Solar spectral actinic flux and photolysis frequency measurements in a deciduous forest

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[1] Within the Emission and Chemical Transformation of Biogenic Volatile Organic Compounds (ECHO) project the photochemistry of biogenic organic compounds in a forest was investigated. In this context, two spectroradiometers were used to determine solar spectral actinic flux and photolysis frequencies within and above a deciduous forest at Jülich, Germany. Locations in the forest and in a small clearing were examined 2 m above ground. Under overcast conditions, photolysis frequencies were within 1–3% and 6–8% of above canopy values at forest and clearing locations, respectively. In a spectral range below 500 nm the canopy was found to act as a gray filter that diminished spectral actinic flux independent of daytime and wavelength. Under clear-sky conditions, diurnal variations within the forest also followed that of diffuse sky radiation above the forest except for sharp peaks from direct sunlight that was incident sporadically at the selected locations. The results under all conditions were in accord with the foliage being opaque toward UV and gaps in the canopy being responsible for the remaining actinic flux. Sky photographs showed that the distribution and size of gaps in the foliage were extremely heterogeneous with patterns changing rapidly upon changing location. Regarding daytime chemical reactions of biogenic compounds within the forest, it was estimated that degradation by OH was reduced by a factor similar to the photolysis frequencies, while potential degradation by NO2 was increased by a factor of ~3 compared with above forest conditions. As a result, it was estimated that minor fractions of 0.8% of isoprene and 3.4% of monoterpenes were degraded by reactions with OH, NO3, and O3 prior to transport into the layer above the forest.


1. Introduction

[2] Forests represent a major source of biogenic organic volatile compounds (BVOCs) in the troposphere, most importantly isoprene, terpenes, sesquiterpenes, and oxygenated compounds like alcohols and aldehydes [e.g., Guenther et al., 1995]. Emissions and deposition of trace gases by forests are controlled by many time-dependent parameters including meteorological conditions (e.g., light and temperature), soil properties (e.g., water availability) and the composition of the plant inventories (e.g., broadleaf trees or conifers) [Guenther et al., 2000; Fuentes et al., 2000]. Owing to this complexity, the impact of BVOC emissions from forests on atmospheric photochemistry, including aerosol formation, are currently not well understood and consequently the regional and global effects on air quality and climate are uncertain.

[3] The Emission and Chemical Transformation of Biogenic Volatile Organic Compounds (ECHO) project aimed to investigate the influence of BVOC emissions on tropospheric photochemistry by combined measurement and modeling activities studying emissions, transport and transformation of trace gases in a typical European mixed forest at Jülich, Germany (50.91°N, 6.41°E). In two field campaigns during the summer seasons of 2002 and 2003 a wide range of instrumentation was used at a tower set up in the forest [Ammann et al., 2004; Kleffmann et al., 2005; Spirig et al., 2005]. Measurements covered of a broad spectrum of organic compounds (including organic nitrates), HOx (OH, HO2), RO2 and NO3 radicals, O3, NOx (NO, NO2), aerosols, meteorological parameters and photolysis frequencies. These activities were complemented by modeling studies and simulation experiments utilizing the atmosphere simulation chamber SAPHIR at Forschungszentrum Jülich, and a wind tunnel at Hamburg University [Aubrun and Leitl, 2004; Aubrun et al., 2005].

[4] Photolysis processes are a key aspect of tropospheric chemistry because photolyses by solar UV produce reactive radicals, most importantly the OH radical. OH radicals largely initiate the degradation of many trace gases including BVOCs. The degradations proceed in terms of complex chain reactions where OH is regenerated from secondarily formed HO2 in reactions with NO or O3. The primary
radical productions in photolysis processes are essential to initiate the chain reactions and to compensate for radical losses by terminating reactions, e.g., by OH + NO2 and HO2 + HO2. For example, a large fraction of primary production of OH results from reaction of electronically excited O(1D) with water vapor,

$$O(1D) + H_2O \rightarrow 2OH$$ (1)

where O(1D) is produced in the UV photolysis of ozone:

$$O_3 + h\nu(\lambda \leq 340 \text{ nm}) \rightarrow O(1D) + O_2$$ (2)

Moreover, tropospheric ozone is formed to a large extent by the photolysis of NO2 followed by the reaction of ground state O(3P) with O2:

$$NO_2 + h\nu(\lambda \leq 430 \text{ nm}) \rightarrow NO + O(3P)$$ (3)

$$O(3P) + O_2 + M \rightarrow O_3 + M$$ (4)

Thus a quantitative treatment of photolysis processes is required for an understanding of tropospheric photochemistry. Reaction (3) for example is quantified by a first-order rate constant \(j(NO_2)\) referred to as photolysis frequency:

$$j(NO_2) = -\frac{d[NO_2]}{dt} \frac{1}{[NO_2]} = \int \sigma(NO_2) \phi(NO) F_\lambda \, d\lambda$$ (5)

The first part of the equation gives a chemical definition of the photolysis frequency in the absence of other NO2 loss or production processes. This definition is therefore not suitable for a determination of \(j(NO_2)\) by measurements of NO2 in complex chemical systems like the troposphere. However, it can be used in simpler, artificial systems like chemical actinometers [e.g., Shetter et al., 2003]. The second part of equation (5) shows the relation with the radiometric quantity spectral actinic photon flux \(F_\lambda\) and the molecular properties of NO2, namely, absorption cross section \(\sigma(NO_2)\) and quantum yield \(\phi(NO)\) of NO + O(3P) formation that are a function of wavelength \(\lambda\). Photolysis frequencies of other photolysis processes are defined accordingly. In Table 1 a selection of important photolysis processes is listed as well as local noon values of photolysis frequencies above the forest on a clear-sky day of the 2003 ECHO campaign. Besides ozone, nitrous acid (HONO) and formaldehyde (HCHO) are important photolytic precursors of tropospheric HOX.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Process</th>
<th>Range, nm</th>
<th>(j, \text{s}^{-1})</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j(O^1D))</td>
<td>(O_3 \rightarrow O(1D) + O_2)</td>
<td>295–325</td>
<td>(2.4 \times 10^5)</td>
<td>15</td>
</tr>
<tr>
<td>(j(H_2O_2))</td>
<td>(H_2O_2 \rightarrow OH + OH)</td>
<td>300–380</td>
<td>(8.3 \times 10^6)</td>
<td>10</td>
</tr>
<tr>
<td>(j(HCHO))</td>
<td>HCHO (\rightarrow H + HCO)</td>
<td>300–335</td>
<td>(2.8 \times 10^5)</td>
<td>20</td>
</tr>
<tr>
<td>(j(HCHO)_m)</td>
<td>HCHO (\rightarrow H_2 + CO)</td>
<td>310–360</td>
<td>(3.4 \times 10^5)</td>
<td>20</td>
</tr>
<tr>
<td>(j(NO))</td>
<td>NO (\rightarrow O(3P) + NO)</td>
<td>310–420</td>
<td>(7.9 \times 10^3)</td>
<td>10</td>
</tr>
<tr>
<td>(j(NO)_m)</td>
<td>NO (\rightarrow O(3P) + NO_2)</td>
<td>400–620</td>
<td>(1.7 \times 10^1)</td>
<td>15</td>
</tr>
<tr>
<td>(j(NO)_m)</td>
<td>NO (\rightarrow NO + O_2)</td>
<td>580–620</td>
<td>(2.1 \times 10^2)</td>
<td>15</td>
</tr>
</tbody>
</table>

*Lower indices \(r\) (radical) and \(m\) (molecular) denote formation of different photoproducts from the same precursor. Wavelength ranges are approximate (tropospheric conditions). Molecular data \(\sigma\) and \(\phi\) (equation (5)) were taken from literature. O3, Malicet et al. [1995] and Matsuura et al. [2002]; HCHO, Merienne [2003]; H2O2, Sander et al. [2003], \(\phi(OH) = 2.0;\) HCHO, Meller and Moortgat [2000] and Atkinson et al. [2004]; HONO, Bongartz et al. [1994], \(\phi = 1.0;\) NO3, Merienne et al. [1995] and Troe [2000]; and NO, Atkinson et al. [2004]. Error estimates include a 6% contribution from the actinic flux measurements and estimated 298 K uncertainties of \(\sigma\) and \(\phi\) from literature.

The relationship between spectral actinic flux and irradiance is complex under natural conditions in particular when parts of the sky are blocked by opaque objects, e.g., trees.

\[ F_\lambda = \int_0^{2\pi} \int_0^{\pi} L_\lambda(\lambda, \vartheta, \varphi) \cos(\vartheta) \sin(\vartheta) \, d\vartheta \, d\varphi \] (6)
investigating local photochemistry based on combined observations of radical species, trace gases and meteorological parameters as intended within the ECHO project. The discussion is focused on the photolysis frequencies $j(O^1D)$ and $j(NO_2)$ which are governed by the wavelength ranges UV-B (300–320 nm) and UV-A (320–400 nm) in good approximation. The results of this work were complemented by profile measurements and long-term measurements of photolysis frequencies at different levels of the ECHO tower using filter radiometers [Bohn et al., 2006].

2. Experimental Method

2.1. Spectroradiometer

[8] Two spectroradiometers similar in construction were used for parallel measurements of downwelling $2 \pi$ sr spectral actinic flux within and above the forest. The instruments were based on thermostated double monochromators (Bentham, DTM 300) [Hofzumahaus et al., 1999]. For each instrument, two 10 m quartz fibers were guiding light from the entrance optics to the monochromators where fiber cross sections were converted from round to rectangular to feed the monochromator entrances without losses. Cochannel operation was achieved in both instruments by utilizing the total slit height of the monochromators (20 mm) for two separate optical paths with slit heights of 7 mm separated by an unused section of 6 mm. In this setup, cross talk between the channels was found to be 0.3% or less. Entrance optics were specially designed for actinic flux reception in one hemisphere with direction-dependent sensitivity using quartz domes (see Figure 1). UV sensitive photomultiplier tubes (EMI, 9250 QB) were used for light detection. A spectral resolution and a step size of 1 nm were used in the most important wavelength range 280–420 nm. Absolute calibration of the spectroradiometers was achieved using a 1000 W irradiance standard (BN-9101, Gigahertz-Optik, PTB traceable) and 45 W secondary standards (Optronic Laboratories) for regular checks. The accuracy of the measured spectral actinic flux was 5–7% considering the uncertainty of the irradiance standard and the characterization of the inlet optics. More information on technical details of the spectroradiometers and uncertainties regarding different photolysis frequencies are given by Hofzumahaus et al. [1999, 2002]. Estimated total uncertainties are listed in Table 1. A constant temperature of 298 K was assumed in the calculation of photolysis frequencies from the actinic flux spectra (equation (5)) to keep the influences of ambient temperature and foliage separated.

[9] Measurements of upwelling radiation were not included in the present study for technical reasons and because the spectral albedo of vegetation-covered surfaces is generally low in the UV range (1–4%) [Feister and Grewe, 1995; Webb et al., 2004]. However, for the visible range spectral actinic flux may have been enhanced by 5–10% above the forest caused by an increased albedo in this spectral range [Feister and Grewe, 1995].

2.1.1. Above Forest Measurements

[10] For reasons of convenience, measurements above the forest were made on top of a building 370 m away from the forest site in southerly direction. A shadow ring was used with one channel to distinguish between direct sunlight and diffuse sky radiation. The setup of the ring is shown in Figure 1. Actinic flux from diffuse sky radiation was measured by the shaded detector and corrected with respect to the solid angle blocked by the ring. Subtraction from the total actinic flux received by the other channel allows to calculate the contribution from direct sunlight. The shadow ring correction was based on the assumption of a time-independent, isotropic radiance distribution. This introduced errors regarding the relative contributions of direct and diffuse sunlight. However, dependent on external conditions, these errors were estimated to be 5% or less [Bohn and Zilken, 2005].

[11] A scanning range 280–550 nm was selected for the measurements above the forest. The upper limit was determined by the decreasing quantum yields of the UV sensitive photomultipliers. In order to save scanning time, 2 nm steps were used in the range 420–550 nm. The corresponding scanning times were about 3 min. The use of wavelength steps of about twice the full width at half maximum in the range 420–550 nm was accepted because this range was considered secondary for photochemistry processes. Except for sporadic instrument failures and breaks for regular calibration, measurements were made continuously while solar zenith angles ($\chi$) were smaller than 96°. Measurement periods are listed in Table 2.

[12] During four weeks of the 2003 campaign also a diode array spectroradiometer (Meteorologie Consult GmbH, Königstein, Germany) was used to measure spectral actinic flux above the forest. This instrument used a similar inlet optic but a combination of a single monochromator and a diode array to measure in a wavelength range 290–700 nm. The spectral resolution was about 2 nm at a pixel width of 0.8 nm. The main advantage of this instrument was the simultaneousness of the measurements in a wide range of wavelengths (also covering $j(NO_2)$) with high time resolution. In this study 1 min averages were recorded.

[13] Above forest measurements of photolysis frequencies were also made on top of the tower at the forest site using $j(NO_2)$ and $j(O^1D)$ filter radiometers [Bohn et al., 2006]. These measurements were made with a high time resolution of 5–7 s. For comparison with the spectroradi-
The data were averaged over the corresponding intervals during the spectroradiometer scans.

### 2.1.2. Forest Measurements

[14] For the forest measurements the scanning range was extended to 280–750 nm. This was accomplished by a further split of the light paths behind the exit slit to feed two additional, red-sensitive photomultipliers (EMI, 9659) protected by cutoff filters (\$C_480\$ nm, Schott) to avoid second-order detection. Above 550 nm a different set of gratings was used reducing spectral resolution to about 2 nm. Caused by the extension of the wavelength range, scanning times were about 4.5 min. For comparison with the above canopy measurements the data were therefore synchronized by linear interpolations.

[15] In the forest the wavelength range was extended to cover the spectral region responsible for NO$_3$ photolysis (Table 1). In contrast to above canopy daytime conditions where $j$(NO$_3$) was considered secondary because of low NO$_3$ concentrations (diminished by photolysis and reaction with NO) this could not be presumed for forest conditions. The spectral range 620–750 nm was included for the sake of completeness to cover PAR and visible radiation (400–750 nm) for potential applications not related to photochemistry.

### 2.2. Field Site and Sky Photography

[16] The instrument operated within the forest was installed in a water-tight housing for outdoor operation. It was located close to the edge of a clearing hosting the ECHO main tower. Figure 2 shows a map of the area and a close-up view of the tower surroundings. The clearing was situated next to a narrow road leading through the forest. The gap in the canopy was almost circular with a diameter of about 15 m. The forest surrounding the ECHO main tower was dominated by large beeches ($Fagus sylvatica$) of about 30 m height. Within a distance of about 50 m there were also some oaks ($Quercus robur$), birches ($Betula pendula$) and smaller spruce ($Picea abies$). Positions in the clearing and in forest unaffected by the clearing were accessible simultaneously within the 10 m quartz fiber ranges. Measurements were made 2 m above ground. During the campaigns positions were changed once to characterize different locations. The measurement sites were denoted forest 1–4.

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**Table 2. Notations of Spectroradiometer Measurement Positions Within and Above the Forest at Different Campaign Periods**

<table>
<thead>
<tr>
<th>Period</th>
<th>Channel 1</th>
<th>Channel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Jun to 4 Jul 2002</td>
<td>Spectroradiometer 1 (SR 1, Forest)</td>
<td>clearing 1 (7 NW)</td>
</tr>
<tr>
<td>6–24 Jul 2002</td>
<td>forest 1 (25 NW)</td>
<td>clearing 2 (5 S)</td>
</tr>
<tr>
<td>28 Jun to 9 Jul 2003</td>
<td>forest 2 (15 SSE)</td>
<td>forest 3a (22 ESE)</td>
</tr>
<tr>
<td>10 Jul to 19 Aug 2003</td>
<td>forest 4 (20 SE)</td>
<td>clearing 2 (5 S)</td>
</tr>
<tr>
<td>15 Jun to 29 Jul 2002</td>
<td>Spectroradiometer 2 (SR 2, Roof)</td>
<td>total (370 SSW)</td>
</tr>
<tr>
<td>30 Jun to 19 Aug 2003</td>
<td>total (370 SSW)</td>
<td>diffuse$^b$ (370 SSW)</td>
</tr>
<tr>
<td>18 Jul to 18 Aug 2003</td>
<td>Spectroradiometer 3 (Diode Array, SR 3, Roof)</td>
<td>$^c$ (370 SSW)</td>
</tr>
</tbody>
</table>

\$^a\$Distances, m, and directions relative to the ECHO tower at the clearing center are given in parentheses. See Figure 2 for comparison.

\$^b\$Measurements with shadow ring.

\$^c\$Total measurements up to 700 nm.

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**Figure 2.** Map of measurement positions listed in Table 2. (left) Overview of the forest at Forschungszentrum Jülich. Hatched areas mark buildings, and gray areas represent forest stands of different compositions. Positions of the tower and the roof site were indicated. (right) Enlargement of the tower surroundings with measurement positions. The bright area marks the approximate extension of the clearing from a fish-eye photograph.
Table 2 and Figure 2 give an overview on relative positions and the respective time periods. Forest 3a and 3b denote two sites that were in direct vicinity to an instrument measuring OH and HO$_2$ radical concentrations within the forest. Except for this period radical measurements were made in the clearing at different levels of the tower [Kleffmann et al., 2005].

LAI measurements in the forest surrounding the main tower gave a mean value LAI = 5.7 [Ammann et al., 2004]. The LAI corresponds to the one-sided area of leaves per unit ground area. The measured LAI was in reasonable agreement with averaged data for temperate deciduous broadleaf forests (5.1 ± 1.8) [Scurlock et al., 2001]. Sky photographs were made to further characterize the measurement sites within the forest by reproducing the angular distributions of gap patterns in the canopy. A conventional camera (Nikon, FM) was used with a suitable objective (Nikkor, fisheye 16 mm f 2.8 D). This combination covered an about 180° field of view along the diagonal of the 24 × 36 mm film. The photographs were taken by directing the camera toward the zenith. The camera was then rotated by 90° to cover higher polar angles also in other directions. The resulting photographs were merged to create a single photograph with reasonable coverage of the upper hemisphere. Photographs were taken during winter and summer seasons to assess the effects of foliage. Examples are shown in Figures 3 and 4.

3. Results and Discussion

3.1. Above Forest Measurements

3.1.1. Contributions of Direct and Diffuse Sunlight

Figure 5 shows two examples of actinic flux spectra obtained above the forest under clear-sky conditions. Total actinic flux as well as contributions of direct sunlight and diffuse sky radiation are shown. At local noon (∼1140 UTC)
a minimum solar zenith angle of 29° was reached on that day (15 July 2003). Accordingly, actinic flux and direct sunlight were at a maximum at this time of day. The contribution of direct sunlight is generally increasing with wavelength caused by decreasing losses by Rayleigh scattering. Moreover, the fluxes under clear-sky conditions are dependent on aerosol optical depths and ozone columns (UV-B). For comparison, Figure 5 (bottom) shows spectra on the same day in the late afternoon at a solar zenith angle of 75°. Fluxes were much lower compared with local noon conditions and the contribution of direct sunlight was strongly reduced in particular toward shorter wavelengths as expected from increased scattering.

[19] Regarding photolysis frequencies, Figure 6 (left) shows diurnal variations of $j(O^1D)$ and $j(NO_2)$ on 15 July 2003. The wavelength ranges of the corresponding photolysis processes (Table 1) resulted in the different shapes of the diurnal variations and the different contributions of direct sunlight. The relative diurnal variations of other photolysis frequencies (except $j(NO_3)$) ranged within these extremes.

[20] In the presence of clouds the situation was obviously more complex in particular under conditions with broken cloud cover and occasional direct sunlight. Figure 6 (right) shows examples from 18 July 2003. Here diffuse sky radiation was temporarily increased by reflections of direct sunlight in clouds. On the other hand, direct sunlight was sporadically blocked by clouds. Consequently, photolysis frequencies were higher or lower compared with clear-sky conditions but lower values were more common. Because of the higher contribution of direct sunlight, these cloud effects were more pronounced for $j(NO_2)$ than for $j(O^1D)$. Under overcast conditions photolysis frequencies were always lower compared with clear-sky conditions at the same time of day. Nevertheless, there were strong and also rapid variations upon changes in cloud thickness (see section 3.2.1).

3.1.2. Comparison of Field Sites Above the Forest

[21] The cloud effects discussed in section 3.1.1 were local and could have affected the measurement sites above the forest differently at a horizontal distance of 370 m (distance tower roof). However, a comparison with the additional above forest filter radiometer measurements of $j(NO_2)$ and $j(O^1D)$ at the tower [Bohn et al., 2006] showed that the roof measurements were a reasonable reference for the forest site. Figure 7 shows correlations of $j(NO_2)$ obtained at the two sites for the complete campaign periods in 2002 and 2003. The correlations were excellent in both years with more than 96% of data similar within 20%. For $j(O^1D)$ a similar result was obtained.

3.2. Forest Measurements

3.2.1. Overcast Conditions

[22] Figure 8 (left) shows variations of photolysis frequencies $j(O^1D)$ and $j(NO_2)$ on 1 July 2002 above the forest and at the ground from positions clearing 1 and forest 1. Conditions on this day were completely overcast. However, there were considerable, sometimes rapid variations in the course of the day. These variations were observed simultaneously at the clearing and forest positions. Plots of photolysis frequencies from these positions as a function of above forest values are shown in Figure 8 (right). As mentioned in section 2.1.2, data sets were synchronized by linear interpolations for this comparison. This procedure
Figure 7. Comparison of above forest measurements of \( j(\text{NO}_2) \) with a filter radiometer at the ECHO main tower (FR) and the spectroradiometer at the roof site (SR 2, total) at a distance of 370 m. Data for the complete campaign periods of (left) 2002 and (right) 2003 are shown, \( N = 13,700 \) (2002), \( N = 14,200 \) (2003).

Figure 8. (left) Diurnal variations of \( j(\text{O}^1\text{D}) \) and \( j(\text{NO}_2) \) on 1 July 2002 (overcast conditions) above the forest (diffuse equals total), and at positions clearing 1 and forest 1 (from top to bottom). Note that the curves for clearing 1 and forest 1 were scaled by factors 7 and 10, respectively. (right) Correlations of forest and clearing data with above forest data. Solid lines indicate linear regressions with slopes of 0.021 (forest) and 0.077 (clearing) for \( j(\text{O}^1\text{D}) \) and 0.023 (forest) and 0.070 (clearing) for \( j(\text{NO}_2) \).
Table 3. Linear Correlation Coefficients $r$ and Mean Ratios $f$ of Photolysis Frequencies Relative to Above Forest Values Under Overcast Conditions

<table>
<thead>
<tr>
<th>Position</th>
<th>Process</th>
<th>$N$</th>
<th>$r$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest 1</td>
<td>$j(\text{NO}_2)$</td>
<td>617</td>
<td>0.985</td>
<td>0.022 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>317</td>
<td>0.941</td>
<td>0.021 ± 0.007</td>
</tr>
<tr>
<td>Forest 2</td>
<td>$j(\text{NO}_2)$</td>
<td>743</td>
<td>0.970</td>
<td>0.010 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>128</td>
<td>0.837</td>
<td>0.011 ± 0.007</td>
</tr>
<tr>
<td>Clearing 1</td>
<td>$j(\text{NO}_2)$</td>
<td>634</td>
<td>0.950</td>
<td>0.067 ± 0.010</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>442</td>
<td>0.965</td>
<td>0.070 ± 0.010</td>
</tr>
<tr>
<td>Clearing 2</td>
<td>$j(\text{NO}_2)$</td>
<td>812</td>
<td>0.965</td>
<td>0.072 ± 0.013</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>511</td>
<td>0.965</td>
<td>0.074 ± 0.013</td>
</tr>
<tr>
<td>Forest 3a</td>
<td>$j(\text{NO}_2)$</td>
<td>601</td>
<td>0.968</td>
<td>0.024 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>313</td>
<td>0.958</td>
<td>0.026 ± 0.006</td>
</tr>
<tr>
<td>Forest 3b</td>
<td>$j(\text{NO}_2)$</td>
<td>589</td>
<td>0.964</td>
<td>0.015 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>266</td>
<td>0.900</td>
<td>0.020 ± 0.015</td>
</tr>
<tr>
<td>Forest 4</td>
<td>$j(\text{NO}_2)$</td>
<td>537</td>
<td>0.980</td>
<td>0.019 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>256</td>
<td>0.963</td>
<td>0.021 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}_2h$</td>
<td>365</td>
<td>0.961</td>
<td>0.022 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}<em>2h</em>{\text{m}}$</td>
<td>329</td>
<td>0.929</td>
<td>0.021 ± 0.004</td>
</tr>
<tr>
<td>Clearing 2</td>
<td>$j(\text{NO}_2)$</td>
<td>557</td>
<td>0.961</td>
<td>0.061 ± 0.011</td>
</tr>
<tr>
<td></td>
<td>$j(\text{O}^1\text{D})$</td>
<td>381</td>
<td>0.971</td>
<td>0.067 ± 0.015</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}_2h$</td>
<td>383</td>
<td>0.910</td>
<td>0.062 ± 0.014</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}<em>2h</em>{\text{m}}$</td>
<td>350</td>
<td>0.924</td>
<td>0.062 ± 0.014</td>
</tr>
</tbody>
</table>

$\text{ECHO Site (Typical)}^b$

- Forest all
- Clearing all

$^a$Conditions are ~8 days in 2002 and ~6 days in 2003. Data were not considered where $j(\text{NO}_2) < 1 \times 10^{-6}$ s$^{-1}$ and $j(\text{O}^1\text{D}) < 5 \times 10^{-8}$ s$^{-1}$ at the forest sites, respectively. Error bars are 1σ.

$^b$The data were considered typical values for the ECHO forest and clearing under overcast conditions.

may have introduced scatter in addition to possible local differences discussed in section 3.1. Nevertheless, the dependencies were linear in good approximation and similar slopes were derived for $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$.

[23] Corresponding results were obtained on other overcast days and for other forest and clearing positions. Table 3 shows a summary of linear correlation coefficients and mean ratios $f$ of photolysis frequencies for all positions from selected overcast days within the different campaign periods. The selection criterion was that on these days the data were considered typical values for the ECHO forest and clearing under overcast conditions.

[24] A linear relationship between above and below canopy spectral actinic flux and photolysis frequencies under overcast conditions was not surprising because the angular distribution of UV sky radiance is usually independent of time and wavelength in good approximation [Grant and Heisler, 1997]. Moreover, similar attenuation factors for different photolysis frequencies pointed toward a wavelength-independent attenuation of actinic flux by the forest. Figure 9 shows actinic flux spectra and ratios of spectra on 17 August 2003 under overcast conditions. This day was selected because the diode array spectroradiometer was operative providing above forest data up to 700 nm. Except for few wavelength positions, measurements of SR 2 (total), SR 2 (diffuse) and SR 3 (diode) above the forest agreed within about 5%. Below 550 nm structures of the spectra were reproduced more precisely by the scanning instruments SR 1 (forest) and SR 2 (roof) because of higher spectral resolutions. This explained the higher scatter of the ratios SR 1/SR 3 in this wavelength range. Spectral resolutions of SR 1 and SR 3 were comparable above 550 nm and consequently the scatter was reduced in this range.

[25] In general the ratios were fairly constant up to 700 nm. In a range 500–650 nm ratios were slightly increased with maxima around 550 nm about 25% (forest) and 10% (clearing) above the means below 500 nm, respectively. The constant ratios below about 500 nm explained the similar attenuation factors for $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ in Table 3. Although $j(\text{NO}_2)$ was affected by the increased fluxes around 550 nm, the integrated effect was not significant within the error limits. At wavelengths above 700 nm actinic flux increased strongly at the forest and the clearing locations. This can be explained by an increased transmission of the foliage. However, no photochemical effect was associated with this increase.

3.2.2. Clear-Sky and Broken Cloud Conditions

[26] Figure 10 shows diurnal variations of photolysis frequencies $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$ on a clear-sky day (15 July 2003) above the forest and at positions clearing 2 and forest 4. Above canopy data of this day were already discussed in section 3.1.1. Below canopy data also exhibited smooth diurnal variations except for sporadic sharp peaks associated with direct sunlight incident through gaps in the foliage. These gaps must have been small compared to the apparent size of the Sun’s disk because the amplitudes of the peaks were much smaller than the contribution of direct sunlight above canopy (mind the
**Figure 9.** (top) Actinic flux spectra obtained on 17 August 2003 at around noon under overcast conditions above the forest (diffuse equals total, and diode), and at positions clearing 2 and forest 4, scaled by factors 7 and 10, respectively (from top to bottom). (bottom) Ratios of spectra from Figure 9 (top).

The results obtained so far were consistent with the foliage being virtually opaque toward radiation at wavelengths below about 500 nm. Thus the simplest perception of transfer of radiation within the forest in this wavelength range is either absorption by the foliage or transmission through gaps. It should be noted that this concept is by no means new and has for example been implemented in instruments for radiometric measurements of LAIs (e.g.,

**3.3. Analysis of Sky Photographs: Canopy Gap Fractions**

The ratios with regard to total actinic flux above the forest were generally decreasing with wavelength up to about 700 nm. Except for the short periods when direct sunlight was received through gaps, the ratios were much smaller compared with overcast conditions. Whether or not this result was applicable for the forest as a whole is discussed in section 3.4. Mean ratios as in Table 3 were not calculated for clear-sky conditions because of the sporadic influence of peaks and obvious nonlinearities.
Consequently, the distribution of gaps was an essential parameter also determining the actinic flux received at a given location.

In Figures 3 and 4, two examples of sky photographs from the ECHO site were shown. At each forest position, photographs were taken during summer and winter seasons. After digitalization these photographs were converted to gray scale and finally black and white images. From these images the fractions of visible sky, denoted canopy gap fractions in the following, as a function of polar angle were derived by binning and averaging the data regardless of azimuth angles. The conversion to black and white images was made by varying the gray scale limits between black and white until the measured attenuation factors of Table 3 were obtained for the different locations upon integration (see equation (7) for comparison):

\[
f = \int_0^{2\pi} \int_0^{\pi/2} \alpha(\vartheta) L(\vartheta) \sin(\vartheta) d\vartheta d\varphi
\]  

For the winter images a measured attenuation factor \( f = 0.33 \) was used [Bohn et al., 2006]. Calculations were made numerically using a standard overcast (SOC) sky radiance distribution [Grant and Heisler, 1997] after 2\(\pi\)-sr normalization:

\[
L(\vartheta) = \frac{1 + b \cos(\vartheta)}{\pi(2 + b)} \quad b = 1.23
\]

This distribution is an empirical description of measured radiances under overcast conditions which can be used in the UV and VIS range in good approximation [Grant and Heisler, 1997].

It should be noted that this analysis of the photographs was considered semiquantitative because the camera did not monitor UV radiation. Moreover, the relationship between brightness and radiance in the photographs was not necessarily linear and may also have depended on polar angle. The idea behind this was that gaps were much

---

Figure 10. (left) Diurnal variations of \(j(O^1D)\) and \(j(NO_2)\) on 15 July 2003 (clear-sky conditions) above the forest (total and diffuse) and at positions clearing 2 and forest 4 (from top to bottom). Note that the curves for clearing 2 and forest 4 were scaled by factors 7 and 10, respectively. (right) Correlations of forest and clearing data with the diffuse fraction of above forest data. Solid lines indicate approximate linear relationships neglecting outliers caused by direct sunlight with slopes of 0.017 (forest) and 0.052 (clearing) for \(j(O^1D)\) and 0.014 (forest) and 0.035 (clearing) for \(j(NO_2)\). Dashed lines indicate the results from overcast conditions (Table 3) for comparison.
Figure 11. (top) Actinic flux spectra obtained on 19 July 2003 around noon under clear-sky conditions above the forest (total, diode, and diffuse) and at positions clearing 2 and forest 4, scaled by factors 7 and 10, respectively (from top to bottom). (bottom) Ratios of spectra from Figure 11 (top).

brighter than foliage allowing a proper distinction also assignable to the UV.

Figure 12 shows canopy gap fractions obtained for the different positions and seasons. During the winter season (Figure 12, top left), i.e., in the absence of foliage, the results looked comparable for the different forest positions and the clearing, except for areas close to the zenith ($\vartheta \leq 30^\circ$). For comparison, above forest conditions for all seasons ($\alpha = 1$) were also indicated.

During summer (Figure 12, top right) the $\alpha$ were strongly reduced by the foliage. Moreover, the results for the different forest sites were very different despite averaging over azimuth angles. This confirmed the impression of strong irregularity evident in Figure 3. The only similarity with the winter data was that sites with low $\alpha$ at small polar angles during the winter season exhibited extremely low $\alpha$ in the same area during the summer season. This was consistent with the site being situated underneath the crown of a tree. The summer data from the clearing increased strongly at $\vartheta \leq 30^\circ$ (also shown in Figure 12 (left) for clarity). Upon weighting the data with $\sin(\vartheta)$ according to equation (8), differences between the forest and the clearing became insignificant during the winter season (Figure 12, middle left). The dashed curve approaching unity at $\vartheta = 90^\circ$ again indicates above forest conditions explaining the strong reduction of photolysis frequencies during the winter season by effective obstruction of the sky at large polar angles. Despite slightly decreasing radiances with increasing polar angle (equation (9)) this explained the strong attenuation $f \approx 0.33$ already during the winter season.

For the summer season weighting with $\sin(\vartheta)$ (Figure 12, middle right) harmonized the overall impression but there were significant differences remaining between the sites. Moreover, in contrast to winter conditions, the clearing site benefited strongly from the gap in the foliage close to the zenith explaining the increased photolysis frequencies compared with the forest sites.

Figure 12 (bottom) indicates the differences between actinic flux and irradiance by weighting $\alpha$ with the product $\sin(\vartheta) \cos(\vartheta)$ (see equation (6)). Here the relative $\vartheta$ dependence of radiance reception was more comparable to above forest conditions because the importance of large polar angles was diminished by the factor $\cos(\vartheta)$. Therefore, compared to actinic flux, attenuation of irradiance was probably less effective and less dependent on the angular distribution of radiance. On the basis of the data of Figure 12, scaling factors for irradiance under overcast conditions were estimated 20–30% greater than for actinic flux. However, no measurements of spectral irradiance were made during the ECHO project.

3.4. Application of Model Gap Fractions

The dotted curves in Figure 12 (right) show a rough mean of canopy gap fractions for the forest sites by fitting a parameterization as a function of polar angle:

$$\alpha(\vartheta)_{\text{forest}} = 0.027 \exp(-5.0(\vartheta/\text{rad} - 0.57)^{4.9})$$  \hspace{1cm} (10)

The coefficient was chosen to meet the mean attenuation factor $f = 0.02$ (Table 3). For the clearing a similar approach was used to produce an analytical description for summer conditions (see dotted curves in Figure 12 (left)):

$$\alpha(\vartheta)_{\text{clearing}} = \alpha(\vartheta)_{\text{forest}} + 0.97 \cdot \exp(-11.5(\vartheta/\text{rad} - 0.02)^{2.9})$$  \hspace{1cm} (11)

The mean canopy gap fractions described by equations (10) and (11) were used to investigate their effect on analytical clear-sky radiance distributions of diffuse sky radiation from literature to reproduce the differences observed between overcast and clear-sky conditions. The day 15 July 2005 was again taken as an example. In Figure 13, forest and clearing data are shown together with modeled data based on photolysis frequencies measured above the forest. The dashed lines were calculated using clear-sky UV-A and UV-B radiance distributions by Grant et al. [1997] for the calculation of $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$, respectively. For example, the following equation was used for the calculation of $j(\text{O}^1\text{D})$ in the forest:

$$j(\text{O}^1\text{D})_{\text{forest,diff}} = j(\text{O}^1\text{D})_{\text{diffuse}} \int_0^{2\pi} \int_0^{\pi/2} \alpha(\vartheta)_{\text{forest}} L(\vartheta, \varphi) \sin(\vartheta) d\vartheta d\varphi$$  \hspace{1cm} (12)
In this equation, $L_J$ is the analytical (2π-sr normalized) UV-B sky radiance distribution by Grant et al. [1997]. For the clearing, a corresponding equation applies by using $\alpha_{\text{clearing}}$ instead of $\alpha_{\text{forest}}$ while for $j(\text{NO}_2)$ the UV-A radiance distribution by Grant et al. [1997] was applied.

The agreement between measured and modeled data in Figure 13 was satisfactory given the simplicity of the approach. Moreover, Figure 13 (right) shows that compared with overcast conditions the effects observed for clear-sky conditions could be reproduced, namely, lower ratios, a nonlinearity for the clearing data and a more pronounced effect for $j(\text{NO}_2)$ (UV-A) than for $j(\text{O}_1\text{D})$ (UV-B) (see Figure 10). Thus these effects were related with the differences in sky radiance distributions and the confined fields of view at forest and clearing positions. The dashed lines in Figure 13 (right) were calculated using the SOC radiance distribution of equation (9) and therefore correspond to the mean attenuation factors given in Table 3.

Figure 12. Results of fish-eye photograph analysis. (top) Canopy gap fraction $\alpha$ as a function of polar angle $\theta$ at winter and summer seasons for the different forest sites (solid lines) and the clearing (dashed lines). The clearing results for the summer season (indicated by dashed lines) are shown for clarity. The dashed line in Figure 12 (left) at $\alpha = 1$ indicates above forest conditions. (middle and bottom) Same as Figure 12 (top) but for the products $\alpha \sin(\theta)$ contributing to actinic flux and $\alpha \times \sin(\theta) \cos(\theta)$ contributing to irradiance, respectively (see text). Dotted curves show rough mean dependencies of $\alpha$ for (left) the clearing and (right) forest positions (equations (10) and (11)).
The dotted curves in Figure 13 (left) indicate the mean total photolysis frequencies expected from diffuse and direct contributions, e.g., for $j(O_1D)$:

$$j(O_1D)_{\text{forest, tot}} = j(O_1D)_{\text{forest, diff}} + j(O_1D)_{\text{direct}} \alpha(x)_{\text{forest}} \quad (13)$$

A comparison of modeled and measured total photolysis frequencies showed that the mean effect of direct sunlight was overestimated by the model. However, this could be explained by the strong variability of the size of the gaps also evident in Figure 3. The diffuse sky radiation incident at a forest position seemed to be dominated by a number of relatively large gaps. The chance that the Sun moved across one of these large gaps was small for a selected location but there were other, few locations in the vicinity where this happened (Sun flecks). If at these locations the Sun was fully visible, the actinic flux was increased very strongly, e.g., by a factor of ~30 for $j(NO_2)$ at around noon. Because this increase affected only confined areas at a time, it remained mostly unobserved. However, the average effect of these bright regions for the forest mean of the photolysis frequencies must have been significant and should be described correctly by equation (13).

On the basis of the model calculations, the integrated, daily fractions of photolysis frequencies $j(O_1D)$ and $j(NO_2)$ received on average at forest and clearing locations were summarized in Table 4 for 15 July 2003. The fractions from diffuse sky radiation were slightly smaller compared with overcast conditions, as expected from Figure 13 (right). The fractions from direct sunlight were similar for clearing and forest positions because in the model treatment the clearing did not receive direct radiation through the main gap in the canopy. Of course, this was only true for the clearing close to ground level. The fractions of total actinic flux for the clearing were different for $j(O_1D)$ and $j(NO_2)$, and also differed significantly from the mean result under overcast conditions ($f = 0.07$, Table 3). However, for the forest the overall effect was very similar for $j(O_1D)$, $j(NO_2)$ and compared with overcast conditions. Thus a mean attenuation factor $f = 0.02$ applied for all conditions close to ground level in...
Taking an above forest photolysis frequency $j(\text{NO}_2)$ of $8 \times 10^{-3} \text{ s}^{-1}$, $[\text{NO}_2]_{\text{PS}} = 390 \text{ pptV}$ was obtained ($T = 298 \text{ K}$, $p = 1000 \text{ hPa}$, $k_{14} = 1.9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ [Sander et al., 2003]). For the clearing and forest positions concentrations of 19 pptV and 10 pptV were calculated, using $j(\text{NO}_2) = 3.0 \times 10^{-3} \text{ s}^{-1}$ and $1.6 \times 10^{-4} \text{ s}^{-1}$, respectively (modeled mean $j(\text{NO}_2)$ of Figure 13). Thus the concentration of NO was expected to be reduced substantially within the forest. Measurements on 15 July 2005 showed significantly lower NO concentrations above the canopy ($\sim 50 \text{ pptV}$) and NO concentrations in reasonable agreement with the PS estimate 9 m above ground at the tower ($\sim 30 \text{ pptV}$) (F. Rohrer, private communication, 2005). The discrepancy above the forest was explainable qualitatively by the presence of RO$_2$ and HO$_2$ radicals and possibly transport processes diminishing the differences between above and below canopy conditions close to canopy top.

[46] With regard to NO$_3$, photostationary state concentrations were estimated considering the following reactions:

$$\text{O}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_3$$  (16)
$$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$$  (17)
$$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$$  (18)
$$\text{NO}_3 + \text{C}_2\text{H}_6 \rightarrow \text{products}$$  (19)
$$\text{NO}_3 + \text{C}_{10}\text{H}_{16} \rightarrow \text{products}$$  (20)
$$\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$$  (21)
$$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}^3\text{P}(\rightarrow \text{NO}_2 + \text{O}_3)$$  (22)
$$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$$  (23)

Formation of N$_2$O$_5$ and its reaction back to NO$_3$ (equations (17) and (18)) cancelled out in the PS approach. Reaction with isoprene ($\text{C}_3\text{H}_6$) and monoterpene ($\text{C}_{10}\text{H}_{16}$) (equations (19) and (20)) were assumed the major loss processes for NO$_3$ in addition to reaction with NO (equation (21)) and photolysis (equations (22) and (23)). The photolyses of NO$_3$ were accounted for by a combined rate constant $j(\text{NO}_3)$. $[\text{NO}_3]_{\text{PS}}$ was then given by

$$[\text{NO}_3]_{\text{PS}} = \frac{([\text{NO}_3] - [\text{NO}_3]_{\text{PS}}) \text{O}_3 k_{16}}{j(\text{NO}_3) + [\text{NO}_3]_{\text{PS}} k_{21} + [\text{C}_3\text{H}_6] k_{19} + [\text{C}_{10}\text{H}_{16}] k_{20}}$$  (24)

For the O$_3$ reaction a rate constant $k_{16} = 3.2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ was used (298 K [Sander et al., 2003]). For $j(\text{NO}_3)$ measured data on 19 July 2003 above the forest (Table 1) and similar attenuation factors as for $j(\text{NO}_2)$ were used. For $[\text{NO}_3]_{\text{PS}}$ calculated and measured concentrations were inserted and $k_{21} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (298 K [Sander et al., 2003]). Isoprene and total monoterpene concentrations were about 2.3 and 0.25 ppbV around noon on 15 July 2003 [Spirig et al., 2005]. For isoprene a rate constant $k_{19} = 7.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ was used [Atkinson and Arey, 2003]. Because different monoterpenes could not be distinguished by the

**Table 4.** Integrated, Modeled Daily Fractions of Photolysis Frequencies Calculated for the Forest and the Clearing 2 m Above Ground With Regard to Above Forest Data on 15 July 2003 (Clear-Sky)

<table>
<thead>
<tr>
<th>Size</th>
<th>Clearing</th>
<th>Forest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>[O3:D]</td>
<td>[NO3]</td>
</tr>
<tr>
<td></td>
<td>0.057</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>0.027</td>
<td>0.025</td>
</tr>
<tr>
<td>Total</td>
<td>0.048</td>
<td>0.037</td>
</tr>
</tbody>
</table>

*On this day the integrated above forest fractions of diffuse sky radiation were 0.70 and 0.54 for $j(\text{O}_3:D)$ and $j(\text{NO}_3)$, respectively.

3.5. Implications for the ECHO Site Photochemistry

[43] Profile measurements of photolysis frequencies in the forest showed that photolysis frequencies dropped rapidly within about 5 m below canopy top followed by a more gradual reduction toward the ground [Bohn et al., 2006]. On average 4% of above forest values were found in a range below about 28 m. Thus the measurements of this work, collected at forest and clearing sites close to ground level were in a range representative for the bulk of the forest.

[44] An important issue regarding the chemistry within the forest is what fraction of reactive BVOCs emitted by plants is injected into the boundary layer and what fraction is already converted within the forest by reactions with OH, NO and O$_3$ [e.g., Makar et al., 1999; Stroud et al., 2005]. At the ECHO site the principal reactive BVOC was isoprene that was emitted during daytime by oak trees in the surrounding forests. Typical maximum concentrations were 2–4 ppbV in the early afternoon [Spirig et al., 2005]. Because OH concentrations were found to be linearly correlated with photolysis frequencies, degradation of isoprene by OH within the forest was estimated negligible except for residence times exceeding about one hour [Bohn et al., 2006]. Within the canopy there may have been an active zone characterized by increased actinic fluxes, strong emissions and slow transport caused by dense foliage but this layer had a very limited extension of a few meters.

[45] In contrast to OH, daytime NO$_3$ radical concentrations could have been increased below canopy as a result of reduced photolysis frequencies and reduced NO concentrations from NO$_2$ photolysis. In a first step, the photostationary equilibrium of NO, NO$_2$ and O$_3$ on 15 July 2005 was examined. At around noon on that day, O$_3$ and NO$_x$ levels were about 50 ppbV and 1.5 ppbV, respectively (F. Rohrer, private communication, 2005). Considering photolysis of NO$_2$ (equations (3) and (4)) and reaction of NO with O$_3$,

$$\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$$  (14)

photostationary state (PS) concentrations of NO were calculated using

$$[\text{NO}]_{\text{PS}} = \frac{[\text{NO}_2]j(\text{NO}_2)}{[\text{O}_3]k_{14} + j(\text{NO}_2)}$$  (15)

Table 4. Integrated, Modeled Daily Fractions of Photolysis Frequencies Calculated for the Forest and the Clearing 2 m Above Ground With Regard to Above Forest Data on 15 July 2003 (Clear-Sky)
For the monoterpenes the (isoprene) above canopy and \(^{1}C_{2}\) was probably increased toward the morning and the \(^{1}C_{2}\) of Isoprene and Monoterpenes With Regard to Reactions 1.0 of 30 (30) above canopy and 10 (30) below canopy. For the monoterpenes noted above, loss rates \(^{3}\) were processed within the forest. These low fractions were compared to the BVOC loss rates using a mean forest height of 28 m below canopy. This revealed that no more than about 0.8% of isoprene and 3.4% of monoterpenes were processed within the forest. These low fractions were consistent with in-forest residence times of BVOCs of the order 2–3 min that were obtained by comparing the BVOC fluxes with the BVOC inventories below canopy as reported by Spirig et al. [2005].

In conclusion, chemistry in the forest at the ECHO site was probably too slow for a significant reduction of net emissions of isoprene and monoterpenes into the boundary layer. However, the situation might have been different for compounds with exceptionally fast rate constants with regard to NO\(_3\) or \(O_3\). Moreover, the relative importance of NO\(_3\) was probably increased toward the morning and the evening when BVOC concentrations and fluxes were lower. More detailed studies considering composition, chemistry and transport are therefore needed to assess the roles of NO\(_3\) and \(O_3\) as daytime reactants within forests.

4. Conclusions

Spectral actinic flux measurements in a deciduous forest at the ECHO field site indicated strongly reduced photolysis frequencies close to ground level. About 2% of

### Table 5. Results of Photostationary State Calculations of NO and NO\(_3\) Concentrations on 15 July 2003 According to Equations (15) and (24)\(^{a}\)

<table>
<thead>
<tr>
<th>Location</th>
<th>Quantity</th>
<th>Above Forest</th>
<th>Clearing</th>
<th>Forest</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j(\text{NO})), (10^{-3}) s(^{-1})</td>
<td>8.0</td>
<td>0.30</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>([N\text{O}]_{ps}), pptV</td>
<td>385 (50)(^{b})</td>
<td>19 (30)(^{c})</td>
<td>10 (30)(^{d})</td>
<td></td>
</tr>
<tr>
<td>(j(\text{NO})), (10^{-3}) s(^{-1})</td>
<td>19</td>
<td>0.71</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>([N\text{O}]_{ps}), pptV</td>
<td>0.08 (0.18)</td>
<td>0.49 (0.46)</td>
<td>0.53 (0.47)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Measured NO above forest.

\(^{b}\)Measured NO at clearing tower (9 m).

\(^{c}\)Estimated maximum NO in forest.

\[^{d}\text{Measured on 15 July 2003.}^{6}\]

\[^{e}\text{Estimated mean by scaling above canopy concentration.}^{6}\]

\[^{f}\text{Mean NO at clearing tower (9 m).}^{6}\]

\[^{g}\text{Calculated NO concentrations.}^{6}\]

### Table 6. Rate Constants \(k\) for Reactions of Isoprene and Monoterpenes With NO\(_3\), OH and \(O_3\), Estimated and Measured Concentrations \(c\) of NO\(_3\), OH, and \(O_3\) Above and Below Canopy, and Estimated Loss Rates \(L\) of Isoprene and Monoterpenes With Regard to Reactions With NO\(_3\), OH, and \(O_3\) at Concentrations of 2.3 pptV (Isoprene) and 0.25 pptV (Monoterpenes), Respectively

<table>
<thead>
<tr>
<th>Location</th>
<th>Quantity</th>
<th>(k) (isoprene), (cm^3) s(^{-1})</th>
<th>(k) (monoterpenes), (cm^3) s(^{-1})</th>
<th>(c) pptV</th>
<th>(L) (isoprene), pptV h(^{-1})</th>
<th>(L) (monoterpenes), pptV h(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above canopy</td>
<td></td>
<td>(7.0 \times 10^{-13})</td>
<td>(1.0 \times 10^{-10})</td>
<td></td>
<td>(10 – 25)</td>
<td>(4200)</td>
</tr>
<tr>
<td>Below</td>
<td></td>
<td>(1.0 \times 10^{-11})</td>
<td>(1.0 \times 10^{-10})</td>
<td></td>
<td>(65 – 75)</td>
<td>(170)</td>
</tr>
<tr>
<td>Above canopy</td>
<td></td>
<td>(0.08 – 0.18)</td>
<td></td>
<td>(0.2)</td>
<td>(5 \times 10^{4})</td>
<td></td>
</tr>
<tr>
<td>Below</td>
<td></td>
<td>(0.46 – 0.53)</td>
<td></td>
<td>(0.008)</td>
<td>(5 \times 10^{4})</td>
<td></td>
</tr>
</tbody>
</table>

\[^{a}\text{Atkinson and Arey [2003]}.^{6}\]

\[^{b}\text{Atkinson and Arey [2003], estimated mean for monoterpenes.}^{6}\]

\[^{c}\text{See Table 5.}^{6}\]

\[^{d}\text{Typical value, measured on 19 July 2003.}^{6}\]

\[^{e}\text{Estimated mean by scaling above canopy concentration.}^{6}\]

\[^{f}\text{Measured on 15 July 2003.}^{6}\]
above forest values were obtained for all relevant photolysis processes under all conditions. In the tower clearing the situation was more complex with attenuation factors varying in a range 4—7%, dependent on conditions (clear-sky or overcast) and wavelength range. Transmission by the foliage below 500 nm was found to be insignificant except for gaps that allowed unblocked view of the sky. The mean distribution of gaps derived from sky photographs explained observed differences between overcast and clear-sky conditions using diffuse sky radiance distributions from literature. Regarding reactive BVOC chemistry in the forest, the strong reduction of photolysis frequencies implied a major disruption of primary OH production and photochemical conversion. On the other hand, a large fraction of monoterpene loss within the forest was attributed to daytime NO₃ radicals that benefited from reduced photolysis and reduced NO concentrations. However, the resulting total in-forest degradations of 0.8% for isoprene and 3.4% for monoterpene were considered insignificant.

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