

## Supplementary information

### 1. Clean MBL data

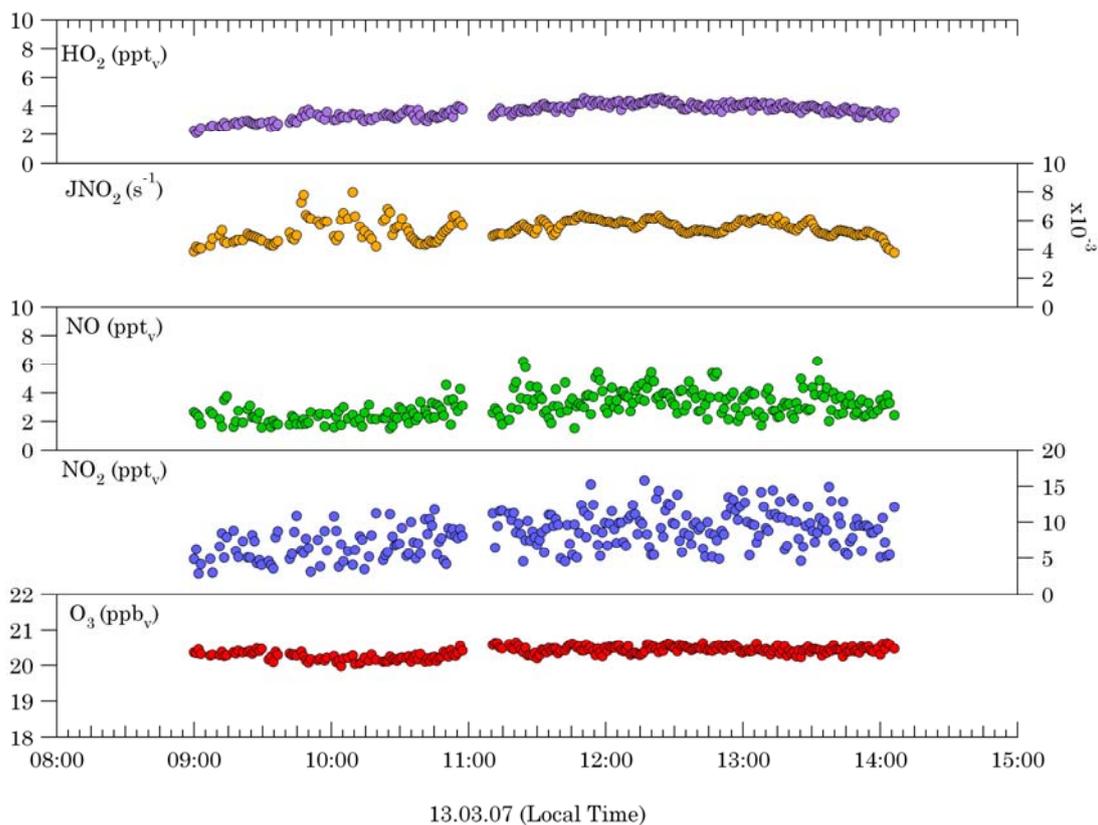
The aim of this study is to investigate the PSS of NO<sub>x</sub> and O<sub>3</sub> in clean background conditions of the southern Atlantic Ocean. Therefore only daytime data where background air masses were measured have been used in this study. All data used in the study are averaged over 1 minute. Analysis and comparison are only done for periods where all parameters required in order to calculate the PSS equations are available. Both GMT and local time, for periods used in this study are presented in table S.1. The start and end coordinates of each period, i.e. longitude and latitude, are also mentioned for geographical orientation.

**Table S.1** Periods of clean background measurements used in this study

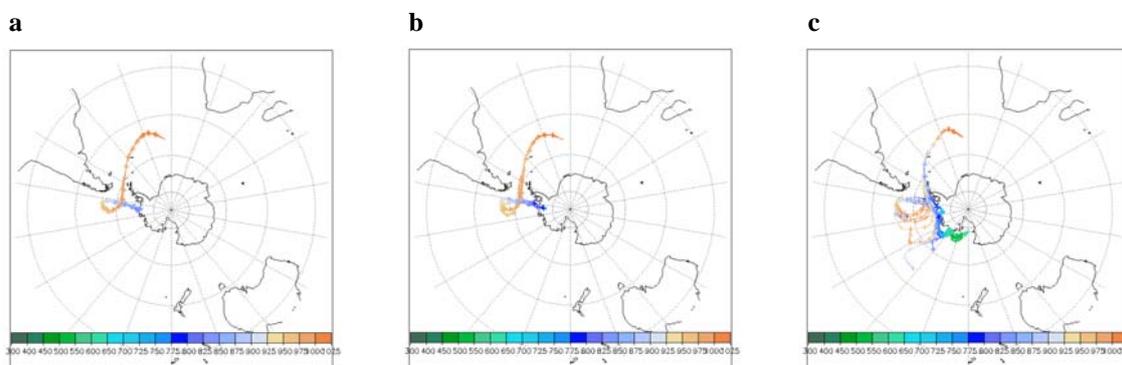
Day	Time(GMT)	Local time	Longitude	Latitude
13.03.2007	09:23 - 14:23	9:00 – 14:06	-5.8 to -4.2	-51.8 to -51.0
14.03.2007	14:56 - 16:45	15:08 – 17:00	3.2 to 3.7	- 46.9 to -46.6
15.03.2007	07:15 - 13:50	7:46 – 14:30	7.9 to 9.9	-44.0 to -42.9
16.03.2007	06:30 – 11:10	7:30 – 12:15	15.0 to 16.5	-40.5 to -39.8
17.03.2007	10:08 - 10:42	11:37 – 12:12	22.5 to 22.7	-36.9 to -37.0

Figures S.1 to S.10 illustrate the periods of clean background measurements carried out during MD 160 and the corresponding back trajectories for the study periods which have been used specifically in the PSS calculations in this chapter. The colour code below each plot is an indication of the pressure level, with a minimum pressure of 300 hPa in dark green corresponding to the free troposphere and a maximum of 1025 hPa in dark orange corresponding to sea surface pressure. Note that air masses with a pressure of more than 900 hPa are from within the marine boundary layer. In general for the period of study, the ten day backward trajectories show that air masses originate from Antarctica and the southern Atlantic Ocean. The majority of the time the air mostly comes from the free troposphere, subsiding to the boundary layer some time before measurement.

The back trajectories show that air masses encountered on March 13th originate from Antarctica. They do not pass over the South American continent and the air masses which are measured subsequently are pristine background air from within the marine boundary layer.

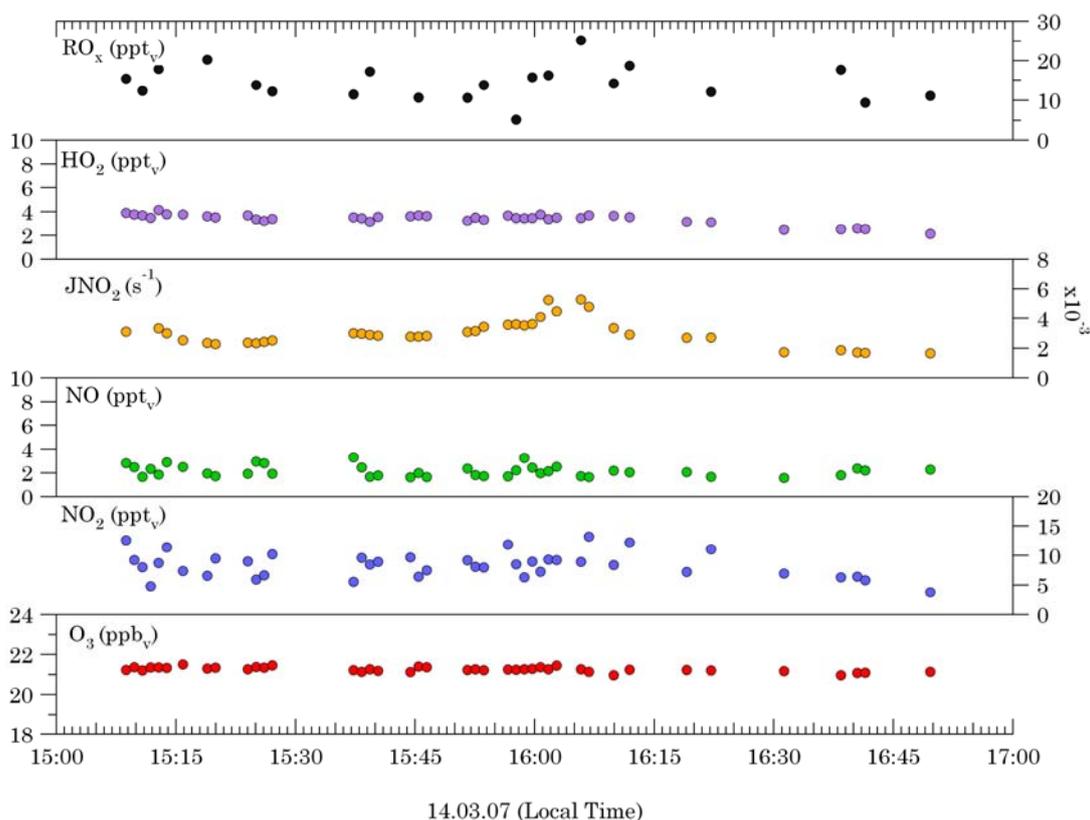


**Figure S.1** Mixing ratios of the measured O<sub>3</sub> (red circles), NO<sub>2</sub> (blue circles), NO (green circles), JNO<sub>2</sub> (yellow circles) and HO<sub>2</sub> (purple circles) in clean background MBL are plotted for the study period on March 13<sup>th</sup> 2007.

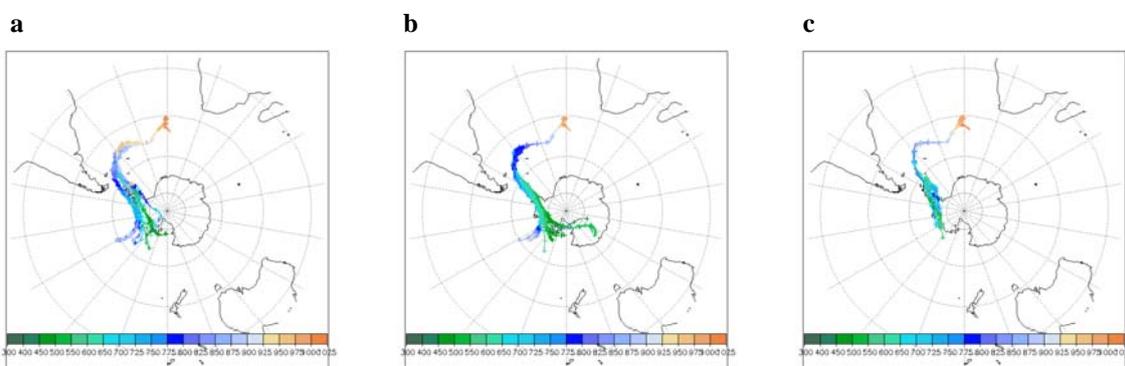


**Figure S.2** Calculated back trajectories for March 13<sup>th</sup> for the period of study. Plots a, b and c correspond to 9:00, 12:00 and 15:00 GMT respectively. The colour bar below each plot is an indication of the pressure level (300 to 1025hPa).

The concentration of trace gases measured during the study period are relatively stable and do not change significantly over the study period. Ozone, NO, NO<sub>2</sub> and HO<sub>2</sub> mixing ratios are on average 20.4 ppb<sub>v</sub>, 3.1 ppt<sub>v</sub>, 8.4 ppt<sub>v</sub> and 3.7 ppt<sub>v</sub> respectively. Average temperature during the study period on March 13 was 3 °C.

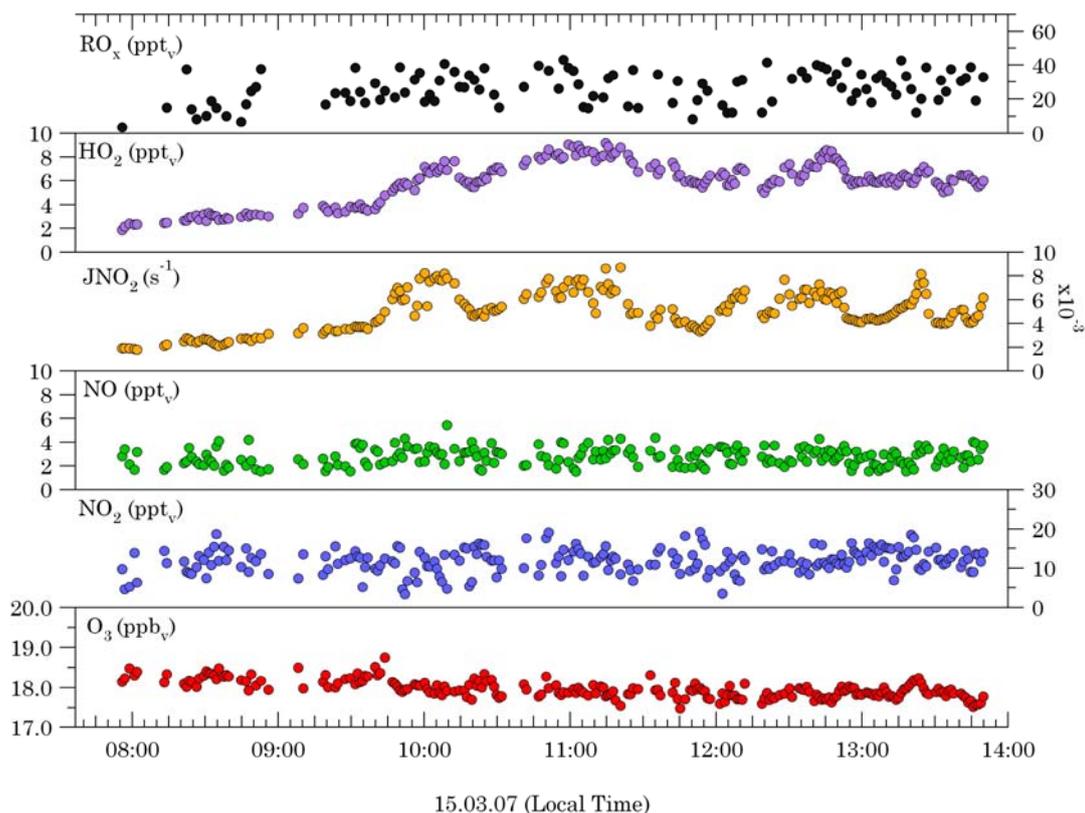


**Figure S.3** Mixing ratios of the measured O<sub>3</sub> (red circles), NO<sub>2</sub> (blue circles), NO (green circles), JNO<sub>2</sub> (yellow circles), HO<sub>2</sub> (purple circles) and RO<sub>x</sub> (black circles) in clean background MBL are plotted for the study period on March 14<sup>th</sup> 2007.

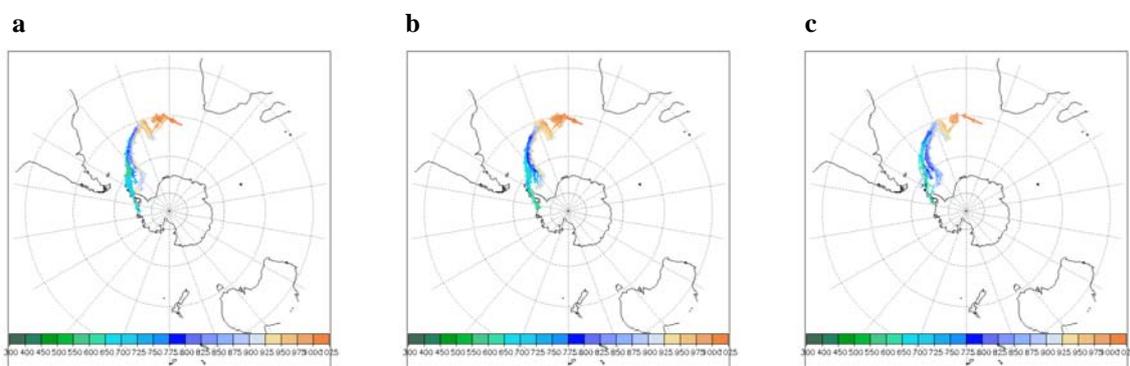


**Figure S.4** Calculated back trajectories for March 14<sup>th</sup> for the period of study. Plots a, b and c correspond to 12:00, 15:00 and 18:00 GMT respectively. The colour bar below each plot is an indication of the pressure level (300 to 1025hPa).

Average temperature during the study period on March 14<sup>th</sup> was 8 °C. Again the 10 day back trajectories indicate that the air masses encountered on March 14<sup>th</sup> originate from the continent of Antarctica, subsiding to the marine boundary layer sometime before subsequent measurement. This period of study is relatively short with very little change in the background values of the trace gases. O<sub>3</sub>, NO, NO<sub>2</sub> mixing ratios are on average 21.3 ppb<sub>v</sub>, 2.1 ppt<sub>v</sub> and 8.4 ppt<sub>v</sub> respectively, whilst the radicals HO<sub>2</sub> and RO<sub>x</sub> have average mixing ratios of 3.4 ppt<sub>v</sub> and 14.3 ppt<sub>v</sub> respectively.

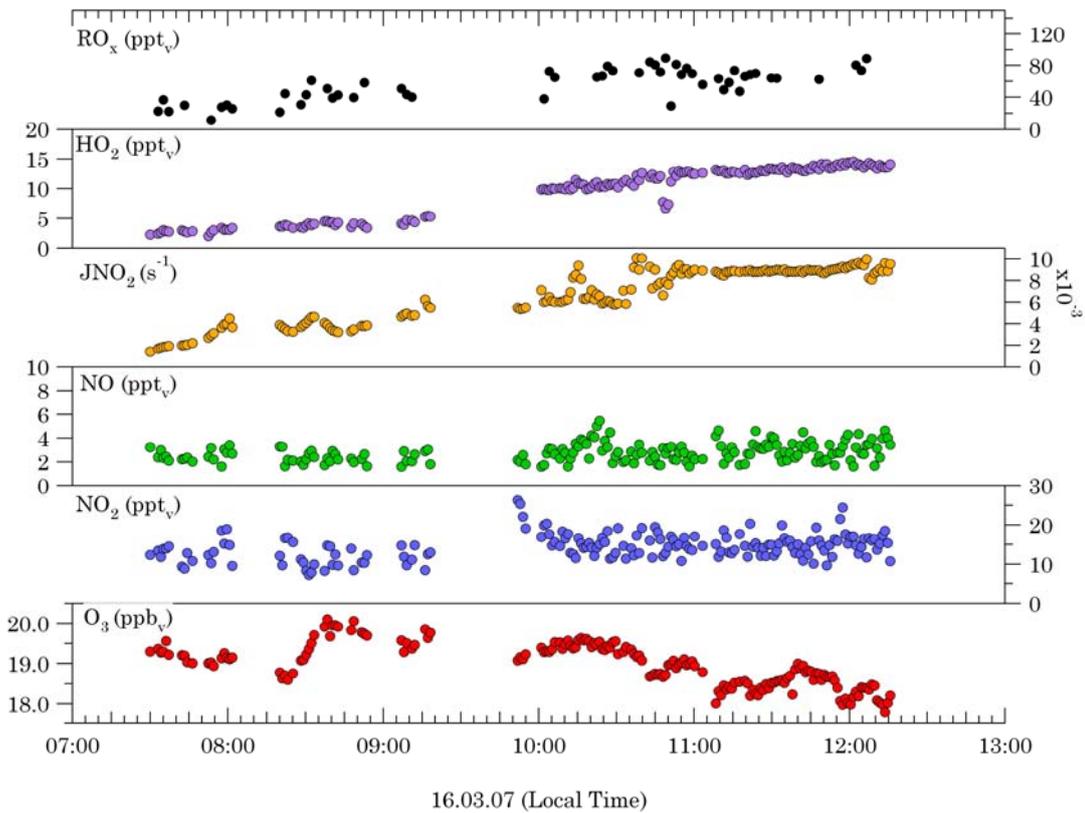


**Figure S.5** Mixing ratios of the measured O<sub>3</sub> (red circles), NO<sub>2</sub> (blue circles), NO (green circles), JNO<sub>2</sub> (yellow circles), HO<sub>2</sub> (purple circles) and RO<sub>x</sub> (black circles) in clean background MBL are plotted for the study period on March 15<sup>th</sup> 2007.

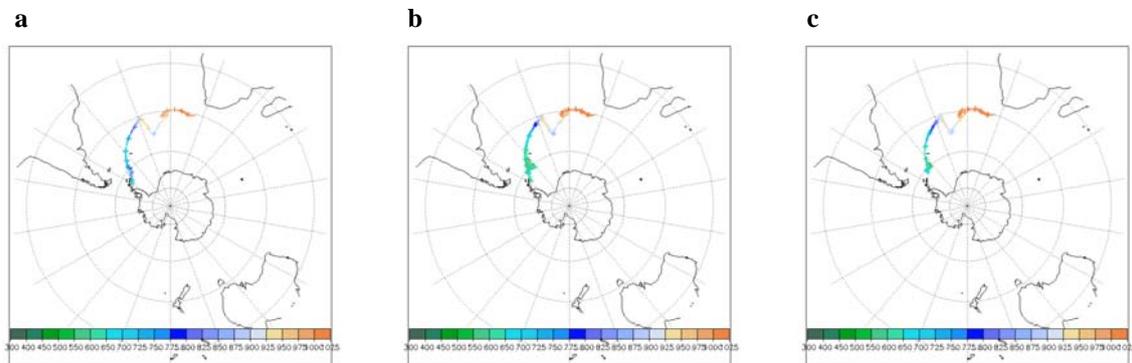


**Figure S.6** Calculated back trajectories for March 15<sup>th</sup> for the period of study. Plots a, b and c correspond to 9:00, 12:00 and 15:00 GMT respectively. The colour bar below each plot is an indication of the pressure level (300 to 1025hPa).

The 10 day back trajectories indicate that the air masses encountered on March 15<sup>th</sup> originate from the shores of Antarctica, subsiding from the free troposphere to the marine boundary layer sometime before measurement. The average temperature during the study period on this day was 11 °C. Again on this day there is very little change in the mixing ratios of O<sub>3</sub>, NO and NO<sub>2</sub> which are on average 18 ppb<sub>v</sub>, 2.8 ppt<sub>v</sub> and 11.8 ppt<sub>v</sub> respectively. However there is a general increase in the HO<sub>2</sub> and RO<sub>2</sub> mixing ratios with time which correlates well with the increase in JNO<sub>2</sub> values and thus the level of photochemical activity.

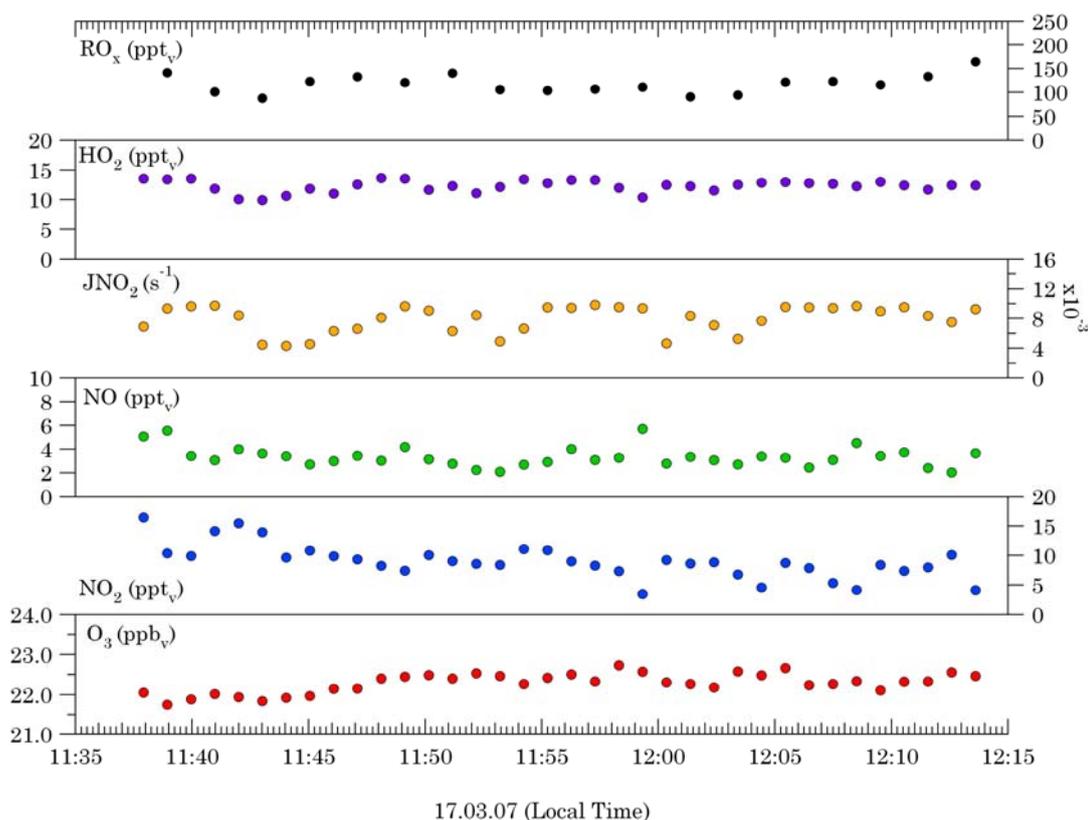


**Figure S.7** Mixing ratios of the measured O<sub>3</sub> (red circles), NO<sub>2</sub> (blue circles), NO (green circles), JNO<sub>2</sub> (yellow circles), HO<sub>2</sub> (purple circles) and RO<sub>x</sub> (black circles) in clean background MBL are plotted for the study period on March 16<sup>th</sup> 2007.

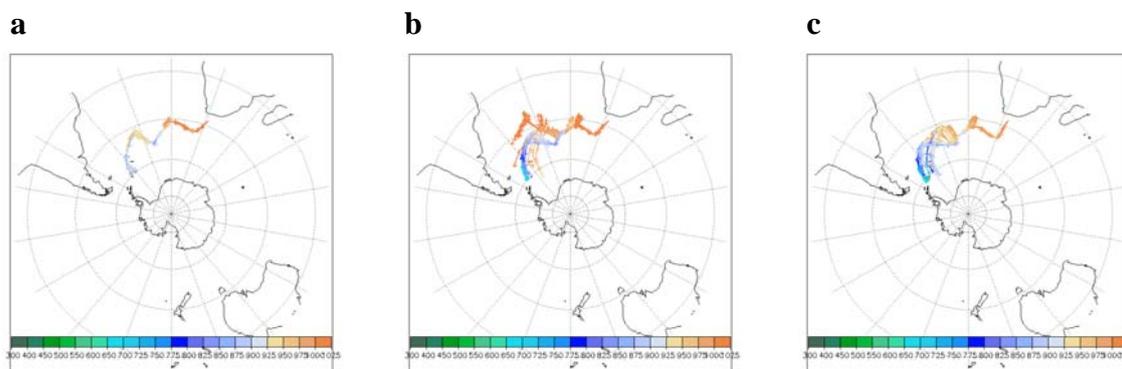


**Figure S.8** Calculated back trajectories for March 16<sup>th</sup> for the period of study. Plots a, b and c correspond to 6:00, 9:00 and 12:00 GMT respectively. The colour bar below each plot is an indication of the pressure level (300 to 1025hPa).

On March 16<sup>th</sup> the ship is two days away from the coast of South Africa. The back trajectories however confirm that the air masses are from the South Atlantic Ocean and are not influenced by the African continent. The average temperature during this study period is on average 16 °C, with temperatures increasing as we go towards South Africa. Mixing ratios of O<sub>3</sub>, NO and NO<sub>2</sub> are on average 19 ppb<sub>v</sub>, 2.8 ppt<sub>v</sub> and 14.4 ppt<sub>v</sub> respectively.



**Figure S.9** Mixing ratios of the measured O<sub>3</sub> (red circles), NO<sub>2</sub> (blue circles), NO (green circles), JNO<sub>2</sub> (yellow circles), HO<sub>2</sub> (purple circles) and RO<sub>x</sub> (black circles) in clean background MBL are plotted for the study period on March 17<sup>th</sup> 2007.



**Figure S.10** Calculated back trajectories for March 17<sup>th</sup> for the period of study. Plots a, b and c correspond to 6:00, 9:00 and 12:00 GMT respectively. The colour bar below each plot is an indication of the pressure level (300 to 1025hPa).

The last period of clean air which is used in this study, March 17<sup>th</sup>, is the result of the ship turning away from its original course so that for the period shown in figure S.9 the wind direction was directly from the front of the ship and therefore clean air masses could be measured for a short period of time. The average temperature on this day was 19 °C. The air masses originate from the southern Atlantic and have already subsided in the MBL for some time before being measured.