Atmos. Chem. Phys. Discuss., 11, C6931–C6947, 2011
www.atmos-chem-phys-discuss.net/11/C6931/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state" *by* Z. Hosaynali Beygi et al.

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Received and published: 26 July 2011

We would like to take this opportunity to thank the referee for the detailed comments and suggestions. We hope that by addressing these questions we have clarified the issues raised. Before addressing the questions raised by the referee we would like to point out, that we believe that the excess NO2 measured during this campaign is not an artifact or a fake signal. We have considered many possibilities during the course of the study and we could not come up with an experimental explanation for the excess NO2 as described in detail in the paper.

Major Comments:

1. I urge the authors to include the NO, NO2, and O3 data in Figure 8 prior to publication. (rather than showing individual days in the supplement). Answer: We agree. A new plot will be added to the revised manuscript including NO, NO2 and O3 as pointed out by the referee.

2a. The authors argue the small correction for NO losses and corresponding NO2 production in the inlet line based on gas phase kinetics. However, I miss a thorough discussion of potential NO conversion on the surface of the inlet line, which might be coated with sea salt. In fact, the NO loss/NO2 production required to explain the deviations from PSS are extremely small in absolute terms! Further, production of NO2 on surfaces might also contribute to the observed deviations. Answer: The loss of NO in the inlet line was tested using the standard calibration and zeroing techniques both upstream and downstream of the instrument, right before the pristine air measurements and on a separate occasion after this period to ensure data quality. Subsequently the NO loss in the line was calculated in percentage. This calibration and zeroing could not be performed more often since it would mean the loss of several hours of data, given our limited resources on a month long ship cruise. The calculations show loss of 2% for NO, which has already been taken into account in calculating the total uncertainty and is not sufficient to explain the high NO2 signal. In fact not only did we not see an increase in the NO2 signal, but our tests indicated that we have a small loss of NO2 in the inlet line. Therefore there is no evidence for the heterogenous production of NO2. We would like to point out again that the observed deviations in the NO/NO2 ratio can be clearly explained via the measured PERCA data, which shows that the potential unknown oxidant is seen by both independent instruments. The probability of two different instruments resulting in calculations that point to the same phenomena is extremely low.

2b. Did the observed NO2 artefact exhibit any dependence on, e.g. time of day/JNO2 or NO2 or history? Answer: What we clearly see is that the excess NO2, has a dependency on JNO2 as described in the paper. We have also looked at other potential parameters but we did not see any dependency whatsoever. We have clearly stated and it is well know that the NO2 signal itself exhibits a clear dependence on JNO2 values and time of day.

2c. Was there a tendency of the fake NO2 signal to decay if zero air was applied for longer periods? The stated rates for the zero air generator are inconsistent with the statement made otherwise in the manuscript about calibrations being performed upstream and downstream of the inlet line. Answer: During our zeroing we did not see any indication for memory effect. The zero level was reached shortly after application and was relatively stable after that point. Not only during this campaign but also on several other campaigns carried out over the course of several years. The stated flow rates for the zero air generators are the actual values from the routine zero gas measurements carried out during the campaign.

2d. As the determination of potential NO losses is one of the crucial points for the validity of the results, the procedures for calibration and zero air addition must be more clearly described, e.g., how and how often calibrations were performed upstream and downstream of the main inlet line. Answer: As already mentioned in the paper calibrations and zeroing downstream of the of the main inlet line were carried out on a daily basis. Upstream calibrations were performed twice during the campaign, right before the pristine air measurements and on a separate occasion after this period. This calibration and zeroing could not be performed more often since it would mean the loss of several hours of data, given our limited resources on a month long ship cruise.

2e. Furthermore, NO losses or oxidation on the surface of the inlet line may be dependent on the actual NO concentration. It is therefore important to know if the calibration was made at high concentrations or close to those observed in ambient air. Answer: During the campaign it was only possible to do calibrations in the mentioned range; this is because low pptv level calibrations (e.g. 50pptv) require the use of large volumes of air in order to dilute the gas. However the linearity of the instrument was tested over a large range of levels prior to the campaign. These tests demonstrated that

changing the concentration of the calibration gas only affected the linearity at very high concentrations (several hundred ppbs), which were beyond the concentration range observed during this campaign. Information derived from the infield calibrations were used in order to correct for sensitivity changes (cts/ppbv) of the instrument on a daily basis. It was observed during the campaign that the sensitivity was relatively stable with average values of 18121 (±49.8)cts/ppb for NO and 10945 (±129.5) cts/ppb for NO2.

3a. I disagree with the statement that the deviation from PSS correlates with JON2. From Fig 5, the clearest correlation is with NO2, which may indeed point to artefacts as a potential cause. Answer: As the referee has pointed out, there may be some sort of dependency at lower concentrations. However once higher concentrations are added to the plot, the dependency reverses. We believe that the phenomena seen here is due to increasing photochemical activity, as the ship moves northwards towards the African continent. Stronger deviation is seen with higher radiation and higher NOx concentration. The correlation between PSS and JNO2 has been illustrated in both figure 4 and 6 and can clearly be observed through the comparison of the colour coding on the plot. Again we would like to mention the discussion on artefacts has been addressed in this study and based on our independent ROx measurements and modeling results we are convinced that there is an additional oxidant which is unaccounted for.

3b. It may help to expand the discussion on the comparison between so-called pristine air and the few pollution events encountered during the cruise. This discussion would have to include potential differences in the experimental setup (e.g., history of the inlet and instruments, cleaning cycles, etc.). Answer: There was no obvious difference in the experimental setup. Due to stack emissions experienced from time to time during the campaign, there was no change in the conditioning of the line. The two pollution events mentioned in this study have only been mentioned for comparison sake and have no other purpose or use in this study. The only information derived is one that is already well know to the scientific community, i.e. confirmation of the well known theory that under high NOx conditions the peroxy radicals do not play a significant role in the photochemical processes governing the NOx-O3 system.

4. A scatter plot of the RO2+HO2 mixing ratio required to explain the deviation from Leighton's ratio (neglecting any potential other oxidants) against those measured (i) by LIF (assuming RO2=HO2) and (ii) measured by PERCA should be included. Such a figure would be of great assistance to the reader for appreciating the need for additional oxidants. It is extremely difficult to judge the differences from the plots shown in the paper. Answer: In order to make comparison easier we have addressed this question using two different methods. First method is based on the referee suggestion, where Measured PERCA data vs. that measured by LIF and also vs. ROx data derived from the PSS equation. The first plot, i.e. the PERCA ROx vs. LIF measured ROx, (assuming RO2=HO2), nicely demonstrates, that our understanding of the radical chemistry in the MBL based on our current understanding and also based on box models and 3D model results accounts for less than 20 % of the measured "peroxy" radicals. The slope we see in the plot is exactly as anticipated with an R2 value of 0.62. The equations for this plot is $y=1.61(\pm0.18)+0.145(\pm0.004)$.

Fig 1.1. PERCA measured ROx vs. LIF measured ROx (assuming RO2=HO2). The red dashed line illustrates the 1:1 line.

The second graph is plotted where PERCA measured ROx vs. PSS derived ROx. The second plot 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 NO2 and undergoes amplification in the PERCA. However due to the fact that one set of data is from actual measurements and the other calculated theoretically, we see a lot of scatter in this plot.

Fig 1.2 PERCA measured ROx vs. PSS calculated ROx. The red dashed line illustrates the 1:1 line.

The second method which helps visually judge the affect of the RO2 and HO2 species

on the Leighton ratio is found below. We have included the calculations and thorough explanations of a detailed step by step comparison. If the editor recommends it we can also incorporate it into the supplementary section of the paper.

A comparison between measured and calculated NO/NO2 ratio: The NO/NO2 ratio was calculated from 1 minute averages of observed NO and NO2 for two days in clean background air masses, i.e. March 13th and 15th. The aim of this comparison is to investigate the effect of HO2 and RO2 radical concentrations on the PSS ratio. The values are only calculated for daytime as the ratio is equal to zero during the night. Also near sunrise and sunset, measured values are less reliable since achievement of PSS is no longer expected due to slower NO2 photolysis. The variation of the observed NO/ NO2 ratio on March 13 is shown in figure 1.3 (red circles with error bars). Provided that the system is in PSS the following ratios are expected to be good approximations for comparison with the observed ratio (for equations please see attached supplement pdf file):

(Equation 1.1)

(Equation 1.2)

(Equation 1.3)

In the above equations k3, k4 and k5 are the reaction rate constants of NO with O3, HO2 and RO2 (reactions R3, R4 and R5 in paper). The three theoretically calculated ratios are also plotted in figure 1.3.

Figure 1.3 Observed NO/NO2 ratios (solid circles with bars) compared with calculated values derived from equation 1.1 (open purple circles), equation 1.2 (open blue squares) and equation 1.3 (dashed green line) for March 13th, 2007.

Since PERCA data is only available from March 14th onwards, equation 1.3 was calculated based on the assumption that RO2 concentrations approximately equal HO2 concentrations. Therefore the RO2 concentrations in this calculation are equal to the concentration of HO2. As can be observed in figure 1.3 the observed NO/NO2 ratio is significantly lower than those theoretically calculated. Equation 1.1, which does not include the effect of HO2 and RO2, has the most significant deviation from the observed ratio. With the addition of HO2 and the theoretically assumed RO2 to equations 1.2 and 1.3 respectively the difference is accounted for to some degree. This may again be an indication that there is a missing chemical mechanism converting NO to NO2, which is not accounted for in the PSS ratio and as a result leads to higher theoretically calculated NO/ NO2 ratios. The average value for each ratio and also the standard deviation, maximum and minimum values are also presented in table 1.1 (tables are included in attached supplement pdf file).

Table 1.1 Average values, standard deviation, maximum and minimum values for March 13th

The difference in equation 1.1 average compared to the observed ratio is extremely high with the value being more than double the value of the observed ratio. With the addition of HO2 to the equation in equation 1.2 the difference slightly decreases. Nevertheless there is still a significant difference of more than 80% between the actual observed values and equation 1.2. The effect of RO2 on equation 1.3 is a decrease in the difference percentage. However, even with this addition the values for equation 1.3 are on average 66% higher than the average observed ratio. The difference between the averages of the observed and theoretically calculated ratios (Δ) is calculated as (see pdf file):

(Equation 1.4)

In the above equation ‘Ratiotheory’ is the average theoretically calculated ratio (equations 1.1, 1.2 or 1.3) and ‘Ratioobs.’ is the averaged observed ratio. Equations 1.1, 1.2 and 1.3 were also calculated for March 15th. For this period a second “equation 1.3” was calculated using the observed data from the PERCA instrument (solid yellow lines). This ratio will be referred to as equation 1.3’. As can be observed in figure 1.4

the observed NO/ NO2 ratio, average of 0.24, is significantly lower than the theoretically calculated ratio, average of 0.75. Equation 1.1, which does not include the effect of HO2 and RO2, has the most significant deviation from the observed ratio. With the addition of HO2 and assumed RO2 to the equation the difference is accounted for to some degree (ratios 1.3 and 1.3’ respectively). However there is still a significant difference between the actual observed values and the theoretically derived values with the values for equation 1.3 being more than double the observed values. With the addition of the observed PERCA data the gap between the observed and calculated equation 1.3’ comes to a minimum. During the morning hours the agreement between the theoretically calculated equation 1.3’ and the observed ratio is excellent. The fact that the PERCA data can close the gap between the theoretically calculated ratios and the observed ratios re-enforces the theory that indeed the high NO2 concentrations measured during the campaign are not due to systematic errors of the CLD instrument. This is strong evidence since the CLD instrument used to measure the NO2 data and the PERCA instrument used to measure the ROx data are completely independent of each other and used separate inlet lines. However they both indicate that based on the observations done in this study that there is an additional missing chemical mechanism converting NO to NO2 in the remote MBL, which is not accounted for in the PSS ratio and therefore leads to much higher theoretically calculated NO/NO2 ratios.

Figure 1.4 Observed NO/NO2 ratios (solid red circles with bars) compared with calculated values derived from equation 1.1 (open purple circles), equation 1.2 (open blue squares), equation 1.3 (dashed green line) and equation 1.3’ (yellow line) for March 15th, 2007

Table 1.2 Average values, STDEV, maximum and minimum values for each ratio on March 15th

Since OH and HO2 were measured independently using a LIF instrument, these values are an asset when comparing total PERCA signal and the RO2 values which can be derived from the PERCA data once HO2 and OH are known. What is interesting is the difference between the assumed RO2 values and the actual RO2 derived from the measured PERCA signal. Even though the PERCA does close the gap between theoretically calculated values and the observed ratio during some periods of the day (figure 1.4) there is still a difference between the average observed ratio and the averaged equation 1.3' for other periods of the day. This could be due to additional unknown chemistry or simply be due to the high uncertainty in the ratio which is expected in low NOx regimes. For a comparison between the observed and calculated NO/NO2 ratio during the pristine conditions mentioned above and a high NOx episode, data obtained during the passing of a 2nd ship on March 15th, has been used. As can be seen in figure 1.5 in contrast to the pristine background period, the observed NO/NO2 ratio is in excellent agreement with the theoretically calculated equation 1.1. In addition the calculation of the Leighton ratio revealed that PSS is established (φ = 1), even without the inclusion of the HO2 and RO2 concentrations into the equation.

Figure 1.5 The observed NO/NO2 ratios (solid red circles) and calculated equation 1.1 (open purple circles) for March 15th 2007 for the high NOx episode resulting from the passing of a second ship.

This confirms the theory that under high NOx conditions the peroxy radicals do not play a significant role in the photochemical processes governing the NOx-O3 system. This indicates that under relatively high NOx conditions the PSS of NOx and O3 seems to be well understood and that the theoretically calculated PSS ratio is in excellent agreement with observed values. It is therefore concluded that the Leighton ratio is only valid for conditions with a significant concentration of NOx and as seen from the above calculations not valid for clean background conditions of the remote MBL. Therefore we conclude that the observed low NO/NO2 ratios suggest a missing chemical mechanism.

5a. There is too little information given in the paper for assessing the quality of the LIF and PERCA measurements. How were the instruments calibrated during the cruise? Was the same calibration source used or have the calibration sources been compared?

Answer: Since both of the instruments used during the campaign (and their calibration methods) have been described in great detail elsewhere, we felt it was sufficient to include only necessary information in the paper. We refer readers who are interested in further information, including detailed description of the instruments and calibrations, to two excellent papers written by the groups that operate them.

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., Fischer, H., Gurk, C., Kluepfel, T., Koenigstedt, R., Parchatka, U., Schiller, C.L., Stickler, A., Williams, J. and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements, Atmospheric Chemistry and Physics, 10, 3759–3773, doi:10.5194/acp-10-3759-2010, 2010.

Parker, A.E., Monks, P.S., Wyche, K.P., Balzani-Loov, J.M., Staehelin, J., Reimann, S., Legreid, G., Vollmer, M.K. and Steinbacher, M.: Peroxy radicals in the summer free troposphere: seasonality and potential for heterogeneous loss, Atmospheric Chemistry and Physics, 9, 1989–2006, doi:10.5194/acp-9-1989-2009, 2009.

Different calibration sources were used and were not compared for this campaign.

5b. The discussion about artefacts in BLC and the PERCA measurement (3.3 and 3.4) mainly repeats well know issues that have partially been described earlier in the paper. I think an important point to discuss (with appropriate figures!) is the difference in "ROx" concentrations determined by PSS and PERCA. This is difficult to quantify from the comparison of Fig. 4 and 7. Answer: The effect of "ROx" concentrations determined by PSS and PERCA on the Leighton ratio has been covered in the answer to point 4 above (including figures).

5c. The PERCA measurements show a clear tendency of increasing ROx concentrations during the time period showed, both at night and during daytime. This may point to an artefact, possibly related to contamination of the inlet. Has this been investigated? Answer: The increasing photochemical activity is due to the ship sailing north and as a direct result of higher temperatures and JNO2 values. The increasing tendency can also be seen in the HO2 and OH as can be observed in figure 8 (see paper). We would also like to point out that unlike most of the other measurements the PERCA instrument was directly situated on top of the atmospheric mast, see figure 3. This makes contamination related to the inlet line highly unlikely.

Technical comments:

1. I would suggest to combining Figs. 4, 6, and 7 in order to make the comparison easier for the reader. Answer: Due to the wealth of information provided by these figures we would prefer to keep the figures as they are instead of overloading all information on one plot. Instead, as the referee has requested, in order to make comparison easier we have provide a series of separate calculations and plots as indicated in point 4 above.

2. There is a lot of redundancy in the experimental sections that should be removed. Simple and well established procedures, such as GPT, do not need lengthy explanations. The same holds for error propagation, which is textbook knowledge and doesn't merit showing lengthy equations. The space should be used for more important details of the data quality as noted above and for expanding the discussion. Answer: In order to exclude the possibility of NO2 artefacs we felt it was necessary to explain the experimental procedure, calibration and zeroing in great detail. Also in order to judge the signal, we felt we had to discuss the error propogation in greater detail.

3. The paragraph on Page 7069, starting at line 4 is not clear and remains inconclusive. It should be reworded and substantiated. Answer: We agree. "The assumption that the reaction rate coefficients of RO2 with NO are similar to that of HO2 has been commonly used in the past. However, it has been suggested that the reaction rate coefficients of RO2 and HO2 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 ROx calculated from the PSS expression ([ROx]PSS). It was found that the reaction rates of NO with HO2 and RO2 are critical for the PSS

estimation and that [ROx]PSS can be influenced by uncertainties in the rate coefficients. Therefore it is recommended that the above assumption should be practiced with caution."

4. I would think that "diel" should be replaced by "diurnal". Answer: We agree.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C6931/2011/acpd-11-C6931-2011-supplement.pdf

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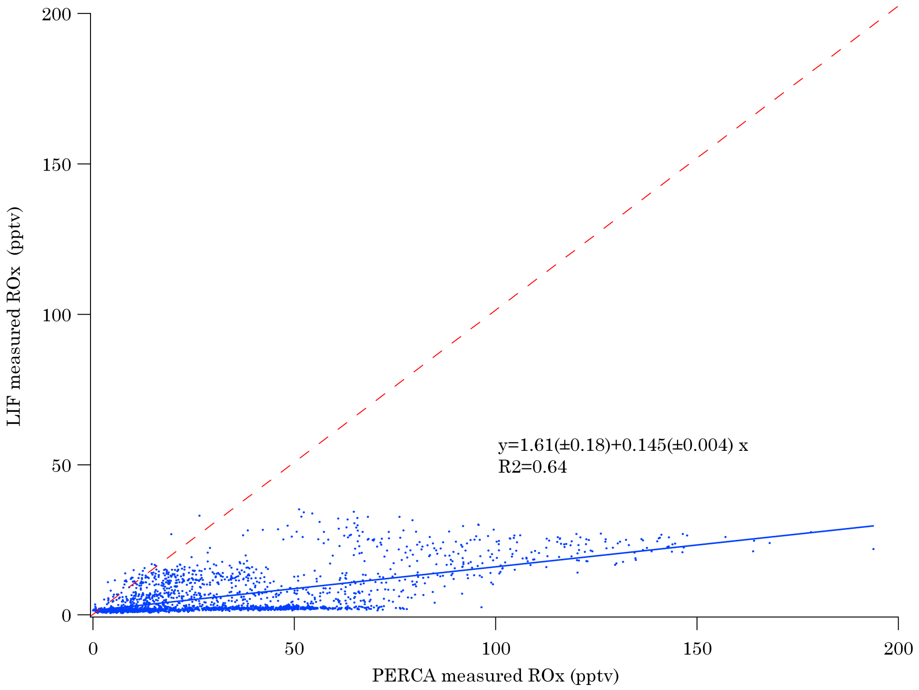
Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7045, 2011.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LIF measured ROx (pptv)
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R2=0.64
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50
100
150
200
PERCA measured ROx (pptv)

Fig. 1.

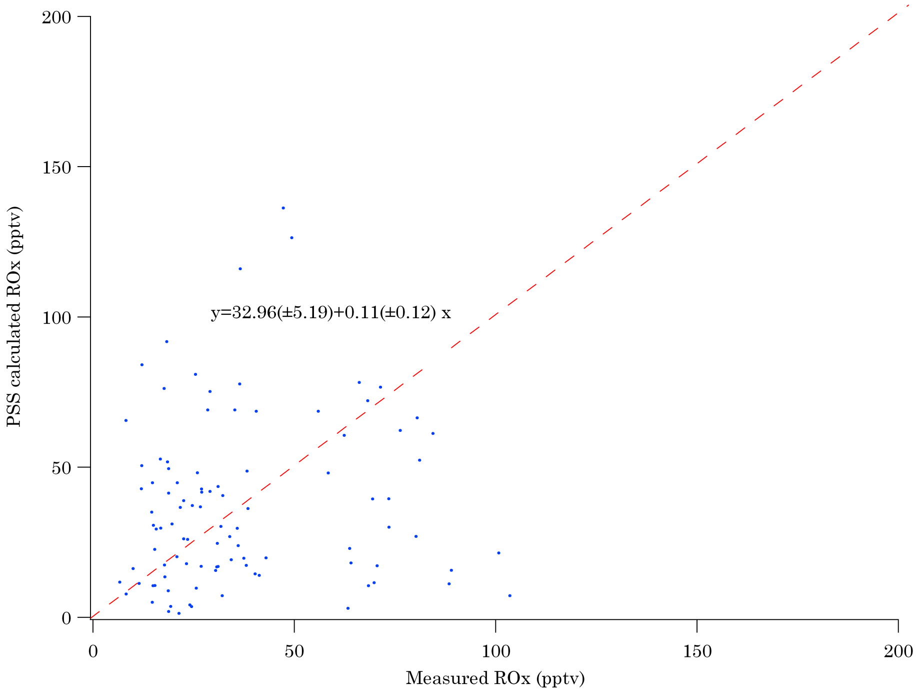
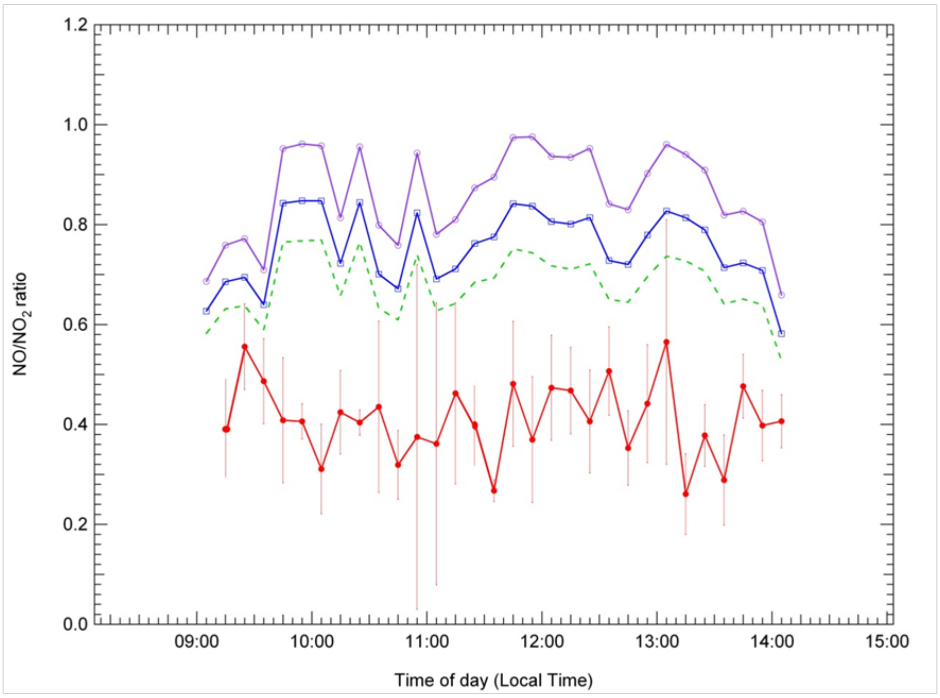

200
150
100
50
0
PSS calculated ROx (pptv)
y=32.96(±5.19)+0.11(±0.12) x
0
50
100
150
200
Measured ROx (pptv)

Fig. 2.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1.2
1.0
0.8
0.6
0.4
0.2
0.0
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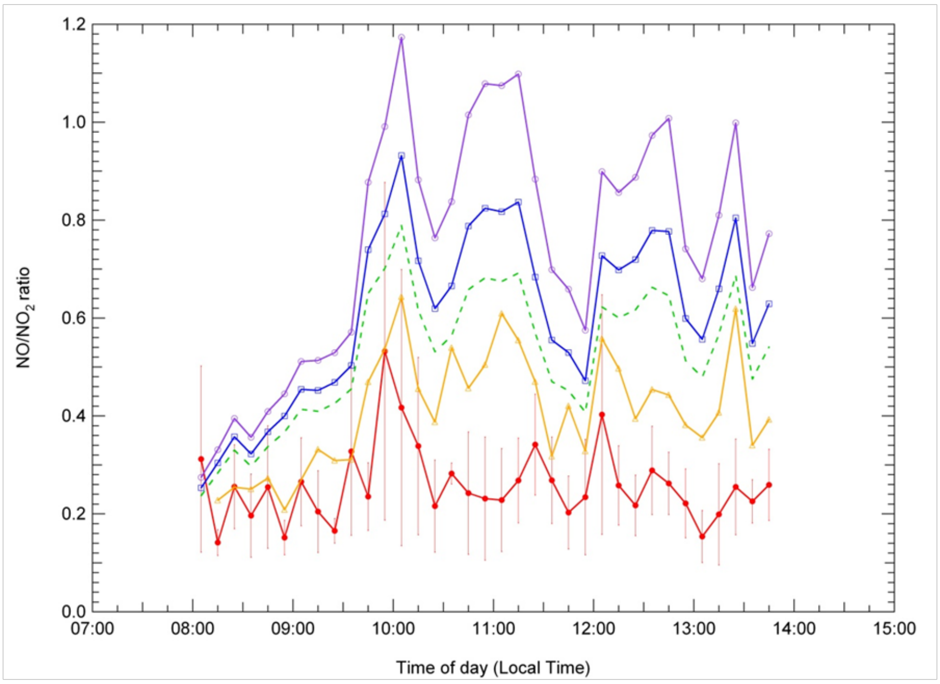
10:00
11:00
12:00
13:00
14:00
15:00
Time of day (Local Time)

Fig. 3.


NO/NO$_2$ ratio
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1.0
0.8
0.6
0.4
0.2
0.0
07:00
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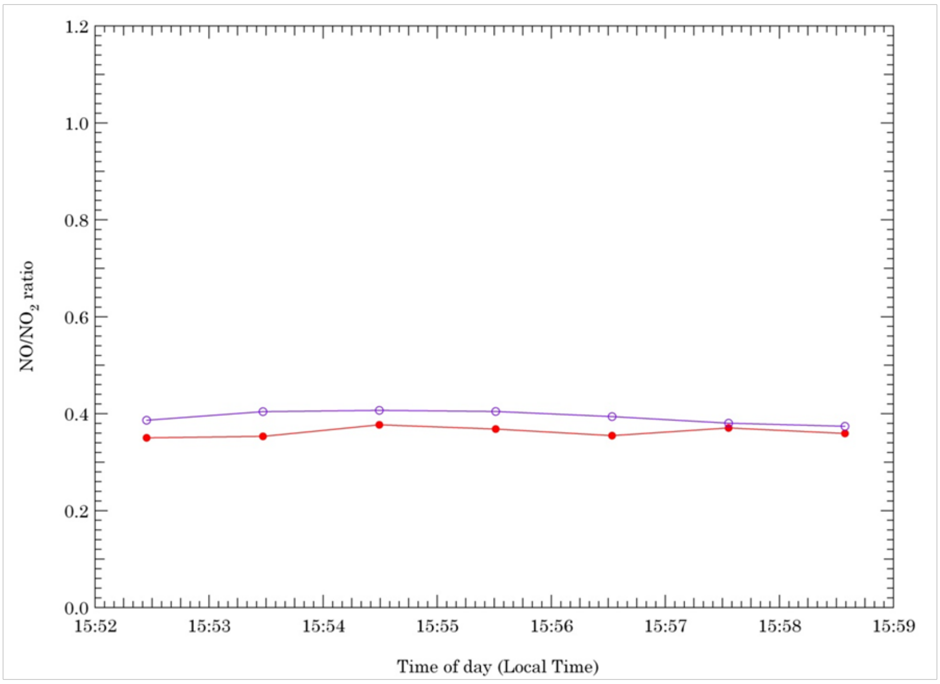
10:00
11:00
12:00
13:00
14:00
15:00
Time of day (Local Time)

Fig. 4.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0.8
0.6
0.4
0.2
0.0
NO/NO$_2$ ratio
15:52
15:53
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15:55
15:56
15:57
15:58
15:59
Time of day (Local Time)

Fig. 5.