

## HO<sub>x</sub> budgets during HO<sub>x</sub>Comp: A case study of HO<sub>x</sub> chemistry under NO<sub>x</sub>-limited conditions

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Received 13 October 2011; revised 20 December 2011; accepted 28 December 2011; published 10 February 2012.

[1] Recent studies have shown that measured OH under NO<sub>x</sub>-limited, high-isoprene conditions are many times higher than modeled OH. In this study, a detailed analysis of the HO<sub>x</sub> radical budgets under low-NO<sub>x</sub>, rural conditions was performed employing a box model based on the Master Chemical Mechanism (MCMv3.2). The model results were compared with HO<sub>x</sub> radical measurements performed during the international HO<sub>x</sub>Comp campaign carried out in Jülich, Germany, during summer 2005. Two different air masses influenced the measurement site denoted as high-NO<sub>x</sub> (NO, 1–3 ppbv) and low-NO<sub>x</sub> (NO, < 1 ppbv) periods. Both modeled OH and HO<sub>2</sub> diurnal profiles lay within the measurement range of all HO<sub>x</sub> measurement techniques, with correlation slopes between measured and modeled OH and HO<sub>2</sub> around unity. Recently discovered interference in HO<sub>2</sub> measurements caused by RO<sub>2</sub> cross sensitivity was found to cause a 30% increase in measured HO<sub>2</sub> during daytime on average. After correction of the measured HO<sub>2</sub> data, the model HO<sub>2</sub> is still in good agreement with the observations at high NO<sub>x</sub> but overpredicts HO<sub>2</sub> by a factor of 1.3 to 1.8 at low NO<sub>x</sub>. In addition, for two different set of measurements, a missing OH source of  $3.6 \pm 1.6$  and  $4.9 \pm 2.2$  ppb h<sup>-1</sup> was estimated from the experimental OH budget during the low-NO<sub>x</sub> period using the corrected HO<sub>2</sub> data. The measured diurnal profile of the HO<sub>2</sub>/OH ratio, calculated using the corrected HO<sub>2</sub>, is well reproduced by the MCM at high NO<sub>x</sub> but is significantly overestimated at low NO<sub>x</sub>. Thus, the cycling between OH and HO<sub>2</sub> is better described by the model at high NO<sub>x</sub> than at low NO<sub>x</sub>. Therefore, similar comprehensive field measurements accompanied by model studies are urgently needed to investigate HO<sub>x</sub> recycling under low-NO<sub>x</sub> conditions.

**Citation:** Elshorbany, Y. F., et al. (2012), HO<sub>x</sub> budgets during HO<sub>x</sub>Comp: A case study of HO<sub>x</sub> chemistry under NO<sub>x</sub>-limited conditions, *J. Geophys. Res.*, 117, D03307, doi:10.1029/2011JD017008.

### 1. Introduction

[2] The hydroxyl radical (OH) has long been known as the primary oxidant in the atmosphere responsible for the oxidation and removal of most natural and anthropogenic

trace gases. The major role of OH in the atmosphere was first recognized by Levy [1971]. Because of its short lifetime (<1 s), OH concentrations are determined by local chemical processes rather than transport. In addition, photochemical oxidation of volatile organic compounds (VOCs) results in

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the formation of other important radical intermediates, hydroperoxy (HO<sub>2</sub>), organic peroxy (RO<sub>2</sub>) and peroxyacyl (RCO<sub>3</sub>) radicals.  $\Sigma\text{RO}_2 + \text{RCO}_3$  are hereafter collectively referred to as RO<sub>2</sub>. Since the OH radical controls the oxidation capacity of the atmosphere, the identification of its sources and sinks in the atmosphere is crucial for the understanding of the tropospheric chemistry under both polluted high NO<sub>x</sub> as well as under low-NO<sub>x</sub> conditions. The term “oxidation capacity” (OC) is defined in the current study as the sum of the respective oxidation rates of the molecules Y<sub>i</sub> (VOCs, CO) by the oxidant X (X = OH, O<sub>3</sub>, NO<sub>3</sub>) [Geyer *et al.*, 2001]:

$$\text{OC} = \sum (k_{Y_i} \cdot [Y_i] \cdot [X]), \quad (1)$$

where  $k_{Y_i}$  is the bimolecular rate constant for the reaction of Y<sub>i</sub> with X (for the argument of using this definition, see Elshorbany *et al.* [2009a]).

[3] Two widely applied chemical schemes to investigate HO<sub>x</sub> (OH+HO<sub>2</sub>) chemistry are the Regional Atmospheric Chemistry Mechanism (RACM) [Stockwell *et al.*, 1997], which uses lumped reactions for organic compounds, and the Master Chemical Mechanism (MCM), a near-explicit chemical mechanism (<http://mcm.leeds.ac.uk/MCM/>). The MCM is based on the original protocol, MCMv2 devised by Jenkin *et al.* [1997], which has been updated and subsequently improved to MCMv3.0 [Saunders *et al.*, 2003; Jenkin *et al.*, 2003]. The aromatic degradation chemistry schemes within MCMv3.0 have been substantially updated, described in MCMv3.1 [Bloss *et al.*, 2005a, 2005b]. The most explicit version, MCMv3.2 incorporates the recent updates of isoprene chemistry [Paulot *et al.*, 2009a, 2009b; Lockwood *et al.*, 2010]. In addition to the more explicit mechanism of isoprene, OH recycling from the reaction of acyl peroxy radicals with HO<sub>2</sub> (based on the IUPAC recommendation for CH<sub>3</sub>C(O)O<sub>2</sub>+HO<sub>2</sub>) has been newly implemented in MCMv3.2. In addition, specialized chemical mechanisms were developed for isoprene, such as the Mainz Isoprene Mechanism (MIM) [Pöschl *et al.*, 2000; von Kuhlmann *et al.*, 2004; Sander *et al.*, 2005] and its updated version MIM2 [Taraborrelli *et al.*, 2009] or the modified version MIM-GK [Geiger *et al.*, 2003; Karl *et al.*, 2006], which can be used alone or in conjunction with other chemical schemes especially for isoprene-rich environments [e.g., Lelieveld *et al.*, 2008; Hofzumahaus *et al.*, 2009; Pugh *et al.*, 2010].

[4] In general, field studies of HO<sub>x</sub> in rural environments showed that OH levels were well simulated during high-NO<sub>x</sub> events (e.g., BERLIOZ [Mihelcic *et al.*, 2003], TOHPE [Mount and Williams, 1997], TORCH [Emmerson *et al.*, 2007], and PRIDE-PRD2006 [Hofzumahaus *et al.*, 2009]). However, under low-NO<sub>x</sub> conditions in isoprene-rich air, modeled OH levels tend to be underpredicted. For example, in a recent field campaign in the rural area of the Pearl River Delta (PRD), China, Hofzumahaus *et al.* [2009] found that modeled OH using a photochemical box model based on RACM updated with MIM-GK, underpredicted measured OH under low-NO<sub>x</sub> conditions. This result was confirmed by measuring the sources and sinks of the OH radical. Thus, they proposed a missing OH source and suggested additional radical cycling (without NO) to fill this gap. Such significant underestimation of OH levels was previously reported over

the pristine forests of Surinam, Guyana and the French Guyana using an atmospheric chemistry model based on MIM [Lelieveld *et al.*, 2008, and references therein]. Recently, a significant OH underestimation was also observed during the OP3 campaign performed at the top of the rain forest canopy near Danum Valley, Malaysian Borneo using a box model based mainly on MIM2 [Pugh *et al.*, 2010, and references therein] or MCM [Whalley *et al.*, 2011; Stone *et al.*, 2011].

[5] In summer 2005, a blind international HO<sub>x</sub> intercomparison (HO<sub>x</sub>Comp) was carried out at Forschungszentrum Jülich (FZJ), which is located in a mixed deciduous forest in a rural environment in Germany [Schlosser *et al.*, 2009; Fuchs *et al.*, 2010]. In addition to HO<sub>x</sub> measurements, a large set of ancillary parameters including OH reactivity, oxygenated volatile organic compounds (OVOCs) and major OH radical precursors were measured during three days (9–11 July) of ambient air sampling. These measurements offer the unique opportunity to investigate the HO<sub>x</sub> chemistry at rural conditions with variable NO<sub>x</sub> levels, based on data from different HO<sub>x</sub> instruments. Two model studies have been performed to analyze the field data. The present work is a case study of the HO<sub>x</sub> budgets of a selected day (10 July), analyses the contributions of primary HO<sub>x</sub> sources and recycling, and compares the measured HO<sub>x</sub> concentrations with box model simulations based on most explicit chemical scheme MCMv3.2. Kanaya *et al.* [2011] extended the model measurement comparison to the other HO<sub>x</sub>Comp days based on RACM with updated isoprene chemistry and investigated the impact of different, recently proposed isoprene mechanisms on the predicted HO<sub>x</sub> concentrations.

## 2. Methodology

### 2.1. HO<sub>x</sub>Comp Campaign

[6] Only a brief description of the campaign is given here. For more details, see Schlosser *et al.* [2009] and Fuchs *et al.* [2010]. The HO<sub>x</sub>Comp campaign took place on the campus of FZJ (50°54'33"N, 06°24'44"E). The campus is situated in a mixed deciduous forest about 2–3 km southeast of the city of Jülich and is surrounded by agricultural areas and main roads. The formal part of the campaign included 3 days of ambient measurements (9–11 July 2005) and 6 days of chamber experiments in the SAPHIR chamber (17–23 July 2005), of which only ambient measurements will be compared to model simulations. During the weekend days 9–10 July 2005, essentially no traffic occurred on the campus [Schlosser *et al.*, 2009]. Of the 3 day ambient measurements, sunny and clear sky conditions were available only on 10 July. On 11 July, HO<sub>x</sub> data were only available until about 14:00 UTC, when a rainstorm evolved and OH reactivity measurements were available only for about 1 h from 13:00 to 14:00 UTC, which causes the 11 July data to be unsuitable for the calculation of experimental HO<sub>x</sub> budgets (see section 3.6). On 9 July, very high NO<sub>x</sub> levels were observed during the daytime, leading to much lower HO<sub>2</sub> levels [Fuchs *et al.*, 2010]. Under these conditions, an average of 9–10 July would mask the low-NO<sub>x</sub> conditions experienced by the measurement site on 10 July (see sections 3.3 and 3.4), which is the main focus of this study. In addition, model simulations of 9–11 July were performed using RACM-based box model [Kanaya *et al.*, 2011].

Therefore, only 10 July is considered here as case study for the simulation and analysis of the radical budgets.

## 2.2. Ambient Measurements

[7] Detailed analyses of the formal blind intercomparison of the different OH and HO<sub>2</sub> measurement techniques are published by *Schlosser et al.* [2009] and *Fuchs et al.* [2010], respectively. In short, OH measurements in ambient air were compared for four different instruments: three laser-induced fluorescence (LIF) instruments operated by Max-Planck Institute Mainz (MPI-LIF); Forschungszentrum Jülich (FZJ-LIF) and the Japan Frontier Research Centre for Global Change (FRCGC-LIF) and one chemical ionization mass spectrometry (CIMS) instrument operated by the Deutscher Wetterdienst (DWD-CIMS), each using its own calibration scheme. In SAPHIR, the OH measurements by the LIF instruments were compared to measured data from the Differential Optical Absorption Spectroscopy (DOAS) instrument operated by FZJ, without participation of the CIMS instrument. All LIF instruments additionally measured HO<sub>2</sub> through the chemical conversion to OH by addition of NO in the gas expansion, followed by LIF detection of the additionally formed OH. Total OH reactivity was measured by the laser-induced pump and probe technique; detailed description of the instrument is published elsewhere [*Yoshino et al.*, 2006, and references therein]. The uncertainty in the reactivity data during the HO<sub>x</sub>Comp was estimated to be 15% [*Kanaya et al.*, 2011].

[8] In SAPHIR, OH measurements by the LIF and DOAS instruments showed very good agreement within 12%, well within the specified calibration errors. In ambient air, however, the regression between pairs of LIF instruments showed slopes between 1.06 (FZJ-LIF versus FRCGC-LIF) and 1.29 (MPI-LIF versus FZJ-LIF), while regressions between CIMS and LIF instruments had slopes between 0.59 (DWD-CIMS versus MPI-LIF) and 0.75 (DWD-CIMS versus FRCGC-LIF). The increased discrepancies in ambient air were possibly caused by inhomogeneously mixed air and/or possible changes of the OH measurement sensitivities that are not accounted for by calibration [*Schlosser et al.*, 2009].

[9] For the HO<sub>2</sub> measurements in SAPHIR, the three LIF instruments were found to agree within the combined 1 $\sigma$  calibration errors (about 30%), when the water vapor mixing ratio in SAPHIR was in the range of (0.6–1.8)% [*Fuchs et al.*, 2010]. Larger systematic deviations were found in dry air. Owing to the relatively high humidity in ambient air, good agreement would be expected, as in the SAPHIR experiments. In fact, the regression of the HO<sub>2</sub> data in ambient air yielded slopes of 1.19 for FRCGC-LIF versus FZJ-LIF, 0.59 for FZJ-LIF versus MPI-LIF and 1.46 for MPI-LIF versus FRCGC-LIF during daytime. The reason for the larger discrepancies compared to the SAPHIR experiments could not be resolved [*Fuchs et al.*, 2010]. One possible reason was discovered after HO<sub>x</sub>Comp. Interference in HO<sub>2</sub> measurements by FZJ-LIF was detected which is caused by cross sensitivity to specific RO<sub>2</sub> radicals [*Fuchs et al.*, 2011]. The interference has been confirmed for the MPI-LIF instrument (T. Dillon (interactive comment, 2011) to *Fuchs et al.* [2011]), and was likely present also in the FRCGC-LIF instrument. The level of interference depends on specific instrumental parameters and may be different for

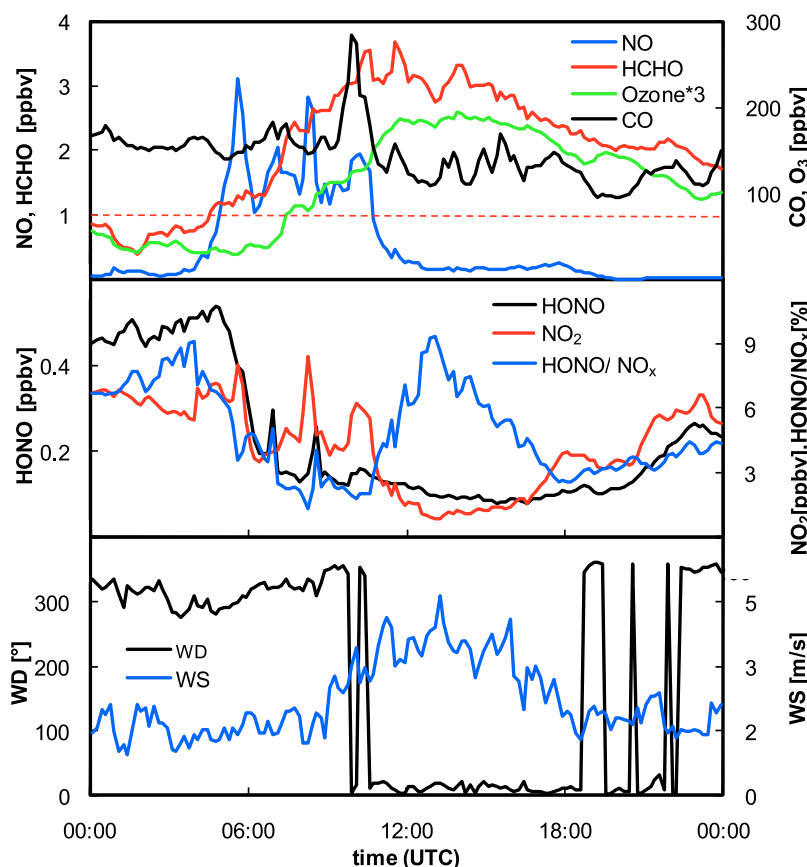
each LIF instrument at HO<sub>x</sub>Comp. So far, it has been characterized for FZJ-LIF only, showing relative sensitivities to RO<sub>2</sub> compared to HO<sub>2</sub> in the range of (50–95)% for peroxy radicals from alkenes, isoprene, MVK, MACR and aromatic compounds [*Fuchs et al.*, 2011]. The interference causes a systematic overprediction of the measured HO<sub>2</sub> concentrations depending on the specific air composition. A detailed description of the experimental setup of the interference experiment for the FZJ-LIF is given by *Fuchs et al.* [2011], which can be used as a guide to characterize the interferences in other LIF instruments.

[10] For the purpose of the comparison between measured and simulated HO<sub>x</sub> concentrations, mean measured OH and HO<sub>2</sub> data by all instruments is used in the current study (see section 3.5). During daytime, the measurements by individual instruments fall into an interval of about  $\pm 30\%$  around their mean. This interval represents the experimental uncertainty of the observations due to systematic differences between the individual instruments. For HO<sub>2</sub>, the interference contributes an additional systematic error, which is discussed in section 3.

[11] Measured trace gases included HONO, HCHO, NO, NO<sub>2</sub>, CO, O<sub>3</sub>, volatile organic compounds (VOCs) and photolysis frequencies  $j(\text{NO}_2)$ ,  $j(\text{O}^1\text{D})$ ,  $j(\text{HCHO})$ ,  $j(\text{HONO})$ . Meteorological parameters including temperature, pressure, relative humidity, wind speed and wind direction were also measured using standard techniques. The time in the current study is reported as UTC. Sunrise, local noon, and sunset occurred at 03:34, 11:40, and 19:45 UTC. Daytime is defined from 06:00 to 18:00 UTC.

## 2.3. Modeling Approach

[12] A zero-dimensional photochemical box model based on the Master Chemical Mechanism, MCMv3.2 (<http://mcm.leeds.ac.uk/MCM>) has been used to evaluate the radical budgets during HO<sub>x</sub>Comp. The MCM photochemical box model system of simultaneous stiff ordinary differential equations (ODEs) was integrated with a variable order Gear's method (FACSIMILE [*Curtis and Sweetenham*, 1987]). The model was constrained by 10 min average values of the following measured parameters:  $j(\text{NO}_2)$ ,  $j(\text{O}^1\text{D})$ ,  $j(\text{HONO})$ ,  $j(\text{HCHO}_{\text{radical}})$ , relative humidity, pressure, temperature, NO, NO<sub>2</sub>, HONO, CO, HCHO, O<sub>3</sub>, and 27 hydrocarbons (including isoprene) and oxygenated VOCs (see section 3.1). The other photolysis frequencies are parameterized within the model using a two stream isotropic scattering model under clear sky conditions [*Hayman*, 1997; *Saunders et al.*, 2003]. The photolysis rates are calculated as a function of solar zenith angle and adjusted by a scaling factor, calculated from the ratio of measured and model calculated  $j(\text{NO}_2)$  values, which takes into account the effects of varying cloud cover and aerosol scattering. Dry deposition terms have been incorporated in the model based on the values of *Sommariva et al.* [2006, and references therein] for HNO<sub>3</sub> (2 cm s<sup>-1</sup>), NO<sub>2</sub> (0.15 cm s<sup>-1</sup>), PAN (0.2 cm s<sup>-1</sup> and assumed the same for the other PANs), O<sub>3</sub> (0.5 cm s<sup>-1</sup>), SO<sub>2</sub> (0.5 cm s<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub> (1.1 cm s<sup>-1</sup>), organic peroxides (0.55 cm s<sup>-1</sup>), methyl and ethyl nitrate (1.1 cm s<sup>-1</sup>) and HCHO (0.33 cm s<sup>-1</sup> and assumed the same for all other aldehydes). Dry deposition terms were calculated as  $V_i/h$  where  $V_i$  is the species-dependent dry deposition velocity and  $h$  is the (time-dependent) boundary layer



**Figure 1.** Ten minute average diurnal profiles of the measured parameters on 10 July during HO<sub>x</sub>Comp. The red dashed line in Figure 1 (top) marks 1 ppbv NO. WD, wind direction; WS, wind speed.

mixing height. In the model, the boundary layer collapses to 300 m during the night at 20:00 UTC and starts to build up during the morning at 06:00 UTC, reaching a height of 1.3 km at 14:00 UTC. This boundary layer depth is maintained until early evening, when the nocturnal boundary layer of 300 m is reestablished. A series of rate of production analyses (ROPA) was carried out in order to identify the most important photochemical processes driving the formation and loss of OH and HO<sub>2</sub>. The MCM photochemical model was run for a period of 5 days, constrained with the same measured campaign parameters each day, to generate realistic concentrations for the unmeasured intermediate species. By the fifth day, free radicals in the model have reached photostationary state. Output from day 5 is used for data evaluation. This model version is henceforth denoted as the base model. Owing to the very large number of reactions and parameters involved in MCMv3.2, it is difficult to determine the model errors. Here, we adopt the  $1\sigma$  model errors for OH (17%) and HO<sub>2</sub> (16%) estimated by Kanaya *et al.* [2011] for the conditions encountered at noontime of 10 July during HO<sub>x</sub>Comp. The model errors consider the propagation of uncertainties of the rate coefficients in a revised RACM based box model and also the errors of measured trace gases and photolysis frequencies used as model input. These uncertainties are also in good agreement with  $2\sigma$  error for OH (42%) and HO<sub>2</sub> (25%), estimated previously using MCM under semi polluted conditions [Carslaw *et al.*, 1999]. Throughout this paper, production

and destruction of a species X are referred to as  $P_x$  and  $L_x$ , respectively.  $P_x$  and  $L_x$  are defined such as  $P_x(Y \rightarrow X)$  when X is produced from Y or by describing the reaction leading to production or loss of X such as  $P_x(Y + Z)$ .

### 3. Results and Discussion

#### 3.1. Field Measurement Results

[13] As shown in Figure 1, two different air masses can be distinguished at the measurement site owing to different wind directions (WD), from the northwest ( $\sim 315^\circ$ ) carrying anthropogenic emissions from the nearby city of Jülich (see section 2.1) during the early morning until around 10:00 UTC, then turning more northerly ( $\sim 10^\circ$ ) with much higher wind speed reaching  $5 \text{ m s}^{-1}$  (see Figure 1) during the rest of the day. Caused by this and by additional diurnal variability of the boundary layer height and the ozone concentration, NO levels ranged from 1 to 3 ppbv during the early morning until around 10:00 UTC and then decreased to less than 1 ppbv during the rest of the day. Therefore, two different chemical regimes have been identified; hereafter referred to as high-NO<sub>x</sub> (06:00–10:00 UTC) and low-NO<sub>x</sub> (11:00–18:00 UTC) periods with average NO mixing ratios of 1.6 and 0.21 ppbv, respectively (see Figure 1). CO and NO<sub>2</sub> showed similar diurnal profiles with average mixing ratios of CO (171, 132 ppbv), NO<sub>2</sub>, (4.65, 1.71 ppbv) during the high- and low-NO<sub>x</sub> periods, respectively. In contrast, HCHO reached a broad maximum of 3.7 ppbv at 11:35 UTC,

**Table 1.** List of Measured Hydrocarbons During HO<sub>x</sub>Comp on 10 July 2005

| Compound                     | Average Mixing Ratio (ppbv) |                 |                 |
|------------------------------|-----------------------------|-----------------|-----------------|
|                              | 06:00–10:00 UTC             | 11:00–18:00 UTC | 06:00–18:00 UTC |
| Ethane                       | 1.55                        | 0.85            | 1.17            |
| Propane                      | 0.99                        | 0.49            | 0.70            |
| i-butane (2-methylpropane)   | 0.20                        | 0.12            | 0.16            |
| i-pentane (2-methylbutane)   | 0.37                        | 0.23            | 0.29            |
| n-pentane                    | 0.20                        | 0.13            | 0.16            |
| n-hexane                     | 0.08                        | 0.05            | 0.06            |
| n-heptane                    | 0.04                        | 0.02            | 0.03            |
| n-octane                     | 0.02                        | 0.04            | 0.03            |
| Ethene                       | 0.53                        | 0.18            | 0.32            |
| Propene                      | 0.31                        | 0.11            | 0.18            |
| i-butene (2-methylpropene)   | 0.07                        | 0.05            | 0.06            |
| trans-2-butene               | 0.04                        | 0.02            | 0.03            |
| cis-2-pentene                | 0.01                        | 0.02            | 0.02            |
| Isoprene                     | 0.37                        | 0.98            | 0.74            |
| Ethine (acetylene)           | 0.18                        | 0.10            | 0.13            |
| Ethylbenzene                 | 0.04                        | 0.02            | 0.03            |
| m- and p-xylene <sup>a</sup> | 0.06                        | 0.02            | 0.04            |
| o-xylene                     | 0.02                        | 0.01            | 0.01            |
| Toluene                      | 0.29                        | 0.11            | 0.20            |
| Benzene                      | 0.24                        | 0.21            | 0.22            |
| Butanal                      | <D <sub>L</sub>             | 0.06            | 0.04            |
| Butanone                     | 0.28                        | 0.13            | 0.19            |
| Methacroleine                | 0.02                        | <D <sub>L</sub> | 0.01            |
| Methylvinylketone            | <D <sub>L</sub>             | 0.11            | 0.07            |
| Propanal                     | 0.03                        | 0.03            | 0.03            |
| Acetone                      | 2.17                        | 3.77            | 3.16            |
| Acetaldehyde                 | 0.86                        | 1.13            | 1.02            |

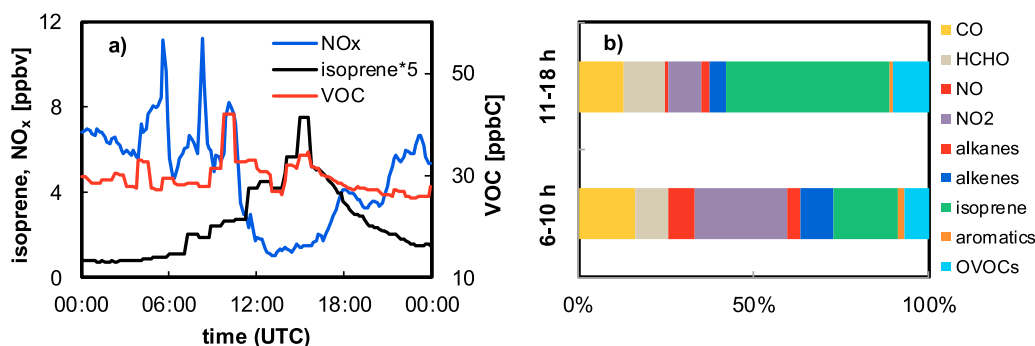
<sup>a</sup>Not constrained to the MCM.

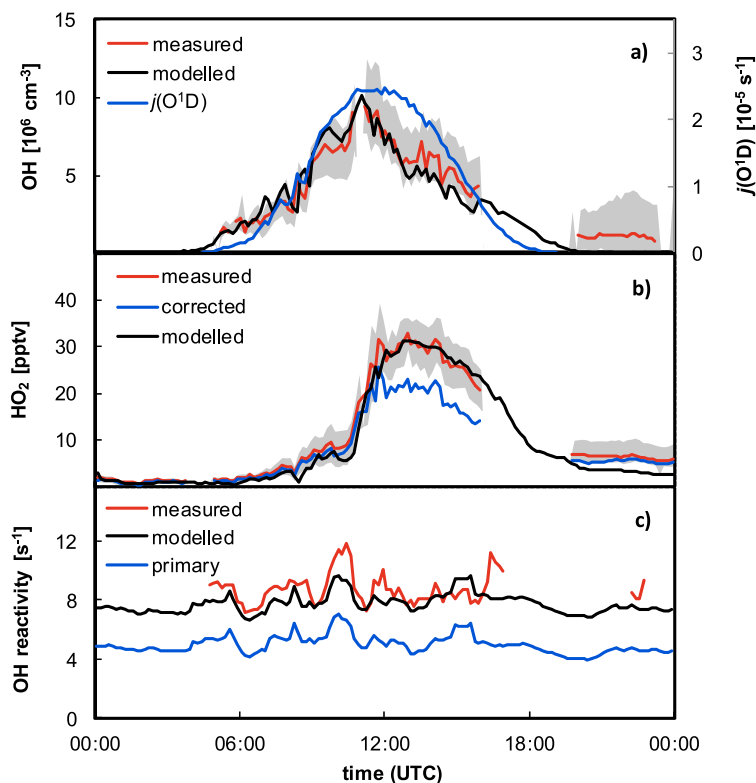
1 h before the ozone maximum mixing ratio of 62 ppbv, due to contributions from secondary photochemical sources (Figure 1).

[14] The HONO/NO<sub>x</sub> ratio showed two maxima (see Figure 1). While the typical nighttime maximum (around 04:00 UTC) can be explained by heterogeneous nighttime sources and the lack of photolysis of HONO, the second maximum during daytime (at around 14:00 UTC) points to a strong daytime source of HONO for which photochemical sources have been proposed [Kleffmann *et al.*, 2005; Kleffmann, 2007]. Similar diurnal profiles of the HONO/NO<sub>x</sub> ratio were also observed under rural [e.g., Acker *et al.*, 2006], remote [e.g., Kleffmann and Wiesen, 2008], and urban conditions [e.g., Elshorbany *et al.*, 2009a, 2010a].

[15] A list of the average mixing ratios of the measured hydrocarbons is shown in Table 1. Measured compounds less than the detection limits (<D<sub>L</sub>) were constrained to the model as zero values while those identified as mixture of two compounds or more were not constrained. The averaged diurnal profiles of VOCs (in parts per billion, ppbC) and NO<sub>x</sub> (ppbv), in addition to the contribution of different species and VOC categories to the primary OH reactivity (see section 3.8) are shown in Figure 2. The relative contribution of the different VOCs during the high- and low-NO<sub>x</sub> periods are alkanes (35, 20%), alkenes (8, 3), isoprene (6, 16%), acetylenes (1, 1%), aromatics (15, 8%) and OVOCs (35, 52%) to the total measured VOCs of about 30 and 31 ppbC, respectively. Unlike NO<sub>x</sub>, the total amount of VOC is almost constant during the day. Thus, the VOC/NO<sub>x</sub> ratio is about 5 during the high-NO<sub>x</sub> period, but reaches a value of about 30 at 13:00 UTC (i.e., VOC-sensitive conditions at VOC/NO<sub>x</sub> < 10 and NO<sub>x</sub> sensitive conditions at VOC/NO<sub>x</sub> > 20; see also section 3.3 [National Research Council, 1991]). In addition, since not all hydrocarbons could be measured by the GC analysis techniques used, similar to other field measurement studies [Elshorbany *et al.*, 2009a; Dusanter *et al.*, 2009, and references therein], a higher VOC/NO<sub>x</sub> ratio is expected. The relative contribution of the different VOC categories to the primary OH reactivity (see Figure 2) varies during the daytime, depending on the NO<sub>x</sub> levels. As expected, NO<sub>x</sub> and anthropogenic emissions of alkanes, alkenes and aromatics had the highest contribution during the high-NO<sub>x</sub> period (06:00–10:00 UTC) while isoprene, OVOCs and HCHO reached their highest contribution during the low-NO<sub>x</sub> period (11:00–18:00 UTC). The OVOC category herein does not include HCHO, which is treated separately due to its particular importance.

[16] The measured diurnal profiles of both OH and HO<sub>2</sub> exhibit similar variations, with maximum values at noontime and concentrations near zero at night (Figures 3a and 3b). The red lines show the mean diurnal profiles measured by all instruments, while the gray area represents the range of measurements by the different instruments, which might be interpreted roughly as a measure of the experimental uncertainty (see section 2.2). The black lines represent the base model results, which show very good agreement (within ± 30%) with the experimental observations both for OH and HO<sub>2</sub>. As pointed out in section 2.2, the measured HO<sub>2</sub> data contain uncorrected contributions by RO<sub>2</sub>. The model calculated RO<sub>2</sub> concentrations from the base model

**Figure 2.** (a) Diurnal variation of measured isoprene, VOCs, and NO<sub>x</sub> mixing ratios and (b) relative contributions of the different VOC categories and other species to the primary OH reactivity.



**Figure 3.** Ten minute average measured and modeled OH, HO<sub>2</sub>, and OH reactivity as well as the corrected measured HO<sub>2</sub> levels due to interferences by RO<sub>2</sub> cross reactions on 10 July. Gray areas determine the minimum and maximum HO<sub>x</sub> levels measured by different instruments.

run have been used to estimate the magnitude of this interference. Based on the cross sensitivities for the different RO<sub>2</sub> species determined for FZJ-LIF [Fuchs *et al.*, 2011], the possible bias is calculated to be +22% and +47% during the high- and low-NO<sub>x</sub> periods, respectively. If we assume that the two other LIF instruments had similar interferences (i.e., cross sensitivities from RO<sub>2</sub> species determined for FZJ-LIF), then the measured HO<sub>2</sub> by FRCGC-LIF and MPI-LIF would have to be reduced by (26, 36)% and (10, 25)% during the high- and low-NO<sub>x</sub> period, respectively. Accordingly, the mean corrected HO<sub>2</sub> data in Figure 3b are smaller than the uncorrected values by 14% at high-NO<sub>x</sub> conditions and 26% at low-NO<sub>x</sub> conditions. After the correction, the modeled HO<sub>2</sub> is still in good agreement with the observations in the morning (within the gray area) but overpredicts the corrected measured HO<sub>2</sub> by a factor of 1.3 to 1.8 during the low-NO<sub>x</sub> period.

[17] Figure 3c shows the measured total OH reactivity (red line) which has a daytime average value of  $8.8 (\pm 0.8) \text{ s}^{-1}$  reaching its maximum of  $11.8 \text{ s}^{-1}$  at about 10:00 UTC and minimum of  $7.2 \text{ s}^{-1}$  at about 06:00 UTC. About 60% of the measured reactivity can be explained by measured trace gases (blue line) during the daytime. A detailed discussion of the model-measurement comparisons for OH, HO<sub>2</sub> and OH reactivity is given in sections 3.5, 3.6 and 3.8.

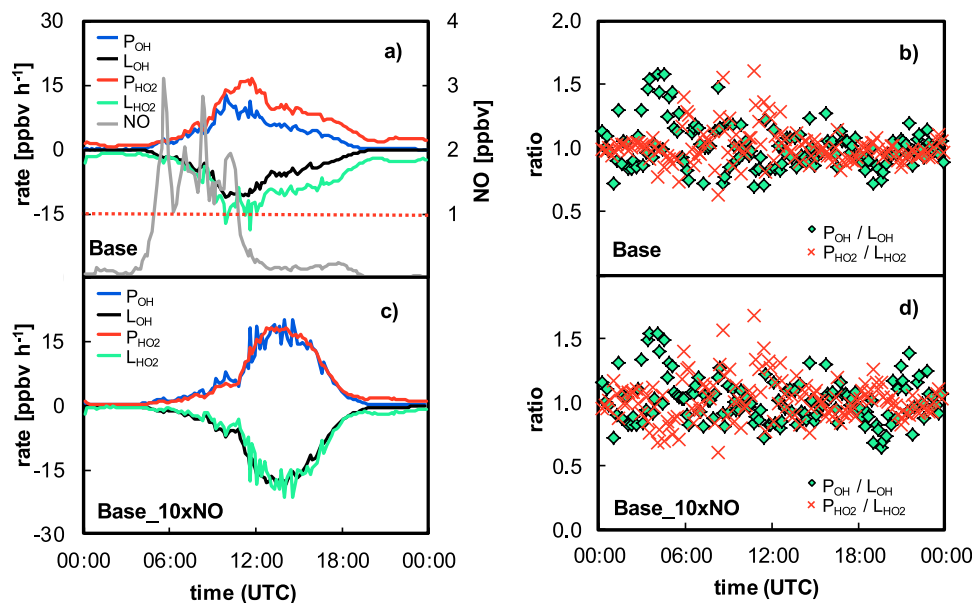
### 3.2. Oxidation Capacity

[18] The oxidation capacity (OC) defined earlier is calculated from the total loss rates of the VOCs and CO due to reactions with OH, O<sub>3</sub> and NO<sub>3</sub> using the MCM model. The

average oxidation capacity of OH, O<sub>3</sub> and NO<sub>3</sub> radicals throughout the entire day is  $1.7 \times 10^7$ ,  $8.6 \times 10^6$  and  $1.8 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$  representing about 63, 31, and 6% of the total oxidation capacity, respectively. During daytime (06:00–18:00 UTC), OH is also the dominant oxidant with an average oxidation rate of  $3.3 \times 10^7 \text{ molecules cm}^{-3} \text{ s}^{-1}$  followed by O<sub>3</sub> and NO<sub>3</sub> of  $7.6 \times 10^6$  and  $1.2 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$  representing 79, 18 and 3% of the total OC, respectively. In contrast, during the night and early morning O<sub>3</sub> was the dominant oxidant. Owing to the dominant contribution of the OH radical to the OC during daytime, the current study focuses only on the HO<sub>x</sub> chemistry analysis during HO<sub>x</sub>Comp.

### 3.3. Modeled HO<sub>x</sub> Budget

[19] The total production and destruction rates of OH and HO<sub>2</sub> calculated by the MCM model are shown in Figure 4a, with ratios of the radical production/destruction shown in Figure 4b. As expected, owing to the very short lifetime of HO<sub>x</sub> radicals, the ratios of the total production to destruction of OH and HO<sub>2</sub> are around unity throughout the day, but highly fluctuating in the early morning due to the large variation of NO<sub>x</sub> (see Figure 4b). In addition, for the hydroxyl radical the ratio reaches a maximum of about 1.6 during the early morning at 04:30 UTC, which may be due to the photolysis of nighttime accumulated HONO. During the high-NO<sub>x</sub> period (06:00–10:00 UTC), when NO levels are  $> 1 \text{ ppbv}$  (see red dotted line in Figure 4a), total production and destruction rates of OH and HO<sub>2</sub> were almost similar. However, when NO levels fall below 1 ppbv, OH

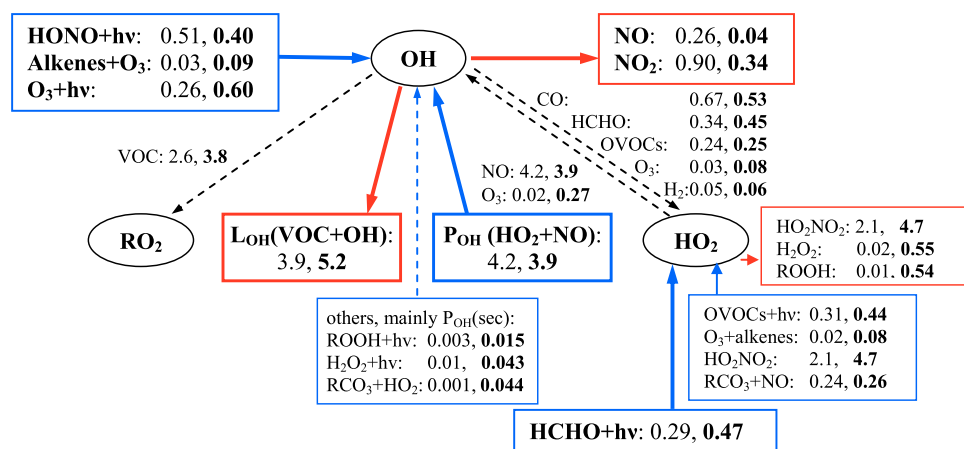


**Figure 4.** (a and c) Total production and destruction rates of OH and HO<sub>2</sub> and (b and d) ratio of production to destruction rates of OH and HO<sub>2</sub>, using the base model (Figures 4a and 4b) in comparison to that of the Base\_10xNO scenario (Figures 4c and 4d). The red dashed line in Figure 4a marks the 1 ppbv NO limit.

total production and destruction rates become much lower than those of HO<sub>2</sub>. This is due to the lower recycling efficiency of HO<sub>2</sub> radicals (i.e., HO<sub>2</sub>+NO→OH) during the low-NO<sub>x</sub> period (see section 3.4). In order to further support the above argument, an additional sensitivity scenario was performed (Base\_10xNO), in which the constrained NO concentrations were increased by a factor of 10. The reason for this is to increase the minimum measured NO concentrations of 0.1 ppbv during the daytime (06:00–10:00 UTC) to reach 1 ppbv, at which an efficient radical recycling (i.e., of HO<sub>2</sub> to OH) occurs (see above). As a result of increasing NO (Base\_10xNO scenario) OH and HO<sub>2</sub> production and destruction rates become similar during the

entire daytime owing to the increased recycling efficiency (Figure 4). Thus, the lower production and destruction rates of OH compared to those of HO<sub>2</sub> (see Figure 4) are consequences of the NO<sub>x</sub>-limited conditions, which also lead to the unsymmetrical profiles observed for both, the measured and modeled OH (see section 3.2).

[20] The main RO<sub>2</sub> production term is due to hydrocarbon oxidation with OH (hereafter referred as L<sub>OH</sub>(OH→RO<sub>2</sub>)) with an average rate of 2.6 and 3.8 ppbv h<sup>-1</sup> during the high- and low-NO<sub>x</sub> periods, which corresponds to about 50 and 70% of the total OH loss rate, respectively (see Figure 5). The main loss of RO<sub>2</sub> is due to its reaction with NO (L<sub>RO2</sub>(RO<sub>2</sub>+NO)) with average loss rates of 2.6 and 3.3 ppbv



**Figure 5.** Average fluxes (06:00–18:00 UTC) of the key radical sources and sinks during HO<sub>x</sub>Comp on 10 July calculated by the MCMv3.2 for the high-NO<sub>x</sub> period in comparison to that of low-NO<sub>x</sub> period (bold letters). The HONO photolysis (HONO+*hν*) represents the gross HONO photolysis (i.e., not the net HONO photolysis defined in the text as P<sub>OH</sub>(HONO)). Units are in ppbv h<sup>-1</sup>.

$\text{h}^{-1}$  for high- and low-NO<sub>x</sub> conditions, respectively, which accounts for most of the HO<sub>2</sub> production. Other important HO<sub>2</sub> sources (hereafter referred to as  $L_{\text{OH}}(\text{OH} \rightarrow \text{HO}_2)$ ) are the reactions of OH with OVOCs, CO, O<sub>3</sub> and H<sub>2</sub> with summed average rates of 1.34 and 1.37 ppbv  $\text{h}^{-1}$  during the high- and low-NO<sub>x</sub> periods, respectively (see Figure 5). The average production rates of HO<sub>2</sub> due to photolysis of HCHO ( $P_{\text{HO}_2}(\text{HCHO} + h\nu)$ ) are 0.29 and 0.47 ppbv  $\text{h}^{-1}$  during the high- and low-NO<sub>x</sub> periods, respectively (Figure 5). One major destruction route of HO<sub>2</sub> is through its reaction with NO ( $L_{\text{HO}_2}(\text{HO}_2 + \text{NO})$ ) with averages of 4.2 and 3.9 ppbv  $\text{h}^{-1}$ , which account for only 65 and 39% of the total HO<sub>2</sub> destruction rate ( $L_{\text{HO}_2}(\text{total})$ ) during the high- and low-NO<sub>x</sub> periods, respectively. This contribution is much lower than that of about 80% reported under urban high-NO<sub>x</sub> conditions [Elshorbany et al., 2009a]. Owing to the higher RO<sub>2</sub> and HO<sub>2</sub> concentrations during the low-NO<sub>x</sub> period (see section 3.2), the relative contribution of the HO<sub>2</sub> self-reaction ( $L_{\text{HO}_2}(\text{HO}_2 + \text{HO}_2)$  leading to H<sub>2</sub>O<sub>2</sub> formation) and its cross reactions with RO<sub>2</sub> ( $L_{\text{HO}_2}(\text{HO}_2 + \text{RO}_2)$  leading to ROOH formation) to the  $L_{\text{HO}_2}(\text{total})$  are about 20 and 40 times higher than during the high-NO<sub>x</sub> period, respectively (see Figure 5). This demonstrates the importance of these reactions under low-NO<sub>x</sub> conditions and therefore, they should be considered when calculating the radical loss budgets under these conditions. The HO<sub>2</sub> loss due to its reaction with O<sub>3</sub> accounts for only 0.3% of the  $L_{\text{HO}_2}(\text{total})$  during the high-NO<sub>x</sub> period but about 3% during the low-NO<sub>x</sub> period. Another important HO<sub>2</sub> destruction path is its reaction with NO<sub>2</sub> to form HO<sub>2</sub>NO<sub>2</sub> with an average loss rates of 2.1 and 4.7 ppbv  $\text{h}^{-1}$  accounting for 32 and 47% of  $L_{\text{HO}_2}(\text{total})$  during the high- and low-NO<sub>x</sub> periods, respectively (Figure 5). However, this loss path is essentially a reversible reaction that leads to HO<sub>2</sub> formation with similar rates.

[21] The main OH loss route is through its reaction with hydrocarbons, followed by reactions with NO and NO<sub>2</sub>. The rates of OH destruction due to CO and hydrocarbons oxidation can be calculated using the following relationships:

$$L_{\text{OH}}(\text{OH} + \text{VOC}) \approx L_{\text{OH}}(\text{total}) - k_{\text{NO}_2 + \text{OH}}[\text{NO}_2][\text{OH}] - k_{\text{OH} + \text{NO}}[\text{NO}][\text{OH}], \quad (2)$$

or alternatively [Elshorbany et al., 2010a],

$$L_{\text{OH}}(\text{OH} + \text{VOC}) \approx L_{\text{OH}}(\text{OH} \rightarrow \text{HO}_2) + L_{\text{OH}}(\text{OH} \rightarrow \text{RO}_2). \quad (3)$$

The average loss rates of OH radicals by reaction with VOCs were similar for both equations and are 3.9 and 5.2 ppbv  $\text{h}^{-1}$ , representing 77 and 93% of the  $L_{\text{OH}}(\text{total})$  during the high- and low-NO<sub>x</sub> periods (see Figure 5), respectively. The rest of the OH loss is caused by its reaction with NO<sub>x</sub>, accounting for 23 and 7% of  $L_{\text{OH}}(\text{total})$  during the high- and low-NO<sub>x</sub> periods (see Figure 5), respectively.

[22] OH production is dominated by the recycling reaction of HO<sub>2</sub> with NO,  $P_{\text{OH}}(\text{HO}_2 \rightarrow \text{OH})$ :

$$P_{\text{OH}}(\text{HO}_2 \rightarrow \text{OH}) = k_{\text{HO}_2 + \text{NO}}[\text{HO}_2][\text{NO}]. \quad (4)$$

The  $P_{\text{OH}}(\text{HO}_2 \rightarrow \text{OH})$  route accounts for 83 and 73% to  $P_{\text{OH}}(\text{total})$ , while production of OH due to HO<sub>2</sub> reaction with O<sub>3</sub> account for 0.4 and 5% during the high- and low-NO<sub>x</sub> periods, respectively (see Figure 5). The next most important

secondary OH sources are the reaction of RCO<sub>3</sub> + HO<sub>2</sub>, the photolysis H<sub>2</sub>O<sub>2</sub> and the photolysis of ROOH and RCO<sub>3</sub>H species (hereafter collectively called  $P_{\text{OH}}(\text{ROOH} + h\nu)$ ) that result from RO<sub>2</sub> cross reactions with HO<sub>2</sub>. The total contribution of these secondary sources (hereafter referred to as  $P_{\text{OH}}(\text{sec})$ ) accounts for only 0.2% of the  $P_{\text{OH}}(\text{total})$  during the high-NO<sub>x</sub> period, but about 2% during the low-NO<sub>x</sub> period.

### 3.4. Radical Propagation

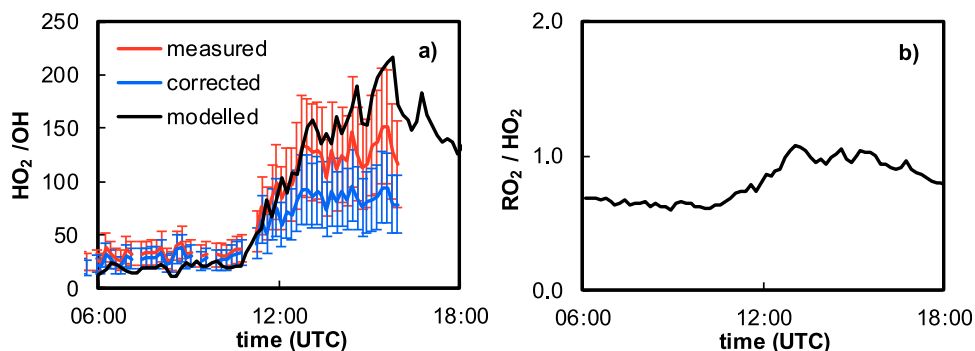
[23] In order to investigate the radical propagation balance between OH secondary radical loss ( $L_{\text{OH}}(\text{OH} + \text{VOC})$ ) and production ( $P_{\text{OH}}(\text{HO}_2 + \text{NO})$ ), a balance ratio (BR) introduced by Elshorbany et al. [2010a] was calculated by the model. The BR ratio is defined as

$$\text{BR} = \frac{P_{\text{OH}}(\text{HO}_2 \rightarrow \text{OH})}{L_{\text{OH}}(\text{OH} \rightarrow \text{HO}_2) + L_{\text{OH}}(\text{OH} \rightarrow \text{RO}_2)}. \quad (5)$$

According to this balance ratio, a BR value of 1 indicates that secondary production and destruction of OH are balanced. A BR < 1 indicates that secondary radical production is smaller than destruction. The latter case may prevail under very low NO<sub>x</sub> conditions, which may lead to a low radical recycling efficiency and consequently, low secondary OH production. The secondary production of radicals is higher than their secondary destruction if BR > 1.

[24] During HO<sub>x</sub>Comp, a modeled BR ratio of 1.07 was obtained during the high-NO<sub>x</sub> period (see Figure 5) indicating almost a balance between the secondary radical loss and production owing to the high recycling efficiency [Elshorbany et al., 2010a]. However, during the low-NO<sub>x</sub> period (11:00–18:00 UTC), a BR ratio of 0.75 was obtained, indicating net secondary radical loss due to a low recycling efficiency. In addition, under low-NO<sub>x</sub> conditions, significant fraction (about 9%) of the OH radical recycling processes occur without NO through  $P_{\text{OH}}(\text{sec})$  and  $P_{\text{OH}}(\text{HO}_2 + \text{O}_3)$ . These recycling processes partially compensate the deficit in the OH budget as a result of the low-NO<sub>x</sub> conditions. Including the other OH secondary sources ( $P_{\text{OH}}(\text{sec})$  and  $P_{\text{OH}}(\text{HO}_2 + \text{O}_3)$ ) in the secondary production term in (5), lead to only a very small increase of 0.7% in the BR ratio to 1.08 during the high-NO<sub>x</sub> period, whereas it increased the BR during the low-NO<sub>x</sub> period by 11% to 0.82. These results confirm our previous conclusion of high recycling efficiency during the high-NO<sub>x</sub> period and lower recycling efficiency during the low-NO<sub>x</sub> period. This lower recycling efficiency is mainly due to the increased HO<sub>2</sub> loss due to the formation of H<sub>2</sub>O<sub>2</sub> and ROOH (see Figure 5) as a result of the low-NO<sub>x</sub> conditions. The total OH production to destruction ratio of unity (see section 3.3) is maintained by the higher OH initiation rate and the lower loss rate by reactions with NO<sub>x</sub> during the low-NO<sub>x</sub> period (see section 3.3). Thus, in contrast to the calculated turnover rates, based on measured HO<sub>2</sub>, OH and OH reactivity (see section 3.3), the primary and secondary sources fill the deficit in the radical budgets during afternoon, thus maintaining the balance between total radical production and destruction (see section 3.3).

[25] The HO<sub>2</sub>/OH ratio is also a measure of the recycling efficiency; a high HO<sub>2</sub>/OH ratio is typical for clean air with low-NO<sub>x</sub> conditions [e.g., Mihelcic et al., 2003; Ren et al.,

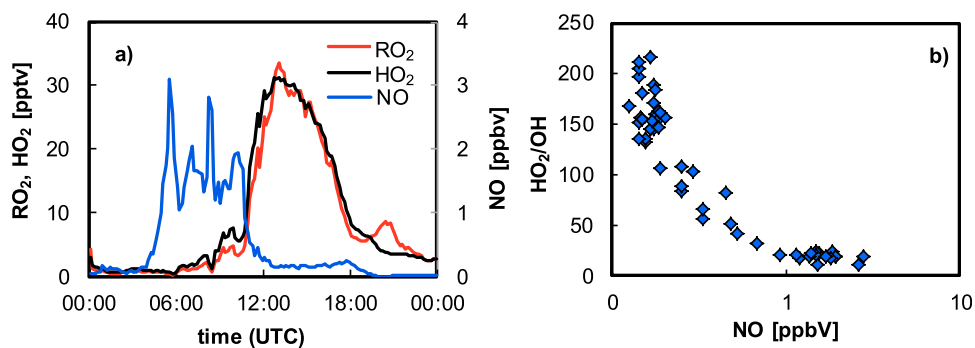


**Figure 6.** Diurnal profiles of modeled, measured, and corrected (for  $\text{RO}_2$  interference) (a)  $\text{HO}_2/\text{OH}$  with  $2\sigma$  error bars, calculated from the propagation error of the relative uncertainties of OH and  $\text{HO}_2$  multiplied by the corresponding  $\text{HO}_2/\text{OH}$  ratio and (b) modeled  $\text{RO}_2/\text{HO}_2$  during the daytime (06:00–18:00 UTC).

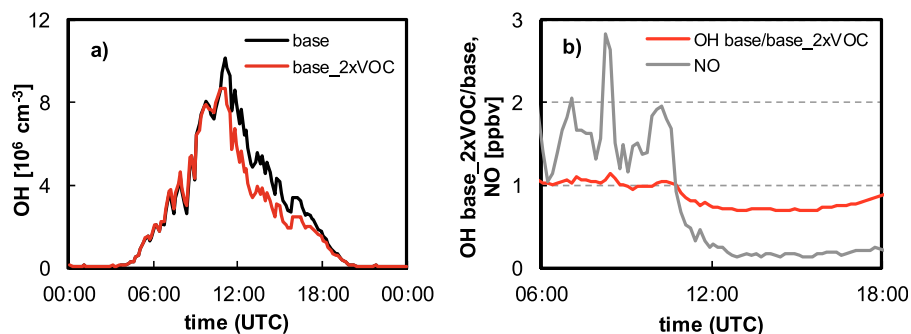
2005; Hofzumahaus *et al.*, 2009], while a low  $\text{HO}_2/\text{OH}$  ratio is typical for polluted air with high- $\text{NO}_x$  conditions and implies a high recycling efficiency toward OH [e.g., Elshorbany *et al.*, 2009, and references therein]. The shape of the measured diurnal profile of the  $\text{HO}_2/\text{OH}$  ratio is well reproduced by the MCM model (see Figure 6) and values are within the measurements uncertainties (see section 3.1). However, if corrected  $\text{HO}_2$  is used to calculate the  $\text{HO}_2/\text{OH}$  ratio, the agreement slightly improves during the high- $\text{NO}_x$  period, but become significantly worse at low  $\text{NO}_x$ . This result shows that the cycling between OH and  $\text{HO}_2$  is better described by the model at high  $\text{NO}_x$  than at low  $\text{NO}_x$ . The low modeled  $\text{HO}_2/\text{OH}$  ratio of 19 indicates high recycling efficiency during the high- $\text{NO}_x$  period (06:00–10:00 UTC), but increases strongly during the low- $\text{NO}_x$  period (11:00–18:00 UTC) with an average value of 125 (see Figure 6) indicating low recycling efficiency. This high  $\text{HO}_2/\text{OH}$  ratio is also in excellent agreement with that measured at Pearl River Delta, China [Hofzumahaus *et al.*, 2009], rural area of central Pennsylvania [Ren *et al.*, 2005], and BERLIOZ [Mihelcic *et al.*, 2003]. Modeled  $\text{RO}_2/\text{HO}_2$  ratio ranges from 0.6 during the high- $\text{NO}_x$  period to 1.0 during the low- $\text{NO}_x$  period (Figure 6). The higher ratio during the low- $\text{NO}_x$  period is also a result of the lower recycling efficiency during this period. In addition, the maximum total peroxy radical ( $\text{RO}_2 + \text{HO}_2$ ) concentrations of 65 pptv during the low- $\text{NO}_x$  period (see Figure 7) is very high in comparison to other similar studies [Mihelcic *et al.*, 2003; Hofzumahaus *et al.*, 2009] and can be explained by the lower NO

concentrations during HO<sub>x</sub>Comp. The maxima in the diurnal profiles of  $\text{RO}_2$  and  $\text{HO}_2$  also coincide with the NO daytime minima as shown in Figure 7. This is also in agreement with the expected anticorrelation between the  $\text{HO}_2/\text{OH}$  ratio and NO as shown in Figure 7, which is in agreement with other studies [e.g., Mihelcic *et al.*, 2003]. The second peak in the  $\text{RO}_2$  diurnal profile at around 20:00 UTC is due to the very low recycling efficiency (i.e.,  $\text{RO}_2 + \text{NO} \rightarrow \text{HO}_2$  and  $\text{HO}_2 + \text{NO} \rightarrow \text{OH}$ ) owing to the extremely small NO values of about 0.01 ppbv at this time.

[26] To further investigate the recycling process, an additional MCM model scenario has been run, in which the concentrations of all constrained VOCs (except HCHO) have been increased by a factor of 2, referred to as Base<sub>2</sub> × VOC. As shown in Figure 8, OH simulated by this scenario matched that simulated by the base model scenario during the high- $\text{NO}_x$  period (within  $\pm 2\%$ ), while it was lower by about 30% during the low- $\text{NO}_x$  period compared to the base model scenario. The excellent agreement between the OH simulations by the base and base<sub>2</sub> × VOC scenarios during the high- $\text{NO}_x$  condition is due to the high recycling efficiency during this time. This result shows that secondary OVOCs are not net sources of OH radicals, in excellent agreement with previous studies under polluted urban conditions [Elshorbany *et al.*, 2009a, 2010a]. The reduction in the OH levels as a result of increasing the VOC levels during the low- $\text{NO}_x$  period is due to the NO-sensitive conditions, under which VOCs act as a net sink of OH



**Figure 7.** (a) Diurnal profiles of modeled  $\text{HO}_2$  and  $\text{RO}_2$  and (b) correlation between modeled  $\text{HO}_2/\text{OH}$  and NO.



**Figure 8.** (a) Simulated diurnal profiles of OH of the base\_2xVOC in comparison to the base model scenario and (b) ratio of the two simulated profiles with measured NO.

radicals due to the low recycling efficiency, in agreement with the conclusion given above.

[27] Very recently, *Mollner et al.* [2010] reported a more precise value for the rate constant  $k_{\text{NO}_2+\text{OH}}$  of  $9.2 (\pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 25 °C and 1 atm of air, which is about 77% of the IUPAC values applied in the MCMv3.2 of  $11.9^{+6.0}_{-3.0} \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In order to test the impact of the new value of the  $k_{\text{NO}_2+\text{OH}}$  on the simulated HO<sub>x</sub> levels, an additional scenario was performed. As expected, only OH, HO<sub>2</sub> and RO<sub>2</sub> levels during the high-NO<sub>x</sub> period were affected and increased by about 11%, while those during the low-NO<sub>x</sub> period were increased by only about 3%. This is due to the high-NO<sub>x</sub> conditions, for which NO<sub>2</sub> reaction with OH is the dominant sink of radicals (see section 3.3). Similarly, *Mollner et al.* [2010] reported a 10% increase in the O<sub>3</sub> levels as a result of using the new values of the  $k_{\text{NO}_2+\text{OH}}$  rate constant, considering that O<sub>3</sub> instantaneous production rate is a function of HO<sub>2</sub> and RO<sub>2</sub> concentrations [e.g., *Elshorbany et al.*, 2009b].

### 3.5. Measured Versus Modeled Radical Levels

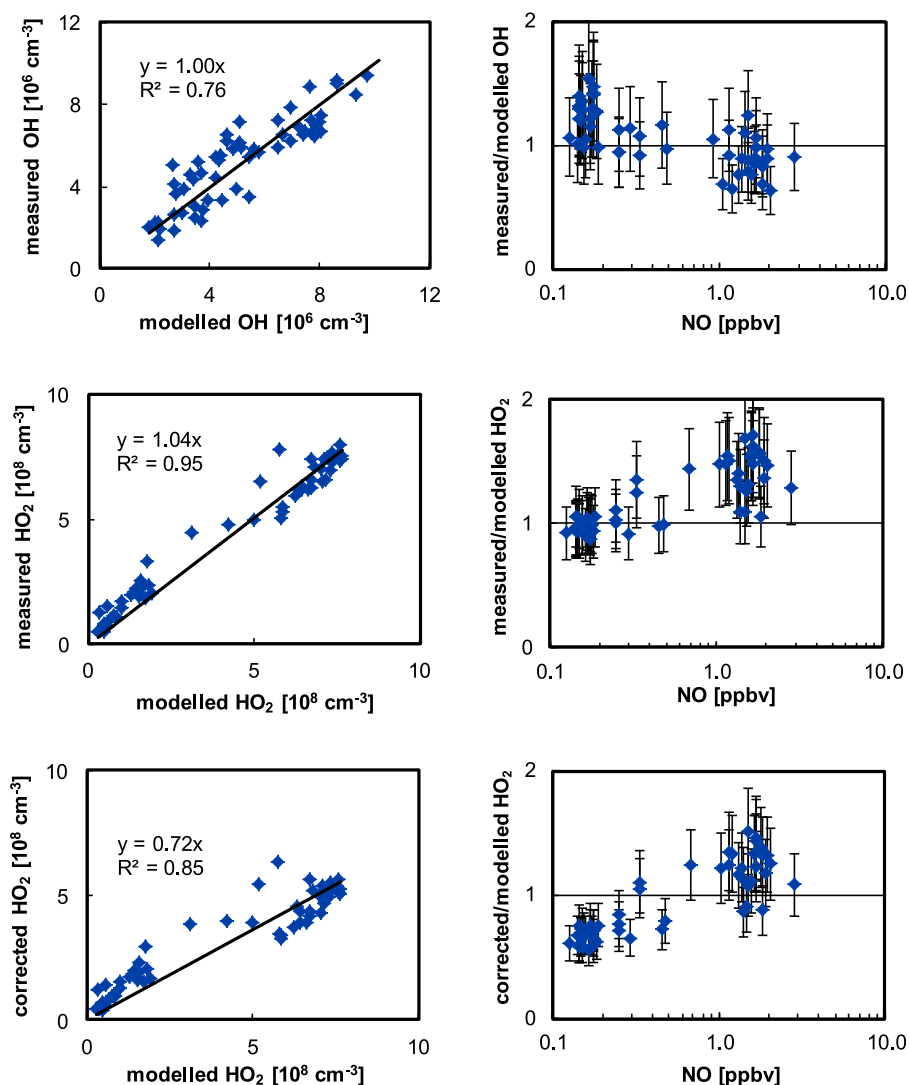
[28] The measured OH diurnal profile reached a maximum of  $9.4 \times 10^6 \text{ molecules cm}^{-3}$  around noon at 11:15 UTC, about half an hour before the maximum  $j(\text{O}^1\text{D})$ , shortly after the high-NO<sub>x</sub> period, and then decreased sharply during the low-NO<sub>x</sub> period owing to the lower recycling efficiency (see section 3.4). Owing to this different photochemical sensitivity during the daytime (i.e., high NO<sub>x</sub>, 06:00–10:00 UTC and low NO<sub>x</sub>, 11:00–18:00 UTC), measured and modeled OH diurnal profiles are asymmetric around the solar noon maximum (see Figure 3). This is due to the low-NO<sub>x</sub> conditions during the time period 11:00–18:00 UTC, for which OH photostationary state equilibrium is shifted toward net OH loss by VOC oxidation (see section 3.4). The measured and modeled HO<sub>2</sub> diurnal profiles are also asymmetric and reach their maximum at about 13:00 UTC, around 1 h after the maximum of  $j(\text{O}^1\text{D})$ . This is due to the high-NO<sub>x</sub> levels which suppress the HO<sub>2</sub> levels only during the high-NO<sub>x</sub> period in the morning (see Figure 3). In contrast to previous studies where modeled OH diurnal profiles were asymmetric, while that measured was symmetric around solar noon [e.g., *Emmerson et al.*, 2007; *Hofzumahaus et al.*, 2009], the asymmetrically distinctive features of the OH and HO<sub>2</sub> diurnal profiles during the high- and low-NO<sub>x</sub> conditions were well reproduced by the MCMv3.2 box model in this study.

[29] The correlation between measured and modeled OH and HO<sub>2</sub> as well as the correlations of the ratio of measured/modeled values versus NO are shown in Figure 9. High correlations between measured and modeled OH and HO<sub>2</sub> values during daytime (06:00–18:00 UTC) with slopes around unity were obtained (see Figure 9). However, when the estimated interference caused by RO<sub>2</sub> cross reactions is considered, the slope between the corrected and modeled HO<sub>2</sub> regression line becomes 30% smaller, indicating a model overprediction of HO<sub>2</sub>. Similar results were also obtained using RACM-based box model [*Kanaya et al.*, 2011]. The correlation between measured/modeled ratio of OH and HO<sub>2</sub> and NO (see Figure 9) shows that OH was slightly overestimated during the high-NO<sub>x</sub> period but shows an increasing underestimation during the low-NO<sub>x</sub> period, reaching 65% at <0.2 ppbv NO (see Figures 3 and 9). In contrast, HO<sub>2</sub> was underestimated during both, high- and low-NO<sub>x</sub> periods by 48 and 17%, respectively. After correction of the HO<sub>2</sub> data for the interference by RO<sub>2</sub>, the agreement improves slightly at NO values above 1 ppb, but a model overestimation of about 40% becomes apparent at low NO values of 0.2 ppb. Although there seem to be NO-dependent trends in the measured/modeled ratios of OH and HO<sub>2</sub>, these trends must be considered carefully owing to the combined model and experimental errors, which are of the order of the observed deviations.

### 3.6. Experimental OH Budget

[30] The total OH production and loss rates determined from measured parameters are compared in Figure 10. The total OH production rate was calculated from the recycling rate of HO<sub>2</sub> ( $k_{\text{NO}+\text{HO}_2} \times [\text{NO}] \times [\text{HO}_2]$ ) in addition to the primary sources ( $P_{\text{R}} = j(\text{HONO})[\text{HONO}] + P_{\text{OH}}(\text{O}_3) + P_{\text{OH}}(\text{alkenes})$ ; see section 3.7). The total OH loss rate was determined from the measured reactivity and concentration of OH ( $k_{\text{OH}} \times [\text{OH}]$ ). For OH and HO<sub>2</sub>, the mean values of FRCGC\_LIF and FZJ\_LIF were used, while the data by MPI\_LIF, which show much higher values (see section 2.2), were treated separately. The ratios of production to destruction of OH ( $P_{\text{OH}}/L_{\text{OH}}$ ) are also shown in Figure 10 for both cases.

[31] When the OH and HO<sub>2</sub> data by FRCGC/FZJ are used (Figure 10), the OH loss rate is found to be almost balanced with the OH production rate at high-NO<sub>x</sub> condition in the morning ( $P_{\text{OH}}/L_{\text{OH}} = 0.93$ ), indicating a closed OH budget. During the low-NO<sub>x</sub> period, however, the production rate is



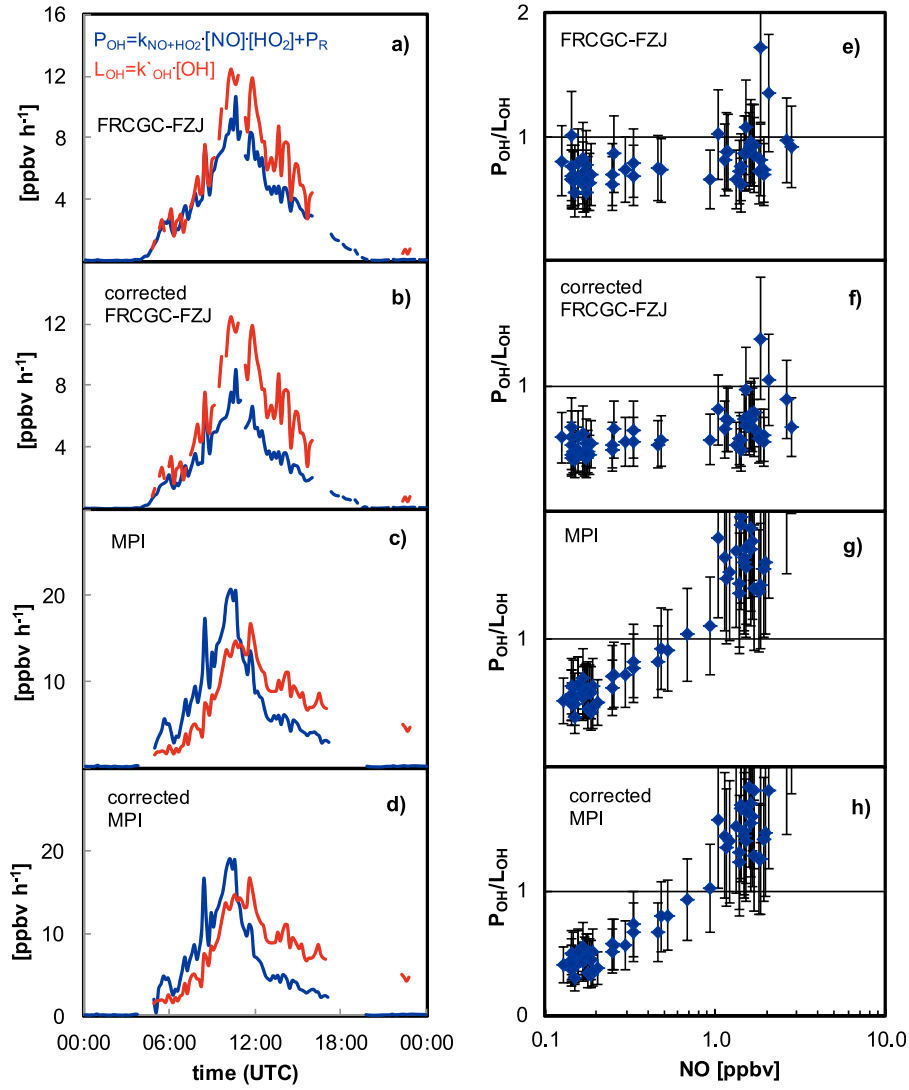
**Figure 9.** Correlation between measured and modeled (top) OH, (middle) HO<sub>2</sub>, and (bottom) corrected HO<sub>2</sub> as well as the correlations of their ratios with NO (on a logarithmic scale) measured during HO<sub>x</sub>Comp. Error bars represent 2 $\sigma$  relative error of the average measured OH and HO<sub>2</sub> levels.

smaller than the loss rate ( $P_{\text{OH}}/L_{\text{OH}} = 0.71$ ), indicating the need for an additional OH source. When the OH and HO<sub>2</sub> data by MPI\_LIF are considered (Figure 10), the OH production rate is found to be consistently larger than the OH sinks in the morning ( $P_{\text{OH}}/L_{\text{OH}} = 1.83$ ). This result is hard to explain, given the expected high recycling efficiency during the high-NO<sub>x</sub> period (see section 3.4), except by systematic errors of the calculated OH budget. At low NO<sub>x</sub>, the production rate is smaller than the loss rate ( $P_{\text{OH}}/L_{\text{OH}} = 0.61$ ), indicating a missing OH source, in qualitative agreement with the result from FRCGC/FZJ (Figure 10). The calculated gap during the low-NO<sub>x</sub> period corresponds to 2.5 and 3.7 ppb h<sup>-1</sup> on average of unaccounted OH sources for FRCGC/FZJ and MPI, respectively. The deficit in the OH budget becomes more apparent when the HO<sub>2</sub> data are corrected for the estimated interferences from RO<sub>2</sub>. As shown in Figure 10, the  $P_{\text{OH}}/L_{\text{OH}}$  ratios calculated using corrected HO<sub>2</sub>, decrease to 0.52 and 0.49 on average for FRCGC/FZJ and MPI, respectively, in average during the low-NO<sub>x</sub> period. Consequently, the deficit in the OH budget increases

to reach 3.6 and 4.9 ppb h<sup>-1</sup> for FRCGC/FZJ and MPI, respectively, on average during the low-NO<sub>x</sub> period. The experimental uncertainty of the missing OH source is about 45%, which represents the error propagation of the uncertainties of the parameters needed for calculation of the turnover rates (see section 2.2). It should be noted here that the result is particularly sensitive to the uncertainty of the HO<sub>2</sub> measurements (and the corrections), because the HO<sub>2</sub>+NO reaction dominates the OH production rate (>70%; see section 3.3). The existence of a missing OH source during HO<sub>x</sub>Comp agrees with findings from other field campaigns in isoprene-rich air at low NO<sub>x</sub>, where efficient OH recycling without NO has been postulated as an additional OH source [Lelieveld *et al.*, 2008; Hofzumahaus *et al.*, 2009; Lu *et al.*, 2011; Whalley *et al.*, 2011].

### 3.7. OH Initiation Sources

[32] OH radical initiation describe processes that lead to the production of new OH radicals which include O<sub>3</sub> photolysis,  $P_{\text{OH}}(\text{O}_3)$ , HONO photolysis,  $P_{\text{OH}}(\text{HONO})$ ,



**Figure 10.** Calculated total OH loss (red,  $k'_{\text{OH}}[\text{OH}]$ ) and production rates (blue,  $k_{\text{OH}+\text{HO}_2}[\text{HO}_2][\text{NO}] + P_{\text{R}}$ , with  $P_{\text{R}} = j(\text{HONO})[\text{HONO}] + P_{\text{OH}(\text{O}_3)} + P_{\text{OH}(\text{alkenes})}$ ). Measured OH and HO<sub>2</sub> data from (a) FZJ\_LIF and FRCGC\_LIF (mean) and (c) MPI used in the calculations. (b) and (d) The corresponding HO<sub>2</sub> data corrected for the recently observed RO<sub>2</sub> interferences of the HO<sub>2</sub> instruments. (e–h) The ratio of production to destruction for each case with the 2 $\sigma$  error bars representing the propagation error of the experimental uncertainties of the parameters used for the calculation.

alkene ozonolysis,  $P_{\text{OH}(\text{alkenes})}$ . For HONO photolysis,  $P_{\text{OH}(\text{HONO})}$ , is given by

$$P_{\text{OH}(\text{HONO})} = j(\text{HONO})[\text{HONO}] - k_{\text{OH}+\text{NO}}[\text{NO}][\text{OH}], \quad (6)$$

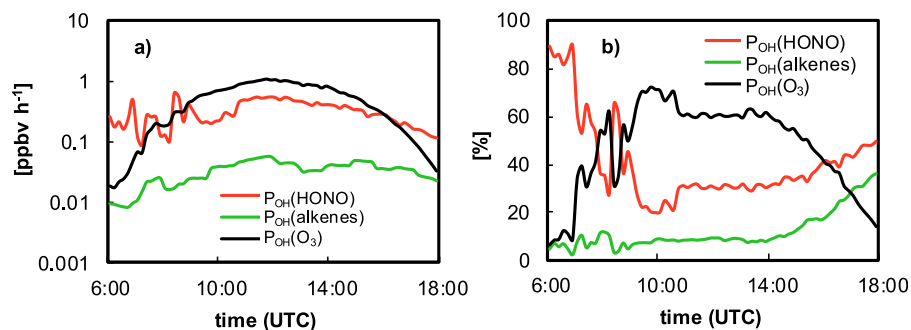
for which only the net OH source rather than the gross HONO photolysis rate is considered. The photostationary state concentration of HONO,  $[\text{HONO}]_{\text{PSS}}$ , defined as

$$[\text{HONO}]_{\text{PSS}} = k_{\text{OH}+\text{NO}}[\text{OH}][\text{NO}] / (j(\text{HONO}) + k_{\text{OH}+\text{HONO}}[\text{OH}]), \quad (7)$$

accounts for about 44% of the measured HONO on average during the high-NO<sub>x</sub> period, in comparison to only 9% during the low-NO<sub>x</sub> period.

[33] The average absolute and relative diurnal contributions of the different net OH sources are shown in Figure 11.

During the high- and low-NO<sub>x</sub> periods, the photolytic sources, namely, photolysis of O<sub>3</sub> (48, 57)% and HONO (46, 34)%, have the highest contributions while alkene ozonolysis contribute only 6 and 9%, respectively. As shown in Figure 11, HONO photolysis has the highest contribution during the early morning but decreases gradually to reach its minimum of about 23% at 10:00 UTC. The relative contribution of HONO photolysis increases slightly after 10:00 UTC owing to the decreased  $[\text{HONO}]_{\text{PSS}}$  levels as a result of decreased NO concentrations. The relative contribution of  $P_{\text{OH}(\text{HONO})}$  becomes stable until around 14:00 UTC, where its relative contribution increases again due to the lower contribution from O<sub>3</sub> photolysis. During daytime (06:00–18:00 UTC) photolysis of O<sub>3</sub> had the highest contribution of 56% followed by photolysis of HONO (36%) and alkene ozonolysis (8%).



**Figure 11.** (a) Primary OH production rates from different sources (logarithmic scale) and (b) their relative contribution.  $P_{\text{OH}}(\text{HONO})$  represents the net HONO photolysis rate defined as  $P_{\text{OH}}(\text{HONO}) = j(\text{HONO}) \cdot [\text{HONO}] - k_{\text{OH}+\text{NO}} \cdot [\text{NO}] \cdot [\text{OH}]$ .

[34] Based on the correlation between the net OH formation by photolysis of HONO,  $P_{\text{OH}}(\text{HONO})$ , and the photolysis frequencies,  $j(\text{NO}_2)$  and  $j(\text{O}^1D)$ , and their different wavelength range Elshorbany *et al.* [2009a] postulated that the photolysis of nitric acid is a minor HONO source under urban conditions. Instead, photolytic sources active at longer wavelengths, like photosensitized conversion of  $\text{NO}_2$  on humic acid surfaces [e.g., Stemmler *et al.*, 2006] or photolysis of nitroaromatic compounds [Bejan *et al.*, 2006], were proposed to be of higher importance. Similarly, analysis for the semirural conditions of this study (see Figure 12) confirms these results. The correlations in Figure 12 show that net HONO formation during the afternoon period is linearly dependent on  $j(\text{NO}_2)$  and shows no significant intercept while the correlation is clearly curved for  $j(\text{O}^1D)$ . This can be explained by the much broader diurnal profile of  $j(\text{NO}_2)$  compared to  $j(\text{O}^1D)$ . Thus, a short-wavelength range photochemical net HONO source [Zhou *et al.*, 2003, 2011] can most probably be excluded for the HO<sub>x</sub>Comp campaign. It worth also noting that HONO formation was recently reported by Su *et al.* [2011] to be a function of temperature (also under dark conditions) rather than being light-dependent at all. Thus, further investigations of HONO daytime sources are still urgently needed.

### 3.8. OH Reactivity

[35] The diurnal profiles of measured and modeled OH reactivity are shown in Figure 3. The modeled OH reactivity,

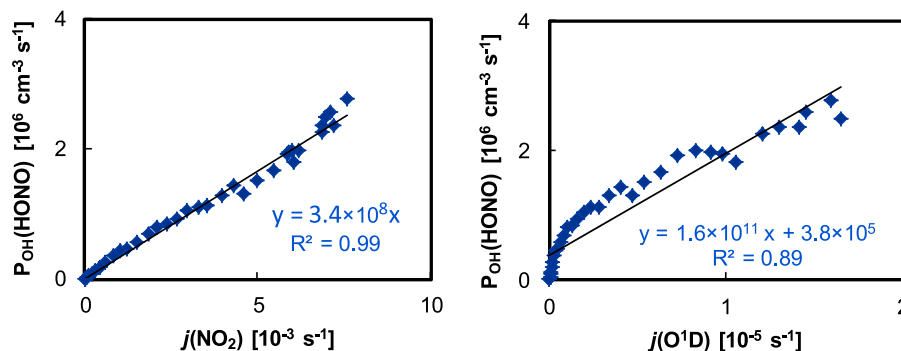
defined as the reciprocal of the OH radical lifetime, has been calculated from

$$\text{OH reactivity} = \frac{L_{\text{OH}}(\text{total})}{[\text{OH}]} \quad (8)$$

The measured OH reactivity during daytime is well reproduced by the model within  $\pm 14\%$  (see Figure 3). The average modeled reactivities during the high- and low- $\text{NO}_x$  periods of  $7.7 \text{ s}^{-1}$  and  $8.2 \text{ s}^{-1}$  are in good agreement (within the experimental uncertainties, see section 2.2) with those measured of  $8.6 \text{ s}^{-1}$  and  $8.6 \text{ s}^{-1}$  (see Figure 3). The calculated primary OH reactivity based solely on the measured species (9) of  $5.3 \text{ s}^{-1}$  and  $5.2 \text{ s}^{-1}$  is much lower than that measured by 38 and 40% during the high- and low- $\text{NO}_x$  periods, respectively (see Figure 3):

$$\text{primary OH reactivity} = \sum k_{\text{OH}+\text{Y}_i} \cdot [\text{Y}_i], \quad (9)$$

where  $k_{\text{OH}+\text{Y}_i}$  is the bimolecular rate constant for the reaction of  $\text{Y}_i$  with OH. A sensitivity test running the base model with and without isoprene as input shows that the enhancement of the modeled reactivity in Figure 3 relative to the primary OH reactivity is mainly caused by model-calculated isoprene degradation products. In another test, isoprene was constrained in the model, but all isoprene oxidation products (e.g., MACR, MVK, and HCHO) were unconstrained. In this case, the modeled concentrations of the isoprene products were found to be significantly larger by varying



**Figure 12.** Correlation between  $P_{\text{OH}}(\text{HONO})$  and (a)  $j(\text{NO}_2)$  and (b)  $j(\text{O}^1D)$  during the afternoon (14:30–20:30 UTC). The linear regression shows that net HONO formation during the afternoon period is linearly dependent on  $j(\text{NO}_2)$  and shows no significant intercept, while the correlation is clearly curved for  $j(\text{O}^1D)$ .

degrees than the corresponding measured values. One possible reason could be that most of the isoprene, which was freshly emitted by the forest around the measurement site, was less photochemically aged than implicitly assumed by the base model. As expected, owing to the increased levels of simulated OVOC, HO<sub>2</sub> and RO<sub>2</sub> and OH reactivity were also increased by different degrees. However, the increase in P<sub>OH</sub>(HO<sub>2</sub>+NO) was almost compensated with the increase in the OH reactivity resulting in only slight changes in the OH levels. In addition, unmeasured, unconstrained isoprene secondary oxidation products, especially the organic peroxide of isoprene (ISOOH) that results from the reaction of the corresponding isoprene peroxy radicals (ISO<sub>2</sub>) with HO<sub>2</sub>, may react with OH at a rate constant that is comparable to that of isoprene and therefore contributes significantly to the OH reactivity and production [e.g., Kubistin *et al.*, 2010; Pugh *et al.*, 2010]. In very clean, pristine air, Kubistin *et al.* [2010] showed explicitly that measured ISOOH reaction with OH contributes 15% to both the total OH loss and production and thus has no net effect on the OH budget. These results are in agreement with our previous studies that showed that photochemically formed OVOCs are not a net OH source [Elshorbany *et al.*, 2009a, 2010b]. Thus, the uncertainty due to the local isoprene emission has little influence on the OH prediction, but causes a possible bias in modeled HO<sub>2</sub>, RO<sub>2</sub> and OH reactivity. A RACM-based box model with updated isoprene chemistry was found to significantly underestimate the measured OH reactivity by 2.5 s<sup>-1</sup>, on average during daytime on 10 July, for which several sensitivity analyses were performed to account for this missed OH reactivity [Kanaya *et al.*, 2011].

[36] Similar to the HO<sub>x</sub>Comp campaign, other studies have also found that the OH reactivity calculated from only measured trace gases underestimates the measured [e.g., Di Carlo *et al.*, 2004; Yoshino *et al.*, 2006; Ren *et al.*, 2006; Lou *et al.*, 2010; Lee *et al.*, 2009; Mogensen *et al.*, 2011] or modeled [Elshorbany *et al.*, 2009a] total OH reactivity. At HO<sub>x</sub>Comp, the OH reactivity split of NO<sub>x</sub>, O<sub>3</sub>, CO, HCHO and OVOCs was determined from their total loss rates due to reaction with OH (calculated by the base model, see Figure 5 and equation (8)). The OH reactivity of NO<sub>x</sub> accounts for 23 and 7% of the total reactivity during the high- and low-NO<sub>x</sub> periods, respectively. Among the VOCs, isoprene and its oxidation products had the highest contribution to the total OH reactivity of 31 and 51% during the high- and low-NO<sub>x</sub> periods followed by CO (13, 10)%, HCHO (7, 8)%, OVOCs (5, 4)%, O<sub>3</sub> (1, 2)% and other VOCs (20, 18)%, respectively. It should also be mentioned that biogenic hydrocarbons (including monoterpenes and sesquiterpenes) other than isoprene are emitted by the forest trees at Forschungszentrum Jülich. For example, Dlugi *et al.* [2010] reported measured values of about 200 ppt of monoterpenes for July 2003, which may add reactivity of the order of 0.5 s<sup>-1</sup>. During HO<sub>x</sub>Comp, monoterpenes were not measured in ambient air and are therefore not considered in the model here.

### 3.9. Conclusion

[37] In this study HO<sub>x</sub> chemistry under NO<sub>x</sub>-limited conditions was investigated through detailed analysis of the radical budgets using the master chemical mechanism, MCMv3.2. The model results have been compared and contrasted with measured radical levels performed

simultaneously by different techniques during the international blind HO<sub>x</sub>Comp intercomparison campaign.

[38] Both modeled OH and HO<sub>2</sub> diurnal profiles lay within the measurement range of all HO<sub>x</sub> measurement techniques with correlation slopes between mean measured and modeled OH and HO<sub>2</sub> values of about unity during daytime (06:00–18:00 UTC). However, when the estimated interference caused by RO<sub>2</sub> cross reactions is considered, the slope between the corrected and modeled HO<sub>2</sub> regression line becomes 30% smaller, indicating a model overprediction of HO<sub>2</sub>. The correlation between measured/ modeled ratio of OH and HO<sub>2</sub> and NO shows that OH was slightly overestimated during the high-NO<sub>x</sub> period but shows an increasing underestimation during the low-NO<sub>x</sub> period, reaching 65% at <0.2 ppbv NO. In contrast, HO<sub>2</sub> was underestimated during both, high- and low-NO<sub>x</sub> periods by 48 and 17%, respectively. After correction of the HO<sub>2</sub> data for their interference by RO<sub>2</sub>, the agreement improves slightly at NO values above 1 ppbv, but a model overestimation of about 40% becomes apparent at low NO values of 0.2 ppbv. In addition, a missing OH source 2.5 and 3.7 ppb h<sup>-1</sup> on average during the low-NO<sub>x</sub> period for FRCGC/FZJ and MPI, respectively, was estimated from the calculated OH budget during the low-NO<sub>x</sub> period. The deficit in the OH budget becomes more apparent when the HO<sub>2</sub> data are corrected for the estimated interferences from RO<sub>2</sub>, reaching 3.6 and 4.9 ppb h<sup>-1</sup> for FRCGC/FZJ and MPI, respectively, on average during the low-NO<sub>x</sub> period. This missing OH source is in qualitative agreement with other previous studies but quantitatively much lower.

[39] The impact of the reported more precise values of  $k_{\text{NO}_2+\text{OH}}$  was estimated and found to increase the measured HO<sub>x</sub> levels only during the high-NO<sub>x</sub> period by 11%.

[40] During the high- and low-NO<sub>x</sub> periods, the photolytic radical initiation sources, namely, photolysis of O<sub>3</sub> (48, 57)%, and HONO (46, 34)% contributed most, while alkene ozonolysis contributed only 6 and 9%, respectively.

[41] The average modeled reactivities during the high- and low-NO<sub>x</sub> periods of 7.7 and 8.2 s<sup>-1</sup> are in good agreement with those measured. Among the VOCs, isoprene and its degradation products had the highest contribution to the total OH reactivity of 31 and 51% during the high- and low-NO<sub>x</sub> periods followed by CO (13, 10)%, HCHO (7, 8)%, OVOCs (5, 4)%, O<sub>3</sub> (1, 2)% and other VOCs (20, 18)%, respectively.

[42] A BR ratio near unity was obtained during the high-NO<sub>x</sub> period (06:00–10:00 UTC), indicating a balance between the secondary radical loss and production owing to the high recycling efficiency. However, during the low-NO<sub>x</sub> period (11:00–18:00 UTC), a BR ratio of only 0.75 was obtained indicating net secondary radical loss due to a low recycling efficiency. In addition, under low-NO<sub>x</sub> conditions, a significant fraction of the OH radical recycling processes occur without NO through P<sub>OH</sub>(sec) and P<sub>OH</sub>(HO<sub>2</sub>+O<sub>3</sub>). These recycling processes partially compensate the deficit in the OH budget as a result of the low-NO<sub>x</sub> conditions. Thus, in contrast to the experimental OH budget calculated based on measured HO<sub>2</sub>, OH and OH reactivity, the initiation sources and other modeled secondary sources fill the deficit in the radical budgets during afternoon, thus maintaining the balance between total radical production and destruction. The measured diurnal profile of the HO<sub>2</sub>/OH ratio is well reproduced by the MCM model within the measurement

uncertainties. However, if corrected HO<sub>2</sub> is used to calculate the HO<sub>2</sub>/OH ratio, the agreement slightly improves during the high-NO<sub>x</sub> period, but becomes significantly worse at low NO<sub>x</sub>. This result shows that the cycling between OH and HO<sub>2</sub> is better described by the model at high NO<sub>x</sub> than at low NO<sub>x</sub>. Similar field model comparison studies are still urgently needed to investigate HO<sub>x</sub> recycling under NO<sub>x</sub>-limited conditions.

[43] **Acknowledgments.** This work was supported by the EU FP-6 program EUROCHAMP (Integration of European Simulation Chambers for Investigating Atmospheric Processes, grant R1I3-CT-2004-505968) and ACCENT (Priority 1.1.6.3. Global Change and Ecosystems, grant GOCECT-2004-505337). We thank F. J. Johnen for assistance with the experiments.

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