

# From biota to chemistry and climate: towards a comprehensive description of trace gas exchange between the biosphere and atmosphere

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**Abstract.** Exchange of non-CO<sub>2</sub> trace gases between the land surface and the atmosphere plays an important role in atmospheric chemistry and climate. Recent studies have highlighted its importance for interpretation of glacial-interglacial ice-core records, the simulation of the pre-industrial and present atmosphere, and the potential for large climate-chemistry and climate-aerosol feedbacks in the coming century. However, spatial and temporal variations in trace gas emissions and the magnitude of future feedbacks are a major source of uncertainty in atmospheric chemistry, air quality and climate science. To reduce such uncertainties Dynamic Global Vegetation Models (DGVMs) are currently being expanded to mechanistically represent processes relevant to non-CO<sub>2</sub> trace gas exchange between land biota and the atmosphere. In this paper we present a review of im-

portant non-CO<sub>2</sub> trace gas emissions, the state-of-the-art in DGVM modelling of processes regulating these emissions, identify key uncertainties for global scale model applications, and discuss a methodology for model integration and evaluation.

## 1 Introduction

Numerous exchange processes take place between the terrestrial biota and the atmosphere that contribute to the regulation of the climate system on timescales from hours to millennia. Frequently highlighted examples are the partitioning of available energy into sensible and latent heat and the uptake and release of carbon dioxide. The former influences the height of the convective boundary layer and the moisture content of the troposphere, thus affecting cloud formation (Pielke et al., 1998; Levis et al., 2000), while the latter drives seasonality and interannual variability of the atmospheric CO<sub>2</sub>



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concentration (Ciais et al., 1995; Denning and Fung, 1995; Keeling et al., 1996). Land surface models describe terrestrial biosphere processes within the climate system and have been expanded to include models of dynamic vegetation and interactive carbon cycles. Indeed, climate model experiments that include an interactive terrestrial carbon cycle have demonstrated potentially large climate-carbon cycle feedbacks that have to be taken into account for future climate projections (Cox et al., 2000; Friedlingstein et al., 2001, 2006).

The need to better quantify trace gas exchange at the land surface has spurred the development of dynamic global vegetation models (DGVMs) (Prentice et al., 2007) which include mechanistic representations of terrestrial biogeochemical cycles and vegetation dynamics. The first generation of DGVMs simulated the global distribution of natural vegetation, represented by a number of generic plant functional types (PFTs), and land carbon and hydrological cycles from diurnal to century timescales. The different processes represented by DGVMs are being expanded substantially to account for the crucial role of terrestrial biota in the regulation of atmospheric composition and climate that goes well beyond that of CO<sub>2</sub> and the surface energy balance. Important gases in this context are methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), both of which are well mixed and potent greenhouse gases (GHGs; Donner and Ramanathan, 1980). Other gaseous species, such as biogenic volatile organic compounds (BVOCs) and the nitrogen oxides NO and NO<sub>2</sub> (together referred to as NO<sub>x</sub>) are much more reactive in the atmosphere than CH<sub>4</sub> and N<sub>2</sub>O. BVOCs and NO<sub>x</sub> affect the lifetime of some GHGs (e.g., CH<sub>4</sub>) and are precursors of others, such as tropospheric ozone (O<sub>3</sub>), and of biogenic secondary organic aerosols (SOA; Denmann et al., 2007).

A number of atmospheric feedbacks have been proposed regarding the magnitude and regional patterns of biosphere-atmosphere exchange of non-CO<sub>2</sub> trace gases (Adams et al., 2001; Gedney et al., 2004; Kulmala et al., 2004; Lerdau, 2007; Sitch et al., 2007). These feedbacks include interactions of these gases and their reaction products with climate, vegetation cover, and the terrestrial cycles of carbon and nitrogen. In addition, emissions of carbonaceous trace gases like CH<sub>4</sub> and isoprene (a highly reactive and important BVOC) can under certain conditions be large enough to impact the interpretation of carbon cycle measurements. Isoprene emissions are of the order 1% of the total carbon assimilated by vegetation (i.e., gross primary productivity) but up to 10% of net ecosystem-atmosphere carbon exchange, NEE (Guenther, 2002). Due to the decoupling of assimilation rates and isoprene emissions under certain conditions this proportion may increase under climate change (Guenther, 2002; Pegoraro et al., 2005; Arneth et al., 2007a). Few studies consider both CO<sub>2</sub> and CH<sub>4</sub> in the context of an ecosystem carbon balance even though CH<sub>4</sub> losses may account for 10–20% of NEE (Friborg et al., 2003; Grant et al., 2003).

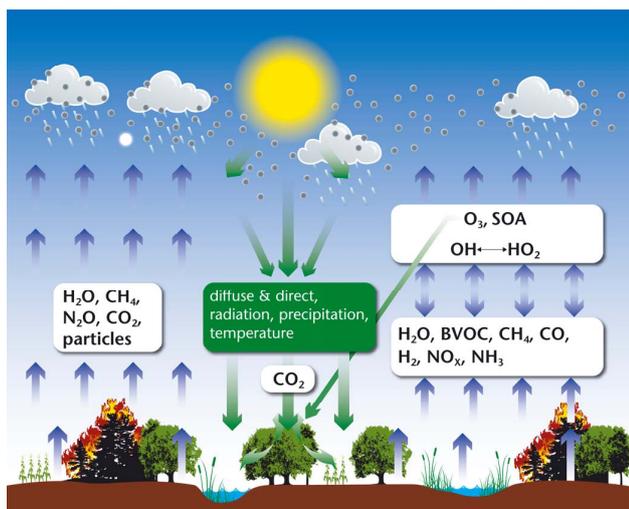
Recent developments in DGVMs aim to represent emissions of climatically relevant non-CO<sub>2</sub> trace gases, to investigate future changes in emissions and associated climate-chemistry feedbacks systematically within unified modelling frameworks. Key processes include interactive carbon and nitrogen cycles, inclusion of fire disturbance, natural wetlands, land use and land cover changes, mechanistic representations of plant BVOC emissions and plant-ozone interactions. We begin with a short overview of the importance of non-CO<sub>2</sub> trace-gas exchange at the land surface for atmospheric chemistry and climate. We then present an overview of DGVM principles, followed by recent developments within the terrestrial biosphere community in expanding DGVMs to incorporate mechanistic, process-based schemes of non-CO<sub>2</sub> trace gas exchange, that are of relevance to the atmospheric chemistry-climate modelling community. Developments are grouped according to the introduction of new land cover types and processes into DGVMs (land use, wetlands, nitrogen cycle, wildfire and hydrogen) and advances in modelling plant physiology (relevant for exchange of BVOC, Ozone and dry deposition). We do not provide a comprehensive review of DGVMs and their performance at simulating vegetation dynamics, land-atmosphere CO<sub>2</sub> and H<sub>2</sub>O exchange in the context of the terrestrial energy balance or land carbon sink strength, as this has been the focus of earlier studies (Cramer et al., 2001; Sitch et al., 2008). We highlight key uncertainties in our ability to model these processes at the global scale, and make recommendations on future DGVM research in this field.

## 2 Importance of non-CO<sub>2</sub> trace gas exchange at the land surface for atmospheric chemistry and climate

### 2.1 Non-CO<sub>2</sub> trace gas exchange at the land surface

Terrestrial ecosystems affect tropospheric composition and climate by emitting and/or absorbing GHGs (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and H<sub>2</sub>O) and other more reactive trace gases (BVOCs, NO<sub>x</sub>, CO, and H<sub>2</sub>). BVOCs also form secondary organic aerosol particles (SOA) by either direct condensation of the BVOC, or the products from chemical reactions. SOA scatter and absorb radiation, and affect cloud formation and precipitation via their ability to act as cloud condensation nuclei (Hoffmann et al., 1997; Hartz et al., 2005; Dusek et al., 2006; Fig. 1). Evapotranspiration determines atmospheric humidity which in turn controls the formation of the hydroxyl radical (OH), the major atmospheric oxidising agent (Derwent, 1995; Monson and Holland, 2001).

Beside H<sub>2</sub>O and CO<sub>2</sub> (which are not the focus of this review) the most important GHGs emitted from terrestrial biota are methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). The chief “natural” biogenic source of CH<sub>4</sub> is anaerobic microbial production in wetlands, with emission estimates between 100 and 231 Tg CH<sub>4</sub> a<sup>-1</sup>. These natural emissions contribute no more



**Fig. 1.** Conceptual overview of terrestrial carbon cycle – chemistry – climate interactions. The land surface affects atmospheric chemistry and climate directly via surface energy partitioning into latent and sensible heat flux (not shown), and emissions of greenhouse gases ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ) and aerosol particles from forests, grasslands, wetlands, agricultural systems, and vegetation biomass burning. Atmospheric chemistry and climate is also affected by atmospheric reactions of reactive trace gases emitted from vegetation, soils and fires ( $\text{H}_2\text{O}$ , BVOC,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ). These contribute to complex oxidation patterns along variable pathways that depend on the overall chemical and physical environment. Reaction kinetics vary greatly, and the lifetime of substances or their reaction products may vary from seconds (e.g., some BVOC) to years (e.g.,  $\text{CH}_4$ ) which in turn determines whether associated chemistry-climate effects are regional or continental to global. The chief oxidising agent is the hydroxyl radical  $\text{OH}$ , while some BVOC react directly with  $\text{O}_3$ . Tropospheric humidity and hence latent heat flux is an important constraint for  $\text{OH}$  formation. The main climate relevance of the atmospheric reactions is to consume or generate  $\text{O}_3$ , formation of secondary organic aerosol (SOA), and effects on the lifetime of  $\text{CH}_4$ . Climate feedbacks in the system occur directly (e.g., via the temperature and/or light response of emissions) or indirectly via climate or, for example,  $\text{O}_3$  effects on vegetation composition, productivity and carbon cycle.

than 15–30% of the global total  $\text{CH}_4$  emission flux which is dominated by anthropogenic sources, primarily from rice agriculture, domestic ruminants and energy production (Denman et al., 2007). Smaller sources in natural ecosystems are termites ( $20 \text{ Tg CH}_4 \text{ a}^{-1}$ ) and wild ruminants ( $5 \text{ Tg CH}_4 \text{ a}^{-1}$ ; Lelieveld et al., 1998). Recent studies suggest a high proportion of  $\text{CH}_4$  emissions occur from tropical wetlands that are permanently or seasonally inundated (Mikaloff Fletcher et al., 2004a,b; Wang et al., 2004; Chen and Prinn, 2006), owing to a combination of a warm and moist climate and high plant productivity. Estimates of the spatial extent of wetlands which account for seasonal changes in inundation and maximum areas under standing water attribute approxi-

mately equal areas to the tropics (including rice paddies) and temperate and boreal regions combined (Prigent et al., 2001). Vegetation composition affects the methane flux to the atmosphere via links with plant productivity and by the proportion of aerenchymatous species present (e.g. mangroves, sedges and rushes), as these species facilitate transport of  $\text{CH}_4$  from anaerobic soil layers to the atmosphere by-passing aerobic layers and the likelihood of oxidation. Keppler et al. (2006) suggest terrestrial plants could be a source of  $\text{CH}_4$  under aerobic conditions, although the magnitude of this flux and mechanisms involved have been the focus of much debate (Houweling et al., 2006; Dueck et al., 2007; Ferretti et al., 2007). Recent evidence supports the existence of a photochemical source of methane from fresh or dry plant material that is affected by amount and type of UV radiation (Vigano et al., 2008). The terrestrial biosphere can also act as a sink for atmospheric  $\text{CH}_4$ . However, uptake by well aerated upland soils is estimated to lie between 9 and  $47 \text{ Tg CH}_4 \text{ a}^{-1}$  (Curry, 2007; Denman et al., 2007; Duttar and Verchot, 2007); therefore this mechanism plays only a minor role compared to the dominating chemical methane oxidation sink (via reaction with  $\text{OH}$ ) in the troposphere.

Biological  $\text{N}_2$  fixation is the largest source of nitrogen to natural ecosystems, currently delivering approximately  $110 \text{ Tg N a}^{-1}$  (Galloway et al., 2004). This flux is rivalled by the application of reactive N as fertiliser created from the Haber-Bosch process in addition to approximately  $40 \text{ Tg N a}^{-1}$  associated with cultivation of nitrogen fixing plants (e.g. from the legume family, with their symbiotic  $\text{N}$ -fixing bacteria in root nodules; Galloway et al., 2004, 2008). Plants are able to take up organic nitrogen from symbiosis with  $\text{N}_2$  fixing bacteria and also directly via root uptake of small-chain organic molecules (Schimel and Bennett, 2004) including proteins (Paungfoo-Lonhienne et al., 2008). More typically, depending on plant species and environmental conditions, N is taken up through the roots in mineral form as nitrate ( $\text{NO}_3^-$ ) or ammonium ( $\text{NH}_4^+$ ) ions derived from mineralization. Natural  $\text{N}_2\text{O}$  emissions, presently about  $11 \text{ Tg N a}^{-1}$  (Galloway et al., 2004), are mainly associated with nitrification and denitrification processes. The magnitude of emissions depends on the availability of N for soil microbial processes and on environmental conditions, especially on soil temperature and moisture conditions (Parton et al., 1996; Li et al., 2000). Tropical rainforests, which are primarily not N limited, grow under conditions of high rainfall and temperature, and support microbial C as well as N turnover. Tropical rainforest soils are therefore major sources of  $\text{N}_2\text{O}$  (Kroeze et al., 1999; Galloway et al., 2004; Werner et al., 2007). But the magnitude of net emissions from particular ecosystems are highly uncertain, owing to the restricted number of measurements, the substantial spatial and temporal variability of fluxes (e.g. Groffman et al., 2006; Seitzinger et al., 2006) and the uncertainty in atmospheric N deposition effects on soil N trace gas emissions (Pilegaard et al., 2006). Enhanced soil  $\text{N}_2\text{O}$  emissions have been reported

for managed agricultural land, which originate from the increased N availability following fertilisation (Forster et al., 2007; Crutzen et al., 2008). The main sink for  $\text{N}_2\text{O}$  is photochemical destruction in the upper troposphere and lower stratosphere, whereas the importance of soils as a sink for  $\text{N}_2\text{O}$  is still unknown (Chapuis-Lardy et al., 2007).

The terrestrial N cycle is also a major source of the reactive nitrogen oxides NO and  $\text{NO}_2$  ( $\text{NO}_x$ ). While  $\text{NO}_x$  represents only a minor fraction of the total N fluxes (normally less than 10%), they are fundamental components of tropospheric chemistry. Similar to  $\text{N}_2\text{O}$ , major natural sources of  $\text{NO}_x$  are associated with soil nitrification and denitrification processes, and the net flux to the atmosphere is estimated at  $5\text{--}8\text{ TgN a}^{-1}$  (Galloway et al., 2004; Denman et al., 2007) but production from biomass burning is also important. On a global scale, emissions from natural sources are much smaller than those from fossil fuel combustion (ca.  $25\text{ TgN a}^{-1}$ ; Jaegle et al., 2005). However, there are indications that the natural flux has been underestimated in the past, owing to the underestimation of the importance and effect of N deposition and the incompletely understood production mechanism of  $\text{NO}_x$  in forest soils (Galloway et al., 2004; Schindlbacher et al., 2004; Pilegaard et al., 2006).

Alongside  $\text{NO}_x$ , BVOCs are an important component of vegetation-chemistry-climate interactions. The term "BVOC" subsumes a vast group of molecules with known (defence, attraction) or debated (range of possible stress-tolerances) functions in plants (Penuelas and Llusia, 2004). Emissions of BVOCs are strongly dependent on plant species (Kesselmeier and Staudt, 1999). Research on their effects on tropospheric chemistry and climate has to date concentrated on the subset isoprene ( $\text{C}_5\text{H}_8$ ) and mono- and sesquiterpenes, and their importance for  $\text{O}_3$  and SOA formation. Isoprene represents approximately one half of the total BVOC emissions (ca.  $1000\text{ TgC a}^{-1}$ ; Guenther et al., 1995) and in terms of carbon matches, or even exceeds, the annual biogenic  $\text{CH}_4$  source. Most studies attribute the majority of isoprene emissions to tropical ecosystems, whereas mono- and sesquiterpenes also have sizeable sources in temperate and boreal regions (Guenther et al., 1995; Arneth et al., 2008a; Spracklen et al., 2008). Emissions of some oxygenated BVOCs can also be large (e.g., methanol, Galbally and Kirstine, 2002) but much less is known about the magnitudes of the biogenic sources of these compounds.

Oxidation of hydrocarbons (including BVOCs and  $\text{CH}_4$ ) is an important source of CO, which in turn is oxidised to  $\text{CO}_2$  via reaction with OH. This reaction with OH means that CO can affect the lifetime of greenhouse gases such as methane. Wild and Prather (2000) estimated that the radiative forcing perturbation caused by an emission of  $100\text{ Tg CO}$  would be the same as that caused by an emission of  $5\text{ Tg CH}_4$ . CO is also emitted directly from both living and decaying vegetation when exposed to sunlight (Warneck, 1999, and references therein), most probably from photooxidation of the plant material, although the exact mechanism is not known.

Source estimates lie in the range  $20$  to  $200\text{ Tg a}^{-1}$  (Sanderson, 2002). A biological sink of CO in soils and production during litter decay may also need consideration, although some studies suggest a smaller contribution to the overall budget than previously thought (Potter et al., 1996; King and Crosby, 2002).

Biomass burning releases a large quantity of aerosols and GHGs directly into the atmosphere, together with precursors of these species, many of which also react with the hydroxyl radical (Andreae and Merlet, 2001). Fire emissions have a strong influence on the interannual variation in the atmospheric growth rates of CO,  $\text{CO}_2$  and  $\text{CH}_4$  and are a major source of uncertainty in radiative forcing calculations (Galanter and Levy, 2000; Ito et al., 2007; Naik et al., 2007). Fire is a natural element in major ecosystems, affecting species composition and canopy structure, and thus indirectly trace gas fluxes (Bond-Lamberty et al., 2007). Estimates for late 20th century global fire-related carbon fluxes range between  $2$  and  $4\text{ PgC a}^{-1}$  (Seiler and Crutzen, 1980; Andreae and Merlet, 2001), representing up to one half of the global CO emissions into the troposphere (Bian et al., 2007; Duncan et al., 2007). Uncertainties in assessing area burnt, variability of burning conditions and changes in global vegetation productivity are large (Seiler and Crutzen, 1980; Andreae and Merlet, 2001; van der Werf et al., 2004).

Over the last centuries anthropogenic land cover and land use changes following human intervention (e.g. deforestation and expansion of agriculture) have been of increasing importance for trace gas exchange. In some regions, an estimated  $80\text{--}90\%$  of all fires are ignited by humans (Denman et al., 2007). Only a few agricultural systems and practices are responsible for half of the anthropogenic  $\text{CH}_4$  emissions (domestic ruminants, rice paddies, and biomass burning) with emissions from cattle and sheep exceeding those from wild ruminants by a factor of five to ten and rice agriculture adding a further  $31$  to  $112\text{ TgCH}_4\text{ a}^{-1}$  to the global emission budget (Denman et al., 2007). Significant emissions of  $\text{N}_2\text{O}$  ( $3.2\text{ TgN a}^{-1}$ ) and  $\text{NO}_x$  ( $2.6\text{ TgN a}^{-1}$ ) are related to the use of mineral and organic fertilizers and thus also to livestock density (Galloway et al., 2004). Fertilizer use within agricultural systems, arable soils and pastures are chief sources of reduced N emissions (referred to as  $\text{NH}_x$ ; Bouwman et al., 2002; Graedel and Crutzen, 1993). Deforestation leads to significant reductions in emissions of isoprene and monoterpenes, which affect regional and potentially global trace gas concentrations. Woody biofuel plantations may increase regional emissions (Lathière et al., 2006; Arneth et al., 2008b); effects of land cover change on emissions of oxygenated BVOC have not yet been extensively studied.

## 2.2 Temporal trends in non- $\text{CO}_2$ trace gas exchange and their atmospheric burden

Increases in  $\text{CH}_4$ , tropospheric  $\text{O}_3$  and  $\text{N}_2\text{O}$  concentrations since pre-industrial times have contributed (average

estimate) radiative forcings of 0.48, 0.35 and  $0.16 \text{ W m}^{-2}$ , respectively (Forster et al., 2007). The combined forcing is equivalent to 60% of the contribution of anthropogenic  $\text{CO}_2$  to global mean radiative forcing in 2005 (Forster et al., 2007).  $\text{N}_2\text{O}$  is a greenhouse gas, approximately 298 times more powerful than  $\text{CO}_2$  (100 year time scale), with an atmospheric lifetime of approximately 114 years and a current rate of atmospheric increase of  $0.25\% \text{ a}^{-1}$  (Forster et al., 2007). Its present radiative forcing is about one third of that of  $\text{CH}_4$ . Methane itself is presently the third most important greenhouse gas after water vapour and  $\text{CO}_2$ , having more than doubled in abundance since pre-industrial times (Forster et al., 2007). Annual anthropogenic sources have increased by 50% since the 18th century (Denman et al., 2007; Lassey et al., 2007), partially due to agriculture but also due to increased human burning activities. Wetland emissions of  $\text{CH}_4$ , including rice paddies, are projected to approximately double by the end of this century in response to climate change, leading to a positive radiative feedback of nearly 5% (Gedney et al., 2004). Although  $\text{CH}_4$  emissions are very sensitive to climate change they have no apparent causal role in the development of late glacial-early interglacial and Holocene climate (Severinghaus et al., 1998; Raynaud et al., 2000). Over the last 10 000 years, the impact of  $\text{CH}_4$  emissions from northern wetlands has been estimated to be a gradually increasing positive radiative forcing, but this reduces the cooling impact of peat  $\text{CO}_2\text{-C}$  uptake only to minor degree (Frolking and Roulet 2007). Biogeochemical models are unable to reproduce the low  $\text{CH}_4$  concentrations at the last glacial maximum (LGM) based on changes in global emission patterns alone. An enhanced LGM atmospheric  $\text{CH}_4$  sink has been invoked due to lower BVOC emissions in the dry, cold environment (Adams et al., 2001; Valdes et al., 2005; Kaplan et al., 2006). However, changes in  $\text{NO}_x$  emissions from fire due to climate change and changes in plant C:N ratio may also have influenced atmospheric oxidation capacity and  $\text{CH}_4$  lifetime (Thonicke et al., 2005). In addition, new process understanding in modelling BVOC suggests substantially altered glacial-interglacial emission trends (Possell et al., 2005; Arneth et al., 2007a). Interest in the global  $\text{H}_2$  cycle has increased as  $\text{H}_2$  fuel cells have been suggested as a replacement for fossil fuel. With a hydrogen economy some leakage of  $\text{H}_2$  is inevitable. An estimated leakage of between 3 and 10% has been associated with an increase of  $\text{H}_2$  of up to 0.6 ppm (Schultz et al., 2003). Technological and infra-structural issues aside, the impact of an increase in  $\text{H}_2$  is still uncertain. However, this doubling in  $\text{H}_2$  concentrations may have the potential to cause reductions in OH, increase lifetimes of  $\text{CH}_4$ , and thus contribute to global warming (Schultz et al., 2003; Warwick et al., 2004).

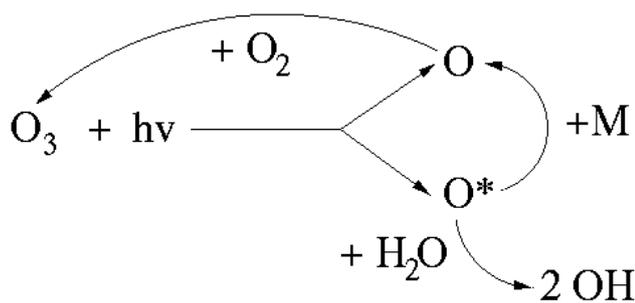
Over the industrial period precursor emissions from fossil fuel and biomass burning have acted to approximately double the global mean tropospheric  $\text{O}_3$  concentration (Gauss et al., 2006). This result is subject to a considerable level of uncertainty, as small changes in assumed pre-industrial BVOC

to  $\text{NO}_x$  ratio, or soil and fire emissions have considerable effect on the pre-industrial  $\text{O}_3$  burden and hence the pre-industrial to present radiative forcing calculations (Mickley et al., 2001; Ito et al., 2007). Uncertainties in future precursor emissions and interactions with climate change, particularly changes in temperature and humidity that affect reaction kinetics paint a complex picture on future regional  $\text{O}_3$  concentrations (Prather et al., 2001; Dentener et al., 2006a; Liao et al., 2006; Stevenson et al., 2006). Two competing effects determine the net  $\text{O}_3$  burden: chemical reactions involved in producing  $\text{O}_3$  will proceed more quickly at higher temperatures, hence greater  $\text{O}_3$  production. But a warmer climate means increased water vapour in the boundary layer, resulting in greater destruction of  $\text{O}_3$ . There will be additional indirect effects from possibly larger  $\text{NO}_x$  emissions from soils,  $\text{NO}_x$  by lightning or changes in isoprene production by vegetation. Sanderson et al. (2003a) projected isoprene emissions to increase by nearly 30% between the 1990s and 2090s due to climate change. These increases resulted in projected summer average surface ozone levels over Europe for 2100 to be 8 ppb larger. However this study neither included the effect of BVOC- $\text{CO}_2$  inhibition in leaves (Sect. 3.6) nor the overall uncertain and contradictory role of VOCs in plant responses to ozone (Fiscus et al., 2005). The former greatly alters future projections of tropospheric  $\text{O}_3$  and OH levels with diverging responses in polluted vs. non-polluted regions (Young et al., 2009).

### 2.3 Processes in the troposphere

Almost all chemical degradation of BVOCs and many other species begin via reaction with the hydroxyl radical, OH. The OH radical is formed during the photolysis of ozone in the presence of water vapour, as illustrated in Fig. 2. Briefly, photolysis of ozone produces an oxygen atom, a proportion of which have sufficient energy to react with water vapour and produce two OH radicals. Some of these high-energy oxygen atoms are quenched via collision with another air molecule (marked as M in Fig. 2) back to a ground state, and reform ozone. The formation of OH is thus principally controlled by the levels of ozone and the flux of radiation.

Other important reactions of BVOCs involve direct oxidation by  $\text{O}_3$  and the night-time reaction with the  $\text{NO}_3$  radical. The  $\text{NO}_3$  radical is formed during the day, but photolyses rapidly, and so its levels are usually very low. At the end of the day, reaction of  $\text{NO}_2$  with  $\text{O}_3$  forms  $\text{NO}_3$  in sufficient levels to oxidise BVOCs. OH also reacts with other important trace gases such as CO, other VOCs, and  $\text{CH}_4$ . These reactions may, overall, act as sources or sinks of OH, depending on, for example, the levels of  $\text{NO}_x$ . They strongly control levels of OH (and hence the oxidising capacity of the troposphere) and the  $\text{CH}_4$  lifetime (Crutzen, 1979; Derwent, 1995; Lelieveld et al., 1998; Pfeiffer et al., 1998; Wang et al., 1998; Sanderson et al., 2003a; Young et al., 2009). Recently, Lelieveld et al. (2008) measured OH levels over a



**Fig. 2.** Production of OH via photolysis of ozone. The photolysis of ozone ( $\text{O}_3$ ) produces oxygen atoms in a ground state (O) or higher energy state ( $\text{O}^*$ ); the latter can react with water vapour to produce 2 OH radicals. Some of the higher energy state oxygen atoms are quenched back to the ground state. The ground state atoms reform ozone.

tropical forest and found they were much higher than model predictions. They proposed that  $\text{HO}_2$  radicals can react directly with large peroxy radicals produced from VOC degradation to produce significant quantities of OH radicals under low  $\text{NO}_x$  conditions. A modified version of their chemistry scheme including these additional reactions produced OH levels that were in much better agreement with the measurements. Aerosols produced from the oxidation of BVOCs can act as cloud condensation nuclei, and surfaces for heterogeneous reactions (Andreae and Crutzen, 1997; Kulmala, 2003).

Hydrogen is not a greenhouse gas itself, but reacts with OH and so may increase concentrations of  $\text{CH}_4$  and other GHGs. The main source of  $\text{H}_2$  is the photolysis of formaldehyde ( $\text{HCHO}$ ), produced from the photochemical oxidation of  $\text{CH}_4$  and VOCs (Price et al., 2007).  $\text{H}_2$  has small biogenic emission sources associated with biological  $\text{N}_2$  fixation (Price et al., 2007), wetlands (Conrad, 1996) and biomass burning. While reaction with OH removes roughly 20% of atmospheric  $\text{H}_2$ , soil uptake is the dominant sink (Price et al., 2007), the exact magnitude depending on soil type, moisture content and temperature (Yonemura et al., 2000; Smith-Downey et al., 2006), or snow cover (Rhee et al., 2006). The present day  $\text{H}_2$  soil sink is estimated to be  $88 \pm 11 \text{ Tg H}_2 \text{ a}^{-1}$  by Rhee et al. (2006) who used seasonal and hemispheric variations in  $\text{H}_2$  and D/H isotopic ratios as constraints. Other estimates range from 40–50 to  $90 \pm 20 \text{ Tg H}_2 \text{ a}^{-1}$  (Seiler and Conrad, 1987; Novelli et al., 1999; Hauglustaine and Ehalt, 2002; Sanderson et al., 2003b; Price et al., 2007) based on measured soil deposition velocities for  $\text{H}_2$  and estimates of the global areas of various soil types.

Tropospheric  $\text{O}_3$  is formed during the photochemical oxidation of CO,  $\text{CH}_4$ , and other VOCs in the presence of  $\text{NO}_x$ , with an additional source from stratosphere-troposphere exchange (e.g., Stevenson et al., 2006). A recent modelling study by Fiore et al. (2009) has examined the impact of foreign and domestic emissions of  $\text{NO}_x$ , CO and VOCs on

ozone levels in four continental-scale regions in the Northern Hemisphere. These authors found that the ozone levels in each region were most sensitive to domestic emissions, but transport of ozone and its precursors from foreign regions was also important. The importance of foreign emissions on domestic ozone levels therefore requires a good understanding of the terrestrial BVOC and  $\text{NO}_x$  emission patterns (e.g., Chameides et al., 1988; Pierce et al., 1998; Wang and Shallcross, 2000; Sanderson et al., 2003a; Barkley Jr. et al., 2004; von Kuhlmann et al., 2004; Folberth et al., 2006; Wu et al., 2007). Wu et al. (2009) showed that the response of ozone levels to changes in emissions of  $\text{NO}_x$  are non-linear outside of the summer months, but are linear during summer, when ozone production is limited by  $\text{NO}_x$  levels. The impact of clouds on regional tropospheric ozone budgets has been studied by Voulgarakis et al. (2009). These authors showed that cloud cover can reduce OH levels and increase isoprene lifetimes by up to 7%. The largest impacts on ozone levels were seen over some marine regions where cloud optical depths are large. High  $\text{O}_3$  concentrations (40 ppb and well above) occur during the northern latitude summer across temperate regions of North America, Eurasia and China, coinciding with the height of the growing season when BVOC emissions, particularly isoprene, are largest. Over tropical regions of India, Amazonia and the Sahel,  $\text{O}_3$  concentrations peak during the dry season, with biomass burning an important source of precursors, alongside emissions of  $\text{NO}_x$  from soils (Kirchhoff et al., 1990; Keller et al., 1991). The most important chemical sink for ozone is photolysis in the presence of water vapour).  $\text{O}_3$  also reacts directly with BVOCs (Bonn and Moortgat, 2003), and dry deposition accounts for approximately 15% of the total  $\text{O}_3$  loss (Stevenson et al., 2006). This process is responsible for the low  $\text{O}_3$  levels observed during the night-time when a shallow boundary layer develops. Non-stomatal deposition on land surfaces such as plant cuticles or soil constitutes 30 to 80% of the total deposition sink (Fowler et al., 2001) with surface resistance decreasing with increasing temperature, solar radiation and relative humidity above 60% (Zhang et al., 2002; Coyle et al., 2009).

$\text{O}_3$  enters leaves via the stomata; the primary effect of chronic  $\text{O}_3$  exposure on plants is to reduce photosynthetic capacity (Ashmore, 2005; Fiscus et al., 2005; Karnosky et al., 2005). However, plants have evolved detoxification mechanisms to counter oxidative stress based on enzymes that utilize ascorbic acid (Plöchl et al., 2000; Fiscus et al., 2005) or possibly BVOCs (Loreto and Velikova, 2001; Fiscus et al., 2005). Reductions in plant assimilation and increasing maintenance costs leads to a reduction in the land carbon sink, and thus implies an indirect radiative forcing of ozone on climate (Sitch et al., 2007).

Secondary organic aerosols, formed as the reaction products of BVOC oxidation, constitute one of the largest uncertainties in the climate system (Forster et al., 2007). SOA affect climate directly by scattering and absorbing radiation,

and act as efficient cloud condensation nuclei (Hartz et al., 2005; VanReken et al., 2005; Dusek et al., 2006). SOA are important for the growth of particles, if not their formation (Hoffmann et al., 1997; Tsigaridis and Kanakidou, 2003; Tunved et al., 2006). Estimates for the present SOA burden vary by a factor of five (Tsigaridis et al., 2005). A considerable part of this uncertainty relates to the incomplete understanding of the biogenic sources. For instance, until recently oxidation of isoprene was thought to produce negligible amounts of SOA, but recent studies have shown that this is not true (Kroll et al., 2006). Isoprene oxidation is estimated to produce between 4.6 and 6.2 Tg SOA  $\text{a}^{-1}$  (Henze and Seinfeld, 2006; Tsigaridis and Kanakidou, 2007). The formation of SOA from biogenic precursors depends on the levels of  $\text{NO}_x$ . For important compounds like isoprene or the terpene  $\alpha$ -pinene, the SOA yield decreased with increasing levels of  $\text{NO}_x$ , whereas the reverse is true for some sesquiterpenes (Kroll et al., 2005, 2006; Ng et al., 2007).

Ammonia ( $\text{NH}_3$ ) has a large agricultural source. Its reaction products (such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ ) also form aerosols which play a key role in cloud formation as cloud condensation nuclei. They provide additional aerosol surfaces which may scatter incoming solar radiation which will impact on tropospheric photochemistry. A global modelling study by Feng and Penner (2007) showed that 43% of the nitrate aerosol and 92% of the ammonium aerosols exist in the fine mode which scatters radiation most efficiently. The continuing reductions in anthropogenic emissions of  $\text{SO}_2$  (the main source of sulphate aerosols) means that formation of ammonium nitrate will increase in importance (Pye et al., 2009). The interaction of  $\text{HNO}_3$  on aerosols has important impacts on tropospheric chemistry. For example, the presence of nitrate in aerosols significantly reduces the conversion of  $\text{N}_2\text{O}_5$  to gaseous  $\text{HNO}_3$  (Riemer et al., 2003) which in turn reduces tropospheric ozone levels (Tie et al., 2003). Overall, SOA formation patterns differ in polluted and clean air environments which will be important to distinguish, e.g., in simulations of preindustrial aerosol burden and concentrations of cloud condensation nuclei (Andreae, 2007).

### 3 Global trace gas exchange modelling

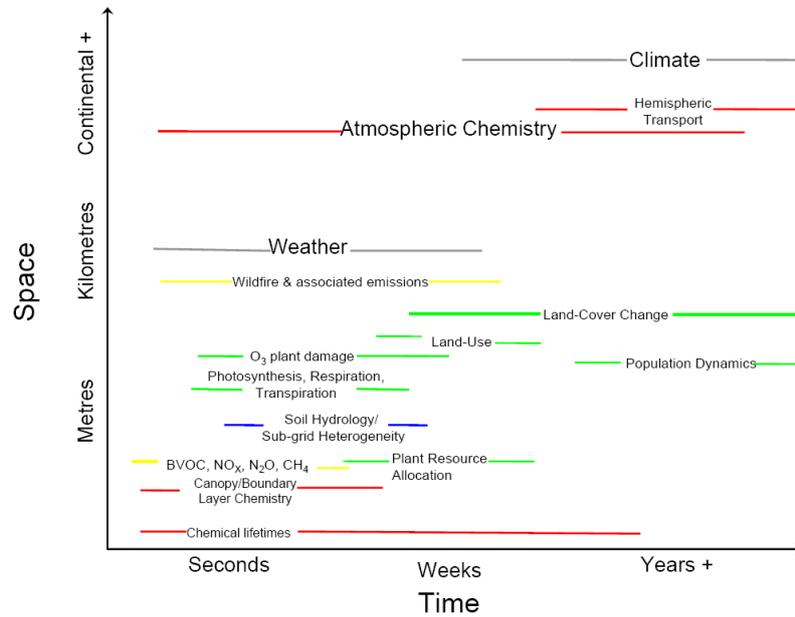
It is evident that surface-atmosphere exchange processes are important for understanding changes in atmospheric composition and radiative forcing from the last glacial maximum to the present day, and for future projections. Biosphere-atmosphere exchange is mediated by physico-chemical and biological processes which are very sensitive to prevailing environmental conditions. Trace gas exchange, ecology, atmospheric chemistry and climate are associated with processes that operate in very different characteristic spatial and temporal scales (Fig. 3) and their incorporation provides a challenge to coupled Earth System models. In addition, many interactions may differ depending on whether

a pristine or polluted environment is considered. Until recently, atmospheric chemistry-transport models (CTMs) relied on emission inventories which assumed constant seasonal or mean-annual emissions over inter-annual to decadal timescales (Prather et al., 2001; Gauss et al., 2006; Stevenson et al., 2006). Coupling CTMs to DGVMs allows the use of emissions which respond to the local climate and surface conditions at high temporal frequencies, as well as a more accurate description of dry deposition and uptake of trace gases by vegetation (Hauglustaine et al., 2005).

#### 3.1 DGVM model structure

In the existing DGVMs plant photosynthesis and autotrophic respiration are simulated in relatively similar ways (e.g., based on models by Farquhar et al., 1980; Collatz et al., 1991). Leaf carbon assimilation and water loss are typically coupled as the models contain a representation of the soil water balance, whereby stomatal conductivity and photosynthesis are reduced in periods with soil moisture deficit. Autotrophic and growth respiration are subtracted from gross photosynthesis, and a set of carbon allocation rules determines plant growth. Plant establishment, growth and mortality are represented, and their response to resource availability (light, water), disturbance and climate extremes underpins simulated population dynamics. Decomposition of dead tissue is described as a function of soil carbon content, temperature and soil moisture. Typically a number of soil pools are distinguished that represent material with different residence times. Some DGVMs have begun to move towards a more detailed representation of canopy dynamics and resource competition by adopting the “gap model” concept where average individuals represent the properties of a certain age cohort of a given PFT (Moorcroft et al., 2001; Smith et al., 2001). While computationally expensive, the gap concept allows the simulation of successional dynamics, reflecting competition between light-demanding and shade-tolerant plants (Smith et al., 2001; Hickler et al., 2004; Miller et al., 2008). For more detailed review of DGVMs see (Cramer et al., 2001; Prentice et al., 2007; Sitch et al., 2008).

Coupling of the carbon and nitrogen cycles is an active area of research within the terrestrial modelling community (Sokolov et al., 2008; Xu-Ri and Prentice, 2008; Thornton et al., 2009). Many DGVMs assign fixed C:N ratios for plant tissues and assume sufficient leaf nitrogen is available for photosynthesis; only few include a coupled soil C and N scheme (Cramer et al., 2001; Prentice et al., 2007). DGVMs require relatively little input: climate, soil type and atmospheric  $\text{CO}_2$  concentration and can be run from (sub)daily to glacial/interglacial time scales. They have been evaluated using flask measurements of  $\text{CO}_2$  from a global network of monitoring stations, eddy covariance data of  $\text{CO}_2$  exchange, field manipulation experiments (e.g. Free-Air-Carbon Enrichment experiments), and field data on net primary productivity (NPP), biomass and soil carbon content



**Fig. 3.** Characteristic spatial and temporal scales associated with DGVMs and climate models, trace-gas biosphere-atmosphere exchange and atmospheric chemistry. Green lines: processes associated with plant physiology/land cover; yellow lines: trace gas emissions; blue: surface hydrology/energy balance; red: chemical transformations and related processes; grey: weather and climate.

(McGuire et al., 2001; Friend et al., 2007; Hickler et al., 2008).

### 3.2 Inclusion of new land cover types and processes in DGVMs

#### 3.2.1 Land use, land cover change and related non-CO<sub>2</sub> trace gas emissions

A substantial fraction of the anthropogenic emissions of non-CO<sub>2</sub> trace gas and particulate matter are due to land use and land cover change (Bruisma, 2003). Already with development of agriculture some 10 000 years ago (Roberts, 1989) humans began to transform the land surface (Olofsson and Hickler, 2007). Historical land use and cover changes are important not only as a large carbon source over the last centuries (Houghton, 1999, 2003) but for pre-industrial non-CO<sub>2</sub> trace gas emissions, e.g., of BVOC and fire related emissions (Arneth et al., unpublished), and hence for pre-industrial to present-day radiative forcing calculations. In the context of climate change, future land use must both supply agricultural products for a growing population (Vitousek et al., 1986), and target new ecosystem services, like soil carbon sequestration or agrofuels (Lal, 2004). Depending on the crop type and its phenology, future climate warming might be locally either advantageous (increased growing period) or detrimental (insufficient vernalization, increased water and heat stress; Lobell et al., 2008) to crop yields. Tropospheric O<sub>3</sub> tends to reduce photosynthesis and yields (Ashmore, 2005).

Accounting for the human influence is therefore crucial for modelling terrestrial trace gas exchange and its climate effects through biophysical and biogeochemical feedbacks. In many land use simulations, agriculture is represented as grassland, by harvesting a fraction of the (natural) productivity or crop growing seasons are prescribed (e.g. McGuire et al., 2001; Feddema et al., 2005). Several studies that parameterised land surface schemes specifically for crops (Challinor et al., 2004; Kothavala et al., 2005; Osborne et al., 2007) have concentrated on short term land-atmosphere interactions. The carbon cycle is not closed, and neither the removal of carbon through harvest nor the long-term soil carbon dynamics were analysed. Recent studies (Davin et al., 2007) estimate past and future cooling due to the biophysical effects of anthropogenic land cover change, while Lobell et al. (2006) relate different cooling levels to crop management.

Biogeochemical impacts of land use and cover change within DGVMs were simulated initially by replacing forests with productive grassland or simply by harvesting a fraction of the (natural) productivity (McGuire et al., 2001). Using a suite of biogeochemical models, McGuire et al. (2001) found the opposing effects of CO<sub>2</sub> fertilization and historical land cover changes to be the two largest factors governing changes in terrestrial carbon storage over the 20th century. Using the DGVM LPJ coupled to the CLIMBER-2 climate model, Brovkin et al. (2004) quantified the effects of historical land cover changes as a biophysical (0.26 °C) cooling due to an increase in northern latitude albedo which was partially offset by a biogeochemical (0.18 °C) warming due to atmospheric CO<sub>2</sub> increases over the last 150 years; for future

land cover change, simulations of the biogeochemical warming largely from tropical deforestation either dominated over the biophysical cooling or amplified the biophysical warming associated with Northern Hemisphere land abandonment, depending on the socio-economic story-line used (Sitch et al., 2005).

Local-scale crop models have been developed by agronomists since the 1970s and are increasingly being applied at larger scales, projecting an increase in production in the northern latitudes due to CO<sub>2</sub> fertilization and warming, while production in the tropical semi-arid areas may decline due to water shortage (Rosenzweig et al., 1993; Parry et al., 1999; Reilly and Schimmelpfenning, 1999; Rosenzweig and Iglesias, 2001; Fischer et al., 2002; Tan and Shibasaki, 2003; Challinor et al., 2007). For a regional application, remote sensing information on canopy height was used to constrain carbon stocks and fluxes calculated with a height-resolved vegetation model (Hurtt et al., 2004). The output of crop models is typically restricted to yield and water requirements although their internal algorithms often include the crop canopy seasonality. Growth processes of individual crops (or crop functional types), have been implemented as an integral part of the modelling framework in three agro-DGVMs which can be run globally or at the regional scale with the coexisting simulation of natural vegetation (see Table 1). Generally, progress in this area allows terrestrial biogeochemical cycle calculations to be explicitly linked with socio-economic scenarios.

In agro-DGVMs, biophysical processes, soil decomposition and some plant physiological processes (e.g. photosynthesis and respiration) are computed using the same formulations (but with adapted parameters) for crops and natural PFTs. Hence these models compute consistent land carbon and water budgets for croplands and natural ecosystems. Other parameterizations are crop-specific, such as the phenological development and carbon allocation to the different pools (e.g. the economically important yield storage organs) during the growing period. Some functions exist only for managed land, like residue processing, crop rotations or irrigation. Two different strategies to implement land-use processes in DGVMs can be distinguished. In the first the parameterizations are built in the host DGVM. For example, algorithms from the EPIC crop growth model (Williams et al., 1989) were adopted in the models Agro-IBIS (Kucharik, 2003) and LPJmL (Sitch et al., 2003; Bondeau et al., 2007). In the second, the DGVM (e.g. ORCHIDEE; Krinner et al., 2005a), is coupled to an agronomy model (e.g. STICS; Brisson et al., 2002) that provides, on a daily time step, the DGVM with all variables that are crop-specific (Gervois et al., 2004). This approach facilitates fast inclusion of any improvement in the agronomical representation.

Agro-IBIS has mainly been developed for continental US agriculture (wheat, maize, soybean), and has been intensively tested for the impacts of different management practises on soil and vegetation C and N pools, crop yields, C and water

fluxes, and N leaching. It was applied to investigate crop yields and environmental problems at the river basin scale (Donner et al., 2004; Donner and Kucharik, 2003) and to quantify the various factors associated with farming practices which drive carbon fluxes (Kucharik and Twine, 2007), while Twine et al. (2004) used it to simulate the biophysical effects of land cover change from natural vegetation to crops.

The coupled ORCHIDEE-STICS model has been developed predominantly for European crops with agriculture described by three generic crop types: wheat-based functions are assumed to represent most of the winter C3-type crops, maize-based parameterizations are used for C4-type crops and soybean-based functions are used for C3-type summer crops. The model has been evaluated against water and carbon fluxes at specific sites, inter-annual yields at the European scale, and is used to simulate the impacts of historical land management on yields and carbon storage in Europe (Gervois et al., 2008) as well as to North American wheat and maize (Gervois et al., 2004).

LPJmL (Bondeau et al., 2007) defines eleven Crop Functional Types (CFTs) and one managed grass. It allows trends in global harvest, vegetation and soil carbon, NPP, water and CO<sub>2</sub> fluxes of the actual vegetation to be simulated and the impact of land use and land cover change globally to be quantified (Bondeau et al., 2007). Zaehle et al. (2007) estimated a carbon sequestration potential of agricultural abandonment and afforestation in Europe of 17–38 TgC a<sup>-1</sup> by 2100, although this was strongly reduced or even offset by climate warming. Müller et al. (2007) produce the inverse picture on the global scale, estimating that the impacts of non-climatic factors on land-use to be as important as the direct climatic factors and CO<sub>2</sub> fertilisation.

Simulations of the greenhouse gases CH<sub>4</sub> and N<sub>2</sub>O, or of NO<sub>x</sub>, with Agro-DGVMs have not yet been attempted but it will be important to assess the impacts of land management on these emissions. In terms of N<sub>2</sub>O, important initial studies have been conducted based on global data assimilation (Stehfest and Bouwman, 2006), and by modelling crop production within the ecosystem model DAYCENT (Stehfest et al., 2007) which provides a tool to simulate the impact of agricultural management on soil nitrogen dynamics and trace gas fluxes. At the regional scale, several groups have used GIS data coupled to ecosystem models to simulate GHG exchange from various land uses, e.g. for rice based agricultural systems in China (Li et al., 2004; Huang et al., 2006), or for grasslands, forests and agricultural systems in Europe or the US (Soussana et al., 2004; Kesik et al., 2005; Del Grosso et al., 2006; Butterbach-Bahl et al., 2008). The next step is to adopt such modules in agro-DGVMs and to analyse the effect of management strategies on emissions reduction, like, for instance, recommended mid-season drainage of rice paddies intended to reduce the CH<sub>4</sub> emissions, or the use of crop residues for biofuel instead of burning.

**Table 1.** Summary overview of three Agro-DGVMs.

DGVM version with crops, land use and land cover change	Original DGVM	main variables simulated	natural PFTs and crops represented and domain of application	model tests of the crop sub-module, or of the combined model (natural vegetation + agriculture)	applications using the crop sub-modules only	applications using the land cover change sub-modules only (i.e. using a simple land use representation within the original DGVM)	applications using both crop and land cover change sub-modules
Agro-IBIS (Kucharik and Brye, 2003)	IBIS (Foley et al., 1996)	– energy, water, carbon, and momentum balance of the soil-plant-atmosphere system – seasonal LAI – C and N pools, crop yields	8 Tree PFTs, 2 grass PFTs, 2 shrubs PFTs + wheat, maize, soybean (crops for the continental US)	– seasonal CO <sub>2</sub> and water fluxes at AMERI FLUX eddy covariance sites – crop yields and N leaching within the Mississippi basin	– impacts of climate and land use management on crop yields and nitrate export (Donner and Kucharik, 2003; Donner et al., 2004) – impacts of crops management on NEP (Kucharik and Twine, 2007)	– impact of the land cover change on terrestrial carbon storage (McGuire et al., 2001)	– impact of land use on the energy and water balance (Twine et al., 2004)
ORCHIDEE-STICS (Gervois et al., 2004; de Noblet-Ducoudré et al., 2004)	ORCHIDEE (Krinner et al., 2005b)	– energy, water, carbon, and momentum balance of the soil-plant-atmosphere system – seasonal LAI – C and N pools, crop yields	7 Woody PFTs + 2 grass PFTs + wheat, maize and soybean (European crops that have also been shown to be valid for the US)	– seasonal CO <sub>2</sub> and water fluxes at eddy covariance flux sites – national crop yields statistics – seasonal and interannual variability of LAI – comparison against CO <sub>2</sub> fluxes from atmospheric measurements		– impact of historical land cover change on climate (Davin et al., 2007)	– impacts of croplands on the European carbon and water budget (de Noblet-Ducoudré et al., 2004) – historical impacts of management on yield and carbon storage (Gervois et al., 2008)
LPJmL (Bondeau et al., 2007)	LPJ (Sitch et al., 2003)	– water and carbon fluxes of the soil-plant-atmosphere system – seasonal LAI – C pools, crop yields	7 tree PFTs + 2 grass PFTs + temperate and tropical cereals, rice, maize, temperate and tropical roots, pulses, sunflowers, groundnuts, rapeseed, grazed or harvested grassland (global)	– seasonal CO <sub>2</sub> fluxes at eddy covariance flux sites – seasonal simulated fPAR against satellite derived fPAR (globally) – national crops yields statistics for wheat and maize – changes in Soil carbon related to land use changes	– comparative impacts of climatic and non-climatic factors on global biogeochemical cycles (Muller et al., 2006) – land use and water use modelling (Lotze-Campen et al., 2005) – bottom-up modelling of the NEP anomaly due to the European 2003 heat wave (Vetter et al., 2008; Jung et al., 2008)	– impact of the land cover change effects on the terrestrial carbon storage (McGuire et al., 2001) – historical and future land cover change impact (biophysical effects and CO <sub>2</sub> increase) on climate (Brovkin et al., 2004; Sitch et al., 2005)	– impact of historical land cover change on green water flow (Gerten et al., 2005) – European vulnerability to climate change (Schroter et al., 2005) – historical impacts of agriculture on the terrestrial carbon balance (Bondeau et al., 2007) – estimated impacts of agriculture on the European and global carbon balance for the 21st century (Zaehle et al., 2007; Muller et al., 2007) – agricultural water consumption & related issues (Rost et al., 2008)

### 3.2.2 Wetlands and methane emissions

CH<sub>4</sub> emissions from wetlands are known to be highly dependent on water table position, temperature and availability of carbonaceous substrate (Walter et al., 2001). This dependence can be seen at both the small (Roulet et al., 1992; Christensen et al., 2003) and the large scale (Bousquet et al., 2006). Similar to natural wetlands, emissions from rice agriculture are also strongly dependent on temperature (Khalil et al., 1989) and water table as defined by irrigation patterns. Drainage of wetlands leads to a shift to more CO<sub>2</sub> instead of CH<sub>4</sub> emissions, whereas restoration will increase CH<sub>4</sub> emissions.

Global estimates of present day CH<sub>4</sub> emissions from wetlands are derived either by using process-based models (bottom-up approach, e.g., Cao et al., 1996; Christensen et al., 1996; Walter et al., 2001; Zhuang et al., 2004) or inverse models (top-down approach, e.g. Fung et al., 1991; Mikaloff Fletcher et al., 2004a; Wang et al., 2004; Chen and Prinn, 2006). A large source of uncertainty is in the wetland distribution itself as most process-based models rely on time-invariant maps of wetland extent. Some process-based models use simplistic empirical relationships between water table depth and CH<sub>4</sub> oxidation rates and do not represent the different CH<sub>4</sub> transport pathways (Cao et al., 1996; Gedney et al., 2004). The widely adopted approach of Walter et al. (2001) is based on soil temperature, NPP and the amount of available substrate, and water-table (derived from a simple hydrological scheme) to model emissions. Recent studies (Wania et al., 2010) include a CH<sub>4</sub> emission model coupled directly into the DGVM to simulate the interactions between vegetation composition, soil temperature, and water table position. This approach has the advantage of modelling interactions between hydrology, vegetation and permafrost, which have not been included previously (Cao et al., 1996; Walter et al., 2001).

Methane models are evaluated using site-specific observations from chamber measurements or flux towers. Influential environmental conditions such as water table position, soil temperature or net primary production at the chamber sites can be readily determined for a small sample area and compared to model output. Chamber measurements have the disadvantage of not always including CH<sub>4</sub> emissions via ebullition, as these highly irregular emissions are often excluded from data sets. Eddy-covariance flux measurements integrate over diffusion, plant-mediated transport and ebullition (Rinne et al., 2007) in an often heterogeneous flux footprint that consist of hummocks, hollows and lawns representing very different micro-habitats (Saarnio et al., 1997). In general, DGVMs do not simulate such spatial heterogeneity given their spatial resolution of typically 0.5 to 1 degrees. However, DGVMs can be run for individual sites or different micro-topographic features. By doing so, they can be used as a tool to explore the impact of small-scale spatial heterogeneity on the simulation of large scale fluxes. Inverse

modelling techniques can help to constrain the process-based models at the regional and global scales. Important limitations arise from lack of suitable observations and uncertainty in the sink terms, e.g. seen in the large spread in estimates of global wetland CH<sub>4</sub> emissions using this approach, 145–231 Tg CH<sub>4</sub> a<sup>-1</sup> (Forster et al., 2007). Satellite measurements of total column CH<sub>4</sub> have also recently become available (Buchwitz et al., 2005; Frankenberg et al., 2005) and developments in inversion techniques have included using isotopic CH<sub>4</sub> data (Mikaloff Fletcher et al., 2004a). Isotopes of carbon (<sup>13</sup>C) and hydrogen (deuterium) can help to localise methane sources, but are yet to be included in a global, process-based methane model.

Simulations of past CH<sub>4</sub> emissions are even more data limited, especially in the distribution and extent of wetlands for the last glacial maximum and during deglaciation (Kaplan, 2002; Valdes et al., 2005). The inter-hemispheric gradient in atmospheric methane levels derived from ice cores can help locate methane sources in the past. Future wetland emissions will depend on warming, directly elevating emission rates and indirectly via changes in the distribution of wetlands (Cao et al., 1998; Gedney et al., 2004; Zhuang et al., 2004). Zhuang et al. (2004) estimate that high latitude emissions have increased over the 20th century and Gedney et al. (2004) predict an approximate doubling of wetlands emissions over the 21st century under the IS92A scenario.

Future climate warming is projected to be most pronounced over high latitudes, regions where frozen soils are prevalent; especially sensitive are frozen soils that currently exist near the freezing point of water. The spatial and temporal dynamics of permafrost and periodic disturbance are crucial in shaping high-latitude landscapes, with important consequences for the spatial extent of wetlands and the exchange of CO<sub>2</sub> and CH<sub>4</sub>. There is increasing evidence that these changes are already occurring across large portions of the Arctic (Serreze et al., 2002; Hinzman et al., 2005). The active layer depth in permafrost areas is likely to change dramatically over the next century (Lawrence and Slater, 2005; Euskirchen et al., 2006; Zhang et al., 2008), thus changing local drainage patterns. The thawing of permafrost could lead to better local drainage leading to drier conditions and therefore reduced CH<sub>4</sub> emissions, but if drainage is impeded, it may lead to enhanced inundation and wetter and warmer conditions favouring higher CH<sub>4</sub> emissions (Christensen et al., 2004). Permafrost and active-layer dynamics are now being developed and incorporated into DGVMs (Venevsky, 2001; Zhuang et al., 2003; Beer et al., 2007; Wania et al., 2009), and used to investigate the relationship between permafrost degradation, wetland-forest carbon dynamics, trace gas emissions and wildfire.

### 3.2.3 Nitrogen exchange in natural and agricultural ecosystems

Several processes govern the flow of nitrogen through terrestrial ecosystems, including nitrogen fixation; uptake by organisms; immobilisation (assimilation of nitrogen into plant and microbial tissue) and mineralisation (decomposition of soil organic matter to  $\text{NH}_4^+$ ); nitrification (biological oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ), denitrification (biological reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to gaseous N), and the perturbation of the natural cycle by anthropogenic nitrogen deposition, and leaching of excess nitrate into groundwater. The division of nitrogen between soil organic matter (C:N~15) and plant biomass (C:N~200) together with the total land N budget and the degree to which plants can alter their C:N ratios will critically determine the ability of terrestrial ecosystems to sequester anthropogenic  $\text{CO}_2$  in the future (Finzi et al., 2007; Thornton et al., 2007; Gruber and Galloway, 2008). However all of these processes are associated with large uncertainties (Holland et al., 1999; Prentice et al., 2000; Dentener et al., 2006b). A major uncertainty with regard to the N cycle, the quantification of  $\text{N}_2$  denitrification losses on site to regional scales, remains an unsolved challenge (Groffman et al., 2009).

At the site scale, a range of process-oriented models with widely varying approaches and degree of detail (Boyer et al., 2006) have been applied with mixed success in natural, semi natural and managed ecosystems to simulate nitrification-denitrification related trace gas emissions. The physico-chemical and biological factors driving nitrification and denitrification depend strongly on microsite conditions. This poses a major challenge for modelling the temporal dynamic of nitrogen trace gas exchange, and more generally for all redox-sensitive sources (e.g.  $\text{CH}_4$  emission versus oxidation) since aerobic and anaerobic zones in soils determine whether oxidative processes (such as nitrification) or reductive processes (such as denitrification) dominate. Simulation of nitrogen oxide fluxes is further complicated by the need to account for the diffusion resistance of soil and canopy and, for  $\text{NO}_x$ , chemical reactions within the canopy that can alter the net flux from the soil surface by up to 50% (Ganzeveld et al., 2002a). Single column canopy transfer schemes for  $\text{NO}_x$  do exist, however, they are yet to be used in conjunction with ecosystem models to simulate nitrogen gas exchanges (Ganzeveld et al., 2002b).

Plot-scale models have been linked to regional databases on soil, land-use and climate to simulate emissions for boreal, temperate and wet tropical forests (e.g., Kesik et al., 2005; Werner et al., 2007), as well as for agriculturally dominated landscapes (Butterbach-Bahl et al., 2004; Gabrielle et al., 2006). However, these upscaling experiments rely heavily on the availability and quality of data on soil physical properties (e.g., Batjes, 2002) and initial conditions for soil and vegetation carbon and nitrogen stocks for model initiali-

sation and parameterisation. The latter requirement suggests the potential usefulness of coupling site-scale emission models into DGVMs that provide spatially explicit information corresponding to local climate and pedographic conditions (see for example, Werner et al., 2007).

Several regional and global studies simulated source emissions of  $\text{NO}_x$ ,  $\text{N}_2\text{O}$  (Potter et al., 1996; Potter and Klooster, 1998; Parton et al., 2001) and  $\text{NH}_3$  (Potter et al., 2003) from soils that were based on process descriptions combined with remote sensing information and vegetation models. At the scale of DGVMs modelling of nitrogen trace gas emissions is still at a very early stage. In general a common structure is applied: N affects gross photosynthesis, transpiration and autotrophic respiration (Field and Mooney, 1986; Sprugel et al., 1995). N availability to plants thereby controls leaf area and plant growth, with the formation of new tissue being subject to plant specific C:N ratios. Plants retain a fraction of leaf N on leaf abscission and thereby influence the quality of litter entering the soil. This N-dependent quality impacts on the decomposability of fresh litter (Anderson, 1973; Jansens and Luysaert, 2009). Decomposition of organic matter results in sequestration or release of mineral nitrogen, depending on the C:N ratio of the decomposing material and the N requirements for the growth of soil microbes. Mineral N dynamics usually account for nutrient competition between soil microbes and plants, and processes of leaching to groundwater, including some protection against leaching resulting from adsorption to clay minerals, and a generic loss term to denitrification dependent on mineral N (e.g. Friend et al., 1997; Thornton et al., 2002). Dickinson et al. (2002) go further by simulating nitrification and denitrification processes as a function of N availability and soil moisture, however, they represent gaseous losses from these processes in a lumped manner.

Recently, algorithms that are based on the adaptation of process-based emission models at the site scale (e.g. DNDC; Li et al., 2000) have been adopted for use in DGVMs (Xu-Ri and Prentice, 2008; Zaehle and Friend, 2009). Taking advantage of the “closed” and consistent N cycle formulation of the DGVMs, these approaches tightly couple the terrestrial C and N cycles, and the process representation of N trace gas production and emissions apply (e.g., an empirically derived split of the soil in aerobic and anaerobic fractions). First model integrations have shown global flux estimates to be within the range of observation based estimates (Xu-Ri and Prentice, 2008; Zaehle and Friend, 2009).

Data on nitrogen trace gas fluxes are still scarce (Stehfest and Bouwman, 2006) and often not all information required to correctly interpret these measurements are available. Fluxes are remarkably variable in response to environmental conditions, vegetation type and management practices and despite recent advances in data availability, these differences are not yet fully understood (Schindlbacher et al., 2004). Site-scale observations of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  soil emissions are biased towards short-term studies in

temperate/boreal croplands, pastures and forests while information from tropical and particular semi-arid and seasonally wet regions is in view of the global importance of this biome types still scarce (e.g. Martin et al., 2003; Brummer et al., 2008). Using space-based observations, Jaegle et al. (2004) have recently suggested that soil  $\text{NO}_x$  emissions from semi-arid regions are significantly contributing to  $\text{O}_3$  enhancement in tropical Africa. A major challenge towards providing a critical benchmark for global scale nitrogen trace gas modelling is the compilation of observations into regional databases, such as in Pilegaard et al. (2006), and in validating and applying space-based observations, as those derived from GOME or Schiamachy.

$\text{N}_2\text{O}$  concentration observed at atmospheric stations can be exploited to evaluate the simulated seasonality of net land-atmosphere  $\text{N}_2\text{O}$  fluxes using CTMs. These measurements can then be used in inversion studies to attribute variations in atmospheric concentrations to sinks and sources according to latitudinal bands and terrestrial versus marine origin, which could provide an integrative benchmark of simulated  $\text{N}_2\text{O}$  fluxes (Hirsch et al., 2006). Large uncertainty exists in such inverse estimates, because the assumed prior net  $\text{N}_2\text{O}$  flux is highly uncertain, but potentially important for the inferred outcome (Hirsch et al., 2006). Also, the atmospheric transport itself contributes substantially to the observed seasonal cycle of  $\text{N}_2\text{O}$  concentrations (Nevison et al., 2007). CTMs can in principle be also used to evaluate emission of  $\text{NO}_x$  by transporting simulated emissions to stations with observed nitrogen deposition. However, N deposition estimates from the current generation of CTMs driven with similar emission fields differ considerably because of differences in the representation of  $\text{NO}_x$  chemistry and deposition processes (Dentener et al., 2006b). The potential to use atmospheric data for the evaluation of large-scale  $\text{NH}_x$  emission modelling is very limited because of the short lifetime of  $\text{NH}_x$  in the atmosphere.

First attempts to study climate change feedbacks suggest NO emissions from forest soils in Europe may increase by 9%, whereas  $\text{N}_2\text{O}$  emissions may decrease by 6% due to predicted changes in temperature and rainfall for the 2030s (Kesik et al., 2006). Land management dominates site to global-scale N trace gas fluxes. Representing land use in DGVMs (see Sect. 3.2.1) is therefore crucial for modelling N trace gas emissions. Fertilizer application to arable land and pastures have been identified as main drivers of N trace gas emissions, owing to its significant effect on site N availability (Forster et al., 2007). Recently Crutzen et al. (2008) estimated that the loss of  $\text{N}_2\text{O}$  from reactive nitrogen (via e.g. fertilization, N deposition, and indirect emissions in the course of cascading) is in the range of 3–5% rather than 2% as used in the IPCC guidelines. This has implications for any land use change from natural towards managed systems and also affects our view on benefits which may possibly be achieved by implementing large scale bioenergy production systems as a measure for climate protection. Furthermore, conversion of

natural systems into pasture or arable systems in tropical regions or the drainage of wetlands for forestry or agriculture have been shown to result in the mobilisation of soil C and N stocks accompanied by pulses of N trace gas emissions lasting up to several years (e.g., Melillo et al., 2001; Smith and Conen, 2004). Even the change from till towards no-till agricultural systems may promote  $\text{N}_2\text{O}$  emissions due to the alteration of the C and N cycles (Six et al., 2004; Li et al., 2005). Further studies with fully coupled vegetation, climate, hydrology and soil biogeochemical models are needed to gain a comprehensive understanding of possible feedbacks of N trace gas exchange due to global change.

### 3.2.4 Fire and fire-related emissions

Fire-related trace gas emissions are estimated using global/regional emission models or global, process-based fire models embedded in DGVMs (Table 2). Emission models combine remote sensing products, databases and inventories to prescribe area burnt, and to estimate fuel loads in order to predict trace gas emissions. Process-based fire models represent fire initiation, spread and effects. Climate data and ecosystem variables governing fuel load and status (provided by the DGVM) serve as input. Model outputs include area and biomass burnt and associated changes in the simulated carbon pools of vegetation and litter.  $\text{CO}_2$  emissions are therefore driven by area burnt, fuel load and fuel consumption. Both groups of fire models rely on biome-specific emission factors (EF) to estimate trace gas emissions. However, the conditions that determine the ratio between flaming and smouldering combustion which determines non- $\text{CO}_2$  trace gas emissions is fixed (Andreae and Merlet, 2001).

Emission models show the influence of extreme fire events and ENSO (van der Werf et al., 2004, 2006) on GHG fluxes to the atmosphere. However, they are limited by the available data-base or satellite information and rely on prescribed assumptions about fire behaviour (surface vs. crown fires) and combustion efficiencies. With improving quantity and quality, remote-sensing products are able to capture real time, continuous global coverage but uncertainties remain regarding reliable products to estimate area burnt, fuel load (driven by vegetation productivity) and land cover (vegetation type, natural vs. non-natural). Fire Radiative Power is a novel development, where the energy content of a fire is detected from remote-sensing fire products and can help to distinguish surface from crown fires and possibly combustion completeness (Wooster et al., 2005).

Process-based fire models in DGVMs try to capture the bi-directional feedbacks between fire frequency, fire effects and vegetation dynamics. Implementation of fire behaviour and intensity within DGVMs, e.g. the SPITFIRE model (SPread and InTensity of FIRE; Thonicke et al., 2009) in the LPJ-DGVM, provide the basis to simulate trace gas emissions. SPITFIRE explicitly accounts for both lightning- and human-caused ignitions. Fire spread only takes place when

**Table 2.** Comparison of emission and process-based fire models.

	Emission models: GWEM (Hoelzemann et al., 2004), GFEDv2 (van der Werf et al., 2004), BWEM (Kasischke et al., 2005)	Process-based Fire-DGVM: MCFire (Lenihan and Neilson, 1998), SPITFIRE (Thonicke et al., 2009) SEVER-FIRE (Venevsky et al., unpublished)
Area burnt	Remote sensing fire product	Simulation of fire initiation and spread
Representation of Vegetation	Actual land cover with varying sensitivity of LC-product used	Potential natural vegetation Integration with crop and land use envisaged
Combustion efficiency	Static combustion efficiency and ratio between crown and surface fire in a biome	Simulating fire behaviour and resulting fuel consumption
Model Application	Limited by years with available satellite observations	Prognostics for different climate conditions

atmospheric conditions are sufficiently dry, a state estimated using the Nesterov Index (Nesterov, 1949), and calculations follow Rothermel's fire spread model (Rothermel, 1972; Wilson, 1982; Pyne, 1995). Surface fire intensity is explicitly simulated. Ignitions which do not generate a sufficiently intense fire do not lead to fire spread. Tree mortality from either crown scorch (Johnson, 1992; Dickinson and Johnson, 2001) or cambial death (e.g., Stephens and Finney, 2002; Rigolot, 2004), the two most important causes for post-fire mortality, are calculated. Process-based fire models can be applied to investigate past, present and future changes in fire and vegetation-fire interactions, e.g. to quantify the contribution of biomass burning to trace gas emission during glacial-interglacial changes (Thonicke et al., 2005; Fischer et al., 2008). Most DGVMs simulate potential natural vegetation under current climate conditions, and estimates of trace gas emissions do not yet capture global fire regimes as determined by actual vegetation cover. An advance will be to incorporate fire models into agro-DGVMs.

Future global fire models will include algorithms to link burning conditions with trace gas emissions, allowing emission factors to reflect conditions, such as the ratio of grass to total litter, fuel moisture, and fire intensity (Hély et al., 2003). Experimental data from controlled burn studies and fire products from remote-sensing, i.e. fire radiative power, are becoming available to evaluate model algorithms of fuel combustion and related trace gas emissions. Process-based global fire models need to reduce uncertainties in quantifying ignitions, especially human-caused fire ignitions, also during past centuries to allow prognostic simulations to estimate changes in human use of fire since pre-historic times. Models of lightning are needed and are especially important

in palaeo-climate applications, where changes in convection and lightning should be consistent with changes in climate. Here fire modellers can benefit from parameterizations in CTMs, which often include a module for NO<sub>x</sub> production by lightning; such modules calculate the number of lightning flashes, and the proportion that strike the ground (Meijer et al., 2001; Schumann and Huntrieser, 2007). Limitations of process-based fire models can be reduced further by considering agricultural and woodfuel burning in DGVMs. Fire models need to be closely linked to ecosystem models, which provide estimates of combustible biomass N (see Sect. 3.2.3). Furthermore, effects of biomass burning on the magnitude and temporal pattern of soil N trace gas emissions (Weitz et al., 1998; Neff et al., 1995), e.g. via changes in energy and water fluxes, N volatilization by pyro-denitrification or changes in soil physical properties need to be taken into account.

### 3.2.5 Hydrogen

Models of the molecular hydrogen cycle have primarily focused on source and sink magnitudes, and the latitudinal distribution and seasonality of atmospheric H<sub>2</sub> concentrations. Unlike many anthropogenically emitted gases, H<sub>2</sub> has higher concentrations in the southern than Northern Hemisphere, which seems to arise from the strong soil uptake. Hauglustaine and Ehhalt (2002) were the first to use a CTM (MOZART) to reproduce latitudinal and seasonal gradients in H<sub>2</sub> concentration. They assumed similar seasonality in surface H<sub>2</sub> sources as for other compounds, for instance both anthropogenic emissions and biomass burning sources of H<sub>2</sub> were scaled to the seasonal cycle of CO. For H<sub>2</sub> sinks, the

seasonality and geographic distribution of the deposition velocity was scaled to Net Primary Productivity. While the observed latitudinal gradient in the Southern Hemisphere and tropics were reproduced in this experiment, data-model mismatches with increasing latitude, especially in the Northern Hemisphere and over the continents suggested that use of NPP for estimating uptake was inaccurate.

Two subsequent studies improved estimates of the velocity deposition by adding temperature dependencies based on observations (Yonemura et al., 2000; Smith-Downey et al., 2006). STOCHEM-CTM was applied using deposition velocities dependent on PFT and soil moisture (Sanderson et al., 2003b), and the GEOS-chem CTM with H<sub>2</sub> uptake inhibited over snow and desert regions (Price et al., 2007). Both studies simulated improved seasonal cycles of H<sub>2</sub> concentration in the Northern Hemisphere and improved latitudinal gradients. Neither model, however, includes a mechanistic treatment of H<sub>2</sub> uptake. The use of a diffusion approach as presented by Smith-Downey et al. (2006), or other diffusion approaches, in a DGVM is an exciting way forward.

### 3.3 Advances in modelling plant physiology

#### 3.3.1 BVOC

The vast majority of regional and global BVOC emission studies to date have concentrated on isoprene and monoterpenes, largely because these represent a significant proportion of the total C emitted annually in the form of BVOC (Guenther et al., 1995). Also leaf measurements on a sufficiently wide range of plants (Kesselmeier and Staudt, 1999) have allowed the development of generalised emission algorithms. Emission models typically specify the emission capacity of a leaf under standardised conditions (arbitrarily chosen to be 30 °C and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> of photosynthetically active radiation). The widely observed short-term response of leaf emissions to temperature and quantum flux is then used as the basis to simulate response of emissions to weather and climate. For isoprene, current algorithms account for the hyperbolic increase in emissions with radiation flux intensity (Guenther et al., 1991, 1993), reflecting its production in the chloroplast (Lichtenthaler et al., 1997). The temperature response of isoprene is based on a modified Arrhenius relationship with a maximum emission at ca. 40 °C. Monoterpenes were originally thought to be all released from storage in the leaf (e.g., specialised storage organs like resin ducts, hairs, or in the cytosol) and the emissions described in terms of a simple exponential function of temperature (Guenther et al., 1991, 1993). However, increasing evidence has emerged that many broadleaf deciduous species that produce monoterpenes do so without storing them, with concurrent emissions in an “isoprene-like” fashion (Staudt and Seufert, 1995; Kesselmeier and Staudt, 1999).

The “Guenther et al. (1993, 1995)” algorithms have been used in a range of global emission studies, and implemented

in a number of DGVMs, although often with static, prescribed vegetation; an overview is presented in Arneth et al. (2008a). An alternative approach couples isoprene emissions to the electron transport rate in the leaf, based on metabolic principles (Niinemets et al., 1999; Arneth et al., 2007b). The model by Arneth et al. (2007b) accounts for a direct CO<sub>2</sub>-isoprene interaction, as found in a range of species where leaf-level emissions increase in plants grown in below ambient CO<sub>2</sub> concentrations and a decrease at higher CO<sub>2</sub> levels – an overview is provided in (Young et al., 2009). Using a simple function that links CO<sub>2</sub>-isoprene inhibition to changes in C<sub>i</sub> (Arneth et al., 2007a) successfully reproduced the available leaf observations. This result provides indirect evidence for substrate competition as the mechanism behind the CO<sub>2</sub> effects (Rosenstiel et al., 2003), however a full mechanistic understanding of the CO<sub>2</sub>-response is still lacking. In addition, the CO<sub>2</sub>-response of emissions may help to explain the short-term decoupling that is often observed between photosynthesis and isoprene emission under conditions of soil water deficit (Pegoraro et al., 2005). The shape of the short-term vs. long-term of isoprene emissions has not yet been resolved yet and it is unclear whether the former would also be applicable for the latter (Wilkinson et al., 2009).

Plant species differ greatly in their capacity to emit isoprene and/or monoterpenes, and a major challenge for modelling global BVOC emissions in the context of DGVMs is the need to specify average standard emission capacities on the PFT level. Although emission capacities are normally adopted from Guenther et al. (1995), values chosen for individual PFTs can vary greatly among DGVMs (Arneth et al., 2008a). Using DGVMs which adopt the gap model concept can help resolve this problem in regions where PFTs can be described to represent individual tree species, for example, in mid to high latitude ecosystems (Arneth et al., 2008b). To date, isoprene estimates vary between ca. 400 and 600 TgC a<sup>-1</sup>. With exception of one study (Schurgers et al., 2009), current global monoterpene estimates are uniformly based on a temperature-dependence of emissions only and have yet to account for the increasing evidence that broadleaf deciduous species tend not to store the produced monoterpenes. The variation in estimates of monoterpene emissions is ca. 30–130 TgC a<sup>-1</sup>, much larger than for isoprene (Arneth et al., 2008a). Model evaluation is difficult since large-scale observational constraints do not exist. Emission estimates based on top-down inversion modelling of satellite formaldehyde retrievals in combination with atmospheric chemistry models are promising, however, suffer at present from large uncertainties in the satellite information retrievals and associated with the chemical reaction pathways (e.g. Palmer et al., 2003). Canopy flux measurements may provide a means to investigate model performance locally (Arneth et al., 2007a; Schurgers et al., 2009). Isoprene and monoterpene emissions have been projected to greatly increase in the future and to have been much lower in past environments, a combination

of the temperature response of emissions and the CO<sub>2</sub> fertilisation effect on vegetation productivity (Guenther et al., 2006, Lathi re et al., 2006). The additional, direct CO<sub>2</sub> response results in more conservative global estimates of isoprene emissions for simulations from the last glacial maximum and into the future due to the counteracting effects of CO<sub>2</sub>-inhibition and temperature stimulation of leaf emissions in such scenarios (Arneth et al., 2007a; Heald et al., 2009).

A number of additional processes need to be accounted for in global BVOC emission models. The capacity of growing leaves to emit isoprene lags development of photosynthesis, with the lag being in cool growth environments (Wiberley et al., 2005). As a consequence, emission capacities vary as leaves age. Leaf emission capacities adapt also to the growth environment, observable in differences between sunlit and shaded leaves, and in a relatively rapid leaf response to short term weather history (Guenther et al., 2006). The latter is crucial if it suggests a tendency to acclimate emission factors in response to climate change (Guenther et al., 2006). Although most current BVOC-enabled DGVMs begin to incorporate at least some of these effects (Arneth et al., 2008a), their parameterisations are as yet empirical and associated with large uncertainty. While these processes have been mostly identified for isoprene they are likely to affect monoterpene emissions as well.

BVOCs contribute to the ubiquitous role of VOCs in atmospheric chemistry and climate due to their reactions involving OH, O<sub>3</sub> and NO<sub>x</sub> that affect lifetime and concentration of GHGs and SOA. BVOC also have a critical role for ecosystem functioning, as floral scents and as substances that protect leaves from herbivory or oxidative stress. Consequently, global emission estimates must account for substances other than isoprene and monoterpenes. In DGVMs, this has been attempted by adopting the Guenther et al. (1995) monoterpene algorithms for other groups of compounds, for example oxygenated BVOC (Lathi re et al., 2006). However the approaches are oversimplified, the required observations to assign emission capacities, and crucial process understanding are missing, particularly for the possibly large emissions of induced BVOC. A recent synthesis of data on sesquiterpene emissions, a group of compounds that are very efficient for SOA formation and that are emitted both constitutively as well as induced, highlighted the numerous difficulties associated with measurements that prevents identification of processes and natural variability required for development of suitable algorithms (Duhl et al., 2008). For methanol, with a terrestrial source at least as large as monoterpenes, a global concept was developed by Galbally and Kirstine (2002) that seeks to account for the observed variation of emissions in response to cellular expansion during vegetation growth.

### 3.3.2 Ozone effects on vegetation

A limited number of continental to global scale modelling studies suggest O<sub>3</sub> induced reductions in productivity and

land carbon storage over North America, Europe, China, and India (Felzer et al., 2004; Ren et al., 2007; Sitch et al., 2007), regions with high levels of human appropriation of primary productivity (Imhoff et al., 2004). A meta-analysis of O<sub>3</sub> experiments has shown reductions in the light-saturated photosynthesis and stomatal conductance in trees of 11% and 13%, respectively, as a likely response of plants to elevated O<sub>3</sub> exposure compared to pre-industrial levels (Wittig et al., 2007). However, McLaughlin et al. (2007) found decreased growth but increased water use in mature forest trees under high ambient O<sub>3</sub> concentrations, with O<sub>3</sub> exposure leading to reduced stomatal control of water loss and delayed stomatal closure at night. Free Air CO<sub>2</sub> Enrichment (FACE) and related experiments using ozone-enriched air indicate a non-linear interaction between plant responses to CO<sub>2</sub> and O<sub>3</sub>. Models of plant-O<sub>3</sub> interactions must be able to replicate results obtained in the enrichment experiments, e.g., for aspen trees (Karnosky, 2003; Karnosky et al., 2005) or at a Swiss grassland site (Volk et al., 2006) where plots are exposed for multiple years to combinations of ambient and elevated concentrations of CO<sub>2</sub> and O<sub>3</sub>.

In recent years there has been a shift towards the use of flux-based assessments (Emberson et al., 2000; Ashmore et al., 2004; Ashmore, 2005). A mechanistic model of plant-O<sub>3</sub>-CO<sub>2</sub> interactions was implemented into the Hadley Centre land-surface model (Sitch et al., 2007). The model assumes a suppression of net leaf photosynthesis by O<sub>3</sub> that varies proportionally to the O<sub>3</sub> flux through stomata above a specified critical O<sub>3</sub> deposition flux. A novel aspect in adopting a flux-gradient approach to modelling leaf gas exchange of both O<sub>3</sub> and CO<sub>2</sub> is that it enables an investigation of not only the individual effects of O<sub>3</sub> and CO<sub>2</sub> acting in isolation on plant physiology, but also of their interaction. These are typically ignored in modelling approaches that are based on cumulative O<sub>3</sub> exposure, e.g. AOT<sub>40</sub> (accumulated dose over a threshold of 40 ppb) metric, rather than on uptake by leaves.

The model of Sitch et al. (2007) was applied using O<sub>3</sub> concentrations previously generated using the STOCHEM chemistry-transport model, which in turn was driven using emissions from the SRES A2 scenario (Sanderson et al., 2003a; Sitch et al., 2007). Results suggest a large negative impact of near-surface O<sub>3</sub> on plant productivity, and a significant suppression of the global land carbon sink of up to 260 PgC by 2100 (Sitch et al., 2007). The additional CO<sub>2</sub> left in the atmosphere caused by O<sub>3</sub>-induced damage to plants constitutes an indirect radiative forcing that could exceed warming due to the direct radiative effect of tropospheric O<sub>3</sub> increases (Sitch et al., 2007). However, elevated CO<sub>2</sub> concentrations provide a degree of protection against O<sub>3</sub> damage via CO<sub>2</sub> induced reductions in stomatal conductance which was found to off-set O<sub>3</sub> suppression of GPP by over one-third (Sitch et al., 2007). Dry deposition fluxes may also change, owing to stomatal closure at elevated CO<sub>2</sub> levels and changes in soil moisture and biogeography. Sanderson et al. (2007) found that surface ozone levels over parts of Europe were

6–8 ppb larger under doubled CO<sub>2</sub> conditions, owing to the reduced dry deposition sink.

Global models currently assume that O<sub>3</sub> effects are representative for all plants and their respective age-classes, and assume a constant O<sub>3</sub> flux response of all plants throughout the growing period. There are significant uncertainties in the response of different plant species to O<sub>3</sub>, especially for tropical ecosystems. Generally, crops are most sensitive, angiosperms intermediate and conifers the least sensitive to O<sub>3</sub> exposure (Reich, 1987). Recent evidence points towards a possible protective role of isoprene and monoterpenes against O<sub>3</sub> damage (Loreto and Velikova, 2001; Fares et al., 2008). Within crop types, wheat is considered sensitive and potato less sensitive to O<sub>3</sub> exposure (Pleijel et al., 2004). But there are disadvantages of sowing O<sub>3</sub> tolerant crop varieties since they tend to have lower yields than non-resistant varieties. Also, only a few studies relate cumulative uptake of O<sub>3</sub> over a growing season to yield reduction for different vegetation types (Karlsson et al., 2004; Pleijel et al., 2004).

#### 4 Future challenges: model integration and evaluation

For an improved representation of non-CO<sub>2</sub> trace gas exchange in global models several scaling problems need to be resolved, associated with increasing resolution and detail of process representation: (i) representation of soils with different physico-chemical properties (i.e. texture, pH) within a DGVM grid cells, (ii) representation of soil moisture heterogeneity and redox status, both in terms of vertical and horizontal sub-grid scale distribution of water, including lateral flows for (seasonal) wetland extent, (iii) representation of vegetation, both in terms of vertical and horizontal sub-grid heterogeneity to appropriately capture vegetation dynamics and trace gas emission interactively, (iv) accounting for within canopy and boundary layer processes affecting both emission and deposition processes, (v) specification of land management practices in terms of fertiliser types and application methods and timing for semi-natural and cropland ecosystems. Moreover, not all DGVMs operate at the short time-steps required to link trace gas emissions and atmospheric chemistry. Progress in these areas is non-trivial due to lack in mechanistic understanding, computational expense as well as structural differences between off-line DGVMs and land surface schemes applied in coupled global models. Hence, there are possible conflicts between model complexity and efficiency. This requires a pragmatic approach to be adopted both in terms of processes as well as evaluation.

By coupling a trace gas enabled DGVM to a CTM, a wide variety of trace gas measurements could be utilised in model evaluation, thereby expanding on the previously developed methodology for carbon, and to evaluate the interdependencies of the various trace gases and GHGs. DGVM outputs can also inform the CTMs about deposition parameters such as LAI, stomatal conductance and roughness length. This

strategy links emissions/sinks of reactive trace gases and concentration observations. Numerous trace-gas measurements are available including historical data from ice-cores (H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>), continuous measurements using high frequency gas chromatographs at a global network of flask (CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub>, CO; Prinn et al., 2000) and aircraft measurements (CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>) (<http://cdiac.ornl.gov/tracegases.html>). In addition isotopes, <sup>13</sup>C (in CO, CO<sub>2</sub>, CH<sub>4</sub>), <sup>14</sup>C (in CO<sub>2</sub>), <sup>18</sup>O,  $\delta^2$ H are available at a subset of stations. However, the appropriate model evaluation protocol is not fully developed and has been attempted only in a few regional studies, and for a limited number of substances (e.g., Palmer et al., 2003; Barkley et al., 2008). A major uncertainty arises since model-data mismatch in trace gas concentrations at monitoring sites may be related to emission estimates, but also to shortcomings in the modelled chemical degradation and transport mechanisms.

#### 5 Outlook

Here we present the collective advances within the DGVM community on simulating non-CO<sub>2</sub> trace-gas exchange at the land surface. At present no single DGVM represents yet all the major non-CO<sub>2</sub> trace gas exchange processes identified in this review. Model intercomparison will be desirable and necessary in the near future once individual DGVMs include representations of all major processes relevant to non-CO<sub>2</sub> trace gas exchange.

While the atmospheric importance of non-CO<sub>2</sub> trace gases is generally understood, their overall climate and atmospheric chemistry effects are uncertain. Apparent, however, from a number of recent studies is that the incorporation of biological process-understanding as part of dynamic emission simulations is important and may yield surprises in the chemistry-climate system. For example, a direct CO<sub>2</sub>-BVOC effect (Arneth et al., 2007a) may lead to larger than thought BVOC emissions at LGM atmospheric CO<sub>2</sub> concentrations. This suggests either larger changes in CH<sub>4</sub> wetland emissions than estimated by biogeochemical models, or invokes additional processes (Lelieveld et al., 2008). However, Wilkinson et al argue for a lower sensitivity of isoprene production at low atmospheric CO<sub>2</sub> levels (Wilkinson et al., 2009). CO<sub>2</sub>-BVOC inhibition also questions the proposed negative temperature feedback of higher aerosol formation from larger BVOC (particularly monoterpenes) emissions in the future (Kulmala et al., 2004), but BVOC-CO<sub>2</sub> interactions in plant species that emit terpenoids from storage are not yet resolved. Together with NO<sub>x</sub>, BVOC are important precursors of O<sub>3</sub>, and reductions in BVOC in a CO<sub>2</sub>-enriched world may reduce regional O<sub>3</sub> concentrations (Young et al., 2009). Future regional changes in near-surface O<sub>3</sub> concentrations are important given the phytotoxicity of O<sub>3</sub> and the potential for considerable reductions in the land carbon sink, constituting indirect radiative forcing of climate (Sitch et al.,

2007). Comparatively low N<sub>2</sub>O emissions are associated with oil palm, and ligno-cellulosic plants (e.g., poplar, willow), compared to other agro-biofuel production for which emission estimates are potentially 2–3 times higher than previously assumed (Crutzen et al., 2008). However almost all fast growing agri-forest tree species are high isoprene emitters (Rosenstiel et al., 2003).

These examples reinforce the important need for an integrated approach to modelling land use, biota, chemistry and climate and the need for a full evaluation of the effectiveness of land management as a tool to mitigate climate change in an integrated DGVM, climate-chemistry model framework. Future DGVMs will be able to simulate spatial and temporal variations in non-CO<sub>2</sub> trace gas exchange at the land surface, thereby going some way to address one of the major sources of uncertainty in atmospheric chemistry, air quality and climate science.

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