Max-Planck-Institut für
Biogeochemie

TECHNICAL REPORTS
12

Quantifying the terrestrial carbon budget of middle latitude ecosystems: the role of Volatile Organic Compounds

by
Krzysztof Stanislaw Katrynski

ISSN 1615-7400

Technical Reports - Max-Planck-Institut für Biogeochemie 12, 2008

Max-Planck-Institut für Biogeochemie
P.O.Box 10 01 64
07701 Jena/Germany
phone: +49 3641 576-0
fax: + 49 3641 577300
http://www.bgc-jena.mpg.de

Quantifying the terrestrial carbon budget of middle latitude ecosystems: the role of Volatile Organic Compounds

Dissertation zur Erlangung des Doktorgrades der
Naturwissenschaften im Fachbereich Geowissenschaften
der Universität Hamburg

vorgelegt von

Krzysztof Stanislaw Katrynski
aus Ostrowiec Swietokrzyski, Polen

Hamburg 2008

Krzysztof Stanislaw Katrynski
Max-Planck-Institute for Biogeochemistry
Hans-Knöll-Str. 10
07745 Jena
Germany

Ph.D. Thesis Supervisors

Prof. Dr. Martin Heimann, *Max-Planck-Institute for Biogeochemistry*
Dr. Armin Jordan, *Max-Planck-Institute for Biogeochemistry*

Ph.D. advisory committee chair

Prof. Dr. Juergen Kesselmeier, *Max-Planck-Institute for Chemistry*

Als Dissertation angenommen
vom Fachbereich Geowissenschafter der Universität Hamburg
auf Grund der Gutachten von

Prof. Dr. Guy Brasseur
und
Prof. Dr. Martin Heimann

Hamburg, den 01. Februar 2008
Professor Dr. Kay-Christian Emeis
(Leiter des Department Geowissenschaften)

ABSTRACT

A substantial amount of carbon flux between biosphere and atmosphere belongs to photosynthesis and respiration activities. During daytime, leaves are affected by sunlight, take up CO_2 from the atmosphere and produce organic carbon for growth. A part of the carbon which is emitted by terrestrial vegetation as biogenic volatile organic compounds (VOC) contributes to the oxidative capacity of the atmosphere, to particle production and to the carbon cycle. With regard to the carbon budget of the terrestrial biosphere, a release of these carbon compounds is regarded as a loss of photosynthetically fixed carbon. The significance of this loss for the regional and global carbon cycles is controversial. I estimated the amount of VOC carbon emitted in relation to the CO_2 taken up, based on my own airborne and micrometeorological flux measurements of VOC concentrations and CO_2 exchange, and on the literature and model data. During two measurement campaigns over the Siberian region a series of experiments was performed. While VOC flux estimates are small in relation to net primary productivity, the amount of carbon lost as VOC emissions might be highly significant relative to net ecosystem productivity. In fact, VOC losses are of the same order of magnitude as net biome productivity. Although it should be assumed that large amounts of these reemissions are recycled within the biosphere, a substantial part can be assumed to be lost into longer-lived oxidation products that are lost from the terrestrial biosphere by transport. However, our current knowledge and measurement technique does not yet allow a reliable estimation of this carbon.

CONTENTS

1.1 The Global Carbon Cycle

Understanding the cycling of carbon, water and nitrogen is a key process in understanding the ecosystem, the biosphere and the entire Earth System. Human activities dramatically change cycles. Fossil fuel combustion has increased the emission of CO_2, CO and other trace gases. These changes affect ecosystems from local, through regional and finally to global change.

Photosynthetic uptake of carbon from the atmosphere and oceans provides the fuel for most biotic processes. The reduced carbon makes up about half of the mass of the Earth's organic matter. Biological systems give off CO_2 when they use organic carbon for growth and metabolism. The controls over the carbon cycle depend on the time scale, ranging from millions of years, by which cycling is controlled by movements of the Earth's crust, to seconds, by which cycling is controlled by the photosynthetic rate and surface-air exchange.

Carbon is distributed among the atmosphere, oceans, land (soils and vegetation), and sediments and rocks. Atmospheric carbon, which consists primarily of CO_2, is the smallest but most dynamic of these pools.

Sedimentary carbonates represent by far the planet's largest carbon pool with persistent carbon stocks that account for more than 60000000 Pg (Falkowski et al., 2000). Fossil fuel reserves and the world's oceans also represent huge carbon reservoirs that account for up to 10,000 and 39,000 Pg of carbon (Schlesinger, 2003). The ocean's surface waters that interact with the atmosphere contain about 1,000 Pg carbon, similar to the quantity in the atmosphere, i.e. 780 Pg C (IPCC 1996, 2001, 2007). The capacity of the ocean to take up carbon is constrained by three categories of processes that operate at different time scales. In the short term, the surface exchange rate depends on wind speed, surface temperature, and the CO_2 concentration of surface waters. The surface of water is a relatively small pool of water that exchanges comparatively slowly with deeper layers because the warm, low salinity layers of the surface water is less dense than deeper layers. Carbon that enters the surface waters is transported slowly to the depths by two major mechanisms. Organic detritus and its calcium carbonate ($CaCO_3$), skeletal content, which form in the euphotic zone, sink to deeper waters, a process termed the biological pump. Bottom-water formation in the polar seas transports dissolved carbon to the depths, a process termed the solubility pump. The terrestrial biosphere contains the largest biological reservoir of carbon, around 2,850 Pg. However, regardless of their small size, these reservoirs play a major part in the planet's short-term circulation of carbon. Atmospheric carbon is primarily present in the form of the inorganic compound CO_2. The amount of carbon represented by CH_4, CO and Non-methane Organic Carbon (NMOCs) is less than 1% of the total atmospheric carbon (IPCC, 1996). Since CO and NMOCs are known to contribute predominantly to the methane and ozone budget (both known as greenhouse gases) they may influence the planet's radiative balance as well (Seinfeld and Pandis, 1997; Atkinson, 2000; Finlayson-Pitts and Pitts, 2000).

There is nearly as much carbon in terrestrial vegetation as in the atmosphere, and there is at least twice as much carbon in soils as in the atmosphere. The terrestrial net primary production (NPP) is slightly greater than that in the ocean, but due to the much larger plant biomass and land, terrestrial plant carbon has a turnover time of about 11 years, compared to 2 to 3 weeks in the ocean. Photosynthetically fixed carbon in chloroplasts turns over on time scales of seconds through photorespiration. Leaves and roots are replaced over weeks to years, and wood is replaced over decades. Carbon in rocks and surface sediments accounts for well over 99% of the Earth's carbon (10^7Pg) (Schlesinger, 1997; Reeburgh, 1997).

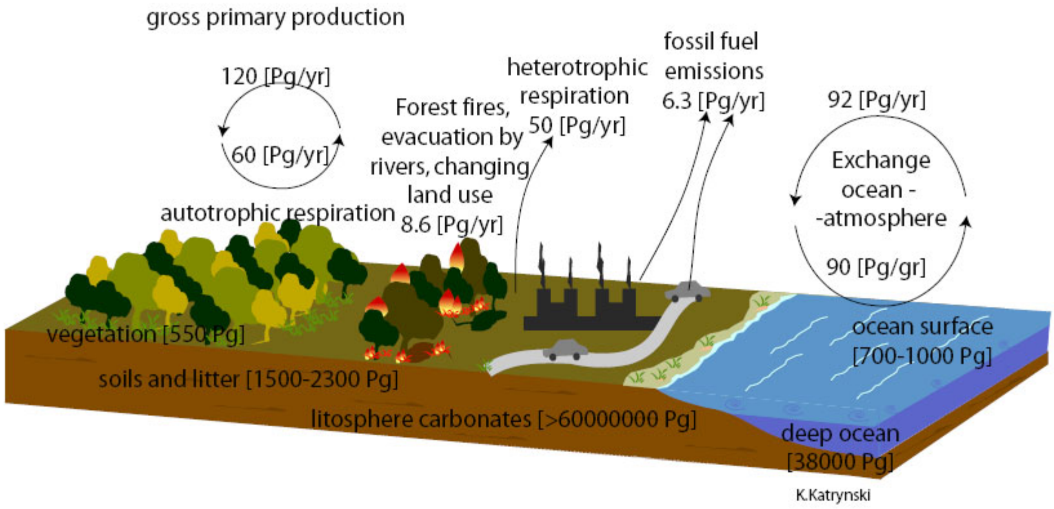


Fig. 1.1 Biogeochemical cycling of carbon within four major reservoirs: atmosphere, oceans, fossil fuels and terrestrial ecosystems (IPCC, 2001).

NPP is about half the gross primary production (GPP; i.e. photosynthetic carbon gain) on land 60 Pg C yr^{-1} (Lloyd and Farquhar, 1996; Waring et al., 1998) out of 120 PgC yr^{-1} (Ciais et al.,1997; Prentice et al. 2001). Around 10 Pg yr^{-1} is left within the ecosystem and is referred to as the net ecosystem production (IPCC 2001). Some part of the carbon is lost during the combustion process (fires), some part is dissolved in rivers and by the harvesting of forest. The ultimate residual of carbon emitted or deposited by an ecosystem is referred to as the net biome production. In accordance with the IPCC 2001 report, during the time period of 1980-1989, the terrestrial sink was estimated at 0.2 (±0.7 PgC yr^{-1}). However, for the period 1989-1998, the terrestrial sink increased to 1.4 (±0.7 PgC yr^{-1}) (IPCC, 2001). On the other hand there are still large uncertainties surrounding the quantity of carbon which is stored and some pathways are not well understood for the carbon cycle.

Some part of this carbon might be realized as Volatile Organic Compounds. According to Kesselmeier et al., 2002b, the emission of these compounds from an ecosystem might be highly significant in relation to net ecosystem productivity (NEP) and is in the same order of magnitude as the net biome productivity (NBP). Since the ultimate atmospheric fate of most of these compounds is oxidation to carbon dioxide, these CO_2 precursors may need to be included in efforts to understand the processes controlling atmospheric global CO_2 concentrations.

In the following chapter a short overview is given on the implication of VOC, their process of emission and chemical pathways into the atmosphere.

1.2 Objective of this work

The main reason for this work was a step in understanding the atmospheric budget of carbon and processes that can predict the effects of pollution control and increasing CO_2. These processes will require an understanding of the trace gas emission from plants. This information will focus on research and provide backgrounds for understanding atmospheric chemistry, the process of reactions and how changes in the atmosphere will affect the natural process. Volatile organic compounds (VOC) are important constituents of the atmosphere. They directly or indirectly affect the oxidative capacity of the atmosphere and thus influence the atmospheric abundance of many other important trace gases. Some VOC have a direct impact on the environment. However, the most important impact of VOC results from complex chemical reactions in the atmosphere. The relation between VOC emissions, atmospheric VOC concentrations and photo-oxidant levels is quite complex. The actual level of VOC and photo-oxidants in the atmosphere is the result of complex interactions between the atmospheric transport of emissions and chemical reactions. Reduction and control strategies for trace gases require a detailed understanding of the processes.

As a consequence of the direct and indirect participation of VOC in most of the relevant reaction cycles it is impossible to understand the chemistry of the troposphere without a quantitative knowledge of the chemistry, distribution and budgets of VOC. For similar reasons studies of atmospheric VOC can also be valuable for atmospheric chemical and transport processes.

Chapter 2 provides an overview and background about biosphere-atmosphere exchange of non-methane organic carbon, a process present and understood in the atmosphere. This chapter also describes the chemical structure, biosynthesis processes and reaction of biogenic volatile organic compounds, as well as inventories of biogenic VOC emission on a global scale.

Chapter 3 gives an overview about the respective experiments performed in the Siberian forest and will discuss the results obtained for BVOC in two measurement campaigns. As the Siberian forest is a large ecosystem which is still poorly understood, a series of aircraft and tower measurement campaigns were performed to gain knowledge of this ecosystem. Information about the process of land classification configuration and data analysis was given. The main achievement of Chapter 3 is information about the concentrations and composition of Biogenic Volatile Compounds over selected sites. The series of measurements were performed over the forest canopy.

Chapter 4 also focuses on the measurements of BVOC, i.e. aircraft measurements in Russia. This chapter presents vertical profiles of VOC obtained by aircraft measurements during measurement campaigns in 2004 and 2005 and their relation to the budget of VOC over a regional scale. A simplified model and techniques have been used to determine fluxes and relation between GPP and BVOC.

Chapter 5 focuses on the measurements in the lower troposphere over north-eastern Poland by using light aircraft and long-term observation of the changes in the regional mixing ratio concentration of trace gases. The results obtained for seasonal changes of selected trace gases have been presented. As the regional observations are important for global changes, this series of experiments is important due to sparse information about the mixing ratios of trace gases over the eastern part of Europe.

2. Volatile Organic Compounds and their atmospheric chemistry

Most volatile organic compounds are emitted by the biosphere with a major impact on the chemistry of the atmospheric boundary layer (Guenther et al., 1995; Monson and Holland 2001; Kesselmeier and Staudt, 1999). In 1960, Went first proposed that natural emission of VOCs from trees and other vegetation could have a significant effect on the chemistry of the Earth's atmosphere. Since that study, numerous researchers have investigated the composition of natural VOCs (Rasmusen and Went, 1965; Rasmussen 1970), their rate of emission (Tingey et al., 1991; Arnts and Meeks 1981; Guenther et al., 1995; Lamb et al. 1983, 1985, 1993) and the distribution of these compounds and their oxidation products in the atmosphere (Isidorov et al., 1985; Fehsenfeld et al., 1992; Montzka et al., 1993, 1995; Yokouchi, 1994). The impact of short-lived VOC extends over the entire troposphere. Due to their reactions with the hydroxyl radical (OH), ozone (O_3), and nitrate (NO_3), they form longer lived intermediates such as carbon monoxide, reactive nitrogen species, aerosols and various carbonyl and carboxyl compounds (e.g. Poisson et al., 2000), the last-named representing a large fraction of acidity in precipitation, particularly in remote tropical areas (Keene et al., 1983).

The term biogenic volatile organic compounds (BVOC) includes organic atmospheric trace gases excluding carbon dioxide and monoxide. Focusing on hydrocarbons but excluding methane, the term non-methane hydrocarbons (NMHC) emerged, while VOCs without methane are termed non-methane VOC (NMVOC). Hence, large numbers of groups of saturated, unsaturated, and oxygenated derivatives are included within VOC. BVOC include the isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids. Emission inventories showed isoprene and monoterpenes as the most dominant compounds. Alcohols and carbonyls are the second groups of compounds after isoprenoids which are the most predominant groups (Kesselmeier et al. 1997) However, one of the consequences of the heterogeneity of VOC is the large number of acronyms in use, each defining a special class of VOC, such as BOVOC (biogenic oxygenated VOC), ORVOC (other reactive VOC), BVOC (biogenic VOC), AVOC (anthropogenic VOC), and finally OVOC (other VOC) for the rest, usually defined by a different lifetime as the main criterion. The last acronym is still open for defining new criteria. The high diversity of VOC, sometimes also falsely summarized in the subgroup non-methane hydrocarbons (NMHC), points to one of the main problems in VOC research, e.g. the large number of different compounds coupled to an equivalent number. For a better knowledge of the concentration and emission of all these compounds in the atmosphere, we need a better description of the exchange processes on a local and regional scale (especially in the poorly investigated Siberian region) and a better understanding of the factors influencing the release of VOC from different biogenic sources (Kimmerer and Kozlowski, 1982; Kimmerer and MacDonald, 1987; Arey et al., 1991 ; Loreto and Sharkey, 1993a; Juuti et al., 1990; Parusel, 1996; Wedel, 1997; Bertin and Staudt, 1996; Staudt, 1997; Kesselmeier et al., 1998a).

There have been a number of efforts to complete inventories of biogenic VOC emission (Lamb et al., 1987, 1993 and Guenther et al., 1995). Emission rate measurements from individual plant species are used with empirical algorithms that account for temperature and for isoprene, light effects to scale up entire geographical regions, based on land use data and biomass density factors. Uncertainties in these inventories are large (Lamb et al., 1993). The last estimated inventories of BVOC for the USA range from 29 to 51 Tg yr^{-1}. However, as a result we have only an approximation, because mitochondrial respiration in leaves declines in the light, when much of the energy for metabolism comes directly from carbon fixation.

On a global scale, the largest BVOC emissions occur in the tropics, with isoprene being the dominant compound emitted. These result from a combination of high temperatures and large biomass densities. On a global basis BVOC emissions far out-traced those of anthropogenic VOC (see Table 2.1 and Table 2.2).

Sources	Isoprene	Monoterpenes	ORVOC[*]	ORVOC[**]	Total VOC
Woods	372	95	177	177	**821**
Crops	24	6	45	45	**120**
Shrubs	103	25	33	33	**194**
Ocean	0	0	2.5	2.5	**5**
Other	4	1	2	2	**9**
Total	**503**	**127**	**260**	**260**	**1150**

Table 2.1: Global Biogenic VOC emission rate estimates by source and class of compounds (Tg yr^{-1})$^{1)}$.

[*]) Defined as having lifetimes <1 day under typical conditions;

[**]) Defined as having lifetimes >1 day under typical conditions;

[1]) Source: Guenther et al. (1995)

Activity	Emission (Tg yr^{-1})
Fuel production/distribution	
Petroleum	8
Natural gas	2
Oil refining	5
Gasoline distribution	2,5
Fuel consumption:	
Coal	3,5
Wood	25
Crop residues (including waste)	14.5
Charcoal	2.5
Dung cakes	3
Road transport	36
Chemical industry	2
Solvent use	20
Uncontrolled waste burning	8
Other	10
Total	142

Table 2.2: Estimated Global Emissions of Anthropogenic VOC.

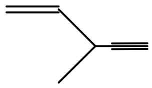
[2]) Source: Middleton et al. (1995)

BVOC are much more reactive than volatile organics that are emitted by anthropogenic activities (Atkinson and Arey, 2003). On a global scale, the emission of BVOC exceeds the emission from anthropogenic sources by a factor of 10 (WMO, 1995).

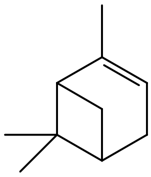
Several thousands of different biogenic VOC and their oxidation products have been identified by analytical techniques (Isidorov et al., 1985; Montzka et al., 1993, 1995; Helas et al., 1997; Yokouchi, 1994; Fall, 1999).

Measurements in woods and agricultural areas coupled with emission studies from selected individual trees and crops have demonstrated the ubiquitous nature of biogenic emissions and the huge number of organic compounds that can be emitted into the atmosphere.

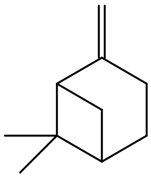
The best known are ethene, isoprene and monoterpenes emitted by terrestrial plants. Each of the compounds is characterized by an olefin double bond that renders the molecule highly reactive in the atmosphere. The typical compound which is emitted by deciduous trees is isoprene C_5H_8. On the other hand, typical compounds that are emitted are terpenes such α-pinene and β-pinene (Rasmussen and Went, 1965).



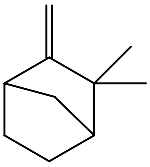
Isoprene



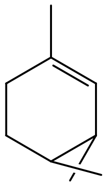
α-Pinene



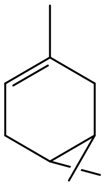
β-Pinene



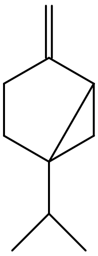
Camphene



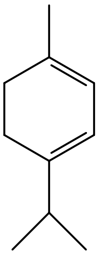
2-Carene



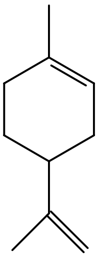
3-Carene



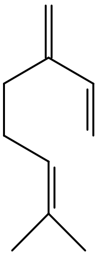
Sabinene



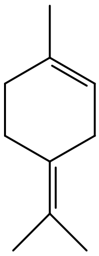
α-Terpinene



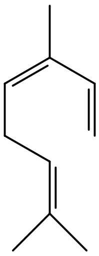
Limonene



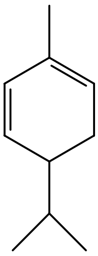
Myrcene



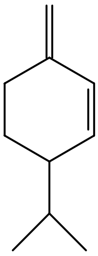
Terpinolene



cis-Ocimene



α-Phellandrene



β – Phellandrene

Table 2.3 Examples of Biogenic Volatile Organic Compounds.

2.1 Monoterpenes and isoprene

Isoprene and monoterpenes belong to the biochemical class of isoprenoids (or terpenoids), whose carbon skeletons are composed of characteristic C_5 units (McGarvey and Croteau, 1995).

Isoprene is the major hydrocarbon emitted into the atmosphere by vegetation and represents a major loss of carbon for plants which has an impact on tropospheric chemistry. It is emitted from a wide variety of mostly deciduous vegetation in the presence of photosynthetically active radiation (PAR), exhibiting a strong increase in emission as temperature increases. Some emission of isoprene is reported from conifer species. The biochemical and biophysical processes controlling the rate of these emissions also appear to be quite distinct. Isoprene emission is regarded as a photorespiration and is photosynthesis-dependent. It has a major role in regulating the oxidative capacity of the troposphere, due to high reaction with OH radical. Isoprene can potentially reduce the effectiveness of methane removal from the troposphere. Isoprene is never stored in plants after its production, but is rapidly lost by volatilization and emission into the atmosphere. Isoprene-emitting species occur in many plants, although out many functional type, but they are more often found in woody plant species than in herbs and crops. They are particularly common in the families *Salicaceae*, *Fagaceae* and *Palmae*, as well as in the genus *Picea* (spruces) and diverse ferns (Sharkey, 1996b; Tingey et al., 1987). However, there are also important exceptions. For example, within the group of evergreen oaks growing in the Mediterranean climate, some species (*Quercus agrifolia*, California live oak) emit exclusively isoprene and others (*Quercusilex*, the European holm oak; *Quercuscoccifera*, the European kermes oak) exclusively monoterpenes, whereas *Quercussuber* (European cork oak), ignoring some trace emissions, emits neither isoprene nor monoterpenes (Staudt et al., 1993; Pio et al., 1993, 1996; Staudt and Seufert, 1995; Seufert et al., 1995; Hansen and Seufert, 1996; Steinbrecher et al., 1997; Kesselmeier et al., 1996, 1997b, 1998b; Bertin et al., 1997; Staudt and Bertin, 1998; Kesselmeier and Staudt, 1999).

2.1.1 Monoterpenes

Emission of monoterpenes has been observed from a variety of plants, including pines (e.g. Juuti et al., 1990; Guenther et al., 1994; Street et al., 1997; Staudt et al., 1997), resin in pine forests (e.g. Pio and Valente, 1998) and in some deciduous trees, such as oaks (Benjamin et al., 1996; Street et al., 1997; Kesselmeier et al., 1997b). Monoterpene emission seems to be triggered by biophysical processes associated with the amount of monoterpene material present in the leaf oils and resin ducts or glands and the vapour pressure of the terpene compounds. Monoterpene emission depends strongly on the temperature of the ambient air, but is not dependent on light. The dependence of natural terpene emission on temperature can result in a large variation in the rate of production of biogenic VOC over the course of a growing season. Some analysis of terpene emission indicates an increase by a factor of 1.5 in ambient temperature from 25°C to 35°C for terpene-emitting species (Lamb et al., 1983). Interestingly, increased emissions have been observed when plants are stressed (Fall, 1999). For example, monoterpene emission rates for a *Monotery* pine increased by factors of 10-50 during rough handling. The temperature dependence of monoterpene emission is often taken into account by multiplying the base emission rate at a reference temperature Ts by the factor $e^{[\beta(T-Ts)]}$, where T is the leaf temperature and β is a coefficient that reflects the temperature sensitivity of emissions (Guenther et al., 1993).

Other products such as diterpenes (number of carbon atoms C_{20}), triterpenes (C_{30}), tetraterpenes (C_{40}) and polyterpenes ($>C_{40}$) are important products of plant metabolism i.e. they act as phytoalexins, produce chemical defence compounds, gibberellin hormones, accessory pigments and electron carrier molecules. However, these compounds are non-volatile, so they have no impact on the chemistry of the atmosphere.

2.1.2 Other NMVOC

The atmospheric concentrations of ethane, propane, and butane range from 1 to 3 ppb (Rudolph, 1995; Lindskog, 1997). Part of these compounds comes from natural gas sources in the range of 6 Tg yr^{-1}. A biomass regarded as a further significant source can be burning with ethane emissions of 6.4 Tg yr^{-1} (Rudolph, 1995).

The main terrestrial biogenic sources of C_2–C_4 alkanes are trees, crops, grass and marshland (Altshuller, 1983) with a possible bidirectional exchange for ethane and propane (Hahn et al., 1991; Steinbrecher et al., 1992). Lichens, mosses, and heather are discussed as potentially relevant sources (Isidorov et al., 1994) and might be of importance for some remote areas without dominant higher vegetation.

Significant biogenic sources are known for ethene, propene, and butene, released at rates of 2.63 and 1.13 and $0.41*10^{10}$ molecules $cm^{-2}s^{-1}$ respectively, from a forest (Goldstein et al., 1996). These values suggest that biogenic emissions of propene and butene exceed anthropogenic ones in the North-east of the U.S.A. and, in addition, that biogenic ethene is equivalent to 50% of the anthropogenic contribution. Hakola et al. (1998) have reported seasonal fluctuations of ethene, propene, and butane emissions by two boreal tree species in the range of 0.5–2 $\mu g g^{-1} h^{-1}$ (LDW, leaf dry weight). Such data point to terrestrial vegetation as the most important source, where agriculturally used crops obviously show a higher percentage of ethane and propene emissions of the total non-methane hydrocarbon emissions than forest trees of a large amount of isoprenoids (Parusel, 1996). Soils are also regarded as sources of ethene (Hahn et al., 1991, 1992; Smith and Cook, 1979). Another significant source of C_2–C_4 alkenes is the oceans. In this case alkenes are not directly produced by marine organisms, but are formed by the photochemical degradation of dissolved organic carbon. Depending on the biochemical process, emission of alkenes from the ocean can reach a level of 5 Tg yr^{-1} (Rudolph, 1997). Sufficient understanding of the plant physiological production is, however, only available for the synthesis of ethene. Global extrapolation of emissions from vegetation is a matter of debate (Kesselmeier et al., 2001).

2.2 Atmospheric chemistry of Biogenic Volatile Organic Compounds (BVOC)

Some of the biogenic VOC are relatively simple compounds such as ethane, but most of them are compounds quite complex in structure. Furthermore, they tend to be unsaturated, often with multiple bonds. As a result they are very sensitive to light and highly reactive. They react easily with OH, O_3 and NO_3 (Atkinson et al., 1995). VOC are quite large and of relatively low volatility, and their polar products are even less volatile. This makes elucidating reaction mechanisms and quantifying product yields quite difficult.

The tropospheric lifetimes of organic compounds due to reaction with OH, NO_3 and O_3 can be estimated by combining the rate constant data with estimated ambient tropospheric concentrations of OH, NO_3 and O_3. The resulting tropospheric lifetimes of a number of organic species, including several biogenic hydrocarbons, are given below. In comparison with other organic species, it should be noted that the atmospheric hydrocarbon lifetimes are relatively short. During the daytime, reactions with OH and O_3 are generally important. On the other hand, the NO_3 radical reaction is dominant during the night-time.

Estimated tropospheric lifetimes of Organic Compounds due to reaction with OH, O_3, NO_3.

	OH [a]	O_3 [b]	NO_3 [c]
n-Butane	5.7 days	-	2.8 yr
Propane	6.6 h	1.6 days	4.9 days
Benzene	12 days	-	-
Toluene	2.4 days	-	1.9 yr
m-Xylene	7.4 days	-	200 yr
Formaldehyde	1.5 days	-	80 yr
Acetealdehyde	11 h	-	17 days
Acetone	66 days	-	-
Isoprene	1.7 h	1.3 days	0.8 h
α-Pinene	3.4 h	4.6 days	2.0 h
β-Pinene	2.3 h	1.1 days	4.9 h
Camphene	3.5 h	18 days	1.5 days
2-Carene	2.3 h	1.7 h	36 min
3-Carene	2.1 h	10 h	1.1 h
d-Limonene	1.1 h	1.9 h	53 min
Terpinolene	49 min	17 min	7 min

Table 2.4

a) *12 hour daytime OH concentration of $1.5*10^6$ molecules cm^{-3} (0.06 ppt)*
b) *24 hour average O_3 concentration of $7*10^{11}$ molecules cm^{-3} (30 ppb)*
c) *12 hour NO_3 concentration of $2.4*10^7$ molecules $^{-3}$ (1ppt)*

Adapted from Seinfeld and Pandies, 1998

A detailed description including several reaction mechanisms for the process of degradation of volatile organic compounds can be found in Seinfeld and Pandies (1997), Finlayson-Pitts (2000), Atkinson 2000, Atkinson and Arrey (2003).

The initial reactions of OH radicals, NO_3 radicals and O_3 with NMOC (including BVOC) have been elucidated over the past two decades (see, for example, Atkinson, 1997, 2000; Calvert et al., 2000) and the reactions of BVOC have been previously reviewed by Atkinson and Arey (1998) and Calogirou et al. (1999).

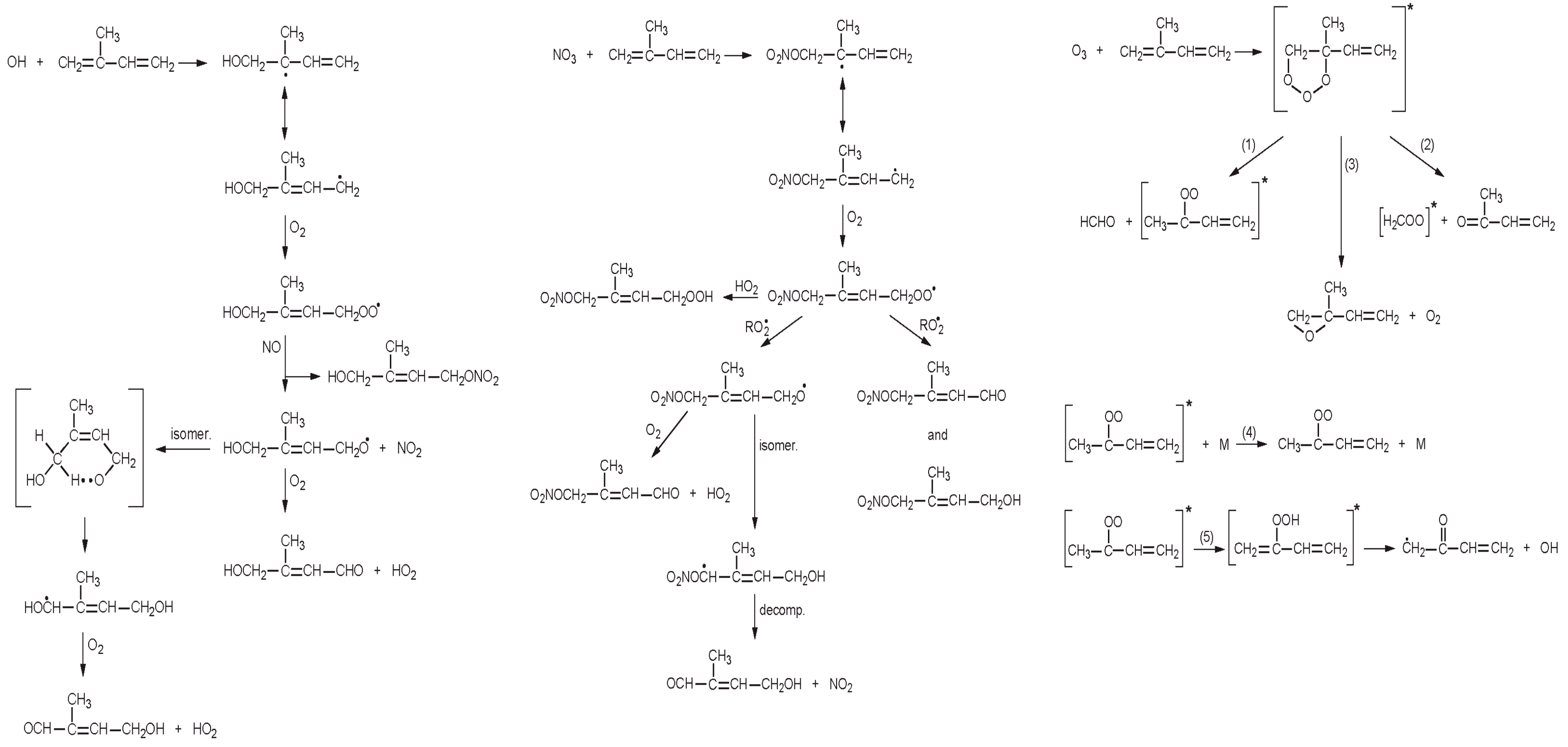


Fig. 2.1 Atmospheric degradation of isoprene by O_3, OH and NO_3 radicals. Reaction pathways given on the left side of the scheme

Oxidation of biogenic compounds initiated by reactions with OH, NO_3 or O_3 leads to the formation of oxygenated or nitrated products with vapour pressures lower than those of starting reactants. Due to their complex molecular structure with double bonds, BVOC are very reactive compounds. Generally we can say that the process of reaction with OH radicals is representative for the major decomposition of BVOC present in the atmosphere. For isoprene, which represents BVOC, there are two general reaction mechanisms listed in Fig. 2.1:

(1) Addition to C=C bonds by OH radicals, NO_3 radicals and O_3,

(2) H-atom abstraction from C–H bonds (and to a much lesser extent, from O–H bonds) by OH radicals and NO_3 radicals.

The H-atom abstraction reactions lead to the formation of alkyl or substituted alkyl radicals. After the reactions to the addition of OH and NO_3 to C=C bonds, the organic peroxy (RO_2) or alkoxy (RO) are formed. In the atmosphere, alkoxy radicals can decompose by C-C bond scission, isomerize by 1,5-H shift through a six-membered transition state or react easily with O_2 (Atkinson, 2000). In Fig. 2.1a the reactions are followed for only one of the six possible hydroxyalkyl radicals (Atkinson, 1997); note that for OH radical addition at the 1-position the initially formed allylic radical $HOCH_2C^{\cdot}(CH_3)CH{=}CH_2$ is in resonance with $HOCH_2C(CH_3){=}CHC^{\cdot}H$ (an analogous situation occurs for OH radical addition at the 4-position), and that isomerization of the 1,4-hydroxyalkoxy radical $HOCH_2C(CH_3){=}CHCH^{\cdot}$ passed through a six-membered transition state (as shown). In Fig. 2b the reaction of NO_3 radicals with isoprene is shown under conditions where RO_2+HO_2 and $RO_2^{\cdot}+RO_2^{\cdot}$ reactions dominate over the RO+NO reactions (note that when NO_3 radicals are present at appreciable concentrations then NO is not, because of the rapid reactions of NO with NO_3 radicals and with O_3). The reactions of O_3 with BVOCs containing C=C bonds proceed by an initial O_3 addition to the C=C bond, to form a primary ozonide which rapidly decomposes via two pathways to a carbonyl plus a ‘‘Criegee intermediate’’ as shown in Fig. 2.1 for isoprene [pathways (1) and (2)]. Note that for cyclic alkenes with an internal double bond (such as a-pinene and 2- and 3-carene), a carbonyl-substituted Criegee intermediate is formed from each primary ozonide decomposition pathway. The initially energy-rich Criegee intermediates react by a number of routes including (a) collisional stabilization to a thermalized Criegee intermediate for dialkyl- and syn-monoalkyl-substituted Criegee intermediates, isomerization to a “hot” hydroperoxide followed by decomposition to an OH radical plus a substituted alkyl radical rearrangement to a “hot” ester followed by decomposition (for example, to CO_2+CH_3CHQCH_2 for the Criegee intermediate of structure [CH_2=$C(CH_3)CHOO$]* formed after initial O_3 addition to the other (3,4-double bond in isoprene). The reactions of O_3 with BVOC and anthropogenic NMOC containing C=C bonds may then be an additional source of OH radicals in the troposphere, including during the night-time (Paulson and Orlando, 1996). Obviously, the importance of a particular BVOC to OH radical production depends on its ambient concentration, its OH radical formation yield, the rate constant for its reaction with O_3, and the O_3 concentration (Paulson and Orlando, 1996). The products observed from the reactions of OH radicals, NO_3 radicals and O_3 with BVOCs are generally consistent with Fig. 2.1, and the individual studies should be consulted for details of the experimental methods and results obtained. The identification and, especially, quantification of many of the products observed or expected to be formed from these reactions (in particular, hydroxycarbonyls, dihydroxycarbonyls, hydroxynitrates, and carbonyl nitrates) have been and continue to be a challenging problem, as evidenced by the lack of a product mass balance for most of the BVOC reactions studied to date.

Generally the main products of isoprene reaction at atmospheric pressure of air, with OH radicals (in the presence of NO), O_3 (in the presence of an OH radical scavenger), and NO_3 radicals are formaldehyde, Methyl vinyl ketone (MVK), Methacrolein (MACR), organic nitrates and 3-Methylfuran.

As a comparison, with the reaction of the monoterpene compounds, for example a-pinene with O_3, 30 different reaction products can be formed. However, these products are less volatile than their precursors, which is why monoterpenes are known to promote the formation of secondary organic aerosol (SOA) particles in the atmosphere. Claeys et al., 2004 postulated that also degradation of isoprene by OH radicals might be a significant source of the SOA formation in tropical environments.

BVOC in combination with anthropogenic NOx have a major influence on the formation of photochemical air pollution which exists in many urban areas. A high concentration of NOx and VOC (primary pollutants) is leading to the formation of secondary pollutants such as PAN (peroxyacetyl nitrate) and O_3. Generally, the net photochemical formation of O_3 depends on the actual NOx mixing ratio. In low polluted areas alkyl peroxy radicals (RO_2) will react with ozone and lead to the formation of alkoxy radicals (RO) and oxygen.

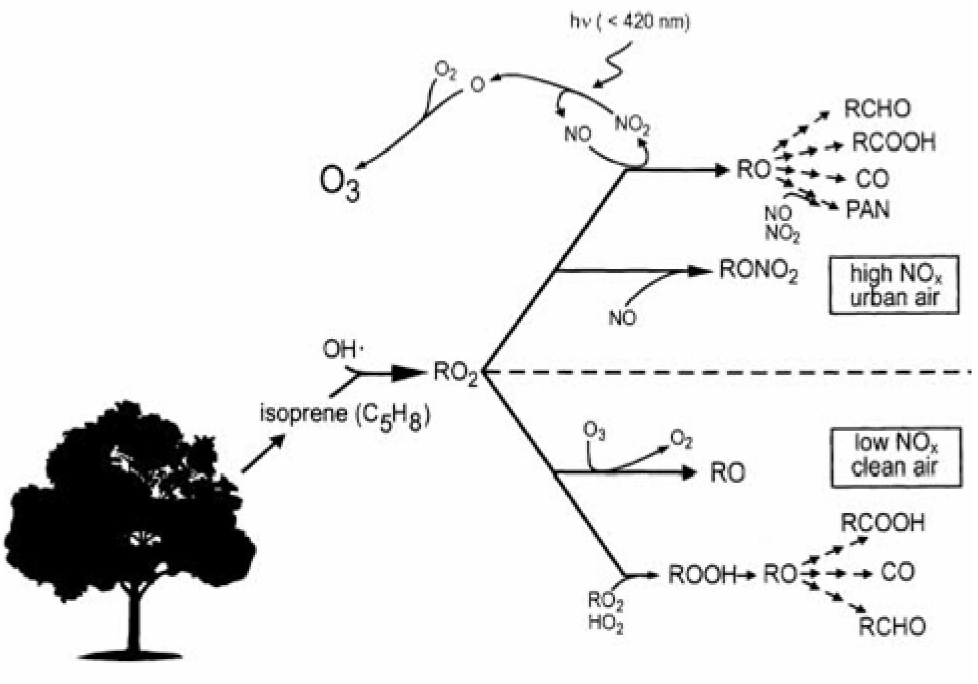


Fig 2.2 Scheme of isoprene reaction with OH radicals in urban air and rural areas.

2.3 Biosynthesis of isoprene

Isoprene emitted from plants is formed from DMAPP by isoprene synthase. This enzyme has a relatively high pH optimum and a requirement for Mg^{2+}, consistent with its location inside the chloroplasts. The molecular weight of isoprene synthase has been reported at 95 KDa *Quercus robur* (Schnitzler et al.,1996), 73 KDa in *Salix discolor* and a doublet of 58 and 62 KDa in aspen (Sharkey and Yeh, 2001). Wildermuth, 1997 showed that thylakoid-bound isoprene synthase activity could be stimulated threefold by the addition of GTP and palmitoyl CoA. Isoprene emission seems to be directly controlled by the activity of isoprene synthase: this activity is correlated with pH in cell plastid. During the night-time, there is no proton increase in the plastid (pH ~ 7). Under the conditions of light, an increase of protons in the tylakoid lumen can be observed. The process causing a pH increase in the stoma to ~8 is optimum for isoprene synthase activity. However, enzymatic activity is also measurable at pH~7, so this process is still not well understood.

2.4 Biosynthesis of terpenes

Terpenes arise from the fundamental precursor isopentenyl diphosphate, which in plants occurs at one of two subcellular locations. The classic acetate/mevalonate pathway (Chappell, 1995) operates in the cytosol compartment in which sesquiterpenes and triterpenes are formed, whereas the mevalonate independent pathway (initiated from pyruvate and glyceraldehyde 3-phosphate) operates in the plastids to provide the monoterpenes, diterpenes, and tetraterpenes (Eisenreichet et al., 1998). Following production of isopentenyl diphosphate and its isomerization to dimethylallyl diphosphate by isopentenyl diphosphate isomerase, the last is condensed with one, two, or three units of isopentenyl diphosphate by specific prenyltransferases at the corresponding subcellular locales to give the respective precursors of the monoterpenes (geranyl diphosphate), sesquiterpenes (farnesyl diphosphate), and diterpenes (geranylgeranyl diphosphate). The terpenoid synthases next convert the respective acyclic precursors, geranyl, farnesyl, and geranyl diphosphate, to the various parent structural derivatives of the different terpene families and so represent the committed enzymes of these pathways (Davis et al., 2000). These enzymes are often called cyclases because most of the products derived from the three central acyclic precursors are cyclic. Terpenoid synthases have been isolated and characterized from several conifer species, but the bulk of this work has been carried out with grand fir (*A. grandis*), a common and widespread species in the Pacific Northwest. The monoterpene synthases of grand fir are very similar to each other (Gijzen et al., 1991), and they differ little in their properties from their counterparts isolated from pine species (Savage et al., 1994). All are operationally soluble proteins with native (monomeric) sizes in the 50–70 kDa range, pI values around pH 6, and pH optima in the pH 6.8 to 7.8 range (generally higher than angiosperm synthases) (Bohlmann et al., 1998; Davis et al., 2000; Wise et al., 1999). They require a divalent metal ion for catalysis (Mg^{2+}, Mn^{2+}, or Fe^{2+}), and activity is stimulated by monovalent cations (Savage et al., 1994); this latter property is not shared by angiosperm synthases. As described in detail by Croteau et al. (2000), an interesting characteristic of monoterpene synthases is their ability to produce more than only one enzymatic product (e.g. pinene synthase may produce either α- or β-pinene). However, all monoterpene synthases use a similar reaction mechanism. The simplest monoterpene synthase reaction is catalysed by limonene synthase, where limonene biosynthesis proceeds via the initial ionisation of GPP by divalent metal ions. The latter ionisation leads to the formation of several rotameric forms of linalyldiphosphate which are then transformed via an α-terpinylcation to limonene.

3. Tower mesurements of VOC over Siberian region.

ABSTRACT

During the EU project, TCOS-Siberia, two measurement campaigns were performed to determine the atmospheric mixing ratios of different species of VOC at the tower stations at Fyodorovskoje and Zotino in Russia. The station Fyodorovskoje is located about 300 km NW of Moscow in European Russia (56 28' N; 32 56' E) and Zotino about 30 km west of the Yenisei River at the eastern edge of the West Siberian Plain (60 45' N; 89 23' N). The most dominant VOC species present in air were isoprene (range 0.5 ppb-1.5 ppb) and monoterpenes such as: α-pinene, camphene, limonene, and β-pinene. Concentration of isoprene oxidation products, i.e. methyl vinyl ketone (MVK) and methacroleine (MACR) were lower than 1 ppb, which indicated the low oxidation capacity of the atmosphere. The ozone data confirmed these subsections (ozone concentration was lower than 30 ppb). Monoterpenes mean concentration was higher than 1 ppb.

3.1 INTRODUCTION

Biogenic volatile organic compounds play an important role in atmospheric chemistry controlling the oxidizing power of the troposphere by affecting sources and sink of O_3 and OH as well as aerosol production (Ketseridis et al., 1976; Atkinson, 1990; Pandis et al. 1991; Fehsenfeld et al., 1992; Andreae and Cruztzen, 1997; Kavouras et al., 1998, 1999; Christoffersen at al., 1998; Calogirou, 1999). Therefore it is of high interest to understand their biogenic production, emission and concentration. A large number of biogenic VOC species is emitted into the atmosphere from the terrestrial vegetation (Warneck, 1998; Guenther et al., 1995; Kesselmeier and Staudt, 1999). Thus, the emission of biogenic VOC plays a central role in the atmosphere, influencing its oxidative capacity. Furthermore, the emission process of VOC may represent a substantial loss of carbon for the biosphere (Guenther, 2002; Kesselmeier et al., 2002b). The specific direct or indirect vegetative sources of these compounds are not well known. Also, the processes of sampling and analysis need the application of considerable techniques for the VOC specification. Therefore there is great interest in the emission pattern and quality of plant species from the boreal zone, especially in the Siberian region which is regarded as a sink of carbon. Bearing in mind the important role of VOC, a description of the atmospheric concentrations and the exchange process on local and regional scales, the biological process and the chemical fate of all these compounds is needed, especially in regions poorly investigated. Several papers describe measurements around boreal forests (Hakola et al., 2000; Rinne et al., 2000). There have been several studies of European boreal ecosystem studies which were the object of intensive research efforts. Biogenic VOC emissions and photochemistry in the boreal regions of Europe were the objective of the BIPHOREP project study, aimed at quantifying the biogenic VOC emissions from boreal forests (e.g. Laurila et al.,1997). However, there are still large gaps in the emission factor data available for detailed emission inventories, especially in remote ecosystems where the species distribution may differ considerably from typical American or Central European vegetation.

The dominant sources of VOC are forests world-wide, one of the most important among them being the Siberian forest. Our knowledge of VOC emission from Siberian forests is still insufficient. Only a few publications describing VOC measurements in Russia are available (Isidorov and Povarov, 2000).

Due to an inadequate database, we still depend on model extrapolation to discuss the chemical process (Guenther et al., 1995). However, some extrapolations which were developed for tropical plants may not accurately simulate emission (Keller and Lerdau, 1999). In addition, biogenic emissions of VOC are affected by a number of factors including temperature, light intensity, plant phenology, injury, stress, etc. (Kesselmeier and Staudt, 1999). Therefore to understand the atmospheric process which is present in nature, data of atmospheric speciation of BVOC and biogenic released under filed conditions are needed. This will increase our knowledge significantly, as atmospheric BVOC concentrations are the product of diverse factors such as biological sources and sinks, meteorology, chemical reaction processes and deposition.

Within the TCOS-Siberia project (Terrestrial Carbon Observation System) we performed field measurements during two intensive field campaigns in the summer of 2004 and 2005 in order to investigate the primary emission of volatile organic compounds from the naturally growing Siberian ecosystem.

We measured the concentrations of a large number of VOC species, such as isoprene and monoterpenes at the tower stations Fyodorovskoje and Zotino.

3.2 TCOS Project Strategy

The principal objective of the project was the implementation of the first components of a continental scale observing system to help determine the net carbon balance of Siberia and its variation from year to year. The complexity of this goal necessitates an integrated top-down and bottom-up approach. In brief, continuous surface flux measurements in key ecosystems at four locations and regular vertical profile measurements from aircraft in the lower troposphere at seven locations will be merged with similar observations at the boundaries of the study domain. These surface and atmospheric observations will then be combined to provide the basis of a continental scale meteorological and biogeochemical modelling framework.

TCOS-Siberia builds on the experience gained in a study evaluating the feasibility of determining the carbon balance of Eastern Europe and Western Siberia by means of atmospheric and surface measurements combined with local process studies (EU project EUROSIBERIAN CARBONFLUX, EV5V-CT95-0116, Heimann, 2000). In that pilot study, a first set of monitoring sites was successfully established. These sites have now been operating for almost several years, providing the basis for a first estimate of the carbon balance of Western Siberia and European Russia.

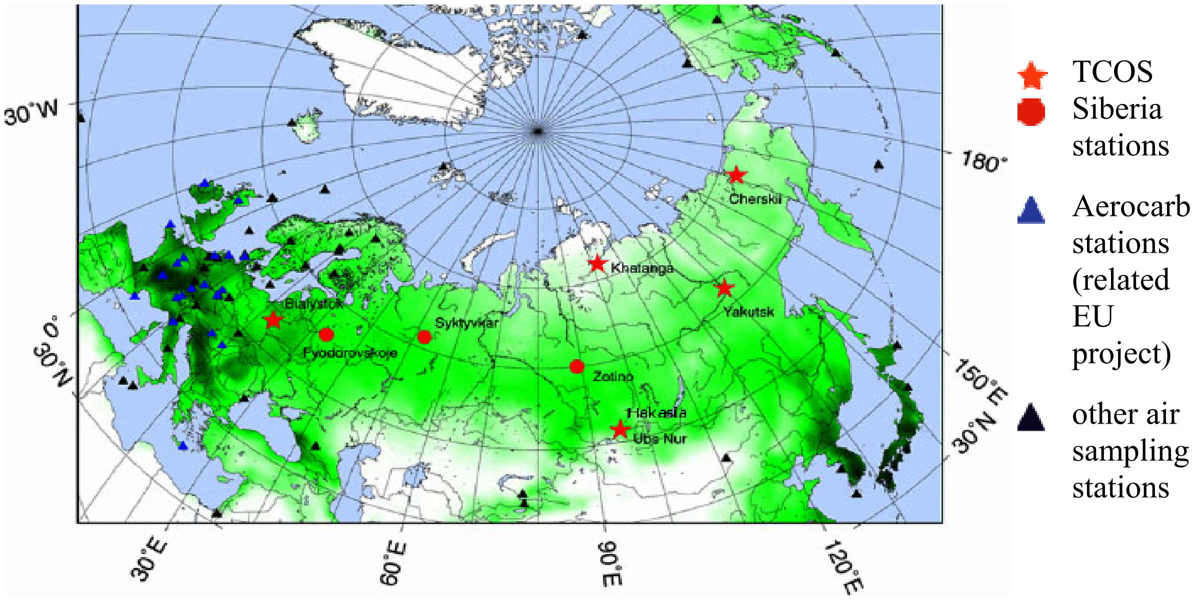


Fig. 3.1 TCOS project sites over the Siberian study region.

The objectives of the proposed TCOS project included, inter alia, the addition of VOC analyses on the tower measurements and in the airborne measurements. The measurements in the boundary layer and the overlying free troposphere within years two and three of the project and determination of their contribution to the atmosphere-canopy carbon fluctuates within the target study area. Those activities were realized by measurement campaigns in 2004 and 2005.

Important aspects of the TCOS project are providing a refined assessment of the carbon balance and its variability in the northern Eurasian continent consisting of the Russian boreal forest zones, the Siberian and European Russian arctic tundra regions and the southern Siberian steppe grasslands.

The focus of this study was the addition of VOC measurements and analyses during two summer campaigns. The regional quantification of the carbon balance by surface flux measurements and by the top-down approach with inverse methods is classically based on concentration measurements of CO_2. Moreover, CO_2 is the climatologically most relevant atmospheric trace gas; there exist several other carbon-containing compounds such as CH_4, CO and Volatile Organic Compounds (VOC), which are also emitted by terrestrial ecosystems in a non-negligible amount. In the atmosphere most of these compounds are rapidly oxidized with lifetimes ranging from hours to a few days (VOC), to several months (CO) and up to a decade (CH_4). These species bypass the flux measurements made with the eddy covariance technique (which determines only the local canopy-atmosphere CO_2 flux), and they are usually not included in inverse atmospheric concentration calculations to infer regional surface carbon balances. In particular, the emissions of VOC (mostly isoprene and monoterpenes, emitted primarily by forests) have recently been shown to constitute a significant contribution to the net carbon balance of the vegetation in selected locations in the tropical area basin (Kesselmeier and Staudt, 1999; Guenther, 2002; Kesselmeier et al., 2002a). A preliminary extrapolation to the globe based on existing measurements in Amazonia and Mediterranean forests yields VOC fluxes that are of the same order of magnitude as the net biome productivity of the global terrestrial biosphere (Kesselmeier et al., 2002a). Simpson et al. (1999) pointed out that present BVOC emission inventories are quite uncertain and some of the tabulated emission rates may differ from actual rates by a factor of 10. One reason for this high uncertainty is the lack of emission data for key species in ecosystems covering a large area, such as tropical and boreal systems.

Within TCOS-Siberia, CO and CH_4 concentrations were routinely analysed from all flasks collected in the aircraft-sampling programme. As a novel measurement component, in TCOS-Siberia additional measurements of VOC were taken on the aircraft-sampling campaigns and directly within and above the canopy during selected periods in summer at the surface flux measuring sites of the TCOS-Siberia project. This information will provide the observational basis to infer the potential corrections quantitatively that have to be applied to the carbon balance estimated by the classical CO_2 only approaches, since VOC are also highly important for the tropospheric chemistry and precursors of aerosols (Andreae and Crutzen, 1997).

3.3 Field Campaigns

During 2004 and 2005, combined airborne and ground-based measurements were performed in selected locations. In 2004, airborne and ground measurements were taken in Fyodorovskoje and Zotino, and in 2005, in Zotino in Central Siberia. Measurements were performed continuously at the area of the flux tower and above the canopy of the forest.

The activities included:

- CBL vertical profile airborne measurements with cartridge sampling, flask sampling and continuous measurements;
- continuous eddy covariance measurements and meteorological parameters recording from the local tower.

Region	Latitude; Longtitude	Land type	Date of campaigns
Fyodorovskoje	56 28' N; 32 56' E	Forest 81 %	19-20.07.2004 (airborne measurements) 22-25.07.2004 (tower measurements)
Zotino	60 45' N; 89 23' N	Forest 80 %	30-31.07.2004 (airborne measurements) 01-05.08.2004 (tower measurements) 12-13.07.2005 (airborne measurements) 15-22.07.2005 (tower measurements)

Table 3.1 Data about land type. Adapted from Glebov, 1969 and Stakanov, 2000.

3.4 Tower measurements

Tower measurements were performed on the eddy covariance tower at two sites, Fyodorovskoje and Zotino. The sampling process usually started between 7-8 a.m. local time and finished between 8-9 p.m. local time, except for two occasions in 2005 during which overnight measurements were performed.

3.4.1 Land Use Classification

The Euro-Siberian region covers the area between 53° and 67° N from the Atlantic coast of Norway at 5° E to the Pacific coast at 170° E. The boreal zone is one of the world's largest forest areas, covering a land surface of 15.8x 10^6 km^2. The region is relatively uniform with respect to species cover. *Picea abies* of Europe is replaced by *Picea obovata* in Finland and NE of European Russia, which then dominates together with *Abies alba* in the dark coniferous taiga of European Russia and *Abies sibrica* in Siberia. Dark coniferous taiga occurs with a different set of species again in the Amur region. *Pinus sylvestris* is the tree species with the largest range of global distribution for any tree species. This is an early successional species along the whole region and dominates on nutrient-poor sandy soils and in bogs. In contrast, *Pinus sibrica* is a central Siberian late successional species forming monotypic stands mainly in wet sites. The genus *Larix* occurs with a range of species in a region almost as broad as that of *P. sylvestris*, but it dominates forests mainly on permafrost soils and in the continental climate of East Siberia (Walter, 1974). The deciduous trees of *Betula* and *Populus* are important throughout the boreal forest belt depending on disturbance. *Betula pendula* and *B. pubescens* are early successional species in many regions of European Russia and Siberia. *Populus tremula* follows disturbance on nutrient-rich and drained soils (Schulze et al., 2002).

The Fyodorovskoje experimental site is located in the Central Forest Reserve (CFR) near the town of Nelidovo (Tver region), about 300 km NW of Moscow in European Russia. The reserve was established in 1931. The eddy tower was mounted in a 150-year-old forest of spruce. The stand is approximately 27 m high, consisting of about 86% *Picea abies* trees and about 14% *Betula spp.* with a total live tree density of 565 ha^{-1} in 2000 (Vygodskaya et al., 2002). This is a widespread forest type in the northern, central-southern taiga, but is mostly limited to the middle and lower parts of soft slopes and shallow depressions. The territory around the tower is fairly heterogeneous. The dominant spruce stand is limited in extent, and within 200-300 m from the tower there are birch and aspen forests as well as windfall of different ages. A comprehensive footprint analysis was made of the area around the tower, taking into account the heterogeneous nature of the vegetation beyond the spruce stand (Sogachev et al., 2002). These authors suggested that 80% of the measured flux comes from within a 200 m radius during the day, with the effective footprint being somewhat larger at night.

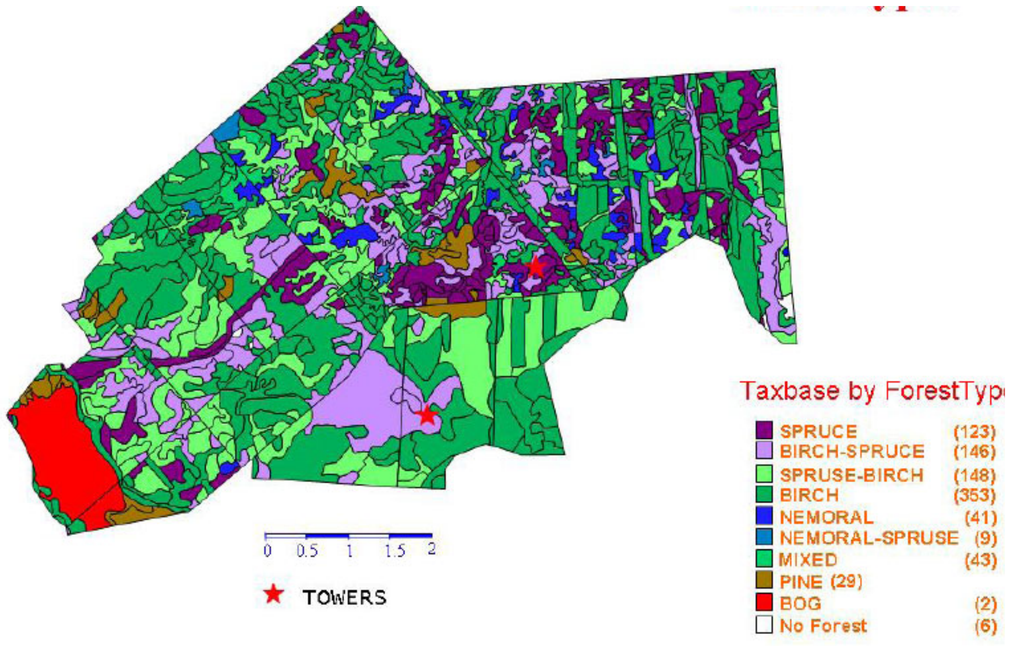


Fig. 3.2 Forest inventory data for the Fyodorovskoje site.

The Zotino site is located near to the village of Zotino, about 30 km west of the Yenisei River at the eastern edge of the West Siberian Plain. The tower was established in a succession pine forest (*Pinus sylvestris*) with a lichen understorey (Wirth et al., 1999). The stand was 200 years old, extending at least 0.5 km in all directions. As with most of the *P. sylvestris* forests in the area, the stand was located on gently undulating, alluvial sand without underlying permafrost. The stand structure was relatively homogeneous with a steam density of 478 ha^{-1}; the basal area was 30 $m^2 ha^{-1}$, LAI 1.5 m^2 and biomass (dry weight) was 10.7 kg m^{-2} (Wirth et al., 1999).

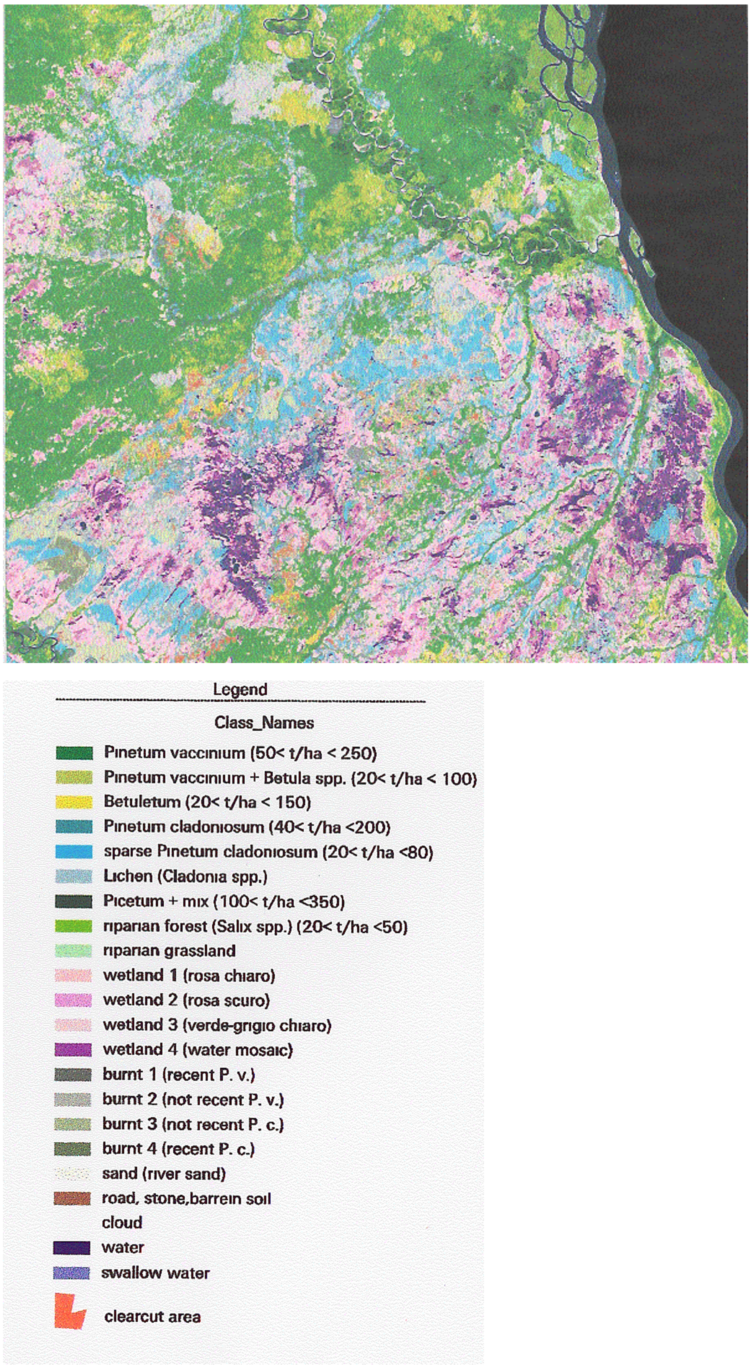


Fig. 3.3 Zotino land cover map. Land cover classification based on LANDSAT ETM+ images of 25.06.2000 and 11.07.2000. Map by Danilo Mollicione, Global Vegetation Monitoring Unit, European Union JRC.

3.4.2 Climatology of the Fyodorovskoje region

Vyshnii Volchek, the oldest weather station in the region, located 100 km north of the study site, shows climatic conditions very similar to those at Fyodorovskoje, the weather station at the central forest reserve (CFR). The station has a long meteorological data record, more than 100 years. There is a slight increase in the annual average temperatures over the last 100 years (0.005 °C yr^{-1}). Temperatures average 20.91±6.4 °C for the period above 10°C average daily temperature. Precipitation may be as low as 400 mm in a dry year (1963) and exceed 800 mm in a wet year (1953), with mainly high summer rainfall in wet years. There is no obvious trend in precipitation. The variation of precipitation is greater in summer, while the variation of temperature is greatest in winter. There is no correlation between annual or summer precipitation and temperature. Summer precipitation (days > 10°C) is about half the total precipitation. The growing season (T > 5°C) lasts on average 172 days (Vygodskaya, 2002).

At Fyodorovskoje the mean wind speed was 3.2 ms^{-1} (1995-1999) with SW to SE, being the prevailing wind direction for 58 % of the time. High wind speeds (4.55 ms^{-1}) come from the SW.

3.4.3 Climatology of the Zotino region

Bor station has been used as a reference station for Zotino. The station is located 80 km to the north, on an inlet of Podkamieniaya Tunguska in the Yenisei River. The climate of the Zotino region is continental, with -26°C average January temperatures and a temperature minimum of <-56°C. The daily maximum temperature can reach 36°C (1999). The monthly average minimum in temperature is -36°C (1969). The annual precipitation in Fyodorovskoje is also the result of a local water cycle of evaporation and convective storms. The absolute maximum precipitation reached 745 mm (1986), while the lowest minimum was recorded in 1938, at 364 mm.

3.5 System Configuration and Data Analysis

Detailed protocols with all observations that might be useful during the process of data analysis were kept in the activity campaign diary.

3.5.1 Measurement equipment. VOC sampling system

For the campaign purposes a new sampling unit was established at the Max Planck Institute for Biogeochemistry in Jena. No commercial unit was available for the purpose. Major effort had to be given to its design and construction. The same kind of sampling unit was used for tower and airborne measurements. The sampling unit can be divided into:

- the inlet part with special tubes and ozone scrubber (MnO_2), to prevent reactions inside the tubes and on the absorbent into the cartridge;
- the pump system (type ETO341FC003, Ansyco, Karlsruhe, Germany), electronic mass flow controller, particle filters (Zeflon);
- the sampling cartridges (Silico steel).

The inlet of the tube was localized at the top of the tower, above the canopy of the forest. For the measurements of volatile organic compounds at ambient air temperature, it is obligatory to remove oxidants from the enrichment step. In particular, interference from the co-trapping of ozone on adsorbent materials and also the reaction of these oxidants with compounds on the adsorbents, may lead to the formation of artifacts. However, an artifact may also be present due to formation from reactions with trapped volatile organics (e.g. Hoffmann et al. 1993; Peters et al., 1994; Hoffmann, 1995; Calogirou et al*.,* 1996). According to Pellizzari and Krost (1984) and Calogirou et al*.* (1996), the degree of decomposition of adsorbed volatile organics is a function of their molecular structure. However, the sensitivity towards an interference of ozone to trapped volatile organics also depends on the type of adsorbent material that is used (carbon type adsorbent material seems to be less sensitive to ozone interferences; Larsen et al., 1997). A detailed overview on these different scrubber techniques is given by Helmig (1997).

From the inlet of the ozone scrubber, the air was pumped by a membrane pump going through a Zeflon filter before entering the system unit. Afterwards, the sampling air can enter the cartridge or go through the outlet via a by-pass. The system was prepared with a special protection part to prevent the cartridge from double filling with air. For sampling, the air flushed the cartridge and VOCs were trapped on the adsorbent. The flow range was from 100-250 ml/min.

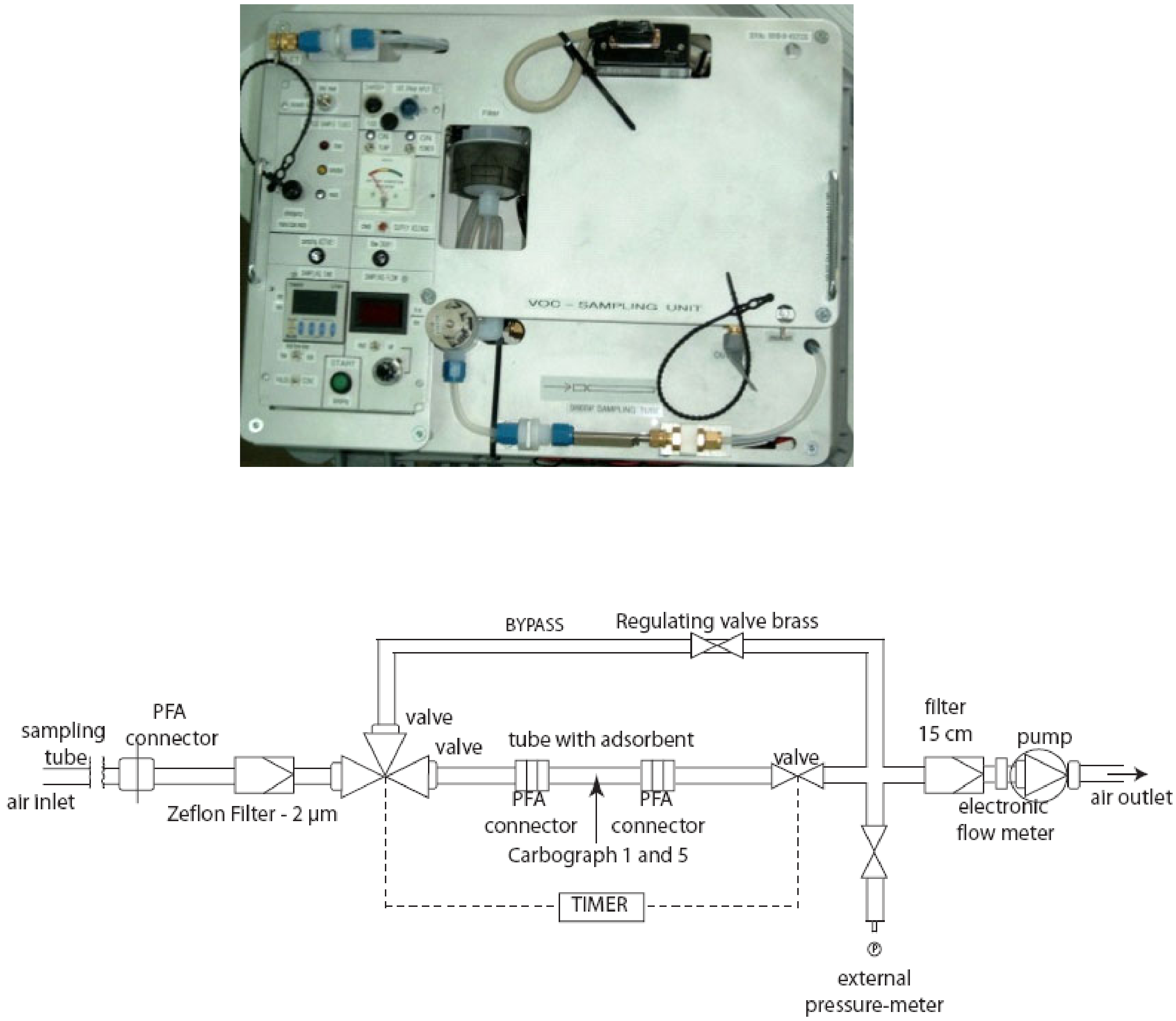


Fig. 3.4 VOC sampling unit used for VOC sampling process.

3.5.1 Eddy covariance measurements

Water vapour, heat and momentum fluxes were measured at a height of 27 m (about 5 m above the average tree height and 4 m above the highest nearby trees). The measurement system consisted of a triaxial sonic anemometer (model Solent R3, Gill Instruments, UK) and a fast response CO_2/H_2O non-dispersive infrared response gas analyzer (model 6262-3, Li-Cor Inc., Lincoln, NB, USA). The air was drawn from an inlet at the top of the tower, 10 cm below the sonic measurement height through BEV-A-Line tubing and two aerosol filters at a flow rate of 5.8 L/min. The fluxes were calculated off-line as a simple covariance of 30 min high-frequency time series of vertical wind velocity with temperature or water vapour density. The time lag between measurements of vertical and solar density due to transport in the tube was estimated by cross-correlation between both time series to be approximately equal at 4.8 s for water vapour. The data were corrected by shifting the time series by the estimated time lag.

3.5.2 Supporting meteorological measurements

Radiative flux measurements included total downward and upward radiation using a pyradiometer (LXG055), and shortwave downward and upward radiation using a Kipp and Zonen pyranometer (CM 14, Kipp and Zonen, Delft, Holland). Additional measurements included air temperature and humidity (HMP 35 D, Vaisala, Helsinki, Finland), and wind velocity (A 100 R, Vector Instruments, USA). These sensors were installed below the sonic anemometer on a boom. At ground level a rain gauge was also installed (Young Instruments, Traverse City, MI, U.S.A.) located in close proximity to the eddy flux tower. At both sites the environmental data were stored as 30 min averages.

3.5.3 Sampling of VOC

VOC were collected on sequential adsorbent beds packed into fused-silica-lined stainless steel cartridges (Perkin–Elmer (U.S.A.)). Sampling of isoprene and monoterpenes was performed by the use of graphitized carbon blacks (GCB). The availability of a graphitic carbon with adsorption features comparable to those of some carbon molecular sieve adsorbents has made it possible to widen the range of polar and non-polar VOCs that can be collected at any relative humidity. Multi-layer traps containing combinations of Carbograph 5 and other hydrophobic sorbents provide a better sensitivity alternative than existing methods. In combination with a stronger adsorbent, traps filled with Carbograph 5 provide results equivalent to those obtained by canister sampling.

The following adsorbents were used for the sampling, 130 mg of Carbograph 1 (90m^2/g) followed by 130mg of Carbograph 5 (560m^2/g). The size of the Carbograph particles was in the range of 20–40 mesh. Carbographs 1 and 5 were provided by Lara s.r.l. (Rome, Italy). Sampling flow rates were 100-250 mL min^{-1}. The adsorption cartridges that were used for VOC measurements during the present study were prepared in 2003 by the MPI-BGC laboratory.

3.5.4 Analysis of VOCs

Desorption and analysis by GC-FID of the trapped samples as well as chromatographic peak evaluation was performed by GC-laboratory group of the MPI for Chemistry in Mainz. For subsequent analyses, the adsorbent cartridges were thermally desorbed under a helium flow at 260°C for 10min (using a Perkin Elmer ATD 400). As described by Kesselmeier et al. (2002a) cartridges filled with Carbograph 1 and 5 were desorbed thermally using a two-step desorption system [Model ATD400, Perkin Elmer, Germany] that was connected to a GC-FID [Model AutoSystem XL, Perkin Elmer, Germany].

In this instrument, desorbed species are refocused on a small quartz tube packed with 20 mg Carbograph 1 and held at 30°C. The quartz tube was then rapidly heated to 280°C and the desorbed compounds were transferred through a heated line to the GC for separation and FID detection (Perkin Elmer Auto system XL GC / FID). Separations were accomplished on two capillary columns connected in series: (Supelco SPB-5,30m 0.25 mm I.D., 0.25 mm film thickness, followed by Hewlett Packard HP-1.30 m 0.25 mm I.D, 0.25 mm film thickness). The temperature programme used for analysis ranged between -10°C and 220°C (-10°C to 40°C at 20°C min^{-1}, 40°C to 145°C at 1.5°C min^{-1}, and 145°C to 220°C at 30°C min^{-1}). Chromatographic separation of one sample was performed within 90 min. Peak detection was accomplished by using a flame ionisation detector (FID).

According to Gottwald (1995), the current produced in the detector is proportional to the mass of volatiles that are detected in this process. In general, the detector consists of a burner that burns a mixture of high purity hydrogen (purity 6.0) (H_2) and synthetic air and an ion collector electrode kept at about -200 V (manufacturer specifications, Perkin Elmer, 1997). For detection of volatiles the H_2 gas flow is mixed with carrier gas derived from the chromatographic column.

As described by Holm (1999), formylium ions (CHO^+) and electrons (e^-) are formed by chemi-ionisation at a yield of approximately one ion per 106 carbon atoms if hydrocarbons are present. In general, the formylium ions are formed by the reaction of hydrocarbon-radicals with oxygen radicals (originating from synthetic air). The hydrocarbon-radicals are derived from methane produced from the hydrogenolysis of VOC inside the flame. Since every 106^{th} carbon atom finally produces a formylium ion, the FID signal derived from hydrocarbons is proportional to the number of carbons present in the original molecule (rule of equal response per carbon). On the other hand, some chemical structures are less sensitive to hydrogenolysis. Holm (1999) reported that a carbon atom bonded to a hetero-atom may or may not be converted to methane, resulting in a lower signal response from the detector. This theory gave the development of the empirical "effective carbon number concept" that defines the relative contribution of different functional groups to the signal response. According to Sternberg et al. (1962), the contribution of different functional groups to the number of "effective carbon atoms" in a molecule varies between zero and 1.0 (see also the studies of Ackmann (1964) and Blades (1976). As described in the publication by Sternberg et al. (1962) for aliphatic, aromatic, and approximately also for olefinic molecules (0.95), the "effective carbon number" is equal to the real carbon number of the molecule. Carbonyl groups on the other hand have no contribution to the effective carbon number. For them the contribution is equal to 0.

As accordance with the procedure described by Komenda (2001), a process of calibration for volatile organics containing no hetero-atoms was obtained by using a gaseous standards mixture containing n-alkenes C_5-C_{10} (n-pentane, n-hexane, n-heptane, n-octane, n-nonane and n-decane) and isoprene, yielding a detector response signal which is proportional to the real carbon number.

Organic compounds evaluated by these analyses are summarized in Table 3.2 For the process of peak identification and integration a commercially available software was used, Turbochrom 4 [Perkin Elmer, Germany]. The identification of compounds was made by their respective retention times.

	Volatile organic compound	Retention time [min]
Alkenes	n-pentane	~14.5
	n-hexane	~18.8
	n-heptane	~26.1
	n-octane	~36.2
	n-nonane	~47.9
	n-decane	~59.9
Hemiterpenes	isoprene	~14.8
Monoterpenes	α-pinene	~52.5
	camphene	~54.3
	sabinene	~56.6
	β-pinene	~58.2
	Δ-3-carene	~61.4
	α-terpinene	~61.8
	p-cymene	~62.1
	limonene	~63.3
	γ-terpinene	~66.4
Carbonyl compounds	MVK	~17.2
	MACR	~16.5

Table 3.2 Volatile Organic Compounds evaluated by GC-FID analysis.

3.5.5 Calculation of Volatile Organic Compound mixing ratios

The calibration of the GC-FID system was performed by the MPI–Ch GC laboratory group. The process of the preparation of calibration standards is a major error source in the analysis of organic compounds. In accordance with the concept of "effective carbon number" and based on the experiments performed by Apel et al. (1994, 2003a, 2003b) and Komenda (2001), the mixing ratios of volatile organic compounds were calculated using a gaseous purity nitrogen standard of stable C_5-C_{10} n-alkenes and isoprene manufactured by Apel-Reimer, Denver, CO, USA]. The mixing ratio of the standard used for GC-FID calibration ranged between 9 and 16 ppb. The standard mixture was sampled from the calibration cylinder under laboratory conditions on adsorbent cartridges resulting in normalized standards ranging between 2 and 75 ng per cartridge (standard conditions 25°C, standards injection number 11 and 29, respectively). After analysis by GC-FID, calibration factors were calculated from the slope of linear regression according to Formula 3.1

$$CalFactor = \frac{Area_{Standard}}{Amount_{standard}} \qquad \text{Formula 3.1}$$

Formula 3.1: Cal Factor- calibration factor [μ Vs ng^{-1}],

Area $_{standard}$ – area of the standards [μVs ng^{-1}],

Amount $_{standard}$ - amount of the standards [ng].

The calibration standard curves are shown respectively in Figure 3.7 and 3.8 for two standards analysed by GC-FID in the years 2004 and 2005. Calibration factors were calculated for all compounds present in the standards mixture. Correlation coefficients (r^2) range between values of 0.97-0.98 for all data obtained in 2004 and values of 0.89-0.99 for standard compounds in 2005.

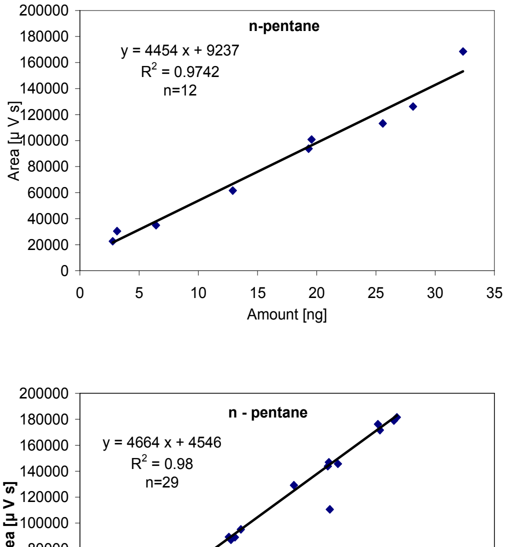


Fig. 3.7 Calibration of n-pentane by use of a gaseous standard mixture [Apel-Riemer, USA] in the years 2004 (left side) and 2005 (right side). Standards of n-pentane were collected on adsorbent traps that were analysed by GC-FID. The slope and intercept of linear regression analysis (grey line) are indicated in the relevant graph for the respective compounds and years.

Table 3.3 shows calibration factors calculated for all standards in 2004 and 2005. However, to obtain better results of the calibration factor, it was decided to do a single calculation of a calibration factor only for all n-alkane standards measured by GC-FID in 2004 and 2005. For 2004 the calculated factor was 4328 μ Vs ng^{-1} and for 2005 it was 4480 μVs ng^{-1}. Differences in the individual n-alkane calibration factors obtained a calibration factor for all compounds for the corresponding year, with a range of ±15% for 2004 and ±10% for 2005.

Volatile organic compound (standard mixture)	year 2004	r^2	year 2005	r^2
n-pentane	4454	0.97	4464	0.98
isoprene	4946	0.97	4622	0.89
n-hexane	4448	0.97	4828	0.99
n-heptane	4376	0.97	4775	0.98
n-octane	4314	0.98	4270	0.92
n-nonane	4300	0.98	4307	0.97
n-decane	4075	0.99	4037	0.99

Table 3.3 Calibration factors (μ Vs ng^{-1}) of hydrocarbons and regression factors (r^2) for the years 2004 and 2005.

3.5.5.1 Calculation of VOC mixing ratios

For GC-FID analysis the calculation of the VOC mixing ratios were in units of ppb in accordance with formula 3.2. The calibration factor was given in units μVs ng^{-1}.

$$\text{Mixing ratio} = \frac{MV}{Cal \quad Factor} \bullet \frac{(Area_{sample} - Area_{Blank})}{SV} \qquad \text{Formula 3.2}$$

Formula 3.2 Area sample = peak area of the sample [μ Vs], Area blank= peak area of the blank [μ Vs], Cal factor = calibration factor [μ Vs ng^{-1}], MV= mole volume of an ideal gas [22.41mol^{-1}, 25°C, 1013hPa], SV= air volume sampled on the respective cartridge [L], Mixing ratio= mixing ratio of the respective compound [ppb].

3.5.6 Applied statistics

The measured data were evaluated using several statistical procedures. The following paragraph will focus on the statistical techniques that were applied.

3.5.6.1 Average, standard deviation and empirical variance

The arithmetic average and the standard deviation of a group of symmetrically distributed data points were calculated by application of the formulae 3.3 and 3.4. Considering the calculation of the standard deviation, the formulae calculate the deviation of random samples from their arithmetic mean. The empirical variance is given as the square of the standard deviation:

$$\text{X}=\frac{\sum x_i}{n} \qquad \text{Formula 3.3}$$

$$\text{S}=\sqrt{\frac{n\sum x_i^{\,2}-\left(\sum x_i\right)^2}{n(n-1)}} \qquad \text{Formula 3.4}$$

Formula 3.3 and 3.4: n=number of data points, s= standard deviation, x= arithmetic mean x_i=single value.

3.5.6.2 Slope, intercept and Pearson product moment correlation coefficient

The slope of the linear regression from a group pair (x_i, y_i) was calculated by formula 3.5.

The y-axis intercept was calculated by use of the linear slope b according to the formula with representing the respective average of all x and y values (formula 3.6).

$$\text{b}=\frac{n\sum x_i y_i-\left(\sum x_i\right)\left(\sum y_i\right)}{n\sum x_i^{\,2}-\left(\sum x_i\right)^2} \qquad \text{Formula 3.5}$$

$$\text{a=y-bx} \qquad \text{Formula 3.6}$$

To give a measure of linear correlation between two datasets (x_i, y_i) the Pearson product moment correlation coefficient was calculated according to formula 3.7, yielding a coefficient ranging between +1 and -1, with +1 and -1 giving the best correction between two data sets.

$$r=\frac{n\sum x_i y_i-\left(\sum x_i\right)\left(\sum y_i\right)}{\sqrt{\left(n\sum x_i{}^2-\left(\sum x_i\right)^2\right)\left(n\sum y_i{}^2-\left(\sum y_i\right)^2\right)}} \qquad \text{Formula 3.7}$$

Formula 3.7 a = intercept of y axis, b- slope of linear regression, n-number of data points or data pairs, r= Pearson product correlation coefficient, x = arithmetic average of all x values, x_i=single value, y = arithmetic average of all y values, y_i = single value, y- axis.

3.5.6.3 T-test

The T-test is an objective measure of whether two averages may be combined in one common one, i.e. both single averages are equal to each other. The T-test is applied by calculation of a test statistic t* that is compared to a tabular value of t. The test statistic t* is calculated according to the formulae 3.8 and 3.9. If $t^*<t$, both average values are equal to each other with the respective likelihood of (95.00% to 99.99%).

$$t^*=\left|\frac{\bar{x}_1-\bar{x}_2}{S_d}\right|\cdot\sqrt{\frac{n_1\cdot n_2}{n_1+n_2}} \qquad \text{Formula 3.8}$$

$$S_d=\sqrt{\frac{(n_1-1)\cdot s_1{}^2+(n_2-1)\cdot s_2{}^2}{n_1+n_2-1}} \qquad \text{Formula 3.9}$$

Formula 3.8 and 3.9: n_1= number of data points in data group 1, n_2= number of data group 2, s_1= standard deviation data group 1, s_2= standard deviation data group 2, x_1= arithmetic average data group 1, x_2= arithmetic average data group 2.

3.5.6.4 Uncertainty of calculated Volatile Organic Compound concentrations

Accuracy, precision and reproducibility are measures for the uncertainty of calculated mixing ratios of volatile organic compounds. Under the assumption that errors were not correlated with each other and are distributed normally, precision can be calculated by error propagation for a single measurement. Reproducibility can be calculated from the average and standard deviation of a series of samples of the same quantity. Since precision and reproducibility are a measure of the repeatability for individual measurements, they will be influenced by random errors. On the other hand, accuracy is a measure of agreement of the calculated and the real concentration and will be influenced by systematic errors.

3.5.6.5 Accuracy of Volatile Organic Compound concentrations

Accuracy is influenced only by systematic errors and is a measure of the deviation between the real and the measured value. An example of systematic errors that will lead to a decreased accuracy of VOC determination is e.g. the application of wrong calibration standard concentrations that may lead to a systematic under- or over-estimation of present VOC mixing ratios. In the following paragraphs, accuracy will be specified by the percentage difference between the measured VOC concentration and the reference VOC concentrations that were set by the permeation device.

3.5.6.6 Precision of VOC concentrations

The precision of all mixing ratios was calculated by Gaussian error propagation and gives the sum of uncertainty of all components used for the calculation of these mixing ratios (calibration factor, sample flow, blank values).

$$\text{Precision}_{\text{MR}} = \left(\frac{\sqrt{\left(Area_{Sample-Blank} \cdot \sqrt{\left(\frac{P_{analyt} \cdot CalFact}{Area_{sample-blank}} \right)^2 + P_{flow}{}^2} \right)^2 + S_{AreaBlank}{}^2}}{Area_{sample-blank}} \right)$$

Formula 3.10

Formula 3.10 Area sample-blank= difference of sample and average blank area [e.g. μ Vs] , Cal Fact= calibration factor [e.g. μ Vs ng^{-1}], MR= missing ratio[e.g. ppb] , P_{flow}= relative uncertainty of flow and volume measurement [%], P_{analyt}= precision of analysis [e.g. ng], Precision $_{MR}$= precision of VOC mixing ratio [e.g. ppb], $S_{AreaBlank}$ =standard deviation of blank values on an area basis [e.g. μ Vs ng^{-1}].

For terms that were linked by multiplication or division during the calculation of the mixing ratios, relative uncertainties were used for error propagation. For terms that were linked by addition or subtraction, absolute uncertainties were used. Formula 3.10 gives an example of precision for the calculation of precision of mixing ratios for the GC-FID analysis. It combines the calculated precision of analysis, flow and the standard deviation of blank values with the factor of calibration and the difference of sample and blank area. Due to the above-mentioned context the precision of analysis and flow were inserted in Formula 3.11 on the basis of relative uncertainties (the relative precision is given by the term: P_{analyt} CalFactor /$Area_{Sample-Blank}$). On the other hand, the precision of blank values (standard deviation) was added as absolute uncertainty on an area basis.

3.5.6.7 Precision of analysis

The analytical precision can be calculated as an uncertainty of the calibration factor from the linear regression of standard concentrations (x-axis) and the associated standard chromatographic peak areas (y-axis) by formulas 3.11, 3.12 and 3.13.

The terms S_o and S_b that are included in formula 3.13 were calculated according to formulae 3.11 and 3.12 with x_i representing the standard amounts and y_i representing the standard areas. The factor Yi represents the calculated standard amount form from regression analysis following Y_i=a + bx.

$$P_{\text{analyt}} = \frac{S_o}{b}\sqrt{\left(\frac{1}{n}\right)+\left(\frac{1}{a}\right)+\left(\frac{S_b}{b}\right)^2 \cdot \left(\frac{Area_{sample-blank} - \left(\sum Area_{s\tan dard} / n\right)}{S_o}\right)^2}$$

Formula 3.11

$$S_o=\sqrt{\frac{\sum (y_i - Y_i)^2}{n-2}}$$ Formula 3.12

$$S=\sqrt{\frac{(n \cdot So^2)}{\left(n \cdot \sum x_i^2 - (\sum x_i)^2\right)}}$$ Formula 3.13

Formula 3.11, 312, 3.13:

a= intercept of the linear regression (calibration curve) [µ Vs], Area sample-blank = difference of sample and average blank area[µ Vs], Area $_{\text{standard}}$ =area of the standard used for calibration[µ Vs], b=slope of the linear regression (calibration curve)[e.g. µ Vs ng^{-1}], n=number of paired values (i.e. number of standards and associated areas), x_i = standard amount or concentration (x-axis)[e.g. ng], y_i= standard area (y-axis) [µ Vs], Y_i= calculated standard amount or concentration from regression analysis (Y_i=a+bx) [e.g. ng].

The precision for this instrument using the same condition of analysis for isoprene is reported in Table 3.4.

Compound	Precision of mixing ratios of isoprene	
	1ppb	10ppb
isoprene	17%	2%

Table 3.4 Precision of mixing ratios of isoprene.

3.5.6.8 Precision of volume and flow

The sampling of air volume was performed by the use of mass flow control flow controller units [size 500 sccm, MKS Instruments, U.S.A.] with a relative precision specified by the manufacturer to 3% of the maximum flow rate; the absolute precision of sampling volume and flow was calculated to 15 ml min^{-1}.

3.5.6.9 Precision of blank values

The average blank values of volatile organic compounds were subtracted from the respective samples on an area basis. Therefore the standard deviation of these average values was used for the calculation of the precision of sample analysis.

3.6 RESULTS

Diurnal fluctuations of ozone (only for the 2005 campaign), light, PAR, temperature, humidity, wind speed and wind directions were measured at the top of the tower above the canopy of the forest at the Fyodorovskoje and Zotino sites (Figures 3.6, 3.7 and 3.8). In 2005, temperature, light and wind speed ratios were similar to those observed in 2004. The main wind direction for the Fyodorovskoje site was from the South-West (SW) and South (S). For the Zotino site the main wind direction was from the North-West (NW) and South (S). The figures presented (3.6-3.8) give an overview of meteorological conditions during the measurement periods.

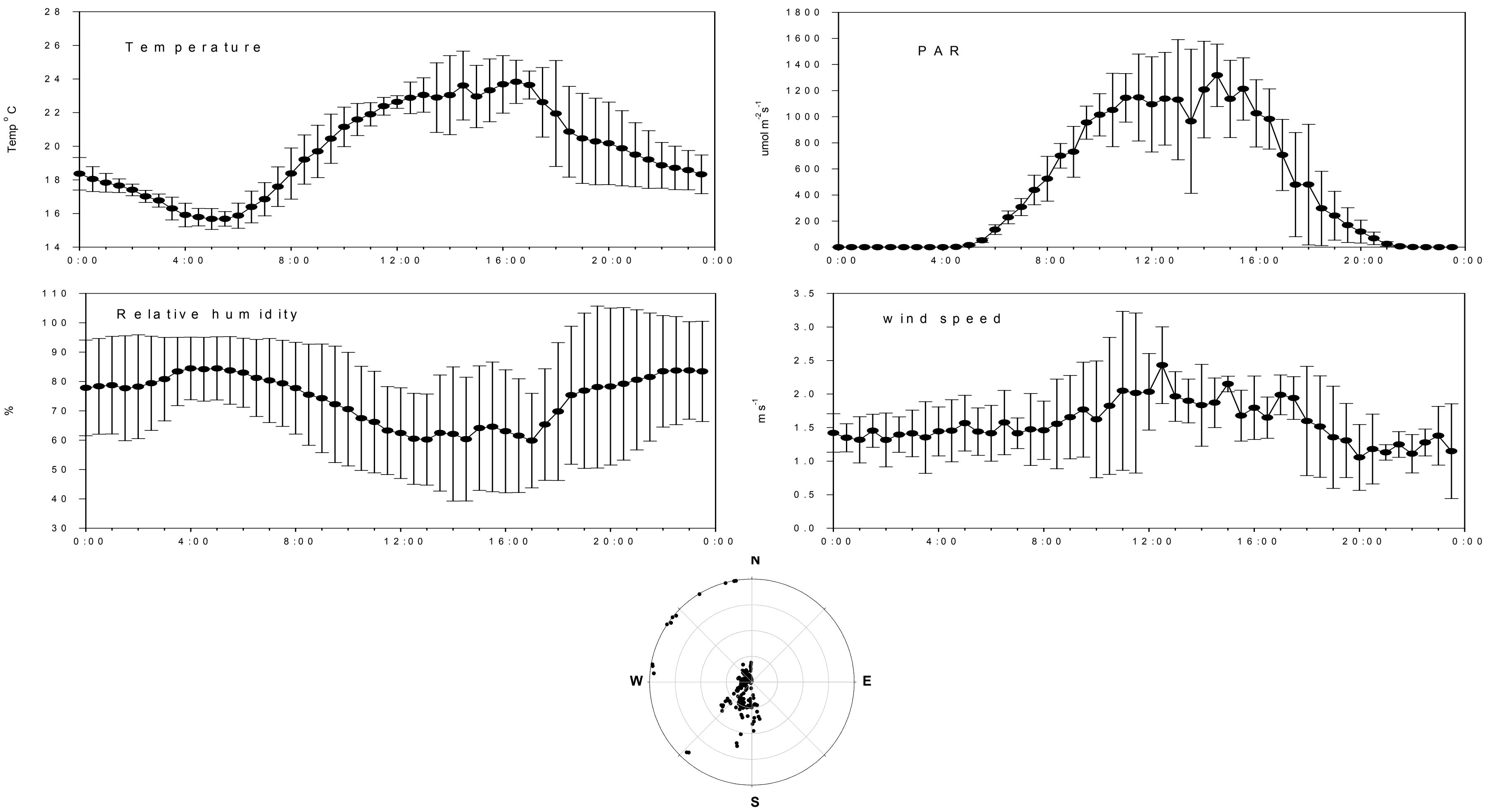


Fig. 3.6 Meteorological conditions: air temperature, photosynthetic active radiation (PAR), relative humidity wind speeds and wind direction, measured at the Fyodorovskoje site. All data are given as a mean value of 30 min averages over several campaign days and the standard deviations (1σ); n= 4 days.

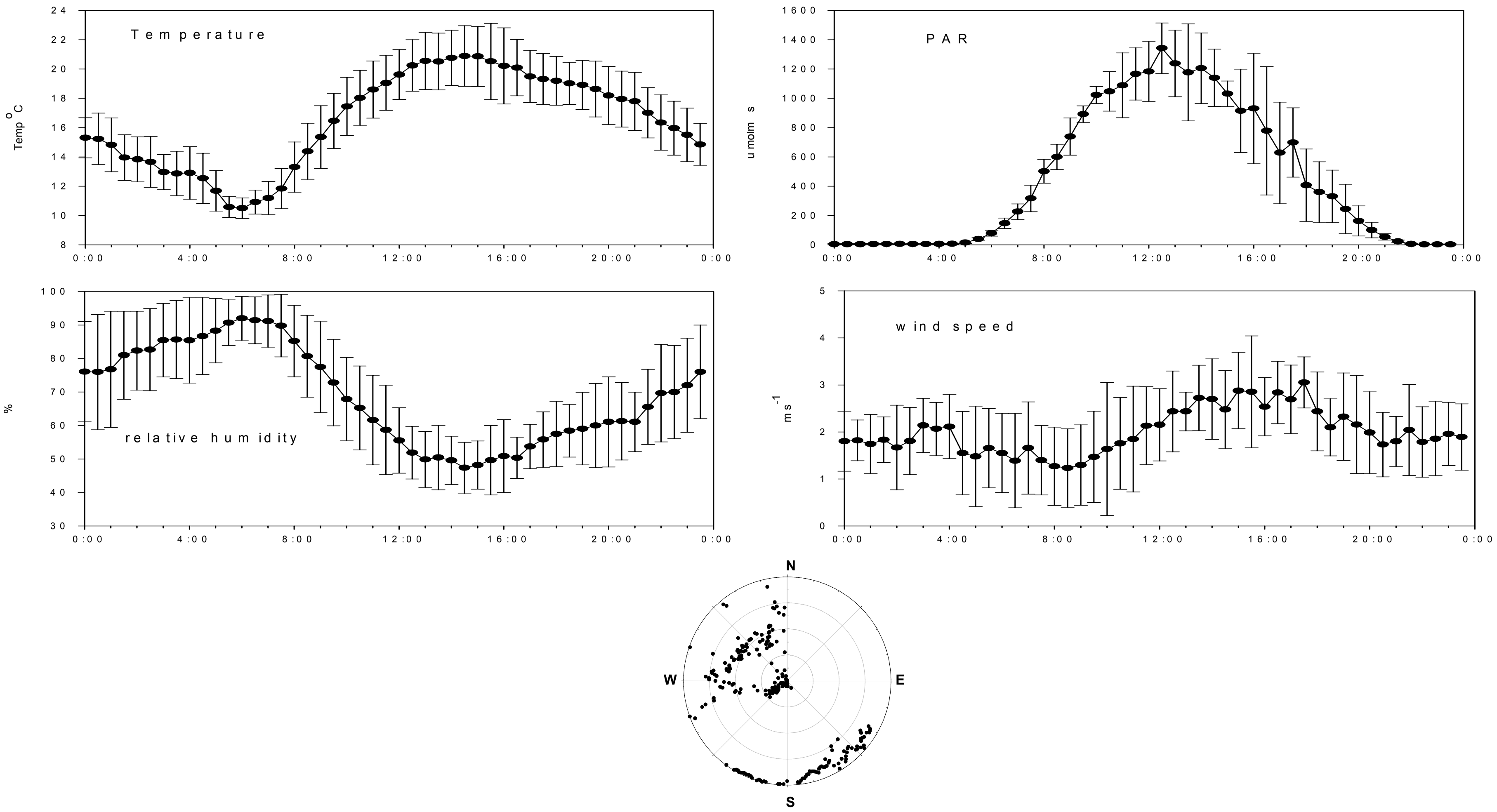


Fig. 3.7 Meteorological conditions: air temperature, photosynthetic active radiation (PAR), relative humidity, wind speed and wind direction as measured at the Zotino site. All data are given as a mean value of 30 min averages over several campaign days and the standard deviations (1σ); n= 5 days.

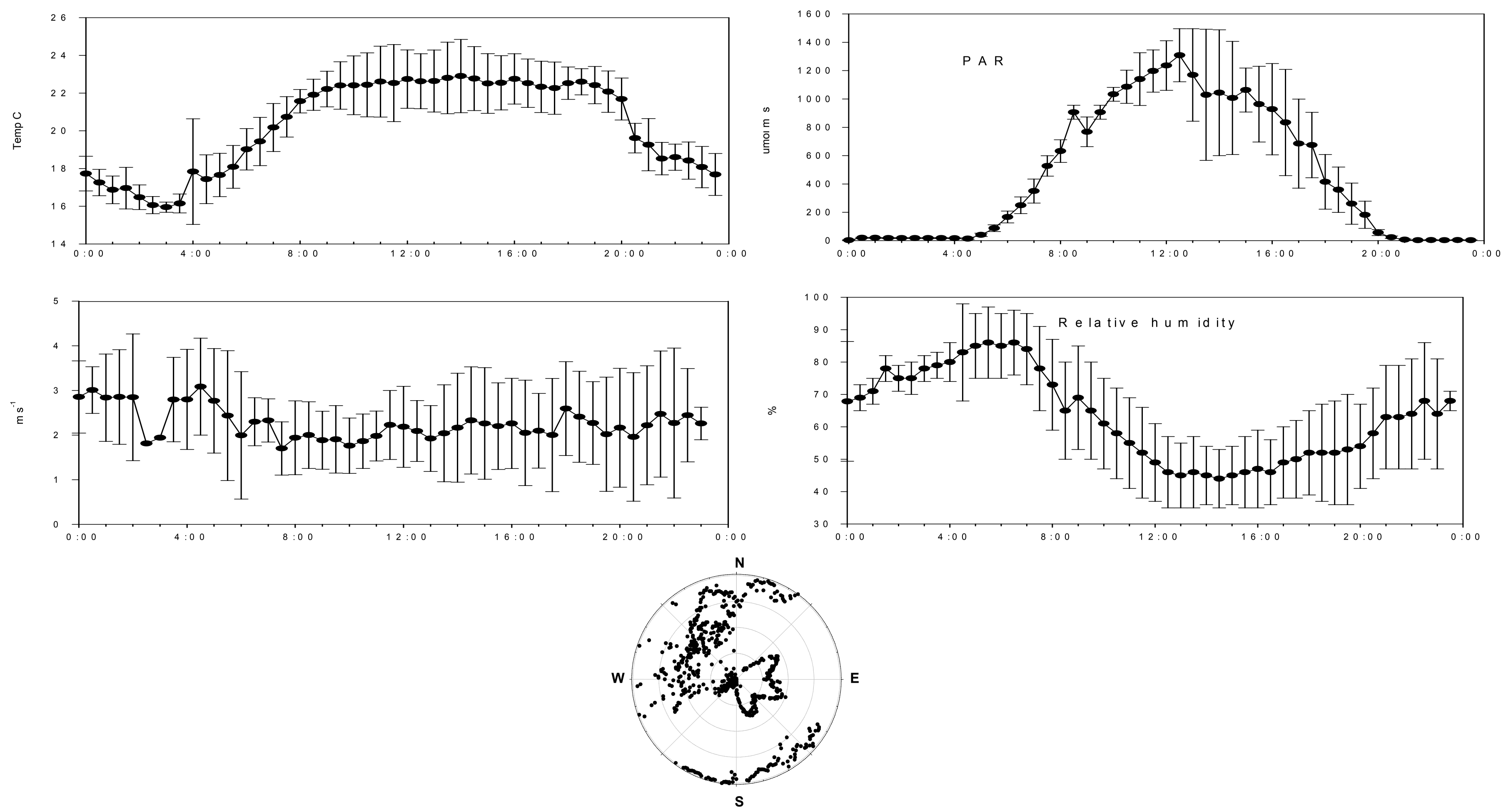


Fig. 3.8 Meteorological conditions: air temperature, photosynthetic active radiation (PAR), relative humidity, wind speed and wind direction as measured at the Zotino site. All data are given as a mean value of 30 min averages over several campaign days and the standard deviations (1σ); n=9 days.

There are two factors which strongly influence the atmospheric composition and chemical process over the Central Siberian region. First, the large forest areas provide the lower atmosphere with reactive compounds of biogenic origin, while also acting as an effective sink for many chemical species e.g. ozone, by dry deposition. Second, the strong seasonal cycle of solar radiation gives rise to a photochemically active summer when the biogenic emissions are most intense.

3.6.1 Ozone concentrations

According to Penkett and Brice (1986), Laurila and Hakola (1996), in the high northern latitude there is a spring maximum of background tropospheric ozone due to the high ozone concentrations in the lower stratosphere and to the photochemical oxidation of ozone precursors which have accumulated in the northern atmosphere during winter. The photochemical oxidation processes are driven by the strong seasonal cycle of the UV-A and UV-B radiation. Unfortunately, the record of ozone concentration measurements is only available for the period of the second campaign in 2005 at the Zotino site (Fig. 3.9).

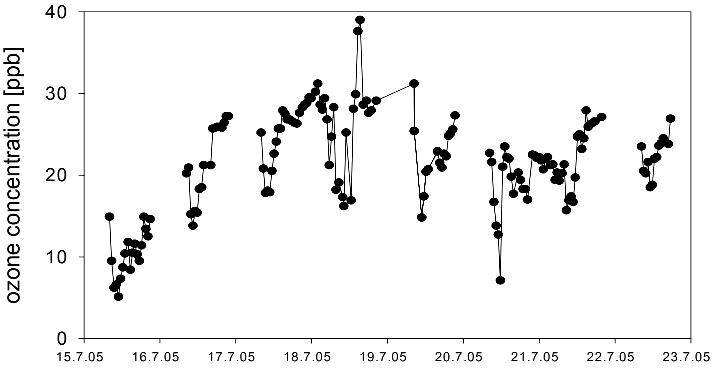


Fig. 3.9 30 min daily ozone concentration averages during the campaign in 2005 at the Zotino site.

Elevated ozone concentrations have detrimental effects on the vegetation process. However, in the Zotino region, 30 minutes daily ozone concentrations were less than 40 ppb. The ozone concentration was not stable and did not show a stable value, but the range of ozone was from 8 ppb to 39 ppb.

3.6.2 Concentrations of biogenic VOCs

The boreal forest is characterized by high foliar biomass densities, which makes it an important source of biogenic VOC. All dominant boreal tree species, Scots pine (Pinus sylvestris), Norway spruce (Picea abies), and birch (Betula pendula) are significant monoterpene emitters (e.g. Simpson et al.,1999; Hakola et al., 1998). α-pinene and β-pinene are the principal emitted compounds emitted, but the monoterpene emission profiles vary considerably between the tree species as well as seasonally.

The biogenic VOC are emitted during the vegetation period. However, some VOC are stored in the needles and can be released at any time. A variety of factors influence isoprene emission rates. Although the mechanism controlling isoprene production is not well known, some studies have correlated long-term and short-term variations in isoprene synthase activity (Kuzma and Fall et al., 1993). Isoprene emissions are coupled to the rate of biosynthesis and are therefore both temperature- and light-dependent (Guenther et al., 1993). Monoterpene emissions are reported to be mainly temperature-dependent (Tingey et al., 1981; Lamb et al., 1985; Juuti et al., 1990). These compounds are stored in the resin ducts of needles, and their emission is regarded as the result of evaporation out of from these storage pools (Dement et al., 1975; Tingey et al., 1980, 1991).

An algorithm to describe monoterpene emissions from plants was established by Tingey et al. (1991), in which the monoterpene emission rates are expressed as a product of a temperature- dependent term and a temperature-normalized standard emission rate. However, this standard emission rate is not a constant but varies because of unknown dependencies of the emissions. (Komenda and Koppmann, 2002).

A good approximation for the growing season in the Siberian region is the period when daily average air temperatures constantly exceed 5ºC. On average, all campaigns were performed during these periods.

Results of VOC levels in the air samples that have been collected are given in Figures 3.10-3.19 and Tables 3.5-3.8. During the two campaigns of the TCOS project, ambient air samples were collected. Monoterpenes were the dominant compound of the VOC species identified by GC/FID, whereas isoprene was present in a lower concentration. However, this composition was not constant for all sites, due to different ecosystem type, different temperature condition and humidity.

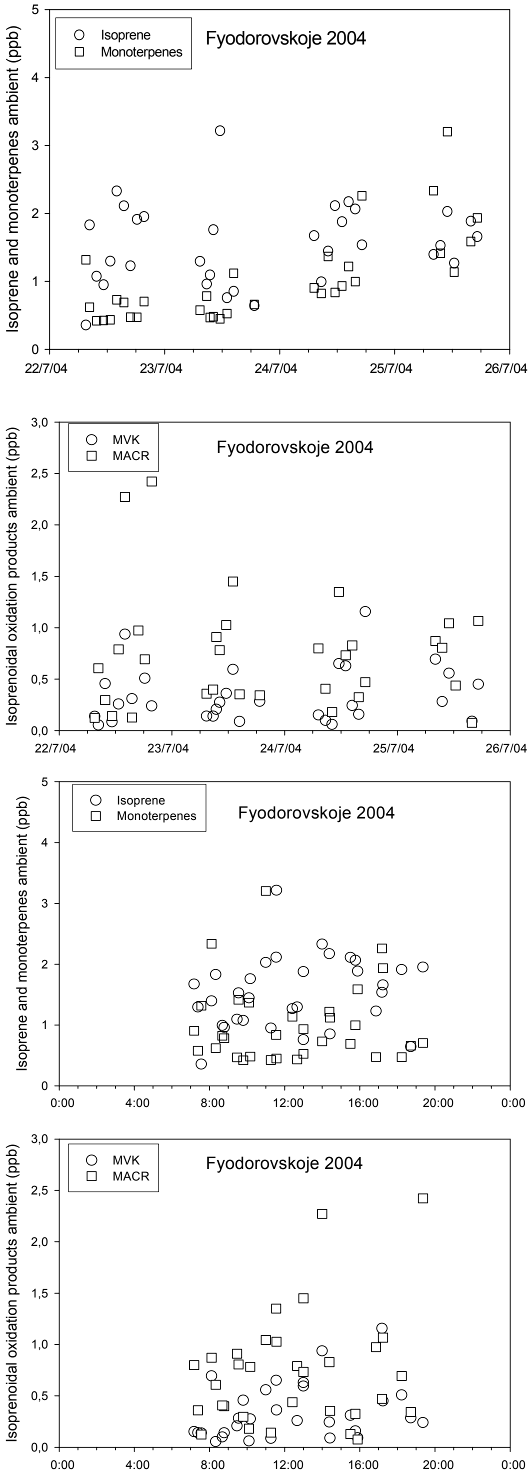


Fig. 3.10 Compilation of daily and diurnal cycles for the isoprenoids and their oxidation products during the campaign in 2004 at the Fyodorovskoje site. MVK= methyl vinyl ketone; MACR=methacrolein.

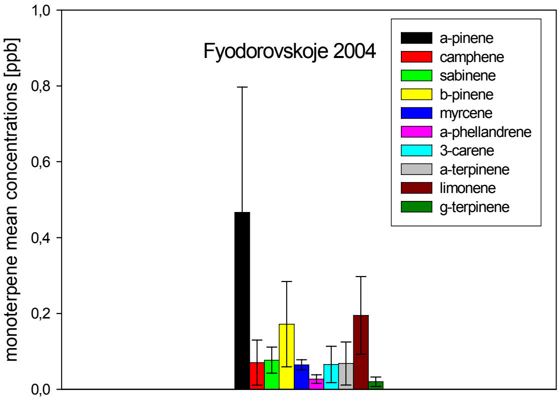


Fig. 3.11 Atmospheric mixing ratios of monoterpenes: α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α- terpinene, limonene, γ-terpinene for Fyodorovskoje site and standard deviation in concentrations for the compounds presented.

VOCs	Mean concentrations [ppb]	Maximum concentrations [ppb]	Minimum concentrations [ppb]
isoprene	1.54	3.21	0.36
MVK	0.34	1.16	0.05
MACR	0.73	2.42	0.08
α-pinene	0.47	1.69	0.15
camphene	0.07	0.25	0.01
sabinene	0.08	0.14	0.01
β-pinene	0.17	0.89	0.03
myrcene	0.06	0.33	0.01
α-phellandrene	0.03	0.18	0.01
3-carene	0.07	0.21	0.01
α- terpinene	0.07	0.16	0.03
limonene	0.19	0.46	0.06
γ-terpinene	0.02	0.15	0.01

Table 3.5 Mean concentrations, maximum and minimum concentrations of isoprene and its oxidation products, i.e. MVK and MACR, and monoterpenes at the Fyodorovskoje site in 2004.

A large number of monoterpene species were identified during measurements with α-pinene, β-pinene, limonene and 3-carene as dominating species for the Fyodorovskoje site. The highest mean concentration was detected for isoprene 1.56 ppb (maximum 3.21

ppb). Higher isoprene values at Fyodorovskoje might be explained by more isoprene-emitting broad leaf species as well as by spruce, which is reported to release isoprene (Street et al., 1996). Some highly reactive monoterpenes were detected, such as myrcene, α-terpinene and α-phellandrene. Of the monoterpenes observed limonene is the most reactive towards the OH-radical and ozone.

Fig. 3.12 Compilation of daily and diurnal cycles for the isoprenoids and their oxidation products during the campaign in 2004 at the Zotino site. MVK= methyl vinyl ketone; MACR=methacrolein.

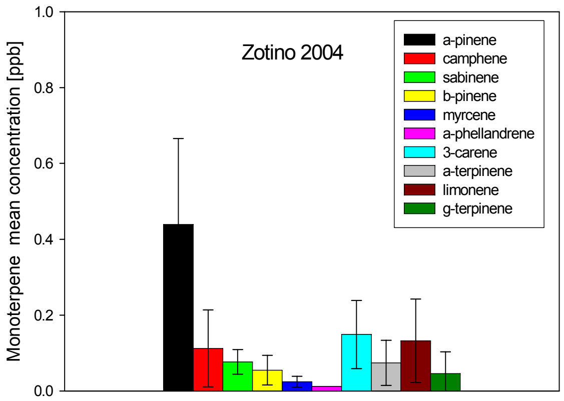


Fig. 3.13 Atmospheric mixing ratios of monoterpenes: α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α- terpinene, limonene, γ-terpinene for Zotino site.

VOCs	Mean concentration [ppb]	Maximum concentration [ppb]	Minimum concentration [ppb]
isoprene	0.56	0.86	0.29
MVK	0.98	1.39	0.02
MACR	0.82	1.70	0.09
α-pinene	0.44	1.06	0.18
camphene	0.11	0.37	0.01
sabinene	0.08	0.25	0.01
β-pinene	0.05	0.14	0.01
myrcene	0.02	0.06	0.01
α-phellandrene	0.01	0.01	0.01
3-carene	0.15	0.39	0.01
α- terpinene	0.07	0.13	0.01
limonene	0.13	0.49	0.03
γ-terpinene	0.05	0.18	0.01

Table 3.6 Mean concentrations, maximum and minimum concentrations of isoprene and its oxidation products i.e. MVK and MACR, and monoterpenes at the Zotino site in 2004.

The Zotino site is a site with a different tree species composition. For the Fyodorovskoje site, spruce is the dominant species as is the pine species for the Zotino site. An interesting situation was observed in the morning when the mixing processes of advection and convective transport are low. This gives a chance for the accumulation process of VOC and high concentrations in the mixed layer.

However, the reason for the low concentrations of some monoterpene species might be their low emission or fast decomposition process. On the other hand, the low ozone concentration (<30 ppb) might suggest that these compounds are emitted in low amounts due to low decomposition after emission.

The differences obtained between the two sites may be caused by the different ecosystem composition. Both sites are located in a mixed forest with dominant coniferous tree species, however with different species.

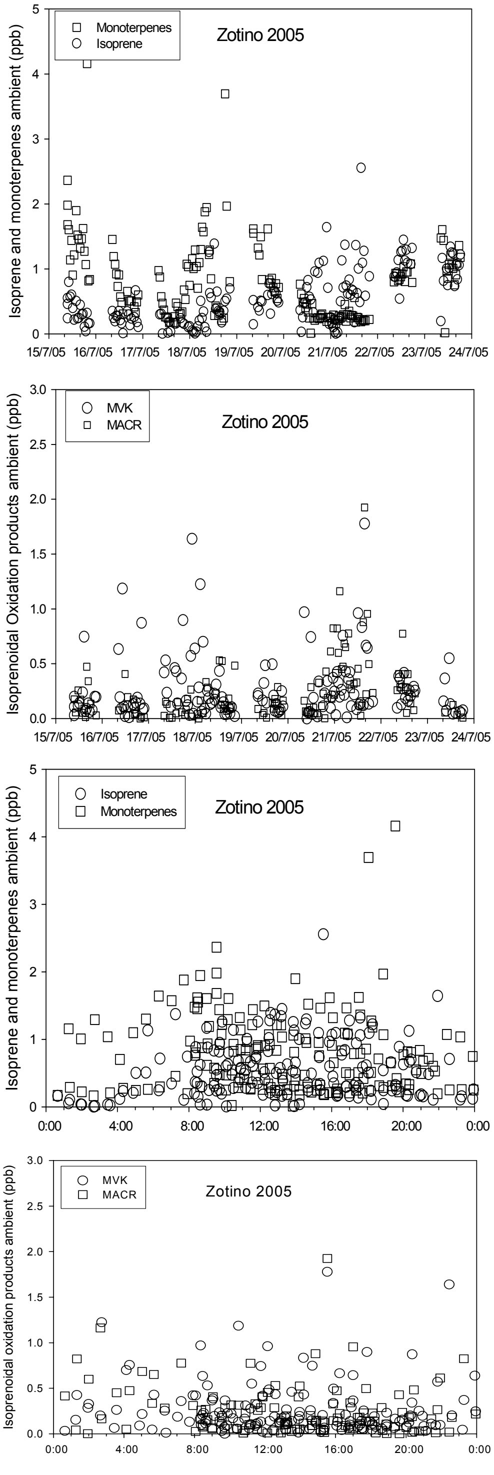


Fig. 3.14 Compilation of daily and diurnal cycles for the isoprenoids and their oxidation products during the campaign in 2005 at the Zotino site. MVK= methyl vinyl ketone; MACR=methacrolein.

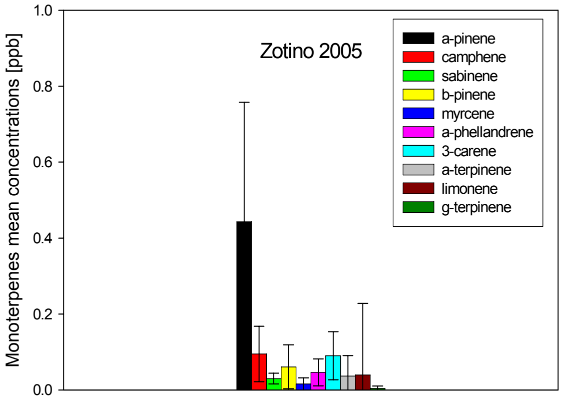


Fig. 3.15 Atmospheric mixing ratios of monoterpenes: α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α- terpinene, limonene, γ-terpinene for the Zotino site.

VOC	Mean concentration [ppb]	Maximum concentration [ppb]	Minimum concentration [ppb]
isoprene	0.56	2.56	0.01
MVK	0.32	1.78	0.01
MACR	0.25	1.93	0.01
α-pinene	0.42	1.57	0.08
camphene	0.09	0.79	0.01
sabinene	0.03	0.32	0.01
β-pinene	0.06	0.57	0.00
myrcene	0.02	0.08	0.00
α-phellandrene	0.05	0.08	0.01
3-carene	0.09	0.40	0.01
α- terpinene	0.04	0.31	0.00
limonene	0.04	0.41	0.04
γ-terpinene	0.01	0.02	0.01

Table 3.7 Mean concentrations, maximum and minimum concentrations of isoprene and its oxidation products, i.e. MVK and MACR, and monoterpenes at the Zotino site in 2005.

During the campaigns in 2004 and 2005 (with overnight measurements), the total monoterpene concentration exhibits a closer relation to temperature than isoprene concentration. On the other hand, an isoprene concentration correlates with PAR. This process is seen well in the overnight measurements in 2005, where isoprene concentrations are very low during the night time, whereas monoterpene concentration is still over 0. On the other hand, isoprene and monoterpene emissions do not depend only on light, but also on temperature (Kesselmeier et al., 1996; Kesselmeier and Staudt, 1999). This behaviour is in close accordance with the source descriptions, isoprene being produced and emitted in the light and the monoterpenes in this special case of dominating coniferous forests being released from storage pools in the needles and trunks.

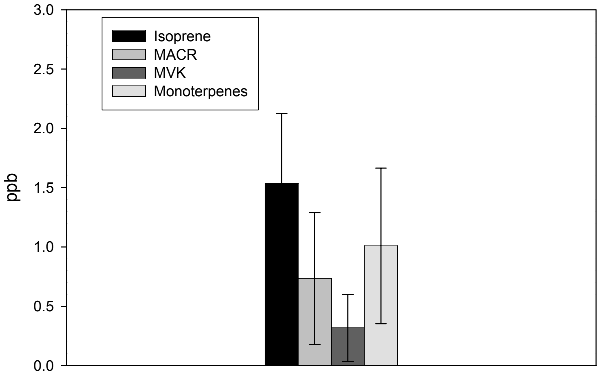
Fig 3.16 contains the data on diurnal and daily cycles for isoprene and for the sum of monoterpenes. In 2004 isoprene reached a maximum of 3.2 ppb around noon at the Fyodorovskoje site, whereas for the Zotino site (in 2004 and 2005), 2.5 ppb was the highest observed value. The higher isoprene values at the Fyodorovskoje site might be explained by more isoprene-emitting broad leaf species or by spruce, which is reported to release a spectrum of emissions. These emissions are strongly correlated with light and temperature. Current investigation shows that the emission factor for spruce can be as high as 24 $ug^{-1}h^{-1}$, suggesting that previous reports on isoprene emissions from coniferous species are significantly underestimated (Hayward et al., 2004). Monoterpenes showed concentrations of 2-2.5 ppb for the Fyodorovskoje site and around 2 ppb for the Zotino site. The most prominent OVOC were MACR and methyl vinyl ketone MVK which are isoprene oxidation products. The concentrations of MVK and MACR reached 2.0-2.5 ppb. However, most of the values were in the range of 0.3-0.5 ppb. The daily fluctuation of monoterpenes and isoprene were observed. It should be kept in mind that all samples were collected above the canopy of the forest where the highest source of emission exists.

The pattern according to which resources in plants are allocated to the production of monoterpenes is the subject of ecological theories, namely the carbon-nutrient balance and growth-differentiation balance hypotheses. Monoterpenes are the species produced in highly specialized organs, i.e. the resin ducts, whose construction and maintenance entail large metabolic costs beyond those of monoterpene synthesis alone (Lerdau and Gershenzon, 1997). Monoterpene emission rates increase with temperature and when the temperatures are high enough, they can also exist during night-time (Schween et al., 1997; Drewitt et al., 1998). Confirmation of this process was also noted during the Zotino campaign in 2005, whereas during the night-time, detectable concentrations of monoterpenes were observed. In contrast, the concentration of isoprene during the night-time was rather low. This can be explained by the process of isoprene production. Isoprene does not accumulate in secretory organs, but is formed inside the chloroplasts of the leaf mesophyll. It is synthesized from a recent process whose potential ecological function is not well understood (Fall and Wildermuth, 1998).

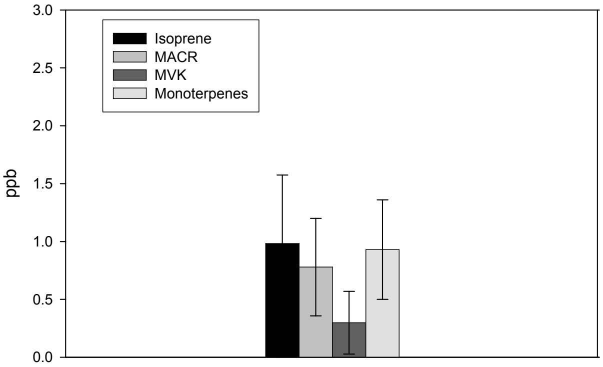
The diurnal cycle of monoterpene concentrations was a result of the diurnal cycle of temperature. Monoterpene emissions from coniferous plants are known to increase exponentially with temperature (e.g. Tingey et al., 1980; Lamb et al., 1985; Juuti et al., 1990). Tingey et al. (1991) explained the emissions of monoterpenes as a result of the diffusion from storage pools in conifer needles. Increasing needle temperatures result in increasing vapour pressures and thus lead to higher emission.

3.6.3 VOC species comparison during the campaigns in 2004 and 2005

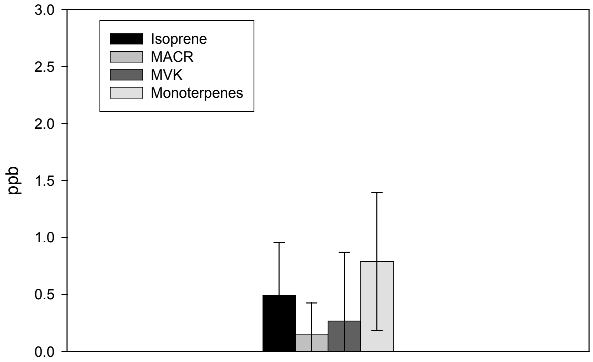
For a good comparison, the results obtained were sorted. To receive more information about monoterpenes, isoprene and its decomposition, certain products, i.e. MVK and MACR, were plotted for each site (Figure 3.16).



Fyodorovskoje 2004; 22-25.07.2004
n=38



Zotino 2004; 01-05.08.2004
n=49



Zotino 2005; 15-24.07.2005
n=172

Fig. 3.16 Overview of the mean values of isoprene, MVK, MACR and monoterpenes investigated at the Fyodorovskoje and Zotino sites (n=number of samples).

As seen in Fig 3.16, the m=mean concentration isoprene for the Fyodorovskoje site is higher than for the Zotino site during the same year. The main reason for this is caused by the species composition. Isoprene is mainly emitted by deciduous trees, whereas coniferous trees emit mostly monoterpenes. At the Fyodorovskoje site, isoprene dominates the composition of measured VOC.

However, the sum of MVK and MACR is higher then the concentration of isoprene. The same situation was observed at the Zotino site in 2004, but the ratio of monoterpenes and isoprene was equal to 1. In 2005 the situation was different. Interestingly, the isoprene mean concentration was lower than the sum of the mean monoterpenes value.

3.6.4 Isoprene, MVK and MACR

In the remote environmental area, the source of MVK and MACR is the processes of isoprene oxidation. Information about oxidation properties of the atmosphere can be determined by the ratio of (MVK+MACR)/isoprene. The average mean values of these ratios found in the study are listed in Table 3.8.

Site	Year of campaign	MVK/MACR	Std. dev.	(MVK+MACR)/Isoprene	Std. dev.
Fyodorovskoje	2004	0.43	0.24	0.68	0.32
Zotino	2004	0.38	0.17	1.10	0.43
Zotino	2005	1.76	0.47	1.22	0.55

Table 3.8 Ratios ppb/ppb Methyl Vinyl Ketone versus Methacrolein (MVK/MACR) and Isoprene oxidation products versus Isoprene (MVK+MACR)/Isoprene during measurement campaigns in 2004 and 2005.

Generally, in 2004 the ratio of MVK/MACR was higher than in 2005 for the Zotino site. However, the ratio oxidation product of isoprene (MVK and MACR) over isoprene was lower in 2004 than in 2005.

According to Montzka et al. (1995), the ratio of (MVK+MACR)/isoprene is not purely photochemically driven, as it is expected to be influenced by the isoprene emission rate and the proximity to emission sources as well as atmospheric mixing. A remarkable situation occurred in 2004, a constancy ratio between two different sites and between different ecosystems. The reason for this situation can be determined by the amount of available NO_x, which is non-linearly related to OH concentrations and is a key variable in the efficient production of MVK and MACR from isoprene concentrations. A similar situation was observed for campaigns in Rondonia, Brazil (for details see Kesselmeier et al., 2002a).

The overall diurnal course of the (MVK+MACR)/isoprene ratios is shown in Figures 3.17-3.19 for each site and campaign, respectively. The relatively higher ratios in the early morning hours are probably caused by factors such as an accumulation in the PBL (wind speed, oxidation process) which serve to remove isoprene preferentially over longer-lived oxidation products (e.g. OH from alkene ozonolysis, NO_3 radical chemistry, dynamic process effects and ozonolysis (Hurst et al., 2001). The ratio MVK/MACR is also a useful parameter in examining the oxidant conditions during the day.

The ratio depends on yields of MVK and MACR from the oxidation process of isoprene and on the relative reaction rates of isoprene, with both MVK and MACR with ozone. Oxidation of isoprene by OH and in the presence of NO_x produces MVK and MACR with respective yields of 32% ad 23% (Tuazon and Atkinson, 1990). In the situation where MVK and MACR did not undergo further oxidation, the ratio of MVK/MACR would consequently be ~1.4. However, MACR is removed through OH radical oxidation more quickly than MVK, which serves to drive up the ambient ratio MVK/MACR. For the process of ozonolysis, relative yields and reaction rates in both cases, isoprene yields and reaction rates are reversed in both cases:

1) isoprene yields more MACR than MVK;
2) MVK reacts more quickly with O_3 than MACR, both of which result in a lower MVK/MACR ratio.

The average daytime values of MVK/MACR for all sites are presented in Table 3.5 and also in Figure 3.17. In 2004 for the Zotino site, daytime ratios were typically 1.16 (±0.34), which is quite close to relative OH production yields of 1.4. In accordance with results obtained by model MESSy by MPICH Mainz, Germany (Jöckel, 2005*)*, values obtained suggest a relatively high O_3/OH ratio, i.e. a relatively low oxidation capacity due to low OH concentrations. With low OH concentrations, subsequent oxidation of longer-lived MVK and MACR is hindered, with the result that the observed, tends to be closer to production yield ratios. The ratio of MVK/MACR was on average much more scattered due to the higher individual uncertainties of MVK and MACR.

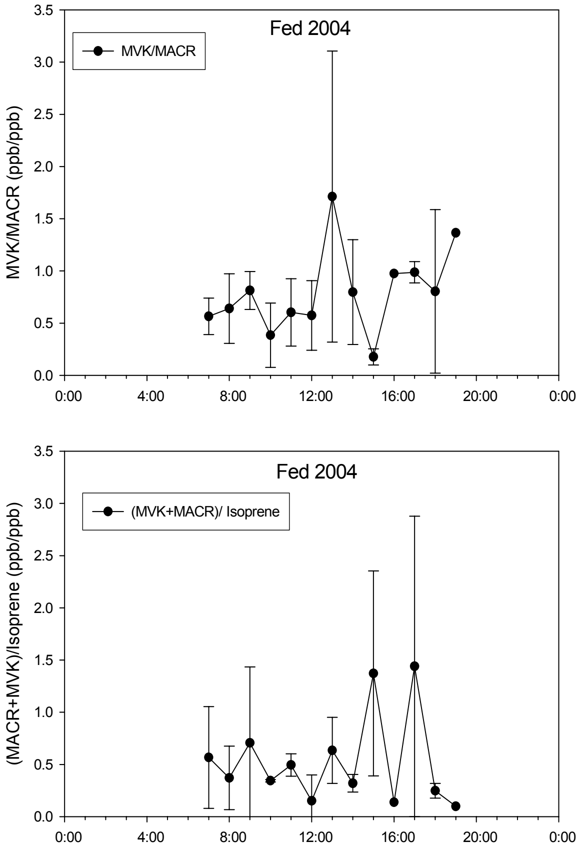


Fig. 3.17 Diurnal cycles of MVK and MACR versus isoprene and MVK/MACR ratios indicating the oxidation capacity during two campaigns in 2004. Data obtained for 2004 were grouped for sampling intervals of 30-80 min and presented as the mean values (±S.D) of data (n=1-4).

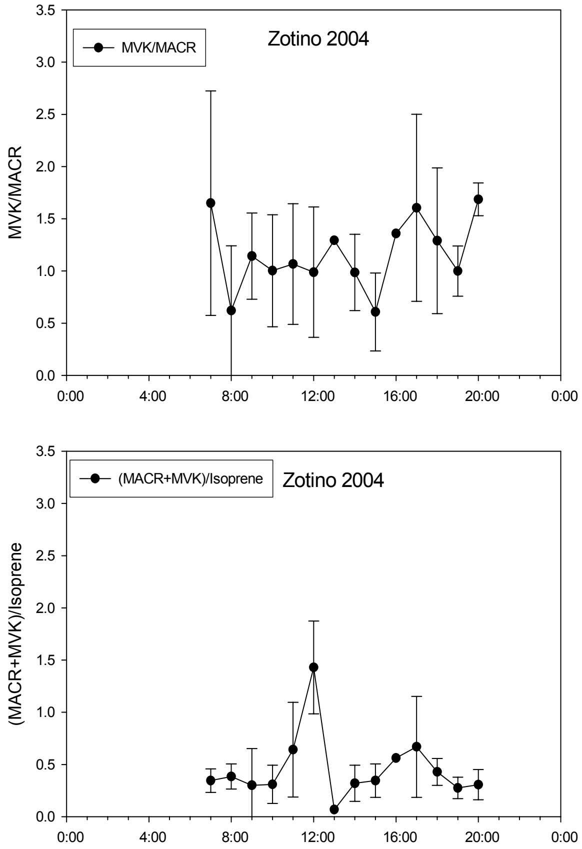


Fig. 3.18 Diurnal cycles of MVK and MACR versus isoprene and MVK/MACR ratios indicating the oxidation capacity during two campaigns in 2004. Data obtained for 2004 were grouped for sampling intervals of 30-80 minutes and presented as the mean values (±S.D) of the data (n=1-4).

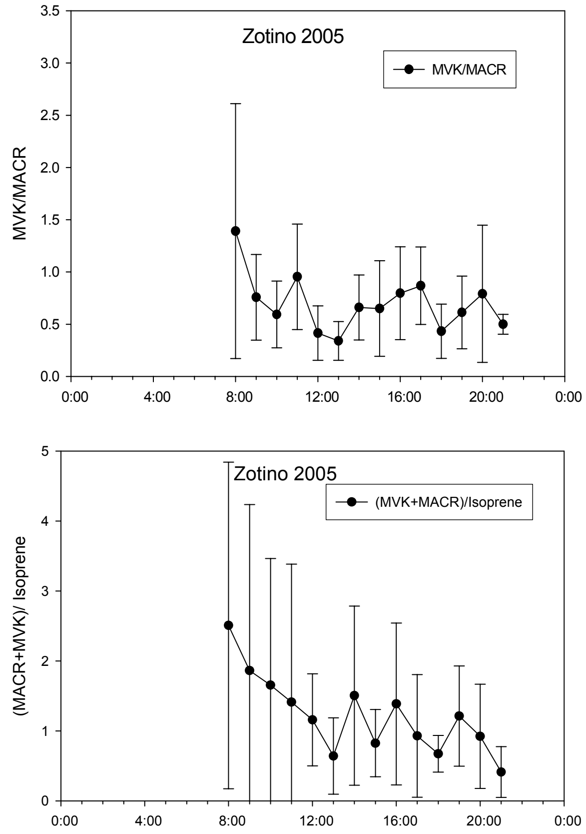


Fig 3.19 Diurnal cycles of MVK and MACR versus isoprene and MVK/MACR ratios indicating the oxidation capacity during two campaigns in 2005. Data obtained for 2005 were grouped for sampling intervals of 40 minutes and presented as the mean values (±S.D) of data (n=2-6).

3.7 Conclusions and discussion

In this study, isoprene and monoterpene concentrations have been measured using sampling cartridges and GC/FID analyses. Biogenic VOC have been measured during two campaigns in 2004 and 2005 in Russia. The data presented give an overview of two measurement campaigns of different VOC species measured in the Siberian forest. Isoprene and monoterpenes were the dominating compounds with different mean concentrations during two campaigns. In 2004 at the Zotino site, the concentration of isoprene was more or less equal to the sum of the concentrations of monoterpenes, whereas in 2005 at the same site, mean values of isoprene were lower than the sum of monoterpenes. The concentrations of α-pinene, β-pinene and camphene were also of a high value. α-Pinene and isoprene were the most abundant compounds throughout the measuring period. Biogenic hydrocarbons contribute significantly to the total reactivity towards the OH radical. During summer months they compromise almost all the measured OH reactivity. Monoterpenes and isoprene concentrations are dependent on the ambient temperature.

There were only small differences between the measurement campaigns in 2004 and 2005 in isoprene and monoterpene concentrations for the Zotino site. Of major importance were the results obtained for the VOC concentrations, which will be used in the modelling process in further studies. Variation in isoprene and monoterpene concentrations caused by different light and temperature have been observed, as far as different ecosystem types are concerned, these variations might also be explained by stresses of plant influence. The high concentration of isoprene at the Fyodorovskoje site might be caused by spruce which was reported to emit isoprene (Street et al., 1996, Lindfors et al., 2000).

The maximum concentration of monoterpenes reached a level of 1.69 for α-pinene. Ambient biogenic VOC measurements from European boreal forests have been reported by Hov et al. (1983) and Janson (1993). Hove et al. found terpene concentration in a forest in Norway varying from 0.8 ppb to 7.1 ppb. Janson reported similar terpene concentrations in a pine forest in Sweden, maximum concentrations being ~ 8 ppb. Hakola et al. 2000 performed measurements of ambient biogenic VOC concentration in a northern part of Europe at a boreal site in Finland with mainly conifer tree species *Pinus sylvestris* and *Picea abies*, as well as some deciduous trees: *Betula pendula* and *Betula pubescens*. The monthly average summer concentrations of isoprene were 0.3 ppb-1.7 ppb and monoterpenes 1.6-3.2 ppb. For detailed comparison see Table 3.9.

ppb	Ilomantsi 1997 1)	Ilomantsi 1998 1)	Fyodorovskoje 2004	Zotino 2004	Zotino 2005
isoprene	0.228	0.35	1.54	0.56	0.56
α-pinene	0.141	0.12	0.47	0.44	0.42
camphene	0.35	0.09	0.07	0.11	0.09
sabinene	0.43	0.24	0.08	0.08	0.03
β-pinene	0.28	0.22	0.17	0.05	0.06
3-carene	0.39	0.26	0.07	0.15	0.09
limonene	0.12	0.08	0.19	0.13	0.04

1) For detailed reference see Hakola et al. (2000).

Table 3.9 Comparison of monthly means of isoprene and monoterpene concentrations obtained during measurements at Ilomantsi (July 1997 and July 1998) with mean isoprene and monoterpene from measurement campaigns in 2004 and 2005.

Results obtained from comparison showed a difference in biogenic VOC concentrations. This difference shows that many factors affect emissions such as temperature, light intensity, plant phenology, injury, stress, etc. (Kesselmeier and Staudt, 1999), making emission inventory difficult. Ambient measurements of biogenic compounds in different environments can help in estimating the performance of such inventories. All the compounds detected, i.e. isoprene and monoterpenes, can be regarded as species which have an impact on aerosol formation as well as being targets for oxidants, and hence can end up in source compounds for organic aerosol particles. Without a better understanding of the processes leading to the emission of isoprene and monoterpenes, estimations of emissions remain uncertain. The data obtained provided information on the natural variability of isoprene and monoterpene concentrations from the Siberian region.

4. Airborne measurements of VOC and calculation of fluxes.

ABSTRACT

Flight measurement campaigns by means of different aircraft were carried out over Siberia region in 2004 and 2005 in two locations: Fyodorovskoje, 300 km to the west of Moscow and Zotino, 500 km to the north of Krasnojarsk in the central Siberian region. Vertical profiles of Biogenic Volatile Organic Compounds (BVOCs), ozone, CO_2, humidity and temperature were obtained. This chapter describes a series of flight campaigns using aircraft to measure BVOC in the atmospheric boundary layer and in a free troposphere. These experiments have been done as part of the TCOS project campaign over poorly investigated Siberian regions. Results of VOC concentration measurements and BVOC flux calculations by a simplified budget approach method are discussed. The range of fluxes obtained varies between 1.39-4.99 $mgCm^{-2}h^{-1}$ for isoprene and 0.49-4.97 $mgCm^{-2}h^{-1}$ for the sum of monoterpenes.

4.1 INTRODUCTION

The composition of the atmosphere system is largely a product of biological activity at the surface. Over 90% of the total volatile organic compounds (VOC) entering the atmosphere are biogenic (Guenther et al 1995). Most of the BVOC entering the atmosphere as a result of emissions from terrestrial ecosystems are highly reactive. Among the major biogenic emissions isoprene and terpenes, especially monoterpenes, are the most abundant. They react easily with ozone, OH and NO_3 radicals.

Most of the BVOC measurements have been performed at the surface or above the canopy of the forests. These may be biased by nearby emission and deposition processes. However, to judge the impact of BVOC, one important part of the information is the quantification of their fluxes. It is desirable to verify larger scale fluxes with measurements as well (Spirig et al., 2004).

About 2.4 PgC of the BVOC per year is emitted into the atmosphere and most of them are oxidized to CO or CO_2. This carbon is regarded as a loss of carbon photosynthetically. The importance of this loss is controversial. The impact of the oxidation of biogenic hydrocarbons on the atmosphere was first noted by Went, 1960. This carbon contributes several percent of the total flow of carbon between landscapes and atmosphere (Went, 1960) but the carbon was mentioned as a potentially significant term in analyses of carbon budgets (Clark 2001, Kesselmeier et al., 2002b). On the other hand, the global average for vegetative surfaces (NPP) is about 7 gC m^{-2} per year but could exceed 100 gm^{-2} per year at some tropical locations. The magnitude of these fluxes on both the landscape and global scales are small relative to the total carbon emission or deposition, but are significant relative to the net fluxes (Guenther, 2002). However, it should be keep in mind that hydrocarbon fluxes are very sensitive to biosphere changes and may vary significantly due to future perturbations.

4.2 Land ecosystems and carbon cycle

Land ecosystems are regarded as the most substantial global carbon sink besides the ocean. Higher plants acquire CO_2 by diffusion through tiny pores (stomata) into leaves and thus to the sites of photosynthesis. The total amount of CO_2 that dissolves in leaf water is about 270 PgC/yr, i.e., more than one-third of all the CO_2 in the atmosphere (Farquhar et al., 1993; Ciais et al., 1997). Around 120 PgC/yr is fixed by the photosynthesis carbon dioxide assimilation of green vegetation (Ciais et al. 1997; Prentice et al. 2001). The amount that is "fixed" from the atmosphere, i.e., converted from CO_2 to carbohydrate during photosynthesis, is known as gross primary production (GPP). This is also the approximate value necessary to support observed plant growth, assuming that about half the GPP is incorporated into new plant tissues such as leaves, roots and wood, and the other half is converted back into the atmosphere. About half of this total carbon is released back to the atmosphere through plant respiration (autotrophic respiration, Ra), leaving about 60 Pg C/yr. This annual plant growth, which is the difference between photosynthesis and autotrophic respiration, is referred to as net primary production (NPP). About 50 Pg C/yr of NPP returns to the atmosphere via decomposition of plant matter and soils. Estimates from remote sensing and atmospheric CO_2 data (Ruimy et al., 1994; Knorr and Heimann, 1995) concur with this value, although there are large uncertainties in all methods. Eventually, virtually all the carbon fixed in NPP is returned to the atmospheric CO_2 pool through two processes: heterotrophic respiration (Rh) by decomposers (bacteria and fungi feeding on dead tissue and exudates) and herbivores; and combustion in natural or human-started fires (Figure 4.1), which ultimately results in the net land uptake of carbon, termed the net biome production (NBP). NBP is estimated to range around 0.2 ± 0.7 Pg C/yr for 1980–1989 and 1.4 ± 0.7 Pg C/yr for 1989–1998. Due to the small ultimate residual sink, each flux of carbon into and out of terrestrial ecosystems should be investigated and accounted for to allow estimates for the processes involved in carbon sequestration in the biosphere. A substantial amount of carbon is re-emitted as volatile organic compounds (VOC) by terrestrial vegetation (Fehsenfeld et al., 1992; Guenther et al., 1995; Kesselmeier and Staudt 1999, Kesselmeier 2002b). The amount of carbon emitted by plants as isoprene, probably the most substantial fraction of isoprenoid emission, accounts for up to 2% of NPP in most cases, but can reach higher values (15–50%) under special conditions (Sharkey et al., 1991a, 1991b, 1996; Sharkey and Loreto, 1993; Harley et al., 1999)

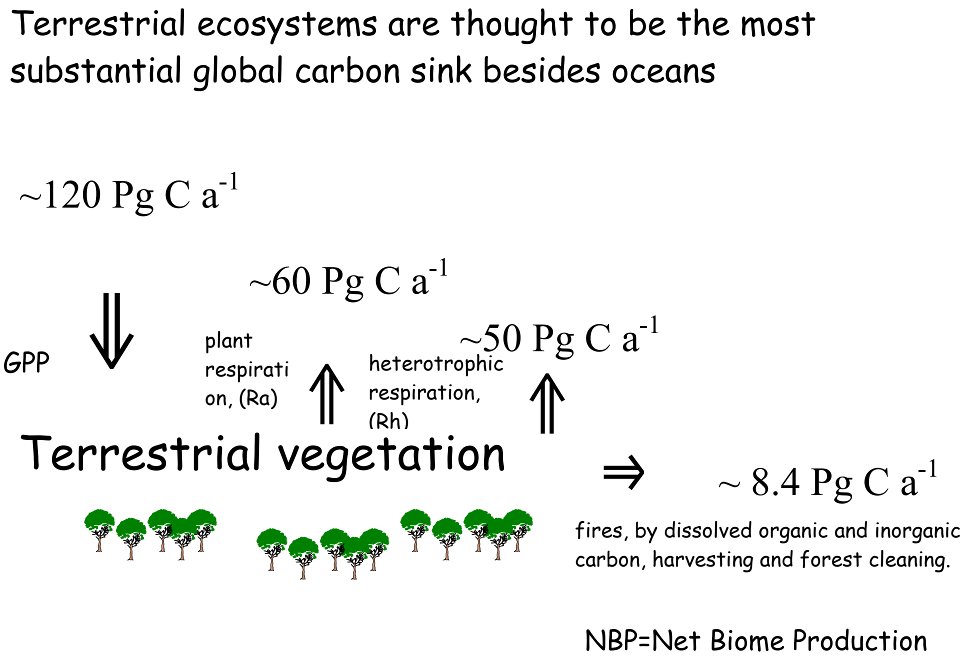


Fig 4.1 Terrestrial ecosystems and their carbon sinks.

4.2.1 Forests

Deforestation has been responsible for almost 90% of the estimated emissions due to land-use change since 1850, with a 20% decrease in the global forest area (Houghton, 1999). Deforestation appears to be slowing slightly in tropical countries (FAO, 1997; Houghton, 2000), and some deforested areas in Europe and North America have been reforested in recent decades (FAO, 1997). Managed or regenerated forests generally store less carbon than natural forests, even at maturity. New trees take up carbon rapidly, but this slows down towards maturity when forests can be slight sources or sinks (Buchmann and Schulze, 1999). To use land continuously in order to take up carbon, the wood must be harvested and turned into long-lived products and trees must be re-planted. The trees may also be used for biomass energy to avoid future fossil fuel emissions (Hall et al., 2000). Analysis of scenarios for future development show that expanded use of biomass energy could reduce the rate of atmospheric CO_2 increase (IPCC 1996; Leemans et al., 1996; Edmonds *et al.,* 1996; Ishitani *et al.,* 1996; IPCC, 2000). IPCC (1996) estimated that slowing deforestation and promoting natural forest regeneration and afforestation could increase carbon stocks by about 60 to 87 PgC over the period 1995 to 2050, mostly in the tropics (Brown *et al.,* 1996).

4.2.2 Net Ecosystem Production

Net ecosystem production (NEP) is the net accumulation of carbon by the ecosystem. It is the balance between carbon which enters and leaves the ecosystem. Most of the carbon enters the ecosystem as gross primary production and leaves through other processes (heterotrophic respiration, leaching, plant volatile emissions, methane flux and disturbance. NEP is an important representative parameter, which explains to us the increment of carbon stored by the ecosystem. NEP determines the impact of the biosphere on their quantity of CO_2 in the atmosphere. NEP is determined by factors that cause an imbalance between carbon gain and loss. NEP varies with season, time since disturbance, inter-annual variation in weather, and long term in the environment. High-latitude ecosystems are a net carbon source and carbon sink in cool years. The direct components of NEP show large temporal variation. Disturbances such as fires and forest harvesting are less important at other times. In ecosystems that have not recently experienced disturbance, NEP is a small net difference between two large fluxes: photosynthetic carbon gain and carbon loss through respiration and leaching. During the season of peak plant growth, NEP is positive because photosynthesis exceeds respiration. In winter, when photosynthesis is low, NEP is negative and it is mainly due to heterotrophic respiration. There is a necessary functional linkage between NPP and heterotrophic respiration. NPP provides the organic material that fuels heterotrophic respiration, and heterotrophic releases the minerals that support NPP. At a steady state, NEP equals zero, regardless of carbon input or climate. Leaching of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) to ground water and streams is a quantitatively important avenue of carbon loss from some ecosystems. Lateral transfer of carbon into or out of ecosystems can be important to long-term carbon budgets of ecosystems. Carbon can move laterally in ecosystems through erosion, deposition by wind, and in water. Disturbance is an episodic cause of carbon loss from many ecosystems. Disturbances such as fires, harvesting of plants or peat can be a major way of carbon losses from ecosystems at the time when they occur.

Because of the sensitivity of NEP to succession status, NEP estimated on the regional scale depends on the relative abundance of stands of different ages. NEP on the regional scales is termed Net Biome Production (NBP) (Schulze et al. 2000). At times of increasing disturbance frequency, NBP is likely to be negative. Conversely, areas that have experienced widespread abandonment of agricultural lands in the last century, as in Europe, may experience a positive NBP.

4.2.3 Net ecosystem exchange (NEE)

Net ecosystem exchange (NEE) provides a direct measure of the net CO_2 exchanged between ecosystems and the atmosphere. One of the main problems in NEE measurements is that we cannot measure most of the component processes directly. Only some components of the ecosystems can be measured, such as accumulation of plant biomass. An important tool in improving our estimates of NEP has been an enhanced ability to measure NEE, which is the net exchange of CO_2 between the ecosystem and the atmosphere. For long period measurements such as intervals of 30 minutes, NEE is equal to NEP. We can estimate that NEE is the balance between GPP and ecosystem respiration

(Reco), which is the sum of plant respiration (R plant) and heterotrophic respiration (R hetero).

$NEE= GPP - (R\ \mathit{hetero} + R\ \mathit{plant}) = GPP - R_{eco}$ Formula 4.1

NEE which excludes flux associated with disturbance and leaching is the largest component of NEP in most ecosystems. GPP (net photosynthesis) is zero in the dark, so NEE is a direct measure of ecosystem respiration (R ecosyst) under these conditions.

$NEE\ dark= -R_{eco}$ Formula 4.2

The total diurnal R ecosyst can be estimated from simple models of R ecosyt as an exponential function of temperature. During the day, NEE is approximately equal to the sum of GPP and ecosystem respiration.

$NEE\ light =GPP -R_{eco}$ Formula 4.3

or

$GPP= NEE\ light + R_{eco}$ Formula 4.4

As a result we are obtaining only an approximation, because mitochondrial respiration in leaves declines in the light, when much of the energy for metabolism comes directly from carbon fixation.

4.2.4 Net ecosystem balance (NECB)

Accordance to the suggestion of Lovett et al. (2006), NEP can be defined as GPP minus R_{eco}. Defined in this way, NEP is conceptually simple and analogous to NPP (photosynthesis minus the respiration of primary producers). It can therefore be unambiguously incorporated into biogeochemical models and is independent of the continually evolving technology of measuring the components of ecosystem C budgets. It was proposed that the term net ecosystem carbon balance (NECB) be applied to the net rate of C accumulation in (or loss from [negative sign]) ecosystems. NECB represents the overall ecosystem C balance from all sources and sinks, physical, biological, and anthropogenic:

NECB = dC/dt

Net fluxes of several forms of C contribute to NECB:

$NECB=-NEE+F_{CO}+F_{CH4}+F_{VOC}+F_{DIC}+F_{DOC}+F_{PC}$ Formula 4.5

Where

NEE is the net ecosystem exchange (the net CO_2 flux from the ecosystem to the atmosphere (or net CO_2 uptake [positive sign]),

F_{CO} is net carbon monoxide (CO) absorption (or efflux [negative sign]);

F_{CH4} is net methane (CH_4) consumption (or efflux [negative sign]);

F_{VOC} is net volatile organic C (VOC) absorption (or efflux [negative sign]);

F_{DIC} is net dissolved inorganic C (DIC) input to the ecosystem (or net DIC leaching loss [negative sign]);

F_{DOC} is net dissolved organic C (DOC) input (or net DOC leaching loss [negative sign]);

F_{PC} is the net lateral transfer of particulate (non-dissolved, non-gaseous) C into the ecosystem (or out of [negative sign]) by processes such as animal movement, soot emission during fires, water and wind deposition and erosion, and anthropogenic transport or harvest. Extrapolation of NECB to larger spatial scales has been termed “net biome productivity” (NBP) (Schulze and Heimann, 1998).

4.3 Experiment

The experiment was performed during two measurement campaigns in 2004 and 2005. More information about characterization of the meteorology, site location (maps) and biosphere composition can be found in Chapter 3.

4.3.1 Measurements

During the years 2004 and 2005, two measurement campaigns with cartridge sampling, flask sampling and in-situ CO_2 measurements, as well as meteorological parameters, were performed using an Antonov 2 (AN- 2) aircraft. The measurements were performed at selected locations. In 2004 airborne and ground measurements were taken in Fyodorovskoje and Zotino, and in 2005 in Zotino in Central Siberia.

Measurements were performed during midday and late afternoon in the area of eddy covariance flux towers with cartridge sampling on the selected levels.

Region	Latitude; Longtitudes	Date of campaigns
Fyodorovskoje	56 28' N; 32 56' E	19-20.07.2004
Zotino	60 45' N; 89 23' N	30-31.07.2004 12-13.07.2005

Table 4.1 Location and date of campaigns performed.

Measurement flights were performed twice per day, i.e. one midday flight and one late afternoon flight. During each flight steel cartridges were sampled at different levels of altitude. In the area of Fyodorovskoje, because of the limitation of the flight duration, cartridges were sampled only at three different altitudes. In the area of Zotino cartridges were sampled at four altitudes.

The flight measurements are highly dependent on weather conditions. All flights were performed during high pressure weather conditions. In addition, the flights were affected by the fixed operational hours of the local operator and the availability of flight areas to the place of the measurements (military area).

4.3.2.1 Atmospheric Boundary Layer

The atmospheric boundary layer is defined as the part of the troposphere that is directly influenced by the presence of the earth’s surface, and responds to surface forcing with a time scale of about an hour or less (Stull, 1999). The typical height of the boundary layer top varies between 100 and 3000m. The process of boundary layer formation is connected with solar heating. The solar heating causes thermal plumes to rise, transporting moisture, heat and aerosols. The plumes rise and expand adiabatically until a thermodynamic equilibrium is reached at the top of the atmospheric boundary layer. The moisture transferred by the thermal plumes forms convective clouds. Thereby the shallow night-time “stable boundary layer” (ABL), growing during daytime because of thermal conversion, converts into the “convective boundary layer” (CBL).

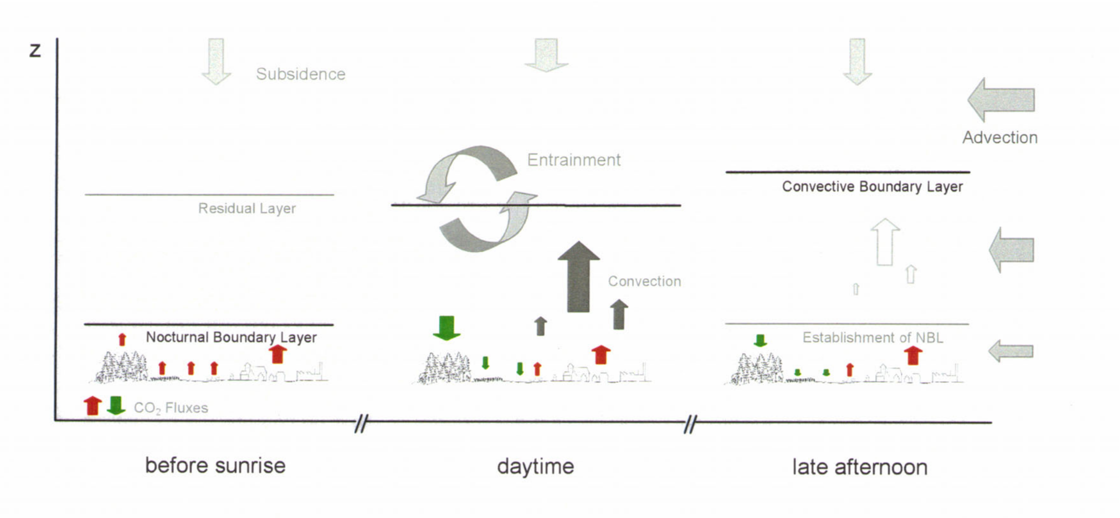


Fig.4.2 Scheme of the CO_2 fluxes and CBL behaviour on a summer day, showing CBL development from the nocturnal/stable boundary layer until the establishment of the next night-time boundary layer.

After this process drier air from the free troposphere penetrates down, replacing rising air parcels. The part of the troposphere between the highest thermal plume tops and deepest parts of the sinking free air is called the entrainment zone. The convective air motions generate intense turbulent mixing. This tends to generate a mixed layer, which has potential temperature and humidity nearly constant with height. When buoyant turbulence generation dominates the mixed layer, it is called a convective boundary layer

(CBL). The lowest part of the boundary layer is called the surface layer. In windy conditions, the surface layer is characterized by a strong wind shear caused by friction.

The boundary layer from sunset to sunrise is called the nocturnal boundary layer. It is often characterized by a stable layer, which forms when the solar heating ends and the radiative cooling and surface friction stabilize the lowest part of the CBL. Above that, the remnants of the daytime CBL form a residual layer. The nocturnal boundary layer may also be convective when cold air adverts over a warm surface. The atmospheric boundary layer can be used for the description of large areas (Rupach et al. 1993, Rupach 1995, 1998, Cleugh et al. 2003).

Based on this approach, several scientific groups started to measure parameters such as energy fluxes or fluxes of climatic relevant trace gases, by aircraft measurements on a larger scale (Lloyd et al. 2001, 2002; Levin et al. 2002, Ramonet et al. 2002). These investigations have been performed over large areas such as Siberia and the Amazon.

4.3.3 Continuous Flight Measurements

4.3.3.1 Airborne measurements

For the accurate vertical profiling of VOC mixing ratios from 100 to 3000m above the canopy, an aircraft (Antonov-2) was employed equipped with the VOC sampler as used for the tower measurements. The twelve profiles reported here were obtained during the period of July-August 2004 and July 2005, just in advance of the intensive tower-based flux measurements. Six of these profile measurements were made around midday (10:00–12:00 local time, LT), and six profile measurements were conducted in the late afternoon (16:00–18:00 LT). For each of the 12 respective flights, a similar flight path and schedule were used. The measurements were performed in two locations. In the first location, after take-off at the airport of Tver and transfer at an altitude of 200 m to the Fyodorovskoje tower site, the profile flight schedule consisted of a continuous profile upwards, from 100m to altitudes of 3000m above the canopy, followed by 2–4 samples collected within the CBL for MLG flux calculations on each flight. The GPS system tracked the aircraft position in longitude, latitude, and altitude. However, transfer of GPS data abroad from Russia was strictly forbidden. In the second location, the plane took off from the Podkamiennaja Tunguska airport, flying according to the same scheme as in the first location. Each of these flight legs allowed for a 20 min cartridge sampling interval (at flow rates of 200 ml min^{-1}). Each flight path covered a length of ca. 25 km to provide sufficient integration time to average spatially over at least several eddies, in order to obtain representative mean CBL concentration profiles. The VOC sampler for solid sorbent cartridges provided the collection of samples on selected types of adsorbents that were analysed by GC-FID to cross-check identification and quantification of VOC species. The CO_2 mixing ratio was measured by an infrared gas analyser (Licor 6251) setup according to Lloyd et al. (2002). After take-off, ambient air from outside the aircraft was continuously drawn through a ca. 5m long 1/4" Teflon tube. The inlet end was forward of all engines in a selected position to minimalize the possibility of sampling exhaust gases, and was equipped with a Teflon filter of 2 μm pore size that was replaced prior to each flight. To avoid possible ozone interference, an ozone scrubber consisting of multiples layers of MnO2-coated copper mesh (Type TO341FC003, Ansyco, Karlsruhe, Germany) was mounted in the sample line ahead of the VOC sampler.

4.3.3.2 Trace gas collection and analysis

For all the measurements, ambient air samples were collected on solid adsorbents for off-line analysis in the lab. The airborne samples were collected on 2-bed graphite carbon adsorbents and analysed using a thermal desorption gas chromatograph with a flame ionization detector (GC-FID) as described in Kuhn et al. (2002; 2004). For the GC-FID technique, calibration was accomplished by use of different gaseous standards containing isoprene, several n-alkanes, methyl vinyl ketone (MVK), and methacrolein (MACR). The detection limit of the method was estimated as the greater of the variability in the blank levels (at the 95% confidence level) or a chromatographic peak three times the noise for each compound, and was typically 25-30 ppt for isoprene and 10 ppt for monoterpenes. Hence, typical uncertainties reached 10% for isoprene at 1 ppb and ranged from 5 to 30% at 100 ppt for monoterpenes, depending on the individual monoterpene peak resolution and blank variability.

Retention features and a selection of biogenic VOCs, their degradation products, calibration and quality assurance procedures are described in detail in Ciccioli et al. (2002). Dominant monoterpene species detected by solid adsorbent analytical systems (CG-FID) were isoprene, α-pinene, camphene and limonene.

Deviations from an ideal atmospheric gradient may be observed if the sample collection period is shorter than the average convective turnover time, i.e., if sampling times do not integrate over several large eddies. With typical horizontal wind speeds of 3 m s^{-1}, and the scale of some convective eddies being as large as the CBL depth, minimum sample times of 15–30 min, or a length of several hundred meters are needed to be integrated over a representative air mass (Lenschow et al., 1980; Lenschow and Stankov 1986).

4.4. Flux estimation by box model method.

For flux estimation a simplified mixed-layer scalar conservation equation was used which can be written as:

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + \frac{\overline{(wc)_{zi}} - \overline{(wc)_{o}}}{zi} = S \qquad \text{Formula 4.6}$$

where C is the mean scalar mixing ratio, U is the mean horizontal wind, t is time, x is the horizontal axis aligned with the mean wind, zi is the height of the mixed layer capping inversion, $(wc)_{zi}$ and $(wc)_{o}$ are the turbulent vertical fluxes of scalar C at the inversion and the surface, respectively, and S is a source or sink of the scalar in the mixed layer. This simplified form assumes that turbulent horizontal fluxes and mean vertical advection are negligible and that the vertical flux profile in the mixed layer is linear. These assumptions are all commonly satisfied in a well-mixed convective boundary layer.

$$\overline{(wc)_{o}} = \overline{(wc)_{zi}} + zi\left(\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + (\mathrm{LC})\right) \qquad \text{Formula 4.7}$$

In this simple box model (BM) estimate of the biogenic hydrocarbon emissions, we assume that the mean mixing ratio has reached a steady state and is homogeneous in space, entrainment flux $(wc)_{zi}$ is negligible and the hydrocarbons are oxidized primarily by OH and O_3 so that the oxidation rate $L(s^{-1})$ is defined as $[k_{OH}OH]+[k_{03}O_3]$ where k_{OH}, k_{O_3} are reaction rate constants and OH and O_3 are mixing ratios of hydroxyl radical and ozone, respectively. Given these assumptions, it becomes

$$\overline{(wc)_o} = ziLC \qquad \text{Formula 4.8}$$

where C is interpretive, as a mixed layer average.

However, there are limitations to these simplifying assumptions. We can evaluate the errors in the fluxes which stem from neglecting the entrainment flux $(wc)_{zi}$, time rate change $zi(\partial C/\partial t)$ and advection $ziU(\partial C/\partial x)$ terms. Estimation entrainment was done using a simple jump model [Lilly, 1968]. Since the lifetime of biogenic VOC is fairly short, it was assumed that their mixing ratio is zero above the boundary layer. The jump in VOC mixing ratio across the planetary boundary layer top is then roughly the mean boundary layer mixing ratio. The entrainment flux is given by the product of the jump in mixing ratio and the mixed layer growth rate (typically 0.05 ms^{-1} during the day). Since entrainment dilutes the mixed layer, neglecting entrainment in the box model causes a systematic underestimate of the surface flux. The underestimate is at most about 1 mg C $m^{-2}h^{-1}$ for isoprene, 0.2 mg C $m^{-2}h^{-1}$ for α-pinene, 0.1 mg C $m^{-2}h^{-1}$ for β-pinene.

The mixing ratio time rate of change $zi(\partial C/\partial t)$ from advection $ziU(\partial C/\partial x)$ using these observations cannot be distinguished, but can be estimated as the magnitude of the sum of them by observing the evolution in the mean mixing ratio profile. The mixing should increase over the course of the day, neglecting advection. This would mean that the box model, which assumes a steady state, again underestimates the surface fluxes. The observations show significant but random trends in the mixed layer over the course of the day. This indicates that the steady state approximation is on the average reasonable and that advection random in sign is the dominant term. The mean time rate of change in mixing ratio is about 0± 1 ppbC h^{-1} for isoprene and 0± 0.5 ppbC h^{-1} for α- and β-pinene. Multiplied by a typical zi, this implies an uncertainty of ± 0.4 mg C $m^{-2}h^{-1}$ isoprene and 0.2 mg C $m^{-2}h^{-1}$ for α- and β-pinene in the box model surface flux estimates.

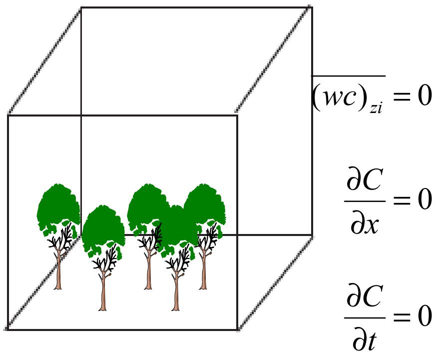


Fig. 4.3 Mixed box technique used for VOCs flux calculation

The next point was an analysis of the uncertainty in the inputs to our box model flux estimate. The largest source of uncertainty is the OH concentration needed to estimate the chemical loss L. An estimation of the chemical loss rate L, OH and ozone rate a coefficient was used (reported by Atkinson, 1990) and the ozone mixing ratios which were measured.

The uncertainty of OH concentration at these sites is caused by lack of measurement data. However, OH concentration data for measurement periods were obtained from a model ECHAM 5. Jacobs et al. 1996 note that direct measurements of OH concentrations in rural areas tend to be lower than those computed from photochemical models. This is most probably because the models underestimate OH sinks which come from oxygenated VOC.

$$\overline{(wc)}_o = zi[VOC](k_{OH}[OH]+k_{03}[O_3] \quad \text{Formula 4.9}$$

4.4.1 OH radical concentration and coefficients

As there are as yet no direct measurements of OH radical concentrations published for typical CBL, an attempt to infer concentrations was done using model Model ECHAM5/ MESSY (Jöckel et al. 2005). Results obtained from the model calculations were used in a further calculation of VOC fluxes.

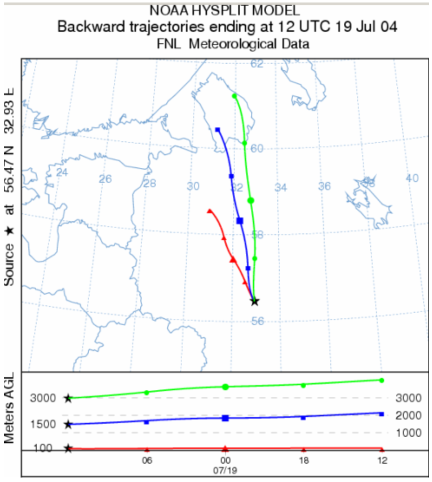
For the calculation of BVOC flux rate coefficients, as for isoprene and selected monoterpenes at 298° K temperature were used and are presented in Table 4.2

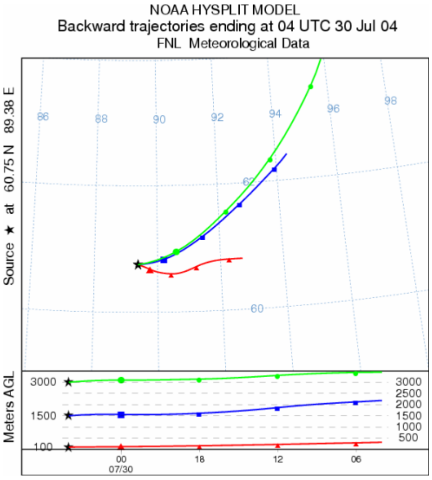
	OH	Ozone	NO_3
	10^{12}k (cm^3 molecule $^{-1}$ s^{-1})	10^{18}k (cm^3 molecule $^{-1}$ s^{-1})	10^{12}k (cm^3 molecule $^{-1}$ s^{-1})
Isoprene	101	12.8	0.68
a-Pinene	53.7	86.6	6.16
Camphene	53	0.9	0.66
Sabinene	117	86	10

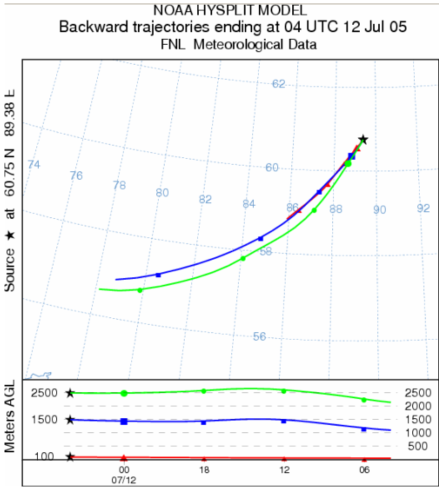
Table 4.2.Rate constants k for the reactions with isoprene and selected monoterpenes with NO_3 radical, OH radical and ozone (Atkinson et al., 2003, 2005)

4.5 Results and discussion

Two measurement campaigns in 2004 and 2005 were carried out in the middle of the summer season. Airborne profile measurements were carried out on two days during July 2004 at the Fyodorovskoje location, and four days in the period between July 2004 and August 2005. In the first location weather conditions were mostly dry and sunny, with foggy mornings. In the second one the weather was mostly dry and very sunny with *cumulus* clouds from time to time. Back trajectories calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model showed a consistent flow of air masses from the North-West (NW) in 2004 for Fyodorovskoje and South-West (SW) for Zotino in the measurement site throughout the experimental period. The air parcel back trajectories for the frame of the individual flights are shown in Figures 4.4, 4.5 and 4.6, respectively. The trajectories showed no evidence of air having passed over the area of the city, nor over the area of large deforestation.







Figs 4.4, 4.5, 4.6 Backward trajectories calculated for selected flights (19.07.2004, 20.07.2004 and 12.07.2005) by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (NOAA/CMDL)

The selected site was chosen as representative of the forest ecosystem in a selected location. The CBL heights, calculated from direct measurements of temperature and humidity (see: Fig. 4.7.2-4.18.2), ranged between 1400 and 2200 m above ground level and were typical mixed layer gradient heights that are expected over Siberian forests. Isoprene and monoterpenes were observed and dominant biogenic VOC observed in ambient air. The mixing ratios of α-pinene, camphene and limonene were more or less at the same range and comprised the detected sum of monoterpene species. Other monoterpenes were detected at the detection limit and were not used in further calculations. The VOC species composition was very similar throughout the boundary layer, when a comparison was made between:

(i) values from the tower-based measurements in the surface layer versus the data observed within the Convective boundary layer, and
(ii) midday versus afternoon values.

Figures 4.7.3-4.18.3 and 4.7.4-4.18.4 show vertical plots of the isoprene, α-pinene, camphene and limonene mixing ratios observed above the canopy during aircraft measurements, which was inferred from surface layer profiles measured simultaneously at four different heights. Isoprene, α-pinene, camphene and limonene mixing ratios followed a clear diel pattern as a function of light and temperature (see also Rinne et al., 2002; Kuhn et al., 2002, 2007). Mixing ratios for isoprene and the sum of three main detected monoterpenes (α-pinene, camphene and limonene) reached a maximum 3.7 ppbC and 3.2 ppbC respectively.

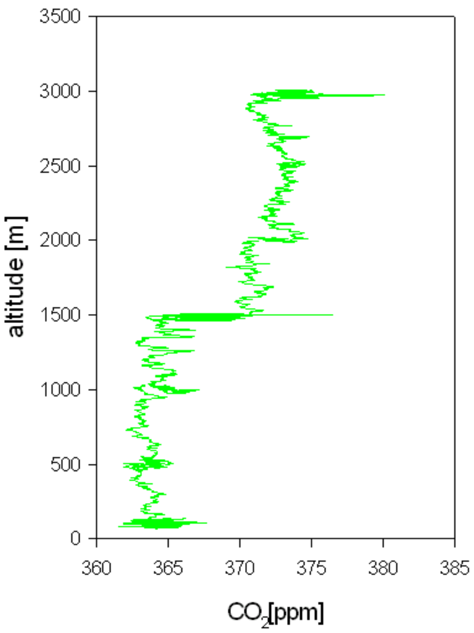


Fig 4.7.1

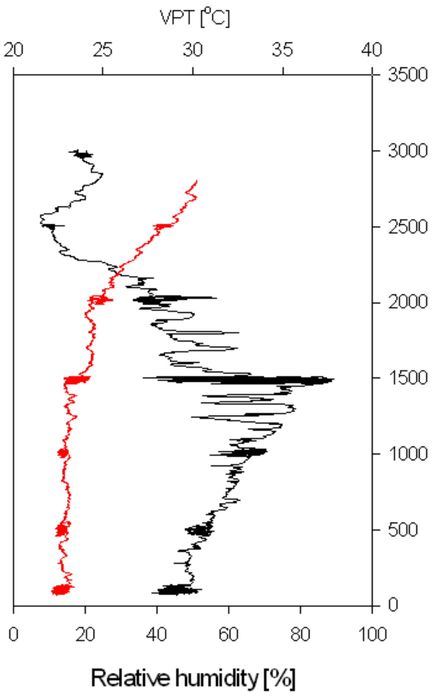


Fig 4.7.2

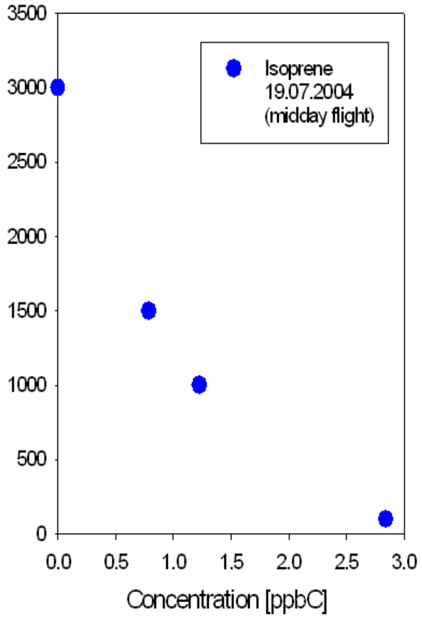


Fig 4.7.3

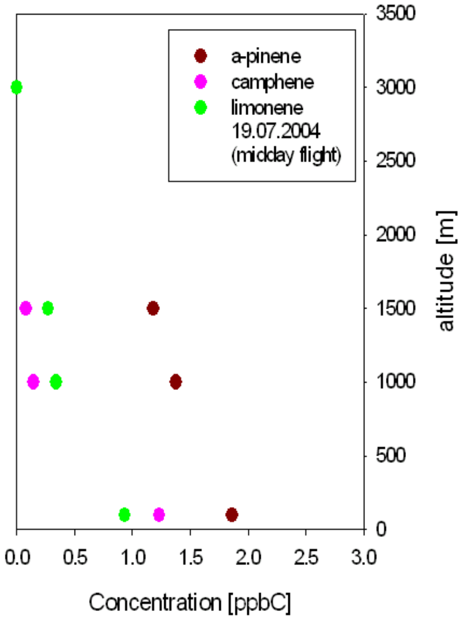


Fig 4.7.4

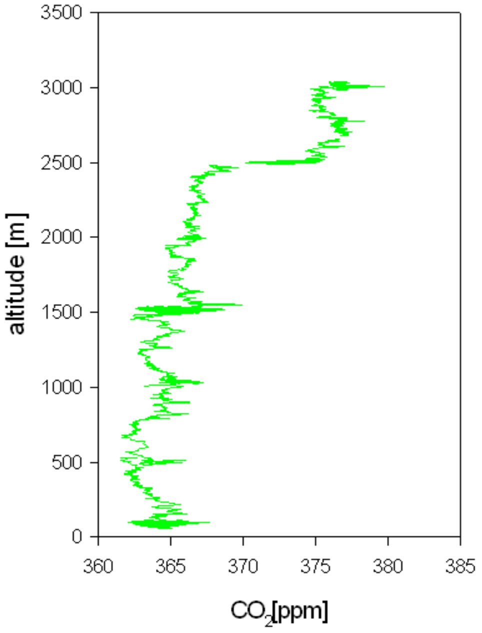


Fig 4.8.1

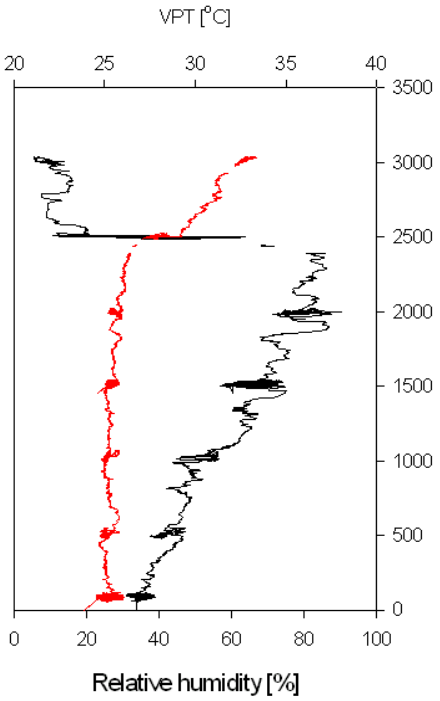


Fig 4.8.2

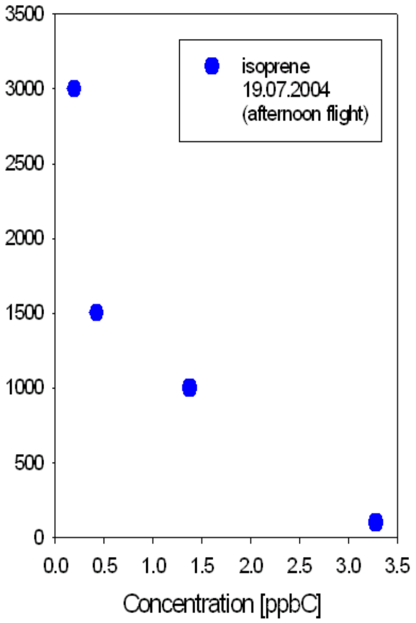


Fig 4.8.3

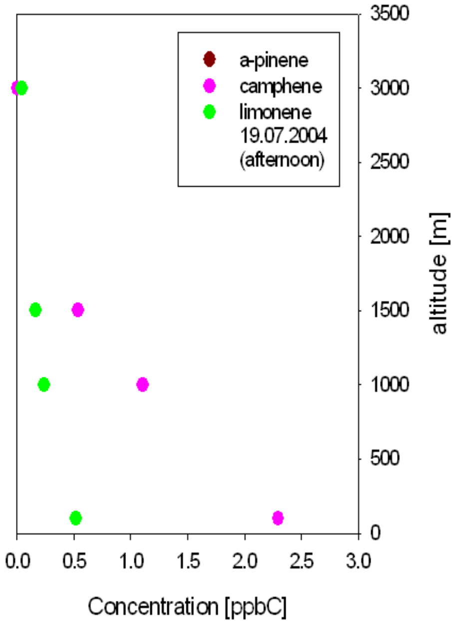


Fig 4.8.4

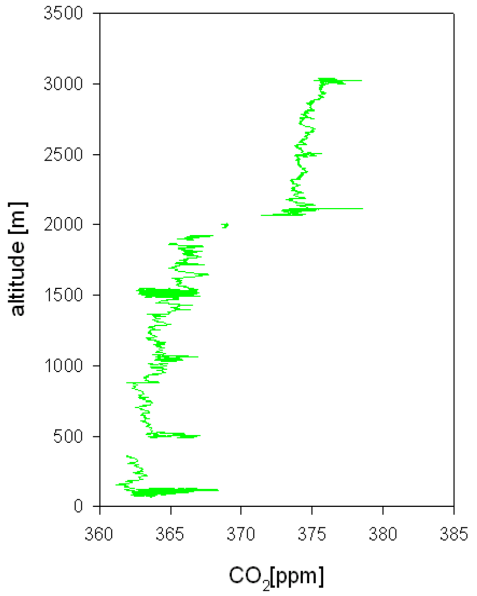


Fig 4.9.1

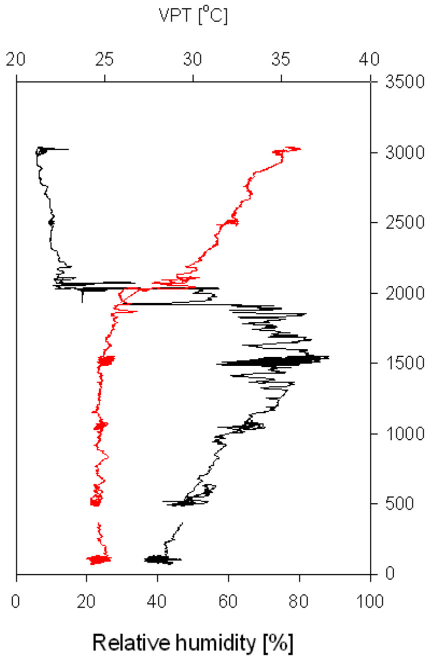


Fig 4.9.2

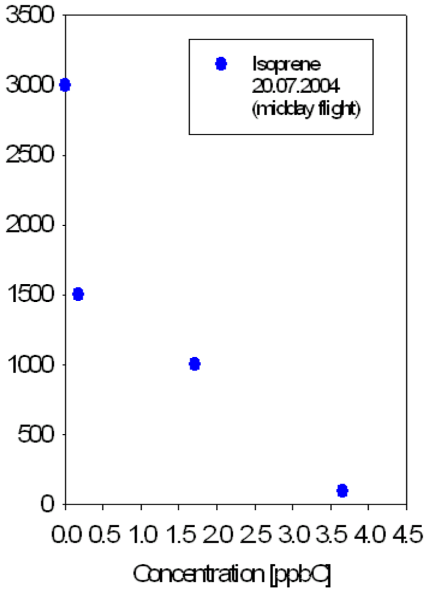


Fig 4.9.3

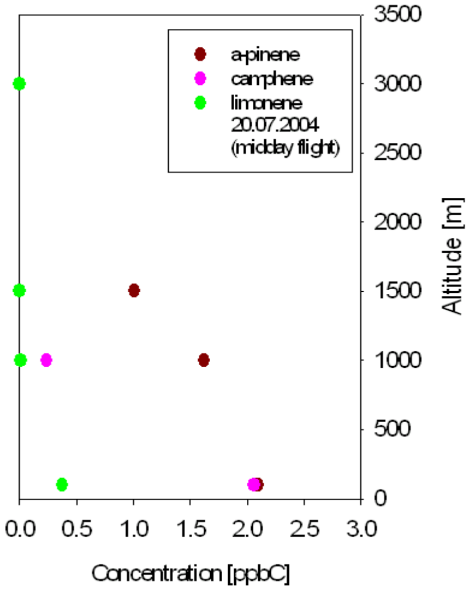


Fig 4.9.4

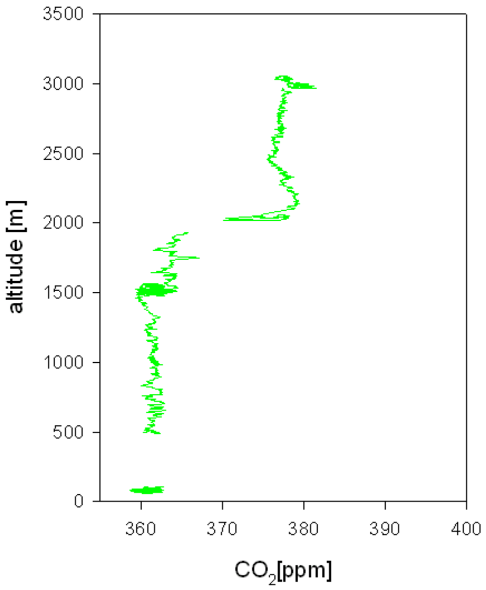


Fig 4.10.1

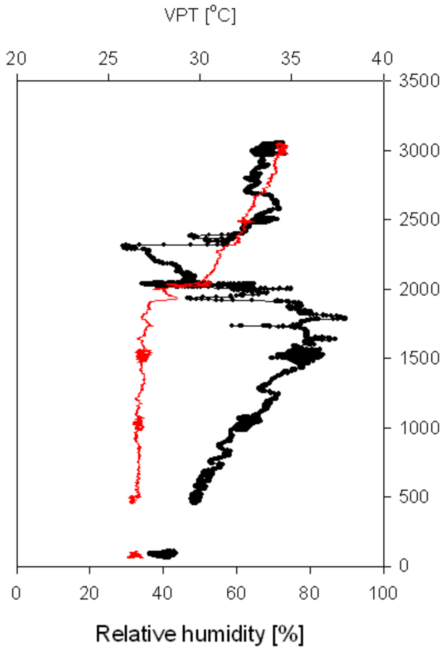


Fig 3.10.2

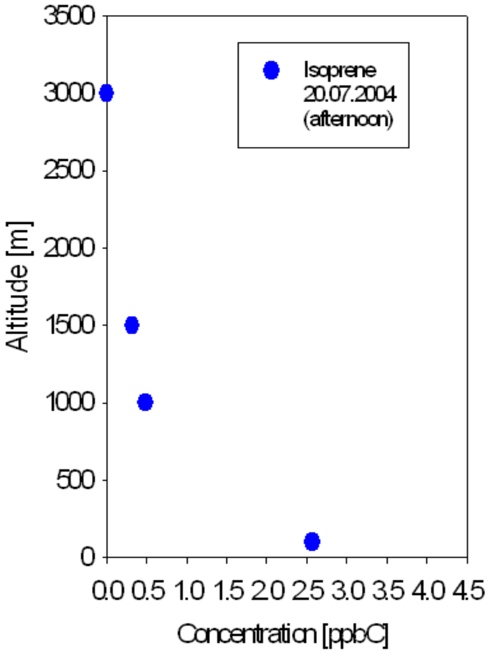


Fig 4.10.3

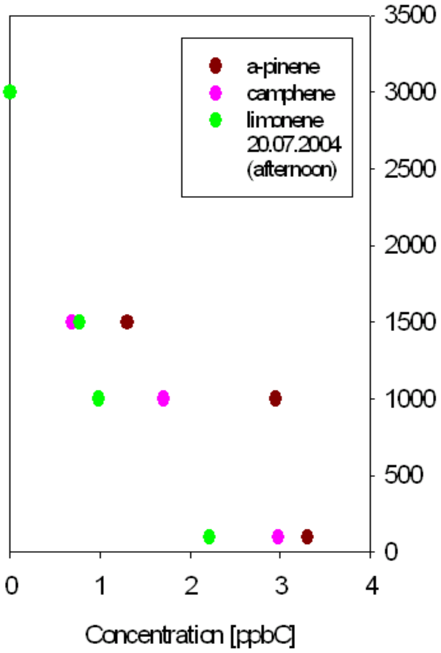


Fig 4.10.4

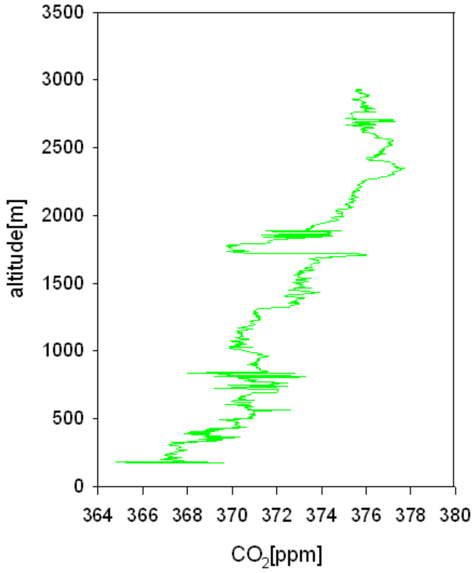


Fig 4.11.1

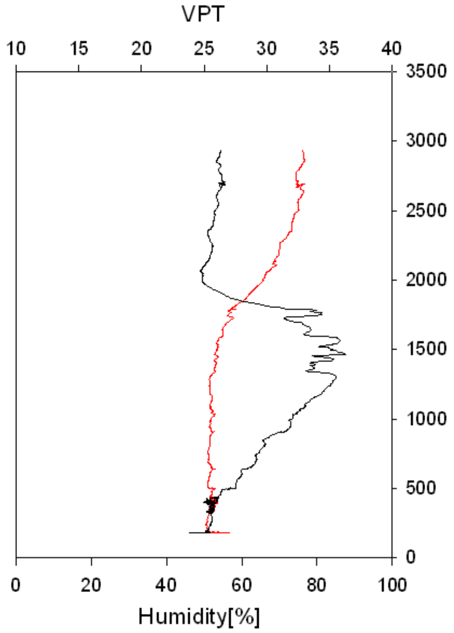


Fig 4.11.2

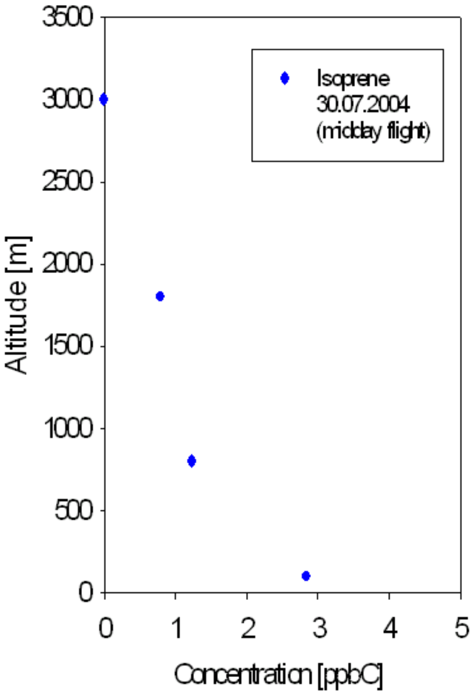


Fig 4.11.3

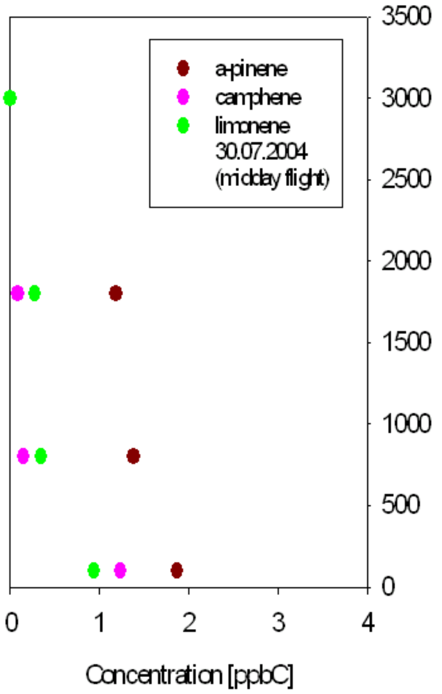


Fig 4.11.4

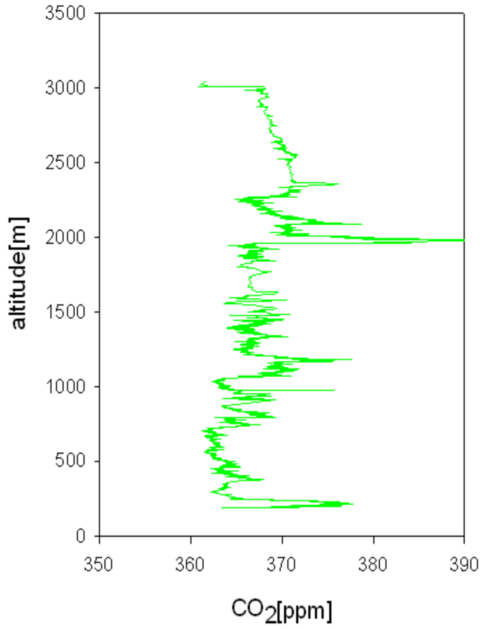


Fig 4.12.1

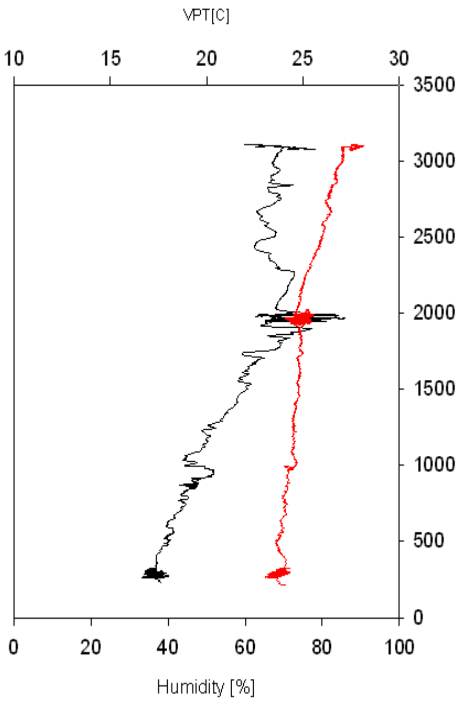


Fig 4.12.2

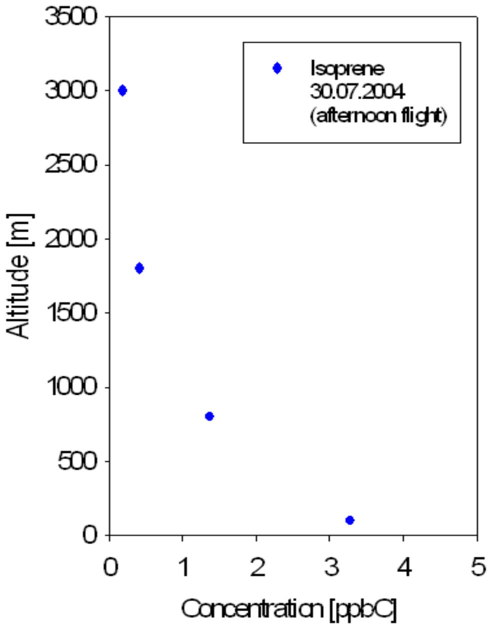


Fig 4.12.3

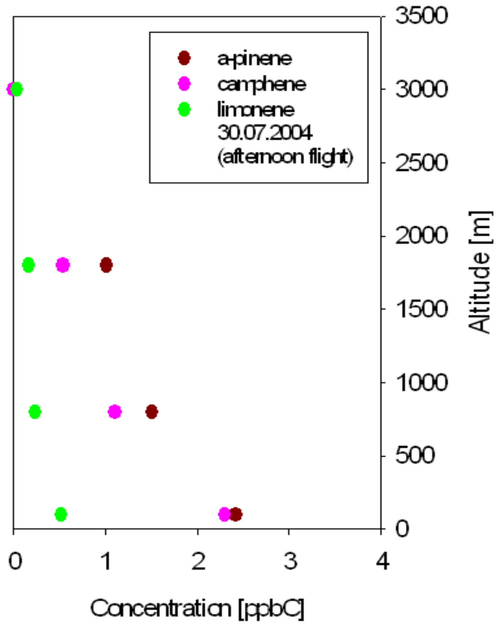


Fig 4.12.4

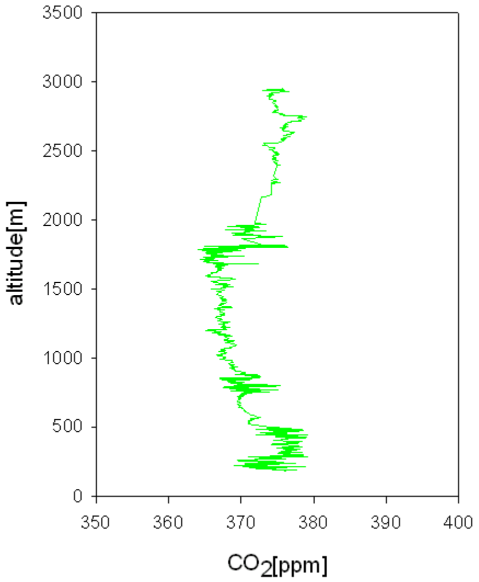


Fig 4.13.1

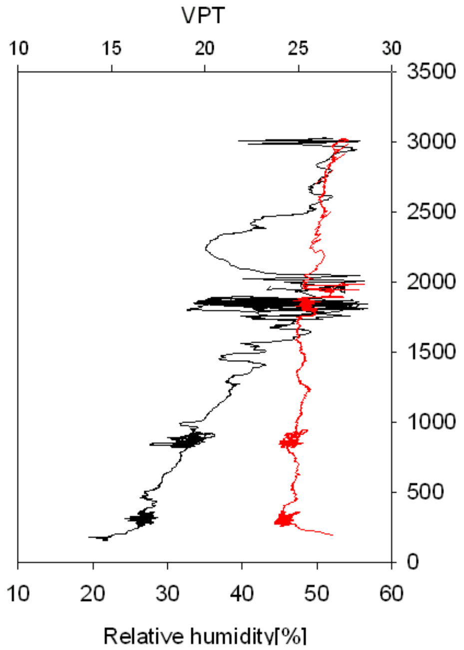


Fig 4.13.2

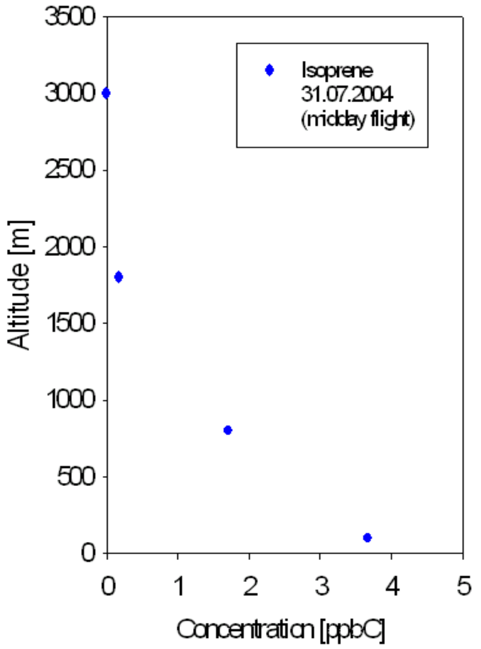


Fig 4.13.3

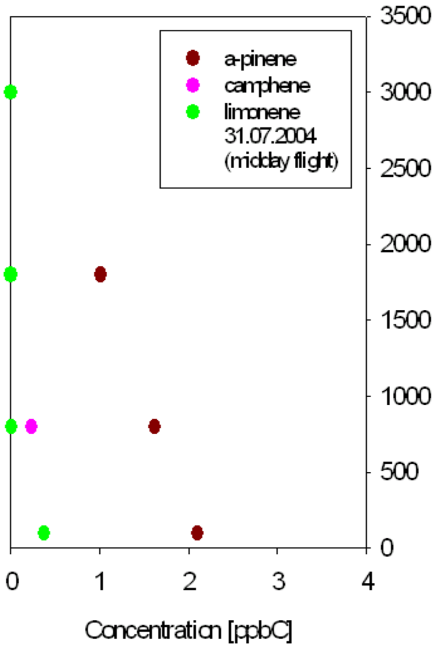


Fig 4.13.4

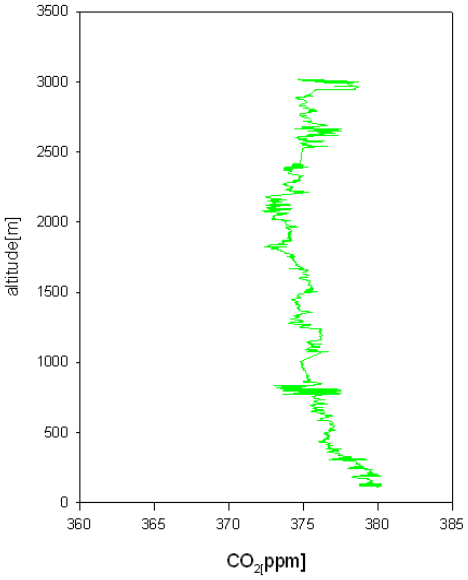


Fig 4.14.1

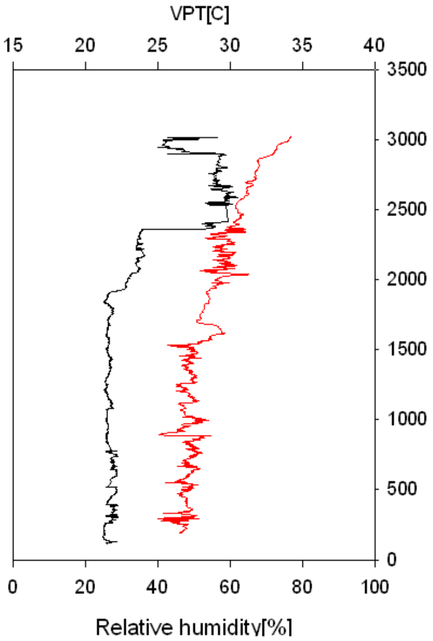


Fig 4.14.2

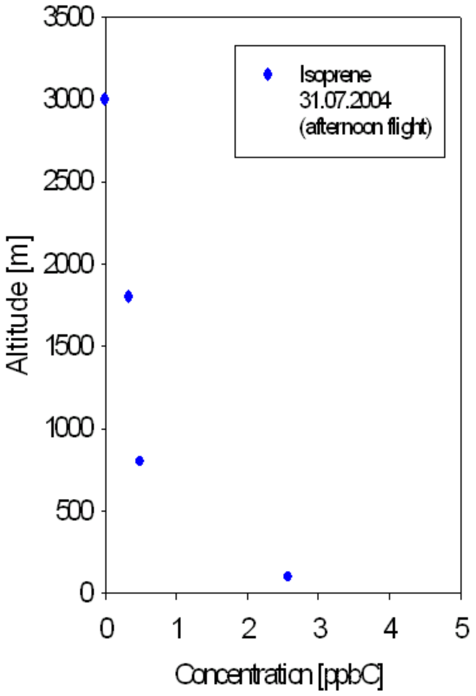


Fig 4.14.3

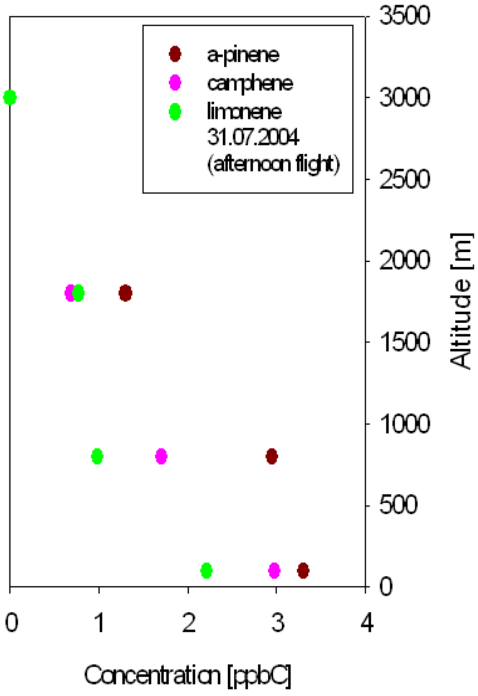


Fig 4.14.4

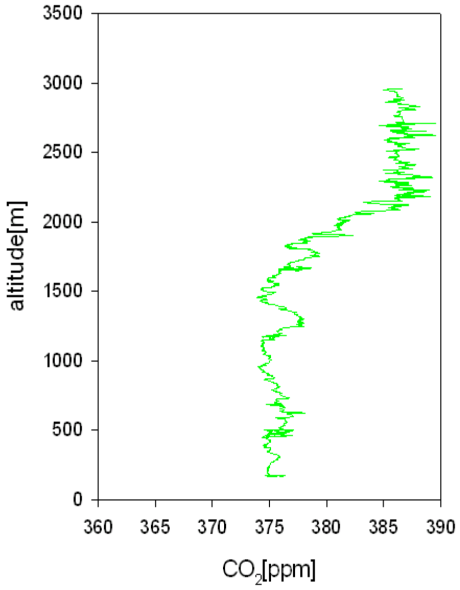


Fig 4.15.1

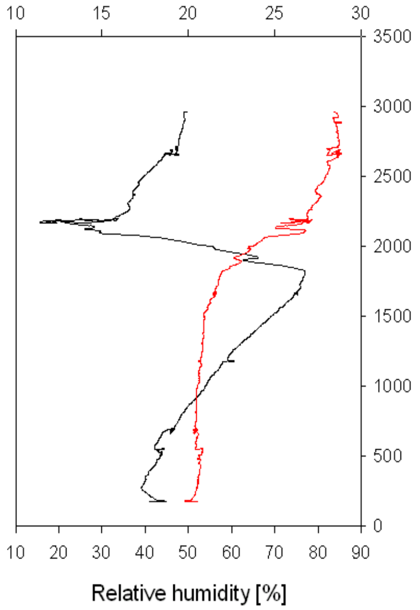


Fig 4.15.2

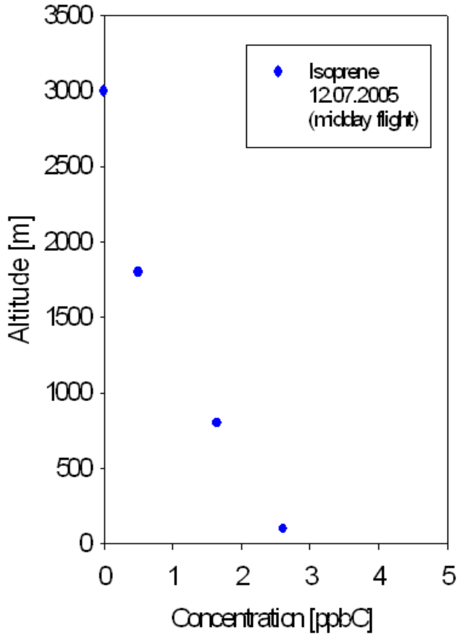


Fig 4.15.3

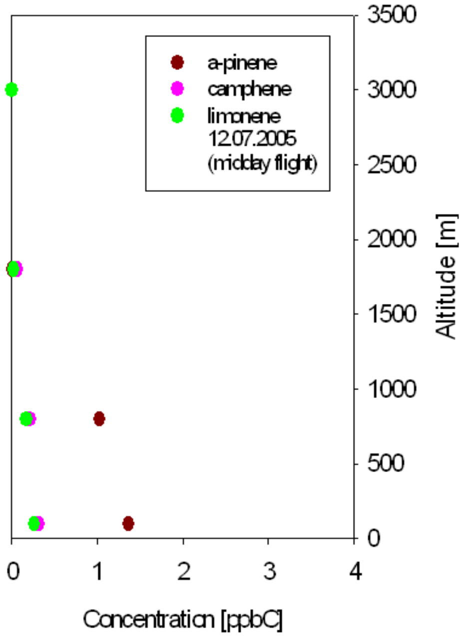


Fig 4.15.4

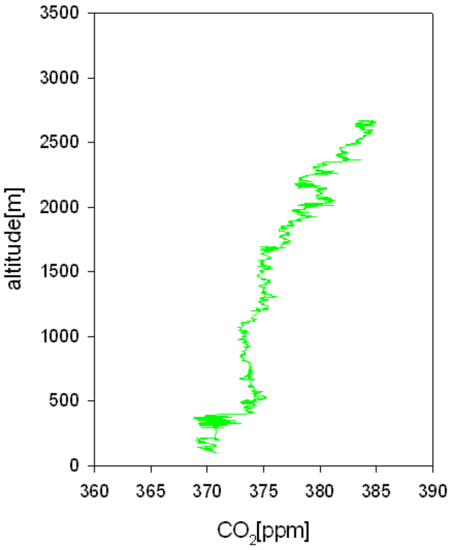


Fig 4.16.1

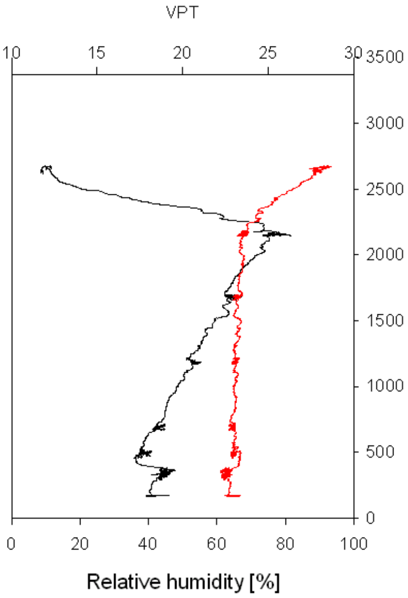


Fig 4.16.2

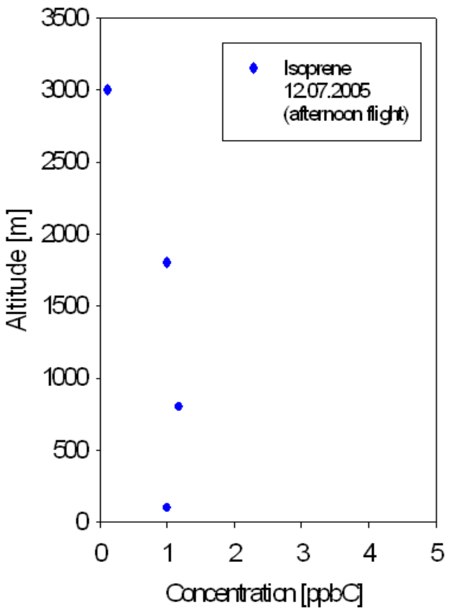


Fig 4.16.3

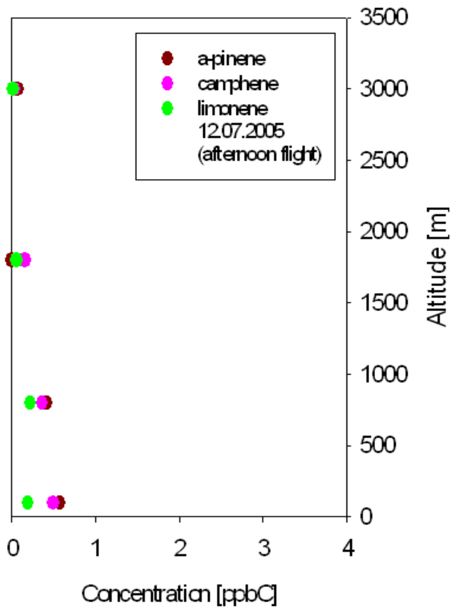


Fig 4.16.4

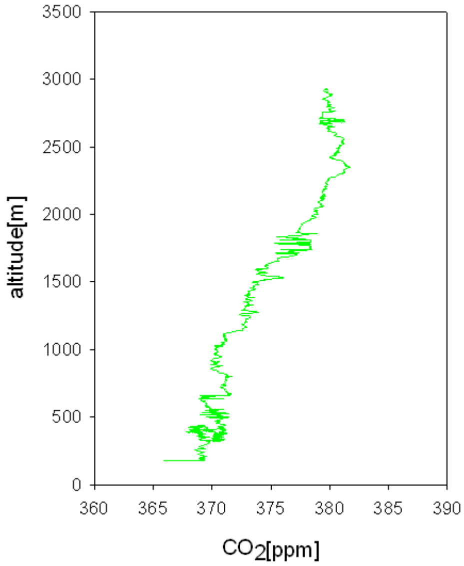


Fig 4.17.1

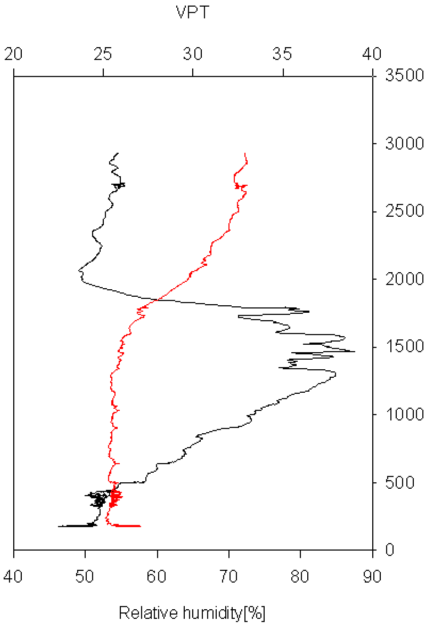


Fig 4.17.2

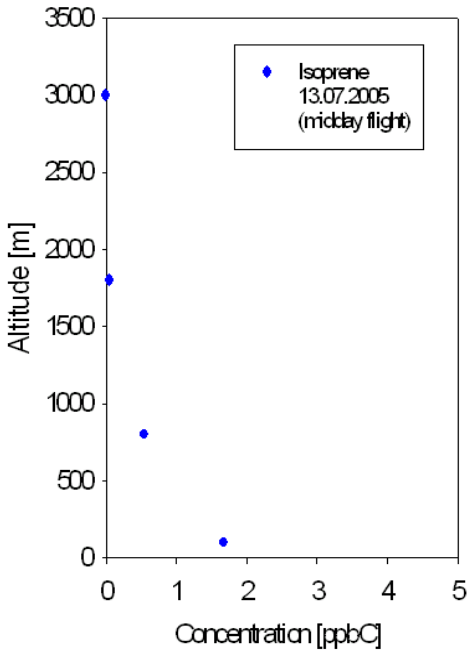


Fig 4.17.3

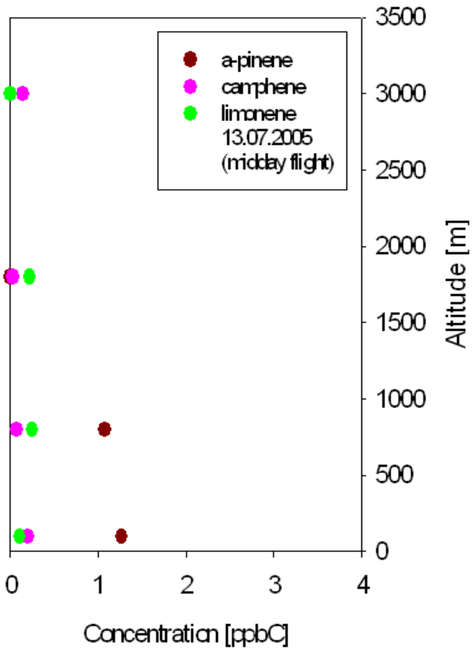


Fig 4.17.4

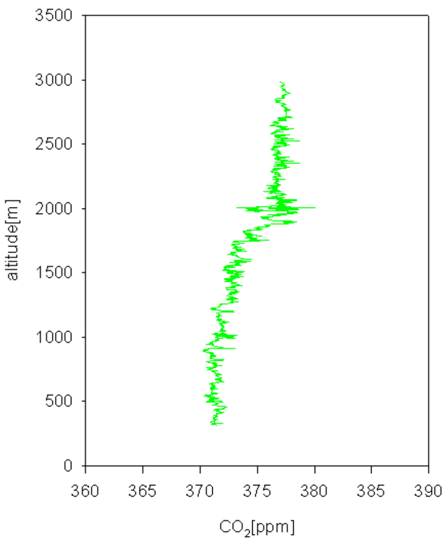


Fig 4.18.1

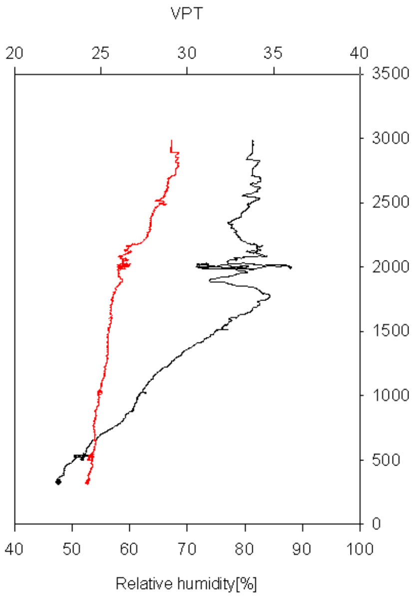


Fig 4.18.2

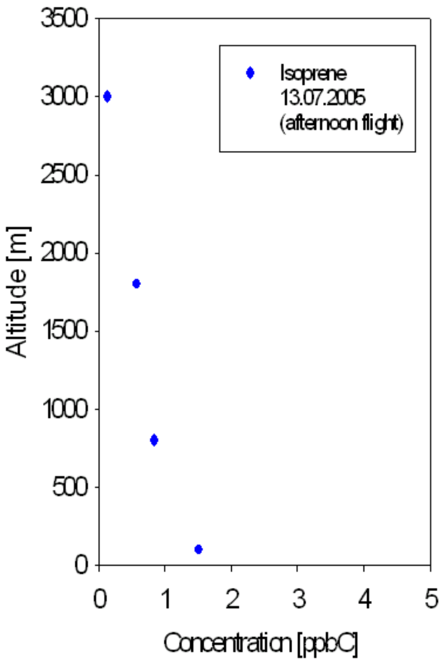


Fig 4.18.3

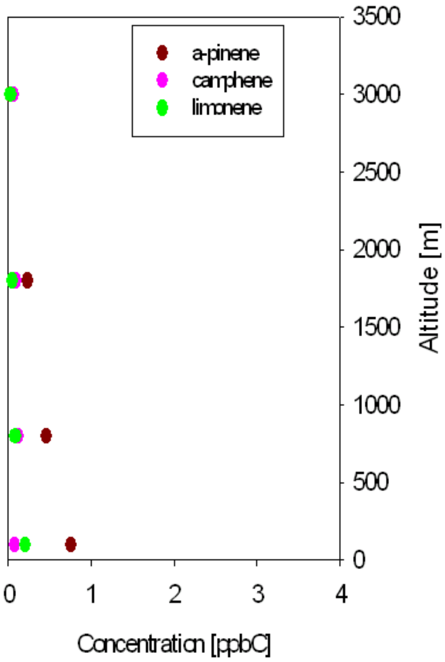


Fig 4.18.4

4.5.1 Implications for the local carbon budget

The total number of twelve VOC profiles between 100 and 3000m above the canopy level were obtained by airborne measurements. Table 4.1 gives an overview of all VOC measurements analysed by GC-FID.

Region	Date of campaigns	Technique of analysis	BVOCs detected
Fyodorovskoje	19-20.07.2004	GC-FID	Isoprene and the sum of monoterpenes (α –pinene, camphene and limonene)
Zotino	30-31.07.2004 12-13.07.2005	GC-FID	Isoprene and the sum of monoterpenes (α –pinene, camphene and limonene)

Table 4.3 Overview of technique used for VOC determination and BVOC detected

The mean profiles of isoprene and α-pinene, camphene and limonene are plotted in Figs. 4.7.3-4.18.3 and 4.8.4-4.18.4; isoprene and monoterpenes showed similar characteristics, both declining strongly with altitude, ranging from 3.7 ppbC for isoprene and 3.2 ppbC for α-pinene to below the detection limit for both compounds above the CBL. The deviation from the mean values is attributable to the day-to-day variability in meteorological conditions, rather than to differences in the general trend of vertical profiles. The strongest concentration gradients were observed close to the surface source (forest canopy) where the sources of emission of VOC exist. The small amounts of isoprene and monoterpenes observed in the free troposphere above the CBL might be caused by the residual layer from the previous day. Another reason might be deep convection penetrating the CBL. The quasi-exponential attenuation during their upward transport within the CBL is controlled by the relative rates of chemical destruction and turbulent mixing of CBL. The similar patterns of isoprene and monoterpenes in the shape of vertical profiles demonstrate the similarities of:

(i) the environmental functions that are driving the emissions

and

(ii) the atmospheric lifetimes under the prevailing oxidation regime.

In general the gradients during the afternoon flights were somewhat less pronounced compared to the midday flights. Meteorological conditions affected both CBL dynamics (processes of mixing), and emission rates. Smaller vertical gradients in the late afternoon may be explained by a reduction of VOC emission due to low radiation intensities close to sunset, rather than by enhanced convective mixing.

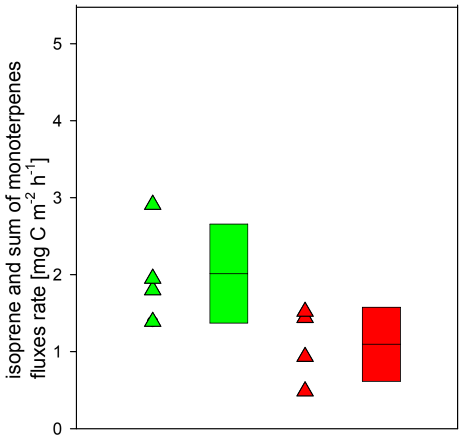
4.5.2 VOC fluxes calculation by box model method (BM)

VOC fluxes were calculated by the BM approach using the concentrations obtained in direct vertical profile measurements. All VOC measurements were accompanied by simultaneous (synchronized in time and sampling period) instruments such as humidity and temperature. The latter was assumed to have the least degree of 25 uncertainties of the flux method applied in this study. Figures 4.19.1-4.19.3 show a comparison of the mean cycle of isoprene and monoterpenes obtained for all campaigns. Mean fluxes measured during the three campaigns using the BM approach are presented in Table 4.4

sites	Isoprene [$mgCm^{-2}h^{-1}$]	SD	Sum of monoterpenes [$mgCm^{-2}h^{-1}$]	SD
Fyodorovskoje (19-20.07.2004)	2.01	±0.64	1.09	±0.48
Zotino (30-31.07.2004)	3.13	±0.85	3.17	±1.28
Zotino (12-13.07.2005)	3.80	±1.02	4.09	±0.72

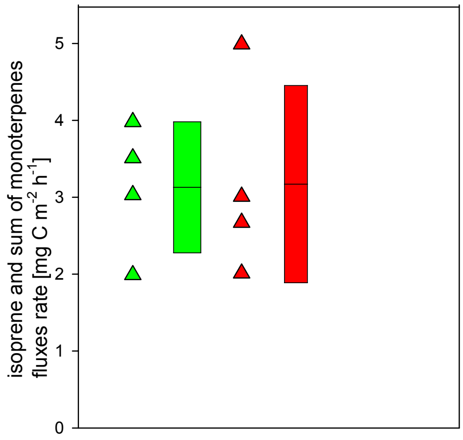
Table 4.4 Mean fluxes and standard deviations (SD) measured during the three campaigns using the BM approach

The maximum fluxes that were calculated with BM were 4.99 $mgCm^{-2}\ h^{-1}$ for isoprene 4.97 $mgCm^{-2}\ h^{-1}$ for the sum of monoterpenes. In general, flux estimates by BM approaches were in reasonable agreement. The canopy scale fluxes, with an estimated footprint area of 50–100 km^2, are assumed to be representative of the combination of the characteristic local-scale landscape elements in this area, including plateaus, rivers, slopes and valleys. The range of VOC flux values observed are difficult to compare due to unavailable data of fluxes for the Siberian region and were not reported previously in the literature. Measured vertical fluxes were roughly proportional to mixing ratios within the boundary layer, as expected for compounds whose atmospheric lifetime is substantially less than one day. Like isoprene, the monoterpenes were also emitted by the vegetation in a light-dependent manner. In agreement with previous studies, there is now increasing evidence that light dependence of monoterpene emissions can be generalized for deciduous tree species in temperate ecosystems (Staudt and Seufert, 1995; Ciccioli et al., 1997; Kesselmeier et al., 1996; Spirig et al., 2005; Dindorf et al., 2006).



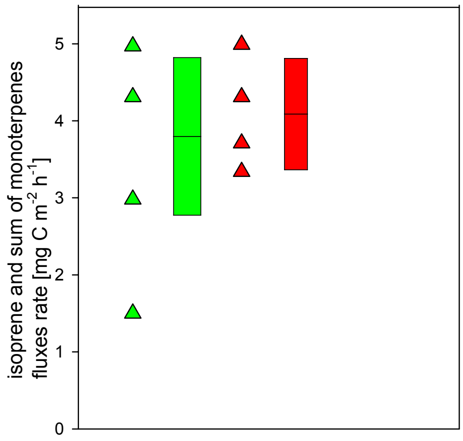
Fyodorovskoje 2004

Fig 4.19.1



Zotino 2004

Fig 4.19.2



Zotino 2005

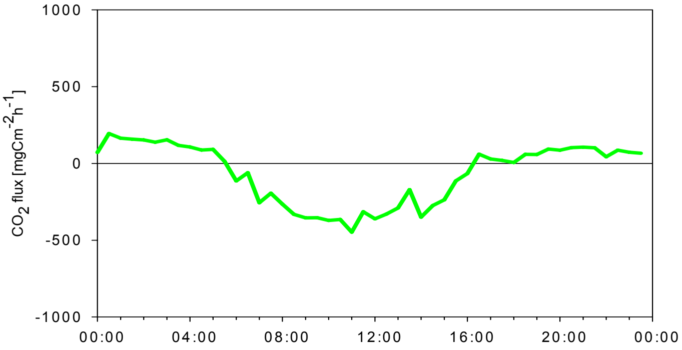
Fig 4.19.3

Figs 4.19.1-4.19.3 show isoprene (green rectangle) and the sum of monoterpenes (red rectangle.) flux rate [mg C m^{-2} h^{-1}] (mean value with standard deviation of the measurements); triangles represent the calculation for a single flight during the measurement campaign.

4.5.3 Comparison with tower-based measurements and NEP, GPP and NEE

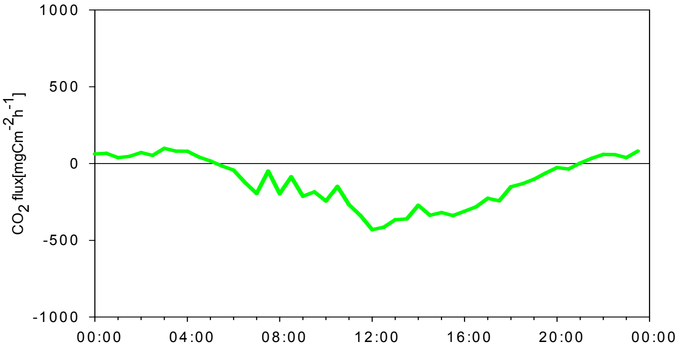
4.5.3.1 Eddy covariance measurements and NEE

BVOC flux measurements for two sites have been compared. Results obtained from eddy covariance measurements of CO_2 (Fig 4.20.1-4.20.3) during the day and night generally showed a diurnal cycle. The final goal of any eddy covariance NEE flux partitioning algorithm is to estimate R *eco* and gross primary production (GPP) from the NEE according to the definition in Formula 4.1. These flux-partitioning algorithms can be classified as those that use only (filtered) night-time data for the estimation of ecosystem respiration. These general approaches have been compared by Falge et al. (2002), resulting in generally good agreement, except in ecosystems where large soil carbon pools exist. Under those conditions, the light-curves derived from daytime data may not well represent the respiratory processes during night-time. Moreover, regressions of light-response curves sometimes tend to yield unstable parameters . The starting point of this analysis was half-hourly eddy covariance CO_2 flux data from sites and vegetation types listed in Chapter 2. Only original data were used in this analysis. All night-time data with non-turbulent conditions were dismissed based on the u*-threshold criterion (Aubinet et al., 2000). The u*-threshold was derived specifically for each site using a criterion similar to the 95% threshold of Reischstein et al. 2002. For five selected days of the month during which measurements were performed, NEE plots were prepared (see Fig 4.20.1-4.20.3). In accordance with formula 4.2, where NEE is a direct measure of ecosystem respiration (R ecosyst) under these night-time conditions, a calculation of NEE for all sites was done. Night-time data were selected according to a global radiation threshold of $20Wm^{-2}$, cross-checked against sunrise and sunset data derived from the local time and standard sun-geometrical routines, and defined as R_{eco} for Fyodorovskoje NEE as 120.63 ± 49.68 $mgCm^{-2}h^{-1}$, whereas for the Zotino site they were 59.44 ± 23.14 $mgCm^{-2}h^{-1}$, 52.68 ± 20.31 $mgCm^{-2}h^{-1}$ in 2004 and 2005 respectively.



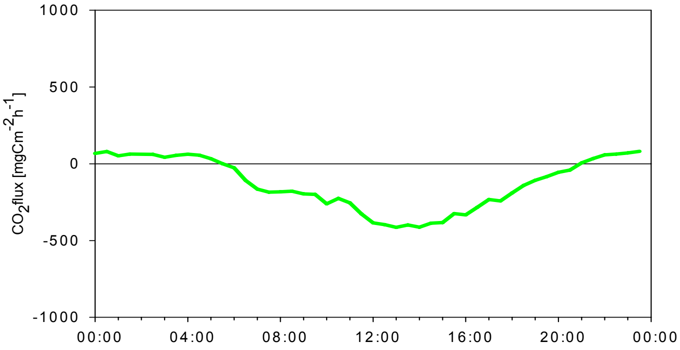
Fyodorovskoje 2004

Fig. 4.20.1



Zotino 2004

Fig. 4.20.2



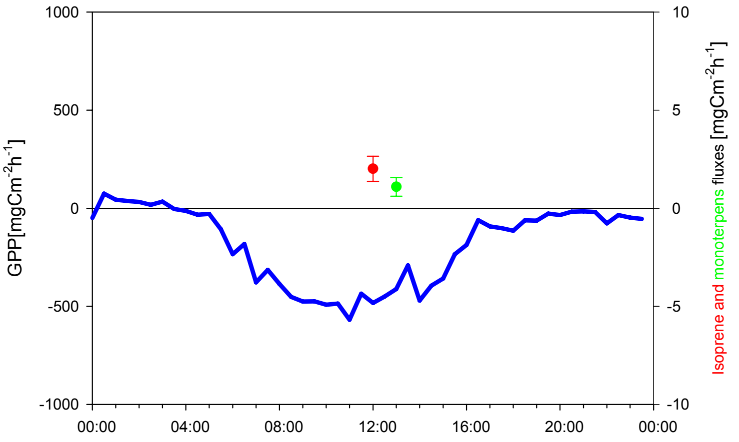
Zotino 2005

Fig. 4.20.3

Figs 4.19.1-4.19.3 NEE calculations for 5 day period.

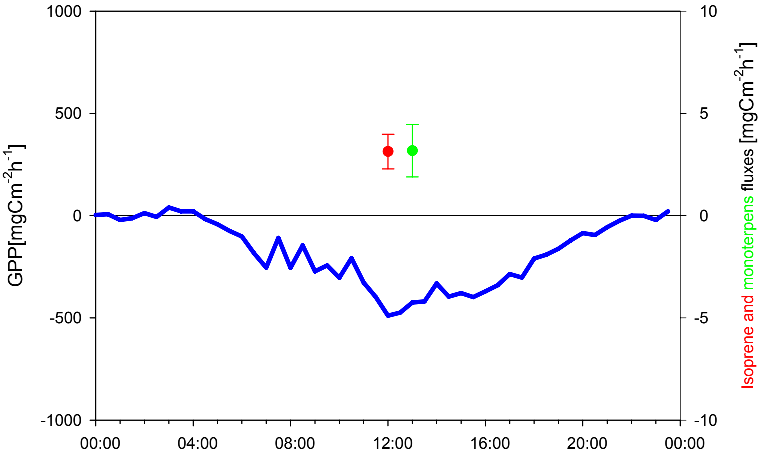
4.5.3.2 Gross Primary Production (GPP) and VOC fluxes

In accordance with Formula 4.4 and GPP, the procedure for flux calculations was applied. The main point of this calculation was the question about reactive carbon released in the form of VOC, which also corresponds to gross primary production (GPP). BVOC were shown to account for as much as several per cent of the GPP, i.e. in case of isoprene: 1.07% for Fyodorovskoje in 2004, 1.77 and 2.1% for Zotino in 2004 and 2005 and, in the case of monoterpenes, 0.58% for Fyodorovskoje in 2004, 1.79 and 2.15% for Zotino in 2004 and 2005 respectively.



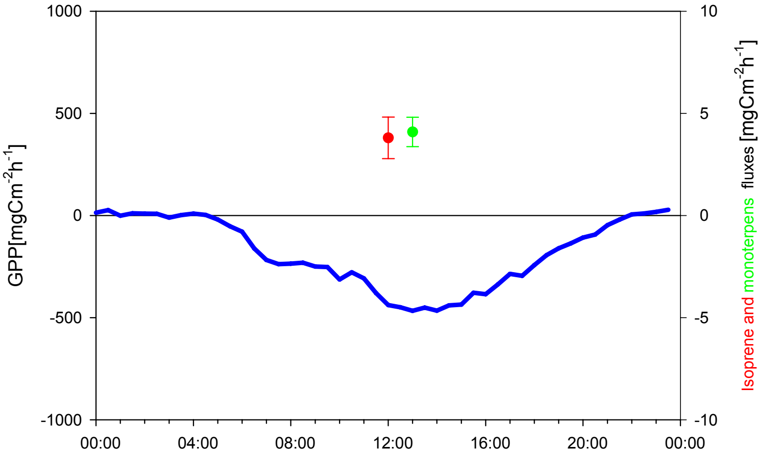
Fyodorovskoje 2004

Fig. 4.21.1



Zotino 2004

Fig. 4.21.2



Zotino 2005

Fig. 4.21.3

Figs 4.21.1-4.21.3 Comparison of GPP and isoprene and monoterpenes fluxes. Please note different scales on the left and right y-axes

4.6 Conclusion

For understanding the effect of spatial and environmental gradients and the ecosystem NEE from eddy data and their relation with VOC, it is essential to estimate their main components, R_{eco}, isoprene and monoterpene fluxes. At the moment a number of studies have been started using a novel technique such as PTR-MS (see Karl et al., 2004 Ruuskanen 2006, Rinne, J., 2007). A quantitative understanding of the processes governing the release of BVOC (e.g. diurnal, seasonal changes) remains a major challenge, and future leaf and canopy level studies will be needed for realistic parameterizations/predictions that can readily be incorporated in existing emission models. The proposed studies will provide key information on the amount of atmospheric carbon sequestered by an important forest ecosystem. This information is crucial to understanding how ecosystems mitigate recent increases in atmospheric carbon dioxide concentration, and the potential of this mitigation to annual variation in climate and future climate change.

The data obtained in this study bring together observations with computer models to provide better tools for analysing future trends in forest growth and carbon uptake. In particular, we will focus on how the process of VOCs mission influences the carbon cycle and how processes in the forest are affected by carbon that is realized as VOC.

5. Trace gas measurements by means of small aircraft in Poland.

Abstract

During the years 2002-2006 a series of regular long-lived trace gas measurements were performed in the lower troposphere over north-eastern Poland by means of small aircraft, as part of the EU-projects AEROCARB, TCOS-Siberia and CarboEurope-IP. The measurements were made about 60 km to the north of Bialystok (53°31'N, 22°40'E) in the area of the Biebrza National Park at intervals of 2-3 weeks. Continuous vertical profiles of temperature, humidity, pressure and CO_2 mixing ratios were obtained, as well as mixing ratios of CO_2, CH_4, CO, H_2, N_2O and SF_6 from flask analyses, which were sampled at altitudes of 300, 500, 1000, 1500, 2000, 2500 metres above ground level. The peak-to-peak amplitude of the seasonal cycle of atmosphere CO_2 within the atmospheric boundary layer (ABL) of 19 ppm is about twice that which was observed in the free troposphere (11.2 ppm). ABL mixing ratios are larger than free troposphere values during winter time, and lower during the summer, reflecting the change of the continental biosphere from its source to a sink. CH_4 mixing ratios do not show a seasonal variability, with the highest values in the ABL during winter. N_2O, CO and H_2 also show a slight seasonal cycle with similar phasing. In contrast, the measured mixing ratios of SF_6 have exhibited a linear increase of 29% since the beginning of 2002 without any significant seasonal variations. The data obtained will be used in the process of trace gas change modelling.

5.1 Introduction

As described in Chapter 3, the main objective of the Aerocarb, TCOS and CarboEurope-IP projects was the development of methodologies and techniques to assess qualitatively and quantitatively the carbon budget on regional scales. One of the fundamental parts of the projects was the provision of data.

During the last few years several theoretical studies have proposed the idea of using the atmospheric boundary layer for the description of larger areas (Klaassen, 1992; Raupach et al., 1993 and 1995; Denmead et al., 1996). Based on these studies several scientific groups started to investigate trace gas ratios and their fluxes using aircraft (Crawford et al., 1996; Langenfelds et al., 1996; Desjardins et al., 1997; Nakazawa et al., 1997; Lloyd et al., 2001 and 2002; Ramonet et al., 2002; Schumacher, 2005).

The drawback of measurements from in-service aircraft such as MOZAIC (Thouret et al., 1998); NOXAR (Brunner et al., 1998) and CARIBIC (Zahn et al., 2002) is that trace gas profiles are often restricted to the vicinity of heavy-duty airports and are thus not representative of the background atmosphere (Fischer et al., 2006). On the other hand, campaign-based data sets (for recent compilation see Emmons et al., 2000) usually provide limited information about seasonal cycles and spatial variations. Here, a series of long-term observations by means of small aircraft are presented, which gives an overview of the seasonal change in trace gases.

The existing and potential feedbacks between the terrestrial ecosystem processes and atmospheric CO_2 concentrations remain a major uncertainty in our understanding of the global carbon cycle. The balance of photosynthesis and ecosystem respiration appears to be strongly influenced by inter-annual variability in climate with discernible effects on the CO_2 concentration.

In the atmosphere the gases are characterized by different mixing ratios as well as different contributions to the greenhouse effect. The amount of the individual gas species is dependent on time and space. The major force of trace gas mixing ratios in the atmosphere is the balance between sources and sink. This balance is highly dependent on biological and chemical activity, the potential reaction of reactive species present in the atmosphere, and the synoptic pattern. The occurrence of trace gases in the atmosphere is mainly dependent on three factors (Vickers and Mahrt, 1997):

- the nature of the sinks and sources,
- their magnitude and persistence,
- their distribution.

Of all the gas species observed, CO_2 is the one which is present in the atmosphere with the highest mixing ratio and which shows the most pronounced periodicity. For the year 2000 the global average of the volume mixing ratio was calculated to be 368 ppm (Keeling et al., 2005), with higher absolute values and a bigger seasonal variation in the northern hemisphere. These changes are caused by the fact that the strongest sources and sinks are located in the continental landmass of the northern hemisphere (Ciais et al., 1995; Prentice et al., 2000).

The main significant terrestrial sources are the respiration of autotrophic and heterotrophic organisms, use of fossil fuels by the transport industry and households (Wittenberg et al., 1998; Anders et al., 1999). Today, we know that CO_2 has increased from its preindustrial level of 280 ppm to more than 380 ppm today. This increase has been demonstrated by Keeling's measurements of carbon dioxide starting in 1958 at Mauna Loa, Hawaii and by the first CO_2 measurements on air bubbles entrapped in Antarctic ice analyzed in the early 1980s at the Climate and Environmental Physics in Bern (Neftel et al. 1985). This data set forms perhaps the most important geophysical record of the century. Meanwhile, the CO_2 increase has been confirmed by other laboratories analyzing several different ice cores.

Besides, for CO_2, air samples were analysed for the mixing ratios of five additional gases: CO, CH_4, N_2O, H_2 and SF_6, which have direct and indirect greenhouse warming potential. Brief characteristics for atmospheric trace gases i.e. sources and sinks, mixing ratio, average change and lifetime are presented in Table 5.1.

	Mixing ratio		**Average change rate ^{3} (yr^{-1})**	**Lifetime in the atmosphere (yr^{-1})**	**sources**	**sink**
	before industrial revolution '1750'	Present				
CO_2	280 ppm	268 ppm	1,6 ppm	50-200	-combustion, -respiration, -CO oxidation.	-assimilation/ organic material, -carbonates.
CO		95 ppb	0.4 ppb	0.2	-combustion, -oxidation of CH4 and VOC, -soils	-oxidation to CO_2, -uptake by soils.
CH_4	700 ppb	1784 ppb	8 ppb	7.9	-bacteria (swamps, bogs, landfills, rice fields), -ruminants, biomass burning	-oxidation to CO and H2.
N_2O	270 ppb	314 ppb	1 ppb	122	-nitrification and denitrification in soils	-only stratosphere.
H_2		531 ppb		1.9	-CH4 oxidation, -combustion of fossil fuels	-uptake by soils.
SF_6	0 ppt	4.2 ppt	0.25 ppt	3200	-anthropogenic: insulation for glass filling, -high voltage plants, aluminum production	-chemically inert.

Table 5.1. Characterization of measured trace gases.

5.2 Isotopic signatures in Carbon Dioxide

Stable isotopes can be used to distinguish and estimate the contribution of different sources of spatially and temporally varying quantities such as CO_2 (Trumbore, 1999). By the implementation of isotope analyses a difference between contributions by vegetation and by insertion of anthropogenic material might be achieved (Ciais et al., 1995; Zondervan & Meijer, 1996; Bakwin et al., 1998).

The standards which were used during this study are the V-PDB (Vienna PeeDeeBelemnite) for delta ^{13}C and the V-SMOW (Vienna Standard Mean Ocean Water) for delta ^{18}O.

5.2.1 ^{13}C in Carbon Dioxide

Under normal conditions plants tend to assimilate the lighter CO_2 molecules more easily than those containing the heavier ^{13}C isotope. By this process the ratio of the carbon isotopes changes, compared to the original air. Plants contain more of the ^{12}C isotope, whereas the concentration of the heavier ^{13}C isotope increases in the ambient air (Lloyd & Farquhar, 1994; Flanagan, 1996). A less negative delta ^{13}C value indicates the assimilation rate of the plant (Trolier et al., 1996; Trudinger et al., 1999). On the other hand CO_2 in respired air from plants is depleted in ^{13}C relative to the atmospheric CO_2, which leads to a dilution resulting in a more negative delta ^{13}C

value (Levin et al., 1995; Kaplan et al., 2002).

CO_2 in baseline air has a delta ^{13}C value about $-8^0/_{00}$ with a seasonal cycle amplitude of 0.05 in the southern hemisphere and $0.8^0/_{00}$ in the northern hemisphere.

For ^{13}C a direct relationship is reflected by the CO_2 mixing ratio: a reduction of the CO_2 mixing ratio with a simultaneous enrichment in ^{13}C indicates an uptake by vegetation. On the other hand an increase in the CO_2 mixing ratio and a depletion of ^{13}C can be attributed to the consumption of organic material.

The basic Keeling plot approach is used for determination of the carbon isotope composition of the source. The atmospheric concentration of a gas in the canopy and adjacent boundary layer reflects the combination of some background atmospheric concentration and variable amounts of that gas added by sources in the ecosystem,

$$c_a=c_b + c_s \qquad \text{formula 5.1}$$

where c_a,c_b and c_s are the atmospheric CO_2 concentrations measured in the ecosystem, the background CO_2 concentration, and the additional concentration component produced by the source, respectively.

For the isotopic ratio, giving a conservation of mass:

$$\delta^{13}C_a\, c_a = \delta^{13}C_b\, c_b + \delta^{13}C_s\, c_s \qquad \text{formula 5.2}$$

where $\delta^{13}C$ represents the carbon isotope ratio of each CO_2 component respectively. Combining formulae 5.1 and 5.2

$$\delta^{13}C_a = c_b(\delta^{13}C_b - \delta^{13}C_s)(1/c_a) + \delta^{13}C_s \qquad \text{formula 5.3}$$

where $\delta^{13}Cs$ is the integrated value of the CO_2 source in the ecosystem.

The background should be represented by the tropospheric $\delta^{13}C$ ratio (global average $-8^{0}/_{00}$), while the ground source/sink can be characterized by its specific carbon isotope discrimination, which can be easily calculated from the intercept of the linear regression between the carbon isotope ratios and the inverse of CO_2 mixing ratio (Keeling 1958, 1961; Pataki et al., 2003).

5.2.2 ^{18}O isotopes in CO_2

Changes of $\delta^{18}O$ in the atmospheric CO_2 are induced by plants, similar to the carbon isotopes. There exist three main sources of ^{18}O in atmospheric CO_2:

- oxygen from soil water taken up by plants,
- oxygen that exchanges with the CO_2 of the ambient air,
- oxygen from CO_2 released by photorespiration.

During the formation of precipitation more ^{18}O condenses, hence the remaining water vapour becomes lighter, whereas the $\delta^{18}O$ of the cloud water increases during ageing (Ciais et al., 1997). Atmospheric CO_2 enters the plants through the stomata. The uptake is restricted by a diffusive kinetic isotope effect, but on the other hand only a few of the oxygen atoms are fixed via photosynthesis (Flanagan et al., 1997).

Plant activity and also soil-respired ^{18}O contributes to the $\delta^{18}O$ ratio of the atmospheric CO_2. Therefore estimates of this rate have to be taken into account when calculating the fraction of plant activity (Miller et al., 1999).

5.3 Material and methods

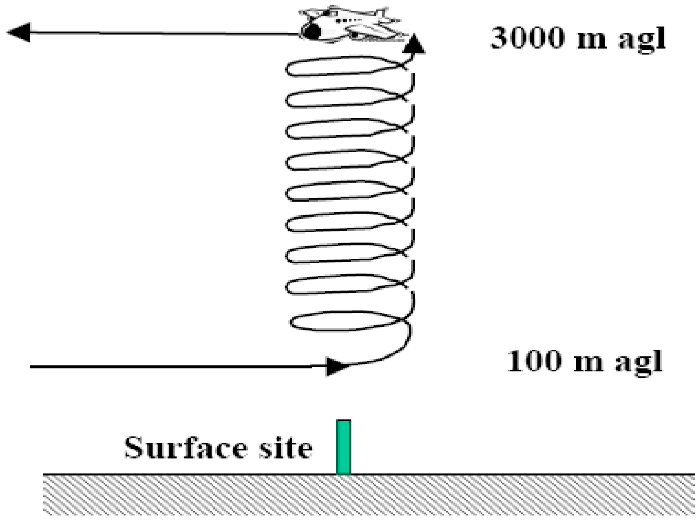
Measurements were taken near Bialystok, about 60 km to the north in the area of the Biebrza National Park, which is situated in the north-eastern part of Poland, in the Podlaskie Region. The north-eastern border of the park is situated close to the Belarusian border and to the south, the boundary of the park is the confluence of the Narew and Biebrza rivers. The Biebrza National Park was established in 1993 and with a total area of 59,223 ha. is the largest of the Polish national parks. The Park area includes 5,075 ha. under strict protection because of marshes and peat lands, unique in Europe, as well as its highly diversified fauna. The main type of ecosystem is forest, agricultural land and wetlands. With the exception of the mountains, this area has a reputation for being the coldest region in Poland. Its climate can be characterized as a combination of continental and sub-boreal. These overlapping characteristics are due to the wide marshy areas that condense moisture on a very large scale and the valley`s unique geological formation. The Biebrza valley is characterized by long winters and a short vegetation growth period. The average year-round temperature is one of the coldest of this type of lowland, the coldest month being February, with temperatures dropping to as low as -5^{0}C. Winters can last up to 117 days with average maximum temperatures below zero. Snow cover can last up to 140 days in the upper basin with a slightly lower timespan in the southern basin. During the spring and autumn, a range of 57 to 66 frosty days is average. July is the hottest month in the Biebrza valley with temperatures averaging out at 17.8^{0}C. The length of the summer ranges from 77 to 85 days, with daytime temperatures averaging 15^{0}C. Foggy nights and misty mornings are quite common and can be seen up to 70 days a year, and usually twice that in the peaty areas of the valley. The cool air of the surrounding uplands flows and touches the warm waters of the Biebrza, which is a quick catalyst for the condensation of water steam which givens the appearance of ground fog.

Fig. 5.1 Bialystok station location

(Picture adapted from DFD: http://www.caf.dlr.de/caf/satellitendaten/bildergalerie/)

5.4 Flight protocol

Flask sampling and in-situ CO_2 measurements were performed using a small aircraft Wilga (type: PZL-104). With an intended frequency of about 2-3 weeks, a local aircraft from Aeroclub Bialystok was employed for atmospheric measurements, flying out of the city of Bialystok. The flights took place at around noon or in the early afternoon during high pressure weather conditions. The plane was equipped with two independent systems, the first for air gas sampling (flask sampling unit) and the second for CO_2 in-situ measurements with instruments for temperature, humidity (probe HMP 45 D from Vaisala) and pressure monitoring (pressure transducer Bricon 411). The inlets of decarbon tubes (polyethylene-coated aluminium-6 mm diameter) were localized at the end of the wing. In this position it was considered that the chances of contamination from the exhaust pipe, located under the body of the aircraft at an angle of 35°, were minimal. Both lines were about 10 m in length. Only a few profiles are available for wintertime. The plane is not prepared for wintertime flights, due to lack of an anti-icing system.



5.5 CO_2 in-situ measurements

Atmospheric CO_2 dry air mixing ratios were continuously analysed by a NDIR analyser system designed at the Max-Planck Institute for Biogeochemistry, Jena, and described in Lloyd et al., 2002. The system is based on a LICOR-6251 infrared gas analyser. The airflow through the LICOR was regulated at 1.5 L/min. The CO_2 mixing ratio was calculated using the customized LiCor software, using the pressure and temperature of the cell. Two calibration gases and one zero gas, nitrogen, all in high-pressure cylinders, were used to recalibrate the data regularly. Calibration gases of 360 ppm and 380 ppm were prepared from ambient air and calibrated by the Institute für Umwelt Physik in Heidelberg. During each flight, calibration gases and nitrogen were used to flow through the LICOR at each flask sampling altitude. The flow amount was 1.5 min for each calibration gas.

5.6 Flask sampling

At each flight altitude (300, 500, 1000, 1500, 2000 and 2500 metres), duplicate flasks were sampled. Flushing and filling each flask took six to seven minutes with the plane circling at a constant altitude in a square (2 km x 2 km) during this time. The air was sucked from the inlets at a rate of about 3-4 L min^{-1}. Whole air samples were pre-dried by passage through a stainless steel cartridge (diameter 1 cm, length 12 cm) filled with magnesium perchlorate-$Mg(ClO_4)_2$ at ambient atmospheric pressure. The sample air was pumped into Duran glass flasks, 1L volume with Teflon PFA O-ring values (Glass Expansion P/L, Melbourne-Australia). A 1 mm filter PTFE was added at the end of the cartridge to avoid loss of material inside the sampling unit. All flasks were pressurized to 0.9 atm above the ambient air (pump KNF-Neuberger, Germany, N86KNDC with EPDM membrane).

5.6.1 Flask analysis

Trace gas concentration analysis is done using two gas chromatography systems. The Gas Analysing Unit 1 (Fig. 5.2) covers the analysis of CO_2, CH_4 and N_2O, whereas the Gas Analysing Unit 2 (Fig. 5.3) has been set up for quantification of SF_6, H_2 and CO. Both systems share an integrated flask analysis system allowing continuous, unattended operation with a flask throughput of 30 air-in-flask samples per day for dual analysis of all species covered. The sample gas is flushed through a ¼ inch tube (l=10 cm) filled with magnesium perchlorate to eliminate residual humidity from ineffectively dried samples. After flushing, the pressure inside the sample loops is equal with the to equilibrate to ambient air before the samples are injected on to the respective precolumns. After the analytes have passed their precolumns and entered their main columns, the Valco 10 port valves are switched back to back-flush the precolumns. After complete detection of CH_4 using GC Agilent 6890 with an FID detector, a valve is switched for directing the column effluent through a hot nickel catalyst. Here CO_2 is converted to CH_4 using hydrogen before detection with the FID.

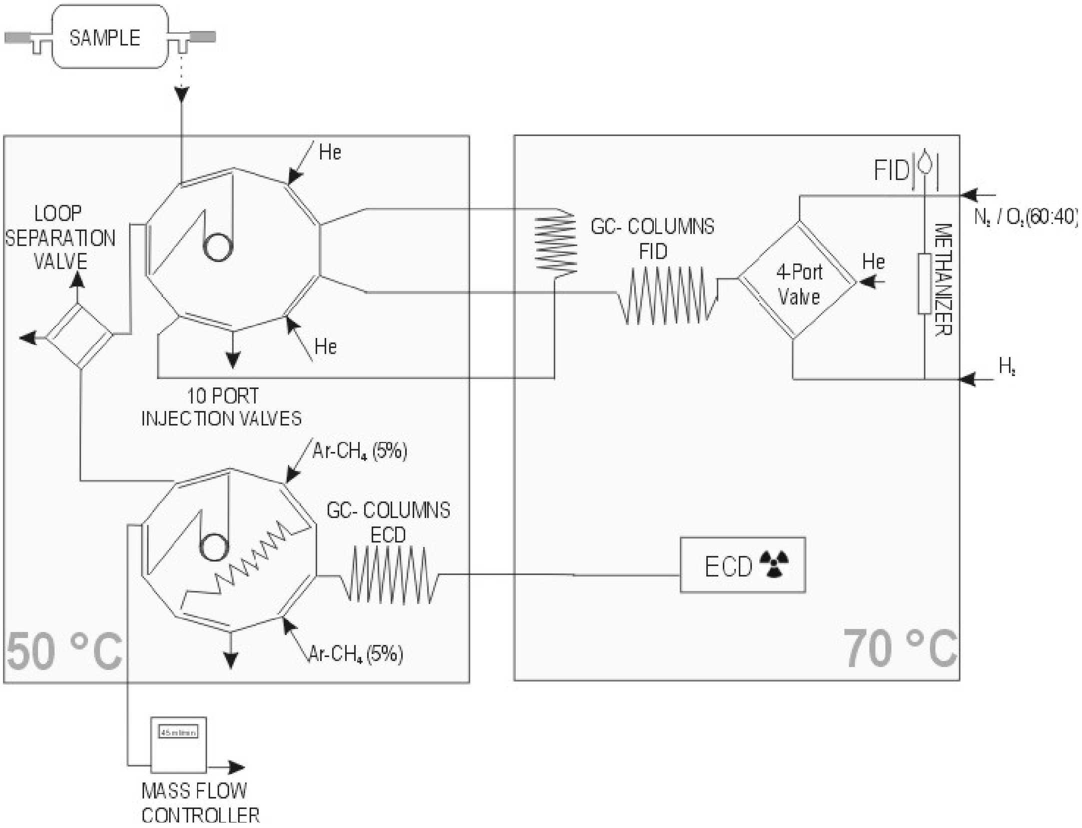


Fig. 5.2 Gas Analysing Unit 1-MPI-BGC Jena.

N_2O was separated from other air constituents in a parallel pre- and main column line and detected on ECD. The trace gas concentrations of unknown samples were inferred from intermittent measurements of precisely calibrated reference gases. Long-term precision was controlled by routinely measuring a quality control standard air. The approach achieved average relative precisions of 0.07% for CH_4 (1.3 ppb at atmospheric mixing ratio levels), 0.02 % for CO_2 (0.08 ppm), 0.04% for N_2O (0.13 ppb).

For SF_6, H_2 and CO quantification, a GC Agilent 6890 with ECD detector was used for SF_6 analysing and a trace Analytical RGA 3HgO detector for CO and H_2. Average recording precisions were 0.3 % for CO (0.5 ppb), 0.5% for SF_6 (0.03 ppt) and 0.4% for H_2 (2 ppb). Details of the instrumentation and experimental procedures are described in detail elsewhere (Jordan and Brand, 2001).

For isotopic analysis, a customized CO_2 extraction unit (BGC-AirTrap) was connected directly to an isotope ratio mass spectrometer (MAT 252, Finnigan MAT, Bremen, Germany). Gas samples were connected to the trapping line with a water trap (dry ice/ethanol) and a CO_2 trap at -196°C in series. CO_2 gas was measured directly from the volume of corresponding line via a capillary to the changeover valve of the mass spectrometer. About 600 mL of sample air was consumed. A correction for the contribution of N_2O to the ion currents of CO_2 were applied in the form of a mass balance calculation using the measured concentration of CO_2 and N_2O in the sample and reference air. Since the start of the measurements in October 2000, the precision of the values used between the working gas tank and the QA air standard on 'Matty' were 0.013‰ ($\delta^{13}C$) and 0.023‰ ($\delta^{18}O$). In March 2002, the 2nd MAT252 ('Cora') started with routine measurements. The precision of both machines was very close. The absolute $\delta^{13}C$ value of the QA reference gas on the VPDB scale was identical on both machines. This difference vanished over time. The overall agreement between the two independent machines was achieved without any machine-specific scale adjustmnt.

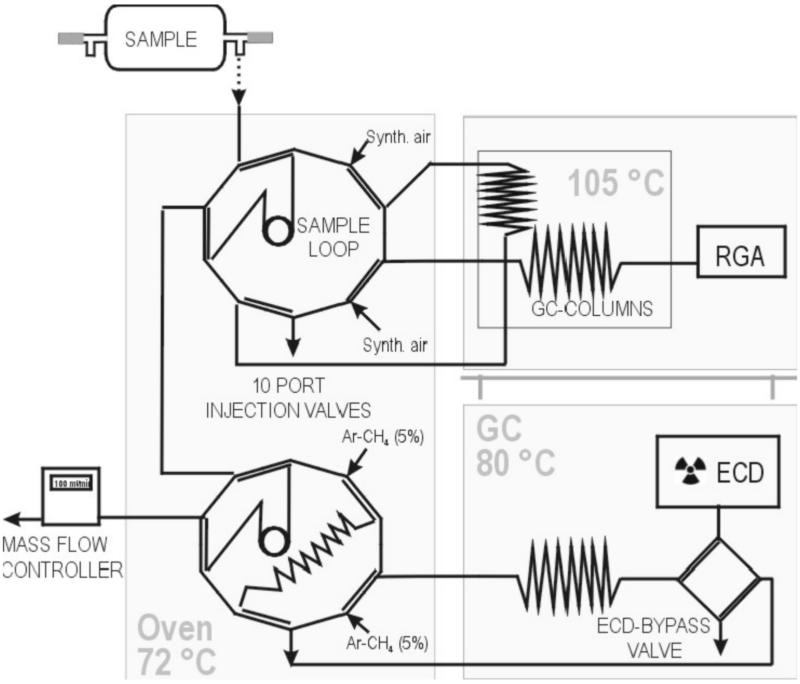


Fig. 5.3 Gas Analysing Unit 2 MPI-BGC Jena

5.7 Results and discussion

5.7.1 Data selection

The flasks were sampled during all flights. Part of those sampled from November 2002-January 2003 and April-June 2003 were rejected from further anlysis. For those flasks a leakage in the transfer line was detected and an extremely high concentration of CO, CH_4 and H_2 in flasks was observed. Results for those flights were rejected.

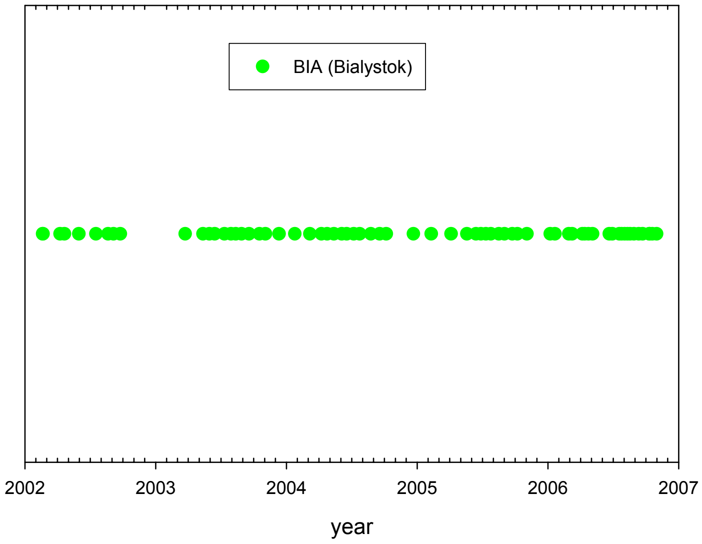


Fig. 5.4. Sampling frequency at the Bialystok measurement site.

5.7.2 Vertical profiles of CO_2, temperature and humidity

Vertical profiles are shown in Figs. 5.5.1-5.5.8 respectively during autumn/winter time and in Figs. 5.6.1-5.6.8 during spring/summer time. On the virtual potential temperature a rapid increase in the potential temperature can be observed, which indicates the end of the BL (boundary layer). The end of the BL was also confirmed by a fast decrease in relative humidity. The relative humidity profiles show an increase in humidity until the end of the BL, then a decrease in relative humidity in the free troposphere.

5.7.2.1 Autumn/winter profiles

Four vertical profiles, showing typical variability observed during late autumn and winter time (January) are presented in Fig. 5.5.1. In winter time, the top of the BL lies on an average lower than in summer. The profiles presented show that the top of PBL is usually about 500-800 m. The CO_2 observed values for the profiles depends on the month of the year when the flight took place. On 24th January 2004 we observed high CO_2 concentration, which systematically decrease up to the top of the BL. Then the CO_2 concentration seems to be quite stable to an altitude of 2100 m, then again increases. Two other profiles seem to be similar, first a quite stable concentration of CO_2 can be observed, and then a tendency for CO_2 to decrease with altitude was observed.

Vertical profiles of the CO mixing ratio showed a tendency for a decrease in CO with altitude. An interesting point can be observed on the 24th January 2004 flight. We observed a high concentration of CO at an altitude of 2500 m, which is different from the pattern of the profile. This observation was accompanied by an increase in CO_2 concentration from an altitude of 2100 m. We suppose that the reason for this may be due to long-term transport.

For the winter/autumn flights the profiles look very similar schematically. With the exception of this one flight on 24th January 2004 we observed an increase in values with altitude. The same pattern can be observed for $^{18}CO_2$.

Generally profiles for CH_4 show the same tendency as profiles of H_2. Profiles of H_2 are shown in Fig. 5.5.5. The lowest concentration of H_2 was observed on 17th October 2003 at an altitude of 300 metres.

5.7.2.2 Spring/summer

Four vertical profiles represent those typically observed in the late spring and summer period, presented in Fig. 5.6.1. We can observe a lower, stable concentration of CO_2 to the end of BL on the profiles, then a fast increase of CO_2 at the beginning of the free troposphere and stabilization of CO_2 concentration up to 2500 m. The lower mean

CO_2 mixing ratio inside BL reflects the strong photosynthetic activity of plants during the summer months. In the profile from the flight on 12th August 2003, the atmosphere seems to be stratified. Generally, with the exception of a few flights, a good agreement between the profile structure of CO_2 concentration and the flask results was observed.

Vertical profiles of CO concentrations showed the structure for a higher concentration of CO in free troposphere, and then in BL.

Spring/summer $^{13}CO_2$ concentrations are shown in Fig. 5.6.7. Generally, this tendency shows an increase in values with altitude to more negatives. Variations in the ^{18}O of CO_2 with altitudes are not as schematic as $^{13}CO_2$.

The CH_4 concentration for summer/spring flights shows an accumulation of methane in the BL. For some profiles a similar concentration of CH_4 can be observed for each altitude.

Figure 5.6.4 shows the vertical structure of hydrogen concentration. Generally, concentration increases linearly with altitude.

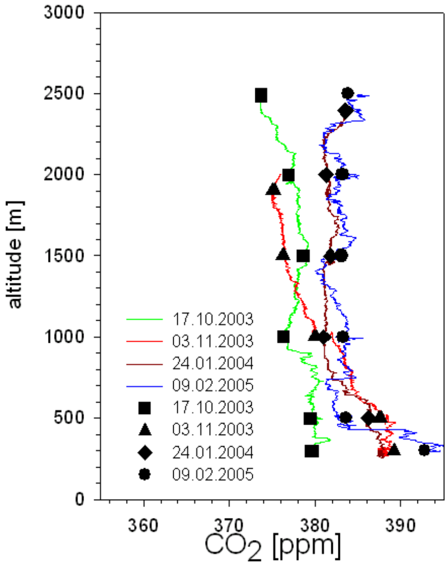


Fig.5.5.1

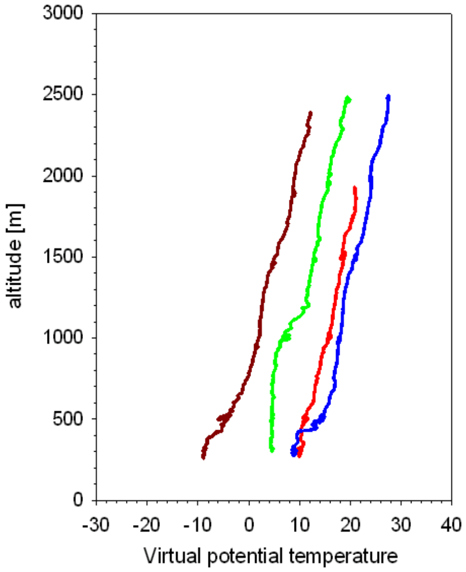


Fig. 5.5.2

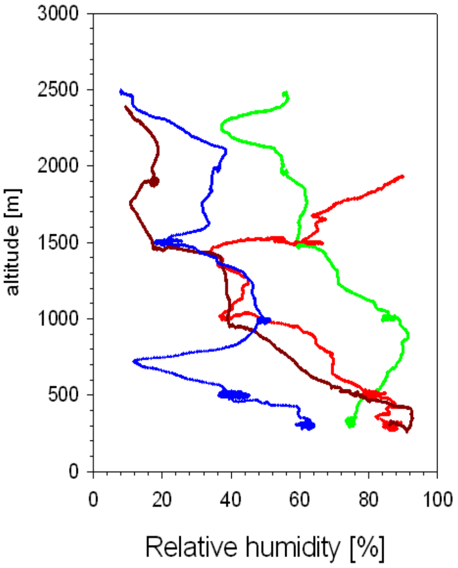


Fig.5.5.3

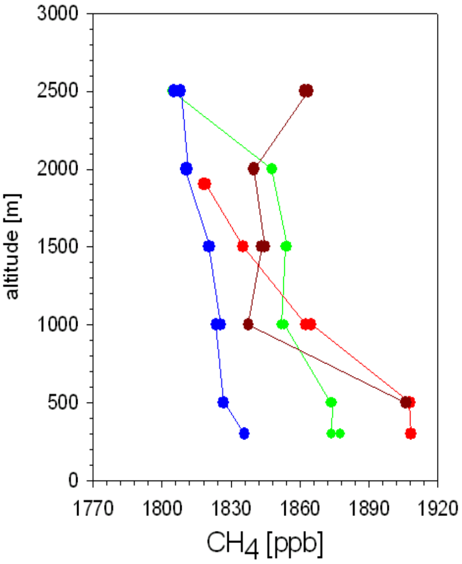


Fig. 5.5.4

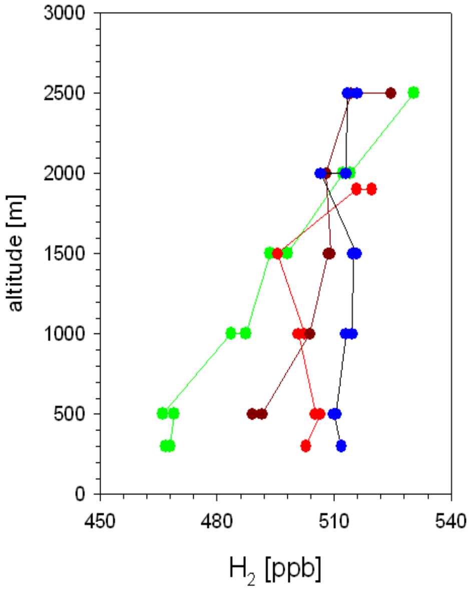


Fig. 5.5.5

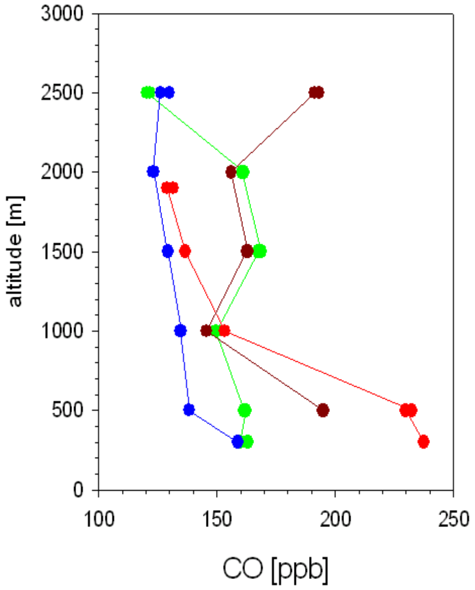


Fig. 5.5.6

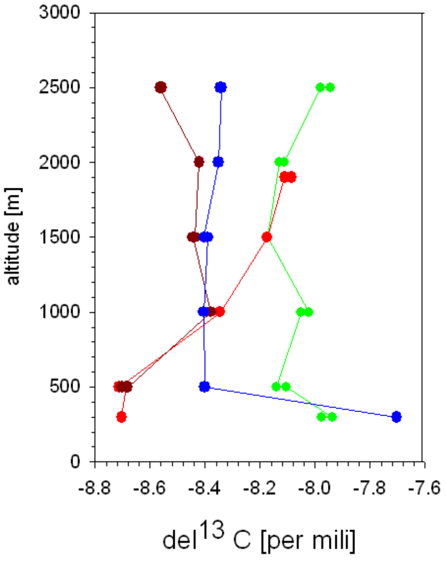


Fig. 5.5.7

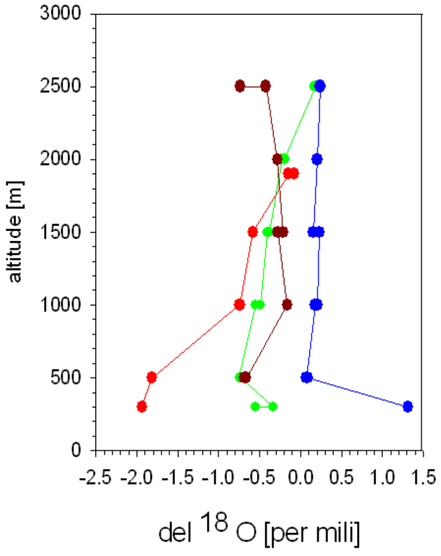


Fig 5.5.8

Figs. 5.5.1-5.5.8. Typical profiles for autumn/winter time. For the continuous and flask profiles: red =17.10.2003 , green=03.11.2003, brown=24.01.2004, blue =09.02.2005.

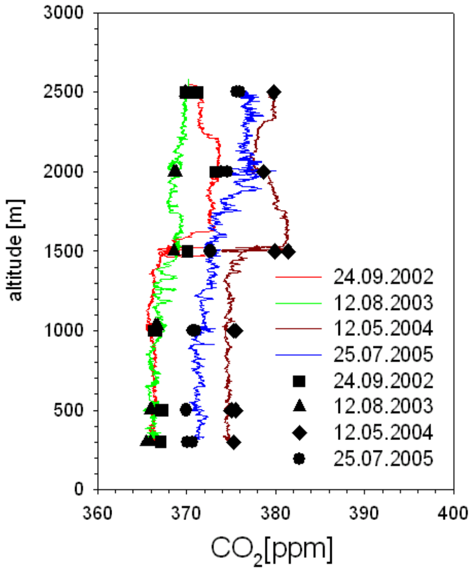


Fig. 5.6.1

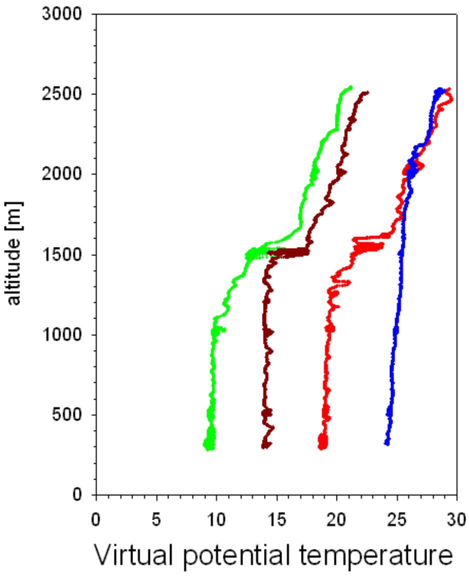


Fig. 5.6.2

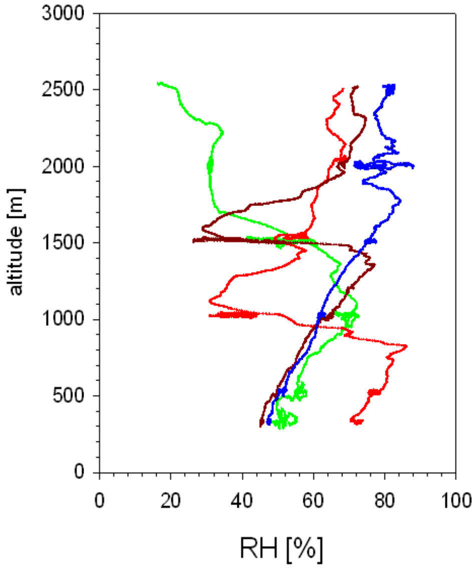


Fig. 5.6.3

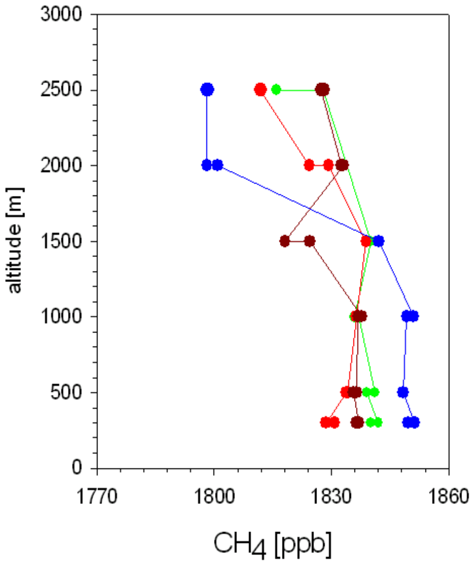


Fig.5.6.4

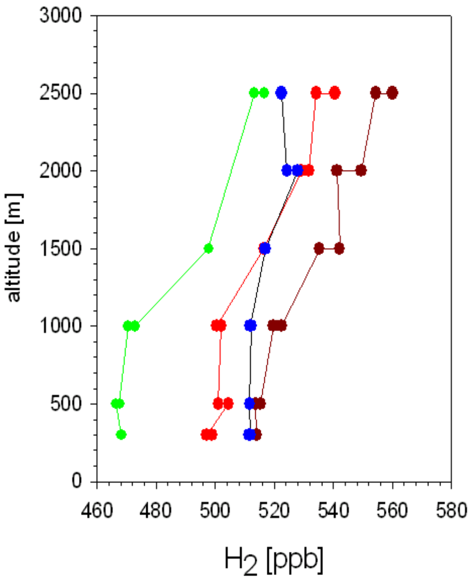


Fig. 5.6.5

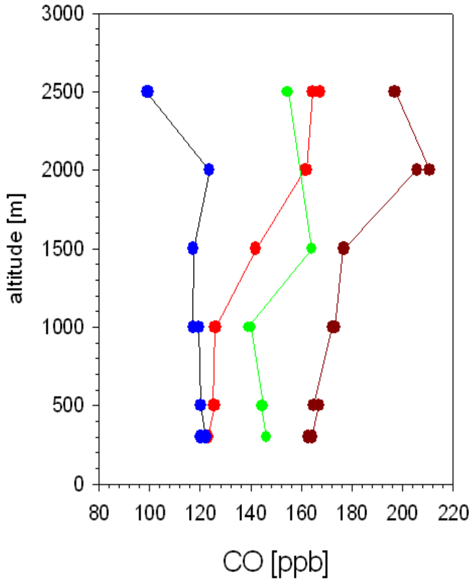


Fig. 5.6.6

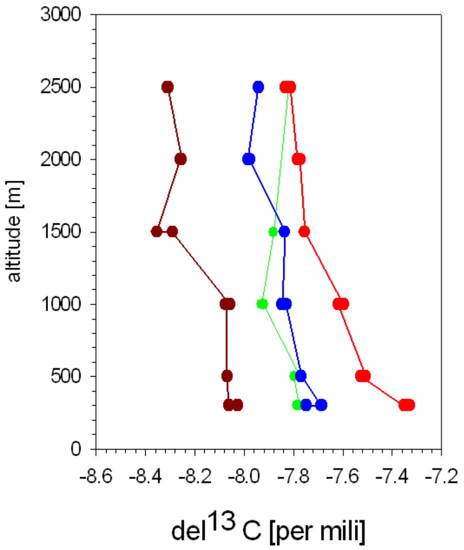


Fig. 5.6.7

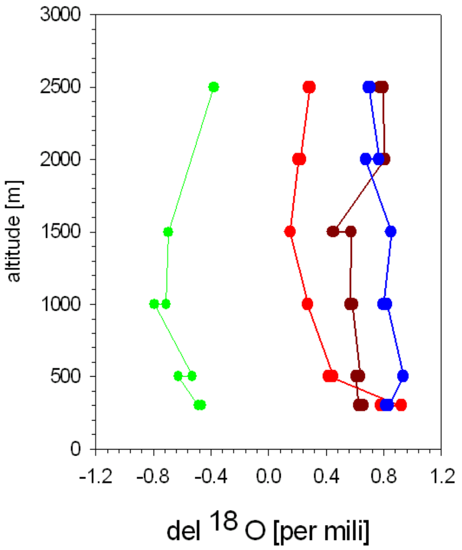


Fig. 5.6.8

Figs. 5.6.1-5.6.8. Typical profiles for spring/summer time. For the continuous and flask profiles: red =24.09.2002, green=12.08.2003, brown=12.05.2003, blue =12.05.2004.

5.8 Boundary layer

The convective boundary layer height depends on many factors. Generally, it depends on the time of year, day and synoptic condition. We tried to estimate the boundary layer heights for our flights, which are presented in Fig. 5.7. Our flights were made during good weather conditions at around noon or in the afternoon. The boundary layer was detected from profiles of temperature, water vapour and CO_2. This calculation is necessary for separating each profile into PBL and free troposphere components. Typically for wintertime, the top of the boundary lies between 400-600 m, whereas for summer time the situation is more flexible. We can say that the boundary layer is between 1500m (1512 above ground level the lowest value observed) and 2300 m (the highest value observed 2302 above ground level) for the summer period.

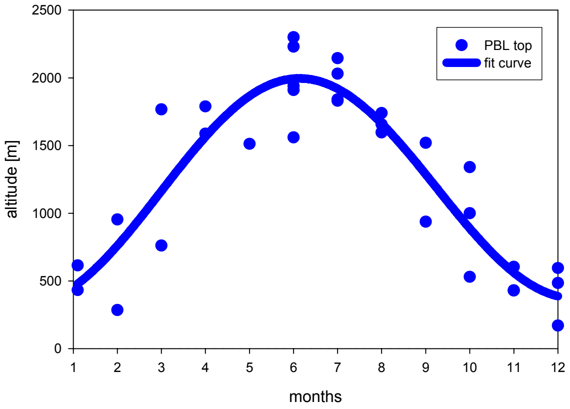


Fig. 5.7 Noon and afternoon boundary layer height vs. function time of year. Some flights are not presented because of difficulties with the estimation of CBL height.

5.9 CO_2 peak-to-peak amplitude

For the Bialystok site the CO_2 seasonal cycle peak-to-peak amplitudes have been calculated within the atmospheric boundary layer (CBL: 19 ppm) and the free troposphere (FT: 11.2 ppm). From these signals a calculation between CBL and FT was made, known as the CO_2 'jump', which will be compared to the simulations from atmospheric transport models. An interesting point which should be noted is that the ‘jump’ of CO_2 for CBL is faster after the winter season than the FT cycle and drops before the FT cycle. That process is connected with an accumulation of CO_2 in the biosphere.

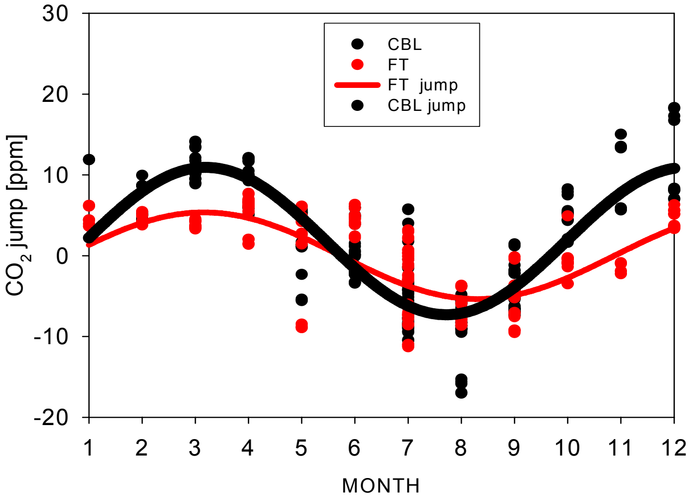


Fig. 5.8 Seasonal CO_2 jump calculated for Free Troposphere (FT) and Convective Boundary Layer (CBL).

5.10 CO_2 concentrations and comparison with other greenhouse gases

The data obtained were divided into two data sets. First, the results for the boundary layer and then for the results for the free troposphere.

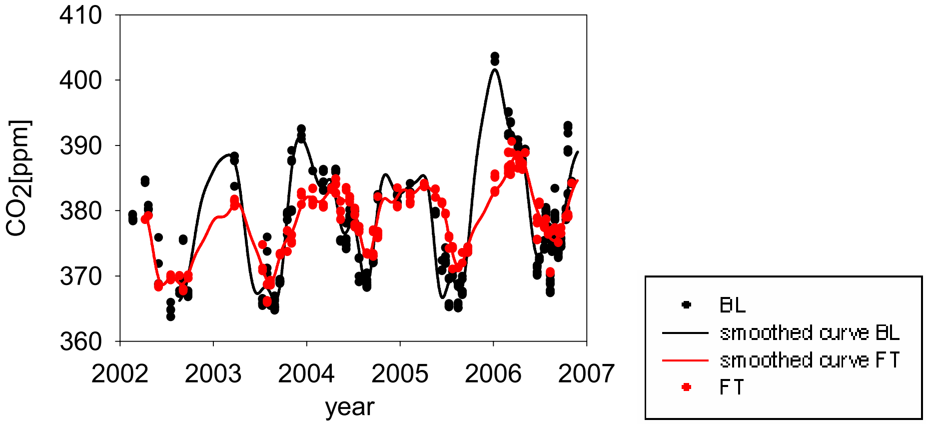


Fig. 5.9.1

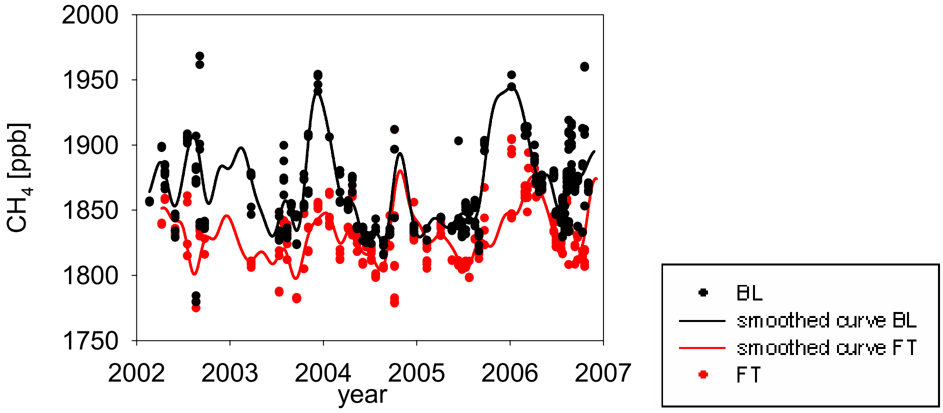


Fig.5.9.2

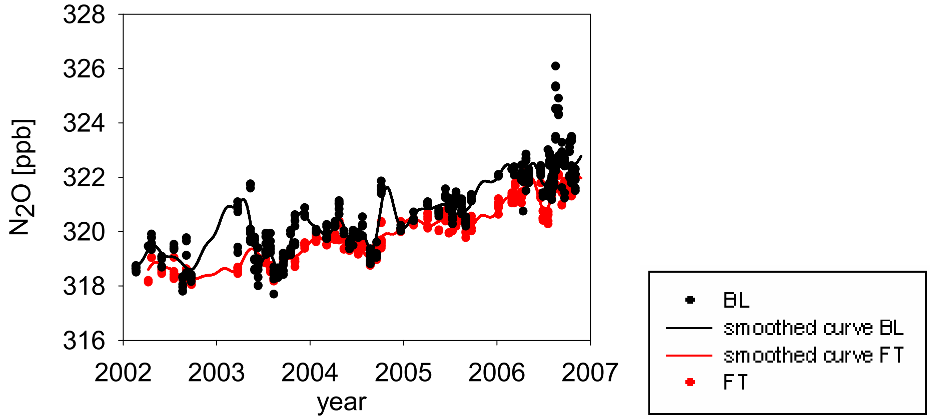


Fig.5.9.3

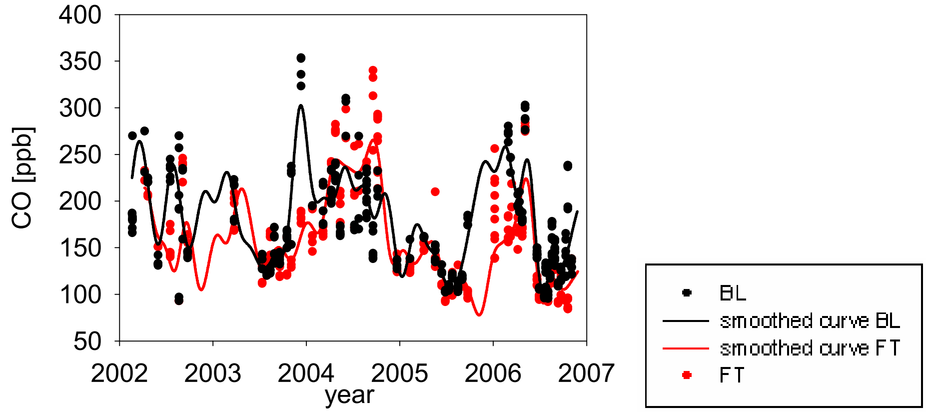


Fig. 5.9.4

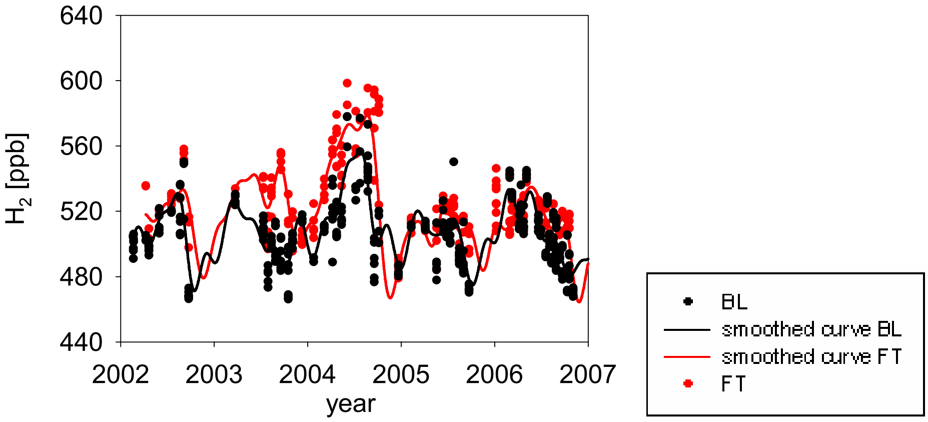


Fig. 5.9.5

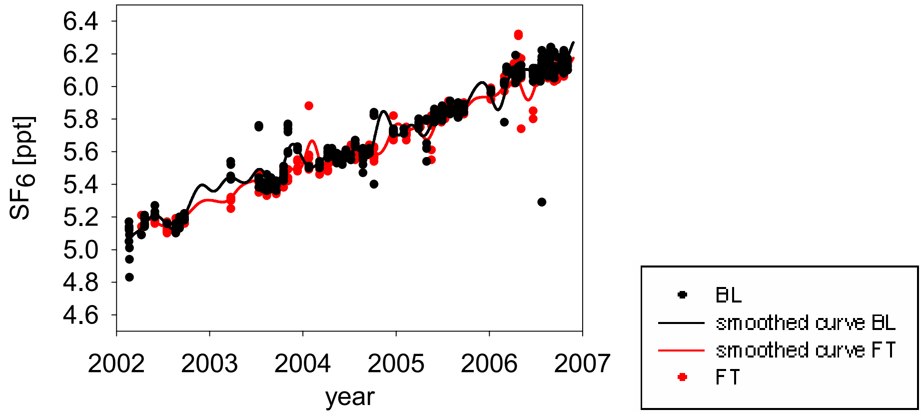


Fig.5.9.6

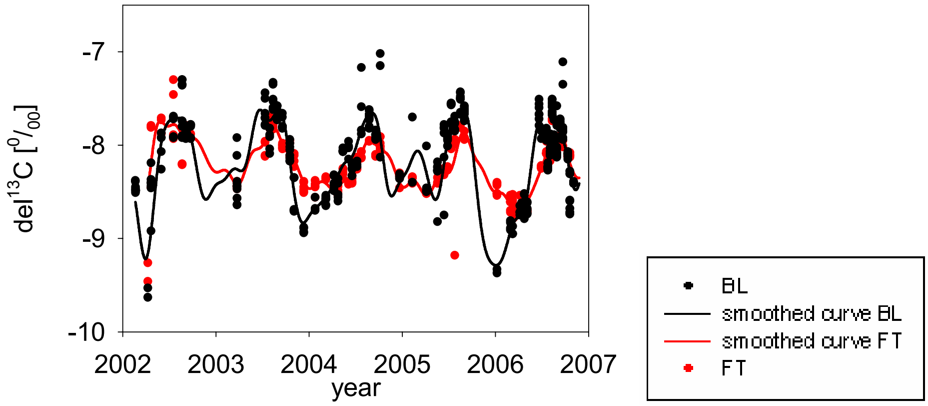


Fig. 5.9.7

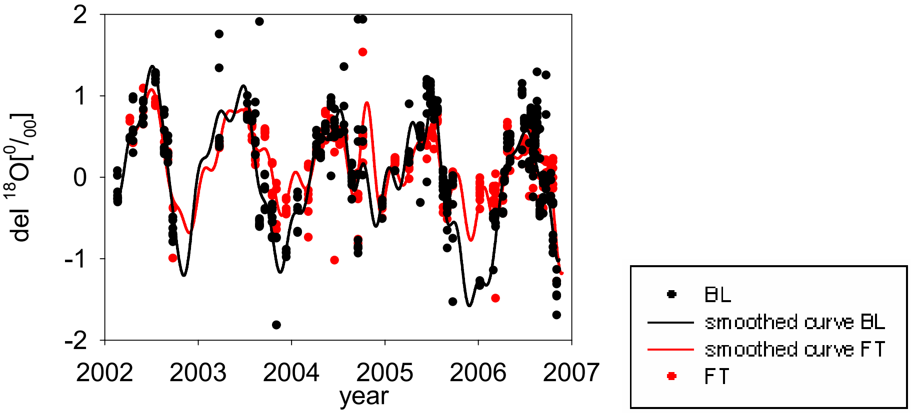


Fig.5.9.8

Figs 5.9.1-5.9.8 Concentrations of CO_2, CH_4, N_2O, *CO*, H_2, SF_6, $\delta^{13}C$, $\delta^{18}O$ *derived from collected flask samples.*

All components show distinct seasonal cycles except for SF_6. In the case of CO_2, regular seasonal changes of CO_2 were observed associated with photosynthetic activity during the vegetation period, seasonal CO_2 exchange and possible influence from anthropogenic emission. The lowest CO_2 concentration was observed during the summer of 2002 (August 2002) and the mixing ratio was equal to 357 ppm, and for the maximum values we observed in the winter of 2002 (December 2002), the mixing ratio of CO_2 was 392 ppm.

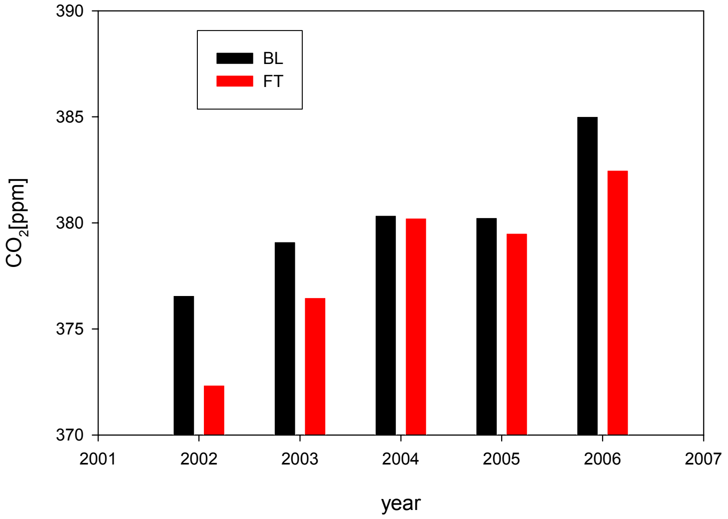


Fig. 5.10 Mean CO_2 concentration observed in the BL and FT at the Bialystok site for all flights.

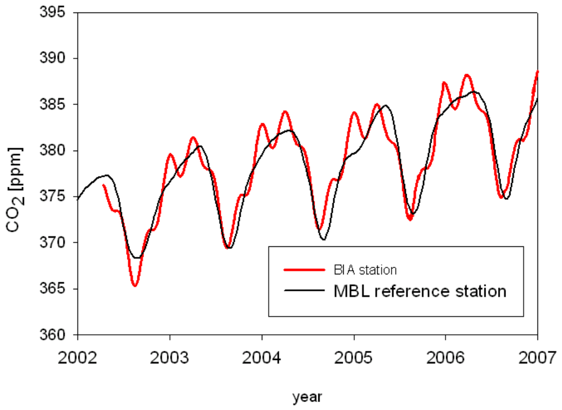


Fig. 5.11 CO_2 trend line (FT) calculated for the Bialystok site and comparison with the MBL reference line Mace Head (NOAA,CMDL).

5.10.1 Seasonal variability of stable isotope ratios of carbon and oxygen in CO_2

The annual mean value mixing ratios show an increase in the CO_2 mixing ratio and a corresponding decrease in $\delta^{13}C$. The $\delta^{13}C$ source signature of this flux is calculated to have a value of -24.65 ‰±0.6‰, similar to other stations (Fyodorovskoje -26‰±1‰ Syktyvkar -27.8‰±0.3‰ and Zotino -27.1‰±0.4‰) (Levin I. et al., 2002). More positive of $\delta^{13}C$ isotopes in flask samples in the BL than in the FT were observed during the summer months.

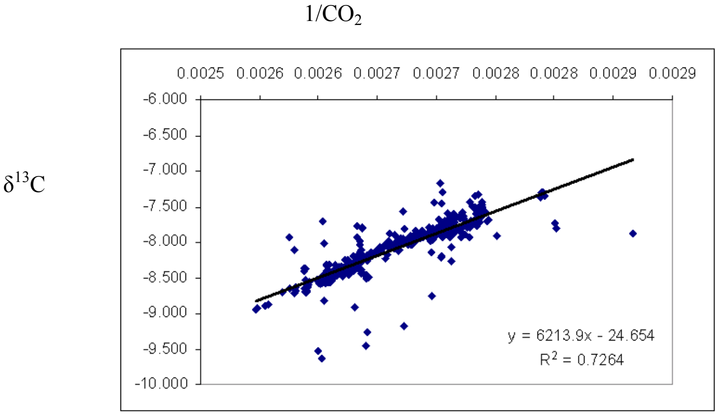


Fig. 5.12 Seasonal variability of oxygen in CO_2 (Keeling plot)($\delta^{13}C$ vs. $1/CO_2$)

This situation represents the enrichment of isotope concentration by photosynthesis. The reverse situation is characteristic in the winter months, when the CO_2 mixing ratio is higher in BL than in FT.

$\delta^{18}O$ in CO_2 data for BL and FT show a small depletion. A minimum of $\delta^{18}O$ occurs in November 2003, whereas the maximum of $\delta^{18}O$ is characteristic for the beginning of the growing period in May.

5.10.2 Seasonal variability of CO, CH_4

The trend of the seasonal cycle of CH_4 with a maximum in the FT, was observed in winter and a minimum in the summer months. We noticed that for all flights the concentration of methane is higher in BL than in FT. In our opinion the situation is caused by local emissions from the marshland. An extreme situation in BL was observed during the winter flight (December 2003), when the concentration of CH_4 was 1951 ppb. Anthropogenic emission due to using a coal as the main source for heating of houses may be one of the main reasons responsible for this.

5.10.3 Seasonal variability of N_2O and SF_6

Our observations show a seasonal cycle of N_2O with a maximum concentration during autumn time and a minimum in late spring. N_2O natural and anthropogenic emissions from soils are generally at their maximum level in spring and early summer (Flessa et al., 1995; Schmidt et al., 2001). This process gives an increasing concentration of N_2O in summer due to the atmospheric mixing process.

SF_6 is chemically a very stable and purely anthropogenic greenhouse gas, with about 80% of the global SF_6 release presumably from leakage in insulation and switching, and 20% from degassing and the purifying of molten reactive metals (Maiss and Brenninkmeijer, 1998). Since the 1970s, atmospheric SF_6 has been increasing globally at a rate of more than 6% per year (Maiss et al., 1996). At the Bialystok measurement station the concentration of SF_6 increased to around 29% from the beginning of 2002. For backward trajectories the analyses show that an increase in the SF_6 concentration is observed during the transport of air masses from the Ukraine.

5.11 Conclusions

This study has demonstrated the appropriateness of multiple tracer analyses and proposed further perspectives for regional experimental investigation. There exist only a few measurements points in Poland for trace gas monitoring. Still, there are some uncertainties which require further observation. These are currently in progress as part of the CarboEurope atmospheric component project with high frequency observations, i.e. one flight per week.

Conclusion

The present dissertation has focused on the measurement of volatile organic carbon compounds and their exchange through biosphere-atmosphere interactions, as well as their concentrations in the atmosphere. Also, a series of experiments to quantify local trace gas concentrations by using small aircraft was performed.

In the case of VOC, the measurement and analysis of biogenic volatiles is a complex task in terms of qualitative and quantitative aspects, and a great variety of analytical techniques has been developed in the past few years. All measurements and analyses were performed with high accuracy, precision, and reproducibility of VOC. To investigate the atmospheric concentrations of VOC a new sampling instrument was developed. During two intensive measurement campaigns a series of sampling was performed over the poorly investigated Siberian region. These experiments comprised the sampling evaluation of VOC over the forest canopy and a series of airborne measurements. Sampling of volatile organics on graphitized carbon blacks, followed by thermal desorption and analysis by gas chromatography coupled to flame ionization detection was the approved method and confirmed the good choice of the method selected. The assessment of data on VOC concentrations is particularly crucial for the evaluation of biosphere-atmosphere exchange processes. As part of the experiments, consecutive field studies in the summers of 2004 and 2005 were performed. In the case of the first location, Fyodorovskoje, located at about 300 km NW of Moscow in European Russia, station measurements over the canopy of the forest showed that the isoprene was the dominant specie with an ambient concentration range of 0.4-3.2 ppb. Mean concentrations of isoprene oxidation products, i.e. methyl vinyl ketone (MVK) and methacroleine (MACR) were lower than 1 ppb. In the case of the second station, Zotino, located to the west of the Yenisei River, the dominant VOC species present in the air was isoprene (range 0.1 ppb-2.5 ppb) and monoterpenes such as α -pinene, camphene, limonene, and β-pinene with the mean concentrations around 1 ppb, which indicated the low oxidation capacity of the atmosphere. Results obtained from comparison showed a difference in biogenic VOC concentrations. This difference shows that many factors affect emissions such as temperature, light intensity, plant phenology, injury and stress, making emission inventory difficult. Ambient measurements of biogenic compounds in different environments can help in estimating the performance of such inventories.

In the case of all the airborne VOC studies, the atmosphere exchange of volatile organics and the results obtained from VOC fluxes showed the importance and relation of VOC to carbon studies. The proposed studies provided key information on the amount of atmospheric carbon sequestered by an important forest ecosystem. The range of fluxes obtained obtained by using a simple Box Model Technique varies between 1.39-4.99 $mgCm^{-2}h^{-1}$ for isoprene and 0.49-4.97 $mgCm^{-2}h^{-1}$ for the sum of monoterpenes and their relation to GPP showed that a crucial point is to include VOC in atmospheric carbon studies.

The observed fluxes showed that VOC may be a substantial and integral part of the regional carbon cycle. Critical limitations in the quest for quantifying the role of VOC in the regional and global carbon budget were found in the uncertainties of both, VOC and CO_2 flux estimates.

BM flux estimates are influenced by the assumptions made on boundary layer turbulence dynamics and atmospheric chemistry, and the oxidation and transport time scales were found to be of similar magnitude. This leads to a coupling between CBL atmospheric chemistry and transport issues, ultimately generating conceptual and practical difficulties in estimating fluxes of reactive scalars such as biogenic VOC.

The airborne approach, using CBL vertical profiles to infer VOC fluxes, included the footprint of the tower-based measurements, but was representative of a significantly larger surface area of several hundred km^2.

According to these promising results, the improvement in knowledge about the Siberian region should result in contributions for the investigation of biosphere-atmosphere exchange processes of volatile organic compounds and their relation to atmospheric carbon.

With a new station in Poland it was proved that local carbon studies are important for regional observations of carbon balance. A series of experiments with small aircraft showed differences between seasonal changes of trace gases in the FT and BL, as well as seasonal changes of trace gas mixing ratios. The aircraft program, started in 2002, has provided a unique set of trace gas observations over the eastern part of the European continent which will serve as an invaluable source of information by investigating quantitatively the associated biogeochemical cycles with these entities. From the first results presented here we can conclude that the gradients observed in CO_2 and stable isotopic ratios in the vertical and across the eastern part of Europe continent are small. As expected, the seasonal amplitudes of CO_2 concentration and stable isotope ratios in CO2 increase towards more continental sites due to large seasonal CO_2 exchange fluxes with the continental biosphere.

However, the largest changes calculated for Bialystok aircraft measurements with double peaks in the winter trend line for the Bialystok site in CO_2 might be caused by heterotropic respiration from soils. In the case of CH_4, seasonal variation in mixing ratios was observed, with an increase of CH_4 concentrations during winter time. However the seasonal concentration of CH_4 during the summer time stayed the same more or less at the same level. N_2O shows small seasonal cycles over Poland which must be associated with the transport pattern in the air masses and the good mixing process due to the time of sampling. In the case of CO, I observed systematic degrees of CO mixing ratios in the FT and BL. This situation might be caused by the CO uptake by soils and the lower number combustion of fossil fuel in Poland. SF_6 does not show any seasonal cycle, only a linear increase of around 6% per year.

The small atmospheric signals observed make high demands on measurement accuracy and, as in our case of a concerted program, with high precision based on inter-laboratory comparability. In fact, the data are a component of a cooperative network and these data will be used successfully in model inversion estimates to derive net European trace gas fluxes.

Outlook

While obviously many questions remain open, this comparison of the VOC emission fluxes with GPP and the discussion of the potential fate of the carbon within the atmosphere makes it clear that VOC emission must be regarded as a substantial loss of biologically fixed carbon from the terrestrial biosphere, significant in relation to GPP and of the same order of magnitude when compared to NBP. To obtain a more reliable estimate of this important term in the carbon budget, more broadly representative measurements of VOC fluxes in relation to CO_2 fluxes, biological process studies, and detailed model calculations on the fate of the emitted VOC are urgently needed.

Newly available techniques might be used for measurements such as PTR-MS. This technique is able to measure compounds with a proton affinity higher than water with a high time resolution of 1 per second compound. This might be of use for obtaining VOC vertical profiles and receiving in-situ measurements of VOC. Hence nearly all VOC can be detected on-line. We could clearly identify the emission of methanol, acetaldehyde, ethanol, acetone, acetic acid, isoprene, monoterpenes and toluene. Such disagreements may have several reasons, such as unclear identification of compounds by the PTR-MS which, however, can be excluded in the case of monoterpenes and some other compounds. Other reasons may involve the use of different tree individuals and different seasonal developmental stages, an explanation which is supported by the enhanced CO_2 assimilation observed. The overall PTR-MS study on VOC emissions looks reliable as it is supported by the relation between carbon assimilated (measured by an infrared gas analyser) and carbon emitted as VOC.

In the case of the Bialystok aircraft measurements, much longer observational records are definitely needed to provide reliable answers to the urgent questions of the role of the great land masses that targeting Europe from the eastern part of the continent in relation to global budgets of atmospheric greenhouse gases. A "footprint" analysis is necessary to find sources of anthropogenic air masses that are targeting Bialystok station.

References

Ackmann, R.G.: Fundamental groups in the response of flame ionisation detectors to oxygenated aliphatic hydrocarbons, Journal of Gas Chromatography, 2, 173-179, 1964.

Altshuller, P.: Review: Natural volatile organic substances and their effect on air quality in the United States, Atmospheric Environment, 17, 2131, 1983.

Andreae, M.O. and Crutzen, P.J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058, 1997.

Apel, E.C., Calvert, J.G., and Fehsenfeld, F.C.: The Nonmethane Hydrocarbon Intercomparison Experiment (Nomhice) - Task-1 and Task-2, Journal of Geophysical Research-Atmospheres, 99, 16651-16664, 1994.

Apel, E.C., Calvert, J.G., Gilpin, T.M., Fehsenfeld, F., and Lonneman, W.A.: Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 4, ambient air (vol 108 art no 4359, 2003), Journal of Geophysical Research-Atmospheres, 108, 2003a.

Apel, E.C., Calvert, J.G., Gilpin, T.M., Fehsenfeld, F., and Lonneman, W.A.: Correction to: Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 4, ambient air, Journal of Geophysical Research-Atmospheres, 108, 2003b.

Arey, J., Winer, A.M., Atkinson, R., Aschmann, S.M., Long, W.D., and Morrison, C.L.: The Emission of (Z)-3-Hexen-1-Ol, (Z)-3-Hexenylacetate and Other Oxygenated Hydrocarbons from Agricultural Plant- Species, Atmospheric Environment Part A-General Topics, 25, 1063-1075, 1991.

Arnts, R., and Meeks, S.A,: Biogenic hydrocarbon contribution to the ambient air of selected areas. Atmosperic Environment 15, 1643—1651, 1981.

Atkinson, R.: Gas-phase troposheric chemistry of organic compounds: a review, Atmospheric Environment, 24A, No. 1, 1-41, 1990.

Atkinson, R., Tuazon, E. C., and Aschmann, S. M.: Products of the gas-phase reactions of O_3 with alkenes, Environmental Science & Technology 29, 1860–1866, 1995.

Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, Journal of Physical and Chemical Reference Data, 26, 215–290, 3931, 1997.

Atkinson, R., Arey, J.: Atmospheric chemistry of biogenic organic compounds. Accounts of Chemical Research, 31, 574 - 583, 1998.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmospheric Environment, 34, 2063-2101, 2000.

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmospheric Environment, 37, S197-S219, 2003.

Bakwin, P. S., Tans, P. P., Hurst, D. F. and Zhao, C.: Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program, Tellus Series B-Chemical and Physical Meteorology, 50B: 401-415, 1998.

BEMA-Project: Special Issue, Atmospheric Environment, 31 (SI), 1997.

Benjamin, M. T., Sudol, M., Bloch, L., and Winer, A. M.,: Low-emitting urban forests: A taxonomic methodology for assigning isoprene and monoterpene emission rates, Atmospheric Environment, 30, 1437–1452, 1996.

Bertin, N. and Staudt, M.: Effect of water stress on monoterpene emissions from young potted holm oak (Quercus ilex L.) trees, Oecologia, 107, 456-462, 1996.

Bertin, N., Staudt, M., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J.L., and Torres, L., : Diurnal and seasonal course of monoterpene emissions from Quercus ilex (L.) under natural conditions - Applications of light and temperature algorithms, Atmospheric Environment, 31, 135-144, 1997.

Blades, A.T.: Ion Formation in Hydrocarbon Flames, Canadian Journal of Chemistry-Revue Canadienne DeChimie, 54, 2919-2924, 1976.

Bohlmann, J., Meyer-Gauen G, Croteau R.: Plant terpenoid synthases: molecular biology and phylogenetic analysis. Proceedings of the National Academy of Sciences U.S.A., 95:4126–33, 1998.

Brown, S., Sathaye, J., Cannell, M , Kauppi, P., Burschel, P., Grainger, A., Heuveldop, J. Leemans, R., Moura Costa, P., Pinard, M., Nilsson, S., Schopfhauser, W., Sedjo, R. Singh, N., Trexler, M., van Minnen, J, Weyers, S.: Management of forests for mitigation of greenhouse gas emissions. In: IPCC Climate Change 1995 - Impacts, Adaptations and Mitigation of Climate Change: Scientific-Technical Analyses, Contribution of Working Group II to the Second Assessment Report of the Intergovernmental Panel on Climate Change [Watson, R.T., M.C. Zinyowera, R.H. Moss and D.J. Dokken (eds.)], Cambridge University Press, Cambridge, pp. 773-797, 1996.

Brunner, D., Staehelin, J. and Jeker, D.: Large-scale Nitrogen Oxide Plumes in the Tropopause Region and Implications for Ozone, Science, 282, 1305-1309, 1998.

Buchmann, N. and. Schulze, E.D: Net CO_2 and H_2O fluxes of terrestrial ecosystems. Global Biogeochemical Cycles 13:3:751-760, 1999.

Calogirou, A., Larsen, B.R., Brussol, C., Duane, M., and Kotzias, D.: Decomposition of terpenes by ozone during sampling on Tenax, Analytical Chemistry, 68, 1499-1506, 1996.

Calogirou, A., Larsen, B.R., and Kotzias, D.:Gas-phase terpene oxidation products: A review. Atmospheric Environment, 33, 1423–1439, 1999.

Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., and Yarwood, G.: The mechanisms of atmospheric oxidation of the alkenes. Oxford University Press, New York, 3904, 2000.

Chappell J.: Biochemistry and molecular biology of the isoprenoid biosynthetic pathway in plants. Annual Review of Plant Physiology in Plant Molecular Biolology 46:521–47, 1995.

Christoffersen, T.S., Hjorth, J., Horie, O. Jensen, N. R., Kotzias, D., Molander, L. L Need, P., Ruppert, L. Winterhalter, R.. Virkkula, A., Wirtz, K. and Larsen, B. R.,: Cis-pinic acid, a possible precursor for organic aerosol formation from ozonolysis of alpha-pinene, Atmospheric Environment, 32, 1657, 1998.

Ciais, P., Tans, P.P., Trolier, M., White J.W.C. and Francey, R.J.: A Large Northern Hemisphere Terrestrial CO_2 Sink Indicated by the $^{13}C/^{12}C$ Ratio of Atmospheric CO_2, Science,Vol.269,no.5227,pp.098-1102,1995.

Ciais, P., Denning, A.S., Tans, P.P., Berry, J.A., Randall, D.A., Collatz, G.J., Sellers, P.J., White, J.W.C., Trolier, M., Meijer, H.A.J., Francey, R.J., Monfray, P., and Heimann, M.: A three-dimensional synthesis study of delta O18 in atmospheric CO2 .1. Surface fluxes, Journal of Geophysical Research- Atmospheres, 102, 5857-5872, 1997.

Ciccioli, P., Fabozzi, C., Brancaleoni, E., Cecinato, A., Frattoni, M., Loreto, F., Kesselmeier, J., Schäfer, L., Bode, K., Torres, L., and Fugit, J.L.: Use of the isoprene algorithm for predicting the monoterpene emission from the Mediterranean holm oak Quercus ilex L.: Performance and limits of this approach, Journal of Geophysical Research-Atmospheres, 102, 23319-23328, 1997.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., and Maenhaut, W. : Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173-1176, 2004.

Clark, J.S., Carpenter, S.R., Barber, M., Collins, S., Dobson, A., Foley, J.A.,Lodge, D.M., Pascual, M.; Pielke, R., Pizer, W., Pringle, C., Reid, W.V., Rose, K. A., Sala, O., Schlesinger, W.H., Wall, D.H., Wear, D.: Ecological forecasts: An emerging imperative Science 293: 657-660, 2001

Cleugh, H.A, Raupach, M.R., Briggs, P.R., Coppin, P.A.: Regional scale heat and water vapour fluxes in an agricultural landscape: An evaluation of CBL budget methods for OASIS, Boundary-Layer Meteorology. 110: 99-137, 2003.

Crawford, T.J, Dobosy, J.R, McMillen R.T., Vogel C.A. and Hicks B.B.: Air-surface exchange measurement in heterogeneous regions: extending tower observations with spatial structure observed from small aircraft, Global Change Biology, 3, 275-285, 1996.

Croteau R., Gershenzon, and Turner, G., J: Distribution of Peltate Glandular Trichomes on Developing Leaves of Peppermint, Plant Physiolgy, 124(2), 655–664, 2000.

Davis, E.M., Croteau, R.: Cyclization enzymes in the biosynthesis of monoterpenes, sesquiterpenes and diterpenes. In Topics in Current Chemistry: Biosynthesis, ed. F Leeper, JC Vederas, 209:53–95. Heidelberg: Springer-Verlag, 2000.

Dement, W. A., Tyson, B. J., and Mooney, H. A.: Mechanism of monoterpene volatilization in Salvia mellifera, Phytochemistry 14, 2555–2557, 1975.

Denmead, O.T. et al: Boundary layer budgets for regional estimates of scalar fluxes, Global Change Biology (3), 255-264, 1996.

Desjardins, R.L., J.I. MacPherson, L. Mahrt, P. Schuepp, E. Pattey, H. Neumann, D. Baldocchi, S. Wofsy, D. Fitzjarrald, H. McCaughey, and D.W. Joiner. Scaling up flux measurements for the boreal forest using aircraft-tower combinations, Journal of Geophysical Research 102 (D24): 29,125-29,133, 1997.

Dindorf, T., Kuhn, U., Ganzeveld, L., Schebeske, G., Ciccioli, P., Holzke, C., Köble, Seufert, G., and Kesselmeier, J.: Significant light and temperature dependent monoterpene emissions from European beech (Fagus sylvatica L.) and their potential impact on the European volatile organic compound budget, Journal of Geophysical Research -Atmosphere, 111, doi:10.1029/2005JD006751, 2006.

Drewitt, G.B., Curren, K., Steyn, D.G., Gillespie, T.J., Niki, H.: Measurement of biogenic hydrocarbon emissions from vegetation in the Lower Fraser Valley, British Columbia, Atmospheric Environment, 32, 3457–3466, 1998.

Edmonds, **J.A**., Wise, M.A, Sands, R.D., Brown, R.A, and Kheshgi, H.S.: Agriculture, Land Use, and Commercial Biomass Energy: A Preliminary Integrated Analysis of the Potential Role of Biomass Energy for Reducing Future Greenhouse Related Emissions. PNNL-111555. Pacific Northwest National Laboratory, Washington, DC, USA, 1996

Eisenreich, W., Schwarz, M., Cartayrade, A., Arigoni, D., Zenk, M.H,: The deoxyxylulose phosphate pathway of terpenoid photosynthesis in plants and microorganisms, Chemical Biology, 5:R221–23, 1998.

Emmons, L. K., Hauglustaine, D.A., Müller, J., Carroll, M.A., Brasseur, G.P, Brunner, D., Staehelin, J., Thouret, V. and Marenco, A. :Data composites of airborne observations of tropospheric ozone and its precursors., Journal of Geophysical Research, vol. 105, D16, 20,497–20,538, 2000.

Falge, E., Baldocchi, D., Tenhunen, J., Aubinet, M., Bakwin, P., Berbigier, P., Bernhofer, C., Burba, G., Clement, R., Davis, K.J.: Seasonality of ecosystem respiration and gross primary production as derived from FLUXNET measurements, Agricultural and Forest Meteorology 113:53–74, 2002.

Falkowski, P., Scholes, R.J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Hogberg, P., Linder, S., Mackenzie, F.T., Moore, B., Pedersen, T., Rosenthal, Y., Seitzinger, S., Smetacek, V., and Steffen, W., : The global carbon cycle: A test of our knowledge of earth as a system, Science, 290, 291-296, 2000.

Fall, R. and Wildermuth, M.C.: Isoprene synthase: From biochemical mechanism to emission algorithm, Journal of Geophysical Research-Atmospheres, 103, 25599-25609, 1998.

Fall, R., Karl, T., Hansel, A., Jordan, A., and Lindinger, W.: Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry, Journal of Geophysical Research-Atmospheres, 104, 15963-15974, 1999.

FAO, 1997: State of the world's forests. FAO, Rome, Italy.

Farquhar, G.D., Lloyd, J, Taylor, J.A, Flanagan, L.B., Syvertsen, J.B., Hubick, K.T,. Wong, S.C, and Ehleringer, J.R.: Vegetation effects on the isotope composition of oxygen in atmospheric CO_2. Nature, 363, 439-443, 1993.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A., Hewitt, C.N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmermann, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, Global Biogeochemical Cycles, 6, 389-430, 1992.

Finlayson-Pitts, B. and Pitts, J.N.: Chemistry of the Upper and Lower Atmosphere, Theory, Experiments and Applications. Academic Press, San Diego, San Francisco, New York, Boston, London, Sydney, Tokyo, 2000.

Fischer, H., de Reus, M., Traub, M., Williams, J., Lelieveld, J., de Gouw, J., Warneke, C., Schlager, H., Minikin, A., Scheele, R., Siegmund, P., Deep convective injection of boundary layer air into the lowermost stratosphere at midlatitudes, Atmospheric Chemistry and Physics 3, 739-745, 2003

Flanagan, L.B., Brooks J.R., Varney, G.T., Berry S.C and Ehleringer. J.R.: Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO_2 in boreal forest ecosystems, Global Biogeochemical Cycles 10, 629-640, 1996.

Flanagan, L.B., Brooks, J.R., Varney, G.T and. Ehleringer, J.R.: Discrimination against $C^{18}O^{16}O$ during photosynthesis and the oxygen isotope ratio of respired CO_2 in boreal forest ecosystems, Global Biogeochemical Cycles 11, 83-98, 1997.

Flessa, H., Dörsch, P. and Beese, F.,: Seasonal variation of N_2O and CH_4 fluxes in differently managed arable soils in southern Germany. Journal of Geophysical Research 100**,** pp. 23115–23124, 1995

Gijzen, M., Lewinsohn E, Croteau R.: Characterization of the constitutive and wound-inducible monoterpene cyclases of grand fir (Abies grandis). Archives of Biochemistry and Biophysics 289:267–73, 1991.

Glebov, F. Z.: Bogs and bogged forests of the forest zone of the left bank of the Yenisei river. NAUKA, Moscow, 132 pp, 1969.

Goldstein, A. H., Fan, S. M., Goulden, M. L., Munger, J. W., and Wofsy, S. C.,: Emissions of ethene, propene, and I-butene by a midlatitude forest, Journal of Geophysical Research-Atmospheres,101, 9149–9157, 1996.

Gottwald, W.: GC für Anwender. In Praxis der instrumentellen Analytik Ed. W. Klein. Verlag Chemie, Weinheim, New York, Basel, Cambridge, Tokyo, 1995.

Guenther, A., Zimmerman, P.R., Harley, P.C., Monson, R.K., and Fall, R.: Isoprene and Monoterpene Emission Rate Variability - Model Evaluations and Sensitivity Analyses, Journal of Geophysical Research-Atmospheres, 98, 12609-12617, 1993.

Guenther, A., Zimmerman, P., and Wildermuth, M.: Natural Volatile Organic-Compound Emission Rate Estimates for United-States Woodland Landscapes, Atmospheric Environment, 28, 1197-1210, 1994.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.:A Global-Model of Natural Volatile Organic-Compound Emissions, Journal of Geophysical Research-Atmospheres, 100, 8873-8892, 1995.

Guenther, A.: The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, Chemosphere, 49, 837-844, 2002.

Hahn, J., Steinbrecher, R., and Stahl,K.,: Study of the emission of lowmolecular weight organic compounds of various plants, EUROTRAC Annual Report 1990, Part 4, BIATEX, 1991.

Hahn, J., Steinbrecher, R., and Slemr, J.,: Study of the emission of low molecular weight organic compounds of various plants, Eurotrac Annual Report, Part 4, BIATEX 1991, Garmisch- Partenkirchen, pp. 230–235, 1992.

Hakola, H., Rinne, J., and Laurila, T.: The hydrocarbon emission rates of tea-leafed willow (Salix phylicifolia), silver birch (Betula pendula) and European aspen (Populus tremula), Atmospheric Environment, 32,1825-1833, 1998.

Hakola, H., Laurila, T., Rinne J. and Puhto, K.: The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site, Atmospheric Environment, Volume 34, Issues 29-30, 2000, Pages 4971-4982, 2000.

Hall, D.O., House, J., and Scrase, I.: An overview of biomass energy. In: Industrial Uses of Biomass Energy: the Example of Brazil [Rosillo-Calle, F., H. Rothman and S.V. Bajay (eds.). Taylor & Francis, London, 2000.

Hansen, U. and Seufert, G.,: The terpenoid emission pattern of Quercus coccifera L. coincides with the emission pattern found with Quercus ilex L, in P. M. Borrell, P. Borrel, T. Cvitas, K. Kelly, W. Seiler (eds), The Proceedings of EUROTRAC Symposium 1996, Computational Mechanics Publications, Southhampton, pp. 235–239, 1996.

Harley, P. C., Monson, R. K. and Lerdau, M. T.: Ecological and evolutionary aspects of isoprene emission from plants, Oecologia, 118, 109–123, 1999.

Hayward, A. Tani, S.M. Owen and N. Hewitt, Online analysis of volatile organic compound emissions from Sitka spruce (*Picea sitchensis*), Tree Physiology, 24, pp. 721–728, 2004.

Heimann, M.: EU project EUROSIBERIAN CARBONFLUX, EV5V-CT95-0116, 2000.

Heimann, M.: Terrestrial Carbon Observing System – Siberia, EU-project, EVK2-2002-00555, 2003.

Helas, G., Slanina, S., and Steinbrecher, R.,:Biogenic Volatile Organic Compounds in the Atmosphere, SPB Acad., The Hague, Netherlands, 1997.

Helmig, D.: Ozone removal techniques in the sampling of atmospheric volatile organic trace gases, Atmospheric Environment, 31, 3635-3651, 1997.

Hoffmann, T., Jacob, P., Linscheid, M., and Klockow, D.: Measurements of Biogenic Hydrocarbons and Their Atmospheric Degradation in Forests, International Journal of Environmental Analytical Chemistry, 52, 29-37, 1993.

Hoffmann, T.: Adsorptive Preconcentration Technique Including Oxidant Scavenging for the Measurement of Reactive Natural Hydrocarbons in Ambient Air, Fresenius Journal of Analytical Chemistry, 351, 41-47, 1995.

Holm, T.: Aspects of the mechanism of the flame ionization detector, Journal of Chromatography A, 842, 221-227, 1999.

Houghton, R. A.: The annual net flux of carbon to the atmosphere from changes in land use 1850-1990. Tellus 51B:298-313, 1999.

Houghton, R.A.: Emissions of carbon from land-use change. Pages 63-76 *in: The Carbon* Cycle (T.M.L. Wigley and D.S. Schimel, editors), Cambridge University Press, New York, NY, 2000.

Hov, O., Schjoldager, J., and Wathne, B. W.,: Measurement and modeling of concentrations of terpenes in coniferous forest air, Journal of Geophysical Research D: Atmospheres, 88, 10679–10688, 1983.

IPCC, Intergovernmental Panel on Climate Change, Contribution of Working Group I to the Second Assessment Report (Houghton, J.T., Meira, L.G., Callander, B.A., Harris, N., Kattenberg, A., and Maskell, K.):Climate Change 1995: The Science of Climate Change, Cambridge University Press, Cambridge, UK,1996.

IPCC, Intergovernmental Panel on Climate Change, Contribution of Working Group I to the Third Assessment Report (Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M.,van der Linden, P.J, Dai, X., Maskell, K., Johnson, C.A.): Climate Change 2001: The Scientific basis, Cambridge University Press, Cambridge, UK, 2001.

IPCC, Intergovernmental Panel on Climate Change, Contribution of Working Group I to the Fourth Assessment Report (Edited by Susan Solomon, Dahe Qin, Martin Manning, Melinda Marquis, Kristen Averyt, Melinda M. B. Tignor and Henry LeRoy Miller): Climate Change 2007: The Scientific basis, Cambridge University Press, Cambridge, UK, 2007.

Ishitani, H., Johansson, T.B. and Al-Khouli, S.: Energy Supply Mitigation Options. In: Climate Change 1995. Impacts, Adaptations and Mitigation of Climate Change: Scientific-Technical Analyses. Contribution of Working Group II to the Second Assessment Report of the Intergovernmental Panel on Climate Change., Watson, R.T.. M.C. Zinyowera and R.H. Moss (eds.), Cambridge University Press, Cambridge, pp. 587-648, 1996.

Isidorov, V.A., Zenkevich, I.G., and Ioffe, B.V.: Volatile Organic-Compounds in the Atmosphere of Forests, Atmospheric Environment, 19, 1-8, 1985.

Isidorov, V. A., Povarov, V. G., Klokova, E. M., Prilepsky, E. B., Churilova, Y.,: Estimation of photochemically active VOC emission by forests of the European part of the former U.S.S.R., in Angeletti, G. and Restelli, G., (eds), Physico-Chemical Behaviour of Atmospheric Pollutants, ECSC-EC-EAEC, Brussels, Luxembourg, pp. 31–40, 1994.

Isidorov V.A. and Povarov, V.G.,: Phytogenic volatile organic compounds emission by russian forests, Ecological Chemistry 9, 10–21, 2000.

Jacob, D. J., Heikes, B.G., Fan, S.-M.,Logan, J.A, Mauzerall, L.M.,Bradshaw, J.D., Singh, H.B, Gregory, G.L, Talbot, G.W, Blake, D.R. and Sachse, G.W: The origin of ozone and NO_x in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin, Journal of Geophysical Research, 101, 24235-24250, 1996.

Janson, R. W.,: Monoterpene emissions from Scots pine and Norwegian spruce, Journal of Geophysical Research D: Atmospheres, 98, 2839–2850, 1993.

Jöckel, P., Sander, R., Kerkweg, A., Tost, H. and Lelieveld, J., Technical Note: The Modular Earth Submodel System (MESSy) - a new approach towards Earth System Modeling, Atmos. Chem. Phys., 5, 433-444, SRef-ID: 1680-7324/acp/2005-5-433, 2005.

Jordan, A. and Brand, W.: Trace gas measurement and quality assurance at the MPI for Biogeochemistry, 11th WMO/IAEA Meeting, Tokyo, 140-144, 2001.

Juuti, S., Arey, J., and Atkinson, R.: Monoterpene emission rate measurements from a Monterey pine, Journal of Geophysical Research-Atmospheres, 95 (D), 7515–7519, 1990.

Kaplan, J.O.; Prentice, I.C; Buchmann, N.: The stable carbon isotope composition of the terrestrial biosphere: Modeling at scales from the leaf to the globe, Global Biogeochemical Cycles 16, art. No.1060, 2002.

Kavouras, I.G., Mihalopoulos, N. and Stephanou, E.G.: Formation of atmospheric particles from organic acids produced by forests, Nature, 395, 683-686, 1998.

Kavouras, I.G., Mihalopoulos, N. and Stephanou, E.G.: Formation and gas/particle partitioning of monoterpenes photo-oxidation products over forests, Geophysical Research Letters, 26, 55-58, 1999.

Keeling, C.D.: The concentration and isotopic abundance of atmospheric carbon dioxide in rural areas, Geochimica and Cosmochimica Acta, 13, 322-334, 1958.

Keeling, C.D: The concentrations and isotopic abundances of carbon dioxide in rural and marine air, Geochimica and Cosmochimica Acta, 24, 277–298, 1961.

Keeling, C. D., Piper, S. C. Bacastow, R. B. Wahlen, M. Whorf, T. P. Heimann, M. and Meijer, H. A.: Atmospheric CO2 and 13CO2 exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications, pages 83-113,in "A History of Atmospheric CO2 and its effects on Plants, Animals, and Ecosystems",Ehleringer, J.R., T. E. Cerling, M. D. Dearing, Springer Verlag(eds.), New York, 2005.

Keene, W. C., Galloway, J. N., and Holden, J. D.: Measurement of weak organic acidity in precipitation from remote areas of the world, Journal of Geophysical Research D: Atmospheres, 88, 5122–5130, 1983.

Keller, M., and Lerdau, M.: Isoprene emission from tropical forest canopy leaves, Global Biogeochemical Cycles, 13, 19-29, 1999.

Kesselmeier, J., Schäfer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J.L., Dutaur, L., and Torres, L.: Emission of monoterpenes and isoprene from a Mediterranean oak species Quercus ilex L. measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project, Atmospheric Environment, 30, 1841-1850, 1996.

Kesselmeier, J., Bode, K., Hofmann, U., Müller, H., Schäfer, L., Wolf, A., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Ferrari, C., Jacob, V., Fugit, J.L., Dutaur, L., Simon, V., and Torres, L.: Emission of short chained organic acids, aldehydes and monoterpenes from Quercus ilex L. and Pinus pinea L. in relation to physiological activities, carbon budget and emission algorithms, Atmospheric Environment, 31, 119-133, 1997a.

Kesselmeier, J., and Bode, K.: Biology needed for the measurements and evaluation of exchange processes, in G. Helas, S. Slanina, and R. Steinbrecher (eds), Biogenic Volatile Organic Compounds in the Atmosphere - Summary of Present Knowledge, SPB Academic Publishers, Amsterdam, The Netherlands, pp. 9–25, 1997b.

Kesselmeier, J., Bode, K., Schäfer, L., Schebeske, G., Wolf, A., Brancaleoni, E., Cecinato, A., Ciccioli, P., Frattoni, M., Dutaur, L., Fugit, J.L., Simon, V., and Torres, L.: Simultaneous field measurements of terpene and isoprene emissions from two dominant Mediterranean oak species in relation to a north American species, Atmospheric Environment, 32, 1947-1953, 1998a.

Kesselmeier, J., Bode, K., Gerlach, C., and Jork, E.M.: Exchange of atmospheric formic and acetic acids with trees and crop plants under controlled chamber and purified air conditions, Atmospheric Environment, 32, 1765-1775, 1998b.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, Journal of Atmospheric Chemistry, 33, 23-88, 1999.

Kesselmeier, J.: Exchange of Short-Chain Oxygenated Volatile Organic Compounds (VOCs) between Plants and the Atmosphere: A Compilation of Field and Laboratory Studies, Journal of Atmospheric Chemistry, 39, 219–233, 2001.

Kesselmeier, J., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Andreae, M.O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S.T., Botelho, M.L., Silva, C.M.A., and Tavares, T.M.: Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia), Journal of Geophysical Research-Atmospheres, 107, 2002a.

Kesselmeier, J., Ciccioli, P., Kuhn, U., Stefani, P., Biesenthal, T., Rottenberger, S., Wolf, A., Vitullo, M., Valentini, R., Nobre, A., Kabat, P., and Andreae, M.O.: Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget, Global Biogeochemical Cycles, 16, doi:10.1029/2001GB001813, 2002b.

Ketseridis, G., Hahn, J., Jaenicke, R., and Junge, C.,: The organic constituents of atmospheric particulate matter, Atmospheric Environment, 10, 603–610,1976.

Kimmerer, T.W. and Kozlowski, T.T.: Ethylene, Ethane, Acetaldehyde, and Ethanol-Production by Plants under Stress, Plant Physiology, 69, 840-847, 1982.

Kimmerer T. W. and MacDonald R.C.: Acetaldehyde and ethanol biosynthesis in leaves of plants, Plant Physiology 84 1204-1209, 1987.

Klassen, W.: Average Fluxes from Hetereogeneous Vegetated Regions, Boundary-Layer Meteorology (4), 329-354, 1992.

Knorr, W. and Heimann, M.: Impact of drought stress and other factors on seasonal land biosphere CO_2 exchange studied through an atmospheric tracer transport model. Tellus, *47B:* 471-489, 1995.

Komenda, M., Parusel, E., Wedel, A., and Koppmann, R.: Measurements of biogenic VOC emissions: sampling, analysis and calibration, Atmospheric Environment, 35, 2069-2080, 2001.

Komenda, M., Koppmann, R.: Monoterpene emissions from Scots pine (Pinus Sylvestris): field studies of emission rate variabilities Journal of Geophysical Research D: Atmospheres 107, D13 10.1029/2001JD000691, 2002.

Kuhn, U., Rottenberger, S., Biesenthal, T., Ammann, C., Wolf, A., Schebeske, G., Oliva, S.T., Tavares, T.M., and Kesselmeier, J.: Exchange of short-chain monocarboxylic acids by vegetation at a remote tropical forest site in Amazonia, Journal of Geophysical Research-Atmospheres, 107, doi: 10.1029/2000 JD000303, 2002.

Kuhn, U., Andreae, M.O., Ammann, C., Araújo, C.,Brancaleoni, E., Ciccioli, P., Dindorf T,Frattoni, M., Gatti, L.V., Ganzeveld, L., Kruijt, B., Lelieveld, J., Lloyd, J., Meixner, F.X., Nobre, A.D., Pöschl, U., Spirig, C., Stefani, P., Thielmann, A., Valentini, R. and Kesselmeier, J.: Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget, Atmospheric Chemistry and Physics, 7, 2855-2879, 2007.

Lamb, B., Guenther, A.,Guy, D., Westberg, H.: A national inventory of biogenic hydrocarbon emissions, Atmospheric Environment, 21, 1695−1705, 1987.

Lilly, D. K.: Models of Cloud-topped Mixed Layers Under a Strong Inversion, Quarterly Journal of the Royal Meteorological Society, 94, 292–309, 1968.

Kuzma, J., and Fall, R.: Leaf isoprene emission rate is dependent on leaf development and the level of isoprene synthase, Plant Physiology, 101**,** 35–440, 1993.

Lamb, B., Westberg, H., Quarles, T., and Flyckt, D.,: Natural hydrocarbon emission rate measurements from vegetation in Pennsylvania and Washington, Report PB84-124981, U.S.Environmental Protection Agency, Nat. Tech. Inf. Serv. Springfield, Virginia, U.S.A, 1983.

Lamb, B., Westberg, H., Allwine, G., and Quarles, T.,: Biogenic hydrocarbon emissions from deciduous rate and coniferous trees in the United States, Journal of Geophysical Research-Atmospheres, 90, 2380–2390, 1985.

Lamb, B., Gay, D., Westberg, H., and Pierce, T.: A biogenic hydrocarbon emission inventory for the USA using a simple forest canopy model, Atmospheric Environment **,** 27A, 1673-1690, 1993.

Langenfelds, R.L., Francey, R.J., Steele, L.P., Fraser, P.J., Coram, S.A. Hayes, M.R., Beardsmore, D.J., Lucarelli, M.P. and Silva, F.R.,: Improved vertical sampling of the trace gas composition of the troposphere above Cape Grim since 1991, in Baseline Atmospheric Program (Australia) 1993, edited by R.J. Francey, A.L. Dick and N. Derek, pp 45-56, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia, 1996.

Larsen, B., Bomboi-Mingarro, T., Brancaleoni, E., Calogirou, A., Cecinato, A., Coeur, C., Chatzianestis, I., Duane, M., Frattoni, M., Fugit, J.L., Hansen, U., Jacob, V., Mimikos, N., Hoffmann, T., Owen, S., Perez-Pastor, R., Reichmann, A., Seufert, G., Staudt, M., and Steinbrecher, R.:Sampling and analysis of terpenes in air. An interlaboratory comparison, Atmospheric Environment, 31, 35-49, 1997.

Laurila, T. and Hakola, H.: Seasonal cycle of C_2-C_5 hydrocarbons over the Baltic Sea and Northern Finland, Atmospheric Environment, 30, 1597-1607, 1996.

Laurila, T., Steinbrecher, R., Kesselmeier, J., Janson, R. and Kellomäki, S., Biogenic VOC emissions and photochemistry in the boreal regions of Europe. In: Larsen, B., Versino, B. and Angeletti, G., Editors, 1997. The Oxidizing Capacity of the Atmosphere. Air Pollution Research Report 60, Commission of the European Communities, Luxembourg, pp. 300–303, 1997.

Leemans, R., Agrawala, S.,Edmonds, J.A., MacCracken, M.C., Moss, R. and Ramakrishnan., S.: Mitigation: Cross-sectoral and other issues. In Climate Change 1995--

Impacts, Adaptation and Mitigation of Climate Change: Scientific-Technical Analyses. Contribution of Working Group II to the Second Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), eds. R.T. Watson et al., 799-822. Cambridge: Cambridge University Press, 1996.

Lenschow, D., Wyngaard, J. C., and Pennel, W.T.:Mean-Field and Second-Moment Budgets in a Baroclinic, Convective Boundary Layer', vol. 37, 1313–1326., 1980

Lenschow, D., and Stankov, B.B: Length Scales in the Convective Boundary Layer, Journal of the Atmospheric Sciences, vol. 43, 1198–1209, 1986.

Lerdau, M. and Gershenzon, J.: Allocation theory and the costs of chemical defenses in plants. pp. 265-277 in: Bazzaz, F. and Grace, J.:Resource Allocation in Plants and Animals (eds.)., Academic Press, San Diego, USA, 1997.

Levin, I., R. Graul, B. and Trivett N.B.A.: Long term observations of atmospheric CO_2 and carbon isotopes at continental sites in Germany, Tellus 47B, 23-34, 1995.

Levin, I., Ciais, P., Langenfelds, R., Schmidt, M., Ramonet, M., Gloor, M., Sidorov, K., Tchebakova, N., Heimann, M., Schulze, E.D., Vygodskaya, N.N, Shibistova O. and Lloyd, J.: Three years of trace gas observations over the EuroSiberian domain derived from aircraft sampling - a concerted action, Tellus 54B, 696-712. 2002.

Lindfors, V., Laurila, T., Hakola, H., Steinbrecher, R., and Rinne, J.: Modeling speciated terpenoid emissions from the European boreal forest. Atmospheric Environment, 34 (29-30), 4983-4996, 2000.

Lindskog, A.,: The influence of the biosphere on the budgets of VOC: Ethane, propane, nbutane and I-butane, in G. Helas, S. Slanina, and R. Steinbrecher (eds), Biogenic Volatile Organic Compounds in the Atmosphere - Summary of Present Knowledge, SPB Academic Publishers, Amsterdam, The Netherlands, pp. 45–52, 1997.

Lloyd, J. and Farquhar, G.D.: ^{13}C discrimination by the terrestrial biosphere, Oecologia 99, 201-215, 1994.

Lloyd, J. and Farquhar, G.D.: The CO_2 dependence of photosynthesis, plant growth responses to elevated atmospheric CO_2 concentrations and their interaction with soil nutrient status. 1. General principles and forest ecosystems, Functional Ecology, 10, 4-32, 1996.

Lloyd, J., Francey, R. J., Mollicone, D., Raupach, M. R., Sogochev, A., Arneth, A., Byers, J. N., Kelliher, F. M., Rebmann, C., Valentini, R., Wong, S. C., Bauer, G. and Schulze, E. D.: Vertical profiles, boundary layer budgets and regional flux estimates for CO_2, its $^{13}C/^{12}C$ ratio and for water vapour above a forest/bog mosaic in central Siberia. Global Biogeochemical Cycles 15, 267-284, 2001.

Lloyd, J., Langenfelds, R. L., Francey, R. L., Gloor, M., Tchebakova, N. M., Zolothukhine, D., Brand, W. A., Werner, R. A., Jordan, A., Allison, C. A., Zrazhewske, V., Shibistova, O. and Schulze, E.-D.: A trace gas climatology above Zotino, central Siberia. Tellus, 54B, 749-767, 2002.

Loreto, F. and Sharkey, T. D.: Isoprene emission by plants is affected by transmissible wound signals, Plant Cell Environment 16, 563–570, 1993.

Lovett, G.M., Cole, J.J, Pace, M.L.: Is net ecosystem production equal to ecosystem carbon storage? Ecosystems, 9: 152–155, 2006.

Maiss, M., Steele, L.P., Francey, R.J, Fraser, P.J., Langenfelds, R.L., Trivett, N.B.A and Levin, I.: Sulfur hexafluoride - a powerful new atmospheric tracer**,** Atmospheric Environment (10-11), 1621-1629, 1996.

Maiss, M., Brenninkmeijer C.A.M.,. Atmospheric SF6: Trends, Sources, and Prospects, Environmental Science and Technology. 32: 3077–3086, 1998.

McGarvey, D.J and Croteau, R.: Terpenoid metabolism, Plant Cell 7: 1015-1026, 1995.

Middleton, P., Stockwell, W., Carter, W.: Aggregation and analysis of volatile organic compound emissions for regional modelling, Atmospheric Environment 24, 1107-1133, 1990.

Miller, J.B.; Yakir, D.; White, J.W.C.; Tans, P.P.: Measurement of $^{18}O/^{16}O$ in the soil-atmosphere CO_2 flux, Global Biogeochemical Cycles,13, 761-774, 1999.

Monson, R. K. and Holland, E.: Biospheric trace gas fluxes and their control over troposheric chemistry, Annual Review of Ecology and Systematics 32:547- 576, 2001.

Montzka, S.A., M. Trainer, P.D. Goldan, W.C. Kuster, F.C. Fehsenfeld, Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere, Journal of Geophysical Research-Atmospheres, 98, 1101-1111, 1993.

Montzka, S. A.,Trainer, M., Angevine, W. M., and Fehsenfeld, F. C.: Measurements of 3-Methyl Furan, Methyl Vinyl Ketone, and Methacrolein at a Rural Forested Site in the Southeastern 15 United-States, Journal of Geophysical Research-Atmospheres, 100 (D6), 11 393–11 401, 1995.

Nakazawa, T.,Sugawara, S.,Inoue, G., Machida, T., Maksyutov S. and Mukai, H. Aircraft measurements of the concentrations of CO_2, CH_4, N_2O and CO and the carbon and oxygen isotopic ratios of CO_2 in the tropospheric over Russia, Journal of Geophysical Research-Atmospheres, 102, 3843-3859, 1997.

Neftel, A., Moor, E., Oeschger, H and Stauffer, B.: Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. Nature 315:45-47. 1985.

Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C.,: Aerosol formation in the photooxidation of isoprene and α-pinene, Atmospheric Environment 25, 997–1008, 1991.

Parusel, E.: Zur Bedeutung der Pflanzen als Quelle leichte Nicht-Methan-Kohlenwasserstoffe für die Atmosphäre. Entwicklung einer Feldmeßmethode und Untersuchungen an Nutzpflanzen und Gehölzen, Sonderheft 167, undesforschungsanstalt für Landwirtschaft, Braunschweig- Völkenrode, 1996.

Pataki, D.E., Ehleringer, J.R., Flanagan L.B., Yakir, D, Bowling D.R, Still, C., Buchmann, N., Kaplan, J.O., Berry, J.A.: The application and interpretation of Keeling plots in terrestrial carbon cycle research. Global Biogeochemical Cycles 17(1), 1022, 2003.

Paulson, S.E., Orlando J.J.: The reactions of ozone with alkenes: An important source of HO_x in the boundary layer, Geophysical Research Letters, Volume 23, Issue 25, p. 3727-3730, 1996.

Pellizzari, E. and Krost, K.: Sampling of Organic-Compounds in the Presence of Reactive Inorganic Gases with Tenax-Gc, Analytical Chemistry, 56, 793-798, 1984.

Penkett, S. A. and Brice, K. A.,: The spring maximum in photo-oxidants in the Northern Hemisphere troposphere, Nature, 319 (6055), 655–657, 1986.

Peters, R.J.B., Duivenbode, J.A.., Duyzer, J.H., and Verhagen, H.L..: The Determination of Terpenes in Forest Air, Atmospheric Environment, 28, 2413-2419, 1994.

Pio, C.A. and Valente, A.R.,: Atmospheric fluxes and concentrations of monoterpenes in resin tapped pine forests. Atmospheric Environment, 32, 683-69, 1998.

Pio, C. A., Nunes, T. V., and Brito, S.,: Volatile hydrocarbon emissions from common and native species of vegetation in Portugal, in J. Slanina, G. Angeletti, and S. Beilke (eds), General Assessment of Biogenic Emissions and Deposition of Nitrogen Compounds, Sulphur Compounds and Oxidants in Europe, E. Guyot SA, Brussels, CEC Air Pollution Research Report 47, ISBN 2-87263-095-3, pp. 291–298, 1993.

Pio, C. A., Nunes, T. V., and Valente, A. R.,: Biogenic hydrocarbon emissions from vegetation in a southern European environment, in P. M. Borrell, P. Borrel, T. Cvitas, K. Kelly, and W. Seiler (eds), The Proceedings of EUROTRAC Symposium 1996, Computational Mechanics Publications, Southhampton, pp. 35–43, 1996.

Poisson, N., Kanakidou, M., and Crutzen P.J,: Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: 3-dimensional modelling results, Journal of Atmospheric Chemistry, 36, 157-230, 2000.

Prentice, I.C., Heimann, M. and Sitch, S.: The carbon balance of the terrestrial biosphere: ecosystem models and atmospheric observations, Ecological Applications, 10: 1553-1573, 2000.

Prentice, I. C., G.D. Farquhar, M.J.R. Fasham, M.L. Goulden, M. Heimann, V.J. Jaramillo, H.S. Kheshgi, C. Le Quéré, R.J. Scholes and D.W.R. Wallace. Chapter 3. The Carbon Cycle and Atmospheric Carbon Dioxide. In: *Climate Change 2001: The Scientific Basis*, J. T. Houghton et al., Eds., Cambridge University Press, New York, NY, 183-237, 2001.

Ramonet, M., Ciais, P., Nepomniachii, I., Sidorov, K.N., Neubert, R,; Langendörfer, U., Picard, D., Kazan, V., Biraud, S., Gusti, M., Kolle, O., Schulze, E.D., Lloyd, J.,: Three years of aircraft-based trace gas measurements over the Fyodorovskoye southern taiga forest, 300 km north-west of Moscow. Tellus, Series B, Chemical and Physical Meteorology 54, 713-734, 2002.

Rasmussen, R. A. and Went, F.W.: Volatile organic material of plant origin in the atmosphere, Proceedings of the National Academy of Sciences U.S.A, 53, 215–220, 1965.

Rasmussen, R.A.: Isoprene: identified as a forest-type emission to the atmosphere, Environmental Science and Technology, 4, 667-71, 1970.

Raupach, M.R, Gillette, D.A., Leys, J.F.: The effect of roughness elements on wind erosion threshold. Journal of Geophysical Research. 98: 3023-3029, 1993.

Raupach, M.R.: Vegetation Atmosphere Interaction and Surface Conductance at Leaf, Canopy and Regional Scales, Boundary-Layer Meteorology (4), 151-179, 1995.

Raupach, M.R.: Influences of local feedbacks on land-air exchanges of energy and carbon, Global Change Biology. 4: 477-494, 1998.

Reeburgh, W. S.: Figures Summarizing the Global cycles of biogeochemically important elements, Bulletin of the Ecological Society of America, (4)78, 260-267, 1997.

Rinne, J., Hakola, H., Laurila, T. and Rannik, Ü.,:Canopy scale monoterpene emissions of Pinus sylvestris dominated forests." Atmospheric Environment 34: 1099-1107, 2000.

Rinne, H., Guenther, A.B., Greenberg, J.P., and Harley, P.C.: Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, Atmospheric Environment, 36, 2421-2426, 2002.

Rinne, J., R. Taipale, C. Spirig, T.M. Ruuskanen, T. Markkanen, T. Vesala, A. Brunner, C. Ammann, A. Neftel, T. Douffet, Y. Prigent, P. Durand & M. Kulmala,: Measuring ecosystem scale VOC emissions by PTR-MS. In Hansel, A., and Märk, T. (Eds.): *3rd* International Conference on Proton Transfer Reaction Mass Spectrometry and its applications - Contributions. January 27th - February 1st, 2007, Obergurgl, Austria. Conference Series, Innsbruck University Press. 76-79, 2007.

Rudolph, J.,: Biogenic sources of atmospheric alkenes and acetylene, in G. Helas, S. Slanina, and R. Steinbrecher (eds), Biogenic Volatile Organic Compounds in the Atmosphere – Summary of Present Knowledge, SPB Academic Publishers, Amsterdam, The Netherlands, pp. 53–65, 1997.

Ruimy, A., Saugier, B., and Dedieu, G.: Methodology for the estimation of terrestrial net primary production from remotely sensed data. *Journal of Geophysical Research* 99:5263-5283, 1994.

Ruuskanen, T.M., P. Kolari, J. Rinne, R. Taipale, M. Kajos, J. Bäck, P. Hari, H. Hakola & M. Kulmala,: PTR-MS measurements of exchange of biogenic volatile organic compounds between boreal forest and atmosphere. In: Kulmala, M., Lindroth, A., and Ruuskanen T.M. (Eds): *Proceedings of BACCI, NECC and FCoE activities 2005*. Report series in Aerosol Science, no 81B, 520-522, 2006

Savage, T.J, Hatch, M.W., Croteau, R..: Monoterpene synthases of Pinus contorta: a new class of terpenoid cyclase. Journal of Biological Chemistry, 269:4012–20, 1994.

Schlesinger, **W. H.:** An Analysis of Global Change, Biogeochemistry , Academic Press, San Diego, CA, 1997

Schlesinger, W.H.: Biogeochemistry. In Treatise on Geochemistry Eds. H.D. Holland and K.K. Turekian.Elsevier BV, 2003.

Schmidt, M., Glatzel-Mattheier, H., Sartorius, H., Worthy, D.E and Levin, I.: Western European N_2O emissions - a top down approach based on atmospheric observations, Journal of Geophysical Research, 106, D6, 5507-5516, 2001.

Schnitzler, J.P., Arenz, R., Steinbrecher, R., and Lehning, A.: Characterization of an isoprene synthase from leaves of Quercus petraea (Mattuschka) Liebl, Botanica Acta, 109, 216-221, 1996.

Schulze, E.D and Heimann, M.: Carbon and water exchange of terrestrial systems. in: Galloway JN; Melillo JM (Eds.): Asian change in the context of global change. Vol. 3. Cambridge University Press, Cambridge. pp. 145-161, 1998.

Schulze, E.-D.: Carbon and Nitrogen Cycling in European Forest Ecosystems, Series: Ecological Studies, Vol. 142, 500 pp., 2000.

Schulze, E-D, Vygodskaya, N.N. , Tschebakova, N., Czimczik, C.I., Kozlov, D., Lloyd, J, Mollicone, D, Myachkova, E., Sidorov, K., Varlagin, A., and Wirth , C., : The Eurosiberian transect: An introduction to the experimental region. Tellus 54B (5):421-428, 2002.

Schumacher, M.: Airborne and ground level flasks sampling for Regional Carbon Budgets- The potential of multiple and isotope analyses, Ph.D. thesis, Hamburg, 2005.

Schween, J., Zelger, M., Wichura, B., Foken, T., Dlugi , R.,: Profiles and fluxes of micrometeorological parameters above and within the Mediterranean forest at Castelporziano. Atmospheric Environment, 31(1):185-198, 1997.

Seinfeld, J.H. and Pandis, S.N.: Atmospheric chemistry and physics: From air pollution to climate change. John Wiley & Sons, Inc., New York, 1997.

Seufert, G., Kotzias, D., Sparta, C., and Versino, B.,: Volatile organics in Mediterranean shrubs and their potential role in a changing environment, in W. C. Oechel and J. M. Moreno (eds),Global Change and Mediterranean Type Ecosystems, Ecology Studies 117 Springer, New York, pp.343–370, 1995.

Sharkey, T. D. and Loreto, F: The biochemistry of isoprene emissions from leaves during photosynthesis, in Trace Gas Emissions From Plants, edited by T. D. Sharkey, E. A. Holland, and H. A. Mooney, pp. 153– 184, Academic, San Diego, Calif., 1991a.

Sharkey, T. D., Loreto, F. and Delwiche, C.F.: High-carbon dioxide and sun shade effects on isoprene emission from oak and aspen tree leaves, Plant Cell Environ., 14, 333–338, 1991b.

Sharkey, T. D., Singsaas, E. L., Vanderveer, P. J. and Geron, C.: Field measurements of isoprene emissions from trees in response to temperature and light, Tree Physiology, 16(7), 649– 654, 1996 a

Sharkey, T. D.: Isoprene synthesis by plants and animals, Endeavour 20, 74–78,1996b**.**

Sharkey, T.D. and Yeh, S.S.: Isoprene emission from plants, Annual Review of Plant Physiology and Plant Molecular Biology, 52, 407-436, 2001.

Simpson, D., Winiwarter, W., Borjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C.N., Janson, R., Khalil, M.A.K., Owen, S., Pierce, T.E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrason, L., and Oquist, M.G.: Inventorying emissions from nature in Europe, Journal of Geophysical Research-Atmospheres, 104, 8113-8152, 1999.

Sogachev, A.F., Menzhulin, G.V, Heimann, M., Lloyd, J.: A simple three-dimensional canopy - planetary boundary layer simulation model for scalar concentrations and fluxes. Tellus, Series B-Chemical and Physical Meteorology, 54, 784-819, 2002.

Spirig, C., Guenther, A., Greenberg, J. P., Calanca, P., and Tarvainen, V.: Tethered balloon measurements of biogenic volatile organic compounds at a Boreal forest site, Journal of Atmospheric Chemistry and Physics, 4, 215–229, 2004.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmospheric Chemistry and Physics, 5, 465- 481, 2005.

Stakanov, V. D., Pleshikov, F. I., Vedrova, E. F. and Verevochkina, L. V.: Carbon storage and dynamics in tree stands of Middle Siberia. In: Biodiversity and dynamic of eosystems in North Eurasia, Vol. 4, part 1, Russian, Acad. Sci. Siberian Branch, Novosibirsik, 119–121, 2000.

Staudt, M., Seufert, G., Kotzias, D., Spartà, C., and Ciccioli, P.,: Holm oak (Quercus ilex) – a strong emitter of monoterpenes, in P. Ciccioli (ed), Proceedings of the 1st Italian Symp. on the Strategies and Techniques for the Monitoring of the Atmosphere Rome, Società Chimica Italiana, Rome, pp. 579–586, 1993.

Staudt, M. and Seufert, G.: Light-Dependent Emission of Monoterpenes by Holm Oak (Quercus-Ilex L.), Naturwissenschaften, 82, 89-92, 1995.

Staudt, M. and Bertin, N.: Light and temperature dependence of the emission of cyclic and acyclic monoterpenes from holm oak (Quercus ilex L.) leaves, Plant Cell and Environment, 21, 385-395, 1998.

Steinbrecher, R., Stahl, K., Slemr, J., and Hahn, J.,: Untersuchung der Emission niedermolekularer organischer Verbindungen durch verschiedene Pflanzen, Final Report, 07 EU 720/2, IFU,Garmisch-Partenkirchen, 1992.

Steinbrecher, R.: Isoprene: Production by plants and ecosystem-level estimates, in G. Helas, S. Slanina, and R. Steinbrecher (eds), Biogenic Volatile Organic Compounds in the Atmosphere Summary of Present Knowledge, SPB Academic Publishers, Amsterdam, The Netherlands, pp.101–114, 1997.

Sternberg, J.C., Gallaway, W.S., and Jones, D.T.L.: The mechanism of response of flame ionisation detectors, In Gas Chromatography, Eds.Brenner, N., Callin J. and Weiss, M.D., Academic press, New York, 1962.

Street, R. A., Duckham, S. C., and Hewitt, C. N.,: Laboratory and field studies of biogenic volatile organic compound emissions from Sitka spruce (Picea sitchensis Bong.) in the United Kingdom, Journal of Geophysical Research-Atmospheres, **101**, 22799–22806, 1996.

Street, R.A., Owen, S., Duckham, S.C., Boissard, C., and Hewitt, C.N.: Effect of habitat and age on variations in volatile organic compound (VOC) emissions from Quercus ilex and Pinus pinea, Atmospheric Environment, 31, 89-100, 1997.

Stull, R.B.: Summary of the 12th Symposium on Boundary Layers and Turbulence. Bulletin of the American Meteorological Society, 79, 85-88, 1998.

Thouret V., Marenco A., Nedelec P., Grouhel C. and Logan J.,:Comparisons of ozone measurements from the MOZAIC airborne programme and the ozone sounding network at eight locations, Journal of Geophysical Research-Atmospheres,103, 19, 25695-25720, 1998.

Tingey, D. T., Manning, M., Grothaus, L. C., and Burns, W. F.: Influence of light and temperature on monoterpene emission rates from slash pine (Pinus elliottii), Plant Physiology , 65, 797–801, 1980.

Tingey, D. T., Evans, R., and Gumpertz, M.: Effects of environmental conditions on isoprene emissions from live oak (Quercus virginiana), Planta 152, 565–570, 1981.

Tingey, D. T., Evans, R., Bates, E. H., and Gumpertz, M.,: Isoprene emissions and photosynthesis in three ferns – the influence of light and temperature, Physiologia plantarum 69, 609–616, 1987.

Tingey, D.T., Turner, D. P, Weber, J.A: Factors controlling the emissions of monoterpenes and other volatile organic compounds. In Sharkey, T.D, Holland E.A, Mooney, H.A, eds., Trace Gas Emissions by Plants. San Diego, CA: Academic, pp. 93–119, 1991.

Trolier, M., White, J.W.C., Tans, P.P., Masarie, K.A., Gemery, P.A.,: Monitoring the isotopic composition of atmospheric CO_2: Measurements from the NOAA Global Air Sampling Network, Journal of Geophysical Research 101: 25,897-25,916, 1996.

Trudinger, C.M., Enting, I.G., Francey, R.J., Etheridge D.M and Rayner P.J.,: Long-term variability in the global carbon cycle inferred from a high-precision CO_2 and $d^{13}C$ ice-core record, Tellus, 51B, 233-24 ,1999.

Trumbore S.: The use of isotopes and tracers for scaling trace gas fluxes. Scaling of trace gas fluxes between terrestrial and aquatic ecosystems and the atmosphere, pp. 257-274, in: A F Bouwman, Ed, Approaches to Scaling of Trace Gas Fluxes in Ecosystems (Elsevier, Amsterdam; 1999).

Vickers, D. and Mahrt, L.: Quality control and flux sampling problems for tower and aircraft data, Journal of Atmospheric and Oceanic Technology,14, 512-526, 1997.

Vygodskaya, N.N., Schulze, E-D, Tchebakova, N.M, Karpachevskii, L.O, Kozlov, D., Sidorov, K.N, Panvyorov, M.I, Abrazko, M.I, Shaposhnikov, E.S, Solnzeva,O.N, Minaeva,T.Y., Jeltuchin, A.S, Wirth, C., Pugachevskii, A.V., : Climatic control of stand thinning in unmanaged spruce forests of the southern taiga in European Russia, Tellus 54B (5) 443-461, 2002.

Waring, R.H., Landsberg, J.J., and Williams, M.: Net primary production of forests: a constant fraction of gross primary production?, Tree Physiology, 18, 129-134, 1998.

Warneck, P.,: Chemistry of the Natural Atmosphere, Academic Press, San Diego, 1988.

Wedel, A.: Bedeutung fluechtiger organischer Verbindungen aus landwirtschaftlich genutzten Pflanzen fuer die Chemie der Atmosphaere, Dissertation an der RWTH Aachen, 1997.

Went, F.W.: Blue Hazes in the Atmosphere, Nature, 187, 641-643, 1960.

Wildermuth, M.C.,: Subcellular location and biophysical regulation of foliar isoprene production (chloroplasts). PhD thesis, University of Colorado at Boulder, 307 pp, 1997.

Wirth, C., Schulze, E-D, Schulze, W., von Stünzner-Karbe D., Ziegler, W., Miljukowa, I., Sogatchev, A., Varlagin, A.B., Panvyorov, M., Grigoriev, S., Kusnetzova, W., Siry, M., Hardes, G., Zimmermann, R. and Vygodskaya, N.N.: Above-ground biomass in pristine Siberian Scots pine forests as controlled by competition and fire. Oecologia 121:66-80, 1999.

Wise, M.L., Croteau R. Monoterpene biosynthesis. In Comprehensive Natural Products Chemistry: Isoprenoids Including Steroids and Carotenoids, ed. DE Cane, 2:97–153. Oxford: Elsevier Science., 1999.

Wittenberg, U., Heimann, M., Esser, G., McGuire, A.D, Sauf W.: On the influence of biomass burning on the seasonal CO_2 signal as observed at monitoring stations, Global Biogeochemical Cycles 12, 531-544, 1998.

WMO, World Meteorological Organization :Scientifc Assessment of ozone depletion: 1994. Global Ozone and Monitoring Project, Report No. 37, Geneva, 1995.

Yokouchi, Y.,: Seasonal and diurnal variation of isoprene and its reaction products in a semi-rural area, Atmospheric Environment, 28, 2651-2658, 1994.

Zahn, A., C.A.M. Brenninkmeijer, W.A.H. Asman, P.J. Crutzen, G. Heinrich, H. Fischer, J.W.M. Cuijpers, and P.F.J. van Velthoven, The budgets of O3 and CO in the upper troposphere: CARIBIC passenger aircraft results 1997-2001, Journal of Geophysical Research-Atmospheres, 107, D17, 4337, doi: 10.1029/2001JD001529, 2002.

Zondervan, A. and Meijer, H.A.J.: Isotopic characteristation of CO_2 sources during regional pollution events using isotopic and radiocarbon analysis, Tellus Series B-Chemical and Physical Meteorology, 4, 601-602, 1996.

Acknowledgments

This thesis was written at the Max Planck Institute for Biogeochemistry in Jena, Germany.

I express my gratitude to Prof. Dr. Martin Heimann for his continual involvement with my work and scientific advice during the writing of my Ph.D. thesis.

I thank Prof. Dr Juergen Kesselmeier for providing me with the practical requirements for VOC measurements and for his considerable help in preparation for the two measurement campaigns in Russia in 2004 and 2005.

Dr. Armin Jordan spent much time in discussions, scientific support and critical review of my work. My heartfelt thanks are due to him and also for his encouraging words of motivation when I started work at the MPI-BGC.

I am grateful to Prof. Dr. Guy Brasseur for support and for reviewing the thesis.

I also thank the local Aeroclub Bialystok in Poland for all the flight measurements and all the pilots "for good starts equal safe landing". I warmly acknowledge the pilots for their excellent work.

Many thanks go to my colleagues from the Max Planck Institute for Biogeochemistry in Jena.

I would also like to thank the people who helped me in the measurements in Russia: Prof. Dr. Zdzislaw Chilmonczyk, Karol Wlosewicz, Andrej Varlagin, Julia Kurbatowa, Olga Shibistova, Galina Zarazhevskaya, Danila Zolothukhine and others.

I want to thank my wonderful wife Danusia and our 3 and a half year old son Brunon. You are in my mind all the time and I felt your support in writing my Ph.D. thesis. Please accept my sincerest apologies for the many times when I was absent from home during my trips in Europe and the campaigns in Russia.

Abreviations list

AcetylCoA

Activated acetic acid, an acetic acid-residual that is bound to Coenzyme

AVOC

Anthropogenic volatile organic compound, a volatile organic released from anthropogenic sources

BL

Boundary layer

BOVOC

Biogenic oxygenated volatile organic compound, an oxygenated volatile organic released from natural sources such as terrestrial vegetation

BVOC

Biogenic volatile organic compound, a volatile organic released from natural sources such as terrestrial vegetation

CBL

Convective boundary layer

CFR

Central Forest Reserve

CH_4

Methane

CMDL

Climate Monitoring & Diagnostics Laboratory

CO

Carbon monoxide

CO_2

Carbon dioxide

DIC

Dissolved Inorganic Carbon

DMAPP

Dimethylallyl-diphosphate, isomer of isopentenyldiphosphate

DOC

Dissolved Organic Carbon

FID

Flame ionisation detector

FT

Free troposphere

GCB

Graphitized carbon blacks

GC

Gas chromatography

GPP

Gross Primary Production

GTP

guanosine-triphosphate, energy-rich compound, consisting of guanosine that is linked to ribose which has a chain of three phosphate groups attached

H_2

Hydrogen

LDW

leaf dry weight

LT

local time

MACR

Methacrolein, one of the major products of the atmospheric decomposition of isoprene

MVK

Methylvinylketone, C_4H_6O, one of the major products of the atmospheric decomposition of isoprene

N_2O

Nitrous oxide

NBP

Net Biome Production

NECB

Net ecosystem balance

NEE

Net Ecosystem Emission

NEP

Net ecosystem production

NMHC

Non methane hydrocarbon, organic compounds that consist from carbon and hydrogen atoms with exception of methane

NMOC

Non methane organic carbon, organic compounds that consist from carbon, hydrogen, and other heteroatoms with exception of methane

NMVOC

Non methane volatile organic compound, volatile organic compounds that consist from carbon, hydrogen,and other hetero- atoms with exception of methane

NOAA

National Oceanic and Atmospheric Administration

NPP

Net primary production

OVOC

Other reactive volatile organic compound, volatile organic compounds that consist from carbon, hydrogen, with exception of methane

PAN

peroxyacetyl nitrate

PAR

Photosynthetic Active Radiation

PFA

Paraformaldehyde

Pg

Peta gram, 10^{15}

ppbC

Parts per billion carbon, 10^{-9}, nmol mol^{-1}

ppb

Parts per billion, 10^{-9}, nmol mol^{-1}

ppm

Parts per million, 10^{-6}, µmol mol^{-1}

ppt

Parts per trillion, 10^{-12}, pmol mol^{-1}

PTFE

Politetrafluoroetylen

SF_6

Sulfur hexafluoride

SOA

secondary organic aerosol

Tg

Tera gram, 10^{12}

VOC

Volatile organic compound