

Extended Executive Summary

Thesis: Carbon and water fluxes from the European terrestrial biosphere.

Trevor Keenan

General Introduction

Every year, every day, every second – indeed, continuously, the Earth is breathing. Carbon, oxygen and water, cycle continuously between the atmosphere and the biosphere. Not only is it breathing carbon and oxygen, as us humans, but there are numerous biogeochemical cycles between the atmosphere, the oceans, and the terrestrial biosphere which constantly renew the vital elements necessary for life. Everything is connected in this huge dynamical system, and, over time, somewhat incredibly, a certain balance has been reached.

The atmosphere is of particular importance due to its crucial role in mediating all energy that enters and leaves earth. Overall, the atmosphere is the component that controls the dominant energy flow in the earth's climate system, and solar radiation from the sun provides the energy to make the weather machine work. Embedded in this process are the biogeochemical cycles that operate on a variety of temporal and spatial scales and help to regulate flows of energy and materials throughout the earth system.

The forests ecosystems of the Earth dominate the biogeochemical fluxes and storage of trace gases from terrestrial vegetation. Terrestrial ecosystems contain about three times more carbon than is found in the atmosphere, with three quarters in the soil and the rest in the aboveground forest structure. Because of the thick humus layer, loose soil, and soil-retaining properties of the trees' long roots, forests are also vitally important for preserving adequate water supplies (Schröter *et al.*, 2005). In addition, the forest provides shelter for wildlife, recreation and aesthetic renewal for people and irreplaceable supplies of oxygen and soil nutrients. In order to better understand their

future, and their potential interactions with future climate, it is necessary to understand their responses to current climatic conditions.

The effect of anthropogenic induced changing climate on Mediterranean forests has already been observed and is expected to continue and perhaps accelerate (IPCC 2007, Summary for Policymakers). Increased temperature and changes in precipitation patterns may affect the capacity of Mediterranean forests to sequester carbon, for example through increased instances of drought (Beniston *et al.*, 2007), thereby providing a positive feed-back to the climate system (Cox *et al.*, 2000). The processes which control the exchange of carbon and water between forests and the atmosphere during drought are, as yet, poorly understood (Loreto and Centritto, 2008; Warren, 2008), and terrestrial vegetation models consistently perform worse in drought stressed environments (e.g., Morales *et al.*, 2005; Jung *et al.*, 2007).

For the Mediterranean climate regions of the world, changes in temperature are expected to exceed the global average, with an overall decrease in precipitation (Giorgi *et al.*, 2004; IPCC, 2007). As a result, hot summer periods and drought events in the Mediterranean basin are likely to increase in frequency (Giorgi, 2006; Beniston *et al.*, 2007). This is of considerable importance given that water is already the main limiting factor to vegetative growth (Boyer, 1982) and a reduction in precipitation could lead to a decrease in water resources, and strong negative impacts on ecosystem integrity (IPCC 2007, Summary for Policymakers). Currently it is unknown exactly how plants react to soil water stress, which makes future predictions of responses of terrestrial vegetation to climate subject to great uncertainty.

Another important component of Mediterranean plant-atmosphere interactions comes in the form of temperature sensitive emissions of biogenic volatile organic compounds (BVOCs), which are emitted by most Mediterranean forests. Although it is not entirely clear why plants emit BVOCs, their presence has been reported to increase plant tolerance to several environmental stresses, i.e. drought stress (see Sharkey *et al.*, 2008 for a review). BVOCs play an important role in plant-insect communication (Laothawornkitkul *et al.*, 2008; Miller *et al.*, 2005) and in regional air chemistry (e.g., Fuentes *et al.*, 2000; Kanakidou *et al.*, 2005). Thus, improving our mechanistic understanding of Mediterranean forest BVOC emissions is highly desirable.

(Exerts in this introduction taken from Keenan, T., S. Sabate and C. A. Gracia (2008), Forest Eco-physiological Models and Carbon Sequestration, in Managing forest ecosystems: The challenge of climate change, edited by F. Bravo et al., pp. 83-102, Springer, Berlin, ISBN 978-1-4020-8342-6.)

Quick Overview

The presented research, undertaken during my PhD studies at CREAM between October 2005 and May 2009, is designed to reduce uncertainty in our understanding of and our ability to model Mediterranean forest carbon and water fluxes. Key weak points in our current knowledge of plant physiology are challenged, from knowledge of leaf scale processes to the calculation of fluxes on regional scales, both in the present and under potential future climate change. The research undertaken has resulted in 8 peer-reviewed publications (7 as lead author), and 3 manuscripts which are currently under review (all as lead author). At the start of 2009, it was decided that five of the then most advanced studies should be selected and used as the basis for my doctoral Thesis. The resulting Thesis focuses on two key issues of uncertainty:

1) Understanding of Mediterranean forest canopy level responses of photosynthesis and transpiration in relation to natural drought cycles

The effect of water stress on plant photosynthesis and stomatal conductance has been widely studied (e.g., Chaves, 1991; Wilson et al., 2000; Chaves et al., 2002). It has long been accepted that stomatal control is the main driver behind photosynthetic response to water stress (e.g., Cornic, 2000), limiting available leaf intercellular carbon, thus slowing down photosynthesis and conserving water ('classical stomatal control'). Yet, the involvement of non-stomatal limitations has also been suggested which takes the form of an additional metabolic or biochemical constraint (e.g., Smirnoff & Stewart, 1985; Maroco et al., 2002; Reichstein et al., 2002).

Changes in mesophyll conductance have been suggested to be one of the possible non-stomatal physiological reactions to stress which can play a part in the limitation of photosynthesis (e.g., Grassi & Magnani, 2005; Niinemets et al., 2005; Warren, 2008). Much debate still remains as to the dynamic between stomatal and non-stomatal

limitations at different levels of water stress (Flexas et al., 2002, 2004; Lawlor & Cornic, 2002; Loreto & Centritto, 2008) and there is large uncertainty as to the role played by stress-related changes in mesophyll conductance. Such uncertainty makes it very difficult to accurately estimate carbon and water fluxes in Mediterranean forests (e.g. Morales et al., 2005), and possible responses to projected climate change scenarios.

We address the problem using a model-data synthesis approach to look at canopy level fluxes, integrating twenty years of half hour data gathered by the FLUXNET network across six Mediterranean sites, with two different vegetation models (ORCHIDEE and GOTILWA+). The results greatly improve the terrestrial vegetation community's ability to model carbon and water fluxes in Mediterranean climate regions, and shed light on the potential role of the different limitations to forest productivity during drought conditions.

2) Understanding and quantification of BVOC emissions from forest canopies.

BVOC emissions from forest canopies are highly sensitive to their driving factors (light and heat). Thus, this leads to large uncertainty when estimating emission responses to these factors. Various different modeling approaches have been developed, but these display large differences in between model sensitivities (Arneeth et al., 2007). This is further complicated by the lack of information on species specific emissions potentials, seasonal variation in emissions (see Grote and Niinemets, 2008), and the unaccounted for potential dependence of emissions on the description of the canopy microclimate. During the elaboration of the presented thesis, we tackled each of these sources of uncertainty independently.

We coupled four emissions models to two process based forest models with contrasting descriptions of canopy microclimate. Simulated emissions are analysed using field data, focusing on model predictions of seasonal cycles in emissions in the Mediterranean region, and model temperature and light responses. A new database of species specific emissions potentials is compiled and used to build a process based model inventory of BVOC emissions. The impact of seasonal changes in emissions is assessed, scaling effects from the leaf to the landscape, and a new mechanistic approach to estimating seasonal changes in emissions is proposed, based on the isoprenoid synthase enzyme. This is the first time that different emissions models are compared based on the same

process based forest models, and that the effect of the choice of forest model or canopy description is assessed. Simulated emissions estimates showed large model-dependent differences, reflecting differences in model temperature responses. This highlights the fact that we are in the early stages of the path towards a full understanding of the processes governing BVOC emissions. Many studies involving modelled future BVOC emissions may need to be revised to take into account the inherent variability introduced by the choice of the emission model used, the choice of the canopy micro-climate model, and overestimations of emissions due to inadequately incorporated seasonality.

Detailed Overview

Chapter 1:

Improved understanding of drought controls on seasonal variation in Mediterranean forest canopy carbon and water fluxes through combined in situ measurements and ecosystem modelling

(Published as: Keenan, T., R. Garcia, A.D. Friend, S. Zaehle, C. Gracia and S. Sabate (2009a), Biogeosciences, 6, 1423-1444.)

Introduction:

Gaps in our knowledge of leaf-level responses to seasonal drought, and how to model them, is potentially a large source of error when modelling Mediterranean-type forest ecosystems due to the strength of the seasonal droughts encountered annually in such ecosystems. The canopy response to drought is important in governing whole-plant abilities to thrive under given conditions. Thus the model description of drought responses must be accurate in order to get the inter-species competitive potential right, and hence be able to better predict vegetation change, in particular in dynamic global vegetation models like ORCHIDEE.

In this chapter, we address the problem of modelling canopy responses to drought from the pragmatic perspective of determining the most straightforward additional parameterisation that can accurately reproduce observed seasonal cycles of carbon and water fluxes across a range of different forest ecosystem types. Using observations of CO₂ and water fluxes over four different forest ecosystems growing in Mediterranean climates, we investigate the relationships between the observed fluxes and estimated seasonal variations in soil moisture. These data are further analysed to determine the relative roles of stomatal and non-stomatal limitations to photosynthesis. The understanding derived from this analysis is then used to adjust two contrasting process-based ecosystem models: GOTILWA+ (Growth Of Trees Is Limited by WAter), a detailed biogeochemical forest growth model (Gracia et al., 1999; Keenan et al., 2008;

<http://www.creaf.uab.es/GOTILWA+>) developed in the Mediterranean region and therefore expected to adequately account for regional specific system behaviour, and ORCHIDEE (ORganizing Carbon and Hydrology In Dynamic EcosystEms), a dynamic global vegetation model (Krinner et al., 2005; <http://ORCHIDEE.ipsl.jussieu.fr>), which has been found to perform poorest in drought-stressed regions (e.g. Jung et al., 2007). Simulations are performed with both models at each of the four sites in order to test the understanding provided by the data analysis.

Methodology used:

FLUXNET site data and data manipulation

Measurements of forest ecosystem carbon and water fluxes were obtained from the FLUXNET database (<http://www.fluxnet.ornl.gov>) for three sites in Mediterranean Europe [Puechabon, in France; Roccarespampani, in Italy; and Collelongo, also in Italy]. A fourth site at a location with a mediterranean-type climate in California (Blodgett) was also chosen. Together, the data used from the four sites amount to a total of eleven measurement years, and cover a broad range of phenological types: temperate broadleaf deciduous, temperate needleleaf evergreen, and temperate broadleaf evergreen types, with varying levels of summer drought stress between the different sites. These monospecific forest stands include the species *Quercus ilex*, *Quercus cerris*, *Fagus sylvatica*, and *Pinus ponderosa*. FLUXNET datasets include measurements of CO₂ and water fluxes integrated to halfhourly time steps (Baldocchi et al., 2001).

Interpreting FLUXNET data

We inverted the FLUXNET measurements to derive soil water content, bulk canopy conductance, and leaf internal carbon concentrations for the parameterisation of the models and for use in the separation of non-stomatal limitations to photosynthesis during periods of low soil water availability. Here we describe in brief the methodology used. For more details, please see Chapter 1 of the Thesis, or Keenan et al., 2009a.

Soil moisture

Analysing responses of observed CO₂ and water fluxes to natural changes in soil moisture requires the seasonal evolution of soil water content to be known. Surface soil

water measurements are often available, but measurements of soil water content over the total soil column are either limited, or not made at most sites, and can show a very different inter-seasonal variation than that of the surface soil water content. In the absence of direct continuous measurements of total soil water content of the soil column, daily soil moisture content (for the entire soil column up to a site specific soil depth) at each site was reconstructed through inverting the evapotranspiration rate (taken to be equivalent to the measured latent heat flux, LHF) and applying this flux to a simple water balance model. This model calculates the balance of the input (precipitation) and outputs (evapotranspiration (LHF), run-off and below-ground drainage) on a daily basis. The main components of the soil water balance, precipitation and LHF were measured, whilst run-off and sub-surface drainage were estimated. Deep soil water content profile measurements during the studied periods were available for the Puechabon and Collelongo sites. These data allowed for a satisfactory validation of the inversion methodology used (see Keenan et al., 2009a Fig. 1).

Canopy conductance.

In order to assess responses of bulk canopy conductance to water to changes in soil water content, we estimate canopy conductance directly from the measured latent heat flux. We assume that the bulk canopy stomatal conductance to water vapour (expressed on a ground-area basis) can be estimated from the observed latent heat flux under conditions of a dry canopy surface conditions and negligible evaporation from the soil surface (such conditions are common in a Mediterranean climate). Bulk canopy stomatal conductance to water vapour, G_c , was then estimated from the measured moisture flux, using a simplified form of the Penman-Monteith equation.

Deriving relationships between bulk canopy conductance, canopy photosynthesis, and soil moisture stress

Bulk canopy conductance models and soil moisture stress.

Ball et al. (1987) proposed an empirical stomatal model (BB model) in which stomatal conductance was expressed as a linear function of the leaf photosynthetic rate, relative humidity at the leaf surface, and the leaf surface CO_2 concentration, under conditions of ample water supply (Ball et al., 1987). This model was later modified by Ray Leuning (BBL model) to use the photorespiratory compensation point and vapour pressure

deficit in place of relative humidity (Leuning, 1995). This BB-type leaf level model has been applied at the canopy scale through the use of bulk canopy level variables (Leuning et al., 1995).

Soil moisture stress has been added to BB-type conductance models through changes in two particular parameters, m , and G_{s0} (the slope and intercept of the regression between the response and the drivers). We looked for possible changes in these parameters using diurnal cycles of net photosynthesis, C_a , v_{pd} , and canopy temperature which were derived from the data under wet and dry conditions. Given canopy stomatal conductance, G_c , for each cycle, $A_n/((C_a - \gamma) \times (1 + (v_{pd}/D_0)))$ was calculated and regressed against estimated G_c . The resulting linear regression allowed for the estimation of the m and G_{s0} parameters for each diurnal cycle. These values were calculated at different soil water levels to assess possible responses to soil water availability.

Non-stomatal conductance-related limitations of photosynthesis due to soil water stress.

Non-stomatal limitations can be identified by simply comparing rates of photosynthesis under similar leaf C_i concentrations, over a soil water gradient. Data relating to a restricted range of leaf C_i concentrations ($220 < C_i < 300$), radiation ($> 250 \text{ W m}^{-2}$), and temperature ($< 25^\circ\text{C}$) was used. Any differences in rates of assimilation under these otherwise non-limiting conditions could then be attributed to non-stomatal soil water effects, rather than changes in the rate of supply of CO_2 to the intercellular spaces, light limitation, or any high temperature effects.

We further analysed the canopy physiological response to soil moisture deficit by estimating the relationship between mesophyll CO_2 concentrations and net photosynthesis. C_i was calculated assuming equilibrium flux of CO_2 . C_i , calculated in this way, allows a first-order canopy-level assessment of the contribution of stomatal vs. non-stomatal limitations to photosynthesis under soil moisture stress. Canopy bulk leaf intercellular CO_2 concentration (C_i) can be calculated using the estimated bulk canopy conductance to carbon, $G_{c\text{CO}_2}$ ($= G_c/1.6$), rates of net photosynthesis derived from the eddy-covariance measurements, and atmospheric CO_2 concentrations.

Ecosystem models

Two contrasting process based ecosystem models were used to ensure the robustness of the conclusions.

GOTILWA+

GOTILWA+ (Growth Of Trees Is Limited by WAter), (Gracia et al., 1999; Keenan et al., 2008; www.creaf.uab.es/GOTILWA+) is a process-based forest growth model that has been developed in the Mediterranean region to simulate tree growth and to explore how it is influenced by water stress, climate, tree stand structure, management techniques, soil properties, and climate (including CO₂) change.

GOTILWA+ simulates carbon and water fluxes within forests in different environments, for different tree species, and under changing environmental conditions, either due to climate or to management regimes. The model treats monospecific stands which can be even or uneven-aged. Individual trees are aggregated into 50DBH (Diameter at Breast Height) classes and calculations are performed for each class. Hourly ecosystem carbon and water fluxes are estimated using meteorological forcing.

GOTILWA+ includes a two-layer canopy photosynthetic model (Wang and Leuning, 1998), coupled to a carbon allocation and growth model and a soil respiration and hydrology model. Each canopy layer is divided into fractions of sunlit (when direct radiation is present) and shaded leaves, with intercepted radiation depending on the time of the day, and the area of leaf exposed to the sun based on leaf angle and the canopy's ellipsoidal leaf distribution. Assimilation rates for sunlight and shaded leaves are calculated using the approach of von Caemmerer and Farquhar (1981), with dependencies on intercepted direct and diffuse radiation, species-specific photosynthetic capacities, leaf temperature, and the concentration of CO₂ within the leaf air spaces. Stomatal conductance is calculated using the BBL model, on a leaf temperature basis. Rates of photosynthesis are dependent on the rate of carboxylation and the proportional rate of electron transport. Each tree cohort is represented by three carbon compartments, leaf, sapwood, and fine roots. Available mobile carbon is allocated to each, and maintenance respiration of each compartment is calculated as a function of temperature. Fine litter fall (i.e. leaves), gross litter fall (i.e. bark, branches) and the mortality of fine roots add to the soil organic carbon content.

ORCHIDEE

ORCHIDEE is a process-based terrestrial biosphere model that simulates terrestrial vegetation and soil energy, water, and carbon fluxes (Krinner et al., 2005). Changes in vegetation structure and distribution in response to environmental forcings are also simulated. ORCHIDEE consists of three major components: (a) SECHIBA, which calculates the exchanges of energy and water between the atmosphere and the land surface; (b) STOMATE, which simulates photosynthesis, carbon allocation, litter decomposition, soil carbon dynamics, and maintenance and growth respiration and (c) the LPJ dynamic vegetation model (Sitch et al., 2003), which simulates long-term changes in the composition and structure of vegetation resulting from sapling establishment, competition for light, and tree mortality. Energy, water, and carbon fluxes resulting from photosynthesis and autotrophic and heterotrophic respiration are calculated on a half-hourly basis, whereas plant growth, phenology, and vegetation structure occur on a daily timestep. Plants in ORCHIDEE used in this study are divided into the following functional types, each with different phenological, physiological, and morphological characteristics: temperate needleleaved evergreen, temperate broadleaved evergreen, temperate broadleaved deciduous, and C3 herbaceous types. In contrast to GOTILWA+, vegetation is represented as an average individual plant, with no accounting for sizedistribution. ORCHIDEE simulates photosynthesis for both C3 (using the method of Farquhar et al., 1980) and C4 (using the method of Collatz et al., 1992) photosynthetic pathways, with stomatal conductance calculated using the BB model. For model parameterisations, plant functional types (PFT) parameters were used, taken from Krinner et al. (2005). Soil water content is treated within two layers, with inputs from precipitation less canopy interception loss, and outputs to sub-surface drainage, runoff, soil evaporation, and transpiration.

Accounting for soil water stress in coupled photosynthesis-conductance models

Two different approaches are frequently used to incorporate the effect of drought stress on the (Farquhar – BB-type) coupled conductance-assimilation model. Tenhunen et al. (1990) originally proposed the application of stomatal limitations under soil moisture stress through applying changes in the slope m of the coupled Farquhar – BB-type model during water stressed periods. This method decreases the empirical scaling coefficient m , with moisture stress, leading to reduced conductance and therefore

reduced internal CO₂ available for assimilation. Changing the slope during water stressed periods has since been commonly adopted, and was the methodology for water stress response applied in the GOTILWA+ model. In GOTILWA+, stomata responded to drought stress through the application of a linear scalar of soil moisture.

The effect of drought stress on the coupled photosynthesis-conductance model (of Farquhar – BB-type) can be implemented through changes in non-stomatal limitations, by reducing photosynthetic potential through the application of a scalar to both the maximum RuBP (ribulose-1,5-bisphosphate) saturated rate of carboxylation, V_{cmax}, and the maximum rate of electron transport, J_{max}. This causes stomatal closure as A_n is reduced in Eqn. (5). The ORCHIDEE model applied a linear scalar in this manner to directly reduce photosynthesis during water stress.

The two approaches were tested in both models, thus avoiding the potential for any model specific biases in results. We used the flux data analysis outlined above to test three hypotheses concerning the responses of canopy net photosynthesis and evapotranspiration to seasonally varying soil moisture supply: 1) directly reducing stomatal conductance by modifying the slope, *m*, within the BB or BBL model is sufficient to explain observed responses, 2) directly reducing J_{max} and V_{cmax} and hence net photosynthesis within the BB or BBL models is sufficient to explain observed responses, and 3) the simultaneous application of both stomatal and non-stomatal limitations is necessary to capture the timing and extent of the water stress induced decrease in CO₂ and water fluxes at each site.

To test the different hypothesis, we parameterised the reduction scalars already in use in both GOTILWA+ and ORCHIDEE from the data for both changes in the slope parameter, *m*, W_{facstoma} and non-stomatal related changes in photosynthesis (W_{facphoto}). These two scalars were parameterised independently for each site and were then applied separately in both GOTILWA+ and ORCHIDEE.

Results:

The results show that canopy conductance and photosynthesis co-vary with soil moisture in a consistent manner using observations from four sites with Mediterranean climates. Stomatal

conductance was found to vary in parallel with photosynthesis, and with only small changes in the fitted slope of the BB or BBL model formulations. Changes in photosynthetic capacity not related to stomatal closure under water stressed conditions were found to be very important at each of the sites studied. Incorporating this knowledge into process-based models suggests that accounting for soil-water mediated reductions of photosynthetic capacity alone is sufficient to adequately model CO₂ and water fluxes during dry and wet periods using either the BB or BBL conductance sub-models. Stomatal regulation of photosynthesis alone is not sufficient to reduce modelled photosynthesis to observed levels during drought periods. Accounting for the empirically-derived non-stomatal soil moisture responses with the derived parameters for each site improved substantially the performance of two ecosystem models, and allowed for the simulation of CO₂ and water fluxes with similar accuracies under both wet and dry conditions. Both models compare well against the FLUXNET data, although GOTILWA+ performed slightly better on average. This study contributes to improving our ability to model and predict carbon and water fluxes in Mediterranean-type forest ecosystems, and thereby to reducing uncertainty in future European terrestrial carbon and water fluxes. These results are of particular importance for any study of the effects of climatic changes on Mediterranean ecosystem functioning. See Keenan et al. (2009a) for a full analysis and interpretation of the results.

Chapter 2

The importance of mesophyll conductance in regulating forest ecosystem productivity during drought periods.

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Introduction:

Mesophyll conductance has historically been assumed to be infinite, with stomatal control given the sole role in the control of photosynthesis in water stressed conditions through the control of the leaf inter-cellular CO₂. However, there is increasing evidence that mesophyll conductance is indeed finite (Flexas *et al.* 2004; Ethier & Livingston 2004; Flexas *et al.* 2008; Niinemets *et al.* 2009), and it has been demonstrated to change during leaf development (Miyazawa & Terashima 2001), with nutrient availability (Warren 2004), with available radiation (Niinemets *et al.* 2006), among other factors. Finite g_m would lead to a lower concentration of CO₂ reaching the chloroplast and any changes in g_m during periods of low soil water availability could potentially play an important role in controlling photosynthetic responses to water stress (Flexas *et al.* 2008; Niinemets *et al.*, 2009).

The logistic complications of making canopy measurements of water stress effects on leaf photosynthesis and g_m over long periods makes it difficult to scale up results to trees in woodland conditions over entire seasons and years. On top of this, only a few studies have used quantitative analysis techniques to separate the different limitations to

photosynthesis (Ellsworth 2000; Wilson *et al.* 2000). These two problems are being approached by recent advances in inverse modelling techniques which allow for the estimation of leaf ecophysiological parameters from eddy-covariance flux data (e.g., Rambal *et al.* 2003; Reichstein *et al.* 2003; Wang *et al.* 2007; Carvalhais *et al.* 2008; Lasslop *et al.* 2008) and recently the consideration of possible limitations of photosynthesis due to a variable mesophyll conductance (Grassi & Magnani 2005).

In this paper, we use data from multiple FLUXNET (<http://daac.ornl.gov/FLUXNET/>) sites to quantify the role of both stomatal conductance and mesophyll conductance in regulating forest ecosystem productivity during drought periods. Both bulk canopy stomatal and mesophyll conductance were calculated from the FLUXNET data, using an inversion of the McNaughton and Black equation (McNaughton & Black 1973), the Harley variable *J* method (Harley *et al.* 1992), and an ecophysiological process based photosynthesis-conductance model coupling (Farquhar *et al.* 1980; Leuning *et al.* 1995) together with a canopy distribution model (Campbell 1986; Dai *et al.* 2004; Keenan *et al.* 2009a), thus describing foliar photosynthesis and conductances as distributed through the canopy. The resulting responses of the bulk canopy leaf intercellular and chloroplast carbon pool concentrations to changes in soil water availability were thus assessed. A quantitative analysis (Grassi & Magnani 2005) allowed for the separation and quantification of the different limitations to forest productivity during drought.

Methodology used:

FLUXNET Site Data and Data Manipulation

The sites chosen cover 6 dominant species, over a wide range of Mediterranean environmental conditions, and include *Quercus ilex*, *Quercus cerris*, *Fagus sylvatica*, *Pinus halepensis*, *Pinus ponderosa*, and *Quercus douglasii*, respectively. Three of the studied sites are situated in Europe (Puéchabon, France; Roccarespampani, Italy; Collelongo, Italy), under the CarboEurope-IP project, one site in Israel (Yatir) and two sites in the United States (Blodgett & Tonzi, California), under the AMERIFLUX project. The most common Mediterranean environments are covered, from a savannah type ecosystem (Tonzi, California) to semi-arid (Yatir, Israel), to mountainous (e.g., Collelongo, Italy; Blodgett, California), across the three continents. FLUXNET provides continuous measurement of carbon dioxide (broken down into net assimilation, and ecosystem respiration) and water fluxes on a seasonal basis with half-hourly discrimination. New flux separation techniques now give the improved level 4 data set (Reichstein *et al.* 2005), used in this study.

Fractional soil water storage

The fractional soil water content was reconstructed from each site by inverting the water fluxes measured by the FLUXNET towers, using the methodology outlined above in Chapter 1.

Both inter-site and inter-annual soil water variability is large, giving a broad range of water stress responses in each of the six species with a particularly strong drought experienced in 2003 at the European sites. The Blodgett site soil water content shows little inter-annual variability due to the lack of inter-annual variability in its climate during the studied period, and small levels of water stress were experienced. In comparison, at Puéchabon, soil water varies over a large range, with levels reaching a

prolonged low during 2003. This drought period is also reflected at the Roccarespampani site, with soil water levels in 2003 reaching half those of 2004. Yatir is a ‘man-made’ forest in a very arid region of Israel and suffers annual periods of strong drought stress. Each site experiences different degrees of water stress related decreases in assimilation rates and observed evapotranspiration. Reconstructed seasonal soil water cycle details are presented in Keenan *et al.* (2009a), and described in Keenan *et al.*, (2009b).

Calculation of bulk canopy conductance and bulk leaf inter-cellular carbon dioxide concentrations

Bulk canopy conductance (G_c) is the leaf-surface conductance to water vapour (g_s) scaled to the canopy level, expressed on a ground-area basis. It can be estimated from the observed latent heat flux under dry canopy conditions and when soil evaporation is negligible. We inverted the McNaughton and Black equation for canopy latent heat flux (McNaughton & Black 1973) to estimate bulk canopy conductance, G_c .

Using the estimated bulk canopy conductance to carbon $G_{c_{CO_2}} (= G_c / 1.6)$, observed rates of net photosynthesis from the eddy-covariance measurements, and atmospheric CO_2 concentrations, canopy bulk leaf intercellular CO_2 concentration (C_i) can be calculated using the simple supply and demand algorithm (See Keenan *et al.*, (2009c) for a full description) As all measurements used in the calculation of bulk conductance have reference above the canopy, boundary layer effects are assumed to be minimal for the calculation of bulk C_i .

Data Selection

The analysed FLUXNET data was filtered to consider only daytime values by selecting data corresponding to half hours with photosynthetically active radiation (PAR) of $400 \mu\text{mol m}^{-2} \text{s}^{-1}$ or greater, and assimilation rates of greater than $2 \mu\text{mol CO}_2 \text{ m}^{-2} \text{s}^{-1}$. Following Harley et al. (1992), only data corresponding to a leaf inter-cellular carbon concentration of between 100 and $300 \mu\text{mol mol}^{-1}$ were used in the calculation of mesophyll conductance. Screening was also performed to remove data relating to precipitation events, and extreme temperatures (below 5° or above 35°). Gap filled data was not considered.

Calculating bulk mesophyll conductance and carbon dioxide concentrations in the chloroplast

The bulk canopy mesophyll conductance, G_m , is the canopy scaled equivalent of leaf internal conductance (g_m) from the sub-stomatal cavities to chloroplasts and was estimated according to the variable electron transport rate method of Harley *et al.* (1992). Cuticular conductance is assumed to have no significant effect on calculations for the range of species and data selected.

Bulk canopy C_c is then a function of the net photosynthesis assimilation rate, bulk canopy conductance to carbon, $G_{c_{\text{CO}_2}}$, and bulk canopy mesophyll conductance, G_m . Please see Chapter 3 of the Thesis, or Keenan et al., (2009c), for a full description of the calculations used.

Quantitative limitation analysis

Using quantitative limitation analysis, it is possible to calculate the limitations imposed on photosynthesis by stomatal conductance (SC_L), mesophyll conductance (MC_L), or

biochemical processes (B_L) at any time of the year, assuming a reference maximum is available. The filtered data was used to separate the three different limitations on maximum photosynthesis, following Grassi & Magnani's (2005) elaboration of Jones (1985). Thus the response of each limitation to changes in soil water availability could be observed.

This approach makes it possible to compare absolute or relative limitations to assimilation over any period of time. The analysis partitions photosynthesis limitations into components related to stomatal conductance, mesophyll conductance and leaf biochemical characteristics (assuming that a reference maximum assimilation rate can be defined as a standard). By explicitly considering mesophyll conductance, it is thus possible to partition non-stomatal limitations among the two underlying mechanisms related to CO₂ diffusion and carboxylation.

Results:

It is as yet unclear as to what processes drive the response of global photosynthesis to drought conditions. Here, we have used a 'scale-down embedded in scale-up' approach (Root & Schneider 1995; Rambal *et al.* 2003), to understand the driving processes behind drought imposed changes in forest carbon and water fluxes. The results of this study highlight the importance of mesophyll conductance in the control of terrestrial vegetation productivity, both in well watered conditions and in response to soil water stress. The concentration of carbon in the chloroplast was shown to potentially be a more reliable estimator of assimilation rates than the inter-cellular carbon concentration. This

is of importance when modelling photosynthetic rates, both in well watered and dry conditions. A strong response of mesophyll conductance to soil water stress was observed at all sites. A complex dynamic was observed at each site between the responses of stomatal and mesophyll conductance limitations to photosynthesis. These results have important implications for regional canopy-level photosynthesis modelling, and may explain the some of the difficulties ecosystem models encounter when modelling carbon and water fluxes in Mediterranean conditions. This could be of particular importance in the estimation of Mediterranean primary production, both in current day conditions and when modelling responses to projected future climate change. See Keenan et al. (2009b) for a full analysis and interpretation of the results.

Chapter 3

Soil water stress and coupled photosynthesis-conductance models: Bridging the gap between conflicting reports on the relative roles of stomatal, mesophyll conductance and biochemical limitations to photosynthesis

(In review: Agricultural and Forest Meteorology)

Introduction:

It was shown in Chapter 1 that part of the reported model deficiency in modeling carbon and water fluxes in the Mediterranean during water stressed periods is due to the assumption of the sole control of stomatal conductance limitations (SCL) over photosynthesis during water stressed periods (Keenan et al., 2009a). The inclusion of empirical ‘non-stomatal’ limitations has been shown necessary to successfully model CO₂ and water fluxes in water stressed environments (e.g. Colello et al., 1998; Reichstien et al., 2002; Rambal et al., 2003; Reichstein et al., 2003; Xu & Baldocchi, 2003), with both CO₂ and water fluxes being accurately modelled during water stressed periods through the reduction of photosynthetic potential (BL) in line with reductions in soil water availability (Keenan et al., 2009a). Such a BL represents the effect of drought on metabolic functioning (e.g. the activity of the Rubisco activase enzyme, denitrogenisation, etc.). These model results suggest that stomatal aperture is driven by photosynthetic demand, and that the stomata do not play an active role in the long term regulation of photosynthesis during water stressed periods. This is controversial, as stomata have been widely reported to play a strong role in regulating photosynthesis during water stress (see Lawlor & Cornic, 2002, for a review). The conclusions from most studies, in particular model studies, were reached without taking into account the possible effects of a finite and changeable mesophyll conductance (g_m).

CO₂ which enters the inter-cellular spaces of the leaf through the stomata diffuses through the mesophyll to the site of carboxylation in the chloroplast. It is becoming increasingly accepted that g_m is finite and variable (Warren, 2008), and that the concentration of CO₂ in the inter-cellular spaces (C_i) differs from the concentration of CO₂ in the chloroplast (C_c) in a manner that is highly variable within species and affected by a range of environmental conditions (e.g. Flexas et al., 2007; Warren, 2008). In Chapter 2 we found that limitations of photosynthesis due

to changes in g_m (MCL) could play a role in plant responses to water stress (Grassi & Magnani, 2005; Galmes et al., 2007; Warren, 2008b; Keenan et al., 2009b). This strengthens the need to incorporate a term that considers g_m in current photosynthesis models, such as that by Farquhar et al. (1980), thus calculating photosynthetic rates based on C_c instead of on C_i .

In the current analysis, different hypothesis are tested, challenging current assumptions regarding the relative roles of SCL, MCL and BL to photosynthesis and conductance, and how to model them, during seasonal water stressed periods in the field. We modified the Farquhar et al. (1980) model to incorporate mesophyll conductance and thus calculated photosynthesis on a C_c basis. This was coupled to the widely used Leuning et al. (1995) version of the Ball-Berry conductance model (Ball et al., 1987), and embedded in the biogeochemical forest growth model GOTILWA+ ('Growth Of Trees Is Limited by Water') (Gracia et al., 1999; Keenan et al., 2008; Keenan et al., 2009a). We could therefore test the effect of the inclusion of a water stress responsive stomatal conductance, mesophyll conductance or photosynthetic potential on modelled CO_2 and water fluxes. CO_2 and water eddy-covariance flux data from the five year period from 2001 to 2005 at the Puechabon Mediterranean *Quercus ilex* forest site in France are used to test model performance during water stressed periods.

Methodology Used:

Fluxnet Site Data

Data and simulations refer to Puechabon State Forest study site, located 35 km NW of Montpellier (southern France) (3°35'45"E, 43°44'29"N, elevation 270 m). Vegetation is largely dominated by a dense over-storey of *Quercus ilex* trees (Allard et al., 2008). Due to its typical Mediterranean-type climate (with warm and wet winters, and hot and dry summers), the water content in summer falls regularly below the value at which water stress limitations to photosynthesis are expected (Rambal et al., 2003), leading to extended seasonal periods of drought stress. The timing and extent of drought conditions varies from year to year, depending on temperature and precipitation. For more details on the site see <http://www.cefe.cnrs.fr/fe/puechabon/>.

Climate, and eddy-covariance CO₂ and water (latent heat flux equivalent) flux Measurements from the period 2001 to 2005 are used, which had an average annual air temperature of 14.5 °C and average annual precipitation of 965 mm. The selected focus year 2002 was wetter (total precipitation 1166 mm) than the long-term average but was also warmer than average, (average temperature for 2002 of 14.7 °C). The high soil water availability during spring, and the relatively high temperatures, led to high production in spring 2002. The corresponding high levels of production related transpiration, and a relatively dry summer which was uninterrupted by strong rainfall events led to a sharp and extended drought period during 2002. This contrast between high spring production and a prolonged uninterrupted summer drought makes 2002 at Puechabon a good example year to test different approaches to modelling soil water stress responses. The valid approaches for 2002 were then tested against the full time series.

Modified photosynthesis model with mesophyll conductance

The photosynthesis model of Farquhar, von Caemmerer & Berry (1980), embedded in the GOTILWA+ forest model (see description in Chapter 1 above) was modified to explicitly calculate mesophyll conductance and therefore accurately calculate the quantity of CO₂ available for assimilation in the chloroplast, through a set of coupled equations. Please see Keenan et al., (2009b) or Chapter 3 of the Thesis for a full description of the equations used.

The effect of the inclusion of g_m in the Farquhar BB-type model coupling (for a non water stressed system) was conducted using three reference values for g_m . This allowed

for the reparameterisation of the photosynthetic parameters J_{\max} and $V_{c\max}$ (following Niinemets *et al.*, 2009b).

The effect of soil water stress on coupled photosynthesis-conductance models

Model studies have shown that the application of B_L is sufficient to accurately model water stress effects on CO_2 and water fluxes (Reichstein *et al.*, 2002; Keenan *et al.*, 2009a), whilst it is commonly upheld that the stomata (SC_L) (e.g., Tenhunen *et al.*, 1990; Cornic, 2000), and the mesophyll (MC_L) (e.g., Warren, 2008a; Keenan *et al.*, 2009b), play a strong role in regulating water stress responses (e.g., Grassi and Magnani, 2005, but see Loreto & Centritto, 2008). We test the following four hypotheses from the literature for the incorporation of the effect of drought stress on the (Farquhar - BB-type) coupled photosynthesis-conductance model:

1) Directly reducing photosynthesis in relation to reductions in soil water availability sufficiently constrains CO_2 and water fluxes during water stressed periods (biochemical limitations, B_L). This incorporates all reported non-conductance limitations.

2) Directly reducing stomatal conductance in relation to reductions in soil water availability is sufficient to explain variation in CO_2 and water fluxes during drought stressed periods (stomatal conductance limitations, SC_L).

3) Directly reducing mesophyll conductance in relation to reductions in soil water availability is sufficient to explain variation in CO_2 and water fluxes during drought stressed periods (mesophyll conductance limitations, MC_L).

4) A combination of conductance limitations (C_L) can accurately simulate the observed flux data ($C_L = SC_L + MC_L$).

We tested the hypotheses by imposing the three limitations, either individually or combined, to: a) photosynthetic potential (B_L), b) stomatal conductance (SC_L), and c) mesophyll conductance (MC_L).

Results:

This work has allowed for a model based assessment of previous suggestions that biochemical limitations, stomatal conductance limitations and mesophyll conductance limitations play some role in the regulation of photosynthesis (Grassi & Magnani, 2005; Loreto & Centritto, 2008), depending on the degree of water stress encountered and the relevant time scales involved. This is the first time that each limitation has been tested on a canopy scale in an eco-physiological model, and shows that, with (and only with) the inclusion of mesophyll conductance, diffusive limitations can explain CO_2 and water flux responses to seasonal changes in soil water availability. This helps in closing the gap between studies (both model and measurement based) which report dominant roles of biochemical changes under water stressed conditions and those which maintain stomatal conductance limitations as the main actor.

It is expected that the future development of a dynamic model for mesophyll conductance which incorporates sensitivity to non-water stress related drivers, and its integration into coupled photosynthesis-conductance models will improve our ability to model CO_2 and water fluxes from terrestrial ecosystems both in well watered and water stressed periods. See Keenan et al. (2009c) for a full analysis and interpretation of the results.

Chapter 4

Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties

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Introduction:

Non-methane biogenic volatile organic compounds (BVOC), emitted by most plant species, is a heterogeneous compound class made up of a wide range of reactive volatile hydrocarbons. European forest species emit large amounts of BVOCs, in particular, volatile isoprenoids: isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) (Arneth et al., 2007; Guenther et al., 1995; Simpson et al., 1999). For many BVOCs, the function for the emitting plants is not entirely clear (Owen and Peñuelas, 2005; Peñuelas and Llusia, 2004), although the emissions seem to play multiple roles in plant protection, in particular during episodes of high photosynthetic photon flux density (Sharkey and Singsaas, 1995), high temperatures (e.g., Peñuelas et al., 2005), oxidative stress (Loreto et al., 2001; Velikova and Loreto, 2005), and biotic stress (van Poecke and Dicke, 2004).

BVOCs play a significant role in atmospheric chemistry (e.g., Kanakidou et al., 2005; Szidat et al., 2006), in particular in the formation of secondary organic aerosols (Kanakidou et al., 2005) and tropospheric ozone at high light intensities and temperatures, and in the presence of NO_x (Fehsenfeld et al., 1992; Monson and

Holland, 2001). Emissions from terrestrial ecosystems also cause a decrease in atmospheric hydroxyl radical (OH) concentrations and thereby result in an increase of the lifetime of methane in the troposphere (CH₄) (Poisson et al., 2000; Roelofs and Lelieveld, 2000). The emissions of BVOC have therefore far-reaching implications for air quality (e.g., Bell and Ellis, 2004), both globally and locally.

The application of emission models is required to accurately describing the responses of emissions to variation in environmental drivers (Grote and Niinemets, 2008). Temperature and radiation have been found to be the main driving factors for the emission of both isoprene and monoterpenes in broad-leaved species (Dindorf et al., 2006; Loreto and Sharkey, 1990). These key findings have driven the development of isoprene and monoterpene emission models from simple empirical models to more process based designs. Early emission modelling methods took an empirical approach, linking emissions directly with climatic variables (Guenther et al., 1995). These have shown to have high predictive power in some, but not in all situations (e.g., Arneth et al., 2007). With an improved understanding of the biochemical reaction pathways for the formation of various plant volatiles, more mechanistic models have evolved (Martin et al., 2000; Niinemets et al., 1999; Zimmer et al., 2000). So far, few attempts have been made to compare the capacity of different emission models to simulate the environmental variability in emissions encountered in the field (Arneth et al., 2007).

Emission models are almost exclusively developed at the leaf level and are then scaled, through spatial and temporal scales, to the canopy, to the stand, and finally to the region level. This requires the coupling of an emission model with a process-based SVAT (soil-vegetation-atmosphere transfer) model. Such models describe leaf scale processes,

set the micrometeorological canopy conditions which drive these processes, and describe the biomass and foliage distribution throughout the canopy (Baldocchi et al., 1999; Grote, 2006; Lamb et al., 1993; Lenz et al., 1997; Schaab et al., 2003).

In this paper, we first embedded three different isoprenoid emission models into a process based terrestrial biogeochemical model (GOTILWA+), thus providing a bottom up approach both to quantify the isoprene and monoterpenes emissions being released into the atmosphere under present day and potential future climate change. Isoprene emission flux measurements were used to compare diurnal and seasonal emission predictions at two forest sites with contrasting forest structure and species composition, one in the south of France and the other in Michigan, USA. We further revised the emission potentials for 80 dominant European forest species both occurring naturally and in forest plantations. Using these basal emission potentials we derive an emission inventory for both isoprene and monoterpenes emissions from European forests under current climatic conditions using the three different modelling approaches. Finally, European forests were used as an example to analyse and compare large scale model performances under future climatic conditions.

Methodology used:

Leaf Level Emission Algorithms

A recent model comparison study highlighted three isoprenoid emission models as possible candidates for regional or global applications (Arneth et al., 2007). The models take contrasting approaches to modelling emissions, each with different assumptions about the way environmental factors limit the emissions and with different levels of

mechanistic detail. Where pertinent, modifications were made in order to ensure consistency between the models (as in Arneth et al., 2007). No direct CO₂ effect on the emissions was applied in the models. The Guenther model (Guenther et al., 1991; 1993) is an empirical model which describes the emission rates by using long-term basal emission factor for isoprene (E_I) and monoterpenes (E_M), and adjusting these basal emission potentials by two empirical factors, one describing the response to light intensity and the other to leaf temperature. The Niinemets et al. model (Niinemets et al., 2002b; Niinemets et al., 1999) for isoprene and monoterpene emissions takes a process-based approach, linking the emission rates to the activity of the synthase enzyme S_S to predict the capacity of isoprenoid synthesis pathway and to foliar photosynthetic metabolism via the photosynthetic electron transport rate, J , to predict substrate availability for isoprenoid synthesis (Niinemets et al., 2002b; Niinemets et al., 1999). Martin et al. (2000) developed a process based approach for isoprene emissions using the knowledge of the biochemical pathway of isoprene synthesis, thus providing a highly mechanistic model.

Species-specific emission potentials

Calculated total emissions are linearly dependent on the assigned emission potentials E_I and E_M that are directly applied in the Guenther et al. model, and determine the isoprenoid synthase activities in the Niinemets et al. and Martin et al. models. The emission potentials have recently been concluded to be one of the most important parameters for modelling regional emissions (Arneth et al., 2008; Grote and Niinemets, 2008). In most large-scale modelling studies, the values initially specified by Guenther et al. (1995) are applied. Since then, much more information has become available and

been integrated into previous estimates (Guenther et al., 2006). It often occurs that very different emission potentials are assigned to a certain functional type or species in different modelling studies, leading to very different results (Arneth et al., 2008 for review). We address this problem through a thorough critical literature review to compile the state of the art knowledge of species-specific emission potentials for 80 species included in the GOTILWA+ forest model.

In this analysis, all previous known reports were reassessed with regards to measurement methods and derivation of standardized emission potentials. As there is considerable uncertainty in actual light and temperature environment in whole-tree and whole-branch enclosure studies that can seriously affect standardization of emission rates, we preferred estimates conducted with single leaf enclosures. As a variety of temperature responses have been used to convert the emission rates to standardized conditions of 30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$, whenever actual response curves were absent, we reconverted the data using the Guenther et al. (1993) original model. Errors due to the use of inappropriate values of leaf dry mass per unit area, M_A , in converting area based relations to mass basis (for instance converting total leaf area based estimates using projected area-based M_A values) were corrected.

Scaling from the leaf to the landscape

The three emission models simulate isoprenoid emissions from any given leaf in dependence on climatic conditions. To scale from the leaf to the landscape, the emission models were coupled to the biogeochemical forest model, GOTILWA+ (previously described). This model described leaf structural and chemical characteristics, and thus foliage physiological potentials. This model also described the microclimatic conditions

and forest structure necessary to scale from the leaf to the canopy, and further to region. Using forest inventories and regional databases of climate on a 10'x10' scale, simulations were run for each of the forest stands in EU15+2.

Scaling from the leaf to the stand: The GOTILWA+ model

Please see earlier description of the GOTILWA+ model, or refer to Keenan et al. (2009d) for a description of the model as used in this Chapter.

Scaling from the stand to the region:

To supply the input data required by the model, an extensive database has been built within the framework of the European ATEAM (Advanced Terrestrial Ecosystem Analysis and Modelling) and ALARM (Assessing Large-scale Risks for biodiversity with tested Methods) projects, connecting diverse information sources at a European level and adapting them to fit the same spatial resolution of 10'x10'. The database contains data related to forest species, forest area cover, forest structure, forest function (photosynthesis, respiration rates), soil hydrology, organic matter decomposition rates and management strategies (Schröter et al., 2005). Area explicit estimates of forest cover were made available which specify the eighty dominant forest species in Europe. Simulations were run with GOTILWA+ for each 10' x 10' scale forested pixel in Europe (EU15 + 2, pre-enlargement Europe, Norway and Switzerland).

Scaling through time:

Simulations were run with each emission model coupled to the GOTILWA+ model for a two hundred year period from 1900 to 2100. From 1900 to 2000, a reconstructed climatic data time series based on the CRU05 (1901-2000) monthly dataset (New,

Hulme, and Jones, 1999) was used, with global atmospheric concentrations of CO₂ from 1901 to 2000 obtained from the Carbon Cycle Model Linkage Project (McGuire et al., 2001). The IPCC socioeconomic analysis (IPCC, 2001, 2007) resolved several possible standard scenarios for CO₂ emissions (A1, A2, B2, B1). Different global circulation models use these scenarios to generate future climatic projections. In this work we have applied the climatic projection for period 2001-2100 generated by the HadCM3 global circulation model using the A2 scenario as an indicator for the effect of possible future climate change on the BVOC emissions. This scenario uses an estimated increase in atmospheric CO₂ to 709 ppm by 2080. Using this scenario, HadCM3 predicts an increase in temperature of 2.8 °C by 2080 for the area included in this study (in comparison to the average temperatures for the 1960-1990 period), and regional changes in precipitation.

Stand scale validation

Recent developments in methodologies such as eddy-covariance techniques provide high quality quantitative measurements of isoprenoid emissions (Spirig et al., 2005). So far, few such measurements are available over forest ecosystems. Here, one relatively short-term series (26-days) of diurnal time-courses of isoprene emissions with a half-hour time-resolution (Arneth et al., 2007) and one long-term series of seasonal time-courses of isoprene fluxes with daily resolution (Pressley et al., 2005; Pressley et al., 2006) are used to validate the implementation of the isoprene models at the canopy level. Three simulations were run at each site, one for each model coupled to the GOTILWA+ model, using stand and species parameters gathered from the literature (Arneth et al., 2007; Goldstein et al., 1998; Waring et al., 1998). Emissions factors were used from a previous modelling study at these sites (Arneth et al., 2007).

Results

The coupling of the three different model approaches (Guenther et al., Niinemets et al. and Martin et al. models) to an ecophysiological forest model provides a unique opportunity to explore the time-dependent changes in modelled biogenic emissions due to differences in model structure and model responses to changes in climatic and physiological processes. The modelled emissions from present day European forests were shown to be independent of the emission model used, with estimates of 1.03 TgC a⁻¹ for isoprene emission and 0.93 TgC a⁻¹ for monoterpenes, giving a consistent emission inventory for BVOCs from European forests. Relative to previous estimates, the differences are moderate and are driven by use of improved emission factor database for 80 European key forest species, as well as implementation on physiological controls on emissions (water stress and phenology).

Coincidence of model estimates of emissions for current and past climatic conditions in Europe suggest that the present day inventories of BVOC emissions provide realistic estimates. However, model-dependent differences in simulated estimates of future emissions of both isoprene and monoterpenes highlight the fact that we are in the early stages of the path towards a full understanding of the processes governing BVOC emissions. This has important implications for any study seeking to model future BVOC emissions. Many studies involving modelled future BVOC emissions may need to be revised to take into account the inherent variability introduced by the choice of the emission model used. Please see Keenan et al. (2009d) for a full description of the results and their implications.

Chapter 5

Seasonality of monoterpene emission potentials in *Quercus ilex* and *Pinus pinea*: Implications for regional VOC emissions modeling

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Introduction:

Natural seasonal cycles are known to have a strong control over the timing of VOC emissions (e.g., Llusia and Peñuelas, 2000; Hakola *et al.*, 2003; Hakola *et al.*, 2006; Holzinger *et al.*, 2006). Climate change already affects seasonal cycles in terrestrial ecosystems, most notably the timing and duration of phenological events such as the onset of budburst and the rates of foliage development and senescence (Peñuelas and Filella, 2001; Bakken *et al.*, 2002; Walther *et al.*, 2002) and is likely to continue to do so in the future (Gitay *et al.*, 2001; Prieto *et al.*, 2009). It is not entirely clear why plants emit VOCs, their presence has been reported to increase plant tolerance to several environmental stresses, i.e. high temperatures. Future changes in environmental conditions are likely to change VOC emissions not only directly through altered temperature effects on the emission rates, but also indirectly due to altered seasonal cycles such as phenological events or enzyme activities. Understanding the overall effect of seasonal cycles on emissions (and potential future changes) is thus necessary to reduce uncertainty in current estimates and future projections of VOC emissions.

The overall uncertainty in our knowledge of the drivers of seasonal dynamics of emissions, and how to model them, is potentially a large source of error when modeling VOC emissions from terrestrial vegetation. In this paper, we focus on monoterpenes (a class of VOCs that consist of two isoprene units and have the molecular formula $C_{10}H_{16}$), and addressed the problem of seasonal dynamics of monoterpene emission potentials by developing seasonal emission factor response functions for two key species in Mediterranean forest ecosystems: the broadleaved evergreen sclerophyll *Quercus ilex* and the evergreen conifer *Pinus pinea*. The response functions were integrated into the Niinemets *et al.* (1999, 2002) monoterpene emission model coupled to the process-based terrestrial biogeochemical model GOTILWA+ (Gracia *et al.*, 1999; Keenan *et al.*, 2008; Keenan *et al.*, 2009a). Simulations were run for these two dominating species over the European Mediterranean region to quantify the effect of the consideration of a seasonally dynamic emissions potential on the total emissions budget for these two species. The simulations were further compared with simulations coupling the commonly used empirical Guenther *et al.* model development, MEGAN, (Guenther *et al.*, 2006), both with and without its seasonal modifications of emissions, to the GOTILWA+ model.

Methodology used:

Studied species

The Holm oak (*Quercus ilex*) is an evergreen sclerophyllous tree native to Mediterranean Europe. It is a strong emitter of monoterpene species (mostly α -pinene, β -pinene, sabinene, myrcene, and limonene), and although its distribution is limited to the Mediterranean region, it contributes more than 25% of the total European forest

monoterpene emissions budget (Keenan *et al.*, 2009a). The aerial coverage of *Quercus ilex* is currently increasing in some mesic areas as the result of warmer temperature and reductions in water availability (Peñuelas and Boada, 2003). The Italian stone pine (*Pinus pinea*) is an evergreen conifer widespread in the European Mediterranean region. It is also one of the strongest monoterpene emitters of European forest species (emitting mostly linalool, trans- β -ocimene, α -pinene, myrcene, and limonene, among others). We assume no emissions from storage ducts, as in both species, the bulk of monoterpenes are emitted in a temperature- and light-dependent manner (Staudt *et al.*, 1997).

Biosphere model platform description

To describe canopy level emissions, and scale the leaf level monoterpene emission models to the region, we coupled both the Niinemets *et al.* and the MEGAN model monoterpene emission models to the process based terrestrial biogeochemical model GOTILWA+ (Growth Of Trees Is Limited by WAter) (Gracia *et al.*, 1999; Keenan *et al.*, 2008), as described in the previous chapter. Please see Keenan *et al.*, (2009e) for a more detailed description.

To scale from the canopy to the region, an extensive database has been built within the framework of the European ATEAM (Advanced Terrestrial Ecosystem Analysis and Modeling) and ALARM (Assessing Large-scale Risks for biodiversity with tested Methods) projects (Keenan *et al.*, 2009d), connecting diverse information sources at a European level and adapting them to fit the same spatial resolution of 10' latitude x 10' longitude (minutes). The database contains data related to forest species, forest coverage, forest structure, forest function (photosynthesis, respiration rates), soil

hydrology, organic matter decomposition rates and management strategies (Schröter *et al.*, 2005). The species distribution database was updated using distribution data compiled by members of the EUFORGEN network (www.euforgen.org; Fady *et al.*, 2004) (updated, 2008). The model set-up used to scale from the leaf to the region has previously been described in Keenan *et al.* (2009d).

2.3. Leaf level monoterpene emissions algorithms

We considered the two leaf level monoterpene emission models most commonly applied to estimate monoterpene emissions on the regional scale (The MEGAN and Niinemets models). Both models take contrasting approaches to modeling emissions, each with different assumptions about the way in which environmental factors limit the emissions and with different levels of mechanistic detail. Where pertinent, modifications were made for consistency between these models (as in Arneth *et al.*, (2007)). No direct CO₂ or water stress effect on the emissions was applied in this modeling exercise. Please see Keenan *et al.* (2009e) for a detailed description of the emissions model coupling to the GOTILWA+ model.

2.4. Derivation and implementation of seasonal response functions

An extensive literature search was performed to identify measurements related to the seasonal variation of the basal monoterpene emission factor (E_M). Data were compiled from studies explicitly looking at seasonal variation in E_M as well as from studies reporting emission rates for several sampling events during the growing season where the measurement date was reported. In all cases, only measurements from fully sun-exposed branches were included. The compiled data for both species exhibited a curve with a maximum between days 200-320 and were fitted by different empirical

functions. The best fit was obtained by an asymmetric exponential function that allows for different rates of increase and reduction in E_M during the growing season (June *et al.*, 2004) to describe the seasonal variation in E_M . The data were fitted through minimizing the least-squares between the measurements and predictions, resulting in a high degree of correlation between the measured and predicted values ($r = 0.83$ for *Quercus ilex* and $r = 0.86$ for *Pinus pinea*).

Modelling protocol

Simulations were run with each emission model coupled to the GOTILWA+ model for each 10' longitude x 10' latitude scale pixel containing *Quercus ilex* or *Pinus pinea* forests in the European Mediterranean region. For parameterization of the forest structural components in GOTILWA+, species-specific parameters for *Quercus ilex* and *Pinus pinea* were applied. Two versions of the Niinemets *et al.* model were considered – one with a fixed tree species-specific emissions potential, and the other varying the emissions potential using the seasonally dynamic response derived. Two versions of the MEGAN model were also used – one without the seasonal parameter modification, and the other applying the MEGAN seasonal modification (based on the previous light and temperature regime). For each tree species, simulations were performed for years from 1900 to 2000, using the reconstructed climatic time-series based on the CRU05 (1901-2000) monthly dataset (New *et al.*, 1999), with atmospheric concentrations of CO₂ from 1901 to 2000 obtained from the Carbon Cycle Model Linkage Project (McGuire *et al.*, 2001).

Results

Our results suggest that monoterpene emissions modelled based on midsummer basal emissions factors will inevitably overestimate the annual total and, more importantly, inaccurately predict the annual pattern of emissions. Emission models including seasonality only as light and temperature history are not capable of catching seasonal changes in emission potential. Therefore, the consideration of seasonality is necessary for any regional monoterpene inventory, and a more thorough understanding will likely be crucial for climate change scenario analyses of VOC emissions for many regions. This is particularly true for areas that exhibit drought stress today or in the future and host VOC emitting plants.

The large reduction in the estimated regional emissions due to the inclusion of seasonality, although here specific to monoterpene and the two studied tree species, are expected to be applicable to any tree species and potentially to other biogenic VOCs. This is likely to have large ramifications on regional and global monoterpene emissions estimates, potentially reducing previous emissions inventories by up to 65% in some areas.

General conclusions

This PhD thesis investigates the exchange rates of carbon and water fluxes from terrestrial forest ecosystems, with a particular focus on combining data analysis with the modeling of the ecophysiological processes which drive them. We have dealt thoroughly with two areas which lead to large uncertainty when modeling carbon and water fluxes from terrestrial vegetation: The effect of water stress on forest productivity, and intermodel differences in BVOC emission estimates. This has led to the following main conclusions:

- 1) The response of the coupled photosynthesis-conductance model represents the main uncertainty when modeling CO₂ and water fluxes from Mediterranean forest ecosystems. This has been shown to be due to the assumption of the sole role of stomatal conductance in the regulation of photosynthesis responses to soil water stress. Through the implication of changes in either photosynthetic potential, or (in conjunction with changes in stomatal conductance) mesophyll conductance, carbon and water fluxes can now be modeled to a similar degree of accuracy during periods of soil water stress as during periods of high soil water availability. Whether biological limitations or a combination of conductance limitations to photosynthesis are dominant during water stressed periods remains an open question, and is most likely to be dependent on the species in question and the degree of soil water stress experienced.
- 2) It has been shown that model predictions of the emissions of BVOCs from European forests agree well under present day conditions but diverge strongly under projected future climatic conditions, due to the different temperature sensitivities of the models. The use of species specific emission potentials and geographical distributions showed that few dominant species contribute the largest portion of the total emissions budget. These will be important focus species for future work, in order to reduce uncertainty in our regional BVOC emissions estimates. Part of this uncertainty derives from lack of knowledge about seasonal variations in the species emissions

potentials. Seasonal variation in emissions potentials was shown to have a very large impact on the regional emissions budget.

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