP) [$\mu\text{mol m}^{-2} \text{d}^{-1}$]	(NEE) was missing, GPP was directly estimated as a saturating function of PPFD. <ul style="list-style-type: none"> data provider P. Kolari 			
Total Ecosystem Respiration (TER) [$\mu\text{mol m}^{-2} \text{d}^{-1}$]	<ul style="list-style-type: none"> TER obtained from NEE and extrapolated to cover the daytime using a temperature regression on organic layer temperature (Kolari et al. 2009) data provider P. Kolari 		X	III

Campaign datasets

Several specific datasets of BVOC concentrations, soil water content and different growth and photosynthesis measurements of Scots pine were used (Table 3). The campaign datasets were modified to represent daily averages, but in the case of BVOC measurements the raw data was further revised for the purposes of this study. In order to make the BVOC dataset representative of the postulated maximum emissions, the day-time medians of the BVOC concentrations were used. The time windows specified for each season represented the time when the sun is high enough to cause atmospheric mixing (Rinne et al. 2005). Furthermore, the daytime observations represented the gas exchange from stomata to air rather than the BVOC deposition to leaves, which may occur during the night. The number of observations varied between seasons due to temporary failures of the measurement system. Although different biogenic sources (trees, ground vegetation, soil) could not be distinguished, wind direction analyses were used to verify that most of the concentrations would represent the local forest.

In Article **II** the shoot CO_2 gas exchange chamber measurements from the SMEAR I and II stations during the years 1999-2005 were utilized. The daily shoot-scale photosynthetic efficiency was estimated by fitting the model to the measured CO_2 exchange while keeping the other model parameters fixed. The quality check of the raw data was done by investigating the daily CO_2 flux profiles during chamber closure. Non-representative measurement data were filtered out before the model fitting.

Table 3. List of the specific campaign datasets used in the study. I= SMEAR-I Värriö site, II= SMEAR-II Hyytiälä site.

Dataset	Raw data description and data providers	I	II	Articles
BVOCs air concentrations [ppbv] in pine forest stand	<ul style="list-style-type: none"> measured masses (M): M33 (refers to methanol), M45 (acetaldehyde), M59 (acetone), M69 (isoprene, MBO), M137 (monoterpene) measurement height upper canopy level, 14 metre height method: PTR-MS analysis samplings: ambient BVOC concentration measured every second or third hour by taking 15-25 samples per hour. campaigns: June 6, 2006 - August 31, 2008 and June 1, 2008- August 31, 2008. data provider: Rinne, Ruuskanen, Taipale, Kajos 		x	III, IV
daily shoot growth daily needle growth [mm/d] in Scots pine	<ul style="list-style-type: none"> on four trees, at four heights in the mornings (9:00 a.m.) at least twice a week, marked main and lateral shoots campaign: shoots May 21 - June 11, needles June 12 - August 8 in 2007. data provider: Korhonen 		x	III
secondary growth [mm/d] in Scots pine stems	<ul style="list-style-type: none"> four representatives of the dominant pine trees, stem diameter recorded at a frequency of once per min method: using linear displacement transducers (LVDT) attached on rectangular steel frames mounted around the stems at about 2 m height. campaign: May 1 - October 31, 2006. data provider: Sevanto 		x	III
soil water content [mm/d]	<ul style="list-style-type: none"> measurements: several locations and depths method: time domain reflectometry (TDR) campaign: summer 2006 data provider: Sevanto (Pumpanen, J. and Ilvesniemi, H. 2005) 		x	III (drought period)
shoot photosynthesis [$\text{CO}_2 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$] in Scots pine	<ul style="list-style-type: none"> the measured shoots located at the top of the canopy, shoots accommodated one age class of needles. method: shoot CO_2, H_2O gas exchange chamber measurements, temperature 70-180 times per day. campaigns: 1999, 2001-2005 for Värriö, 1999-2005 for Hyytiälä data provider: Kolari, ref. Article II 	x	x	II

3.2.3. State of development (S) model

The State of development (S) model by Mäkelä et al. (2004) was tested, and the relation between photosynthetic efficiency β and (S) was refined with the Scots pine shoot photosynthesis measurements at two different locations, Värriö (Lapland) and Hyytiälä (Southern Finland) in Article II. For the internal stage of the photosynthetic machinery in boreal evergreen conifers, the State of development (S) model uses the photosynthetic efficiency (Pelkonen and Hari 1980). The efficiency parameter (β) is part of the function

representing the light response $f(I)$ of the biochemical reactions, where γ ($\mu\text{mol m}^{-2} \text{s}^{-1}$) is a parameter describing the shape of the light response of the photosynthetic biochemistry, and the photosynthetic efficiency β (m s^{-1}) reflects the state of the photosynthetic functional substances (pigments, enzymes, or membrane pumps). The relationship between β and the state of development (S , “the temperature history”), can be calculated by using the optimum stomatal control model and the S model together with field measurements (Fig. 7). Using the optimum stomatal control model and the measured CO_2 exchange data and PPF, the seasonal course of the key photosynthetic parameters can be derived, and the temperature dependence can be studied. Day-time respiration was estimated from the measurements of night-time CO_2 exchange.

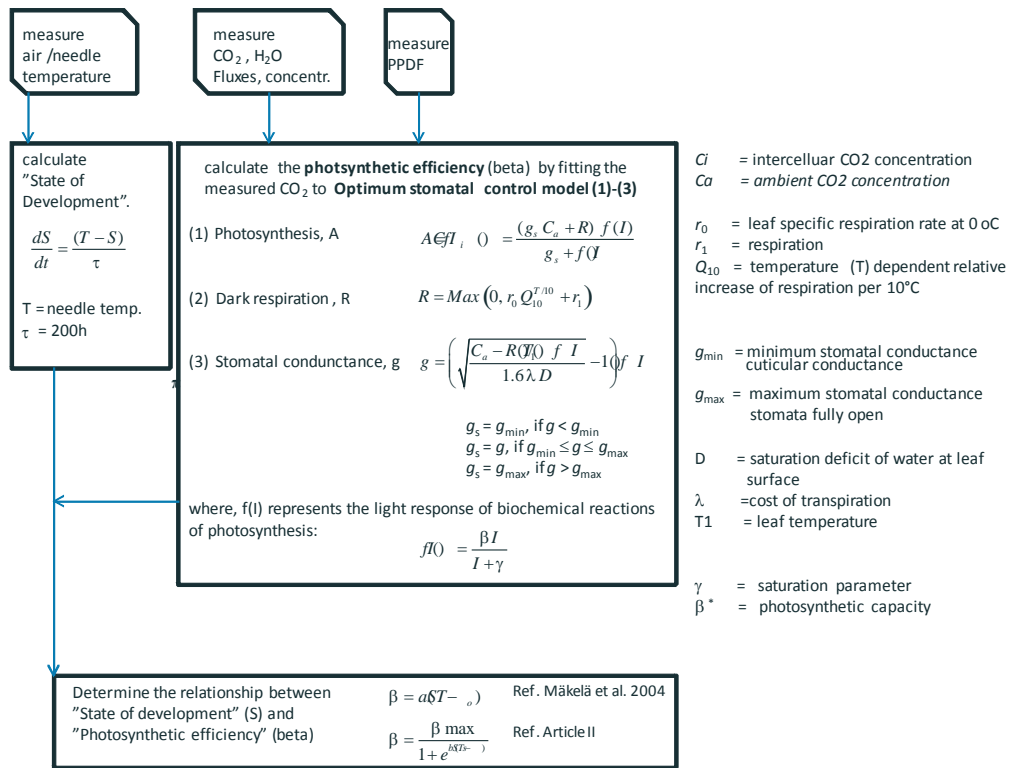


Figure 7. The flow chart for how to determine the relationship between the “State of development” (S) and the “Photosynthetic efficiency” (β). First the measurement of the hourly air temperature, CO_2 and H_2O fluxes and concentrations and light (PPFD) are used for the determination of daily photosynthetic efficiency (beta). Assigning the major part of the parameters of the optimal stomatal control model fixed, the day-to-day variation of alfa, beta and gamma are estimated by fitting the model to the data. Then the temperature history is calculated based on ambient temperature data. The relation between beta and temperature history is determined.

3.2.4. BVOC models

One of the main focuses of the work was on the analysis and modelling of the BVOC concentration data in Articles **III** and **IV**. The applicability of the S model to predict BVOC air concentrations was also analysed in Article **IV**.

BVOC concentration models were tested and developed in Article **III** and **IV**. The first model was an exponential temperature model (T-model) where the day-time median BVOC concentration, y , (in ppbv) was represented as an exponential function of the daytime median air temperature (Eq. 1 in Table 4), where a and b are the parameters fitted using the 2006-2007 dataset.

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 variable, S , (Mäkelä et al. 2004) (Table 4., Eq.2). Here the approach by Gray et al. (2006), where the basal emission rate depends on the temperature history, was followed. In the T-S model, the temperature part was identical to that of the T-model (Eq. 1 in Table 4), with the state-of-development (S) included in the model as an additional exponential term. In a boreal forest, the parameter S , the state-of -development, formulated by Makelä et al. (2004), followed the ambient temperature (T °C) in a delayed manner with a time constant of 200 h.

The third model was a trigger model, which responded to relatively high ozone and PPFD, and aimed at improving the performance of the T-S model (Eq. 2) for peak concentrations (Fig. 8). With the ozone concentrations > 40 ppb and relative PPFD > 0.015 , the T-S model is stressed (see Table 4, Eq. 3). All the models were first fit to the 2006-2007 dataset, with the model parameters (a , b , c , f) being determined based on residual analysis (minimum sum of residuals). The models were then tested with the dataset collected in summer 2008.

Table 4. *The basic equations and factors of the BVOC concentration models.*

BVOC Model type	Equation	Factors	Articles
T-model Eq. 1	$y_1 = ae^{bT}$	T =day-time mean temperature (C°) a, b parameters	III, IV
T-S-model Eq.2	$y_2 = ae^{bT} + ce^{fS}$	T= day-time mean temperature (C°) S = state of development (C°) a, b = parameters	IV
Trigger model Eq.3	$q=(1+A+B)y_2$	A, B parameters for T-S model	IV

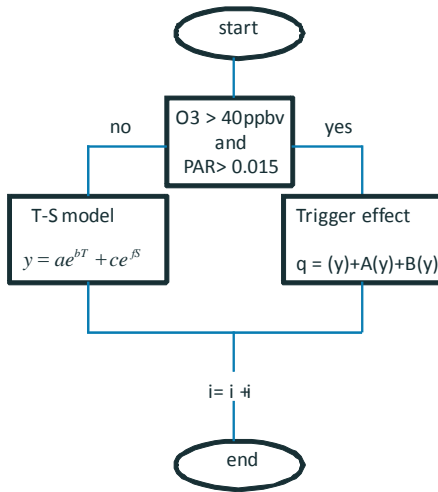


Figure 8. The flow chart of the Trigger model (Article IV). The T-S model was run for each day except for days when O_3 and PFD were over their threshold values. For days when O_3 and PFD are above their threshold values, the T-S model is weighted.

4 RESULTS

4.1. Role of temperature

4.1.1. Phenological modelling

In Article I parameter values for ten different phenological models were estimated and then compared to each other. Temperature was the primary driver in all the models studied. The essential aspect of the model comparison was the possibility to use separate datasets for model estimation and evaluation. The use of separate test data better indicated the performance of the phenological models.

Considering the ten studied models, the simplest, the Thermal Time (TT) type model, had only one estimated parameter, while the most complicated model, Promoter-Inhibitor model, had ten. When comparing the external RMSE values of the Jyväskylä datasets between the models the Thermal Time model had the smallest RMSE values: 3.4 for 1896 to 1952 and 3.1 for 1953 to 2002 (Table 5). The most complicated models (the Promoter-Inhibitor and the Unified model) fit the Oulainen dataset well, and had the lowest internal RMSE values. However, when tested with the Jyväskylä data, the external RMSE values were the largest compared to the other models.

In Article I it is argued that these complicated models were over-parameterized and fit the random noise in the data, losing the real features of plant phenological control. In a boreal forest, the thermal time approach provides an easily accessible practical tool, and the estimated parameter values are valid over large areas of the forest, in this case, that in central Finland.

Table 5. Internal and external values of the square root of the mean of the squared errors (RMSE, days) of the phenological models in predicting *Betula* bud burst. The internal RMSE represents the best fit of the parametrised models, the external RMSE represents the evaluation of the model for test data, while the systematic RMSE represents the systematic part of the external RMSE describing the ability of the model to adjust to variations in the data (modified from Article I).

Phenological Model	Oulainen-Ohineva data 1952-2002	Jyväskylä test data 1896 to 1952		Jyväskylä test data 1953 to 2002	
	RMSE internal	RMSE external	RMSE systematic	RMSE external	RMSE systematic
1) Thermal Time model *parametrized threshold	2.5	3.4	2.2	3.4	3.2
2) Thermal Time model, *Sarvas -rate function	2.4	3.6	2.3	3.4	3.2
3) Thermal Time model, *fixed start date	2.8	4.1	2.7	3.1	2.8
4) Sequential model	4.0	5.5	4.1	4.2	3.9
5) Sequential model, *parametrized functions	2.6	4.5	2.7	4.3	3.5
6) Parallel model	2.3	3.7	2.3	3.8	3.5
7) Parallel model, *fixed starting dates	2.4	4.1	2.6	3.9	3.5
8) Promoter-Inhibitor model	2.3	9.9	2.2	6.9	3.1
9) Unified model	3.2	4.7	3.1	8.5	3.9
10) Unified model, *parametrized starting date	2.0	3.5	2.0	3.7	2.8

4.1.2. Photosynthetic efficiency

In Article II the relationship between the photosynthetic efficiency (β) and the theoretical state-of-development of photosynthesis (S) were tested, and comparisons of multi-annual time series of shoot gas exchange measured under different climatic regimes along with meteorological measurements were performed.

The relationship between temperature history and the seasonal pattern of photosynthetic efficiency in Scots pine at both the southern (Hyytiälä) and northern boreal sites (Värriö) were investigated. The S model (Pelkonen and Hari 1980, Mäkelä et al. 2004) was validated as a modelling tool describing the photosynthetic efficiency over a wide range of boreal forest. The development of photosynthetic efficiency followed very closely the seasonal course of the ambient temperature history as indicated by S (Fig. 9). This was demonstrated by comparing the annual course of photosynthetic efficiency (β), estimated from the chamber measurements, with the state of development (S) derived from the ambient temperature. The same result was obtained at both Värriö and Hyytiälä; thus, the seasonal pattern of photosynthetic efficiency in the southern boreal zone as well as at the northern boreal timberline consistently followed the state of acclimation derived from the air temperature history.

The other important observation was that the differences in the observed relationships between photosynthetic efficiency and state of development (S) were small between the southern and the northern trees. In the temperature range between 0°C and 10°C, the

photosynthetic efficiency was almost linearly related to the state of development, i.e., a variable describing the ambient temperature history. Overall the relationship between the state of development (S) and photosynthetic efficiency was sigmoid. A rapid temperature response of photosynthetic efficiency could be observed at temperatures around zero. The difference in the rate of development between the north and the south was small, and the recovery of photosynthetic development in trees growing at their native sites did not indicate a noticeable difference between north and south. However, during warm spells (summer) the photosynthetic efficiency in Lapland continued to increase with increasing temperature, whereas in southern Finland the temperature response of photosynthetic efficiency saturated.

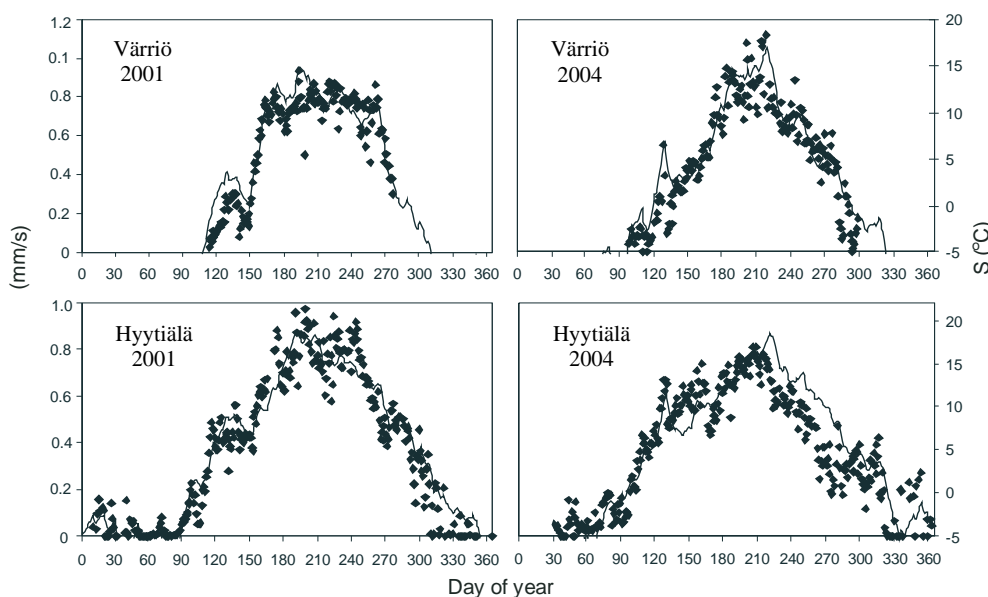


Figure 9. The annual course of photosynthetic efficiency (β) (left axis) estimated from the chamber measurements, and state of development (S) (right axis) derived from the ambient temperature at Värriö in 2001 and 2004, and at Hyttiälä in 2001 and 2004. The time constant τ in the calculation of S was 200 h (Dots indicate the photosynthetic efficiency, S is indicated with a line) (Figure adapted from Article **II**).

4.1.3. Atmospheric BVOC daytime concentrations

In works **I** and **II** the central role of temperature in driving the biological activity of boreal forest trees was examined. It was shown that temperature-based formulations can capture the phenological development and photosynthetic efficiency. The BVOC air concentrations were analyzed and the first attempts at modelling the concentrations were undertaken (**III**). In this task the results of **I** and **II** were taken into consideration. It was postulated that, despite the myriad BVOC atmospheric chemistry interactions, the concentrations in a boreal forest can be represented by a function of temperature and proxies of biological activity.

The major results of the analysis of the BVOC daytime air concentration time series inside a boreal forest stand (Fig. 10) were 1) phenological events and other biological activity proxies can be associated with the high concentrations of BVOCs, 2) BVOC daytime concentrations are inter-correlated, 3) a seasonal progress of BVOC daytime concentrations can be detected and 4) all the studied BVOC concentrations were best correlated with daytime median air temperature.

In Article **III**, the secondary growth of stem (summer 2006 data), shoot and needle growth (spring, summer 2007 data) were compared to BVOC concentrations. Especially, the methanol concentration variation and growth were associated with the growth measurements of Scots pine. Furthermore, springtime concentrations peaks were associated with the timing of bud burst. Since no phenological data of the timing of bud burst was available from Hyytiälä, the BVOC concentration peaks were compared with the average dates of bud burst obtained from statistics (Lappalainen and Heikinheimo 1992); the Thermal Time model was also applied.

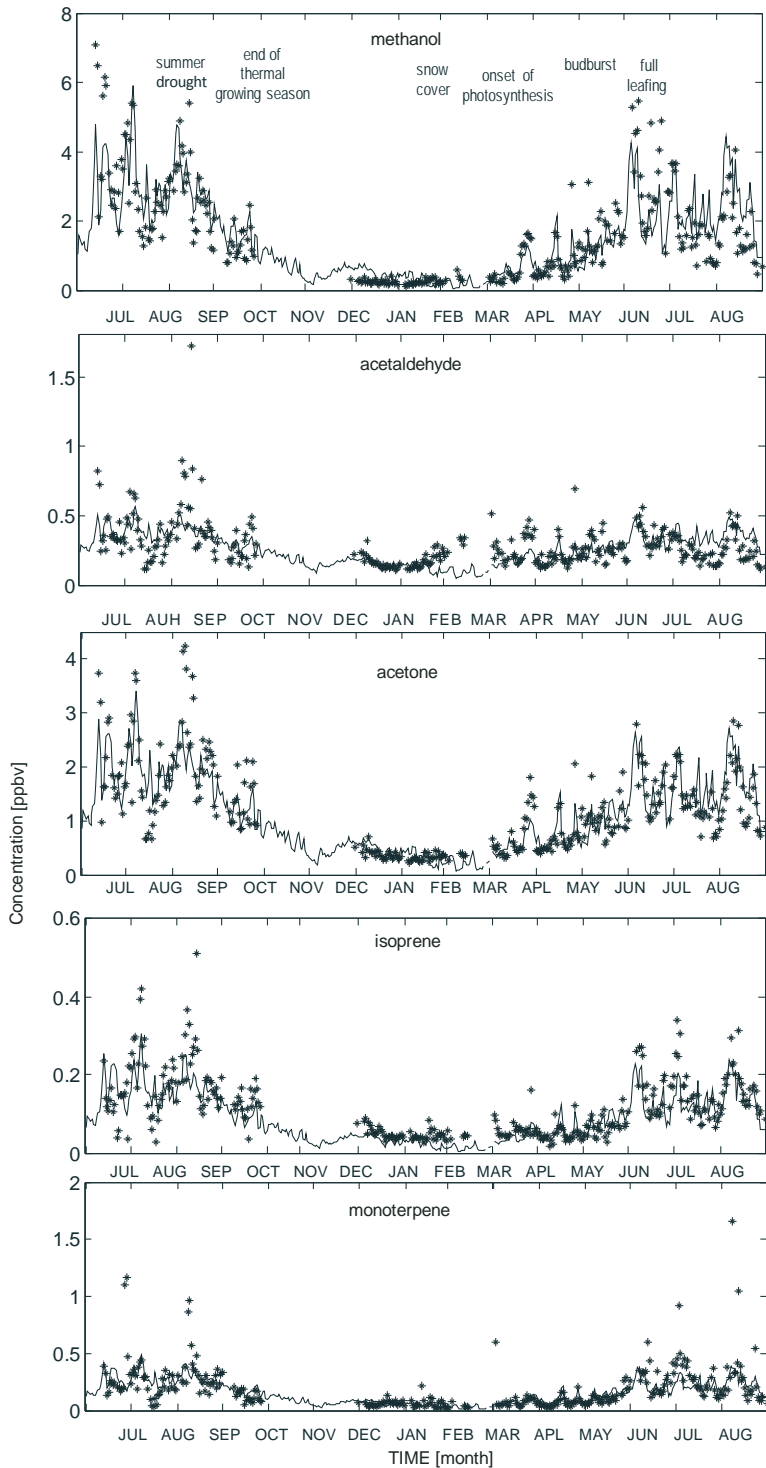


Figure 10. Day-time medians (crosses) of BVOCs and temperature model (line), time period June 2006 – May 2007 from the SMEAR-II station, Hyytiälä (modified from Articles III, IV).

The concentrations of the compounds were significantly correlated with each other. The peak concentrations occurred simultaneously for all compounds, except for the monoterpenes in June 2006. This happened even though the biological processes synthesizing the various BVOCs are different. The highest correlation was between methanol and acetone (0.91). The acetone concentration was also well-correlated with the concentrations of the other compounds. The correlations of monoterpene concentrations with other compounds were lowest (Article **III**).

All the compounds except acetaldehyde showed clear seasonal differences in the monthly daytime median concentrations. The concentrations had a minimum in the winter and a maximum in summer. Acetaldehyde concentrations were almost independent of the season (Article **III**).

The major part of the variation in the BVOC daytime concentrations was best explained by an exponential function depending only on air temperature. The addition of a new explanatory variable, the state of development (S), to the T model improved the model slightly. This use of S, the theoretical state-of-development-of photosynthesis, was based on the knowledge that in boreal evergreen species, seasonal changes in photosynthetic activity are pronounced (Article **IV**).

Occasional high BVOC concentrations could be explained either by direct environmental triggers or by environmental triggers changing the internal response of the plant. In order to explain the pronounced concentrations' variation, especially the high daily concentrations' values, the T-S model was modified to include environmental triggers that could increase the concentrations momentarily (Article **IV**). Of the studied triggers that improved the model most were a high ozone concentration and a high photosynthetically active photon flux density (PPDF) compared to the seasonally available radiation. The Trigger model described the peak concentrations somewhat better than the T or T-S model, i.e., the level of explanation was slightly improved with the trigger model explaining 30-71 % of the total variation (Fig. 11). The trigger coefficients of the Trigger model describing the effect of ozone were positive in all the studied compounds, indicating a positive correlation between BVOCs and an ozone concentration over 40 ppb.

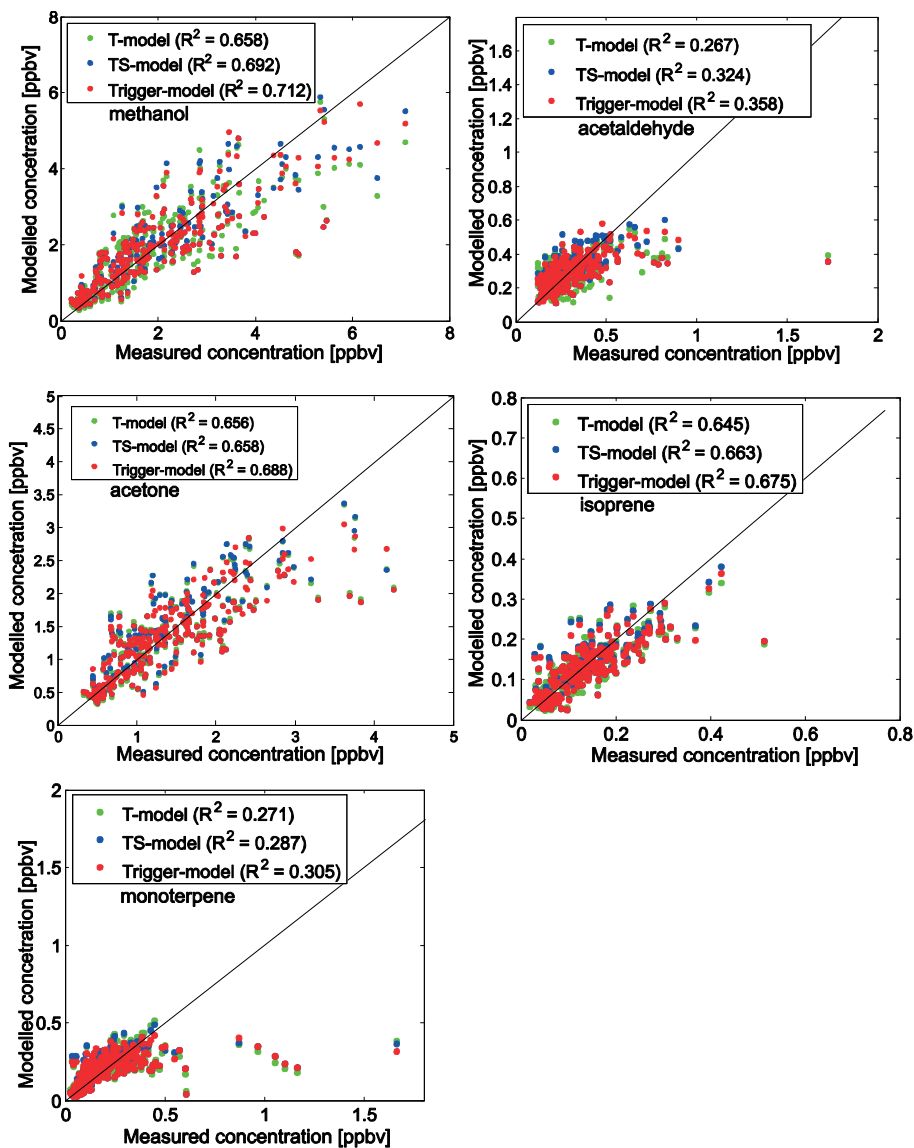


Figure 11. The modelled (T-model $y = ae^{bT}$ green, TS-model $y = ae^{bT} + ce^{fS}$ blue, Trigger model red) versus observed daytime BVOC concentrations from the dependent dataset 2006-2007 at the SMEAR-II station (Article IV).

4.2. Long-term trends in spring phenology

In Article V the onset of spring phenology and the long-term trends of 31 species at the Oulainen-Ohineva site ($64^{\circ}13'N$, $24^{\circ}53'E$) in Central Finland were analyzed. The species studied represented a wide range including deciduous trees, shrubs, grasses, 18 species of migratory birds and six insect species. The duration of the species-specific time series varied from 4 years up to 54 years during the observation period of 1952-2005. Statistically significant advancing trend in the timing of spring phenology was only found for five

species, but not, however, for the tree species studied. The highest advancement trend was observed for bird cherry (*Prunus padus*) with 7 days per 45 years, whereas for birch (*Betula* spp.) the corresponding value was only 1 day in 53 years of observations.

5 DISCUSSION

5.1 Temperature as the main driving factor in a boreal forest

This study focused on the role of temperature as a driving factor for the various different biological processes in a boreal forest. The role of temperature was considered from different perspectives and on different spatial and temporal scales over the area of Finland. The results were based on phenological and SMEAR station datasets that were exceptional in terms of volume, length and quality. The crucial part of this study was based on the BVOC concentration data, which represents one of the longest existing in-situ concentration datasets (Holzinger et al. 2006).

An optimal balance in the timing of the active growth and rest periods is essential for the survival of boreal trees. Their seasonal activity is a result of long-term adaptation (Kramer 1994, Hänninen 1995, Linkosalo et al. 2000) to a high seasonal temperature range of up to 60°C (Drebs et al. 2002). The genetic adaptation of trees to temperature conditions so as to optimize the time of onset of growth in spring is the ultimate process controlling their seasonal activity. The role of temperature as the main driving factor behind the onset of bud burst in a boreal forest has been incorporated into the phenological model approach (Sarvas 1972, 1974; Cannell and Smith 1983, Hänninen 1990). The phenological model comparison of this study (Article I) showed that the Thermal Time model provides the best prediction accuracy for the timing of budburst in current climate conditions. Proper timing of the release of frost resistance is also critical for maximizing photosynthetic production, which is also significantly controlled by temperature. The sigmoid relationship between temperature history and the seasonal pattern of photosynthesis history was demonstrated in both the southern and the northern boreal pine forests (Article II), which consolidates earlier results (Mäkelä et al. 2004) on the connection between temperature history and photosynthetic capacity.

In this study, the major part of the BVOC daytime concentration variation was also described by an exponential function depending only on air temperature (Articles II, III, IV). However, an analysis of the role temperature plays in BVOCs processes is more complex compared to that for the annual cycle and photosynthetic efficiency. Although the result is in line with BVOC emission rates, which increase exponentially with increasing temperature (Guenther et al. 1995, Filella et al. 2007), the ambivalence of the effects of atmospheric chemistry on BVOC air concentrations remains. In principle, the BVOC air concentrations in a boreal forest are the end result of the BVOC emissions affected by atmospheric chemistry (Atkinson and Arey 2003). At the present time, measurements of atmospheric BVOC concentrations made by proton transfer reaction mass spectrometry offer the longest datasets of BVOCs, and are the only data available for studying the seasonal variation of BVOCs. The measurement setup can be directly installed to represent forest-scale concentrations (Ruuskanen et al. 2009, Taipale et al. 2008), but the ambient BVOC concentrations in a forest represent a situation where the emitted BVOCs of local biota are affected by atmospheric chemistry. As long as atmospheric mixing is high and the measurements are made at the top canopy level (Rinne et al. 2009), and anthropogenic sources can be excluded, understanding the behaviour of daytime BVOC concentrations could be based on BVOC

emission biology. In this study, the atmospheric BVOC concentrations were considered and modelled from the biogenic source perspective. The main aim was to connect the BVOC concentrations of five simultaneously- measured compounds to their biogenic source, the tree emissions. Parallel in-situ measurements of BVOC emissions and air concentrations were lacking in this study, but by using daytime concentration measurements near the biological source, inside the forest, the link between emission and concentration was maximized. The overall representative value of the concentrations was considered as further justified when the daytime concentrations were found to be highly inter-correlated (Schade and Goldstein, 2005). Furthermore, the seasonal progress of BVOC daytime concentrations showed a similar behaviour to that of biological activity (photosynthesis) (Article III).

Despite the fact that atmospheric chemistry complicates the explanation of atmospheric BVOC concentrations, the study showed that the signal of photosynthetic efficiency can be detected in a pine forest. The BVOC model was improved by adding a photosynthetic efficiency proxy, the state of development (S), to the T model. The link between temperature history and photosynthesis and thus to emission efficiency has already been demonstrated in the field conditions for pinus (*Pinus ponderosa*) in western North America (Grey et al. 2006) and for oak (*Quercus alba*, *Quercus rubra* L) in North Carolina USA (Sharkey et al. 1999).

Temperature explained the major part of the BVOC concentration variation, but failed to capture the extreme concentrations. Fast changes are typical for BVOC emissions, and could be related to several kinds of environmental changes (temperature, light, drought) but also to different plant physiological processes or ontogenic structures. Phenological events 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 give rise to emission peaks, especially those of methanol, in the spring (Schade and Goldstein 2006). There have been some earlier attempts to relate the bud burst via the corresponding effective temperature sum to a single emission peak. For example, a fixed temperature sum has been used to predict the initiation of the isoprene emission and the terpene emissions from *Betula pendula* (Hakola et al. 2000). These observations indicate the link between a tree's physiological status and its phenology, its BVOC emissions and their concentrations. In this study, too, intensive spring or early summer shoot and needle growth was related to high ox-VOCs concentrations.

Fast changes could also be related to stress-induced BVOCs emissions, which is one of the key uncertainties in all current emission models (Niinemets 2009). It is estimated that tropospheric ozone concentrations will increase in the future (IPCC 2007). The effects of high ozone concentrations on biological activity and on atmospheric chemistry are contradictory (Ashmore 2005). Above a certain ozone threshold concentration, stress-induced BVOC are emitted (see Fuhrer et al. 1997, Karlsson et al. 2004, Loreto and Fares 2007), but at the same time atmospheric ozone depletes atmospheric BVOC (monoterpene) concentrations (Spanke et al. 2001). The question as to which ozone effect becomes dominant, is related to the atmospheric lifetime of the BVOC. In Article IV the high isoprene and monoterpene peaks were poorly explained by high ozone concentrations, and obviously the regulation of isoprenoid concentrations in the boundary layer above a Scots pine forest includes some as yet unattributed factors. However, as a whole, the effect of ozone was positive for all the compounds studied. This is the first time that a positive relationship between ozone and high VOC concentrations has been shown in natural conditions in a boreal forest, indicating that the effect of ozone stress on trees is the more

dominant process as compared to the atmospheric chemistry. This verifies an earlier observation of the positive correlation between ozone treatments and the increased VOC and terpene emission rates of *Pinus halepensis* L. (Peñuelas et al. 1999).

5.2 Future BVOC emissions linked to changes in the annual cycle

The latest climate prediction for Finland suggests that the thermal winter (the period when the daily mean temperature remains below 0°C) will be significantly shortened, especially in Southern Finland (Jylhä et al. 2009). Furthermore the temperature sum of the growing season will increase (Jylhä et al. 2009). The phenological model comparison (Article I) determined that Thermal Time model provides the best prediction accuracy under current climate conditions for the onset of the growing season of deciduous trees. In the Thermal Time model, a clear assumption was that the buds have been sufficiently chilled and that the dormancy release is related to environmental conditions that can be modelled with a fixed starting date. In future, the main question is related to the acclimation of the photosynthesis of deciduous trees and coniferous species in winter conditions (Öquist and Huner 2003). In the current climate, the chilling requirement is met early in the winter, but in warmer conditions the onset of biological activity in deciduous trees could be delayed due to insufficient chilling. However, this is not probable. The few available lab experiments have shown that the temperatures above 0 °C are the most effective chilling temperatures (see Aron and Gat 1991). Under the current climate, trees have adapted their chilling requirement to avoid damage by either late spring frosts or early autumn frost (Hänninen et al. 1990). The effect of temperature variations on the length of the growing season of trees and on their biological activity is a key issue when estimating future BVOC emissions (Peñuelas and Staudt 2010). An increasing photosynthesis, growth and leaf area would have a significant impact on the integrated annual BVOC emissions, and on their temporal and regional dynamics at the stand and ecosystem level. Phenological models provide a tool to estimate the length of the growing season. Although the Thermal Time model was shown here to be the best phenological model, for predictions of future BVOC emissions the relevance of chilling to the timing of bud burst under elevated temperature conditions may be of major importance for model predictions. This is the case for deciduous trees (Fig. 12).

However, the effect of a warmer winter could be more stressing for conifer species. The wintertime photosynthetic efficiency of conifers may increase the emissions directly due to photosynthesis. Field observations have shown that photosynthesis can take place in winter conditions (Sevanto et al. 2006). Also laboratory experiments have indicated that deacclimation, the fast (60h) and full recovery of the photosynthesis (photosystem II) of a Scots pine, can take place in low light and room temperature conditions (Ottander et al. 1995). In this study, a rapid temperature response of photosynthetic efficiency was observed at temperatures around zero (Article II). Furthermore, the temperature history related to the seasonal photosynthetic efficiency of conifers showed a similar type of relationship at both southern and northern Finland sites (Article II). In spring, at low temperatures, the photosynthetic efficiency was very low, but not zero. At both sites the photosynthetic efficiency seemed to saturate in summer (a sigmoid relationship). This observation supports the view that pine forests may have a greater potential to increase annual photosynthetic production in a warming climate, especially in winter. If the efficiency is saturated, any possible future increase in annual photosynthesis in southern Finland will be mainly due to a longer growing season, not higher summertime temperatures.

Of the conifer species, Norway spruce (*Picea abies*) emits monoterpene, acetone and acetaldehyde (Isidorov et al. 1985, Cojocariu et al. 2004, Rinne et al. 2009, Steinbrecher et al. 1997) and Scots pine is a strong methanol, acetone and acetaldehyde-emitting species (Janson et al. 1999, Komenda and Koppmann 2002, Rinne et al. 2008). Due to the different dynamics of the dormancy period in coniferous and deciduous trees, the species compositions plays a significant role, when the future BVOC emissions of a boreal forest are to be estimated. In Finland, the conifer species (*Pinus*, *Picea*, *Abies*, *Larix*) dominate the deciduous tree species (*Alnus*, *Betula*, *Populus*). The most common evergreen tree species of the boreal forest in Finland are Scots pine (*Pinus sylvestris*), which represents 65% of the area of Finnish forests and Norway spruce (*Picea abies*), which represents correspondingly 27% (Metsätieteellinen vuosikirja 1993). The most common deciduous tree species is birch (*Betula* sp.), which is the third most common tree species in Finland. Other commonly-growing species are rowan (*Sorbus aucuparia*), alder (*Alnus incana*) and aspen (*Populus tremula*).

If temperature increases and the photosynthetic efficiency of conifers is not saturated in summer but rather continues to increase, increased BVOC emissions in summer can also take place. Additionally, if the photosynthetic efficiency is sustained during the wintertime an increase in monoterpene emissions could also take place. In contrast to conifers, the BVOC production of deciduous tree species in Finland could remain at the same level in a warmer climate. Whilst the chilling is delayed, the onset of bud burst and leaf development may occur at the same time or even earlier. Hänninen (1991) has estimated that, despite the delayed chilling, the onset of bud burst in deciduous trees may be advanced as much as four weeks. This study suggests that the photosynthetic efficiency will be saturated in summer.

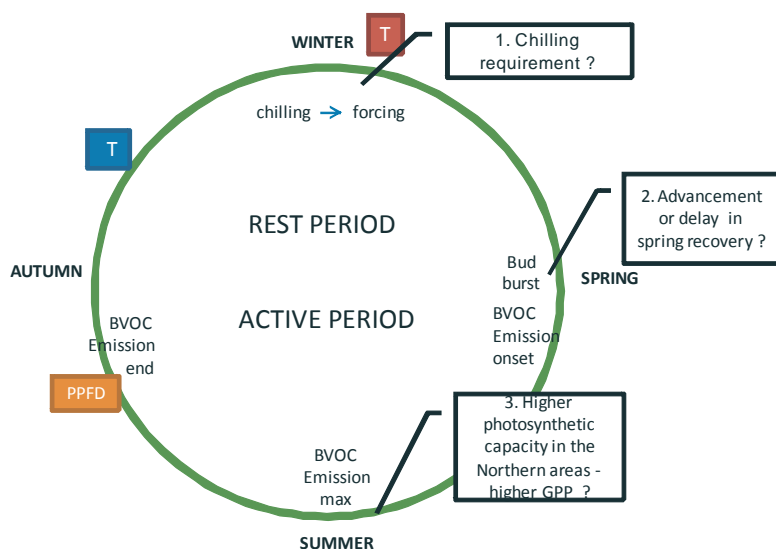


Figure 12. Schematic figure pointing out the critical issues (1-3) of the annual cycle affecting the total amount of BVOC in a warmer climate in northern latitudes.

Due to the winter dormancy of boreal trees and the seasonal variation of photosynthesis, the main features of the seasonal control (Article I) and photosynthesis efficiency (Article II) of boreal trees should be incorporated into a BVOC emission model, especially, when estimates of future BVOC emissions in a boreal forest and in northern latitudes are made.

5.3 Need for long-term phenological observations

The empirical phenology models used in global climate simulations use only a few local-scale observations that represent only a fraction of the global bioclimatic diversity (Penueals et al. 2008). Furthermore, due to herbivores-induced BVOCs, long-term phenological datasets covering several interacting species (prey-predator, pollinator - pollinated tree species) are also needed for estimating future BVOC emissions (Peñuelas and Filella 2001, Peñuelas and Staudt 2010). Analysis of an intensive European phenological dataset has indicated that the spring recovery of biota has already advanced by 10 days (Menzel and Fabian 1999). Contrary to the commonly-reported significant advancement in spring phenology, in this study no statistically significant advancement of the spring recovery of birch, rowan or bird cherry living near the northern limits of their distribution areas in the boreal vegetation zone was detected (Article V). The range between the earliest observation and the latest observation was, however, one month, indicating the high inter-annual variation of the tree species studied. Similar results, i.e., of no distinct change in long-term phenological trends, have been presented for some plant species growing in the most northern part of Europe, i.e., on the Kola Peninsula (Kozlov and Berlina 2002, Shutova et al. 2006).

The result of the non significant advancement in the spring recovery of deciduous trees raises questions on the effect of warm winters and to the status of the chilling requirement at this particular single site among the northern latitude sites. Linkosalo et al. (2009) have demonstrated that in a 150 year period the pooled time series over Central Finland on the timing of the spring recovery including the budburst of silver birch (*Betula pendula*) and the flowering of bird cherry (*Prunus padus*) and rowan (*Sorbus aucuparia*) has advanced by 3.3–11.0 days per century. In general, the trend analysis of Article V demonstrates how important it is to obtain data with a wide spatial coverage. The studied trends, over a 54 year period, were considered reliable. In general, phenological data from a single location are considered valuable if they exist as part of a long run of years, usually more than 20 (Sparks et al. 2000).

In addition to obtaining plant phenological data with a wide spatial coverage, it is as important to have parallel observations on several species. The wider ecological viewpoint is also related to BVOC emissions. BVOCs emissions are stimulated not only by the climate factor but also as a defence against herbivores attack (Dicke 2009). In Article V, an indication of an advanced trend in spring phenology was found for 17 out of 23 species. The trend was clearest for animal species: *Rana temporaria* (7.62 days per 54 years), *Formica rufa* (12.21 days per 42 years), *Ficedula hypoleuca* (22.15 days per 18 years) and *Grus grus* (13.98 days per 54 years). The changes in plant phenology and bird migration show that climate warming may lead to a decoupling of species interactions, for example between birds, plants and their pollinators or herbivores (Peñuelas and Filella 2001, Dicke 2008). Due to the complexity of interaction between BVOC emissions, species interactions and the atmosphere it is not possible to include all the affecting factors in the emission models; however a knowledge of the observed trends should be taken into account when emission predictions are evaluated.

6 CONCLUSIONS

The results obtained in this thesis have expanded our knowledge of phenological modelling and photosynthetic efficiency in a boreal forest. The fundamental status of the Thermal Time model in predicting the onset of spring recovery was confirmed. However, sequential models are the more appropriate tools when the onset of the growing season is estimated in a warmed climate. A similar type of relationship between photosynthetic efficiency and temperature history, the state of development, was found in both southern and northern boreal forest stands. This result draws attention to the critical question of the seasonal efficiency of coniferous species to emit organic compounds, especially, monoterpenes in a warmer climate. New knowledge was gained on the temperature dependence of biogenic volatile organic compound concentrations in a boreal forest stand. Regarding seasonal progress, the inter-correlation of the BVOC concentrations indicated a link to biological activity, and temperature was detected as the main driving factor for the concentrations. The effect of photosynthetic efficiency on air concentrations was also found. However, in addition to temperature, other factors, like O₃ stress, may play a significant role here, especially when the high emission peaks are considered.

This study has shown, that it is important to take into consideration aspects of the annual cycle of biological activity and the photosynthetic efficiency, as well as the species compositions, when the effect of climate change on boreal forests and future BVOC concentrations and emissions are to be estimated.

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