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Diurnal behavior and temporal patterns of atmospheric peroxy radicals in a semi-urban area during summer 2016

MASTER THESIS



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Abstract

Peroxy radicals (HO_2+RO_2) are greatly involved in the oxidative capacity of the atmosphere together with the hydroxyl radical (OH). They are produced mostly by the photolysis of ozone followed by the reaction of the $O(^{1}D)$ atoms with water molecules. They play a key role in the formation or depletion of ozone depending on the ambient concentration of NO_x . Multiple techniques were developed to measure peroxy radicals in the field. One of them is the peroxy radical chemical amplification (PeRCA), which was used in the summer campaign 2016 carried out by the institute of environmental physics in the semi urban area of Bremen on the roof of the institute. During the campaign on sunny days RO_2^* mixing ratios of up to 140 pptv were measured. The midday peak was found to be isochronal with the peak in radiation. Further the morning rush hour peak could be identified in the mixing ratio of NO and NO₂ followed by the build up of ozone in the afternoon. The NO_x emission peak during rush hours belated the build up of ozone when compared to mixing ratios during weekends. A broadening of the diurnal cycle of RO_2^* mixing ratios could be identified on weekends. At night repeating emission patterns could be identified in the mixing ratio of the trace gases measured as well as in the relative humidity and temperature changes varying along with the variations of the trace gases. It is suggested that a local source is momentary repeatedly releasing air masses with increased NO, NO₂, and CO mixing ratio.

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1 Introduction

Atmospheric radicals, HO_2 and RO_2 , where R represents an organic group, play a key role in the chemistry of the troposphere alongside the hydroxyl radical OH despite their low abundance in the atmosphere. Their high reactivity results in a very short lifetime [J. H. Seinfeld, 1998, J.M. Wallace, 2006, Monks, 2005] which, depending on composition of the ambient air as HO₂ can have a lifetime of ~ 1 minute in clean air conditions. They are involved in many reactions with several species, in clean atmospheric conditions dominated by natural trace species, and also with species characteristic for anthropogenically polluted areas e.g. hydrocarbons [Green et al., 2006]. Peroxy radicals are closely involved in the depletion and production of tropospheric ozone, depending on the local atmospheric composition, [Mihelcic and Müsgen, 1985] and other species typical for photochemical smog events. The hydroxyl radical OH initiates a reaction chain which is the major sink for most atmospheric trace gases. The concentration of OH radicals is coupled with the concentration of ozone which reaches a peak at noon [Monks, 2005]. As OH originates from the photolysis of ozone to oxygen and $O(^{1}D)$ and the subsequent reaction with water vapour forming OH. Therefore the peak concentrations of OH usually follow the ones of ozone assuming no other major reactions involving OH are taking place. The formation of OH originating from the photolysis of ozone happens to only a fraction of $\sim 1\%$ of the O(¹D) atoms while the remaining part returns to the ground state via quenching [Monks, 2005]. In the marine boundary layer 10% of the photochemically produced $O(^{1}D)$ results in OH. However, this reaction is not the only source of OH. Photolysis of species like formaldehyde also play a big role in the production of OH, as does the reaction of ozone with alkenes, leading to production of OH at night time as no light is required [Ren et al., 2003].

The reaction of the hydroxyl radical with hydrocarbons results in the production of organic peroxy radicals, which in turn can react with O_2 forming HO_2 . The complex interaction of the reactions and the low mixing ratios (pptv range) result in the measurement of radicals being a difficult task. However, as they are a key factor for understanding the chemical processes in the atmosphere and since they can be used as indicators of the oxidative capacity of the atmosphere, a notable number of measurement studies has been done in the past 30 years [Clemitshaw, 2010, Kartal et al., 2010, and references herein]. Because of their coupled chemistry with ozone and NO_x , peroxy radicals are mostly considered in combination with these species as well as concentrations of ozone, volatile organic compounds and meteorological data. The most frequently used method to quantify peroxy radicals is the method of chemical amplification developed by Cantrell and Stedman [Cantrell and Stedman, 1982]. The University of Bremen has been using the PeRCA (Peroxy Radical Chemical Amplification) method in multiple campaigns in the last years, using a DUALER (DUAl channel peroxy radical chemical amplifiER)[Andrés-Hernández et al., 2013, 2010].

In the summer of 2016 the Institute of Environmental Physics of the University of Bremen carried out a campaign measuring air quality parameters as well as peroxy radicals on the semi-urban conditions of the institute itself in order to characterize the chemical behavior of the lower troposphere in the semi urban area. Peroxy radicals were measured using the PeRCA method on the roof of the institute. Furthermore, the abundance and diurnal variation of NO_x , CO and ozone were measured while simultaneously recording meteorological parameters as well as the global radiation and photolysis rate of NO_x . This paper presents the theoretical background and the experimental setup to this study.

2 Theoretical background

2.1 Role of the troposphere

The troposphere is the lowest layer of the atmosphere. It is characterized by decreasing temperature with altitude and within which most cloud formations occur. The pressure is decreasing vertically throughout the entire atmosphere logarithmically which means that the troposphere contains $\sim 80\%$ of the atmospheric mass. The hydrostatic equation

$$\frac{\delta p}{\delta z} = -g\rho \tag{1}$$

describes the decrease of pressure with increasing height, where p is the pressure, z the height, g the gravitational acceleration and ρ the density of air. Therefore, at the height of 5 km the pressure has decreased by 50%. The temperature decrease can be described by

$$\Gamma = -\frac{\delta T}{\delta z} \approx 6.5 \frac{K}{km} \tag{2}$$

here T denotes the temperature and Γ the lapse rate. The lapse rate depends on the humidity so dry air has a lapse rate of approximately $10Kkm^{-1}$ and moist air of ~ $5Kkm^{-1}$. The troposphere reaches a height of 9 to 16 km depending on the latitude and present temperature [J.M. Wallace, 2006]. Also rapid vertical mixing takes place in the troposphere. The trace species in the troposphere are highly dependent on the emissions from the surface, naturally and anthropologically. 80% of the CH₄ is emitted naturally from recently decayed organic materials. Biological processes, as the conversion of N₂ into NH₃, are performed by lifeforms such as microbes and bacteria. Volatile organic compounds (VOC's) are emitted by plants and anthropologically. The most abundant trace gases are argon, CO₂, neon, helium and methane (CH₄). Further, hazardous gases as ozone (concentrations in the ppbv range) and carbon monoxide (CO, concentration in the ppbv range) are present. The most important chemical species are listed in table 1. The chemical composition of the troposphere depends on surface conditions. Marine, forested and urban areas each have characteristic chemical emissions into the atmosphere. Biological

Gas	Chemical formula	Fraction of volume of air occupied by the species	Residence time	Major sources
Nitrogen	N ₂	78.084 %	1.6×10^7 years	Biological
Oxygen	O ₂	20.946 %	3000-4000 years	Biological
Argon	Ar	0.934 %	-	Radiogenic
Carbon Dioxide	CO_2	379 ppmv	3-4 years	Biological, oceanic, combustion
Neon	Ne	18.18 ppmv	-	Volcanic
Helium	He	5.24 ppmv	-	Radiogenic
Methane	CH_4	1.7 ppmv	9 years	Biological, anthropogenic
Hydrogen	H_2	0.56 ppmv	~ 2 years	Biological, anthropogenic
Nitrous oxide	N ₂ O	0.31 ppmv	150 years	Biological, anthropogenic
Carbon monoxide	СО	40-200 ppbv	$\sim 60 \text{ days}$	Photochemical, combustion, anthropogenic
Ozone	O ₃	10-100 ppbv	days - weeks	Photochemical
Nonmethane hydrocarbons	-	5-20 ppbv	variable	Biological, anthropogenic
Halocarbons	-	3.8 ppbv	variable	Mostly anthropogenic
Hydrogen peroxide	H ₂ O ₂	0.1-10 ppbv	1 day	Photochamical
Formaldehyde	HCHO	0.1-1 ppbv	$\sim 1.5 \text{ h}$	Photochemical
Nitrogen species	NOy	10 pptv-1 ppmv	variable	Soils, anthropogenic, lightning
Ammonia	NH ₃	10 pptv-1 ppbv	2-10 days	Biological
Sulfur dioxide	SO_2	10 pptv-1 ppbv	days	Photochemical, volcanic, anthropogenic
Dimethyl sulfide	CH ₃ SCH ₃	10-100 pptv	0.7 days	Biological, oceanic
Hydrogen sulfide	H_2S	5-500 pptv	1-5 days	Biological, volcanic
Carbon disulfide	CS_2	1-300 pptv	$\sim 120 h$	Biological, anthropogenic
Hydroxyl radical	OH	0-0.4 pptv	$\sim 1 \text{ s}$	Photochemical
Hydroperoxyl radical	HO ₂	0-5 pptv	-	Photochemical

Table 1: Typical range of mixing rations at dry tropospheric air at a pressure of 1 atm, residential times and sources of the most abundant gases in the troposphere. Source: [J.M. Wallace, 2006](p.155)

factors, such as vegetation and the fauna type, and also anthropogenic factors play a role. NO_x (NO+NO₂) concentrations are highly determined by vehicle emissions and therefore depend on population density [Alvarez et al., 2008]. While natural sources emitted in the year 2000 estimated 13.5 Tg NO_x, anthropogenic sources were responsible for 30.5 Tg NO_x . Regarding CO the distribution is even more drastic. 150 Tg were emitted naturally and 1000 Tg anthropogenically [J.M. Wallace, 2006].

The concentration of most trace gases in the troposphere does not change significantly when averaged globally over a specific time period. Thus, the rate of production and the rate of depletion must be equal. On this basis the lifetime of a species is defined as

$$\tau = \frac{M}{F} \tag{3}$$

with τ being the residence time or lifetime of a species, M the mass of the constituent in the atmosphere in kg and F the removal rate in $kg \cdot s^{-1}$. Lifetimes of trace gases in the troposphere vary from 1 s to 100 years. Non-reactive species with long lifetimes show rather uniform concentrations on the spatial scale and also a rather uniform vertical distribution. CFCs with a lifetime of ~ 100 years can even enter the stratosphere where they are known to destroy the stratospheric ozone layer.

2.2 Air pollution

The composition of the atmosphere can significantly influence the quality of life and future development in a specific area. Air pollution is a growing problem in many populated areas. It is defined as " $[\cdots]$ a situation in which substances that result from anthropogenic activities are present at concentrations sufficiently high above their normal ambient levels to produce a measurable effect on humans, animals, vegetation, or materials." [J. H. Se-infeld, 1998, p.49]. The main source of pollutants are products of combustion. In theory, the combustion of hydrocarbons leads only to the formation of CO₂ and H₂O. An example is given in reaction R1 [Schmidt-Rohr, 2015].

$$C_8H_{18} + 12.5O_2 \longrightarrow 8CO_2 + 9H_2O \tag{R1}$$

In reality however, the necessary mixing relation for R1 to happen is not given so that species such as CO and unburned hydrocarbons are emitted. The process of the combustion of hydrocarbons is used in many fields of energy production. Power plants, whether energy gain by burning of coal, oil, gas or wood, and motor vehicles, all use the same principle. Additionally, combustion leads to formation of NO. As the combustion process results in high temperature, molecular nitrogen is converted to NO at temperatures below $\sim 4500 \text{ K}$ [J.M. Wallace, 2006, p.178].

$$O_2 + M \longleftrightarrow 2 O + M$$
 (R2)

$$2 O + 2 N_2 \iff 2 NO + 2 N$$
 (R3)

$$2 \operatorname{N} + 2 \operatorname{O}_2 \longleftrightarrow 2 \operatorname{NO} + \operatorname{O}_2$$
 (R4)

$$O_2 + N_2 + M \iff 2 \operatorname{NO} + M$$
 (R5)

with M being any molecule. As can be seen in reactions R2-R5, the reaction is in steady state at constant temperatures leading to maximum NO concentrations at ≥ 3500 K. But the hot air parcel leaving the combustion area cools down and the much lower temperature of the ambient air slows the reverse reactions down. This results in NO enriched air being released into the atmosphere. Depending on the type of fuel also other types of pollutants may be released during the combustion process. An example is SO₂, which leads to acid rain and nitrogen-containing fuel is leading to an additional source of NO [J.M. Wallace, 2006, p.178]. Besides the emission rates, the distribution of pollutants by winds, vertical transport and chemical removal, as well as dry and wet deposition, determine the severeness of air pollution locally [J.M. Wallace, 2006, p.176]. Inverse temperature profiles over areas with high emission rates of pollutants can lead to formation of so called "smog" events. Smog is derived from the words smoke and fog and is divided into two types, classical and photochemical smog. The first occurs under cold and moist conditions, where particulate matter (PM) dissolves in fog droplets as does SO₂ reacting to sulfuric acid. Contrary to the classical smog, photochemical smog is found in hot dry areas and is determined by secondary pollutants. It is characterized by a wide variety of chemical species such as ozone, CO, hydrocarbons and NO_x [J.M. Wallace, 2006, p.180]. Ozone in the troposphere is naturally present due to the steady state of the reactions R6-R8:

$$NO_2 + h\nu \longrightarrow NO + O$$
 (R6)

$$O + O_2 + M \longrightarrow O_3 + M$$
 (R7)

$$O_3 + NO \longrightarrow NO_2 + O_2$$
 (R8)

However, these reactions result in a null cycle and background concentrations of ozone are approximately ~ 30 ppbv [J.M. Wallace, 2006, p.180], [J. H. Seinfeld, 1998, p. 292], [Ehhalt et al., 1991]. In reality, ozone mixing ratios can reach up to 500 ppbv. This means that some other processes are present which oxidize NO to NO_x without the consumption of ozone. Here the OH radical becomes important. It initiates a chain reaction reacting with methane, CO and CH₃CHO as shown in R9-R12.

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$
 (R9)

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$$
 (R10)

$$CO + OH + O_2 + M \longrightarrow CO_2 + HO_2 + M$$
 (R11)

$$OH + CH_3CHO \longrightarrow H_2O + CH_3CO$$
 (R12)

The radicals of this process, in this example HO_2 and CH_3O_2 , in turn initiate reactions that convert NO into NO₂ following the reactions R13-R14, respectively.

$$CH_3O_2 + NO \longrightarrow NO_2 + CH_3O$$
 (R13)

$$HO_2 + NO \longrightarrow NO_2 + OH$$
 (R14)

The OH peroxy radical resulting from R14 then starts the cycle over from reaction R9/R11/R12 [Moelders and Kramm, 2014].

Also the product of reaction R12 enters a series of reactions resulting in the formation of CH_3 and CH_3COO_2 . The later substance reacts with NO₂ forming the peroxyacetyl nitrate (PAN), which is another hazardous substance, produced as shown in the reaction R15. The vapor of the colorless explosive liquid PAN is a major eye irritant [J.M. Wallace, 2006].

$$CH_3COO_2 + NO_2 \longrightarrow CH_3COO_2NO_2$$
 (R15)

The chain productions of HO and HO_2 (reactions R9-R14) are terminated by their reaction with NO_2 and HO_2 respectively, as shown in reactions R16-R18

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$
 (R16)

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$
 (R17)

$$CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$$
 (R18)

The subsequent reactions of CH_3OOH are still poorly understood [Moelders and Kramm, 2014, p.209].

2.3 Radicals in the troposphere

Radicals are chemical species having the outer orbital occupied with only one electron. They are therefore highly reactive. Most commonly referred to as free radicals, they originate from reactions where weak bonds break and the molecule remains with an unpaired electron [Pryor, 1966]. In general a quick reaction with other species results in further free radicals as shown in figure 1. Sunlight is a strong factor concerning the abundance of peroxy radicals. Figure 1 summarizes main day time reactions occurring in the troposphere [Clemitshaw, 2010].



Figure 1: Day time tropospheric chemistry of the formation of O₃, H₂O₂, ROOH,RONO₂, RO₂NO₂, HO₂NO₂, HONO, HONO₂, CH₂O and other carbonyls via OH initiated oxidation of VOCs or NMHCs and CO in the presence of NO and NO₂. Source: [Clemitshaw, 2010]

In the following the most important radicals in the atmosphere are described.

2.3.1 Hydroxyl radical

Despite its low abundance (see table 1), especially in winter time [Moelders and Kramm, 2014, p.210], the hydroxyl radical plays an essential role in tropospheric chemistry due to its high reactivity with almost any molecular species [J. H. Seinfeld, 1998], resulting in an extremely short life time (table 1). In the absence of light, NO₃ is a major oxidant in the atmosphere but is quickly photolysed at wavelengths $\lambda < 700$ nm by the reaction

$$NO_3 + h\nu \longrightarrow NO + O_2$$
 (R19)

and at the wavelength $\lambda < 580$ nm by the reaction

$$NO_3 + h\nu \longrightarrow NO_2 + O$$
 (R20)

This gives NO_3 during the day a lifetime of ~ 5 s making the hydroxyl radical the dominant oxidant during the day [J.M. Wallace, 2006, Moelders and Kramm, 2014].

Ozone is photolysed by ultraviolet light (reaction R21). Most $O(^{1}D)$ react via quenching back to ozone as shown in reactions R22 and R23.

$$O_3 + h\nu(\lambda \le 320 \text{ nm}) \longrightarrow O_2 + O(^1D)$$
 (R21)

$$O(^{1}D) + M \longrightarrow O(^{3}P) + M$$
 (R22)

$$O(^{3}P) + O_{2} + M \longrightarrow O_{3} + M$$
(R23)

But about 1% of the exited $O({}^{1}D)$ molecules, react with water molecules according to reaction R24 to form hydroxyl radicals. At wavelength $\geq 320nm$, ozone is also photolysed to form O₂ and O, but the singular oxygen is then a $O({}^{3}P)$, which does not react with H₂O molecules [Ehhalt et al., 1991]. Thus, the net reaction for the production of hydroxyl radicals can be given as showed in R25

$$O(^{1}D) + H_{2}O \longrightarrow 2OH$$
(R24)

$$O_3 + H_2O + h\nu(\lambda \le 320 \text{ nm}) \longrightarrow O_2 + 2 \text{ OH}$$
 (R25)

Over marine areas, the fraction of excited $O(^{1}D)$ atoms generating OH can reach 10% [Monks, 2005]. Although the photolysis of ozone followed by the reaction with water vapour is the main source of OH production, several other photolysis sources of OH exist including the photolysis of HONO, HCHO, H₂O₂, acetone and the reaction of methane with $O(^{1}D)$ [Monks, 2005]. The peak concentrations are reached in the afternoon in relation with ozone photolysis rate $j(O(^{1}D))$. Typically up to 3×10^{6} molecules cm^{-3} are present [J.M. Wallace, 2006, Monks, 2005], which, assuming standard temperature and pressure results in 0.12 pptv as shown in

$$n = \frac{pV}{RT} = \frac{1.01325 \cdot 10^5 Pa \cdot 10^{-6} m}{8.314 J \cdot mol^{-1} \cdot K^{-1} \cdot 298.15 K} = 4.0876 \times 10^{-5} mol$$

$$= 2.4616 \times 10^{19} \text{molecules}$$
(4)

In this equation 1cm^3 was used for V (volume), 1013.25 hPa for p (pressure), R represents the gas constant, n the amount of the substance in mol and T the temperature (in this example the standard temperature of 25°C was used). This means that we have 4.0876×10^{-5} mol or 2.4616×10^{18} molecules per 1 cm³. In this example 3×10^6 of them are OH molecules. 1 pptv means the presence of $\frac{1}{10^{12}}$ OH molecules in the total of 2.4628×10^{18} molecules of air in one $\rm cm^3,$

$$\frac{3 \times 10^6 \text{molecules} \cdot cm^{-3}}{2.4628 \times 10^{19} \text{molecules} \cdot cm^{-3}} = 0.12 \text{pptv}$$

OH is responsible for the removal rate of, amongst others, 85% CO, 90% of CH_4 and 90% of isoprene [Monks, 2005]. Furthermore the OH radical is responsible for the removal of a large number of species like sulfur dioxide, ammonia, trichloroethane and hydrogen sulfide [J.M. Wallace, 2006, p.163]. OH has been therefore called the detergent of the atmosphere [Crutzen and Zimmermann, 1991]. The main fate of the OH radical is the reaction with CO and methane as already described by reactions R9 and R11.

Furthermore the OH radical can also react with NO_2 if the NO_2 concentrations are sufficient, to form HNO_3 which is a terminating process for the NO_x and the HO_x cycle [Monks, 2005]. HNO_3 , (as well as H_2O_2 , a product of the terminating process of HO_2), is soluble and is removed from the atmosphere by wet deposition.

It becomes clear that these reactions lead to hydroperoxy radicals and organic peroxy radicals. Due to its high reactivity and the complex interaction with other species, OH can not be considered isolated. Figure 2 summarizes the OH chemistry in the troposphere.

Due to high irradiation rates and humidity, OH concentrations in the tropics are estimated to be the highest throughout the atmosphere and due to elevated CO concentrations in the northern hemisphere as a result of anthropogenic activities, OH levels are predicted to be 20% lower in the northern hemisphere, as CO consumes OH (see equation R11). [J. H. Seinfeld, 1998] estimates the following concentrations of OH:

Day time (summer)	$5-10 \times 10^6$ molecules $\cdot $ cm ⁻ 3	$\sim 2 - 4 pptv$
Day time (winter)	$1-5 \times 10^6 \text{molecules} \cdot \text{cm}^-3$	$\sim 0.4 - 2pptv$
Night time	$< 2 \times 10^5$ molecules $\cdot $ cm ⁻ 3	< 0.4 pptv

Table 2: Measured and theoretical estimates of [OH] in the troposphere indicate the given ranges. Source: [J. H. Seinfeld, 1998]

2.3.2 Hydroperoxyl radicals

The main source of hydroperoxy radicals (HO_2) is the hydroxyl radical by its reaction with CO (see reaction R11). But also the reaction of ozone with OH is a source of HO_2 as shown in reaction R26.

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (R26)

The chemistry of HO₂ is therefore closely coupled to the OH radical, described above [Monks, 2005]. Due to their concentrations being up to 100 times higher compared to the concentrations of OH [Monks, 2005] and the coupled chemistry, it is useful to summarize HO and HO₂ radicals as HO_x. In conditions of low NO_x concentrations, HO₂ can react with ozone to form OH radicals leading to ozone destruction (reaction R27).



Figure 2: Reaction cycle of OH and HO₂ (collectively designated HO_x). The calculation simulates an airmass observed between 09:08h and 11:30h, 20.05.1983 at Deuselbach. Numbers in boxes are calculated concentrations of *molecules* cm^{-1} ; numbers on arrows are the conversion rates of HO_x (cm⁻³s⁻¹) resulting from reactions with the relevant trace gases. Mixing ratios were calculated assuming standard temperature and pressure. Source: [Ehhalt et al., 1991]

$$HO_2 + O_3 \longrightarrow OH + 2O_2$$
 (R27)

In NO_x rich environments the oxidation of NO to NO_2 also has to be considered [Burkert et al., 2001a]. HO₂ oxidizes NO to NO₂ (reaction R28), without the consumption of ozone. This leads to production of ozone as becomes clear from reaction R6-R8.

$$HO_2 + NO \longrightarrow OH + NO_2$$
 (R28)

One sink, already mentioned in section 2.2, is the self reaction of the hydroperoxyl radical (reaction R17) or with organic peroxy radicals (an example in reaction R18) to form organic hydroperoxides. Furthermore, in marine environments, especially in high latitudes, halogen species are also a sink for HO_2 in their chain reaction (R29-R32) of ozone removal [Burkert et al., 2001a].

$$Br + O_3 \longrightarrow BrO + O_2$$
 (R29)

$$BrO + HO_2 \longrightarrow BrOH + O_2$$
 (R30)

$$BrOH + h\nu \longrightarrow Br + OH$$
 (R31)

$$Net: O_3 + HO_2 \longrightarrow 2O_2 + OH \tag{R32}$$

2.3.3 Organic peroxy radicals and alkoxy radicals

Alkoxy peroxy radicals, denoted as RO_2 , are species generated by the oxidation of hydrocarbons by HO, NO_3 , Cl and O_3 . The hydrocarbons are emitted into the atmosphere from vegetative sources and anthropogenic activity [Heard and Pilling, 2003]. Depending on the environmental regime RO_2 radicals can take part in different reaction types. In high NO_x environments, they predominantly oxidize NO to NO_2 as is shown in the reactions R35-R39.

$$OH + RH \longrightarrow H_2O + R$$
 (R33)

$$R + O_2 + M \longrightarrow RO_2 + M$$
(R34)

$$\mathrm{RO}_2 + \mathrm{NO} \longrightarrow \mathrm{RO} + \mathrm{NO}_2$$
 (R35)

$$RO + O_2 \longrightarrow HO_2 + RCHO$$
 (R36)

$$2(\mathrm{NO}_2 + \mathrm{h}\nu(\lambda < 420nm) \longrightarrow \mathrm{NO} + \mathrm{O}(^{3}\mathrm{P})) \tag{R37}$$

$$2(O(^{3}P) + O_{2} + M \longrightarrow O_{3} + M)$$
(R38)

$$Net : RH + 4O_2 \longrightarrow RCHO + 2O_3 + H_2O$$
(R39)

In NO_x low environments ([NO] ~ 1-10 pptv) other reactions dominate [Khan et al., 2015, Lightfoot et al., 1992]. During night time reactions of RO₂ with NO₃ take place and in maritime condition reactions with BrO or ClO take place (equivalent to reaction R29-R32). [Burkert et al., 2001a] suggest an overall ozone production at $[NO_x] > 40$ pptv and an overall ozone destruction at $[NO_x] < 40$ pptv.

Some typical removal processes are already mentioned in section 2.2 (reactions R16-R18). Further removal processes would be reactions R40-R43 [Kartal et al., 2010].

$$HO + NO + M \longrightarrow HONO + M$$
 (R40)

$$\mathrm{RO}_2^* + \mathrm{surfaces} \longrightarrow \mathrm{non\,radical\,products}$$
 (R41)

$$OH + HO_2 \longrightarrow H_2O + O_2$$
 (R42)

$$HO_2 + NO_2 + M \longrightarrow HO_2NO_2 + M$$
 (R43)

Furthermore, reactions with NO or NO_2 can lead to $RONO_2$ and RO_2NO_2 , respectively, representing another removal reaction for HO_x and NO_x [Heard and Pilling, 2003].

2.4 State of the art of peroxy radical measurement techniques

Multiple approaches have been developed for the measurement of radicals. This work refers to the PeRCA technique, however a number of other techniques, which are frequently used are described here. [Brookes, 2009] provides an overview of present techniques with their individual advantages and disadvantages as well as their accuracies, times of residence and detection limits, shown in table 3. Due to the scope of this work not all methods in the table are mentioned in the following. Table 5 shows a summary of campaigns using the LIF technique and table 4 summarizes all recent campaigns involving the measurements of peroxy radicals, which is also taken from Brookes [2009].

Technique	Time res.	Accuracy	Detections	Dreg	Cana
Technique	(s)	(%)	limit (pptv)	I IOS	Collis
PeRCA $([RO_2^*])$	60	±40	1	relatively low cost, portable, sensitive to HOx and RO ₂ , simple detection method	Non-specific integrated response, varying sensitivity by radical, indirect, interferences, dangerous reagents
PerCIMS/ROxMas $([HO_x], \sum ([R_iO_2])$	15	± 40	0.4	Highly sensitive CIMS detection, fast response, separated HOx and RO ₂	Indirect, varying efficiency of RO_2 conversion suppression
PeRCA-LIF $([RO_2^*])$	60	± 10	2.7-3.6	Sensitive to HOx and RO ₂ , highly sensitive LIF detection	Non-specific integrated response, varying sensitivity by radical, indirect, interferences, dangerous reagents, more complicated detection method
LIF/FAGE $([HO_x])$	30	$\pm 35 (OH), \\ \pm 31 \\ (HO_2)$	0.006 (OH), 0.006-0.04 (HO ₂)	Direct OH, highly sensitive LIF detection, fast response	Inderect HO_2 , more complicated detection method, no RO_2
$\begin{array}{c} \text{ROxLIF} \\ ([HO_2], \sum [R_i O_2]) \end{array}$	60	±20	$0.08(HO_2), \\ 0.28 \\ (\sum [R_1O_2])$	Sensitive to HOx and RO ₂ , highly sensitive LIF detection, fast response, minimized interferences	Non-specific integrated response to RO_2 , indirect HO_2 and $\sum R_iO_2$, varying sensitivity by radical, more complicated detection method
$MIESR ([HOx], \\ \sum_{alkyl} [R_{alkyl}O_2], \\ [CH_3C(O)O_2]]$	1800	± 5	20	Specificity, absolute, calibration standard, quantifiable sampling losses	Long sampling time, low sensitivity, practicality in field, offline, cryogenic sample storage

Table 3: Summary of established radical measurement techniques. Sampling times are typical of ambient measurements, accuracies are typical values, detection limits have been converted to pptv equivalent at STP. Detection limits often determined from signal/noise over a period greater than typical time resolution of published data. Source: [Brookes, 2009]

Year	Campaign	Location	Technique(s)	Platform	References
2003	TORCH I	Writtel, Essex, UK	PeRCA, FAGE	Ground	Emmerson & Carslaw et al. (2007), Lee et al. (2006b), Jacob(2006)
2004	TORCH II	Waybourne, Norfolk, UK	PeRCA , FAGE	Ground	Jacob (2006)
2004	ITOP	Horta Airport, Faial, Azores	PeRCA, FAGE	Aircraft	Parker (2000)
2005		Jungfraujoch, Switzerland	PeRCA	Ground	Parker (2007), Parker et al. (2009)
2005	CHABLIS	Halley, Antarctica	$\begin{array}{c} \text{PeRCA,} \\ \text{FAGE} \end{array}$	Ground	Bloss et al. (2007)
2005	GABRIEL	Suriname, Guyana	FAGE	Aircraft	Lelieveld et al. (2008)
2005	SAPHIR	Juelich, Germany	MIESR, FAGE, ROxLIF, CIMS	Ground	Fuchs (2206) Fuchs et al. (2008)
2005	HOxCOMP	Juelich, Germany	MIESR, FAGE, ROxLIF, CIMS	Ground	Fuchs (2006), Fuchs (2008)
2006	MIRAGE	Veracruz, Mexico	PerCIMS	Aircraft	Shon et al. (2008)
2006	MCMA/ MILAGRO	Mexico City, Mexico	FAGE	Ground	Dusanter et al. (2009)
2006	TEXAQS	Gulf of Mexico	PeRCA	Ship	Sommariva et al. (2009)
2006	INTEX-B/ MILAGRO	Houston, Texas; Honolulu, Hawaii; Anchorage, Alaska	FAGE	Aircraft	Sigh et al. (2009), Mao et al. (2009)
2006	AMMA	Niamey, Niger	PeRCA, FAGE	Aircraft	Brookes (2009)
2006	AMMA	Ouagadougou, Burkina Faso	PeRCA	Aircraft	Andres- Hernandez et al. (2009)
2007	OOMPH	Southern ocean-Indian Ocean	$\begin{array}{c} \text{PeRCA,} \\ \text{FAGE} \end{array}$	Ship	
2007	LAMP	Leicester, UK,	PeRCA	Ground	
2008	OP3 Phase I	Bukit Atur, Borneo, Malyasia	PeRCA, FAGE	Ground	
2008	OP3 Phase II	Bukit Atur, Borneo, Malyasia	PeRCA, FAGE	Ground	
2008	OP3 Phase II	Kota Kinabalu, Borneo, Malyasia	PeRCA, FAGE	Aircraft	
2009	SOLAS	Cape Verde	PeRCA	Ground	

Table 4: Overview of recent campaigns involving the measurements of atmospheric radicals. Source: [Brookes, 2009]

2.4.1 MIESR

So far, the only direct measurement for peroxy radicals is the Matrix Isolation Electron Spin Resonance Spectroscopy (MIESR). It can distinguish between NO, NO₂, HO₂, $CH_3(O)O_2$ and RO₂. This method traps radicals from the ambient air in a polycrystalline D₂O matrix at a temperature of 77 K. Each sampling point takes 30 minutes and

the samples are evaluated in the laboratory by electron spin resonance spectroscopy [Mihelcic et al., 1993]. However, it has limited application possibilities in field studies due to long sampling times and off-line analysis [Fuchs et al., 2009, Mihelcic and Müsgen, 1985]. Nevertheless it has been in used in several campaigns for ground based measurements. In the BERLIOZ campaign in 1998 it was used in a forested area 50 km away from Berlin, Germany, and showed good agreements with the results from the PeRCA instruments. In this study also night time radical formation was observed [Mihelcic et al., 2003]. In 1990 the MIESR technique was used in a ground based study in southern Germany to investigate the night time chemistry of radicals [Mihelcic et al., 1993].

2.4.2 ROxMas/PerCIMS

ROxMas, a technique introduced by Reiner et al. [1997], uses the amplification by chemical conversion of peroxy radicals to gaseous sulfuric acid via a chain reaction with NO and SO₂. The detection is performed via ion molecule reaction mass Spectrometry (IMR-MS). This technique was tested in a ground based study in the urban area of Hamburg and in a forested area near Heidelberg, Germany in the summer of 1995. The results were compared with a model study and agreed with expected values, but no reference measurements with other instruments were done. This technique yields small chain lengths and short reaction times reducing possible losses. The low background concentration of H_2SO_4 and the high sensitivity of the system permits measurements of very low concentrations of peroxy radicals [Reiner et al., 1997]. Hanke et al. [2001] introduce in the year 2001 a technique using the same chemical amplification of peroxy radicals but detecting the H_2SO_4 by chemical ionosation mass spectrometry (CIMS). This technique was used for an airborne study over the Pacific [Cantrell et al., 2003b], where the flights were conducted from 24.02.2001 to 10.04.2001, and over the North American continent [Cantrell et al., 2003a] where flights were performed between February and May 2000.

2.4.3 LIF

Another class of measurement techniques is the laser-induced fluorescence (LIF) method. In was introduced by Hard et al. [1984] and uses the fluorescence of species in the gasphase under low-pressure conditions. This technique is however measuring OH radicals and the HO₂ radicals by the conversion to OH. In order to measure the OH radicals, the air sample is drawn into a low-pressure chamber with a vacuum pump and the OH is detected by its excitation with a laser at a wavelength of 308 nm [Brune et al., 1998]. It was successfully used in field studies in marine areas [Creasey et al., 2003] and the polluted area of New York [Ren et al., 2003] as well as in central Tokyo. In the later HO₂ peak values of 5.7 pptv in summer and 1.1 pptv in winter were measured and also night time mixing ratios of 0.7 pptv and 2.6 pptv in winter and in summer respectively were detected [Kanaya et al., 2007]. Furthermore, this technique was used to measure HO and HO₂ concentration in wintertime in the PUMA campaign in the time between the 16th January and 18.02.2000 4 km outside Birmingham on the campus of the University [Heard et al., 2004]. It has been shown that [OH] correlates with $j(O^1D)$ and winter time studies are therefore important in order to understand the oxidizing capacity of the atmosphere, when UV radiation is low [Heard and Pilling, 2003]. In the study of Heard et al. [2004] it was found that, surprisingly, the [OH] was reduced only by a factor of 2 while the OH production from the photolysis rate of ozone decreased by a factor of 15 in comparison with the summertime values. HO_x mixing ratios were also measured in the lower stratosphere using the LIF technique with chambers at low pressure, often called FAGE, detecting HO₂ concentrations of 15 pptv on board of the NASA DC-8 aircraft during the SUCCESS campaign [Brune et al., 1998]. Another airborne study was performed in Suriname [Martinez et al., 2010].

In most of the studies model calculations were performed parallel to the measurements. As HO_x radicals have a short life time, their concentration is argued to be dependent only on local concentrations of species like O_3 , VOCs and NO_x . This zero-dimensional chemical box models are often used to compare calculated concentrations to measured data. The ratio between the calculated and measured concentrations is also shown in table 5, where radical measurements using the LIF technique and the measured OH and HO_2 concentrations, and NO and NO_x mixing ratios are summarized. One study not mentioned in table 5, focused on the comparison of measurement data and modeled data is presented by Sommariva et al. [2004]. This study took place in Australia in order to study free radical concentrations in extremely unpolluted areas in austral summer between 18th January and 18th February 1999 at the Cape grim Baseline Atmospheric Pollution Station at the north-west tip of Tasmania. The ground based study used the LIF method to measure HO_x concentrations in the clean southern marine boundary layer. For both OH and HO_2 the model overestimated the measured data. A similar approach has been done before, during the LAFRE experiment, which had a sample site 55 km away from downtown Los Angeles during September 1993. The study used the fluorescence assay with gas expansion (FAGE) technique and in the study period of 3 days, good agreement with modeled data was found in the morning and evening time periods, however the model overestimated the radical concentration by 50% during midday [George et al., 1999]. Similar difficulties were detected in the field study of the campaign OKIPEX during July and August 1998 at Oki Island in Japan in marine environment, where the model overestimated HO_2 concentrations, measured with the LIF technique, during the day by a factor of 2 during the midday [Kanaya et al., 2000]. Also in forested area condition of the PROPHET campaign in northern Michigan in summer 1998, modeled data overestimates the OH and HO_2 concentrations as shown by Tan et al. [2001]. Additionally a large number of studies were made measuring OH concentrations with the LIF technique, including two studies of atmospheric chemistry, with a measurement of OH radicals in the antarctic region and compared with modeled data. While in [Jefferson et al., 1998], modeled calculations of

				~				0			
Campaign	Site	Month, Year	[OH] (calc./obs ratio)	[OH2] (calc./obs ratio)	ON	NO_{x}	[OH] (calc./obs ratio)	[OH2] (calc./obs ratio)	NO	NOx	References
LAFRE	Claremont (34° N), USA, 55km downwind from Los	Sep 1993	$6 imes 10^{6}(1.5)$	2×10^8 (~ 1.5)	1-5 ppbv	15-50 ppbv	$0-1 imes 10^6 \ (\sim 1)$	$\begin{array}{c} 0-5\times 10^7\\ (\sim 1) \end{array}$	0-10 ppbv	20-100 ppbv	George et al. [1999]
BERLIOZ	Angeles Pabstthum (52.85° N), Germany, $\sim 50 km$ NW of Berlin	Jul- August 1998	$8 \times 10^{6} (1.33)$	$8 imes 10^8 \ (\sim 1)$	0.1 - 1.5ppbv	1.5 - 7ppbv	$< 3.5 imes 10^5$	$3 imes 10^7$	< 30 pptv	3-4pbbv	Holland et al. [2003], Platt et al. [2002]
PUMA	Birmingham University (52°26'N), USA, $\sim 4 \text{ km from}$ the city center	Jun- Jul 1999	$\begin{array}{c} 3\times10^{6} \\ (0.58) \end{array}$	3×10^{8} (0.56)	2.7 - 4.2 ppbv	9.3 - 18.6 ppbv	NA	NA	NA	NA	Heard et al. [2004], Emmerson et al. [2005]
PUMA	as above	Jan-Feb 200	$2 imes 10^{6}$ (0.50)	3×10^8 (0.49)	4.5 -20.4 ppbv	13.8 -43.4 ppbv	NA	NA	NA	NA	Heards et al. [2004], Emmerson et al. [2005]
SOS	Nashville (36° 11.4' N), USA, $\sim 8 \text{ km}$ northeast of the downtown area	Jun-Jul 1999	$1 imes 10^{7}(0.75)$	$\begin{array}{c} 30 \text{ pptv} \\ (0.64) \end{array}$	0.5 -2 ppbv	NA	$1 imes 10^{6} (0.01 ext{ -0.1})$	4 pptv (0.13 -0.5)	< 0.1 - 10ppbv	NA	Martinez et al [2003]
PMTACS	New York (Queens College), USA, (40°44'15"N), in the Borough of Queens	Jun-Aug 2001	7×10^{6} (0.91)	1×10^8 (0.81)	3-35 ppbv	20-50 ppbv	$7 imes 10^5$ (0.17)	8×10^{6} (0.78)	3-10 ppbv	20-35 ppbv	Ren et al. [2003]
PMTACS	as above	Jan-Feb 2004	1×10^{6} (0.83)	$\begin{array}{c} 0.7 \ \mathrm{pptv} \\ (0.17) \end{array}$	20-50 ppbv	30-50 ppbv	$\begin{array}{c} 0.01 \text{ pptv} \\ (0.18) \end{array}$	0.2 pptv	0-100 ppbv	20-50 ppbv	Ren et al. [2006]
(Rural ennsylvania)	rural Pennsylvania, USA (40°43'N) Marico City Marico	May- Jun 2002	4.6×10^{6} (1.25)	$\begin{array}{c} 13 \text{ pptv} \\ (0.83) \end{array}$	0.5 - 2.5 ppbv	5-9 ppbv	$\overrightarrow{6\times10^5}$ (1.25)	2 pptv (2)	0.5-0.8 ppbv	4-6 ppbv	ren et al. [2005]
MCMA	$\sim 7 \text{km} (19^{\circ}25^{\circ}\text{N})$	Apr 2003	$\begin{array}{c} 7\times10^{6} \\ (1.30) \end{array}$	$\begin{array}{c} 40 \text{ pptv} \\ (1.27) \end{array}$	typically i1 ppbv	20-110 ppbv	0.02-0.05 pptv (0.93)	typically 5 pptv (0.8)	NA	20-35 ppbv	Shorley et al. [2006]
UK TORCH	Writtle College (52°N), England, ~ 40 km NE of 1 mag	Jul-Aug 2003	$2 imes 10^{6} \; (1.2)$	$8 \times 10^7 \ (1.1)$	2.9 ppbv	10.8 ppbv	$4\times10^5~(\sim2)$	$\begin{array}{c} 4 \times 10^7 \\ (\sim 1.3) \end{array}$	NA	10-25 ppbv	Emmerson et al [2007], Lee et al. [2006]
MPACT - IV	London Tokyo (35°39'N, 139°41'E)	Jan- Feb 2004	$\begin{array}{c} 1.5 \times 10^{6} \\ (0.93, 1.23) \end{array}$	1.1 pptv (0.48-0.88)	8.1 ppbv	26.3 ppbv	$1.8 imes 10^5$ (0.32-0.78)	$\begin{array}{c} 0-3 & \mathrm{pptv} \\ (0.44\text{-}1.47) \end{array}$	5.6 ppbv	37.4 ppbv	Kanaya et al. [2007]
IMPACT-L	as above	Jul-Aug 2004	6.3×10^{0} (0.86)	$\begin{array}{c} 9.4 \ \mathrm{pptv} \\ (1.29) \end{array}$	2.6 ppbv	12.0 ppbv	3.7×10^{2} (0.24)	0-8 pptv (0.63)	2.2 ppbv	14.3 ppbv	Kanaya et al. [2007]



OH correlated with observed levels within 30%, the model used in Chen et al. [2001] overestimated OH level at NO < 120 pptv and underestimated OH levels at NO > 380 pptv.

2.4.4 PeRCA

A technique introduced by Cantrell and Stedman [1982] has been broadly used in field studies to measure the sum of peroxy radicals, denoted as $\mathrm{RO}_2^* = [HO_2] + \sum [RO_2]$. This technique is described in section 3 in more detail. Briefly, it converts peroxy radicals into NO_2 and measures the abundance of NO_2 using its chemiluminescence with luminol. Several marine, continental and airborne studies were performed using this technique. Studies in marine environments have been carried out on research vessels. They observed RO_2^* mixing ratios in the range of 40-80 pptv in the case of Burkert et al. [2001a] which reports data of the ALBATROSS campaign performed on board of the Polarstern in the Atlantic Ocean during the years 1996 and 1991 and 30-60 pptv in the case of Andrés-Hernández et al. [2001], which presents data of the AEROSOLS99 campaign, where two voyages from Norfolk, Virginia to Cape Town, South Africa and from Cape Town to Mauritius in the time of January and February 1999 were carried out. Both studies measured night-time signals in the range of 10 pptv. Multiple studies were performed in Mace Head, Ireland, measuring marine conditions. Fleming et al. [2006] presents the data of the NAMBLEX campaign in the summer of 2002, where daily maxima of 10 to 40 pptv were measured. Carslaw et al. [1999] showed good agreement of modeled data with the measured data of the EASE96 field campaign performed during July and August 1996 at the Mace Head Atmospheric Observatory. The ground based measuring campaign DOMINO, which was held from 21st November and 8th December 2008 at the Atmospheric Sounding Station in El Arenosillo in Spain, distinguished between marine and continental air masses from larger cities using both, LIF and PeRCA method to determine the oxidative capacity of the air [Sinha et al., 2012]. RO^{*}₂ were measured and daylight maxima between 10 and 50 pptv were found. Due to anthropogenic organics an intense organic peroxy radical formation took place leading to mixing ratios of up to 60-80 pptv [Andrés-Hernández et al., 2013]. Also a large number of studies using the PeRCA technique were performed in clean and forested areas. In the FIELDVOC'94 campaign, carried out in Tábua, 70 km east of the Atlantic coast, between the 17th of June until the 12th of July 1994, RO_2^* mixing ratios of up to 260 pptv were detected. It has also been found that these mixing ratios correlate with the concentrations of isoprene [Burkert et al., 2001b]. Also high mixing ratios of RO_2^* (up tp 200 pptv) were found in the ROSE campaign, which took place in a forest preserve in west-central Alabama. Here most of the oxidation rate (70%) could be accounted to isoprene [Cantrell et al., 1992]. While most of the studies mentioned above were taken over a shorter period of time, the MLOPEX 2 campaign measured peroxy radicals in time periods distributed over the whole year on Mauna Loa, however the peroxy concentrations did not vary by a lot as did the photolysis rate of ozone. The differences in measured concentration rates were due to overhead scattered clouds reducing the photochemical activity. Overall, $[RO_2^*]$ reached up to 40 pptv and night-time values of up to 10 pptv were observed [Cantrell et al., 1996]. Also a number of airborne measurements of RO_2^* were performed as reported in Andrés-Hernández et al. [2010].

3 Peroxy Radical Chemical Amplification technique

The PeRCA technique uses a chain reaction of RO_2^* , converting NO into NO₂ as described by the reactions R44-R48. This reaction chain naturally takes place in the atmosphere but is strongly favoured by the addition of NO and CO in abundance. The NO₂ can be detected using different measurement techniques. In this study its chemiluminescent reaction with a luminol solution is used (described in more detail in section 3.2). The amount of light released is proportional to the [NO₂] in the sample. The detected amount of NO₂ is then proportional to the amount of the sum of RO₂^{*} in the ambient air and the signal is amplified by the chain length (CL) of the chain reaction converting RO₂^{*} in NO₂. In the presence of NO and CO, RO₂^{*} reacts as described by the chain reactions R44-R48.

$$RCHO_2 + NO \longrightarrow NO_2 + RCHO$$
 (R44)

$$RCHO + O_2 \longrightarrow HO_2 + RCO$$
 (R45)

$$HO_2 + NO \longrightarrow NO_2 + HO$$
 (R46)

$$HO + CO + M \longrightarrow COOH + M$$
 (R47)

$$HOOC + O_2 \longrightarrow HO_2 + CO_2$$
 (R48)

The chain length (CL) is defined as

$$CL = \frac{\Delta[NO_2]}{[RO_2^*]} \tag{5}$$

It describes how many NO₂ molecules are produced for each molecule of RO_2^* and depends on the propagation and termination reactions. The chain reaction is terminated by the reactions R40-R43 and the reactions R16-R18, already described in section 2.3, section 2.2, and furthermore reaction R49 [Kartal et al., 2010].

$$OH + NO_2 + M \longrightarrow HONO_2 + M$$
 (R49)

At higher $[NO_x]$ reaction R49 becomes important [Lightfoot et al., 1992]. The main sink is considered to be the formation of HONO (reaction R40) [Cantrell et al., 1993]. Further sinks would be wall reactions. Negligible reactions are OH + HO₂ and the radical reaction with ozone. The OH + HO₂ reaction is relatively slow and the ozone is consumed by the NO. Because most of the odd hydrogen radicals are HO_2 , in this measurement the concentration of HO_2 is approximated as the sum of HO and HO_2 .

In order to measure the amount of the present peroxy radicals in the ambient air, NO is added to the sampled air mass. Additionally, CO is added, to convert the OH, the product from reaction R46, to HO_2 , which can start the chain reaction R47-R48 over. This leads to an amplification of the signal as multiple NO_2 molecules are produced for each peroxy radical. CO is added alternating with N_2 in front of the reactor. While CO is added in the front of the reactor (close to the sample inlet), which is from now on called the amplification mode, N_2 is added in the back of the reactor and vice versa (from here on called background mode). N_2 is not reacting with OH and therefore prevents further amplification. It is added in order to minimize pressure changes in the reactor. Due to the high reactivity of the peroxy radicals, it is assumed that in the background mode all radicals have been terminated and no amplification takes place when the flow reaches the end of the reactor where the CO is added. During the time period when N_2 is added, the background signal of NO₂ is measured ($[NO_2]_{BG}$ in equation 6). This is not only the signal of the ambient NO_2 ([NO₂]_{ambient} in equation 6), but also of other species which in the presence of NO are converted into $[NO_2]_{other}$, as is ozone or are thermally decomposed species in the reactor such as PAN (see equation R15). In order to differentiate between this background concentration of NO₂ ($[NO_2]_{BG}$) from the signal from the RO^{*}₂, this background has to be subtracted from the NO_2 concentration in the amplification mode and calculate the ΔNO_2 (equation 6 and 7).

$$[NO_2]_{BG} = ([NO_2]_{ambient} + [NO_2]_{other}) + CL \cdot [RO_2^*]$$

$$\tag{6}$$

$$\Delta[NO_2] := [NO_2] - [NO_2]_{meas} = CL \cdot [RO_2^*]$$

$$\tag{7}$$

The ΔNO_2 between the time period of amplification and the time period of background is interpreted as the radical signal multiplied with the chain length (see equation 5), where OH and $\sum RO$ are neglected [Horstjann et al., 2014]. As $\sum (RO_2) \gg \sum (RO)$, the calibrated chain length is representative for $\sum (RO_2)$ [Burkert et al., 2001b]. The possible chain length of the reactions R44-R45 was approximated by Cantrell and Stedman [1982] to be between 100 and 3000. However, in that paper the loss reactions were underestimated and CL's reported in laboratory and field studies range approximately between 40 and 1000 [Hastie et al., 1991]. Green et al. [2006] mentions, that CLs between 150 and 300 can be achieved easily. The chain length is therefore different for each setup and has to be calibrated individually for each reactor [Burkert et al., 2001a, Horstjann et al., 2014]. The CL calibration is described in section 5.1.4.

The NO_2 produced in the reactor is subsequently transported to a detector which, in this study, is based on the chemiluminescence of a luminol solution. The amount of light produced by the chemiluminescence is proportional to the NO₂ in the sample [Green et al., 2006]. It was first suggested by Hastie et al. [1991], that larger RO_2^* react more slowly with NO and the loss to $RONO_2$ is significant. Thus it was assumed that the PeRCA system is more sensible to lighter RO_2^* . However, it was shown, that the rate coefficient of the reaction of RO_2^* with NO does not decrease with increasing carbon mass and the chain length of the amplification reaction is similar for larger RO_2^* and HO_2 [Eberhard and Howard, 1997].

3.1 Effect of humidity on the amplification chain length

The CL of the reactions R44-R48 describes the number of times a peroxy radical cycles through the reactions before it is being lost and the concentration of RO_2^* can be determined through the division of the $[NO_2]$ by the CL (equation 5) as it is described in section 3. Therefore it is a crucial parameter for the performance of the instrument. As the humidity of the ambient air has an important impact on the CL, careful determination of the influence of the humidity on the chain length has to be done. Mihele and Hastie [1998], Mihele et al. [1999] and Reichert et al. [2003] performed a number of tests in order to study this effect showing that the CL decreases nonlinearly with increasing relative humidity (RH). Mihele et al. [1999] found that the rate of wall loss for the HO_2 radicals was twice the rate for the organic radicals. In the study of Mihele and Hastie [1998] the CL showed a decrease of 50% at 40% humidity compared to the CL at dry conditions. Mihele and Hastie [1998] suggests three mechanisms which could be responsible for the decrease: an increased radical loss to the walls of the reactor, an increase in the rate of the reaction R40 or a decrease in the chain reaction of reactions R44-R48. In order to test the influence of wall loss reactions at increased humidity, the change in chain length was tested while the reactor wall was heated to 60°C reducing the amount of adsorbed water on the walls of the reactor. The results were compared to outcomes under same conditions but without the reactor walls being heated. Figure 3 displays the results of this test.

The data shows much less impact of humidity when the walls were heated and therefore less water was adsorbed. To identify the impact of an increase of the reaction rate of reaction R40, the NO concentration was set to 12 ppmv which leads to a removal of 92% of radicals by reaction R40 (27% for 2 ppmv). This change also leads to a reduction in the sensitivity of the CL in presence of water. The experiment was also performed with reactors having a different surface to volume ratio and resulted in similar results. Mihele and Hastie [1998] consider the water vapor-dependent wall loss rate less significant due to the large diameter of the reactor used in the study. The study suggests that as $\sum RO_2$ are typically not very hydrophilic, only HO₂ is responsible for reactions with water forming H₂O clusters. Further, it suggests that the amount of this is expected to increase with relative humidity but that these clusters are less stable at higher temperatures. As a



Figure 3: Change in the chain length of the radical amplifier with absolute humidity in the reactor for identical gas composition but for different reactor wall temperatures. Source [Mihele and Hastie, 1998]

result of this study, Mihele and Hastie [1998] give multiple suggestions to exclude errors in the CL due to humidity of ambient air. The first is to heat the walls of the reactor, which however would lead to an increase in the rate of radical production of species such as PAN. The second suggestion is to take humidity data parallel to radical measurements and perform CL calibrations in dependence of humidity. Further measures could be the operation at low pressure conditions. For this solution also all other rates of the reactions involved decrease and would require a new setup. The use of a humidity filter is excluded due to the reactivity of the radicals.

The CL dependence on humidity was also studied at the IUP and similar but not identical results were found. The study of Reichert et al. [2003] determined the influence of the humidity on the CL in a glass reactor, with an inlet of 4 mm internal diameter which expands in a cylinder of 2 cm diameter, which was also used during the summer campaign 2016. The study excludes the influence of wall losses as the only explanation for the decrease observed in the CL. The results are shown in figure 4 and are compared to the results of Mihele and Hastie [1998] and Stöbener [1999].

It was tested whether the CL sensitivity is dependent on absolute H_2O concentration or on the relative humidity. Therefore tests at different temperatures and humidities were performed. At the conditions of this study (278 K < T < 330K) the CL seems to depend on relative humidity rather than on absolute water content [Reichert et al., 2003]. The study uses a three dimensional physiochemical model to simulate possible water dependent processes involved in the amplification. As a result three processes were identified which can explain the observed CL variations connected to relative humidity (reactions R50-R52).



Figure 4: Ratio of CL_{wet}/CL_{dry} obtained at 20°C for the setup used by the IUP setup. The data are plotted versus the RH in the reactor. For comparison the results reported by Mihele and Hastie [1998] and the data obtained by Stöbener [1999] at the IUP are added

$$\rm CO + HO_2 \xrightarrow{nH_2O} \rm CO_2 + OH$$
 (R50)

$$NO + HO_2 \xrightarrow{nH_2O}$$
 non radical products (R51)

$$OH + CO \xrightarrow{nH_2O}$$
 non radical products (R52)

Reichert et al. [2003] also suggests a gas reaction involving the formation of a water complex with two H₂O molecules. The reaction of HO₂ with water to HO₂ \cdot n(H₂O) was proposed by Cox and Burrows [1979]. HO₂ \cdot n(H₂O) may then react with NO to a product other than NO₂ as shown in reaction R53 reducing the CL.

$$HO_2 \cdot n(H_2O) + NO + M \longrightarrow HNO_3 + nH_2O + M$$
 (R53)

3.2 Detection of NO_2 by chemiluminescence

Luminol (5-amino-2,3-dihydro-1,4-phthalazine dione) is known to emit chemiluminescence while reacting with oxidizing species. Maeda et al. [1980] describes a method to detect NO₂ by its reaction with luminol. The study found the maximum chemiluminescence intensity for luminol concentrations between 3×10^{-4} and 3×10^{-3} M (equals 0.053148 g/l to 0.53148 g/l). Furthermore an alkaline environment is needed to achieve light emission. To achieve this, potassium hydroxide (KOH) is added to the solution. A minimum of

other gas	concentration in ppmv	relative signal response (*)
none	-	1.00
СО	1.1×10^5	1.00
1,2-dichloroethylene	$1.0 imes 10^4$	1.01
propylene	1.1×10^{5}	1.00
ozone	0.08	1.53
ozone	0.3	2.70
SO_2	16.6	1.25
CO_2	$4.0 imes 10^3$	0.68
CO_2	1.2×10^{4}	0.27

Table 6: Interferences from other gases at NO₂ mixing ratio of 3.8 ppmv, a luminol concentration of 1×10^{-3} M and a KOH concentration of 5×10^{-2} M. *: Signal for NO₂ + other gas/signal for NO₂. Source: [Maeda et al., 1980]

 10^{-5} M (0.0028 g/l) of potassium hydroxide is needed to detect chemiluminescence. The chemiluminescence is increases proportionally to KOH concentration until a maximum concentration of 1.0 M (56.11 g/l). But at KOH concentrations higher than 0.1 M (5.6 g/l) oxygen reacts with luminol leading to interferences of the NO₂ determination. The reaction of luminol with NO₂ is shown in figure 5.



Figure 5: Basic chemiluminescence reaction between luminol and NO₂. Source: [Wang et al., 2016]

Maeda et al. [1980] performed a number of experiments to determine the interferences by other gases, especially pollutants typical for polluted air masses. Table 6 lists the signal response for 3.8 ppmv NO₂ in the presence of other pollutants. It shows that ozone and sulfur dioxide interfere positively and carbon dioxide negatively with the initial signal. Furthermore, it shows that the change in the interference is not linear with the mixing ratio of the species.

The interference of SO_2 could be solved by the addition of 0.01 M (1.26043 g/L) of Na₂SO₄ simultaneously increasing the signal of NO₂. At a concentration of 0.1 M (12.6043 g/L) Na₂SO₄ the interference from ozone could be minimized. The negative interference of CO₂ with the signal could be removed by increased KOH concentrations. At a concentration of 1.0 M (56.11g/L) of KOH in the solution the CO₂ interference could be removed independently of the concentration of the CO₂ in the ambient air. Based on this study, Maeda et al. [1980] gives a suggestion for the composition of the luminol solution (see table 7).

It has to be stated that the detector response is non-linear below a few ppbv of NO_2 . In order to assure that all measurements are in the linear response region of the instrument,

luminol concentration	$1 \times 10^{-3} {\rm M}$	$0.17716 { m g/L}$
[KOH] if sample contains CO ₂	$5 \times 10^{-2} \mathrm{M}$	$2.8055~{\rm g/L}$
[KOH]	1.0 M	$56.11 { m g/L}$
[Na ₂ SO ₃]	$1 \times 10^{-2} \mathrm{M}$	1.26043 g/L
$\begin{bmatrix} [Na_2SO_3] & \text{for the} \\ \text{determination of} \\ NO_2 & \text{in the} \\ \text{presence of ozone} \end{bmatrix}$	$1 \times 10^{-1} \mathrm{M}$	$12.6043~{ m g/L}$

Table 7: Luminol solution as suggested by Maeda et al. [1980]. Source: [Maeda et al., 1980]

a constant offset of 20 ppbv NO_2 is usually added [Hastie et al., 1991, Kelly et al., 1990]. In the case of the present study 40 ppbv NO_2 were added to assure the linear response.

4 Summer campaign 2016 in Bremen

The summer campaign of 2016 at the University of Bremen aimed to investigate the trace gas chemistry of the site, which is considered as semi-urban. A continuous data set of NO_x , CO, O_3 , RO_2^* , the photolysis rate of NO_2 ($j(NO_2)$), and meteorological data: wind speed and direction, relative humidity, temperature and pressure. The campaign was started on the 27th of July 2016 and ended on the 26th of September 2016. The sampling area was chosen to be the roof of the Institute of Environmental Physics (IUP) of the University, right above the 5th floor of the institute. The coordinates are 53°06'13.8"N, 8°50'58.6"E. In figure 6 the sample area is displayed, with the location of the institute pointed out. The semi-urban character of the site is clearly recognizable. The north and east of the site are dominated by farm fields, while the south and west of the site are dominated by urban structures including a harbor. Additionally, the waste-fed heating plant of the city of Bremen is located in westward direction from the sample site in a distance of 2.68 km. This heating plant could have a major influence on the measurements. It is also marked in figure 6. Figure 7 shows the close up view on the IUP, where the red circle marks the position of the experimental setup.



Figure 6: Satellite picture of the sample site surroundings. The sample site and the waste-fed energy plant are marked. The distance between is marked with the red line and measures 2.68 km. To the north mostly fields are present. The south is dominated by urban structures. Source: Google Earth



Figure 7: Satellite image of the sample area. Source: Google maps

4.1 Experimental setup

As mentioned in section 3, the PeRCA method was used for the measurement of the RO_2^* . In the campaign a dual-channel system was applied, hence two systems were measuring simultaneously, each 60 s in the amplification mode and 60 s in background mode, alternating. Therefore, two reactors were sucking air by a shared vacuum pump. To each reactor the addition gases, NO, CO and N₂, were added individually. Each of the gas flows for each reactor was controlled by a flow controller (FC) of the company "Bronkhorst" which, in turn, was controlled by the operating computer. After the sample passes the reactor, it flows through the detector where NO₂ reacts in a chemiluminescence reaction with the luminol, emitting light, which is measured by the detector. The build up of the detector shown in figure 8.

The photodiode is covered with a "Whatman" glass fiber filter paper through which the luminol solution and the sample air are flowing as shown in figure 8. As the two sample lines each lead to an individual detector, two individual experimental setups, called system 1 and system 2, exist. If only one system is used, the background NO_2 signal during the



Figure 8: Left: Inner view of the luminol detector schematically. The reaction zone and the photodiode are separated by quartz glass. Source: [Kartal et al., 2010]. Right: Photo of the inner view of the detector used

amplification mode has to be interpolated using the measurements taken before and after. The advantage of the dual channel principle is that the background signal of NO_2 does not have to be interpolated. While one system is in amplification mode, the other is in background mode, thus continuous background and amplification measurements can be taken. This results in decreasing uncertainties of the measurement. Furthermore, as both systems are completely independent, with individual gas lines and flow controllers, separated detectors and individual control, it is possible for each system to be calibrated or maintained individually while the other system is still operating. However, the two systems share the same power source and the pump for the luminol solution flowing through the detector, as well as the vacuum pump. A rough sketch of the experimental setup is shown in figure 9.

The two reactors are installed in a height of 3.5 m above the roof with a horizontal distance of 0.3 m in between. Each reactor has an individual supply of CO, N₂ and NO. Three-way magnetic valves regulate whether the signal is in amplification or background mode by adding CO in the front and N₂ in the back of the reactor for the signal mode and vice versa for the background mode (see section 3). A picture of one reactor is displayed in figure 10. The reactor is located inside a hangar which keeps the reactor fixing in the tube that again is holding the reactor in place as seen in figure 11. The reactor is covered with a heating foil (orange cover of the glass reactor also seen in figure 10) and a PT100 temperature sensor is installed in the reactor in order to control the temperature.

The luminol detectors are located on the ground, covered by a canvas in order to prevent direct sunlight exposure. Following the reaction in the reactor the sample is transferred to the detector in a 4 m 1/4" Teflon tube, which is protected from the sunlight by a black coat (in order to prevent photolysis of NO₂). Shortly ahead of the detector (approximately 40 cm) additional NO₂ (45 ppbv) is added to assure that the linear re-



Figure 9: Rough sketch of the experimental setup used in the summer campaign 2016. The yellow arrows indicate the luminol flow, the red arrows the sample flow and the green arrows represent the voltage output from the detectors. Not considered in the figure are the flow controllers, controlled by the computer and the flow of the gases added at the inlet of the reactors, as well as the power supply.

sponse of the chemiluminescence of NO_2 and the luminol solution is achieved (see section 3.2). The setup is shown in figure 11. The sample lines (number 3) precede the sample air from the reactors (number 1+2) to the detectors (number 5), which are covered by the canvas. In the box (number 6), the system controlling units are located (number 4). This includes the flow controllers for CO, NO, N₂, and the exhaust, as well as the power supply for the three-way magnet valves, controlling the amplification and background mode, and also the temperature regulation, the data acquisition (DAQ) cards for the communication



Figure 10: Picture taken inside the laboratory of one reactor used in the campaign. 1: glass reactor; 2: reactor inlet; 3: addition point of NO; 4: front of the reactor, in the amplification mode, addition point of CO, in the background mode addition point of N_2 ; 5: heating foil covering the glass reactor; 6: NO_2 scrubber; 7: PT100 temperature sensor inserted in the reactor; 8: back end of the reactor, in the amplification mode, addition point of N_2 , in the background mode addition point of CO; 9: three-way magnet valve, for alternate addition of CO and N2 to the front. The second magnet valve can not be seen in this picture

of the computer and the devices and the computer itself. The flow controllers for the NO_2 are located in the box underneath the plane, in which the luminol detectors are placed. Next to the reactors the temperature and humidity sensor are mounted (number 7). Above, the wind speed and wind direction devices are attached (not seen in this picture). The total flow rate in the sample lines is 1 l/min in both systems, out of which 0.2% are NO, 9% CO and 9% N₂. The NO₂ offset, added later in the line, was usually set to 45 ppbv.

4.2 NO₂ calibration

During the measurement campaign the NO_2 detectors were regularly calibrated over the day in order to evaluate variations in the sensitivity associated to significant changes in ambient temperature. Calibrations usually started between 05:00 and 08:00 UTC.

In this campaign 0.886 g of luminol, 22.44 g KOH, 63.02 g Na₂SO₃ and 30 ml isopropanol were used for a 10 l solution. This composition was empirically optimized over multiple years by the TROLAS group of the University of Bremen. The emitted light is detected by a photo diode which gives an output voltage proportional to the light from the chemiluminescence and therefore proportional to the NO₂ concentration in the sample. The NO₂ calibration determines how the signal of the detector responds to a given concentration of NO₂.

Due to technical reasons, synthetic air (SA) could not be added to the reactors easily for the NO₂ calibrations, which forced to perform the NO₂ calibrations on top of the background signal leading to a low stability of the calibration and hence to a higher uncertainty in the NO₂ calibration results. To improve the quality of the calibration, a calibration sequence was chosen which had a background measurement in-between calibration steps.



Figure 11: Experimental setup of the summer campaign 2016. 1 and 2: reactors of system 1 and 2 respectively in a protective tube; 3: sample line from the reactor to the detector (1/4") teflon tube, covered by a black coat), gas lines from the flow controllers to the reactor (1/8") teflon tubes); 4: control units: flow controllers, temperature control unit, power supply for the magnetic valves, operating computer, DAQ cards; 5: box with luminol detector, including luminol source and waste, covered by a plane; 6: Box, protecting all units mentioned in 4 and the vacuum pump

The calibration steps were 45 ppbv, 55 ppbv, 45 ppbv, 65 ppbv and 45 ppbv. An example of a typical NO_2 calibration signal during the campaign can be seen in figure 12.

5 Analysis Methods

Throughout the campaign, it was realized that the PeRCA signal was not performing as expected. The two systems did not seem to be independent and produced high noise. Although all possible sources of this behaviour were checked during the campaign no reason for was found. To observe this behaviour one of the reactors (alternating) was connected to SA during specific time periods with the purpose to isolate the variations in the signal due to a malfunction from real signals, and to find the source. However, no source could be identified. During the preparation for the laboratory work after the campaign, it was discovered that the grounding for one of the detectors was loose, which resulted in the


Figure 12: NO₂ calibration in the morning of the 19.09.2016. The upper graph shows the calibration of system 1, the lower graph the calibration of system 2

dependency of the detector signals on each other, as the detectors were following each other. This problem could then be fixed on the 29.11.2016 and the characterization could be performed without interference. The consequences for the campaign data are presented in section 5.2.3.

5.1 System characterization in the Laboratory

5.1.1 FC calibration

After the end of the summer measurements, the system was brought to the laboratory to be characterized during the period from the 28.11.2016 to the 23.12.2016. The parameter of interest was the CL and its dependency on RH in the system.

The Gilibrator was used to calibrate the FC. It shows the real flow in the FC using N_2 . Pressure and temperature were measured in laboratory during the calibration to bring the flows to standard conditions. The flows measured by the Gilibrator had to be normalized to standard conditions in order to get the true correction slope. The correction slopes were also forced to zero as it was tested that at the set point zero no flow is coming through the FCs. For the analysis of the data the relation of the set values to the real values and the relation of the read values to the real flow was needed.

5.1.2 NO₂ calibration

During the whole lab work one of the reactors was connected to the source while the other was placed alongside it as shown in figure 13. For the NO₂ calibrations, both systems were sampling SA. The system was operating in background mode during the calibrations. A known amount of NO₂ was added to the system on top of the NO₂ offset of 45ppbv. The sensitivity of the detector to the light emitted by the photochemical reaction of NO_2 and the luminol could be measured in voltage. The mixing ratio of NO_2 in the system can be calculated from equation 8. The NO_2 signal is read in [V] and converted to [ml].



Figure 13: Reactor setup in the laboratory. Left: Reactor (2) connected to the source (1) with the opened light chamber (3) to the UV lamp (4). Right: Placement of both reactors in the laboratory.

$$[NO_2] = \frac{NO_2 \cdot FC_{NO_2} \cdot B}{Ex \cdot FC_{ex}}$$
(8)

With NO₂ being the [NO₂] in [ml], Ex the exhaust flow in [ml], FC_{NO_2} the correction slope of the FC of NO₂, FC_{ex} the correction slope of the FC for the exhaust flow and the real concentration of the NO₂ gas bottle B.

$$\Delta[\mathrm{NO}_2] = \left|\frac{B}{Ex \cdot FC_{ex}}\right| \cdot x_1 + \left|\frac{\mathrm{NO}_2 \cdot FC_{NO_2}}{Ex \cdot FC_{ex}}\right| \cdot x_2 + \left|\frac{\mathrm{NO}_2 \cdot FC_{NO_2} \cdot B}{(Ex \cdot FC_{ex})^2}\right| \cdot x_3 \tag{9}$$

Equation 9 shows the calculation of the error of $[NO_2]$, where x_1 denotes the error of the correction slope of the NO₂, FC, x_2 the error of the true values of the NO₂ bottle mixing ratio and x_3 the error of the slope for the exhaust correction slope.

The corrected NO₂ mixing ratio is plotted against the corresponding signal measured by the detectors in voltage. The first 15 points were discarded, as approximately 15 s are needed for the flow to reach the detector and stabilize. Periods corresponding to instrumental failure were also omitted. The slope a, considering the error of each individual [NO₂] as σ_i , was then calculated as

$$a = \frac{S_{xx} \cdot S_y - S_x \cdot S_{xy}}{\varpi} \tag{10}$$

$$S \equiv \sum \frac{1}{\sigma_i^2} \tag{11}$$

$$S_x \equiv \sum \frac{x_i}{\sigma_i^2} \tag{12}$$

$$S_y \equiv \sum \frac{y_i}{\sigma_i^2} \tag{13}$$

$$S_{xx} \equiv \sum \frac{(x_i)^2}{\sigma_i^2} \tag{14}$$

$$S_{xy} \equiv \sum \frac{x_i \cdot y_i}{\sigma_i^2} \tag{15}$$

$$\varpi \equiv S \cdot S_{xx} - (S_x)^2 \tag{16}$$

The intercept of the regression line is not of interest in this analysis. The error of the slope was calculated as

$$\sigma(a) = \sqrt{\frac{S}{\varpi}} \tag{17}$$

Additionally, for each NO₂ calibration the moisture in the system, the amount of minutes per step and the coefficient of determination, R^2 per point were noted. The R^2 was calculated as

$$R^{2} = 1 - \frac{\sum (y_{i} - \hat{y}_{i})^{2}}{\sum (y_{i} - \bar{y})^{2}}$$
(18)

Where \bar{y} is the average of the regression, \hat{y}_i is the individual point approximated by the regression and y_i is the individual point. This coefficient allows to estimate the discrepancy between the data and the estimation. In this case it shows the stability of the calibration.

The NO_2 calibration slopes were analysed for their dependency on RH. The slope varies over time depending on multiple factors, hence the dependency of the slope results on RH was considered individually for each day.

5.1.3 O_3 calibration

In order to determine the mixing ratio of ozone produced during the HO₂ calibration by the photolysis of oxygen, the ozone calibration is done previous to the HO₂ calibration (equation R56 and R57 in section 5.1.4). The reactor used is connected to the source. Inside the source a SA flow is going through a chamber in which a mercury lamp is producing UV light. The chamber is flushed with N₂. In the chamber reactions R56 and R57 take place. As the air flow enters the reactor, all O₃ is converted to NO₂ as described in reaction R8. Both systems were calibrated 8 times. At a lower flow the residence time of the SA in the UV lamp chamber increases, hence more O₂ can be converted to O₃ as the reaction rate is constant. Different SA flow rates and the residence times in the light chamber were tested for their influence on the [O₃] produced. For the calibration, the UV lamp chamber alternated between an opened state for 8 minutes and a closed state for 5 minutes. While the chamber was closed no photolysis took place. As the chamber was opened light induced the reactions R56 and R57 followed by reaction R8 in the reactor. The difference in signal height of the detector was divided by the NO_2 calibration slope to calculate the present $[O_3]$. For all analysis methods the first 180 points of each step were removed, as the PMT (photo multiplier) detector of the lamp needs 3 minutes to stabilize after the chamber was opened. The stabilization time of 3 minutes was determined empirically. For this decision, different attempts were made to get a signal and background line which is not influenced by the switching. Figure 14 shows how the stability of the signal and the background line depend on the amount of points removed. Only after cutting 180 points is each of the lines (PMT signal plotted in black) straight.

For the analysis of the O₃ calibration different methods were used. For the first method (1), the signal (chamber open) and the background (chamber closed) was interpolated over the entire calibration time, excluding the first 180 points, and calculating the difference between each signal and background point. Out this set of differences the average was calculated. For the second method (2), an average of all values (excluding the first 180 data points) for each signal or background step was taken, the difference identified, and an average of these values was found. In all calibrations performed, the signal is measured first, hence when applying this method, the average of a background step is always subtracted from the average of the previous signal. In the case of an unstable baseline, this method is not reliable, as it would overestimate the wanted delta between signal and background in case of a decreasing background and underestimate it in case of an increasing background. The third method (3) used the difference between the average of the background signal of each step and as the background signal the averaged value from the interpolation of the background before and after the individual signal step. For the fourth method (4) this procedure was done vice versa. The error of each result was calculated from the standard deviation of the $[O_3]$ gotten from the individual method and the standard deviation of the voltage of the lamp measured by the PMT. The error of the final result given in $[O_3]/V$ is calculated as

$$\left(\frac{\delta z}{z}\right)^2 = \left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2 \tag{19}$$

where z is the final result, δz the final error, x the O₃ concentration and δx the standard deviation and y the voltage measured by the PMT with δy being the standard deviation of the PMT signal. The four different methods and their errors were compared in the analysis. Further results were calculated using the first method as it has far more individual [O₃]/V points. The first method is more exact, despite having a higher standard deviation due to a higher amount of points.



Figure 14: Signal and background voltages of the PMT are given ind black and red. The signal from the NO_2 detector is given in green, the background in blue. The data set from the 01.12.2016 is taken as an example. In the first plot 0 data points after each switching are removed. In the second plot 15 data points are removed. in the third plot 45, in the fourth 120 and in the fifth 180 data points are removed and the missing data interpolated linearly. As only in the last plot no influence of the switching is seen, for the analysis of the O_3 calibration 180 data points (the first 3 minutes) were removed

Each fit is performed with the weight w which is calculated as

$$w = \frac{1}{\sigma^2} \tag{20}$$

LabVIEW finds the amplitude, power and offset by minimizing the residue according to

$$\frac{1}{N}\sum w_i(f_i - y_i)^2 \tag{21}$$

Here N is the length of the data set, w_i is the i^{th} element of the weight, f_i is the i^{th} element of the best power fit and y_i is the i^{th} element of the $[O_3]/V$ value.

5.1.4 HO₂ calibration

The CL calibration determines the amount of NO_2 molecules produced by one peroxy radical molecule. It depends on the propagation and termination reactions described in section 2.4.4. The CL calibration of each reactor used in the summer campaign was performed by the production of a determine mixing ratio of radicals from the UV photolysis of water in the presence of oxygen at a wavelength of 185 nm as described by Schultz et al. [1995]. The UV light produces equal amounts of HO₂ and OH as shown in reaction R54 and R55.

$$H_2O + h\nu (\lambda = 185 \text{ nm}) \longrightarrow OH + H$$
 (R54)

$$H + O_2 + M \longrightarrow HO_2 + M$$
 (R55)

When CO is added, the OH radicals are converted into HO_2 (see reaction R47 and R48) hence for every H_2O molecule which undergoes the photolysis, two HO_2 molecules are produced. Oxygen also has a photolysis reaction at the same wavelength. Reactions R56 and R57 show the production of ozone by the photolysis of oxygen.

$$O_2 + h\nu \longrightarrow 2 O(^{3}P)$$
 (R56)

$$O(^{3}P) + O_{2} + M \longrightarrow O_{3} + M$$
(R57)

Therefore, for each O_2 molecule two O_3 molecules are formed. The production rates of HO_2 and O_3 can be described by

$$P_{HO_2} = \sigma_{H_2O}^{185} \cdot q_1^{185} \cdot \theta^{185} \cdot [\text{H}_2\text{O}]$$
(22)

$$P_{O_3} = \sigma_{O_2}^{185} \cdot q_4^{185} \theta^{185} \cdot [O_2] \tag{23}$$

where θ represents the photon flux, σ_M^{185} is the absorption cross section and q_i^{185} is the overall quantum yields at 185 nm. For each H₂O molecule two HO₂ molecules are produced and for each O₂ molecule two O₃ molecules are produced, the quantum yield equals 2. Neglecting potential losses of H₂O and O₃ the concentration of HO₂ can be described by equation 24 where q_M^{185} cancels out.

$$[HO_2] = \frac{\int \sigma_{H_2O}^{185} \cdot q_1^{185} \cdot \theta^{185} \cdot [H_2O]}{\int \sigma_{O_2}^{185} \cdot q_4^{185} \cdot \theta^{185} \cdot [O_2]} \cdot [O_3] = \frac{\sigma_{H_2O}^{185} \cdot [H_2O]}{\sigma_{O_2}^{185} \cdot [O_2]} \cdot [O_3]$$
(24)

The absorption cross section of water is known and the effective absorption cross section of O_2 is determined in the laboratory. The only unknown remains the ozone concentration which is determined in the ozone calibration as described in section 5.1.3. The known concentration of HO_2 is then converted inside the reactor into NO_2 by the process described in section 2.4.4, where NO is added to the sample flow to convert the radicals into NO_2 molecules. The amount of detected NO_2 and the known amount of HO_2 is used to determine the chain length for the specific setup (see section 3, equation 5). As in the setup of the campaign, two reactors are used. Each reactor has to be calibrated individually before and after the campaign, since the CL calibration cannot be easily carried out during fieldwork.

5.2 Data analysis

5.2.1 NO_2 calibration used

During the campaign multiple NO₂ calibrations were performed daily. However, the NO₂ calibration slope varies strongly with multiple factors such as filter age and temperature. For practical reasons, it was not possible to perform NO₂ calibrations at all times. To get an estimation of the actual NO₂ slope, the measured results were interpolated for each second of the campaign. Figure 15 shows the result of this interpolation over the entire campaign period. The NO₂ calibration used for the analysis of the RO₂^{*} data, is plotted with the running mean of the ambient temperature using of 1 hour and 1 day. Although the correlation coefficient of the temperature running mean and the NO₂ calibrations performed compared to the frequency of temperature change, an anti correlation can be seen. By zooming into an example day set, as shown in figure 16, one can also observe an anti correlation of the NO₂ calibration slope with the temperature with an running mean of 1h. Although no factor could be found, it can be said that the NO₂ calibration slope decreases with increasing temperature



Figure 15: NO_2 calibrations slope (black) over the time period of the campaign with the temperature running mean of 1 hour (blue) and 1 day (red)



Figure 16: NO_2 calibrations slope (black) over the time period from 30.08.2016 to the 03.09.2016 with the temperature running mean of 1 hour (blue) and 1 day (red)

5.2.2 CL used

The CL varies with the ambient relative humidity. The CL calibration was performed at 3%, 20%, 40% and 60% RH for each detector, hence the dependency of the CL on humidity for each reactor was determined in the laboratory work via the interpolation of the results. Hence, for each RO₂^{*} data point a CL could be calculated in dependency of the RH. However, during the laboratory work it was not possible to achieve RH above 60% in the system. The RH dependency is expected to decrease continuously following the calculated function shown by [Andrés-Hernández et al., 2001]. However, an extrapolation of the CL dependency on RH results in high error ranges witch can not be determined. To avoid unknown errors in the data set, all data measured under a RH above 75% were discarded.

5.2.3 RO_2^* data analysis

Throughout the campaign, it was realized that the PeRCA signal was not performing as expected. The two systems did not seem to be independent and produced high noise. Although all possible sources of this behaviour were checked during the campaign no reason was found. To observe this behaviour one of the reactors (alternating) was connected to SA during specific time periods with the purpose to isolate the variations in the signal due to a malfunction from real signals, and to find the source. However, no source could be identified. During the preparation for the laboratory work after the campaign, it was discovered that the grounding for one of the detectors was loose, which resulted in the dependency of the detector signals on each other, as the detectors were following each other. This problem was fixed on the 29.11.2016 and the characterization could be performed without interference. It is possible that during the campaign, while system 2 was in signal mode and signal 1 in background mode, system 2 was pulling system 1 up, leading to a higher background signal. On the other hand, while being in background mode system 2 might have pulled the signal of system 1 down, decreasing the signal of system 1. The stronger the signal of system 2 was the stronger this influence is suggested to be. However, no systematic pattern could be found. Figure 17 shows the RO_2^* data, measured by system 1 and 2 on one of the days of the campaign. Until 20:00 UTC system 1 seems to give a pattern mirrored to the one of system 2. On the contrary, after 20:00 UTC both systems give a similar result. An error in the analysis leading to this phenomenon could be excluded. Hence, for the following presentation and discussion of results all data of system 1 is discarded.



Figure 17: Example of the relation between system 1 and 2 during the measurement campaign

A LabVIEW routine was developed to evaluate the results of the campaign. The average of each background and amplification signal period of each system was calculated resulting in 1 minute averages of the signals. These averages were interpolated over the whole day, resulting in two continuous data arrays with the frequency of 1 minute each. In this way a change in the NO₂ offset could be excluded from the influences on the result as accurate as possible. Time periods of NO₂ calibrations were excluded. The delta of the amplification and background signal was calculated and divided by the interpolation of all NO₂ calibration slopes measured during the campaign. The result is divided by the CL calculated from the RH. RO_2^* measured at RH over 70% were discarded due to the high uncertainty of the CL value at higher RH. The resulting mixing ration of RO_2^* is smoothed over 30 minutes, due to the noise of the signal. Known sources of error were excluded.

6 System calibration results

6.1 Calibrations of the flow controllers

All FC were tested to be closed at an input of 0 ml. The results of the calibrations for the NO_2 and the exhaust FC can the seen in table 8 and 9.

	Calibration slope	error
NO ₂ -FC sys1	1.109	0.071
NO ₂ -FC sys2	1.096	0.062
Exhaust-FC sys1	1.071	0.046
Exhaust-FC sys2	1.029	0.019

Table 8: FC calibration of the set point value to the true value considering the ambient temperature and pressure

	Calibration slope	error
NO_2 -FC sys1	1.106	0.0109
NO_2 -FC sys2	1.091	0.0115
Exhaust-FC sys1	1.069	0.0166
Exhaust-FC sys2	1.027	0.0130

Table 9: FC calibration of the read value to the true value considering the ambient temperature and pressure

6.2 NO₂ calibration

For each calibration performed in the laboratory from the 28.11.2016 to the 23.12.2016, the slope, intercept, R^2 , and standard deviation for the slope and intercept were calculated from all points, excluding the first 15 s of each step. It was found that the baseline of the signal was decreasing over the day in all calibrations performed. An example is given in figure 18. It can be seen that the stability of the baseline improves over the day as the regression line matches the measured points poorly for the first calibration and with an increased accuracy for the later calibration results. The decrease of the baseline can be linked to the switch off of the N₂ and CO gases over the night as mentioned in section 5.1.2. By defining the slope of the calibration using a regression line, the result gets biased to higher values. In this case the R^2 can be used as an indicator for the stability of the baseline. Table 10 shows the slope, R^2 and time after the start of the laboratory work (min. after CO) for the calibrations shown in figure 18. It is becomes clear that the R^2 increases with the time passed and the slope decreases.



Figure 18: Exemplary NO₂ calibration results performed on the 05.12.2016. The slope and intercept of the regression lines for the NO₂ calibration decreases with time over the day. The match of the regression line with the measured points increases over time indicating a increased stability of the system

Time	Slope [V/ppbv]	R^2	min. after CO
09:49	0.032286	0.971484	61
11:14	0.0307 96	0.997862	145
17:07	0.0289 36	0.999329	499

Table 10: Exemplary NO₂ calibration results performed on the 05.12.2016. The resulting slope decreases with the time passed from the opening of the CON_2 lines, while the R^2 increases.

To avoid the influence of the decreasing baseline, the baseline of each calibration was interpolated from the first to the last calibration step and subtracted from the individual calibration points. On the one hand, this procedure improved the accuracy of the resulting slopes and on the other hand, the intercept of the regression line vanishes. However for the purpose of this calibration only the slope is of interest.

Removing the baseline from the calibration leads to a decrease of the calculated regression line. In figures 19 and 20 the black line shows the NO₂ calibration slope without the baseline removal and the red line after the baseline removal. The dashed lines are added for better visual clearness and do not indicate values between the points. The blue bars indicate the R^2 before and the green bars after the baseline removal. In the cases where the calibration was done with only increasing steps, no correction could be done as the baseline could not be defined. These slopes are marked in figures 19 and 20 with pink circles. In all other cases the corrected slope is smaller compared to the original slope.



Figure 19: NO₂ calibration slope results for system 1 over the course of the laboratory work without (black line) and with (red line) the background removal. The R^2 without (blue bars) and with (green bars) background removal. The violet circles mark the calibration witch were performed with the return to the background, hence no background removal could be done



Figure 20: NO₂ calibration slope results for system 2 over the course of the laboratory work without (black line) and with (red line) the background removal. The R^2 without (blue bars) and with (green bars) background removal. The violet circles mark the calibration with were performed with the return to the background, hence no background removal could be done

This effect increases for calibration slopes with higher R^2 before the background removal. The dependency can be approximated for system 1 with

$$\Delta_{slope} = R_{before}^2 \cdot (-0.04671) + 0.04670 \tag{25}$$

and for system 2 with

$$\Delta_{slope} = R_{before}^2 \cdot (-0.05723) + 0.05721 \tag{26}$$

where Δ_{slope} is the decrease in the the NO₂ calibration slope after the removal of the background and R_{before}^2 is the R^2 coefficient before the removal of the background. This approximation is taken from a linear regression of all points as shown in the figures 21 and 22.



Figure 21: Decrease of the regression slope of the NO₂ calibration over the R^2 before the correction for the results of system 1



Figure 22: Decrease of the regression slope of the NO₂ calibration over the R^2 before the correction for the results of system 2

For further analysis only the corrected slopes are considered. The R^2 values are also not shown as after the correction all R^2 values are above 0.99 and therefore the goodness of the regression line is assured. Due to this instability of the baseline, a calibrations setup is to be preferred, which returns to the baseline as often as possible in order to be able to get a reasonable interpolation of the baseline.

In order to define the variability of the NO₂ calibration slope, all calibrations performed at an RH above 3% were removed from the mean and standard deviation calculations and marked in pink in figures 23 to 25 as an influence of the RH on the result is expected. The remaining calibration results were divided in three major sections: 28.11.2016 - 08.12.2016, 12.12.2016 - 19.12.2016 and 20.12.2016 - 23.12.2016. These sections are further called period 1, 2, and 3. These periods were chosen in regard with the events which influenced the sensitivity of the detectors. After the 12.12.2016 the luminol filters were changed. On the 20.12.2016 the detectors were switched. On the 09.12.2016 NO₂ calibration were performed only under wet conditions. The results and variabilities of the slopes are given in table 11 and the corresponding plots are shown in the figures 23 to 25. The mean of all NO₂ calibration slopes made under dry conditions in the considered time period is shown with the black line and the 1.5 σ is given with the red line. The blue points show the all NO_2 calibration slopes measured in this period. The data points during which on one of the systems RH was used are marked in pink. The variability in system 1 is 5.3%, 2.03%and 2.3% in period 1, 2, and 3 respectively. The variability of system 2 is 6.72%, 1.135% and 5.88% for system 1, 2, and 3 respectively. However, in system 2 the calibration result of the 19.12.2016 was taken out of this summary. The extremely low slope was noticed during laboratory work and as a consequence the detectors were switched. Inclusion if this point would lead to a mean of 0.037932 and a standard deviation of 0.00692608, leading to an error of 18.25 %.

system 1			system 2		
period	mean [V/ppbv]	std [V/ppbv]	period	mean [V/ppbv]	std $[V/ppbv]$
1	0.030272	0.00161	1	0.041348	0.00278
2	0.026587	0.00054	2	0.041390	0.00047
3	0.040374	0.00093	3	0.021773	0.00128

Table 11: Mean and standard variation of the NO_2 calibration slope results performed in the laboratory for each period and system



Figure 23: NO₂ calibration results during the first laboratory work time period given with blue dots, the mean with a black line and the 1.5 σ with the red lines for system 1 on the top and for system 2 on the bottom



Figure 24: NO₂ calibration results during the first laboratory work time period given with blue dots, the mean with a black line and the 1.5 σ with the red lines for system 1 on the top and for system 2 on the bottom



Figure 25: NO₂ calibration results during the first laboratory work time period given with blue dots, the mean with a black line and the 1.5 σ with the red lines for system 1 on the top and for system 2 on the bottom

The calibrations were made under different RH, expecting a change in the NO₂ calibration slope. It is expected that only the system connected to the source is affected by the RH. However, in figure 26 and 27 it can be seen that the humidity in the source seems also to affect the NO₂ calibration slope in the other system. From the 17.12.2016 on system 2 was connected to the source. In figure 26 and 27 the time in which the system was not connected to the source is put in a black box. Furthermore it shows that, as expected and described in section 3.1, the NO₂ calibration slope decreases with increasing RH.



Figure 26: NO_2 calibration results over the course of the laboratory work for system 1 with the lower and upper boundary given in the black, red and green lines respectively and the RH with the blue bars. The black box marks the time in which the system was connected to the source



Figure 27: NO_2 calibration results over the course of the laboratory work for system 2 with the lower and upper boundary given in the black, red and green lines respectively and the RH with the blue bars. The black box marks the time in which the system was connected to the source

In period 1 (figure 23), system 1 is connected to the source. The influence of the RH on the slope is inside the 1.5 σ range, except the last calibration which was made under an RH of 60% for the system under RH influence and for system 2 all calibration at this time are inside the 1.5 σ range. No influence of the RH in the connected system on the remaining system can be identified.

During period 2 (figure 24) system 1 is still connected to the source and all calibration slopes which are influenced by RH are outside the 1.5 σ mark for the connected system.

Therefore it can be said that with a variability of 5% as in period 1, the influence can not be detected, but when the system runs more stable with a variability of 2% the influence of an RH over 20% can be distinguished with a probability of 86.66% (1.5 σ). During the same period system 2 was not connected to the source, nevertheless the data points during which system 1 was influenced by RH were taken out to calculate the mean and the standard deviation and treated as in system 1 in order to see if the system which is not connected to the RH is really influenced or this appearance underlies the variation of the data. After eliminating the data point of the 19.12.2016 for above mentioned reasons, only 3 data points are left leading to a very small variability of 1.135%. The data point that was discarded is marked in green. Even within of this 1.5 σ the first two marked points (first is 20% RH; second is 40% RH)are not clearly distinguishable. The last marked point is representing the NO₂ calibration slope made while the other system had 60% RH in the lines. It seems to be distinguishable, but with only 3 data points the statistic is not reliable.

During period 3 (figure 25) system 2 is connected to the source and is influenced by the RH. In the lower plot of figure 25 it is shown that the 40% and 55% RH (second and third marked point) are distinguishable outside, while the 20% are inside the 1.5 σ mark. In this case (similar to period 1) the variability is 5.9% where the data point influenced by 20% is inside the 1.5 σ mark, the data point influenced by 40% RH is close to the marking line and the higher (60%) is clearly distinguishable. The variability of system 1 during this period is 2.3% but the data points which were taken while the source was producing RH are not distinguishable. Hence in order to see an influence of the RH on the NO₂ calibration slope the RH has to be at least 40% and the system has to be stable enough to have a variability of 2-3%. It is therefore shown that the impression that the system which has no RH in the system is still influenced by it (indication for a leak) is not supported.

The dependency of the NO_2 calibration slope on the RH was considered for each day individually and lead to very similar dependencies. Figure 28 and 29 show to which degree the RH is influencing the slope and the results are summarized in table 12.

	system 1	system 2		
date	decrease rate $[[V/ppbv]/\%RH]$			
09.12.2016	-0.000065	date	mean $[[V/ppbv]/\%RH]$	
13.12.2016	-0.000061	20.12.2016	-0.000152	
14.12.2016	-0.000071	21.12.2016	-0.000070	
16.12.2016	-0.000062	22.12.2016	-0.000070	
16.12.2016	-0.000063	mean	-0.0000973	
mean	-0.0000644	std	0.0000473	
std	0.000004			

Table 12: NO_2 calibration slope dependency on RH increase measured on different days and averaged for each system

Apart from the dependency measured on the 20.12.2016 the results are relativity similar. Considering all results, the data from the 20.12.2016 are calculated to be an outlier using the Grubbs test. After the removel of the outlier an average of -0.000066 could be calculated with an standard variation of 0.00000424. The dependency of the slope from the RH can be therefore described with

$$S_{RH} = S_{dry} - (RH \cdot 0.000066) \tag{27}$$

Where S_{RH} is the NO₂ calibration slope at wet conditions, S_{dry} is the NO₂ calibration slope measured at dry conditions and RH is the relative humidity at which S_{RH} is measured. As the detectors were switched on the morning of the 20.12.2016, an unstable system from the interruption of the change could be the reason for the outlier in the data set. This hypothesis would also explain the first data point in the upper plot of figure 25 being clearly higher while all following dry calibrations are very similar.



Figure 28: Dependency of the NO_2 calibration slope on RH for system 1



Figure 29: Dependency of the NO_2 calibration slope on RH for system 2

6.3 O₃ calibration

The O_3 calibrations were analysed by the 4 methods described in 5.1.3. The overview of the O_3 calibration results is given in figure 30 considering all 4 methods. All 4 methods lie within 1 σ error bars of each other. In figure 31 it can be seen that method 1 overall has a rather high relative error due to a large data set, as mentioned in 5.1.3. The results on the 19.12.2016 were unexpectedly low, having high relative errors (figures 30 and 31). As mentioned in 6.2, the NO₂ calibration slope on that day was very low and was excluded from the analysis, leading to a high error in the conversion of the ΔV to $[O_3]$. The O_3 calibration results were also identified to be outliers as well as the NO₂ calibration results on the same day, using the Grubbs' test, a statistical test to detect outliers. For this reason the data on the 19.12.2016 are not further considered in the analysis. The results depend on the residence time of the SA flow on the UV light chamber with a volume of 3078.76 mm². The SA flow used in for each O₃ calibration is given with the pink bars. High SA flow lead to lower O₃ production.



Figure 30: Overview of all O₃ calibration results and the 1 σ error range applying all 4 method and the used SA flow given with the pink bars



Figure 31: Relative errors of all O_3 calibration results of each methods

In order to define the dependency of the calibration result on the residence time in the chamber, the O_3 calibration was performed using different SA flows of 2, 5, 7 and 9 L/min flows. It is expected that the $[O_3]$ concentration produced is decreasing with a higher SA flow, as the air spends less time in the UV lamp chamber and hence less O_2 can be photolysed to O_3 .



Figure 32: All O_3 calibration results plotted against the SA flow used. Top left: analysis using the interpolation method; top right: analysis using the averaging method; bottom left: analysis using the interpolation of the signal method; bottom left: analysis using the interpolation of the background method

Figure 32 shows the dependency of the O_3 calibration result on the SA flow for all four methods. Here the results of the calibrations performed on the 19.12.2016 are added to demonstrate the deviation of the results of these calibrations from the whole set of O_3 calibration results. Table 13 shows the summary of the parameters for the different fits for each of the methods.

The exponential fit is described as

$$f(x) = a \cdot \epsilon^{x \cdot b} \tag{28}$$

The power fit as

$$f(x) = d \cdot x^e \tag{29}$$

and the polynomial fit as

$$f(x) = \sum_{j=0}^{m} c_j \cdot x^j \tag{30}$$

with x representing the residence time in the light chamber and f(x) the $[O_3]/V$ measured.

Method	Exponential fit		Polynomial fit			Power fit	
1	a	b	c_1	c_2	c_3	d	е
1	581.012	19.83	5.35	31950	78782.6	52033.3	1.12
2	634	18.97	11.24	32424.4	76176.3	51953.3	1.11
3	611.45	19.3103	257.00	22137.3	3 156680	51230.3	1.11
4	493.99	21.72	98.3	28481.4	110411	48757.4	1.07

Table 13: Constants for each fitting approach of the O_3 calibration for each method when including the measurement with a residence time of 0.0923628 s

The power fit approximation seems to give the best fit for all methods used. The dependency on the residence time was calculated only for the first method, as it is found to be the most appropriate (see chapter 5.1.3). Here the power fit approximation has parameters of $d = 52033.3 \pm 2099.62$ and $e = 1.12 \pm 0.011803$, being close to a linear dependency.



Figure 33: Left: $[O_3]$ produced depending on the residence time in the light chamber including the $[O_3]$ produced using an SA flow of 2 L/min. Right: $[O_3]$ produced depending on the residence time in the light chamber excluding the $[O_3]$ produced using an SA flow of 2 L/min

Using all the data points means including all the O₃ calibrations results, where δ V was divided by each of the dry NO₂ calibration slopes performed on that day. Hence, one O₃ calibration can lead to multiple O₃ results, if multiple NO₂ calibrations were performed on this day. As depending on the NO₂ calibration used the result varies and all are possible, both are taken into the data set. However, the O₃ calibration with the residence time of 0.0923628 s was performed only once, and divided by 5 different NO₂ calibration slopes, which shifts the weight of the individual data points for the fits. Hence a second set of fits was performed excluding this calibration results. The results can be seen in figure 33 on the right hand side. The associated constants are $d = 43422.3 \pm 10489.9$ and $e = 1.0653 \pm 0.069$ for methods 1 and the constants for the methods 2-4 are given in table 14.

Method	Exponer	ntial fit	Polynomial fit		Power fit		
1	a	b	c_1	c_2	c_3	d	e
T	351.39	35.32	98.10	25529.6	185174	43422.3	1.06
2	634.45	18.97	11.24	32425	76176.3	51953	1.11
3	611.45	19.31	257.00	22137.3	156680	51230.3	0.96
4	493.993	21.72	98.300	28481.4	110411	48757.4	1.07

Table 14: Constants for each fitting approach of the O_3 calibration for each method when excluding the measurement with a residence time of 0.0923628 s

For the calculation of the chain length only the $[O_3]/V$ values are important, which were measured at a residence time of 0.0263894 s as it is the residence time of the SA flow in the UV light chamber which was used during the HO₂ calibrations. The [V] represents the voltage produced by the PMT measuring the light intensity of the UV lamp.

The results at this residence time using the power fit which includes the values at a residence time of 0.0923628 s would lead to $[O_3]/V$ values of 895 ± 15 . The power fit approximation excluding this values leads to a $[O_3]/V$ value of 904 ± 15 . The mean of all values at this residence time, 911.27. is scarcely outside the 1 σ error range of the first approach and inside the 1 σ error range of the second approach, hence it is used for the HO₂ calibration analysis.

$6.4 \quad HO_2 \text{ calibration}$

CL calibrations were performed under different RH conditions (3%, 20%, 40%, 60%). The calibration with the RH of $\leq 5\%$ are considered as dry calibrations. In table 15 the CL results are given with the corresponding RH in the system. The first point was found to be an outlier using the Grubbs' test among all CL results at dry conditions.

As expected and described in chapter 3.1 the CL decreases with increasing RH. The decrease can be approximated with an exponential decay (equation 28) where $a = 125.399(\pm 6.191)$ and $b = -0.02517(\pm 0.0048)$ for system 1 and $a = 164.842(\pm 3.625)$ and $b = -0.0269(\pm 0.0014)$ for system 2, the fits being shown in figure 34 and 35. The error

System 1			System 2	
Date	CL	RH		
05.12.2016	150.916603	3	Date CL RH	
06.12.2016	111.280702	3	20.12.2016 142.677426 3	
07.12.2016	111.248881	3	21.12.2016 157.280615 3	
13.12.2016	109.291352	3	22.12.2016 162.792348 3	_
14.12.2016	108.348382	3	20.12.2016 96.9963092 20	_
15.12.2016	110.854884	3	20.12.2016 95.907581 20	
16.12.2016	110.055547	3	21.12.2016 55.318150 40	=
13.12.2016	74.984837	20	21.12.2016 51.353820 40	_
16.12.2016	75.431631	20	22.12.2016 33.099079 60	=
14.12.2016	45.432231	40	22.12.2016 38.216408 60	_
15.12.2016	29.405727	60	i	=

Table 15: CL calibration results for each system at different RH

of the $[HO_2]$ is determined by the error in the $[O_3]/V$ value, which is constant and the error of the NO₂ slope, which both are constant for each HO₂ calibration and the NO₂ calibration slope leading to negligible errors ranges. The confidence range of the regression is marked in blue in the figures 34 and 35.

Using Grubb's test, the first CL calibration result of system 1 was identified as an outlier and the fit was then repeated without the point. The parameters changed to $a = 118.633(\pm 0.5205)$ and $b = -0.02331(\pm 0.0004)$ (shown in figure 36)



Figure 34: CL change over RH in the system for system 1

To be able to compare the results with the results from figure 4 in chapter 3.1, the fit was plotted in the same way, as figure 4 plotting the ratio of the CL at a higher RH and the CL at dry conditions. The dependence measured in this study lies between the one performed by Mihele and Hastie [1998] and the data obtained by Stöbener [1999] at the IUP and is shown in figure 37 and 38 for system 1 and 2 respectively.



Figure 35: CL change over RH in the system for system 2







Figure 37: Dependency of the CL on RH for system 1



Figure 38: Dependency of the CL on RH for system 1

From this curve the RO_2^* mixing ratio measured during the campaign over the summer can be calculated by dividing the delta [NO2] by the CL.

7 Campaign data results and discussion

This section presents the results of the measurement campaign. The data taken from the 06.08.2016 to the 21.09.2106 were considered in the analysis. The analysis of data will focus on the investigation of potential variables affecting the diurnal variation of RO_2^* , focus of the present work.

Due to software editing features, RO_2^* is represented in all plot legends as ROx. As mentioned in 5.1.2 a failure in the grounding of system 1 affected the detector signal and as a consequence only data from system 2 are considered in the analysis.

7.1 Data overview

All data of the gases and RO_2^* in the first step were used to calculate a diurnal average mixing ratio. Figures 39 to 43 show the averaged variation of the mixing ratios of RO_2^* , NO, NO₂, O₃ and CO respectively over the whole campaign time. For better visual clarity the plot legend was left out.



Figure 39: Variation of the mixing ratio of RO_2^* , averaged over the whole campaign time in black and individual days given in colours

The measured RO_2^* mixing ratio average was found to be between 20 and 40 pptv over the course of the day. The maximum is found at 12:00 UTC slightly exceeding 40 pptv. Apart from the expected peak at noon, a secondary build up of RO_2^* was observed after 18:00 UTC. After 23:00 and 06:00 UTC the data remains sparse due to the high RH in the night hours. The mixing ratio ranged between 0 and 150 pptv over the measurement campaign. Of all days, 15 were classified as clear and sunny conditions and 21 were classified as cloudy. Out of these 21 days, 7 had RH above 70% throughout the entire day. As the lab calibrations of the RH effect in the chain length were carried out up to 60%, all measurements at higher RH are subject to high inaccuracies and were discarded from the data set. This influence is studied more in detail in section 7.3. The remaining days had alternating sunny and cloudy conditions.



Figure 40: Variation of the mixing ratio of NO averaged over the whole campaign time in black and individual days given in colour



Figure 41: Variation of the mixing ratio of NO_2 averaged over the whole campaign time in black and individual days given in colour



Figure 42: Variation of the mixing ratio of O_3 averaged over the whole campaign time in black and individual days given in colour

For the variation of the CO mixing ratio no mean was calculated. The mixing ratio of CO does not show a typical diurnal pattern with peaks at specific times of the day, but it is determined by a rather stable concentration over the course of a day with individual short, but high peaks. An average over all days would not show a diurnal variation but would be influenced by individual peaks at different times of the day, hence lifting the averaged value up. Figure 43 depicts the high variability of the CO diurnal variation over the whole period. The typical background mixing ratio of CO was found to be between 200 and 400 ppbv with individual short term peaks reaching up to 1000 ppbv.



Figure 43: Variation of the mixing ratio of CO, individual days given in colour

For NO and NO₂ it is possible to identify a more regular pattern likely related to traffic sources of emission. A morning rush hour peak in the NO and the NO₂ mixing ratios is observed reaching on average 10 and 20 ppbv respectively, followed by the build up of ozone from 08:00 UTC until the late afternoon at 17:00 UTC reaching on average 45 ppbv with a maximum of 110 ppbv and a minimum of 17 ppbv at noon. The NO₂ mixing ratio shows a second peak between 16:00 and 23:00 UTC of on average 10 ppbv with individual days reaching up tp 57 ppbv. A clear minimum of $[NO_2]$ is reached at 14:00 UTC going close to 0. It is feasible that a potential isochronal NO peak is consumed by the build up of ozone and converted to NO₂. Occasionally the peaks of $[NO_2]$ measured at night, between 18:00 UTC and 02:00 UTC exceed the expected peak of the morning rush hour.

7.2 Influence of local emissions

In immediate distance to the IUP building, a major city road is located which leads to the other side of the city. Only 1.5 km to the north is a freeway connecting Bremerhaven (as well as surrounding villages) to the city of Bremen. Therefore, it is to be expected that the traffic emissions of the rush hours leave trails in the measurements of the trace gases. Indeed, a clear peak between 04:00 and 08:00 UTC is registered in the mixing ratios of NO and NO_2 during weekdays which can not be observed on weekends as shown in figures 44 and 45. While during the morning rush hour a clear peak can be seen in the NO and NO_2 mixing ratios during weekdays, the mixing ratio of NO does on average not rise during the expected evening rush hour around 15:00 UTC as shown in figure 44. Individual peaks can be seen however after 18:00 UTC on weekdays which is after the expected time of an evening rush hour on weekdays. The mixing ratio of NO_2 has a clear increase averaged over all work days after 16:00 UTC on weekdays. An increase in the NO₂ mixing ratio can also be observed on weekends but less profound. On the weekends (figure 45, bottom plot) an average mixing ratio of 10 ppby NO_2 is observed with a minimum between noon and 16:00 UTC at approximately 0-3 ppbv NO₂. In the time from midnight to 10:00 UTC the average (black line) is dominated by four days with NO_2 mixing ratios in the range typical for weekdays (figure 45, top plot). These days are the 10.09.2016, 11.09.2016 and 17.09.2016.



Figure 44: Top: NO mixing ratio in [ppbv] observed on all weekdays from the 08.08.2016 to the 23.09.2016. The legend is not shown for visual clarity. Bottom: NO mixing ratio in [ppbv] on all weekends from the 06.08.2016 to the 25.09.2016. Time is given in UTC



Figure 45: Top: NO₂ mixing ratio in [ppbv] observed on all weekdays from the 08.08.2016 to the 23.09.2016. The legend is not shown for visual clarity. Bottom: NO₂ mixing ratio in [ppbv] on all weekends from the 06.08.2016 to the 25.09.2016. Time is given in UTC

On the 10.09.2016 the observed NO mixing ratios were also clearly over the average (in brown in figure 44). From the 10.09.2016 to the 18.09.2016 a local event, "Maritime Woche" was hosted in the city of Bremen. This could explain an increase in the traffic close to the measurement site during the preparation phase immediately before the event. Additionally, on the evening of the 16.09.2016 a fireworks display was held. The traces of these fireworks could be observed in the mixing ratios of NO₂ and NO (figure 46).



Figure 46: Mixing ratios NO, NO₂, O₃ and CO on the evening of the 16.09.2016 when a fireworks display was taking place in the city

Concerning O_3 mixing ratios, the effect of traffic emissions is not expected to be that obvious in the diurnal variation as this is also affected by transport and deposition and is a secondary pollutant. However, there is a slight difference observed between work and weekend days, related to the magnitude of the peak emissions during rush hours. On top of the variations due to different photochemical activity (sunny and cloudy days) it can be observed that the increase of O3 in the mornings starts slightly earlier on the weekends without the dip at 06:00 UTC, as the emissions of NO are generally lower.

However, in both cases mixing ratios increase from 06:00 UTC until noon and remain stable until 16:00 UTC, followed by a slow decrease until the minimum at 17:00 UTC is reached, where a new cycle is starting. The starting decrease in the mixing ratio of O_3 coincides with the starting increase of NO₂ mixing ratios. Hence it can be reasoned that NO is emitted and oxidises to NO₂ with ozone as described in section 2.2 reaction R8. It remains unsettled what the source of the emissions after 16:00 UTC is which is seen for NO only on weekdays and for NO₂ also during the nights of the 3 days identified above.



Figure 47: Top: O_3 mixing ratio in [ppbv] observed on all weekdays from the 08.08.2016 to the 23.09.2016. The legend is not shown for visual clarity. Bottom: O_3 mixing ratio in [ppbv] on all weekends from the 06.08.2016 to the 25.09.2016. Time is given in UTC

Similarly to the O_3 mixing ratio, the effect of traffic in the diurnal evolution of RO_2^* is expected to be partly hidden by other influencing factors like solar radiation (see section 7.3). While ozone has a longer lifetime and can be brought by transport of air masses, the short lived RO_2^* are influenced by multiple local factors. However, as in O_3 , the diurnal cycle is slightly broader in weekend days in the absence of the NO rush hour peaks.



Figure 48: Top: Ro_2^* mixing ratio in [pptv] observed on all weekdays from the 08.08.2016 to the 23.09.2016. The legend is not shown for visual clarity. Bottom: RO_2^* mixing ratio in [pptv] on all weekends from the 06.08.2016 to the 25.09.2016. Time is given in UTC

7.3 Diurnal variation on clear, sunny days

As described in section 2.3 the formation of peroxy radicals is closely related to the irradiation at the surface. Therefore, sunny and cloudy days were investigated separately (see figure 49). Despite the high variability between the individual days, a clear pattern can be seen in these sunny days. The peroxy radical mixing ratio increases with increasing radiation and its maximum coincides with the maximal irradiation (see figures 49 and 50).

The ozone mixing ratio is closely related to the RO_2^* mixing ratio. Table 16 displays the peak ozone mixing ratios of each day used in figure 49. The highest ozone mixing ratio was achieved on the 26.08.2016 (110ppbv). Figure 49 shows that the same day also has the highest RO_2^* mixing ratio peak, followed by the 14.09.2016, the 13.09.2016 and 12.09.2016 with peak ozone concentrations of 80. 85 and 75 ppbv respectively. Also all of these days have high ambient temperatures varying from 26 to 34 °C during the day and reach the highest temperatures between noon and 16:00 UTC. The 17.08.2016 shows the lowest O₃ mixing ratios and the lowest temperature (< 25°C) of the sunny days. On the 19.08.2016, which is considered a sunny day with a temperature of 26°C and a peak solar irradiance of 850 W/m^2 , no RO₂* mixing ratio peak was observed.

On days with predominantly cloud covered sky, no increase of average RO_2^* mixing

ratios during noon was observed (figure 49 bottom). However, individual days feature peaks of up to 110 pptv. It must be kept in mind, that the high RH on cloudy days affect the accuracy of the RO_2^* measured, as discussed in section 5.2.2. Data subject to high inaccuracies (RH > 75%) were not considered in the present analysis. Due to the high RH on the cloudy days less data could be considered on the cloudy days.



Figure 49: Top: Measured diurnal peroxy radical mixing ratio variation in [pptv] on sunny, clear days with a temperature variation from 23-35 °C. 15 days were classified sunny and clear with a radiation patterns shown in figure 50. Bottom: Measured diurnal peroxy radical mixing ratio variation in [pptv] on days with predominant cloud coverage. 21 days were classified cloudy



Figure 50: Top: Solar irradiation data measured on the dates between the 17.8.2016 and the 15.09.2016 listed in the legend. Bottom: solar radiance data measured on cloudy days in the legend of the lower plot of figure 49, not shown for visual reasons
Date	peak [O ₃] in [ppmv]	max. Temp. [°C]	solar radiance $[W/m^2]$
17.08.2016	45	23	840
19.08.2016	60	26	850
24.08.2016	65	32	720
25.08.2016	75	34	735
26.08.2016	110	32	690
31.08.2016	65	28	710
06.09.2016	50	26	780
07.09.2016	55	30	690
08.09.2016	65	30	656
09.09.2016	55	27	690
10.09.2016	75	28	620
12.09.2016	75	32	610
13.09.2016	85	33	605
14.09.2016	80	31	600
15.09.2016	55	28	620

Table 16: Peak concentrations of ozone in [ppbv], maximum temperature in [°C] and maximal solar radiance in $[W/m^2]$ on the chosen sunny, clear days

7.4 Influence of wind direction

The 26.08.2016 has a course of ozone mixing ratio over the day that is clearly different from the other working days and also reaching the highest O_3 mixing ratios of 110 ppbv at noon. Striking is the peak around noon (figure 51, green line). Overall, the RO_2^* and O_3 diurnal variations agree reasonably. After 12:00 UTC the RO_2^* mixing ratio decreases shortly followed by a drastic increase of the mixing ratio up to 140 pptv at 13:15 UTC. At high NO₂ mixing ratios the production of RO_2^* is hindered by the consumption of the RO_2^* via the reaction R43 described in section 2.3.3. As the NO₂ mixing ratio decreases, the $[RO_2^*]$ builds up and a change in the $[O_3]$ variation slope is noticeable at 08:30 UTC due to the role of the radicals in the production of O_3 .



Figure 51: Variation of O_3 an RO_2^* mixing ratios measured on the 26.08.2016

A second increase in the O_3 variation slope can be observed at 11:00 UTC. The change in wind direction, wind speed (figure 53), temperature and humidity at 11:00 UTC indicate a change in the air mass sampled at the site (figure 52).



Figure 52: Wind direction, RH and temperature measured on the 26.08.2016



Figure 53: Variation of wind speed measured on the 26.08.2016

This pattern is not observed that clearly in the RO_2^* diurnal variation. Two clear peaks of RO_2^* can be identified, at noon and at 13:15 UTC. The first peak clearly overlaps with the RH peak at noon, which is measured in a different air mass from a new wind direction. A smaller local maximum in the RO_2^* mixing ratio simultaneous to a small local maximum is also found at 14:00 UTC.

Similarly, a sudden wind direction change from S to NE brings different air masses. Contrary to the effect observed on the 26.08.2016, which only influences the mixing ratio of ozone, increased RH and CO and NO₂ mixing ratios at noon are noticeable(figures 54 and 55). Furthermore, on the 28.08.2016 the O₃ mixing ratio decreases sharply from 90 ppbv to 60 ppbv one hour after the wind direction changed (figure 55).



Figure 54: Variation of wind direction measured on the 28.08.2016 with temperature and RH



Figure 55: Variation of the mixing ratios of O_3 , CO, NO and NO₂ measured on the 28.08.2016

The diurnal evolution of RO_2^* and the solar irradiance agree very reasonably (figure 56), increasing constantly until 10:45 UTC when cloud coverage starts to dominate the conditions, leading to a drop in the RO_2^* mixing ratio. This can also be noticed in the change in the diurnal variation of O_3 . At 12:40 UTC a permanent cloud coverage until 13:20 UTC leads to a drop in the temperature and an increase in RH. The dropped solar irradiance causes a drop in the RO_2^* mixing ratio of 65 pptv, which might partly explain the drop of 30 ppb observed in O_3 . This period is followed by 2 hours of alternating conditions between overcast sky and clear sky. The RO_2^* mixing ratio increases to 50 pptv. A second cloud cover from 14:30 UTC to 15:30 UTC causes a second drop of the $[RO_2^*]$ followed by a decrease in the O_3 mixing ratio. The wind direction changes from NE to NW at 16:10 UTC. In this case O_3 increases 30 ppbv at the time of the change in the wind direction.



Figure 56: Variation of the mixing ratios of O_3 and RO_2^* , RH and solar irradiance measured on the 28.08.2016

Contrarily, no significant changes in wind direction over the course of these days were measured on the 10.08.2016 (figure 57). The wind direction varies between N and NE continuously and the wind speed stays between 2 and 5 m/s, thus changes in the mixing ratio of the measured species are not related to a specific wind direction. However, the temperature and RH vary greatly between 10:00 and 18:00 UTC with 4 periods of low temperature resulting in high RH. The temperature varies between 10°C and 17°C while the RH varies between 50% and 85%. Relatively low O₃ mixing ratios are observed over the course of the day as well as low NO₂ mixing ratio until 18:00 UTC (figure 58).



Figure 57: Variation of wind direction measured on the 20.08.2016 with temperature and RH



Figure 58: Variation of wind direction measured on the 20.08.2016 with temperature and RH

The mixing ratio of RO_2^* in these conditions is dominated by the solar irradiance as can be seen in figure 59. Five periods with enduring cloud coverage can be identified: 09:00-09:40, 10:15-11:15, 12:10-12:45, 13:50-14:30 and 15:50-16:45 UTC. In all of these periods a drop in the mixing ratio of RO_2^* is measured and an increase to mixing ratios of up to 30 pptv is measured during the continuously sunny periods around 07:30, 08:40, 11:40 and 13:00 UTC.



Figure 59: Variation of the mixing ratios RO_2^* and solar irradiance measured on the 10.08.2016

In all three cases discussed above, the solar irradiance is determining the overall variation of the $[RO_2^*]$ variation contrary to the mixing ratios of CO, NO₂ which are largely influenced by transport and O₃ which is influenced by local chemistry as well as by transport and deposition, in which case the mixing ratio would depend on the wind direction.

7.5 Night time emissions

During night time periods, after 18:00 UTC no emission of CO or NO_x from traffic is expected. However, on several evenings increased mixing ratios of NO_2 or CO were observed. NO_2 is the product of the reaction of O_3 and NO. During the night the boundary layer of the atmosphere decreases due to lower temperatures, confining the O_3 mixing ratios. At night time NO_2 is not photolysed, thus mixing ratios of NO_2 are increasing if NO is present. Chosen days with typical emission patterns for these events are shown in the figures 60 to 64. Two different features after 16:00 UTC are observed, when mixing ratios of the measured species are expected to decrease. On the one hand side short-lived NO_2 peaks of 7-10 ppbv, lasting for 30-60 minutes and occurring multiple times over the night and on the other hand rising NO_2 mixing ratios up to 40 ppbv over a time span of multiple hours. Generally, the former is associated with N to NW winds (figure 60). The last could not be related to specific wind directions (figure 61). On multiple days, an overlap of both features could be seen. On these days S winds were registered. Figure 63 shows the measurement site with the surroundings and the wind directions. NE from the measuring site a waste powered energy plant is located, which is known to power combustion processes at night. Directly N from the measurement site the chemical waste handling station of the university is located. However, the emission hours do not overlap with the assumed operating hours of the station. No systematic behaviour for weekdays and weekends could be found.



Figure 60: Wind direction and the mixing ratios of O_3 , NO, CO and NO₂ after 16:00 UTC on days on which multiple short time mixing ratio peaks were observed



Figure 61: Wind direction and the mixing ratios of O_3 , NO, CO and NO₂ after 16:00 UTC on days on which an overall build up of NO₂ mixing ratio was observed



Figure 62: Wind direction and the mixing ratios of O_3 , NO, CO and NO₂ after 16:00 UTC on days on which multiple short time emissions were observed as well as a build up of $[NO_2]$



Figure 63: Map of the surrounding of the measurement site with wind directions marked as measured during the campaign. The Measurement site is marked with the smaller red circle in the middle

On several days, NO₂ mixing ratios up to 55 ppbv were measured as shown in figure 64. On most of these days unexpectedly high RO_2^* mixing ratios over 50 pptv were measured as well. A relation to the build up of NO₂ is possible. In the first plot in figure 64 on the left side it can be seen that the RO₂^{*} correlates with the NO₂ mixing ratio between 18:30 and 20:30 UTC. Two [NO₂] peaks are observed at 19:15 and 19:45 UTC. Simultaneously [RO₂^{*}] increases while [O₃] decreases. Also, in the third and fifth left plot of figure 64 the RO₂^{*} is varying with the NO₂. Contradictory on the 09.09.2016, which is displayed as the fourth left plot in figure 64, the RO₂^{*} mixing ratio varies with the mixing ratio of ozone contra-wise to NO and NO₂.



Figure 64: Wind direction and the mixing ratios of O_3 , NO, CO and NO₂ after 16:00 UTC on days on which surprisingly high $[NO_2]$ were reached

On the 19.08.2016 a short time RO_2^* mixing ratio peak of up to 100 pptv was measured as can be seen in figure 65. As at 21:00 UTC solar irradiance is at 0, the source of the production of the high mixing ratio of radicals is unknown. CO and NO mixing ratios remain constant. However, in the mixing ratio of O₃ a sudden increase is registered 15 minutes after the abrupt increase in RO_2^* indicating the oxidation of NO without the consumption of ozone. As the RO_2^* mixing ratios drop back to lower values of around 15 pptv, an increase in the mixing ratio of NO₂ can be seen.



Figure 65: Mixing ratios of RO_2^* , CO, O₃, NO and NO₂ measured on the 19.08.2106

7.6 Range of the error

The total error in the measured RO_2^* can be calculated by

$$\Delta RO_2^* = \sqrt{\left(\frac{1}{CL} \cdot \Delta NO_2\right)^2 + \left(\frac{NO_2}{CL^2} \cdot \Delta CL\right)^2}$$
(31)

Where ΔRO_2^* is the absolute error of the RO_2^* mixing ratio, CL the chain length, ΔNO_2 the detection limit of the detector, NO_2 the measured NO_2 mixing ratio signal and ΔCL the absolute error of the CL. The CL depends on the relative humidity and the signal/noise ratio during the CL calibration deteriorates with increasing humidity. Related to this and to the stability of the RH during the calibration, only CL up to 60% humidities could be performed during the laboratory characterisation (see section 6.4).

Under standard controlled laboratory conditions and SA sampled, the detector noise was at average $\sim \pm 0.005$ V (as calculated from the standard deviation of individual steps during the NO₂ calibrations) and an average NO₂ calibration slope of 0.042 V/ppbv was calculated, hence NO₂ mixing ratios above 0.125 ppbv can be distinguished from the noise. The error of the NO₂ calibration slope remains below 1%.

The CL error range for CL measured at RH between 3% and 60% was between ± 2 and ± 4 (see section 6.4). The CL for system 2 measured in the lab varied between 164 \pm

3 and 34 ± 2 for 3% and 60% RH respectively. As mentioned above the accuracy of the CL is therefore dependent on the RH conditions and varies between 1.83% and 5.88%. At RH < 3% a CL of 164 ± 3 is obtained and the corresponding NO₂ calibrations are based on NO₂ controlled mixing ratios varying between 1 and 30 ppbv above the NO₂ offset (see section 5.1.2). According to equation 31 and combining the uncertainty in the CL and the NO₂ detector, the uncertainty in the RO₂^{*} mixing ratios for RH < 3% vary between approximately 0.8 and 3.4 pptv. Similarity, at a RH of 60% a CL of 34 ± 2 is obtained and identical controlled NO₂ mixing ratios for RH < 60% vary between ± 4 pptv and ± 52 pptv.

The RO_2^* mixing ratios determined during the measurement campaign underlie higher inaccuracies compared to the measurements in the laboratory under controlled conditions due to two main influencing factors. Firstly it was not possible to carry out an automatic NO₂ calibration sampling SA during the day as initially planned. Due to interferences likely related to the long tubing from the gas cylinders in the laboratory to the measurement site on the roof terrace and the low NO and NO₂ flow required, high interferences disturbed the signal in the calibration setup. Therefore, short calibrations were carried out manually when possible, at the same time trying to minimize the loss of measurements. Secondly, the RH was frequently close or over 60%. Apart from potential condensation effects in the inlet, the error of the CL interpolation to this range of RH can only be estimated.

During the campaign, the noise of the detector increased and was calculated to be ± 0.05 V (calculated from the standard deviation of individual steps during the NO₂ calibration). The NO₂ calibration slope varied around 0.04 V/ppbv. Thus the detection limit was 1.25 ppbv NO₂. For an RH of 30%, at a CL of 75, the error of the RO₂^{*} mixing ratio for a signal of 1 ppbv NO₂ is calculated to be at ± 16.6 pptv. Typically RH of 50%, with a CL of 45, were measured at day time periods during the campaign. At this RH the error of the RO₂^{*} mixing ratio is calculated to be ± 27.8 pptv. the error of the mixing ratios measured at RH above 75% is estimated to be $\sim 70\%$. The smoothing of the data set over 30 minutes over periods with no clear indication of a change in the conditions, as was done in this work, decreased partly the error in the determination of the diurnal variation.

8 Summary and conclusion

The mixing ratios of RO_2^* , CO, NO₂, NO and O₃ were measured during an intensive period in the summer of 2016 between the 06.08.2016 and the 21.09.2016 in order to investigate the main variables and parameters affecting the diurnal evolution of peroxy radicals in a semi urban measurement site. For the analysis of the data of this campaign the following steps were undertaken: • The sensitivity of the detectors and the CL for both reactor were characterized in the laboratory. In particular the dependency of the CL on RH for each reactor was investigated. For system 1 a CL of 110 was found at dry conditions with a dependency on RH as

$$CL = 118.63(\pm 0.52) \cdot \epsilon^{RH \cdot -0.023(\pm 0.00)}$$

For system 2 a CL of 153 was found at dry conditions with a dependency on RH as

$$CL = 164.842(\pm 3.625) \cdot e^{RH \cdot -0.027(\pm 0.01)}$$

- During the campaign, multiple NO₂ calibrations were performed daily to correct the variations of the sensitivity of the luminol detectors with the temperature.
- The dependency of the O_3 mixing ratio concentration produced during the HO_2 calibration was determined in dependency of the residence time in the UV light chamber. The dependency was found to follow an power fit

$$O_3 = 52033.3(\pm 2099.62) \cdot x^{1.12(\pm 0.015)}$$

• Software routines were developed using LabVIEW for the acquisition and validation of the data.

Main conclusions of this work can be summarised as follows:

- RO₂^{*} mixing ratios between 0 and 140 pptv were measured, on average varying between 20 and 40 pptv over the course of the day. During the measurement campaign 15 days were classified as sunny (clear sky) and 21 days as cloudy.
- The diurnal evolution of RO₂^{*} is characterised by reaching a maximum at the maximum solar radiance (11:30 UTC) varying between 3 and 140 pptv on sunny and between 0 and 110 on cloudy days. On average a mixing ratio of 60 pptv was calculated at noon for sunny days, and 30 pptv for cloudy days.
- The RO₂^{*} and solar radiance diurnal variations mostly show a very reasonable agreement, indicating the solar irradiance to be a dominant factor in the formation of radicals.
- There was no clear relation observed between the wind direction and the observed RO₂^{*} mixing ratios, indicating no significant changes in the composition of radical precursors in the air masses arriving at the measurement site.

- During the night time measurements on 11 different days unexpectedly high RO₂^{*} mixing ratios were observed during periods of high NO₂ mixing ratios. The chemistry behind this build up is not analysed here as it is beyond the scope of this work. Additionally, these measurements underlie increased inaccuracy, due to increased RH during most night time periods.
- The influence of local traffic emission sources was seen in the measurements of the mixing ratios of NO₂ and NO. During the morning rush hour NO mixing ratios of up to 58 ppbv were measured. On average a peak during the rush hour of 10 ppbv was calculated. On weekends no peak at the same time was found. This signal from the rush hour was also seen in the mixing ratios of NO₂ with an average of 20 ppbv mixing ratio.
- For NO₂ a second build up peak at 21:00 UTC was found reaching on average 12 ppbv.
- On weekdays as well as on weekends the average O₃ mixing ratio build up from 08:00 UTC with peak mixing ratios of 45 ppbv at 14:00 UTC. Despite the variation of the O₃ mixing ratio due to different photochemical activity, on weekdays the build up of [O3] is belated due to a drop during the morning rush hour caused by the emission of NO.
- The influence of the local emission from traffic was seen on the RO₂^{*} mixing ratio in a broadening of the diurnal cycle.

The RO_2^* mixing ratio data was limited to periods with a RH below 75% due to an increase of the uncertainty in the CL. This fact restricted the data set, especially during evening and night periods. A method for the calibration of the instrument at higher RH could increase the data set for future measurements.

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