Experimental chemical budgets of OH, HO_2 and RO_2 radicals in rural air in West-Germany during the JULIAC campaign 2019

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Abstract.

Photochemical processes in ambient air were studied using the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany. Ambient air was continuously drawn into the chamber through a 50 m high inlet line and passed through the chamber for one month in each season throughout 2019. The residence time of the air inside the chamber was about one hour. As the research center is surrounded by a mixed deciduous forest and is located close to the city Jülich, the sampled air was influenced by both anthropogenic and biogenic emissions. Measurements of hydroxyl (OH), hydroperoxyl (HO_2) and organic peroxy (RO_2) radicals were achieved by a laser-induced fluorescence instrument. The radical measurements together with measurements of OH reactivity (k_{OH}, the inverse of the OH lifetime) and a comprehensive set of trace gas concentrations and aerosol properties allowed for the investigation of the seasonal and diurnal variation of radical production and destruction pathways. In spring and summer periods, median OH concentrations reached 6×10^6 cm^{-3} at noon, and median concentrations of both, HO_2 and RO_2 radicals, were 3×10^8 cm^{-3}. The measured OH reactivity was between 4 and 18 s^{-1} in both seasons. The total reaction rate of peroxy radicals with NO was found to be consistent with production rates of odd oxygen ($O_X = NO_2 + O_3$) determined from NO_2 and O_3 concentration measurements. The chemical budgets of radicals were analysed for the spring and summer seasons, when peroxy radical concentrations were above the detection limit. For most conditions, the concentrations of radicals were mainly sustained by the regeneration of OH via reactions of HO_2 and RO_2 radicals with nitric oxide (NO). The median diurnal profiles of the total radical production and destruction rates showed maxima between 3 to 8 ppbv h^{-1} for OH, HO_2 and RO_2. Total RO_X (OH, HO_2~~,~~ and RO_2) initiation and termination rates were below 3 ppbv h^{-1}. The highest OH radical turnover rate of 13 ppbv h^{-1} was observed during a high-temperature (max 40°C) period in August. In this period, the highest HO_2, RO_2 and RO_X turnover rates were around 11, 10 and 4 ppbv h^{-1}, respectively. When NO mixing ratios were between 1 ppbv to 3 ppbv, OH and HO_2 production and destruction rates were balanced, but unexplained RO_2 and RO_X production reactions with median rates of 2 ppbv h^{-1} and 0.4 ppbv h^{-1}, respectively, were required to balance their destruction. For NO mixing ratios above 3 ppbv, the peroxy radical reaction rates with NO were highly

uncertain due to the low peroxy radical concentrations close to the limit of NO interferences in the HO_2 and RO_2 measurements. For NO mixing ratios below 1 ppbv, a missing source for OH and a missing sink for HO_2 were found with maximum rates of 3.0 ppbv h^{-1} and 2.0 ppbv h^{-1}, respectively. The missing OH source consisted likely of a combination of a missing inter-radical HO_2 to OH conversion reaction (up to 2 ppbv h^{-1}) and a missing primary radical source (0.5 – 1.4 ppbv h^{-1}). The dataset collected in this campaign allowed to analyze the potential impact of OH regeneration from RO_2 isomerization reactions from isoprene, HO_2 uptake on aerosol, and RO_2 production from chlorine chemistry on radical production and destruction rates. These processes were negligible for the chemical conditions encountered in this study.

1 Introduction

The hydroxyl (OH) radical is the dominant daytime atmospheric oxidant. It reacts with most trace gases in the troposphere and thereby controls the rate of their removal and chemical transformation. In the lower troposphere, OH is primarily produced by solar photolysis of ozone (O_3) and nitrous acid (HONO). The reaction of OH with trace gases leads to the formation of hydroperoxy (HO_2) or organic peroxy (RO_2, with R = organic group) radicals, which undergo further radical reactions. Generally, these reactions are cyclic chain reactions, in which OH, HO_2, and RO_2 are converted into each other, while at the same time emitted pollutants are oxidized and converted into secondary pollutants such ozone and oxygenated volatile organic compounds (OVOCs). Because the conversion of radicals occurs on a time scale of seconds to minutes, they are often referred to as the RO_X family (OH + HO_2 + RO_2). The most important radical reactions in the lower are summarized in Table 1. Understanding the radical chemistry is the basis for reliable predictions of the atmospheric lifetime and chemical transformation of air pollutants and climate-relevant gases by atmospheric chemistry models (Stone et al., 2012).

The level of agreement between simulated and observed radical concentrations in various environments shows the degree of understanding of the underlying radical chemical mechanism. Even though good agreement is found in some cases (Tan et al., 2001; Konrad et al., 2003; Mihelcic et al., 2003; Lelieveld et al., 2008; Kubistin et al., 2010; Whalley et al., 2011), there are significant unexplained discrepancies between modelled and measured OH in forested regions ~~(Wolfe et al., 2011; Kim et al., 2013; Hens et al., 2014; Wolfe et al., 2014; Griffith et al., 2016)~~ (Wolfe et al., 2011; Griffith et al., 2013; Kim et al., 2013; Hens et al., 2014; Wolfe et al., 2014) and of HO_2 and RO_2 in polluted areas (Ren et al., 2003; Ren et al., 2006; Kanaya et al., 2007; Dusanter et al., 2009; Chen et al., 2010; Ren et al., 2013; Brune et al., 2016; Tan et al., 2018; Slater et al., 2020; Whalley et al., 2021), while different results are found depending on the abundance of nitric oxide (NO) in rural environments (Hofzumahaus et al., 2009; Lou et al., 2010; Elshorbany et al., 2012; Kanaya et al., 2012; Tan et al., 2017).

A chemical budget analysis using measured OH, HO_2 and RO_2 radical concentrations can help assessing the strength of different radical production and loss paths. This allows to identify possible missing chemical processes by comparing the total production and destruction rates for the different radicals as concentrations are expected to be in steady-state due to their short chemical lifetime. A large number of measurements needs to be available (e.g., OH reactivity, OH, peroxy radicals), therefore, there have been only few studies focusing on the analysis of the chemical budget for OH radicals so far (Handisides et al., 2003; Hofzumahaus et al., 2009; Brune et al., 2016; Whalley et al., 2018; Tan et al., 2019; Whalley et al., 2021).

Results from field campaigns in China showed a larger OH radical destruction rate compared to its production rate in the afternoon, which points to an unaccounted OH radical source. Discrepancies were highest, when NO mixing ratios were lower than 2 ppbv (Hofzumahaus et al., 2009; Tan et al., 2019; Whalley et al., 2021). On the other hand, studies in urban areas in California (Brune et al., 2016) and in London (Whalley et al., 2018) as well as in a rural area in Hohenpeissenberg (Handisides et al., 2003) showed no significant gap between the OH production and destruction rates. Recently, radical measurements including RO_2 enabled the investigation of HO_2, RO_2, and RO_X production and destruction rates in field campaigns in China (Tan et al., 2019; Whalley et al., 2021). Tan et al. (2019) showed that a RO_2 loss process was required in a campaign in Wangdu in summer, while HO_2 production and destruction rates were balanced. This suggests a missing conversion of RO_2 to OH in addition to the reaction of peroxy radicals with NO. Furthermore, Whalley et al. (2021) found large imbalances between peroxy radical production and destruction rates in Beijing indicating a substantially slower propagation of RO_2 to HO_2 radicals than anticipated.

In this study, OH, HO_2, and RO_2 radical concentrations as well as OH reactivity, the inverse of the OH radical lifetime, were measured in the atmospheric simulation chamber SAPHIR on campus of Forschungszentrum Jülich (FZJ), Germany, in the Jülich Atmospheric Chemistry Project Campaign (JULIAC). Ambient air was sampled from 50 m height into the SAPHIR chamber. From this data set, a chemical budget analysis of OH, HO_2, RO_2 radicals, and their sum (RO_X) was done using measured concentrations allowing to investigate, if all radical production and destruction processes were accounted for during spring and summer.

Table 1. Chemical reactions and rate constants used for the analysis of the chemical budgets of radicals. Values of reaction rate constants are given for standard conditions (298 K, 1 atm). Actual numbers are used for the calculations.

	Reaction	k(298 K, 1 atm) / $cm^3\,s^{-1}$	k_{ERR}[a]	Reference
Radical initiation reactions				
R1	$HONO+hv \rightarrow OH + NO$	j_{HONO}[b]		
R2	$O_3+hv \rightarrow O^1D+O_2$	j_{O1D}[b]		
R2a	$O^1D+H_2O \rightarrow 2OH$	2.1×10^{-10}	±13%	IUPAC
R2b	$O^1D+M \rightarrow O^3P+M$	3.3×10^{-11}	±10%	IUPAC and JPL
R3	$HCHO+hv \rightarrow 2HO_2 + CO$	j_{HCHO}[b]		
R4	$CH_3CHO+hv\rightarrow CH_3O_2+HO_2+ CO$	j_{CH3CHO}[b]		
R5	alkenes+$O_3\rightarrow$OH, HO_2, RO_2+products			
R5a	propene+$O_3\rightarrow$ products[c]	1.0×10^{-17}	±20%	IUPAC
R5b	cis-but-2-ene+$O_3\rightarrow$ product[d]	1.3×10^{-16}	±12%	IUPAC
R5c	1-pentene+$O_3\rightarrow$ products[e]	1.0×10^{-17}	±20%	MCMv3.3.1
R5d	2-hexene+$O_3\rightarrow$ products[f]	1.1×10^{-17}	±20%	MCMv3.3.1
R5e	isoprene+O_3 → products[g]	1.3×10^{-17}	±10%	MCMv3.3.1
R5f	α-pinene+O_3 → products[h]	9.6×10^{-17}	±20%	IUPAC
Radical interconversion reactions				
R6	$HCHO+OH+O_2\rightarrow CO+H_2O+HO_2$	8.5×10^{-12}	±10%	IUPAC
R7	$CO+OH+O_2\rightarrow CO_2+HO_2$	2.3×10^{-13}	±6%	IUPAC
R8	VOCs+$OH+O_2 \rightarrow RO_2+H_2O$	[j]		
R9	$RO_2+NO\rightarrow$products+HO_2+NO_2	8.6×10^{-12}	±30%	Jenkin et al. (2019)
R10	$HO_2+NO\rightarrow OH+NO_2$	8.5×10^{-12}	±13%	IUPAC
R11	$HO_2+O_3\rightarrow OH+2O_2$	2.0×10^{-15}	±29%	IUPAC
Radical termination reactions				
R12	$NO_2+OH\rightarrow HNO_3$	1.0×10^{-11}	±30%	IUPAC
R13	$NO+OH\rightarrow HONO$	9.7×10^{-12}	±13%	IUPAC
R14	$RO_2+NO\rightarrow RONO_2$	4.6×10^{-13}	±30%	Jenkin et al. (2019)
R15	$RO_2+RO_2\rightarrow$products	3.5×10^{-13}	±50%	Jenkin et al. (2019)
R16	$RO_2+HO_2\rightarrow ROOH+O_2$	2.3×10^{-11}	±50%	Jenkin et al. (2019)
R17	$HO_2+HO_2\rightarrow H_2O_2+O_2$	4.5×10^{-12}[i]	±20%	IUPAC
Isoprene reactions				
R18	isoprene + OH → products	1.0×10^{-10}	±8%	IUPAC
R19	isoprene–RO_2 (1,6-H shift) → products + OH	0.01–0.06 s^{-1}		Peeters et al. (2014)
Cl reactions				
R20	$ClNO_2+hv\rightarrow Cl+NO_2$	j_{ClNO2}[b]		
R21	$Cl_2+hv\rightarrow 2Cl$	j_{Cl2}[b]		
R22	VOCs+$Cl\rightarrow RO_2$+HCl	[j]		

[a] 1σ uncertainty

[b] Measured photolysis frequencies

[c] Yield for OH: 0.36, HO_2: 0.10, RO_2: 0.42 from Novelli et al. (2021)

[d] Yield for OH: 0.36, HO_2: 0.15, RO_2: 0.51 from Novelli et al. (2021)

[e] Yield for OH: 0.32, HO_2: 0.09, RO_2: 0.37 from Novelli et al. (2021)

[f] Yield for OH: 0.48, HO_2: 0.11, RO_2: 0.59 from Novelli et al. (2021)

[g] Yield for OH: 0.26, HO_2: 0.26 from Malkin et al. (2010)

[h] Yield for OH: 0.8 from Cox et al. (2020)

[i] at 1% water vapour mixing ratio

[j] Highly variable depending on the specific VOC.

2 Methodology

2.1 The JULIAC campaign

The Jülich Atmospheric Chemistry Project (JULIAC) campaign was conducted at Forschungszentrum Jülich (FZJ, 50.9° N, 6.4° E), Germany. The project consisted of four one-month long intensive campaigns studying atmospheric chemistry in ambient air in each season throughout 2019. The location is surrounded by a deciduous forest and is located in a rural environment near a town, Jülich (33,000 inhabitants), 25 km northeast, 40 km west, and 43 km southwest from three large cities, Aachen, Cologne and Düsseldorf, respectively. Therefore, ambient air is influenced by both biogenic and anthropogenic emission sources.

The investigation of the photochemistry was performed in the SAPHIR chamber, which was equipped with a large set of instruments measuring radicals, trace gases and aerosol (Table 2). The SAPHIR chamber has a cylindrical shape and is made of a double-wall Teflon (FEP) film. A slight overpressure (35 Pa) is maintained in the chamber and the space between the two films is permanently flushed with pure nitrogen (Linde, purity: > 99:99990 %) to prevent outside air penetrating the inner chamber. The

Table 2. Specification of instruments used in the JULIAC campaign for the analysis in this work.

Species	Measurement technique	Time resolution	Limit of detection (1σ)	1σ accuracy
OH	LIF	270 s	0.7×10^{6} cm^{-3}	18%
OH	DOAS	134 s	0.8×10^{6} cm^{-3}	6.5%
HO_2	LIF	47 s	1×10^{7} cm^{-3}	18%
RO_2	LIF	47s	2×10^{7} cm^{-3}	18%
OH reactivity (k_{OH})	LP-LIF	180 s	0.2 s^{-1}	10%
Photolysis frequencies	Spectroradiometer	60 s		18%
O_3	UV photometry	60 s	0.5 ppbv	2%
NO_X ($NO+NO_2$)	Chemiluminescence[a]	60 s	NO: 20 pptv NO_2: 30 pptv	NO: 5 % NO_2: 7%
CO, CO_2, CH_4, H_2O	Cavity ring-down spectroscopy	60 s	CO and CH_4: 1 ppbv CO_2: 25 ppbv H_2O: 0.1 %	5%
HONO	LOPAP	180 s	5 pptv	10%
HCHO	Cavity ring-down spectroscopy	300 s	0.1 ppbv	10%
$ClNO_2$	I-CIMS	60 s	2.8 pptv	8.5%
VOCs	PTR-TOF-MS	30 s	15 pptv	14%
	VOCUS PTR-TOF-MS	30 s		
Aerosol surface area	SMPS	7 min	10nm – 1μm	N/A

[a] NO_2 was converted to NO before detection using a custom-built photolytic converter.

chamber is equipped with a shutter system allowing the air to be either shielded from or exposed to solar radiation.

In the JULIAC campaign, ambient air was sampled at a high flow rate of 660 m^3 h^{-1} from 50 m high inlet line (104 mm inner diameter, SilcoNert® coated stainless steel) by means of an oil-free turbo blower (Aerzener Maschinenfabrik, AERZEN Turbo G3 Typ: TB 50-0.6 S). Large particles (>10 µm diameter) were removed by a SilcoNert® coated cyclone (LTG, ZSB-6). The temperatures in the inlet line and cyclone were controlled to be slightly higher than ambient temperature (+1 to 2 ˚C) to avoid water vapor condensation in the inlet system. A 3/2-way valve directed part of the air (flow rate of 250 m^3 h^{-1}) into the chamber. Two fans inside the chamber ensured fast mixing on a time scale of a few minutes. As a result, the chamber behaved as a continuously stirred photochemical flow reactor with a mean residence time of air of 1.1 h. During the transition time of 3.5 s from the tip of the inlet to the SAPHIR chamber, atmospheric RO_X radicals are lost on walls, but concentrations are rapidly re-established in the sampled ambient air inside the sunlit chamber.

The use of the chamber as a flow reactor has advantages compared to field measurements in the open air. Perturbations of the studied chemistry due to local emissions of VOCs or NO_X can be avoided. Transient fluctuations of reactants in the sampled air, for example due to spikes of NO from passing cars, are smoothed out in the chamber. Due to the homogeneous mixing, instruments connected to the chamber measure the same air composition and segregation effects on reaction rates are insignificant.

The air composition could be influenced by the inlet line and chamber surfaces. As the whole inlet line is heated and chemically inert due to the SilcoNert® coating, no relevant wall loss or desorption of trace gases is expected from the inlet. This assumption was confirmed by comparing OH reactivity measured at several positions of the inlet line. No significant differences were found between measurements, if the air was either sampled upstream of the cyclone or downstream of the blower. Wall losses of trace gases (VOCs, NO_x, O_3) inside the SAPHIR chamber were found to be negligible in previous experiments (e.g., Kaminski et al., 2017, Rolletter et al., 2020).

Nitrous acid (HONO) and formaldehyde (HCHO) are known to be emitted from the chamber film when it is exposed to solar radiation (Rohrer et al. (2005)). These emissions significantly increase the concentrations of HONO and HCHO in the chamber. Due to the transmission through the Teflon film and shading from construction elements of the chamber, the absolute actinic flux density is reduced by 20 to 40 % compared to outside the chamber. It is worth noting, however, that the relative spectral distribution of the solar radiation is not changed by the transmission through the chamber film (Bohn and Zilken, 2005).

The floor underneath the chamber is heated by the solar radiation. Although it is not in direct contact to the foil, the air temperature in the chamber was on average 0.7°C higher during winter and autumn and 1.9°C higher during spring and summer than the temperature outside of the chamber at daytime. Since photochemistry was studied in the chamber, all data of chemical and physical conditions shown in this work refer to conditions inside the chamber.

The measurements in the campaign were at least once a week interrupted for calibration and maintenance of instruments. Some days were also excluded from the analysis in this work because the chamber shutter system was kept closed to protect the chamber film during bad weather from strong wind gusts and/or precipitation. Reference experiments with clean synthetic air were performed to investigate possible changes in the strength of chamber emissions and to check for instrumental backgrounds. In addition, chemical actinometry experiments, in which NO_2 was photolyzed in synthetic air, were performed before and after each intensive period. The comparison of actinometric and spectroradiometric j_{NO_2} values was used to track and correct for changes in light transmission due to aging of the chamber wall (Bohn et al., 2005).

2.2 Instrumentation

2.2.1 OH, HO_2 and RO_2 radical and OH reactivity (k_{OH}) measurements

OH, HO_2, and RO_2 radicals were measured by the FZJ – LIF which included a newly developed chemical modulation reactor (CMR) for interference-corrected measurements of OH radicals (Cho et al., 2021). The signals of the instrument were calibrated against well-defined radical concentrations that were produced from water photolysis in synthetic air at a wavelength of 185nm using radiation of a mercury lamp. A detailed description of the LIF instrument and its calibration can be found in previous publications (Holland et al., 2003; Fuchs et al., 2008; Fuchs et al., 2011; Fuchs et al., 2012).

Shortly, the OH radical is sampled through a nozzle with a 0.4 mm diameter pinhole and is excited by a pulsed laser at a wavelength of 308 nm in a low-pressure (4 hPa) fluorescence cell. The emitted resonant fluorescence is detected with a time delay by a time-gated micro-channel plate detector (MCP). In the JULIAC campaign, a chemical modulation reactor (CMR) was implemented on top of the OH cell to quantify potential interferences. This is achieved by periodically removing ambient OH by an OH scavenger that is injected in the reactor (propane, Air Liquide, purity>99.95%, (5.0±0.1) % mixture in nitrogen) before the air enters the fluorescence cell. During the campaign, the observed interference could be fully explained by the well-characterized interference from the photolysis of ozone in humid air inside the detection cell. No evidence for an unexplained interference was found (Cho et al., 2021). The limit of detection for OH was 0.7×10^6 cm^{-3} and the accuracy was 18 % (1σ).

OH radical concentrations were also measured by differential optical absorption spectroscopy (DOAS) using a multiple folded light path for absorption inside along the chamber. The DOAS technique is a calibration-free technique (Hausmann et al., 1997; Schlosser et al., 2007; Schlosser et al., 2009). The limit of detection was 0.8×10^6 cm^{-3} and the 1σ–accuracy was 6.5 %. Due to a technical laser problem, the DOAS instrument was not available in spring.

HO_2 radicals were detected by the LIF instrument in a separate detection cell, where HO_2 is chemically converted to OH radicals in the reaction with NO (Air Liquide, 1% NO in N_2, purity > 99.5 %) that is injected in the fluorescence cell (Fuchs et al., 2011). During the JULIAC campaign, two different concentrations (2.5×10^{13} cm^{-3} and 1.0×10^{14} cm^{-3}) of NO in the fluorescence cell were used to observe possible interference from specific RO_2 radicals as highlighted by Fuchs et al. (2011). No difference between HO_2 measurements at high and low NO concentrations was found suggesting that there was no significant interference from RO_2.

In addition, the sum of OH, HO_2, and RO_2 (RO_X) was measured by the RO_X-LIF system. Air is sampled into a chemical converter (pressure of ~ 25 hPa), where a mixture of NO (Air Liquide, 500 ppmv NO in N_2, purity > 99.5%) and CO (Air Liquide, 10% CO in N_2, purity > 99.997%) is injected. The NO converts RO_2 radicals to HO_2 radicals and CO converts OH radicals formed from the reaction of HO_2 radicals with NO back to HO_2. Therefore, an equilibrium between OH and HO_2 is established. Concentrations are chosen, so that the equilibrium is on the side of HO_2. In a low-pressure cell downstream of the converter HO_2 radicals are converted to OH radicals by injecting excess NO (Air Liquide, pure NO, purity>99.5%) (Fuchs et al., 2008) that shifts the equilibrium between OH and HO_2 to OH. The RO_2 concentration is obtained from the difference between the sum measurement of RO_X and measurements of OH and HO_2 concentrations in the other two detection cells. The RO_2 detection sensitivity was calibrated for methyl peroxy radicals (CH_3O_2) which are produced from the reaction of OH with methane (CH_4) in the calibration system. The resulting calibration is also applicable to the majority of other atmospheric alkyl peroxy radicals (Fuchs et al., 2008; Fuchs et al., 2011) and recent laboratory tests performed with a variety of VOCs including monoterpenes and chained alkanes for the CO and NO mixing ratios applied in the RO_X converter during the JULIAC campaign showed a decrease of less than 15% of sensitivity as compared to methyl peroxy radicals which is within the accuracy of the instrument.

The signals in the HO_2 and RO_2 detection systems contain a background signal observed when NO is injected into the detection cells, even if no radicals are present in the air sampled. The background signal can be characterized when the inlet of the detection system is overflown with synthetic air, which is part of the calibration procedures. During JULIAC the background varied from calibration to calibration and was often larger than the smallest signals measured in ambient air from the chamber (Table S1). The highest background signals obtained from calibrations is therefore regarded as an upper limit and the variability is considered as an additional uncertainty in the measured HO_2 and RO_2 concentrations. HO_2 and RO_2 background signals, which are subtracted in the evaluation of HO_2 and RO_2 measurements, were taken from reference experiments in the dark clean chamber, when no HO_2 or RO_2 radicals are expected. The subtracted signals for each period are available in Table S1and in most cases were equivalent to concentrations lower than 1×10^7 cm^{-3} for both HO_2 and RO_2 measurements.

The total OH reactivity (k_{OH}), the inverse of the chemical lifetime of OH radicals, was measured in ambient air by a laser-flash photolysis LIF instrument (Lou et al., 2010; Fuchs et al., 2017). A high concentration of OH radicals is produced by flash photolysis (266 nm, 1 Hz repetition rate) of ozone in humid air (Reaction R2) in a flow tube that is on top of an OH fluorescence cell. The pseudo first-order decay of OH in the chemical reactions with atmospheric reactants is measured, giving directly the OH reactivity.

2.2.2 Other trace gases, aerosol properties and photolysis frequencies measurements

A comprehensive set of instruments operated during the JULIAC campaign (Table 2) analyzed the air composition inside the chamber. Photolysis frequencies inside the chamber were derived from ~~the~~ solar actinic flux densities measured by a spectroradiometer mounted on the roof of the nearby institute building. Chamber values were calculated using a model approach considering shading effects and the influence of the chamber film (Bohn et al., 2005; Bohn and Zilken, 2005). Formaldehyde (HCHO) was detected by cavity ring-down spectroscopy (Picarro, G2307, Glowania et al. (2021)). NO and NO_2 were measured by chemiluminescence (Eco Physics, TR780, NO_2 conversion by a custom-built photolytic converter). In addition, HONO was measured by long-path absorption photometry (LOPAP, Kleffmann et al. (2006); Häseler et al. (2009)), CO, CO_2, CH_4, and H_2O by cavity ring-down spectroscopy (Picarro, G2401), and O_3 by UV absorption (Ansyco-41M and Thermo scientific-49I). Volatile organic compounds (VOCs) were detected by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon) (Jordan et al., 2009) and a VOCUS PTR-TOF-MS instrument (Aerodyne). The VOCs included in this study are listed in Table S2 and include isoprene and some carbonyl compounds. Total aerosol surface area was determined from measurements by a scanning mobility particle sizer (SMPS). In the summer and autumn periods, nitryl chloride ($ClNO_2$) was detected by a chemical ionization mass spectrometer using iodine as reagent ion (I-CIMS) (Sommariva et al., 2018; Tan et al., 2022).

In addition to measurements in the chamber, concentrations of O_3 and NO_X were also measured in the inlet system before the air flowed into the SAPHIR chamber. For these measurements, a combined system (Eco Physics, $CraNO_X$) consisting of an ozone photometer and a chemiluminescence instrument for NO_X was deployed. Measurements were used to determine the photochemical ozone production in the JULIAC campaign. Further description of the measurement set-up and concept of the evaluation will be discussed in details in a further publication.

2.3 Chemical budget calculations

A chemical budget analysis, similar as in Tan et al. (2019) and Whalley et al. (2021), was applied for OH, HO_2, RO_2 and the sum of all three radicals (RO_X) to the data set from the JULIAC campaign. All reactions typically considered to be relevant for the generation and destruction of these radicals are considered (Table 1). Rate constants and their uncertainties were mainly taken from IUPAC recommendations (Atkinson et al., 2004; Atkinson et al., 2006; Cox et al., 2020) or more recent studies. If not otherwise specified, radical production and destruction rates are calculated from measured concentrations of reactants.

2.3.1 Chemical budget of OH radicals

The production rate of OH radicals includes primary production reactions (Reaction R1, R2 and R5) and radical interconversion reactions (Reaction R10 and R11):

$$\mathrm{P_{OH}} = j_{\mathrm{HONO}}[\mathrm{HONO}] + \varphi_{\mathrm{OH}} j_{\mathrm{O^1D}}[\mathrm{O_3}] + k_{10}[\mathrm{NO}][\mathrm{HO_2}] + k_{11}[\mathrm{O_3}][\mathrm{HO_2}] + \Sigma\{{\varphi_{\mathrm{OH}}}^{i} k_5^{i}[\mathrm{alkene}]^{i}[\mathrm{O_3}]\} + \mathrm{P_{OH,Isop.}} \quad (1)$$

Here, φ_{OH} is the effective OH yield of the ozone photolysis including the reaction of excited oxygen atoms $O(^1D)$ with H_2O producing two OH radicals. ${\varphi_{\mathrm{OH}}}^{i}$ is the OH yield of the ozonolysis reaction of alkenes, and k_5^i represents the rate constants of the corresponding reactions.

$P_{OH,Isop}$ is the effective production of OH radicals from unimolecular reactions (1,6-hydrogen shift reactions) of isoprene-RO_2 radicals (Z-δ-RO_2-I and II, Peeters et al. (2014)) and the subsequent chemistry of products.. As there was no measurement of speciated RO_2 radicals, isoprene-RO_2 radical concentrations are estimated from steady-state conditions considering their production from the reaction of isoprene with OH and their destruction in bimolecular reaction (reaction rate k_{bi}) and unimolecular reactions (bulk reaction rate $k_{\mathrm{bulk\ 1,6\text{-}H}}$ as defined in Peeters et al. (2014)):

$$[\mathrm{RO_2(isop.)}]_{\mathrm{SS}} = \frac{k_{18}[\mathrm{Isoprene}][\mathrm{OH}]}{k_{\mathrm{bi}}+k_{\mathrm{bulk\ 1,6-H}}} \tag{2}$$

$$k_{\mathrm{bi}} = (k_9 + k_{14})[\mathrm{NO}] + k_{15}[\mathrm{RO_2}] + k_{16}[\mathrm{HO_2}] \tag{2a}$$

Bimolecular loss reactions include reactions with NO (Reaction R9 and R14), RO_2 (Reaction R15) and HO_2 (Reaction R16). The OH production from isoprene-RO_2 isomerization reactions is simplified in the calculation of the total OH production in this work by assuming that each isomerization reaction produces rapidly one OH radical from the subsequent reactions of products such as photolysis of hydroxy-peroxy aldehyde (HPALD). In this case, the radical production rate is equal to the loss rate of the isoprene-RO_2 due to isomerization reactions ($\mathrm{D_{Z-\delta-RO_2,Isop.}}$):

$$\mathrm{P_{OH,Isop.}} = \mathrm{D_{Z-\delta-RO_2,\ Isop.}} = k_{\mathrm{bulk\ 1,6-H}}\,[\mathrm{RO_2(isop.)}]_{\mathrm{SS}} \tag{4}$$

The total loss rate of OH radicals for the chemical budget analysis is determined by the product of the total OH reactivity (k_{OH}) and the OH radical concentration:

$$\mathrm{D_{OH}} = k_{\mathrm{OH}}[\mathrm{OH}] \tag{5}$$

2.3.2 Chemical budget of HO_2 radicals

The production rate of HO_2 radicals includes primary reactions (Reaction R3, R4 and R5) and interconversion reactions (Reaction R6, R7 and R9, Table 1):

$$\mathrm{P_{HO_2}} = 2\,j_{\mathrm{HCHO}}[\mathrm{HCHO}] + k_6[\mathrm{HCHO}][\mathrm{OH}] + k_7[\mathrm{CO}][\mathrm{OH}] + k_9[\mathrm{NO}][\mathrm{RO_2}] + \Sigma\{\varphi_{\mathrm{HO_2}}{}^{i} k_5^{i}[\mathrm{alkene}]^{i}[\mathrm{O_3}]\} \tag{6}$$

Here, the photolysis frequency of HCHO (j_{HCHO}) include only paths generating radicals. $\varphi_{\mathrm{HO_2}}{}^{\mathrm{i}}$ is the HO_2 yield from the ozonolysis of alkenes. The reactions of OH with H_2 and O_3 are not considered due to their negligible contributions to the HO_2 production.

The loss rate of HO_2 is determined by the reactions with NO (Reaction R10), O_3 (Reaction R11), RO_2 (Reaction R16) and HO_2 (Reaction R17):

$$\mathrm{D_{HO_2}} = (k_{10}[\mathrm{NO}] + k_{11}[\mathrm{O_3}] + k_{16}[\mathrm{RO_2}] + 2k_{17}[\mathrm{HO_2}])[\mathrm{HO_2}] \tag{7}$$

Here, the humidity dependence of k_{17} was taken into account. The reaction of HO_2 radicals with NO_2 is not included as the thermal decomposition of peroxynitric acid (HO_2NO_2) forming back HO_2 radicals and NO_2 is instantaneous for the temperatures experienced during the JULIAC campaign.

In a sensitivity calculation (Section 4.2.3), potential loss of HO_2 due to heterogeneous uptake on aerosol is investigated. The first order loss rate ($k_{\mathrm{het.}}$) can be described as:

$$k_{\mathrm{het.}} = \frac{\gamma_{\mathrm{eff.}} \cdot \nu_{\mathrm{HO_2}} \cdot [\mathrm{AS}]}{4} \tag{8}$$

$\nu_{\mathrm{HO_2}}$ is the mean molecular velocity of HO_2 (4.44×10^5 cm s^{-1} at 298 K), [AS] is the measured aerosol surface area concentration, and $\gamma_{\mathrm{eff.}}$ is the effective uptake coefficient.

2.3.3 Chemical budget of RO_2 radicals

Primary sources of RO_2 radicals include all oxidation reactions of VOCs with OH, Cl, NO_3 radicals and O_3. As the number of measured VOC species in this study was limited (Table S2) and because it is generally difficult to capture the entire spectrum of atmospheric VOCs (Goldstein and Galbally, 2007; Lou et al., 2010), the measured total OH reactivity (k_{OH}) can be used to calculate the RO_2 radicals production from the reactions of VOCs with OH. First, the contributions from CO, NO, NO_2, HCHO and O_3 is removed from the measured OH reactivity as these species do not form RO_2 radicals in the reaction with OH. It is then assumed that the remaining fraction can be attributed to organic compounds (VOC reactivity (k_{VOC})) including measured and unmeasured VOCs, which produce RO_2 radicals in their reaction with OH.

For some aromatics, such as toluene, benzene, xylene, etc., the prompt formation of HO_2 is expected by their reaction with OH (Nehr et al., 2011; Nehr et al., 2014; Jenkin et al., 2019). However, in this campaign, their concentrations were small and their average contributions to the OH reactivity from VOCs were only 2.8%. Therefore, their potential impacts on the RO_2 production are negligible (less than 1%).

In addition, RO_2 production from ozonolysis needs to be included. In this work, only the reactions of measured organic compounds are considered. The contribution to the RO_2 production from the oxidation of VOCs by the NO_3 radical was negligible during daytime due to the low VOC load (low OH reactivity), so that NO_3 destruction by photolysis and reaction with NO dominated.

Reactions of chloride (Cl) also produce RO_2 radicals, but the concentration was not measured in the JULIAC campaign. However, one of the most important precursor species, nitryl chloride ($ClNO_2$), was detected during the campaign (except in spring, Tan et al. (2022)). $ClNO_2$ can accumulate during nighttime, but it is photolyzed after sunrise yielding NO_2 and Cl atoms (Reaction R20). Assuming as an upper limit that each Cl atom reacts with a VOCs (Tanaka et al., 2003), the RO_2 production rate from Cl radicals can be calculated as:

$$\mathrm{P_{RO_2,Cl}} = j_{\mathrm{ClNO_2}}[\mathrm{ClNO_2}] \tag{9}$$

The total RO_2 production rate is then calculated as:

$$\mathrm{P_{RO_2}} = k_{\mathrm{VOC}}[\mathrm{OH}] + \sum\left(\varphi_{\mathrm{RO_2}}{}^{i} k^{i}_{\mathrm{R5}}[\mathrm{alkene}]^{i}[\mathrm{O_3}]\right) + \mathrm{P_{RO_2,Cl}} \tag{10}$$

Here, $\varphi_{\mathrm{RO_2}}{}^{\mathrm{i}}$ is the RO_2 yield from the ozonolysis of alkenes species (Table 1).

With respect to the destruction rate of RO_2, its reactions with NO, HO_2, and other RO_2 and unimolecular reactions of specific isoprene-RO_2 radicals ($\mathrm{D_{Z-\delta-RO_2,Isop.}}$) (Eq. 4) are considered in this work:

$$\mathrm{D_{RO_2}} = ((k_9 + k_{14})[\mathrm{NO}] + 2k_{15}[\mathrm{RO_2}] + k_{16}[\mathrm{HO_2}])[\mathrm{RO_2}] + \mathrm{D_{Z-\delta-RO_2,\ Isop.}} \tag{11}$$

2.3.4 Chemical budget of RO_X radicals

In the chemical budget of the sum of OH, HO_2 and RO_2 (RO_X), inter-radical conversion reactions cancel out and only initiation and termination reactions are included. Therefore, the RO_X radical budget analysis allows to investigate if primary radical source reactions or termination processes are missing in the chemical mechanism used (Table 1).

The production rate of the RO_X radicals is given by the sum of rates from radical initiation reactions (Reaction R1-R5, R20-R22, Table 1):

$$\mathrm{P}_{\mathrm{RO_x}} = j_{\mathrm{HONO}}[\mathrm{HONO}] + \varphi_{\mathrm{OH}} \mathrm{j}_{\mathrm{O^1D}}[\mathrm{O_3}] + 2 j_{\mathrm{HCHO}}[\mathrm{HCHO}] + \sum\left((\varphi^{\mathrm{i}}_{\mathrm{OH}} + \varphi^{\mathrm{i}}_{\mathrm{HO_2}} + \varphi^{\mathrm{i}}_{\mathrm{RO_2}}) k^{\mathrm{i}}_5 [\mathrm{alkene}]^{\mathrm{i}} [\mathrm{O_3}]\right) + \mathrm{P}_{\mathrm{RO_2,Cl}} \qquad (12)$$

Radicals can be additionally produced from the photolysis of other oxygenated organic compounds (OVOCs, e.g., Reaction R4) not included in Eq. 12. Their potential impact is further discussed in Section 4.2.2.

The loss rate of the RO_X radical is calculated by the sum of rates from radical termination reactions (Reaction R12-R17):

$$\mathrm{D}_{\mathrm{RO_x}} = (k_{13}[\mathrm{NO}] + k_{12}[\mathrm{NO_2}])[\mathrm{OH}] + k_{14}[\mathrm{NO}][\mathrm{RO_2}] + 2k_{15}[\mathrm{RO_2}]^2 + 2k_{16}[\mathrm{HO_2}][\mathrm{RO_2}] + 2k_{17}[\mathrm{HO_2}]^2 \qquad (13)$$

2.3.5 Uncertainties in the calculated production and destruction rates

The uncertainty of each production or loss rate is calculated by Gaussian summation of the 1σ errors of the measured quantities (Table 2) and the uncertainties of the reaction rate constants (Table 1).

For reactions of RO_2 with NO (Reaction R9, R14), HO_2 (Reaction R16) and RO_2 (Reaction R15), generic rate constants are used for the sum of RO_2 radicals (Table 1, Jenkin et al. (2019)). Rate constants of the NO reaction with RO_2 derived from hydrocarbons (<C_5) and with oxygenated peroxy radicals range from 7.7×10^{-12} $cm^3 s^{-1}$ to 1.1×10^{-11} $cm^3 s^{-1}$ (Jenkin et al., 2019). The 1σ-uncertainty of the rate constants varies from 6 to 30 %. In the error calculations here, an upper limit value of 30 % is applied. However, for reactions of RO_2 with HO_2 and with RO_2, the range of rate constants varies by more than an order of magnitude. In the calculations, an uncertainty of 50% is used for the reaction rate constants of RO_2 with HO_2 and with RO_2.

As there are no measurements of speciated RO_2 radicals, a yield of 5% for the formation of organic nitrates is assumed for all RO_2 but the yield can vary between 1% for methyl peroxy radicals (CH_3O_2) and more than 20 % for RO_2 from monoterpene species. This simplification can introduce systematic errors in the calculations (Section 4.2.1).

2.4 Odd oxygen production rate

In the troposphere, ozone is formed exclusively by the oxidation of NO to NO_2 through reaction with RO_2 (Reaction R9) and HO_2 (Reaction R10), followed by NO_2 photolysis (Fishman and Carney, 1984; Sillman et al., 1990; Kleinman et al., 2002).

During the day, the photolysis of NO_2 and the back reaction of NO with O_3 form a rapid photochemical equilibrium between O_3 and NO_2. The sum of O_3 and NO_2 is therefore defined as odd oxygen (O_X) (Han et al., 2011; Goldberg et al., 2015). The relative composition of O_X depends on the NO_2 photolysis frequency and the NO concentration. For the conditions of the spring and summer periods in the JULIAC campaign, O_X consisted predominantly (> 85%) of O_3.

In this work, the net production rate of O_X (P_{Ox}) was determined experimentally from the increase of O_X in the sunlit SAPHIR chamber. Furthermore, measurements of radicals and NO_X were used to calculate P_{Ox} from the rate of O_X formation reactions (Reaction R9, R10), and O_X loss by the reaction of NO_2 with OH (Reaction R12) (Mihelcic et al., 2003; Cazorla et al., 2012; Niether et al., 2022)):

$$\mathrm{P}_{\mathrm{O}_\mathrm{X},\mathrm{net}} = k_9[\mathrm{NO}][\mathrm{RO}_2] + k_{10}[\mathrm{NO}][\mathrm{HO}_2] - k_{12}[\mathrm{NO}_2][\mathrm{OH}] \tag{14}$$

This calculation neglects minor O_x destruction processes such as the reaction of O_3 with NO_2, OH, HO_2 ~~or~~ , Cl or alkenes since they did not play a notable role during the day in this campaign.

3 Results

3.1 Data quality of radical measurements

Performing measurements in the SAPHIR chamber allowed to test the accuracy of radical measurements in different ways that are typically not available in field experiments. First, OH radicals was measured by 2 independent instruments, the OH-DOAS and LIF instruments (Cho et al., 2021). Second, the O_X production rate calculated from measured concentrations of HO_2 and RO_2 could be compared to the observed increase of O_X concentrations in the chamber, which can be solely attributed to chemical reactions. This is possible, because other factors typically impacting the O_X concentration in field experiments such as transportation processes are not effective.

OH concentrations were measured by the LIF instrument applying the chemical modulation scheme and the DOAS in the winter, summer and autumn periods of the campaign. As OH concentrations were close to the limit of detection in autumn and winter, a meaningful comparison of measurements was only possible for the summer period. A detailed comparison of measurements can be found in Cho et al. (2021). In general, the OH measurements of the two instruments agreed within their measurement errors (Table 1) giving a slope of 1.1±0.02 in a linear regression analysis. The good agreement confirms that the newly developed chemical modulation system of the LIF instrument allowed for interference-free OH concentration measurements for conditions of the campaign. Only in the period from 22 to 26 August, which was characterized by exceptionally high temperatures (30 to 40°C), OH concentrations measured by the LIF instrument were systematically higher by 25% than those measured by the DOAS instrument for unknown reasons (Cho et al., 2021). OH concentrations measured by the DOAS instrument were used for the analysis of the radical budgets in this period.

Net O_X production rates were determined from the measured increase of O_X concentrations in the chamber and compared to calculations from the turnover rates of HO_2 and RO_2 reactions with NO. This calculation takes also the NO_2 loss due to its reaction with OH into account (Eq. 14). The odd oxygen production rate did not exceed 1 ppbv h^{-1} in winter and autumn due to the general low photochemical activity in these seasons. In spring and summer, the O_X production rate showed clear diurnal variations with noontime maxima that reached up to 16 ppbv h^{-1}. In these seasons, both methods for determining the O_X production rate agreed within ±15 % (1σ). Observed discrepancies were less than 1 ppbv h^{-1}, when NO mixing ratios were lower than 1 ppbv, but reached values of 3 ppbv h^{-1} for NO mixing ratios of 3 - 4 ppbv NO. The largest discrepancy of 8.5 ppbv h^{-1} was found in the morning on 29 April, when the NO mixing ratio exceeded 9 ppbv. High NO values suppressed HO_2 and RO_2 concentrations to values below 2.0×10^7 cm^{-3}, which is within the range of the background corrections for the HO_2 and RO_2 measurements (Table S1). Under these conditions, an erroneous background subtraction may have caused the observed discrepancies.

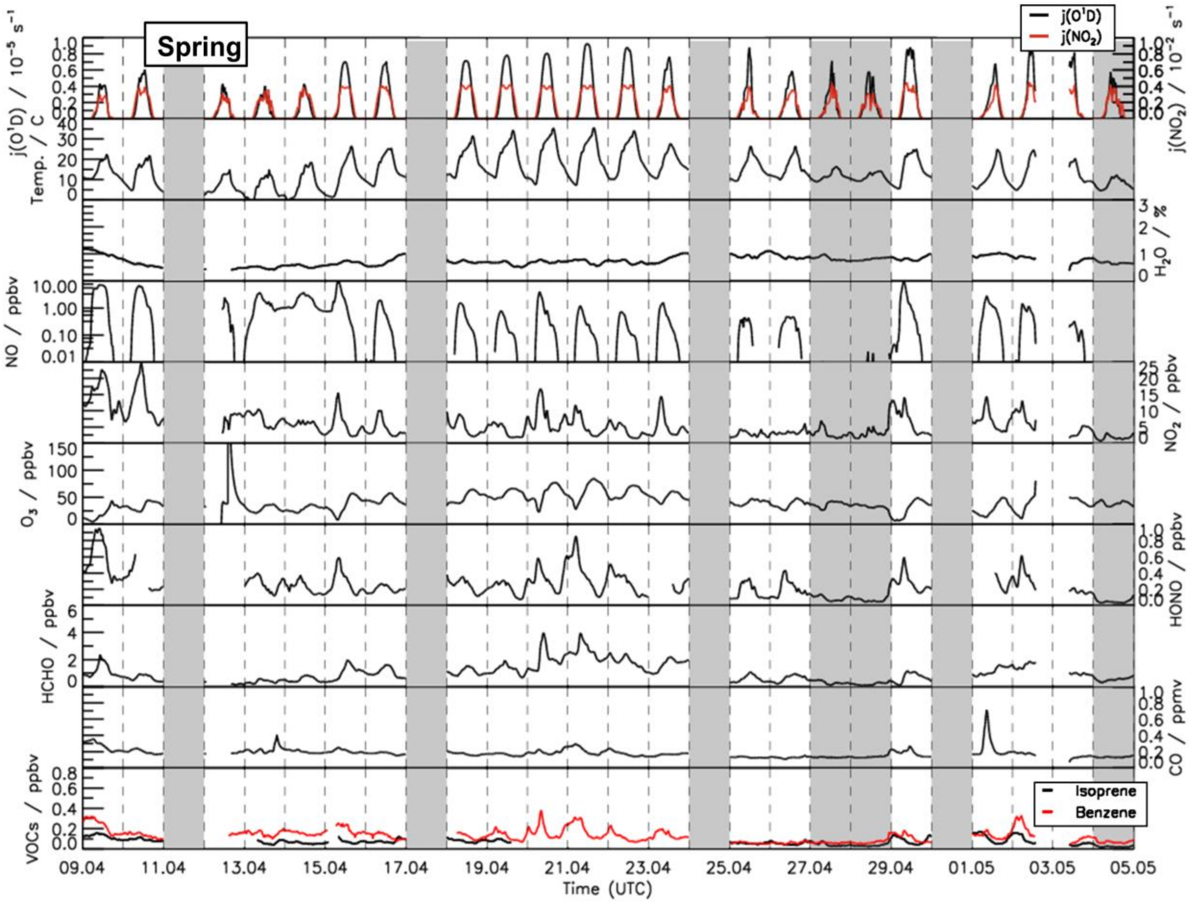

Figure 1: Time series of temperature and trace gas concentrations during the spring period of the JULIAC campaign (Cho et al., 2022). Vertical dashed lines denote midnight. Grey shaded areas indicate calibration days, when no measurements were done and days when the chamber roof was closed due to bad weather conditions.

3.2 Meteorological and chemical conditions during the JULIAC campaign

A broad range of meteorological and chemical conditions was encountered during the JULIAC campaign. During the winter and autumn periods (Fig. S1 and S2), the sky was often overcast and it rained frequently. Temperatures were generally below 10℃ and the photolysis frequencies of ozone (j_{O1D}) and nitrogen dioxide (j_{NO2}) mostly remained below 1.5×10^{-6} s^{-1} and 2×10^{-3} s^{-1}, respectively. During spring and summer, temperatures in the chamber were up to 35℃ in mid-April and 40℃ between 24 and 31 August (Fig. 1 and 2). Photolysis frequencies in the chamber were 1×10^{-5} s^{-1} (j_{O1D}) and 4×10^{-3} s^{-1} (j_{NO2}).

The air was sampled at all times from 50 m above ground. The temperature at different heights measured between 5 m and 120 m at a meteorological tower near the SAPHIR chamber showed that the air was well mixed within this height range during the day. Therefore, it can be assumed for the chemical composition of the air sampled into the chamber to be representative for the air within the atmospheric boundary layer. At night, vertical temperature profiles showed atmospheric stratification below 100 m. The air at 50 m can be assumed to be isolated from the ground and therefore not being affected by surface emissions or deposition on surfaces at the ground.

Overall, relatively clean air was sampled during the whole JULIAC campaign indicated by CO and NO mixing ratios below 0.3 ppmv and 2 ppbv, respectively. Concentrations of anthropogenic organic compounds (e.g. benzene and toluene) were low with mixing ratios of less than 0.5 ppbv. Even though the measurement site is surrounded by a deciduous forest, the concentrations of biogenic organic compounds such as isoprene and monoterpenes were also low (median 0.8 ppbv and 0.15 ppbv, respectively) compared to previously reported values measured on the campus of FZJ in summer, when isoprene concentrations ranged between 0.5 to 4 ppbv (Komenda et al., 2003; Spirig et al., 2005; Kanaya et al., 2012). A possible reason for the low values could be damages of trees from severe droughts in the previous year (BMEL, 2021).

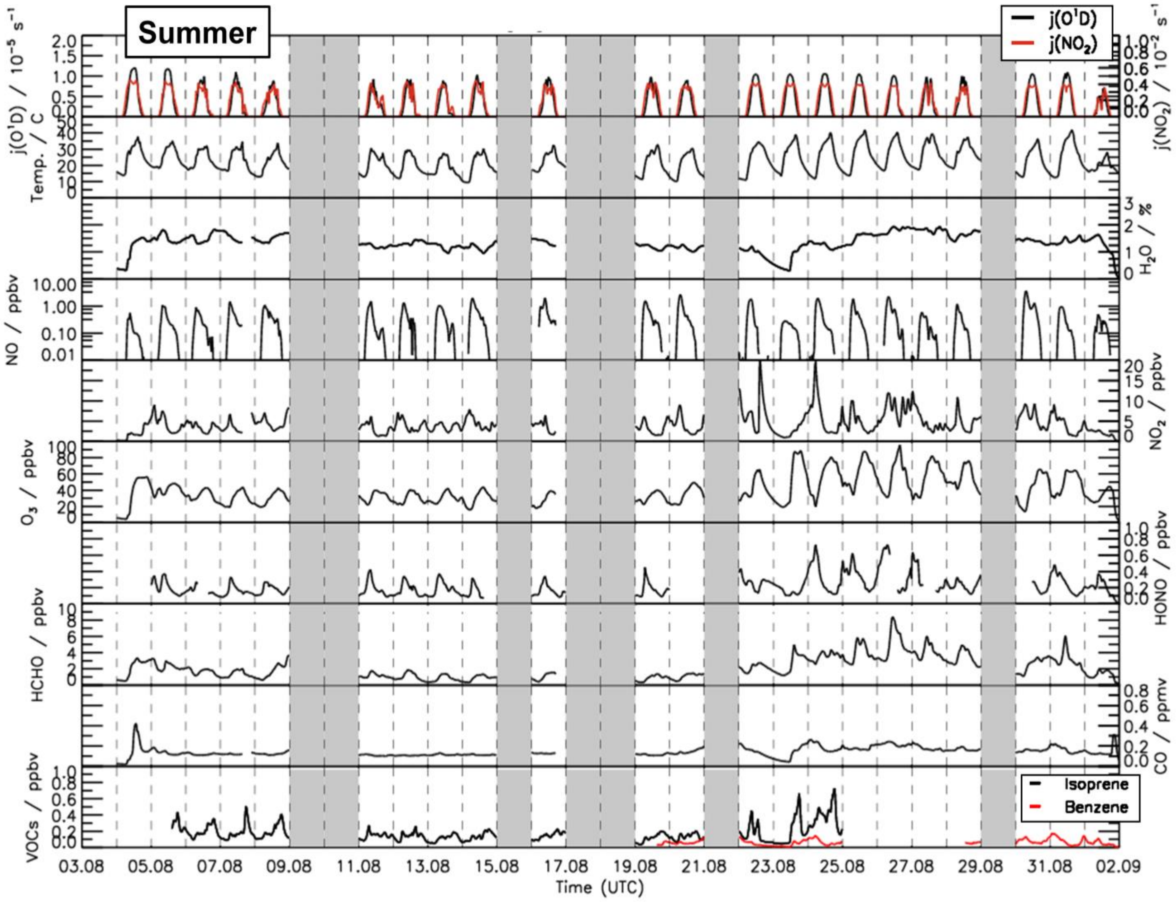

Figure 2: Time series of temperature and trace gas concentrations during the summer period of the JULIAC campaign (Cho et al., 2022). Vertical dashed lines denote midnight. Grey shaded areas indicate calibration days, when no measurements were done and days when the chamber roof was closed due to bad weather conditions.

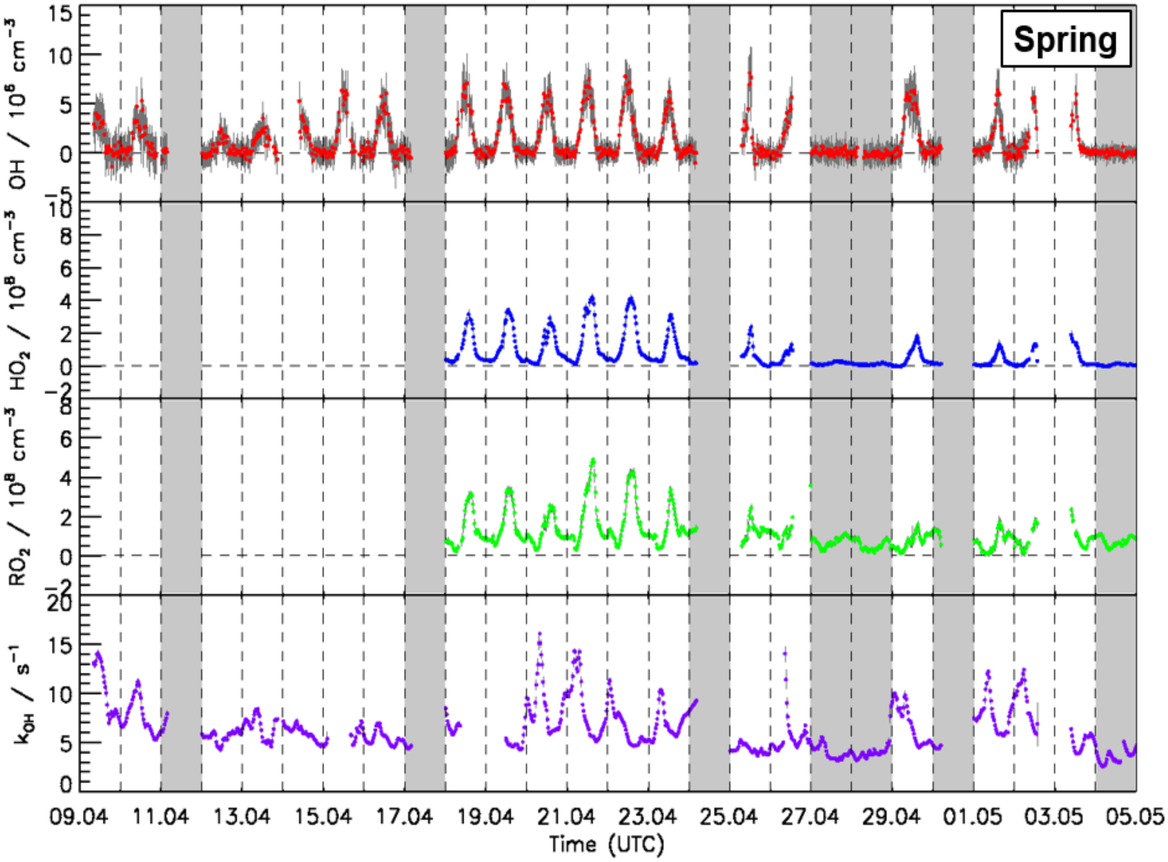

Figure 3: Time series of OH, HO_2, and RO_2 radical concentration measured by the FZJ-LIF-CMR instrument and measurements of the OH reactivity (k_{OH}) measured in the spring period of the JULIAC campaign (Cho et al., 2022). Vertical bars represent 1σ statistical errors. Vertical dashed lines denote midnight. Grey shaded areas indicate calibration days when no measurements were done and days when the chamber roof was closed due to bad weather conditions.

3.3 OH, HO_2, and RO_2 radical concentrations and OH reactivity during winter and autumn periods of the JULIAC campaign

During winter (Fig. S3) and autumn (Fig. S4), daytime OH radical concentrations were below 1×10^6 cm^{-3}, mainly due to a low primary radical production. Daytime peroxy radical (HO_2 and RO_2) concentrations during these periods were also very low with average values below 2×10^7 cm^{-3} (Fig. S5) close to the limit of detection of RO_2 radicals (Table 2) and within the uncertainty of the background corrections for HO_2 and RO_2 (Table S1). During winter and autumn, HO_2 concentrations typically increased in the morning and reached peak concentrations of 2×10^7 cm^{-3} at noon. Concentrations decreased in the evening and night with minimum values right before sunrise. In contrast, nighttime RO_2 concentrations increased to values between 3 to 4×10^7 cm^{-3} after sunset, when the chemical loss due to their reaction with NO became negligible, while RO_2 radicals were still produced from reactions of VOC with NO_3 and O_3. NO concentrations were essentially zero at that time, because NO production by the photolysis of NO_2 stopped and NO rapidly reacted with ozone. RO_2 radical concentrations decreased in the morning to values that were similar to that of HO_2 radicals as can be expected for conditions with high NO mixing ratios, which lead to a fast loss of RO_2 and HO_2 in their reactions with NO.

The measured OH reactivity (k_{OH}) ranged between 4 and 33 s^{-1} during winter and autumn periods. The highest value was observed on 21 January, when a highly polluted plume containing 50 ppbv of NO was sampled.

The measured OH reactivity can be compared to OH reactivity calculated by summing up the product between measured OH reactant concentrations and their reaction rate constants with the OH radical. On average, 1.3 s^{-1} (18 %) of the measured OH reactivity could not be explained by the measured OH reactants during the winter and autumn periods (Fig. S5). NO_X, CH_4, CO, and VOCs contributed approximately 43, 3, 20 and 13 %, respectively, to the measured OH reactivity.

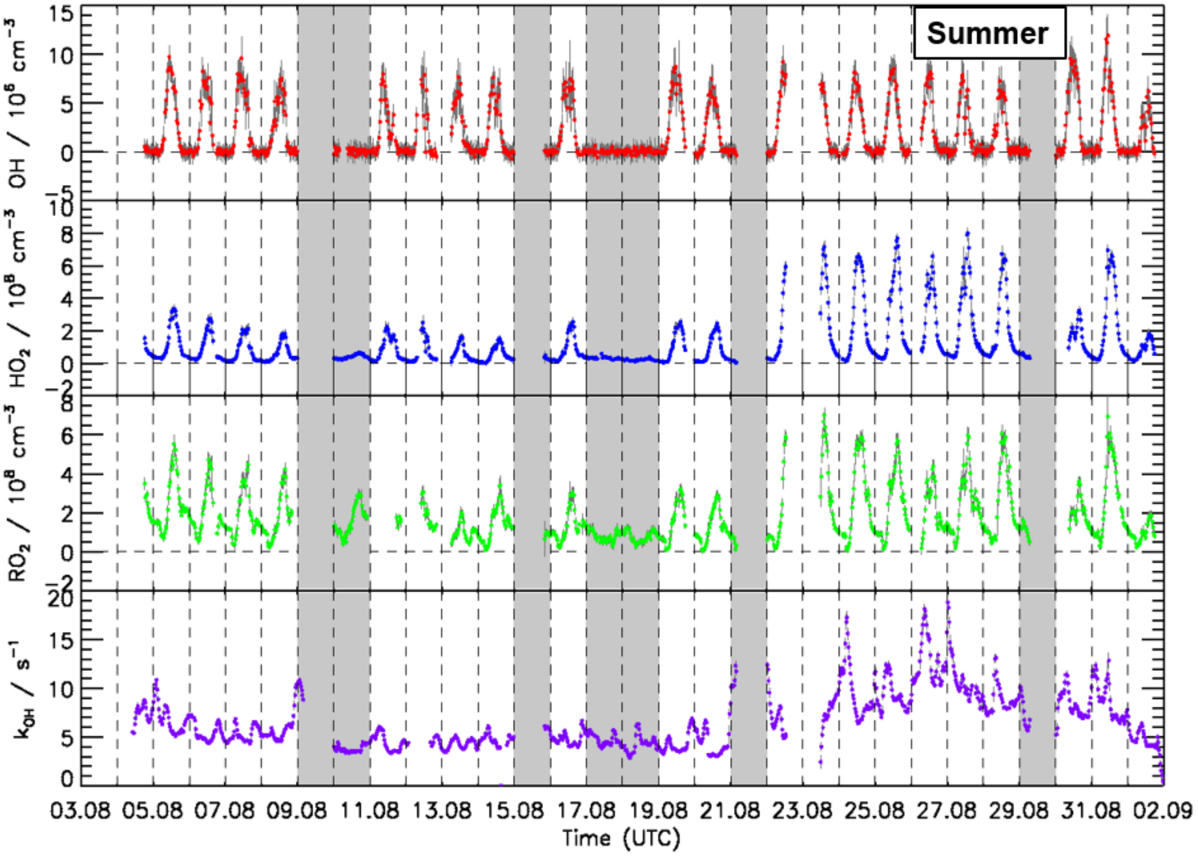

Figure 4: Time series of OH, HO_2, and RO_2 concentration measured by the FZJ-LIF-CMR instrument and measurements of the OH reactivity (k_{OH}) in the summer period of the JULIAC campaign (Cho et al., 2022). Vertical bars represent 1σ statistical errors. Vertical dashed lines denote midnight. Grey shaded areas indicate calibration days when no measurements were done and days when the chamber roof was closed due to bad weather conditions.

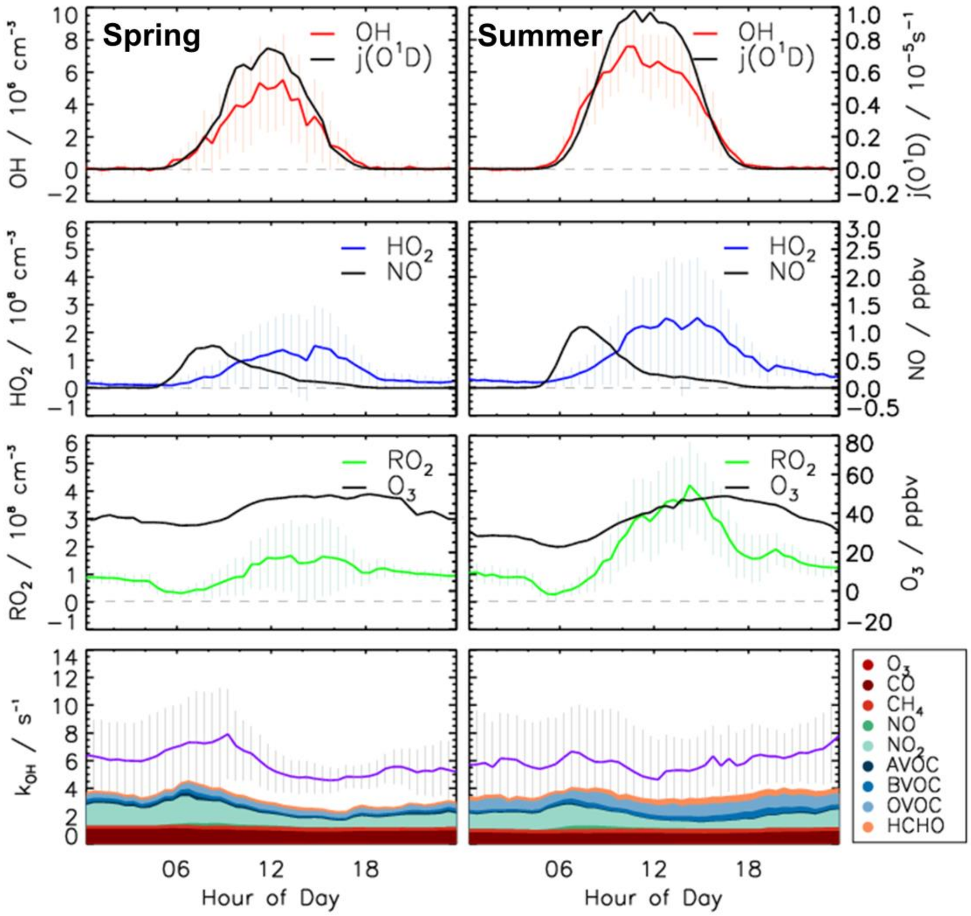

Figure 5: Median values of the diurnal profiles of OH, HO$_2$, RO$_2$, k_{OH}, j_{O1D}, NO~~,~~ and O$_3$ measured in the spring and summer periods of the JULIAC campaign. Colored areas represent the contributions of measured reactants to the total OH reactivity. Vertical lines give 25th and 75th percentile values.

3.4 OH, HO$_2$, and RO$_2$ radical concentrations and OH reactivity during the spring and summer periods of the JULIAC campaign

During spring and summer (Fig. 3, 4 and 5), maximum daytime OH concentrations were between 6 and 8 $\times$ 10^6 cm^{-3}. The highest OH concentration (1.2×10^7 cm^{-3}) occurred on 31 August. The diurnal OH concentration profile shows a high correlation with the ozone photolysis frequency (j_{O^1D}) as observed in previous field campaigns (e.g., Ehhalt and Rohrer (2000); Handisides et al. (2003); Holland et al. (2003)).

Unfortunately, the measurements of HO$_2$ and RO$_2$ radicals were not available for the first two weeks of the spring campaign due to a malfunction of the instrument. Daily maximum HO$_2$ and RO$_2$ concentrations were in the range of 2 to 4×10^8 cm^{-3} during the spring period and the first half of the summer period. Maximum HO$_2$ and RO$_2$ concentrations were 8.0×10^8 cm^{-3} and 7.0×10^8 cm^{-3}, respectively, during the second half of summer period. In spring and summer, peroxy radical concentrations showed a distinct diurnal pattern. Both HO$_2$ and RO$_2$ radical concentrations were suppressed in the early morning (between 04:00 and 07:00) due to the reaction with elevated NO mixing ratios of up to 1.5 ppbv. Maximum peroxy radical concentrations were usually reached in the afternoon (~14:00), when NO concentrations were lowest.

The measured OH reactivity values were in the range of 4 to 18 s^{-1}. High values were observed between 23 and 31 August due to high emissions of biogenic volatile organic compounds (BVOCs) from plants at high ambient temperatures. The OH reactivity that cannot be attributed to the measured OH reactants was on average, 2.5 s^{-1} (40%), which is much higher than observed in the winter and autumn periods (Fig. S5). CO and CH_4 contributed 10% and 4%, respectively. Due to the high emissions of biogenic organic compounds in spring and summer, the attributed contribution of organic compounds to the total measured OH reactivity was 20 % and the contribution of NO_X was only 19 %, much less compared to the winter and autumn periods. Isoprene had the largest contribution among all VOCs accounting for up to 5 % of the total measured OH reactivity. Unfortunately, the number of detected VOC species in the JULIAC campaign was small (Table S2). ~~This, however, does not impact the analysis in this study as the measured OH reactivity is used to determine the loss rate of OH radicals.~~

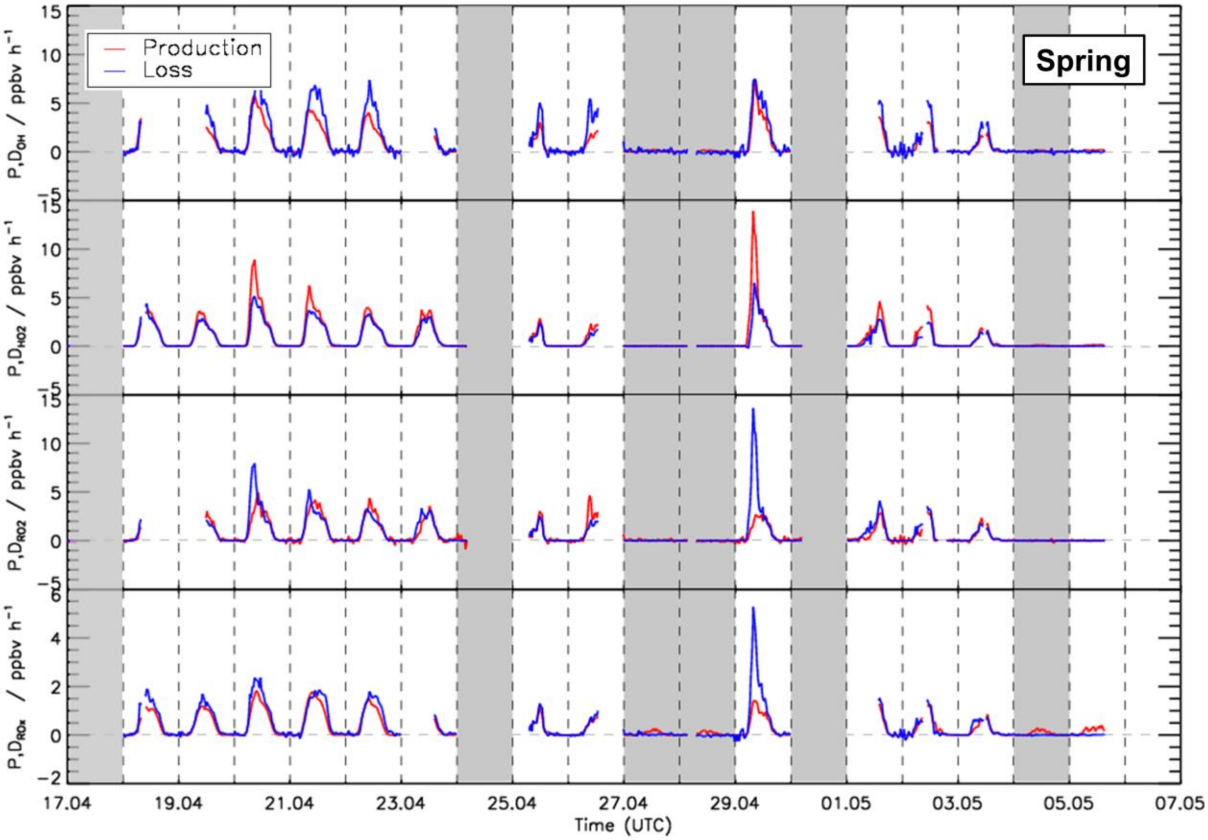

Figure 6: Time series of total production and destruction rates of OH, HO_2, RO_2, and RO_X radicals in the spring period of the JULIAC campaign. Vertical dashed lines denote midnight. Grey areas indicate calibration days and days when the chamber roof was closed.

In the JULIAC campaign, nighttime OH concentrations were clearly below the limit of detection of the FZJ-CMR-LIF instrument (0.7×10^6 cm^{-3}). When all nighttime data are averaged, mean OH concentrations with 1σ standard errors of $(3 \pm 1) \times 10^4$ cm^{-3} and $(5 \pm 3) \times 10^4$ cm^{-3} are obtained for the spring and summer periods, respectively. These low values support the absence of instrumentally produced OH and indicate a very low nocturnal OH production at 50 m height in the absence of NO and solar UV.

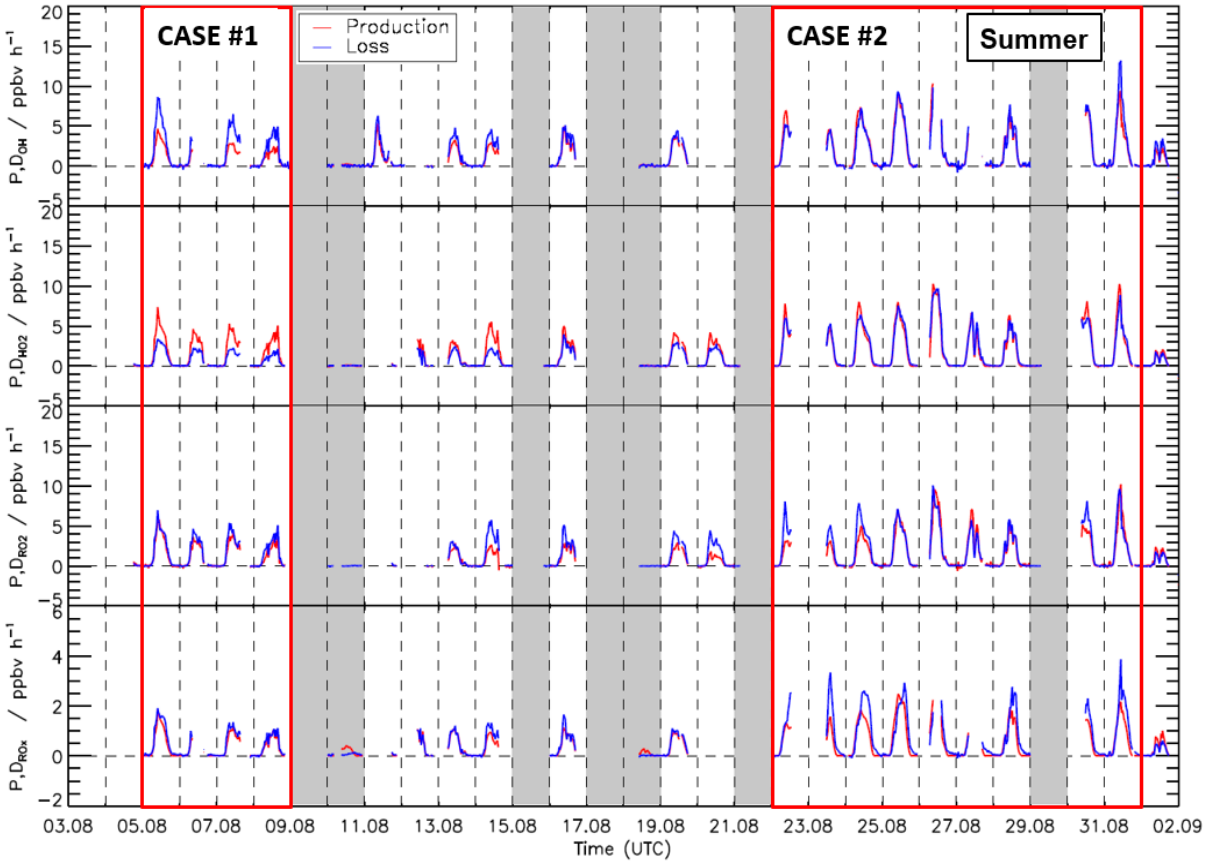

Figure 7: Time series of total production and destruction rates of OH, HO_2, RO_2, and RO_X radicals in the summer period of the JULIAC campaign. Vertical dashed lines denote midnight. Grey areas indicate calibration days and days when the chamber roof was closed. The red boxes denote periods that are discussed in more detail (Case 1 and Case 2).

3.5 Chemical budgets of OH, HO_2, RO_2 and RO_X radicals in the spring and summer periods

Due to the very low photochemical activity observed in autumn and winter, which resulted in radical concentrations close to the detection limit of the instrument, the chemical budget analysis is only discussed for data from the spring and summer periods. It focuses on daytime conditions.

Time series of turnover rates of reactions involving OH, HO_2, RO_2 and RO_X radicals in the spring and summer periods are presented in Fig. 6 and 7, respectively, and median diurnal profiles in Fig. 8. Typical daytime turnover rates of OH, HO_2 and RO_2 radicals were between 3 ppbv h^{-1} and 10 ppbv h^{-1}. The rates of RO_X production and destruction ranged from 1 ppbv hr^{-1} to 3 ppbv hr^{-1}, which is 2 to 4 times lower than those of OH, HO_2, and RO_2, because radical conversion reactions cancel out. The highest OH turnover rate of 13 ppbv h^{-1} was observed on 31 August, when the air temperature in the chamber reached up to 40˚C. Unusually high turnover rates for HO_2, RO_2, and RO_X radicals occurred on 29 April with values of 14 ppbv h^{-1}, 15 ppbv h^{-1}, and 4 ppbv h^{-1}, respectively, when the NO mixing ratio exceeded 9 ppbv. For the reasons stated in Section 3.1, the HO_2 and RO_2 data on this date are considered highly uncertain and were excluded from further analysis of the chemical budgets.

Diurnal variations of total radical production and destruction rates, as well as of the contributions of the most important reactions, are shown as median values for the entire spring and summer period in Fig. 8. For OH, the reaction of HO_2 with NO (Reaction R10) was the dominant production pathway contributing more than 70 % to the total production rate in both spring and summer periods. The photolysis of HONO (Reaction R1) was the most important primary OH source during daytime contributing approximately 20 % to the total OH production. The reaction of HO_2 with ozone (Reaction R11), the photolysis of ozone (Reaction R2), and the ozonolysis of alkenes (Reaction R5) contributed less than 3 % to the total OH production. The maximum median total OH production rate of 3.5 ppbv hr^{-1} was observed in the morning shortly after the peak NO concentration in both spring and summer (Fig. 5). Values gradually decreased until sunset. Median total OH destruction rates were higher than production rates and reached up to 5 ppbv hr^{-1} and 6 ppbv hr^{-1} at noon in spring and summer, respectively. The contributions of different reactions to the total OH destruction rate is described by the contribution of OH reactants to the OH reactivity (Section 3.4, Fig. 5).

Short-lived radicals are expected to be in a steady state, and therefore radical production and destruction rates must be balanced. An imbalance between the calculated rates indicates inaccurate data or a missing radical production or destruction process. The daily peak of the OH production rates was typically lower than the destruction rate by approximately 1.8 ppbv h^{-1} in the spring and 2.5 ppbv h^{-1} in the summer period (36 and 43 % of the total OH destruction rate). These discrepancies are higher than the uncertainty of the calculation (Fig. 8).

80% of the HO_2 production rate consisted of the reaction of RO_2 with NO (Reaction R9). The remaining part of the HO_2 production rate was due to the photolysis of formaldehyde (9 %) and the reaction of formaldehyde with OH (10 %). Other reactions producing HO_2 played a minor role (< 1 %). The HO_2 destruction was mostly due to the reaction of HO_2 with NO (Reaction R10) contributing on average 88 % to the total production rate. The loss due to reaction of HO_2 with RO_2 radicals (Reaction R16) contributed on average 9 % to the total loss.

Median values of the total HO_2 destruction and production rates were well balanced in the spring period, with the production rate being slightly higher than the destruction rate. The maximum difference of 1 ppbv hr^{-1}, however, was insignificant compared to the uncertainty of the calculation. A similar tendency but more pronounced feature was observed in summer. Here, the median value of production rate was higher than that of the destruction rate by 1.8 ppbv hr^{-1} (38 % of the total HO_2 production rate) but differences were variable (Fig. 7). This aspect is discussed in more detail for two periods (Sections 3.7 and 3.8), which exhibited different degrees of imbalances in the radical budgets.

The RO_2 production rate was dominated by the reaction of VOCs with OH (Reaction R8). The contributions of ozonolysis of measured alkenes to the RO_2 production were very small (less than 1 %). The reaction of RO_2 with NO (Reaction R9) dominated the RO_2 destruction and contributed more than 90 % to the total loss rate. In the late afternoon, the RO_2 termination reaction with HO_2 gained in importance with contributions of up to 10 %. Although slight imbalances of up to 1 ppbv were observed in the early morning, the RO_2 production and destruction rates were generally balanced within the uncertainty of calculations in both spring and summer.

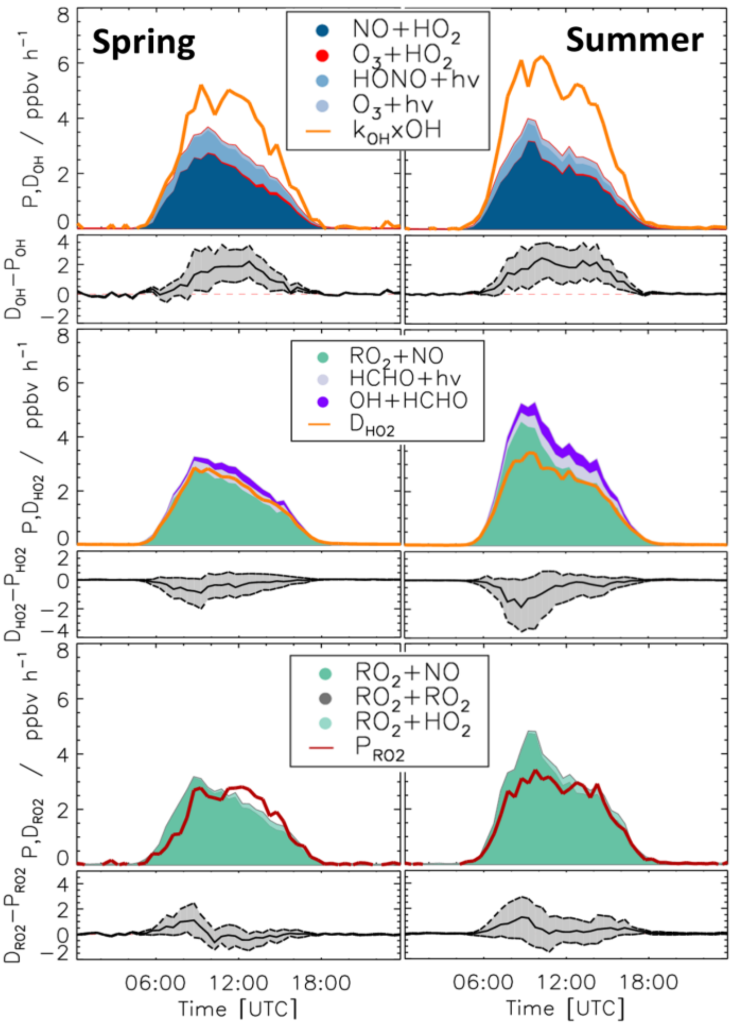

Figure 8: Median values of production and destruction rates of OH, HO_2, and RO_2 radicals in the spring and summer periods of the JULIAC campaign, with data from 29 April excluded. In addition, the differences between the destruction and production rates are shown. Grey areas indicate the 1σ uncertainty derived from experimental errors of the measured quantities (Table 2) and of the reaction rate constants (Table 1). The reactions that have insignificant contributions to the production or destruction rates are not shown.

Figure 9 shows the calculated RO_X production and destruction rates. The photolysis of HONO (Reaction R1), HCHO (Reaction R3) and O_3 (Reaction R2) were the dominant processes initiating radical chemistry and contributed to the total RO_X production rate on average 45 %, 38 % and 15 %, respectively, in both periods. In the morning, the reaction of OH with NO_2 (Reaction R12) was the most important radical termination process contributing up to 65 % to the total RO_X destruction rate. In addition, due to relatively high NO mixing ratios in the early morning, the reactions of OH with NO (Reaction R13) and RO_2 with NO, which yields organic nitrate (Reaction R14), were also significant radical termination processes contributing 13 % and 17 % to the total RO_X destruction rate, respectively. In the afternoon, radical self-reactions (Reaction R15 – R17), and, in particular, the reaction of RO_2 with HO_2 (Reaction R16), dominated the RO_X destruction due to the low NO and NO_2 mixing ratios. In both periods, spring and summer, the total RO_X destruction rate was slightly higher than the production rate, in particular, in the afternoon. The imbalance was up to 0.5 ppbv h^{-1}, which is higher than the uncertainty of the calculations.

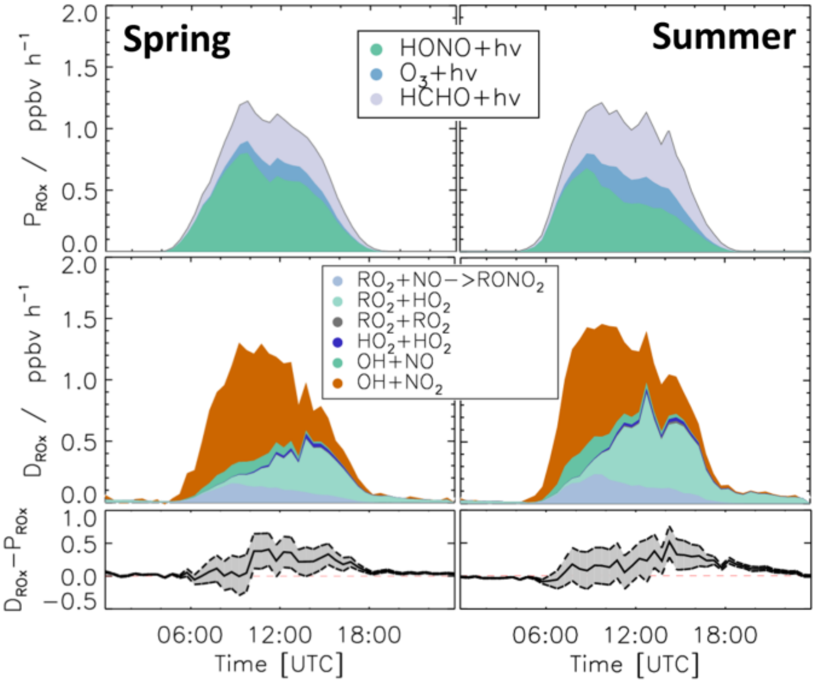

Figure 9: Median values of production and destruction rates of RO_X radicals during the spring and summer periods of the JULIAC campaign. In addition, the differences between the destruction and production rates are shown. Grey areas indicate the 1σ uncertainty derived from experimental errors of the measured quantities (Table 2) and of the reaction rate constants (Table 1). The reactions that have insignificant contributions to the production or destruction rates are not shown.

Meteorological and chemical conditions were variable especially in the summer period causing variations in the balance between radical production and destruction rates (Fig. 7 and Table S3). In the following, the chemical budgets with the largest and smallest observed imbalances are discussed: August 5-8 (Case 1) and August 22-31 (Case 2).

3.5.1 Case 1: 5 - 8 August 2019

For the period between 5 and 8 August, relatively low NO mixing ratios (maximum: 1 ppbv, median: 0.26 ppbv) and typical summer temperature for this region (median: 27˚C) were observed (Fig. 10 and Table S3).

As for the whole summer period (Fig. 8), the reactions of peroxy radicals with NO (Reaction R9, R10) dominated the inter-radical conversion reactions of OH, HO_2 and RO_2 in this period (Fig. 10). A significant imbalance between the OH production and destruction rates of up to 3.0 ppbv h^{-1} (51 % of the total OH destruction rate) is found, which cannot be explained by the uncertainty of the calculations. The total HO_2 production rate was 2.0 ppbv h^{-1} higher than the destruction rate (48 % of the total HO_2 production rate), whilst the RO_2 production and destruction rates were well balanced. Relatively small but nevertheless significant differences between RO_X production and destruction rates (0.5 ppbv h^{-1}) were observed during daytime (Fig. 11).

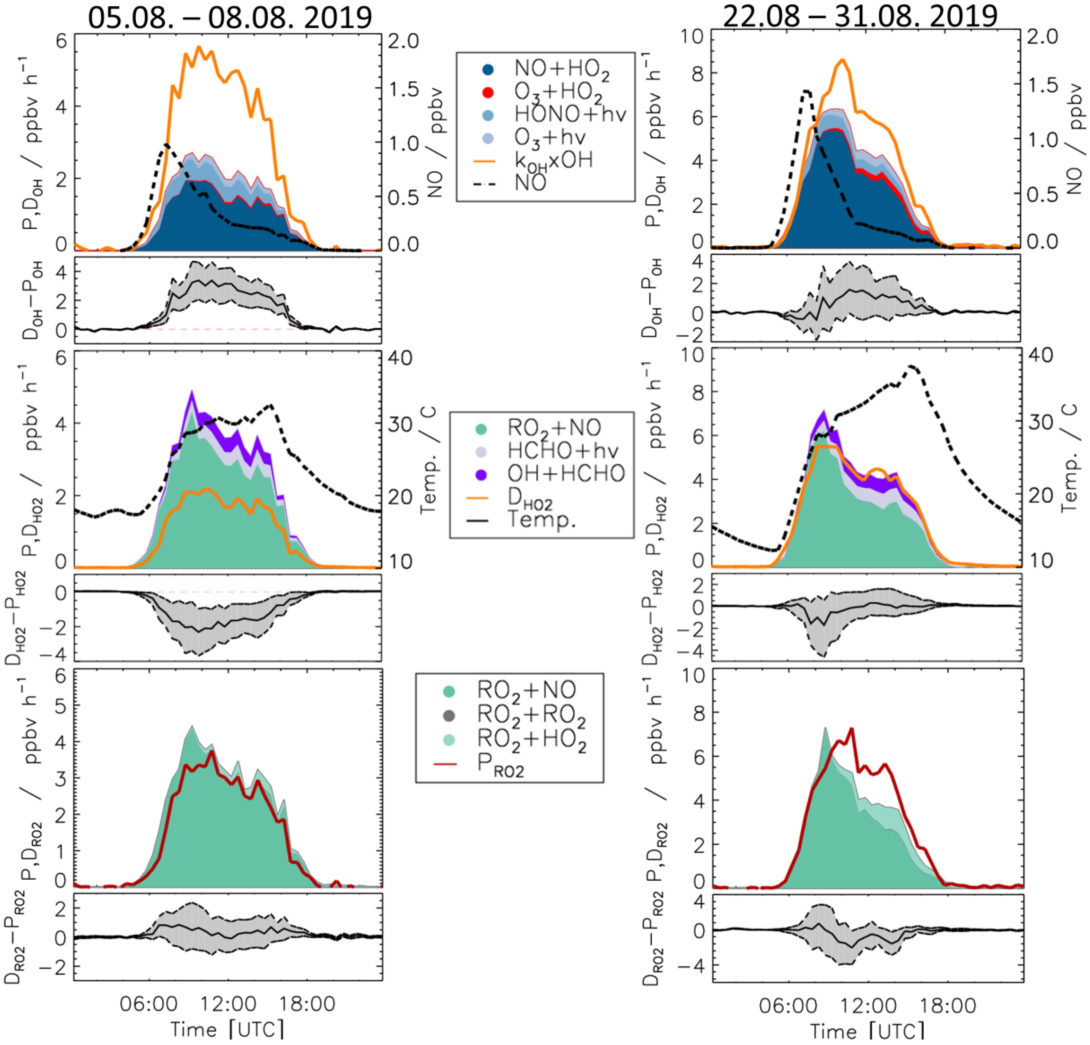

Figure 10: Production and destruction rates of OH, HO_2, and RO_2 radicals for Case 1 (05.08. - 08.08 2019) and Case 2 (22.08 - 31.08 2019). In addition, the differences between the destruction and production rates are shown. Grey areas give the 1σ uncertainty derived from experimental errors of the measured quantities (Table 2) and of the reaction rate constants (Table 1). The reactions that have insignificant contributions to the production or destruction rates are not shown.

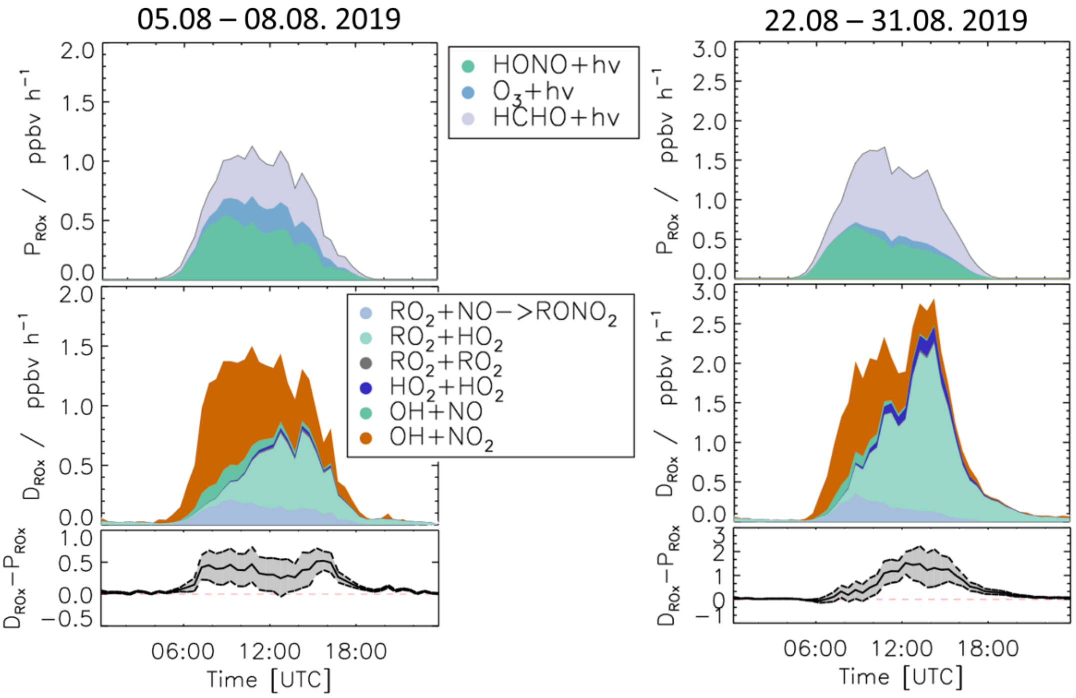

Figure 11: Production and destruction rates of RO_X for the periods of the case studies (Case 1 and Case 2). In addition, the differences between the destruction and production rates are shown. Grey areas indicate the 1σ uncertainty derived from experimental errors of the measured quantities (Table 2) and of the reaction rate constants (Table 1). The reactions that have insignificant contributions to the production or destruction rates are not shown.

3.5.2 Case 2: 22 - 31 August 2019

During the period from 22 to 31 August, the temperature was generally high and reached a maximum value of 42°C inside the chamber. The concentrations of radical precursors, HONO, HCHO and O_3, were higher than those observed in Case 1 (Table S3). Ozone mixing ratios reached values up to 100 ppbv, while daytime NO mixing ratios were similar as in Case 1 (<1.5 ppbv, median value of 0.22 ppbv). The conditions outside the chamber were characterized by stagnant air (wind speed < 4 m/s at 50 m height) with no precipitation. At these conditions, vigorous biogenic emissions can be expected (Vilà-Guerau de Arellano et al., 2009; Sarkar et al., 2020). Enhanced biogenic VOC emissions and their photochemical degradation can therefore explain the higher VOC and HCHO concentrations in Case 2 compared to the cooler period beginning of the month (Table S3). The larger VOC reactivity and comparable OH concentrations resulted in HO_2 and RO_2 concentrations that were approximately 2 to 3 times higher than in Case 1 (Table S3).

Imbalances between the radical production and destruction rates were a factor of 2 smaller in the warmer and more photochemically active period of Case 2 compared to Case 1. OH destruction rates were up to 1.5 ppbv h^{-1} (25 % of the total OH destruction rate) higher than the total production rate (Fig. 10). The HO_2 production and destruction rates agree within ±1 ppbv h^{-1}. The contributions from photolysis of

HCHO and the reaction of HCHO with OH to the HO_2 production rate were larger compared to other periods with values of up to 15% and 13%, respectively, due to high HCHO mixing ratios of up to 8 ppbv (Fig. 2). The RO_2 production and destruction rates showed imbalances by up to 1.5 ppbv h^{-1} in the late afternoon.

While HONO photolysis was the dominating RO_X source during most of the time in spring and summer (Fig. 9), HO_2 production from the photolysis of HCHO was the most important primary radical source in Case 2 due to the high concentration of HCHO (Fig. 11). Although the chemical budgets for each radical species were essentially closed within the experimental uncertainty, the total loss rate of RO_X was consistently higher than the production rate during daytime. The deviation was higher than the experimental uncertainty and reached a maximum value of 1.4 ppbv h^{-1} at noontime.

3.5.3 NO dependence of radical production and destruction rates

One of the most influential parameters for the radical chemistry is the concentration of NO, since the reaction with NO dominates the conversion rate of RO_2 to HO_2 (Reaction R10) and HO_2 to OH (Reaction R9) (Fig. 10). Figure 12 shows the NO dependence of median values of the calculated production and destruction rates for the different radicals for the spring and summer period.

For OH, the production rates are consistently lower than the destruction rates by about 1.5 ppbv h^{-1} for NO mixing ratios lower than 1 ppbv NO. At higher NO, the OH budget is balanced within the experimental uncertainty. For HO_2, an inverse pattern is observed. Below 1 ppbv NO, the production rate is higher than the destruction rate by about 1 ppbv h^{-1}. Only for lowest NO mixing ratios, the production and destruction rates are balanced. For NO mixing ratios above 1 ppbv, the chemical budget of HO_2 is essentially closed. For NO mixing ratios of 3.5 ppbv, the difference between production and destruction rate is noticeably high with 4 ppbv h^{-1} but has also a large uncertainty. For RO_2 radicals, the chemical budget is closed for NO mixing ratios below 1 ppbv but an increasing discrepancy between the loss and production rates is observed with increasing NO mixing ratios. While the production rate is relatively constant with a value of 2.5 ppbv h^{-1}, the loss rate increases to values of up to 7.5 ppbv h^{-1} at 3.5 ppbv NO. The budget of RO_X, in which radical inter-conversion reactions cancel out, is mostly balanced over the whole range of NO. Only for lowest and highest NO mixing ratios the destruction rate is 0.6 ppbv h^{-1} higher than the production rate.

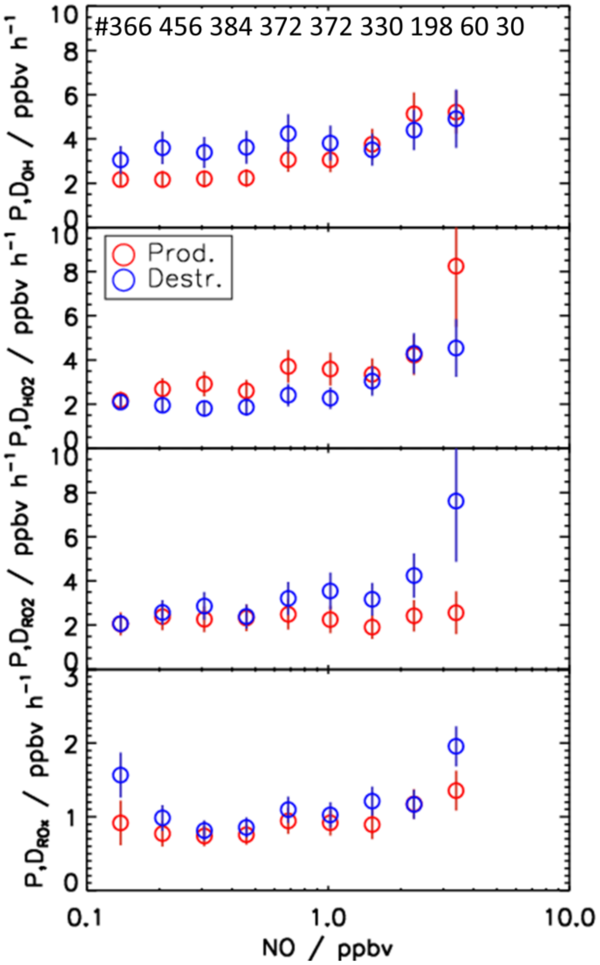

Figure 12: NO dependence of median production and destruction rates of OH, HO_2, RO_2, and RO_X radicals. Median values include all data from the spring and summer periods of the JULIAC campaign (NO intervals: ln(NO) = 0.4 ppbv). Vertical bars represent the 1σ uncertainty from experimental errors of the measured quantities (Table 2) and of the reaction rate constants (Table 1). The number of data points in each NO bin is represented on the top panel.

4 Discussion

4.1 Discrepancies in the chemical budgets of radicals

The highest imbalances in the chemical budgets of radicals are found for OH radicals. In spring and summer, their production rate was consistently lower than the loss rate (Fig. 8). This deficit was largest beginning of August (Case 1, Fig. 10) when the discrepancy reached (3.0±1) ppbv h^{-1}.

Imbalances in the radical budgets can be observed for different reasons. They can be caused by missing processes or incorrect rate constants in the calculations of the production or destruction rates (Section 4.2). It is also possible that measured concentrations that are used for the calculation contain unknown errors.

The technically difficult radical measurements have a large potential for artefacts (Hofzumahaus and Heard, 2016). Precautions were taken to minimize measurement interferences for OH and HO_2 in this campaign:

- The measurements of OH by the LIF instrument were interference-corrected using chemical modulation and agreed with simultaneous OH measurements by the DOAS instrument within the experimental uncertainties. The measured OH reactivity quantifies the total chemical loss rate of OH caused by atmospheric reactants and has a total accuracy of 10%. Thus, the destruction rate of OH, which is the product of the concentration and reactivity of OH, is known within 20 % and is unlikely biased by unknown OH interferences or unknown atmospheric reactants.
- The O_X production rate calculated from the reaction of peroxy radicals with NO agrees with the measured increase of O_X concentrations within ±1 ppbv h^{-1} for most conditions (Section 3.1). As more than 70 % of the OH production is due to the reaction of HO_2 with NO (Reaction R10), a bias of more than 1 ppbv h^{-1} due to an unaccounted HO_2 measurement error seems unlikely.
- The analysis of the chemical budget of OH in previous chamber experiments performed at various chemical conditions showed no evidence for a missing OH source originating from chamber wall effects (Kaminski et al., 2017; Fuchs et al., 2018; Novelli et al., 2018; Rolletter et al., 2019; Rolletter et al., 2020).

Thus, there is no evidence for instrumental errors that are not included in the estimated errors of the calculated turnover rates. The observed imbalances in the OH budget of up to 3 ppbv h^{-1} are therefore most likely due to a missing OH source.

The missing OH production is correlated with the imbalance in the HO_2 budget, for which the production rate is larger than the loss rate at low NO mixing ratios (Fig. 12). This is most clearly seen in the period of Case 1, when the discrepancy reaches (2.0±1) ppbv h^{-1} (Fig. 10). The production rate of HO_2 is nearly equal to the RO_2 loss rate ($P_{HO2} \approx D_{RO2}$) because both are controlled by the reaction of RO_2 with NO (Reaction R9). Furthermore, the RO_2 loss rate is well balanced by the RO_2 production rate within the experimental uncertainty of ±1 ppbv h^{-1} (Fig. 8 and 10). Thus, there is no hint that the calculated turnover rate of the RO_2 + NO reaction had a bias higher than 1 ppbv h^{-1}. In addition, turnover rates of the reactions of HO_2 and RO_2 with NO producing ozone are consistent with the observed O_X increase in the chamber (Section 3.1). This suggests that these rates are correct in the chemical budget analysis. For the above reasons, the discrepancy between HO_2 production and destruction rates is most likely due to a missing HO_2 loss process and not by measurement errors of HO_2, RO_2 or NO.

RO_X destruction rates are generally higher than the production rates but differences are on average lower than 0.5 ppbv h^{-1} (Fig. 9). In the periods of Case 1 and Case 2, the corresponding discrepancies reach 0.5 ppbv h^{-1} and 1.4 ppbv h^{-1}, respectively (Fig. 10). If these discrepancies were due to a missing primary OH source, they could also explain a small part (17 %) of the imbalance in the chemical OH budget in Case 1, and the complete imbalance in the OH budget in Case 2.

It is difficult to identify the exact cause for the differences in OH and HO_2 budgets observed for Case 1 and 2 only with the available data. Case 2 was characterized by high temperature with increased BVOC emissions and high levels of HCHO (Table S3). No clear correlation was found between the ratio of the production and destruction rates of the radicals and the concentration of chemical species such as NO, NO_2, O_3, HCHO, etc. A weak correlation was observed with temperature with an improved balance in the budgets the higher the temperature was. This could indicate that the unaccounted processes become less competitive for high radical turnover rates with chemical conditions being dominated by organic compounds from biogenic emissions.

In conclusion, the radical budget analysis suggests the presence of a missing OH source and a missing HO_2 loss process with a similar turnover rate at NO mixing ratios below 1 ppbv for typical temperatures in summer. The opposing imbalances in the OH and HO_2 budgets could be due to an unknown mechanism that converts HO_2 to OH, or they could indicate a missing primary OH source and a similar fast, but independent termination reaction removing HO_2. The remaining imbalance in the RO_X budget would be consistent with an unaccounted primary OH source. This fits best the observations in Case 2 characterized by high temperatures and VOC emissions.

For NO mixing ratios that are higher than 1 ppbv, production and destruction rates of OH and HO_2 radicals are generally balanced (Fig. 12). An exception is observed for HO_2 for highest NO mixing ratios of 3.5 ppbv, for which the production rate is 3.5 ppbv h^{-1} higher than the loss rate.

For RO_2, the radical budget is not closed, but the loss rate increases with NO in contrast to the production rate. The difference reaches a value of 5 ppbv h^{-1} at 3.5 ppbv NO. In the same range of NO mixing ratios, the odd oxygen production rate (P_{Ox}) calculated by peroxy radicals (Eq. 14) overestimates the observed increase in the O_x mixing ratio by about 3 ppbv h^{-1}. This difference points to a systematic error in the peroxy radical measurements explaining a considerable part of the imbalance in the RO_2 budget. A reduction of the RO_2 concentration by 3×10^7 cm^{-3} would reduce the HO_2 production rate by 3 ppbv h^{-1} and resolve the discrepancy in the odd oxygen production calculations for the highest NO mixing ratio. The presumed bias in the RO_2 measurement may be caused by an incorrect background subtraction that becomes most relevant at high NO concentrations (Section 3.1). However, even after correction of this bias a discrepancy in the RO_2 budget would remain requiring an additional RO_2 source of approximately 2 ppbv h^{-1} to be balanced.

Further information on the nature of the missing RO_2 source can be obtained from the chemical budget of RO_X, for which the production rate is 0.5 ppbv h^{-1} smaller than the loss rate at 3.5 ppbv NO (Fig. 12). This discrepancy cannot be explained by the instrumental uncertainties in HO_2 and RO_2 measurements, because the RO_X budget at high NO in the morning was dominated by OH reactions with NO_2 and (Fig. 9). Thus, the imbalance in the RO_X budget at high NO indicates a missing primary radical source, which on a single day (29 April) even reached 3 ppbv hr^{-1} (Fig. 6). As the OH budget is balanced for most of the time and the corresponding HO_2 budget does not require an additional HO_2 source, a missing primary RO_2 source is a likely explanation for the discrepancy in the RO_X budget. This would also explain part of the imbalance in the RO_2 budget at high NO concentrations.

4.2 Potentially missing chemical processes

The above discussion shows that imbalances between calculated production and destruction rates are highly variable over time and change with chemical conditions. As main general features in spring and summer, the radical budget analysis indicates unaccounted OH production processes with a typical strength of 1.5 – 3 ppbv h^{-1} at low NO concentrations, which coincides with a missing HO_2 sink of 1 – 2 ppbv h^{-1}. At high NO mixing ratios (> 1 ppbv), the radical budgets for OH and HO_2 radicals are relatively well balanced, but RO_2 production processes of about 2 ppbv h^{-1} appear to be missing in the RO_2 radical budget. In the following, potential reasons for the observed discrepancies in the radical budgets are discussed.

4.2.1 Differences in the chemical behavior of specific RO_2 radicals

As no speciated RO_2 radicals were detected but the sum of all RO_2 species, effective rate coefficients for the reaction of all RO_2 species with NO (Reaction R9, R14), RO_2 (Reaction R15), and HO_2 (Reaction R16) are used from structure-activity relationship (SAR) by Jenkin et al. (2019) for the calculations of turnover rates. Potential systematic errors due to this simplification for reactions of RO_2 with RO_2 and HO_2 are expected to be negligible due to their small contributions to the total turnover rates.

In contrast, the reaction of RO_2 with NO plays an important role in the chemical budgets of HO_2 and RO_2. The reaction has one channel that converts RO_2 to HO_2 (Reaction R9) and one radical termination channel that produces organic nitrates ($RONO_2$) (Reaction R14). The unknown speciation of RO_2 causes uncertainty with respect to the total rate constant of the RO_2 + NO reaction ($k_9 + k_{14}$). An effective value of 9×10^{-12} cm^{-3} s^{-1} was taken from (Jenkin et al., 2019). A high limit for the total rate coefficient of RO_2 +NO (for example 1.1×10^{-11} cm^{-3} s^{-1}, 298K for c-$C_5H_9O_2$) would slightly increase the imbalances between production and destruction rates for HO_2 and RO_2 radicals by 13 % for both spring and summer. A lower limit would be the rate constant of the reaction of methyl peroxy radicals (CH_3O_2) with NO having a value of 7.7×10^{-12} cm^{-3} s^{-1} (298 K)., Applying this number in the calculations for HO_2 production and RO_2 destruction rates (Fig. S6) for the period when observed discrepancies in the HO_2 budget were highest (Case 1) further improves the already well balanced budget of RO_2 radicals. This also reduces the imbalance between HO_2 destruction and destruction rates, but the effect is rather small (approximately 10%) and not sufficient to explain the total difference. For the other periods such as the spring period and the period of Case 2, a reduced reaction rate would worsen the observed imbalances.

An additional uncertainty in the HO_2 production rate comes from the assumed yield of organic nitrates in the reaction of RO_2 with NO. Typical organic nitrate yields range from 5 % to 20 % (Jenkin et al., 2019). The low limit value is applied in the calculations above. Using a value of 20 % decreases the discrepancy between HO_2 production and destruction rates from 2.0 to 1.5 ppbv h^{-1} for the period of Case 1.

It is worth noting that the organic nitrate yield is generally higher for larger hydrocarbons, but the rate constant for the RO_2 + NO reaction is also often higher, so that there are compensating effects in the production efficiency of HO_2. In addition, it is expected that only a fraction of RO_2 radicals is produced from large hydrocarbons due to the major composition of RO_2 would be methyl peroxy radicals.

For the above reasons, the unknown speciation of RO_2 is unlikely the reason for the observed imbalances in the HO_2 budget that are most prominent in the period of Case 1.

4.2.2 Unaccounted primary radical sources

Primary RO_X radical production that may not be appropriately accounted for in the calculations could be OH, HO_2, and RO_2 production from the ozonolysis of alkenes. Only few alkene compounds were measured in the JULIAC campaign. The contribution from the ozonolysis of these alkenes to the radical production was very small with values in the range of 0.005 to 0.03 ppbv h^{-1} (Section 3.5). The ozonolysis of small alkenes such as propene and cis-2-butene that were not measured but are often abundant for example in forested areas (Goldstein et al., 1996; Rhew et al., 2017), may have significantly contributed to the radical production.

The potential impact of unmeasured alkenes on the primary radical production is tested by assuming that the OH reactivity that cannot be explained by measured OH reactants (on average, 2.5 s^{-1}) originates from 1.5 ppbv propene and 1.0 ppbv cis-2-butene. The radical production by ozonolysis of the additional propene and cis-2-butene increases the production from ozonolysis of measured species by more than an order of magnitude in both spring and summer periods of the JULIAC campaign (Fig. S7) The discrepancies between the total RO_X production and destruction rates is significantly decreased for the period of the 2 Case studies by approximately 0.2 ppbv h^{-1}. However, the additional OH production is by far insufficient to explain the missing OH source that was generally found during the JULIAC campaign. In addition, the corresponding OH and O_3 reactivity from the additional alkene compounds is about a factor of 6 larger than of alkenes (e.g., ethene, propene, trans-2-butene, cis-2-pentene) that were measured in ambient air next to the SAPHIR chamber in the HOxComp campaign in July 2005 (Elshorbany et al., 2012; Kanaya et al., 2012). In addition, during the HOxCOMP campaign the modelled OH reactivity could be matched with the measured reactivity by including either additional primary emissions (Kanaya et al., 2012) or model-produced oxygenated secondary products (Elshorbany et al., 2012). Neither of the additional species contributed enough to close the radical budgets. If it is assumed that the missing OH reactivity (2.5 s^{-1}) is all due to glyoxal (9 ppb) an additional OH production of 0,3 ppb h^{-1} could be expected. This would still not be enough to close the radical budget suggesting that unmeasured OVOCs do not play a large role.

The photolysis of oxygenated organic compounds is another source for radicals that could be underestimated in the calculations. Only the photolysis of HCHO is included in the production rate of HO_2 and RO_X at all times of the campaign. In addition, acetaldehyde (CH_3CHO), methyl vinyl ketone (MVK), methacrolein (MACR), and methylglyoxal were measured during part of the campaign and were not included in the analysis in Section 3. Calculations show that radical production rate from their photolysis was less than 0.1 ppbv h^{-1}. Thus, photolysis of unmeasured OVOCs was very likely unimportant in the present study. This is consistent with similar small contributions from photolysis of OVOCs other than HCHO found in in the HOxComp campaign (Kanaya et al., 2012).

The photolysis of $ClNO_2$ constitutes a primary radical source (Reaction R20, R22) that can be found in coastal environments (e.g., Osthoff et al. (2008)) and mid-continental regions (e.g., Thornton et al. (2010)). The availability of $ClNO_2$ data during the summer period allowed assessing the potential impact of its photolysis on the RO_2 radical production (Eq. 9). Due to the low mixing ratio of $ClNO_2$ of less than 0.4 ppbv (Tan et al., 2022), the RO_2 production from Cl oxidation processes was insignificant (<0.1 ppbv h^{-1}) and cannot explain the observed discrepancies in the primary production and destruction rates of radicals in the summer period and in the case studies. The instrument detecting $ClNO_2$ was not available in the spring period of the campaign. Therefore, the extent to which $ClNO_2$ photolysis contributed in spring, for example to the large missing RO_x source (up to 3 ppbv hr^{-1}) on 29 April, remains unknown.

4.2.3 Unaccounted radical termination reactions

Heterogeneous uptake of HO_2 on aerosol is a potential termination reaction that is not included in the HO_2 and RO_X destruction rates above. However, the impact of including the heterogeneous HO_2 loss on aerosol surface (Eq. 8) on the total loss rate is insignificant (less than 1 %), even if a high effective uptake coefficient of 0.2 is assumed (Fig. S7).

As HO_2 uptake is a radical termination process, its relative contribution to the total RO_X loss rate can be higher compared to the relative contribution to the total HO_2 loss rate. However, the only notable influence would be for the period of Case 2 (8 % of total RO_X loss rate), when the aerosol surface area concentration was high with values of up to 3.0×10^2 μm^2 cm^{-3}.

The estimate for the heterogeneous HO_2 loss rate has a high uncertainty because the uptake coefficient highly depends on the aerosol properties that were not fully characterized in this campaign. Previous laboratory investigations showed a large variability for the uptake coefficient with values ranging from 0.08 to 0.6 depending on the aerosol chemical composition and the physical state (George et al., 2007; Taketani et al., 2008, 2009; George et al., 2013; Lakey et al., 2015; Song et al., 2020; Tan et al., 2020). Even the largest reported HO_2 uptake coefficients cannot explain the observed differences in the chemical budget of HO_2 radicals. Therefore, heterogeneous HO_2 reactions can be ruled out as an explanation for the unexplained HO_2 loss rate.

4.2.4 Unaccounted radical inter-conversion reactions

In the last decade, it has been discovered that unimolecular reactions of RO_2 can significantly increase atmospheric OH concentrations in low-NO environments where they can compete with the reaction of RO_2 with NO. The most important, atmospherically relevant example is the production of OH from the isomerization of isoprene-RO_2 radicals (Peeters et al., 2009; da Silva et al., 2010; Peeters and Müller, 2010; Crounse et al., 2011; Fuchs et al., 2013; Peeters et al., 2014; Teng et al., 2017; Novelli et al., 2020). The SAPHIR chamber is surrounded by a deciduous forest that emits isoprene especially in summer. Compared to previous campaigns on the campus where up to several ppbv of isoprene were measured (Komenda et al., 2003; Spirig et al., 2005; Kanaya et al., 2012), concentrations were relatively low during the JULIAC campaign (< 0.4 ppbv, on average).

The effect of the conversion of RO_2 to OH by the isomerization of isoprene-RO_2 (Eq. 4)is tested in the analysis of the OH and RO_2 budgets. In the afternoon of days in the spring period and the period of Case 2, the total OH production increases only 1 % due to the low isoprene mixing ratios (< 0.2 ppbv) and the competition of unimolecular reactions with bimolecular reactions of RO_2 with NO. Even in the summer period, when isoprene mixing ratios were up to 0.8 ppbv, the contribution of isomerization reactions from isoprene-RO_2 radicals to the total turnover rate of RO_2 is still small with values of less than 4 %. This implies that unimolecular decomposition reactions of isoprene-RO_2 radicals made a minor contribution to the RO_2 destruction and OH production rates.

Another known isomerization process that produces OH applies to RO_2 that are formed by OH oxidation of methacrolein (MACR) (Crounse et al., 2012; Fuchs et al., 2014), which is an oxidation product of isoprene. MACR mixing ratios were up to 0.5 ppbv in the JULIAC campaign. Because the rate constant for the OH reaction of MACR is smaller than for isoprene, OH regeneration from MACR-RO_2 radicals is even less important than from isoprene-RO_2.

For acyl and carbonyl peroxy radicals it was shown that the reaction of RO_2 with HO_2, which mainly forms hydroperoxides (ROOH) (Reaction R16), can produce OH with yields up to 80% (Hasson et al., 2004; Dillon and Crowley, 2008; Groß et al., 2014; Praske et al., 2015; Winiberg et al., 2016; Fuchs et al., 2018; Jenkin et al., 2019). It is also noteworthy that the rate constant for the reaction of HO_2 with this class of RO_2 species is almost a factor of 2 higher than for other RO_2 species (Jenkin et al., 2019). However, even if it is assumed that all the measured RO_2 are acyl and carbonyl peroxy radicals, the formation of OH from their reaction with NO could only explain up to 0.5 ppbv h^{-1} of the imbalances in both OH and HO_2 budgets.

Studies in the remote marine boundary layer show that HO_2 to OH conversion mediated by halogen oxides (XO, X = Cl, Br, I) (e.g., Bloss et al. (2005); Sommariva et al. (2006); Kanaya et al. (2007); Stone et al. (2018); Fan and Li (2022)) can significantly contribute to the interconversion of radicals and destroy ozone:

$$HO_2 + XO \rightarrow HOX + O_2 \tag{R23}$$

$$HOX + h\nu \rightarrow OH + X \tag{R24}$$

$$XO + NO \rightarrow NO_2 + X \tag{R25}$$

$$X + O_3 \rightarrow XO \tag{R26}$$

This conversion mechanism would only be effective at low NO, when the consumption of XO by NO (Reaction R25) is comparatively slow and when X is not depleted by other reactions as in the case of Cl by reactions with VOCs (Reaction R22).

For BrO, the rate constants for Reaction R23 and R25 are about the same (2.1×10^{-11} cm^{-3} s^{-1} at 298 K, (J. B. Burkholder, 2019). Thus, the reaction of BrO with HO_2 would only be dominant, if the NO concentration were smaller than the concentration of HO_2, i.e., less than 10 pptv in this campaign. For IO, the situation is similar and NO mixing ratios would need to be less than 40 pptv. Such low NO mixing ratios were not observed during daytime and rule out significant halogen oxide mediated HO_2 to OH conversion. The required XO concentrations to achieve an HO_2 loss rate of 1 ppbv h^{-1} at an HO_2 concentration of 2×10^{8} cm^{3} would be 66 pptv BrO or 16 pptv IO, which exceeds the abundances reported for marine environments, where halogen sources are known to exist, by more than an order of magnitude. For these reasons, halogen oxide chemistry cannot explain the missing HO_2 sink and missing OH source in this study.

4.3 Comparison with results from other field campaigns

Although the chemical and physical conditions were partly influenced by the chamber properties (Section 2.1), the radical concentrations observed during spring and summer were within the range of values that have been observed in other field studies in summertime in urban and suburban areas (Tan et al., 2001; Ren et al., 2003; Kanaya et al., 2007; Mao et al., 2010; Lu et al., 2013; Brune et al., 2016; Tan et al., 2017; Whalley et al., 2018; Tan et al., 2019). The impact of the decreased solar radiation by the chamber transmission on the radical production was compensated by the radical production from the photolysis of HONO and HCHO emitted from the chamber film.

This effect is also shown in the relationship between the OH concentration and the photolysis frequencies of ozone, j_{O^1D} (Section 3.4). The slope (8.0×10^{11} cm^{-3} s^{-1}) of the correlation for the data from the

JULIAC campaign is much higher than obtained for data in other field campaigns in similar environments (Ehhalt and Rohrer, 2000; Handisides et al., 2003; Holland et al., 2003; Tan et al., 2017) due to the high OH production by the photolysis of chamber-produced HONO (Reaction R1). This is further confirmed by the similarity in OH and HO_2 radical concentrations between this campaign and what was observed in the HOxComp campaign when measurements were performed in front of the SAPHIR chamber for 3 days in July 2005 (Elshorbany et al., 2012).

In contrast, daytime OH concentrations observed during winter and autumn in the JULIAC campaign were lower than OH concentrations observed in previous wintertime field campaigns (Heard et al., 2004; Ren et al., 2006; Kanaya et al., 2007; Tan et al., 2018; Ma et al., 2019). This is due to the lower photolysis frequencies in the chamber compared to outsides, which is not compensated by chamber-produced HONO in wintertime, because the emission strength is low at low temperature and low solar radiation.

Very low nighttime OH concentration in all seasons of the JULIAC campaign (Section 3.4) is consistent with observations in previous field campaigns in rural areas in Germany (Ehhalt and Rohrer, 2000; Handisides et al., 2003; Holland et al., 2003), in which nighttime OH concentrations were less than 1×10^5 cm^{-3}. However, in several other field studies performed in urban areas, nighttime OH concentrations were in the range of 0.2 to 3×10^6 cm^{-3}, for example in China (Lu et al., 2014; Rohrer et al., 2014; Tan et al., 2017; Tan et al., 2018; Ma et al., 2019; Tan et al., 2019; Wang et al., 2019; Whalley et al., 2021), in the US (Martinez et al., 2003; Brune et al., 2016; Griffith et al., 2016), and in the UK (Ren et al., 2003; Vaughan et al., 2012). In these studies, the high nighttime OH concentrations could not be explained by model predictions and raised questions about the presence of potential interferences in nighttime OH signals measured by LIF instruments (Mao et al., 2012; Lu et al., 2014; Novelli et al., 2014).

Similar studies investigating the chemical budgets of OH, HO_2, RO_2, and RO_X radicals like in this study have been performed for data from field campaigns in a suburban area in the Pearl River Delta (PRD), China, in autumn 2014 (Tan et al., 2019), and in central Beijing, China, (Whalley et al., 2021) in summer 2017.

Tan et al. (2019) observed median values of turnover rates of OH, HO_2 and RO_2 radicals ranging from 10 to 15 ppbv h^{-1}, while rates for RO_X initiation and termination rates were on the order of 3 to 4 ppbv h^{-1} during daytime for chemical conditions affected by anthropogenic emissions. From the comparison between the radical production and destruction rates, a missing OH source and a missing RO_2 sink with a similar rate up to 7 ppbv h^{-1} (45 % of the total OH turnover) were found at low NO mixing ratios below 1 ppbv, while HO_2 production and destruction rates were balanced. The authors suggested that an additional chemical mechanism is required that efficiently converts RO_2 to OH without the involvement of NO. One possibility proposed by Tan et al. (2019) is that HO_X radicals are formed from the auto-oxidation of specific RO_2 species which include multifunctional groups such as -OH, -OOH, or -CHO groups.

The analysis of the chemical budget of OH radicals in the JULIAC campaign shows that an unaccounted OH source with a rate ranging between 2 and 3 ppbv h^{-1} (about 50 % of the total OH destruction rate) is required at low NO mixing ratios to balance OH production and destruction rates. This rate is smaller than the rate determined in Tan et al. (2019). However, considering that the OH radical turnover rates in the JULIAC campaign were about half compared to values in the campaign in the PRD area, the relative importance of the unaccounted OH source was comparable in both campaigns. However, the mechanism suggested by Tan et al. (2019) is likely not the only explanation for discrepancies in the radical budgets observed in this study. In the JULIAC campaign, to balance the budget of RO_2 radicals rather requires an additional radical source than additional loss processes particularly at high NO mixing ratios above 1 ppbv, and the missing OH sources are likely originating from an HO_2 to OH conversion process and/or a missing primary OH source.

Whalley et al. (2021) also investigated the chemical budgets for radicals over a wide range of NO mixing ratios (0.1 to 104 ppbv) from measurement performed in central Beijing, China. Compared to the results in Tan et al. (2019) and to results in this study, the rates of RO_X initiation and termination reactions were 2 to 4 times higher. Also, the rates of radical propagation reactions for OH, HO_2 and RO_2 radicals were 5 to 10 times higher due to fast inter-radical conversion reactions at conditions with high concentrations of NO. Similar to the results in this study, an OH source with a high rate of up to 15 ppbv h^{-1} (50 % of the total OH destruction) was required to balance OH production and destruction rates for low NO mixing ratios. This unaccounted OH source is more than 3 times higher than that determined in the JULIAC campaign and in the campaign in China reported by Tan et al. (2019). The HO_2 production rate observed in Beijing largely exceeded the destruction rate by 3 to 5 times for low NO mixing ratios. In contrast, production and destruction of RO_2 and RO_X radicals were well balanced. On the other hand, results for conditions of low NO concentrations, production and destruction of OH radicals were balanced at high NO mixing ratios, while very high imbalances of up to 50 ppbv h^{-1} were observed for HO_2 and RO_2 radicals. Whalley et al. (2021) showed that reducing the rate constant of the reaction between RO_2 and NO by a factor of 10 could close the gaps between production and destruction rates. The authors suggested that the presence of a significant fraction of RO_2 radicals from the oxidation of large and multifunctional VOCs such as monoterpenes and long-chain alkanes could explain observations. These radicals can undergo multiple RO_2 to RO_2 conversion reactions by unimolecular isomerization of alkoxy radicals (RO), which are formed from the reaction of RO_2 with NO, so that no HO_2 is produced. Such a RO_2 radical reaction chain would be equivalent to an increased chemical lifetime of RO_2 radicals, if RO_2 species cannot be distinguished by instruments like in the sum measurements performed by RO_X-LIF instruments. Whalley et al. (2021) showed that RO_2 production by this mechanism would largely reconcile discrepancies between modelled and measured RO_2 concentrations (the model-measurement ratio decreases from 6.2 to 1.8), if the OH reactivity that could not be accounted for by measured OH reactants is attributed to α-pinene.

Applying a reduced rate constant for RO_2 to HO_2 propagation reactions as suggested in Whalley et al. (2021) in the calculations in this study could help explaining the observed discrepancies between HO_2 and RO_2 production and destruction rates. The largest effect is expected when high NO mixing ratios up to 10 ppbv like on 29 April is experienced. In this case, a high reduction of the rate constant by a factor of 2 for all measured RO_2 would be required to close the observed gaps between production and destruction rates. Reduced reaction rate constants of the RO_2+NO reaction could be expected for RO_2 from large VOCS. However, the fraction of these RO_2 species is expected to be small for conditions of this campaign, even if OH reactivity that is not explained by measured OH reactants is attributed to large VOCs. Therefore, it seems unlikely that the mechanism suggested by Whalley et al. (2021) affects the observed discrepancies in the radical budgets in this study.

It is interesting to point out that similar discrepancies in the OH and HO_2 budgets have been observed during the HOxComp campaign in July 2005 (Elshorbany et al., 2012). Although measurements were only done for 3 days and despite that these were 14 years earlier than measurements in this work, the chemical composition was similar with comparable values of NOx, O_3, isoprene concentrations and of OH reactivity. As observed in this study, a missing OH radical source in the range of 2 to 4 ppbv h^{-1} was needed to close the OH budget for low-NO chemical regimes. The lack of measured RO_2 radicals did not allow to perform a measurement-only budget for HO_2 radicals. Nevertheless, model calculations overestimated measured HO_2 radicals after the correction for RO_2 radical interferences (Fuchs et al., 2011) by up to 30% at low NO (Elshorbany et al., 2012; Kanaya et al., 2012). Like in this study, good agreement was found between modelled and measured OH and HO_2 radical concentrations only if an unknown loss process for HO_2 radicals that would recycle OH was introduced.

4.4 Potential role of the missing radical processes on the evaluation of the ozone production rate

The good agreement of the odd oxygen production rates calculated by the two different methods (Section 3.1) not only gives high confidence in the measured peroxy radical concentrations but also confirms the current chemical understanding of tropospheric ozone formation from the reaction of peroxy radicals with NO. Therefore, results demonstrate that accurate predictions of radical concentrations in atmospheric models are crucial to accurately predict the surface ozone level.

However, the significant level of the missing radical processes found in this study implies the difficulties in the prediction of the radical concentrations by the models without constraining radicals by their measurements. In low NO mixing ratios, there are two opposing effects of the missing radical processes on the O_3 formation. At first, a missing OH source and therefore an underestimation of OH concentrations by the models would lower the loss of NO_2 by the reduced reaction rate with OH, and essentially produce more O_3 by its photolysis. Furthermore, the production of RO_2 would be under-predicted due to the lower OH concentrations in the models. At the same time, an unexplained HO_2 sink would result in the over-prediction in HO_2 concentrations and thus O_3 production. In high NO environments, missing RO_2 and RO_X production processes would result in an underestimation of the O_3 production.

5 Summary and conclusions

Ambient measurements of atmospheric radicals, trace gases, and aerosol properties were performed during the Jülich Atmospheric Chemistry Project campaign (JULIAC) using the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany. Ambient air was continuously drawn at a high rate into the chamber (1 hour residence time) through a 50 m high inlet line for one month in each season throughout 2019.

For parts of the campaign, measurements of OH concentrations were achieved by two different methods, laser-induced fluorescence with a chemical modulation system for zeroing (FZJ-LIF-CMR) and differential optical absorption spectroscopy (FZJ-DOAS). Measurements of both instruments agreed within 11 % (Cho et al., 2021).

The production rate of odd oxygen (O_X) was determined by using either measured HO_2 and RO_2 concentrations or O_3 and NO_2 concentrations measured in the chamber and in the incoming flow. Results showed excellent agreement between the two different methods confirming that HO_2 and RO_2 are responsible for the formation of tropospheric O_3 and giving additional confidence in the reliability of peroxy radical concentration measurements performed in the JULIAC campaign.

An analysis of the chemical budgets of OH, HO_2, RO_2 and RO_X radicals was performed for data obtained in the spring and summer periods of the campaign. On average, daytime radical turnover rates ranged between 3 to 6 ppbv h^{-1} and 4 to 10 ppbv h^{-1} in spring and summer, respectively, for OH, HO_2 and RO_2 radicals, while total rates of RO_X initiation and termination reactions were below 2.0 ppbv h^{-1}. For most conditions, radical production and destruction rates highly depended on the turnover rate of the reaction of peroxy radicals with NO. For the total turnover rate of the sum of all radicals (RO_X), the photolysis of HONO and HCHO contributed most to the primary radical production and the reactions of OH with NO_2 and RO_2 with HO_2 dominated the radical termination processes.

Differences between radical production and destruction rates were often small and below the accuracy of the calculations in the JULIAC campaign in winter and autumn. However, for both spring and summer, an additional OH source is required to explain the observed discrepancy between production and destruction rates. The OH production rate of this source would need be on average 2 ppbv h^{-1} and 3 ppbv h^{-1} in the spring and summer period, respectively. This discrepancy is in the same range as observed for measurements at the same location during the HOxComp campaign in July 2005 (Elshorbany et al., 2012).

Discrepancies between production and destruction rates of OH radicals were highest for conditions with low NO mixing ratios in this study. This is similar to findings in other field campaigns in China (Tan et al., 2017; Tan et al., 2019; Whalley et al., 2021). The high reliability of radical data in this study gives further confidence that the discrepancies arise from unaccounted chemical processes rather than from instrumental artefacts.

The highest unaccounted OH source with a rate of 3.0 ppbv h^{-1} (51 % of the observed total OH destruction rate) is observed in the period from 5 August to 8 August (Case 1), when NO mixing ratios were less than 1 ppbv and median maximum temperature in the chamber were 31°C. At the same time, an additional HO_2 destruction process with a rate of up to 2.0 ppbv h^{-1} is required to balance the HO_2 production rate, while production and destruction rates for RO_2 radicals are well balanced. The opposing imbalances in the OH and HO_2 budgets could be due to an unknown mechanism that converts HO_2 to OH, or this could indicate a missing primary OH source and a similar fast, but independent termination reaction removing HO_2. If an unknown HO_2 to OH conversion mechanism played a major role, it would not explain the complete rate of the missing OH source. Since the missing OH source is slightly larger than the rate of the missing HO_2 sink, part of the missing OH source could have been originated from a missing primary OH production process, ~~his indicates that an unaccounted HO_2 to OH radical propagation process could be present. In addition, part of the missing OH source could have been originated from a missing primary OH production process,~~ because also a small difference between the total RO_X production and destruction rates are observed. The missing RO_X source was up to 0.5 ppbv h^{-1} for Case 1, but was even higher with a rate of 1.4 ppbv h^{-1} in the summer, when temperature was highest (Case 2). Since the calculated reaction rate of the HO_2 and RO_2 radicals with NO were able to reproduce the observed O_X production within 1ppbv h^{-1}, the unknown missing processes do not seem to have a direct impact on net ozone production.

For NO mixing ratios in range of 1 to 3 ppbv, production and destruction rates for OH and HO_2 radicals were balanced, while additional sources of RO_2 and RO_X having on average rates of 1.6 ppbv h^{-1} and 0.4 ppbv h^{-1}, respectively, were required to balance their production and destruction rates. Therefore, part of the missing RO_2 source can be explained by a primary radical source, but the remaining RO_2 source is still unresolved.

For high NO mixing ratios above 3 ppbv, 4 to 5 ppbv h^{-1}, large discrepancies between production and destruction rates of HO_2 and RO_2 radicals were found, but the calculations for these conditions have a higher uncertainty due to low HO_2 and RO_2 concentrations close to background signals. Whereas the imbalance in the budget for HO_2 radicals is due to an unaccounted loss processes, an additional RO_2 production processes is required to close the chemical budget for RO_2 radicals. For the same conditions, a primary RO_X source with a rate of 0.5 ppbv h^{-1} was needed to balance the RO_X destruction rate. Therefore, the missing primary RO_X source is likely an unaccounted primary RO_2 source.

Production of radicals from the oxidation of organic compounds by chlorine could have been one additional source. Unfortunately, the potential impact of chlorine chemistry could not be examined in the spring periods, when these conditions were experienced, because $ClNO_2$ measurements were not available. During times when $ClNO_2$ concentrations were measured, chlorine chemistry initiated by the photolysis of $ClNO_2$ did not significantly contribute to the radical production.

For chemical conditions when the contribution of the reaction of HO_2 with NO to the OH production was reduced, i.e. at lower NO levels, other radical formation pathways such as isomerization reactions of RO_2 radicals, OH formation from ozonolysis of alkenes or photolysis of multifunctional organic compounds could gain in importance and need to be properly accounted for. These processes remain relatively poorly constrained due to the lack of direct measurements of e.g., multifunctional organic compounds.

Although the exact mechanism for the missing production or destruction processes for OH, HO_2 and RO_2 radicals could not be determined from measurements in this campaign, knowing the magnitudes of the missing radical processes gives indicative information about the disagreements of model simulations and observations for radicals and secondary air pollutants.

More investigations of the chemical budgets of radicals for example in environments with high NO mixing ratios including the determination of the impact of chlorine chemistry and with a detailed characterization of the chemical composition of air masses with respect to the presence of complex organic compounds would be beneficial for the understanding of radical chemistry as well as of the formation of secondary air pollution such as ozone.

Code and data availability

Data of the JULIAC campaign analyzed in this work is available from the Jülich Data repository (https://doi.org/10.26165/JUELICH-DATA/3J80BW, Cho et al., 2022).

Author contributions

AH designed JULIAC campaign and organized it together with HF and FH. CC performed the measurements of radicals, analyzed the data, and wrote the paper together with AN and HF. All co-authors contributed with data and helped the writing by intensive discussions of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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