

INVERSE MODELLING OF TRACE GAS EXCHANGE AT
CANOPY AND REGIONAL SCALES

By

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Statement of originality

This thesis, except where otherwise acknowledged, is the original work of the author. The ideas upon which this thesis was based were developed by the author in consultation with her supervisors, including but not restricted to: design of the field experiment with Jon Lloyd and Michael Raupach; development of the inverse Lagrangian approach with Michael Raupach; and incorporation of plant physiological constraints with Graham Farquhar. All three supervisors contributed significantly to interpretation of the results. Advice on investigation of model errors was received from Peter Rayner.

The model code was written by the author after drawing from examples of the inverse Lagrangian code obtained from Michael Raupach and Ray Leuning, and the sun/shade canopy code obtained from Tania June. The final coding was almost entirely original, except for various subroutines called from the IMSL Fortran 90 Math Library.

This work relies on the use of field data collected as part of the Eurosiberian Carbonflux Project in central Siberia. Many of the data (including all samples for isotopic analysis) were collected by the author personally, but the field campaign and general instrumentation set up was carried out by a number of people from the Max Planck Institute of Biogeochemistry (MPI-BGC) and the V.N. Sukachev Institute of Forests, notably including Olaf Kolle and Karl Kübler. Isotopic analysis of CO₂ for the canopy study was carried out by Willi Brand and Roland Werner at MPI-BGC. That for the regional study was carried out by Roger Francey and others at CSIRO Atmospheric Research. Nitrogen content and carbon and oxygen isotope analyses of plant matter were carried out by Sue Wood at the Environmental Biology laboratory, Research School of Biological Sciences. Oxygen isotopic analyses of precipitation, soil water and water vapour was carried out by the author at that laboratory.

Signed

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Abstract

This thesis deals with the estimation of plant-atmosphere trace gas exchange and isotopic discrimination from atmospheric concentration measurements. Two space scales were investigated: canopy and regional. The canopy-scale study combined a Lagrangian model of turbulent dispersal with ecophysiological principles to infer vertical profiles of fluxes of CO₂, H₂O and heat as well as carbon and oxygen isotope discrimination during CO₂ assimilation, from concentration measurements within a forest. The regional-scale model used a convective boundary layer budget approach to infer average regional isotopic discrimination and fluxes of CO₂ and sensible and latent heat from the evolution during the day of boundary layer height and mean concentrations of CO₂ and H₂O, temperature and carbon and oxygen isotope composition of CO₂.

For the canopy study, concentrations of five scalar quantities, CO₂, ¹³CO₂, C¹⁸O¹⁶O, H₂O and temperature, were measured at up to nine heights within and above a mixed fir and spruce forest in central Siberia over several days just after snow melt in May 2000. Eddy covariance measurements of CO₂, H₂O and heat fluxes were made above the canopy over the same period, providing independent verification of the model flux estimates. Photosynthesis, transpiration, heat exchange and isotope discrimination during CO₂ assimilation were modelled for sun and shade leaves throughout the canopy through a combination of inversion of the concentration data and principles of biochemistry, plant physiology and energy balance.

In contrast to the more usual inverse modelling concept where fluxes are inferred directly from concentrations, in this study the inversion was used to predict unknown parameters within a process-based model of leaf gas and energy exchange. Parameters relating to photosynthetic capacity, stomatal conductance, radiation penetration and turbulence structure were optimised by the inversion to provide the best fit of modelled to measured concentration profiles of the five scalars. Model results showed that carbon isotope discrimination, stomatal conductance and intercellular CO₂ concentration were depressed due to the low temperatures experienced during snow melt, oxygen isotope discrimination was positive and consistent with other estimates, radiation penetrated further than simple theoretical predictions because of leaf clumping and penumbra, the turbulence coherence was lower than expected and stability effects were important in the morning and evening.

For the regional study, five flights were undertaken over two days in and above the convective boundary layer above a heterogeneous pine forest and bog region in central Siberia. Vertical profiles of CO₂ and H₂O concentrations, temperature and pressure were obtained during each flight. Air flask samples were taken at various heights for carbon and oxygen isotopic analysis of CO₂. Two budget methods were used to estimate regional surface fluxes of CO₂ and plant isotopic discrimination against ¹³CO₂ and C¹⁸O¹⁶O, with the first method also used to infer regional sensible and latent heat fluxes. Flux estimates were compared to ground-based eddy covariance measurements. Model results showed that afternoon estimates for carbon and oxygen isotope discrimination were close to those expected from source water isotopic measurements and theory of isotope discrimination. Estimates for oxygen isotope discrimination for the morning period were considerably different and could be explained by contrasting influences of the two different ecosystem types and non-steady state evaporative enrichment of leaf water.

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Chapter 1

Introduction

1.1 Plant-atmosphere interactions

The extent to which plants modulate atmospheric composition is a topic that has been of interest to researchers for several decades, but which has in recent years gained particular importance due to the pressing need to be able to predict atmospheric and global climate response to rising carbon dioxide concentrations.

Environmental factors that influence photosynthetic rate will necessarily influence atmospheric CO₂ concentration: understanding how these variables interact is essential for developing a capacity to predict plant response and feedback to varying environmental conditions. We have already learned much about plant-atmosphere interactions on a variety of scales. Leaf-level studies have shown us that photosynthetic uptake of CO₂ regulates and is regulated by the difference in concentration of CO₂ within and outside the leaf and the rate at which it diffuses into or out of the leaf through the stomata (Jarman, 1974; von Caemmerer and Farquhar, 1981; Evans *et al.*, 1986). Biochemical theory has led to increasingly robust models of photosynthesis in C₃ plants at the sub-leaf scale (Hall and Björkman, 1975; Farquhar *et al.*, 1980), which describe the influence of irradiance and nitrogen availability on photosynthetic rate in the chloroplast. Leaf photosynthesis can be modelled in an analogous manner provided that chloroplast light response is constant throughout the leaf and photosynthetic capacity is in proportion to absorbed irradiance

(Farquhar, 1989). Physiological models have been developed from theory (Cowan and Farquhar, 1977) and experiment (Wong *et al.*, 1985; Ball *et al.*, 1986; Leuning *et al.*, 1995) to describe environmental regulation of stomatal conductance, through variables such as humidity or vapour pressure deficit, temperature and irradiance.

Extending this knowledge of leaf-level processes to the canopy scale has proved non-trivial (see §1.3). Simple big-leaf models which calculate a weighted average conductance and assimilation rate for the whole canopy have been shown to be inadequate in many cases except with site-specific tuning (Norman, 1993; Raupach, 1995; de Pury and Farquhar, 1997). A more generally applicable approach considers sunlit and shaded leaves separately (eg. Sinclair *et al.*, 1976; Norman, 1980; Smolander, 1984; de Pury and Farquhar, 1997), and more rigorous still are multi-layer models which consider sunlit and shaded leaves at a number of levels within the canopy (eg. de Wit, 1965; Leuning *et al.*, 1995; and many other studies). The more detailed treatment of light penetration in the sun/shade and multi-layer models comes at the cost of computational and conceptual simplicity (especially in the multi-layer models) and introduction of additional unknowns such as the vertical distribution of photosynthetic capacity. These kinds of models are usually coupled to the atmosphere assuming simple gradient-diffusion transport, which describes turbulent transport of scalar quantities such as CO₂ in a manner analogous to molecular diffusion. As will be discussed in a later section (§1.2.1), more sophisticated turbulent transport models are now being used to provide the link between leaf and canopy scalar source distribution and atmospheric concentrations. Projecting these influences to the regional scale is facilitated with theories of atmospheric boundary layer physics (Stull, 1988; Garratt, 1992), and the influence of regional fluxes on global atmospheric concentrations may be determined through the use of global atmospheric transport models (eg. Heimann and Keeling, 1989; Heimann, 1995; Denning *et al.*, 1995, 1999; Sellers *et al.*, 1996, 1997).

The exact manner in which observations or models of energy and trace gas exchange are scaled up in time and space is a topic of continuing research. Studies of leaf and canopy scale plant-atmosphere interaction as described above are usually carried out by

biologists, and often use a “forward” modelling approach. Here theories from plant physiology and biochemistry are used to describe plant-atmosphere exchange processes and the effects of these processes on atmospheric concentrations at equal and larger scales are investigated. In contrast, studies at regional to global scales, generally carried out by meteorologists or atmospheric physicists, often use an “inverse” modelling approach, where plant-atmosphere exchange processes are inferred from observations of atmospheric concentrations either explicitly within the model formulation or implicitly by assessment of initial flux estimates based on agreement between modelled and measured concentrations. More generally, an inverse approach is one that uses a set of observations to infer something about the processes causing those observations, and this approach may incorporate forward modelling of some or all of the system. Additional information at regional scales may be obtained from remotely sensed data, from which correlations have been derived between surface spectral characteristics, leaf area index and ecosystem productivity.

A challenge of the past two decades has been to try to wed forward and inverse, process-based and observation-based approaches, utilising the advantages of each (Jarvis and McNaughton, 1986; Luxmoore *et al.*, 1991; Running and Hunt, 1993; Schimel *et al.*, 1993; Jarvis and Dewar, 1993). There now exist many regional and larger scale models incorporating canopy-scale modules which represent biological response and feedback to atmospheric conditions in much greater detail than was present in previous models (Avissar and Pielke, 1989; King *et al.*, 1989; Rastetter *et al.*, 1992; Pielke *et al.*, 1993; Baldocchi and Meyers, 1998; Sellers *et al.*, 1996; Noone *et al.*, 2001). A significant limitation to this approach is computational demand, and there remains a need to effectively simplify and parameterise small-scale processes in large-scale models in a manner based on sound principles. An example of the evolution of scaling-up approaches is the discovery of the importance of the diffuse radiation component, which in early canopy models and even now in many regional to global models is completely ignored, yet it is the likely cause for leaf area indices in forests often far exceeding values expected from consideration of direct radiation interception (Hollinger *et al.*, 1994; Roderick *et al.*, 2001, though other

factors such as nutrient availability and competition for light may be involved); and for the inferred large positive anomaly in global carbon uptake in the two years following the Mt Pinatubo eruption in 1991 (Roderick *et al.*, 2001; Gu and Baldocchi, 2001). Similarly, the observation of counter-gradient fluxes in tall forest canopies showed that the prevailing (gradient-diffusion) transport model linking leaf fluxes to atmospheric concentrations was over-simplified for such applications (Denmead and Bradley, 1985; Finnigan and Raupach, 1987).

These considerations form the basis of the motivation behind this thesis. The study presented here is a detailed investigation of plant-atmosphere interactions at canopy and regional scales with a focus on interpretation of atmospheric concentrations in terms of plant energy and gas exchange. The study has two parts: the first describes canopy-scale models and measurements aimed at partitioning the fluxes of carbon dioxide, water vapour, sensible heat and carbon and oxygen isotope discrimination between the soil and canopy. A secondary investigation deals with prediction of regional scale carbon dioxide fluxes and isotopic discrimination using measurements of atmospheric composition in the convective boundary layer. In both parts, a combination of forward and inverse approaches was used with the aims of: (i) gaining additional information on the key parameters and processes involved in plant-atmosphere exchange; (ii) identification of limitations to generalisation of parameters and how these may be overcome; and (iii) assessment of factors complicating interpretation of atmospheric concentrations. The studies were undertaken at a field site in central Siberia, with ecological, physiological and meteorological measurements within a mixed coniferous forest being undertaken during snow-melt in May 2000, and intensive aircraft measurements carried out above a nearby forested region in mid-summer in July 1998.

The remainder of this chapter will be devoted to introducing methods and concepts used in this study. An overview of inverse modelling methods is given, in general (§1.2) and at canopy (§1.2.1) and regional (§1.2.2) scales. Physiologically-based methods for investigating plant-atmosphere trace gas exchange are reviewed in §1.3, and an introduction

to the scope of isotopic applications is given in §1.4. A qualitative description is then given of the models developed in this thesis (§1.5). Chapter 2 provides a full description of the canopy-scale study: the model components (§2.1); the field site and measurements (§2.2); comparison of modelled fluxes and concentration profiles with measurements (§2.3); and discussion of interesting results and model deficiencies (§2.4). The regional-scale study is similarly described in Chapter 3. Finally, general conclusions drawn from the two studies are discussed in Chapter 4.

1.2 Inverse modelling

A central problem of atmospheric modelling is the elucidation of surface exchange processes from atmospheric measurements. This procedure is an example of inverse modelling, where underlying processes are modelled from observations of their effects: here the observed CO₂ molecules (or any other entity of interest) are traced back over time and space through the atmosphere to their various sources. Atmospheric inverse modelling methods offer the potential to reveal information about surface exchange processes that are not readily measured, and the concept can be applied at various scales from sub-canopy to globe (eg. Evans *et al.*, 1986; Lloyd *et al.*, 1996; Enting *et al.*, 1995).

Atmospheric inverse modelling problems are inherently unstable (Enting, 1993). Atmospheric transport and turbulent mixing smooth out fine-scale variation in source distributions, which means that small errors in atmospheric concentration measurements can translate to very large errors in implied source distributions when the inversion is applied. In addition, inverse problems are typically under-determined: though the number of data may be significantly greater than the number of parameters to be determined, the parameters are often not sufficiently independent for the emergence of a unique optimal solution (Heimann and Kasibhatla, 1999; Press *et al.*, 1992). To counter these problems it is usually necessary to make use of *a priori* information to constrain the inversion (eg. Enting *et al.*, 1995). For discussion of various methodologies and difficulties encountered

in atmospheric inverse modelling problems, as well as practical applications, see Kasibhatla *et al.* (1999).

1.2.1 Canopy-scale atmospheric inversions

Gradients in atmospheric concentrations above vegetation canopies are commonly used to provide information on surface flux magnitudes. In the surface layer of the atmospheric boundary layer over horizontally homogeneous terrain, the relationship between vertical fluxes and time-averaged vertical gradients is modelled in a manner analogous to molecular diffusion in laminar flow (Kaimal and Finnigan, 1994). This approach is known as gradient-diffusion theory or K-theory, and according to this theory kinematic fluxes and concentration gradients are linearly related with proportionality constant K , the eddy diffusivity, specific to the entity being considered (momentum, heat, moisture etc.). The manner in which this theory is applied depends on the nature of the surface (degree of roughness) and the atmospheric stability (Kaimal and Finnigan, 1994), the simplest case being flow in neutral stability over flat, uniform terrain.

The presence of a plant canopy alters the character of turbulent transfer. The surface layer within and above a vegetation canopy can be divided into three regions: the canopy sublayer from the ground to the top of the canopy; the roughness sublayer from the top of the canopy to a height z_* (about 3 times the canopy height); and the inertial sublayer from z_* to the height at which Coriolis effects outweigh the surface influence (Raupach and Thom, 1981). Turbulent exchange in the inertial sublayer can be described by Monin-Obukhov similarity theory (Monin and Obukhov, 1954), where mass and momentum fluxes are universal functions of $(z - d)/L$, the height z above the apparent surface momentum sink d (which is about 0.75 of the canopy height in moderately dense canopies) divided by the Obukhov length L . The Obukhov length is a scaling parameter relating to atmospheric stability that in convective conditions may be interpreted as being proportional to the height at which buoyant production of turbulence outweighs shear production (Stull, 1988). Forms for surface fluxes in terms of vertical gradients and $(z - d)/L$ using Monin-Obukhov

similarity theory have been determined empirically to fit data from field experiments (see for example Kaimal and Finnigan, 1994).

In the canopy and roughness sublayers turbulent exchange is directly affected by the presence of the canopy elements. In the canopy sublayer, turbulence is generated by wake production in the low pressure regions on the lee side of the plants, as well as by shear production in the region near the top of the canopy where the wind speed rapidly declines (Raupach *et al.*, 1986, 1996). Flexing of plant parts may also contribute to turbulence production (Finnigan, 1985). This turbulent production is then transmitted to the roughness sublayer by turbulent diffusion. The Monin-Obukhov relationships therefore need to be modified for application in the roughness sublayer, accounting for additional contributing length scales and enhanced eddy diffusivity values (Cellier and Brunet, 1992; Kaimal and Finnigan, 1994).

The Bowen ratio method avoids the need to parameterise eddy diffusivities by considering the ratio of sensible to latent heat flux (the Bowen ratio, $\beta = H/\lambda_E E$) in terms of the ratio of vertical gradients in temperature and vapour pressure, assuming the eddy diffusivities for heat and moisture to be the same (eg. Jarvis *et al.*, 1976). Energy balance is then used, with measurements of net radiation, to partition surface energy fluxes between sensible and latent heat. This method can then be applied to fluxes of other scalars if the eddy diffusivities are assumed to be equal.

Gradients in concentrations *within* vegetation canopies (that is, in the canopy sublayer) have also, more recently, begun to be used to infer either total canopy flux or its variation with height. Two approaches differing in frame of reference are utilised for this task: Lagrangian and Eulerian. Both these approaches have been used successfully to describe the characteristics of turbulent dispersal within plant canopies and to relate leaf-level fluxes to concentrations within canopies (higher-order Eulerian models: Paw U and Meyers, 1989; Katul and Albertson, 1999; Ayotte *et al.*, 1999; Katul *et al.*, 2001; Lagrangian models: Raupach, 1989a,b; Leclerc and Thurtell, 1990; Warland and Thurtell, 2000; and hybrid models utilising aspects of both approaches: Siqueira *et al.*, 2000; Lai *et al.*, 2000).

Eulerian models make use of fixed-coordinate statistics averaged over an ensemble of realisations of the flow, in practice represented by time and/or space averages. The Eulerian statistics evolve according to conservation equations which contain unknown contributing terms. In order to achieve closure of these equations approximations have to be made to the unknown terms, and the order of the moment equations at which the parameterisation is made determines the order of closure for a particular model. An advantage of the Eulerian approach is that often only single-point measurements can be made in the field, which are appropriate for analysis in a fixed frame of reference. Eulerian models also incorporate the wind-field implicitly, whereas Lagrangian models require this to be predetermined. A major disadvantage of the Eulerian approach is the need to make assumptions relating moments to gradients, a procedure which at first order (K-theory) has been found to cause serious errors for high intensity structured turbulent regions such as within tall plant canopies (Denmead and Bradley 1985, 1987), and which remains theoretically flawed at higher orders.

Lagrangian models use a fluid-following framework, the advantage of which is that it is much better able to account for the history of particle trajectories and the influence of this on future trajectories. On the down side, these models require prior knowledge of the wind field and measurements made in the Eulerian framework must be converted to Lagrangian statistics *via* assumptions and approximations which may not be well understood or may be unrealistic in certain conditions.

1.2.2 Regional-scale atmospheric inversions

The integrating properties of the convective boundary layer allow the influence of surface exchange processes on the atmosphere to be quantified and estimates of fluxes of trace gases and plant isotopic discrimination to be made. Concentrations of trace gases within the atmospheric boundary layer reflect exchange processes occurring at the surface over a regional scale (10^2 to 10^4 km²). On days of high radiation load, low winds and clear skies, turbulence driven by thermal convection mixes air within the atmospheric boundary

layer so that concentrations of scalar quantities such as CO_2 and its isotopes, H_2O and potential temperature are approximately constant with height. The influence of inhomogeneities at the surface are therefore smoothed in the atmosphere and the signal present in the evolution of atmospheric concentrations through the day represents the weighted average surface flux over the region. Mixing within the convective boundary layer (CBL) occurs rapidly (~ 15 min., Stull, 1988) relative to the time scale for substantial changes in surface fluxes (~ 1 hr except near sunrise and sunset, from eddy covariance observations in various ecosystems). This allows simple mass-balance approaches to relate average CBL concentrations to surface flux magnitudes. These approaches are collectively called CBL budget methods, and may be partitioned into “differential” CBL methods and “integral” CBL methods according to whether the conservation equations are integrated in time before application (Raupach *et al.*, 1992). The methods have been used successfully to model diurnal growth of the depth of the mixed layer and/or its scalar content (eg. McNaughton and Spriggs, 1986; Denmead *et al.*, 1996; Cleugh and Grimmond, 2001) and to infer average regional fluxes of sensible and latent heat and CO_2 from diurnal changes in corresponding scalar concentrations over both homogeneous and heterogeneous landscapes (eg. Brutsaert and Mawdsley, 1976; Munley and Hipps, 1990; Raupach *et al.*, 1992; Denmead *et al.*, 1996; and Cleugh and Grimmond, 2001).

1.3 Process-based modelling of canopy mass and energy exchange

An alternative to the inverse modelling approach to gaining information on plant-atmosphere exchange is the process-based or “forward” modelling approach. Here knowledge of plant physiology, biochemistry and thermodynamics is used to construct a model of exchange processes. This model is then coupled to the atmosphere using a description of turbulent transfer (which may be one of those used in the inverse models) to relate these processes to atmospheric concentrations above and within the canopy. In this manner concentration measurements above the canopy may be used to provide boundary conditions for the

canopy-atmosphere exchange problem. As mentioned in §1.1, this approach can be taken to varying degrees of complexity, ranging from the simplest big-leaf models (leaf properties and fluxes averaged over the entire canopy), to two-leaf models (averaged over sun and shade leaves), more recently three-leaf models (averaged over Rubisco-limited sun leaves, electron transport-limited sun leaves and electron transport-limited shade leaves), and to multi-layer models (no vertical averaging before integration over the canopy except due to finite-difference approximation).

Process-based canopy models make use of understanding of leaf-level fluxes gained from experimental and theoretical approaches, including open or closed chamber leaf gas exchange experiments investigating variation of assimilation rate and/or carbon isotope discrimination with environmental variables (eg. von Caemmerer and Farquhar, 1981; Evans *et al.*, 1986); biochemical investigations of the photosynthetic carbon reduction and photorespiratory carbon oxidation cycles, enzyme kinetics and electron transport at the chloroplast level (eg. von Caemmerer and Farquhar, 1981; and many other studies); studies of radiation penetration within the leaf in relation to chloroplast distribution (eg. Evans, 1995; Vogelmann and Han, 2000); and theoretical considerations linking leaf and sub-leaf processes with environmental variables such as the constraint on stomatal aperture imposed by water loss (eg. Cowan, 1977; Cowan and Farquhar, 1977). Scaling these processes from the leaf to the canopy can to some extent be carried out as the sum of individual leaf contributions, treating the canopy as a single large leaf with vertically varying properties. The most significant property that is generally now not scaled in this manner is the radiation absorption (de Pury and Farquhar, 1997). Radiation penetration in canopies differs from that in leaves because sunflecks penetrate deep into the canopy. This means that while the time-averaged radiation profile may follow the same exponential decline with cumulative leaf area that is shown in leaves with cumulative chloroplast area, the instantaneous profile does not: leaves low in the canopy at times receive much more radiation than the time-averaged profile would predict. The non-linear response of photosynthesis to radiation makes this distinction important, and leaf-based canopy

models that do not account for sunfleck penetration will overestimate canopy photosynthesis (de Pury and Farquhar, 1997; Wang and Leuning, 1998). These considerations have led to canopy models being classed according to their treatment of radiation absorption (big-leaf, two-leaf, three-leaf and multi-layer). Additional factors lending complexity to radiation absorption models, but which may be accounted for to varying degrees, include leaf angle distribution; consideration of radiation components of different wavelengths and their corresponding leaf absorptances; variation of reflectance and transmission with leaf angle; penumbral effects; and non-uniform leaf distribution (leaf clumping) (see for example Lemeur and Blad, 1974; Norman and Jarvis, 1975; Goudriaan, 1977; Ross, 1981; Stenberg, 1996a; Ross *et al.*, 1998; Palmroth *et al.*, 1999).

1.4 The use of isotopes of CO₂ as indicators of exchange processes

Isotopic fractionation occurs during many physical and chemical processes because the heavier atom or molecule, while maintaining the general physical and chemical properties of the lighter isotope, moves or reacts slower in mass-limited kinetic processes such as gaseous diffusion and chemical reactions, and in equilibrium processes such as phase changes in a closed system (the steady-state result of two opposing kinetic processes). Knowledge of the degree of fractionation during a particular process allows us to discern when and how much that process is occurring by looking at the isotopic composition of the remaining substrate. Conversely, knowledge of the rate of occurrence of a process can be used to determine the fractionation during that process, which can be used to validate models for use in other applications. In cases where a reactant is converted into a product and both are available for analysis, fractionation factors can be determined directly by comparison of their isotopic compositions.

In relation to plant-atmosphere interaction, the important processes involving isotopic fractionation of carbon isotopes of CO₂ are diffusion of CO₂ into and out of the stomata and carboxylation by the enzyme Rubisco during CO₂ fixation (Farquhar *et al.*, 1989a;

Brugnoli and Farquhar, 2000). There is evidence to suggest that respiration involves little if any isotopic fractionation (Lin and Ehleringer, 1997; Gillon and Griffiths, 1997), but releases a pool of isotopically distinct CO₂, of composition acquired during fixation, into the ambient air. Contrary evidence, however, suggest discriminations of 3-6‰ may occur during leaf dark respiration (Duranceau *et al.*, 1999, 2001; Ghashghaie *et al.*, 2001). The degree of fractionation, if any, is likely to vary among species and environmental conditions (Ghashghaie *et al.*, 2001), and the discrimination signature of leaf-respired CO₂ must be offset to some degree by that of soil-respired CO₂ in order to conserve mass. Observations over many species are well represented without recourse to inclusion of respiratory fractionation (Farquhar *et al.*, 1989a; O'Leary, 1993), and until a clear understanding is gained of isotope effects during respiration from the various plant and soil compartments and their response to environmental conditions, neglect of this fractionation may be justified.

The relative importance of the two events causing carbon isotope fractionation during CO₂ assimilation depends on the rate of supply of CO₂ to the sites of carboxylation, which is limited by the stomatal conductance. At very low stomatal conductance fewer molecules reach the sites of carboxylation and a higher proportion of available molecules are fixed, resulting in less discrimination by the carboxylation enzyme and total discrimination is dominated by that during diffusion through the stomata. Conversely, at very high stomatal conductance intercellular CO₂ concentration approaches the ambient concentration and discrimination is dominated by the carboxylation reaction (Farquhar and Lloyd, 1993).

Oxygen isotopes of CO₂ paint a considerably more complicated picture because the species (CO₂ molecules of a particular isotopic composition) is not conserved: the oxygen atoms in CO₂ exchange with those in H₂O. Consideration must therefore be given to all possible sites of contact with water where exchange may occur. Water in the chloroplasts and soil are considered to be the two most important pools for exchange of oxygen isotopes of CO₂ in plant-atmosphere interaction (Farquhar *et al.*, 1993). Only about $\frac{1}{3}$ of the CO₂ which diffuses into the leaf is actually fixed: the remainder comes into isotopic equilibrium

with the chloroplast water in a reaction catalysed by the enzyme carbonic anhydrase, and then returns to the ambient air subject to fractionation during diffusion through the stomata. CO_2 respired from roots and soil microbes diffuses through the soil, acquiring the isotope signature of soil water to varying degrees at various depths depending on soil type, soil water content and temperature, and fractionating as it diffuses out of the soil. Another process potentially complicating the budget of oxygen isotopes of CO_2 is the “invasion” effect, where CO_2 diffuses from the ambient air into the soil, partially equilibrates with soil water and diffuses out again, resulting in no net CO_2 flux (Tans, 1998; Miller *et al.*, 1999). Similar mass-conserving exchange may occur with other water pools in a plant canopy such as dew or free water on plant and soil surfaces.

The strong coupling between isotope discrimination and plant physiological properties such as stomatal conductance and intercellular CO_2 concentration lead to distinctive isotope signatures in ecosystems of different plant species, functional type and climate conditions (Körner *et al.*, 1991; Lloyd and Farquhar, 1994; Brooks *et al.*, 1997a; Buchmann *et al.*, 1998; Flanagan, 1998). In addition, the signature associated with isotope exchange between atmospheric CO_2 and the oceans is considerably different to that with the terrestrial biosphere (Francey and Tans, 1987; Farquhar *et al.*, 1993). This has enabled the carbon and oxygen isotope composition of atmospheric CO_2 (both carbon and oxygen) to be used as additional constraints in global atmospheric inversions to partition CO_2 flux between continents and oceans (eg. Tans *et al.*, 1993; Francey *et al.*, 1995; Enting *et al.*, 1995; Ciais *et al.*, 1995, 1997; Rayner *et al.*, 1999; Peylin *et al.*, 1999). Recently, process-based hydrological modelling has been combined with the global flask network CO_2 and isotope composition data to map the oxygen isotope discrimination over a fine-scale global grid (Noone *et al.*, 2001). These studies demonstrate the importance of developing a good understanding of the variations in carbon and oxygen isotope discrimination on daily, seasonal and interannual scales and the dominant causes of these variations.

1.5 Combining atmospheric inversion, micrometeorology and plant physiology

The canopy and regional scale models presented here have been reported elsewhere (Styles *et al.*, 2002a, 2002b). The implementation of the canopy-scale model as reported here is slightly different to that of Styles *et al.* (2002a), with corresponding small differences in results. That study did not incorporate oxygen isotope composition of CO₂, and used a slightly different parameter optimisation scheme. As the content of this thesis includes and surpasses the content of those papers, no further reference will be made to them except to indicate some of those small differences.

1.5.1 Canopy-scale model

In the canopy-scale study presented here the canopy source distribution is specified through the use of a multi-layer sun/shade photosynthesis and energy balance model and Lagrangian localised near-field theory of turbulent dispersal is used to determine profiles of ¹³CO₂, C¹⁸O¹⁶O, CO₂ and H₂O concentrations and of temperature in the canopy. Four canopy parameters relating to maximum photosynthetic capacity, the ratio of marginal water loss to carbon gain and radiation penetration into the canopy, together with the ground fluxes of CO₂, H₂O and heat, are fitted by the inversion procedure to provide optimal agreement with the measured concentration profiles. Two additional parameters describing within-canopy turbulence structure are also optimised.

The inverse Lagrangian approach for modelling source/sink distributions from concentration measurements has been used successfully for determining source distributions of heat in wind tunnel studies (Raupach, 1989a); evaporation in millet (Dolman and Wallace, 1991); heat and ammonia in corn (Denmead *et al.*, 2000a and Harper *et al.*, 2000); CO₂, H₂O and heat in a rice canopy (Leuning *et al.*, 2000) and CO₂ in a pine forest canopy (Katul *et al.*, 1997). These studies all applied the model to individual tracer species with no use of mutual constraints and no analysis of interaction between source strengths of different species.

Most multi-layer and big-leaf canopy models make use of energy constraints to couple water and heat fluxes. These kinds of models have been used in conjunction with Lagrangian dispersal theory in the forward mode to obtain near-field concentration contributions within canopies. Huber *et al.* (1999) used this approach to infer air and leaf temperature, from which isoprene emissions could be estimated; while van den Hurk and McNaughton (1995) and McNaughton and van den Hurk (1995) explored the effect of the near-field contribution on the energy balance within a two-leaf model. Baldocchi (1992) used biochemical, physiological and micrometeorological principles to describe source/sink strengths and compared two Lagrangian random walk models, inferring total canopy fluxes and within-canopy concentration profiles from these. Gu *et al.* (1999) used a similar approach to partition CO₂, H₂O and sensible heat fluxes between the soil, understorey and overstorey of a boreal aspen forest. Soil flux in all these studies was either modelled independently or estimated from above-canopy measurements. None of these studies made use of the Lagrangian turbulent transfer theory in inverse mode, where canopy concentration measurements are used not only to assess the validity of the model, but also to drive the output of unknown parameters or variables.

The model and measurements presented here provide a means to investigate several important characteristics of canopy trace gas exchange. These are: (i) the partition of fluxes between the soil and canopy; (ii) estimation of parameters involved in photosynthesis (maximum photosynthetic capacity), stomatal conductance (marginal water loss per marginal carbon gain), radiation penetration (extinction coefficients for diffuse and direct radiation) and turbulence structure (Lagrangian time scale); (iii) determination of carbon and oxygen isotope discrimination during CO₂ assimilation and its vertical and diurnal variation; (iv) determination of physiological properties (intercellular CO₂ concentration, vapour pressure deficit, stomatal conductance, leaf water isotopic enrichment) and their vertical and diurnal variation.

Other methods dealing with result (i) include combining above-canopy eddy covariance measurements with scaled up chamber measurements of soil, leaf and stem fluxes (Ryan

et al., 1996; Law *et al.*, 1999); measuring soil fluxes directly with below-canopy eddy covariance instruments (Baldocchi *et al.*, 1997, 2000; Shibistova *et al.*, 2002); extrapolating night-time respiration fluxes based on temperature regressions (Goulden *et al.*, 1996); and the use of isotopic composition of CO₂ to differentiate between the isotope discrimination signals from photosynthesis and respiration (Yakir and Wang, 1996; Bowling *et al.*, 2001). In contrast to the present study, many of these methods are applicable to partitioning carbon dioxide fluxes only, most require eddy covariance measurements, and none utilise the information available in the vertical structure of concentration profiles within the canopy, nor the constraint provided by measuring several trace gas species simultaneously.

In relation to result (ii), it is possible to measure all of these quantities, usually requiring intensive, time and equipment-consuming methods. For example to measure the radiation extinction coefficients would require several sensors to obtain sufficient spatial coverage and determine the vertical decline with leaf area: examination of Figure 2 of Kellomäki and Wang (2000b) implies the use of 1200 sensor locations to determine the diffuse and direct extinction coefficients for short wave radiation in a Scots pine canopy. The present method is appealing not only for the ease in obtaining required measurements but also because it relies on no assumptions or prior knowledge of these parameters, so that a result contrary to expectations may reveal processes or information that would otherwise go unnoticed.

Results (iii) and (iv), the vertical and time-variation of isotopic discrimination and physiological properties, are not easily obtained in a forest canopy. Much work has been carried out in recent extensive ecosystem investigations such as the Boreal Ecosystem-Atmosphere Study (BOREAS) in boreal North America and the Large Scale Biosphere-Atmosphere Experiment (LBA) and other studies in Amazonia, providing important observational evidence of diurnal and seasonal changes in ecosystem discrimination and gas exchange and canopy concentrations (Buchmann *et al.*, 1996; Brooks *et al.*, 1997b; Flanagan *et al.*, 1996, 1997, 1999; Kruijt *et al.*, 1996; Lloyd *et al.*, 1996; Buchmann *et al.*, 1997; Moreira *et al.*, 1997; Sternberg *et al.*, 1998). To avoid the need for high resolution of

spatial and temporal measurements, leaf measurements may be made and interpolated or scaled up to the canopy and in time with appropriate assumptions. The present method of gleaning information from atmospheric concentrations causes no disturbance to ambient conditions and is able to resolve properties within the canopy as well as of the canopy as a whole. It is therefore less subject to sampling and measurement error, relying more on the accuracy of formulation of the exchange processes within the model.

1.5.2 Regional-scale model

The regional-scale study presented here compares two budget methods for inferring surface CO₂ fluxes and carbon and oxygen isotope discrimination during CO₂ assimilation over a forest and bog region in central Siberia in July 1998. The first method is also used to infer regional sensible and latent heat fluxes. The two budget methods investigated here use similar scalar conservation considerations. Despite both effectively being integral CBL (ICBL) methods, this label will be applied to the first method, which utilises the idealised properties of the CBL to find an analytical solution to the surface fluxes. The second method, referred to as the “height integration method”, is more numerical in its approach, calculating the molar difference in the sampled air column over the integration period. These and similar boundary layer budget methods have been used with reasonable success to infer regional fluxes of a variety of trace gases, including CO₂ (eg. Raupach *et al.*, 1992; Denmead *et al.*, 1996; Levy *et al.*, 1999; Lloyd *et al.*, 2001); sensible heat (eg. Barr *et al.*, 1997; Barr and Betts, 1997); latent heat (eg. McNaughton and Spriggs, 1986; Denmead *et al.*, 1996; Barr *et al.*, 1997; Barr and Betts, 1997; Lloyd *et al.*, 2001); and methane (eg. Denmead *et al.*, 2000b; Wratt *et al.*, 2001).

The ICBL budget method was only recently for the first time applied to the carbon isotope composition of CO₂ to infer regional carbon isotope discrimination during photosynthesis (Lloyd *et al.*, 1996; Lloyd *et al.*, 2001). This study is the first to additionally infer regional oxygen isotope discrimination. The application of the methods to inference of plant isotope discrimination requires interpretation based on ecophysiological theory

of CO₂ assimilation and isotopic fractionation during diffusion and fixation. Estimates of isotope discrimination obtained from atmospheric inversions such as presented here have the potential to reveal weaknesses in simplified physiological models, showing when and to what degree additional complicating processes are important. The comparison of the two budget approaches highlights strengths and weaknesses in both, and assesses the importance and validity of assumptions commonly adopted in CBL budget methods.