Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state

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Abstract. Ozone (O3) is a photochemical oxidant, an air pollutant and a greenhouse gas. As the main precursor of the hydroxyl radical (OH) it strongly affects the oxidation power of the atmosphere. The remote marine boundary layer (MBL) is considered an important region in terms of chemical O3 loss; however surface-based atmospheric observations are sparse and the photochemical processes are not well understood. To investigate the photochemistry under the clean background conditions of the Southern Atlantic Ocean, ship measurements of NO, NO2, O3, J(NO2), HO2, OH, ROx and a range of meteorological parameters were carried out. The concentrations of NO and NO2 measured on board the French research vessel Marion-Dufresne (28°S–57°S, 46°W–34°E) in March 2007, are among the lowest yet observed.

The data is evaluated for consistency with photochemical steady state (PSS) conditions, and the calculations indicate substantial deviations from PSS (ϕ > 1). The deviations observed under low NOx conditions (5–25 pptv) demonstrate a remarkable upward tendency in the Leighton ratio (used to characterize PSS) with increasing NOx mixing ratio and JNO2 intensity.

It is a paradigm in atmospheric chemistry that OH largely controls the oxidation efficiency of the atmosphere. However, evidence is growing that for unpolluted low-NOx (NO + NO2) conditions the atmospheric oxidant budget is poorly understood. Nevertheless, for the very cleanest conditions, typical for the remote marine boundary layer, good model agreement with measured OH and HO2 radicals has been interpreted as accurate understanding of baseline photochemistry. Here we show that such agreement can be deceptive and that a yet unidentified oxidant is needed to explain the photochemical conditions observed at 40°–60°S over the Atlantic Ocean.

1 Introduction

The remote MBL occupies about 25% of the Earth’s surface and provides optimal conditions to study baseline photochemical processes (Monks et al., 1998; Penkett et al., 1997). Ozone plays a central role in atmospheric chemistry as the primary precursor of OH radicals through its photodissociation by solar ultraviolet radiation (Levy, 1971). In the troposphere, including the MBL, O3 is formed through the oxidation of NO into NO2 (Crutzen et al., 1994; Logan, 1981). The subsequent photodissociation of NO2 yields ground state oxygen, which combines with molecular oxygen:

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad (\lambda < 424 \text{ nm}) \]  

\[ \text{O} + \text{O}_2(+\text{M}) \rightarrow \text{O}_3(+\text{M}) \]  

(M is an air molecule that removes excess energy)

In turn, ozone can regenerate the NO2, which together with Reactions (R1) and (R2) constitutes a null-cycle:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  

In conditions where NO-to-NO2 conversion is dominated by Reaction (R3), the overall process can be described by the “Leighton ratio” \( \varphi \), representing photostationary steady state (PSS), typically achieved within minutes (Leighton, 1961):

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\[ \varphi = \frac{J_{NO_2}[NO_2]}{k_3[O_3][NO]} \]  

Equation (1)

\( J_{NO_2} \) is the photodissociation frequency of NO\(_2\) and \( k_3 \) the rate coefficient of Reaction (R3). In the polluted high-\( NO_x \) atmosphere \( \varphi \) is unity (Carpenter et al., 1998; Parrish et al., 1986; Thornton et al., 2002; Yang et al., 2004). In moderately polluted environments radical reactions play a proportionally larger role in the conversion of NO to NO\(_2\) and \( \varphi \) is typically \( > 1 \) (Hauglustaine et al., 1999; Mannschreck et al., 2004; Ridley et al., 1992; Volz-Thomas et al., 2003). In this case the reactions of peroxy radicals \( HO_2 \) and RO\(_2\) with NO compete with Reaction (R3) (R represents an alkyl group, in the clean marine atmosphere mostly CH\(_3\)O\(_2\) from CH\(_4\) oxidation) (Crutzen et al., 1994).

In fact by only considering Eq. (1) we are disregarding additional reactions which are expected to be important at low \( NO_x \), i.e. that of NO with \( HO_2 \) and RO\(_2\). Thus we need to expand the denominator of Eq. (1) with the following reactions to account for the NO\(_2\) source terms:

\[ HO_2 + NO \rightarrow NO_2 + OH \]  

Equation (R4)

\[ RO_2 + NO \rightarrow NO_2 + RO \]  

Equation (R5)

By rearranging in order to calculate the NO\(_2\) concentration at PSS we obtain:

\[ [NO_2]_{\text{calculated}} = \frac{(k_3[O_3] + k_4[HO_2] + k_5[RO_2])[NO]}{J_{NO_2}} \]  

Equation (2)

Several researchers have actually used the measured deviation from \( \varphi = 1 \) to estimate the concentration of peroxy radicals (Cantrell et al., 1997; Hauglustaine et al., 1999; Mannschreck et al., 1986; Ridley et al., 1992; Thornton et al., 2002). There is a general disagreement among the theoretically calculated RO\(_x\) concentrations and the observed and modeled calculated RO\(_x\). This is also the case in the study as discussed below.

One cause for such disagreement could be an unknown or non-quantified oxidation pathway which can result in the additional oxidation of NO to NO\(_2\). Since it is unaccounted for in the Leighton ratio this leads to a significant overestimation of the theoretically calculated RO\(_x\) compared to measured or model calculated RO\(_x\). One additional pathway leading to deviations of \( \varphi = 1 \), relevant for the MBL, is the reaction of NO with halogen monoxides (XO) (Carpenter et al., 1998; Read et al., 2008; Yang et al., 2004). XO (ClO, BrO or IO) can convert NO to NO\(_2\) via the reaction:

\[ XO + NO \rightarrow NO_2 + X. \]  

Equation (R6)

Halogen oxides have been observed in remote marine regions (Yang et al., 2004) and possible XO contribution to the PSS of NO\(_x\) and O\(_3\) is discussed in more detail below.

Deviations also occur when loss processes for O\(_3\) other than Reaction (3) become significant, so that O\(_3\) is no longer in steady state. The additional loss processes can be O\(_3\) photolysis, reactions of O\(_3\) with NO\(_2\), alkenes and radicals. At sunrise and sunset deviations are expected from unity due to small \( J_{NO_2} \) values, therefore steady state assumptions are not valid.

If the reaction time is not sufficient after perturbations in concentration of gases in the air mass e.g. due to source pollution, then PSS assumption is not valid. The decomposition of reservoir species such as Peroxy Acetyl Nitrate (PAN) as additional NO\(_2\) sources can also result in deviations from PSS. Reaction rates in the Leighton equation are also important for PSS calculations. The calculated ratios are significantly influenced by the uncertainties in the reaction rates of \( k_1, k_2 \) and \( k_3 \). Uncertainties in the measured values of \( J_{NO_2}, O_3, NO, NO_2 \) and RO\(_x\) are another important factor. It is vitally important to carry out accurate, precise and simultaneous measurements of the mentioned species in order to better understand the causes for deviations.

Here we present evidence that, indeed, PSS photochemistry is well characterized in polluted conditions, including the MBL. But in the low-\( NO_x \) conditions encountered during a ship cruise, sailing between the southern tips of South America and South Africa in the austral summer of 2007, we observed major deviations in \( \varphi \) that cannot be reconciled with the prevalent theory, indicating a major gap in our understanding of baseline atmospheric photochemistry.

2 Experimental

2.1 Cruise MD160

The Marion Dufresne cruise, referred to as MD160, took place during the late austral summer, from 1 March 2007 in Punta Arenas, Chile (70.85\(^\circ\)W, 53.12\(^\circ\)S), to 23 March 2007 in La Réunion Island (55.36\(^\circ\)E, 21.06\(^\circ\)S). The cruise was part of the OOMPH project (Ocean Organics Modifying Particles in both hemispheres, see: www.atmosphere.mpg.de/enid/oomph). The ship crossed the southern Atlantic Ocean from west to east between approximately 60\(^\circ\)S to 20\(^\circ\)S (Fig. 1). In this region of the globe strong westerlies prevail and severe weather and sea conditions are common, as indicated by the terms “Roaring Forties” and “Furious Fifties”.

During the first part of the campaign drifting icebergs from Antarctica were often encountered, associated with cold air from the Southern Ocean. During this period cloud cover was extensive with periods of rain and sometimes snow. In contrast, during the second part of the campaign, cruising towards the African continent, both the temperature and radiation levels increased. The westerly wind speeds varied in strength from calm conditions up to 33 m s\(^{-1}\). Occasionally, gale force winds (>17 m s\(^{-1}\)) occurred. The average wind speed was 10 m s\(^{-1}\) during the first half and 8 m s\(^{-1}\) in the second part of the campaign. Further details can be found in (Williams et al., 2010).
Fig. 1. The Marion Dufresne cruise track over the South Atlantic Ocean.

2.2 Instrumental methods

The most common meteorological measurements were performed, and in addition also balloon soundings, flux measurements and calculations of air flow dynamics and turbulence around the ship. In situ gas phase measurements included O$_3$, CO, OH, HO$_2$, RO$_x$ (RO + RO$_2$ + HO$_x$), NO and NO$_2$ concentrations as well as organic species like dimethyl sulphide (DMS), isoprene and halocarbons. Measurement of photodissociation frequencies were also performed on board the ship. The NO$_x$ and non-methane hydrocarbon concentrations measured were among the lowest reported to date. During pristine background conditions average ozone mixing ratios were 19.6 ($\pm$0.6) ppbv and NO$_x$ mixing ratios 13.4 ($\pm$5.8) pptv ($\pm1\sigma$ standard deviation). Note that the NO$_x$ data used in the following calculations exclude those that were below the total uncertainty ($2\sigma$) of the NO and NO$_2$ measurements, 1.5 and 2.2 pptv, respectively, though the results and conclusions are robust and consistent by including all data. We focus on the period 13–18 March 2007 during which a complete data set was obtained in air that spent at least 10 days over the Southern and South Atlantic Oceans and Antarctica without contact with air masses near the South American and African continents (Hosaynali Beygi, 2010).

2.2.1 NO$_x$ and O$_3$ measurements

The instrument used to measure NO$_x$ and O$_3$ is a high resolution and highly sensitive 3-channel chemiluminescence detector (CLD, ECO-Physics CLD 790 SR) which carries out simultaneous in situ measurements of NO$_2$, NO and O$_3$. The instrument was originally manufactured as a two channel system by ECO Physics Inc., Dürnten, Switzerland, and has been modified. One important modification has been the addition of a third channel for the measurement of O$_3$ (Hosaynali Beygi, 2010).

To guarantee data quality, calibrations were performed during the campaign via the addition of a standard gas directly to the sample lines of the 3 channels. NO in N$_2$ (2.191 $\pm$ 0.044 ppmv, Air Liquide, Germany) was used as a calibration gas. The gas had a flow of 3.93 sccm and was diluted to mixing ratios of approximately 2 ppbv by synthetic air (SA). This standard was compared to a primary standard (4.83 $\pm$ 0.05 ppmv, NIST, USA) before and after the campaign. The NO and NO$_2$ channels were calibrated at least once per day.

Bottled synthetic air (Air Liquide, Germany), a zero air generator and a Purafil cartridge were employed in order to achieve optimum zeroing conditions for the CLD instrument. The bottled synthetic air used had a purity of 5.0 (corresponding to 99.9990 %) and the air consisted of a mixture of O$_2$ (20.5 %) and N$_2$ (the rest) produced by Air Liquide, Germany.
Table 1. Average and standard deviation of zero gas measurements for NO.

<table>
<thead>
<tr>
<th>Date</th>
<th>Average “zero gas” (pptv)</th>
<th>STDEV “zero gas” (1σ, pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.03.07</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>14.03.07</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>15.03.07</td>
<td>0.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Since the synthetic air can potentially contain interfering species a zero air generator was used. The zero air generator (CAP 30, Headline Filters GmbH, Germany) consisted of Pd and Pt catalysts and operated at a temperature of 370°C. It was primarily used to remove hydrocarbons, aerosols and fine dust from bottled air used for zeroing of the instrument. Prior to the campaign the effects of a different variety of Purafil compounds were tested on the quality of the zero air in the laboratory. To avoid Purafil dust contamination, filters were used to prevent contamination of the inlet line and reaction chambers by the Purafil cartridge. The average and standard deviation of zero gas measurements for the NO channel are presented in Table 1. The indicated values have been calculated using the original 2 s data.

The conditions under which the measurements were performed were ideal in terms of testing the zeroing of the instrument. Since measurements were made in a pristine region without direct anthropogenic source pollution, it may be assumed that night time values measured during these periods are based on the complete conversion of NO to NO$_2$. Due to the lack of solar radiation the back-conversion of NO$_2$ to NO does not take place and therefore in a remote location without local NO$_x$ sources the NO mixing ratio is expected to equal zero. The standard deviation of the measured night time values was compared to the standard deviation of the SA measurements. They were in very good agreement, which corroborates the high quality (purity) of the synthetic gas (Tables 1 and 2).

The background signal of the three channels was determined with SA measurements and corrected for in the data. The detection limit (DL) of the measured species in this study was determined based on the reproducibility of the SA measurements carried out on a daily basis throughout the campaign. The DL, based on a 2σ confidence level and 60 s integration time, is 0.47 pptv, 0.51 pptv, and 18.2 pptv for the NO, NO$_2$ and O$_3$ channels, respectively.

Table 2. Observed night time NO during pristine background conditions.

<table>
<thead>
<tr>
<th>Date</th>
<th>Median night time (pptv)</th>
<th>Average night time (pptv)</th>
<th>STDEV night time (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.03.07</td>
<td>0.12</td>
<td>0.12</td>
<td>1.31</td>
</tr>
<tr>
<td>14.03.07</td>
<td>0.18</td>
<td>0.18</td>
<td>1.32</td>
</tr>
<tr>
<td>15.03.07</td>
<td>0.84</td>
<td>1.01</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Fig. 2. BLC spectral information. The narrow wavelength range of the solid state LED’s avoids effects of interfering species (source: BLC instrument manual, Droplet measurement technologies, USA).
was the case during the campaign). The CE is also affected by the flow rate. High flow rates result in shorter residence times within the BLC and consequently lead to a lower CE. The residence time within the BLC was 1 s.

High specificity is achieved by the narrow spectral output of the LEDs. The peak absorption cross section for NO\(_2\) is at 390–400 nm, i.e. the wavelength range of the LEDs. This precludes the conversion of potential interfering species such as HONO, NO\(_3\) and PAN (Fig. 2). This is discussed in more detail in Sect. 3.3.

The efficiency of the converter has been determined by gas phase titration (GPT) of NO with O\(_3\), before and during the campaign using a commercial instrument (ANSYCO GmbH, Karlsruhe, Germany). The calibration technique is based on the rapid gas phase reaction between NO and O\(_3\) to produce stoichiometric quantities of NO\(_2\). For this purpose both synthetic air and NO calibration gas were used. The quantitative knowledge of this reaction is such that when the NO concentration is known, the concentration of NO\(_2\) can be determined. O\(_3\) is added to NO in a dynamic calibration system, and the NO channel of the CLD detector is used as an indicator of changes in NO concentration. A UV lamp is located inside the GPT instrument to generate O\(_3\). Upon addition of O\(_3\), the decrease in NO concentration observed in the calibrated NO channel is equivalent to the concentration of NO\(_2\) produced. From these values the CE of the BLC can be estimated.

As mentioned above, standard GPT, calibrations and zeroing of the instrument were carried out which are considered adequate to calculate the uncertainty and conversion efficiency. The efficiency of the BLC did not change significantly throughout the course of the campaign. The conversion efficiency during the period of study was 59\% with an uncertainty of ±1.8\%. The average and standard deviation of zero gas measurements for the NO\(_2\) channel are presented in Table 3. There is ~10 pptv offset during zeroing of the instrument. This offset was not seen once the blue light converter (BLC) was switched off. To correct for this the offset has been subtracted from the measurements; therefore, NO\(_2\) values after correction are approximately 10 pptv lower than the measured signal.

The O\(_3\) channel was calibrated using a commercial O\(_3\) calibrator, (model TE49C, Thermo instruments GmbH, Germany) several times during the campaign. The only gas required for this measurement is SA which is fed directly into the O\(_3\) calibrator. Subsequently, O\(_3\) is produced by the O\(_3\) calibrator based on the specified set points e.g. 0 ppbv, 10 ppbv, 20 ppbv, ... 100 ppbv, etc. The value measured by the CLD is read and compared to the actual set point value of the O\(_3\) calibrator.

The precision of the NO, NO\(_2\) and O\(_3\) channels deduced from the sum of the DL and the reproducibility of the infield calibrations was 0.47 pptv +2.68\% (of total reading) for NO, 0.51 pptv +2.68\% for NO\(_2\) and 0.02 ppbv +1\% for O\(_3\), based on a confidence level of 2\(\sigma\) and 60 s integration time.

The accuracy is calculated based on the total sum of the accuracy of the calibration standards used and also the uncertainty due to the offset corrections. The accuracy for the NO\(_2\) channel additionally contains the uncertainties in the conversion efficiency of the BLC. The accuracy is 1.4 pptv +2\% for the NO channel, 1.5 pptv +2\% for the NO\(_2\) channel and 0.5 ppbv +1\% for the O\(_3\) channel.

The total uncertainty of the mixing ratio of a species can be determined by using the error propagation equation

\[
(\Delta C)^2 = \left(\frac{\partial C}{\partial E_1}\Delta E_1\right)^2 + \left(\frac{\partial C}{\partial E_2}\Delta E_2\right)^2 + \left(\frac{\partial C}{\partial E_3}\Delta E_3\right)^2 + ... \tag{3}
\]

\(E_x\) represents the different parameters with their uncertainties (\(\Delta E_x\)). Hence the total uncertainty based on the calculations of precision and accuracy is 1.5 pptv +3.3\% (of total reading) for the NO channel, 2.2 pptv +5.3\% for the NO\(_2\) channel and 0.5 pptv +1\% for the O\(_3\) channel.

The CLD instrument was setup inside a container which was located on the deck of the ship (Fig. 3). Air was sampled through a Teflon inlet line which was mounted on top of the atmospheric mast 10 m above the foredeck and approximately 20–25 m above the sea surface. From there an inlet line was installed to the container. The Teflon inlet line was placed inside black tubing in order to prevent photochemistry taking place in the inlet line. The total length of the inlet line was 17.1 m and consisted of 1/2" Teflon tubing (outer diameter). The last meter of the inlet line consisted of 1/4" Teflon tubing.

During the campaign the membrane pump maintained a flow of 19.2 SLM. The instrument preserved a total flow rate of 2.25 SLM by the use of a scroll pump. A peroxide analyzer (Aero-laser AL2021) shared the inlet line with the CLD instrument and applied a flow of 3 SLM. Therefore a total flow of 24.45 SLM was maintained in the inlet line. This corresponds to a retention time of 3.4 s. The data was corrected for the residence time.

Inlet line calibrations and zeroing were carried out using a commercial GPT instrument. The standard GPT procedure is followed once in front of the inlet line and subsequently without the inlet line, directly connected to the instrument. Through a series of steps and comparison of the measured values in the two modes the amount of NO lost in the line can be estimated. For the MD160 campaign it is estimated that NO loss due to residence in the inlet line is less than 2\%. Note that zero gas calibrations with and without the inlet line rule out potential memory effects. There were also concerns regarding the inlet perturbations on NO\(_2\) e.g. PAN decomposition. The amount of NO\(_2\) produced in the inlet line through the reaction of NO with O\(_3\) was calculated for different periods of the study. It was found that the contribution due to this reaction was of the order of 1\% or less of the total NO\(_2\) mixing ratio.

With regard to PAN decomposition, it is important to stress that PAN is relatively stable under the conditions the measurements were carried out, due to the low temperatures,
which varied on average between 3 °C and 11 °C from 13 to 15 March, respectively. We calculated that PAN under the measurement conditions has an average lifetime of more than 1 day (see Sect. 3.3). We also calculated that in order for PAN to produce 7 pptv of additional NO\textsubscript{2}, via thermal decomposition very high concentrations of PAN would be needed, i.e. at least several hundred pptv, which was not observed during the campaign.

2.2.2 Radical and \( J_{\text{NO}_2} \) measurements

For the data analysis several parameters measured with other instruments were used. The most important details of the instruments are presented next.

OH and HO\textsubscript{2} were measured with the HORUS instrument (HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy), which uses laser-induced fluorescence (LIF) of the OH molecule, based on the fluorescent assay by gas expansion (FAGE) technique. A detailed description of the instrument is given in (Martinez et al., 2010). The time resolution for OH and HO\textsubscript{2} detection is 10 s. The precision for a 60 s integration time and a confidence level of 1σ is 0.017 pptv for OH and 0.1 pptv for HO\textsubscript{2}. The accuracy is ±35 % for a confidence level of 2σ. The DL of the instrument is defined as the 2σ precision, assuming it is limited by the background noise.

The photodissociation rate of NO\textsubscript{2}, \( J_{\text{NO}_2} \), was measured using two (up- and downward) 2\( \pi \)-steradian (sr) filter radiometers (Meteorologie Consult GmbH, Germany), thus providing 4\( \pi \)-sr photodissociation rates. The instrument has a precision of 5 % for 1 s data and an accuracy of 10 %. The basic design is adopted from the device described by (Junkermann et al., 1989). The principles of \( J_{\text{NO}_2} \) filter radiometry are explained by (Volz-Thomas et al., 1996). The radiometer is annually calibrated at the research centre FZ-Jülich. Long term calibrations show a small variation (below 2 %, 1σ) during one year.

RO\textsubscript{x} was measured using a peroxy radical chemical amplifier (PERCA). The PERCA technique was introduced in the early 1980s (Cantrell et al., 1997) and has been widely used since then (Parker et al., 2009). The detector is calibrated by the addition of NO\textsubscript{2} and the chain length is calibrated by the addition of known concentrations of CH\textsubscript{3}O\textsubscript{2}. During MD160 the instrument was placed on top of the atmospheric mast above the foredeck. The PERCA instrument is sensitive to humidity hence a water correction is applied to all data. One data point was obtained per minute, however due to calibrations actual measurements are available every other minute. The uncertainty in the PERCA measurements leads to an accuracy of 36 %. The uncertainty and DL of the relevant instruments used in this work are summarized in Table 4. For each measurement the total uncertainty is determined by the highest of the two values (pptv or %).

Fig. 3. Schematic of the Marion Dufresne to illustrate the position of the instrument container (black box) relative to the atmospheric mast (Zorn et al., 2008).
Table 4. Total uncertainty of the instrumentation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>Total uncertainty</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>CLD</td>
<td>1.5 pptv + 3.3 %</td>
<td>0.47 pptv</td>
</tr>
<tr>
<td>NO₂</td>
<td>CLD and BLC</td>
<td>2.2 pptv + 5.3 %</td>
<td>0.51 pptv</td>
</tr>
<tr>
<td>O₃</td>
<td>CLD</td>
<td>0.5 ppb + 1 %</td>
<td>18.2 pptv</td>
</tr>
<tr>
<td>J_NO₂</td>
<td>Filter radiometer</td>
<td>11 % (2σ 1 s)</td>
<td>1.5 × 10⁻⁶ (s⁻¹)</td>
</tr>
<tr>
<td>HO₂</td>
<td>LIF instrument</td>
<td>0.1 pptv + 35 %</td>
<td>0.2 pptv</td>
</tr>
<tr>
<td>OH</td>
<td>LIF instrument</td>
<td>0.017 pptv + 35 %</td>
<td>0.034 pptv</td>
</tr>
<tr>
<td>RO₂</td>
<td>PERCA</td>
<td>10 pptv + 36 %</td>
<td>10 pptv</td>
</tr>
</tbody>
</table>

3 Results and discussions

3.1 Back trajectory calculations and data filtering

Meteorological data and the Lagrangian Analysis Tool (LAGRANETO) were used to calculate the 10-day back trajectories of the air masses (Wernli and Davies, 1997).

Every 3 h about 10 trajectories were started within a 30 min time interval at the ship position along the cruise track. The path of the trajectories was calculated using three-dimensional wind fields from the European Centre for Medium-Range Weather Forecasts (ECMWF). For the analysis, 6-h operational global analyses are complemented by intermediate 3-h forecasts interpolated onto a horizontal grid with a resolution of 1° latitude/longitude. The horizontal resolution of the model is 25 km using 91 vertical levels. The computational time step for trajectory calculations is 30 min.

The 10-day back-trajectories show that the air masses came from the Southern and South Atlantic Ocean until 21st March, and that they originated mostly in the free troposphere, subsiding to the boundary layer before the measurements. Considering the air mass origins over the Antarctic continent and the surrounding oceans, the likelihood of anthropogenic contamination is small.

Depending on the wind direction and speed, the ship exhaust can be a source of contamination. During some periods wind from the rear gave rise to local pollution, which could be easily identified in many of the trace gas measurements. To exclude these events, measurement data with exhaust contamination were removed. The optimum filtering process was selected after considering a range of techniques and criteria. For the data used in PSS calculations additional J_NO₂ filtering and a filter based on the uncertainty of the channels were applied.

The criteria for data exclusion included the wind direction relative to the direction of the ship, and signs of exhaust contamination in the CLD data. Pollution was observed when the wind came from 55° and 275° relative to the ship (0° is the cruise direction). Further, a rigorous NO filter (based on 2 s measurements) was applied by removing outliers (3σ relative to the 24 h average).

To carry out precise and accurate PSS calculations two additional filters were used. In the remote MBL the NO and NO₂ concentrations are very low and close to the detection limit of the instrument. To ensure data quality a third filter was set up using the total uncertainty based on the calculations of precision and accuracy of the NO and NO₂ channels. Any data point which was below the total uncertainty limit of the relevant channel was excluded. The 2σ uncertainty for the NO and NO₂ channels are 1.5 pptv and 2.2 pptv, respectively. To investigate the influence of this procedure, PSS calculations were carried out both with and without the uncertainty filter. The results of the two sets of calculations did not show significant differences.

Furthermore, PSS calculations are sensitive to uncertainties in J_NO₂. At low J_NO₂ values, e.g. during sunrise and sunset, deviations from PSS are expected. Therefore only data for J_NO₂ > 0.001 s⁻¹ have been used.

3.2 The Leighton ratio

Figure 4 presents the Leighton ratios based on our observations in the unpolluted MBL. Considerable deviations from unity are evident, as predicted by previous studies.
(Hauglustaine et al., 1999; Mannschreck et al., 2004; Parrish et al., 1986; Volz-Thomas et al., 2003). However, noteworthy is the trend in $\varphi$ in the low-NO$_x$ regime, at variance with previous reports, and consistently observed during several days. If RO$_2$ were a significant contributor to NO-to-NO$_2$ conversion, it would have been expected that the maximum influence on $\varphi$ and deviations from unity occur at the lower end of the NO$_2$ axis, i.e. around 3 pptv, and that the divergence decreases with increasing NO$_2$. This tendency is actually observed in the moderately polluted air masses near South Africa (70–400 pptv NO$_2$) and close agreement is found for an air mass that was polluted by a passing ship (~1 ppb$_v$) (Fig. 4).

The $J_{\text{NO}_2}$ colour coding shows that the maximum deviations are not at the lowest NO$_2$ and $J_{\text{NO}_2}$ values, far from the established theory. In fact, for NO$_2$ mixing ratios less than 10 pptv and $J_{\text{NO}_2}$ below $3.4 \times 10^{-3}$ s$^{-1}$ we find that $\varphi \approx 1$ (within the uncertainty range). What is observed is that the maximum deviations in the unpolluted MBL occur at the highest NO$_2$ mixing ratios (10–20 pptv) and the highest solar radiation intensities (proportional to $J_{\text{NO}_2}$). This clearly indicates the importance of NO$_x$-mediated photochemistry. Unfortunately, no data are available for the 20–60 pptv NO$_2$ (30–100 pptv NO$_x$) regime, and we anticipate that a reverse tendency to that for 3–20 pptv NO$_2$ (5–30 pptv NO$_x$) may occur and an increasing dominance of Reaction (R3).

Next we analyze to what degree $\varphi \neq 1$ conditions can be explained by conventional theory, in particular by considering measurement uncertainties, and then also by making some assumptions about parameters that were not directly observed. The uncertainty in $\varphi$ in the low-NO$_x$ regime is mainly related to the NO and NO$_2$ measurement data.

For NO$_x$ mixing ratios in the pptv range the uncertainty resulting from the measurement of NO and NO$_2$ dominates the overall uncertainty, which increases with decreasing NO$_x$. Uncertainty estimates for PSS calculations have been reported to be up to 60% (Mannschreck et al., 2004). The overall uncertainty in the Leighton ratio $\varphi$ can be calculated through the sum of the individual uncertainties in each parameter using the following equation:

$$\Delta\varphi = \sqrt{\varphi^2 \sum (\frac{\Delta X_i}{X_i})^2}$$

(4)

$X_i$ represents $J_{\text{NO}_2}$, NO, NO$_2$, HO$_2$, O$_3$ and RO$_2$, depending on which form of the PSS equation is used. For example, for Eq. (1) the uncertainty is calculated as:

$$\Delta\varphi = \sqrt{\varphi^4 \left( \left( \frac{\Delta J_{\text{NO}_2}}{J_{\text{NO}_2}} \right)^2 + \left( \frac{\Delta \text{NO}_2}{\text{NO}_2} \right)^2 + \left( \frac{\Delta \text{O}_3}{\text{O}_3} \right)^2 + \left( \frac{\Delta \text{RO}_2}{\text{RO}_2} \right)^2 + \left( \frac{\Delta \text{NO}_x}{\text{NO}_x} \right)^2 \right)}$$

(5)

With the addition of parameters to the equation, the uncertainties are added to the total uncertainty. The uncertainties can be expressed as a function of the NO$_2$ mixing ratios. We estimate the 2$\sigma$ uncertainty in $\varphi$ at approximately 93%, 71%, 63% and 11% for NO$_2$ mixing ratios of 3, 5, 10 and 100 pptv, respectively.

As mentioned before by only considering Eq. (1), we are disregarding additional reactions which are expected to be important at low NO$_x$, i.e. that of NO with HO$_2$ and RO$_2$. Therefore in a further step Eq. (2) was used in order to calculate the NO$_2$ concentration at PSS. For this calculation we initially adopt [HO$_2$]$\approx$[RO$_2$], a reasonable assumption for conditions in which hydrocarbon chemistry is dominated by methane (Crutzen et al., 1994), hence [RO$_2$]$\approx$[CH$_3$O$_2$] (to be evaluated below). Our analysis indicates a 2$\sigma$ uncertainty of [NO$_2$]$_{\text{calculated}}$ based on Eq. 2) of about 108%, 89% and 82% at NO$_2$ mixing ratios of 3, 5 and 10 pptv, respectively.

If this expansion of Eq. (1) by including Reactions (R4) and (R5) would adequately account for NO-to-
This may again be an indication for an unknown photochemical change. In fact it is the same as for the classic Leighton ratio. That is, the maximum deviation seen in Fig. 7 is substantially lower compared with the values in Figs. 4 and 6. The trend seen in the deviation from \(\psi=1\) as a function of NO\(_2\) and \(J_{\text{NO}_2}\) in the pristine background air masses does not change. In fact it is the same as for the classic Leighton ratio. This may again be an indication for an unknown photochemically driven oxidant that can convert NO to NO\(_2\) and therefore leads to significant deviation from unity in the Leighton ratio.

The values for the passing ship period have not changed and are similar to those plotted in Fig. 4. This is a strong confirmation of the relative insignificance of RO\(_x\) reactions in high NO\(_x\) regimes.

Total uncertainties were calculated for the Leighton ratio, for several NO\(_2\) mixing ratios and are estimated to be 158\%, 147\% and 131\% for NO\(_2\) mixing ratios of 3, 5 and 10 pptv respectively. The uncertainties are higher than in previous cases due to the additional uncertainties in the peroxy instrument.

It is remarkable that the addition of PERCA derived peroxy radical concentrations causes such a strong change in the Leighton ratio and can to a large degree compensate for the high NO\(_2\) concentrations measured by the CLD instrument. Figure 8 presents time series of observed \(J_{\text{NO}_2}\) and radical species in addition to NO\(_x\) and O\(_3\). Maximum OH mixing ratios reach up to \(\sim0.3\) pptv, HO\(_2\) \(\sim17\) pptv and RO\(_x\) \(\sim150\) pptv. As the mixing ratios of the highly reactive OH and RO are low it may be assumed that their contribution to RO\(_x\) is minor. As a consequence maximum RO\(_2\) mixing ratios would exceed 100 pptv, clearly inconsistent with the above assumption that RO\(_2\) \(\approx\)HO\(_2\).

This assumption can be tested with a chemical box model, constrained by our measurements, and with output of a global chemistry-transport model.

A photochemical steady-state box model was used to simulate the ambient HO\(_x\), OH and CH\(_3\)O\(_2\) concentrations (RO\(_2\) \(\approx\)CH\(_3\)O\(_2\)). The model was set up and constrained using data obtained on the MD 160 cruise. The parameters used to constrain the box model are: H\(_2\), CH\(_4\), H\(_2\)O\(_2\), CH\(_3\)OOH, O\(_3\), NO, CO, latitude, longitude, pressure, air temperature, H\(_2\)O, JO\(_1\)D, \(J_{\text{NO}_2}\), and a number of photolysis rates based on radiation calculations using measured \(J_{\text{NO}_2}\) as input, JCHO\(_2\), JCOH\(_2\), JH\(_2\)O\(_2\), JCH\(_3\)OOH and JNO\(_3\). Steady state concentrations of OH, HO\(_2\) and CH\(_3\)O\(_2\) were calculated according to the method of (Kubistin et al., 2010). A model data point was calculated whenever the complete set of relevant data was available within a 10 s time period.

Under steady state conditions the production and loss rates for the radical species balance:

\[
\frac{d[X]}{dt} \approx 0 = P_x - L_x
\]

where \(P_x\) represents the total production and \(L_x\) the loss rate. By this approach the diurnal profiles of the radicals and their average concentrations could be reproduced well, as shown in Fig. 9. Figure 10 demonstrates that according to these calculations HO\(_2\) and CH\(_3\)O\(_2\) concentrations are very similar. This is in line with the observed CO/CH\(_4\) ratio, as expected according to the prevailing theory of atmospheric radical photochemistry, because the production of HO\(_2\) and...
Fig. 8. Measured diurnal profiles of NO, NO$_2$, O$_3$, $J_{\text{NO}_2}$, OH, HO$_2$ and RO$_x$ (note that NO$_x$ and O$_3$ data have been filtered for stack emissions).

Fig. 9. Comparison of model results with observations of OH and HO$_2$ (for NO < 20 pptv).

CH$_3$O$_2$ are dominated by the reactions of CO and CH$_4$ with OH, respectively.

A further test of the assumption of HO$_2$ \( \approx \) CH$_3$O$_2$ \( \approx \) RO$_2$ is based on calculations with an atmospheric chemistry general circulation model (AC-GCM). The ECHAM/MESSy Atmospheric Chemistry (EMAC) model describes lower and middle atmosphere processes and their interactions with oceans, land and human influences (Jöckel et al., 2010; Kerkweg et al., 2008). The dynamical core atmospheric general circulation model is the 5th generation European Centre Hamburg model ECHAM5 (Roeckner et al., 2006).

EMAC was applied in the T42L90-resolution, i.e. with a spherical truncation of T42 (corresponding to about $2.8^\circ \times 2.8^\circ$ latitude/longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. The model time step in this resolution is 12 min. Data from the model were sampled at each time step along the OOMPH transect. The results corroborate that for the clean background period until 17 March 2007
Fig. 10. Results from the chemical box model for daytime HO$_2$ and CH$_3$O$_2$, obtained by constraining the model with the measurements of non-radical species.

Fig. 11. Results from the global EMAC model for HO$_2$ and CH$_3$O$_2$. The model grid cells correspond with the locations and time periods of the measurements and the results shown in Fig. 10.

(EMAC predicts somewhat enhanced pollution influences thereafter, related to its coarse resolution), during daylight hours RO$_2$ and HO$_2$ concentrations are about equal (Fig. 11). A closer look at the RO$_2$ specie as predicted by EMAC, i.e. CH$_3$O$_2$, C$_3$H$_5$O$_2$, C$_3$H$_7$O$_2$ and C$_4$H$_9$O$_2$, reveals that CH$_3$O$_2$ is in fact the dominant RO$_2$ specie and that the mixing ratios of the other species compared to CH$_3$O$_2$ are negligible. Therefore based on EMAC predictions we can assume that RO$_2$ ≈ CH$_3$O$_2$. As mentioned above, based on previous knowledge this is a reasonable assumption for conditions in which hydrocarbon chemistry is dominated by methane.

The results from both the box model and EMAC corroborate the expectation that RO$_2$ ≈ CH$_3$O$_2$ ≈ HO$_2$. Therefore this assumption is valid based on current knowledge of the MBL chemistry and represented by state-of-the-art models. The realistic representation of HO$_x$ by our constrained box model, in agreement with the global model, is supported by the favourable comparison between the model output and measurements (Fig. 9). However at the same time a significant inconsistency results from the comparison of model calculated and measured RO$_x$ data. A number of studies have been carried out in which measurements of peroxy radicals have been compared with PSS-based calculations and model results, typically under moderately polluted (>50 pptv NO$_x$) or highly polluted conditions (up to several ppbv NO$_x$) (Cantrell et al., 1997; Carpenter et al., 1998; Hauglustaine et al., 1999; Ridley et al., 1992; Volz-Thomas et al., 2003). Generally, RO$_2$ concentrations calculated by the PSS assumption were significantly higher than the directly measured values. It is remarkable that both our

Fig. 12. PERCA measured RO$_x$ vs. RO$_x$ based on LIF measured HO$_2$ and an estimate of CH$_3$O$_2$ (assuming RO$_2$=CH$_3$O$_2$ and that CH$_3$O$_2$ ~HO$_2$). The red dashed line illustrates the 1:1 line.

Fig. 13. PERCA measured RO$_x$ vs. PSS calculated RO$_x$. The red dashed line illustrates the 1:1 line.
Fig. 14. Results from the chemical box model, constrained by the measurements, assuming a Leighton ratio of \( \varphi = 1 \).

PSS-derived and observed RO\(_x\) are much higher than those predicted by the models and based on previous knowledge, which is demonstrated in Figs. 12 and 13, which show a scatter plot of RO\(_x\) based on LIF measured HO\(_2\) and an estimate of CH\(_3\)O\(_2\) (assuming RO\(_2\)=CH\(_3\)O\(_2\) and that CH\(_3\)O\(_2\) \~ HO\(_2\)) and PSS derived RO\(_x\) versus measured RO\(_x\), respectively. Figure 12 nicely demonstrates that our understanding of the radical chemistry in the MBL based on our current understanding and also based on box models and 3-D model results accounts for less than 20% of the measured “peroxy” radicals. The equation is RO\(_x\)(HO\(_2\)+CH\(_3\)O\(_2\)) = 0.25 RO\(_x\)(PERCA) − 0.59. The slope we see in the plot is as anticipated with an \( R^2 \) value of 0.64. Figure 13 confirms that the atmosphere (PSS) and the PERCA see similar results, i.e. similar amounts of “peroxy” radicals or more generally peroxy radicals plus a mystery oxidizer that converts NO to NO\(_2\) and undergoes amplification in the PERCA. The equation in this case is RO\(_x\)(PSS) = 1.27 RO\(_x\)(PERCA) − 10.63. Although the data scatter around the 1:1 line, the correlation coefficient is rather poor.

This difference can be interpreted in two ways. First there may be systematic errors involved in measuring and calculating RO\(_x\) and RO\(_2\). Second there is an unknown photochemical oxidant that converts NO into NO\(_2\). The process apparently maintains the OH/HO\(_2\) relationship, as indicated by Fig. 9; and the effects vanish as NO\(_x\) increases. The fact that the RO\(_x\) mixing ratios are so high suggests that the PERCA instrument is also sensitive to the unknown oxidant (to be discussed below). Actually, the RO\(_x\) measurements provide independent observational support of an unknown oxidant that causes the anomalous Leighton ratios.

### 3.3 BLC and potential interfering species

The peak absorption cross section for NO\(_2\) is at 390–400 nm, i.e. the wavelength range of the LEDs. This precludes the conversion of potential interfering species such as HONO, NO\(_3\) and PAN (Fig. 2).

Furthermore, based on the very low PAN concentrations calculated by our atmospheric chemistry general circulation model (EMAC, discussed in article) and PAN measurements during the campaign, which were below the DL of the instrument (10 pptv), potential interferences from this species are highly unlikely, as several hundred pptv would be required to cause significant effects through thermal decomposition. Also due to the relatively low temperatures during the cruise, the lifetime of PAN was calculated to be about 1.2 days, indicating that it is thermally stable under the measurement conditions.

To investigate which species could cause possible interferences in the BLC, the absorption cross sections (ACS) of many species were studied and compared to the ACS of NO\(_2\) for three different wavelengths, i.e. 390, 395 and 400 nm (source: the MPI-Mainz spectral atlas at http://www.atmosphere.mpg.de/enid/2295). Species which have been suggested as potentially interfering are PAN, nitrous and nitric acid (HONO and HNO\(_3\)), alkyl nitrates (e.g. methyl nitrate and ethyl nitrate), and halogen nitrates (BrONO\(_2\), ClONO\(_2\), CINO, ClNO, ClNO\(_2\) and BrNO\(_2\)). The results of this study are summarized in Table 5.

The NO\(_2\) equivalent of each species needed to produce 7 pptv of additional NO\(_2\) was calculated and is listed in Table 5. A dash in the table means that there is no corresponding ACS for the species in the wavelength of interest.

From Table 5 it can be concluded that these species may not be expected to cause significant interferences in the BLC. BrNO\(_2\) is the only specie with an ACS close enough to that of NO\(_2\) at the wavelength of interest. However calculation of the mixing ratio of BrNO\(_2\) needed to produce 7 pptv of NO\(_2\) shows that on average 26 pptv would be required, which we consider highly unlikely in view of the model calculations presented in the article.
is added to the air mixture containing RO$_2$ by Chemical Amplification (PERCA) method. In a study by (Perner et al., 1999) it was observed that the method is sensitive to ClO$_x$ (Cl+ClO+ClO$_2$). It was found that ClO$_x$ is reduced by NO to Cl atoms which react with CO in the presence of O$_2$:

\[ \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \]  (R13)

\[ \text{Cl} + \text{CO} + \text{M} \rightarrow \text{CICO} + \text{M} \]  (R14)

The reaction sequence which is initiated oxidizes CO to CO$_2$ and NO to NO$_2$:

\[ \text{CICO} + \text{O}_2 + \text{M} \rightarrow \text{CICO}_3 + \text{M} \]  (R15)

\[ \text{CICO}_3 + \text{NO} \rightarrow \text{Cl} + \text{CO}_2 + \text{NO}_2 \]  (R16)

The chain length for ClO$_x$ species in the study by Perner et al. was reported to be 300 ± 60. In parallel peroxy radicals are indicated with a chain length of 160 ± 15. Therefore the chain length for ClO$_x$ is approximately a factor of two larger than that of the peroxy radicals. It is actually possible that the ClO$_x$ chain length could be up to a factor of 10 higher compared to the peroxy radical chain length (J. N. Crowley, personal communication, 2009). This would of course have a significant impact on the total observed “RO$_x$ signal”. Thus the chemical amplification method is not specific and does not indicate which radical chain is observed. Therefore the PERCA signal can be defined as:

\[ \text{PERCA signal} = \text{RO}_2 + \text{RO} + \text{HO}_2 + \text{OH} + \text{X} \]  (7)

X in the above equation is the additional unknown oxidant that can oxidize NO to NO$_2$ in the atmosphere and therefore lead to the high NO$_2$ levels measured during the campaign.

The possibility that unidentified NO-to-NO$_2$ conversions have affected our PERCA measurements actually reconciles the above two interpretations. The unexpected high RO$_x$ mixing ratios as measured with the PERCA instrument, being up to an order of magnitude higher than of measured HO$_2$ and of modelled HO$_2$ and RO$_2$ provides independent observational support for the presence of an unknown oxidant. Furthermore, its production is likely to be catalytic as it produces a strong signal in the PERCA instrument.

3.4 PERCA method and potential interferences

The most widely used method to measure RO$_x$ is based on the Peroxy Radical by Chemical Amplification (PERCA) technique (Cantrell et al., 1993; Penkett et al., 1997). NO is added to the air mixture containing RO$_2$ and HO$_2$, yielding NO$_2$, which can be detected by several methods. The PERCA method was also employed in our measurement campaign (Fleming et al., 2006). An inherent problem is that oxidants in addition to RO$_2$/HO$_2$ that convert NO into NO$_2$ are detected ambiguously. For example, it has been shown that halogen oxides (ClO$_x$), especially in the presence of CO, catalytically oxidize NO. The measurement principle of the PERCA method is based on the OH/NO$_2$ radical catalysed simultaneous chain oxidation of CO to CO$_2$ and NO to NO$_2$:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]  (R7)

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]  (R8)

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  (R9)

RO$_2$ measurement first requires the conversion of RO$_2$ to HO$_2$ via the following reactions:

\[ \text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{RO} \]  (R10)

\[ \text{RO} + \text{O}_2 \rightarrow \text{RCHO} + \text{HO}_2 \]  (R11)

\[ \rightarrow \text{R-CO-R} + \text{HO}_2 \]  (R12)

Subsequently HO$_2$ is detected through the same cycle as the first three reactions mentioned above. Therefore any oxidant that converts NO to NO$_2$ and has a sufficiently long chain length (i.e. the number of conversion cycles that occurs before termination) can be detected via the chemical amplification method. In a study by (Perner et al., 1999) it was observed that the method is sensitive to ClO$_x$ (Cl+ClO+ClO$_2$).
3.5 Halogen monoxides, DMS and the Leighton ratio

Several researchers have proposed that halogen monoxides can represent an “unknown oxidant” and drive $\phi$ away from unity, although their studies did not pertain to baseline MBL chemistry (Mannschreck et al., 2004; Matsumoto et al., 2006). Further, Read et al. (2008) conclude that biologically active regions of the tropical Atlantic Ocean release reactive halogens (up to 2.5 pptv BrO) and destroy ozone. This contrasts with our measurements in a region of very low biological activity. The part of the numerator in Eq. (2) between parentheses would have to be expanded by another term $k_d[XO]$, with X representing e.g. bromine. Both our chemical box and global chemistry-transport models include comprehensive descriptions of halogen chemistry in the MBL. Our model calculations indicate only very low concentrations of BrO in the measurement region (well below 1 pptv), one reason being that in the remote MBL the sea salt aerosol is hardly acidified by strong acids (e.g. $H_2SO_4$) of natural and anthropogenic origin. Back-calculating from Eq. (2), assuming that $[NO_2]_{\text{observed}}/[NO_2]_{\text{calculated}}$ is unity, implies that a BrO mixing ratio up to $\sim 100$ pptv would be required. This would represent a “bromine explosion” leading to the depletion of $O_3$ and $NO_x$, which is not observed.

We have used the chemical box model, which includes a comprehensive description of halogen chemistry (Kerkweg et al., 2008) to investigate the potential role of bromine in the observed deviation of the Leighton ratio. We constrained the model with the observations and applied an artificial emission of Br$_2$ from the sea salt aerosol (or a surface source) and increased the entrainment of ozone from the free troposphere to prevent its complete chemical destruction. For a Leighton ratio $\phi=1$ the simulated mixing ratio of BrO ranges from a few to more than 100 pptv at low to high solar intensity, respectively (Fig. 14a). These BrO mixing ratios are orders of magnitude higher than those simulated with a three-dimensional global model (Kerkweg et al., 2008). If the marine boundary layer chemistry would sustain such high BrO mixing ratios, it would be extremely difficult to explain the observed $O_3$ levels of $\sim 20$ ppbv. Figure 14b shows that 10–30 pptv BrO, for example, destroys 5–15 ppbv $O_3$ during the day, which would give rise to a strong diurnal cycle of $O_3$ in the boundary layer, which is not observed. Although we do not exclude that halogen chemistry takes place, it seems highly unlikely that reactive bromine accounts for the “mystery” oxidant.

The contribution of DMS has been considered as a potential source of peroxy radicals as this compound was measured during the campaign. However, the ship sailed across regions with very low biological activity at the time of the measurements, and mixing ratios of DMS, and other volatile organic compounds (VOCs) such as isoprene, were rather low, i.e. DMS averaged about 50 pptv, which is too low to have a significant effect.

3.6 Uncertainty related to rate coefficients

The uncertainty related to the rate coefficients of relevant reactions, $k_i$, is of course part of the overall uncertainty of the PSS calculations. It is believed that whilst $k_i$ does in fact contribute to the overall uncertainty of the results, there is little dispute over the actual $k_i$ values themselves. This was noticed in the sensitivity tests carried out on the PSS calculations using two studies of rate coefficients (e.g., Atkinson et al., 2004; Sander et al., 2006).

The two rate coefficients agree well within the range of uncertainty. Therefore it is concluded that the large deviations seen in the Leighton ratios cannot be due to the relatively insignificant uncertainty in the $k_i$ values.

The assumption that the reaction rate coefficients of RO$_2$ with NO are similar to that of HO$_2$ has been commonly used in the past. However, it has been suggested that the reaction rate coefficients of RO$_2$ and HO$_2$ could be critical for PSS calculations of ROx (Matsumoto et al., 2006). Therefore a sensitivity test was carried out in relation to rate coefficients, in this case specifically for RO$_x$ calculated from the PSS expression ($[RO_x]_{\text{PSS}}$). It was found that the reaction rates of NO with HO$_2$ and RO$_2$ are critical for the PSS estimation and that $[RO_x]_{\text{PSS}}$ can be influenced by uncertainties in the rate coefficients. Therefore it is recommended that the above assumption should be practiced with caution.

4 Conclusions

Our measurements provide compelling evidence of the presence of an unknown oxidant. It might only convert NO into NO$_2$, but also has the potential of participating in catalytic oxidant cycles, as indicated by the PERCA measurements. Note that even though the uncertainties increase with decreasing NO$_2$, at the very lowest levels of 3–5 pptv $\phi$ approaches one (Fig. 4), which argues against a measurement error to explain the exponentially increasing $\phi$-values at NO$_2$ mixing ratios up to 20 pptv. Although it is widely accepted that the oxidation chemistry of the troposphere is dominated by reactions with OH (Crutzen et al., 1994; Heard and Pilling, 2003; Logan et al., 1981), a growing number of studies exposes discrepancies between model calculations and observations in low-NO$_x$ conditions (Brune et al., 1998; Falloona et al., 2000; Hofzumahaus et al., 2009; Lelieveld et al., 2008; Stevens et al., 1997; Thornton et al., 2002). It is noteworthy that models and measurements of HO$_x$ in the remote MBL generally agree well, which has been optimistically interpreted as a consistent understanding of baseline photochemistry (Heard and Pilling, 2003; Sommeriva et al., 2004). However, taking all indications into account rather suggests that something important is missing in our understanding of baseline photochemistry.
Appendix A

Abbreviations and acronyms

ACS  Absorption cross sections
BLC  Blue light converter
CE   Conversion efficiency
CH$_3$O$_2$ Methyl peroxy radical
CLD  Chemiluminescence detector
DL   Detection limit
DMS  dimethyl sulfide
ECHAM European Centre Hamburg general circulation model
EMAC ECHAM/MESSy Atmospheric chemistry model
GPT  Gas phase titration
HO$_2$ Hydroperoxy radical
J$_{NO_2}$ Photolysis rate of NO$_2$
LED  Light emitting diodes
LIDAR Laser detection and ranging
LIF   Laser induced fluorescence
MBL  Marine boundary layer
MD   Marion Dufresne
MESSy Modular earth sub-model system
MPI  Max Planck Institute
NO   Nitrogen oxide
NO$_2$ Nitrogen dioxide
NO$_x$ Total sum of active nitrogen oxides (NO+NO$_2$)
OH   Hydroxyl radical
OMOPH Organics over Ocean Modifying Particles in both hemispheres
PAN Peroxy acetyl nitrate
PERCA Peroxy radical chemical amplifier
ppb, parts per billion
pptv parts per trillion
PSS  Photostationary state
RO$_2$ Organic peroxy radical
RO$_x$ Total sum of organic peroxy radicals
SA   Synthetic air
Sccm Standard cubic centimetres per minute
SLM  Standard liter per minute
STDEV Standard deviation
UV   Ultraviolet
VOC  Volatile organic compound

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