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# Experiments on forest/atmosphere exchange: Climatology and fluxes during two summer campaigns in NE Bavaria

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## Abstract

During two summer field campaigns in 2001 and 2002, biosphere / atmosphere exchange fluxes of energy, gases, and particles were quantified in a Norway spruce forest in NE Bavaria at 775 m a.s.l. The overall goal of the BEWA campaigns was to study the influence of the emissions of reactive biogenic organic volatile compounds (BVOC) on chemical and physical processes in the atmosphere, and an overview over the meteorological conditions, experimental frame, and the achieved results is provided. A rigorous quality assurance / quality control plan was implemented. From analysis of meteorological conditions and experimental success, golden day periods were selected for coordinated data analysis. These periods cover typical summertime conditions with various wind directions, $NO_x$ mixing ratios between 2 and 10 ppb, and $O_3$ mixing ratios ranging between 13 and 98 ppb. Diurnal patterns of trace gas concentrations resulted from the dynamics of the boundary layer, from regional atmospheric processes (for example production of $O_3$ in the atmosphere), and deposition. Turbulence also exhibited a diurnal pattern indicating thermal production during daytime and calm conditions during nighttime. However, in many cases, turbulence was often well developed during the nights. Horizontal advection of air masses into the trunk space occurred due to the patchiness of the forest. Nevertheless, for most conditions, the application of a one-dimensional model to describe the vertical exchange processes was appropriate. Therefore, the use of one single meteorological tower to study biosphere / atmosphere exchange is valid. Measured turbulent vertical exchange fluxes were estimated to be representative within an error of less than 25 %. The results for VOC concentrations and fluxes were rather heterogeneous. Both model and measurements demonstrated that the Norway spruce trees acted as a weak source of formaldehyde.



**Key words:**

atmospheric boundary layer, biogenic volatile organic compounds, BVOC, Norway spruce, quality assurance of flux data, surface exchange fluxes, ozone fluxes, turbulent exchange


## I Introduction

Biogenic volatile organic compound (BVOC) emissions greatly contribute to total VOC emissions into the atmosphere (Guenther et al., 1995). Their contribution to atmospheric processes, including the formation and growth of aerosol particles, is estimated to be very significant significant (Andreae and Crutzen, 1997; Griffin *et al.,* 1999). Considerable research has been carried out on emissions of BVOC to the atmosphere, but so far there is no detailed study of fluxes of these

compounds from forest canopies in Germany. The BEWA2000 research cluster was initiated to address this gap in atmospheric research.

BEWA 2000 comprised experimental and modeling activities at various scales. A key component consisted of two integrated field experiments during the summers of 2001 and 2002 at the Norway spruce forest site *Waldstein* in NE Bavaria. This site was selected because spruce is an important tree species in Germany, and because the site is an established ecosystem research site with extensive historical data and knowledge concerning ecosystem fluxes and processes (Matzner, 2004). This contribution sets an overview of the site and the experiments in 2001 and 2002. Data quality assurance activities are presented in detail, an overview over the meteorological and air chemistry is given, and VOC mixing ratios and fluxes are described. The applicability of a one-dimensional model to describe vertical fluxes at our experimental site is discussed. Further details on BEWA2000 results are given in a series of separate papers in this issue (Valverde-Canossa *et al*, Held *et al.,* 2004, Held and Klemm*,* Forkel, *et al.,* , Ganzeveld*, et al.,* , A, Ganzeveld *, et al.,* , B, Grabmer, *et al.,* , Graus, *et al.,* , Grote, *et al.,* , Magel*, et al.,* , Müller*, et al.,* , Plewka*, et al.,* , Smiatek*, et al.,* , Spittler, *et al.,*).

## II Site and Experimental Phases

The experimental ecosystem research site *Waldstein* is located in the *Fichtelgebirge* mountain range, NE Bavaria, at an altitude of approximately 800 m a.s.l. This area exhibited one of the highest degree of forest decline symptoms in Europe in the 1980s. During that period acid precipitation and its impact on pollutant and nutrient cycling was extensively studied (Schulze et al., 1989). After the mid 1980, the emissions of precursors of acid precipitation in Europe were reduced, and subsequently, the air concentrations of $SO_2$ and the deposition rates of sulfate and other acidifying compounds to the forest decreased as well (Klemm and Lange, 1999; Matzner, 2004). As a consequence, but also due to extensive liming activities of the soils on acidic, mainly granitic bedrock of the region, the forest health recovered.

The experimental site is located within the *Lehstenbach* catchment 1 km to the SW of the "Bergkopf" summit (857 m a.s.l.) The catchment covers an area of about 4 $km^2$. The forest is dominated by planted Norway spruce, with patches of stands of various age classes. Ecosystem balance studies have been performed here since 1988 (Matzner, 2004). A 30 m scaffolding walk-up tower at the *Weidenbrunnen* site, at 50°08'32"N, 11°52'04"E, 775 m a.s.l., is located close to the watershed and in a terrain that slopes to the SSW with an angle of about 5°. The forest extends approximately 6.5 km to the SW, 2.5 km to the W, and 5.5 km to the E. A detailed footprint analysis showed that the source area (90% of the biosphere/atmosphere fluxes) is about 15 ha in the

cases of a highly unstable stratification of the boundary layer, 40 ha for unstable cases, 100 ha for neutral stratification, and 750 ha for a stable boundary layer (Klemm and Mangold, 2001). Independent of wind direction and stability, the source area is in most cases covered with spruce forest of 60–120 year stand age, except in the highly stable cases where the influence from the agricultural area to the west may not be excluded. These situations were excluded from data analysis anyway due to poorly developed friction velocities (see section IV). Towards the SE there are further mountain ranges, also covered with spruce forest. Although these areas host small towns and motorways, air masses advecting from the SE make surface contact with a more or less homogeneous spruce forest cover.

At the meteorological tower, the spruce stand was planted in 1945, is up to 19 m high and about 200 m × 200 m large. At distances more than about 50 m to the W and E, respectively, the spruce tree height is 25 - 30 m. A 100 m × 100 m open field with forest nursery ("*Pflanzgarten*") is located at a distance of 200 m to the W from the tower. A forest road of 6 m width crosses from WNW to ESE at a distance of 100 m to the N from the tower. This road is hardly used by any vehicles. To the N of this road, the 150 year old spruce trees are about 27 m high and exhibit a relatively open trunk space. This stand is called *Coulissenhieb* and was used within the BEWA 2000 experiment for the quantification of soil fluxes. Within the forest considerable gaps between trees have developed and horizontal advection of air parcels into the trunk space can not be ruled out.

The projected leaf area index (LAI) for the tower site was determined in 1997 to be 5.3 $m^2\ m^{-2}$ (Alsheimer, 1996). Multiplication of this number by 2.57 gives the total leaf area (per ground area). The projected stem and twig area per ground area is 1.14 $m^2\ m^{-2}$. Assuming cylindrical stems and twigs, the total stem and twig area is computed as 1.14 $m^2\ m^{-2} \times \pi$. The total projected surface area index (SAI), including leaves, stems and twigs, is (5.3 + 1.14) $m^2\ m^{-2}$. The distribution of LAI and SAI with altitude above ground is detailed in Klemm *et al*. (2005). About 80 % of the surface area is between 7 and 14 m above ground.

The spruce trees at the tower site show heavy symptoms of forest decline, with yellowing of needles, loss of needles, and breaking of tree tops due to heavy snow load during winters. Single dead trees in the direct vicinity of the tower were removed every year to protect the installed infrastructure from falling stems. To prolong the lifetime of the forest stand, liming with dolomite, $CaMg(CO_3)_2$, was performed in the vicinity of the tower in November 1999, and around the tower site itself in December 2001.

The meteorological routine program at the tower is operational since 1993. Table 1 shows the measurements at the tower during the BEWA 2000 campaign. Trace gas measurements of NO, $NO_2$, $NH_3$, $O_3$ and $SO_2$ were performed in the *Pflanzgarten* forest clearing, with the air inlet at 3 m

above ground. NO, $NO_2$, $NH_3$, and $SO_2$ were measured within the routine program and with standard techniques: NO was detected with gas phase chemiluminescence of activated $NO_2$ after reaction of NO with $O_3$, $NO_2$ was measured as NO after reduction on a 300 °C molybdenum converter, and $SO_2$ was measured with gas phase UV-fluorescence. Ammonia ($NH_3$) was measured as electric conductivity in aqueous solution after stripping the gas phase in a rotating annular denuder (Wyers *et al.*, 1993). During the BEWA experiments, the bulk particle composition was also measured at the *Pflanzgarten* site with a high volume sampler. During selected time periods, surface exchange fluxes of $O_3$ was measured with eddy covariance (Klemm et al., 2004), and those of NO, $NO_2$, and VOC (C5 – C10), were quantified with dynamic chambers (Butterbach-Bahl *et al*., 1997) in the *Coulissenhieb* site. Eddy covariance measurements of the exchange of $O_3$ were also realized at this site during a short time period in 2002. Measurements were made during the periods 09.07.2001 - 03.08.2001 and 24.06.2002 - 02.08.2002 and data quality assurance activities took place during the periods 09.07.2001 - 14.07.2001 and 24.06.2002 - 30.06.2002.

## III Data quality assurance

A rigorous independent quality assurance and quality control (QAQC) program was implemented and realized. A set of data quality objectives (DQO, Table 2) was developed for each parameter of the routine measurement programs jointly with the data generators. Quality assurance (QA) plans were implemented that defined the steps to be followed for acquiring quality assured data. Data quality was ultimately assessed through system and performance audits that were conducted prior, during, and after the field campaigns.

For trace gas measurements, all continuously operating instruments were intercompared and assessed against the QA-reference instruments using ambient air. These additional QA-reference instruments operated completely independently within a truck, using their own air inlet manifold. Special emphasis was devoted to intercomparisons between QA-reference instruments and the routine analyzers, whereby the respective instruments operated concurrently measuring outside air over an extensive time period. During this QA-phase, instrument malfunctions and deviations from the QA reference instruments were identified early-on and corrected prior to the actual field experimental phase. To assure the traceability to international standards, all instruments including the spare instruments were calibrated with the QA transfer standards. Problems were identified with the NO and $SO_2$ instruments since their minimum detection levels (MDL) were close to the ambient concentration at the site at times. These instruments were therefore closely re-evaluated with calibration gases to reconfirm their MDL and their agreement at higher levels with the appropriate QA reference instruments. Upon completion of all QA-checks, all instruments complied with the data quality objectives.

For the standard meteorological parameters air temperature (T), relative humidity (rH), and air pressure (p), the routine instruments operated concurrently with the reference instruments side by side in the field, measuring the ambient air over an extensive time period. No problems were identified with the parameters T and rH. For p, an offset of -4.6 hPa was identified during the 2002 experiment, and p was corrected in the main data set after completion of the experimental phase. No QA plan was implemented for the mean horizontal wind speed and wind direction.

Reference measurements were not possible for the QA assessment of micrometeorological data, because no accepted standard instrument or method exists. However, intercomparison of ultrasonic anemometer data from the participating research groups proved helpful for the subsequent, quantitative interpretation of turbulent fluxes, because eddy covariance methods and instruments were not identical among the different groups Mean vertical wind speed (w), sonic temperature ($T_s$, calculated from the speed of sound), friction velocity (u*), and the standard deviation of mean vertical wind speed ($\sigma_w$), sonic temperature ($\sigma_{Ts}$) and of kinematic heat flux ($w'T_s'$) were each compared on the basis of 30 minute intervals of measurements. In this case, the QA activity referred solely to the relative instrument performances of the employed ultrasonic anemometers as mounted on the experimental tower.

There are further sources of error or uncertainty for the eddy covariance measurements, such as non-stationarity of the meteorological conditions, insufficiently developed turbulence regime, or perturbation of the wind field for a given anemometer at a given wind direction. These types of error were analyzed and filtered according to Foken and Wichura (1996) by the respective data generators. The QA assessment reported here was realised in double-blind mode and refers exclusively to source data of high quality.

Regressions indicate the relative precision of the micrometeorological parameters of groups 2 and 3 versus group 1, respectively. Table 3 shows that there is an offset of the measured sonic temperatures. Different groups' measurements of sonic temperature varied, due to differences in the ultrasonic anemometers or their internal software. However, these systematic deviations do not affect the meteorological or flux data. More important are the slopes of the standard deviations of $T_s$ of 0.89 and 0.93, indicating a deviation of up to 11 % of the temperature fluctuations. The squared regression coefficients of 0.79 and 0.92 indicate reasonable agreement. The agreement of the kinematic heat fluxes of the research groups agree within 16 % (slopes 0.93 and 0.84, respectively, $R^2$ values 0.85 and 0.79), indicating reasonable agreement. For the mean vertical winds, the agreement seems unsatisfactory. Potential sources of this disagreement, such as different positioning of the anemometers at the tower and resulting dependence of the vertical wind on the wind direction, have not been further investigated, because the mean of the vertical wind is not used

for flux calculations. More important are the parameters uncertainty of w, $\sigma_w$, and friction velocity, u*, because they directly influence the flux computations. For $\sigma_w$, the agreement between the groups is excellent. For u*, the slopes of 0.89 and 0.93 (with squared regression coefficients of 0.84 and 0.70, respectively), indicate acceptable, though not perfect agreement. Overall, we conclude that the physical quantification of the relevant turbulence parameters agrees within less than 10 % deviation between the research groups on average, with higher variability to be accepted in single data points. This quality of agreement has to be taken into consideration for all further quantitative interpretation of flux data derived from eddy covariance measurements within the BEWA experiments.

## IV Meteorological Conditions

*Meteorology and air chemistry*

Backward trajectories (travel paths) for air masses arriving at the *Waldstein* site every 12 hrs within the experimental periods 2001 and 2002 were calculated by use of the HYSPLIT model (Draxler and Rolph, 2003; Rolph, 2003). In Figure 1, we present a subset of trajectories, based on an arrival time of 13:00 CET on each of the golden days (for definition see below).

During 2001, all analysed air masses originated NW of the site, having spent considerable time within the boundary layers of northern Germany, Netherlands, Belgium, or northern France, respectively. Even air masses associated with easterly winds at the site did not represent a strong eastern European influence, but originated mostly in Central Europe. For 2002, two separate classes of trajectories appear: From 20.07.2002 through 23.07.2002, the air masses travelled over the North Sea, then over the Netherlands and Belgium into Central Europe before arriving at the site. Between 28.07.2002 and 31.07.2002, the air masses mostly travelled over eastern central Europe including the Bohemian basin before arriving at the *Waldstein*.

Table 4 summarizes some meteorological average data for the experimental phases 2001 and 2002. The experimental period 2001 was more favorable for the study of biogenic emissions of VOC from the vegetation. In 2001, the temperature was higher and the relative humidity lower. Although more precipitation was recorded in 2001 compared to 2002, the period 2002 was more humid. Overall, precipitation in 2002 fell during 16.6% of the whole time period, whereas precipitation occurred for only 3.6% of the time in 2001. About one third of the total precipitation fell on 16.07.2001, and no precipitation occurred between 22.07.2001 and 02.08.2001. The higher humidity in 2002 is also confirmed by the average leaf wetness, which is significantly higher in 2002 than in 2001.

Average $NO_x$ mixing ratios were 4.05 ± 1.33 ppb (average ± 1σ) in the 2001 period and 4.65 ± 1.47 ppb in the 2002 period. The medians for the entire years 2000, 2001, and 2002 were 4.6 ppb, 5.4

ppb, and 5.0 ppb, respectively (Klemm, 2004). The $NO_x$ mixing during the experimental periods were thus within the normal range of the $NO_x$ levels, with tendency to the lower end. This reflects the annual cycle of $NO_x$ that exhibits lower values during the summer seasons, when the boundary layer is typically deeper than in winter. The ammonia mixing ratios in 2002 (median 1.2 ppb) were also comparable to typical values for 2000 (0.91 ppb), 2001 (1.51 ppb), and 2002 (0.64 ppb). The 2001 period, however, exhibited extraordinarily high $NH_3$ mixing ratios (median 3.5 ppb). A high proportion of air masses travelling over areas of intense animal farming (c.f., Fig. 1) probably contributed to high $NH_3$ values. The average ozone mixing ratios were not very different in 2001 and 2002, respectively, but reflect conditions that were typical for the summer seasons at that site.

From the meteorological conditions during the experimental periods and from the availability and technical quality of data of the various research groups, golden day-periods were defined. For these periods, the best and most interesting results were expected from integrated and interdisciplinary data analysis, and therefore the data work focussed mainly on these periods. The golden day periods were: 21.07.2001 – 02.08.2001; 20.07.2002 - 23.07.2002; 28.07.2002 - 31.07.2002. In addition, the 12.07.2002 was identified to be very interesting for aerosol particle dynamics studies. Data from12.07.2002 are not included in this paper.

Figures 2 and 3 show selected results of the continuous measurements during the golden day-periods 2001 and 2002. In 2001, it was a dry and warm summer period. The winds originated from easterly / north-easterly directions between 22.07.2001 and 30.07.2001. The five-day backward air trajectories (Fig. 1) indicate that the air masses reaching the site had not travelled long distances, but originated mostly in NW Central Europe. Typical source areas for potential contamination with pollutants are the areas of Germany, Denmark, and at times Great Britain. Nevertheless, the $NO_x$ mixing ratios between 1.2 ppb and 10.5 ppb indicate no large contamination of the air masses reaching the site. Often, the $NO_x$ mixing ratios exhibited a diurnal behavior with lower values during the days. This indicates that deeper mixing layers lead to higher dilution of the rather freshly emitted $NO_x$. More clearly pronounced are the diurnal patterns of $O_3$. The nocturnal decrease is mainly caused by dry deposition of $O_3$ to the surface, whereas steep increase during the morning hours indicated downward mixing of ozone-rich air from the residual layer. The extraordinarily high mixing ratio on 31.07.2001 was associated with winds from the W. Although the backward trajectory yields no indication for an abrupt change of air mass origin on 31.07.2001, there are indications that free tropospheric air is well represented on that day (Fig. 1). A peak mixing ratio of 81 ppb can be explained by regional photochemical ozone forming processes within the boundary layer, as predicted with the one-dimensional model (Forkel *et al*, this issue). Mixing ratios higher than that are due to advection air masses with relative enrichment of ozone.

The friction velocity u* also exhibits a pronounced diurnal behavior with maxima above 0.5 m $s^{-1}$ during the daylight hours. A large portion of the turbulence is thermally induced. Nighttime minima are typically between 0.1 and 0.3 m $s^{-1}$. During the period with westerly winds on 30. and 31.07.2001, the highest nighttime minima were observed. These data indicate that turbulent exchange is reduced during nighttime. However, in many cases the turbulence regime remains well developed throughout nighttime.

The two 4-day-periods of golden days in 2002 differ from each other (Fig. 3). Westerly winds between 20.07.2002 and 23.07.2002 were associated with 3 - 5 ppb $NO_x$ in air masses. The wind speeds were low (average of 0.45 m $s^{-1}$ for this period). A diurnal pattern for $O_3$ is apparent only on 20.07.2002 and 21.07.2002, when the temperature reached maxima above 20 °C. During the second period from 28.07.2002 to 31.07.2002 with easterly winds, the daytime maximum temperatures increased until 30.07.2002, and the patterns of $NO_x$ and $O_3$ are typical for a summertime photochemical episode. The friction velocity follows a similar diurnal pattern, indicating thermal activity to be the driver for the development of turbulence near the surface. Nighttime minima of u* are often above 0.3 m $s^{-1}$, indicating a well developed turbulence regime. A thunderstorm with rain and a temperature drop of 6 K within one hour terminated this period on the afternoon of 31.07.2002.

Results for the golden day periods in 2001 and 2002 show that some trace gases are advected with the boundary-layer air masses arriving at the site. Additional concentrations appear to be driven by vertical exchange with the underlying surface (forest vegetation) and with the free troposphere, and also by chemical reactions within the boundary layer air masses.

*Wind profiles within the forest*

The wind regime within the forest stand is characterized through average profiles in Figure 4. From all 10 minute wind speed profiles at the tower as measured during the 2001 campaign, six average profiles were computed. For the first average profile, all individual profiles with wind speeds between 0 and 1 m $s^{-1}$ at the 32 m level were combined. For the second average profile, all individual profiles with wind speeds between 1 and 2 m $s^{-1}$ were combined, and so forth. The maximum wind speed at 32 m was 5.85 m $s^{-1}$, so this procedure yielded 6 average profiles (Figure 4). Two important conclusions can be drawn: First, the wind speed profiles 2 - 6 (top level wind speeds > 1 m $s^{-1}$) of the three levels above the tree tops (32 m, 25 m, and 21 m above ground) exhibit log-normal shape (analysis not displayed in Fig. 4, squared regression coefficients with altitude > 0.99). The zero points of the five profiles are at 11.1 m, 12.3 m, 11.9 m, 11.4 m, and 11.0

m above ground. The average zero displacement height (plus roughness length) of the forest is thus 11.5 m, which is 61 % of the maximum tree height.

Secondly, all six average profiles exhibit higher wind speeds at 2 m above ground than at 10 m above ground, respectively. This clearly shows that there is advective forcing within the trunk space. The patchiness of the forest with varying stand heights and canopy structures apparently allows for such forcing at all observed wind speeds.

## V Fluxes of energy, $H_2O$, and $CO_2$

Figure 5 shows two important parameters of the energy balance and the measured $CO_2$ exchange at the tower site for the golden day-periods 2002. The short-wave radiation balance complements the meteorological parameters in Fig. 5. The energy balance is a one-dimensional computation of the vertical energy fluxes. It is the sum of the short wave radiation balance (average 241 W $m^{-2}$ for the periods shown), the long wave radiation balance (average -66 W $m^{-2}$), minus the soil heat flux (80 W $m^{-2}$), the buoyancy flux (as measured with eddy covariance, average 69 W $m^{-2}$), and the latent heat flux (eddy covariance, average 74 W $m^{-2}$). Energy storage within the vegetation is neglected. The energy balance averages -48 W $m^{-2}$, which is -20 % of the shortwave incoming radiation. The measured soil heat flux was suspiciously high, but repeated service of the heat flux plates did not affect the results. Thus, the energy balance is closed within about 20%. An important contribution to the non-closure of this type of energy balance is most likely a result of the advection of air masses into the trunk space as indicated in section IV.

From the data in the lower panel of Figure 5 (thin dark line), an average deposition flux of $CO_2$ of -4.2 µmol $m^{-2}$ $s^{-1}$ is computed. Rebmann et al. (2004) found average fluxes of $CO_2$ for the months of July and August of the years 1997 through 2000 between -1.17 and +0.44 µmol $m^{-2}$ $s^{-1}$ with an average of -0.53 µmol $m^{-2}$ $s^{-1}$. This shows that the net $CO_2$ uptake during the golden days period 2002 was very high. During the golden day period 2001, the average $CO_2$ uptake (-4.5 µmol $m^{-2}$ $s^{-1}$), and thus the activity of the vegetation, was at least as high as in 2002, although this number is less reliable due to data gaps. The average evapotranspiration flux of 1.6 mmol $H_2O$ $m^{-2}$ $s^{-1}$ (golden day period 2002, 1.8 mmol $H_2O$ $m^{-2}$ $s^{-1}$ for the golden days 2001) is at the upper end of values computed for the months of July and August (monthly averages 0.7 - 1.4 mmol $H_2O$ $m^{-2}$ $s^{-1}$, after Rebmann *et al*., 2004). The biological activity of the forest was thus very high during the 2002 golden day period, and probably even higher in the corresponding 2001 period, as compared to average conditions typical for the same time of year.

The grey line in the lower panel of Figure 5 shows the $CO_2$-exchange as measured with the single branch enclosure technique. On 20.07.2002, the agreement between branch enclosure and the eddy

covariance technique is very good. On 23.07.2002, 28.07.2002, and 29.07.2002, the fluxes of the branch enclosure deviate from the eddy covariance measurements. During these days, different individual branches were used for the measurement. These data show that scaling up from single branch experiments to the stand scale is problematic because branches or twigs with activity above (or below) average may have been used for individual experiments. From these results alone, deviations of ~100% may be attributed to single measurements.

## VI Ozone

The turbulent exchange flux of ozone has been quantified at the tower site since 1998 (Klemm and Mangold, 2001, Klemm *et al.,* 2004). Most of the ozone deposition flux (about 85 %) is taken up by the canopy (Klemm et al., 2004). During the BEWA campaign 2002, the measured ozone deposition flux was for the first time compared with turbulent exchange flux within the *Coulissenhieb* forest stand, and with soil emission fluxes of NO. For the 20.07.2002, the measured deposition to the ground was exactly equal to the measured emission flux of NO (0.92 nmol $m^{-2}$ $s^{-1}$).

Figure 6 shows ozone mixing ratios for 20.07.2002. The $O_3$ mixing ratio outside and inside the forest agree very well between 06 and 18 hrs, indicating good mixing of air masses into the forest. During this time period, turbulence above the forest was well established (Fig. 3). Before 06 hrs and after 18 hrs, however, the meteorological conditions were very different. The mixing ratio of $O_3$ within the forest was higher than outside. This somewhat surprising result seems to indicate relatively poor mixing of air inside and outside the forest. The forest trunk space appears to be a reservoir of $O_3$-rich air, while the air masses outside and above the canopy are depleted in $O_3$ through deposition. The modelled $O_3$ mixing ratio above the forest is in good agreement with the measurement. In particular the diurnal cycle is well represented in the model. However, the modelled data tend to be lower by about 3 - 10 ppb than the measured daytime data. The modelled $O_3$ mixing ratio decreases from the layer above the forest into the trunk space, as deposition takes place and there is no efficient source of $O_3$ within the stand. Therefore, a higher mixing ratio within the stand at night cannot be predicted with the model.

Overall, the model is able to predict the production of ozone. Further it indicates that the regional production of ozone can be described using the one-dimensional model approach. There are some limitations with respect to the transport of air into the trunk space and back. Observations suggest that lateral advection of air masses, enriched with $O_3$, into the trunk space, leads to identical mixing ratios within and outside the forest. The patchiness of the forest suggests that such a mechanism is possible; however,we consider this effect to be small. At night, situations may occur when the $O_3$ mixing ratio in the trunk space is larger than above. Once $O_3$-rich air is mixed into the trunk space

during the daytime, it is not subject to any efficient deposition or other sink process, and once the mixing ratio above the canopy decreases (for example due to dry deposition and limited refilling of the reservoir from above during calm nights), the trunk space will be enriched relative to the stable atmospheric boundary layer just above. Under these conditions, and also hours later, when turbulence picks up again, an emission flux of $O_3$ from the trunk space upward may occur, as often observed for this site (Klemm and Mangold, 2001).

## VII Volatile Organic Compounds

The role of volatile organic compounds (VOC) in the physical and chemical processes within the atmospheric boundary layer was a main focus of the BEWA campaign. Of special interest was the contribution of biogenic VOC (BVOC) on the formation and dynamics of aerosol particles. These aspects are discussed in detail in Held *et al*. (2004). The chemical characterization of particulate matter with focus on biogenic compounds was performed using high-volume filter samples collected at 12 and 24 m altitude above ground, and GC-MS analysis (Plewka *et al., this issue*).

In this section, we provide an overview of the concentrations and fluxes of VOC as they were measured during the golden day periods of the campaigns 2001 and 2002 (Table 5). The various measurement datasets were obtained using different measurement techniques and different sample time integration periods (between 2 min and 60 min per individual measurement cycle).

The completeness of the datasets for the golden day periods varied. These factors contribute to significant deviations and uncertainty in the data. Furthermore, systematic differences were observed for some compounds that were measured by more than one research group. The acetaldehyde and acetone data of group 1, using DNPH cartridge sampling and GC analysis in the laboratory, are often higher than those of group 4, using the PTR-MS technique. An extensive laboratory intercomparison of the two techniques showed no large differences (data not shown). Thus it remains unclear so far as to why the DNPH method yielded larger mixing ratios of carbonyls in comparison to the PTR-MS technique when both systems were used in the field.

VOC fluxes were measured with a relaxed eddy accumulation technique using PTR-MS (Graus *et al., this issue*), yielding 30-minute averages. Whereas in summer 2001 one PTR-MS system was connected to a REA-sampling system for the entire experimental period, in 2002 two PTR-MS systems were set up for VOC flux measurements using REA technique, as well as disjunct eddy sampling (DES) and an enclosure sampling system to determine direct VOC emissions from individual branches (enclosure measurements, Grabmer *et al., this issue*). At times between conducting the flux measurements, the PTR-MS systems acquired VOC mixing ratios in the ambient air within, as well as above, the canopy.

The average isoprene mixing ratio during the golden day period of 2002 was 0.27 ppb at both levels (17 m and 32 m above ground). The average isoprene emission fluxes, as measured by group 4 were 0.64 ±1.6 nmol $m^{-2}$ $s^{-1}$ (mean ± one standard deviation) in 2001 and 0.23 ± 0.36 nmol $m^{-2}$ $s^{-1}$ in 2002, which are in rather good agreement with the modelled emission fluxes of 0.42 nmol $m^{-2}$ $s^{-1}$ and 0.39 nmol $m^{-2}$ $s^{-1}$, respectively. Terpenes, which are also emitted from spruce trees, were present at mixing ratios similar to those of isoprene, with average emission fluxes of 0.73 ± 1.1 nmol $m^{-2}$ $s^{-1}$ in 2001 and 0.55 ±0.67 nmol $m^{-2}$ $s^{-1}$ in 2002. The high average mixing ratios and emission fluxes of all BVOC measured in 2001 compared to those measured in 2002 indicate that the forest was more physiologically active during the golden day period in 2001. This is consistent with the meteorological data shown in Table 4.

Measurements of $H_2O_2$ and organic peroxide mixing ratios (see Table 5) and surface fluxes were carried out by application of the relaxed eddy accumulation technique (REA) during the 2001 experimental period. Profile measurements of peroxide mixing ratios at 32 and 14 m were made to qualitative check on the flux direction, and therefore, on the performance of the REA system. Mean surface exchange fluxes of $H_2O_2$ of –0.8 ± 0.3 nmol $m^{-2}$ $s^{-1}$, methylhydroperoxide (MHP) of -0.03 ± 0.03 nmol $m^{-2}$ $s^{-1}$ and hydroxymethylhydroperoxide (HMHP) of – 0.7 ± 0.5 nmol $m^{-2}$ $s^{-1}$ were obtained. REA and profile measurements show that the dry deposition process primarily controls the $H_2O_2$ and MHP surface exchanges. The controlling factor for $H_2O_2$ deposition fluxes was found to be turbulence, while that for the MHP was surface resistance (Valverde-Canossa *et al., this issue*).

The mixing ratio and flux data of formaldehyde are given in Figure 7 for 20.07.2002 and 23.07.2002. For both days, mixing ratios at 12 m and 24 m were not significantly different. This confirms results from the analysis of $O_3$ data suggesting that mixing mixing of canopy air with masses directly above is well established. The seven available data points of the HCHO mixing ratio measurements at the leaf level, as realized in empty branch enclosure chambers by group 2, however, indicate large differences. On both days, they are lower than those of the direct DNPH method (group 1). On 20.07.2002, the deviation is by a factor of 4. Possible reasons for this disagreement may be adsorption or reaction at the enclosure walls or in the pumps which were used for flushing ambient air through the enclosures.

On 20.07.2002, the CACHE model HCHO data are about half those of the measured data (direct DNPH method) at 12 m and 24 m above ground. The CACHE model data are more similar to the data from enclosure chambers (between 12 and 18 hrs, see Fig. 7). On 23.07.2002, the modelled data agree well with the measured data in the range between 1.6 and 2.0 ppb during the afternoon hours.

In the model, the ecosystem may act as net source (on 20.07.2002) or as a net sink (on 23.07.2002) for formaldehyde. The branch enclosure experiments show an emission of formaldehyde on 23.07.2002 while the model predicts deposition. Emission of formaldehyde by the leaves of trees is a well known phenomenon (Kesselmeier et al., 1997; Kreuzwieser et al., 2002) which has also been described for Norway spruce (Janson et al., 1999, 2001; Cojocariu et al., 2004) and other conifers (e.g. Kesselmeier et al., 1997). Parameterisation studies showed that formaldehyde exchange of Norway spruce is dependent on temperatures, relative humidity and transpiration of the leaves. The biochemical pathways underlying the production and emission of this carbonyl by leaves are still not completely understood (Kesselmeier and Staudt 1999), nor is deposition of formaldehyde to the surfaces of the forest

In addition to formaldehyde, mainly acetaldehyde and acetone were emitted by Norway spruce needles as determined by enclosure measurements and detection by both DNPH coated silica gel cartridges (with HPLC) and PTR-MS. Like formaldehyde emissions, the release of acetaldehyde and acetone showed a clear diurnal pattern with higher emissions during midday than at night. Canopy flux measurements in a Pinus ponderosa plantation revealed similar patterns for acetaldehyde and acetone emission (Schade and Goldstein, 2001, 2002).

## VIII Concluding discussion

It is the purpose of this contribution to offer an overview over the BEWA field campaigns in the *Fichtelgebirge* mountain range in NE Bavaria during the summers of 2001 and 2002. The exchange of matter, in particular VOC, between the Norway spruce forest and the atmosphere, was studied in an integrated experiment. The scope of the BEWA campaigns was to develop further understanding of the surface/atmosphere exchange on the physical and chemical processes in the atmospheric boundary layer.

The *Waldstein* study site is an experimental forest, well suited for such intensive programs, because (i) a planted Norway spruce forest represents one of the major types of ecosystems, typical for the central European middle altitude ranges between 500 and 1200 m a.s.l., (ii) long term ecosystem research activities at that site offer a good understanding of the plant physiology, nutrient and pollutant fluxes within the ecosystem, and meteorological processes (Matzner, 2004), and (iii) because the site offers excellent logistical opportunities including power supply and a meteorological tower.

We found that, on the time scale of the golden day -periods in 2001 and 2002, the closure of the one-dimensional energy balance is within 20 %;. therefore, any measured vertical turbulent exchange fluxes of gases or particulates are probably not reliable with a precision better than 20 %.

The quality control of micrometeorological techniques (i.e. ultrasonic anemometers) indicates a precision of 10 % (or better) between parallel setups. It is not clear from our data if these two sources of error are independent from each other or if the instrumental uncertainty is already included within the uncertainty of the energy balance. We conclude that the precision of vertical exchange flux measurements lie within ± 25 % confidence for the BEWA experiments.

Long-term quantification of vertical fluxes of gases such as $CO_2$ and $H_2O$ are associated with large uncertainties and sources of large errors, mainly due to gaps in the data series resulting from instrument failures and data losses during times of poorly developed turbulence (Rebmann *et al.,* 2004). Our approach to select shorter experimental time periods and select high quality data for further analysis leads us to believe that the 25 % precision, as indicated above, represents a maximum margin of error for these types of measurements. On the single branch level, however, the heterogeneity is much larger and deviations between single measurements on the order of a factor of two must be expected.

A possible cause of error lies in the patchiness of the forest. We showed that impulse and gases (ozone) could enter the trunk space without leaving a corresponding signature at the canopy-top level. Vertical escape of these scalars doubtlessly jeopardizes the applicability of a one-dimensional model or the applicability of a one-tower measurement to quantify vertical fluxes with acceptable spatial representativeness. Upward fluxes of ozone, as observed at the top level of the meteorological tower (Klemm and Mangold, 2001), may result from such transport. However, the CACHE model (Forkel *et al*., *this issue*) successfully described the magnitude and diurnal behaviour of the ozone fluxes and the profile of ozone concentrations within the stand for most of the time during the BEWA experimental phases. We conclude that the model is a suitable tool for our purposes.

On a regional scale, gases and particles are certainly advected to the site. The *Waldstein* represents a remote site in central Europe. Spikes of primary pollutants (*i.e.*, $NO_x$) occur rarely at this experimental site, and diurnal behavior of $NO_x$ and $O_3$ (Figs. 2 and 3) can be almost completely understood considering the boundary dynamics and deposition processes. It is predominantly the vegetation cover itself and its interaction with the atmospheric boundary layer that leads to dynamics of trace gases (and particles) on short time scales.

For VOC, the general picture is less homogeneous. A general overview of the predominant concentrations at the *Waldstein* site could was presented for the first time (Table 5). However, some of the fluxes are uncertain. The ambient mixing ratios of formaldehyde predicted with the atmospheric model CACHE agree reasonably well with the measured data. Modelled formaldehyde fluxes exhibit alternating net emission and net depositional fluxes. On 23.07.2002, CACHE predicts

a net deposition while simultaneously branch enclosure measurements show emissions, suggesting that the spruce leaves act as a weak source for formaldehyde. These data do not necessarily contradict each other, as the enclosure measurements represent the process at the leaf level, while the model data reflect the net ecosystem response. It remains unclear under what exact conditions sinks within the ecosystem (stems, understorey vegetation, soil) are stronger than the principal formaldehyde source (leaves). The same could be true for other carbonyls (acetaldehyde, acetone) that have been shown to be emitted by vegetation with the branch enclosure technique. Conversely, good agreement between ecosystem and leaf level flux patterns was observed for isoprenoids (Cojocariu et *al., this issue*, Grabmer *et al., this issue*, Graus *et al., this issue*). Further research should aim at solving this problem in understanding the biogeochemistry of HCHO and other VOC over spruce forests.

In addition to the overview presented in contribution about climatology, fluxes, and techniques, this interdisciplinary and integrated research approach, as realized in the BEWA project, yielded an improved understanding of parameters and mechanisms driving forest / atmosphere interaction on local and regional scales. An operational tool has been developed to estimate VOC emissions with high spatial and temporal resolution (Smiatek and Steinbrecher, *this issue*). A new canopy chemistry emission model explicitly describes canopy effects on VOC emissions (Forkel *et al., this issue*). The role of VOC emissions on particle formation has been identified, and the growth of ultrafine particles has been quantified (Held *et al.,* 2004).

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**Table 1:** Meteorological measurements at the scaffolding tower during the experimental phases 2001 and 2002. Radiation measurements include the four parameters incoming and outgoing short wave and long wave radiation, respectively, and the photolysis rates for $NO_2$, ($J_{NO2}$), and for $O_3$ to $O^1D$, ($J_{O1D}$). The turbulent flux measurements of at 32 m height above ground are important parameters in the energy balance computation.

| **parameter** | **height above ground / m** | **comment** |
|---|---|---|
| 3D-wind | 32 m | turbulence measurement |
| wind direction | 32 m | vane |
| wind speed | 32 m, 25 m, 21 m, 18 m, 16 m, 10 m, 2 m | cup anemometer |
| $CO_2$, $H_2O$, $O_3$ | 32 m | fluxes (eddy covariance technique), Rebmann *et al*., 2004, Klemm and Mangold, 2001 |
| VOC (C5 – C10) | 30 m, 17 m | fluxes (REA technique) and concentrations (Grabmer *et al., this issue*; Graus *et al., this issue*) |
| peroxides | 32 m, 14 m | concentrations at 32 m and 14 m (profile), fluxes at 32 m (REA, only 2001) (Valverde-Canossa *et al., this issue*) |
| precipitation | 31 m | intensity |
| air temperature | 31 m, 30 m, 25 m, 21 m, 2 m | |
| air humidity | 31 m, 30 m, 21 m, 2 m | |
| radiation | 30 m | |
| visibility | 25 m | as indicator for presence and density of fog |
| fog | 25 m | chemical composition: inorganic ions (Wrzesinsky *et al.,* 2004) |
| particles | 24 m, 12 m | size separated chemical composition: inorganic ions, elemental carbon, organic carbon, organic acids, aldehydes (Plewka *et al., this issue*) |
| carbonyls (C1 – C12) | 24 m, 12 m | concentration measurements (Müller *et al., this issue*) |
| particles | 22 m | size distributions, fluxes (Held *et al.,* 2004; Held and Klemm*, this issue*) |
| leaf wetness | 13 m | Klemm *et al.,* 2002 |
| carbonyls (C1 – C5), alcohols (C1 – C4), VOC (C5 – C10) | 12 m | concentration and fluxes at leaf level (Kreuzwieser *et al., this issue*) |
| soil heat flux | -0.05 m | 3 heat flux plates |
| soil temperature | -0.05 m -0.1 m -0.2 m -0.5 m | |

**Table 2:** Data quality objectives (DQO) for air chemistry and meteorological routine parameters. For trace gas concentration measurements, the minimum detection levels (MDL) are also given.

| **Parameter** | **abbreviation** | **DQO** | | **MDL** |
|---|---|---|---|---|
| | | **accuracy** | **precision** | |
| nitrogen oxide | NO | 10 % or 1 ppb* | 5 % or 0.5 ppb* | 1 ppb |
| nitrogen dioxide | $NO_2$ | 15 % or 1.5 ppb* | 10 % or 1 ppb* | 2 ppb |
| sulfur dioxide | $SO_2$ | 15 % or 2 ppb* | 10 % or 2 ppb* | 2 ppb |
| ozone | $O_3$ | 10 % or 2 ppb* | 5 % or 1 ppb* | 2 ppb |
| air temperature | T | 0.5 K | 0.3 K | - |
| relative air humidity | rH | 10 % | 5 % | - |
| air pressure | p | 1 hPa | 0.5 hPa | - |

*whichever is larger

**Table 3:** Regression analyses of micrometeorological data (30 minute averages) between group 2 and group 1, and between group 3 and group 1, respectively, for the 2002 data sets. Results are given in the form $y = a \cdot x + b$, where y are data from group 2 (or group 3, respectively), x are data from group 1, a is the slope of the regression line, b the offset, and $R^2$ the squared regression coefficient. The data set sizes are typically a few hundred.

| **parameter** | **unit** | **group 2** | | | **group 3** | | |
|---|---|---|---|---|---|---|---|
| | | **a** | **b** | **$R^2$** | **a** | **b** | **$R^2$** |
| **$T_s$** | °C | 1.40 | 0.65 | 0.99 | 0.94 | 1.52 | 0.99 |
| **$\sigma_{Ts}$** | °C | 0.89 | 0.02 | 0.79 | 0.93 | 0.01 | 0.92 |
| **u*** | m $s^{-1}$ | 0.89 | 0.07 | 0.84 | 0.93 | 0.07 | 0.70 |
| **$w'T_s'$** | K m $s^{-1}$ | 0.93 | 0.00 | 0.85 | 0.84 | 0.00 | 0.79 |
| **w** | m $s^{-1}$ | 0.73 | 0.06 | 0.63 | 0.75 | 0.03 | 0.71 |
| **$\sigma_w$** | m $s^{-1}$ | 1.01 | 0.02 | 0.94 | 1.01 | 0.03 | 0.92 |

**Table 4.** Averages of meteorological and air chemistry parameters during the two campaigns in 2001 and 2002.

| | **09.07.2001 – 03.08.2001** | **24.06.2002 – 02.08.2002** |
|---|---|---|
| **air temperature** | 16.3 °C | 15.2 °C |
| **relative air humidity** | 69 % | 76 % |
| **sum precipitation** | 55 l $m^{-2}$ | 46 l $m^{-2}$ |
| **leaf wetness** | 0.10 | 0.17 |
| **solar radiation** | 217 W $m^{-2}$ | 211 W $m^{-2}$ |
| **wind speed** | 2.4 m $s^{-1}$ | 2.5 m $s^{-1}$ |
| **NO** | 0.25 ppb | 0.55 ppb |
| **$NO_2$** | 3.8 ppb | 4.1 ppb |
| **$NH_3$** | 3.5 ppb | 1.2 ppb |
| **$O_3$** | 40 ppb | 42 ppb |

**Table 5:** Trace gas mixing ratios as measured during the golden day-periods 2001 and 2002 by various research groups at the *Waldstein* site. All mixing ratios are given in units ppb. N is the number of individual measurements. For analytical details concerning groups 1 and 3 see Müller et al. (*this issue*), group 2 see Cojocariu *et al.*, (*this issue*), group 4 see Graus *et al.,* (*this issue*), group 5 see Graus *et al.,* (*this issue*) and Grabmer et al. (*this issue*), and group 6 see Valverde-Canossa et al. (*this issue*). The model data represent individual times every 30 minutes.

| | 2001 | | | | 2002 | | | |
|---|---|---|---|---|---|---|---|---|
| | **N** | **mean** | **max** | **min** | **N** | **mean** | **max** | **min** |
| $O_3$ | 1858 | 48 | 98 | 16 | 1122 | 49 | 78 | 13 |
| NO | 1831 | 0.20 | 1.67 | 0 | 1122 | 0.43 | 2.25 | 0.01 |
| $NO_2$ | 1830 | 3.8 | 10.4 | 1.2 | 1122 | 3.5 | 8.1 | 1.8 |
| $SO_2$ | 1858 | 1.5 | 12.5 | 0 | 1122 | 0 | 3.55 | 0 |
| $NH_3$ | 1287 | 5.4 | 19 | 1.4 | 1079 | 1.5 | 7.0 | 0.25 |
| **group 1** | | | | | | | | |
| formaldehyde | 303 | 1.97 | 4.64 | 0.55 | 356 | 2.12 | 9.91 | 0.34 |
| acetaldehyde | 303 | 1.87 | 5.47 | 0.51 | 356 | 1.21 | 4.86 | 0.22 |
| acetone | 303 | 3.70 | 11.61 | 1.06 | 356 | 4.01 | 13.30 | 1.22 |
| propionaldehyde | 303 | 0.15 | 0.28 | 0.05 | 356 | 0.12 | 0.47 | 0.00 |
| methylethylketone | 303 | 0.89 | 2.51 | 0.03 | 356 | 0.94 | 6.18 | 0.09 |
| trans-2-hexenal | 302 | 0.09 | 0.35 | 0.01 | 356 | 0.07 | 0.55 | 0.00 |
| pinonaldehyde | 139 | 0.03 | 0.14 | 0.01 | 356 | 0.01 | 0.11 | 0.00 |
| nonanal | 254 | 0.04 | 0.16 | 0.00 | 356 | 0.04 | 0.46 | 0.00 |
| **group 2** | | | | | | | | |
| formaldehyde | 30 | 3.12 | 7.63 | 1.59 | 19 | 2.63 | 5.29 | 0.96 |
| acetealdehyde | 30 | 4.41 | 7.96 | 2.60 | 21 | 2.12 | 5.33 | 0.66 |
| acetone | 30 | 4.69 | 7.58 | 3.20 | 21 | 2.23 | 3.55 | 0.90 |
| **group 3** | | | | | | | | |
| formaldehyde | 225 | 1.29 | 1.92 | 0.63 | -- | -- | -- | -- |
| **group 4** | | | | | | | | |
| methanol | 266 | 6.30 | 12.36 | 2.49 | 77 | 4.28 | 6.56 | 1.31 |
| acetaldehyde | 266 | 2.75 | 14.86 | 0 | 77 | 0.95 | 2.35 | 0.31 |
| acetone + propanal | 266 | 5.28 | 10.83 | 2.12 | 77 | 4.13 | 6.14 | 1.42 |
| isoprene | 266 | 0.50 | 2.41 | 0 | 92 | 0.27 | 0.49 | 0.08 |
| methylvinylketone + methacrolein | 266 | 0.29 | 1.63 | 0.46 | 77 | 0.22 | 0.43 | 0.06 |
| sum of monoterpenes | 266 | 0.43 | 1.66 | 0.01 | 92 | 0.24 | 0.69 | 0.02 |
| **group 5** | | | | | | | | |
| a-pinene | 34 | 0.14 | 2.13 | 0.01 | 37 | 0.21 | 0.75 | 0.04 |
| b-pinene + sabinene | -- | -- | -- | -- | 37 | 0.27 | 0.62 | 0.10 |
| **group 6** | | | | | | | | |
| $H_2O_2$ | 439 | 0.33 | 0.96 | 0.00 | -- | -- | -- | -- |
| methyl hydroperoxide | 439 | 0.06 | 0.28 | 0.00 | -- | -- | -- | -- |
| hydroxymethyl hydroperoxide | 439 | 0.0004 | 0.15 | 0.00 | -- | -- | -- | -- |
| **model** | | | | | | | | |
| formaldehyde | 576 | 1.58 | 2.58 | 0.66 | 432 | 1.41 | 2.62 | 0.56 |
| OH *1000 | 576 | 0.1123 | 0.4172 | 0.0051 | 432 | 0.0826 | 0.3820 | 0.0023 |
| $O_3$ | 576 | 47 | 84 | 21 | 432 | 43 | 71 | 8 |
| a-pinene | 576 | 0.361 | 0.820 | 0.026 | 432 | 0.325 | 1.123 | 0.054 |
| limonene | 576 | 0.159 | 0.336 | 0.045 | 432 | 0.142 | 0.442 | 0.049 |
| isoprene | 576 | 0.158 | 0.437 | 0.000 | 432 | 0.153 | 0.617 | 0.000 |
| metacroleine | 576 | 0.217 | 0.569 | 0.055 | 432 | 0.215 | 0.629 | 0.044 |

**Figure 1:** 120-hour backward trajectories of air masses arriving at the *Waldstein* site during the golden days 2001 and 2002, respectively, at 12 hrs UT, which is 13 hrs CET. Open symbols indicate travel of the respective air mass outside the mixed layer, full symbols indicate travel within the mixed layer. Dates indicate arrival dates of individual trajectories.

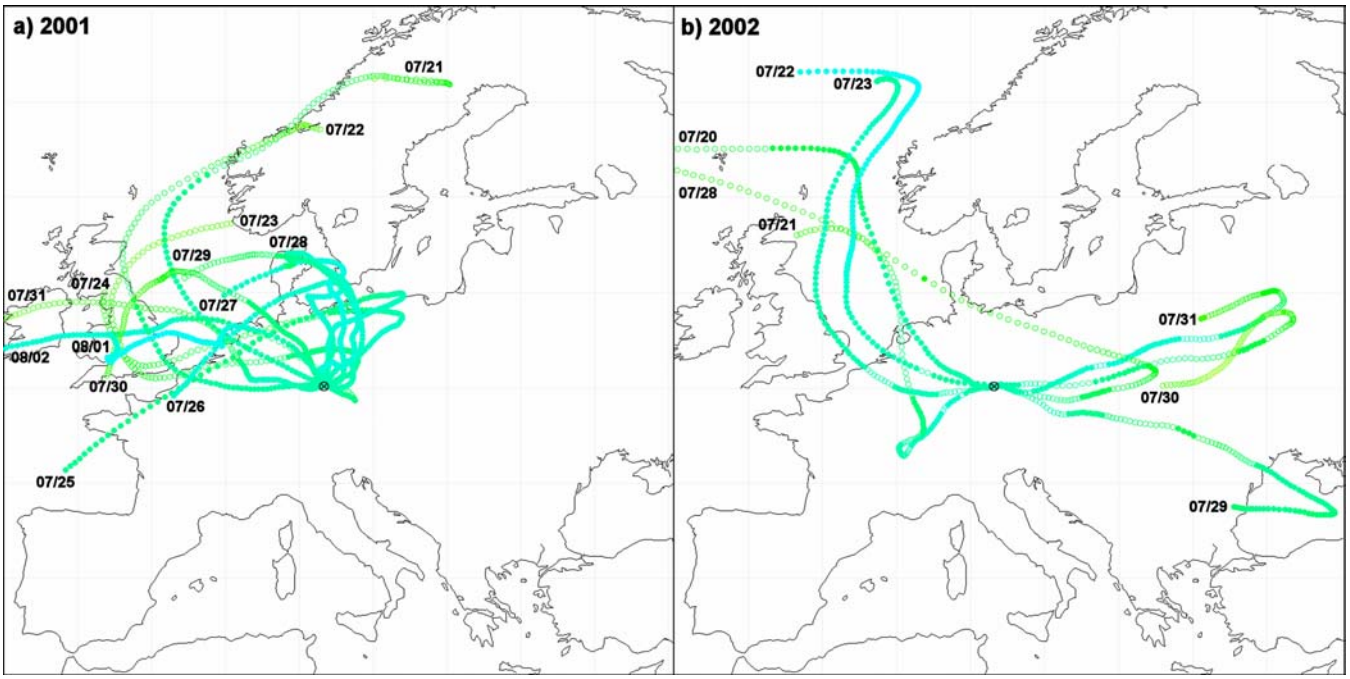
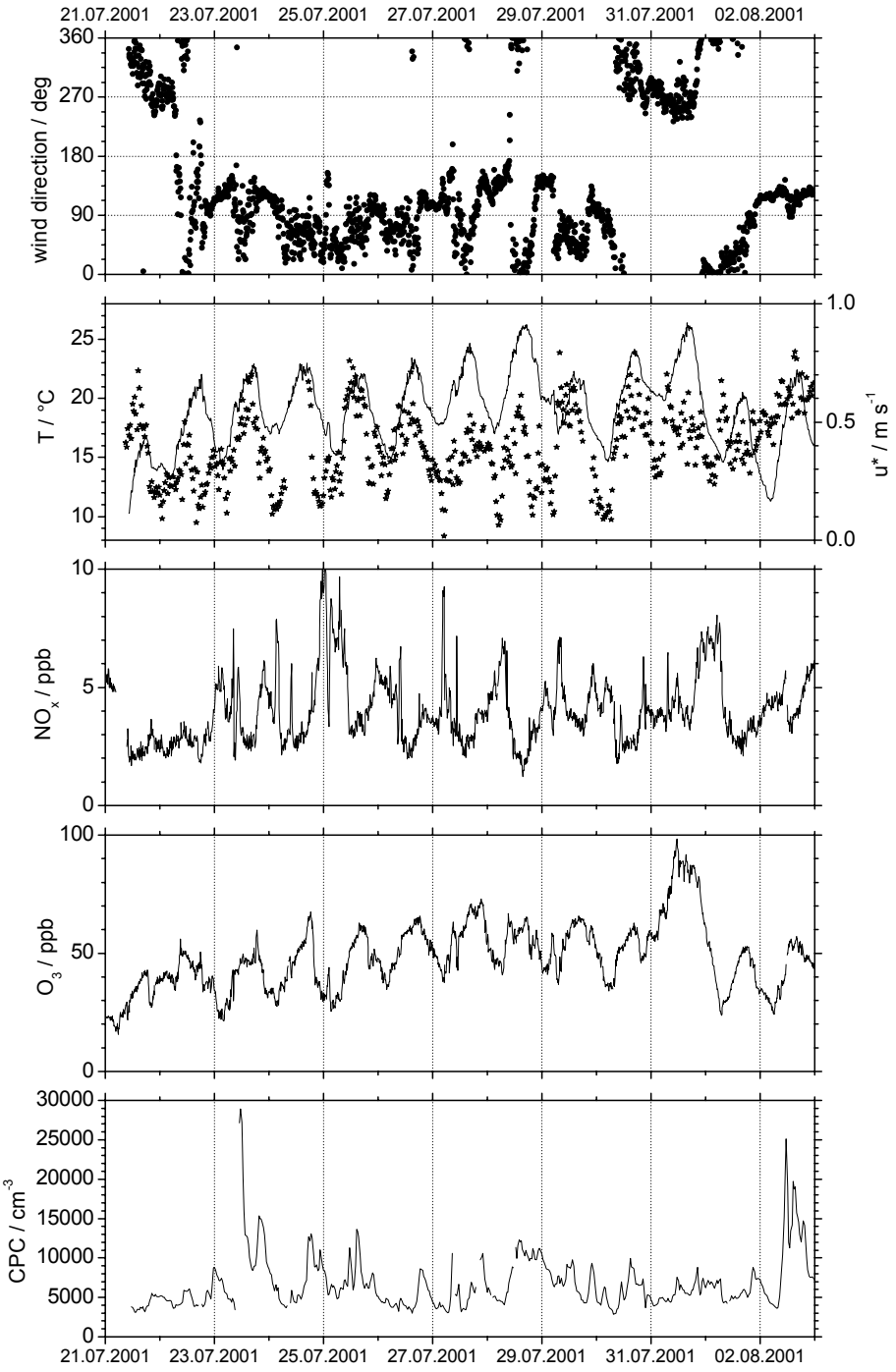
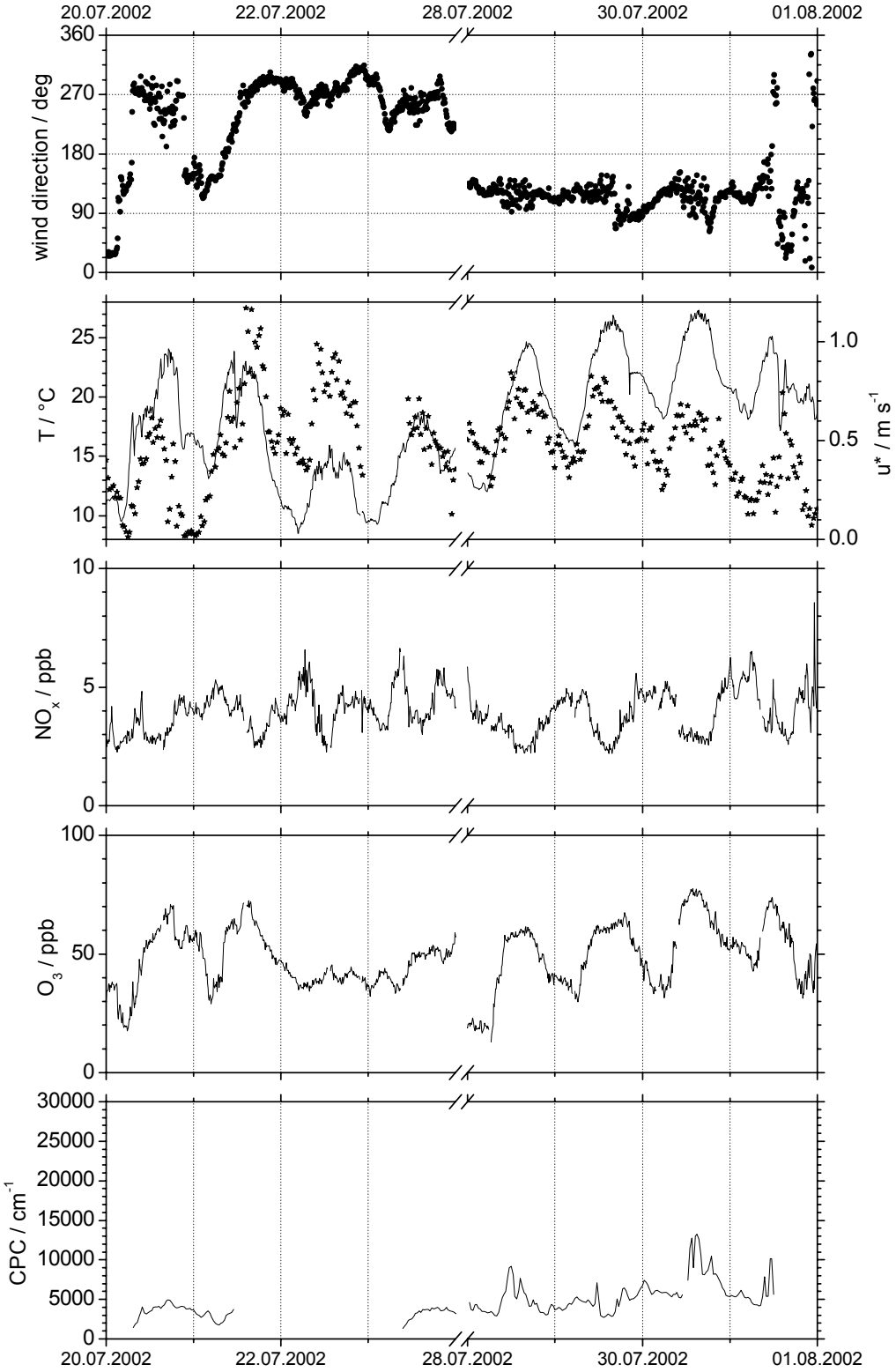


**Figure 2:** Meteorology and air chemistry parameters for the golden day-period 2001. All data are displayed as 10-minute-averages except the friction velocity u*, which is given in 30-minute averages (asterisks in second panel). Tick labels are marked with the respective dates at 00:00 hrs Central European Time, which is one hour ahead of UTC. CPC means total particle number concentration for particles with diameter > 11 nm.



1 **Figure 3:** Same as Figure 1, but for the golden day periods 2002.




2

**Figure 4:** Average profiles of the wind speed as measured during the 2001 golden days. Lines in left hand graph are averages for wind speeds at the top level (32 m above ground) between 0 and 1 m $s^{-1}$, 1 and 2 m $s^{-1}$, 2 and 3 m $s^{-1}$, 3 and 4 $ms^{-1}$, 4 and 5 m $s^{-1}$, and 5 and 6 m $s^{-1}$, respectively. The right hand graph shows the latter 5 profiles at the three upper levels, with logarithmic scaling of the height axis, and the extrapolations of the profiles to zero wind speed (logarithmic profiles).

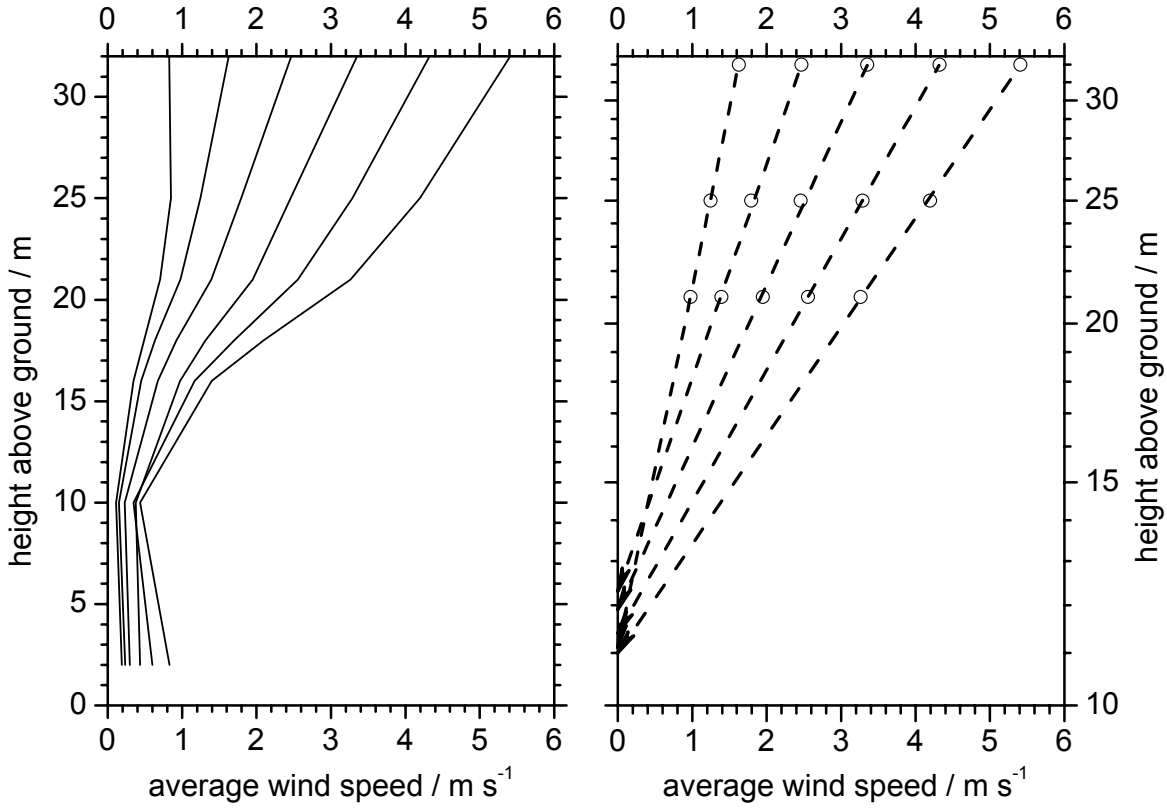


**Figure 5:** Energy balance and $CO_2$ flux during the golden day periods 2002. Upper panel: Short wave radiation balance (full line), energy balance (dotted line). For clarity of presentation, the buoyancy flux, latent heat flux, long wave radiation balance, and soil heat flux are not shown. Lower panel: $CO_2$ flux as measured with the eddy covariance method (thin dark line) and with the single branch enclosure technique (broad, grey line). All data refer to the ground area as reference.

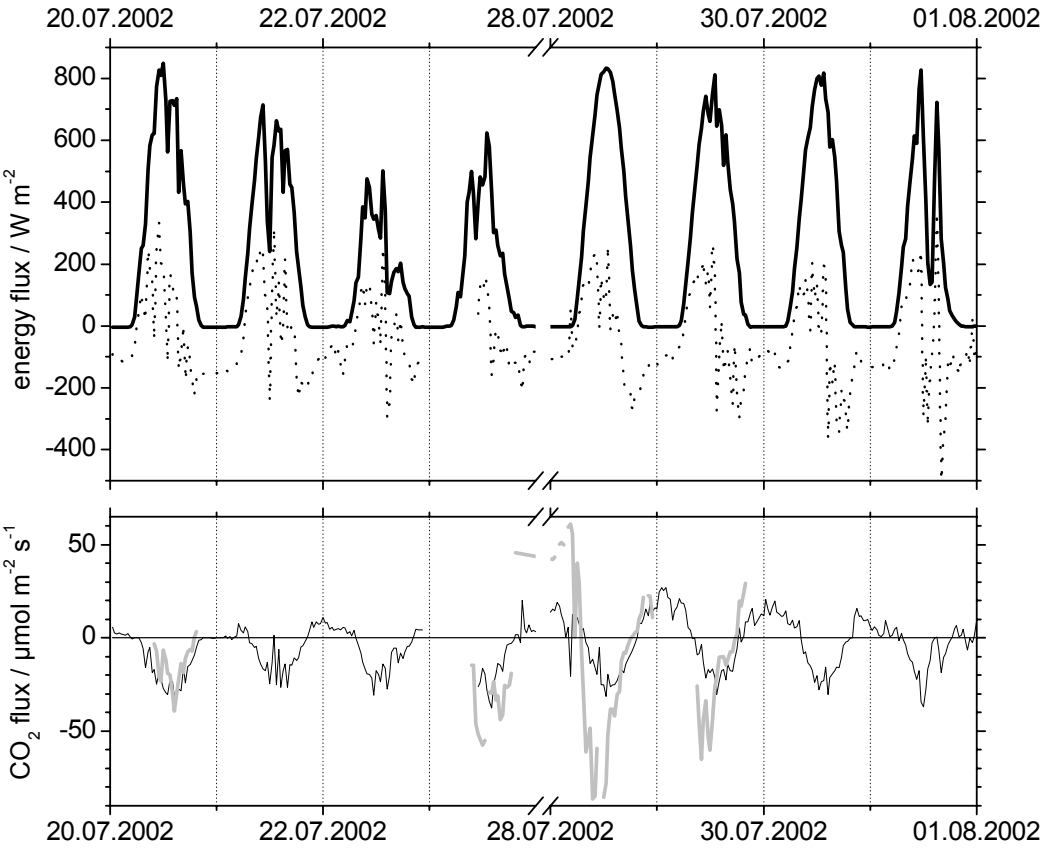


**Figure 6:** Ozone mixing ratios at the *Waldstein* site on 20.07.2002. Full black line: measured $O_3$ outside the forest; dotted black line: measured inside the forest (3 m above ground); full grey line: modelled $O_3$ above the forest canopy (30.8 m above ground); broken grey line: modelled $O_3$ inside the forest (1.9 m above ground).

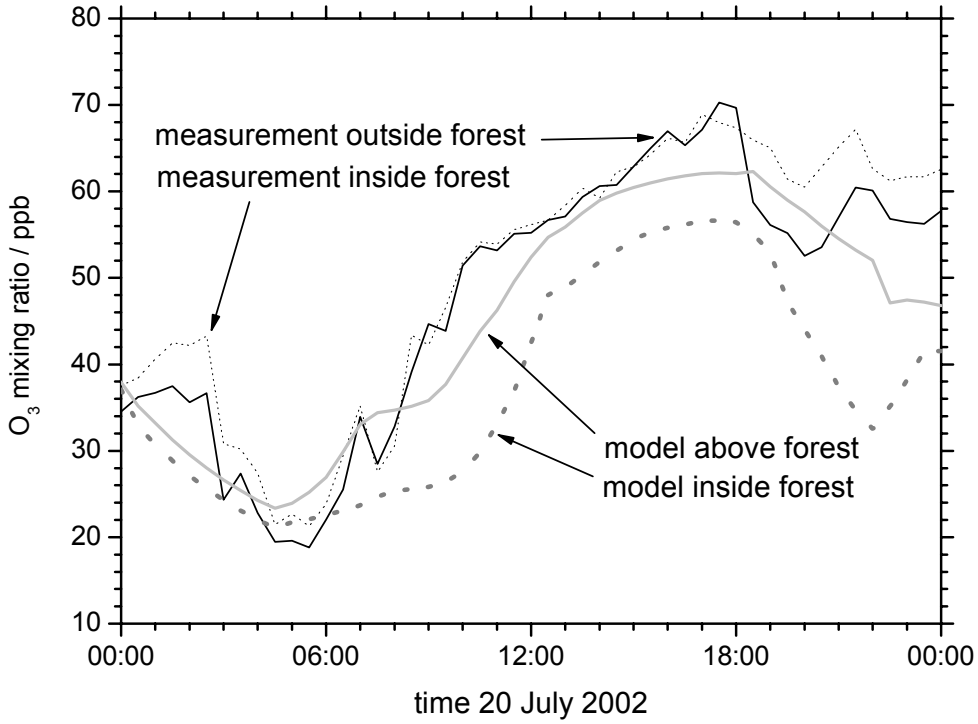


**Figure 7:** Formaldehyde mixing ratios (top panel) and exchange fluxes (lower panel) during two days of the 2002 experiment. Tick labels are marked with the respective dates at 00:00 hrs Central European Time The dashed line shows the CACHE model results. Full lines show measurements with the DNPH cartridge method at the 24 m level of the tower (thick line) and at the 12 m level (thin line). Dots show branch enclosure experiment data as performed on trees in immediate proximity of the tower, at about 13 m above ground.