Observation of strong NOx release over Qiyi Glacier, China

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Abstract. NOx is released from sunlit snowpack surfaces, and this significantly influences the oxidizing capacity of the clean boundary layer atmosphere and the potential interpretation on the historical atmospheric composition recorded in the ice core. The Tibetan Plateau is an important snow-covered region in the northern midlatitudes, with strong solar radiation and relatively high NO₃⁻ in snow/ice. Released NOx on the glacier surface of the Tibetan Plateau should have a higher concentration than in Antarctic and Arctic regions. To verify this hypothesis, field observations were carried out at 4600 m asl in Qiyi Glacier in late August 2004. In late August, the surface ultraviolet-B (UVB) radiation level at 4600 m asl in Qiyi Glacier reached >4.5 W/m² and was increased by the strong reflection of snow/ice and clouds against the sun, and strengthened by the topographical effect. The concentrations of NO₃⁻ and NH₄⁺ in water from melting snow were hardly detected, but the average concentration (±1σ) of NO₃⁻ in snow samples was 8.7 ± 2.7 μmol/L. Strong correlations were observed between NOx (NO₂) mixing ratios and UVB radiation levels in the Tibetan glacier. Vertical experiments revealed a negative gradient of NOx (NO₂) mixing ratios from the glacier snow surface to a height of 30 cm. As a result of the high levels of UV radiation and high NO₃⁻ concentrations in snow/ice, the mixing ratios of NOx released by fresh snow in Qiyi Glacier in late August reached to several parts per billion (ppbv) and were approximately 1 order of magnitude higher than those observed in polar regions. This observation provides direct evidence to support the research hypothesis and confirms that the release of high concentrations of NOx in the boundary layer of highland glaciers and snow surfaces.

1 Introduction

NOx and other gases may be released from sunlit snowpack in Antarctic and Arctic regions, significantly influencing the oxidizing capacity of the polar boundary layer atmosphere and the potential interpretation of the historical atmospheric composition recorded in the ice core (Honrath et al., 1999; Summer and Shepson, 1999; Davis et al., 2001; Mauldin et al., 2001; Zhou et al., 2001; Domine and Shepson, 2002; Honrath et al., 2002; Jone and Wolff, 2003; Mauldin et al., 2004; Wang et al., 2011). The ice core record of nitrate was used for the estimation of preindustrial NO emission levels (Preunkert et al., 2003). This promotes scientific awareness and research on the importance of photochemical processes on polar ice surfaces (Bottenheim et al., 2002; Davis et al., 2004; J. Erbland et al., 2013; Van Dam et al., 2015; Bock et al., 2016; Chan et al., 2018). NOx release in the photolysis experiments of natural snow was observed not only in polar regions but also in midlatitudes...
during winter (Honrath et al., 2000). Therefore, solar radiation–induced release of NOx or other trace substances from snow/ice is a common phenomenon. Cotter et al. (2003) proposed a possible mechanism of snow nitrate (NO$_3^-$) photolysis to produce NO/NO$_2$, and this mechanism has been confirmed by laboratory research (Boxe et al., 2003; Jacobi and Hilker, 2007) and many field observations (Jones et al., 2000; Dibb et al., 2002). More complicated and further improved mechanism can be found in the following researches (Wren et al., 2011; Domine et al., 2013; Morenz and Donaldson, 2017) and review paper by Bartels-Rausch et al. (2014).

The Tibetan Plateau, with an area of 2,500,000 km$^2$, is an important snow-covered region in the northern midlatitudes. The characteristics of clean air, high altitude (>4000 m on average), and high surface albedo (including snow/ice reflection) subject this region to high levels of solar radiation (Chen et al., 2015). Its lower atmosphere has a strong photochemical oxidizing capacity with strong photolysis of surface O$_3$ and high production potential of OH radicals as high as 4–5 $\times$ 10$^{-5}$ s$^{-1}$ and 1–4 $\times$ 10$^6$ s$^{-1}$, respectively (Lin et al., 2008). Under the influence of the westerlies and Asian monsoons, the chemical compositions of snow in the northern and southern regions of the plateau are different, but the NO$_3^-$ concentration in the Tibetan Plateau (1.7–4.2 μmol L$^{-1}$) is higher than that (0.23–2.0 μmol L$^{-1}$) in Arctic and Antarctic regions (Li et al., 2000; Xiao et al., 2002). Therefore, photochemical reactions in the snow surface must be stronger and the NOx concentration must be higher in the Tibetan Plateau than in Arctic and Antarctic regions. To verify this hypothesis, this paper reports observations of NOx concentration and ultraviolet-B (UVB) radiation levels in late August 2004 on the surface of Qiyi Glacier (July 1 Glacier), Tibetan Plateau.

2 Site, observations, and methods

The observation of NOx on the surface of Qiyi Glacier (39.241°N, 97.756°E, 4600 m asl) was conducted from 26 to 31 August 2004. Qiyi Glacier is located in the hinderland of Qilian Mountains and is approximately 116 km away from the southwestern border of Jiayuguan City, Gansu Province. The glacier is situated on the slopes with a gradient of <45°, and its terminus is facing north (Fig. 1). The altitude of the glacier summit is 5150 m, and that of the frontier glacier tongue is approximately 4300 m. At 4600 m asl, it’s belonged an ablation zone of the glacier with occasional summer snowfall.

NO$_2$ was measured through chemiluminescence using the LMA-3D Luminox monitor (Unisearch Associates Inc., Ontario, Canada). Air was drawn through the LMA-3D vacuum pump and allowed to flow across a fabric wick saturated with a specially formulated luminol solution. When NO$_2$ encounters the wick, the luminol oxidizes and produces chemiluminescence (in the region of 425 nm). A photomultiplier tube measures the light produced and converts it into a signal that is proportional to the NO$_2$ concentration. The air is passed through a converter, where NO in the air is oxidized to NO$_2$. The detection limit is <10 ppt NO$_2$, and the response time is 0.2 s. The sample inlet was close to the snow surface (<3.0 cm). Solar UVB radiation levels (280–320 nm) were measured using a UVB pyranometer (Model UVB-1, Yankee Environmental Systems Inc., MA, USA). The measurement technique involves the use of colored glass filters and a highly stable UV-sensitive fluorescent phosphor to stop all of the sun’s visible light and convert UV photons into visible light, which is then measured using a solid-state
photodetector. The response time of the UVB-1 pyranometer is approximately 0.1 s. The winds were measured using Model 05103 Wind Monitor (R.M. Young Company, Michigan, USA). The relative humidity measured using a Assmann ventilation dry and wet meter. The snow samples were collected from nonmelted snow on the glacier surface, and the water samples were collected from melting snow from high altitudes flowing in an ice ditch. A DIONEX2100 ion chromatograph (AS14 column for anion separation and CS12 column for cation separation) was used for ion analysis on the samples. Power was supplied by a HONDA SHX2000 gasoline generator, which was 100 m away from the analyzers. The line between the observation and generator positions was perpendicular to the dominant wind direction (katabatic and anabatic winds).

The Tropospheric Ultraviolet-Visible Radiation Model (TUV4.1 version, Madronich and Flocke, 1997; https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model) was used to simulate ground UVB radiation on clear sunny days. The changed input parameters are summarized as follows. The total ozone amounts overhead were obtained from Total Ozone Mapping Spectrometer data, and the values from 26 to 30 August were 297, 291, 282, 275, and 273 DU, respectively. The aerosol optical thickness at 340 nm was set at 0.19. The vertical profiles of ozone, air density, and air temperature in the northern region of the Tibetan Plateau (32‒40°N, 70‒110°E) were obtained from SAGE-II satellite remote sensing data (the NASA Langley Research Center, USA, http://www.sage2.larc.nasa.gov/data/v6_data/Version 6.2). The surface albedo was set at 0.9. The model results are presented in Fig. 2. Treatments similar to the TUV model were applied in the UVB simulation for the north valley of Qomolangma (Lin et al., 2008).

3 Result

It snowed heavily during 22–23 August 2004, and then it was cloudy; the wind speed was strong on 24–25 August. Measurements were obtained from this fresh snow surface from 26 August, through its melting and spoilage processes, and no new snowfall was noted in the following observation days. After heavy snowfall, 26 August was the first sunny day. The wind was strong around noon and in the afternoon, and relatively low in the morning and evening. The clouds drifted one after another, and the UVB radiation level exhibited large variations during the daytime. Signs of Loess dust falling into glaciers were clearly identified around this time (Figure S1).

3.1 Measurement and simulation of UVB radiation

Figure 2 shows the diurnal variation in UVB radiation levels measured using the UVB-1 during the observation period. UVB radiation levels could exceed 4.5 W/m², which was much higher than the radiation level measured at noon in June (3.8 W/m², with a lower solar zenith at noon) at an altitude of 5050 m (Lin et al., 2008) and at Zhongshan Station (69°22'S, 76°22'E), Antarctica (Zheng et al., 2020). The highest UVB value on clear days (27 and 29 August) was lower than that on cloudy days (26, 28, and 30 August). The measured UVB values were higher than the simulated values even when the surface albedo value was set at 0.9 (Fig. 2). In the daytime of 28 and 29 August, the relative humidity was 61%–94%, with a water vapor density
of 2.1–4.6 g/m$^3$. During 12:00–15:00 on 31 August 2004, six surface albedos in different places on the glacier were obtained using a UVB pyranometer (UVB-1). The measured albedo values on 31 August 2004 varied from 0.24 to 0.58, with an average of 0.42 ± 0.11 (Table 1). The values were lower than ultraviolet albedos (0.70–0.90) over the fresh snow surface (Blumthaler and Ambach, 1988; Chen, 1995; Feister and Grewe, 1995).

### 3.2 Inorganic ion concentrations in snow and water samples

Table 2 lists the inorganic ion concentrations in snow and water samples. Samples were collected during the daytime. SO$_4^{2-}$ was the most abundant anion, followed by Cl$^-$ and NO$_3^-$, and Ca$^{2+}$ was the most abundant cation, followed by Na$^+$ and Mg$^{2+}$ (Table 2). The concentrations of NO$_3^-$ and NH$_4^+$ in the snow samples were much higher than those in the water samples, in which NO$_3^-$ and NH$_4^+$ in the water samples was difficult to detect. The average concentration ($±1σ$) of NO$_3^-$ in 10 snow samples was 8.7 ± 2.7 μmol/L (0.44 ± 0.13 ppm (w/w)), which was much higher than that in Antarctic (0.4–2.0 μmol/L) and Arctic (1.9–2.6 μmol/L) snow/ice regions (Li et al., 1995; Xiao et al., 2002).

### 3.3 Relationships between NOx and UVB

Figure 3 shows variations in the mixing ratios of NO$_2$ and NOx and UVB radiation level on 26 August 2004. Before 16:00, the LMA-3D was used for continuously measurement for 1 or 2 hours in fixed NO$_2$ or NOx mode. At 16:00, the instrument switched to automatic switching mode, and NO$_2$ and NOx were measured in turns for 1 minute. The change in NOx (NO$_2$) concentration corresponded well with the increase and decrease in UVB radiation, and a clear correlation was observed between them (Fig. 3 and Fig. S2). When the UVB radiation level was high, the concentration of NOx (NO$_2$) could reach magnitudes of several parts per billion, approximately 1 order of magnitude higher than that observed in polar regions (Ridley et al., 2000; Davis et al., 2001; Davis et al., 2004a). After sunset, the concentration of NOx (NO$_2$) gradually decreased to the background level at night. Hence, a sunlit condition was a key factor influencing NOx (NO$_2$) concentrations on the surface of ice and snow. According to the slopes in Fig. S2, with 1 unit change in UVB radiation level, NO$_2$ and NOx changed 0.47 and 1.17 ppb, respectively. NO$_2$ accounted for 40.2% of the total NOx.

In the following days, the snow melted further. Strong correlations were observed between NOx (NO$_2$) and UVB (Fig. S3–S5), similar to the observations on 26 August, but with much lower mixing ratios of NOx and NO$_2$. On 30 August, we cleared the remaining surface snow near the observation region, and the sample inlet was deployed near the glacier ice surface. Figure 4 shows variations in NO$_2$, NOx, and UVB on 30 August 2004, and Fig. S6 shows correlations between NOx (NO$_2$) and UVB.

On the glacier ice surface, a strong relationship was observed between NOx (NO$_2$) and UVB radiation levels. However, unlike on the snow surface, the ratio of NO$_2$ to NOx on the glacier ice surface was approximately 90%, which means that NO$_2$ rather than NO was directly released from the ice surface. In addition, the levels of NOx (NO$_2$) released on the glacier ice surface were much lower and more fluctuating than those on the fresh snow surface.
Wind speed can be an important factor influencing the processes of snowpack release and air dilution. To weaken the influence of these processes on the relationship between NOx and UVB, the corresponding data of NOx, NO2, and UVB radiation at different binned wind speeds (0.5 m/s as an interval) were calculated, and the relationships between the binned NOx (NO2) mixing ratios and UVB radiation levels are shown in Fig. 5. Similar results were obtained from no binned data (Fig. S2), but with a lower ratio (30.8%) of NO2 to NOx. Gaseous NO2 was the main product of NO3− photolysis in snow or ice (Jones et al., 2000; Dibb et al., 2002; Jacobi and Hilker, 2007), and only those NO2 on the snow surface can be directly released into the air; the remaining NO2 is further photodissociated into NO (Dubowski et al., 2001; Boxe et al., 2005). Our observations confirm these conclusions.

Similarly, to determine the influence of wind speed on NOx (NO2) release by weakening the influence of UVB on the relationship between NOx and wind speed, data on wind speed, NOx level, and NO2 level were reclassified according to the UVB binned data (0.5 W/m2 as an interval), and the relationships between the binned wind speed and NOx (NO2) were obtained (Fig. 6). Significant correlations were observed between NOx (NO2) and wind speed, indicating that wind speed could promote NOx (NO2) release from the snowpack, and the close values of slopes also indicated the same effect of wind on NO and NO2 release rates.

### 3.4 Variations in vertical NOx distribution at different sample heights

On 27 August 2004, experiments were conducted with three sampling inlet heights (1.5, 3.0, and 30 cm above the surface level every 5 minutes) to obtain vertical changes in NOx/NO2 concentrations, and the results are shown in Fig. 7. NOx (NO2) mixing ratios at a height of 30 cm were always lower than those at heights of 3.0 and 1.5 cm (except around 13:00) (Fig. 7). During 12:00–14:00, when the UVB radiation levels were high but wind speeds were low, the differences in NOx (NO2) level at heights of 1.5 and 3.0 cm were greater than those at other times. On average, the mixing ratios of NOx (NO2) at heights of 1.5, 3.0, and 30 cm were 0.38 (2.28), 0.44 (0.28), and 0.33 (0.25) ppbv, respectively. These results indicated a decreasing trend of NOx (NO2) concentration with height; that is, the concentrations near the ground were higher than those at a height of 30 cm, which further indicates that the source of NOx (NO2) was sunlit snow or ice. The gradients were significantly higher than those observed in Antarctica (Jones et al., 2001), where a difference of only several parts per trillion (pptv) was observed at a height difference of 2.5 m.

### 4 Discussion

Surface albedo can significantly contribute to UV radiation over the snow/ice surface. The measured values of albedo were lower than ultraviolet albedos (0.70–0.90) over the fresh snow surface (Blumthaler and Ambach, 1988; Chen, 1995; Feister and Grewe, 1995). Furthermore, the particle size and moisture content of the snow affected the glacier albedo. Glaciers melt during the summer. The melting of snow crystals under higher temperatures during the daytime increases the water content.
During the night, when the temperature drops, the recrystallization effect causes increases in snow particle size, thereby reducing the albedo. Another important factor was the deposition of sand and dust (Fig. S1), which blow from surrounding barren mountains as a result of strong winds, making the snow dirty and leading to easy absorption solar radiation, causing the snow particles to melt and the water content to increase, thus reducing the UV albedo.

As stated above, the measured UVB values were higher than the simulated values even when the surface albedo value was set at 0.9, which value can be only found in fresh snow. Albedo is not the only factor to enhance the surface UV radiations. In the Tibetan plateau, studies have observed high surface solar radiation in summer at values frequently larger than the solar constant owing to cloud reflection overhead (Kou et al., 1975; Ren et al., 1999; Li et al.,2000). Although multiple reflections on the cloud overhead might lead to an increase in the ground UVB radiation level, the measurement values on clear and cloudless days (27 and 29 August) were significantly higher than simulated values. A complex terrain might be one of the biggest influence factors. Qiyi Glacier is a valley-shaped glacier, and UVB radiation was observed at a gently sloping mountainside. This might collect strong solar radiation as a result of reflection by the snow covering mountain peaks, resulting in high radiation levels recorded by the instrument. Therefore, model challenges will be faced on simulating the solar radiations over a mountain-valley-shaped glacier surface.

O$_3$ data were not available during observation because of instrument malfunction. However, other observations (Zhu et al., 2006; Lin et al., 2015; Xu et al., 2016) have proven that the background O$_3$ mixing ratio in the Tibetan Plateau is high (Hourly mean can be as high as 100 ppbv and the monthly mean can be as high as >60 ppbv) due to its high altitude. In the daytime of 28 and 29 August, the relative humidity measured using a Assmann ventilation dry and wet meter was 61%–94%, with a water vapor density of 2.1–4.6 g/m$^3$. Additionally, strong UV radiation and abundant water vapor promote OH radical generation through O$_3$ photolysis, which might indicate that glacier surface air has a high oxidizing capacity.

$$O_3 + hv (\lambda \leq 330 \text{ nm}) \rightarrow O (^1\text{D}) + O_2$$

(1)

$$O (^1\text{D}) + H_2O \rightarrow 2\text{OH}$$

(2)

The concentrations of NO$_3^-$ and NH$_4^+$ in the snow samples were much higher than those in the water samples, in which NO$_3^-$ and NH$_4^+$ in the water samples was difficult to detect. This phenomenon might indicate a quick loss of NO$_3^-$ during the melting process under sunlight. However, we only collected limited number of water samples, so it was difficult to determine whether this phenomenon was universal.

Strong correlations were observed between the NOx (NO$_2$) mixing ratios and UVB radiation levels obtained from Qiyi Glacier, Tibetan Plateau. The correlations were much more significant than the findings in the North and South pole regions, where no such direct and strong correlations were reported. Moreover, the mixing ratios of NOx released by fresh snow in Qiyi Glacier in late August reached up to several parts per billion (ppbv), approximately 1 order of magnitude higher than those observed in the polar region. This observation provides direct evidence to support the hypothesis that the concentrations of NOx released on the glacier surface of the Tibetan Plateau are higher than those in Antarctic and Arctic regions. Due to the limited covering areas of mountain-valley glaciers which are less than the huge covering areas in Antarctic and Arctic regions, the photochemical generation NOx left from the snowpack in Tibetan plateau might be more easily to be transported to somewhere.
else by advection, and hardly return to the snow by deposition through the reaction between NOx and HOx to form HNO₃ and HO₂NO₂ (Honrath et al., 2002; Oncley et al., 2004; Munger et al., 1999; Cohen et al., 2007), resulting in the loss of nitrogen in the snow. High levels of NOx release certainly affect atmospheric chemical processes in the boundary layer of highland glaciers and snow surfaces as well as the conversion equation of snow/ice records to real atmospheric concentrations.

5 Conclusions

In late August, the surface UVB radiation level at 4600 m asl in Qiyi Glacier reached >4.5 W/m² and was enhanced by the strong reflection of snow/ice and clouds against the sun, which was strengthened by the topographical effect. At Qiyi Glacier, a clear phenomenon of dust/sand deposition exists, which helps to absorb sunlight, promotes the melting of ice and snow, increases the air humidity, and reduces the surface albedo. The average concentration (±1σ) of NO₃⁻ in 10 snow samples was 8.7 ± 2.7 μmol/L, but NO₃⁻ was barely detected in three melting snow (water) samples. Very strong correlations were observed between the NOx (NO₂) mixing ratios and UVB radiation levels obtained from Qiyi Glacier, Tibetan Plateau. Vertical experiments showed a negative gradient of NOx (NO₂) mixing ratios from the glacier snow surface to a height of 30 cm. Moreover, the mixing ratios of NOx released by fresh snow in Qiyi Glacier in late August reached up to several parts per billion (ppbv). This might be due to strong UV radiation and much higher NO₃⁻ concentrations in snow/ice in the Tibetan Plateau comparing with that in Antarctic and Arctic regions. Further in-depth researches needed to access the effect of such high levels of NOx release on the atmospheric chemical processes in the boundary layer of highland glaciers and snow surfaces.

Author contributions

WL and TZ designed the research plan. WL, FW, and TZ carried out the observation. CY contributed the idea on data analysis. WL wrote the manuscript with scientific input from all co-authors.

Competing interests

The authors declare that they have no conflicting interests.

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Table 1. Surface albedos measured on 31 August 2004 in different places at Qiyi Glacier

| Place No | Average albedo | Standard deviation | Measurement time on 31 August |
|----------|----------------|-------------------|-------------------------------|
| 1        | 37.7%          | 8.0%              | 11:40–12:00                   |
| 2        | 57.8%          | 3.0%              | 12:00–12:30                   |
| 3        | 44.3%          | 2.6%              | 12:30–12:55                   |
| 4        | 42.4%          | 5.0%              | 12:55–13:06                   |
| 5        | 23.4%          | 0.5%              | 13:06–13:20                   |
| 6        | 45.4%          | 4.1%              | 13:20–13:45                   |

Table 2. Concentrations of inorganic ions in snow and water samples of Qiyi Glacier (values in ppm by weight)

| Sample     | Sample time | [Cl]  | [NO₃⁻] | [SO₄²⁻] | [Na⁺]  | [NH₄⁺] | [K⁺]  | [Mg²⁺] | [Ca²⁺] |
|------------|-------------|-------|--------|---------|--------|--------|-------|--------|--------|
| Water #1   | 2004-8-31   | 0.55  | <0.01  | 0.63    | 0.47   | <0.01  | 0.05  | 0.56   | 2.89   |
| Water #2   | 2004-8-31   | 0.28  | <0.01  | 1.00    | 0.73   | 0.03   | 0.05  | 0.54   | 4.11   |
| Water #3   | 2004-8-30   | 0.65  | <0.01  | 0.80    | 0.73   | 0.01   | 0.10  | 0.48   | 3.00   |
| Snow #1    | 2004-8-27   | 0.65  | 0.34   | 1.17    | 0.57   | 0.10   | 0.09  | 0.14   | 5.43   |
| Snow #2    | 2004-8-27   | 0.49  | 0.26   | 0.76    | 0.22   | 0.06   | 0.05  | 0.10   | 3.69   |
| Snow #3    | 2004-8-27   | 0.76  | 0.45   | 1.51    | 0.46   | 0.08   | 0.09  | 0.21   | 9.24   |
| Snow #4    | 2004-8-27   | 0.71  | 0.48   | 1.42    | 0.46   | 0.08   | 0.08  | 0.12   | 6.07   |
| Snow #5    | 2004-8-27   | 0.54  | 0.37   | 1.05    | 0.27   | 0.06   | 0.04  | 0.47   | 6.58   |
| Snow #6    | 2004-8-27   | 0.55  | 0.34   | 0.99    | 0.25   | 0.03   | 0.05  | 0.34   | 5.44   |
| Snow #7    | 2004-9-29   | 1.86  | 0.56   | 0.66    | 1.25   | 0.56   | 1.18  | 0.38   | 2.11   |
| Snow #8    | 2004-8-29   | 0.82  | 0.53   | 0.63    | 0.31   | 0.37   | 0.43  | 0.43   | 2.23   |
| Snow #9    | 2004-8-29   | 0.41  | 0.68   | 0.82    | 0.07   | 0.14   | 0.04  | 0.19   | 3.47   |
| Snow #10   | 2004-8-29   | 0.31  | 0.39   | 0.26    | 0.02   | 0.19   | 0.08  | 0.19   | 1.74   |
Figure 1: Contour map of Qiyi Glacier and the observation site.

Figure 2: Diurnal variations in UVB radiation levels at 4600 m asl at Qiyi Glacier.
Figure 3: Variations in the mixing ratios of NO$_2$ and NOx and UVB radiation levels on 26 August 2004. The data were averaged in 1 minute.

Figure 4: Variations in the mixing ratios of NO$_2$ and NOx and UVB radiation on 30 August 2004. The data were averaged in 10 minutes.
Figure 5: Correlations between NOx (NO$_2$) and UVB radiation levels under different wind speed bins (0.5 m/s as an interval) on 26 August 2004.

Figure 6: Correlations between NOx (NO$_2$) and wind speed under binned UVB radiation on 26 August 2004.
Figure 7: Variations in NOx and NO₂ mixing ratios at different heights (the error bar is 1 standard deviation).