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Long-term study of biogenic volatile organic compound exchanges in a forest ecosystem

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Résumé

La biosphère terrestre et plus particulièrement les écosystèmes forestiers émettent de grande quantité de composés organiques volatiles (COV) qui ont un impact significatif sur les caractéristiques chimiques et physiques de l'atmosphère. Les COVs sont notamment des précurseurs dans la formation de l'ozone et des aérosols organiques secondaires. L'isoprène et les monoterpènes dominent largement les émissions totales de COVs et le méthanol est un des COVs les plus abondants dans l'atmosphère en raison de son temps de demi-vie plus élevé par rapport aux deux premiers.

L'objectif principal de cette thèse a été d'étudier (au moyen de la technique de la covariance de turbulence et d'un spectromètre de masse par réaction de transfert de proton) les mécanismes d'émissions et/ou de dépositions de COVs (isoprène, monoterpènes et méthanol) à l'échelle d'un écosystème forestier en climat tempéré (Vielsalm, Belgique), constitué de plusieurs espèces (*Fagus sylvatica*, *Abies alba*, *Picea Abies*, *Pseudotsuga menziessi*).

La technique de la covariance de turbulence est particulièrement adaptée pour l'étude des mécanismes d'émissions/dépositions de COVs à l'échelle d'un écosystème puisqu'elle ne perturbe pas le fonctionnement de l'écosystème et qu'elle a une très bonne résolution temporelle (1/2h). Elle a été utilisée sur le site de Vielsalm pendant une période de plusieurs mois sans interruption majeure dans les mesures.

Une première campagne de mesure a été réalisée entre le début juillet 2009 et la fin novembre 2009 et une seconde a été réalisée entre la fin mars 2010 et la fin novembre 2010. Simultanément aux mesures par covariance de turbulence des échanges de VOC, les paramètres climatiques contrôlant les mécanismes d'échange ont été également mesurés. Durant ces deux campagnes, les flux de méthanol, d'acétaldéhyde, d'acétone, d'isoprène, de méthyle vinyle cétone/méthacroléine, de monoterpènes, d'acide acétique (2010) et d'acide formique (2010) ont été mesurés. Les émissions observées les plus importantes ont été celles de l'isoprène et des monoterpènes ainsi que de méthanol qui contrairement au deux premiers présentait aussi des dépositions. Notre thèse s'est donc naturellement focalisée sur l'étude de ces trois flux, vu le rôle important que présentent ces trois composés dans la chimie atmosphérique et donc l'intérêt de la communauté scientifique à affiner les paramétrisations des modèles d'échanges écosystème/atmosphère de ces composés. L'étude des flux d'isoprène, de monoterpènes et de méthanol ont permis de rédiger trois articles originaux constituant le corps principal de cette thèse.

En raison de l'hétérogénéité de l'écosystème étudié, la première étude indispensable a été d'identifier quelles étaient les espèces émettrices de COVs. Pour cela, un modèle d'empreinte de flux a été utilisé en combinaison avec une carte des espèces présentes sur le site. Cette analyse a mis en évidence que le principal émetteur de monoterpènes était le *Fagus sylvatica* et que dans une moindre importance, l'*Abies alba*, le *Picea Abies* et le *Pseudotsuga menziessi* étaient également des émetteurs. Contrairement à la littérature, l'analyse a montré que l'*Abies alba* était probablement un émetteur d'isoprène mais la présence de *Picea Abies* connu comme étant un émetteur d'isoprène n'a pas permis d'être catégorique à ce sujet.

Les flux d'isoprène ont été observés uniquement pendant le jour contrairement aux flux de monoterpènes qui ont été observés le jour et la nuit. L'analyse des flux diurnes a montré clairement que la température et la lumière sont les deux principales variables contrôlant les émissions. La combinaison de cette analyse avec l'étude de la relation étroite existante entre les émissions d'isoprène/monoterpènes et la photosynthèse ont permis de mettre en évidence les mécanismes de production biosynthétique *de novo* des plantes, aspect original à l'échelle d'un écosystème. La présence d'émissions nocturnes de monoterpènes a permis de déterminer que la production *de novo* de monoterpènes directement émise dans l'atmosphère (comme pour l'isoprène) n'était pas la seule source contribuant aux émissions observées. Le déstockage de réservoirs de monoterpènes localisés au niveau des organes des plantes ou du sol peuvent être également des sources de monoterpènes. L'étude de la relation entre les flux d'isoprène/monoterpènes et la lumière en séparant les conditions nuageuses et ensoleillées a montré que pour une même intensité de lumière, les émissions étaient plus importantes en conditions nuageuses qu'en conditions ensoleillées. De la même manière, l'étude de la relation entre les flux d'isoprène et la photosynthèse en conditions nuageuses/ensoleillées a permis de supposer que la production *de novo* d'isoprène est plus importante dans les feuilles situées au-dessus du couvert végétal que les feuilles situées à l'intérieur du couvert. La mesure à long-terme des émissions d'isoprène et de monoterpènes a permis d'étudier l'évolution saisonnière de ces mécanismes observés et d'encore mieux les comprendre. En plus de la compréhension des mécanismes, cette étude a également permis de quantifier l'évolution saisonnière des paramètres essentiels à la modélisation des émissions d'isoprène/monoterpènes.

Les échanges de méthanol ont été généralement positifs (émissions) pendant le jour et négatifs (dépostions) pendant la nuit. De manière globale, les dépositions de méthanol ont été prédominantes en été et en automne mais ont été minoritaires au printemps. En moyenne, le site de Vielsalm s'est comporté comme un puits de méthanol ce qui va à l'encontre de toutes les autres études existantes jusqu'à présent. Un modèle original a été développé afin d'identifier les mécanismes responsables des émissions/dépostions de méthanol à court-terme et à long-terme. La cohérence entre les mesures et les simulations du modèle a suggéré que les principaux processus contrôlant les échanges de méthanol en été pouvaient être dus, à court-terme, à l'adsorption/désorption de méthanol (soluble dans l'eau) au niveau des films d'eau présents à la surface des feuilles et/ou présents à la surface du sol et à long-terme, dus à la destruction du méthanol par un processus de dégradation biologique et/ou chimique présent également à la surface des feuilles et/ou du sol. L'étude de la différence entre les mesures et le modèle, au printemps, a permis de mettre en évidence la présence d'une éventuelle production biosynthétique de méthanol par les plantes. Cette production semblait être contrôlée principalement par la température mais elle n'a pas pu être mise en évidence durant l'été en raison de la dominance des processus d'adsorption/désorption de méthanol.

La littérature sur les échanges écosystèmes-atmosphère d'isoprène, de monoterpènes et, dans une moindre mesure, de méthanol est abondante. Néanmoins, l'originalité de notre étude tient à l'échelle spatio-temporelle utilisée. En effet, nous travaillons à l'échelle de l'écosystème et non de la feuille ou de la branche comme dans la plupart des études. De plus, nos mesures couvrent une échelle temporelle allant de la demi-heure à la saison complète de végétation, ce qui reste encore très rare dans la littérature. Ceci nous à permis d'améliorer la compréhension des mécanismes de production et d'échanges de ces composés. Plus spécifiquement, l'étude des flux de méthanol est unique à l'heure actuelle dans sa description et sa compréhension des mécanismes de dépositions.

Summary

The terrestrial biosphere, especially forest ecosystems, emits large quantities of volatile organic compounds (VOCs) which have a significant impact on the atmosphere's chemical and physical characteristics. In particular, VOCs are precursors in the formation of ozone and secondary organic aerosols. Isoprene and monoterpenes dominate the total VOC emissions, and methanol is one of the most abundant atmospheric VOCs due to its longer half-life than the other two.

The main objective of this thesis was to investigate (using the eddy covariance technique and a proton-transfer-reaction mass spectrometer) the mechanisms of VOC (isoprene, monoterpene and methanol) emission and/or deposition at the scale of a temperate climate forest ecosystem (Vielsalm, Belgium) comprising several species (*Fagus sylvatica*, *Abies alba*, *Picea Abies* and *Pseudotsuga menziessi*).

The eddy covariance technique is very suitable for studying VOC emission/deposition mechanisms at ecosystem level as it does not interfere with the functioning of the ecosystem and it has very good temporal resolution (half an hour). It was used for several months at the Vielsalm site without any major interruption to the measurements.

The first measurement period ran from early July to late November 2009 and the second from late March to late November 2010. As well as measuring the VOC exchanges by eddy covariance, the climate parameters controlling the exchange mechanisms were also measured. During both these periods the methanol, acetaldehyde, acetone, isoprene, methyl vinyl ketone/methacrolein, monoterpene, acetic acid (2010) and formic acid (2010) fluxes were measured. The highest emission levels observed were isoprene and monoterpenes along with methanol, which unlike the first two also showed depositions. The thesis therefore naturally focused on studying these three fluxes, in view of the important role played by these three compounds in atmospheric chemistry and hence the scientific community's interest in refining the parametrisation of these compounds' ecosystem/atmosphere exchange models. The study of the isoprene, monoterpene and methanol fluxes has been written up in three original articles which form the main body of this thesis.

Because of the heterogeneity of the ecosystem studied, the first essential study concerned the identification of VOC-emitting species. This was done with the aid of a flux footprint model combined with a map of the species occurring on the site. This analysis showed that the main monoterpene emitter was *Fagus sylvatica* followed, to a lesser extent, by *Abies alba*, *Picea Abies* and *Pseudotsuga menziessi*. In contrast to the literature, the analysis showed *Abies alba* to be a probable isoprene emitter but the presence of *Picea Abies*, a known isoprene emitter, ruled out absolute certainty on that point.

The isoprene fluxes were observed by day only, unlike the monoterpene fluxes which were observed both day and night. Diurnal flux analysis clearly showed temperature and light to be the two main variables controlling emissions. Combining this analysis with a study of the close relationship between isoprene/monoterpene emissions and photosynthesis revealed the plants' *de novo* biosynthetic production mechanisms, an original aspect at ecosystem scale. From the occurrence of nocturnal monoterpene emissions it was possible to determine that *de*

novo monoterpene production emitted directly into the atmosphere (as in the case of isoprene) was not the only source of the emissions observed. Withdrawals from monoterpene sinks located in plant organs or in the soil can also be monoterpene sources. Studying the relationship between isoprene/monoterpene fluxes and light, distinguishing between cloudy and sunny conditions, showed that for the same light intensity the emissions were higher in cloudy conditions than in sunshine. Similarly, a study of the relationship between isoprene fluxes and photosynthesis in cloudy/sunny conditions suggested that *de novo* isoprene production is greater in leaves above the canopy than in leaves within the canopy. Long-term measurement of isoprene and monoterpene emissions enabled seasonal changes in the mechanisms observed to be studied and more fully understood. As well as providing an understanding of the mechanisms, this research also resulted in quantification of the seasonal changes in the key parameters for modelling isoprene/monoterpene emissions.

Methanol exchanges were generally positive (emissions) by day and negative (depositions) at night. Overall, methanol depositions were predominant in summer and autumn but in the minority in spring. On average, the Vielsalm site behaved like a methanol sink, which contradicts all the other research published to date. An original model was developed for identifying the mechanisms responsible for short-term and long-term methanol emissions/depositions. The consistency between the measurements and the model simulations suggested that the main processes controlling methanol exchanges in summer could be attributed, in the short term, to (water-soluble) methanol adsorption/desorption occurring in the films of water on leaf surfaces and/or on the soil surface and, in the long term, to methanol destruction by a biological and/or chemical degradation process also occurring on the surface of leaves and/or the soil. A study of the difference between the measurements and the model, in spring, indicated the possibility of biosynthetic methanol production by the plants. This production was apparently controlled mainly by temperature, but it could not be shown in summer when methanol adsorption/desorption processes dominated.

The literature on ecosystem-atmosphere exchanges of isoprene, monoterpenes and, to a lesser extent, methanol is extensive. Nevertheless, what makes this research original is the spatio-temporal scale used. We are in fact working at ecosystem scale, and not at leaf or branch scale as in most other cases. Moreover, our measurements cover a timescale from half an hour to a full growing season, which is rarely found in the literature. This has resulted in a better understanding of these compounds' production and exchange mechanisms. To be precise, the methanol flux study is currently unique in its description and understanding of the deposition mechanisms.

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List of Abbreviations

Abbreviation	Definition
ACD/NCAR	Atmospheric Chemistry Division/National Center for Atmospheric Research
ANOVA	A two-way ANalysis Of VAriance
AVOC	Anthropogenic Volatile Organic Compound
BVOC	Biogenic Volatile Organic Compound
C1-C3	Compounds family with 1-3 carbons
C10	Monoterpenes
C15	Sesquiterpenes
C20	Diterpenes
C30	Triterpenes
C40	Tetraterpenes
C5	Isoprene
C5-C6	Compounds family with 5-6 carbons
CAPRI	Common Agricultural Policy Regional Impact
CCN	Cloud Condensation Nuclei
CFC	ChloroFluoroCarbons
CLC	Corine Land Cover map
COS	CarbOnyl Sulfide
DEC	Disjunct Eddy-Covariance
DEC-MS	Disjunct Eddy-Covariance by Mass Scanning
DMADP	DiMethylAllyl DisposPhate
DMS	DiMethylSulfides
DOX/MEP	The 2-DeOXyxylulose-5-phosphate/2-MethylErythritol-4-Phosphate pathways
EC	Eddy-Covariance
ECMWF	European Centre for Medium Range Weather Forecast
EPA	Environmental Protection Agency
E/N	The ratio of the electric field strength E and the buffer gas number density N in the drift tube of the PTR-MS
FPP	Farnesyl diPhosPhate

Abbreviation	Definition
G97	Model of Guenther (1997)
GGPP	GeranylGeranyl diPhosPhate
GIS	Geographic Information System
GLC	Global Land Cover
GPP	Geranyl diPhosPhate
HC	Health Canada
HFC	HydroFluoroCarbons
ICP Forests	International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests
IMPECVOC	Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems
IPCC	Intergovernmental Panel on Climate Change
IPP	IsoPentenyl diphosPhate
ISPS	Isoprene synthase enzyme
LVOC	Low Volatile Organic Compound
MBO	2-Methyl-3-Butene-2-Ol
MEGAN	Model of Emissions of Gases and Aerosols from Nature
MODIS	Moderate Resolution Imaging Spectroradiometer
MVA	The acetate/MeValonAte pathways
m/z	Mass-to-charge
NMVOC	Non Methane Volatile Organic Compound
NPI	National Pollutant Inventory of Australia
NVOC	Non-Volatile Organic Compound
ORVOC	Other Reactive Volatile Organic Compound with a lifetime < 1 day
OVOC	Other Volatile Organic Compound with a lifetime > 1 day
oxVOC	Oxygenated Volatile Organic Compound
PFA	PerFluoroAlkoxy Teflon®
ppbv	Mixing ratio from parts per billion by volume
ppmv	Mixing ratio from parts per million by volume
pptv	Mixing ratio from parts per trillion by volume
PTR-MS	The proton-transfer-reaction mass spectrometer
SVOC	Semivolatile organic coumpound
SOA	Secondary Organic Aerosols
STP	Standard Temperature and Pressure

Abbreviation	Definition
Td	Physical unit of the ratio E/N: 1 Townsend = 10−17 V cm2
UV-B	Ultraviolet B (315-280 nm)
VOC	Volatile Organic Compound

List of Symbols

Symbol	Definition	Unit
$\boldsymbol{\alpha}$	Empirical parameter in C	Pa
$\boldsymbol{a}$	Slope coefficient	mol mol^{-1}
$\boldsymbol{A}$	Empirical parameter in R_t	Dimensionless
$\boldsymbol{\beta}$	Temperature dependence parameter	K^{-1}
$\boldsymbol{b}$	Intercept coefficient	mol m^{-2} s^{-1}
$\boldsymbol{c}$	Concentration of an atmospheric compound	µmol m^{-3}
$\boldsymbol{C}$	Capacity of the water films to store methanol	m^3 m^{-2}
$\boldsymbol{C_L}$	Function describing the $PPFD$ dependence of isoprene/monoterpene emissions	Dimensionless
$\boldsymbol{C_{L1}}$	Saturation C_L value	µmol m^{-2} s^{-1}
$\boldsymbol{C_P}$	Air specific heat	J kg^{-1} K^{-1}
$\boldsymbol{C_R}$	Component of C that depends on P	m
$\boldsymbol{C_{R0}}$	Residual capacity of C	m
$\boldsymbol{C_T}$	Function describing the T_a dependence of isoprene and monoteperne emissions	Dimensionless
$\boldsymbol{D}$	Water vapour pressure deficit	Pa
$\boldsymbol{F}$	Eddy-covariance flux density	µmol m^{-2} s^{-1}
$\boldsymbol{F_1}$	Net methanol flux exchange	µmol m^{-2} s^{-1}
$\boldsymbol{F_2}$	Flux methanol degradation in aqueous phase	µmol m^{-2} s^{-1}
$\boldsymbol{F_3}$	Methanol exchange by the adsorption/desorption of methanol in water films	µmol m^{-2} s^{-1}
$\boldsymbol{E_{G97}}$	Newly synthesized isoprene/monoterpenes emission	µmol m^{-2} s^{-1}
$\boldsymbol{GPP}$	Gross Primary Production	µmol m^{-2} s^{-1}
$\boldsymbol{H}$	Sensible heat flux	W m^{-2}
$\boldsymbol{i}$	Index denoted successive time period intervals	
$\boldsymbol{j}$	Index denoted successive time period intervals	
$\boldsymbol{K_H}$	Henry's law constant	Dimensionless (water/air partition ratio)
$\boldsymbol{LAI}$	Leaf area index	m^2 m^{-2}
$\boldsymbol{M_{aa}}$	Methanol concentration in the atmosphere	µg m^{-3}

Symbol	Definition	Unit
M_{aw}	Methanol concentration in the air at the water film surface	µg m^{-3}
n	Number of data point	
N	Number of disjunct PTR-MS samples during T	
NEE	Net ecosystem exchange	µmol m^{-2} s^{-1}
ψ	q/C_R	µg m^{-3}
P	Precipitation	mm
$PPFD$	Photosynthetic Photon Flux Density	µmol m^{-2} s^{-1}
q	Total methanol content in the water film reservoirs	µg m^{-2}
ρ	Air density	kg m^{-3}
R	Gas constant	J mol^{-1} K^{-1}
R^2	Coefficient of determination	
R_{net}	Net radiation	W m^{-2}
R_t	Gas-phase resistance to the methanol transfer in the surface boundary layer	S m^{-1}
SEF	Standard emission factor	µmol m^{-2} s^{-1}
S_w	Soil humidity	m^3 m^{-3}
τ	Lifetime of methanol in the water films	s
t	Time	s
T	Time averaging of eddy-covariance flux	s
T_a	Air temperature	°C or K
T_l	Leaf temperature	K
TER	Total Ecosystem Respiration	µmol m^{-2} s^{-1}
T_H	Water temperature	K
t_{lag}	Lag time between w and c	s
u^*	Friction velocity	m s^{-1}
U	Wind velocity	m s^{-1}
VAI	Vegetation area index	m^2 m^{-2}
w	Vertical wind velocity	m s^{-1}

Chapter 1

General introduction

1 Volatile organic compounds (VOC)

The term 'Volatile Organic Compound' (VOC) is more of a regulatory term than a scientific one. Scientifically, all compounds containing carbon other than carbon oxides and inorganic carbonates and bicarbonates are considered organic. In chemistry a volatile compound is one that readily evaporates under normal conditions. The ambiguity of the VOC classification derives from the non-specific term 'normal conditions'. Under European Union legislation, a VOC is any organic compound with an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa (European Union Directive 2004/42/CE, 2008). The United States Environmental Protection Agency (EPA) considers a VOC as any organic compound that participates in atmospheric photochemical reactions, except those designated by the EPA as having negligible photochemical reactivity (EPA www.epa.gov). Health Canada classifies VOCs as organic compounds with boiling points in the range of 50 to 250°C (HC www.hc-sc.gc.ca). For the National Pollutant Inventory (NPI) of Australia, a VOC is any chemical compound based on carbon chains or rings with a vapor pressure greater than 0.01 kPa at 20°C, that participate in atmospheric photochemical reactions (www.npi.gov.au). In the scientific community, several acronyms are used to classify the great diversity of VOCs (Kesselmeier and Staudt, 1999). The acronyms BVOC (biogenic VOC) and AVOC (anthropogenic VOC) are used to distinguish the origin of VOC emitted by natural and anthropogenic sources, respectively. From these both groups, there are subgroups, such as oxVOC (oxygenated VOC), CFC (chlorofluorocarbons) and HFC (hydrofluorocarbons). Other terminology refers to the atmospheric lifetime of VOCs, such as OVOC (other VOC with a lifetime > 1 day under typical tropospheric conditions) and ORVOC (other reactive VOC with a lifetime < 1 day under typi-

cal tropospheric conditions). Methane is an exception into VOC classification because its low reactivity (atmospheric lifetime ~ 10 years) and its importance as a greenhouse gas; it is often distinguished from other VOCs by the acronym NMVOC (non-methane VOC).

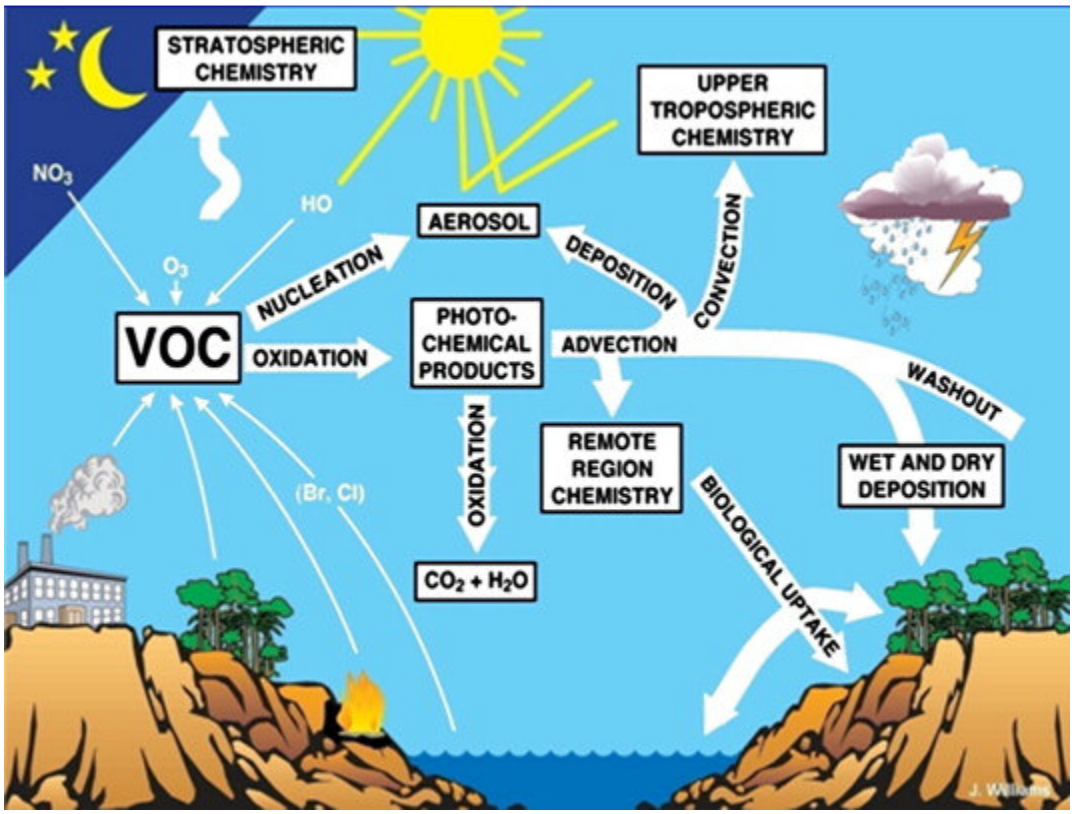

Figure 1.1 Schematic representation of the main processes driving the chemical composition of the lower atmosphere (from (Monks et al., 2009)).

The atmospheric mixing ratio of NMVOCs ranges from a few 10^{-9} g m^{-3} (pptv) to several 10^{-6} g m^{-3} (ppbv), and they account for less than 1% of the total atmosphere (Seinfeld and Pandis, 2006). They vary greatly both spatially and temporally and are influenced by several factors, including surface emission distributions, boundary layer exchanges, large-scale advection, shallow and deep convection, chemical and photochemical transformations, wet deposition/scavenging and dry deposition (Brasseur, 2003; Granier, 2004). Globally, NVOC mixing ratios decrease with altitude for all compounds. They also decrease from lower to higher carbon numbers within one class of compounds, due to both the lower emission rates and the shorter lifetimes of the higher hydrocarbons. Large quantities of NMVOCs are emitted into the troposphere from anthropogenic and biogenic sources (terrestrial ecosystems, plant decay, soil and ocean). To

date, several thousand NMVOC species have been identified. Despite their low mixing ratios, NMVOCs have profound effects on indoor air quality and climate due to their ability through chemical degradations to form aerosol particles (see § 3.2.2) or greenhouse gases (see § 3.2.1, § 4) and to determine the oxidative atmospheric photochemistry (see § 3.2). Figure 1.1 shows the main processes affecting the NMVOC composition of the Earth's lower atmosphere.

2 NMVOC sources

2.1 Anthropogenic sources

The anthropogenic contribution to the atmosphere is determined largely by the exploitation of fossil fuels (coal, oil and gas) that release a great variety of organic compounds such as acyclic alkanes, cyclic alkanes, monoaromatics and diaromatics (Hewitt, 1999). The solvents industry, biofuel combustion, agricultural practices and waste management also contribute to anthropogenic emissions, but they account for less than the fossil fuels sector. Another important source of anthropogenic emissions is biomass burning, which could be regarded as a natural process. These emissions are the most difficult to assess because of the spatial and temporal variability of burning. The global emissions of anthropogenic AVOCs are estimated to be 103 Tg/year (Brasseur, 1999).

2.2 Biogenic sources

The terrestrial biosphere is the dominant source of atmospheric VOCs (BVOCs). These compounds consist of alkenes, aldehydes, ketones, esters, ethers, alcohols, acids and isoprenoids (Arey et al., 1995; Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). The isoprenoid compounds contain isoprene (C_5H_8), monoterpenes (two isoprene units) and sesquiterpenes (three isoprene units) are released mainly by forestry ecosystems. Isoprene and monoterpene emissions dominate the total BVOC emissions. They are generally characterized as volatile, poorly water-soluble and very reactive compounds with a strong fragrance. Using the model developed by Guenther et al. (1999; 1995), global BVOC emissions amount to about 1150 Tg (C) yr^{-1} and are made up of 44% isoprene, 11% monoterpenes, 22.5% other reactive BVOCs and 22.5% other BVOCs. Table 1.1 (Fall, 1999) gives an overview of the estimated annual global emissions of major BVOCs, with their primary natural sources.

Table 1.1 The estimated annual global emissions of major BVOCs with their primary natural sources and their atmospheric lifetime (based on Fall et al. 1999).

Species	Primary natural sources	Estimated annual global emissions (Tg (C) yr^{-1})	Reactivity (averaged atmospheric lifetime in days)
Isoprene	Plants	175-503	0.2
Monoterpenes	Plants	127-480	0.1-0.2
Other reactive VOCs (e.g. acetaldehyde, 2-methyl-3-buten-2-ol, hexenal family)	Plants	~260	<1
Other less reactive VOCs (e.g. methanol, ethanol, formic acid, acetic acid, acetone)	Plants, soils	~260	>1
Dimethylsulfide	Oceans	15-30	<0.9
Ethylene	Plants, soils, oceans	8-25	1.9

Although the emission rates of single oxygenated BVOC species can be relatively small, their total amount can reach the same magnitude as those of isoprene and monoterpenes. Methanol, acetone and acetaldehyde are the most abundant oxygenated BVOCs in the C1-C3 group of carbon (Cx with x the number of carbon) release by many ecosystems, including forests and grasslands (Brunner et al., 2007; Custer and Schade, 2007; Holzinger et al., 2000; Hörtnagl et al., 2011; Karl et al., 2002c; Nemecek-Marshall et al., 1995; Schade et al., 2010; Seco et al., 2007; Spirig et al., 2005). In particular, formic and acetic acid has been found to be emitted by European oak and pines trees (Kesselmeier et al., 1997). Another set of oxygenated BVOCs released mainly after leaf damage is a group of C5-C6 compounds, known as the hexenal family (Hatanaka, 1993). Almost all plants seem to produce these compounds (Hatanaka et al., 1987), of which (2E)-hexenal and (3Z)-hexenol are the most important. The mechanisms driving BVOC production are located mainly at the leaf level, depending on the environmental conditions and their modulation by the canopy architecture. In

contrast, BVOC exchanges processes depend on the time scale (especially for reactive BVOC) and the spatial scale at leaf, plant and canopy level.

The ocean biosphere (Brasseur et al., 2003) can also release BVOC compounds: organohalides, cyanides and organic sulfur coumpounds, especially dimethylsulfides (DMS) and carbonyl sulfide (COS), produced by photochemical processes at the surface or by biological activity. At the global scale, the total amount of BVOC emissions from the oceans is clearly less important than that from terrestrial ecosystems.

2.2.1 Environmental controls on isoprenoids emissions

Isoprenoids are synthesized in all green plants through the condensation of two five-carbon intermediates: isopentenyl diphosphate (IPP) and dimethylallyl disposphate (DMADP). The biosynthesis of these universal precursor compounds proceeds along different metabolic pathaways: via the classical acetate/mevalonate (MVA pathways in the cytoplasm (and in the endoplasmic reticulum) and via the 2-deoxyxylulose-5-phosphate/2-methylerythritol-4-phosphate (DOX/MEP) pathway in a plant's chloroplasts (more details in: (Eisenreich et al., 2004; Lichtenthaler, 1999; Rohmer et al., 1993; Rohmer et al., 1996), as illustrated in Figure 1.2. The sesquiterpenes (C15), triterpenes (C30) and polyterpenes are produced in the cytoplasm, whereas the isoprene (C5), monoterpenes (C10), diterpenes (C20) and tetraterpenes (C40) are produced within a plant's chloroplasts (Croteau et al., 2000; Owen and Peñuelas, 2005). Many isoprenoids could be vital for biochemical and physiological functions, as well as for the healthy function and survival of all plant species (Owen and Peñuelas, 2005).

2.2.1.1 Isoprene

Most isoprene emitting plants are woody species; only a few crop species produce isoprene (Kesselmeier et al., 1997). Isoprene is produced by many families, but there are many cases where a family has both emitters and non-emitters. For example, although all North American species in the oak genus are high isoprene emitters, many European oaks are non-emitters (Seufert et al., 1997). Isoprene synthesis usually occurs in the leaf/needle's chloroplasts from the catalysis of DMADP by the enzyme isoprene synthase.

Ambient temperature and photosynthetically active radiation are the best-known variables affecting isoprene emission rates in the short-term. Emissions increase exponentially with ambient temperature (Figure 1.3) due to the temperature dependence of the

participating enzymes (Guenther et al., 1993). Above 40°C, emissions are expected to decline because of reduced enzyme activity. Isoprene emissions are also regulated by ambient light conditions, reflecting the close link between emissions and their production from photosynthetic products (IPP, DMADP). Isoprene emissions are regarded as a function of light (Figure 1.3) and they follow a saturation curve. Several studies (Delwiche and Sharkey, 1993; Funk et al., 2004; Karl et al., 2002b; Loreto et al., 1996) have shown that photosynthetically assimilated carbon is the principal source of carbon used in the formation of isoprene (more than 80%: Funk et al., 2004) in the absence of

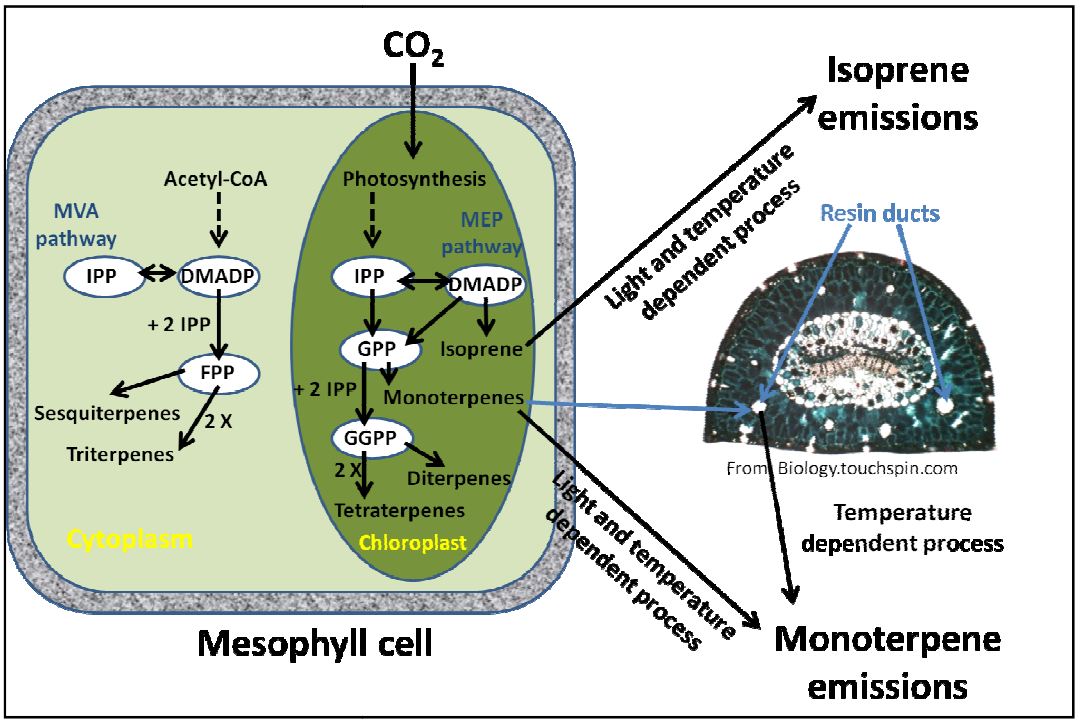

Figure 1.2 Biosynthesis of isoprenoid compounds in a plant cell: the DOX/MEP pathway for the biosynthesis of isoprene, monoterpenes, diterpenes and tetraterpenes and the MVA pathway for the biosynthesis of sesquiterpenes and triterpenes. The isoprene and monoterpene emission processes are highlighted and a cross-section of a pine needle is represented with the localization of the resin ducts. IPP-isopentenyl diphosphate, DMADP-dimethylallyl disposphate, GPP- geranyl diphosphate, GGPP- geranylgeranyl diphosphate and FPP- farnesyl diphosphate (based partly on Litchenthaler et al. 2007).

drought and thermal stress. In the case of stress, the plant uses alternative carbon sources that differ from the DOX/MEP pathway in order to maintain isoprene production (Funk et al., 2004). After production, isoprene is emitted directly into the atmosphere mainly through the stomata, but is not controlled by the stomatal aperture. The stomatal insensitivity of the emission has been explained by the rapid build-up of isoprene partial pressure within the leaf gas-phase, such that the decrease in stomatal con-

ductance is balanced exactly by increases in the diffusion gradient from the internal air space to the ambient air (Niinemets et al., 2004).

On a long-term basis, temperature and light acclimation effects might affect enzymatic activities and influence the emission strength of a individual plant (Lehning et al., 1999), which could lead to seasonality effects, as observed by several authors (Fuentes et al., 1999; Geron et al., 2000a; Monson et al., 1994; Sharkey et al., 1999). Leaves that develop in full sun emit isoprene at a higher rate than those that develop in shade (Harley et al., 1997; Sharkey et al., 1991). A leaf's ability to emit isoprene is also clearly influenced by its phenology: very young leaves do not emit isoprene, mature leaves emit at a maximal rate and, as leaves senesce, the emission capacity gradually declines, although studies indicate that isoprene emission is less sensitive than photosynthesis to decreasing soil moisture (Pegoraro et al., 2004; Pegoraro et al., 2005; Sharkey and Loreto, 1993). The impact of drought stress directly affects stomatal conductance and creates biochemical limitations of photosynthesis (Sharkey and Loreto, 1993). Both photosynthesis reduction and stomatal closure are expected to adversely affect isoprene emission by altering the carbon supply to the DOX/MEP pathway. In fact, isoprene emission is resistant to moderate drought stress until that stress becomes heavy (inhibitions of photosynthesis). This resistance is induced by the production of isoprene from carbon sources (stored carbon) other than photosynthesis, possibly related to respiration or starch breakdown (Loreto and Schnitzler, 2010). Finally, there is growing evidence that changes in the composition of the atmosphere (e.g., increased CO_2 and increased ozone) could affect isoprene production/emission capacity but the effect reported in the literature is sometimes conflicting (Loreto and Schnitzler, 2010; Peñuelas and Staudt, 2010). Nitrogen availability (Harley et al., 1994), UV-B radiation (Harley et al., 1996) and physical stress (Alessio et al., 2004) could also influence isoprene emission activity.

2.2.1.2 Monoterpenes

Monoterpene (C10) compounds consist of two isoprene units with a great structural diversity: more than 1000 different structures have been determined. Only a few of them, however, are emitted by plants in amounts that are significant for atmospheric chemistry (Geron et al., 2000b). The most abundant monoterpenes are: α-pinene, β-pinene, limonene, Δ^3-carene, myrcene, sabinene, camphene, β-phellandrene, α-thujene, terpinolene, α-terpinene, γ-terpinene, ρ-cymene and ocimene. Together, these account for 95% of the estimated total monoterpene emissions (Guenther et al., 1994; Owen et

al., 2001). Monoterpenes are generally biosynthesized as a product of DMADP and IPP condensation through the enzymatic monoterpene synthase (Croteau et al., 2000) in the leaf/needle's chloroplasts.

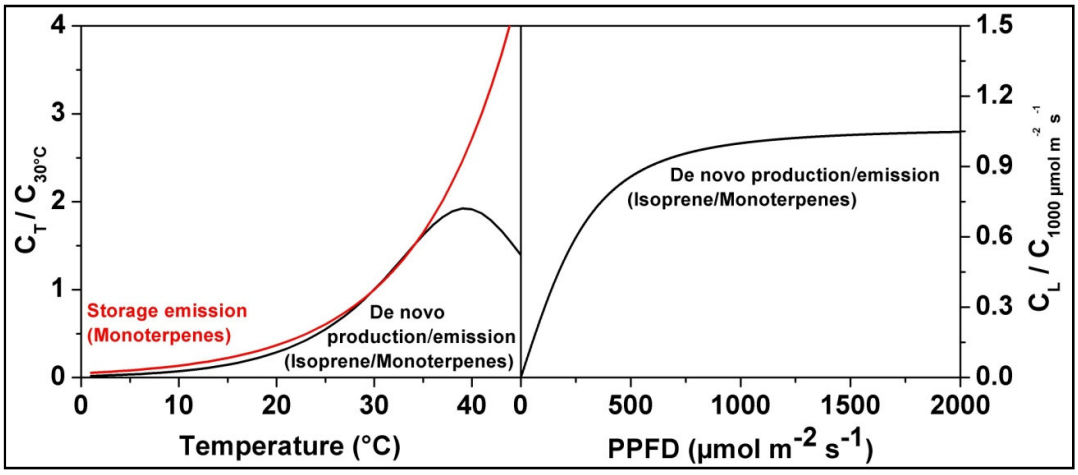

Figure 1.3 Response of isoprene/monoterpene production/emission to temperature (C_T) and light (C_L), normalized to standard conditions (30°C, 1000 µmol m^{-2} s^{-1}). Based on Guenther et al. (1993).

As in the case of isoprene synthesis, monoterpene synthesis is light and temperature dependent (Figure 1.3) but, unlike isoprene, monoterpene can be stored in large pools in plant organs (Figure 1.2) (resin canals in pine needles, resin blisters in firs and the glandular dots in leaves of the citrus family, Lerdau et al., 1997), which act as a buffer and can maintain emission under short-term climatic changes, even if the synthesis rate is affected. Monoterpene emission is therefore assumed to result mainly from the volatilization from storage organs and, for this reason, only the effects of temperature on the gas vapor pressure in plant tissue and on the resistance along the emission pathway are considered (Lerdau et al., 1997; Monson et al., 1995; Tingey et al., 1991). Some plants also emit monoterpenes without significant intermediate storage. These monoterpenes are emitted into the air through the stomata (emissions are not controlled by the stomatal aperture, as in the case of isoprene) directly after synthesis (Bertin et al., 1997; Demarcke et al., 2010b; Dindorf et al., 2005; Kesselmeier et al., 1997; Kuhn et al., 2002; Rinne et al., 2002; Staudt et al., 2000). In the long-term, temperature and light acclimation effects could also affect enzymatic activities, as in the case of isoprene, which influences monoterpene emissions and could therefore lead to seasonality effects (Demarcke et al., 2010b; Dindorf et al., 2005; Sabillón and Cremades, 2001; Staudt et al., 2003). Unlike isoprene, monoterpene emissions seem to be inhibited by drought stress (Delfine et al., 2005; Lavoir et al., 2009; Llusia and Penuelas, 1998; Šimpraga et

al., 2011b). It is unclear whether or not alternative carbon sources could be used to generate monoterpenes under drought conditions (Loreto and Schnitzler, 2010). The effect of drought, like other stressors factors affecting plant BVOC emissions, can depend on the level of stress or damage caused to the plant by drought (Peñuelas and Staudt, 2010). It is probable that monoterpene emissions are affected by the same stresses that affect isoprene emissions.

2.2.2 Ecophysiological role of isoprenoids in plants

The function of most isoprenoids is not well known and is a matter of debate. For many years, these compounds were thought simply to be functionless end products of the metabolism, or metabolic wastes. More recently, it has been suggested that many isoprenoids have important ecological functions in plants by acting as a protection agent against consumption by herbivores and infection by microbial pathogens (Paré and Tumlinson, 1999). They have also been shown to serve as attractants for pollinators and seed-dispersing animals and as agents of plant-plant competition (Dudareva et al., 2006).
Isoprene might protect photosynthesis from the damage caused by high temperatures (Sharkey and Singsaas, 1995). Some monoterpenes might also provide this thermoprotection (Peñuelas and Llusià, 2002). It has also been hypothesized that isoprene can help to protect cell photosynthetic structures against reactive oxygen species (Loreto et al., 2004; Loreto and Velikova, 2001). Isoprene is not emitted by all plant species and cannot have a universally essential role in plant function. For isoprene-emitting species, however, isoprene has certain ecophysiological roles that are, in non-emitting species, fulfilled by other compounds or other mechanisms (Owens and Penuelas, 2005).

2.2.3 Environmental controls of short-chain oxygenated compound emissions

Oxygenated VOCs can be emitted or taken up (see § 3.1) by plants. The direction of the exchange is thought to be determined, at least partly, by the atmospheric mixing ratios, because gases move along the concentration gradient between the inner and outer parts of the leaf/needle. The biosynthetic production mechanisms within a plant are known in some cases and they differ for each oxVOC. Within plant tissues:

- **acetone** can be produced by the cyanogenic pathway, leading to the production of hydrogen cyanide and, as a by-product acetone (Fall, 2004). Acetone can be also produced through litter decomposition (Warneke et al., 1999).
- **methanol** can be produced by the demethylation of pectin during cell wall formation (Fall and Benson, 1996). It can be also produced through litter decomposition (Warnecke et al., 1999).
- **acetaldehyde** can be produced by the oxidation of ethanol mediated by alcohol dehydrogenase in leaves. Under anoxic conditions, ethanol can be produced from ethanolic fermentation in roots and transported to leaves via the transpiration stream (Kreuzwieser et al., 2004).

Unlike isoprene and monoterpene emissions, solubility influences the atmospheric exchange of oxVOCs. These compounds all have high water solubility in common, as shown by their Henry's law constants. The magnitude of Henry's law constant is: for methanol 4.6 10^{-1} Pa m_{aq}^3 mol_{aq}^{-1}; for acetaldehyde 6.3 Pa m_{aq}^3 mol_{aq}^{-1} and for acetone 3.9 Pa m_{aq}^3 mol_{aq}^{-1}. These are low values compared with those of highly volatile isoprene and monoterpenes which are of the order of 10^3 Pa m_{aq}^3 mol_{aq}^{-1} (Sander, 1999). For highly water-soluble compounds, the exchange is more affected by stomatal conductance, depending mainly on Henry's law constant (Niinemets et al., 2004; Niinemets and Reichstein, 2003). Another characteristic of plant-emitted short-chain oxVOC emission rates is their exponential increase with temperature. This suggests that emissions could originate from an internal pool and/or that enzymatic activities are involved and similar to the responses of isoprene/monoterpenes emissions to temperature (Figure 1.3). Emission responses to light were described by Harley et al. (2007) for methanol and by Jardine et al. (2008) for acethaldehyde. The dependence of acetone emission on light seems to be less clear (Grabmer et al., 2004).

3 Deposition and scavenging of BVOCs in the atmosphere

Since BVOC concentrations do not all simply increase with time, there must logically be one or more removal processes (sinks) acting on these compounds. The most important sink for BVOCs in the atmosphere is chemical degradation (as described in § 3.2). Some BVOC compounds in the atmosphere can also be photolysed by sunlight and others can be efficiently removed physically by dry deposition on surfaces (terrestrial sur-

faces such as vegetation, water surfaces such as the ocean, and aerosol surfaces) or by wet deposition in rain driven by solubility. The maximum amount of BVOC that can be taken up into drop water depends on Henry's law constant and the rate of deposition depends on the BVOC concentrations in the atmosphere and in the drop water. The transport of BVOCs from the atmosphere to terrestrial surfaces is driven by turbulent transfer and by surface processes that determine the potential degradation of BVOCs. Generally, deposition involves mainly short-chain oxygenated BVOCs but significant deposition fluxes of monoterpenes and sesquiterpenes have recently been observed by Ruuskanen et al. (2011) above grassland.

3.1 Deposition of short-chain oxygenated compounds

Uptake can occur at multiple spatial scales through the absorption of gas-phase oxVOCs via the stomata into the mesophyll or via foliar surfaces and soil whose properties as sinks for a range of oxVOCs vary with the humidity and the presence of surface water (Figure 1.4) and are influenced, sometimes strongly, by the presence of other gases (Fowler et al., 2009). The diffusion of adsorbed oxVOCs through the aqueous pores of the cuticle might also play an important role in absorption, as described for organic ions (Schreiber, 2005). The stomata, however, probably constitutes the most important way through which plants absorb short-chained oxVOCs. Within leaves, the oxVOCs can be recycled by the plant and/or stored in the water inside the plant tissues. For example, Rottenberger et al. (2004) reported the existence of enzymatic pathways in leaves taking acetaldehyde into the general metabolism.

The presence of water on foliar surfaces might be due to rain and/or to microscale liquid water layers formed on the foliar surfaces (and on the other external plant surfaces) by the condensation of water vapor originating from the atmosphere or plant transpiration (Burkhardt et al., 2009). The oxVOCs present in the water could be supplied by rain (wet deposition) and/or by the solubility of atmospheric oxVOCs. If not adsorbed through the cuticule, oxVOCs could be revolatilized with the evaporation of water films, as a result of a decrease in atmospheric concentration through the action of atmospheric turbulence (friction velocity). In addition, oxVOCs might react with other atmospheric chemical species on the cuticle itself and/or be consumed by microorganisms present on the leaf (and on other external plant surfaces) that use the ox-

VOCs as a source of energy and carbon (e.g., the methylotrophic bacteria are known to consume methanol; Duine and Frank, 1980).

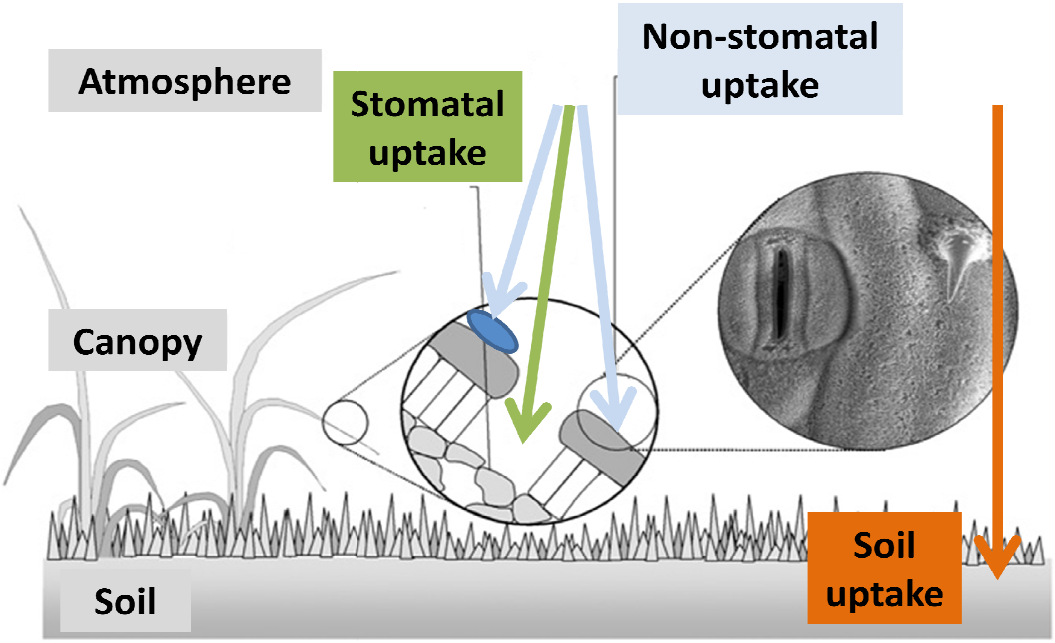

Figure 1.4 Illustration of the different sinks for oxVOC compounds on terrestrial surfaces, notably through the stomata or via foliar surfaces and soil where thin water films might be present under high humidity conditions. Adapted from Folwer et al. (2009).

3.2 Atmospheric chemistry of BVOCs

Once emitted into the atmosphere, BVOCs are generally very reactive (they are much more reactive than AVOCs) (Atkinson and Arey, 2003) and they influence the oxidation capacity of the troposphere by reacting mainly with the hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3), as well as by direct photolysis. The lifetimes (i.e., the time required for the concentration of BVOCs to decrease to a fraction 1/e of the initial concentration) of BVOCs are controlled mainly by theses oxidants concentrations, but they also depend on time of day, season, latitude, cloud cover and the presence of other reactive compounds (see Table 1.1 for a lifetime estimate of the mains BVOCs). The reactions of BVOCs with OH radicals dominate the daytime chemistry of the troposphere. During the day, OH radical are produced mainly by the photolysis of tropospheric O_3 and the subsequent reaction of electronically excited atomic oxygen $O(^1D)$, with water vapor (Atkinson and Arey, 2003; Isaksen et al., 2009). An additional, but smaller source of OH radicals is the ozonolysis of alkenes, which does not require

sunlight. At night, when the concentration of OH radicals is negligible, the oxidation of BVOCs is driven by NO_3 radicals. The oxidation by NO_3 radicals is also present during the day, but has a little effect because of the rapid reaction of NO_3 radicals with NO and its short lifetime in sunlight (Warneck, 2000).

In combination with anthropogenic NOx emissions, BVOCs lead to the formation of photochemical air pollution, especially tropospheric O_3. In addition, the oxidation of some BVOCs (monoterpenes and isoprene) can lead to the formation of secondary organic aerosols (SOAs) (Claeys et al., 2004; Hoffmann et al., 1997). The O_3 and the SOA formations affect air quality, human health (Pöschl, 2005) and ecosystems; they also influence the Earth's climate.

3.2.1 Tropospheric ozone formation and destruction

Tropospheric O_3 production during the day depends on the concentration of VOCs (including methane and NMVOCs) and NOx (Atkinson, 2000). O_3 is formed photochemically from the photolysis of NO_2:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (R1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (M = air) \qquad (R2)$$

and because O_3 reacts rapidly with NO:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R3)$$

The sequence of R1 to R3 therefore results in an equilibrium between NO, NO_2 and O_3, with neither net formation nor loss of O_3, as illustrated in Figure 1.5 A.

If VOCs (including methane and NMVOCs) are introduced into the system (Figure 1.5 B), their photochemical degradation leads to the formation of hydroperoxide (HO_2) and alkyl peroxy radicals (RO_2). These HO_2 and RO_2 radicals react with NO, converting NO to NO_2:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R4)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (R5)$$

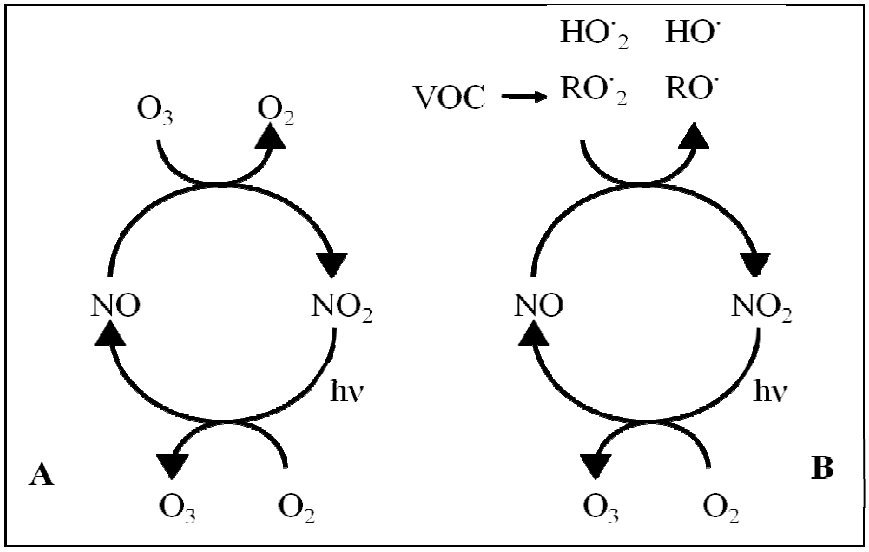

Figure 1.5 Schematic representation of photochemical production of tropospheric O_3. Photoequilibrium of NO-NO_2-O_3 (A); net formation of tropospheric O_3 through the introduction of VOCs into the stable NO-NO_2-O_3 system (B). Adapted from Atkinson (2000).

The common sink of O_3 is missing from the photoequilibrium state, leading to a net formation of tropospheric O_3 (Figure 1.5 B). At low NO mixing ratios (< 10-30 pptv; Logan, 1985), however, HO_2 reacts with itself, with RO_2 or with O_3, leading to a net destruction of tropospheric O_3.

The complex relationship between O_3, NO_x and VOC can be illustrated by isopleth plots. Figure 1.6 shows an example of the O_3 mixing ratio as a function of the NO_x and VOC mixing ratio. In this figure it is possible to identify two regimes with different O_3-NO_x-VOC sensitivities. When the NO_x mixing ratio is low and the VOC mixing ratio is high, O_3 increases quasi-linearly with increasing NO_x (NO_x sensitive regime) and changes little in response to increasing VOC. When the NO_x mixing ratio is high and the VOC mixing ratio is low (VOC sensitive regime), O_3 increases with decreasing NO_x. Naturally, the impact of the individual VOC species on tropospheric O_3 formation depends on their reactivity and their atmospheric degradation mechanism. The contribution to O_3 formation of a VOC emitted in a certain quantity at a certain place depends greatly on the ambient conditions (meteorology and concentrations of trace gases, particularly NO_x), as well as on the time scale over which the ozone build-up occurs.

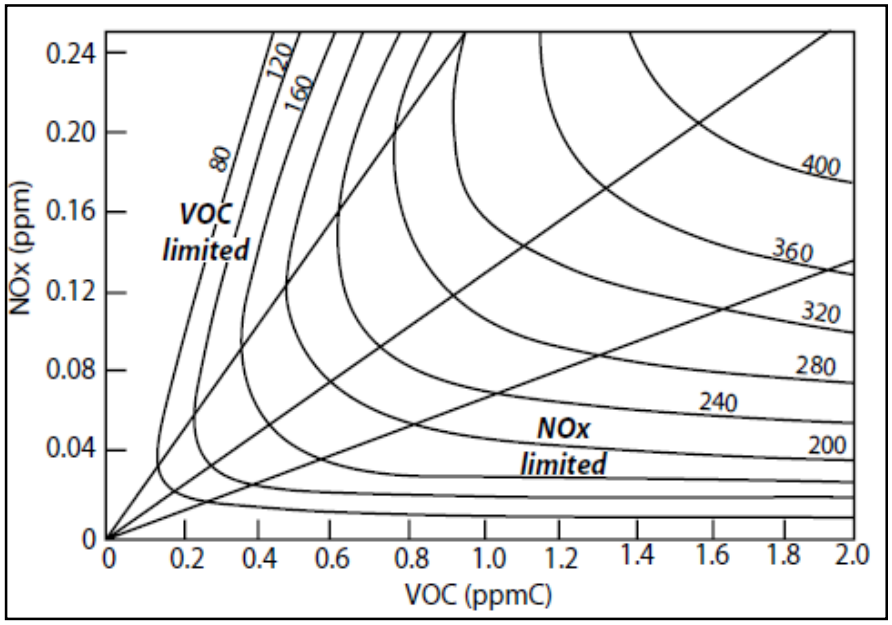

Figure 1.6 Ozone isopleth diagram showing the nonlinear response of O_3 to VOCs and NO_x (From NRC, 1991).

3.2.2 Secondary organic aerosol formation

Atmospheric aerosols are liquid or solid particles suspended in the air. The so-called primary aerosols are released directly by human activity (e.g., industrial escapement, car exhaust, manifold combustion) or naturally (e.g., fire forest, volcanic ash, desert dust, pollen). In the atmosphere they can also be created by the oxidative processes of NMVOCs, especially the terpenoïds (isoprene, monoterpenes and sesquiterpenes), leading to the formation of SOAs. The total budget of SOAs formed in the atmosphere is very uncertain, with estimates in the literature ranging from 12 to 1640 Tg (aerosol) yr^{-1} (Pierce et al., 2012). This uncertainty is due to the limited understanding of the principal SOA precursor gases, including the relative contribution of BVOCs and AVOCs, the magnitude of their emissions and the uncertainty about the number of atmospheric degradation processes that could produce a range of oxidized products that might or might not contribute to SOA formation (Carslaw et al., 2010; Kanakidou et al., 2005).

Gaseous organic components can be transformed into SOAs and incorporated into existing particles via several pathways (Fuzzi et al., 2006):

- New particle formation. Semivolatile organic coumpounds (SVOCs) are formed from oxidation processes and participate in the nucleation and growth of new

aerosol particles. This is the dominant source of particle number in the atmosphere (Kulmala and Kerminen, 2008).

- Gas-particle partitioning. SVOCs are formed by gas-phase oxidation and are taken up by pre-existing aerosol or cloud particles.
- Heterogeneous or multiphase reactions. Formation of low volatility or non-volatile organic compounds (LVOCs, NVOCs) by the chemical reaction of VOCs or SVOCs at the surface or in the bulk of aerosol or cloud particles.

Nucleation occurs when condensable vapors occurs high enough concentrations for them to collide to form stable clusters before re-evaporating (Kulmala and Kerminen, 2008). These stable clusters (diameter about 1nm) could become cloud condensation nuclei (CCN) if they continued to grow through the condensation of more vapor. Whether or not a particle acts as CCN depends on its size, composition, hygroscopicity and the maximum supersaturation of water reached within the cloud. Typically, particles must have dry diameter of 50 nm or larger to nucleate cloud droplets (Seinfeld and Pandis, 2006). The ultra fine particles are highly susceptible to coagulation scavenging by larger particles. There is competition between growth and coagulation to determine whether or not a newly formed particle will grow to become a CCN (Pierce et al., 2012). The SOA must be removed from the atmosphere through oxidation, or through wet or dry deposition.

4 BVOCs in the context of climate change

It is now widely acknowledged that biological processes in terrestrial ecosystems broadly affect the Earth's atmosphere and climate system, which implies potentially significant feedback effects on current global changes in atmosphere and climate arising from human activities (Peñuelas et al., 2009; Peñuelas and Staudt, 2010). The potential feedback effects on climate involving BVOC are illustrated in the Figure 1.7.

Climate models suggest that, during the 21st Century, the mean global temperature will increase by 1-6°C (with a best estimate of 2-3°C) (Meehl et al., 2007). We know that a rise in temperature exponentially increases the emission of most BVOCs in the short-term. Peñuelas and Llusià (2003) suggested that increasing mean global temperature by 2-3°C could enhance global BVOC emissions by 25-45%. The recurrence of very high temperatures (above 40°C) episodes (especially in the tropics) could also lead to a decrease in BVOC production because of reduced enzyme activity production. In addition,

global warming not only lengthens the growing season (Myneni et al., 1997), but also alters latitudinal and altitudinal treelines (Wilmking et al., 2004). Forest dieback at lower latitudes has already occurred, with an upward and northward expansion of boreal forests (Kittel et al., 2000).

Climates models also predict a change in precipitation frequency and intensity in response to increasing surface temperature (Meehl et al., 2007). In semiarid and Mediterranean climates, accelerated soil water depletion in summer and reduced precipitation will increase drought and associated heat stress in summer (Peñuelas and Staudt, 2010), affecting BVOC emissions (see § 2.2.1.1).

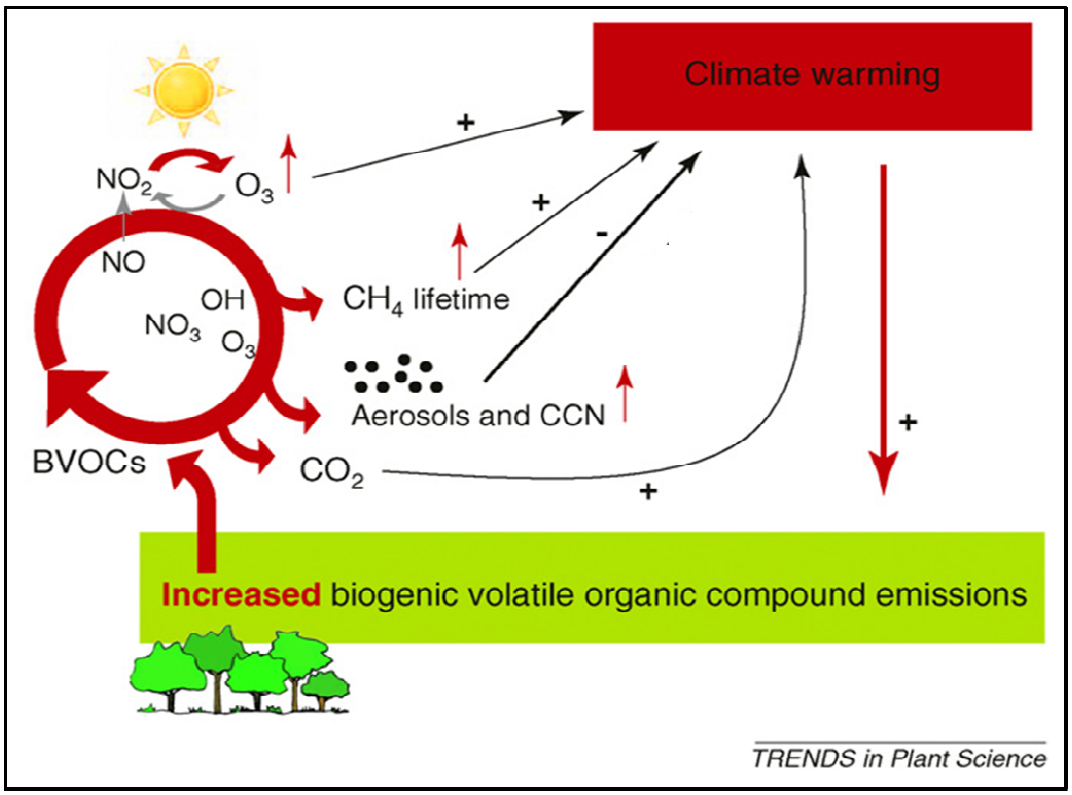

Figure 1.7 Effects of increased BVOC emissions on atmospheric chemistry and climate. Schematic representation of the coupling of enhanced BVOC emissions and atmospheric and climatic changes (adapted from Penuelas and Staudt, 2010).

Rising atmospheric CO_2 concentrations due to anthropogenic activities (IPCC, 2007) could increase the productivity and standing biomass of plants, at least in the short term and indirectly increase BVOC production and emission (Körner, 2006). As noted for isoprene in § 2.2.1.1, contradictory observations have shown that an increase in CO_2 induces varied (increase, decrease or no significant effects) effects on BVOC emissions at the levels of whole plant, the shoots or the leaves (Laothawornkitkul et al., 2009). Various factors, including plant species, age, experimental duration and CO_2 concentra-

tion could explain these contrasting results. It is likely that the concentration of tropospheric O_3 will increase in the coming decades, in terms of either of higher background concentrations and/or frequency of air pollution (IPCC, 2007). As mentioned for isoprene in § 2.2.1.1, an increase in O_3 could positively/negatively affect BVOC production/emission, but contradictory observations have been reported depending on the experimental conditions (temperature, applied O_3 concentrations), species, type of BVOCs and seasons (Peñuelas et al., 1999).

An increase in BVOC emissions can lead to a reduction in the oxidation capacity of the troposphere by depleting the level of OH radicals, inducing an increase in the atmospheric lifetime of the greenhouse gas methane; thereby contributing to global warming (Atkinson and Arey, 2003). An increase in BVOC emissions can also lead to an increase in the production of tropospheric O_3 (greenhouse gas), depending on NO_x concentration (see § 3.2.1). In addition, SOAs affect climate directly by scattering and absorbing radiation and indirectly by influencing cloud properties through the CCN (Forster et al., 2007). An increase in BVOC emissions increases SOA/CCN concentration, leading to more reflective clouds (Twomey, 1977) with potentially longer lifetimes (Albrecht, 1989). As a result, the amount of solar radiation reaching the surface of Earth is reduced with a consequent cooling effect (Goldstein et al., 2009). SOAs and clouds can also affect canopy photosynthesis by increasing the relative proportion of diffuse radiation at the Earth's surface. The carbon sequestration in the canopy is enhanced under conditions with a high proportion of diffuse radiation compared to conditions with the same total radiation but with a lower proportion of diffuse radiation (Gu et al., 2002; Knohl and Baldocchi, 2008), providing another indirect, and potentially negative, feedback on global warming.

5 Global BVOC budget modeling

As described above, BVOCs play an important role in air chemistry and climatic processes, and regional-scale emission/deposition inventories are needed in order to predict regional air quality and simulate future climatic conditions (Karl et al., 2009; Keenan et al., 2009). This requires applying emission models that accurately describe the responses of emissions to variation in environmental factors.

Early BVOC emission modeling methods took an empirical approach, describing monoterpene emission rates as a function of temperature and isoprene emission rate as a func-

tion of temperature and radiation (Guenther, 1997; Guenther et al., 1995; Guenther et al., 1993). The model developed by Guenther et al. (1993, 1995, 1997), originally for isoprene emissions but also for monoterpene emissions from *Fagus sylvatica* (Dindorf et al., 2005; Holzke et al., 2006; Moukhtar et al., 2005), described newly synthesized emissions dependent on instantaneous light and temperature as:

$$E_{G97} = SEF.C_L.C_T$$

where SEF [µg m^{-2} s^{-1}] is a standard emission factor (i.e., the emission rate at standardized conditions; 30°C, 1000 µmol m^{-2} s^{-1}) for the type of vegetation considered; C_L and C_T describe the response of the emissions to instantaneous radiation and temperature, respectively. Both these functions are represented in Figure 1.3.

To date, most BVOC modeling has been done on the basis of the Guenther et al. (1993) algorithm. In recent years, however, it has become increasingly evident that the SEF is not constant. Apart from instantaneous $PPFD$ and temperature, as explained in § 2.2.1, additional short- and medium-term factors play an important role in modifying emission rates. The parameterization of emissions rates has been extended in the Model of Emissions of Gases and Aerosols from Nature (MEGAN), the algorithm developed by Guenther et al. (2006) and optimized for isoprene emissions. MEGAN incorporates the effects of leaf age, soil moisture and the temperature and light conditions of the previous day.

Emission models are developed almost exclusively at the leaf level and are then scaled up, spatially and temporally, to the canopy, the stand, and finally the region level. This bottom-up modeling approach (Figure 1.8) requires climatic forcing variables, information on plant leaf area, architecture of plant stands, species composition, BVOC emission potentials as input data and the coupling of the BVOC emission model with a canopy environment model (Guenther et al., 2006). The most important variable in modeling BVOC emissions is the BVOC emission potential (Arneth et al., 2008; Grote and Niinemets, 2008) represented by the standard emission factor (SEF). The SEF strongly varies among species from values near zero to more than 100 µg g(LDW)$^{-1}$ h^{-1} and can be very different for species of the same genus (Kesselmeier and Staudt, 1999). The great variability in the emission factor estimates is currently not understood and could generate great differences in the estimation of global BVOC emissions. Recently, Arneth et al. (2008) summarized and compared several models predicting annual and global isoprene fluxes and obtained a global average of 516 Tg C yr^{-1}, with an 11%

standard deviation (55 Tg C yr^{-1}). Curiously, a similar picture does not emerge from simulation estimates of global monoterpene emissions. For these compounds, the variation around the mean is considerably larger, the standard deviation (37 Tg C yr^{-1}) being 40% of the mean (91 Tg C yr^{-1}). There is no apparent reason why the spread in monoterpene emission rates should be so much larger than isoprene emission rates. Both are based on similar model set experiments, and differences in vegetation type, physiological activity or canopy characteristics should have very similar effects on isoprene and monoterpene emissions. This shows that further observations are needed on order to improve the accuracy of isoprene and monoterpenes modeling.

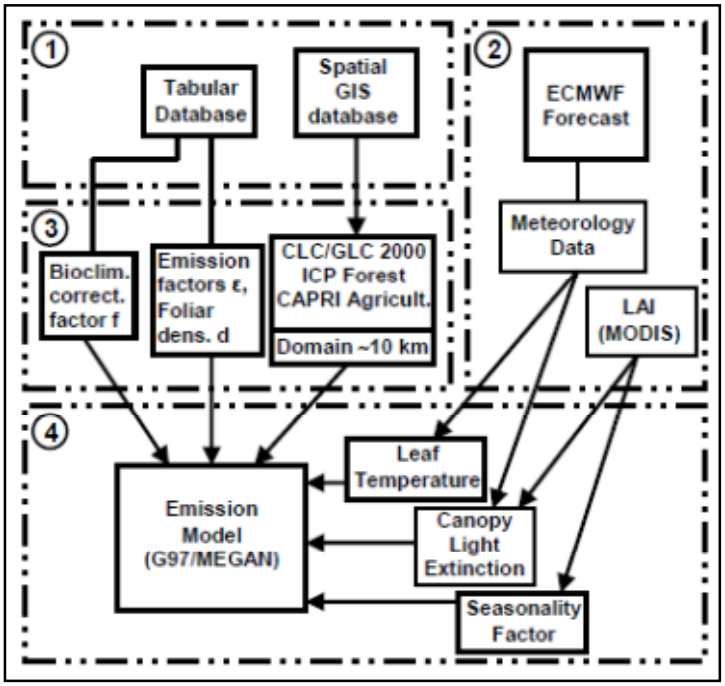

Figure 1.8 Global BVOC emission model. Schematic overview (from Karl et al., 2009).

Several modeling studies conducted to quantify the source of global methanol (the second most abundant organic gas in the atmosphere after methane) have produced a wide range of values for global annual emission estimates, from 123 to 343 Tg yr^{-1} (Jacob et al., 2005; Millet et al., 2008; Tie et al., 2003). The global sink budget is also uncertain, with estimates ranging from 40 to 284 Tg yr^{-1} (Jacob et al., 2005; Millet et al., 2008; Tie et al., 2003). These uncertainties are due mainly to the lack of available measurements that can provide constraints on methanol sources and sinks, which are typically limited in terms of temporal and spatial resolution, leading to limited knowledge about emission and deposition mechanisms. The uncertainty about the methanol

budget is greater than that about the isoprene and monoterpene budgets because of the very few studies on estimating methanol emission potential from plant growth (Kesselmeier and Staudt, 1999), and also because of the presence of deposition mechanisms that do not exist in the isoprene and monoterpene budgets.

6 Sampling BVOC emissions/depositions

In the past decade, numerous studies have measured BVOC emissions from various plant species. The results were reviewed by Kesselmeier and Staudt (1999) and regularly updated via the online Lancaster University database (UK) and the ACD/NCAR database. The choice of sampling device or method used to determine VOC emissions at small or large scales depends on many factors (e.g., the research question being addressed, whether it is primarily laboratory-based or field-based, the relative importance of technical issues surrounding environmental controls, and the physico-chemical properties of the VOCs being investigated) (Hewitt et al., 2011). To date, the enclosure method is the most widely used way of measuring VOC emissions from plants at the leaf or branch level. This technique consists of enclosing a leaf or branch in a cuvette ventilated at a constant rate. The emission from the plant components is then deduced from the concentration difference between incoming and outgoing air. The enclosure method, however, is not without its problems (Hewitt et al., 2011). It can take a long time to achieve equilibrium and a genuine emission rate. When the emission rate of compounds from the plant is low, concentrations in the headspace will also be low. Reducing the flow rate through the cuvette will increase the VOC concentration, but can lead to condensation of transpired water vapor. Consequently, this can reduce the $PPFD$ and alter emission rates, and can lead to the adsorption of some water-soluble VOCs on the cuvette surfaces and to the destruction of extremely reactive VOC (Niinemets et al., 2011). Extrapolating leaf or branch-level emission measurements to give canopy-scale emission rates provides information on emitted compounds and source strength. It can also provide emission input to atmospheric chemistry models for regions or vegetation types where canopy-scale measurements have not been made (as explained in § 5). The extrapolation of these measurements to the whole canopy scale introduces substantial uncertainties (Guenther et al. 2006) because of the limited understanding of chemical sink and deposition losses within vegetation canopies, artificially disturbed emission rates due to the enclosure, differences between the functioning of individual ecosystem com-

ponents (e.g., leaves) and the entire ecosystem and limited sample size within the enclosure (relative to the whole landscape). In addition, BVOC cuvette studies usually cover only a small part of the growing season, centered on time periods when BVOC emissions are thought to be important, and are still too limited by the natural variability in BVOC emissions; sources of variation include tree-to-tree variability, the acclimation of leaf to sun or shade environments and vertical gradients in BVOC emission potentials.

In contrast to enclosure methods, micro-meteorological techniques offer a way of measuring interactions between plant canopies and the atmosphere without disturbing the local environment. When applied over homogeneous canopies, these techniques can provide temporally and spatially integrated estimates of the VOC exchange occurring from the area upwind of the measurement point, called the flux footprint area. These features make micro-meteorological techniques ideal for monitoring long-term whole-ecosystem responses to environmental factors and for computing a precise BVOC balance of the whole-ecosystem, and they provide insight into new BVOC emission/deposition mechanisms not detected by enclosure measurements. The most direct micro-meteorological flux measurement technique is the eddy covariance (EC) technique. In this study, the directness and accuracy of EC (described in Chapter 2, §3.1) made it an attractive method for sampling VOC emissions at the canopy scale.

Chapter 2

Objectives & Outlines

1 Objectives

1.1 The IMPECVOC project

A Belgian project known as the Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems (IMPECVOC; www.impecvoc.ugent.be) was implemented during the 2006-2011 period to investigate BVOC emissions from deciduous and coniferous tree species in Belgium's forest ecosystems. A bottom-up approach was followed beginning with enclosure measurements (leaf/branch level) on saplings in growth chambers, followed by enclosure measurements on a mature tree in outdoor conditions and ending with stand level measurements using a micro-meteorological method. The chosen tree species were European beech, Douglas fir and Norway spruce. European beech has always been considered as a low isoprene and monoterpenes emitter. Recently, however, branch enclosure measurements indicated that it could be classified as a high monoterpene emitter (Dindorf et al., 2005). Norway spruce is reported to emit monoterpenes, as well as isoprene and acetone (Janson and de Serves, 2001). Douglas fir is known to emit monoterpenes (Pressley et al., 2004).

Within the framework of the IMPECVOC project, the research objectives of this thesis were:

- to measure BVOC exchange at stand level and over the long-term above a mixed forest (European beech, Douglas fir, Norway spruce, Abies alba) in the Belgian Ardenne (Vielsalm site).
- to characterize the relationship between BVOC emissions/depositions, climatic variables and photosynthesis fluxes under different relevant phenological conditions (i.e., leaf development, fully leafed period, senescence and leafless period).

- to propose standard emission factors and improved BVOC emission/deposition algorithms in order to improve the estimation of BVOC emissions from Belgian forests.

1.2 Papers included in the thesis

This thesis is arranged in three papers, each one being characteristic of a step in the author's research. The papers included in this thesis are:

Paper I: *Q. Laffineur, M. Aubinet, N. Schoon, C. Amelynck, J.-F. Müller, J. Dewulf, H. Van Langenhove, K. Steppe, M. Simpraga, B. Heinesch,* 2011. **Isoprene and monoterpene emissions from a mixed temperate forest.** *Atmospheric Environment*, 45, 3157-3168.

Paper II: *Q. Laffineur, M. Aubinet, N. Schoon, C. Amelynck, J.-F. Müller, J. Dewulf, H. Van Langenhove, K. Steppe, B. Heinesch,* 2012. **Light regime impact on isoprene and monoterpene emissions from a mixed temperate forest.** *Atmospheric Environment*, submitted.

Paper III: *Q. Laffineur, M. Aubinet, N. Schoon, C. Amelynck, J.-F. Müller, J. Dewulf, H. Van Langenhove, K. Steppe, B. Heinesch,* 2012. **Abiotic and biotic control of methanol exchanges.** *Atmospheric Chemistry and Physics*, 12, 1-14.

All three papers are based on ecosystem-scale BVOC flux measurements performed at the mixed forest site of Vielsalm, using the micro-meteorological method known as 'disjunct eddy-covariance' (DEC) (see § 3.1). A proton-transfer-reaction mass spectrometer (PTR-MS) was used to continuously measure several BVOC mixing ratios (see § 3.2). The dataset used in **Paper I** extended from July to October 2009 and the dataset used in **Papers II** and **III** extended from June 2009 to September 2010 (winter was not included).

The objectives of **Paper I** were to:

- describe and quantify the climatic control of isoprene and monoterpene emissions
- derive standard emission factors
- investigate the coupling between isoprene/monoterpene emissions and assimilated CO_2
- investigate the seasonal evolution of the standard emission factors and the response of isoprene/monoterpene emissions to temperature and light, in order to

see how isoprene/monoterpene production pathways within the plant can alter over time.

The objectives of **Paper II** were to:

- investigate the impact of the diffuse/direct radiation on isoprene/monoterpene canopy emissions over the whole growing season
- investigate the coupling between isoprene/monoterpene emissions and assimilated CO_2 under diffuse and direct radiation.

The objectives of **Paper III** were to:

- disentangle the abiotic and biotic drivers of the methanol emissions/depositions
- develop an original model for estimating the respective contributions to the net flux of, first, the methanol adsorption/desorption in water film present in the ecosystem and, second, methanol degradation
- use the model residuals to isolate biogenic emissions and to identify their driving variables.

The author of this thesis carries the main responsibility for the BVOC flux data treatment and flux analysis (**Papers I**, **II** and **III**). Data acquisition (meteorological data, BVOC data) and CO_2 flux measurements were undertaken by B. Heinesch, and the PTR-MS was operated by N. Schoon and C. Amelynck. The site was maintained by the technicians M. Yernaux, A. Debacq and H. Chopin.

2 Methodology

2.1 Disjunct eddy covariance

The most direct micrometeorological method for studying the gas exchange between a canopy and the atmosphere is the eddy-covariance (EC) method. It requires high-frequency simultaneous measurements of the concentration of an atmospheric compound (c) and vertical wind velocity (w). It can be demonstrated (Foken et al., 2012) that, under given conditions, the covariance between the eddy components of these variables ($c' = c - \bar{c}; w' = w - \overline{w}$) can be equated to the flux

$$F = \overline{w'c'} = \frac{1}{T}\int_0^T w'(t).c'(t)dt$$

where the overbar denotes time-averaging (T). These two components must be measured with a short instrumental time response in order to take account of the high frequency fluctuations contributing to the flux. Typically, sampling frequencies used in EC measurement are 5-10 Hz. The three-dimensional wind is commonly measured by an acoustic anemometer where each component of the wind (u,v,w) is obtained from the differences in time it takes for an acoustic signal to travel the same path in opposite directions. The EC is used to measure fluxes of any scalar if their concentration can be measured rapidly enough by gas analyzers. Currently, it is most often used to measure CO_2 and H_2O fluxes (Aubinet et al., 2012a). For many other atmospheric constituents there are no sensors that are fast enough for traditional EC measurements, although recently the PTR-MS has been applied for the EC measurement of VOCs (Ammann et al., 2006; Bamberger et al., 2010; Hörtnagl et al., 2011; Karl et al., 2001; Rinne et al., 2001; Spirig et al., 2005).

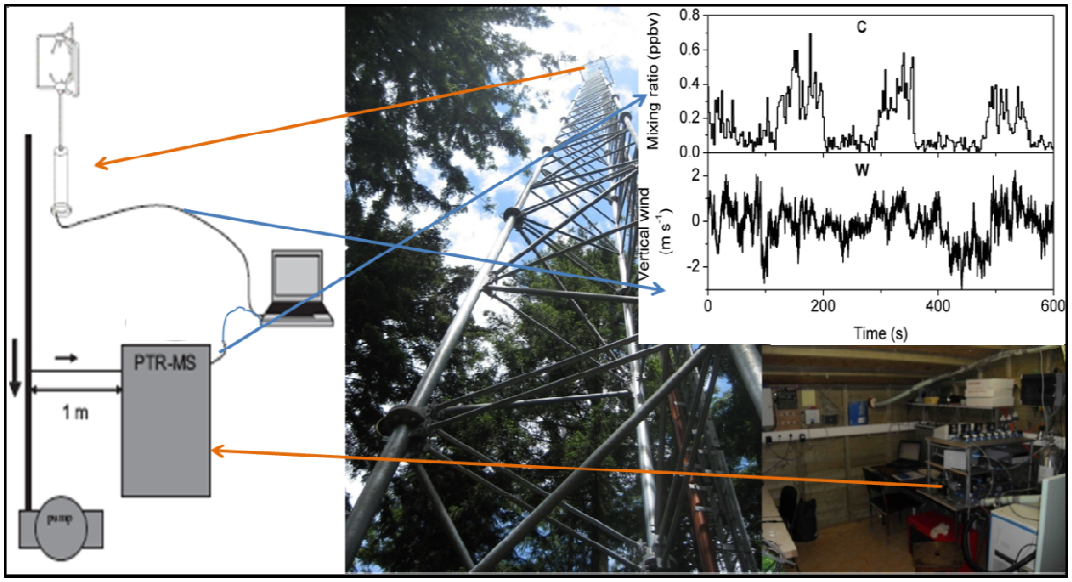

Figure 2.1 Schematic representation of the experimental set-up, with the sonic anemometer at the tower top measuring the vertical wind velocities (w) and the PTR-MS at the tower base measuring the VOC mixing ratio (c).

A PTR-MS allows the VOC concentration fluctuations to be measured in real time with a fast instrumental response time (see § 3.2). As it is unable to measure ion intensities at more than one mass at a time, however, the ion signal intensities at the masses of interest are measured in a cyclic way, producing a disjunct concentration time series for each mass. Using this approach, the disjunct EC by mass scanning (DEC-MS) method (Rinne and Ammann, 2012), the flux is determined by the covariance between the discrete

function of the time series of c' and the subsampling of the continuous time series of w':

$$F = \frac{1}{N}\sum_{i=1}^{N} w'(t_i - t_{lag}).c'(t_i)$$

where N is the number of disjunct PTR-MS samples during T and t_{lag} is the lag time between w and c. This lag time is the time taken to draw the ambient air sample from the inlet close to the sonic anemometer sensing volume to the PTR-MS. At Vielsalm, the sonic anemometer was placed at the top of the tower at a height of 52 m and the PTR-MS was located at the base of the tower (Figures 2.1 and 2.2), giving a sampling line length of 62 m. Although DEC-MS is the most direct method for studying gas exchanges between the canopy and the atmosphere, some corrections must be applied to the measured fluxes. These corrections are described in details by Aubinet et al. (2012a).

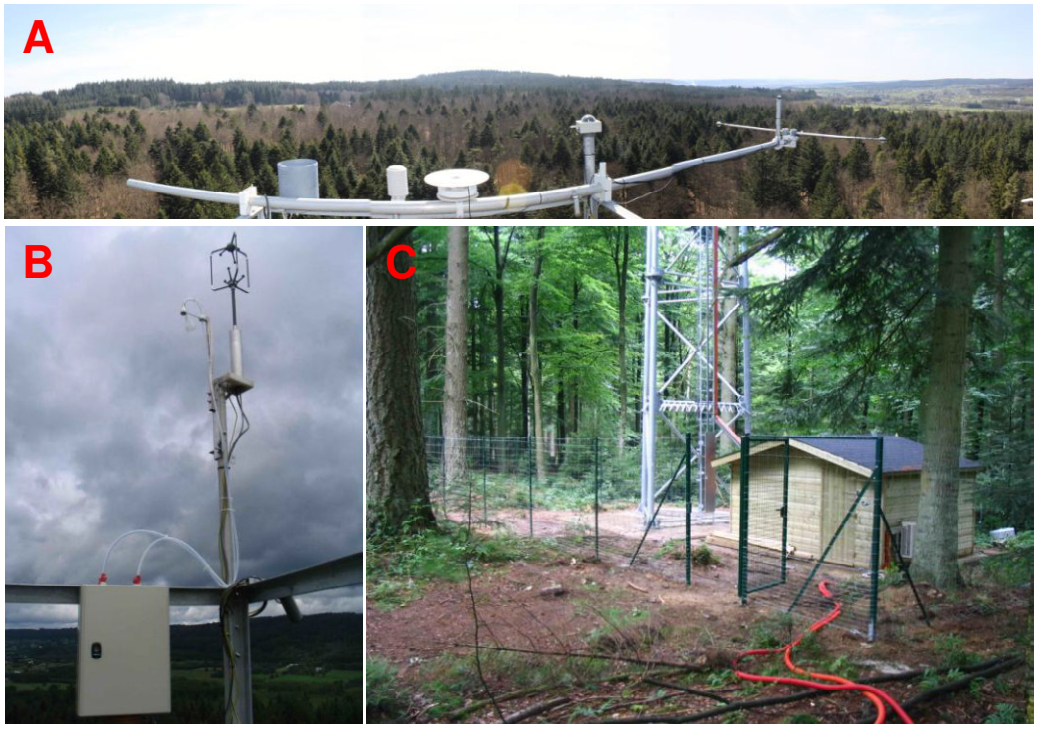

Figure 2.2 View from the tower top showing radiation sensors (a), the air sampling inlet close to the sonic anemometer (b) and the tower base with the shelter housing the PTR-MS and acquisition systems (c).

2.2 PTR-MS

The proton-transfer-reaction mass spectrometer (PTR-MS) is an excellent instrument for VOC analysis. More details on the PTR-MS technique are given be by Lindinger et al. (1998), de Gouw and Warneke (2007) and Blake et al. (2009). A shorter description is provided here.

In proton-transfer-reaction mass spectrometry, the air to be analyzed is continuously pumped through a drift tube reactor, and a fraction of the VOC is ionized in proton-transfer reaction with hydronium ions (H_3O^+):

$$H_3O^+ + VOC \rightarrow VOCH^+ + H_2O$$

The advantage of using proton transfer reactions is that it is a soft ionization method and therefore does not lead to fragmentation of the product ions. The mass of the product ion equals the VOC mass increased by one. At the end of the drift tube, the reagent and product ions are measured by a quadrupole mass spectrometer, and the product ion signal is proportional to the VOC mixing ratio. A PTR-MS allows numerous VOCs of atmospheric interest to be monitored with a high sensitivity (10-100 pptv) and rapid response time (1-10 sec). In addition, air samples can be introduced directly into the drift tube without sample preparation or pre-concentrations, allowing for on-line monitoring of VOC emissions. A major disadvantage is that a PTR-MS determines only the mass product ions, which is not of course, a unique indicator of VOC identity. For example, at the ion signal m/z 137, several monoterpene species can be detected without distinction. Nevertheless, the ion signal at m/z 137 has always been considered to be a good estimator ion of the sum of monoterpenes (de Gouw and Warneke, 2007). In this study, the ion signal at m/z 87 was used because it is typical for C_5 alcohols, which might interfere with the detection of isoprene because these alcohols are known to have an important fragment ion at the same m/z value of protonated isoprene (m/z 69) (de Gouw and Warneke, 2007; Demarcke et al., 2010a). At the ion signal m/z 33 (methanol), the oxygen isotopes ($^{16}O^{17}O^+$) (Spirig et al. 2005) are also detected and could bias the methanol measurements.

3 Generality on BVOC measurements at Vielsalm

Routine measurements of BVOC fluxes at the Vielsalm site started on 10 July 2009 and ran through to 17 November 2009 (131 days). In 2010, measurements started on 26 March and ended on 18 November (236 days). During these periods there was an overall BVOC flux data coverage of 83% (69% after removing the PTR-MS background measurements, PTR-MS calibration and maintenance events). Data gaps were due to power cuts and problems with the source or the detector of the PTR-MS. The flux dataset constitutes more than 12000 half-hours per compound allowing robust statistical analysis. This database encompasses all the meteorological and phenological situations that occurred during these 13 months at Vielsalm (e.g., night-day, hot-cold, sunny-cloudy, wet-dry, full vegetation-senescence), with the exception of the winter when the fluxes were expected to be very low. It is worth mentioning that the measurements continued in 2011, including the winter period and that an in-canopy vertical concentration profile was implemented as well as a DEC system in the trunk-space. These 2011 data are not included in the present thesis.

3.1 BVOC emissions

Ten ion species representative of BVOCs were selected for routine measurements: methanol (m/z 33), acetaldehyde (m/z 45), formic acid (m/z 47, added in 2010), acetone (m/z 59), acetic acid (m/z 61, added in 2010), isoprene (m/z 69), methyl vinyl ketone and methacrolein (m/z 71), fragment of monoterpenes (m/z 81), methylbutenol and possibly others (m/z 87) and the sum of monoterpenes (m/z 137), in addition to the PTR-MS reactant ion species (H_3O^+ at m/z 21and $H_3O^+.H_2O$ at m/z 39).

An overview of mixing ratio and fluxes is given in Figures 2.3 and 2.4, respectively. During the two measurement periods, the most important fluxes measured at Vielsalm were the monoterpenoids (m/z 137) flux and the isoprene (m/z 69) flux. Both these fluxes were positive indicating that the flux was always oriented from the surface towards the atmosphere, and had a diurnal cycle. At night, isoprene fluxes were close to zero, whereas monoterpene fluxes remained slightly positive. The methanol (m/z 33) flux was also important (third position) at Vielsalm but exhibited a complex emission/deposition behavior that was also observed for acetaldehyde (m/z 45) and acetone (m/z 59).

Based on this general analysis, in the research for this thesis we focused on the isoprene and monoterpene emissions and on the methanol exchange. The analysis of these first two fluxes is detailed in Chapters 3 and 4, where the production and exchange processes are described through the seasonal evolution of the flux measurements. The observations of methanol deposition (and acetaldehyde and acetone deposition) at the Vielsalm site generally contradicted the results reported in experimental studies where methanol emissions dominate the measurements, with occasional methanol depositions occurences. In Chapter 5, the abiotic and biotic drivers of the methanol emissions/depositions are described in the context of the development of an original model.

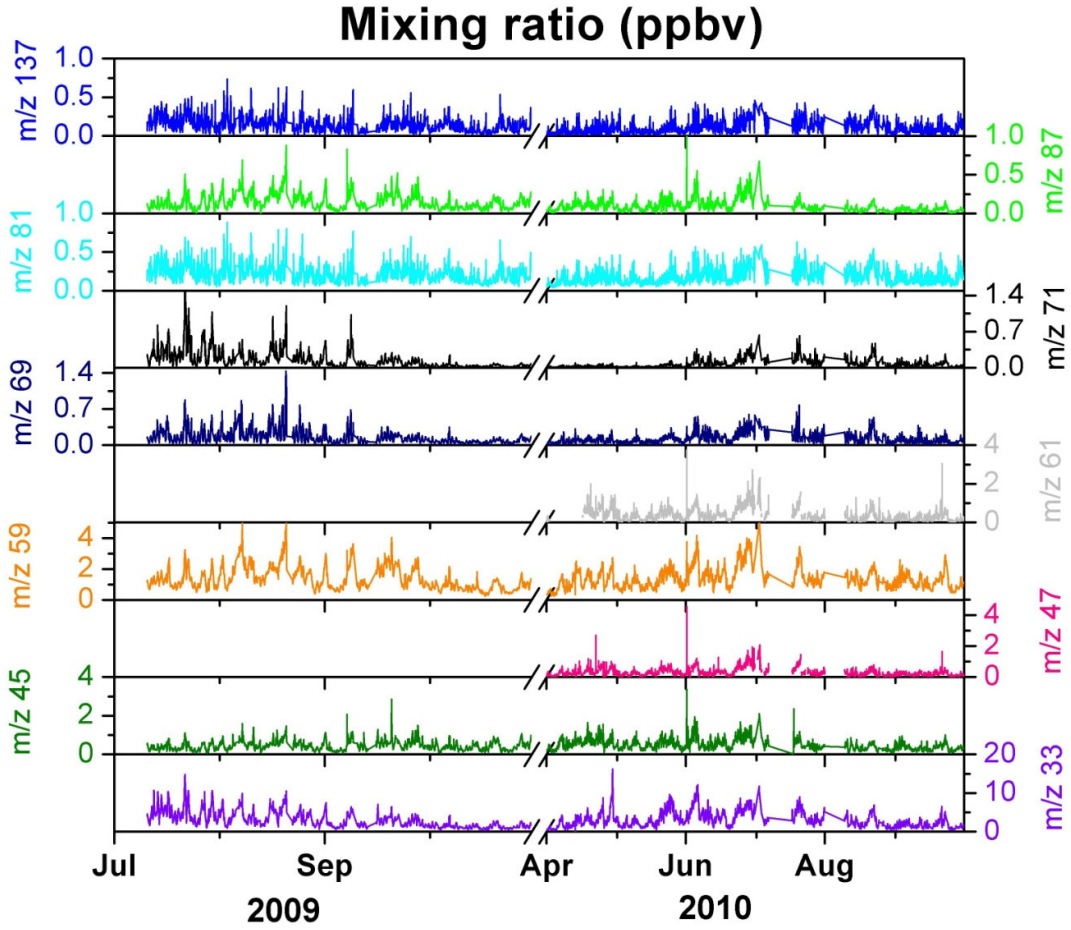

Figure 2.3 Overview of the filtered (see Chapter 3, Section 2.5) dataset of the BVOC mixing ratio obtained at Vielsalm in 2009 and 2010. All mixing ratios are given in ppbv.

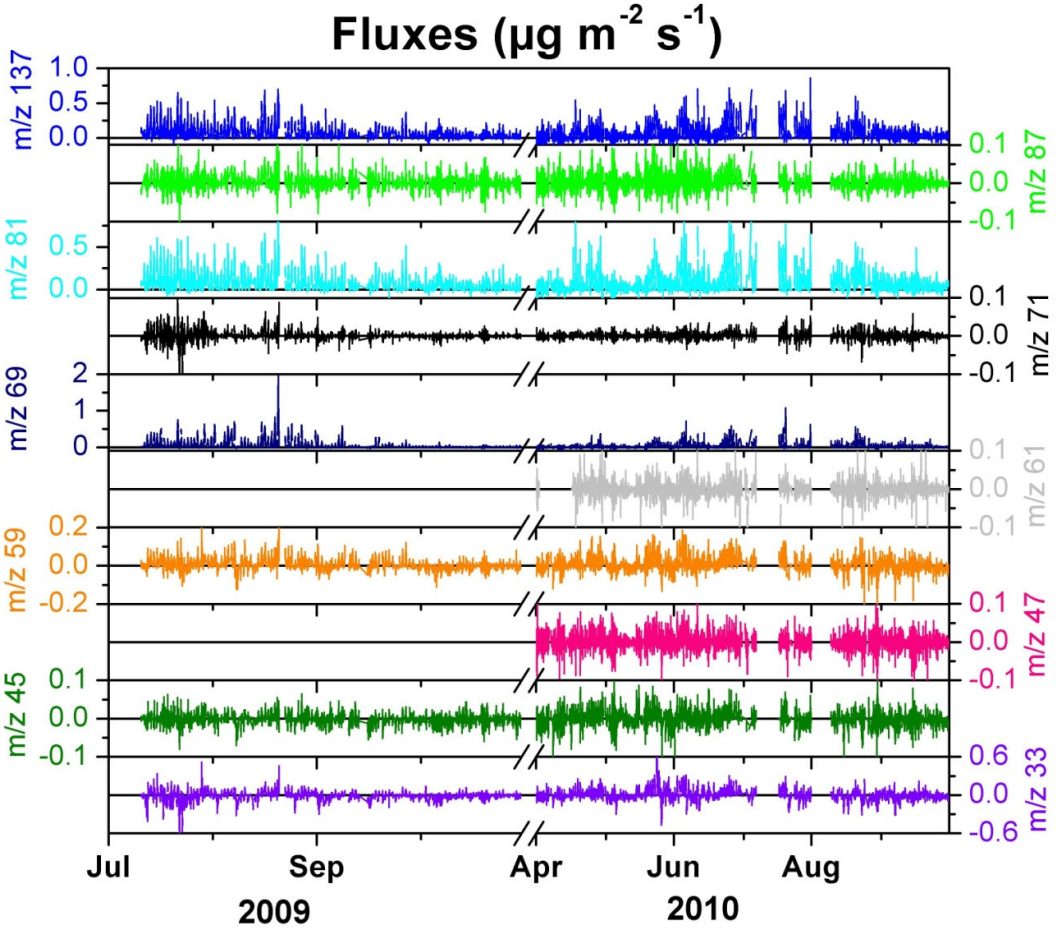

Figure 2.4 Overview of the filtered (see Chapter 3, Section 2.5) dataset of the BVOC fluxes obtained at Vielsalm in 2009 and 2010. All fluxes are given in µg $m^{-2}s^{-1}$.

Chapter 3

Isoprene and monoterpene emissions from a mixed temperate forest

1 Introduction

Isoprene and monoterpenes are the most abundant biogenic volatile organic compounds (BVOCs) emitted by terrestrial vegetation, particularly by forests. Global isoprene and monoterpene emissions are estimated to be 460 TgC yr^{-1} and 117 TgC yr^{-1}, respectively, representing 80% of the total BVOC emissions (Lathière et al., 2006). Isoprene and monoterpenes have a significant impact on atmospheric chemistry and physics. The degradation of BVOCs can lead to an increase/decrease in the production of tropospheric ozone (O_3), depending on the nitrogen oxide (NO_x) concentration (Atkinson, 2000). Their very short reaction time (Atkinson, 2000) with hydroxyl (OH) radicals can modify the oxidative capacity of the atmosphere and increase the lifetime of other chemical compounds such as methane (Ortega et al., 2007). Isoprene and monoterpene oxidation initiates and favours the production of secondary organic aerosols (Kanakidou et al., 2005), compounds that can have a direct and indirect influence on the Earth's radiative budget (Peñuelas and Staudt, 2010).

BVOCs are produced mainly by bio-chemical processes in leaves. Isoprene and monoterpene biosynthesis takes place in chloroplasts (Wildermuth and Fall, 1996) through the 1-deoxy-D-xylulose 4-phosphate/2-C-methylerythritol 5-phosphate (DOXP/MEP) pathway (Eisenreich et al., 2004; Lichtenthaler, 2007). The first enzyme in this biosynthesis pathway catalyses the formation of DOXP from D-glyceraldehyde 3-phosphate and pyruvate, both intermediate products of photosynthesis. After six other enzymatic reactions, DOXP is transformed in isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMADP). This DMADP is transformed into isoprene by the isoprene synthase enzyme (ISPS) and monoterpenes are synthesized as a product of DMAPD and IPP condensation through the enzymatic monoterpene synthase (Croteau et al., 1988). There is another IPP and DMADP synthesis pathway in the

cytosol (Lichtenthaler, 2007; 1997) leading to the formation of sesquiterpenes, triterpenes and polyterpenes, but the IPP exchange between the two biosynthesis pathways apparently does not occur under physiological standard conditions (Lichtenthaler, 2007). Several studies (Delwiche and Sharkey, 1993; Funk et al., 2004; Karl et al., 2002b) have shown that photosynthetically assimilated carbon is the principal source of carbon used in the formation of isoprene (more than 80%: Funk et al. (2004)) in the absence of drought and thermal stress. Brüggemann and Schnitzler (2002) showed a positive correlation between net carbon assimilation and DMADP content in leaves, as well as between DMADP content in leaves and isoprene emission. Isoprene (monoterpene) production is therefore regulated by the ISPS (monoterpene synthase) activity and by the availability of DMADP in leaves, the latter depending on the enzymatic activity of the DOX/MEP pathway (Brüggemann and Schnitzler, 2002; Fischbach et al., 2002; Wiberley et al., 2008).

In addition, under conditions of drought and thermal stress, it has been observed that the *de novo* carbon constituting the BVOC skeleton is partly replaced by carbon coming from alternative sources that are not directly dependent on photosynthesis (Funk et al., 2004). In addition, in the case of isoprene, Owen and Penuelas (2005) formulated the hypothesis that if other BVOCs such as diterpenes and tetraterpenes are synthesized episodically by the plant (thermal protection, defence against pathogens,...) via the DOXP/MEP pathway, available DMADP can be reduced, leading to a decrease in isoprene emission.

After their production, isoprene and monoterpenes are emitted directly to the atmosphere mainly through the stomata. In the case of monoterpenes, a fraction of the production can be stored temporarily in the plant before progressively diffusing in the plant tissues and being emitted into the atmosphere (Fuentes et al., 2000; Kesselmeier and Staudt, 1999).

To date, very few studies have presented simultaneous ecosystem-scale micrometeorological measurements of isoprene, monoterpenes and CO_2 fluxes over several months (Fuentes et al., 1999; Holst et al., 2010; Holzinger et al., 2006; Pressley et al., 2006). Such measurements performed over shorter periods, from several days to several weeks (Gallagher et al., 2000; Grabmer et al., 2004; Greenberg et al., 2003; Rinne et al., 2001; 2007; 2000; Spirig et al., 2005), cannot cover the seasonal evolution of BVOC emissions. Knowing this evolution, however, is crucial for reducing uncertainties in regional emission models and for a better understanding of the emission mechanisms. There are also numerous studies of BVOC emissions using cuvettes (Kesselmeier and Staudt, 1999) which allow, under controlled conditions, to pinpoint the drivers of these emissions. These studies are often limited in time and it is

more difficult to obtain statistically reliable relationships at the ecosystem spatial scale due to the challenge of having enough replica.

In this study, we present ecosystem-scale flux measurements of isoprene and monoterpenes between a mixed forest and the atmosphere, using the disjunct eddy-covariance (DEC) technique (Rinne et al., 2001). This technique is the best suited for long-term monitoring in real conditions and at the ecosystem scale without disturbing the ecosystem. Our dataset extends from July to October 2009, thus covering the Belgian summer and the first part of autumn.

Our objectives were to (i) describe and quantify the climatic control of these emissions, (ii) derive standard emission factors, (iii) investigate the coupling between BVOC emissions and assimilated CO_2 and (iv) investigate the seasonal evolution of the above-mentioned parameters in order to see how BVOC production pathways within the plant can alter over time.

2 Material and methods

2.1 The Vielsalm site

The forested site is at Vielsalm in the Belgian Ardenne forest (50°18'18.20''N, 5°59'53.15''E altitude: 450 m). Its topography is smoothly sloping (3%) in a north-westerly direction. The climate is temperate maritime. The soil is 50-100 cm deep and is classified as a dystric cambisol. The vegetation is a mixture of coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) about 40 m high, Norway spruce (*Picea Abies* [L.] Karst.) about 32 m

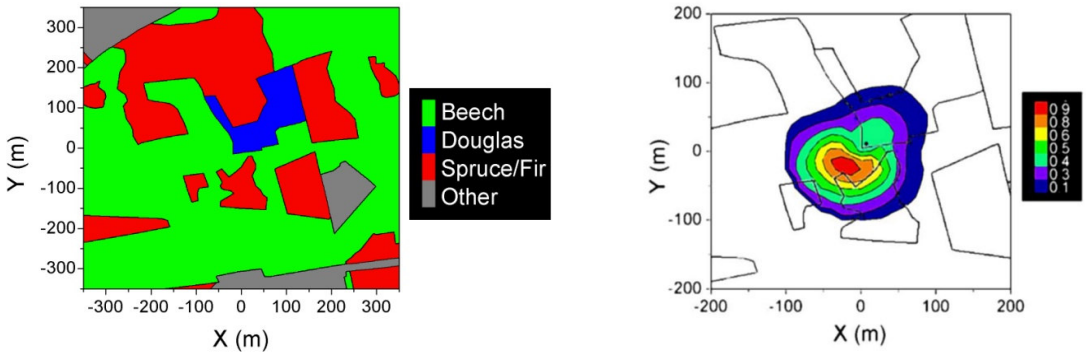

Figure 3.1 Left: Land-use map around the tower. Right: Normalised and cumulated day footprint from July to September superimposed on the vegetation map (red colour corresponds to the region that contribute the most to the flux). Tower location: (0,0) , North direction: (0,Y).

high, Silver fir (*Abies alba* Miller) about 32 m high, and deciduous species, mainly beeches (*Fagus sylvatica* L.) about 28 m high. Figure 3.1 represents the vegetation distribution around

the tower. There are more details about the site in (Aubinet et al., 2001; 2002) and (Laitat et al., 1999).

2.2 Disjunct eddy covariance

The technique used to measure ecosystem BVOC fluxes is the disjunct eddy-covariance (DEC) derived from the eddy covariance method (Ammann et al., 2006; Karl et al., 2001; 2004; 2002c; Rinne et al., 2001; Spirig et al., 2005) which is generally used to measure CO_2 and H_2O fluxes (Aubinet et al., 1999). The flux is computed as the covariance of vertical wind velocity component and BVOC concentration. These two components must be measured with a short instrumental time response in order to take into account the high frequency fluctuations contributing to the flux. For BVOC fluxes, proton transfer reaction-mass spectrometry (PTR-MS) allows the concentration fluctuations of BVOCs to be measured in real time with a fast instrumental response time (see below). Conventional PTR-MS instrument with a quadrupole mass spectrometer (used in this study) does not enable ion intensities to be measured at more than one mass at a time; the ion signal intensities in the masses of interest are measured in a cyclical way, which produces a disjunct concentration time series for each mass. Two methods can then be used to compute the turbulent flux (Hörtnagl et al., 2010). The first (Spirig et al., 2005) consists of filling the missing data in the concentration time series by simply repeating the closer measured concentration with a sampling frequency identical to the one of the vertical velocity component. The second (Karl et al., 2002c) consists of under-sampling the vertical velocity component time series with a sampling frequency identical to the PTR-MS cycle. The first method will act as a low-pass filter and the use of an empirical correction function can be contemplated (Bamberger et al., 2010). The second method increases the random error on the fluxes but does not increase the systematic error (Lenschow et al., 1994) as long as the under-sampling period is shorter than the turbulent integral time scale (typically between 15 and 60 s over forests). In this study, we used the second method (under-sampling) for flux computation, with an under-sampling period of 2 s. From the empirical relationship deduced by Turnipseed et al. (2009), the additional random error originating from this under-sampling was 10%.

Our system comprised a sonic anemometer (model SOLENT 1012R2, Gill Instruments Ltd, Lymington, UK) and an hs-PTR-MS (Ionicon Analytick GmbH, Innsbruck, Austria). The sonic anemometer was placed at the top of a tower at a height of 52 m and measured the three wind velocity components continuously at a sampling frequency of 20.8 Hz. Ambient air was

continuously sampled close to the sonic anemometer through a main sampling line (PFA tubing: Fluortechnik-Wolf) 60 m long and 6.4 mm inner diameter, with a flow rate of 9 STP L min^{-1} (Standard Pressure and Temperature conditions corresponded to 1013.25 hPa and 273.15 K) and was slightly heated above ambient temperature. A part of this air flow (0.1 STP L min^{-1}) was drawn into the PTR-MS through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The time lag between the sonic anemometer measurements and the PTR-MS measurements was computed for each half-hour by shifting one-time series relative to the other until the absolute maximum covariance between the two-time series was determined. We used the filled-time series as proposed by Spirig et al. (2005) and described above to determine the time lag (but not to compute fluxes as already mentioned). This approach allowed an easier timelag determination and is similar to the averaging approach proposed by Taipale (2010). The mean time lag found using this method was 14.8 s, close to 12.9 s, the theoretical value computed from the flow rate and the inlet line volume. This experimental mean time lag was used as the default value when we didn't found a maximum in the covariance function inside the [10 s, 18 s] time window. The data streams coming from the two instruments were logged on a single computer in order to optimise synchronization. We measured the ion signals at mass to charge ratio m/z 21 (primary hydronium ions: $H_3^{18}O^+$), m/z 33 (methanol), m/z 39 (water cluster ion), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 69 (isoprene), m/z 71 (methyl vinyl ketone and methacrolein), m/z 81 (fragment of monoterpenes), m/z 87 (methylbutenol and possibly others) and m/z 137 (monoterpenes). The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. This dwell time was required for limiting significant noise contribution from the PTR-MS. The dwell time had little influence on flux loss (Hörtnagl et al., 2010). BVOC fluxes were computed using the EUROFLUX methodology (Aubinet et al., 1999). Means were computed using block average over 30 min periods, and 2D rotation was applied. High frequency losses due mainly to the damping of concentration fluctuations in the sampling line were corrected experimentally following the method reported by Aubinet et al. (2001) using a transfer function determined by a comparison of the sensible heat flux co-spectra and the m/z 69 flux co-spectra. From this unique transfer function, a correction factor was deduced which was applied to the BVOC fluxes. For example, for a wind speed of 3 m s^{-1} (mean value of our dataset), we obtained a correction factor of 1.49.

2.3 PTR-MS operation

There are detailed descriptions of the PTR-MS technique in Lindinger et al. (1998), de Gouw et al. (2007) and Ammann (2004). In our study, PTR-MS was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2), with E the electric field and N the ambient air number density in the flow/drift tube. During the measurements, the instrumental background was determined every 4 hours by sampling BVOC-free air, obtained by sending ambient air through a heated catalytic converter for 15 min (the last 8 min being used for the calculation of the mean background values). The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every two or three days using a gravimetrically prepared mixture of these gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA) that contained approximately 500 ppbv isoprene, α-pinene and sabinene and about 1 ppmv methanol, acetaldehyde and acetone, with an accuracy of 5%. The compounds were further diluted (2-12 ppbv range) using a dynamic dilution system.

The ion signal at m/z 87 was followed because it is typical for C_5 alcohols, which might interfere with the detection of isoprene because these alcohols are known to have an important fragment ion at the same m/z value of protonated isoprene (m/z 69) (de Gouw and Warneke, 2007; Demarcke et al., 2010a). A comparison of measured fluxes and concentrations calculated from the ion signals at m/z 69 and 87, however, indicated (data not shown) that there is no important contribution of C_5 alcohols to the ion signal at m/z 69. The ion signal at m/z 137 has always been considered to be a good estimator ion of the sum of monoterpenes (de Gouw and Warneke, 2007).

2.4 Meteorological measurements

Measurements of relevant meteorological variables were performed as half-hourly averages, including total and diffuse fraction of photosynthetically active radiation (Sunshine sensor type BF3, Delta-T Devices Ltd, Cambridge, UK), air temperature and humidity (RHT2, Delta-T Devices Ltd, Cambridge, UK) at a height of 50 m, soil humidity (ThetaProbe, Delta-T Devices Ltd, Cambridge, UK) at a depth of 20 cm, and precipitation and atmospheric pressure (MPX4115A, Motorola, Phoenix, USA).

2.5 Data filtering

Throughout the measurement period, in some cases, mixing ratios of methanol and monoterpenes were abnormally high for the wind direction sector 230-270° (Figure 3.2), which was also the main wind direction. In this direction, a wood panel factory was 3 km from the tower. This industrial process is known to emit high levels of monoterpenes (due to wood grinding).

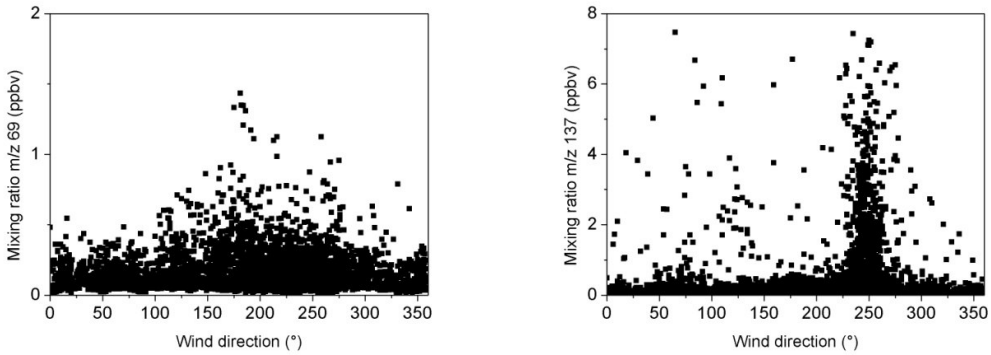

Figure 3.2 Wind direction dependence of m/z 69 and m/z 137 mixing ratios.

The factory was not located inside the main day flux footprint (90%), but this source was probably so important, compared with biogenic sources, that it influenced our measurements. The suspected anthropogenic origin of these monoterpene emissions was confirmed by the lack of a relationship between wind direction and mixing ratios of isoprene (Figure 3.2). The measurements spoiled by anthropogenic emissions should therefore be rejected from the data-set. A filtering criterion based on wind direction only would have been too restrictive in view of the intermittent activity of the factory and the huge amount of data that would have been lost. We therefore used a filtering criterion based on the variance of the monoterpene mixing ratio. When the factory was functioning, this variance was very high for the 230°-270° wind sector compared with other sectors, where it never exceeded 0.08 $ppbv^2$ during the day and 0.03 $ppbv^2$ during the night (data not shown). These high values must be the consequence of the huge difference in monoterpene mixing ratios between air emitted by the factory and ambient air. The relatively short distance between the factory and the tower did not allow complete mixing of the air, resulting in important mixing ratio fluctuations and therefore in strong disturbances of the ecosystem flux measurements. The application of the flux variance criterion rejected 17% of the monoterpene data. The isoprene data were not affected by the factory activity and were therefore not filtered.

The system detection limit was estimated using a procedure proposed by Wienhold et al. (1994) and Spirig et al. (2005). They proposed computing the covariances of concentrations

and vertical velocities delayed by time lags so large that the covariance should theoretically have been zero. The detection limit was then defined as three times the standard deviation of the covariance for these time lag ranges. In practice, we used -180 s to -160 s and 160 s to 180 s as the time lag ranges. These confidence intervals were useful as quality criteria for individual flux estimations, but became useless when flux estimations were treated as statistical means in order to get rid of the noise.

2.6 Data treatment and analysis

2.6.1 Emission algorithm

To analyse the meteorological responses of isoprene and monoterpene emissions, we used an algorithm derived from those proposed by Guenther et al. (1993; 1997). We modelled the temperature and radiation dependence of isoprene and monoterpene emissions as:

$$E_{G97} = SEF.C_L.C_T \quad (1)$$

where *SEF* is the standard emission factor describing emissions under standard conditions ($PPFD$ = 1000 µmol m^{-2} s^{-1}, T_a = 30°C), and C_L and C_T are functions describing the photosynthetic photon flux density (*PPFD*) and the air temperature (T_a) dependence, respectively. In this study, air temperature was used as a surrogate for leaf temperature.
C_T was modelled as:

$$C_T = \exp(\beta.(T_a - 303.15)) \quad (2)$$

where β [K^{-1}] is the temperature dependence parameter,
and C_L as:

$$C_L = \frac{C_{L1}PPFD}{\sqrt{1000^2(C_{L1}{}^2-1)+PPFD^2}} \quad (3)$$

where C_{Ll} [µmol m^{-2} s^{-1}] is the saturation C_L value. The expression 2 is generally used to describe the monoterpene emissions from storage pools. The temperature response of isoprene/monoterpenes emission from *de novo* production is commonly represented by a temperature response of enzymatic activity that decreases above 40°C due to the enzyme denaturation (Guenther et al., 1993). These temperatures were never observed in our dataset therefore we used the expression 2 in our data adjustment to represent both the temperature response of *de novo* isoprene/monoterpene production and monoterpene emissions form pools.

Expression 3 from Guenther et al. (1993) was rearranged in order to depend on only one parameter, C_{LI}.

We adjusted these equations to our data by using non-linear least square fitting based on the Levenberg-Marquardt algorithm from Origin software 7.0 (OriginLab Corporation).

2.6.2 Footprint model

The footprint analyses were performed with a two-dimensional analytical footprint software tool proposed by Neftel et al. (2008) according to the Kormann-Meixner footprint model (Kormann and Meixner, 2001). The inputs of the model are information provided by the eddy covariance system (friction velocity, Obukhov length, standard deviation of lateral wind speed, measurement height and horizontal wind speed).

2.6.3 Gross primary production computation

The gross primary production (GPP) was inferred by deducting the total ecosystem respiration (TER) to the net ecosystem exchange (NEE) measured by eddy covariance. TER was inferred by extrapolation to the whole day of night-time NEE measurements, since plant assimilation can be considered to be zero at night. An algorithm proposed by Reichstein et al. (2005) for the respiration response to soil temperature based on night flux measurements was used for the extrapolation.

3 Results

3.1 Micrometeorological and flux seasonal evolutions

The seasonal evolution of air temperature, $PPFD$, wind direction, friction velocity (u^*), soil moisture (S_W) and precipitation are given in Figure 3.3. Mean air temperature was 16.8°C, 13.6°C and 8.4°C for July-August, September and October 2009, respectively. Maximum temperature (30.3°C) was reached on 20 August and minimum temperature (−1.7°C) on 15 October (the first frost appeared on 14 October). In July, the noon $PPFD$ values went up to 1500 and 300 µmol m^{-2} s^{-1} under sunny and cloudy conditions, respectively. In October they reached 800 and 150 µmol m^{-2} s^{-1}, respectively. The main wind direction was W-SW (50%), but E-SE (15%) and NE (10%) directions were also observed. Soil moisture measured at 0.2 m below the soil surface diminished progressively in August and September, from 0.38 m^3 m^{-3} to 0.26 m^3 m^{-3} (field capacity: 0.43 m^3 m^{-3}, wilting point: 0.15 m^3 m^{-3}). During this

period, precipitation was quite sparse, occurring on about one or two days every 10 days. More intense precipitation in early October increased soil moisture rapidly up to 0.33 m^3 m^{-3}.

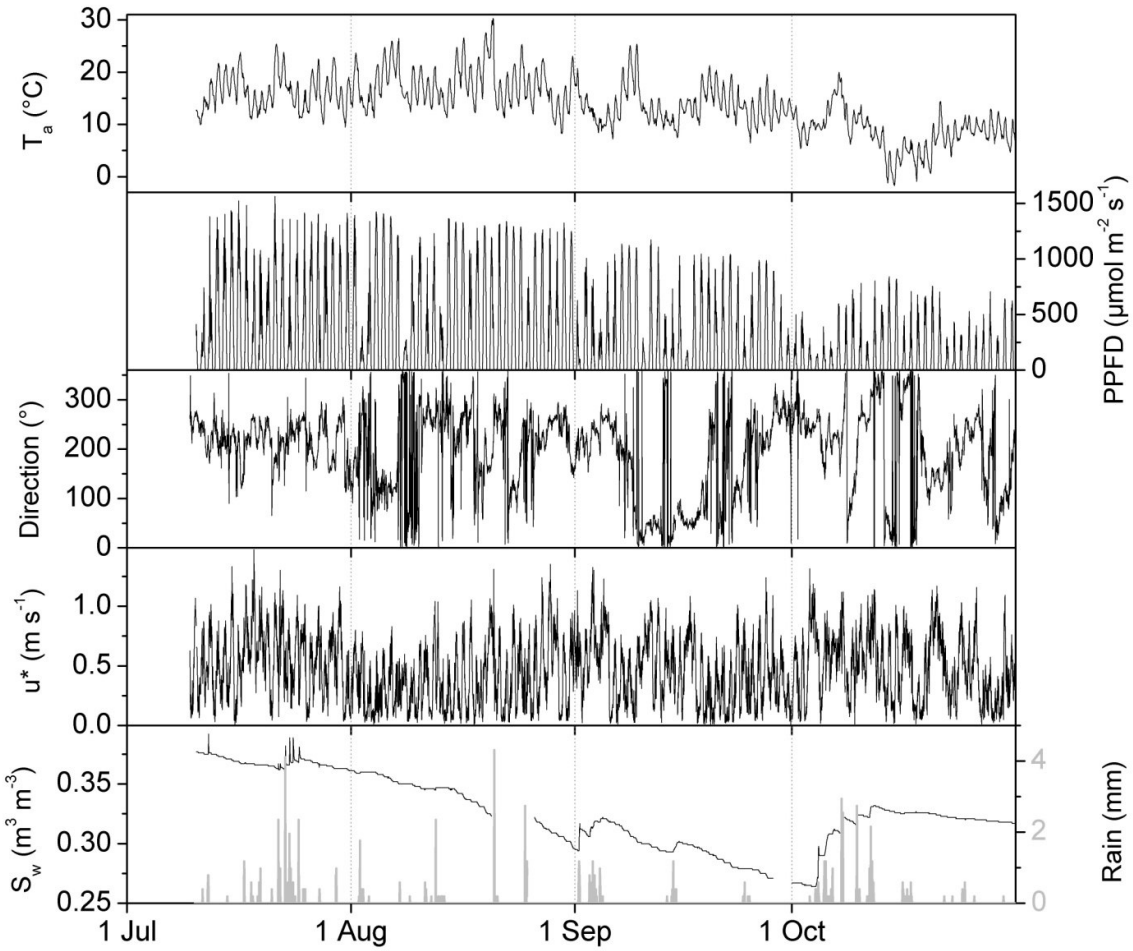

Figure 3.3 Temporal evolution of relevant meteorological parameters between 10 July 2009 and 31 October 2009: air temperature (T_a), Photosynthetic Photon Flux Density (*PPFD*), wind direction, friction velocity (u^*), soil humidity (S_W) and precipitation.

Time series of measured isoprene and monoterpene fluxes are presented in Figure 3.4. The measurements covered 88% of the period, data gaps being due either to partial or total system failures or to background noise measurement and PTR-MS calibration (12%). The grey lines correspond to data that could not be considered as different from zero on the basis of the detection limit criterion described in section 2.5.

Both fluxes were always positive, which indicates that the flux was always oriented from the surface towards the atmosphere, and presented a diurnal cycle. At night, isoprene fluxes were close to zero, whereas monoterpene fluxes remained slightly positive. Maximum flux values were observed for both components on 20 August (isoprene: 1.96 µg m^{-2} s^{-1}; monoterpenes: 0.69 µg m^{-2} s^{-1}), which corresponded to the warmest day of the 2009 season. The last signifi-

cant fluxes of isoprene and monoterpenes were observed on 28 September and 7 October, respectively, the latter date corresponding to the last day of the season where the temperature slightly exceeded 20°C. Only data measured between July and September were used in the rest of the study. During this measurement period, no biotic stress on trees was visually detected, nor was any alteration of the GPP signal observed.

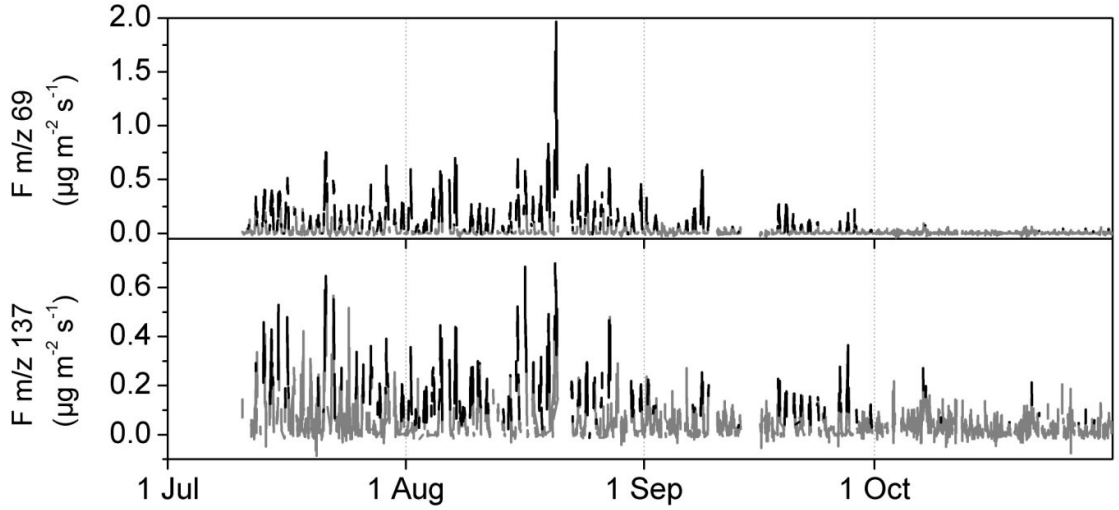

Figure 3.4 Temporal evolution of isoprene (m/z 69) and monoterpene (m/z 137) fluxes throughout the measurement period. The grey parts of the curves represent measured fluxes that are not significantly different from zero.

The land cover map and footprint climatology corresponding to the July-September period are shown in Figure 3.1. The contribution to the flux from the NE wind direction (Douglas fir) appears small compared with that of *Fagus sylvatica*, *Picea abies* and *Abies alba*.

A two-way analysis of variance (ANOVA) was performed in order to analyse the relative impact of radiation and temperature on the fluxes. Response to temperature appeared dominant as it contributed up to 44% and 22% of the isoprene and monoterpene flux variance, respectively, whereas the $PPFD$ response contributed up to 14% and 10%, respectively.

3.2 BVOC flux response to temperature

The relationships between BVOC fluxes and air temperature are shown in Figure 3.5 for July, August and September. They show that both isoprene and monoterpene emissions increased with temperature. Fitting Equations 1 and 2 to the data allowed the temperature sensitivity, β to be estimated and the emission factor to be standardized at 30°C, $SEF.C_L$. Their mean values for each month and each compound are given in Table 3.1.

Isoprene fluxes were characterized by systematically larger temperature sensitivities and standardization factors than monoterpene fluxes. Below 30°C, these two parameters affected the

relationship in opposite ways, so that isoprene fluxes were larger than monoterpene fluxes at high temperatures but lower at low temperatures. In addition, the temperature sensitivities of both components and the isoprene temperature standardized emission factor ($SEF.C_L$) did not evolve significantly with season.

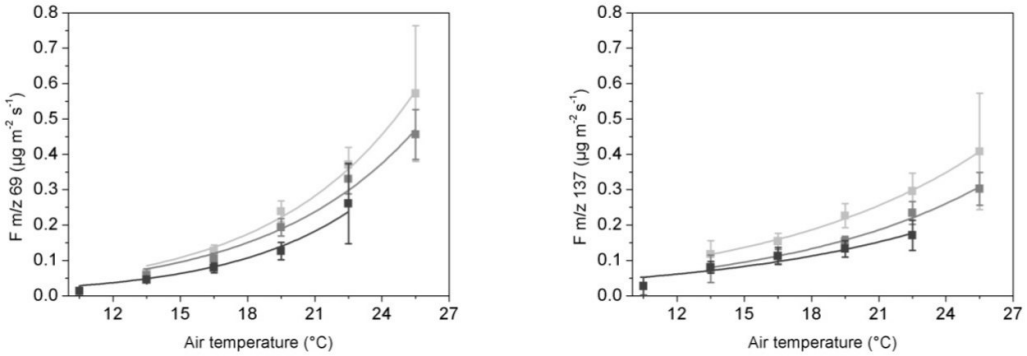

Figure 3.5 Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes in relation to the air temperature (n≥14, error bars are 95% confidence intervals) for July (light grey), August (grey) and September (dark grey) during the day.

Under night-time conditions, the isoprene flux was zero but there was still a slight monoterpene flux. This emission appeared to be related to temperature, as shown in Figure 3.6. By adjusting Equation 2 to the measurements, a temperature sensitivity of 0.061 ± 0.017 K^{-1} was found with an SEF (C_L=1) equal to 0.093 ± 0.019 µg $m^{-2}s^{-1}$ (estimate ± standard error).

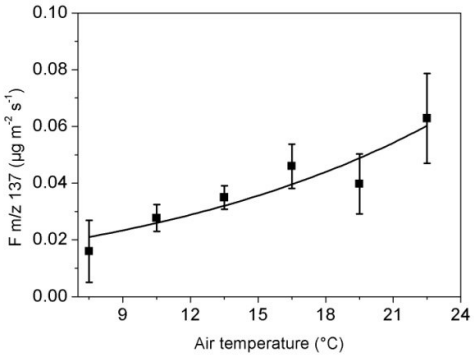

Figure 3.6 Bin average of monoterpene (m/z 137) fluxes ($u^* > 0.3$ m s^{-1}) in relation to the air temperature (n≥14, error bars are 95% confidence intervals) during the night from July to September.

3.3 BVOC response to PPFD and GPP

Figure 3.7 represents the response to $PPFD$ of monoterpene and isoprene fluxes standardized with temperature. To this end, each flux was divided by Equation 2 parameterized with the temperature sensitivities given in Table 3.1. The increase of fluxes with $PPFD$ was clear. Sa-

turation coefficients, C_{L1}, were deduced by fitting Equation 3 on these relationships. The results are given in Table 3.1.

Table 3.1 Fitting coefficients of *Ta* and *PPFD* dependence according to Equation 1, 2 and 3.

	Isoprene			*Monoterpenes*		
	July	**August**	**September**	**July**	**August**	**September**
β[a]	0.16±0.01	0.15±0.01	0.18±0.02	0.10±0.01	0.11±0.01	0.10±0.02
$SEF.C_L$[b]	1.07±0.08	0.93±0.10	0.90±0.09	0.65±0.02	0.51±0.03	0.38±0.09
C_{L1}[c]	2.35±0.20	2.10±0.43	1.55±0.24	1.65±0.08	1.37±0.08	1.03±0.08
SEF[d]	0.91±0.01	0.83±0.02	0.56±0.02	0.74±0.03	0.54±0.03	0.27±0.03

[a] units of β: K^{-1}
[b] units of $SEF.C_L$: µg m^{-2} s^{-1}
[c] units of C_{L1}: µmol m^{-2} s^{-1}
[d] units of SEF: µg m^{-2} s^{-1}

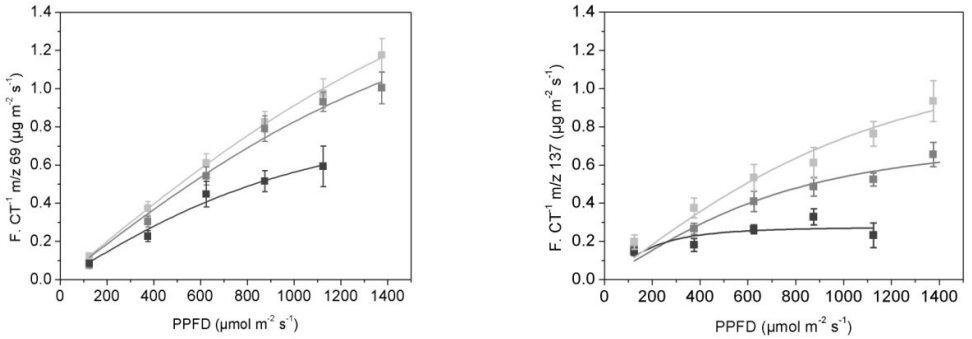

Figure 3.7 Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C in relation to *PPFD* (n≥14, error bars are 95% confidence intervals) for July (light grey), August (grey) and September (dark grey).

Both saturation fluxes tended to decrease during the season. For monoterpene fluxes, the decrease was quite regular, whereas for isoprene it was not significant between July and August but was more pronounced in September. Saturation of the flux response to *PPFD*, however, was observed only once, in September, for the monoterpene fluxes.

Finally, there was a clear response of temperature-standardised BVOC fluxes to *GPP* (Figure 3.8). Both fluxes were found to increase linearly with absolute *GPP* in July. The slopes and their standard errors were $-5.54\ 10^{-4} \pm 1.69\ 10^{-5}$ (intercept: $-1.310^{-3} \pm 3.67\ 10^{-4}$ µmol m^{-2} s^{-1}) and $-1.99\ 10^{-4} \pm 9.70\ 10^{-6}$ mol mol^{-1} (intercept: $-2.53\ 10^{-4} \pm 2.10\ 10^{-4}$ µmol m^{-2} s^{-1}) for isoprene and monoterpenes, respectively. In September, the isoprene flux response to *GPP* (slope: $-2.78\ 10^{-4} \pm 2.84\ 10^{-5}$ mol mol^{-1}; intercept: $-2.13\ 10^{-4} \pm 5.37\ 10^{-4}$ µmol m^{-2} s^{-1}) was still linear, whereas that of monoterpene saturated rapidly.

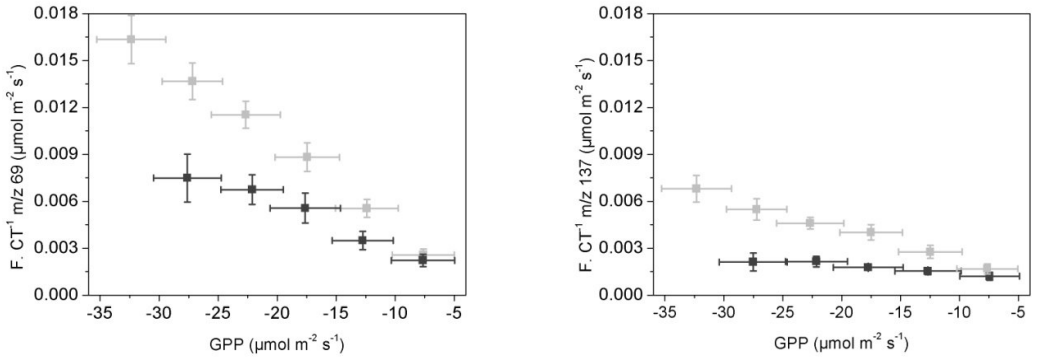

Figure 3.8 Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C (n≥14, error bars are 95% confidence intervals) in relation to the gross primary production (*GPP*) for July (light grey) and September (dark grey).

3.4 Standard emission factors

The seasonal evolution of *SEF* is presented in Figure 3.9. The *SEF* for both isoprene and monoterpenes decreased during the season. The decrease was clearer for monoterpenes than for isoprene, the *SEF* remaining quite stable and lower than 0.5 µg m^{-2} s^{-1} after the end of August. This trend was also significant for isoprene but less pronounced and partly masked by a larger day-to-day variability.

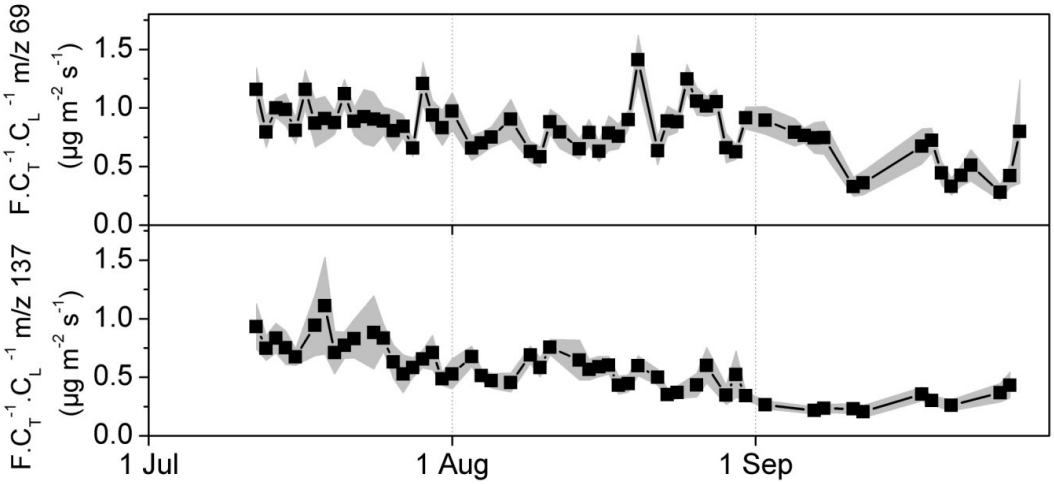

Figure 3.9 Mean diurnal evolution (*PPFD* > 300 µmol m^{-2} s^{-1}) of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and *PPFD* (1000 µmol m^{-2} s^{-1}). The grey area represents the 95% confidence intervals.

Finally, an *SEF* dependence on friction velocity was also found, as shown in Figure 3.10. In both cases, fluxes were found to increase with u^*, the increase being more pronounced for isoprene than for monoterpenes and showing saturation at high u^* (see below).

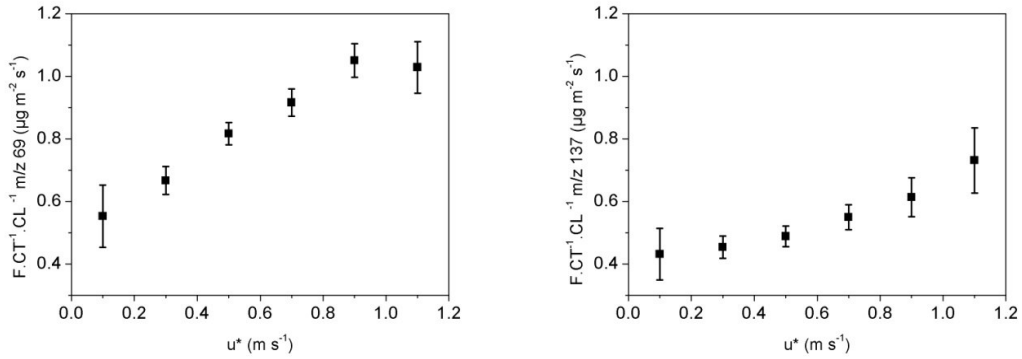

Figure 3.10 Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PFFD (1000 µmol m^{-2} s^{-1}) in relation to the friction velocity (u^*).

4 Discussion

4.1 Impact of tree species on fluxes

The footprint climatology (Figure 3.1) suggested that, during the observation period, the fluxes originated mainly from the south-west, a zone covered predominantly by *Fagus sylvatica* and *Picea abies*/*Abies alba,* and to a lesser extent from the north-east, where Douglas fir predominated. Footprint analysis (data not shown) suggested that the flux measured by the eddy covariance system never came from a unique source, but more often from a mixture of species. Under these conditions, it was difficult to characterize univocally the emission characteristics of each emitting species. By combining the footprint analysis (Figure 3.1b) with the land use map (Figure 3.1a), we found that monoterpene flux increased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%. This suggests that *Fagus sylvatica* emits more monoterpenes than the other species of the ecosystem, which accords with previous studies (Holzke et al., 2006; Moukhtar et al., 2005; Tollsten and Müller, 1996). Other species could also contribute to the emissions of monoterpenes, such as *Abies alba* (Moukhtar et al., 2006) or *Picea abies* (Filella et al., 2007). However, Moukhtar (2006) showed that *Fagus sylvatica* should emit at least 10 times more than *Picea abies* or *Abies alba*, which accords with our footprint analysis.

The analysis also showed that the isoprene flux decreased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%, suggesting that this beech is not an isoprene source, as already reported by Moukhtar et al. (2005) and Tollsten and Müller (1996). Moukhtar et al. (2006) also found that *Abies alba* was not an isoprene source, but Filella et al. (2007) showed

that *Picea abies* could be one. This would suggest that *Picea abies* was the sole species on the site emitting isoprene. This is not incompatible with our results, but cannot be validated by the footprint analysis because the contribution of this species to the measured flux never exceeded 40%. Given these results, in the following discussion we will consider the forest as a whole without trying to discriminate between the emitting species. The changing fluxes contribution of the major emitters due to the spatial heterogeneity combined with the changing wind direction and atmospheric stability will introduce variability on the flux that can be seen as a random error. This additional source of random error is compensated by the fact that given the important data coverage, our further analyses will always be performed on statistics containing an important number of realisations. A systematic error could also potentially be introduced in our seasonal evolution analyses if the flux footprint also presents a seasonal evolution. This effect, although present, is rather limited since the flux species contribution for each month (July, August and September) was respectively equal to 66.2 ± 2.0; 60.1 ± 1.6 and 49.8 ± 2.6 % for *Fagus sylvatica* and was respectively equal to 19.3 ± 1.1; 21.5 ± 1.1 and 24.1 ± 1.3 % for *Picea abies/Abies alba*.

4.2 Temperature response of BVOC emissions

BVOC flux temperature dependency is characteristic of an enzymatic reaction and could therefore characterize the isoprene or monoterpene synthases as well as the enzymatic reactions of the DOXP/MEP pathway. It is unlikely to be related to photosynthesis because this process is not very sensitive to temperature in the investigated range. No seasonal evolution of temperature sensitivity was observed, suggesting that this factor is an enzyme property that is independent of climatic conditions or leaf age. During the measurement period, it is possible that the β values were slightly distorted by the correlation that could exist between warm and sunny conditions. This effect is limited because we have shown that temperature is the main driving emission parameters. The values we observed for monoterpenes were close to those reported by Guenther et al. (1993), which varied between 0.057 and 0.144 K^{-1}. For isoprene, temperature sensitivity was slightly larger than 0.13 K^{-1}, the value obtained by adjustment of expression 2 on the Guenther et al. (1993) C_T relation.

4.3 Night-time monoterpene flux

There could be several reasons for the observed night-time monoterpene flux. First, it could result from de-storage. Unlike isoprene, some of the monoterpene production can be stored in

plant tissues from which it can diffuse progressively to the atmosphere where it is volatilized (Lerdau et al., 1994; 1997; Tingey et al., 1991). The release of monoterpenes is controlled by their concentration within tissues and by their temperature-dependent vapor pressures. This process is much slower than the direct diffusion that follows production and could therefore be responsible for the flux observed at night. However, several studies (Demarcke et al., 2010b; Dindorf et al., 2005; Holzke et al., 2006; Moukhtar et al., 2005) have shown that, in the absence of light, emissions of monoterpenes from *Fagus sylvatica* were small or, in some cases, close to zero, suggesting that storage pools play only a marginal role in *Fagus sylvatica*. For coniferous species, storage pools are known to be located in resin ducts (Fuentes et al., 2000). Night-time monoterpene fluxes have never been observed in *Abies alba*, so far as we know, but they have been observed by Grabmer et al. (2004) using DEC above a *Picea abies* forest (Germany). They found fluxes of about 0.02 µg m^{-2} s^{-1} at T_a ~ 15°C, which is comparable in magnitude with those observed in our study for a similar temperature. With regard to storage pool capacity, we did not observe significant differences between monoterpene fluxes at the beginning and the end of the night (data not shown), suggesting that the fluxes are not rapidly depleted and therefore storage pools could be important. Ghirardo et al. (2010) also showed that the contribution of pool emissions to total monoterpene emissions may be significant for *Picea abies* (66.5%).

A second reason for monoterpene night-time fluxes could be soil production through various mechanisms. Litter decomposition has the potential to contribute significantly to these fluxes (Isidorov et al., 2010), especially fresh litter (Hayward et al., 2001). An emission from the storage pools of the roots with a mechanism similar to needle storage emissions can also contribute to monoterpene emissions (Janson, 1993; Lin et al., 2007), as well as the activity of specific micro-organisms (Schulz and Dickschat, 2007). Hayward et al. (2001) observed 30°C standardized emissions (July) varying between 0.008 and 0.01 µg m^{-2} s^{-1} from an undisturbed forested soil under Sitka spruce (United Kingdom). Hellén et al. (2006) observed fluxes between the detection limit and 0.1 µg m^{-2} s^{-1} for a forested soil under Scots pine (Finland), the maximum value being observed during spring and average values below 0.007 µg m^{-2} s^{-1} being observed in summer. However, our fluxes were at least one order of magnitude higher than those observed by Hayward et al. (2001) and Hellén et al. (2006).

Night-time emission processes were also present during the day, but their contribution to fluxes was at least 10 times lower than the contribution of *de novo* synthesized monoterpene emissions. The C_T obtained for each month was therefore influenced mainly by the biosynthe-

sis process of monoterpenes. In summary, it is likely that night-time monoterpene fluxes resulted from both de-storage in the conifers and soil emission. However, the results of the literature survey suggest that de-storage fluxes would be at least one order of magnitude larger than those of soil emission.

4.4 BVOC flux response to PPFD/GPP

There are strong correlations of BVOC fluxes with $PPFD$ and GPP, as the latter two variables themselves are well correlated. It is therefore not easy to determine the true causal relations.
A direct correlation between BVOC fluxes and GPP appears to be the most logical hypothesis because DMADP (the isoprene and monoterpene precursor) is a sub-product of photosynthesis. The linear relationship observed in July would suggest that DMADP (via GPP) was the main limiting factor in BVOC synthesis. Penuelas and Llusià (1999) had already found a linear relationship between monoterpene emission and GPP in a Mediterranean ecosystem during summer. They concluded that monoterpene precursors originated from photosynthetic activity. Under these conditions, the response to $PPFD$ would be a direct consequence of the dependence on GPP.
However, we cannot completely discard the hypothesis of a direct dependence of other synthesis reactions on light. Wildermuth and Fall (1996) discussed the possibility of the direct impact of light on ISPS activity by covalent modifications. However, Lehning et al. (1999) and Brüggemann and Schnitzler (2002) have shown that ISPS activity undergoes no intra-day variation, making it more likely that the light-dependency of isoprene emission results directly from the GPP response to light. The slope of the BVOC/GPP relationship depends on enzymatic activity. It is therefore likely that the decrease in this slope during the season corresponded to a decrease in this activity. Schnitzler et al. (1997) and Mayrofher et al. (2005) stressed a seasonal evolution of ISPS activity in *Quercus robur* and *Populus* X *canescens*, respectively, showing an activity decrease after the summer. Fischbach et al. (2002) observed a similar effect on the monoterpene synthase activity of *Quercus ilex*. This seasonal decrease could be due to a leaf acclimation to temperature and radiation (Lehning et al., 1999) that could affect enzymatic activity over the long term. For *Fagus sylvatica*, leaf senescence could also have contributed to the decrease in monoterpene synthase activity. The non-linearity of the BVOC emissions to GPP responses in September and the appearance of saturation at a large GPP clearly indicates that other factors limit the BVOC synthesis. The limitation appears to be more critical for monoterpenes than for isoprene and could be due to saturation in

the substrate of the enzyme activity through the DOXP/MEP pathway and/or saturation in the substrate of the monoterpene synthase activity and (to a lesser extent) of the isoprene synthase activity during the season.

In the case of isoprene, a DMADP reallocation to the production of diterpenes, tetraterpenes and monoterpenes, which eventually results in the decreased production of isoprene, has been proposed by Owen and Penuelas (2005). However, the occurrence of this mechanism is unlikely in our study as it generally takes place when there is stress, but no heat or drought stress was detected during the measurement period.

4.5 Response of SEF to friction velocity

There are several possible explanations for the SEF response to friction velocity. In the case of CO_2 fluxes, similar behavior is generally observed that can be explained by the lack of atmospheric turbulence and the development of other transport processes (Aubinet, 2008). This process would affect similarly BVOC fluxes but it can explain CO_2 or BVOC fluxes underestimations for low u^* at night-time only because the alternative transport processes do not develop during the day. The two most likely explanations are linked to O_3 transport and the chemical lifetime of BVOCs in the atmospheric boundary layer. The possibility of an adsorption/desorption process on ecosystem surfaces was discarded because neither isoprene nor monoterpene depositions were ever observed in this study.

In the first explanation, an increase of u^* would denote an intensification of turbulent mixing in the canopy and therefore an increase in O_3 supply in the canopy, which could activate BVOC synthesis. Several studies have highlighted the existence of a stimulation process of isoprene (Calfapietra et al., 2009; Fares et al., 2006; Velikova et al., 2005) and monoterpene emissions (Loreto et al., 2004) when leaves are exposed to high O_3 concentrations (100-300 ppb). This emission could be a protection mechanism against oxidation. Apart from this, O_3 deposition and O_3 vertical gradients are known to be controlled by the efficiency of turbulent mixing in the canopy that is driven by friction velocity (Jäggi et al., 2006; Karlsson et al., 2006; Pleijel et al., 1996). Ozone concentration in the canopy should therefore increase with u^* and tend towards above-canopy concentration at high u^* values. This hypothesis was confirmed by independent measurements made at a station 300 m from our site that showed an increase in O_3 concentration with u^* during the day (data not shown).

The difference in behaviour between isoprene and monoterpenes could be explained by different sensitivities of the emitting tree species to the stimulation by O_3 due to differences in O_3 absorption capacity or the possible presence of other anti-oxidative compounds.

The second explanation involves the limited BVOC chemical lifetime. Upon emission, a BVOC might be oxidized (degraded) through reaction with other atmospheric compounds, mainly OH and to a lesser extent O_3 and the nitrate radical, before reaching the measurement point. As the footprint zone expands under low u^*, the distance between the BVOC source point and the measurement system generally increases, increasing the extent of chemical degradation. By combining a footprint model with a chemical degradation model, and assuming an abundance of 0.25 pptv (i.e., 6 x 10^6 molec. cm^{-3}) for OH, Rinne et al. (2007) showed that when u^* was equal to 0.5 m s^{-1} (measurement height: 22 m; source height: 11.2 m), the flux loss could reach 10%. This value of OH is typically observed in summer in the USA (Ren et al., 2008) or in August, in Germany, near Jülich (Dlugi et al., 2010), and is probably similar at the Vielsalm site. The loss calculated in our case was higher but this could be due to the distance between the emitting canopy and the measurement location, which is about twice as large at Vielsalm than at Hyytiala. However, it is still difficult to quantify the flux loss through chemical degradation in order to validate this hypothesis.

5 Summary and conclusions

This study is one of the first to have collected data on monoterpene, isoprene and CO_2 fluxes simultaneously and continuously over several months. This extensive dataset allowed an analysis to be conducted of the flux responses to climate and their seasonal evolution.

Temperature appeared to be the most important driving variable of BVOC fluxes, followed by solar radiation. During the day, the temperature response was found to be exponential and probably reflected the temperature activation of enzymatic reactions in the DOXP/MEP biosynthetic pathways. The flux response to radiation was probably controlled by the $GPP/PPFD$ response. This was confirmed by the linearity of the relationship between BVOC fluxes and GPP. The slope of this relationship, characterizing the enzyme activity through the biosynthesis pathway decreased during the season. This was probably modulated by leaf acclimation to environmental conditions. For monoterpenes, leaf senescence and acclimation might take place simultaneously, especially in September. In September, at high GPP, BVOC fluxes no longer depended on GPP. The seasonal decrease in the enzymatic activity and the

saturation in the substrate of this enzymatic activity at a given GPP threshold could explain this behavior.

During the night, the isoprene flux was zero but small emissions of monoterpenes were found, showing a temperature dependency. These emissions were probably due to the volatility of monoterpenes stored in the needle resin ducts of coniferous species. There could also be a contribution from the soil through litter decomposition, from roots or from micro-organisms.

An increase in temperature- and radiation-standardized BVOC fluxes (mainly isoprene) with u^* was found. This surprising relationship could be due to a stimulation of isoprene emissions by exposure to O_3, the O_3 concentration in the canopy increasing with u^*. Complementary measurements of O_3 fluxes should be performed to test this hypothesis. The relation BVOC fluxes/u^* could be also due to the distance between the BVOC source point and the measurement system that generally increases under low u^* thereby increasing the extent of BVOC oxidation.

Finally, long-term measurements of BVOC fluxes at the ecosystem scale allowed a temperature dependence function and a $PPFD$ dependence function necessary to compute a standard emission factor to be deduced for each month. In this study, the $PPFD$ dependence function has been transformed from Guenther et al. (1993) by using only one fitting parameter, making it easier to study the seasonal variation of the standard emission factor. These factors are crucial for regional emission modelling, and a more in-depth analysis of their seasonal evolution for different ecosystems in real-field conditions would help to improve these emission predictions.

Chapter 4

Impact of diffuse light on isoprene and monoterpene emissions from a mixed temperate forest

1 Introduction

Biogenic Volatile Organic Compounds (BVOCs) emitted by terrestrial vegetation, particularly forests, dominate the global BVOC emissions. Forest ecosystems release mainly isoprene and monoterpenes into the atmosphere. The global isoprene and monoterpene emissions have been estimated at 412-601 TgC yr^{-1} and 30-128 TgC yr^{-1} (Arneth et al., 2008), respectively, representing the main BVOC emissions. Isoprene and monoterpenes play an important role in tropospheric chemistry and in the Earth's radiation budget. Their oxidation products are important precursors for ozone (O_3) production/destruction, depending on the nitrogen oxide (NO_x) concentration (Atkinson and Arey, 2003). The atmospheric reactions of isoprene and monoterpenes can also have an important influence on the tropospheric concentration of hydroxyl (OH) radicals, thereby influencing the atmospheric lifetime of methane (Ortega et al., 2007).

In addition to their importance in tropospheric gas phase chemistry, isoprene and monoterpene oxidation initiates and favors the production of compounds that can partition into the particulate phase, forming secondary organic aerosols (SOAs) (Hallquist et al., 2009; Kanakidou et al., 2005). SOAs have both a direct and indirect effect on atmospheric radiation. The direct effect is caused by the scattering and absorption of solar radiation by SOAs, whereas the indirect effect derives from their important role in the growth of cloud condensation nuclei. The total budget of SOAs formed in the atmosphere is also very uncertain, with estimates published in the literature ranging from 12 to 1,640 Tg yr^{-1} (Pierce et al., 2012). The uncertainties about the SOA and isoprene/monoterpene budgets could be due partly to the potential feedback between the terrestrial biosphere, atmospheric aerosols and climate

(Carslaw et al., 2010). The main driver of this feedback is the strong control that climate exerts over the emission of BVOCs. Increases in temperature are likely to lead to increased BVOC emissions (Fuentes et al., 2000; Šimpraga et al., 2011a) and aerosol concentrations, resulting primarily in increased aerosol radiative cooling and a potential negative feedback mechanism (Carslaw et al., 2010; Kulmala et al., 2004). Aerosols and clouds can also affect the functioning of the biosphere in terms of its effect on canopy photosynthesis by increasing the relative proportion of diffuse radiation at the Earth's surface. Carbon sequestration in the canopy is enhanced under conditions where there is a high proportion of diffuse radiation compared with conditions with the same above-canopy total radiation but with a lower proportion of diffuse radiation (Gu et al., 2002; Knohl and Baldocchi, 2008). Since the metabolic production pathways of isoprene and monoterpenes are closely linked to photosynthesis (Lichtenthaler et al., 1997), an increase in diffuse radiation could also increase isoprene and monoterpene emissions at the same temperature. This opportunity hypothesis was mentioned briefly by Sharkey et al. (1991), but no ecosystem-scale micrometeorological measurements of BVOCs conducted to date have shown this effect. At a global scale, this latter effect could partly compensate for the aerosol radiative cooling effect on global BVOC emissions, but probably does not mask it because temperature is the main driver of BVOC emissions.

Our objective was to investigate the impact of the light regime (proportion of diffuse radiation) on isoprene and monoterpene canopy emissions without any artificial disturbance to the emissions and over the whole vegetation season. For this purpose, we used an eddy-covariance dataset of isoprene, monoterpene and CO_2 fluxes measured at stand level in a temperate forest. In order to highlight the behaviour of canopy emissions under different radiation regimes, the dataset was divided into two classes: clear sky conditions and cloudy conditions and the relationship between emissions/radiation and emissions/gross primary production (GPP) were analysed for these two datasets.

2 Material and methods

2.1 Measurement site

The experimental site is a forest ecosystem at Vielsalm in the Belgian Ardenne forest (50°18'18.20''N, 5°59'53.15''E; altitude 450 m). Its topography is smoothly sloping (3%) in a NW direction. The climate is temperate maritime. The soil is 50-100 cm deep and is classified as a dystric cambisol. The vegetation in the tower flux footprint is a mixture of: conifer-

ous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) about 40 m high, Norway spruce (*Picea abies* [L.] Karst.) about 32 m high and Silver fir (*Abies alba* Miller) about 32 m high; and deciduous species, mainly beeches (*Fagus sylvatica* L.) about 28 m high. A more detailed description of this site is given by Aubinet et al. (2001; 2002) and Laitat et al. (1999).

2.2 Instrumentation and BVOC sampling

An ultrasonic anemometer (model SOLENT 1012 R2, Gill Instruments Ltd, Lymington, UK) was placed at a height of 52 m and continuously measured the three wind velocity components at a 20.8 Hz sampling frequency. Ambient air was continuously sampled close to the sonic anemometer through a 60 m-long sampling line with an inner diameter of 6.4 mm, (PFA tubing: Fluortechnik-Wolf) at a flow rate of 9 STP L min^{-1} (Standard Temperature and Pressure corresponding to 1,013.25 hPa and 273.15 K). The sampling line was heated to an average of 12°C above ambient temperature. Part of this air flow (0.1 STP L min^{-1}) was drawn into a gas analyser through a 1.2 m-long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The data streams from the two instruments were logged on a single computer in order to optimise synchronization.

The measurements of relevant meteorological variables were performed at a 0.04Hz sampling frequency and averaged over half an hour. They included the total and diffuse fraction of photosynthetically active radiation ($PPFD$, Sunshine sensor type BF3, Delta-T Devices Ltd, Cambridge, UK), air temperature and humidity (RHT2, Delta-T Devices Ltd, Cambridge, UK) at a height of 50 m and atmospheric pressure (MPX4115A, Motorola, Phoenix, USA).

VOC mixing ratios were measured by a conventional quadrupole-based high-sensitivity Proton Transfer Reaction - Mass Spectrometry instrument (hs-PTR-MS, Ionicon Analytick GmbH, Innsbruck, Austria). Detailed descriptions of the PTR-MS technique are given by Lindinger et al. (1998), de Gouw and Warneke (2007) and Ammann et al. (2004). The instrument was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2), where E is the electric field and N the ambient air number density in the flow/drift tube. Ion signals were measured in a cyclic way at 10 mass-to-charge (m/z) ratios in 2009 and 12 in 2010, including m/z 21 ($H_3^{18}O^+$), m/z 69 (protonated isoprene) and m/z 137 (protonated monoterpenes). As such, a disjunct time series was produced for the ion intensities at each m/z value. The dwell time for m/z 69 and m/z137 was 200 ms, ending precisely in a measurement cycle length of

2.212 s in 2009 and 2.852 s in 2010. During the measurements, the instrumental background was determined every 4 h by sampling BVOC-free air, which involved sending ambient air through a heated catalytic converter for 15 min (the last 8 min being used to calculate the mean background values). The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every 2 or 3 days using a gravimetrically prepared mixture of these gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA) that contained approximately 500 ppbv isoprene, α-pinene and sabinene and about 1 ppmv methanol, acetaldehyde and acetone, with an accuracy of 5%. The compounds were further diluted (2-12 ppbv range) using a dynamic dilution system. There are more details in Laffineur et al. (2012; 2011).

2.3 Disjunct eddy-covariance

The technique used to measure ecosystem BVOC fluxes is the disjunct eddy-covariance by mass scanning technique (Karl et al., 2002; Rinne et al., 2001; Rinne and Ammann, 2012). The flux is computed as the covariance of the vertical wind velocity component and the disjunct VOC mixing ratio time series for each mass. These two components must be measured with a short instrumental time response in order to take account of the high frequency contributions to the flux. For BVOC fluxes, PTR-MS allows the mixing ratio fluctuations of BVOCs to be measured in real time with a fast instrumental response time. More details on the flux computation methodology are given in Laffineur et al. (2012; 2011).

2.4 Source identification

The footprint analysis made by Laffineur et al. (2011) suggested that the flux measured by the eddy-covariance system did not come from a unique source, but rather from a mixture of species. Under these conditions, it was difficult to unequivocally characterize the emission of each species. Laffineur et al. (2011), however, found that *Fagus sylvatica* was the greatest monoterpene emitter in the ecosystem, with other species such as *Abies alba* and *Picea abies* also contributing to the monoterpene emission, but in a much lower proportion, probably less than 10%. Important isoprene emissions were found in the SW sector of our site, which is covered mainly by *Fagus sylvatica* and *Abies alba*. As the former is reported, in the literature, not to be an isoprene source (Moukhtar et al., 2005), this suggested that *Abies alba* could be the main isoprene emitter in this sector. This did not accord with findings reported by Moukhtar et al. (2006), who stated that *Abies alba* does not produce isoprene, but a recent study

based on cuvette measurements showed that *Abies alba* trees native to our experimental site behaved as substantial isoprene emitters (Pokorska et al., 2012). A contribution from *Picea abies* was also expected (Filella et al. 2007). Finally, *Pseudotsuga menziesii* is also known (Moukhtar et al., 2006) to produce monoterpenes and isoprene. In this study, however, we did not use isoprene and monoterpene fluxes for which *Pseudotsuga menziesii* was known to be an important contributor, for reasons explained below (§ 2.6).

2.5 Gross primary production computation

Gross primary production (GPP) was inferred by deducting total ecosystem respiration (TER) from net ecosystem exchange (NEE) measured by eddy-covariance. TER was inferred by extrapolation to the whole day of night-time NEE measurements, since plant assimilation can be considered to be zero at night, using an algorithm devised by Reichstein et al. (2005). In our study, a positive GPP corresponded to a flux oriented from the atmosphere towards the surface, whereas a positive isoprene and monoterpene flux is oriented in the opposite direction. This particular convention was used to facilitate the interpretation of the relationship between the isoprene and monoterpene fluxes and the GPP.

2.6 Data treatment

In addition to standard quality control procedures (Laffineur et al., 2011), some filtering/standardisation was applied to the flux data prior to analysis. First, a filtering criterion based on wind direction was applied. At Vielsalm, there is a covariation between the individual species contribution to the total flux and the cloud cover: the NE sector, from which the wind blows during anticyclonic conditions and which is characterized by more frequent clear sky conditions, is planted mainly with *Pseudotsuga menziesii*. In contrast, the SW sector, from which the wind blows during cyclonic events and which is characterized by a temperate climate and cloudier conditions, is covered mainly by *Fagus sylvatica* (Aubinet et al., 2002). This covariation could have introduced an undesirable complexity into the analysis because *Pseudotsuga menziesii* is a potential monoterpene and isoprene emitter and because we wanted to focus on the impact of cloud cover on the flux and not on the inter-species emission differences. Data on the wind blowing from the NE sector (330°-90° N) were therefore not used in the dataset.

Second, isoprene and monoterpene fluxes were standardised by temperature, following Laffineur et al. (2011). In this latter study, which used the 2009 dataset, we had already high-

lighted the major effect of temperature on isoprene and monoterpene fluxes. The standardisation was therefore necessary in order to study the dependence of further drivers of isoprene and monoterpene fluxes, such as $PPFD$ and its partitioning into its diffuse and direct parts. In addition, temperature standardisation prevented a possible temperature bias in the flux comparison between cloudy and clear sky conditions. The standardisation involved dividing the measured flux by the function describing the temperature dependence modelled as:

$$C_T = \exp(\beta.(T_l - 298.15)) \quad (1)$$

where β [K^{-1}] is the temperature dependence parameter and T_l [K] is the leaf temperature estimated as (Hoyaux et al., 2008):

$$T_l = T_a + \frac{H.U}{\rho.C_p.u_*^2} \quad (2)$$

where T_a [K] is the air temperature, H [W m^{-2}] is the sensible heat flux, ρ [kg m^{-3}] is the air density, C_p [J $kg^{-1}K^{-1}$] is the air specific heat, and u_* [m s^{-1}] and U [m s^{-1}] are the friction and the average wind velocity, respectively. Here we used a standardisation temperature of 25°C instead of the commonly used 30°C because it is more representative of average conditions at the site, thereby limiting the standardisation error.

Table 4.1 Fitting coefficient (β [K^{-1}]) of T_l dependence according to equation (1) for isoprene and monoterpene fluxes measured under clear sky and cloudy conditions in June, July, August and September 2009 and 2010 with the standard error on β and where R^2 is the coefficient of determination.

	β	R^2
Isoprene-clear sky		
June	0.12 ± 0.02	0.43
July	0.14 ± 0.01	0.73
August	0.14 ± 0.01	0.67
September	0.20 ± 0.01	0.72
Isoprene-cloudy		
June	0.17 ± 0.03	0.50
July	0.13 ± 0.01	0.50
August	0.17 ± 0.01	0.68
September	0.17 ± 0.02	0.28
Monoterpenes-clear sky		
June	0.10 ± 0.02	0.29
July	0.11 ± 0.01	0.43
August	0.12 ± 0.01	0.56
September	0.10 ± 0.02	0.11
Monoterpenes-cloudy		
June	0.17 ± 0.03	0.46
July	0.13 ± 0.01	0.39
August	0.11 ± 0.01	0.55
September	0.12 ± 0.02	0.26

The seasonal evolution of standardised isoprene and monoterpene fluxes being similar in 2009 and 2010 (results not shown), the 2009 and 2010 data were grouped and analysed by month (July, August and September, June data being available only for 2010) to reinforce the statistical study. The β parameters deduced from the regression analysis of the relationships flux-T_l are given in Table 4.1.

3 Results

3.1 Meteorological conditions

The seasonal evolution (2009 and 2010) of air temperature, $PPFD$, wind direction, friction velocity and precipitation were presented in detail in Laffineur et al. (2012; 2011). The summers of 2009 and 2010 were characterized by temperatures higher (mean temperature: 15.7°C

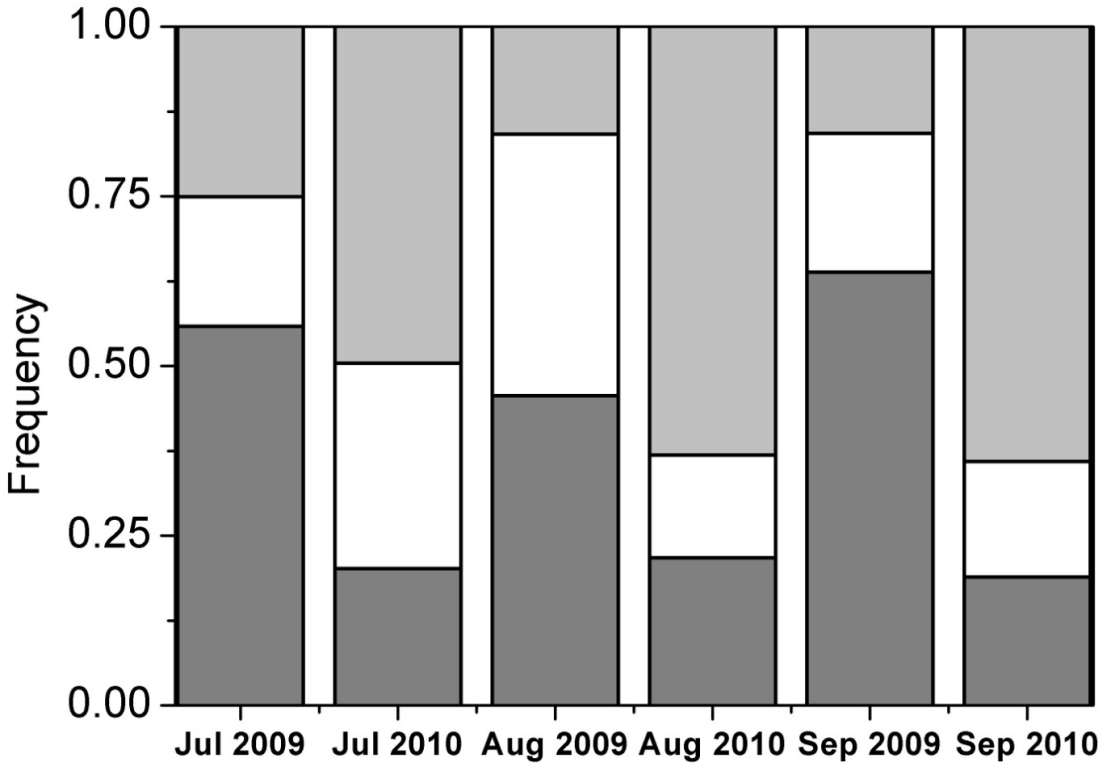

Figure 4.1 Occurrence of cloudy (dark grey) conditions (0.6 ≤ fraction of diffuse to total radiation ≤ 0.9) and clear sky (white) conditions (fraction of diffuse to total radiation ≤ 0.4), and when the fraction of diffuse to total radiation > 0.9 or included between 0.4 and 0.6 (light gray), during July, August and September in 2009 and 2010.

in July-August-September 2009, and 15.2°C in July-August-September 2010) than the regional standard (14.6°C). There was more rain in August 2010 (215 mm) than in August 2009 (54 mm). The occurrence of clear sky conditions (fraction of diffuse to total radiation ≤ 0.4)

and cloudy conditions (0.6 ≤ fraction of diffuse to total radiation ≤ 0.9) during the measurement periods are given in Figure 4.1. The cloudy conditions were at least twice more frequent in 2009 than in 2010. Clear sky conditions were twice as frequent in July 2010 than in July 2009, three times as frequent in August 2009 than in August 2010 and similar in September in the two years.

3.2 BVOC fluxes/PPFD relationship

Figures 4.2 and 4.3 represent the response to *PPFD* (Fig. 4.2A, 4.3A) and *GPP* (Fig. 4.2B,

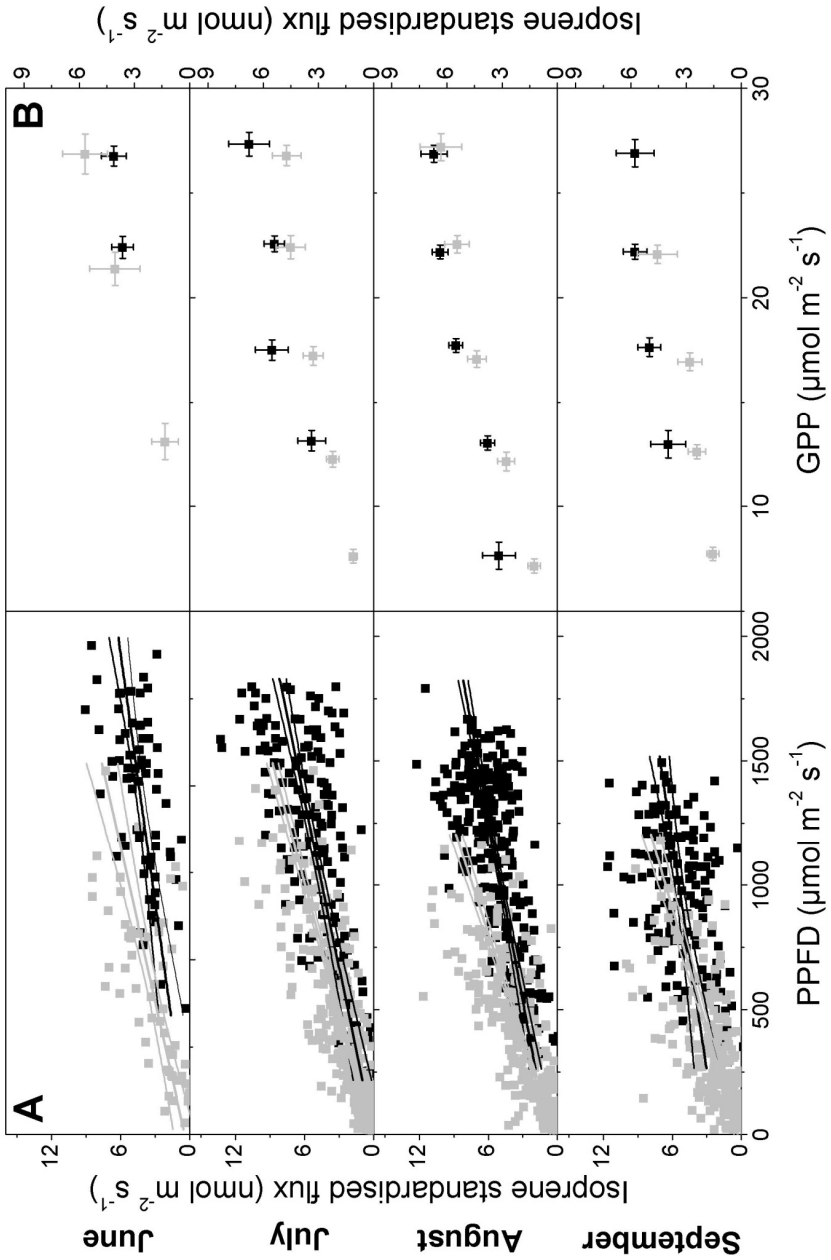

Figure 4.2 Isoprene fluxes standardised at 25°C in relation to *PPFD* (A) and bin average of isoprene fluxes standardised at 25°C in relation to *GPP* (B), with separation between cloudy (■) and clear sky (■) conditions for June, July, August and September in 2009 and 2010. In A, the main line represents the linear regression with its confidence bands (95%). In B, the error bars are 95% confidence intervals.

4.3B) of temperature-standardised isoprene and monoterpene fluxes for cloudy and clear sky conditions, respectively. In both cases, the emissions increased quasi-linearly with $PPFD$, as reported by Laffineur et al. (2011). The linear regression results are given in Table 4.2. At equal $PPFD$, the standardised isoprene and monoterpene flux was significantly higher in

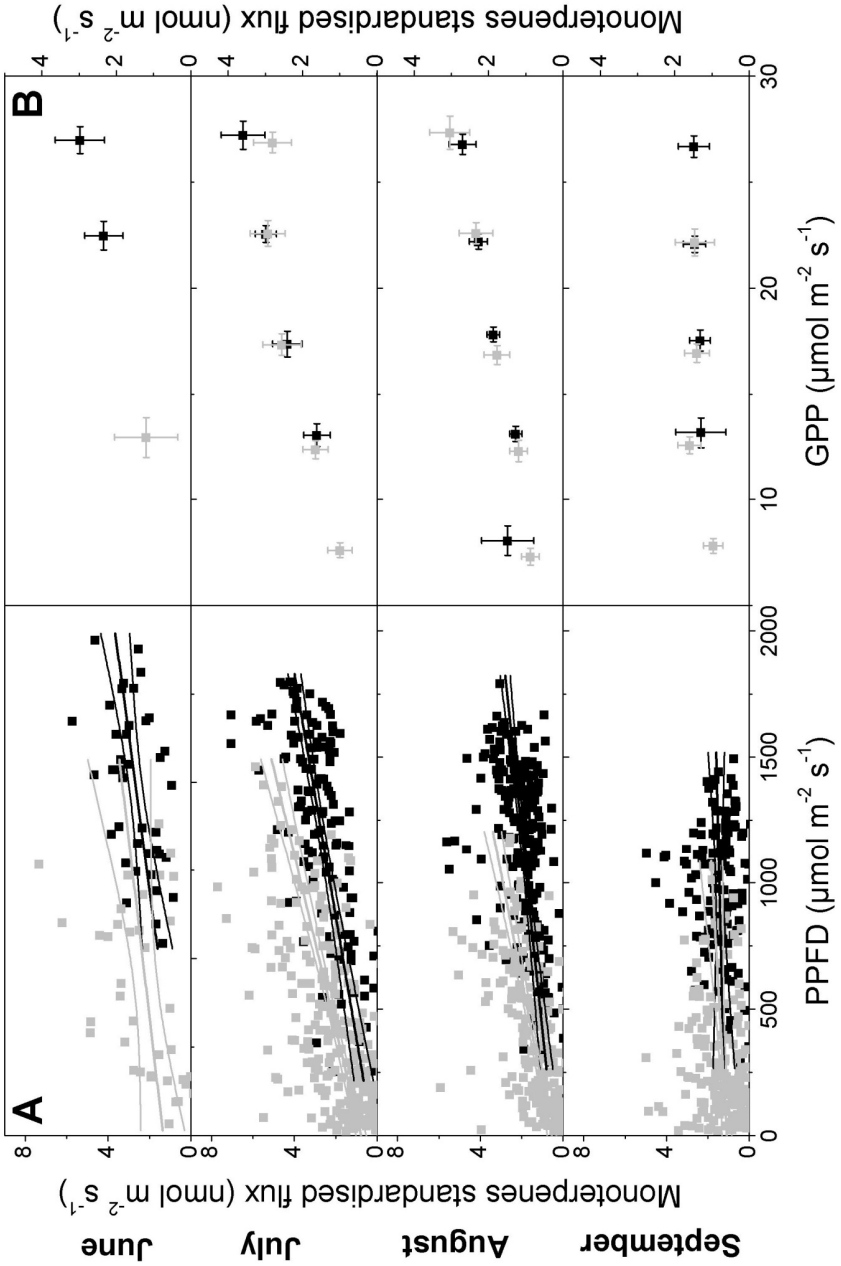

Figure 4.3 Monoterpene fluxes standardised at 25°C in relation to *PPFD* (A) and bin average of isoprene fluxes standardised at 25°C in relation to *GPP* (B), with separation between cloudy (■) and clear sky (■) conditions for June, July, August and September in 2009 and 2010. In A, the main line represents the linear regression with its confidence bands (95%). In B, the error bars are 95% confidence intervals.

cloudy conditions than in clear sky conditions, this result being observed throughout the summer for isoprene but only in July and August for monoterpenes. The limited number of flux measurements in June and the lack of any $PPFD$ control on monoterpene flux in September could explain the absence of significant differences between cloudy and clear sky conditions. For both cloudy and clear sky conditions, the slope coefficient increased between

June and July. For monoterpenes, under both conditions, the slope coefficient decreased quite regularly during the following period. In the case of isoprene, the slope coefficient remained almost constant during the following period in clear sky conditions. In cloudy conditions, the slope coefficient reached a maximum in August before to decrease in September.

Table 4.2 Linear fitting coefficients of the isoprene and monoterpene flux/*PPFD* relationship under clear sky and cloudy conditions for June, July, August and September, where: a is the slope coefficient [mol mol^{-1}] with its standard error; b is the intercept coefficient [mol m^{-2} s^{-1}] with its standard error; R^2 is the coefficient of determination; and n is the number of points.

	a	b	R^2	n
Isoprene-clear sky				
June	$(3.1 \pm 0.1) \times 10^{-6}$	$(0.2 \pm 0.8) \times 10^{-9}$	0.30	67
July	$(4.5 \pm 0.4) \times 10^{-6}$	$(0.0 \pm 0.5) \times 10^{-9}$	0.45	169
August	$(4.0 \pm 0.3) \times 10^{-6}$	$(0.8 \pm 0.3) \times 10^{-9}$	0.43	276
September	$(3.3 \pm 0.7) \times 10^{-6}$	$(2.2 \pm 0.7) \times 10^{-9}$	0.12	148
Isoprene-cloudy				
June	$(4.8 \pm 0.7) \times 10^{-6}$	$(0.4 \pm 0.5) \times 10^{-9}$	0.46	58
July	$(5.7 \pm 0.2) \times 10^{-6}$	$(0.2 \pm 0.1) \times 10^{-9}$	0.68	309
August	$(7.1 \pm 0.3) \times 10^{-6}$	$(0.3 \pm 0.2) \times 10^{-9}$	0.63	273
September	$(6.3 \pm 0.4) \times 10^{-6}$	$(0.3 \pm 0.2) \times 10^{-9}$	0.48	257
Monoterpenes-clear sky				
June	$(1.6 \pm 0.5) \times 10^{-6}$	$(0.4 \pm 0.7) \times 10^{-9}$	0.22	39
July	$(2.1 \pm 0.2) \times 10^{-6}$	$(0.2 \pm 0.3) \times 10^{-9}$	0.41	133
August	$(1.3 \pm 0.2) \times 10^{-6}$	$(0.5 \pm 0.2) \times 10^{-9}$	0.22	231
September	$(0.3 \pm 0.3) \times 10^{-6}$	$(1.1 \pm 0.3) \times 10^{-9}$	0.01	128
Monoterpenes-cloudy				
June	$(1.4 \pm 0.8) \times 10^{-6}$	$(0.1 \pm 0.5) \times 10^{-9}$	0.10	39
July	$(2.9 \pm 0.2) \times 10^{-6}$	$(0.8 \pm 0.1) \times 10^{-9}$	0.37	260
August	$(2.3 \pm 0.2) \times 10^{-6}$	$(0.5 \pm 0.1) \times 10^{-9}$	0.32	203
September	$(0.7 \pm 0.3) \times 10^{-6}$	$(1.1 \pm 0.1) \times 10^{-9}$	0.01	186

3.3 BVOC fluxes/GPP relationship

The relationships between isoprene and monoterpene temperature-standardised fluxes and GPP are shown in Figures 4.2B (isoprene) and 4.3B (monoterpenes). Isoprene fluxes increased linearly with absolute GPP and were significantly lower (except in June) at equal GPP in cloudy conditions than in clear sky conditions for GPP between 5 and 20 µmol m^{-2}

s^{-1}. For monoterpenes, no significant difference between clear sky and cloudy conditions was observed.

4 Discussion

At similar total $PPFD$, isoprene and monoterpene fluxes were found to be higher in cloudy conditions than in clear sky conditions. This could be due to differences in either GPP or enzymatic activity between the different light regimes. These two possibilities are discussed below.

4.1 Radiative transfer properties

The fact that, at similar $PPFD$, GPP can be greater in cloudy conditions than in clear sky conditions is well recognized and has been discussed in the literature, especially by Gu et al. (2002), Knohl and Baldocchi (2008) and Roderick et al. (2001). This was also observed at

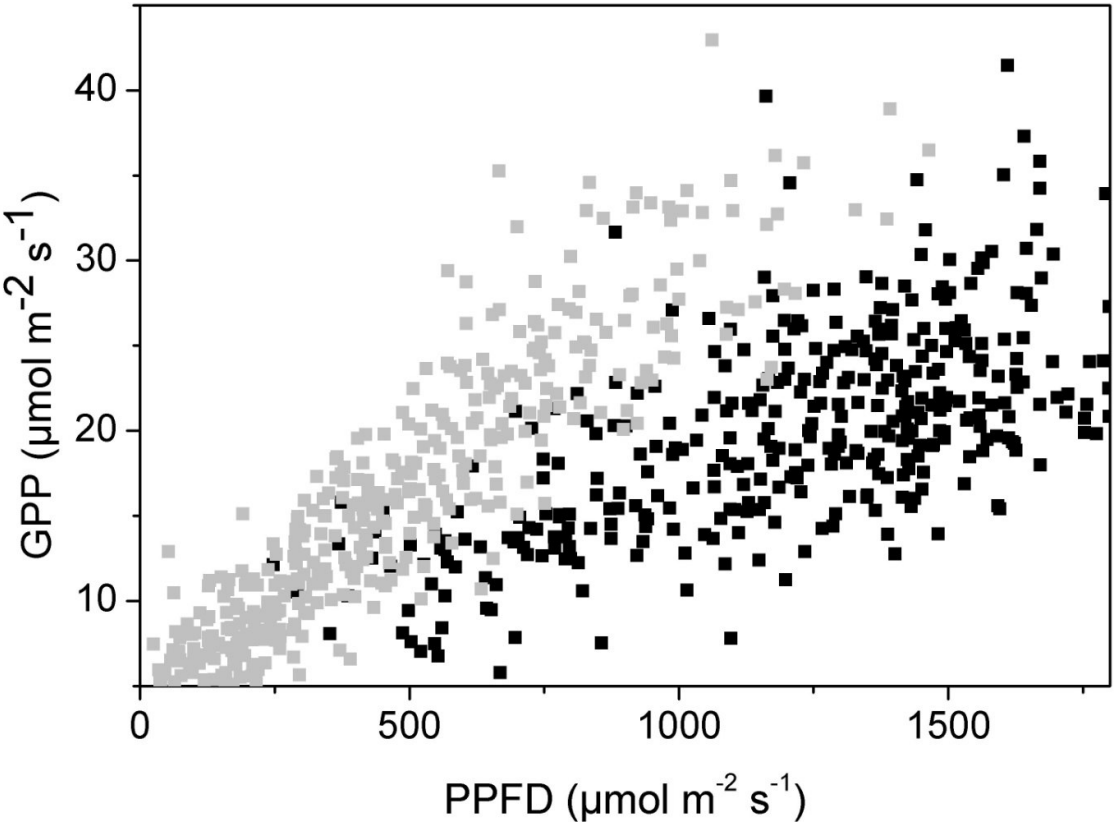

Figure 4.4 GPP in relation to $PPFD$, with separation between cloudy (■) and clear sky (■) conditions for July, August and September in 2009 and 2010.

Vielsalm, as shown in figure 4.4. The commonly accepted explanation is that this is due to the difference between diffuse and direct radiative transfer regimes in plant canopies, coupled with the nonlinearity of the photosynthesis response to $PPFD$. Diffuse radiation is known to better penetrate the canopy than direct radiation. Consequently, at similar above-canopy incident $PPFD$, as the sun leaf photosynthesis is the same under clear and cloudy conditions, the shade leaves within the canopy receive more radiation in cloudy conditions than in clear conditions, and thus photosynthesise more, inducing an overall increase in the whole canopy assimilation. Other potential explanations for the increased net CO_2 sink could include a reduction in respiration due to a temperature decrease, or an increase in stomatal conductance due to a reduction in vapor pressure deficit, as investigated by Knohl and Baldocchi (2008), but these factors were found to be of a minor importance.

As isoprene and monoterpenes are photosynthesis by-products (Delwiche and Sharkey, 1993; Loreto et al., 1996), a similar direct and diffuse radiation effect on their emissions would be expected, which could partially explain the results depicted in Figures 4.2A and 4.3A. Nevertheless, since we also observed an influence of sky conditions on isoprene fluxes at equal GPP (Fig 4.2B), this suggests that the radiative transfer process is not the sole isoprene flux driver.

4.2 Enzymatic activity effect

At the Vielsalm site, an initial study on the interaction between photosynthesis and isoprene and monoterpene emissions was conducted by Laffineur et al. (2011). They observed a linear relationship between temperature-standardised isoprene and monoterpene fluxes and GPP that resulted directly from the GPP response to light. This relationship characterized the enzyme activity along the isoprene and monoterpenes biosynthesis pathway. In the current study, we observed that at equal GPP the standardised isoprene fluxes were lower during cloudy conditions than during clear sky conditions (Fig. 4.2B). This would mean a lower overall enzymatic activity (along the isoprene biosynthesis pathway) in the canopy in cloudy conditions than in clear sky conditions. One possible explanation of this could be a difference in the enzymatic activity of shade and sun needles. Sharkey et al. (1991; 1996) showed that the isoprene emission rate/CO_2 assimilation rate ratio in oak trees was significantly lower in shade than in sun leaves, due probably to leaf acclimation to temperature and radiation (Lehning et al., 1999). Despite the lack of direct experimental confirmation of this effect at the needle scale for the species at the Vielsalm site, and because, in the present case, the relative contribution of the

shade needles to flux (isoprene and GPP) was more important under cloudy conditions than under clear sky conditions, we suggest that lower enzymatic activity along the isoprene biosynthesis pathway of shade needles could explain the difference. The observed effect could also be due to a different flux footprint in cloudy conditions than in clear sky conditions, leading to different isoprene emitters and carbon assimilators between cloudy and clear sky conditions. We expect this effect to play a minor role, however, because the observations showed that isoprene fluxes increased regularly with GPP in the 5-20 µmol m^{-2} s^{-1} range (in clear and cloudy sky conditions) in contrast to a potential footprint effect that could induce an irregular increase.

Contrary to isoprene emissions, no difference was found between monoterpene emissions at similar GPP in clear and cloudy conditions. This could be because, at Vielsalm, several species (deciduous and coniferous) contribute to the monoterpene emissions, leading to more complex processes. In addition, part of the monoterpene emissions could be due to de-storage processes (Laffineur et al., 2011). Finally, the PTR-MS instrument measures the total monoterpene mixing ratio and does not allow a compound separation, which makes it more difficult to understand the possible differences in enzymatic activity along the monoterpene biosynthesis pathway under clear and cloudy sky conditions.

5 Conclusions

This study is to our best knowledge the first to investigate, at the ecosystem scale, the relationship between isoprene and monoterpene emissions and GPP under cloudy and clear sky conditions. We observed that, together with a higher CO_2 assimilation rate, isoprene or monoterpene fluxes are enhanced under conditions with a high proportion of diffuse radiation (cloudy conditions) compared to conditions with a lower proportion of diffuse radiation (clear sky conditions), at equivalent temperature and above-canopy total radiation. Since those BVOCs are produced from intermediate products of photosynthesis, this result is coherent with a higher input in the isoprene and monoterpene metabolic production pathway. We have also shown, however, that for isoprene the whole-canopy enzymatic activity of the metabolic production pathway is lower under cloudy conditions than under clear sky conditions. The fact that we observed an increase in the emissions under cloudy conditions suggests that the former effect is more important than the latter one.

It is likely that the mechanisms behind these observations are linked to the better penetration of diffuse radiation in the canopy. Shade leaves/needles receive more radiation in cloudy con-

ditions than in clear sky conditions, thereby enhancing the BVOC emissions of the whole canopy, an effect well known for CO_2 in the flux community. A more important contribution of shade leaves/needles associated with their lower enzymatic activity would also lead to the observed reduced whole-canopy enzymatic activity in cloudy conditions.

Studies related to global warming suggest that an increased temperature would lead to increased BVOC emissions and aerosol concentrations, resulting in increased aerosol radiative cooling and a potential negative feedback mechanism. With increased aerosol concentrations being associated with more diffuse radiation, our study suggests that this feedback is itself subject to secondary feedback through radiative canopy transfer and vertical enzymatic activity gradient in the canopy. In the context of current knowledge, more investigation is needed to understand more precisely the effect of these mechanisms on BVOC emissions and to reduce the uncertainty about the global BVOC and biogenic aerosol budgets.

Chapter 5

Abiotic and biotic control of methanol exchanges

1 Introduction

Methanol is the second most abundant organic gas in the atmosphere after methane (Jacob et al., 2005; Singh et al., 2001). Its mixing ratio can easily exceed 10 ppbv above forests during the growing season (Karl et al., 2003; Schade and Goldstein, 2001, 2006). Methanol plays a minor but non-negligible role in atmospheric chemistry (Harley et al., 2007; Jacob et al., 2005). It reduces atmospheric oxidation capacity due to its reactions with hydroxyl radicals (OH), producing formaldehyde (CH_2O) and hydroperoxyl radicals (HO_2), thereby increasing the tropospheric ozone concentration (Tie et al., 2003). The chemical atmospheric lifetime of methanol is from 5 to 12 days (Atkinson, 2000; Galbally and Kirstine, 2002; Jacob et al., 2005; Millet et al., 2008; Tie et al., 2003). Several modelling studies (Galbally and Kirstine, 2002; Heikes et al., 2002; Jacob et al., 2005; Singh et al., 2000; Stavrakou et al., 2011; Tie et al., 2003) have focused on the global methanol budget. These studies show that the principal methanol source in the atmosphere is vegetation (60-80%) and that the major sinks are the reaction with OH in gas-phase (40-70%) and dry deposition on land (20-30%). These modelling efforts, however, remain characterized by huge uncertainties. Estimations of global emission by plants vary between 75 (Singh et al., 2000) and 280 (Heikes et al., 2002) Tg yr^{-1} and estimations of global sinks through OH reaction and dry deposition vary between 133 (Galbally and Kirstine, 2002) and 234 (Tie et al., 2003) Tg yr^{-1}. These uncertainties are due mainly to a lack of available measurements, which are typically limited in terms of temporal and spatial resolution, leading to limited knowledge about emission and deposition mechanisms. To date, about 15 studies (see a partial review of them in Seco et al. (2007)) have measured and quantified methanol exchange above a variety of ecosystems (mainly forests and grasslands) using a variety of techniques (relaxed eddy accumulation and disjunct eddy-

covariance). These studies usually cover only a small part of the vegetation season, centred on time periods when biogenic emissions are thought to be important, and are still too limited in terms of the variety of ecosystems that are potential methanol emitters. Among these techniques, disjunct eddy-covariance is the most suitable for long-term monitoring of the ecosystem exchange in real-undisturbed conditions (Rinne et al., 2001). It has been used in several methanol studies (Bamberger et al., 2010; Brunner et al., 2007; Custer and Schade, 2007; Holst et al., 2010; Karl et al., 2001; Karl et al., 2003; Karl et al., 2005; Karl et al., 2004; Karl et al., 2002a; Langford et al., 2010; Spirig et al., 2005), but none of them (at the exception of Hörtnagl et al., 2011 above a temperate mountain grassland) proposed a year-round follow-up of the exchange. In addition, although methanol dry deposition has been observed occasionally or more regularly in some studies (Custer and Schade, 2007; Holst et al., 2010; Karl et al., 2005; Karl et al., 2004; Langford et al., 2010; Schade et al., 2010; Spirig et al., 2005), very few of these studies paid detailed attention to the underlying mechanisms.

In this study, we present long-term ecosystem-scale measurements of methanol fluxes exchanged between a heterogeneous temperate forest and the atmosphere, obtained using the disjunct eddy-covariance by mass scanning. Our dataset covers more than one vegetation period (winter is not included), with a total composite coverage of 10 months. The main result of the study is that, on a long-term scale, the site behaved as a methanol sink in contrast to what has been found at other sites. In order to better understand these results, abiotic and biotic drivers of the methanol emissions/depositions were disentangled. An original model was developed in order to estimate the respective contributions to the net flux of the methanol adsorption/desorption in water films present in the ecosystem and of methanol degradation. Model residuals were then used to isolate biogenic emissions and to identify their driving variables.

2 Material and methods

2.1 Measurement site

The experimental site is a forest ecosystem located at Vielsalm in the Belgian Ardennes forest (50°18’18.20’’N, 5°59’53.15’’E; altitude 450 m). Its topography is smoothly sloping (3%) in a north-westerly direction. The climate is temperate maritime. The soil is 50-100 cm deep and is classified as a dystric cambisol. The vegetation in the tower flux footprint is a mixture of: coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) about 40 m

high, Norway spruce (*Picea abies* [L.] Karst.) about 32 m high, Silver fir (*Abies alba* Miller) about 32 m high; and deciduous species, mainly beeches (*Fagus sylvatica* L.) about 28 m high. A more detailed description of this site is given by Aubinet et al. (2001; 2002) and Laitat et al. (1999).

2.2 Instrumentation and BVOC sampling

An ultrasonic anemometer (model SOLENT 1012 R2, Gill Instruments Ltd, Lymington, UK) was placed at the top of a tower at a height of 52 m, and it continuously measured the three wind velocity components at a sampling frequency of 20.8 Hz. Ambient air was continuously sampled close to the sonic anemometer through a main sampling line (PFA tubing: Fluortechnik-Wolf) 60 m long and 6.4 mm inner diameter, with a flow rate of 9 STP L min^{-1} (Standard Pressure and Temperature conditions corresponded to 1013.25 hPa and 273.15 K). The sampling line was wrapped with two heating cables (20 W/m) and three thermistors were placed along the line to monitor the heating. The output of the thermistors showed that the line was on average 12°C above ambient temperature. Part of this air flow (0.1 STP L min^{-1}) was drawn into a gas analyser through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The data streams coming from the two instruments were logged on a single computer in order to optimise synchronization.

Measurements of relevant meteorological variables were performed at a sampling frequency of 0.04Hz and averaged over half an hour, including total and diffuse fraction of photosynthetically active radiation: $PPFD$ (Sunshine sensor type BF3, Delta-T Devices Ltd, Cambridge, UK), net radiation: R_{net} (Q7.1, REBS, Seattle, WA,USA), air temperature and humidity (RHT2, Delta-T Devices Ltd, Cambridge, UK) at a height of 50 m, soil moisture content (ThetaProbe, Delta-T Devices Ltd, Cambridge, UK) at a depth of 20 cm, and precipitation and atmospheric pressure (MPX4115A, Motorola, Phoenix, USA). A global Vegetation Area Index (VAI) was deduced from $PPFD$ measurements above and below the canopy, as described by Aubinet et al. (2002).

VOC concentrations were measured by a conventional hs-PTR-MS (Ionicon Analytick GmbH, Innsbruck, Austria) equipped with a quadrupole mass spectrometer. Detailed descriptions of the PTR-MS technique are given by Lindinger et al. (1998), de Gouw et al. (2007) and Ammann (2004). The PTR-MS was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2), where E is the electric field and N the ambient air num-

ber density in the flow/drift tube. The ion signals were measured in a cyclic way (which produces a disjunct time series for each mass) at mass to charge ratio m/z 21 (primary hydronium ions: $H_3^{18}O^+$), m/z 33 (protonated methanol), m/z 39 (water cluster ion), m/z 45 (protonated acetaldehyde), m/z 59 (protonated acetone), m/z 69 (protonated isoprene), m/z 71 (protonated methyl vinyl ketone and methacrolein), m/z 81 (fragment of protonated monoterpenes), m/z 87 (protonated methylbutenol and possibly others) and m/z 137 (protonated monoterpenes). In 2010, m/z 47 (protonated formic acid) and m/z 61 (protonated acetic acid) were added. The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. During the measurements, the instrumental background was determined every 4 h by sampling BVOC-free air, obtained by sending ambient air through a heated catalytic converter for 15 min (the last 8 min being used for the calculation of the mean background values). The background measurements for m/z 33 (protonated methanol) may be somewhat more complicated than the background measurements for the other compounds. Indeed, the measured background signal at m/z 33 consists of the real instrumental background at m/z 33 and the oxygen isotopes ($^{16}O^{17}O^+$) (Spirig et al. 2005). Background measurement was generated from ambient air just at the bottom of the tower, which can be somewhat more humid than the air from the top of the tower, which can have a small influence on the strength of the O_2^+ signal (m/z 32) and its second isotope. Once a month of 2010, we have estimated that the error caused by this effect on your m/z 33 measurements was less than 3%.

The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every two or three days using a gravimetrically prepared mixture of these gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA) that contained approximately 500 ppbv isoprene, α-pinene and sabinene and about 1 ppmv methanol, acetaldehyde and acetone, with an accuracy of 5%. The compounds were further diluted (2-12 ppbv range) using a dynamic dilution system. More details can be found in Laffineur et al. (2011).

2.3 Disjunct eddy-covariance

The technique used to measure ecosystem BVOC fluxes is disjunct eddy-covariance by mass scanning (Karl et al., 2002; Rinne et al., 2001). The flux (F_{VOC}) is determined by the covariance of the discrete function between the time series of vertical wind velocity $w(t)$ and VOC concentration $C_{VOC}(t)$ over an averaging period of 30 min (T):

$$F_{VOC} = \frac{1}{N}\sum_{i=1}^{N} w'(t_i - t_{lag}).C'_{VOC}(t_i)$$

with w', C'_{VOC}, the instantaneous deviations from the mean value of w and C_{VOC} respectively, N the number of disjunct PTR-MS samples (790 in 2009 and 605 in 2010 due to the addition of two other masses in the measurement cycle) during T and t_{lag} the lag time between w and C_{VOC} induced by the distance between inlet and PTR-MS. The time lag was computed for each half-hour by shifting one-time series relative to the other until the absolute maximum covariance between the two-time series was determined. We used the filled-time series as proposed by Spirig et al. (2005) to determine the time lag (but not to compute fluxes). This approach allowed an easier time lag determination and is similar to the averaging approach proposed by Taipale et al. (2010). The mean time lag found using this method was 14.8 s for methanol and others BVOCs, close to 12.9 s, the theoretical value computed from the flow rate and the inlet line volume. This experimental mean time lag was used as the default value when we didn't found a maximum in the covariance function inside the [10 s, 18 s] time window. Methanol fluxes were computed using block average over 30 min periods, and 2D rotation was applied. Stationarity test (Foken and Wichura, 1996) was not applied in this study as in Brunner et al. (2007), because fluxes would hardly pass the test (more than 40% of data would have been rejected) and because this filtering did not increase the quality of our methanol data. A filter linked to anthropogenic influence (Sect. 2.4) and a stability filter (Sect. 4.3.1) were applied. Over the course of the two measurements campaigns 10138 half-hourly fluxes for methanol were recorded, of which 5481 passed all filtering criteria.

High frequency losses due mainly to the damping of concentration fluctuations in the sampling line were corrected experimentally following the method reported by Aubinet et al. (2001) using a transfer function determined by a comparison of the sensible heat flux co-spectra and the m/z 69 flux co-spectra. From this unique transfer function, a correction factor was deduced which was applied to the BVOC fluxes. For example, for a wind speed of 3 m s^{-1} (mean value of our dataset), we obtained a correction factor of 1.49. More details on the flux computation methodology are given by Laffineur et al. (2011).

2.4 Data filtering

In the 230-270° wind direction sector, which was also the main wind direction, methanol fluxes could be contaminated by the activities of a wood panel factory, 3 km from the tower.

Wood panel production is known to emit high levels of monoterpenes and methanol (Nicholson, 2003). Although not located inside the main day flux footprint, defined as the 90% level contribution to the total flux (footprint analyses were performed with a two-dimensional analytical footprint software tool proposed by Neftel et al. (2008) in line with the Kormann-Meixner footprint model (Kormann and Meixner, 2001)), this source was probably so important compared with forested ecosystem sources that it influenced our measurements. Flux measurements spoiled by anthropogenic emissions were therefore rejected, using a filtering criterion based on the variance of the monoterpene mixing ratio. Indeed, it is easier to define a threshold on the monoterpenes variance than on the methanol variance to exclude precisely the data affected strongly by factory emissions (27 % of data 2009-2010 was rejected). Figure 5.1 shows the effect of the monoterpenes variance filtering on the methanol mixing ratio. The monoterpenes variance seems to be a sufficiently robust criterion to exclude methanol data affected by the factory. The filtering suppresses also data points outside the factory direction but in a small number of cases in comparison with the number of data point that succeed the test. This procedure was described in detail by Laffineur et al. (2011).

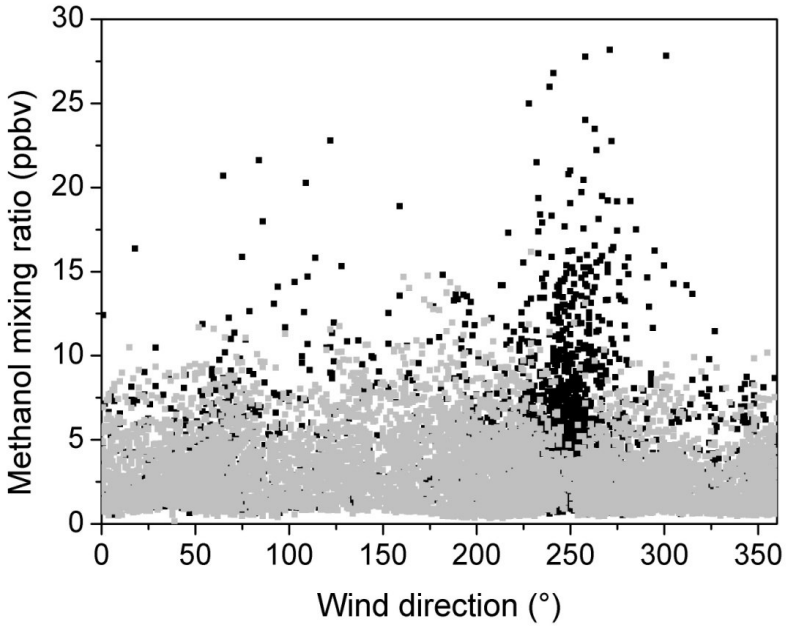

Figure 5.1 The black points represent the methanol flux data (2009-2010) deleted by the monoterpenes variance filtering. The light grey points represent the data that succeed the test.

In contrast with CO_2 fluxes (Aubinet et al., 1999), u^* filtering was not applied here. The methanol flux is not controlled by a continuous production process (like respiration in the case of CO_2) that works independently of the presence or absence of turbulent transport. The dependence of the methanol flux on turbulence (see § 4.2.) corresponds here to a real process

(not a measurement artefact), so that any data filtering with a criterion based on turbulence could lead to flux overestimation (Aubinet et al., 2012b).

3 Methanol adsorption/desorption model

The empirical adsorption/desorption model is represented by the electrical analog scheme presented in Fig. 5.2. Net methanol flux exchange by the ecosystem with the atmosphere is characterized by F_1 [µg m^{-2} s^{-1}]. This flux consists of two components: the first one (F_3) corresponds to adsorption/desorption in water films present in the ecosystem; and the second one (F_2) corresponds to methanol degradation in aqueous-phase, possibly by methylotrophic organisms. This sink was postulated to deal with the negative methanol budget on a long-term time scale (see § 4.3.2).

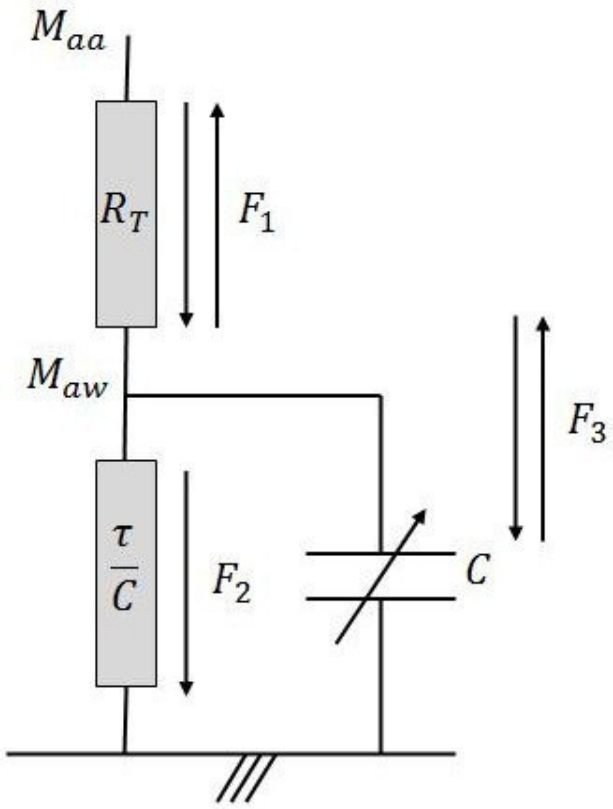

Figure 5.2 Electrical analogy for methanol adsorption/desorption/degradation processes. F_1 represents the net methanol flux exchange, F_3 represents the adsorption/desorption of methanol in water films (represented by the capacity: C), F_2 represents the methanol degradation (represented by the resistance: τ/C), M_{aw} and M_{aa} represent the methanol concentration in the air at the water film surface and in the atmosphere, respectively, and R_t represents the gas-phase resistance to the methanol transfer in the surface boundary layer.

The net flux with the atmosphere is written as:

$$F_1 = \frac{1}{R_t}(M_{aw} - M_{aa}) \quad (1),$$

where M_{aw} [µg m^{-3}] and M_{aa} [µg m^{-3}] represent the methanol concentration in the air at the water film surface and in the atmosphere, respectively, and R_t [s m^{-1}] represents the gas-phase resistance to the methanol transfer in the surface boundary layer. Sign convention is that a positive flux is directed towards to the atmosphere and a negative flux towards the surface. Considering that molecular diffusion transport is negligible compared to turbulent transport, R_t might be approximated by the aerodynamic resistance of in-canopy air space (Mihailovic et al., 2009; Pul and Jacobs, 1994) in a very straightforward way:

$$R_t = \frac{1}{A.u^*} \quad (2),$$

where A is an empirical parameter and u^* [m s^{-1}] is the friction velocity. The aerodynamic resistance above the canopy can be considered negligible compared with this resistance.

In this model, we consider that the methanol reservoir in the ecosystem is made of water films present on leaves and wet soil surfaces that can adsorp/desorp methanol. In these conditions, M_{aw} can be related to the total methanol content in the water film reservoirs of the ecosystem (q [µg m^{-2}]) by:

$$M_{aw} = \frac{q}{C} \quad (3),$$

where C [m^3 m^{-2}] represents the capacity of the water films to store methanol as suggested by Sutton et al. (1998) in the context of ammonia exchange. This constant depends on Henry's law constant, K_H [dimensionless (water/air partition ratio)], and on the free water present in the ecosystem. The dimensionless Henry's law constant of methanol is given by (Warneck, 2006):

$$K_H = \frac{1000.R.298.15\left[e^{-12.46}e^{5312.4/T_H}\right]}{101325} \quad (4),$$

where R [J mol^{-1} K^{-1}] is the gas constant and T_H [K] represents the temperature that we have considered to be the air temperature (T_a).

A complete description of the free water content would require establishing a detailed ecosystem water balance, which is not available here. We therefore approximated it by a function of air humidity as suggested by Van Hove and Adema (1996), Burkhardt and Eiden (Burkhardt

and Eiden, 1994) and Burkhardt et al. (2009) and the precipitation during the preceding days. Dependence on air humidity (see § 4.3.1) was computed by:

$$C = K_H . \frac{C_R}{\left[1-\exp\left(-\frac{D}{\alpha}\right)\right]} \quad (5),$$

where D [Pa] is the water vapour pressure deficit, α [Pa] is an empirical parameter and C_R [m] is the component of the capacity that depends on the precipitation (P [mm]) of the preceding days. Without information on the leaf/soil water balance from precipitation, C_R was computed simply by a linear dependence on cumulated precipitation of the 10 preceding days (480 half-hours):

$$C_R = C_{R0} + \sum_{i=0}^{480} P_i \quad (6),$$

where C_{R0} is a residual capacity.

Methanol degradation is described by a diffusion flux (F_2) and characterized by a resistance τ/C :

$$F_2 = -\frac{q}{\tau} \quad (7),$$

where τ [s] represents a time constant, characteristic of the methanol lifetime in the water films in the absence of adsorption or desorption.

Using Kirchhoff's circuit law, we can write:

$$F_3 = F_1 - F_2 = -\frac{dq}{dt} \quad (8).$$

By introducing (1)-(3) and (7) in (8) and approximating the equation by finite differences, we get:

$$q_j = q_{j-1} - \Delta t \left[A . u^* . \left(\frac{q_{j-1}}{C} - M_{aa}\right) + \frac{q_{j-1}}{\tau}\right] \quad (9),$$

where Δt is the integration time, fixed in this study to one half-hour (1800 s) and index j denotes successive **time period** intervals.

By introducing expression (9) of q into (3) and then into (1), we then get:

$$F_{1,j} = A . u^* . \left[\frac{q_j}{K_H . \frac{C_{R0} + \sum_{i=0}^{480} P_i}{\left[1-\exp\left(-\frac{D}{\alpha}\right)\right]}} - M_{aa}\right] \quad (10).$$

Finally, the complete model given by equation (10) depends on four empirical parameters: A, τ, C_{R0} and α.

4 Results

4.1 Micrometeorological and methanol flux evolutions

The seasonal evolution of air temperature (T_a), photosynthetically active radiation ($PPFD$), water vapour pressure deficit (D), precipitation (P), friction velocity (u^*), methanol ambient mixing ratio and methanol flux is shown in Fig. 5.3.

Summer and autumn 2009 were characterized by high temperatures (mean temperature in July-August-September 15.7°C) for the region, except at the end of October (8.4°C). August and September were relatively dry with cumulated rain close to only 50 mm. The temperature conditions during spring 2010 were normal for the region (mean temperature in April-May-June 10.9°C), except during the first half of May, which followed the bud break of *Fagus sylvatica* on 1 May and was colder and cloudier than average. The April-May-June period was, however, dry, with cumulated rain of only 86 mm. Summer 2010 was also characterized by high temperatures (mean temperature in July-August-September 15.2°C), especially between 7 and 14 July. The highest D (> 0.8 kPa) were observed mainly between the end of June and the end of July 2010. In contrast with 2009, August 2010 was very rainy, with cumulated rain of 215 mm. The annual mean temperature (cumulated rain) in the region was 8.5°C (939 mm) and 7.4°C (896 mm) in 2009 and 2010 respectively.

The atmospheric methanol concentration course in the spring and summer periods was similar and varied between 0.8 and 8.7 ppbv (5^{th} centile and 95^{th} centile), with a mean of 3.5 ppbv. In autumn, the methanol concentration was close to 2.0 ppbv. Methanol fluxes were bi-directional. The highest deposition fluxes were observed in July 2009 and in August-September 2010 (up to -0.6 µg m^{-2} s^{-1}), while the highest emissions (up to 0.6 µg m^{-2} s^{-1}) were observed during the second half of May 2010 and the beginning of June 2010. To a lesser extent, emissions were observed during July-August 2009 and during the second half of April 2010 and the end of June 2010.

Figure 5.4 shows the mean diurnal evolution of the methanol flux in the summer in 2009 and 2010 and in spring 2010. In both cases, the flux was generally positive during the day and negative at night, but in spring the fluxes shifted towards more positive values compared with summer, the net daily flux being roughly twice as large in spring as in summer. As a result,

the net daily flux was negative in summer (deposition dominates) and positive in spring

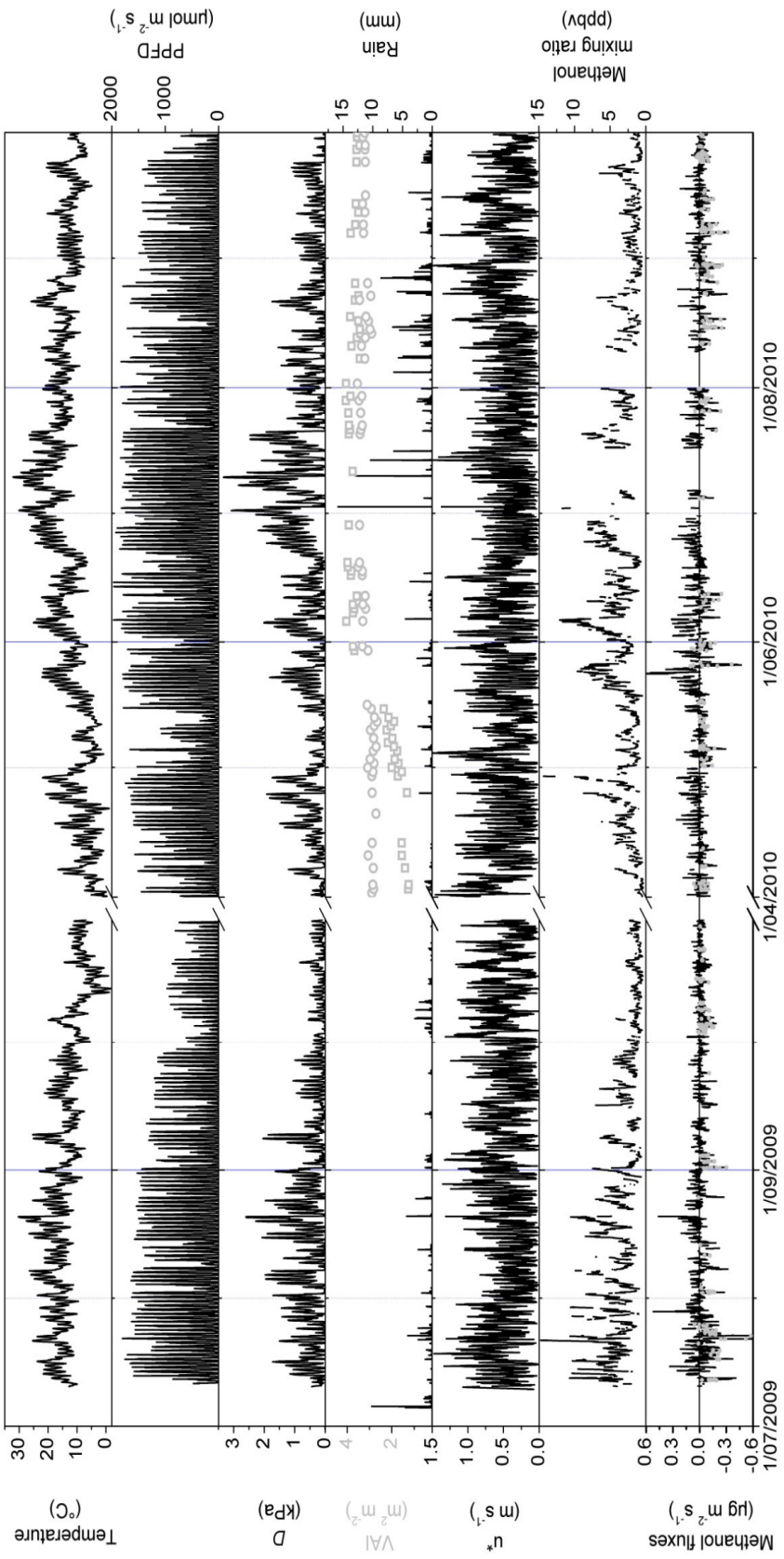

Figure 5.3 Temporal evolution of meteorological variables, methanol mixing ratio and methanol flux between 10 July and 31 October 2009 and between 1 April and 30 September 2010: air temperature (T_a), *PPFD*, vapour pressure deficit (*D*), precipitation, vegetation area index (VAI) of beeches (□) and Douglas (○), friction velocity (u^*), ambient methanol mixing ratio and methanol fluxes (the rain events are identified with grey points).

(emission dominates). For the whole measurement period, deposition was generally less pronounced in the beginning of the night than at the end.

4.2 Main drivers of methanol flux

In order to determine the main drivers of methanol fluxes, their relationships with the main meteorological variables (radiation, air temperature, water vapour pressure deficit, friction velocity, atmospheric methanol concentration) were tested. Only the most relevant relationships are presented here. The clearest response of methanol flux to climatic variables is the one to water vapour pressure deficit (Fig. 5.5). At low D, fluxes are mainly negative, indicating methanol deposition. The flux increases with D, and tends towards a positive and constant value above $D = 1$ kPa. The influence of humidity on the methanol exchange can be seen in Fig. 5.3 where deposition is systematically observed during or following precipitation.

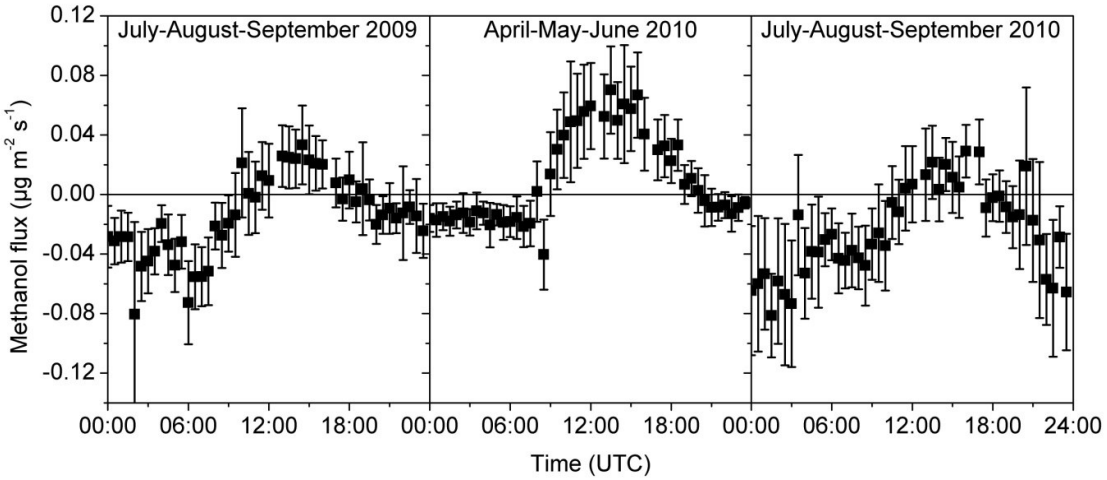

Figure 5.4 Mean diurnal evolutions of methanol flux (error bars are 95% confidence intervals).

A linear dependence between the ratio of F to M_{aa} and u^* was also found (Fig. 5.6), only when wet conditions ($D < 0.15$ kPa) were selected (and $R_{net} > -20$ W m^{-2}, explanation below). In these wet conditions, M_{aw} can be close to zero, the ratio F to M_{aa} thereby representing a deposition velocity (see § 4.3.1 and Foken et al. (2008)). Similar relationships were observed for day and night. Slope (parameter $-A$ in the model) and intercept coefficients were equal to -0.055 ± 0.004 and -0.0018 ± 0.0022 m s^{-1} ($R^2 = 0.36$), respectively, for the day and equal to -0.060 ± 0.002 and -0.0043 ± 0.0011 m s^{-1} ($R^2 = 0.58$), respectively, for the night. For the whole measurement period, the mean u^* was 0.4 m s^{-1}, which corresponds to a deposition velocity of 2.4 cm s^{-1}.

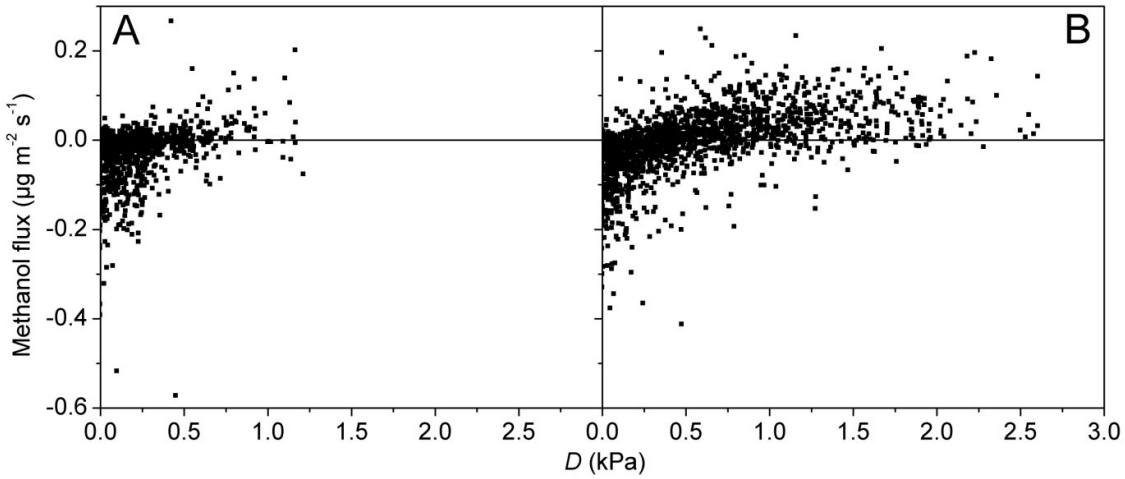

Figure 5.5 Vapour pressure deficit (*D*) dependence of methanol flux in night (A) and day (B) conditions for July-August-September 2009.

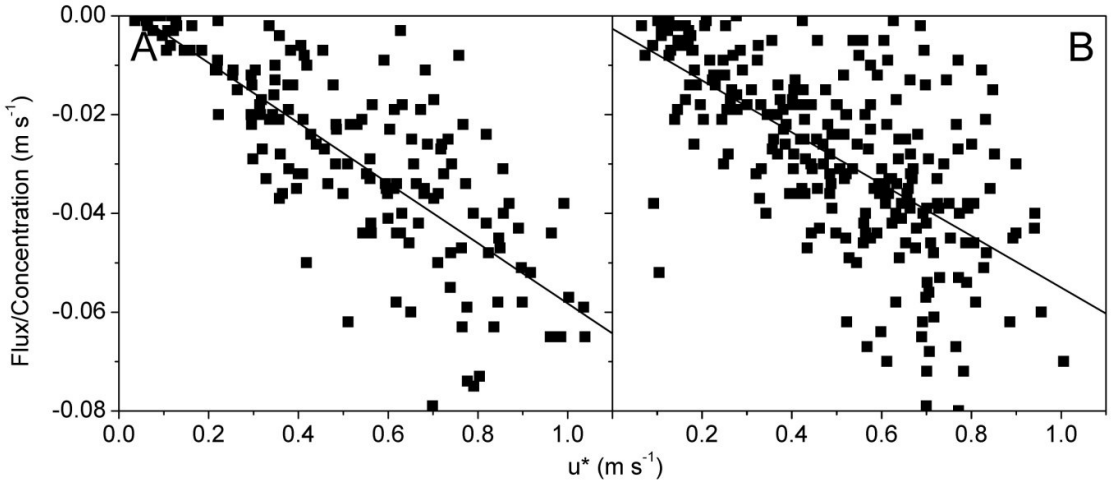

Figure 5.6 Relationship between the ratio methanol flux/ambient methanol concentration and the friction velocity (u^*) in night (A) and day (B) conditions for July-August-September 2009, respecting these conditions: flux < 0 µg m^{-2} s^{-1}, D < 0.15 kPa and R_{net} > –20 W m^{-2}.

The relationship between methanol exchange and temperature appeared to be complex (Fig. 5.7), with the most important negative fluxes being observed between 10 and 20°C and the most important positive fluxes between 15 and 25°C.

4.3 Bi-directional methanol flux modelling

The methanol deposition quantities increased strongly with increasing air humidity, indicating that water on the leaf and/or soil surface plays a major role in the interaction of methanol with leaf and/or soil surfaces. This is due to microscale liquid water films and/or droplets formed on external plant/soil surfaces through condensation of water vapour on the leaf/soil surface

or through rain or fog droplets from the atmosphere. The dependence of the deposition velocity on u^* (Fig. 5.6) indicates that turbulent transport is the main resistance driving deposition. The complex response of deposition to air temperature could be due to the interaction between the temperature dependency of methanol solubility (Henry's law) in water and of air saturation deficit.

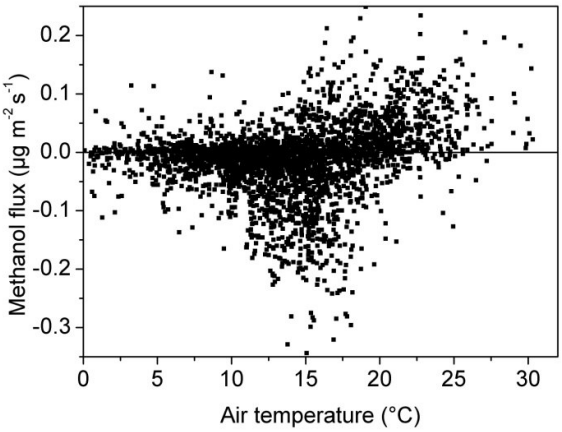

Figure 5.7 Methanol flux in relation with the air temperature for July-August-September 2009.

Our observations therefore strongly suggest that methanol fluxes could be driven by the adsorption/desorption process of methanol in water films that are present in the ecosystem. We have used the model developed in section 3 to prove this hypothesis.

The model has 5 input variables (T_a, u^*, M_{aa}, D and P) and 4 site-specific parameters (A, τ, C_{R0} and α). In this section, the model will first be calibrated (§ 4.3.1) and validated (§ 4.3.2) on data sets where the abiotic processes appear dominant (i.e., in summer). The model will then be used (§ 4.3.3) to compute the abiotic component in spring. Finally, abiotic flux simulations will be combined with measurements in order to isolate the biogenic contributions to the fluxes and these fluxes will be analysed more deeply. Calibration will be performed on summer 2009 data (July to September) and validation on summer 2010 data.

4.3.1 Model calibration (summer 2009)

The calibration was performed in three steps. First, for parameter A, the value found in § 4.2 (Fig. 5.6) above was retained, selecting night conditions when stomata are closed to limit the possible effect of biogenic emissions on the parameter A. Second, α was also deduced from the results of § 4.2 (Fig. 5.5). A function of the type:

$$f(\alpha) = \psi.\left[1 - \exp\left(-\frac{D}{\alpha}\right)\right]$$

was adjusted on the relationship between $M_{aw}.K_H(T_a)$ and D (Fig. 5.8), $\psi = \frac{q}{C_R}$ being a free parameter (corresponding to a residual concentration) and M_{aw} being deduced from Equation (1) by using our measurements (M_{aa}, u^* and $F_1 = F_{measured}$). We obtained $\alpha = 588 \pm 69$ Pa ($R^2 = 0.44$).

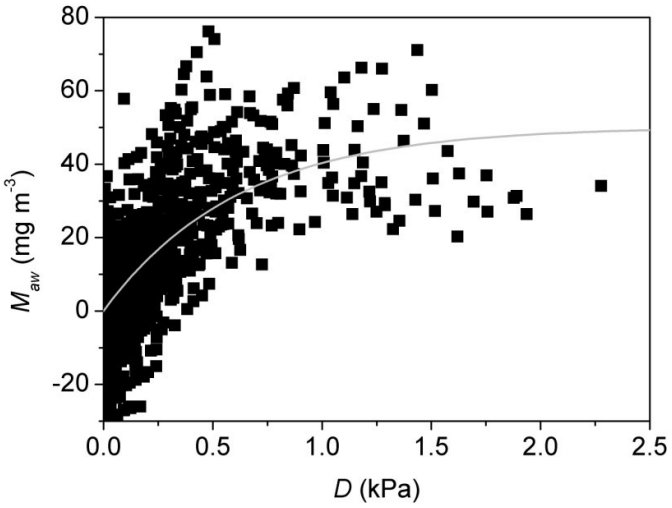

Figure 5.8 Relationship between the concentration of methanol (M_{aw}) in the water films and the vapour pressure deficit (D) for July-August-September 2009. The negative value is due to the modeled uncertainty of M_{aw} (± 20 mg m^3).

Third, the last two parameters (τ, C_{R0}) were estimated by minimising the square root differences between modelled and measured cumulated fluxes. This provided $C_{R0} = 0.176$ m and $\tau = 82.8$ hours, the latter corresponding to a half lifetime of 57.4 hours. If C_{R0} is interpreted as the minimum total height of water films in the ecosystem, its value may look unrealistically high. This is probably because we use air temperature for the computation of the Henry's law constant instead of the temperature of the water films at the soil surface. This latter temperature is not available, but is usually lower than the air temperature, leading to a systematic underestimation of K_H compensated by a high fitted C_{R0}.

In the above calibration and in the subsequent validation phase, we rejected data with net radiation below -20 W m^{-2} because in these atmospheric conditions (11% of the dataset after the anthropogenic filtering) the oversimplified parameterisation chosen for R_t in equation (2) underestimates the in-canopy aerodynamic resistance (Pul and Jacobs, 1994). In summer, the comparison between measured mean diurnal evolution of methanol fluxes without (Fig. 5.4) and with R_{net} filtering (Fig. 5.9A) shows that, under stable atmospheric conditions, the turbulent exchange is dampened, therefore limiting the exchange. Without R_{net} filtering, the model would have predicted unrealistically strong deposition (result not shown) during these events.

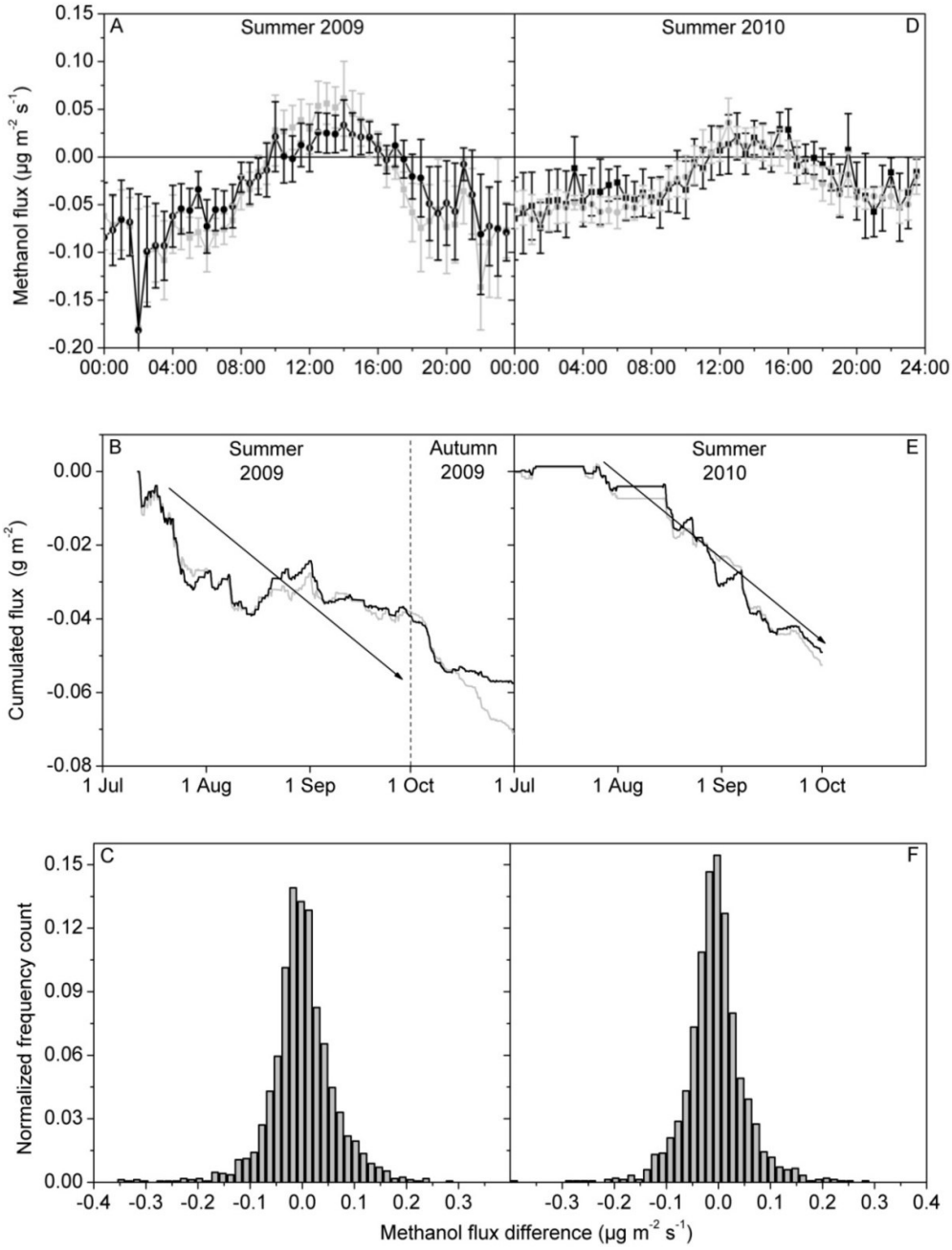

Figure 5.9 Mean diurnal flux evolution of modelled (grey line) and measured (black line) methanol flux for the summer 2009 (A) and for the summer 2010 (*D*) with $R_{net} > -20$ W m^{-2} (error bars are 95% confidence intervals), temporal evolution of cumulated measured (black line) and modelled (grey line) methanol flux for the summer 2009 (B) and the summer 2010 (E), distribution of the difference between the measured and modelled methanol flux for the summer 2009 (C) and the summer 2010 (F).

In the case of long data gaps (more than 10 days), the model lacks information on the temporal evolution of total methanol content in the water films. Several days are needed after the measurement recovery to allow reliable modelling. Such data gaps did, for instance, occur in

2010, the first one in July and the second at the beginning of August. In these cases, we discarded the results obtained less than 4 days after the measurement recovery.

After calibration, the model was able to reproduce the intra-day (Fig. 5.9A) as well as the long-term (Fig. 5.9B) flux dynamics. The frequency distribution of the differences between measurements and simulations (Fig. 5.9C) is characterized by a mean and a median close to zero and by a standard deviation of 0.065 $\mu g\ m^{-2}\ s^{-1}$. This standard deviation probably originates from the random errors introduced by the DEC method (Hörtnagl et al., 2010) and by the spatial distribution of sources/sinks that can affect measurements, especially at low wind speed (Richardson et al., 2006). The effect of these random errors was limited in time by performing the model calibration on cumulated fluxes instead of using individual half-hours. The cumulated flux shows a linear decrease with time (Fig. 5.9B). This decrease is due to methanol degradation that affects the long-term evolution of the modelled flux. The slope of this long-term evolution, representing the mean degradation methanol flux, is $-7.42\ 10^{-3}\ \mu g\ m^{-2}\ s^{-1}$. The fluctuations of the cumulated flux around this linear decrease are due to adsorption/desorption mechanisms that, unlike degradation, are short-term effects.

4.3.2 Model validation (summer 2010)

Once calibrated with the summer 2009 data, the model reproduced faithfully the observed mean diurnal flux evolution in summer 2010 (Fig. 5.9D). Measured and modelled cumulated fluxes were also in good agreement (Fig. 5.9E) and were characterized by a linear decrease similar to that in the calibration phase. In the period from 28 August to 5 September, the model first under-estimated and later over-estimated the depositions. At the beginning of this period, heavy rains occurred and the effect of this is probably poorly represented by the model through Equation (6) on a short-time scale (< 10 days). The frequency distribution of the deviation measurements-model (Fig. 5.9F) is characterized by a mean and a median close to zero and by a standard deviation of 0.057 $\mu g\ m^{-2}\ s^{-1}$.

Other divergences were observed in autumn 2009, from 15 October onwards, and also in April 2010 (data not shown), during which the model over-estimated the deposition. One reason could be that during both these periods the deciduous trees are leafless, while the model had been parameterised (Equation 5) on the basis of measurements taken during the full-leaf period. This could lead to an overestimation of the water film capacities during these periods.

4.3.3 Flux partitioning during transitional phenological phases (spring 2010)

The model was then applied to spring (May 2010, Fig. 5.10). As the model computes only the abiotic contribution to the fluxes and the methanol degradation, its residuals (measurement minus modelling) during this period should therefore represent the biogenic emissions. Time evolutions of the residuals and their driving variables have been investigated.

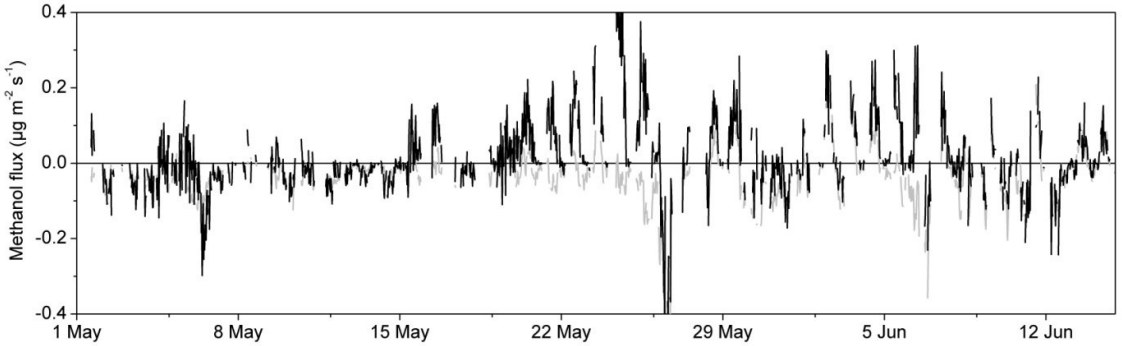

Figure 5.10 Temporal evolution of measured (black line) and modeled (grey line) methanol flux between 1st May and 15th June 2010.

The model residuals during the day become increasingly significant from 20 to 27 May, reaching a maximum value of 0.6 µg m^{-2} s^{-1}. During this period, when leaves are almost at their full development stage (see VAI, Fig. 5.3), the model residuals cannot be explained by an overestimation of the water film capacities as suggested for the divergence observed in autumn. Indeed, a possible increase in foliar surface should instead reduce these residuals.

As the biogenic fluxes are known to respond mainly to temperature (Custer and Schade, 2007; Filella et al., 2007; Folkers et al., 2008; Harley et al., 2007) and to $PPFD$ (Brunner et al., 2007; Harley et al., 2007), we investigated the relationships of the model residuals to these two variables. The results are presented in Fig. 5.11.

Residuals increase with temperature (Fig. 5.11A) and can be fitted using an exponential relation:

$$F_{Methanol} = SEF_{30°C}.\exp(\beta.(T_a - 303.15))$$

where $SEF_{30°C}$, the standard emission factor at 30°C was found to be 0.76 ± 0.11 µg m^{-2} s^{-1} and β, the temperature dependence parameter, 0.12 ± 0.01 $°C^{-1}$ ($R^2 = 0.38$).

On the other hand, no obvious relationship (slope coefficient not significantly different from zero, $p = 0.1$) between the model residuals standardized with air temperature and $PPFD$ was found (Fig. 5.11B).

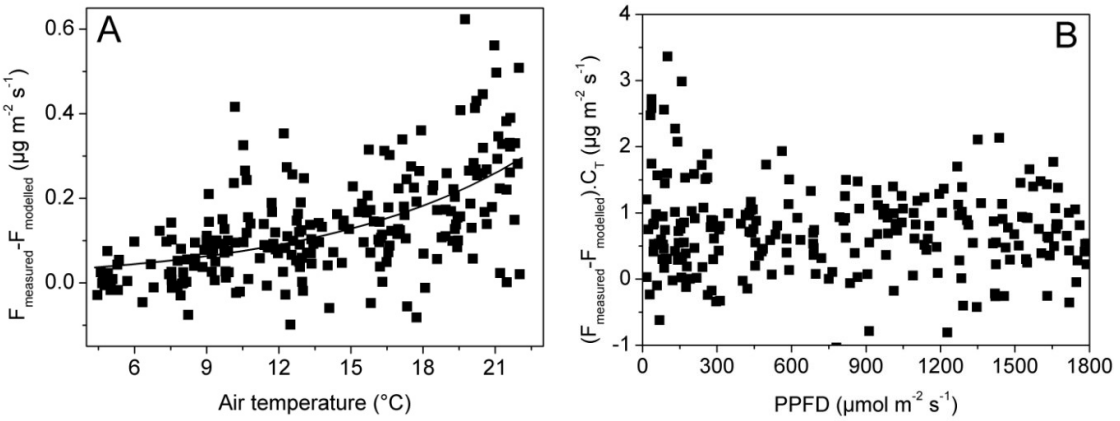

Figure 5.11 Relation between the difference of measured/modelled methanol flux and the air temperature (A), relation between the difference of measured/modelled methanol flux standardised at 30°C and the *PPFD* (B) between 15th and 27th May 2010.

5 Discussion

5.1 Comparison with previous flux studies at the ecosystem scale

This study reports a temperate forest behaving as a net methanol sink (−0.057 ± 0.012 mg m^{-2} h^{-1}) over a 7-month period (April 2010 to September 2010) and, given the fact that net emissions are not expected during winter, most probably as a sink on an annual basis. This result contradicts most studies published on methanol exchange by forests to date (Karl et al., 2004, 2005; Schade et al., 2010; Spirig et al., 2005), which reported generally positive fluxes and a positive net budget during their measurement periods. Methanol deposition was observed only occasionally in these studies, with a maximum deposition up to 0.15 µg m^{-2} s^{-1} for Spirig et al. (2005) over a temperate forest, still four times lower than our maximum deposition. The sole negative net budget over two measurement periods (April-May 2008: −0.02±0.02 mg m^{-2} h^{-1} and June-July 2008: −0.04±0.02 mg m^{-2} h^{-1}) was observed by Langford et al. (2010) above a tropical rainforest.

One of the main reasons for these differences is probably that most of these studies were conducted over short periods corresponding with sunny weather conditions and vegetation development, during which biogenic emission dominated. If our study had been limited to spring, it would also have reported such a positive methanol net budget with occasional depositions. The detection of the alternation between day emission and night deposition and of the long-term methanol degradation was possible only because of long-term measurements performed after the single production period.

MEGANv2.1, the state-of the-art empirical upscaling emission algorithm (Stavrakou et al., 2011), is parameterised using emission factors and deposition velocities derived from a compilation of the above-mentioned ecosystem-scale studies. The proposed standard emission factor for growing leaves of northern temperate forests (0.67 µg m^{-2} s^{-1}) is close to our result (0.76 µg m^{-2} s^{-1}).

In this model, dry depositions are accounted for by using a linear dependence of the deposition velocity on the LAI, increasing from 0 to 0.75 cm s^{-1} when LAI increases from 0 to 6 m^2 m^{-2}. Our results contrast with this parameterisation. Our calculated average deposition velocity (2.4 cm s^{-1}) is 10 times higher than the mean deposition velocity observed by Karl et al. (2004) above a tropical rain forest (0.27 ± 0.14 cm s^{-1}) and more than twice as high than the maximum velocity of 1.0 cm s^{-1} observed by Karl et al. (2005) above a *Pinus taeda* plantation and than the deposition velocity of 1.1± 0.9 cm s^{-1} observed by Schade et al. (2010) above a *Fagus sylvatica* forest. However, it is worth mentioning that in our study we selected only wet atmospheric conditions (and $R_{net} > -20$ W m^{-2}) for the deposition velocity calculation (see § 4.2), whereas other studies used their whole dataset. For comparison, we obtained a deposition velocity of 1.78 ± 0.08 cm s^{-1} without filtering, still higher than in previous studies.

Our study therefore questions the measured and modelled net methanol budget in forest ecosystems. The presence of an adsorption/desorption process of methanol in water films and of a methanol degradation process could significantly modify the methanol budget on short- and long-term scales.

5.2 Processes responsible for methanol depositions/emissions

5.2.1 Adsorption/desorption process

The good agreement between our simulations and the measurements in summer, especially the good reproduction of the intra-day variability of the methanol exchange, suggests that methanol adsorption/desorption in water films is the main process controlling net methanol ecosystem exchange in the short-term. This is due to the high solubility of this compound in water compared with other BVOCs (Sander, 1999).

5.2.2 Degradation processes

In addition, the observation of a negative cumulated flux on a long-term scale in summer reflects the existence of methanol degradation processes in the ecosystem. Several degradation mechanisms have been identified in literature.

The possibility of stomatal deposition during the day followed by the oxidation of methanol into formaldehyde in the leaf was reported by Gout et al. (2000). However, this process would imply a higher deposition velocity during the day than at night, because the stomata are closed at night. Since no significant difference was observed in the deposition velocity during the day or night (Fig. 5.6), we assume that this process was negligible at our site compared with the adsorption/desorption mechanism in water films.

Another possibility would be consumption by methylotrophic bacteria, organisms that preferentially use methanol as source of energy and carbon through an enzymatic reaction (Duine and Frank, 1980). These organisms are known to be common on leaf surfaces (Holland and Polacco, 1994) and soil (Hiraishi et al., 1995). Romanovskaya et al. (2001) reported a natural colonization of methylotrophic bacteria on leaves, occurring mainly via air transfer. The degradation of methanol could also be due to the reaction of methanol in the aqueous-phase with OH radicals (Elliot and McCracken, 1989). This chemical reaction might occur in water films present on leaf and soil surfaces. Based on our sole dataset, we were not able to identify the precise origin of this degradation mechanism and whether it occurs on leaf and/or soil surfaces. Nevertheless, we found a mean degradation rate of $-7.42\ 10^{-3}$ µg m^{-2} s^{-1} and a half lifetime for methanol in water films of 57.4 hours. This latter value is in agreement with Howard et al. (1991) who found a half lifetime in a wet soil of between 1 and 7 days.

5.2.3 Biogenic emission processes

We considered that biogenic emissions occur mainly in spring. Leaf methanol emission is usually considered to be two to three times lower for mature leaves than for young leaves (Karl et al., 2003; Nemecek-Marshall et al., 1995). It is therefore likely that, in summer, leaf emissions might be negligible compared with the methanol adsorption/desorption in water films. We therefore associated biogenic emission with the model residual only for spring.

Between 20 and 27 May (Fig. 5.10), these residuals showed an exponential increase with temperature (Fig. 5.11A), indicating an enzymatic mechanism and/or destorage from an internal pool. This enzymatic mechanism can be attributed to the demethylation of pectin that occurs during the leaf/needle cell wall expansion (Fall and Benson, 1996) and also to root

growth (Folkers et al., 2008), this entire methanol production being emitted through the stomata (Galbally and Kirstine, 2002). In support of this hypothesis, the fitted temperature sensitivity factor was found to be 0.12 ± 0.01 $°C^{-1}$, comparable with previous enclosure studies (β = 0.06±0.003 $°C^{-1}$ (*Fagus sylvatica*) for Fillela et al., 2007 and β = 0.082 $°C^{-1}$ (*Picea abies*) for Folkers et al., 2008). (Filella et al., 2007; Folkers et al., 2008; Harley et al., 2007).

The attribution of biogenic emissions due to leaf/needle growth to a specific tree species is a difficult exercise because of the mixed composition of the stand. In the 20-27 May period, during which the most significant emissions were observed, footprint analysis reveals that a contribution to the total flux of 40% or more by *Fagus sylvatica, Pseudotsuga menziesii* and *Picea abies/Abies alba* occurred during 50, 36 and 24% of the time, respectively. Since *Fagus sylvatica* was the main contributor during this period and since its leaves were still not at their full development stage at that time, we attribute the main part of the growth-linked biogenic emission to that species, but we cannot exclude a contribution of *Pseudotsuga menziesii* and *Picea abies/Abies alba,* since they also contribute to flux and are known to have their bud break at the end of April and mid-May, respectively (Lebourgeois et al., 2002).

The emission we observed (Fig. 5.10) did not coincide exactly with the *Fagus sylvatica* bud break, which started on 1 May 2010. This is probably because the following 15 days were characterized by cold conditions (T_a < 9°C) which hindered biogenic emissions (Fig. 5.10). From 15 May onwards, the air temperature increased and the highest residuals were found.

Methanol can also be produced through litter decomposition occurring mainly in autumn (Gray et al., 2010; Warneke et al., 1999). This would agree with an increase of the model residuals observed in autumn, but we have already noted that our model was not designed to handle the LAI change occurring during this period. In the absence of trustworthy information produced by the model, it was not possible to determine if methanol production from the litter was really present in autumn and/or if a seasonal decrease of methanol degradation occurred.

In contrast to the enclosure study of Folkers et al. (2008) (*Fagus sylvatica*) and the DEC study of Brunner et al. (2007) (grassland), we did not observe any clear dependence of the biogenic emissions on $PPFD$, whereas $PPFD$ is known to regulate stomatal conductance, which in turn controls leaf emissions for soluble compounds such as methanol (MacDonald and Fall, 1993; Niinemets et al., 2004). This dependence could have been blurred by two processes: (i) the biogenic emission computation procedure as model residuals standardised with air temperature and (ii) the leaf development dynamics that occurred throughout the period when biogenic emissions were analysed.

6 Summary and conclusions

This study presented and analysed long-term measurements of ecosystem-scale methanol exchange over a forest. It showed that the site behaved as a methanol sink for most of the measurement period, which contradicts results generally reported in experimental studies and the estimates of methanol exchanges based on emission modelling.

A simple model was developed in order to identify the mechanisms responsible for this sink. The results suggest that the main processes controlling methanol exchanges in summer are on a short-term scale, the methanol adsorption/desorption by water films and, at longer term, the methanol degradation.

The production of methanol associated with leaf development, as generally observed in some preceding studies, was also detected at our site, but it was limited to a short period in spring and did not constitute the largest contribution to the net ecosystem exchange. This would suggest that abiotic and methanol degradation processes play a more important role than previously assumed and that measurements focusing only on the growing period could strongly bias the annual methanol budget of ecosystems by neglecting these processes. This highlights the need to develop long-term measurements in order to obtain accurate estimates of net methanol exchanges at the ecosystem level.

Different processes responsible for methanol degradation and operating at the soil or leaf level were suggested, but none of them could ultimately be retained. Additional measurements are needed to elucidate the precise origin of this degradation.

These results suggest that the adsorption/desorption and degradation processes play a more important role than previously expected in the site methanol balance. In addition, these processes could affect other organic compounds that are similarly or more soluble than methanol as, for example, the precursors to secondary organic aerosol issue from isoprene oxidation, from aromatic compounds... This needs to be investigated for different types of ecosystems using long-term (at least one season) continuous measurements. The model and the procedure presented here could be adapted for each site and each compound in order to separate the abiotic and biogenic component of the fluxes.

Chapter 6

Conclusions & Perspectives

1 General conclusions

This study is one of the first to propose continuous measurements at stand level over 2 years of BVOC exchange between a mixed temperate forest and the atmosphere. The investigations were focused on the isoprene, monoterpene and methanol exchanges, considered the most abundant compounds released by forest ecosystems. At the global scale, isoprene and monoterpenes dominate the total BVOC emissions, and methanol is the most abundant NMVOC compound in the atmosphere. Due to their reactivity with the main oxidants in the atmosphere ($OH^{\cdot}$, O_3, $NO_3^{\cdot}$), these BVOCs are thought to contribute significantly to atmospheric chemistry. In order to estimate BVOC emissions from terrestrial vegetation, several models have been developed (Guenther et al. 2006; Bey et al. 2001; Stavrakou et al. 2011) based on empirical observation. Accurate, stand-level, long-term, non-enclosure BVOC flux measurements are required in order to better calibrate and validate these models and improve their accuracy. In addition, the long-term flux measurement perspective will help to improve knowledge about the processes driving VOC emission/deposition, currently documented using cuvette or chamber techniques, but scarcely or sporadically observed at the ecosystem scale. These processes are not fully understood at the ecosystem scale, which may result in large uncertainties in the modelling approach.

The first, technical challenge for this analysis was to measure the isoprene and monoterpenes exchange above the canopy knowing that these compounds have a short lifetime; the BVOC detection techniques had to sensitive and have a fast response time. This problem was solved thanks to the use of the DEC by mass scanning method and the use of a PTR-MS, the most developed on-line analyser of VOC apart from the very recently developed PTR-time-of-flight (PTR-TOF) mass spectrometer. Particular attention was paid to technical/methodological aspects in order to:

- limit gaps in the data set by ensuring a rigorous maintenance (e.g., filters changing, remote control monitoring)
- ensure the quality of data concentrations through frequent PTR-MS calibration, zero-air measurements and data synchronisation between the sonic anemometer and the PTR-MS
- reduce the time for air transported to the analyser in order to limit the chemical degradation of BVOCs
- limit adsorption/desorption effects of isoprene, monoterpenes and (especially) methanol onto the walls of the sampling line; this wall effect was limited by heating the line and filters
- limit the high frequency damping of BVOC mixing ratio fluctuations in the tube and propose adequate spectral corrections to compensate this attenuation.

Another challenge in the analysis of BVOC emission/deposition at Vielsalm was the heterogeneity of the site in terms of vegetation cover and the subsequent difficulty in clearly identifying the BVOC emitters. Adequate data filtering and the use of a footprint model, combined with the land-use map, helped to overcome this problem.

1.1 Isoprene and monoterpene emissions

The combination of a footprint model with the land use map enabled us to discover that monoterpenes were released mainly by *Fagus sylvatica*. *Abies alba* and *Picea abies* contributed to the monoterpene emissions, but in lower proportions. In contrast to reports in the literature (Moukhtar et al., 2006), we found that *Abies alba* was probably the main emitter of isoprene. This assumption was recently confirmed by Pokorska et al. (2012) in their cuvette study.

1.1.1 Diurnal emissions

The most important diurnal drivers of isoprene and monoterpene emissions observed at the Vielsalm site were temperature and light. These drivers were parameterized using the well-known empirical relationships proposed by Guenther et al. 1993. We propose, however, an original adaptation of the two fitting-parameter light dependence function described by Guenther et al. (1993). We showed that these parameters were not independent and therefore proposed a formulation with a unique fitting parameter. This new formulation would simplify the light parametrisation used in the MEGAN model (Guenther et al. 2006). The establish-

ment of the temperature and light dependence function allowed the standard emission factors for isoprene and monoterpenes to be computed. This enable us (Muller et al., submitted) to react to the paper published by Hewitt et al. (2012) who claimed that isoprene emissions are under circadian control, resulting in a reduction of isoprene emissions worldwide when this circadian control is taken into account in emission algorithms. Muller et al. (submitted) showed that the circadian control observed with oil palm appears to be an extreme case compared with our measurements and therefore can not be included in estimates of global terrestrial isoprene emissions.

The *de novo* biosynthesis of isoprene/monoterpenes in leaves was the main process driving the observed emissions. This was reflected both by the exponential dependence of fluxes on temperature (due to the temperature activation of enzymatic reactions in the DOXP/MEP biosynthetic pathways) and by the dependence of fluxes on light and on GPP (light acting on GPP and providing higher inputs in the DOXP/MEP biosynthetic pathways.

We interpreted the ratio between isoprene/monoterpene fluxes and GPP as the enzyme activity of these BVOC production pathways. We showed that this activity decreased throughout the growing season and was probably modulated by leaf acclimation to environmental conditions. For monoterpenes, released mainly by beeches, leaf senescence and acclimation could take place simultaneously, especially in September. In September, at high GPP, BVOC fluxes no longer depended on GPP. The seasonal decrease in enzymatic activity and the saturation in the substrate of this enzymatic activity at a given GPP threshold could explain this behavior.

In addition to the seasonal trend, the isoprene/monoterpene flux was greater under cloudy conditions than under clear sky conditions with equivalent temperature and total radiation. The better penetration of diffuse radiation through the canopy compared with direct radiation could explain this effect, which is well known in the CO_2 flux community. The observation of this effect using cuvette or chamber measurements is more difficult, clearly illustrating the need for BVOC flux measurements at the ecosystem scale. The whole-canopy isoprene enzymatic activity of the metabolic production pathway, however, was observed to be lower under cloudy conditions than under clear sky conditions at equivalent temperature. A more important contribution of shade needles, associated with their expected lower enzymatic activity, would explain the observed reduced whole-canopy enzymatic activity in cloudy conditions. The fact that we observed an increase in emissions under cloudy conditions suggests that the former effect is more important than the latter one. Both these mechanisms indicate a potential impact on the climate, but the interactions between the aerosol concentrations and the BVOC emissions are complex. An increase in the aerosol concentrations, induced by global

warming increasing the BVOC emissions, leads to more diffused radiation that enhances the BVOC emissions but also results in more radiative cooling, which reduces the BVOC emissions. Further investigation is needed to understand more precisely this potential climate feedback and to reduce the uncertainty about the global BVOC budget and the global biogenic aerosols budget.

1.1.2 Nocturnal emissions

During the night there were no isoprene emissions and only a small monoterpene emissions, one order of magnitude lower than during the day. The main nocturnal driver of the monoterpene emissions was temperature. The absence of carbon assimilation by the vegetation rules out *de novo* biosynthetic production as an explanation of these emissions, pointing to the temperature-dependant volatilization of the monoteprenes from storage organs of coniferous species (no storage organs for beeches) as the process likely to be responsible for these emissions. In addition, soil could contribute to nocturnal emissions through litter decomposition, from roots or micro-organisms. These whole potential sources were also present in the day, but were at least 10 times lower than the *de novo* biosynthetic production.

1.2 Methanol depositions/emissions

Methanol exchange is currently under-represented in published studies despite methanol being one of the most abundant VOCs in the atmosphere. Most papers published to date deal with isoprene and monoterpene measurements. The dataset presented in this thesis contradicted most other studies because our measurements showed the site to be a net sink of methanol for most of the year (apart from spring/early summer), whereas published studies from various ecosystems show methanol emissions for most of the time.

Most of these studies, however, are based on limited datasets that do not cover a large range of climatic and phenological conditions. Recently, Hörtnagl et al. 2011 proposed a year-round follow-up of the methanol exchange above managed temperate mountain grassland. In contrast to this study, their measurements did not show significant methanol deposition, but they found that management events (e.g., grass cutting) were the largest perturbations of methanol exchange. We suggest that between two successive management events (grass cutting), grass growth (producing methanol) could hide or disturb the eventual methanol deposition on water films likely to be present on the grass leaves. Another recent study by Fares et al. (2012),

measuring BVOC exchanges over 1 year above a Valencia orange orchard, showed methanol depositions occurring mainly during the night.

An original simple model was developed in order to identify the mechanisms responsible for methanol depositions/emissions in the short-term and for the sink in the long-term, as observed in our study. The good agreement between the model simulations and the measurements suggested that the main processes controlling methanol exchanges in summer could be, in the short-term, methanol adsorption/deposition by water films on leaf surfaces or on the soil and, in the long term, methanol degradation by methylotrophic bacteria operating at the soil or leaf level and/or by chemical reactions in the water films of methanol in the aqueous-phase with OH radicals. This point remains to be clarified.

The production of methanol associated with leaf development, as generally observed in previous studies, was also detected at our site, but it was limited to a short period in spring and did not constitute the largest contribution to the net ecosystem exchange. This would suggest that abiotic and methanol degradation processes play a more important role than previously assumed and that measurements focusing only on the growing period could strongly bias the annual methanol budget of ecosystems by neglecting these processes. This highlights the need for long-term measurements in order to obtain accurate estimates of net methanol exchanges at the ecosystem level. Our observations show that the EC method is the most appropriate for studying methanol depositions and that cuvette measurements might be less efficient because of the presence of multiple sources and sinks in the ecosystem and the perturbation induced by the cuvette environment itself.

The dataset of methanol mixing ratio obtained at Vielsalm helped partly to validate a new algorithm (MEGANv2.1) developed by Stavrakou et al. (2011) for estimating methanol emissions from plants. This algorithm is based on net ecosystem fluxes, and accounts for the effects of light, temperature, and leaf age the same way as for isoprene emissions in the MEGAN model developed by Guenther et al. (2006).

1.3 Friction velocity effect

In this thesis, for some BVOC species we were also confronted with the underestimation problem that affects the CO_2 fluxes measured by EC during the night (Aubinet et al., 2012b). This problem results mainly from atmospheric processes that hinder the turbulent transport of CO_2. Nocturnal CO_2 is produced mainly by soil respiration that works independently of the presence or absence of turbulent transport. In our case, a careful and specific analysis was

needed for each BVOC to determine whether or not the flux decrease under low turbulence was the result of a measurement artifact or of a real flux slowing down. This analysis permits to complete the redaction of the Chapter 5 (Nighttime flux corrections) of Aubinet et al. (2012) by highlighting the impact of the night flux error on fluxes other than the CO_2 flux. In this context, monoterpenes and methanol fluxes present interestingly contrasted responses. On the one hand, monoterpene fluxes, after standardization with temperature in order to avoid any confounding effect of this parameter with friction velocity, decreased under low turbulence in the same way as for CO_2 fluxes. As the monoterpenes were released from storage organs independently of the presence or absence of turbulent transport, it appeared that this decrease was due to a measurement artifact. On the other hand, methanol deposition fluxes were also found to depend on friction velocity but, in this case, it appeared that this was due to a real process because the flux was not controlled by production/desorption process, resulting instead from a diffusive exchange between a reservoir (water films) and the atmosphere.

During the day, in contrast to the CO_2 fluxes, an increase in temperature- and radiation-standardized isoprene/monoterpene fluxes (mainly isoprene) with friction velocity was observed. This surprising result was very difficult to explain without complementary measurements, but two assumptions were put forward. The first supposed a stimulation of isoprene emissions by exposure to O_3, the O_3 concentration in the canopy increasing with friction velocity. The second assumption involved the effect of the chemical destruction of isoprene that depends on its chemical lifetime and the effectiveness of the turbulent transport between the emitter and the measurement point.

2 Perspectives

Several hypotheses have been put forward in this work that need to be confirmed and new questions have been raised that require more investigation before they can be answered. Here, we describe new activities being undertaken outside our work and suggest possible additional measurements that could be considered.

The EC technique has great advantages, but it has also some limits. It gives only the net flux exchanged between the ecosystem and the atmosphere, and therefore, the partitioning of this net flux between its different components, such as biological or physical emissions/sinks at the leaf and/or soil level, is often a difficult task, as can be seen in this work. The joint use of leaf enclosure methods and soil chambers together with EC is probably the best way to gain insights into this source/sink distribution, but this type of work would be very expensive and

labour intensive because of the presence at Vielsalm of four potential BVOC emitter species with a canopy height of at least 30 m. To handle statistically the natural variability of BVOC emission for each species, it would be necessary to measure the BVOC emissions from several replicates of each species on 'typical' branches/leaves, representing environmental conditions. Leaves should be sampled in sunlight and shaded positions, since the SEF may vary with illumination and temperature history within the canopy. With two replicates for each species and with six cuvettes by replicate, we would need at least 48 cuvettes, and that is without even taking soil chambers into account! This type of activity is not scheduled in the short-term at Vielsalm but other more pragmatic lines of action have been initiated.

First, a vertical profile of ambient BVOC concentration measurements was installed in 2011 with the aim of answering partly or totally, several questions raised in this thesis. A vertical profile of ozone (O_3), nitrogen oxides (NO_x) and hydroxyl radical (OH) would also be useful for this task.

Second, a BVOC DEC system was installed in the trunk-space in 2011, the PTR-MS being shared between above and below-canopy measurements. This system should allow estimates to be made of the contribution of the soil to the net exchange. It remains to be proved, however, that these measurements are valid because under-canopy conditions often challenge the underlying assumptions for turbulent flux computation, especially for reduced sampling rates inherent in the DEC method. Nevertheless, examples in the literature give hope that, even for a close canopy like that at Vielsalm, fluxes could be valid (Launiainen et al., 2005; Misson et al., 2007; Subke and Tenhunen, 2004).

The analysis of the data from these two systems is ongoing, but the results should help to disentangle the respective contribution of the leaves and the soil surface to the net exchange for all measured BVOCs, especially for those investigated in this work. For example, the seasonal and diurnal evolution of a specific BVOC profile and trunk-space flux and the cross-comparison among different BVOCs families (e.g., soluble or not, with expected biogenic sinks or not) will provide useful information.

With regard to methanol, more experimental investigations and an improvement of the adsorption/desorption model are needed. We are left with the following questions: Do methylotrophic bacteria exist? If so, where are they located (e.g., on leaves, in the ground)? What is the population density of these bacteria? Bacterial identification on leaf and ground surfaces would be the most direct way of answering these questions. Leaf wetness measurements would also be useful; they could be carried out using electrodes clipped to the leaf surfaces (Burkhardt et al. 2009). The measurement of the electrical conductance would allow leaf wet-

ness to be better quantified and improve Equation (5) in Chapter 4. In addition, the installation of soil humidity sensors at ground surface would improve measurements of the surface water balance of the ecosystem.

Other important and more general questions include: Are the depositions also important for other forested sites in similar climates? Are these depositions a common feature in all ecosystems under various climatic conditions and what is their importance in the annual methanol budget of these ecosystems? Are the depositions also important for other soluble OVOCs, such as acetone and acetaldehyde? The coupling between this model and a biogenic methanol emission model would allow the deposition and emission contributions to the methanol fluxes to be separated more accurately. The model should be tested further with methanol flux measurements from sites other than Vielsalm. It should also be tested for other soluble BVOCs, such as acetaldehyde and acetone, although in contrast to methanol a stomatal deposition is known to exist for these compounds. Datasets are now available and synthesis activities are starting in which the analysis proposed in Chapter 5 could be used as a guideline.

The newly developed PTR-TOF (Graus et al., 2010; Jordan et al., 2009; Ruuskanen et al., 2011) improves the EC measurements of VOCs. The PTR-TOF can measure 10 Hz time series of full mass spectra with a mass accuracy sufficient to determine chemical formulas. The features of the PTR-TOF enable simultaneous measurements to be made of the EC fluxes of all protonated VOCs, no longer restricting the flux measurements to a pre-selected set of a limited number of compounds, as in the case of a classic PTR-MS. Determining simultaneous EC fluxes will open up the possibility of screening fluxes for a wide range of VOCs and will lead to an improved understanding of VOC biosphere-atmosphere-interactions. Unfortunately, this technology is still very expensive.

In this thesis, we have not investigated the effect of plant stress on emissions although we know that stress can drastically alter the emission capacities of plants and change their BVOC emission pattern. No obvious evidence of severe stress conditions was observed during the 2 years of our work. If severe abiotic stress such as drought or heat stress can be discarded, based on our measurements, however, we have to recognized that ozone and biotic stress were not investigated, even if obvious damages to the leaves was never observed. Insights into stress impact could be gained by measuring of turbulent above-canopy ozone fluxes and by a following-up plant physiological stress markers (e.g., using physiological and biochemical parameters indicative of the stress experienced by the plant, such as: chlorophyll fluorescence and oxidative damage markers). These improvements are not likely to be made in the near

future at Vielsalm, but will be developed, we hope, in future BVOC investigations conducted by the research teams involved in this thesis work.

Chapter 7

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Curriculum Vitae

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Current position

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Academic background

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Orientation: Geophysics
Grade : High Distinction
University of Liège, Belgium

Thesis *Etude des flux de CO_2 échangés par une jeune forêt mixte dans la région de Jalhay au lieu-dit "La Robinette"*

2003-2004 **Master of Physics**
Grade : Distinction
University of Namur, Belgium

Thesis *Etude in situ de films minces Co/GeS et Co/$SnSe_2$ par spectroscopie de photoélectrons : mode de croissance et réactivité*

Working experience

2007-2011 **Research assistant** at **Gembloux Agro-Bio** Tech, University of Liège, Unité de Physique des Bio-systèmes.

Project: **Infrastructure for Measurements of the European Carbon Cycle** (**IMECC**-6th Framework Programme of the European Commission)

Project: **Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems** (**IMPECVOC**-Belgian Federal Science Policy)

Training course

2004 Within the framework of my Master thesis: one week of intensive work in the infrastructures of the Hamburg Synchrotron radiation Laboratory (Hasylab-DESY) Hamburg, Germany.

International publications

2012 **Q. Laffineur**, M. Aubinet, N. Schoon, C. Amelynck, J.-F. Muller, J. Dewulf, K. Steppe, B. Heinesch, *Impact of diffuse light on isoprene and monoterpene emissions from a mixed temperate forest*, Atmospheric Environment, Submitted.

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International conference speaker

2012 **Q. Laffineur**, *What can we learn from LIDAR-ceilometer measurements?*, Royal Meteorological Institute of Belgium (RMI), 27 June 2012.

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