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“Study of ozone depletion events in the Weddell Sea, Antarctica during the Winter Weddell Outflow Study from August until October 2006”

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Abstract

So-called ozone depletion events have been investigated since their first appearance in the mid 1980s. They are characterized as drops of the ozone levels in the lower troposphere in a timescale of minutes to several days and have mostly been observed in polar regions. Chemical catalytic cycles known as the bromine explosion generate reactive bromine atoms that destroy surface ozone and lead to an increase of the BrO vertical column. These chemical reactions are linked to sea ice covered regions as well as insolation and are limited to the springtime in both polar regions.

Ozone depletion events have already been well-probed in the Arctic Ocean. However in Antarctica only ozone concentrations observed at coastal and inland sites have been analysed. During a scientific cruise ("Winter Weddell Outflow Study") with the German research vessel Polarstern ozone investigations were performed for the first time in the north-western Weddell Sea southward of the South Orkney Islands. Several meteorological parameters were recorded as well. Furthermore a 2-channel multiaxis DOAS (Differential Optical Absorption Spectroscopy) instrument allowing the detection of BrO was installed onboard and data from the SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) sensor were used. The entire data was analysed to investigate the connection between the ozone concentrations, the prevailing meteorological conditions and the BrO vertical column during ozone depletion events in the Weddell Sea. During the Winter Weddell Outflow Study four ozone depletion events were recorded. The investigations allowed a distinction between chemically and meteorologically induced ozone depletion events. The meteorologically induced ODEs were characterized by the advection of air masses already depleted in ozone. Using backward-trajectories, the origin of the depleted air masses was detected.

The ozone concentrations and the BrO VC observed onboard have been compared. The similar increase of the BrO concentration and decrease of the ozone concentration indicates that the ozone depletion events measured onboard were in fact activated by the presence of Br in the atmosphere.

Ozone measurements at the German research station Neumayer as well as at the British station Halley were also analysed. The origin of the depleted air masses reaching the RV Polarstern and both Antarctic stations is identical. In the majority of cases, the chemical reactions destroying ozone took place over the Central Weddell Sea. In most cases, enhanced BrO vertical columns were observed simultaneously in the same region.

Finally the role of low pressure systems in the generating of BrO was analysed. High wind speeds favour the turbulent mixing and, therefore, the increase of salinity and reactive bromine atoms in the boundary layer. Since low pressure systems are often accompanied by high wind speeds, a link between low pressure systems and enhanced BrO vertical columns is proposed.

Zusammenfassung

Der plötzliche Abfall der Ozonkonzentration in der Troposphäre ist bereits seit Mitte der achtziger Jahre bekannt. Katalytische Prozesse, die sogenannte "Bromexplosion", erzeugen reaktive Bromatome, die in weiterer Folge bodennahes Ozon zerstören und zu einem Anstieg der BrO Vertikalsäule führen. Diese chemischen Reaktionen sind allerdings an das Vorhandensein von Meereis und solarer Einstrahlung gebunden. Sie sind daher auf die Polarregionen und auf die Frühlingszeit beschränkt.

In der Arktis sind die sogenannten "Ozone depletion events" schon zahlreich erforscht worden, in der Antarktis hingegen gibt es nur Messungen an den Küsten- sowie Inlandstationen, aber keinerlei Beobachtungen direkt in den Meeresregionen. Während der Forschungsreise "Winter Weddell Outflow Study" im Frühling (August-Oktober) 2006 an Bord des deutschen Polarschiffes "Polarstern" wurden zum ersten Mal Ozondaten im Weddellmeer, Antarktis gesammelt. Weiters wurden meteorologische Parameter gemessen und die BrO Vertikalsäule anhand eines DOAS-Messgerätes (Differential Optical Absorption Spectroscopy) ermittelt.

Ziel der Arbeit ist es nun diese erworbenen Ozondaten zu analysieren und mit Ozondaten der Forschungsstationen Neumayer (GER), Halley (GB) und Cape Point (ZA) zu vergleichen. Eventuelle Zusammenhänge zwischen der Ozonkonzentration, den vorherrschenden meteorologischen Bedingungen und der BrO Vertikalsäule sollen erläutert werden. Weiters soll geklärt werden, ob es Unterschiede zwischen dem Ablauf der "Ozone depletion events" in beiden Polarregionen gibt.

Résumé

La chute soudaine de la concentration d'ozone troposphérique a été découverte pour la première fois dans les années 80. Des réactions catalytiques, connues comme la "bromine explosion" génèrent des atomes de brome réactifs qui menent à une hausse de l'oxyde de brome (BrO) dans la colonne d'air. Cependant ces réactions chimiques sont liées à la présence de banquise et du rayonnement solaire. Ces évènements sont donc limités aux régions polaires et n'ont lieu qu'au printemps.

En Arctique, les chutes de l'ozone ont largement été suivies depuis leur découverte. En Antarctique, par contre, les concentrations de l'ozone troposphérique sont mesurées par les stations de recherches côtières ou à l'intérieur du continent mais n'ont jamais été suivies en milieu marin. Les premières mesures d'ozone troposphérique en milieu marin de l'Antarctique ont eu lieu lors de l'éxpédition "Winter Weddell Outflow Study (WWOS)" en printemps 2006 à bord du navire allemand "Polarstern". Le domaine exploré s'étend de l'Afrique du Sud jusqu'au nord-ouest de la mer de Weddell jusqu'au Sud de l'archipel des Orcades du Sud. De nombreux paramètres météorologiques ainsi que la colonne d'air de BrO ont également été mesurés durant cette éxpédition.

L'objectif de ce stage est d'analyser les données d'ozone collectées pendant la WWOS et de les comparer avec les observations des concentrations d'ozone faites aux stations de recherche Neumayer (GER), Halley (GB) et Cape Point (ZA). L'existence de liens entre la concentration d'ozone, les paramètres météorologiques et la colonne d'air de BrO doit être validée. De plus, les évènements de chutes de l'ozone en Arctique et en Antarctique seront comparées.

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Eidesstattliche Erklärung

Ich erkläre hiermit, dass ich diese Arbeit selbst verfasst, alle verwendeten Quellen zitiert und mich keiner unerlaubten Hilfsmittel bedient habe.

Datum und Unterschrift

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Chapter 1

Introduction

According to the IPCC Fourth Assessment Report: Climate Change 2007, surface ozone is an important greenhouse gas, whose global radiative forcing increased by 0,35 Wm^{-2} since pre-industrial time [Forster et al., 2007]. Hence, it is important to understand the behaviour of surface ozone on a global to local scale. According to Vingarzan [2004], "*the ozone concentration in any given region is affected by formation, destruction, transport and deposition of ozone*". This study investigates the first ozone measurements in the Weddell Sea ever done and further examines the sudden destruction and the transport of surface ozone.

The sources and sinks of surface ozone are various. Solar radiation has an important impact on the ozone concentration - it can act as sink as well as source of ozone - hence, ozone cycles vary widely on geographical scales [Helmig et al., 2007]. Surface ozone is additionally removed from the atmosphere by deposition. Major sources of surface ozone are downward mixing from the stratosphere as well as chemical reactions of anthropogenic NOx in the presence of sunlight [Simpson et al., 2007].

According to Helmig et al [2007], the tropospheric ozone concentration in the polar regions, especially Antarctica, is barely affected by the generation of ozone due to anthropogenic NOx as nearly no human population or industries are residing in those regions [Helmig et al., 2007]. Hence, the ozone concentration primarly depends on natural chemical processes, downward mixing from the stratosphere and synoptic transport [Helmig et al., 2007]. Comparing the annual mean ozone background level (defined as *"the fraction of ozone present in a given area that is not attributed to anthropogenic sources of local origin"* [Vingarzan, 2004]) measured at different sites in the Arctic as well as in Antarctica to the background ozone at monitoring sites worldwide, reveals that the ozone background level over the polar regions is not as low as in the clean boundary layer over maritime regions, where the circumjacent ocean acts as a sink of ozone [Helmig et al., 2007]. This comparision is based on data from polar research stations located at the coast. Especially in Antarctica, measurements over maritime regions are almost inexistent.

As already mentioned, solar radiation acts as a sink of ozone. During the polar night no solar radiation reaches the polar regions, hence, the atmospheric lifetime of ozone *"reaches up to 100 days, which is the longest of any environment on Earth"* [Helmig et al., 2007]. Deposition is the only sink of surface ozone during the polar night.

Due to the absent solar radiation during the polar night and the continuous insolation during the polar day, the annual ozone cycles are well defined. Excluding ozone depletion events happening in the southern spring, the highest ozone concentration values in Antarctica are recorded in the southern winter (June, July and August), the period with lowest ozone concentration is the southern summer (December, January and February) [Helmig et al., 2007] (see section 3.1.).

As the ozone concentration depends on synoptic transport [Helmig et al., 2007], which in turn is influenced by the land mass distribution [King and Turner, 1997], the recorded ozone data in the Arctic and in Antarctica (at coastal sites as well as inland sites) reveal some differences. According to Helmig et al. [2007], the mean ozone concentration in the Arctic is 5 ppbV higher than in Antarctica mainly provoked by the enhanced transport of ozone-rich air from lower latitudes into the Arctic. For example, during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment conducted between 4 February to 23 May 2000 [Emmons et al., 2003], the importance of synoptic transport of ozone-rich air masses was pointed out. In the Arctic, between February and May, the tropospheric ozone increased by 4.6 ppbV $month^{-1}$ between 60° and 85°N latitude due to transport of ozone from lower latitudes [Helmig et al., 2007]. Furthermore, the seasonal ozone cycle has a larger amplitude at Antarctic sites than in the Arctic [Helmig et al., 2007]. Some differences in the ozone concentration are also present between coastal and inland sites in Antarctica as well as in the Arctic. At both Summit (Greenland, 3212 m amsl) and South Pole (Antarctica, 2830 m amsl) the annual mean ozone concentration is higher than at coastal measuring points [Helmig et al., 2007]. This enhanced ozone levels could be caused by photochemical production of ozone due to high NOx levels generated by the photo-denitrification of the Antarctic snowpack [Legrand et al., 2009].

In the Southern Hemisphere the ozone concentration at the surface is further influenced by an intensified UV radiation due to the minimum of stratospheric ozone over the Antarctic continent between October and December. The higher levels of UV radiation at the surface and the resulting increase in NO_x fluxes from the snow lead to a rise in the chemical production of the ozone concentration [Helmig et al., 2007, Legrand et al., 2009].

Ozone depletion events are events where ozone suddenly drops from background level to near zero levels in a timescale of minutes to several days before recovering again. They were first discovered at polar sunrise in the mid 1980s at Point Barrow, Alaska and at Alert,

Canada [Barrie et al., 1988]. Later it has been confirmed, that ODEs are widespread near the surface in the Arctic and Antarctica [Simpson et al., 2007].

ODEs can be chemically induced, meteorologically controlled or a combination of both. Meteorologically controlled ODEs are defined as the *"advection of ozone depleted air and therefore are rapid on their onsets and are characterized by changes in wind speed and wind direction*" [Simpson et al., 2007]. In contrast chemically controlled ODEs occur during low wind speed and a stable boundary layer. They are normally slower in their onsets [Simpson et al., 2007]. The recovery of the ozone concentration is primarly determined by the approach of ozone-rich air masses, hence, meteorologically controlled [Simpson et al., 2007, Jacobi et al., 2010]. Ozone depletion events happen almost always over the frozen ocean [Jacobi et al., 2010, Simpson et al., 2007], hence, the ozone concentration generally drops in the boundary layer, whereas the ozone concentration in higher layers in at background levels [Jones et al., 2010]. The physical behaviour of the atmosphere strongly influences the vertical extent of an ozone depletion event. Hence, in the majority of the cases, ODEs are limited by the height of the inversion [Jones et al., 2010, Jacobi et al., 2006] which prevents the downward mixing of ozone rich air masses from the upper troposphere [Lehrer et al., 2004]. Occasionally, due to vertical transport of ozone-depleted air masses, ozone concentration at the surface is at background level, whereas the ozone concentration at higher altitude is depleted [Jones et al., 2010] (compare Jacobi et al. [2009]).

The different meteorological conditions between the Arctic and Antarctica have an important influence on the local ozone concentrations.

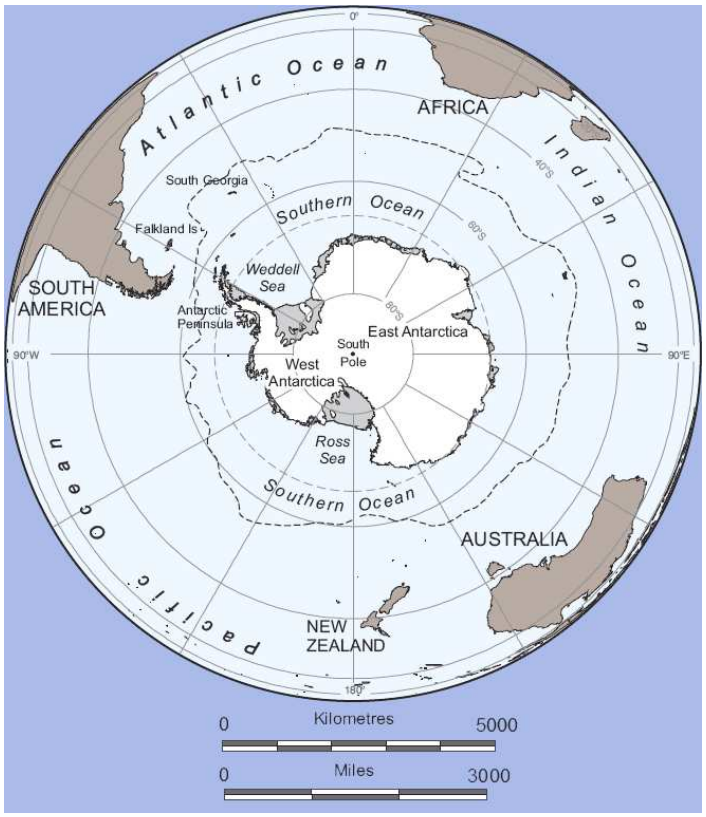


Figure 1.1: *Map of the Antarctic continent. Image credit: British Antarctic Survey (**http://map-of-antarctica-with-boltss.pics-grabber.appspot.com/**).*

The distribution of the land masses differs strongly in the Arctic and in Antarctica. Whereas the Arctic region is dominated by a generally sea-ice covered polar ocean and surrounded by land masses, the South Pole is situated on the Antarctic continent with an average height of 3000 m and surrounded by a circumpolar ocean (Figure 1.1.). Although the physical geography of both polar regions is contrary, some similarities due to the high latitude exists. Due to the lower sun elevation in higher latitudes and the high albedo of snow and ice, the surface radiation balance is mostly negative in both polar regions. Another distinctive commun aspect is the surface inversion induced by the strong radiative cooling. Temperature increases of more than 30°C within the lowest 100 m have been observed in the Arctic as well as Antarctica. The temperature inversions tend to be stronger on the Antarctic continent than in the Arctic [King and Turner, 1997, Rasmussen and Turner, 2003].

The negative surface radiation balance in both polar regions is compensated by the advection of warmer air masses from lower latitudes. As they reach the higher latitudes, they

cool down and their density increases and they are forced to subside. This leads to distinct high pressure systems in the polar regions. Whereas the polar highs are similar in the Northern and Southern Hemisphere, the behaviour of low pressure systems indicate significant differences.

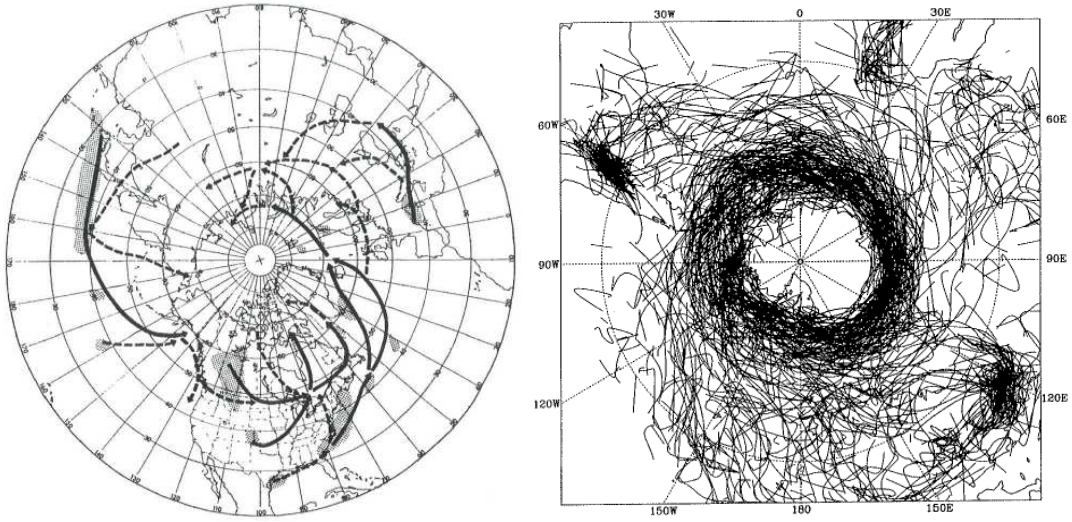


Figure 1.2: *Principal northern hemisphere depression tracks in January in the Arctic. Major tracks are indicated by the solid lines, secondary tracks (less frequent and less well defined) by broken lines (left) [Rasmussen and Turner, 2003]. Tracks of all depressions around Antarctica in southern summer between 1985-1989 (right) [King and Turner, 1997].*

As the Arctic Ocean is surrounded by continents extending into middle and lower latitudes, the low pressure systems in the Northern Hemisphere move in a meridional direction advecting warm, moist air into the Arctic. However, in the Southern Hemisphere, the high plateau of the continent Antarctica represents a major barrier for low pressure systems. They are forced to move east as soon as they reach the continent and thus move in a zonal direction. In Antarctica, the Weddell Sea is a region with increased mesocyclogenesis. Due to the lower extent of sea ice in southern summer, the development of mesocyclones in the Weddell Sea is greatest in this period of the year. Low pressure systems in this area tend also to develop, when already mature depressions are situated east of the Weddell Sea. The cyclonic rotation induces advection of cold air from the continent which results in a strong low-level temperature gradient favouring cyclogenesis [King and Turner, 1997, Rasmussen and Turner, 2003]. In the Arctic a correlation between synoptic systems and the ozone concentration was observed; a likewise correlation in Antarctica was not found yet.

The destruction of ozone in the polar regions is induced by halogen chemistry [Simpson et al., 2007, Friess et al., 2004, Jones et al., 2009]. As *"large and persistent areas of elevated BrO"* [Simpson et al., 2007] are regularly observed in regions where ozone was depleted over the Arctic Ocean [Simpson et al., 2007, Barrie et al., 1988] as well as over the ocean surrounding Antarctica [Friess et al., 2004, Hollwedel et al., 2004], a correlation between increase of reactice bromine species and ozone depletion was proposed. In Antarctica, elevated BrO levels have only been measured in coastal areas as well as over the sea ice belt around the continent [Lehrer et al., 2004].

Different chemical reaction cycles exist containing halogens that destroy ozone in the boundary layer in the polar regions [Simpson et al., 2007]:

- self reaction of halogen oxides:

$$2 * (Br + O_3 \rightarrow BrO + O_2) \tag{1.1}$$

$$BrO + BrO \rightarrow 2Br + O_2 \tag{1.2}$$

  Bromine reacts with ozone generating BrO and oxygen. Two BrO molecules react to recycle two bromine atoms.

- cross reaction between two different halogen oxides, which is one order of magnitude faster than the self reaction [Simpson et al., 2007].

$$BrO + ClO \rightarrow Br + Cl + O_2 \tag{1.3}$$

- reactions of halogen oxides with the hydroperoxyl radical (HO_2):

$$Br + O_3 \rightarrow BrO + O_2 \tag{1.4}$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{1.5}$$

$$HOBr + h\nu \rightarrow Br + OH \tag{1.6}$$

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \tag{1.7}$$

Since all three chemical reaction cycles destroy ozone, they are possible propagation reactions during the ozone depletion events in the polar regions. But, according to Simpson et al. [2007], *"these cycles do not increase the reactive stock of halogen atoms and halogen oxides (Br and BrO)",* contrarily to a chemical process called "bromine explosion":

$$HOBr_{(g)} \rightarrow HOBr_{(aq)} \tag{1.8}$$

$$HOBr_{(ad)} + Br^{-}_{(aq)} + H^{+} \rightarrow H_2O + Br_{2(aq)} \tag{1.9}$$

$$Br_{2(aq)} \rightarrow Br_{2(g)} \tag{1.10}$$

$$Br_{2(g)} + h\nu \rightarrow 2Br_{(g)} \tag{1.11}$$

$$Br_{(g)} + O_3 \rightarrow BrO_{(g)} + O_2 \tag{1.12}$$

$$BrO_{(g)} + HO_2 \rightarrow HOBr_{(g)} + O_2 \tag{1.13}$$

The catalytic cycles of the bromine explosion leading to the destruction of ozone are well known. Gaseous HOBr is absorbed and reacts with aqueous Br^{-}, which results in the production of Br_2. Once Br_2 is in the gas phase, it is photolysed forming two reactive bromine atoms [Vogt et al., 1996]. In this heterogeneous chemical process, one reactive bromine species (HOBr) leads to the release of two reactive bromine atoms (Br) in the gas phase, which again destroy two ozone atoms [Simpson et al., 2007]. Hence, the bromine explosion results in an exponential growth of the reactive bromine concentration and also an exponential decrease of the ozone concentration in the atmosphere [Simpson et al., 2007, Jacobi et al., 2006].

Whereas the chemical reactions leading to ozone depletion in the polar regions have been identified, the process inducing the reactive halogen species to enter the gaseous phase is still open to some discussion [Lehrer et al., 2004]. Sea salt is the source of the enhanced BrO observations in the polar regions [Lehrer et al., 2004, Jacobi et al., 2006, Jones et al., 2009].

The importance of sea salt deposited on snowpacks [Jones et al., 2010] or the contribution of sea salt aerosols [Lehrer et al., 2004, Wagenbach et al., 1998] in the generating of reactive bromine in the polar troposphere is still unresolved.

According to Jacobi et al. [2006] and Kaleschke et al. [2004], frost flowers are the most likely sources of reactive bromine in the polar regions. As sea water freezes, a thin liquid film with enhanced salinity remains on top of the first-year sea ice [Lehrer et al., 2004]. Frost flowers are ice crystals forming on the surface of fresh sea ice (see Figure 1.3.).

Figure 1.3: *"Field of frost flowers on an area of new ice observed and sampled during the ice station on 8 October (left). Example of a needle-shaped frost flower crystal sampled on the new ice area (right)." [Jacobi et al., 2009]*

A 1-dimensional model developped by Lehrer et al. [2004] gives information about the vertical distribution of ozone, HOBr, Br_2 radicals and BrO before and during an ozone depletion event. The ozone concentration is homogeneous in the first 500 m height whereas BrO decreases with height. As Br_2 is photodissociated, it is only present a few meters over the sea ice ($<$ 5 m). HOBr is destroyed by chemical reactions over the surface, thus, it increases with height.

Considering frost flowers as the main source of reactive bromine in the polar regions, first year sea ice as well as radiation are necessary to initiate an ozone depletion event. These conditions are only encountered in spring. Hence, ODEs only occur during the polar sunrise [Jones et al., 2009].

As indicated before, the bromine explosion is a heterogeneous reaction between the gaseous and the condensed phase [Simpson et al., 2007]. According to Jones et al. [2009], two different possibilities facilitate the contact between these two phases. On the one hand a stable and well-stratified boundary layer as well as low wind speed can lead to an enhancement of the concentration of reactants in the first few meters above the surface. On the other hand high wind speed (above 12 ms^{-1}) leads to blowing snow [Jones et al., 2009]. If particles with high salinity are lifted and attain the boundary layer, the bromine explosion can be induced under these conditions.

Ozone mixing ratios as well as meteorological parameters and BrO vertical column have been observed during the expedition 'Winter Weddell Outflow Study' between 24 August and 29 October 2006. One of the main challenges of this study was to follow the development of ozone to improve the knowledge about tropospherical ozone depletion events (ODEs). Investigations were performed in the north-western Weddell Sea southward of the South Orkney Islands [Jacobi et al., 2009] (see below).

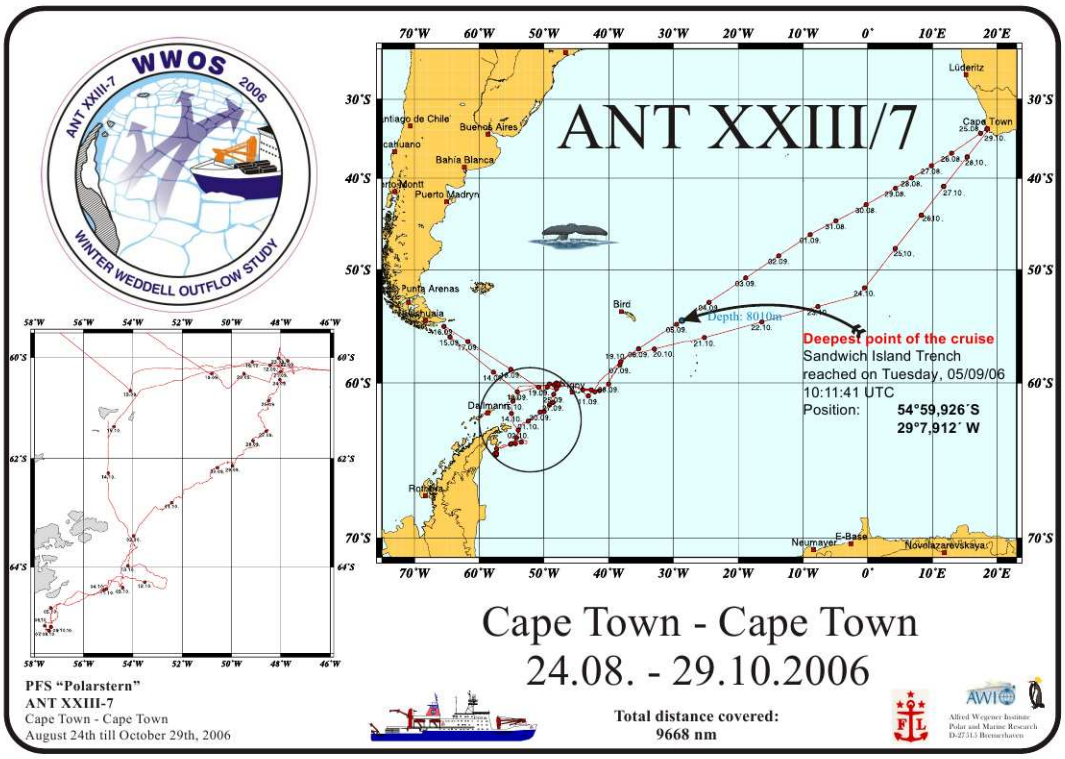


Figure 1.4: Itinerary of the research vessel 'Polarstern' between the 24 August 2006 and 29 October 2006.

To verify the connection between the ozone concentration and the BrO vertical column in the troposphere, additional BrO observations were performed onboard of the research vessel. The further comparison of BrO measurements onboard and satellite BrO observations permitted to gain even more informations about the ozone depletion events.

Chapter 2

Methods

2.1 Ozone measurements

2.1.1 Ozone measurements onboard of the RV Polarstern

Ozone measurements were performed on board of the RV Polarstern during the cruise ANT 23/7 between 27 August and 21 October 2006. Measurements started with an interval of 10 minutes in the beginning of the expedition until 31 August 2006; 11h40. Thereafter the interval was changed to 5 minutes until the end of the expedition.

Ozone mixing ratios were determined using a commercial detector (O341M, Ansyco GmbH, Karlsruhe, Germany), which is based on UV Photometric detection at 254 nm and which was used on board during previous cruises [Jacobi and Schrems, 1999, Jacobi et al., 2006]. The detector was installed in a heated laboratory container placed on the compass deck (the upper most deck) of the ship and was equipped with an unheated inlet line consisting of approximately 2 m of 0.4 cm ID perfluoroalkoxy tubing. The outboard end of the inlet line was shielded with a sea spray deflector and was mounted on the front rail of the deck approximately 25 m above sea level. The inlet line was regularly controlled by visual inspection. The ozone values were internally averaged and stored as 5-min or 10-min averages. Ship borne measurements of ozone can generally be disturbed by possible contamination originating from the exhaust of the ship's engines since they are powerful sources of nitrogen oxides ($NO + NO_2$). Nitrogen oxides can modify ozone concentrations by removing ozone due to the reaction with NO or by forming ozone due to photochemical processes. Therefore, ozone mixing ratios obtained during relative wind directions outside a corridor of $\pm 110^\circ$ or at relative wind speeds lower than 2 m s^{-1} were discarded. Only corrected data were used for further analysis. The full and corrected data sets are shown in Figure 2.1.

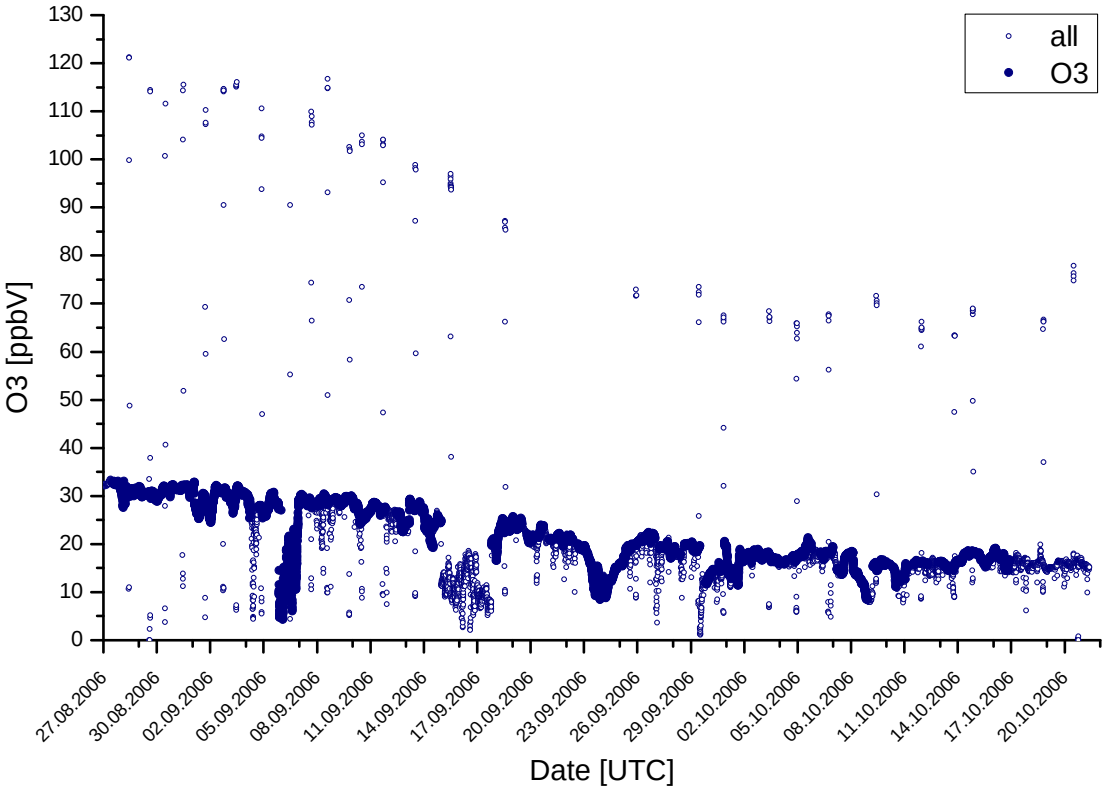


Figure 2.1: *Time series of all ozone measurements including calibration measurements (open blue circles). The filled circles indicate the remaining data set after removing data for periods of potential contamination (see text) and calibration.*

During the expedition, the performance of the detector was regularly controlled using an internal ozone generator producing a stream of air with a defined ozone mixing ratio. The results of these control measurements are displayed in 2.2. Obviously, the values of the control measurements were decreasing during the expedition probably due to a decrease in sensitivity of the detector caused by the deterioration of the light source and / or the deposition of sea salt on the optical elements of the measuring cell. A similar overall trend is also apparent in the ozone time series for ambient air.

The ozone control measurements show a constant value between the beginning of the measurements until 4 September; 08:19 (Period 1); between 4 September; 08:19 and 28 September; 16:14 the values of the control measurements decrease steadily (Period 2). After 28 September; 16:14 (Period 3), the control measurements were again constant (see Figure 2.2.).

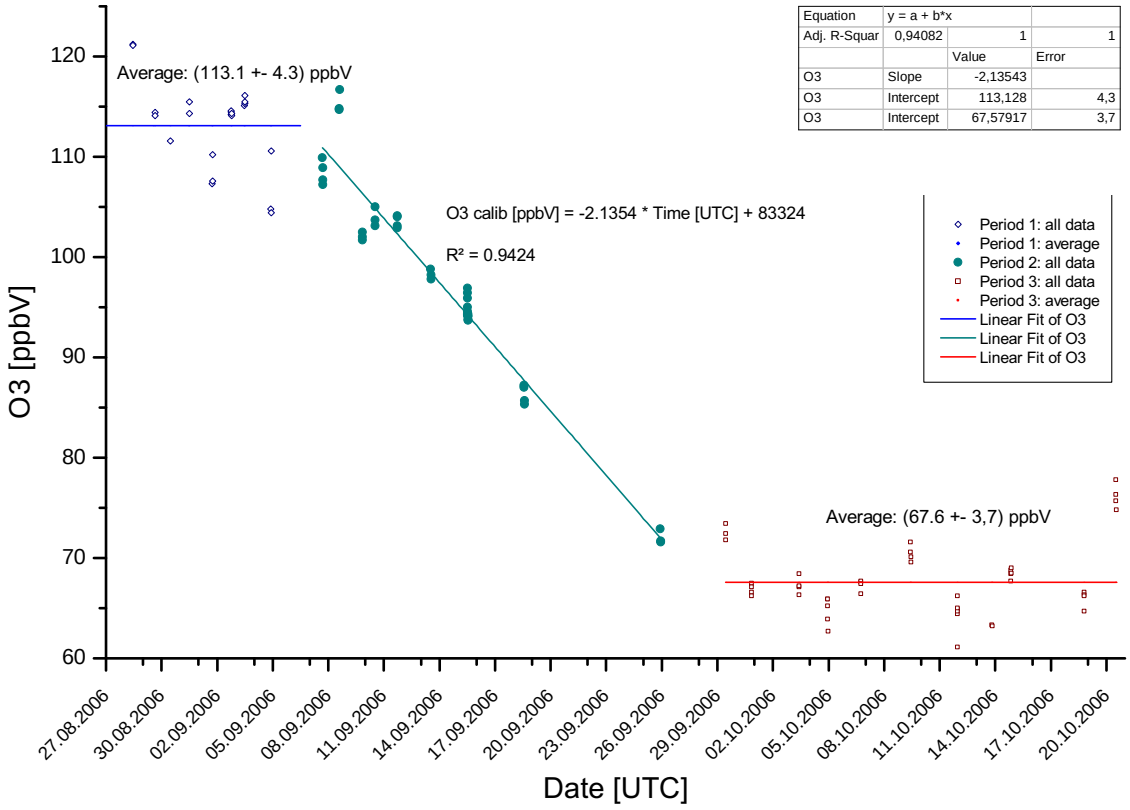


Figure 2.2: *Trends of the ozone control measurements*

The results of the control measurements were used to correct the obtained ozone time series for ambient air according to the three defined periods.

- Period 1: Values are constant. The average value of the control measurements corresponds to (113.1±4.3) ppbV. This mixing ratio compares well to control measurements of the same instrument performed during previous experiments. Therefore, the value of this period is considered as a reference for the mixing ratio of the internally generated air stream with a constant ozone mixing ratio. No correction for the raw ozone mixing ratio $[O_3]_{raw}$ in period 1 is necessary.

$$x_{new} = [O_3]_{raw} \tag{2.1}$$

- Period 2: The values during period 2 decrease linearly as a function of time. The linear regression for this period delivers equation 2.2. with a correlation coefficient of $R^2 = 0.9424$.

$$y_i = -2.1354 * x_i + 83324 \tag{2.2}$$

where x_i corresponds to the time elapsed since 01 January 1900 in days. Using this formula it is possible to correct all raw ozone mixing ratios according to equation 2.3:

$$x_{new} = \frac{113.1}{y_i} * [O_3]_{raw} \tag{2.3}$$

- Period 3: The values remained constant with an average of (67.6±3.7) ppbV. Therefore, the sensitivity of the detector decreased by almost 40 % compared to the beginning of the measurement period. To correct the raw values all data points were adjusted according to equation 2.4.:

$$x_{new} = \frac{113.1}{67.6} * [O_3]_{raw} \tag{2.4}$$

Figure 2.3. summarizes the time series of the raw and the final corrected ozone mixing ratios.

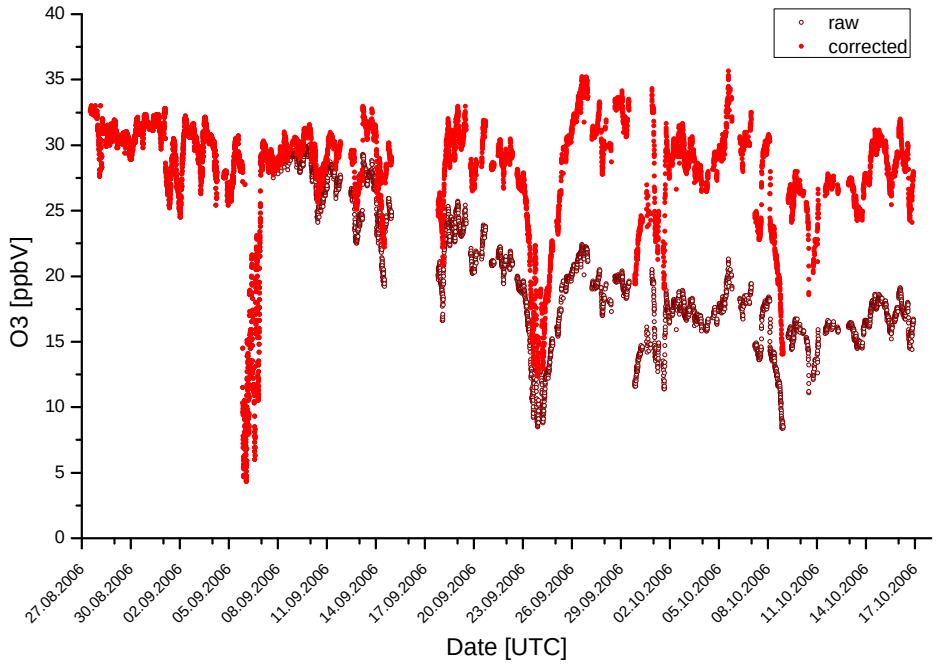


Figure 2.3: *Raw and corrected ozone concentration*

Normally, the estimated error of the O_3 measurement is in the order of 1 ppbV [Jacobi et al., 2009]. Due to the correction of the recorded values, the error needs to be reevaluated.

The error estimation was done for each period separately.

- Period 1: The relative error of corrected data only consists of the relative error of the arithmetic average of the ozone control concentrations during this period and the relative error of the individual ozone values. To simplify the estimate, the error is calculated using average values for the recorded and corrected ozone values: $[O_3]_{measured,Period1}$= 30.1 ppbV; x_{new}= 27.6 ppbV.

$$\left|\frac{\triangle x}{x_{new}}\right| = \left|\frac{\triangle Av[O_3]_{contr}}{Av[O_3]_{contr}}\right| + \left|\frac{\triangle [O_3]}{Av[O_3]_{measured,Period1}}\right| \tag{2.5}$$

$$\left|\frac{\triangle x}{x_{new}}\right| = \left|\frac{4.3}{113.1}\right| + \left|\frac{1}{30.1}\right| \tag{2.6}$$

  The relative error of Period 1 corresponds to 7% or around 2 ppbV.

- Period 3: The relative error consists of the sum of the relative error of the arithmetic average of the ozone control concentration during Period 1, the relative error of the arithmetic average of the ozone control concentration during Period 3 and the relative error of the individual ozone values. Again, calculations are done by using the averaged values for the recorded and corrected ozone values: $[O_3]_{measured,Period1}$= 16.4 ppbV; x_{new}= 27.5 ppbV.

$$\left|\frac{\triangle x}{x_{new}}\right| = \left|\frac{\triangle Av[O_3]_{contr,Period1}}{Av[O_3]_{contr,Period1}}\right| + \left|\frac{\triangle Av[O_3]_{contr,Period3}}{Av[O_3]_{contr,Period3}}\right| \left|\frac{\triangle [O_3]}{Av[O_3]_{measured,Period3}}\right| \tag{2.7}$$

$$\left|\frac{\triangle x}{x_{new}}\right| = \left|\frac{4.3}{113.1}\right| + \left|\frac{3.7}{67.6}\right| + \left|\frac{1}{16.4}\right| \tag{2.8}$$

  As a result, the relative error of Period 3 amounts to 15% or around 4 ppbV.

- Period 2: The relative error of Period 2 increases steadily between 7 and 15%.

2.1.2 Ozone measurements at other research stations in the southern Atlantic

Ozone concentrations have continuously been measured at three stations around the South Atlantic Ocean.

Neumayer is a German research station in Antarctica located on the Ekstrom Ice Shelf and lies close to sea level. It is specialised in geophysical, meteorological and atmospheric chemistry measurements. The data from 2006 used for comparison are issued from the Neumayer Station II. It opened in 1992 and is located at 70.6° S, 8.3° W. At Neumayer ozone concentration is measured with a UV absorption monitor similar to the detector used onboard of Polarstern [Helmig et al., 2007, Weller et al., 2007]. The ozone concentration is automatically measured every hour.

The British research station Halley is located on the Brunt Ice Shelf in the East of the Weddell Sea. The predominant wind direction is East keeping a number of polynyas open [Helmig et al., 2007]. The Antarctic Survey Station was opened in 1956 and operates throughout the year. The scientific activities primarily consist in atmospheric sciences, but also in geology and glaciology. The data analysed were obtained at Halley VI at the position 75.6° S, 26.6° W. Halley data were provided by the British Antarctic Survey. Ozone monitoring was performed with continuously operating UV absorption monitors [Helmig et al., 2007]. The ozone concentration was recorded with an interval of 10 minutes at Halley. Ozone data were provided by Anna Jones from the British Antarctic Survey in Cambridge, UK.

The research station Cape Point is located near the Cape of Good Hope in South Africa. It is specialised in measurements of trace gases (CO, CO_2, CH_4, N2O, O_3, CFCs), aerosols as well as meteorological parameters (pressure, wind, temperature, solar irradiance and others). It is located at 34.4° S, 18.5°E.

The Antarctic research station Neumayer as well as the South African station Cape Point contribute to the Global Atmosphere Watch (GAW) Programme. Information about the GAW Programme can be found at `www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html`. Data for both stations were retrieved from the World Data Centre for Greenhouse Gases (`http://gaw.kishou.go.jp/wdcgg/`), where they are stored at 1-hour averages.

2.2 BrO measurements in the Weddell Sea

2.2.1 Differential Optical Absorption Spectroscopy (DOAS)

The Differential Optical Absorption Spectroscopy (DOAS) is a remote sensing method to determine concentrations and total amounts of atmospheric trace gases from measurements of solar radiation in the UV, visible, and NIR spectral range. The basic principle used in DOAS is absorption spectroscopy. Solar radiation travelling through the atmosphere is partly absorbed by trace constituents along the way following Lambert-Beer's law. The radiation intensity at the end of a light path therefore depends on:

- the initial intensity
- the length of the light path
- the total amount of the absorber along the light path
- the absorption strength of the species of interest

Further details can be found at `www.doas-bremen.de/doas_tutorial.htm`.

2.2.1.1 MAX-DOAS

From 27 August until 25 October continuous measurements were performed with a ship-borne 2-channel multiaxis DOAS instrument installed in the air measurement container. The collected spectra of the UV-channel allowed the simultaneous detection of BrO, O_3, nitrogen dioxide (NO_2), oxygen dimer (O_4), and chlorine dioxide (OClO) [Jacobi et al., 2009].

2.2.1.2 Sciamachy - Scanning Imaging Absorption Spectrometer for Atmospheric Chartography

In this study satellite data from the SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) sensor were used. It is also based on the DOAS method. As the measurements are sensitive to both stratospheric and tropospheric BrO, the stratospheric component must be accounted for before retrieval of the tropospheric amount. The stratospheric column was approximated with $4*10^{13}$ molecules cm^{-2} and subtracted from the total column observed. The data were provided by Andreas Richter from the University of Bremen, Germany (`http://www.iup.uni-bremen.de`).

2.3 Meteorological data

2.3.1 Meteorological measurements on board of RV Polarstern

Standard meteorological data are routinely collected onboard the RV Polarstern. Information about the meteorological observatory on board can be found on the homepage of the Alfred Wegener Insitute for Polar and Marine Research (`http://www.awi.de/en/infrastructure/ships/polarstern/meteorological_observatory`). A full description of the installed instrumentation can be found in König-Langlo et al. [2006]. Retrieval of data from the Data Acquisition and Management System for Marine Research Archive System is possible starting from `dship.awi.de`.

The following meteorological data were used in this study:

- Pressure [hPa]
- Temperature [°C]
- Dew Point [°C]
- Humidity [%]
- Wind direction [°]
- Wind velocity [m/s]
- Visibility [m]
- Insolation [W/m^2]

2.3.2 ECMWF - The European Centre for Medium-Range Weather Forecasts

The ECMWF is an intergovernmental organisation supported by 34 States, based in Reading in the United Kingdom. Data and more information about the European Centre for Medium-Range Weather Forecasts can be found on the website: `www.ecmwf.int/`.

The global reanalysis used is the ERA-Interim reanalysis. It is an "interim" reanalysis containing data since 1989 until present. Fields are analysed for 00:00, 06:00, 12:00 and 18:00 UTC every day. Each parameter at every level is stored as a field of grid points at N128 Gaussian Grid resolution dividing the latitude in 256 latitude numbers between 89.46282° and -89.46282° latitude. Analysis data are available for surface levels as well as pressure, model, isentropic and potential vorticity levels.

ERA-Interim is a four dimensional variational analysis.

Following data were retrieved from the reanalysis daily ERA-Interim fields:

- Mean sea level pressure
- 10 metre U and V wind components
- Sea-ice cover
- Boundary layer height

2.4 Other data

2.4.1 Hysplit - Hybrid Single-Particle Lagrangian Integrated Trajectory

The Hysplit model is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations. Information about the operating of the Hysplit model can be found on the homepage of the "NOAA - Air Ressources Laboratory" (`http://www.arl.noaa.gov/HYSPLIT_info.php`). It is possible to run the model interactively on the Web. The trajectories used to describe the movement of the air parcels during ozone depletion events are archive trajectories computed with NCEP global Reanalysis data from 1948 to present.

Chapter 3

Results and Discussion

3.1 Ozone concentrations

To compare the time series at the different research stations in the southern Atlantic and onboard the RV Polarstern, it is necessary to average the recorded values within a common time interval. Ozone data from the German research station Neumayer and the South African station Cape Point are available every hour, hence, the intervals of the data at Halley as well as those collected on board of Polarstern were averaged to obtain 1-hour averages.

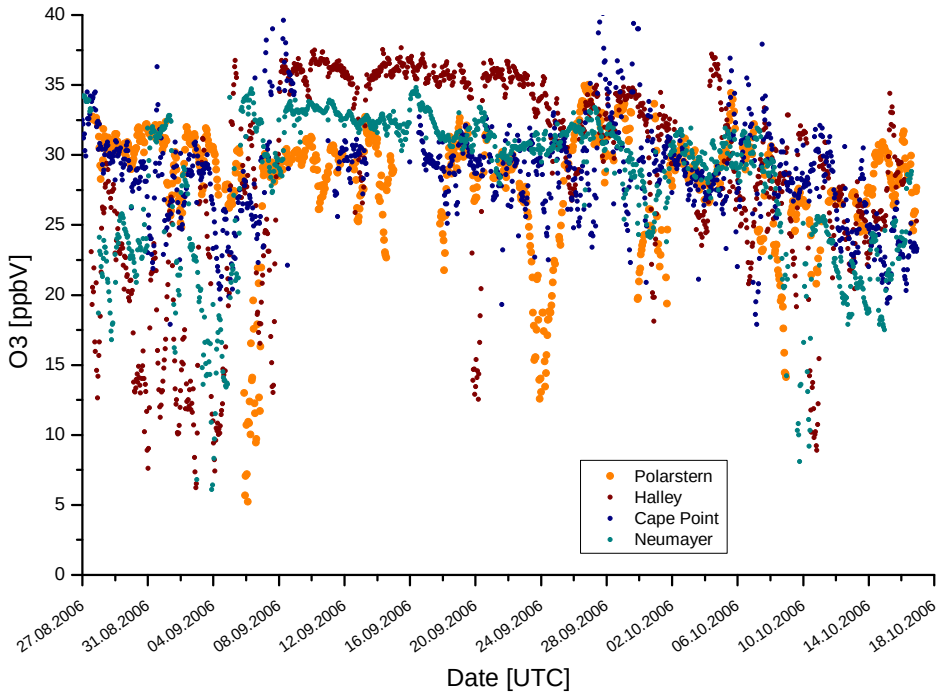


Figure 3.1: *Time series of ozone concentration on board of Polarstern and at Halley, Neumayer and Cape Point between 27 August and 17 October 2006*

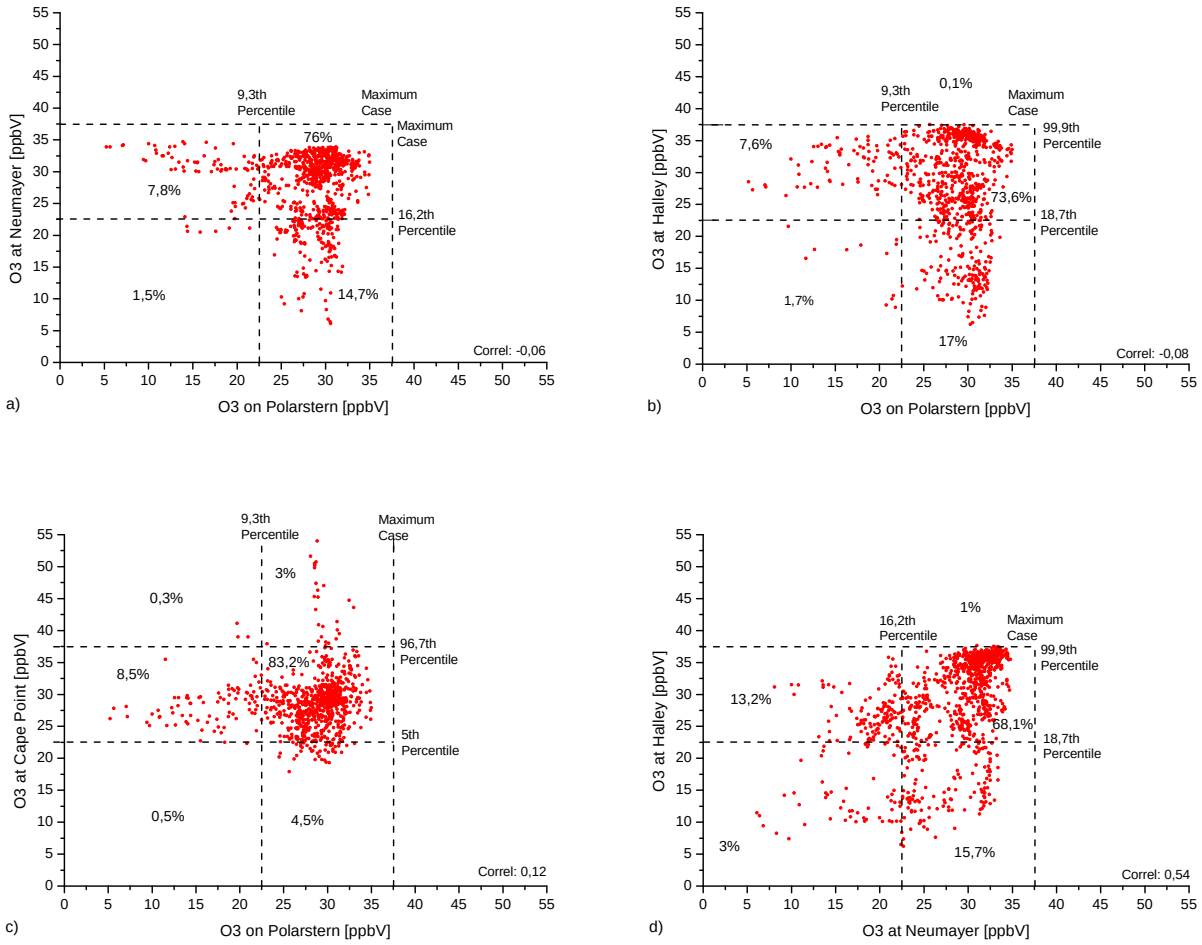


Figure 3.2: *Correlations between the ozone concentrations measured at Neumayer (a), at Halley (b), at Cape Point (c) and on board of Polarstern and at Halley and Neumayer (d) between 26 August and 17 October 2006.*

Figure 3.2. illustrates correlations of the ozone concentration measured on board of Polarstern and at Neumayer (Figure 3.2.a), at Halley (Figure 3.2.b) and at Cape Point (Figure 3.2.c), respectively. The median of the ozone concentration is around 30 ppbV on board of Polarstern and at the research stations in the southern Atlantic (see Table 3.1.). The intervals plotted in figure 6 are defined as ±25% of the median.

All graphs indicate that ozone remains at background level during extended periods at each research station. Background level is considered as an ozone concentration between 22.5 and 37.5 ppbV, at least at this period of the year. It demonstrates that at these locations ozone depletion events only happen during limited periods and only in and around the Weddell Sea. The lowest concentration observed at Cape Point corresponds to 17.9 ppbV.

The correlation between the ozone data collected on board of Polarstern and at Neumayer (Figure 3.2.a) and on board of Polarstern and at Halley (Figure 3.2.b) display a similar behaviour. About 75% of the data are simoultaneously at background level at both locations. Ozone depletion events take place at one of the two Antarctic stations whereas the ozone concentration on the research vessel Polarstern do not decrease (around 15% in both cases). Ozone depletion events only happening on board of Polarstern are rare (7.8% and 7.6%). These asynchronous events can be explained by the geographical distance between the itinerary of the research vessel Polarstern and the Antarctic stations Neumayer and Halley respectively. Nevertheless simultaneous drops of the ozone concentration on Polarstern and one of the Antarctic stations were observed. However, these simultaneous events remain uncommon ($< 2\%$).

The Antarctic research stations Neumayer and Halley are both located on the Eastern Coast of the Weddell Sea within a distance of 800 km. The correlation of the ozone concentration between these stations is shown in Figure 3.2.d. Compared to stations that are distant (Polarstern and Neumayer (a) or Polarstern and Halley (b)), the percentage of ozone drops happening at the same time at Neumayer and Halley is twice as high (3%). Again about 70% of the ozone data are at background level simultaneously at both stations. The percentage where ozone depletion events happen at Neumayer whereas the ozone concentration at Halley remains at background level and vice versa is uniformly distributed (13.2% and 15.7%).

Finally, the ozone concentrations on board of Polarstern and at Cape Point in South Africa (Figure 3.2.c) indicate no correlation (0.12). The ozone concentration on the South African Coast seems to be somewhat lower than in the Weddell Sea (compare Figure 3.3.) and there is no significant ozone depletion event at Cape Point during the observed period. However, peaks in ozone concentration probably due to pollution are regularly observed at the South African station Cape Point (3%) [Brunke et al., 2010].

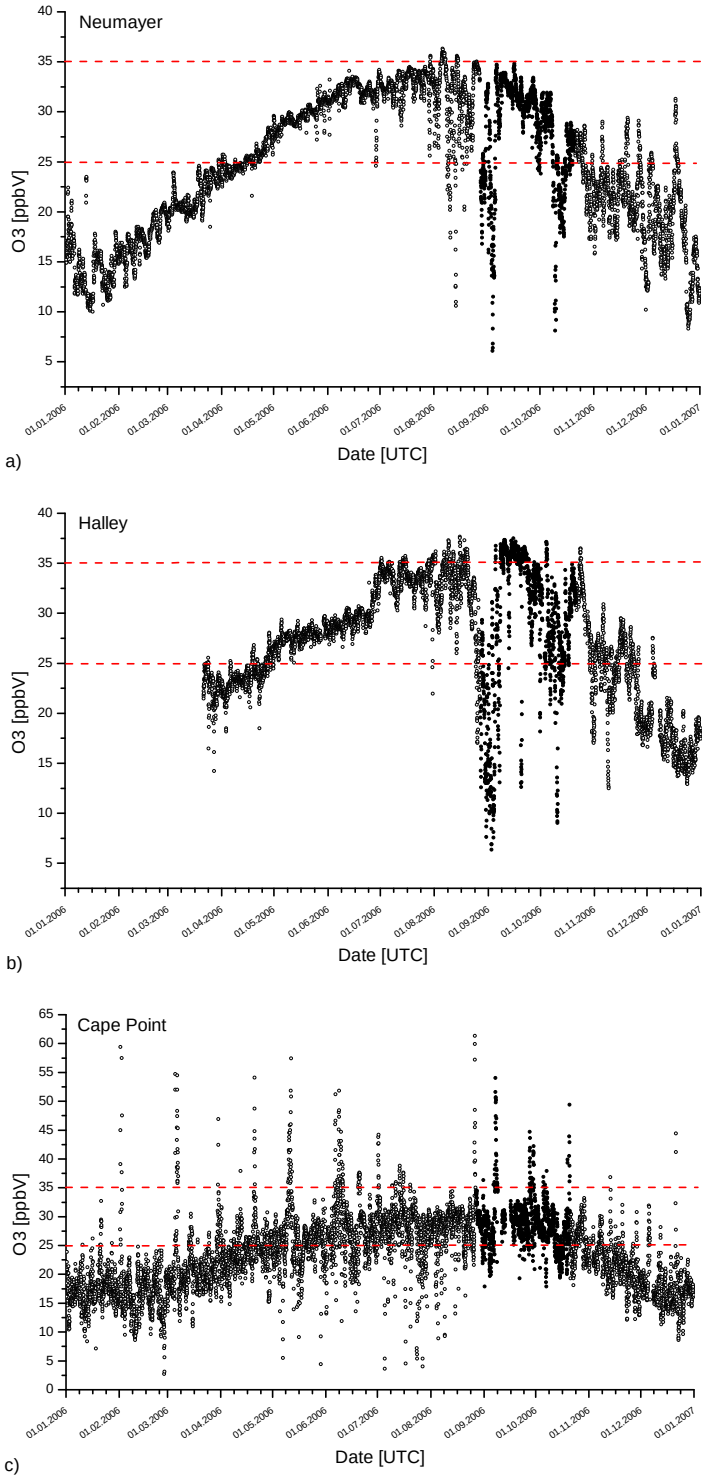


Figure 3.3: *Annual records of surface ozone for the stations Neumayer (a), Halley (b) and Cape Point (c) for 2006. The filled circles indicate the period where the the Winter Weddell Outflow Study took place. Note the different scales (40 vs. 65 ppbV) in a) and b) compared to c).*

According to Helmig et al. [2007] the months with highest ozone in Antarctica are observed in winter (June to August), seasonal minima are mainly observed from December to February. Ozone depletion is mostly driven by halogen chemistry, most notably bromine. Photolysis of Br_2 generates Br radicals that can destroy O_3 [Jones et al., 2010, Simpson et al., 2007]. During the Polar night, no photolysis takes place and the ozone concentration increases to background level.

At the South African station Cape Point, the period where the mean ozone concentration is highest begins earlier than at the Antarctic stations and the maximum ozone concentration is reached earlier in the season. In addition, the amplitude of the ozone concentration at Cape Point is smaller (from around 15 ppbV in summer to approximately 30 ppbV in winter compared to a minimum of 10 ppbV and a maximum of 35 ppbV at the Antarctic stations Neumayer and Halley).

At Neumayer (a) and Halley (b) ozone depletion events are typically observed between August and November. No ozone depletion event took place during this period at the South African research station Cape Point (Figure 3.3.c). Nevertheless, some sudden ozone drops are also observed at Cape Point between May and September.

		Mean	Median	< 0.5 Median	> 1.5 Median
		[ppbV]	[ppbV]	[%]	[%]
Neumayer	2006	24.9	25.1	3.6	0.0
Neumayer	27 Aug.-17 Oct. 2006	28.1	30.3	3.0	0.0
Halley	2006 [I]	27.2	27.8	1.2	0.0
Halley	27 Aug.-17 Oct. 2006	29.6	30.9	10.3	0.0
Halley	2003 [II]	24.3	27.1	8.5	0.0
Cape Point	2006	26.4	24.1	2.0	2.2
Cape Point	27 Aug.-17 Oct. 2006	28.8	28.9	0.0	1.2
Polarstern	27 Aug.-17 Oct. 2006	28.0	29.3	2.9	0.0

Table 3.1: *Mean, Median and percentage of data lower than 0.5-median value and higher than 1.5-median value of the ozone time series at Neumayer, Halley, Cape Point and onboard of Polarstern. Analysed periods range from 27 August to 17 October 2006 as well as for the entire year 2006, at Halley for the year 2003.*

Table 3.1. provides the mean and the median of the ozone timeseries for 2006 at both Antarctic stations Neumayer and Halley and at the South African research station Cape Point as well as of the ozone timeseries for the period between 27 August and 17 October 2006 at

[I] only from 21 march to 31 december
[II] data from Helmig et al. [2007]

the research stations Neumayer, Halley and Cape Point and onboard of the research vessel Polarstern. The difference between the mean and the median value provides an indication of isolated events with strongly depleted or enhanced ozone. Additionally Table 1 indicates the percentage of the hourly data that fell below and above 0.5 and 1.5 times the annual median ozone value and the median ozone concentration to determine either extremely high or low ozone values during the Winter Weddell Outflow Study. The ozone timeseries measured at Halley in 2006 are incomplete, the mean and the median of these data must therefore be regarded with caution. For comparison the mean and median of the ozone time series of 2003 at Halley are provided [Helmig et al., 2007]. Table 1 indicates that the mean ozone concentration at the Antarctic stations Neumayer and Halley as well as at the South African station Cape Point are very similar. As the expedition Winter Weddell Outflow Study took place in the end of the winter of the Southern Hemisphere, the mean and the median of the ozone concentration of this period are slightly higher than the annual mean in the observed area (compare Figure 3.3.). Comparing the percentage of the hourly data that fell below 0.5 times the median ozone concentration between 27 August and 17 October 2006 reveals a high rate of ozone drops below this arbitrary limit at the research station Halley. It demonstrates that frequent ozone depletion events took place at the Antarctic station (compare figures 3.2.b and 3.3.b). In 2003, 8.5 % of the data met the $<$ 0.5-times annual median criteria (see Table 1).

As already seen in Figure 3.2.c no ozone depletion events took place between 27 August and 17 October 2006 at Cape Point. This is confirmed by Table 1: the percentage of data meeting the $<$ 0.5-times median criteria for this period equals 0.0%.

Table 1 also suggests that the annual mean ozone value, which, evidently, will be more influenced by events with extreme high or low ozone concentration, exceeds the median value at Cape Point. Additionally Cape Point is the only station in the observed area where some data meet the $>$ 1.5-times median criteria for the period between 27 August and 17 October 2006 as well as for the entire year 2006. This underlines the frequency of periods with elevated ozone concentration (compare Figure 3.3.c). Since such high ozone concentrations were only encountered at the South African research station and not at the Antarctic stations, they can be interpretated as pollution peaks [Brunke et al., 2010].

3.2 Link between ozone concentrations and meteorological conditions

Ozone depletion events are defined as sudden drops of the ozone concentration on a timescale of minutes to several days [Simpson et al., 2007]. Two different processes can cause the sudden decrease of the ozone concentration: They can be meteorologically controlled or chemically induced. In this chapter, the meteorological causes of the four ozone depletion events that happened during the Winter Weddell Outflow Study will be investigated.

Previous measurements in 2003 and 2007 in the Arctic revealed that low ozone levels represented the normal state of the boundary layer of the Arctic Ocean in springtime (in 2003 more than 55 % and in 2007 more than 66 % of all ozone observations were below 5 ppbV, which was used to define ozone depletion events) [Jacobi et al., 2010]. These decreases in ozone were in many cases accompanied by increases in pressure and vice versa. Similarly, ozone concentrations and local air temperatures were positively correlated during the fast ozone transitions [Jacobi et al., 2010]. The available data sets were investigated for the relationships between O_3, pressure and air temperature. Further investigations indicated the connections between the sudden changes in ozone concentration and air mass changes. Hence, according to Jacobi et al. [2010], the transition between low and high ozone over the Arctic Ocean is related to lows entering the region from lower latitudes. These lows induce changes in the transport of air masses leading to simultaneous changes in meteorological variables like pressure and temperature as well as ozone concentration.

The main factor for depressions to develop in higher latitudes in the southern hemisphere is an intense meridional temperature gradient in the troposphere. Due to the higher albedo of snow and ice, the surface radiation on and around the continent Antarctica is mostly negative and the cooling of the lower troposphere happens faster in higher latitudes than in middle latitudes [König-Langlo et al., 1998]. The polar front separates the cold polar air to the south and the more temperate air masses to the north in the Southern Hemisphere. This region is favorable for baroclinic waves to generate and further develop into low pressure systems [King and Turner, 1997]. This leads to a low Index exposure and a trough-ridge system. The "Index-exposure" is defined as the absolute value of the difference between two geopotential-fields in different latitudes. Under these conditions, the vorticity term must be considered. The following Omega-equation [Holton, 2004] describes the behaviour of pressure systems and depicts the cyclonic rotation of low pressure systems and the anticyclonic rotation of high pressure systems.

$$\left[\vec{\nabla}^2 + \frac{f_{0^2}}{\sigma}\frac{\partial^2}{\partial p^2}\right]\omega = -\frac{f_0}{\sigma}\frac{\partial}{\partial p}\left[-\vec{v}_g.\vec{\nabla}\left(\frac{1}{f_0}\vec{\nabla}^2\Phi + f\right)\right] + \frac{1}{\sigma}\vec{\nabla}^2\left(-\vec{v}.\vec{\nabla}\frac{\partial\Phi}{\partial p}\right) \tag{3.1}$$

∇^2 is the Laplacian Operator; f and f_0 are the Coriolis parameter in s^{-1}. f_0 is a constant value defined as $f_0 = 2\Omega sin\varphi_0$ whereas f is a function of the latitude $f = 2\Omega sin\varphi$ where φ indicates the latitude in degrees and Ω is the rotation rate in s^{-1}. The static stability is described by σ. ω indicates the generalised velocity in ms^{-1} and $-\vec{\nabla}^2\Phi$ the relative vorticity in s^{-1} where Φ is the geopotential in gpm. The geostrophic wind is described by $\vec{v_g}$, thus $-\vec{v_g}.\vec{\nabla}$ is the advection with the geostrophic wind in ms^{-1}.

According to the Omega-equation (Equation 3.1.), the combination of negative vorticity advection and warm air advection in the Southern Hemisphere leads to the ascent of the air mass. This can result in a cyclonic depression.

The repartition of land masses in the Southern Hemisphere differs largely from the Northern Hemisphere. These differences influence the behaviour of pressure systems. Whereas in the Northern Hemisphere the low pressure systems penetrate into the Arctic Ocean, the depressions that develop over the Southern Oceans first move in a zonal direction. Therefore, the low pressure systems are already in a mature stage when they reach the Antarctic continent. Since Antarctica consists of a high plateau, the depressions are unable to penetrate far into the interior of the continent. They usually turn towards the east and again move in a zonal direction parallel to the coast in a latitude band of 60 to 70° South (see Figure 3.4.). This region is known as the circumpolar trough [King and Turner, 1997].

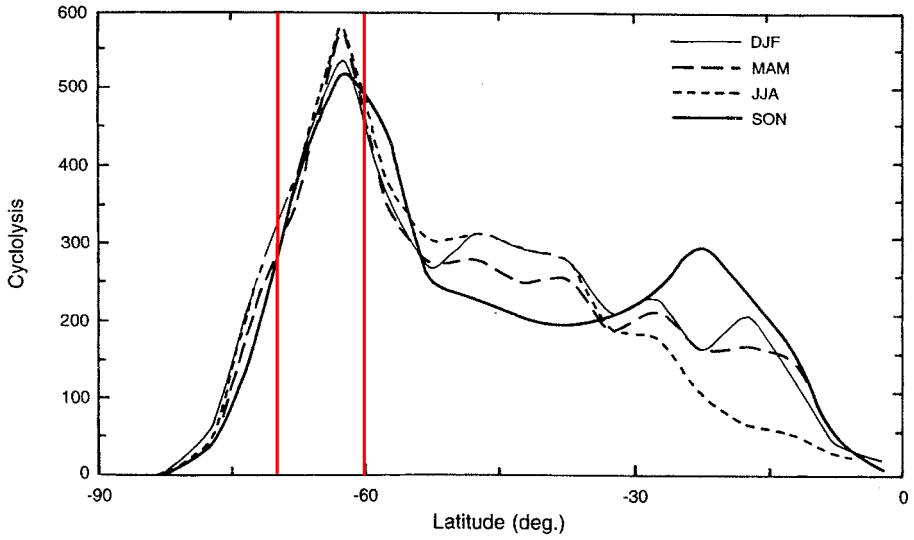


Figure 3.4: *The total count of cyclogenesis in 5° latitude bands for summer (June, July, August), autumn (September, October, November), winter (December, January, February) and spring (March, April, May), for the period 1975-1989 [King and Turner, 1997].*

Figure 3.4. illustrates the number of low pressure systems as a function of the latitude showing that the maximum of cyclones resides in the circumpolar trough between 60 and 70° South. Further south the number of cyclones decreases rapidly as the high altitude of the Antarctic continent prevent the low pressure systems to move in a southern direction.

The horizontal temperature gradient between middle and high latitudes needed for the development of large-scale cyclones shows two maxima around the equinoxes. Hence, the circumpolar trough is strongest in spring and autumn [Schlosser et al., 2011]. The RV Polarstern was situated in the circumpolar trough during the Winter Weddell Outflow Study in spring 2006. Therefore, it is possible that large-scale cyclones had an impact on the ozone concentration.

Besides large-scale frontal cyclones, a potential for non-frontal developments exists near the Antarctic coast and especially in the Weddell Sea. Katabatic and drainage winds from the interior of the continent can lead to higher convergence and upward motion over the ocean. Additionally large surface fluxes of sensible as well as latent heat from the surface of the water to the atmosphere arise when cold continental air moves over the ocean. This can lead to baroclinic instability [Heinemann, 1990]. According to Heinemann et al. [1990], non-frontal developments increase with increasing southern latitude.

Hence, during the entire cruise the RV Polarstern was situated in regions with enhanced

cyclogenesis. The connection between pressure, air temperature and ozone concentration is investigated for this cruise.

During the Winter Weddell Outflow Study, ozone depletion events were defined as ozone drops below 70% of the mean ozone concentration (compare table 1), corresponding to 19 ppbV. The ozone time series recorded onboard of the research vessel Polarstern reveals four occasions with ozone concentrations below this threshold between 27 August and 17 October 2006 (see Figure 3.5.).

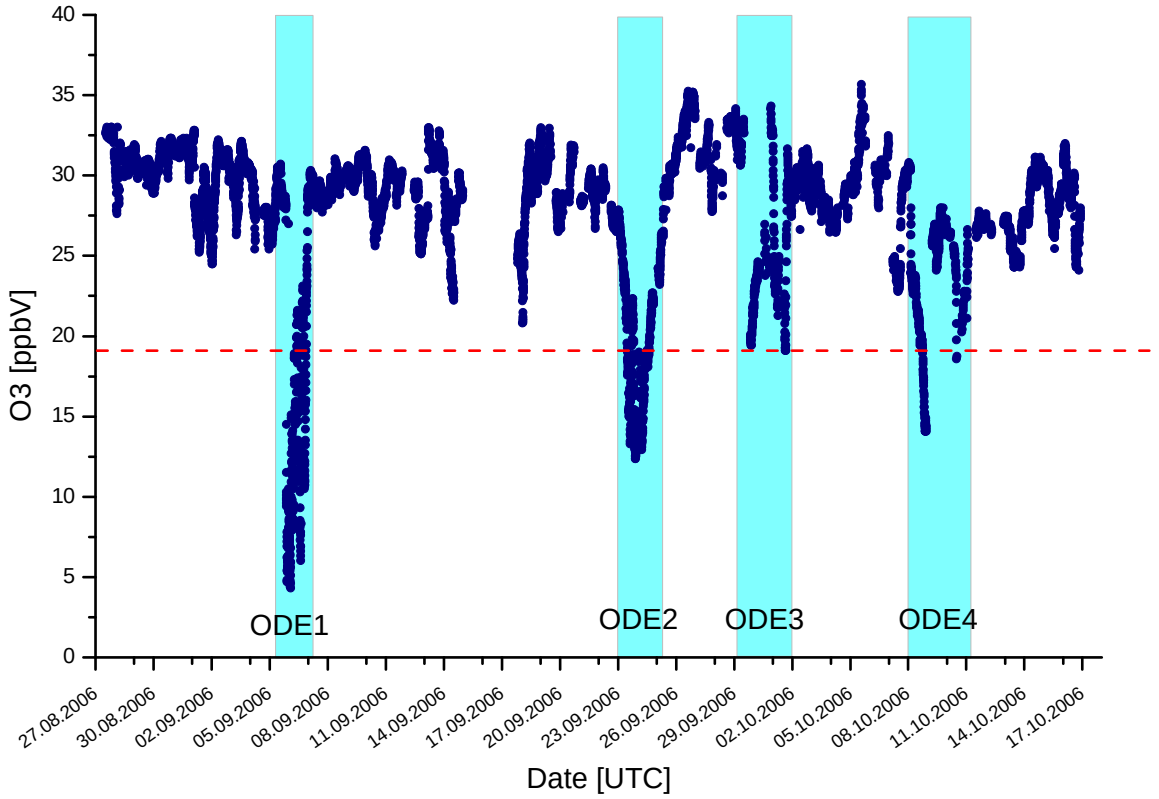


Figure 3.5: *Corrected ozone concentration onboard of the research vessel Polarstern during the Winter Weddell Outflow Study between 27 August and 17 October 2006.*

The first ozone depletion event (ODE1) took place between 05 September 2006, 20:35 and 07 September 2006, 00:15. The ozone concentration dropped below 5 ppbV in only one hour and lastet only one day. During the second ozone depletion event between 23 September 2006, 01:05 and 25 September 2006, 09:35, the period with low ozone level lasted longer. The ozone concentration dropped below 15 ppbV. The third ozone depletion event happened

between 29 September 2006, 11:45 and 01 October 2006, 18:35. The ozone concentration barely dropped below the threshold of 19 ppbV. The last ozone depletion event was the longest. It started on 08 October 2006 at 02:05 and lasted until 11 October 2006, 16:15.

Besides ozone concentration, standard meteorological data (pressure, temperature, dew-point etc.) were measured onboard of the research vessel Polarstern. These local observations were used for the following analyses.

			Correlation R^2	Correlation R^2
		Date & Time	Air pressure - O3	Air temperature - O3
ODE1	Drop	05.09.06, 20:35 - 05.09.06, 21:55	(- 0.10)	(+ 0.69)
	Rise	06.09.06, 19:25 - 07.09.06, 00:15	+ 0.98	+ 0.97
ODE2	Drop	23.09.06, 01:05 - 23.09.06, 14:05	(- 0.90)	(+ 0.55)
	Rise	24.09.06, 05:55 - 25.09.06, 09:35	(+ 0.47)	+ 0.43
ODE3	Drop	30.09.06, 21:55 - 01.10.06, 04:25	- 0.89	+ 0.96
	Rise	01.10.06, 15:45 - 01.10.06, 18:35	(+ 0.33)	+ 0.98
ODE4	Drop	08.10.06, 02:05 - 08.10.06, 21:35	(+ 0.72)	(+ 0.03)
	Rise	10.10.06, 12:15 - 11.10.06, 16:15	+ 0.91	+ 0.62

Table 3.2: *Correlation between ozone concentration and air pressure and ozone concentration and air temperature, respectively, during the ozone depletion events 1 to 4 onboard of Polarstern between 27 August and 17 October 2006. (Figures can be found in the annexes).*

The correlation coefficients obtained from linear regressions of the air pressure and the ozone concentration during the 4 detected ozone depletion events are shown in Table 2. The correlations based on changes below 3 hPa regarding air pressure and changes below 3°C concerning air temperature are considered as not significant enough and are put in parentheses. The coefficient of determination R^2 ranges from -0.89 to +0.98. The correlation between air pressure and ozone concentration is positive (increase of the air pressure) during the rise of the ozone concentration (range between +0.91 and +0.98). Only one coefficient of determination is retained describing the correlation during the drops of the ozone concentration. Hence no statement can be made regarding the correlation between air pressure and sudden ozone decrease.

Table 2 also indicates the correlation between the air temperature and the ozone concentration during the 4 ozone depletion events. Considering the changes in air temperature exceeding 3°C, the coefficient of determination R^2 is positive during both drops and rises of the ozone concentration. R^2 ranges from +0.43 to +0.98. Ozone concentration and air temperature decline or increase simultaneously.

In summary, there is no consistent statistical relationship between the ozone concentration and the air pressure but a certain connection between the air temperature and the ozone

concentration. To examine if the ozone depletion events were related to changes in the air mass, the prevailing meteorological conditions are analyzed more precisely for each ozone depletion event. This analysis is based on the re-analysis data of The European Centre for Medium-Range Weather Forecasts (ECMWF) and back trajectories using the Hysplit Model to allow the determination of the origin of the air masses related to either high or low ozone concentration.

3.2.1 Decrease of the ozone concentration between 05.09.06, 20:35 - 05.09.06, 21:55

According to Figure 3.6, an intense low pressure system was located south of the RV Polarstern during this period. As the ozone decrease lasted only one hour, the air pressure onboard did barely change. Hence, no correlation exists between air pressure and ozone concentration in this case (see Table 3.2.). The low pressure system located south-east as well as a high pressure system situated north-east of the research vessel did not particularly intensify or move during the ozone depletion.

Figure 3.7. shows the standard meteorological parameter measured onboard of the research vessel as well as the ozone concentration between 19:00 and 22:00 on 05 September 2006 indicating the sudden drop of the ozone concentration.

The graph reveals a similar increase of the wind velocity (from below 5 ms^{-1} to more than 15 ms^{-1}). The additional decrease and subsequent increase of the air pressure indicates a frontal system that passed the research vessel. The visibility improves abruptly as well. The change of the wind direction (from north-west to south-west) indicates a change of the origin of the air masses. The air masses arriving from north-west contained background ozone levels. With the wind change to south-west, ozone depleted air reached the research vessel and the ozone concentration measured onboard decreased. In this case, the sudden drop of the measured ozone concentration can be explained by the change of air masses due to a frontal system.

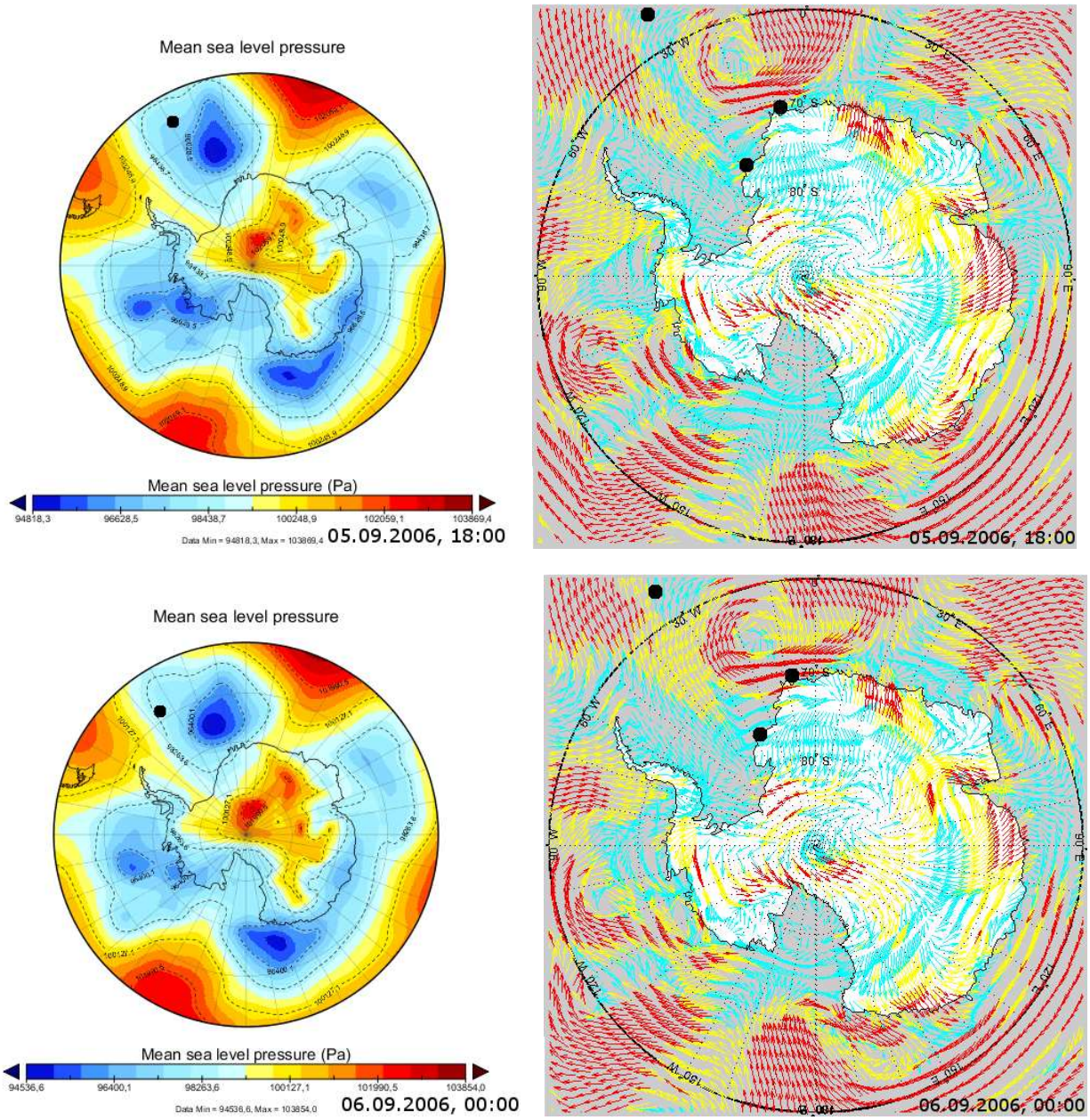


Figure 3.6: *Mean sea level pressure, wind direction and wind speed between 05.09.2006, 18:00 and 06.09.2006, 00:00. The black point in the mean sea level pressure map indicates the position of the research vessel Polarstern. The black points in the wind map represent the location of the research stations Neumayer and Halley and the research vessel Polarstern. The wind speed is divided into three categories: The blue arrows represent wind speeds below 8 m s^{-1}, the yellow ones wind speeds between 8 m s^{-1} and 12 m $s^{-1}$and the red arrows wind speeds above 12 m s^{-1}. Note that the Antarctic plateau has an average height of 3000 m. The reduction of pressure from the stations in the interior of the continent to mean sea level pressure can be inaccurate since the temperature structure of the fictitious air column between the station and the mean sea level has to be estimated.*

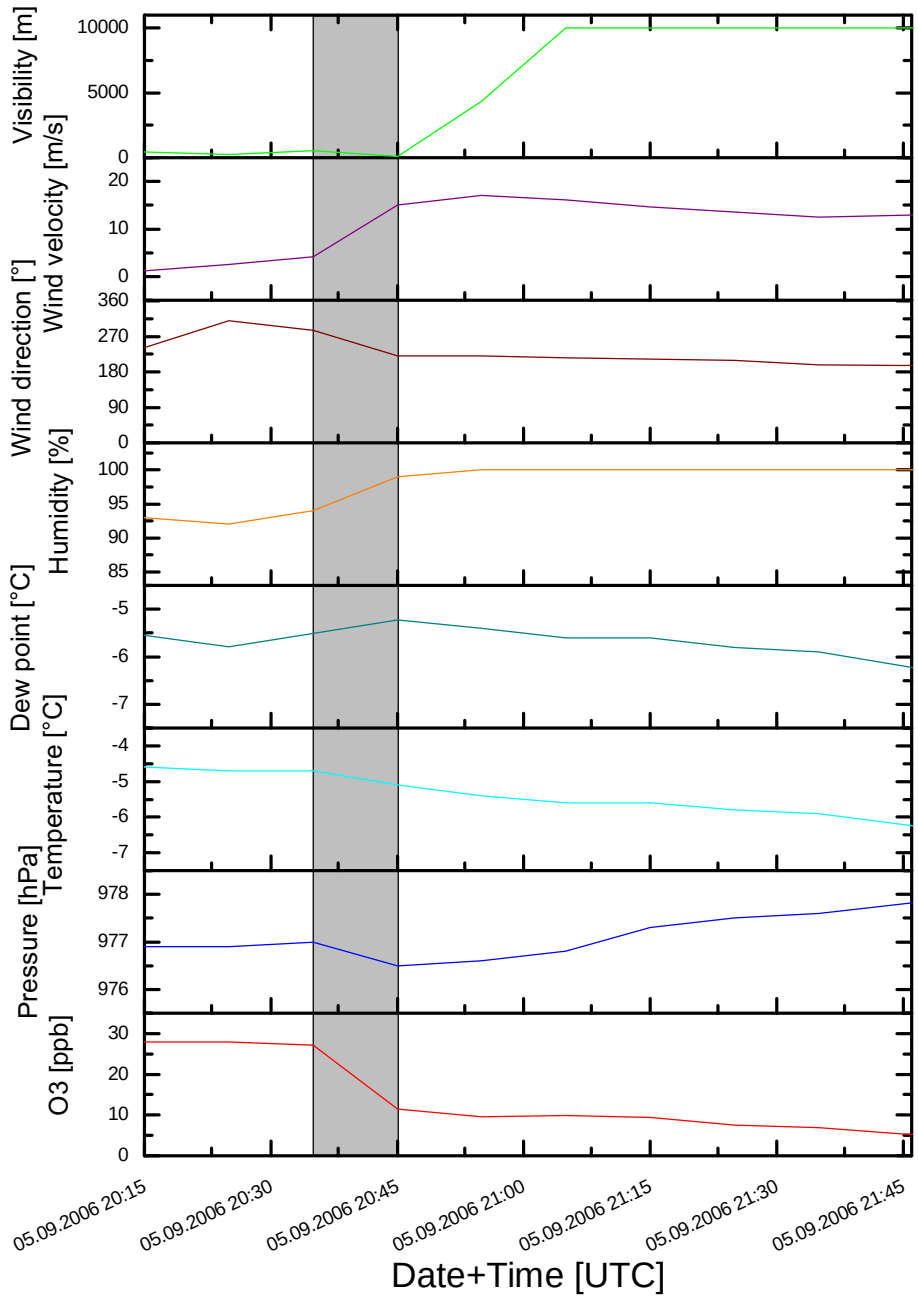


Figure 3.7: *Visibility, wind velocity, wind direction, humidity, dew point, temperature, pressure and ozone concentration during the first ozone depletion measured by the research vessel Polarstern in southern spring 2006. The period with continuously decreasing ozone concentration is indicated by the shaded area.*

3.2.2 Increase of the ozone concentration between 06.09.06, 19:25 - 07.09.06, 00:15

As illustrated in Figure 3.8., on 06.09.2006, 12:00, Polarstern was influenced by the same low pressure system located south-east of the ship as during the drop of the ozone concentration. As this low pressure system weakened and the high pressure system situated north-west of the research vessel moved south-east, the air pressure measured on board increased. Simultaneously the wind direction onboard of the research vessel changed from south-south-west to south-west and furthermore to west and the wind speed decreased from between 8 and 12 m $s^{-1}$to below 8 m s^{-1}. With the approach of this high pressure system from the north and the change of the wind direction, the ozone concentration increased.

Figure 3.9. shows the 120-hour backward trajectories before (18:00) and during the increase of the ozone concentration (20:00 and 22:00) on 05 September 2006. It reveals the change of the origin of the air masses. Whereas the air masses reaching the research vessel at 18:00 originated from east of the Antarctic Peninsula, the air masses observed at 20:00 and 22:00 were coming from the high plateau of the continent. Before the increase of the ozone concentration (18:00), the trajectories reveal that the air masses originated from over 500m height, therefore from the free atmosphere and not from the boundary layer. According to Jones et al. [2010], ozone depletions in higher layers are observed occasionally. In this case, ozone depleted air masses seem to have been transported down from higher altitudes into the boundary layer.

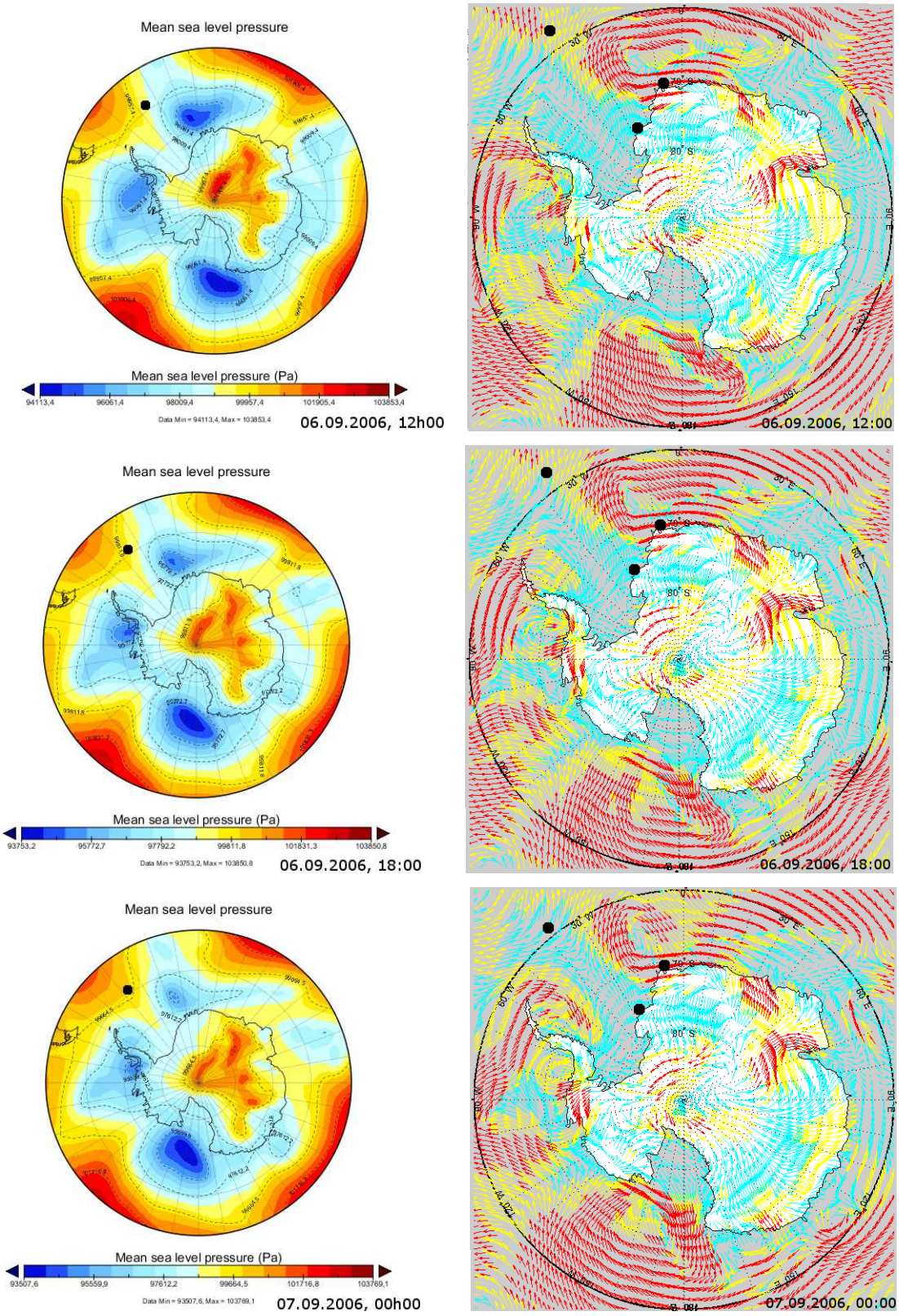


Figure 3.8: *Mean sea level pressure, wind direction and wind speed between 06.09.2006, 12:00 and 07.09.2006, 00:00. See Figure 3.6.*

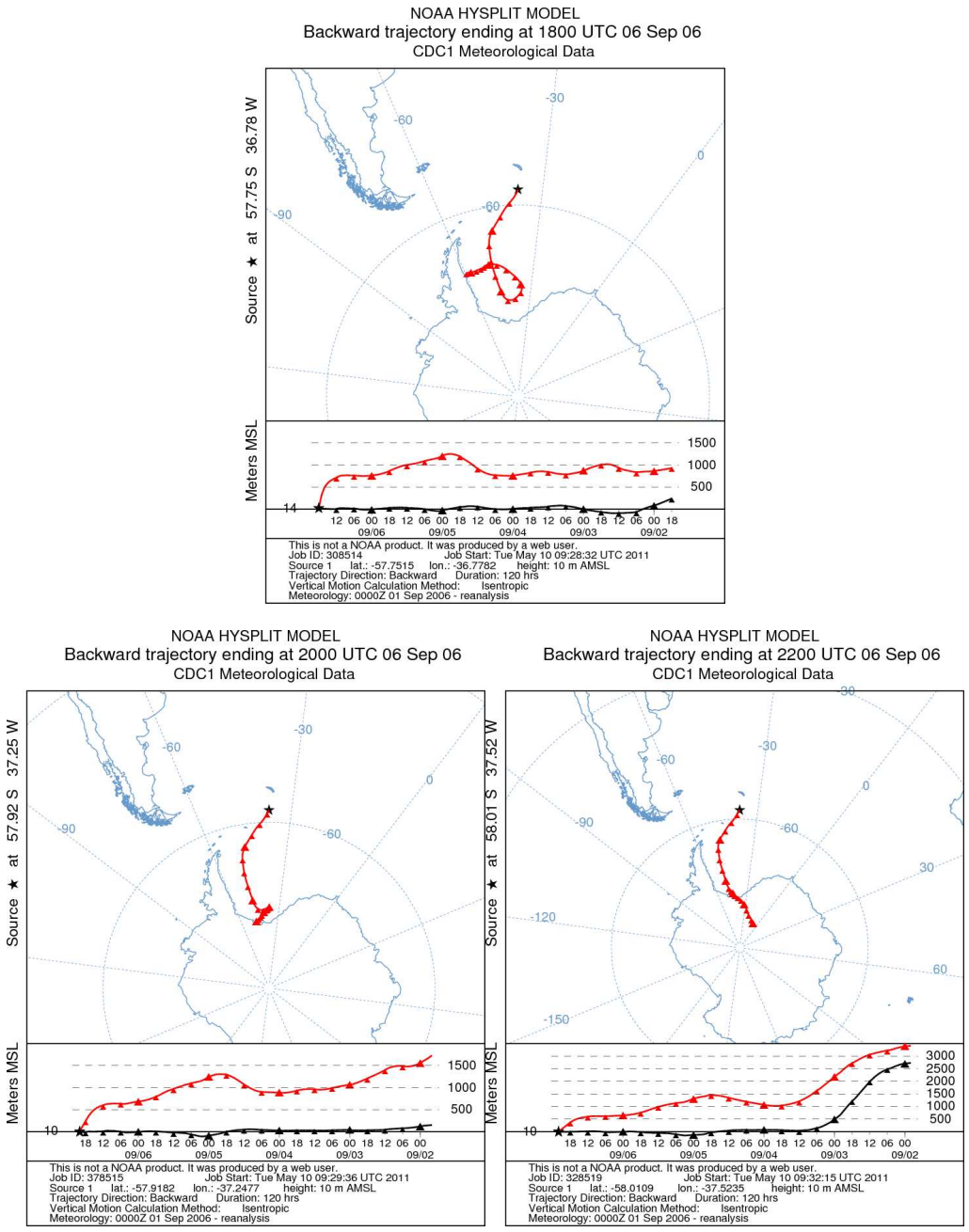


Figure 3.9: *120-hour backward trajectories for the research vessel Polarstern. Trajectories are shown for the period between 18:00 UTC and 22:00 UTC on 05 September 2006. Starting point of the trajectories are the actual ship's positions. The red line on the bottom indicates the altitude of the trajectory, the black one illustrates the terrain height in meters. Note that the time axis runs from right to left.*

3.2.3 Decrease of the ozone concentration between 23.09.06, 01:05 - 23.09.06, 14:05

According to Figure 3.11., on 22.09.2006, 18:00, the wind direction and the wind speed measured onboard of the RV Polarstern was strongly influenced by a low pressure system located east of the ship. Hence the wind direction was south-south-west and the wind speed between 8 and 12 m s^{-1}. On 23.09.2006, during the course of the day, a high pressure system located west of the reserch vessel approached and the wind direction turned sligthly to south. As the low pressure system located east intensified simoultaneously, the wind measured onboard increased in speed (above 12 m s^{-1}). With the approach of this high pressure system from the west, the intensification of the low pressure system situated east and the resulting increase of the wind speed, the ozone concentration decreases.

According to figure 3.10., the air parcels reaching the research vessel Polarstern at 00:00 and 02:00 UTC on 23 September 2006 originated both over the Weddell Sea.

As the chemical reactions depleting ozone take place on the surface, ozone depletion events mostly take place in the boundary layer. Vertical observations of ODEs mostly show low ozone concentrations in the boundary layer whereas the ozone in higher layers is at background levels. Hence, it is important to examine the height of the air parcels reaching the research vessel before and during the drop of the ozone concentration. The boundary layer height around the research vessel was around 500 m. By comparing both trajectories, an important difference becomes obvious. The air parcels reaching the research vessel at 00:00 UTC (before the sudden ozone depletion) entered the boundary layer only a few minutes before finally arriving at the research vessel. Therefore, no chemical destruction could have taken place before the ozone concentration was measured onboard. Contrarily, the air parcels reaching Polarstern at 02:00 on 23 September 2006 entered the boundary layer on 21 September 2006, 18:00 (see Figure 3.10.). In that case chemical depletion could have taken place while the air parcels stayed in the boundary layer and could have been transported to the position of Polarstern afterwards. Both air masses reaching the RV before and during the decrease of the ozone concentratration originated over the Antactic continent, crossing the Weddell Sea.

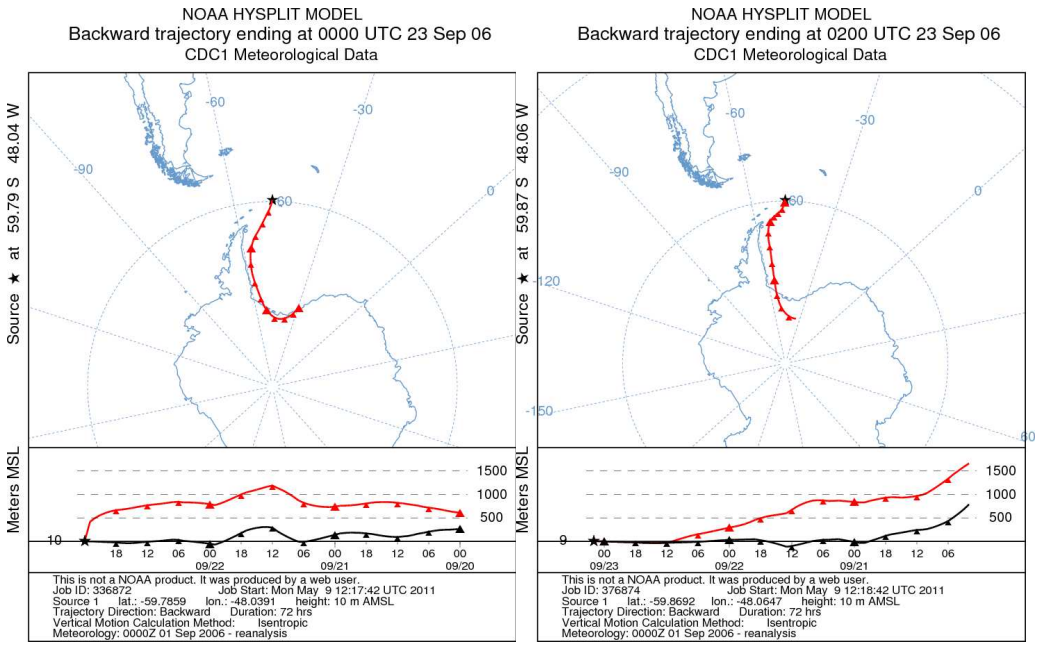


Figure 3.10: *72-hour backward trajectories for the research vessel Polarstern. Trajectories are shown for the period between 00:00 UTC and 02:00 UTC on 23 September 2006. See Figure 3.9.*

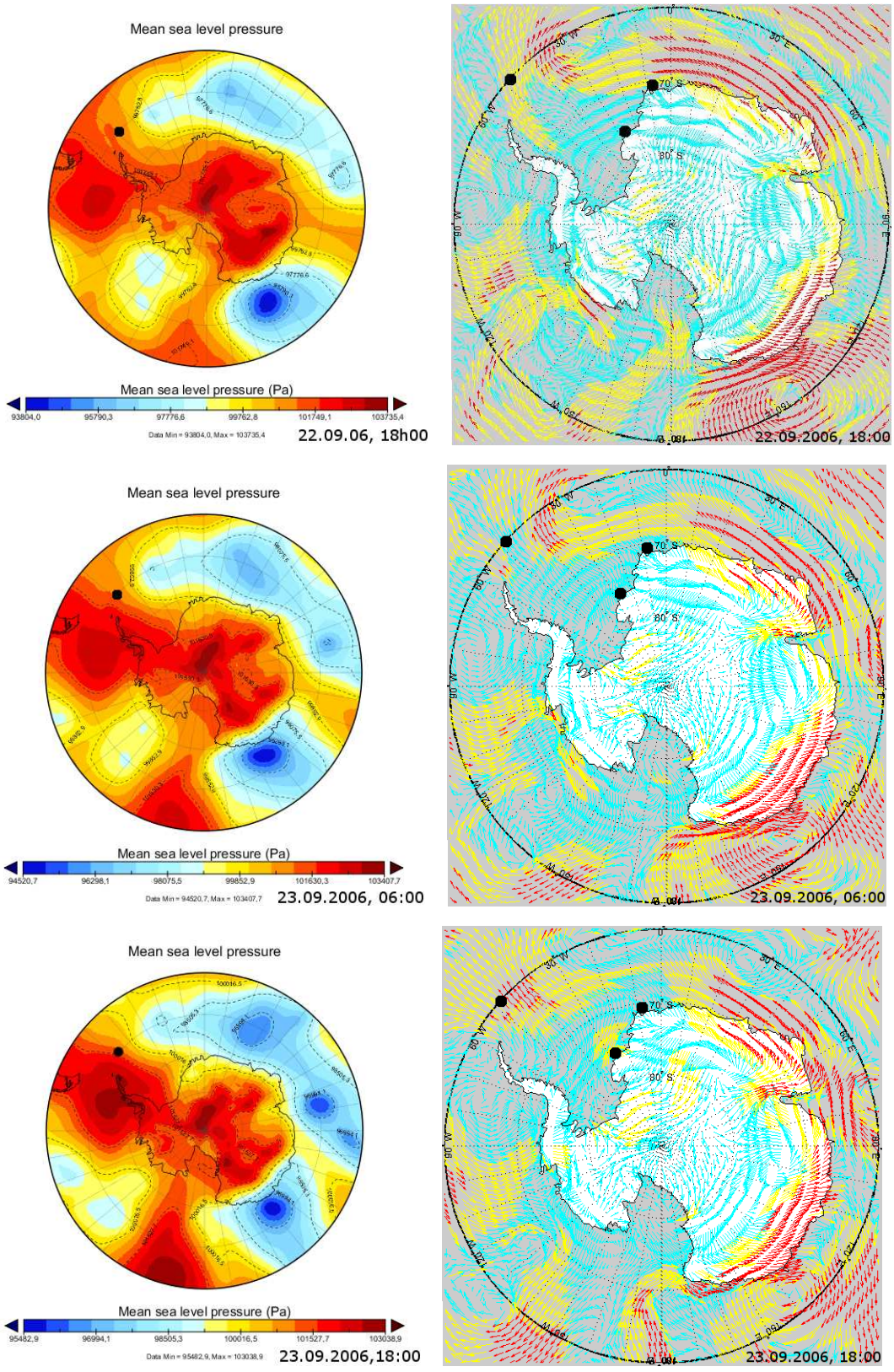


Figure 3.11: *Mean sea level pressure, wind direction and wind speed between 22.09.2006, 18:00 and 23.09.2006, 18:00. See Figure 3.6.*

3.2.4 Increase of the ozone concentration between 24.09.06, 05:55 - 25.09.06, 09:35

As illustrated in Figure 3.12., the high pressure, that already had been affecting the meteorological conditions during the decrease of the ozone concentration, was located west of the measuring point and again influenced the wind direction and speed measured onboard. Although this system weakened, it approached the research vessel and thus the air pressure measured onboard increased. The wind direction stayed south in the beginning of the ozone increase onboard. In contrast, the wind speed decreased from above 12 m $s^{-1}$to below 8 m s^{-1}. As the high pressure system moved north-east, the wind direction changed to south-west on 25.09.2006.

According to Figure 3.13, the air parcels reaching the RV on 24 September 2006, 00:00 UTC during the period with low ozone concentration originated from Queen-Maud-Land on the Antarctic continent and did not leave the boundary layer. In the beginning of the increase of the ozone concentration, no change of the wind direction was determined onboard (Figure 3.12.); nevertheless a change of the origin of the air masses took place. At 07:00, the air parcels arrived from the interior of the continent. But they also passed the boundary over the Weddell Sea. On 25 September 2006, 00:00 (see Figure 3.13.), the provenance of the air masses observed on board changed again. Originating from Queen-Maud-Land, the air parcels ascended into the free troposphere as they reached the Weddell Sea. They passed the Antarctic Peninsula before reaching again the boundary layer and finally the RV Polarstern. Hence, the origin of the air mass changed at least two times during the rise of the ozone concentration.

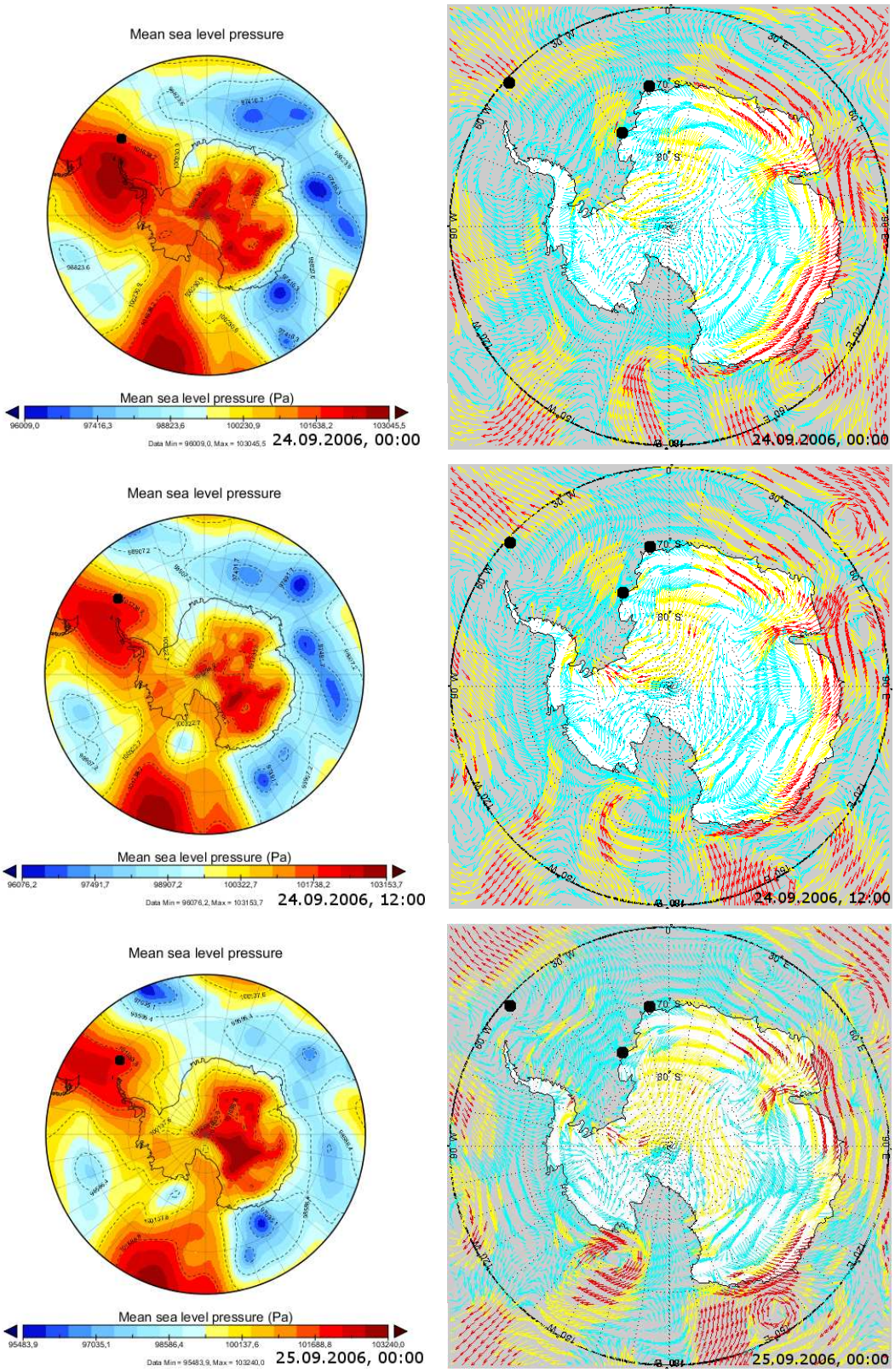


Figure 3.12: *Mean sea level pressure, wind direction and wind speed between 24.09.2006, 00:00 and 25.09.2006, 00:00. See Figure 3.6.*

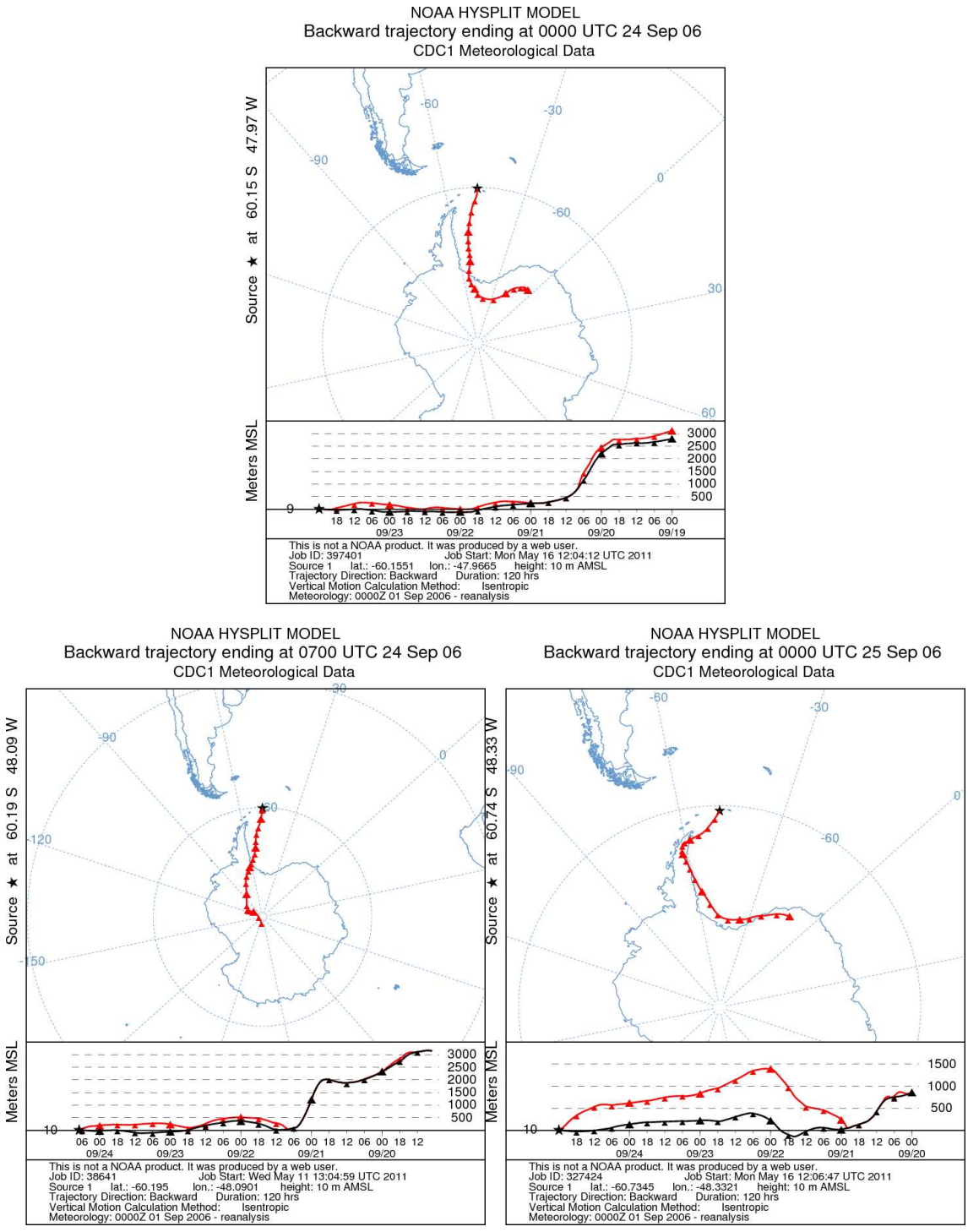


Figure 3.13: *120-hour backward trajectories for the research vessel Polarstern. Trajectories are shown for the period between 00:00 UTC on 24 September 2006 and 00:00 UTC on 25 September 2006. See Figure 3.9.*

3.2.5 Decrease of the ozone concentration between 30.09.06, 21:55 - 01.10.06, 04:25

During this period a weak low pressure system was located north-east of the Antarctic peninsula, only a few kilometers away from the research vessel Polarstern. As the low pressure system filled up, the air pressure measured on board increased. Due to the low intensity of this system, the wind direction measured on board was primarily influenced by the wind circulation around the Antarctic Peninsula. Hence the wind direction alternated between west and south-west with a constant speed of less than 8 m s^{-1}during this period. According to Figure 3.15. there was no air mass change that could have induced the decrease of the ozone concentration measured onboard of the research vessel Polarstern. As the BrO map (Figure 3.14.) indicates an elevated vertical column north-east of the Antarctic Peninsula on 30.09.2011, the ozone depletion event could have been chemically induced.

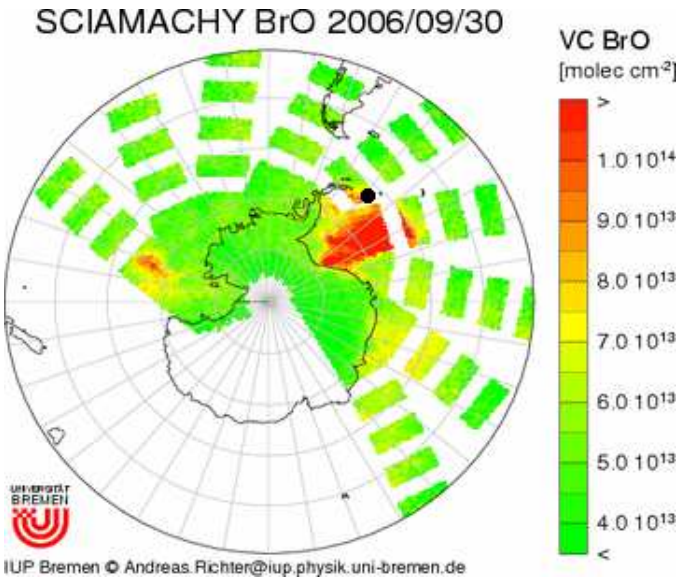


Figure 3.14: BrO vertical column on 30.09.2006.

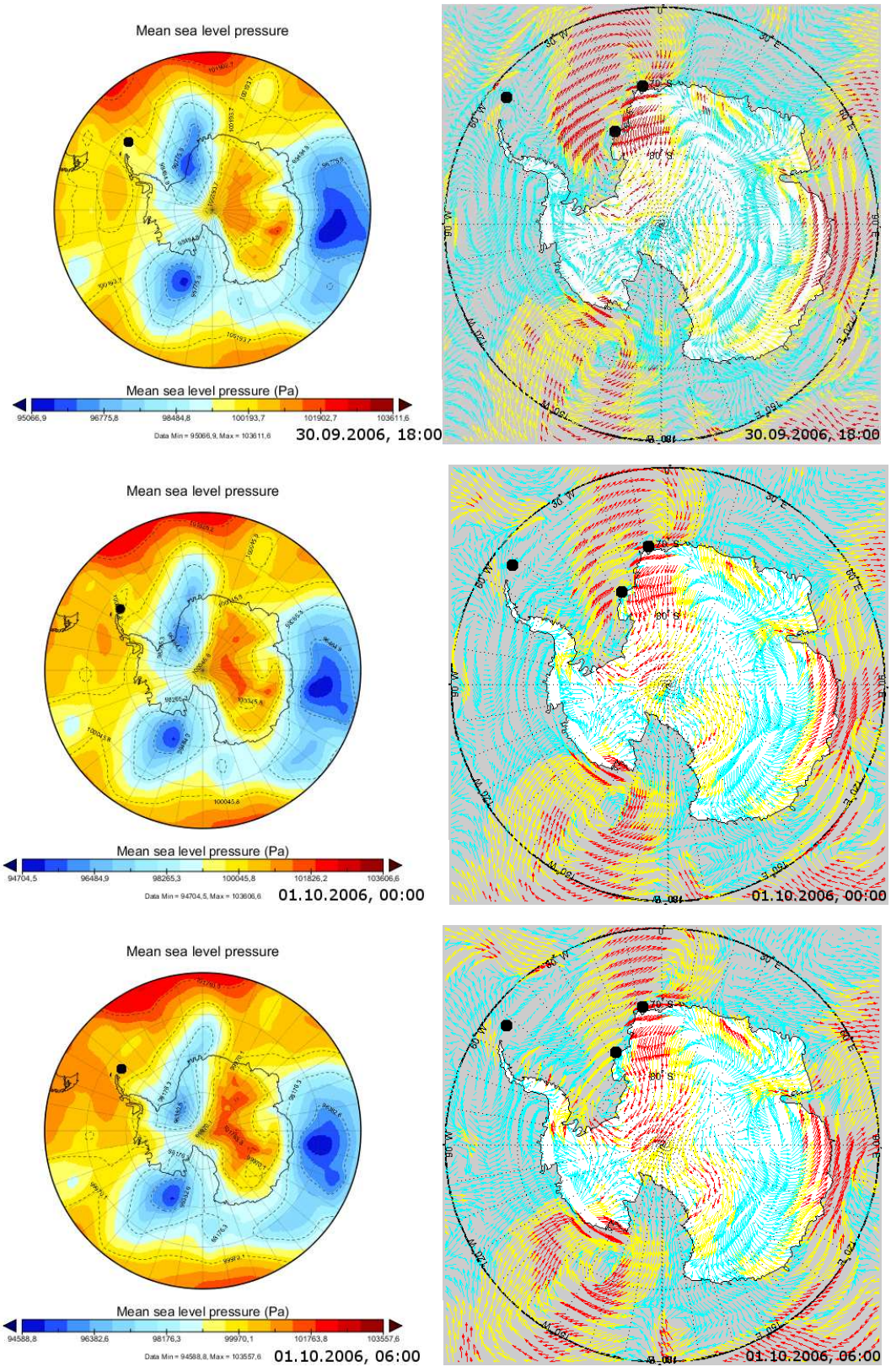


Figure 3.15: *Mean sea level pressure, wind direction and wind speed between 30.09.2006, 18:00 and 01.10.2006, 06:00. See Figure 3.6.*

3.2.6 Increase of the ozone concentration between 01.10.06, 15:45 - 01.10.06, 18:35

According to Figure 3.16., on 01.10.2006, 12:00, the high pressure system north of the Antarctic Peninsula, that already had been affecting the meteorological conditions during the decrease of the ozone concentration, has increased in intensity. The airmasses transported along the southern rim, either had to overflow or to circulate around the Antarctic Peninsula. As the research vessel Polarstern was situated in the area, where the air masses circulated around, the wind direction was west to south-west. With the intensification of the high pressure system, the pressure onboard increased. The wind speed exceeded 8 m s^{-1}at 18:00.

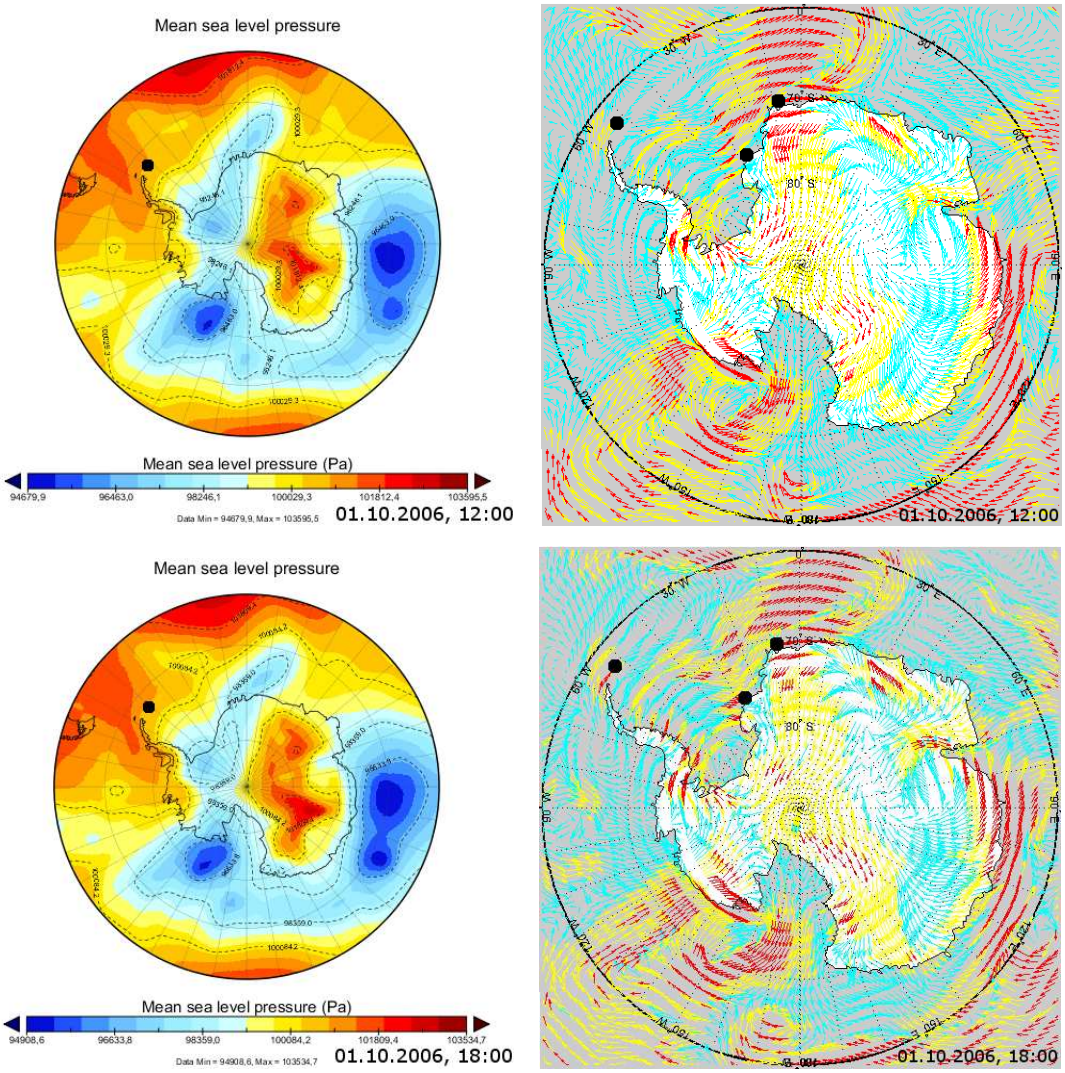


Figure 3.16: *Mean sea level pressure, wind direction and wind speed between 01.10.2006, 12:00 and 02.10.2006, 00:00. See Figure 3.6.*

3.2.7 Decrease of the ozone concentration between 08.10.06, 02:05 - 08.10.06, 21:35

As illustrated in Figure 3.17., on 08.10.2006, 00:00, the research vessel Polarstern is located between a high pressure system to the south-east and a low pressure system to the north-east. According to these two systems and the proximity of the Antarctic Peninsula, the wind direction on board is south-east. As the high pressure system weakens, the pressure onboard decreases slightly and the wind direction turns south. With the weakening of the high pressure system south-east and the consequential change of the wind direction bringing air masses from the Weddell Sea, the ozone concentration decreased.

According to Figure 3.18., the air parcels reaching the research vessel Polarstern at 01:00, 03:00 and 12:00 UTC on 08 October 2006 originated all from the same region. But comparing the height of the trajectories reveals a difference that could have influenced the ozone concentration. The air parcels reaching the research vessel at 01:00 UTC (before the ozone depletion) were forced to ascend due to small scale wind systems two days before arriving at Polarstern. In contrast, the air parcels reaching the research vessel during the ozone depletion (03:00 and 12:00) were continously in the boundary layer.

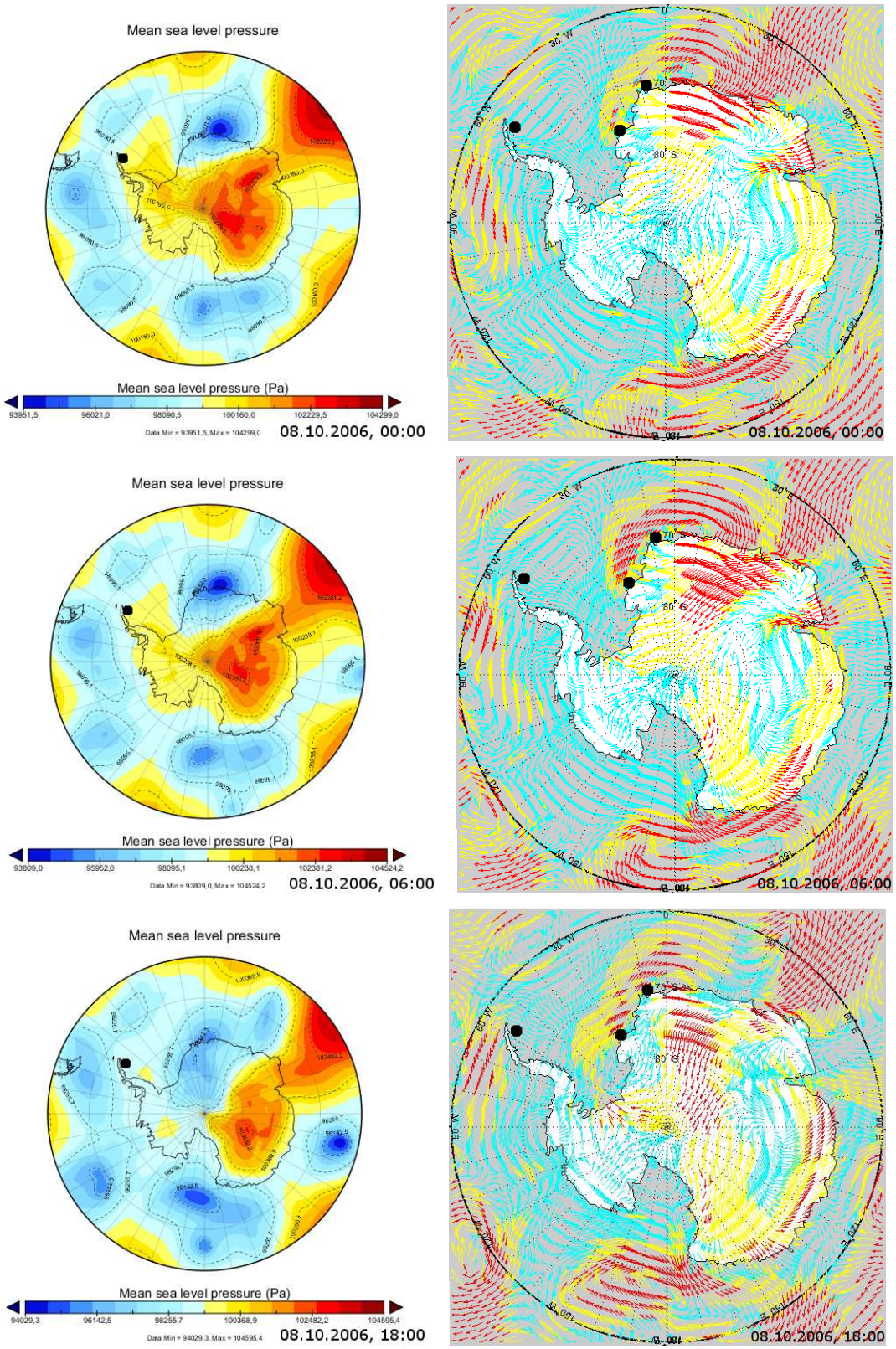


Figure 3.17: *Mean sea level pressure, wind direction and wind speed between 08.10.2006, 00:00 and 08.10.2006, 18:00. See Figure 3.6.*

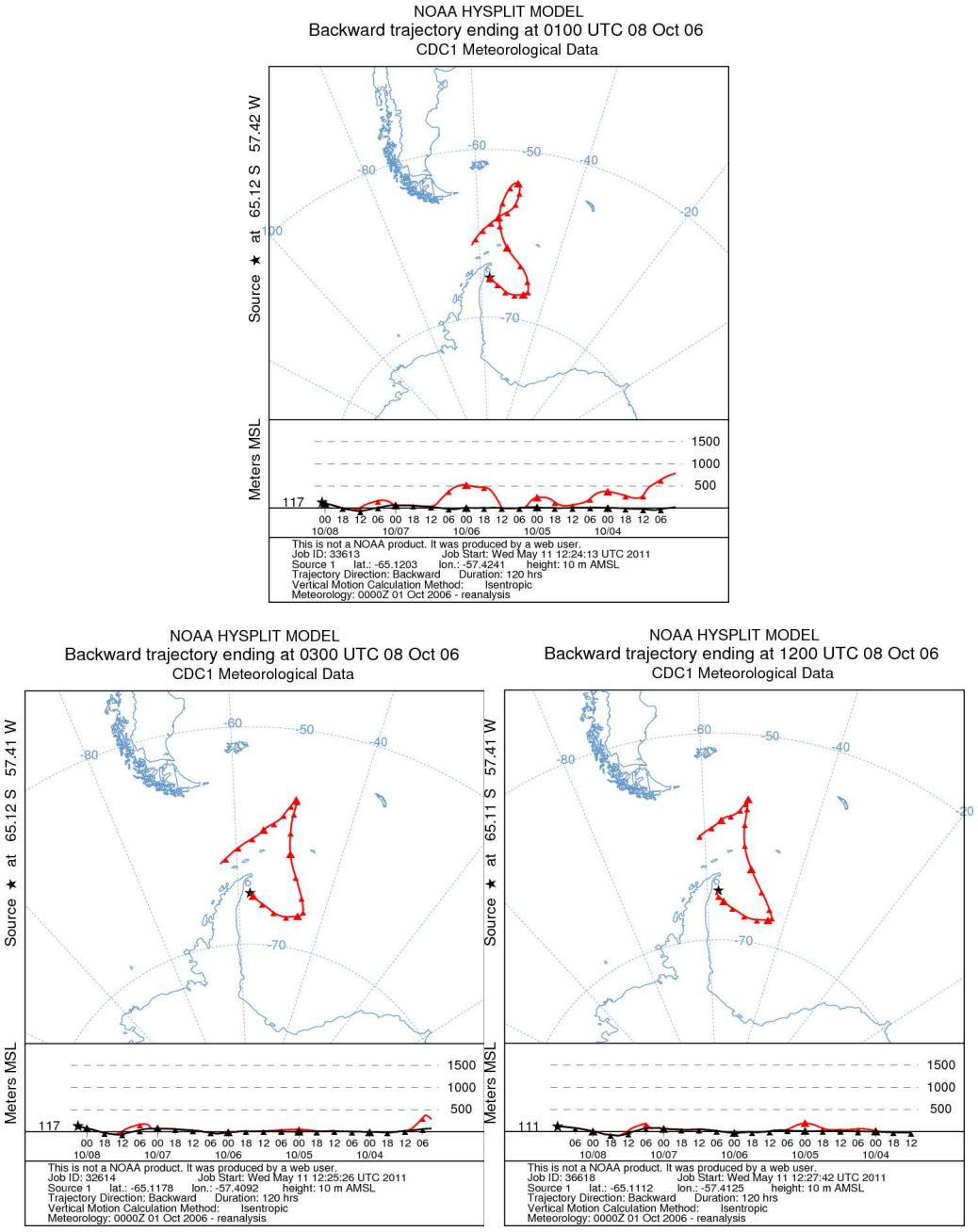


Figure 3.18: *120-hour backward trajectories for the research vessel Polarstern. Trajectories are shown for the period between 01:00 UTC and 12:00 UTC on 08 October 2006. See Figure 3.9.*

3.2.8 Increase of the ozone concentration between 10.10.06, 12:15 - 11.10.06, 16:15

On 10.10.2006, 06:00 (see Figure 3.19.), the wind direction onboard of the research vessel was influenced by a col that extended from the Antarctic Peninsula to the Prime Meridian. Polarstern was situated south of this divergence area, hence the wind direction was north. As the high pressure system located over the South American continent approached during the course of the day, the air pressure onboard rose. Simultaneously the wind direction changed from north to west, thus the air masses overflowed the Antarctic Peninsula before reaching the research vessel. The wind speed remained below 8 m s^{-1}. With the approach of this high pressure system from the north-west and the change of the wind direction constraining the air masses to cross the Antarctic Peninsula, the ozone concentration increased.

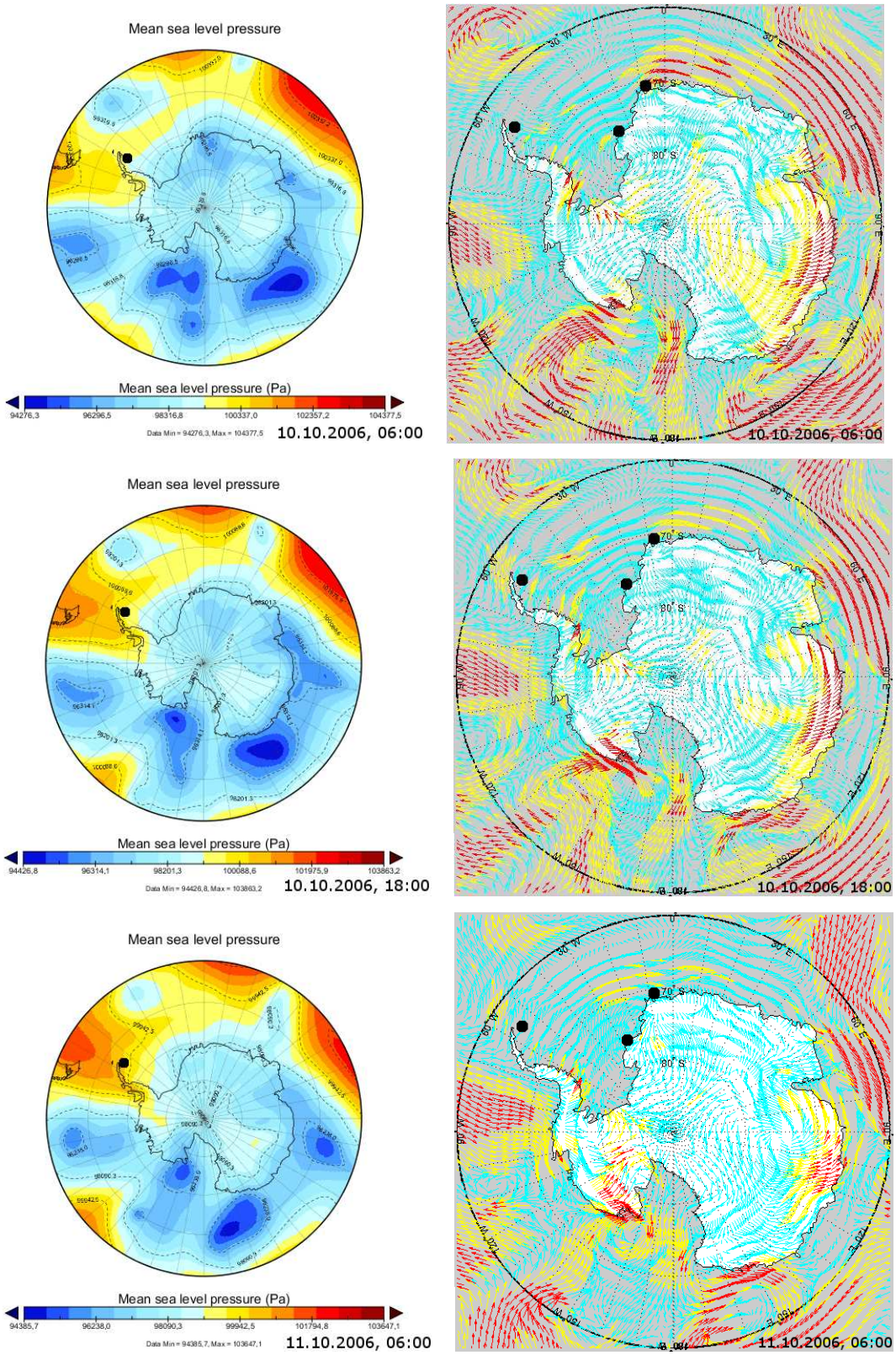


Figure 3.19: *Mean sea level pressure, wind direction and wind speed between 10.10.2006, 06:00 and 11.10.2006, 06:00. See Figure 3.6.*

3.2.9 Conclusion

The meteorology in the Southern Atlantic, especially in the Weddell Sea is dominated by two different synoptical systems. On the one hand, low pressure systems often form in the circumpolar trough and move in a zonal direction parallel to the coast [King and Turner, 1997]. On the other hand, intense high pressure systems form over the South American Continent. As they move eastwards, they influence the wind systems in the Weddell Sea.

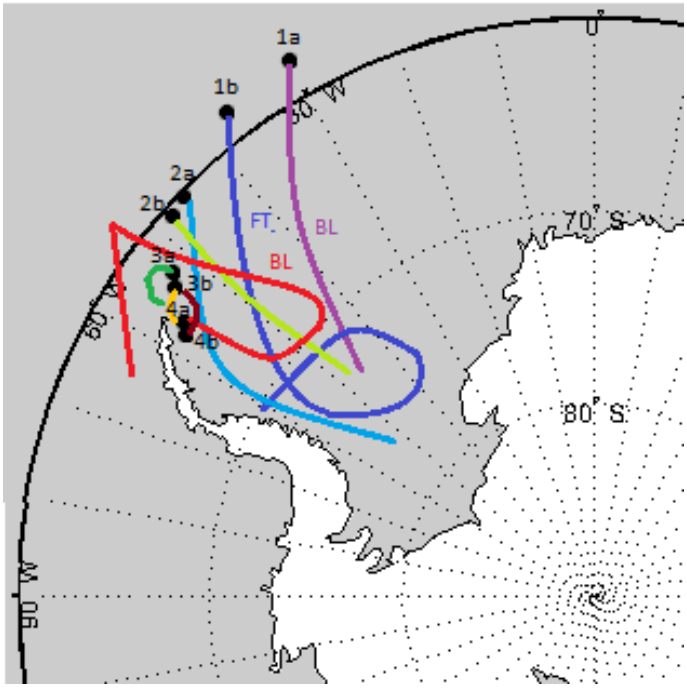


Figure 3.20: *Schematical trajectories during the sudden decreases (indicated by 1a, 2a, 3a and 4a respectively) and before the increase (indicated by 1b, 2b, 3b and 4b respectively) of the ozone concentration during the four ozone depletion events observed onboard of the RV Polarstern. The black points indicate the approximate ship's positions, the lines the associated trajectories calculated for an arrival height of 10 meters above the mean sea level. "BL" ("boundary layer)" signifies that the air masses stayed in the boundary layer before reaching the RV Polarstern. "FT" ("free troposphere") indicates that the air parcels stayed in a height superior than 500 m above mean sea level before reaching the ship.*

During the ODE1 (1a and 1b) and the ODE2 (2a and 2b) the air masses originated from the Weddell Sea. The air parcels resided in the boundary layer where chemical destruction could have taken place, exept for the trajectory 1b (before the increase of the ozone concentration during ODE1) originating from higher layers, from an altitude of 700 to 1200 m approximately during the 120 hours before reaching the ship (see Figure 3.9.). It demonstrates that ozone depleted air masses can reside in higher layers and can be mixed downwards into the boundary layer. Whether the ozone concentration was depleted in the boundary layer and was transported in higher layers by local wind systems or the ozone depletion took place in

the free troposphere, can not be determined with the available data. The ODE3 (3a and 3b) seem to be a local chemically controlled event as no air mass changes took place. The 4th sudden decrease of the ozone concentration during the Winter Weddell Outflow Study (4a) was initiated by the transport of air masses originating from west of the Antarctic Peninsula and passing trough the boundary layer above the Weddell Sea. The trajectory 4b, indicating the path of the air parcels reaching the RV Polarstern before the increase of the ozone concentration during ODE4, reveals a local chemically induced depletion of the ozone concentration. Hence, the ODE4 seems to be meteorologically induced and intensified by a local depletion of the ozone concentration.

Comparing the meteorologically controlled ozone depletions in southern spring 2006 reveals that most of the depleted air masses (ODE 1, 2 and 4) were transported from the interior of the Weddell Sea to the observational sites. However, also local processes at the northwestern rim of the Weddell Sea can contribute to the destruction of ozone (ODE3).

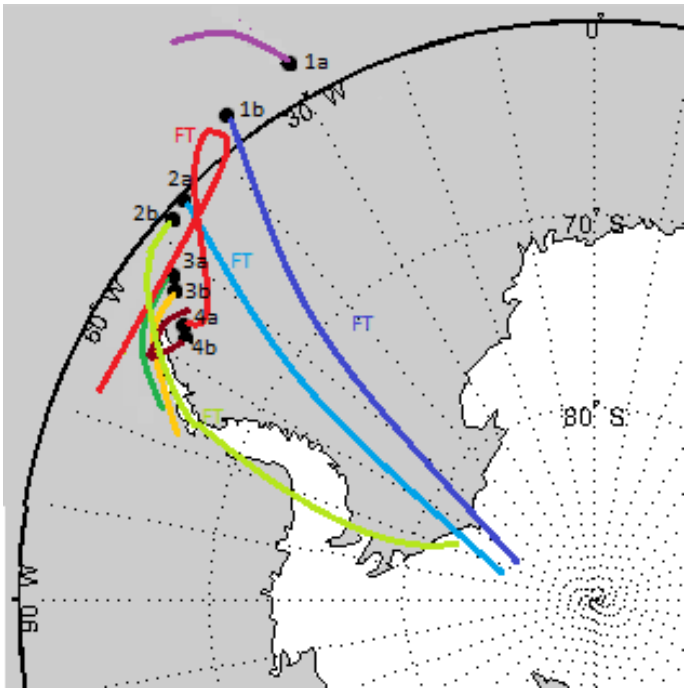


Figure 3.21: *Schematical trajectories before the sudden decrease (indicated by 1a, 2a, 3a and 4a respectively) and during the increase of the ozone concentration (indicated by 1b, 2b, 3b and 4b respectively) during the four ozone depletion events observed onboard of the RV Polarstern. The black points indicate the approximate ship's positions, the lines the associated trajectories calculated for an arrival height of 10 meters above the mean sea level. "FT" ("free troposphere") indicates that the air parcels stayed in a height superior than 500 m above mean sea level before reaching the ship.*

The air masses residing in and around the Weddell Sea are influenced by the low pressure systems developing in the circumpolar through and the high pressure systems approaching from the South American continent. The interaction between those two synoptical systems sometimes constrains air parcels to circulate around or overflow the Antarctic Peninsula. The eight trajectories in Figure 3.21. represent the origin of the air masses before the sudden drop and during the increase of the ozone concentration. Figure 3.21. reveals that the trajectories during ODE3 (3a, 3b) and ODE4 (4a, 4b) as well as during the increase of the ozone concentration after the second ozone depletion event (2b) circulated around the Antarctic Peninsula. Before the first decrease of the ozone concentration (1a), the air parcels arrived from north-west due to a low pressure system situated south of the position of the RV. The air masses during the increase of the ozone concentration of the first ODE (1b) as well as the air parcels reaching the RV before the second decrease of the ozone concentration (2a) originated both from the interior of the Antarctic continent and resided in layers above the boundary layer (500 to 1500 over terrain height level for 1b and 500 to 1000 m over terrain height level for 2a) before being measured onboard. During the ODE3 (3a and 3b), the air masses mainly resided in the boundary layer while circulating around the Antarctic Peninsula. Before the 4th sudden ozone depletion (4a), the air masses circulated around as well, but resided in a height of 500 m for a short time of two days before arriving at the ship. Hence, downward mixing of ozone-rich air masses from layers above the boundary layer could be possible.

During the Winter Weddell Outflow Study, the air masses reaching the RV and causing the increase of the ozone concentration to background level as well as the air masses measured onboard before a sudden decrease of the ozone concentration originated all from the interior of the Antarctic Continent, the Southern Atlantic or west of the Antarctic Peninsula. Those, which passed the Weddell Sea resided in the free troposphere, where in these cases no chemical reactions took place.

During the Winter Weddell Outflow Study, the meteorologically controlled ozone depletion events revealed an important similarity. It seems that the ozone depleted air masses always passed the Weddell Sea before reaching the RV Polarstern. Additionally the air masses causing the sudden meteorologically controlled ozone decreases during the Winter Weddell Outflow Study crossed the boundary layer above the Weddell Sea. Only in one case (1b, Figure 3.21.) already depleted air masses from the free troposphere were transported downwards to the ship. In contrast the meteorologically controlled increases of the ozone concentration seem to be linked to the presence of high pressure systems south-east of the South American continent. The trajectories during ODE3 and ODE4 as well as during the increase of the ozone concentration after the second ozone depletion event reveal air masses circulating around the Antarctic Peninsula before being measured onboard.

According to Figure 3.20., chemical destruction of ozone happened mainly in the boundary layer above the Weddell Sea. The depleted air masses were transported abroad whereas the air masses approaching from west of the Antarctic Peninsula were rich in ozone and caused an increase of the ozone concentration onboard (Figure 3.21.).

The analysis indicate a considerable difference between ozone depletion events over the Arctic Ocean and the Weddell Sea. According to Jacobi et al. [2010], during the observations in 2003 and 2007 in the Arctic Ocean, low ozone mixing ratios constitued the prevailing state of the boundary layer (55% in 2003 and 66% in 2007 of all ozone observations were below the limit used to define ozone depletion events) and this depleted state was only interrupted by episodes with elevated ozone mixing ratios. Contrarily, on the north-western rim of the Weddell Sea, ozone concentration was mostly at background level and only 6.1% of the data were below the threshold of 19 ppbV used to specify ozone depletion events during the Winter Weddell Outflow Study. In the Arctic Ocean, the increase of the ozone concentration to background level was linked to the approach of low pressure systems from the South bringing air masses from lower latitudes. Furthermore, the ozone mixing ratio decreased quickly as soon as the low continued to move farther north. As a result, over the Arctic Ocean, decreases in ozone were often accompanied by increases in pressure and vice versa. In contrast, the ozone concentration in the Weddell Sea was only partly linked to meteorological systems and there was no consistent correlation between the ozone concentration and the air pressure, and the ozone concentration and the air temperature, respectively. Whereas the ozone decrease seem to be dependent on air masses arriving from the interior of the Weddel Sea, ozone increases were often induced by the approach of high pressure systems from the South American Continent.

Most of the ozone drops observed onboard of the RV Polarstern during the Winter Weddell Outflow Study are induced by already depleted air masses approaching from southern latitudes and crossing the Weddell Sea. Obviously chemical destruction of ozone mainly takes place in the boundary layer above the Weddell Sea.

However, an ozone depletion does not necessarily take place as soon as the air masses cross the Weddell Sea before reaching the measuring point.

Figure 3.22. illustrates a 120-backward trajectory on 16 october 2006 staying in the boundary layer over the Weddell Sea. Reaching the RV Polarstern, the ozone concentration stayed at background level (26,6 ppbV), no ozone depletion took place.

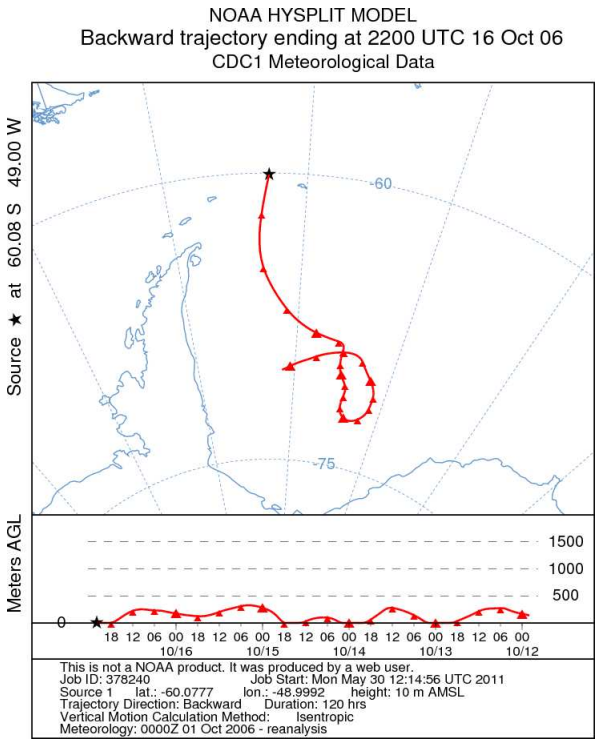


Figure 3.22: *120-hour backward trajectory on 16 october 2006, 22:00. Starting point is the actual ship position.*

To get informations about the percentage of trajectories passing the Weddell Sea and bringing air masses with low ozone concentration, two trajectories - at 00:00 and 12:00 UTC - have been plotted for each day between 27 August and 17 October 2006. On 31 August 2006, 00:00, no data were available. Hence, a total of 103 trajectories has been obtained for the period where the Winter Weddell Outflow Study took place.

As already seen before, only 6.1 % of the total ozone concentration measured during the WWOS was considered as depleted ozone concentration.

Trajectories	N° of trajectories	Depleted ozone	Background ozone
- All	103	6.1 %	93.9 %
- Crossing the Weddell Sea	31 (30.1 %)	35.5 %	64.5 %
- Crossing the Weddell Sea $<$ 500 m	7 (6.8 %)	58.5 %	41.5 %

Table 3.3: *Distinction between trajectories bringing air masses with depleted ozone concentrations and air masses with background ozone mixing ratios. Further distinction between trajectories crossing the Weddell Sea in any height and crossing the Weddell Sea in the boundary layer (below 500 m height).*

During the Winter Weddell Outflow Study, between 27 August and 17 October 2006, 30.1 % of the trajectories crossed the Weddell Sea in different heights before reaching the RV Polarstern. Only one third of the air parcels passing the Weddell Sea were low in ozone concentration when they arrived at the ship, whereas the remaining air masses contained background ozone mixing ratios.

58.5 % of the air masses crossing the boundary layer above the Weddell Sea before reaching the ship were depleted in ozone during the Winter Weddell Outflow Study whereas 41.5 % of the air masses contained ozone concentration at background level.

According to this, the probability of ozone depletion rises from 6.1 % to 35.5 % as soon as the trajectories pass the Weddell Sea and even reaches 58.5 % when the air masses remain in the boundary layer above the Weddell Sea.

The results indicate that, in southern spring, the probability of an ozone depletion event is elevated when the air masses passed the boundary layer above the Weddell Sea before reaching the measuring point.

In the Arctic, the percentage rate of ODEs is higher in the Central Arctic Ocean compared to coastal sites. This analysis reveals that the conditions seem to be very similar in Antarctica. Ozone depletion events are probably much more frequent in the interior of the Weddell Sea compared to the edge, where the WWOS took place. In fact, the percentage rate of ozone depletion events in the Arctic Ocean and in the interior of the Weddell Sea could be very similar.

3.3 Chemistry

According to Simpson et al. [2007], chemical processes lead to ozone depletion events in the polar regions. These local chemical processes are initiated by an elevated concentration of Br in the boundary layer reacting with ozone and therefore creating BrO as key intermediate for the destruction of ozone. The BrO concentration was measured onboard of the research vessel during the Winter Weddell Outflow Study using the Differential Optical Absorption Spectroscopy (DOAS) (see section 6.5.). BrO data were provided by Dr. Andreas Richter from the Institute of Environmental Physics, University of Bremen.

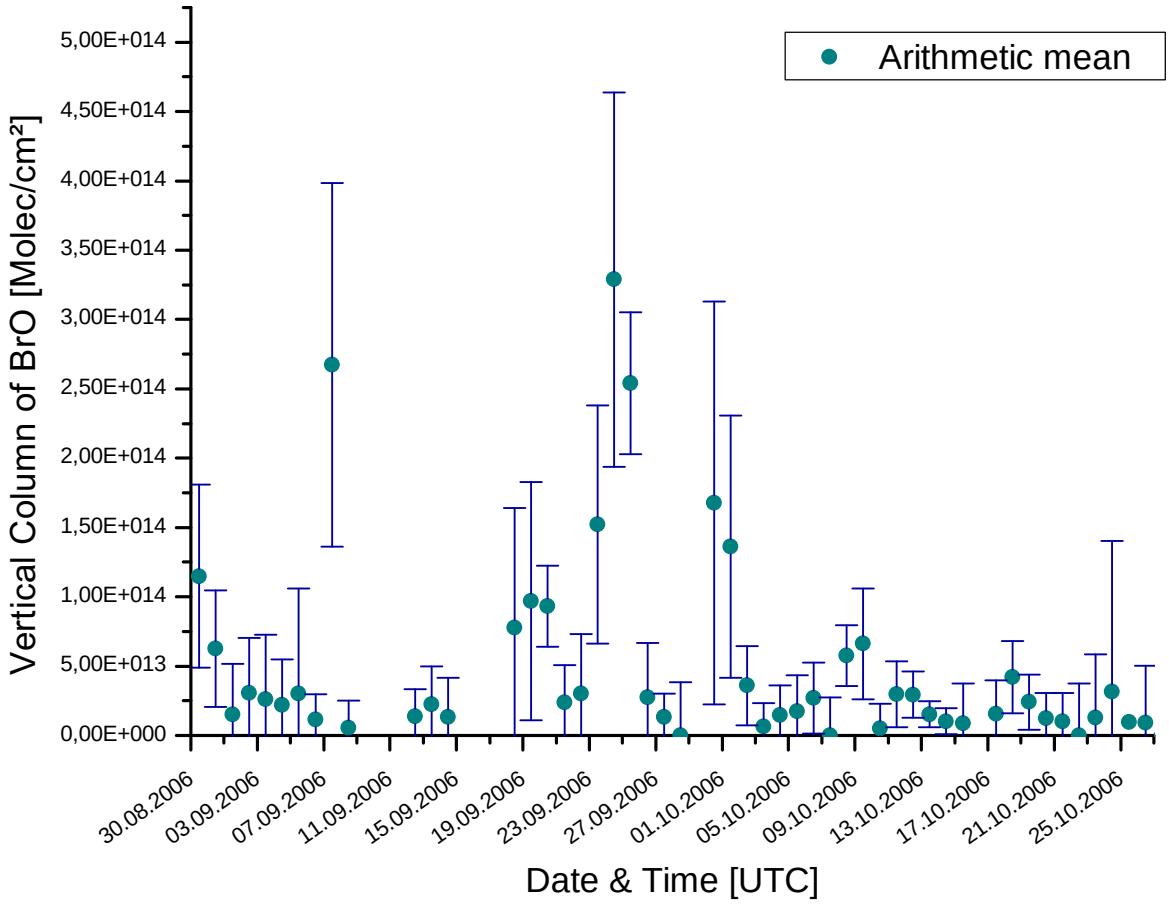


Figure 3.23: *Daily means of the BrO vertical columns measured onboard with a MAX-DOAS instrument between 30 August 2006 and 27 October 2006. The bars indicate the estimated error.*

Figure 3.23 indicates the daily mean BrO vertical columns during the Winter Weddell Outflow Study. Since aerosols have a significant impact on the measurements the absolute value of the data is strongly dependent on the amount of aerosols present along the light path in the atmosphere (`http://www.doas-bremen.de/doas_tutorial.htm`). The effect can be estimated with the help of the visibility measured onboard of the research vessel. Depending on the visibility, the data must be divided by a coefficient of 3 to 5 to correct the data. Since a detailed calculation of the radiative transfer in the atmosphere is required to correct the observed vertical columns, the observations can only be used for a qualitative comparison with the observed ozone concentrations.

As revealed by Figure 3.23., there are several events where the BrO concentration measured onboard increased for periods between one to three days.

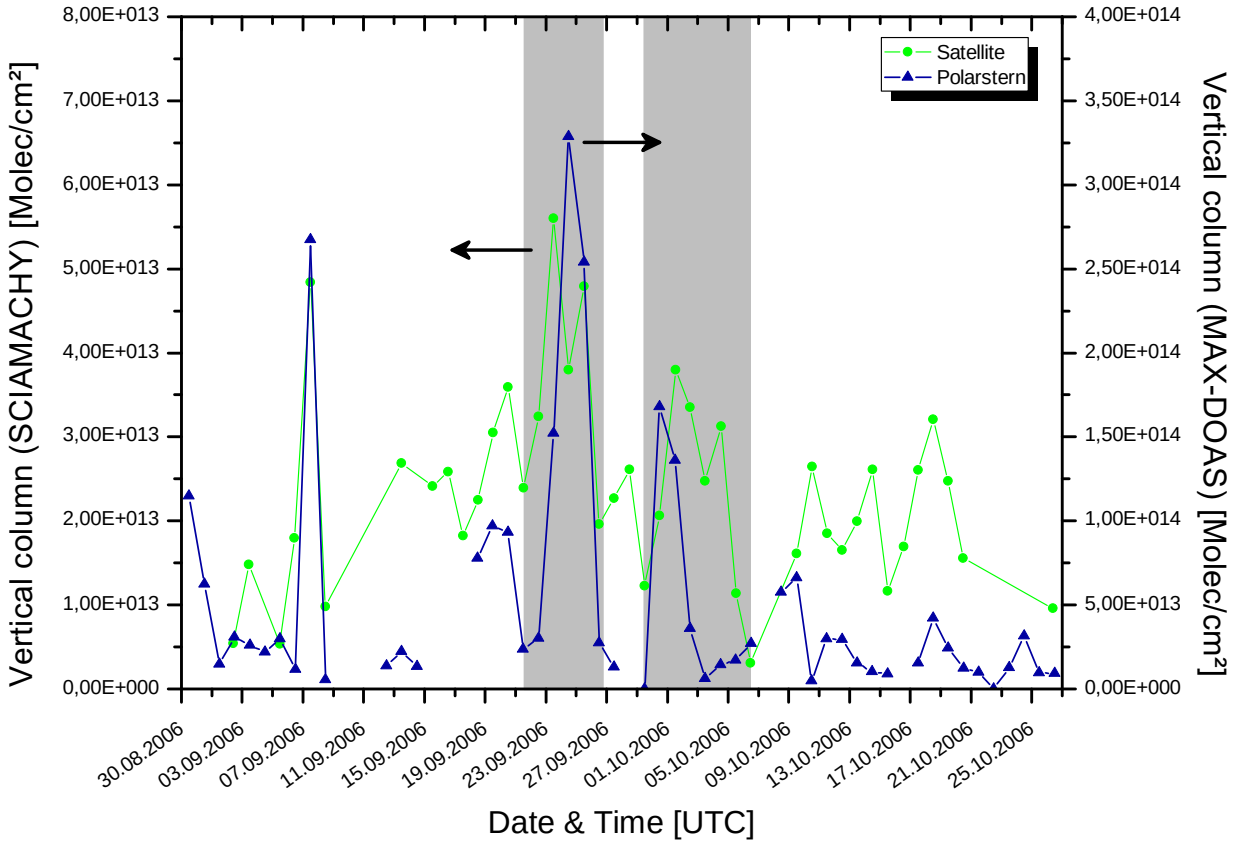


Figure 3.24: *Comparison between the BrO concentration observed by the SCIAMACHY instrument and the BrO concentration measured onboard using the MAX-DOAS.*

Figure 3.24. shows a comparison of BrO data measured onboard of the research vessel during the Winter Weddell Outflow Study on the one hand and detected by the satellite on the other hand. The data measured by the SCIAMACHY instrument represent the BrO vertical colums within a radius of 200 km around the RV Polarstern whereas the MAX-DOAS instrument measures the vertical column within a smaller radius.

According to Figure 3.24., both BrO time series have the same trend indicating that both SCIAMACHY data as well as MAX-DOAS data can be used for further comparisons with ozone concentration during the Winter Weddell Outflow Study.

The shaded areas in figure 3.24. reveal two periods, where the SCIAMACHY as well as the MAX-DOAS time series indicate a similar increase of the BrO concentration but which do not happen simultaneously. During the first period, between 21 and 26 september 2006, the increase of the BrO data measured by SCIAMACHY started earlier than those collected onboard of the RV. Hence, the maximum of the BrO vertical column was as well reached before in the data recorded by the satellite. It indicates that the BrO increased first within a radius of 200 km around the RV Polarstern before actually reaching the RV itself. During the second period, between 30 september and 03 october 2006, the time series reveal that the BrO vertical column measured by the MAX-DOAS instrument onboard of the RV rose quicker than the data collected by the satellite. It suggests that the BrO vertical column was denser above the research vessel than within the radius of 200 km around it.

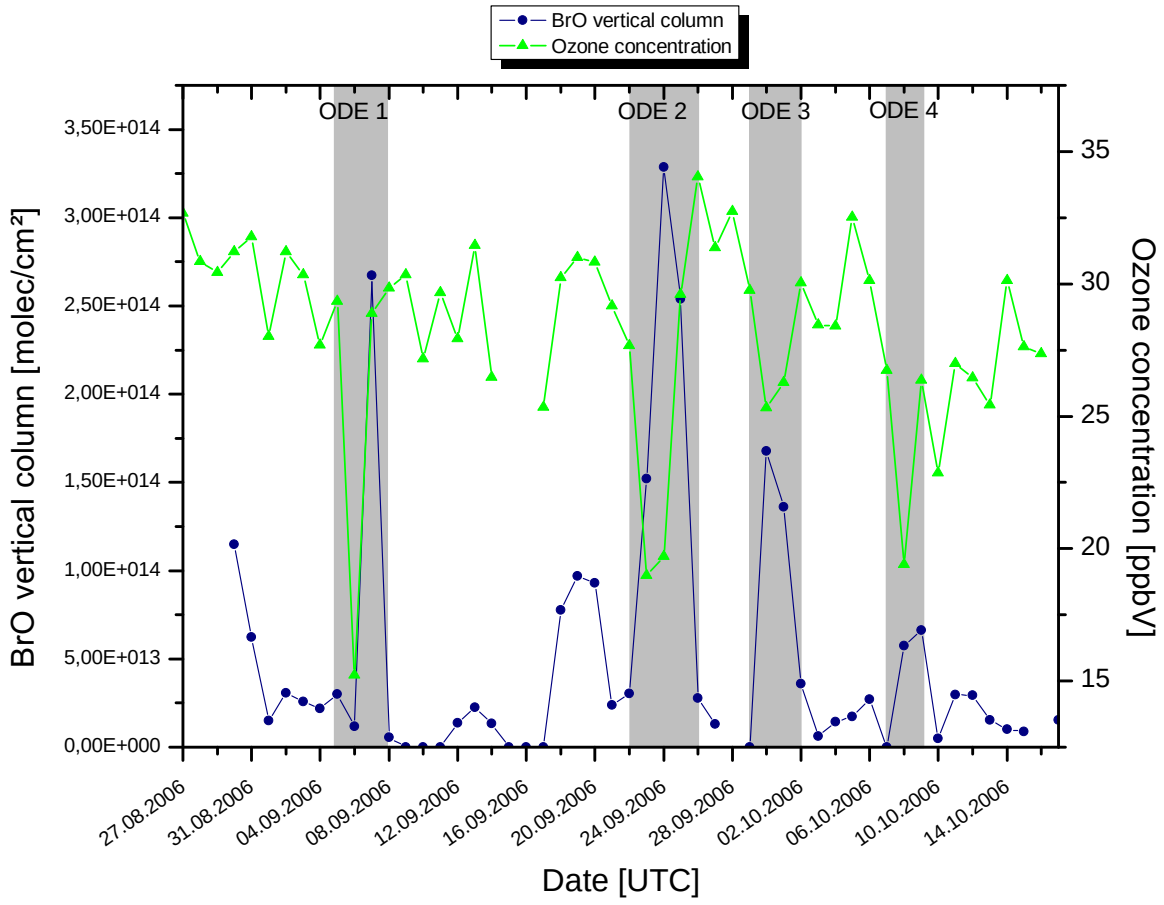


Figure 3.25: *Daily mean of the BrO concentration and the ozone concentration measured onboard during the Winter Weddell Outflow Study. The shaded area indicates the observed ozone depletion events.*

Since the DOAS method to detect BrO only operates during daylight hours, the daily mean is actually a mean for the daily insolation period. To directly compare the different time series of BrO and ozone, daily means of the ozone concentration were calculated for the same period for each day. The used lower limit to determine the insolation period corresponds to 20 W/m^2.

Figure 3.25 shows the calculated daily means of the ozone concentration together with the daily means of local BrO concentration between 27 August and 17 October 2006. During the four ozone depletion events (ODE 1 to 4) the BrO concentration measured onboard also varied. Especially during the events 2, 3 and 4, the ozone concentration and the BrO concentration were highly anti-correlated. As the ozone concentration dropped below the background level concentration, the BrO concentration increased similarly.

The halogen radical Br reacts with ozone, forming a halogen oxide molecule BrO [Simpson et al., 2007]. The similar increase of the BrO concentration and decrease of the ozone concentration indicates that the ozone depletion events measured onboard were in fact activated by the presence of Br in the atmosphere.

The two peaks in the BrO time series measured by the SCIAMACHY and the MAX-DOAS and with a delay in time (see shaded areas in Figure 3.24.) occur simoultaneously with the ozone depletion events 2 and 3 (compare Figure 3.25.). Section 8 revealed that the ozone depletion event between 23 and 25 september 2006 (ODE2) was meteorologically controlled. According to this, the BrO data (Figure 3.24.) indicate that the regionally measured data (SCIAMACHY) increased earlier than the local BrO data (MAX-DOAS) which again indicates a meteorologically controlled ODE. In contrast, between 30 september and 1 october 2006 (ODE2), the BrO vertical column attained its maximum first locally (onboard of the RV) before rising regionally (in a radius of 200 km). It indicates that ODE2 was initiated by local chemical destruction.

The BrO time series reveals two other peaks, one at the beginning of the record as well as one starting on 17 September and lasting until 21 September 2006 during which ozone remained at background levels. As the MAX-DOAS measures the BrO concentration in a vertical column extending from the ground to the upper limit of the troposphere, the collected data do not provide any information about the exact altitude, where the observed BrO was located. According to Jones et al. [2010], ozone depletion can be observed at several kilometers altitude while ozone concentration at the surface is at background level. Concerning the two BrO peaks that apparently had no influence on the ozone concentration measured onboard, it is assumed that the increased BrO concentration resided above the boundary layer, while the ozone concentration in the boundary layer was not affected.

3.4 Ozone concentrations at other Antarctic stations

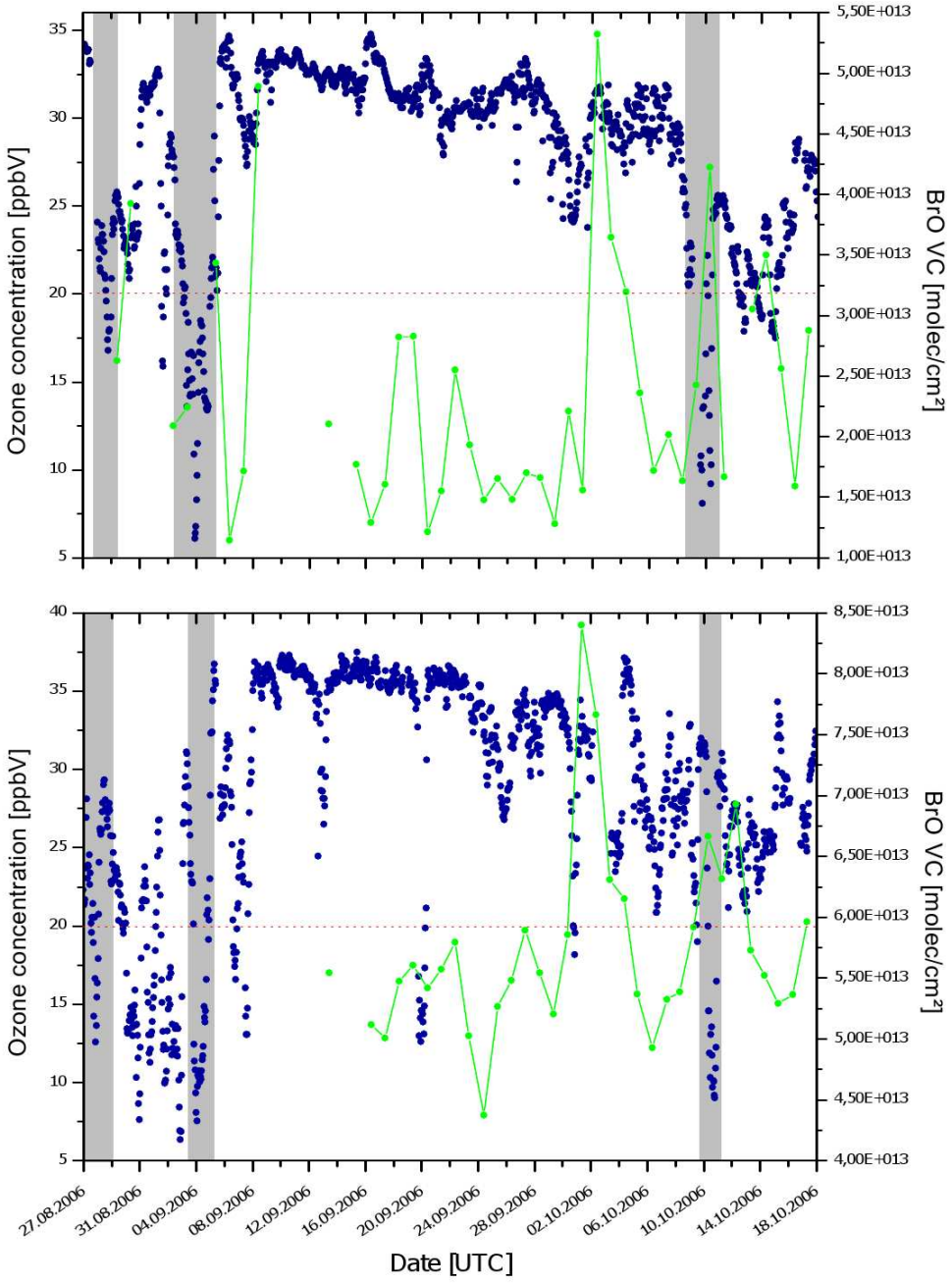


Figure 3.26: *Ozone concentration measured at the Antarctic research stations Neumayer (top) and Halley (bottom) and BrO vertical column within a radius of 200 km around both research stations measured with the SCIAMACHY satellite between 26 August and 17 October 2006. The shaded areas indicate the ozone depletion events happening simultaneously at both Halley and Neumayer.*

Ozone data were also collected at the German Antarctic research station Neumayer [König-Langlo and Loose, 2007] as well as at the research station Halley.

For both stations, ozone depletion events between 26 August and 17 October 2006 were specified as ozone drops below 70% of the mean ozone concentration, corresponding to 20 ppbV. The ozone time series recorded at Neumayer reveals four events with ozone concentrations below the threshold during the measuring period (see Figure 3.26). At Halley, the ozone concentration dropped seven times below 20 ppbV (see Figure 3.26.). Only the ozone depletion events happening simultaneously at both stations will be investigated (see Figure 3.26., shaded areas).

3.4.1 ODE1

Between 27 and 31 August 2006, ozone dropped one time below 20 ppbV at the research station Neumayer and three times at the British station Halley.

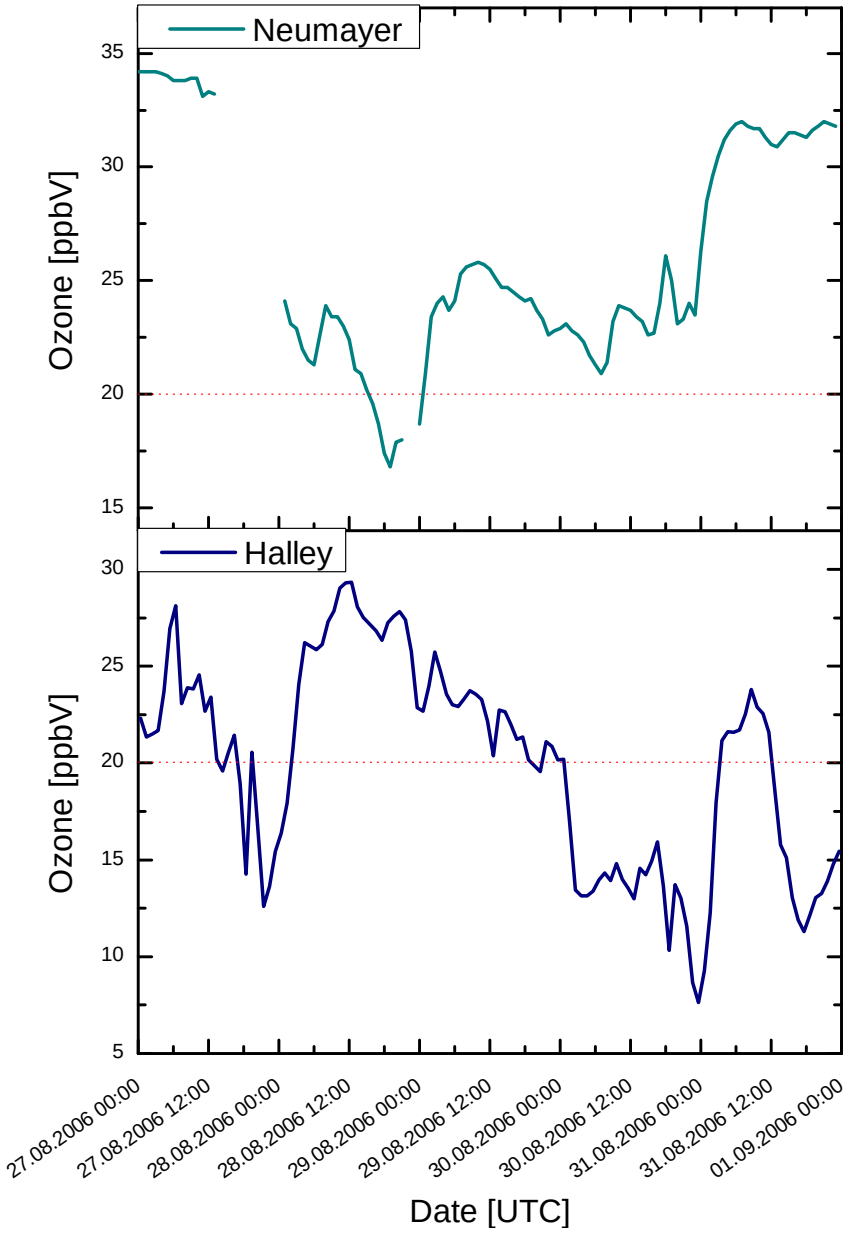


Figure 3.27: *Ozone concentration at the stations Neumayer and Halley between 27 and 31 August 2006.*

At the Antarctic station Neumayer, the sudden ozone depletion seemed to be linked to a change of the wind direction.

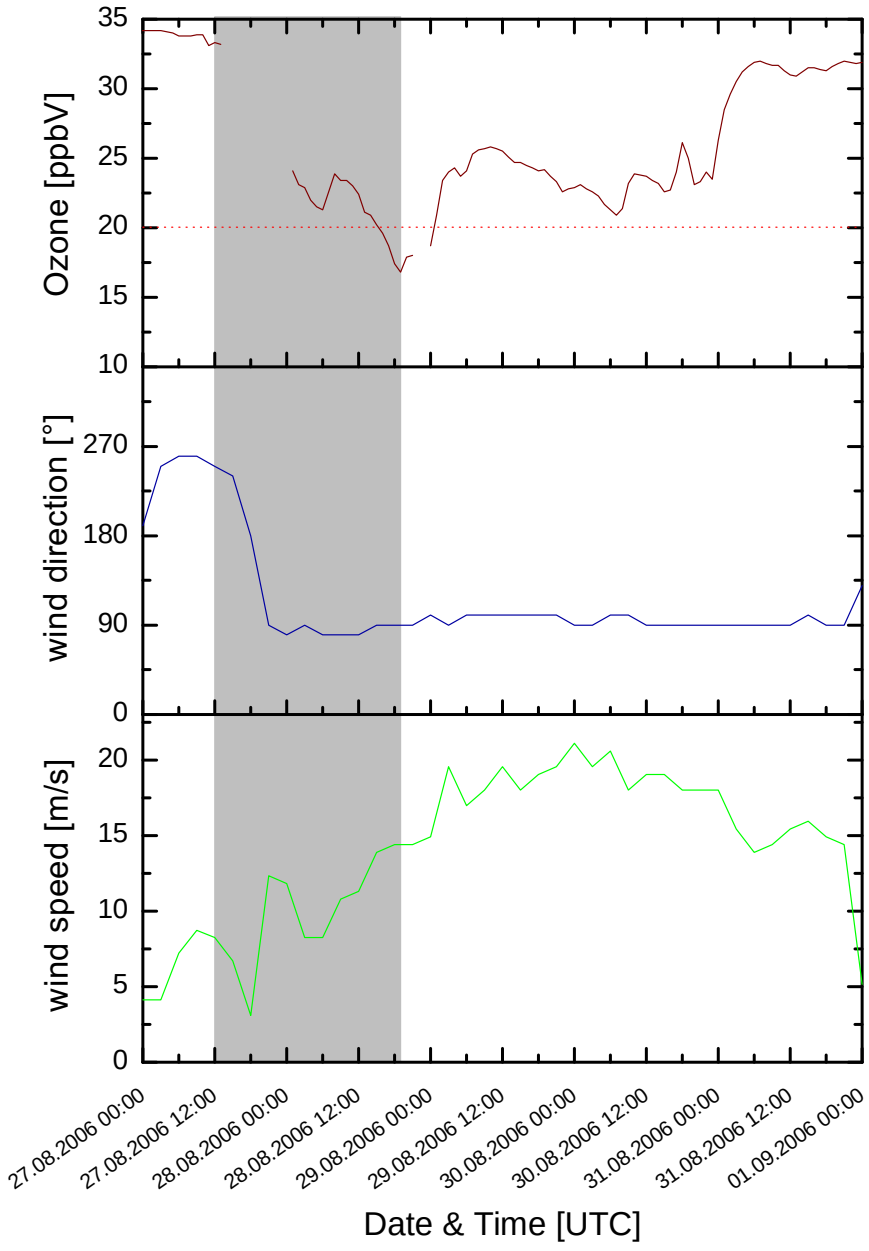


Figure 3.28: *Ozone concentration, wind direction and wind speed at the research station Neumayer between 27 and 31 August 2006. The shaded area represents the period of the ozone decrease.*

Figure 3.28. represents the ozone concentration, wind direction and wind speed at Neumayer for the period of the ozone depletion event. The ozone concentration dropped at the same time as the wind direction changed from south-west (250°) to east (90°). Additionally the wind increased from approximately 7 to 15 ms^{-1} until the ozone concentration reached its minimum (17 ppbV).

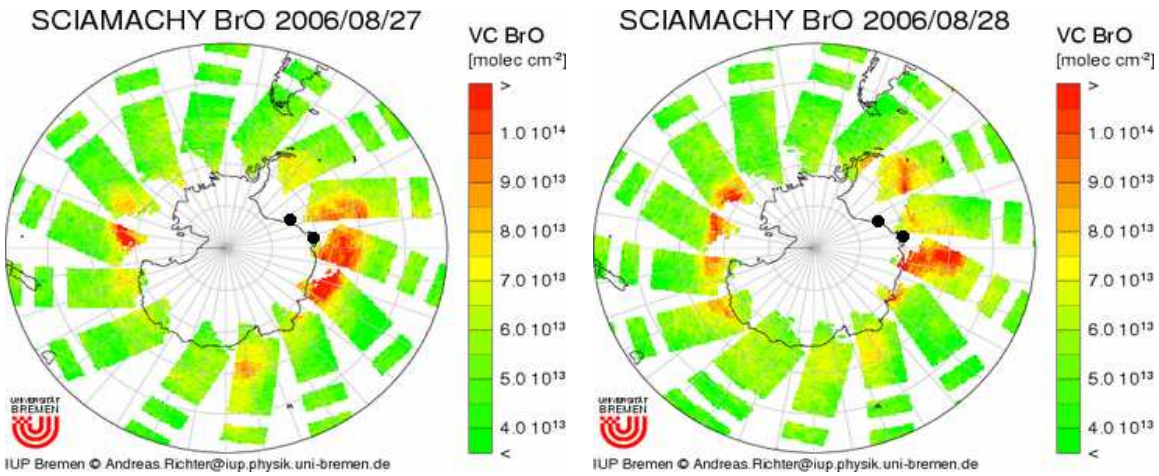


Figure 3.29: *BrO vertical column on 27 and 28 August 2006.*

Figure 3.29. reveals elevated BrO vertical columns east of the research station Neumayer on 27 and 28 August 2006. Next to the station, no data are available. Due to the simultaneous drop of the ozone concentration and the sudden change in wind direction, it is probable that ozone depleted air masses were transported to the station. As the BrO enriched air masses moved eastwards, the ozone concentration again increased at Neumayer on 29 August 2006.

At the British research station, no wind data nor BrO data are available. As the backward trajectories reaching the station before and during the ozone depletion event are similar, no statement can be made about this ozone depletion event on Halley.

3.4.2 ODE2

Between 01 and 05 September 2006, ozone dropped two times below 20 ppbV at the research station Neumayer and at the British station Halley (Figure 3.30.).

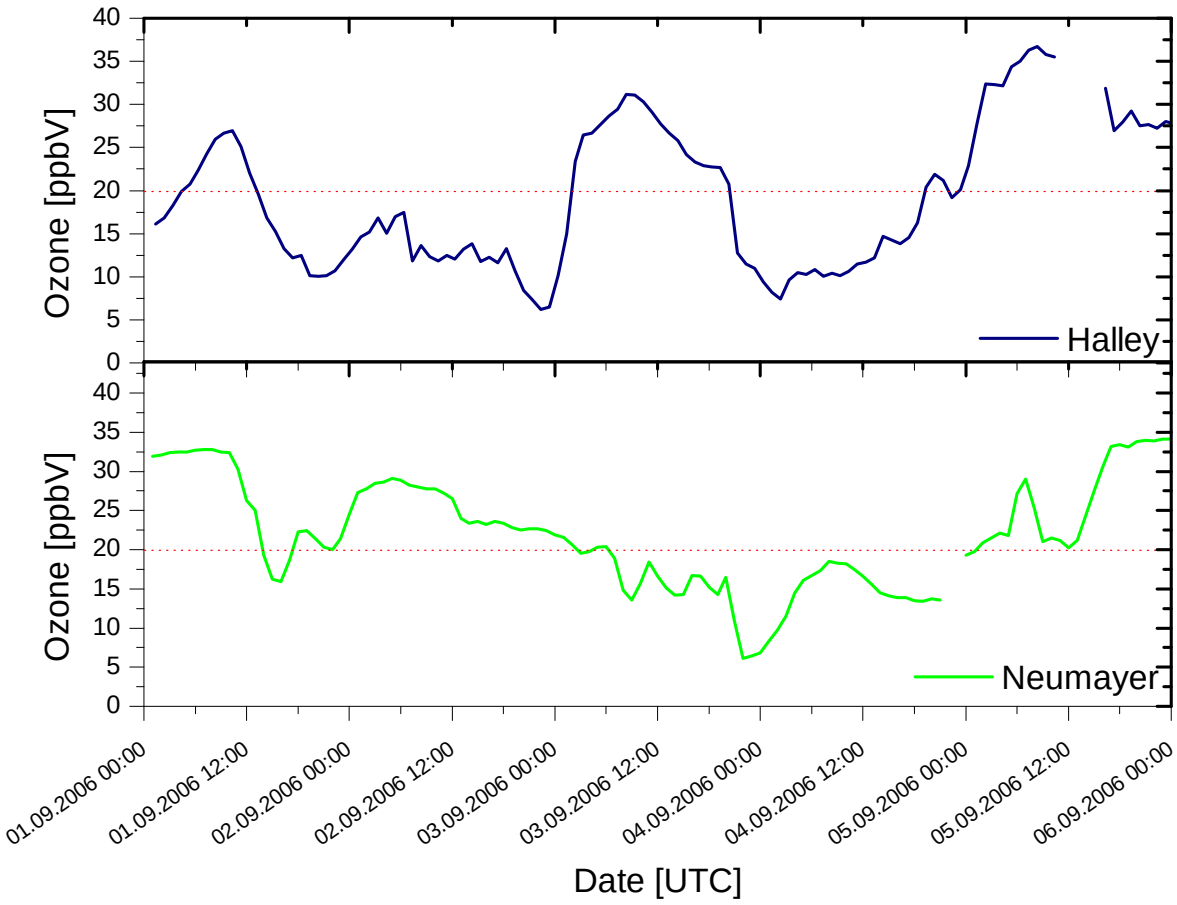


Figure 3.30: *Ozone concentration at the stations Neumayer and Halley between 01 and 05 September 2006.*

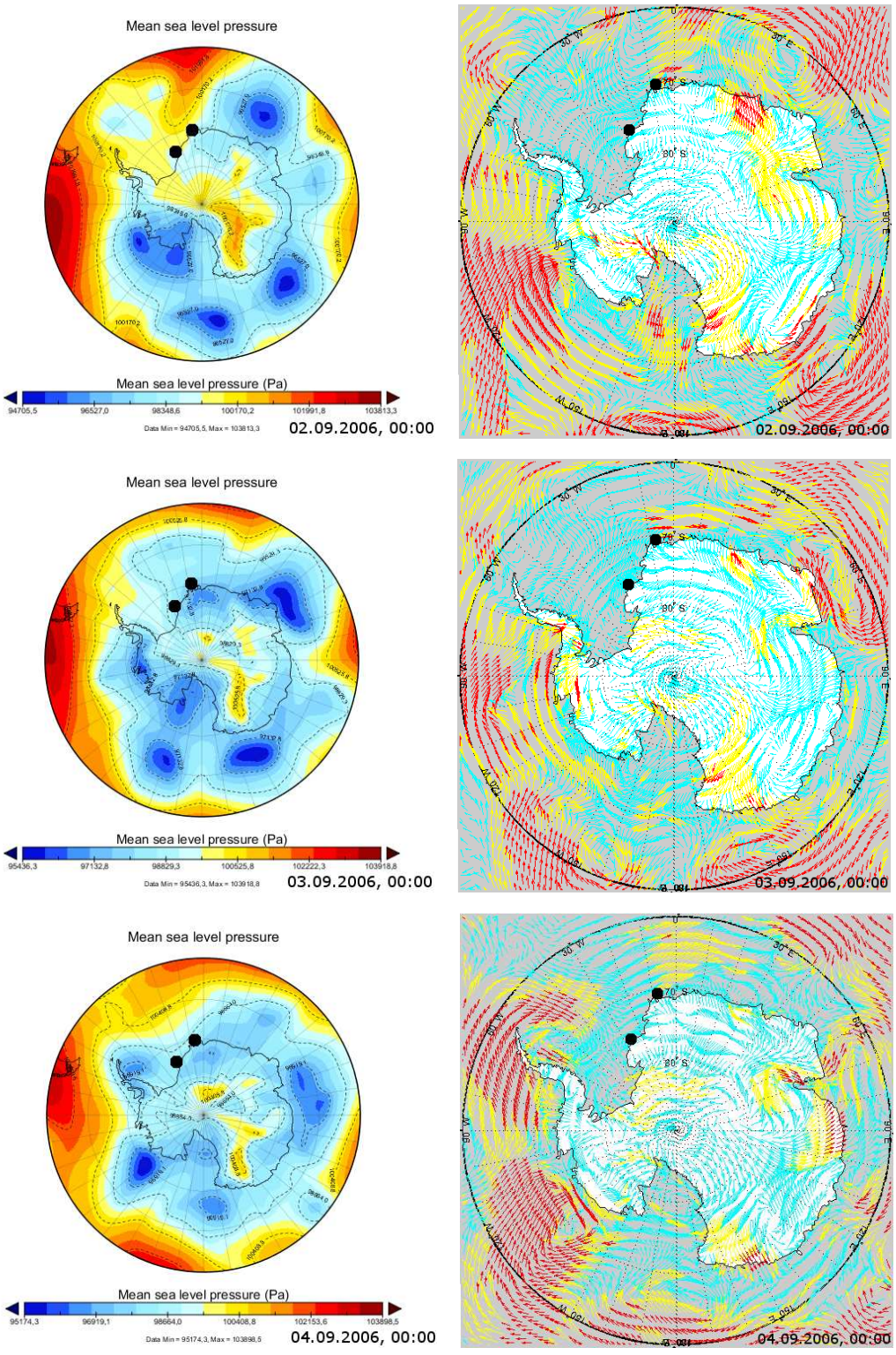


Figure 3.31: *Mean sea level pressure and wind maps on 2, 3 and 4 September 2006. The two Antarctic research stations Neumayer and Halley are indicated by a black circle.*

The ozone concentration at Neumayer as well as at Halley between 1 and 5 September 2006 was considerably influenced by three different synoptical systems. On the one hand a high pressure system situated in the southern Atlantic brought ozone-rich air masses from northern latitudes into the area of the Weddell Sea and broader to the Antarctic stations Halley and Neumayer (see Figure 3.31., 02.09.2006, 00:00). On the other hand a low pressure system developped over the research station Neumayer. As it intensified, the high pressure system had to move northwards. Hence, the anticyclonical rotation of the low pressure system influenced both the air masses reaching Neumayer and also the air parcels arriving at Halley a few hours later (see Figure 3.31., 03.09.2006, 00:00). In both cases, the air masses originated from the Weddell Sea. Additionally a second low pressure system passed the Antarctic Peninsula on 4 September 2006 (see Figure 3.31.). Again ozone-rich air masses reached the Weddell Sea and were further transported to the Antarctic stations.

At Neumayer, the ozone concentration dropped on 1 September 2006 between 08:00 and 16:00, where the ozone concentration reached a minimum of 15.9 ppbV. The air masses were influenced by a low pressure system situated north-east of the station at that time. Hence, as revealed by the 120h-backward trajectory (Figure 3.32., left), the air masses originated from the eastern coast of the continent, where the BrO vertical column exceeded $1*10^{14}$ molecule/cm^2 on 27 August 2006 (Figure 3.32., right).

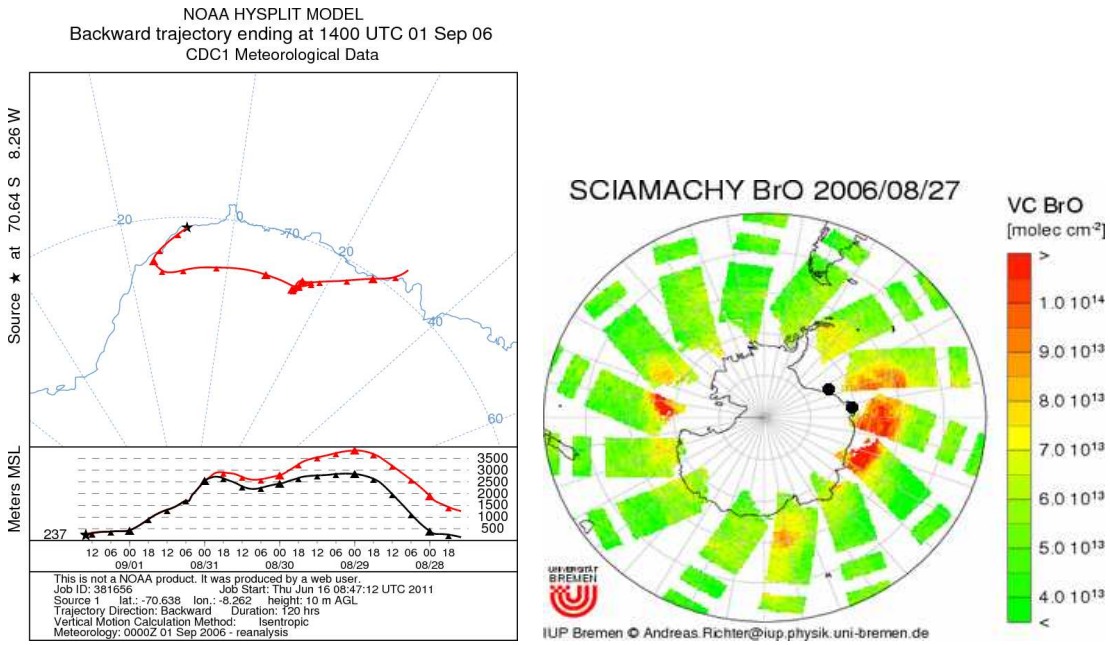


Figure 3.32: *120 hours-backward trajectory reaching Neumayer on 1 September 2006, 14:00 (left) and vertical column of BrO on 27 August 2006.*

As already indicated in figure 3.31., between 2 and 3 September 2006, a low pressure system developped over the research station Neumayer and influenced the origin of the air masses reaching both Antarctic stations. Simultaneously the ozone concentration at Neumayer drops from 22.5 ppbV at 20:00 on 2 September to 6.1 ppbV at 22:00 on 3 September and at Halley from 31.2 ppbV at 08:00 on 3 September to 7.4 ppbV at 02:00 on 4 September.

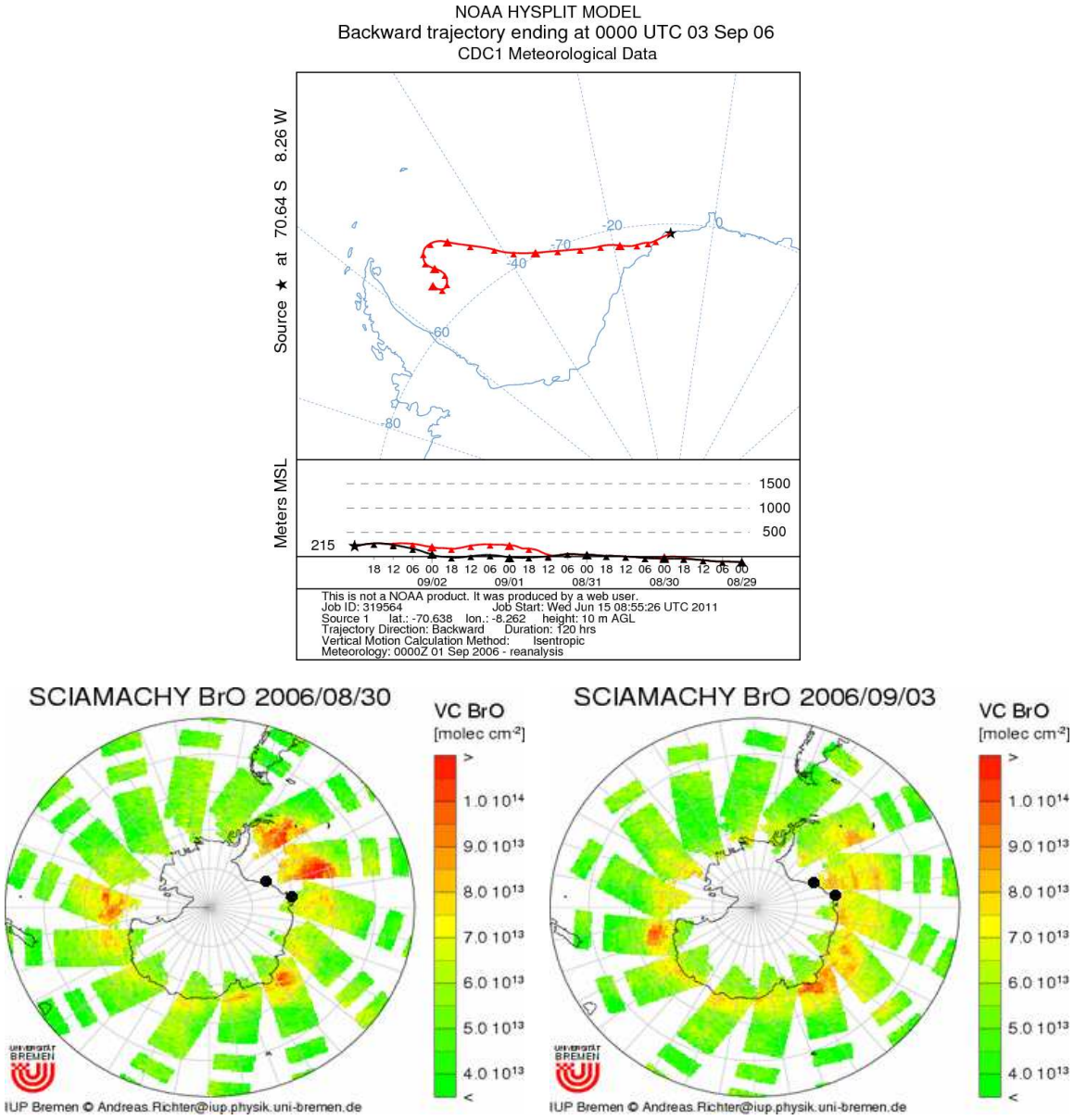


Figure 3.33: *120 hours backward trajectory reaching Neumayer on 03 September 00:00 (top). BrO vertical column maps on 30 August and 03 September 2006 (bottom).*

At Neumayer, the ozone depletion seemed to be meteorologically as well as chemically controlled. In the beginning of the decrease, the 120 hours backward trajectory reveals that the air masses passed the boundary layer over the Weddell Sea on 30 and 31 August, where the BrO vertical column exceeded $1*10^{14}$ molecules/cm^2. Between 12:00 and 18:00 on 3 September 2006, the ozone concentration remained constant at about 15 ppbV; simultaneously, the 120 hours back trajectory reaching Neumayer at 12:00 reveals a change of the air masses, originating from the interior of the continent. The sudden decrease of the ozone concentration between 18:00 and 22:00 with a minimum of 6.1 ppbV as well as the ozone depletion event at Halley on 3 September were chemically induced. The BrO map indicates an elevated vertical column around both Antarctic stations for this period.

At Halley, the backward trajectories do not change before and during the ozone depletion event. As neither BrO data nor meteorological data are available for this period, the causes for the ODE can not be further interpreted.

3.4.3 ODE3

Another ozone depletion event took place simultaneously at both Antarctic research stations Neumayer and Halley. At Neumayer, ozone concentration was at background level until a sudden drop on 09 October 2006 18:00, where the ozone concentration reached a minimum of 7 ppbV. After increasing during the night, it dropped again below 10 ppbV before finally reaching background level on 10 October 2006 12:00. At Halley the ozone concentration decreased below 10 ppbV on 10 October 2006 before rising again.

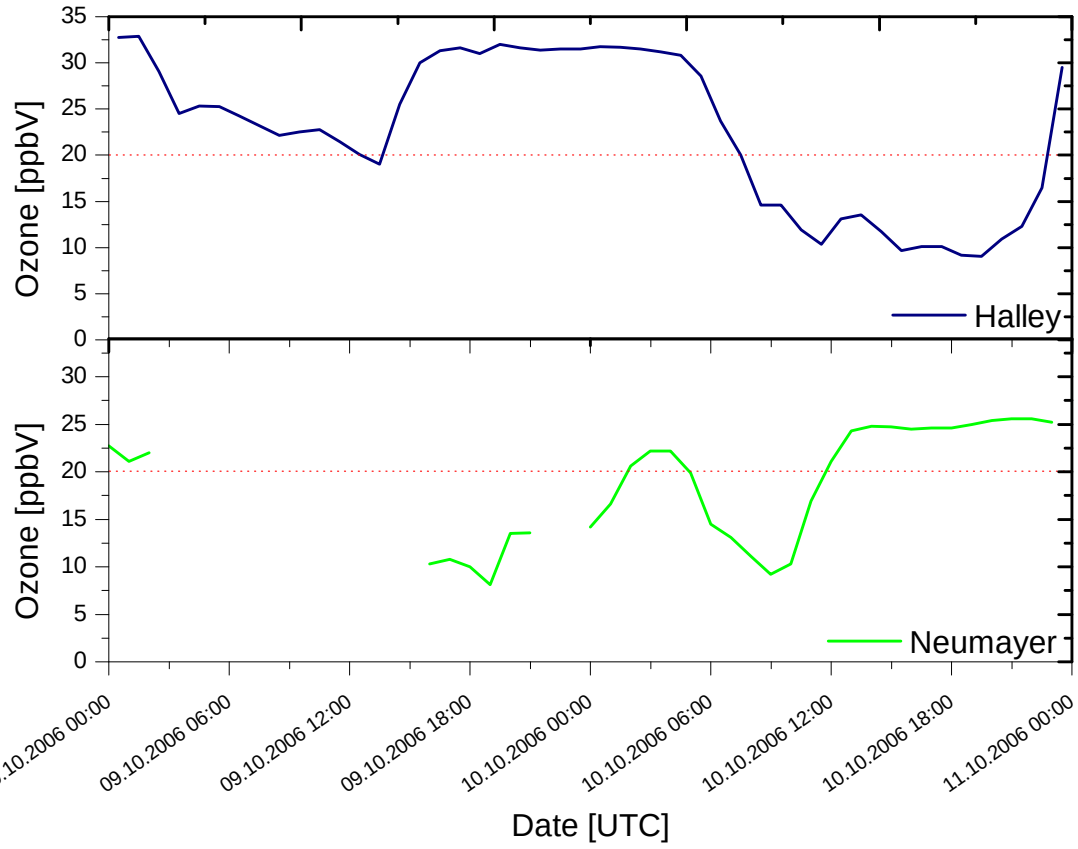


Figure 3.34: *Ozone concentration at the stations Neumayer and Halley between 09 and 10 October 2006.*

Between 08 and 11 October 2006, several synoptical systems influenced the trajectories of the air masses reaching Neumayer as well as Halley.

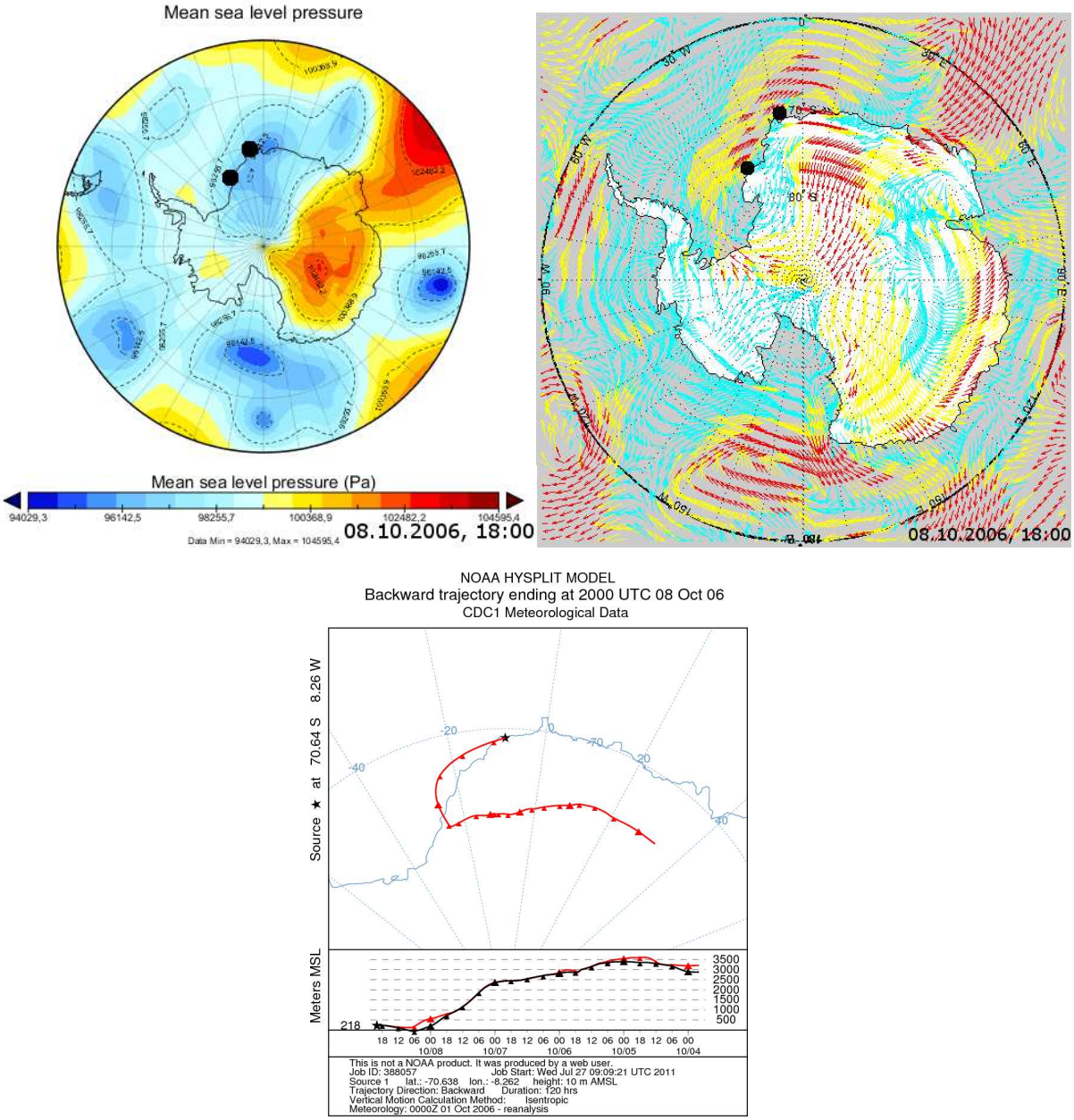


Figure 3.35: *Mean sea level pressure, wind direction and wind speed at 10m on 08 October 2006, 18:00 and the 120h-backward trajectory reaching Neumayer on 08 October 2006, 20:00.*

Influenced by a low pressure system located right over the Antarctic station Neumayer, the trajectories reaching the research station transport air masses from Queen Maud Land in the interior of the continent containing background level ozone concentration.

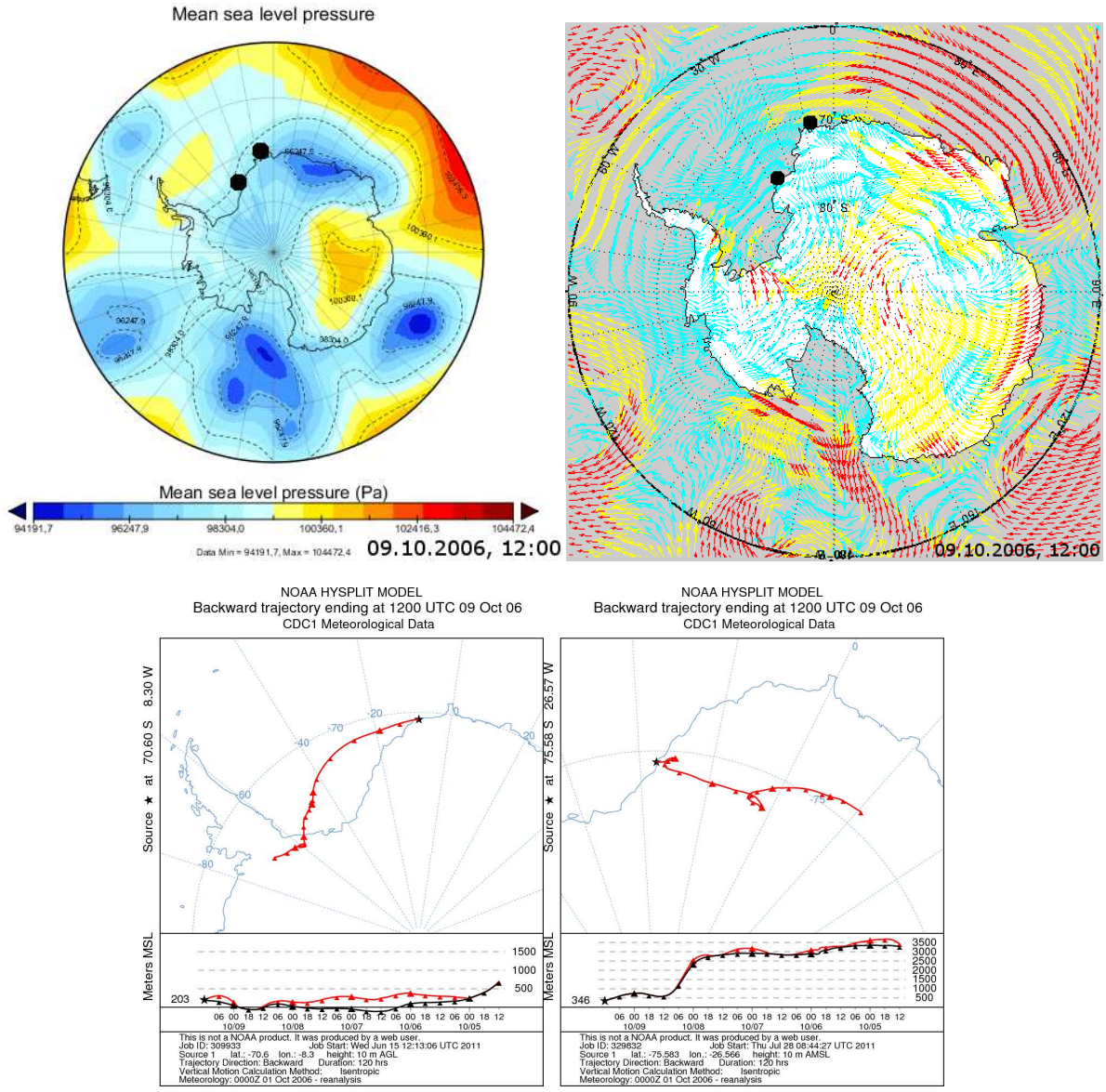


Figure 3.36: *Mean sea level pressure, wind direction and wind speed at 10m on 09 October 2006, 12:00 and the 120h-backward trajectory reaching both stations Neumayer (bottom left) and Halley (bottom right) on 09 October 2006, 12:00.*

The 120h-backward trajectory reaching Neumayer on 09 October 2006, 12:00 is influenced by two synoptical systems. A high pressure developping over the Weddell Sea and lower air pressure along the eastern coast of the Weddell Sea have an impact on the local wind direction and wind speed, hence, the wind direction in the central Weddell Sea is west. Thus, the trajectory reaching Neumayer on 09 October 2006, 12:00 originates from the boundary layer over the Weddell Sea. No ozone data are available between 09 October 2006 02:00 and 16:00 at the station Neumayer. As the ozone concentration dropped already to 10.3 ppbV

at 16:00 (22 ppbV at 02:00), it can be assumed that the ozone depletion started earlier than 16:00. At 12:00, the trajectory brought air masses originating from the Weddell Sea (see Figure 3.36.). It is probable, that the ozone was depleted over the Weddell Sea, and already depleted air masses reached the research station at 12:00.

The air masses reaching Halley on 09 October 2006, 12:00 were influenced by a third synoptical system. The low pressure system that was situated right above the station Neumayer 16 hours earlier (see Figure 3.35.) moved eastwards (see Figure 3.36.). Hence, the trajectories originated from Queen Maud Land. According to the ozone measurements performed at the research station, ozone was at background level at that time.

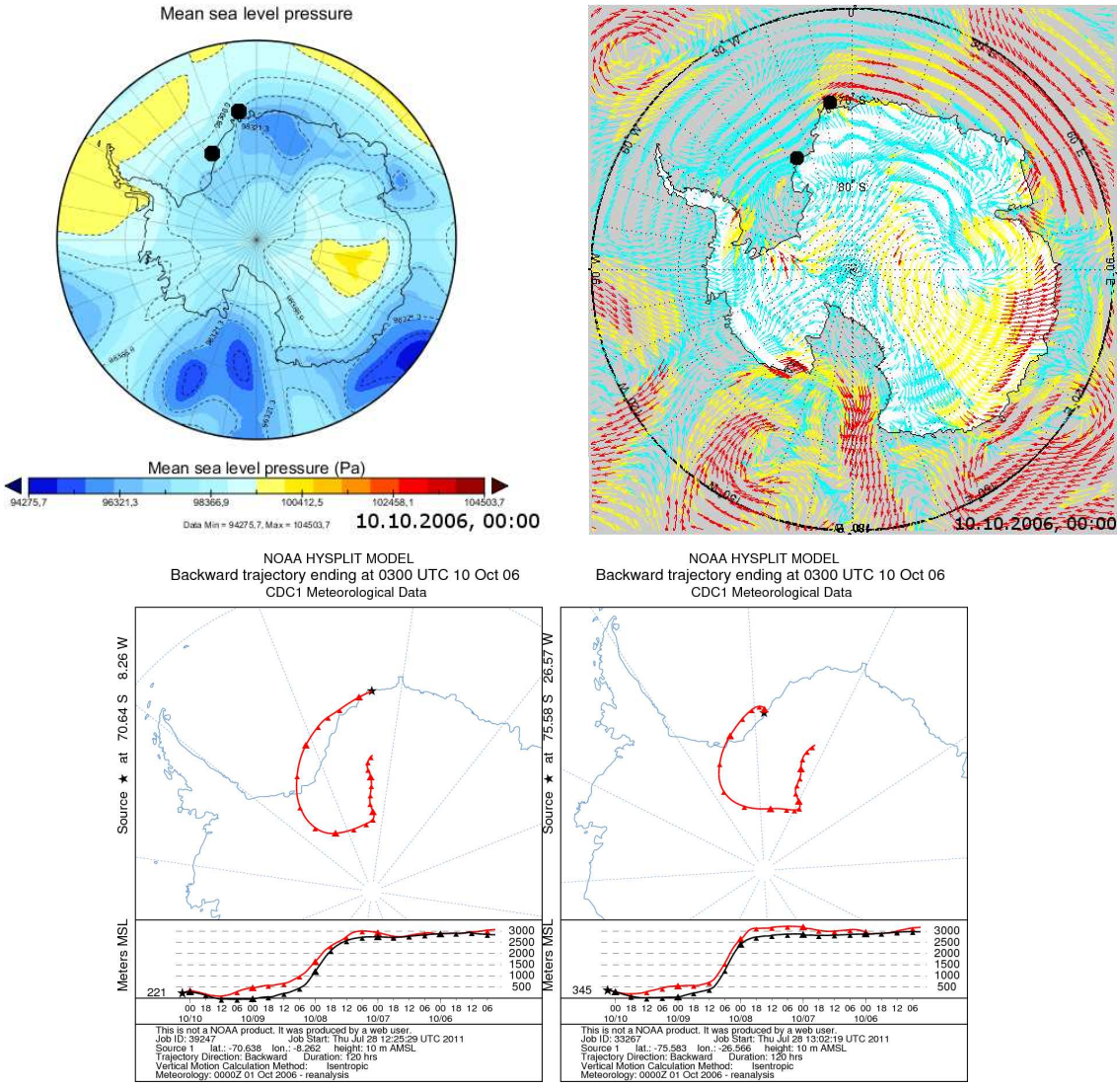


Figure 3.37: *Mean sea level pressure, wind direction and wind speed at 10m on 10 October 2006, 00:00 and the 120h-backward trajectory reaching both stations Neumayer (bottom left) and Halley (bottom right) on 10 October 2006, 03:00.*

The trajectories reaching the research stations Neumayer and Halley are both influenced by a low pressure systems that developped south-west of Halley. The air masses originated from the interior of the continent and only passed the eastern coast of the Weddell Sea before arriving at Neumayer and Halley, respectively. Ozone concentration was at background level at both research stations on 10 October 2006, 03:00.

At Halley, the ozone depletion event takes place shortly after:

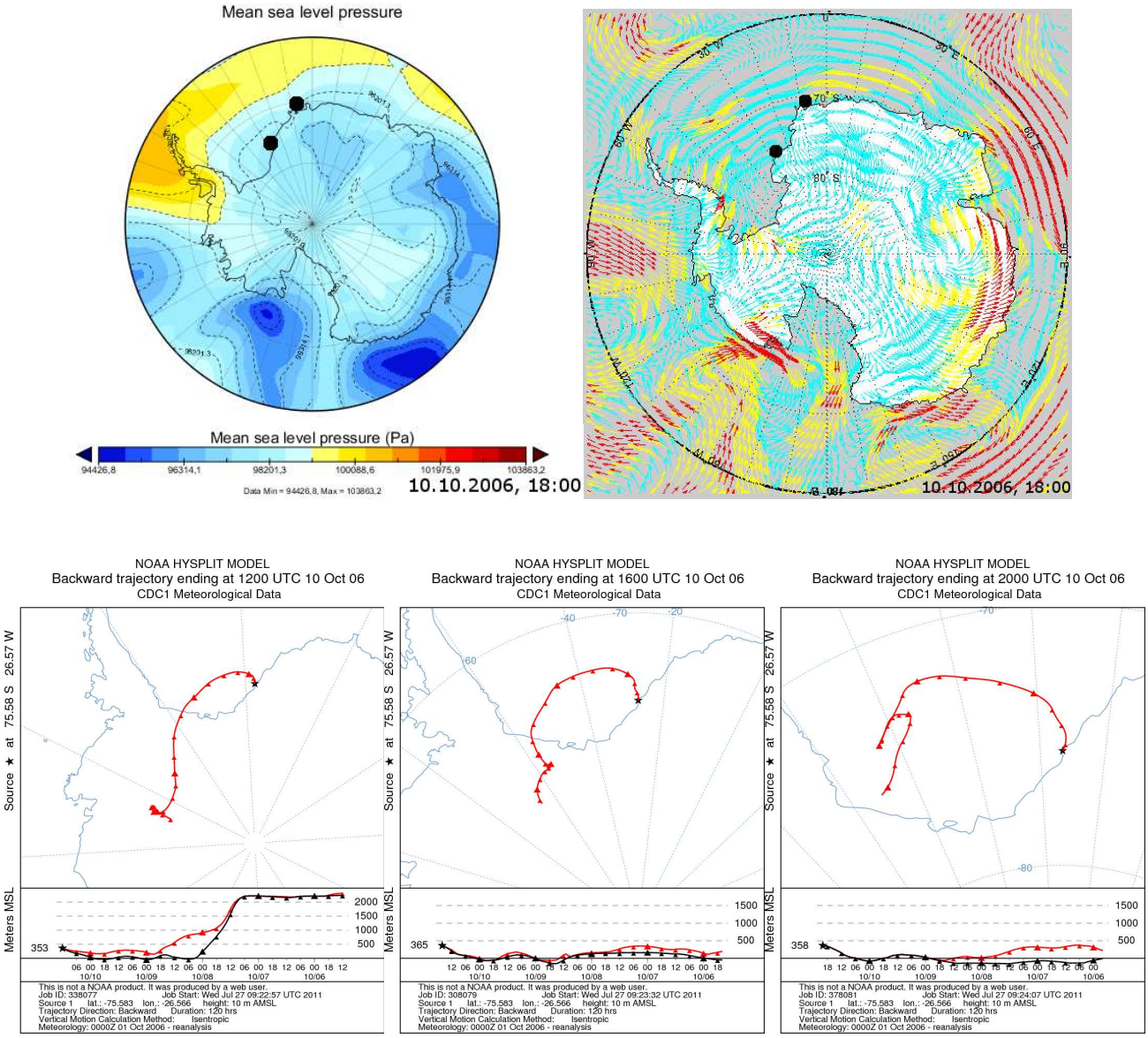


Figure 3.38: *Mean sea level pressure, wind direction and wind speed at 10m on 10 October 2006, 18:00 and the 120h-backward trajectory reaching the station Halley on 10 October 2006, 12:00, 16:00 and 20:00.*

The low pressure system that was situated south-west of Halley a few hours before, hardly moved east causing a sudden change of the air masses reaching Halley. The trajectories indicate, that the air masses originated from the boundary layer over the Weddell Sea. Simultaneously, the ozone concentration measured at the Antarctic station dropped below 20 ppbV and reached a minimum of 8.9 ppbV at 20:00.

Comparing the trajectories reaching Neumayer and Halley during ODE3 reveals that the air masses inducing the drop of the ozone concentration at both stations crossed the Weddell Sea during the same period.

3.4.4 Conclusion

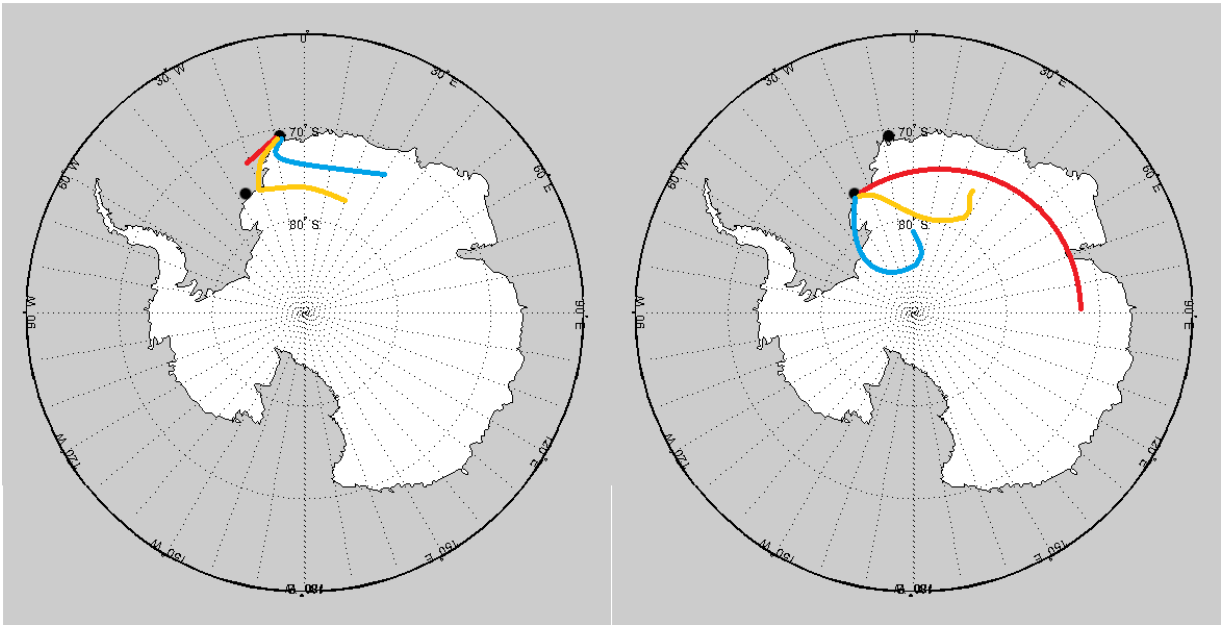


Figure 3.39: *Schematical 120h backward trajectories before the sudden ozone depletion events simultaneously observed at Neumayer (left) and Halley (right). The red trajectory indicate ODE1, the yellow one ODE2 and the blue one ODE3.*

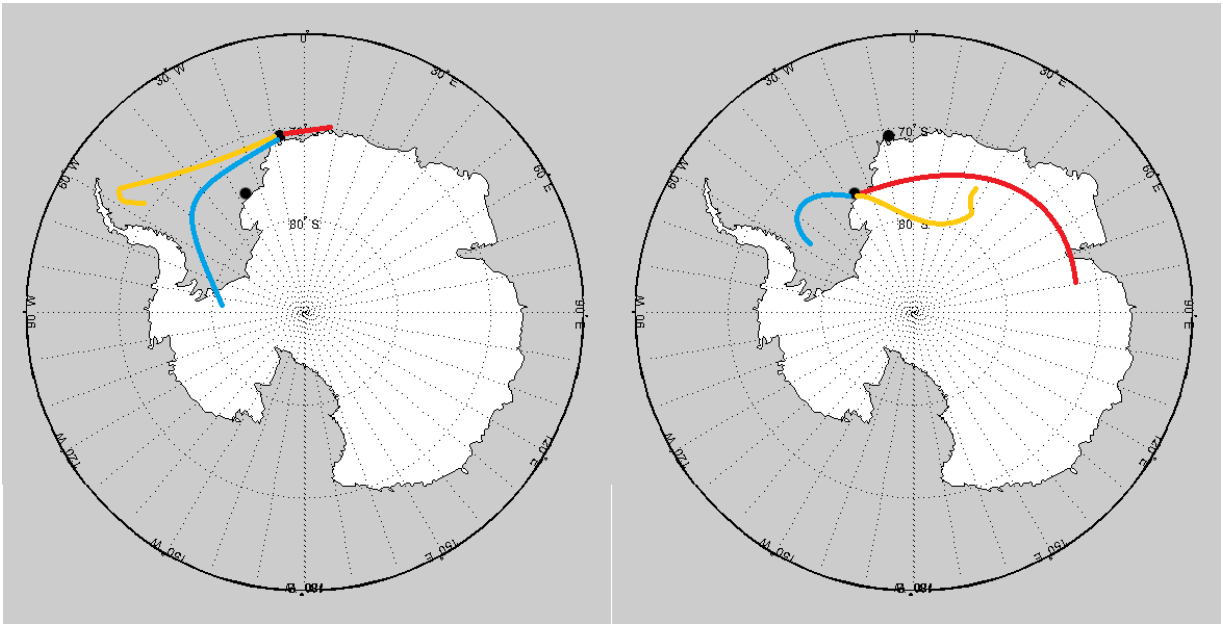


Figure 3.40: *Schematical 120h backward trajectories during the sudden ozone depletion events simultaneously observed at Neumayer (left) and Halley (right). The red trajectory indicate ODE1, the yellow one ODE2 and the blue one ODE3.*

At Neumayer, all ozone depletion events that have been investigated were induced by altering synoptical conditions initiating a change of the origin of the air masses reaching the research station. The 120h-backward trajectories clearly indicate that the air masses causing the drops of the ozone concentration during ODE2 as well as ODE3 originate from the Weddell Sea. Furthermore the air masses provoking the third decrease of the ozone concentration at the British station Halley arose as well from the interior of the Weddell Sea. Hence, the chemical reactions destroying the ozone concentration seem to take place again over the Weddell Sea.

The air masses containing low ozone are transported eastwards out of the Weddell Sea, thus, ODEs at Neumayer can also be initiated by air masses approaching from the east. ODE1 for example is induced by a change of the origin of the air masses. The wind turns east and air masses with low ozone concentration attain the research station.

At Halley, local processes can have an important influence on the ozone concentration. As the research station is predominantly exposed to wind from the east, a number of polynyas are kept open during the period of extended sea ice [Helmig et al., 2007]. These polynys are a probable source of sea salt aerosols that can lead to a local decrease of the ozone concentration. During ODE1 and ODE2 the trajectories do not change. It is a possible indicator for a chemically induced ozone depletion events. As neither BrO data nor meteorological data are available, an unambiguous assignment can't be done.

3.5 Link between BrO and low pressure systems

No consistent correlation has been found between pressure systems and ozone concentration in the north-western edge of the Weddell Sea (see Section 3.2.). But a connection between low pressure systems and enhanced BrO vertical columns and associated low ozone concentration has already been mentionned by Jones et al. [2010]. Since synoptic-scale depressions as well as polar lows are often accompanied by high wind speeds, saline snow can be lifted into the boundary layer and chemical reactions generating BrO can be induced (see Chapter 1). According to Jones et al. [2009], snow remains in a layer 10 cm above the surface, when the wind speed ranges between 8 ms^{-1} and 12 ms^{-1}. Above 12 ms^{-1}saline particles are lofted into the boundary layer and "blowing snow" is generated [Jones et al., 2009]. Hence wind speed exceeding 12 ms^{-1} in combination with high salinity can be a significant indicator for saline blowing snow that can generate BrO and therefore deplete ozone in the atmosphere. Enhanced wind speed generated by a passing low pressure system can also lead to the formation of polynas. The prevalent low temperatures lead to a freezing of the sea water surface forming fresh sea ice which is favorable for the creation of frost flowers [Jacobi et al., 2006, Kaleschke et al., 2004]. Frost flowers are an important source of reactive bromine and can induce the depletion of ozone. As a result low pressure systems accompanied by high wind speeds can generate an important BrO vertical column and provoke a drop in the ozone concentration.

3.5.1 Case study: 04 - 07 September 2006

The mean sea level pressure represented in Figure 3.42. indicates a low pressure system passing the Antarctic Peninsula and reaching the Weddell Sea on 04 September 2006. As it moved eastwards it coalesced with a second low pressure system reaching the eastern Weddell Sea from the north. It further moved south towards the Antarctic research station Neumayer before finally filling up and dissolving.

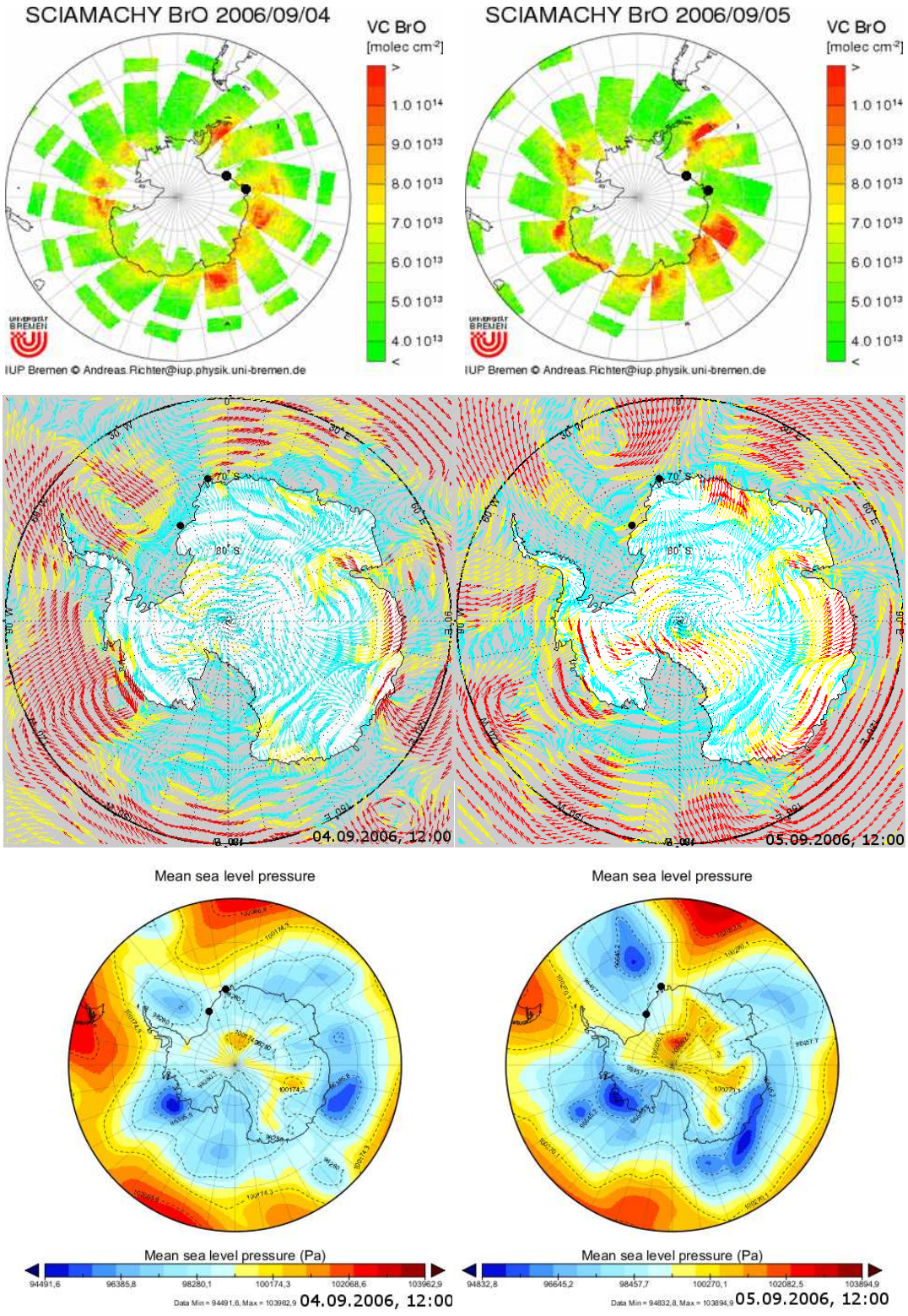


Figure 3.41: *BrO vertical column, wind speed and mean sea level pressure on 04 and 05 September 2006, see Figure 3.6. Note that the Prime Meridian is oriented differently in the map of the BrO vertical column.*

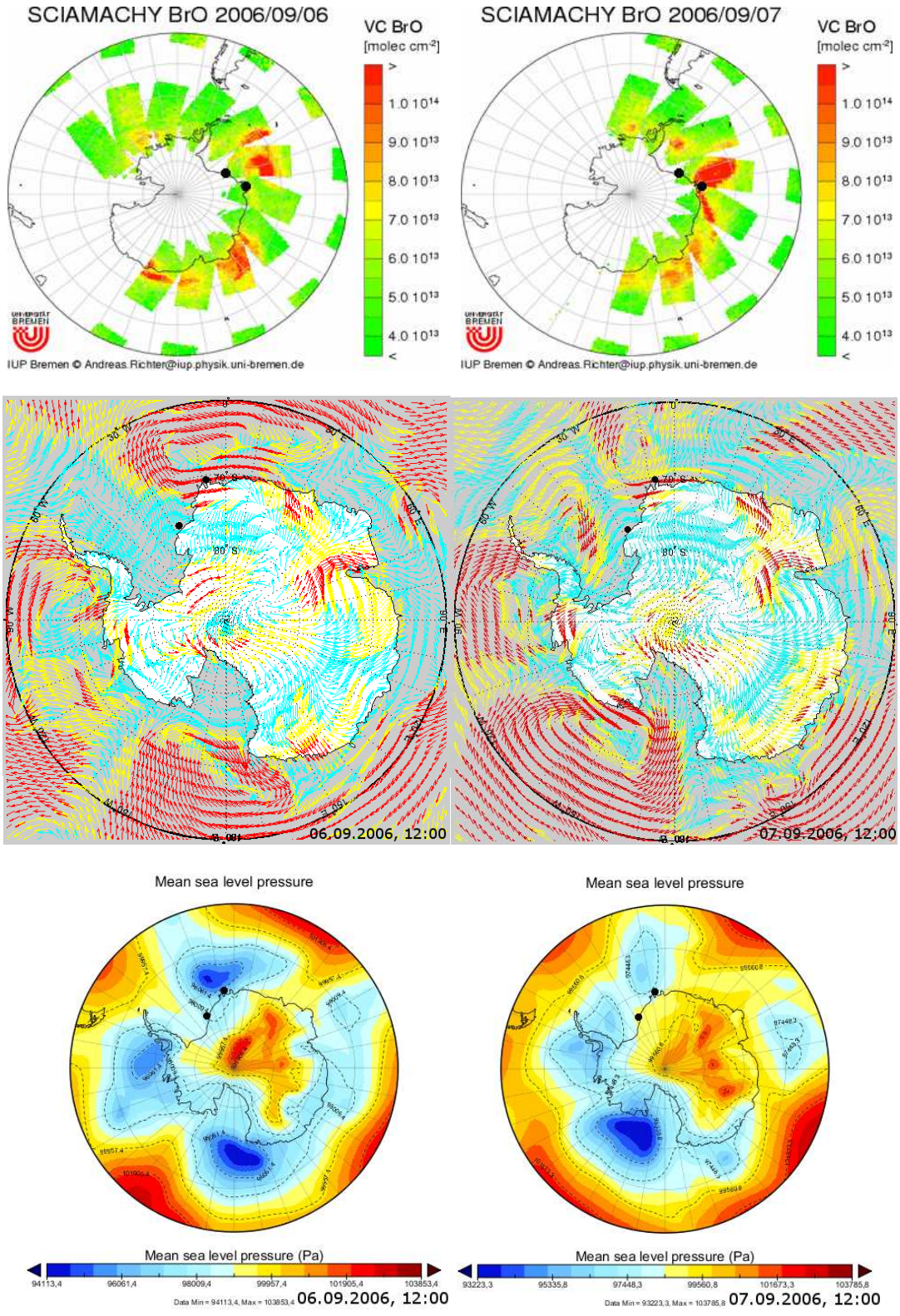


Figure 3.42: *BrO vertical column, wind speed and mean sea level pressure on 06 and 07 September 2006. (See Figure 3.41.)*

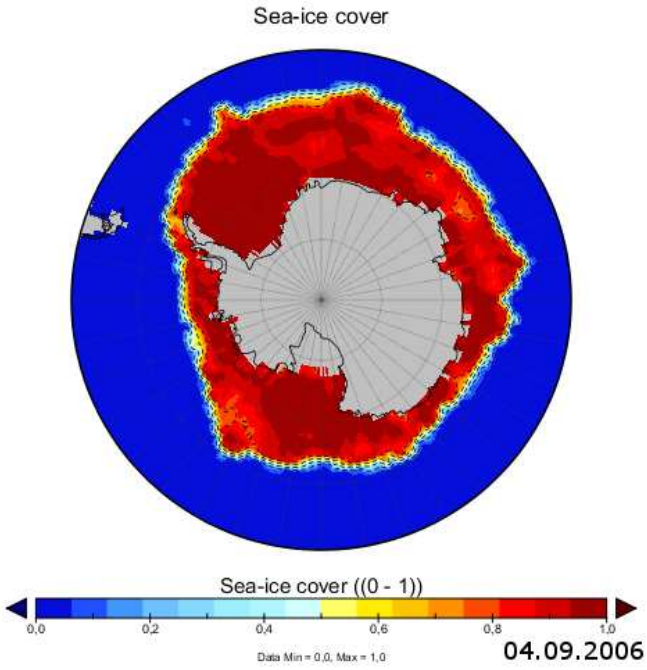


Figure 3.43: *Sea ice cover around the continent Antarctica on 04 September 2006.*

According to Figure 3.43. the Weddell Sea was covered with sea ice on 04 September 2006. Because the 10m wind speed exceeded 12 ms^{-1} on the western and the eastern flank of the low pressure system (see Figure 3.42.), it is possible that saline snow was lifted in the boundary layer. The BrO map on 04 September 2006 indicates an elevated vertical column near the Antarctic Peninsula, on the western flank of the low pressure system. Apparently the combination of sea ice and high wind speed led to chemical reactions generating BrO and depleting ozone.

When the low pressure system moved eastwards on 05 September 2006, the BrO vertical column diminushed next to the Antarctic Peninsula and increased at the actual western flank of the low pressure system, where the wind speed again exceeded 12 ms^{-1}. With only one BrO map per day, it is difficult to determine whether the elevated BrO vertical column was induced close to the Antarctic Peninsula on 04 September 2006 and afterwards advected by the low pressure system as it moved eastwards or if the high wind speeds (above 12 ms^{-1}) on the western flank of the low pressure system on 05 September 2006 induced another increase of the BrO vertical column. Furthermore it is difficult to explain why the BrO vertical column increased only on the western flank of the low pressure system on 04 and 05 September 2006 although the wind speed on the eastern flank exceeded 12 ms^{-1}as well.

The wind speed, coming along with the low pressure system approaching the research station Neumayer from the north on 06 September 2006, reached again values above 12

ms^{-1} and the BrO vertical column increased in this region. As the low pressure system was stationary with constant wind speed above 12 ms^{-1}on the southern and northeastern flank between 06 and 07 September 2006 before finally filling up on 08 September 2006, the BrO VC increased again on 07 September 2006.

3.5.2 Case study: 29 September - 02 October 2006

Comparing the BrO vertical column and the mean sea level pressure between 29 September and 02 October again reveals that the enhanced BrO VC was induced by a low pressure system situated in the north-western Weddell Sea (see 3.43., top). As the low pressure system moved eastwards, the BrO VC in the center of the Weddell Sea increased. Reaching the eastern coast of the Weddell Sea, the low pressure system splitted and formed to independent cyclones. One of them turned eastwards and led again to an increase of the BrO vertical column on it's actual position.

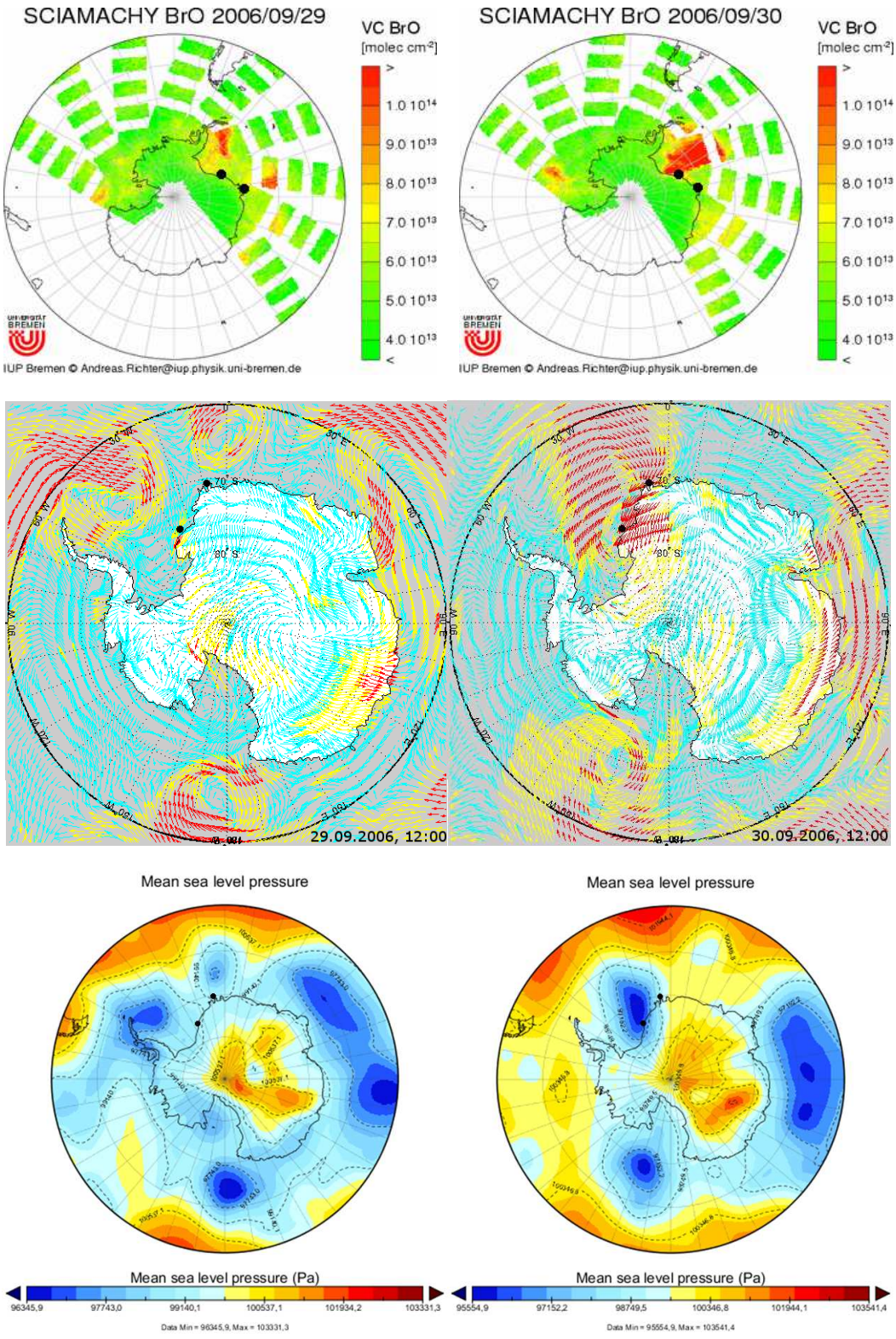


Figure 3.44: *BrO vertical column, wind speed and mean sea level pressure on 29 and 30 September 2006. (See figure 3.41.)*

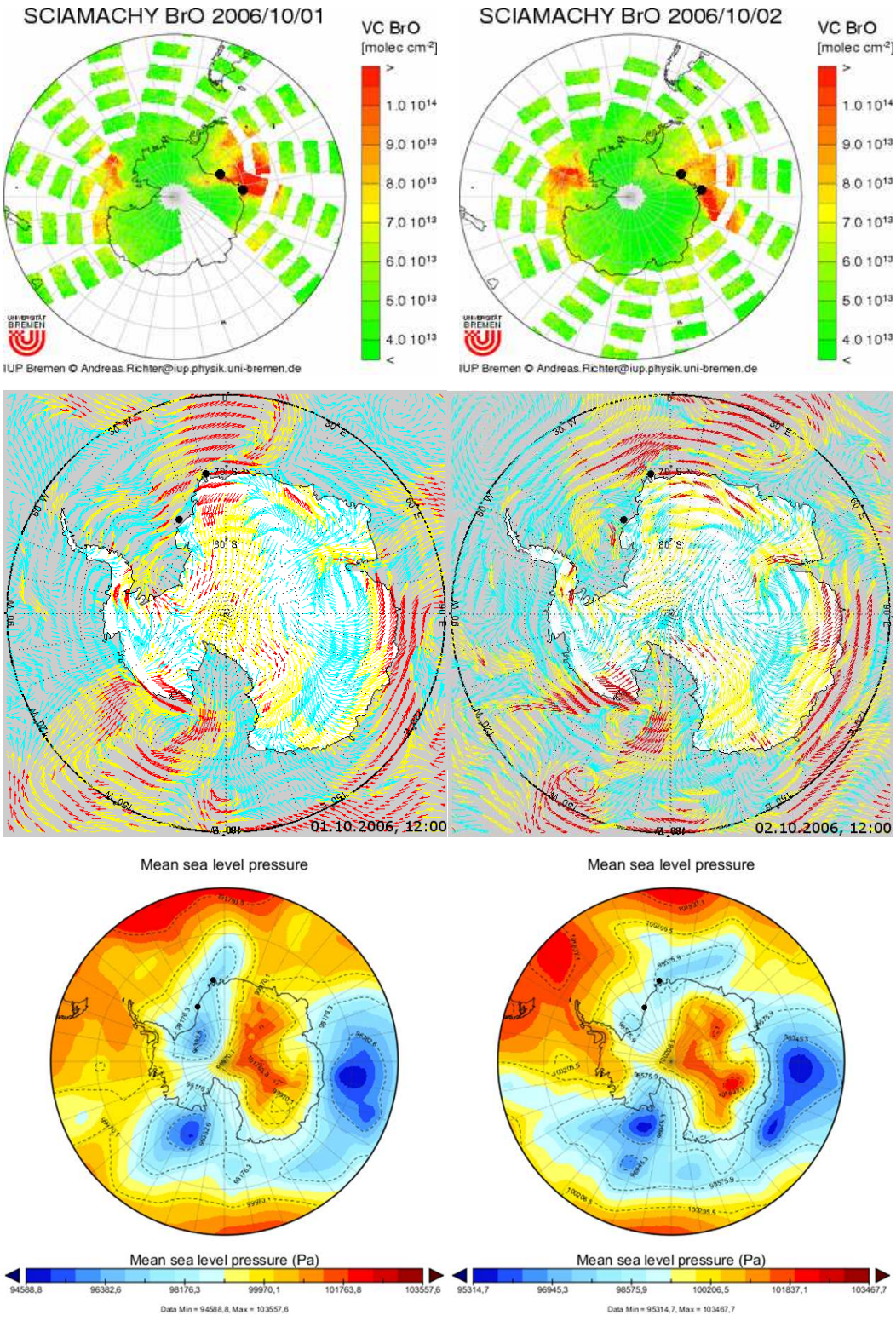


Figure 3.45: *BrO vertical column and mean sea level pressure on 01 and 02 October 2006. See Figure 3.41.*

In both cases low pressure systems accompanied by high wind speeds probably led to blowing snow dispersing saline particles. Those induced a chemical reaction forming BrO. As the low pressure systems moved further, the reactions were activated at the actual positions of the cyclones.

In the first case, the reactions were activated on the western flank of the actual positions of the cyclone. In the second case, the regions in the Weddell Sea with wind speeds exceeding 12 ms^{-1} coincided with the enhanced BrO vertical column. Hence, in both cases the enhanced BrO VC seemed to be induced by the passage of a low pressure system from west to east over the Weddell Sea.

Both case studies reveal another similarity. Although the low pressure systems developped west of the Antarctic Peninsula, the reactions releasing BrO only took place as soon as the low pressure system reached the Weddell Sea. As photolysis is necessary to generate reactive bromine atoms (see Chapter 1), the insolation is an important factor to induce an increase in the BrO vertical column. According to Figure 3.43. the sea ice west of the Antarctic Peninsula extended less to the North (70° South) than in the Weddell Sea where the sea ice reached 60° South. Hence, the time duration of the insolation is less over the sea ice in the Bellinghausen Sea than over the sea ice in the Weddell Sea. Consequently the probability of photochemical reactions generating reactive bromine atoms is elevated in the Weddell Sea comparing to west of the Antarctic Peninsula.

Cyclones are unable to enter the continent and therefore have to turn eastwards and move parallel to the coast in the circumpolar trough situated in the latitude band 60 to 70° South [King and Turner, 1997]. Figure 3.46. represents the tracks of all depressions between 1985-1989. It illustrates the frequency of low pressure systems in the circumpolar trough.

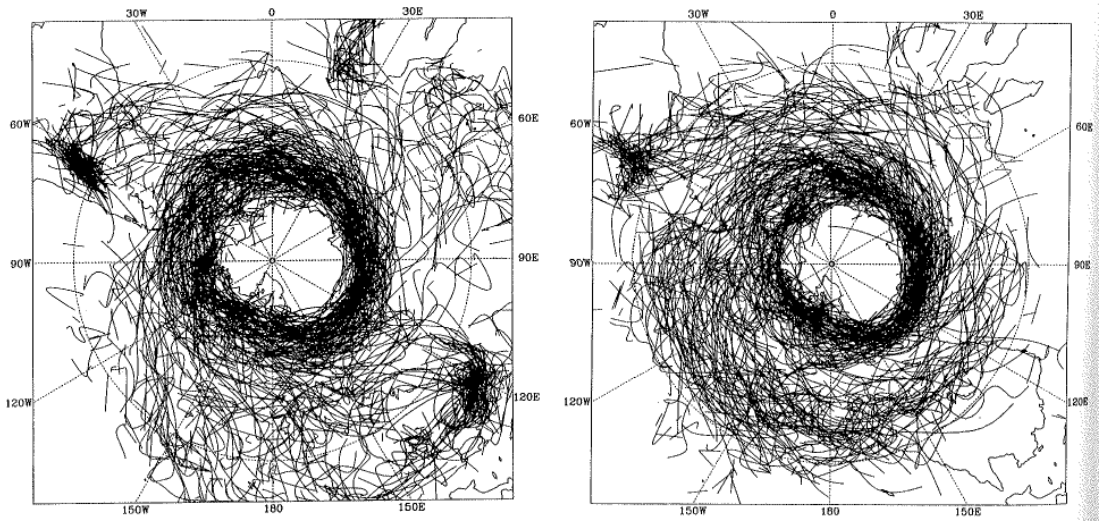


Figure 3.46: *Tracks of all depressions in summer (left) and winter (right) between 1985-1989. [King and Turner, 1997]*

BrO is released when cyclones, accompanied by high wind speed, move over saline snow residing on sea-ice. As cyclones move eastwards as soon as they reach the continent, the released BrO stays between the latitude band 60 and 70° South and does not move further north. This is one possible explanation for the absence of ozone depletion events at Cape Point in the southern spring (see Section 3.1.).

The connection between low pressure systems and the ozone concentration in the Arctic Ocean and in the Weddell Sea is opposite. Whereas low pressure systems bring air masses rich in ozone into higher latitutes and therefore induce an increase of the ozone concentration in the Arctic, low pressure systems in the Weddell Sea seem to generate BrO and lead to a drop of the ozone concentration.

Chapter 4

Summary and Conclusions

Ozone concentrations measured onboard of the research ship Polarstern during the Winter Weddell Outflow study between August and October 2006 were analyzed and compared to observations at other research stations located on the East coast of the Weddell Sea as well as the research station Cape Point in South Africa. Background concentrations of 25 to 35 ppbV were comparable for the studied period at all four locations. Ozone depletion events were characterized as drops of the ozone concentration from background levels below 70 % of the mean ozone concentration. The observations show that ozone depletion events occured at all locations, except at Cape Point. They were more frequent on the eastern coast of the Weddell Sea than onboard of the research vessel, which remained close to the Antarctic Peninsula or to the northern rim of the Weddell Sea. The fact, that no sudden decreases of the ozone concentration were observed at the South African station, confirms that ozone depletion events only occur at higher latitudes.

During the Winter Weddell Outflow Study, four ozone depletion events have been identified onboard of the RV Polarstern. Averaged, the ODEs lasted two days before the ozone concentration recovered. The minimum ozone concentration varied for each ODE (ODE1: 4.3 ppbV; ODE2: 12.4 ppbV; ODE3: 19.0 ppbV; ODE4: 14.0 ppbV).

Ozone depletion events can either be meteorologically (advection of ozone depleted air masses) or chemically induced (chemical removal of ozone occurs close to the measuring point). The meteorological conditions during the four ODEs were explicitly investigated to determine the causes of the drop of the ozone concentration. At first, the correlation between air pressure, air temperature and ozone concentrations onboard of the RV Polarstern were analysed. Since no distinctive correlation exists, the focus was put on the analysis of the synoptical situation in and around the Weddell Sea. By means of local wind maps, the mean sea level pressure in and around Antarctica as well as backward trajectories reaching the research vessel, the ozone depletion events could be defined as either meteorologically or chemically controlled. According to the meteorological parameter, ODE1, ODE2 as well as

ODE4 were meteorologically induced by a change in the origin of the air masses. In contrast, during ODE3 ozone was mainly removed locally by chemical processes.

During the WWOS BrO data were also collected onboard of the RV Polarstern. The BrO data were compared to the collected ozone data. During all ODEs elevated BrO vertical columns were observed. Additional BrO satellite observations permitted again to distinguish between chemically and meteorologically induced ozone depletion events onboard of Polarstern. According to these data, the BrO vertical column during the ODE3 increased primarily in proximity of Polarstern before rising in a radius of 200 km around the ship observed by the satellite. It confirms that this ozone depletion event was in fact driven by local chemistry. During ODE2, the BrO data increased first in a radius of 200 km around Polarstern. The subsequent rise of BrO was detected by the MAX-DOAS onboard of the research vessel. This delay between satellite and local BrO concentrations confirms that during this event ozone was rather removed away from the observational site and that the ozone decrease was caused by the advection of ozone-poor air masses.

Satellite observations of the BrO vertical column in austral spring 2006 in Antarctica revealed that BrO was mainly generated in the Weddell Sea before being transported to the east by low pressure systems. The increased development of low pressure systems due to a strong temperature gradient in the region between 60°S and 70°S latitude in the Weddell Sea could have been a reason for enhanced BrO development in this region. Additionally, low pressure systems tend to fill up and dissipate before reaching the Antarctic Peninsula rather than pass it. Hence, BrO clouds infrequently approach the Weddell Sea from the West.

The backward trajectories of the meteorologically induced ozone depletion events ODE1, ODE2 andODE4 revealed that the air masses causing the decrease of the ozone concentration mostly originated from the boundary layer over the Weddell Sea. The subsequent increases to background levels were again initiated by an air mass change bringing either air masses from higher layers or from other regions than the Weddell Sea. Ozone depletion events at the German station Neumayer as well as the British station Halley were also investigated. The analyses of the backward trajectories reaching both stations during ODEs indicates as well that the ozone depleted air masses mostly originated from the Weddell Sea.

Even if the chemical cycle of destruction of the ozone concentration is identical in both the Arctic and Antarctica, the processes do not follow the same pattern.

	Arctic	WWOS
Definition of ODE	2003 & 2007: < 5 ppbV	2006: < 19 ppbV
Percentage of ozone concentration below the limit defining ODEs	2003: > 55 % 2007: > 66 %	2006: 6.1 %
Correlation between ozone and pressure systems	Low pressure systems induce an increase of the ozone concentration	Low pressure systems can generate BrO clouds

Table 4.1: *Ozone depletion events in the Arctic compared to Antarctica.*

In both the Arctic and Antarctica, the meteorological conditions play an important role in the depletion of ozone. Whereas low ozone concentration is a prevailing state in the Central Arctic Ocean [Jacobi et al., 2010] interrupted only by the approach of low pressure systems bringing ozone-rich air masses from lower latitudes, low pressure systems present in the Weddell Sea tend to generate BrO and consequently deplete ozone. The high wind speed during low pressure systems can lead to the formation of polynyas and to enhanced dispersion of sea salt aerosols or can induce saline blowing snow generating the bromine explosion. Nevertheless, no definite correlation between ozone concentration and air pressure could be found in the Weddell Sea.

During the WWOS, ozone depletion events were defined as drops below 19 ppbV, but only 6.1 % of the data decreased below this limit. Ozone depletion events are even less pronounced at Dumont d'Urville, a French station on the East coast of Antarctica [Legrand et al., 2009] and inexistant in the interior of the continent [Helmig et al., 2007]. In contrast, low ozone concentration is a prevailing state during springtime in the boundary layer of the Arctic Ocean (55 % in 2003, 66 % in 2007) and ozone data often drop below detection limit. During the WWOS, the measurements took place in the north-western edge of the Weddell Sea. In fact, no ozone data from the midst of the Weddell Sea exist. The comparison with data from the interior of the Arctic Ocean are therefore difficult. The backward trajectories plotted for the entire period of ozone measurements in the Weddell Sea revealed that around 60 % of all trajectories crossing the boundary layer over the Weddell Sea before reaching Polarstern transported air masses depleted in ozone. This analysis indicates that ozone depletion events are probably much more frequent in the midst of the Weddell Sea compared to the edge, where the ozone measurements took place. Hence the percentage rate of ODEs in the Arctic Ocean and the interior of the Weddell Sea could in fact be very similar.

Ozone depletion events were already well probed in the Arctic Ocean, whereas observations in the Weddell Sea in Antarctica are recent. As the ozone data measured onboard of the RV Polarstern in 2006 are the first data collected in this region, it is recommendable to perform further research campaigns to examine this area. Investigations of data collected on the Antarctic coast can not be compared to ozone data measured in the Arctic Ocean, hence. Ozone observations onboard of Polarstern only revealed few drops of the ozone concentration below 70 % of the mean concentration, but the subsequent analysis of the trajectories reaching the research vessel revealed that the Weddell Sea seems to be more affected by low ozone concentration. Hence, particularly ozone measurements in the interior of the Weddell Sea would be of great interest.

The exact role of low pressure systems during ozone depletion events in the Weddell Sea is not yet ascertained and needs to be further investigated in future research campaigns. Furthermore, data about the vertical distribution of the ozone concentration during an ODE induced by a low pressure system would be important to collect and analyse.

Finally comparison of BrO data from satellites and from Max-DOAS positionned on the RV Polarstern permitted to distinguish between meteorologically and chemically induced ozone depletion events. In further research campaigns it is required to use both methods to study the causes of sudden decreases of the ozone concentration.

Chapter 5

Annexes

5.1 Wind direction and wind speed computed with Matlab

As the ECMWF wind data are only available as U and V wind component data, a program plotting the total wind speed and direction was developped. The program has been computed in Matlab for the area south of 60°S. The wind speed is subdivided in three categories: below 8 m s^{-1}, between 8 m s^{-1} and 12 m $s^{-1}$and above 12 m s^{-1}.

5.2 Matlab-Code

```
datenU=xlsread(,‘);
u=datenU;
datenV=xlsread(,‘);
v=datenV;

Antarctica = shaperead(’landareas’, ’UseGeoCoords’, true, ... ’Selector’,{@(name)
strcmpi(name,{’Antarctica’}), ’Name’});
figure;
worldmap(’south pole’)
setm(gca,’Grid’,’on’);
setm(gca,’GLineStyle’,’:’);
setm(gca,’GColor’,[0 0 0]);
setm(gca,’PLabelLocation’,[-70 -80]);
setm(gca,’MLabelLocation’,30);
setm(gca,’PLabelMeridian’,0);
setm(gca,’MLabelParallel’,-60);
setm(gca,’GLineWidth’,0.01);
setm(gca,’FontSize’,9);
```

```
lat=90:-1.5:-90;
lon=-178.5:1.5:180;

[mlat,mlon] = meshgrat(lat,lon);
[x,y] = mfwdtran(mlat,mlon);

ff=(u.*u+v.*v).^0.5;

drehUu=-cos(mlon*(pi/180));
drehUv=-sin(mlon*(pi/180));
px=u.*drehUu+v.*drehUv;

drehVu=sin(mlon*(pi/180));
drehVv=-cos(mlon*(pi/180));
py=u.*drehVu+v.*drehVv;

for(ii=113:121)
for (i=1:240)
if (mod(i,(ii-111))~=0)
px(ii,i)=NaN;
py(ii,i)=NaN;
x(ii,i)=0; y(ii,i)=0;
end
end
end

[z0,s0]=find(ff<8);
[z8,s8]=find(ff>8 & ff<12);
[z12,s12]=find(ff>12);

px0=zeros(121,240);

for (k=1:length(z0))
px0(z0(k),s0(k))=px(z0(k),s0(k));
end
py0=zeros(121,240);
for (k=1:length(z0))
py0(z0(k),s0(k))=py(z0(k),s0(k));
end
x0=zeros(121,240);
for (k=1:length(z0))
x0(z0(k),s0(k))=x(z0(k),s0(k));
end
```

```
y0=zeros(121,240);
for (k=1:length(z0))
y0(z0(k),s0(k))=y(z0(k),s0(k));
end

px8=zeros(121,240);
for (k=1:length(z8))
px8(z8(k),s8(k))=px(z8(k),s8(k));
end
py8=zeros(121,240);
for (k=1:length(z8))
py8(z8(k),s8(k))=py(z8(k),s8(k));
end
x8=zeros(121,240);
for (k=1:length(z8))
x8(z8(k),s8(k))=x(z8(k),s8(k));
end
y8=zeros(121,240);
for (k=1:length(z8))
y8(z8(k),s8(k))=y(z8(k),s8(k));
end

px12=zeros(121,240);
for (k=1:length(z12))
px12(z12(k),s12(k))=px(z12(k),s12(k));
end
py12=zeros(121,240);
for (k=1:length(z12))
py12(z12(k),s12(k))=py(z12(k),s12(k));
end
x12=zeros(121,240);
for (k=1:length(z12))
x12(z12(k),s12(k))=x(z12(k),s12(k));
end
y12=zeros(121,240);
for (k=1:length(z12))
y12(z12(k),s12(k))=y(z12(k),s12(k));
end
```

```
find(x0)
h0 = quiver(x0,y0,px0,py0,'c');
trimcart(h0)

find(x8)
h8 = quiver(x8,y8,px8,py8,'y');
trimcart(h8)

find(x12)
h12 = quiver(x12,y12,px12,py12,'r');
trimcart(h12)

geoshow(Antarctica, 'FaceColor', 'white');

%Polarstern
[sx,sy]=mfwdtran( , )
h = scatter(sx,sy,'ok')
trimcart(h)

%Neumayer
[ssx,ssy]=mfwdtran(-70.638,-08.262)
hh = scatter(ssx,ssy,'ok')
trimcart(hh)

%Halley
[sssx,sssy]=mfwdtran(-75.583,-26.566)
hhh = scatter(sssx,sssy,'ok')
trimcart(hhh)
```

5.3 Correlations between air pressure and ozone concentration and between air temperature and ozone concentration

5.3.1 ODE1

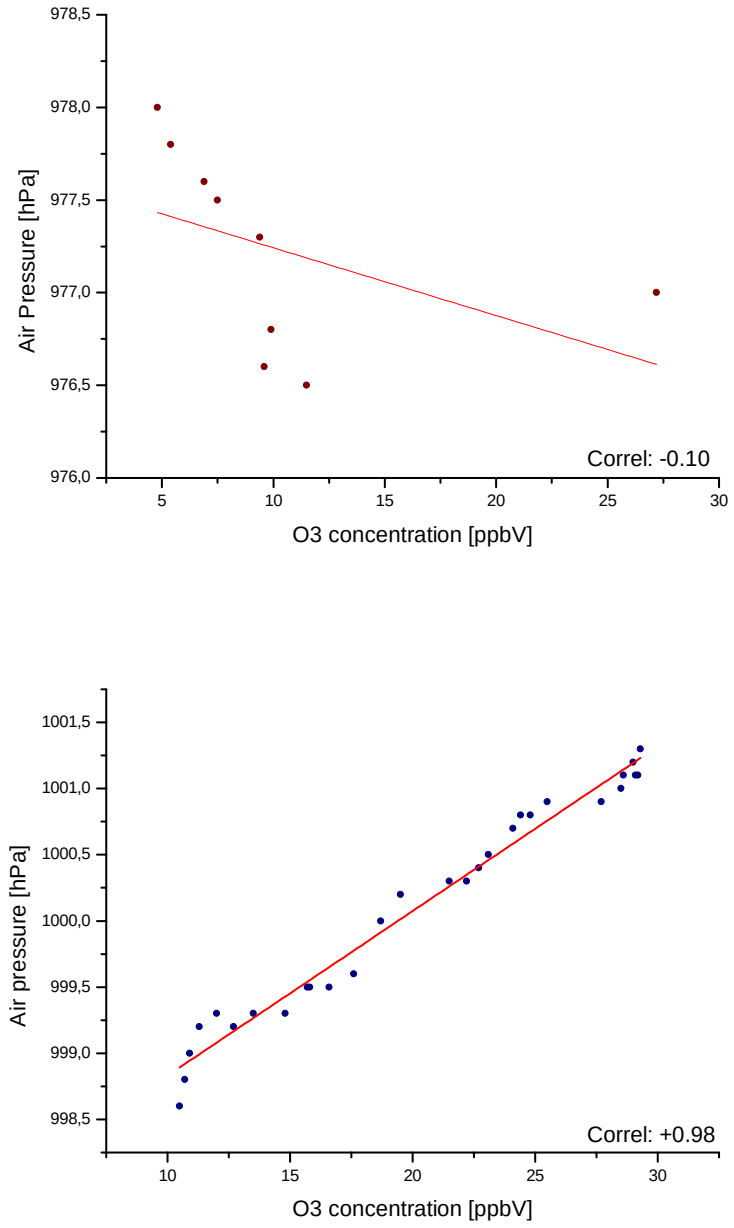


Figure 5.1: *Correlation between the air pressure and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE1.*

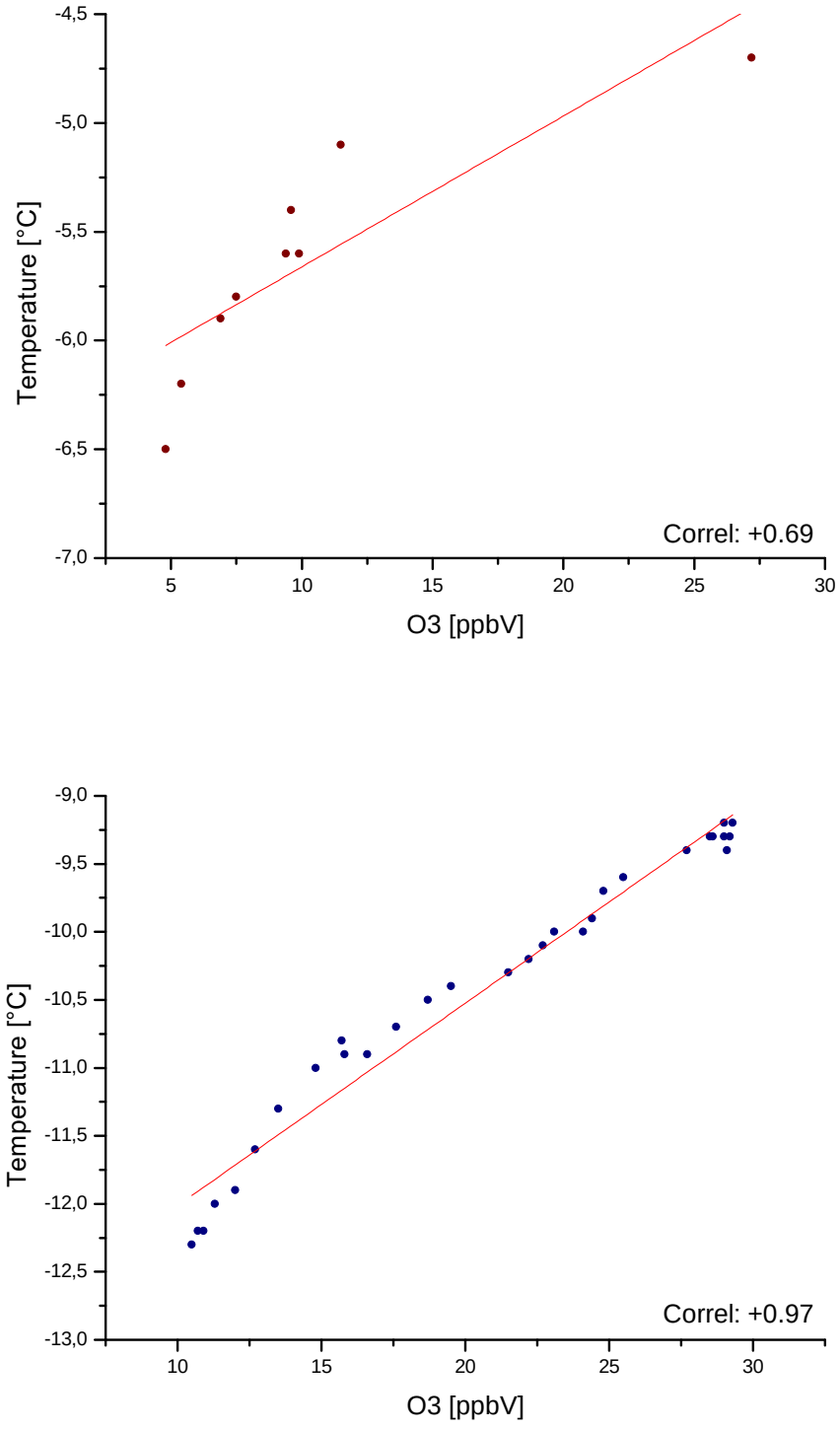


Figure 5.2: *Correlation between the air temperature and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE1.*

5.3.2 ODE2

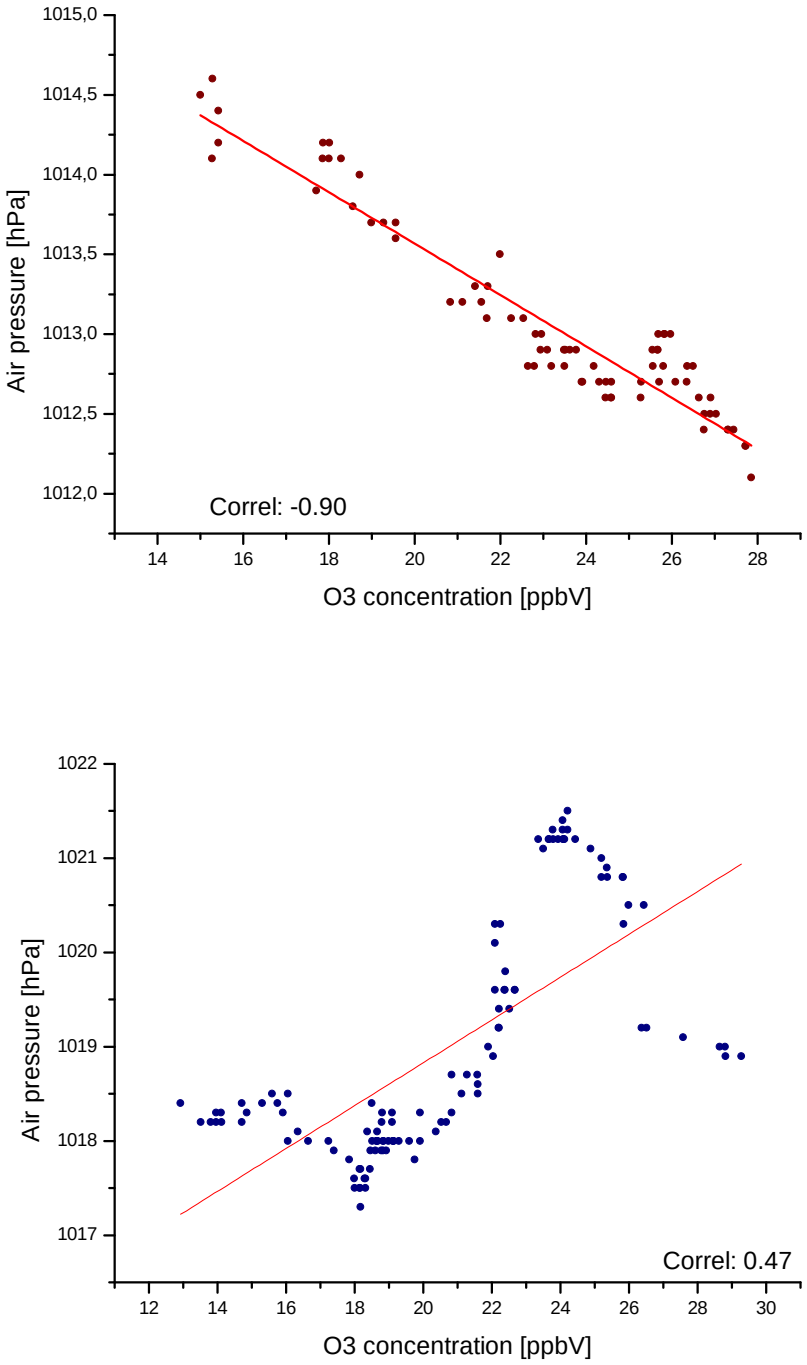


Figure 5.3: *Correlation between the air pressure and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE2.*

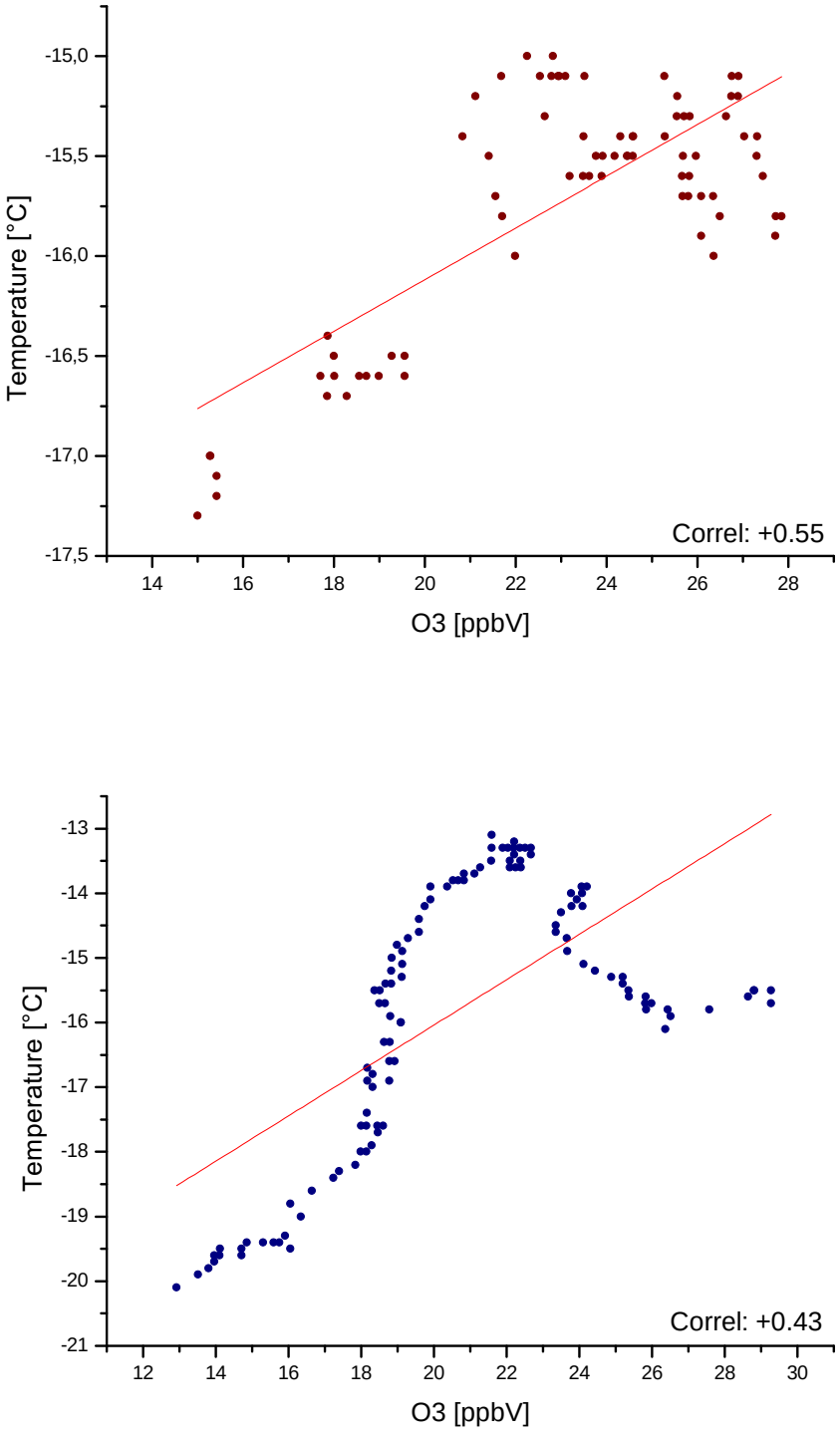


Figure 5.4: *Correlation between the air temperature and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE2.*

5.3.3 ODE3

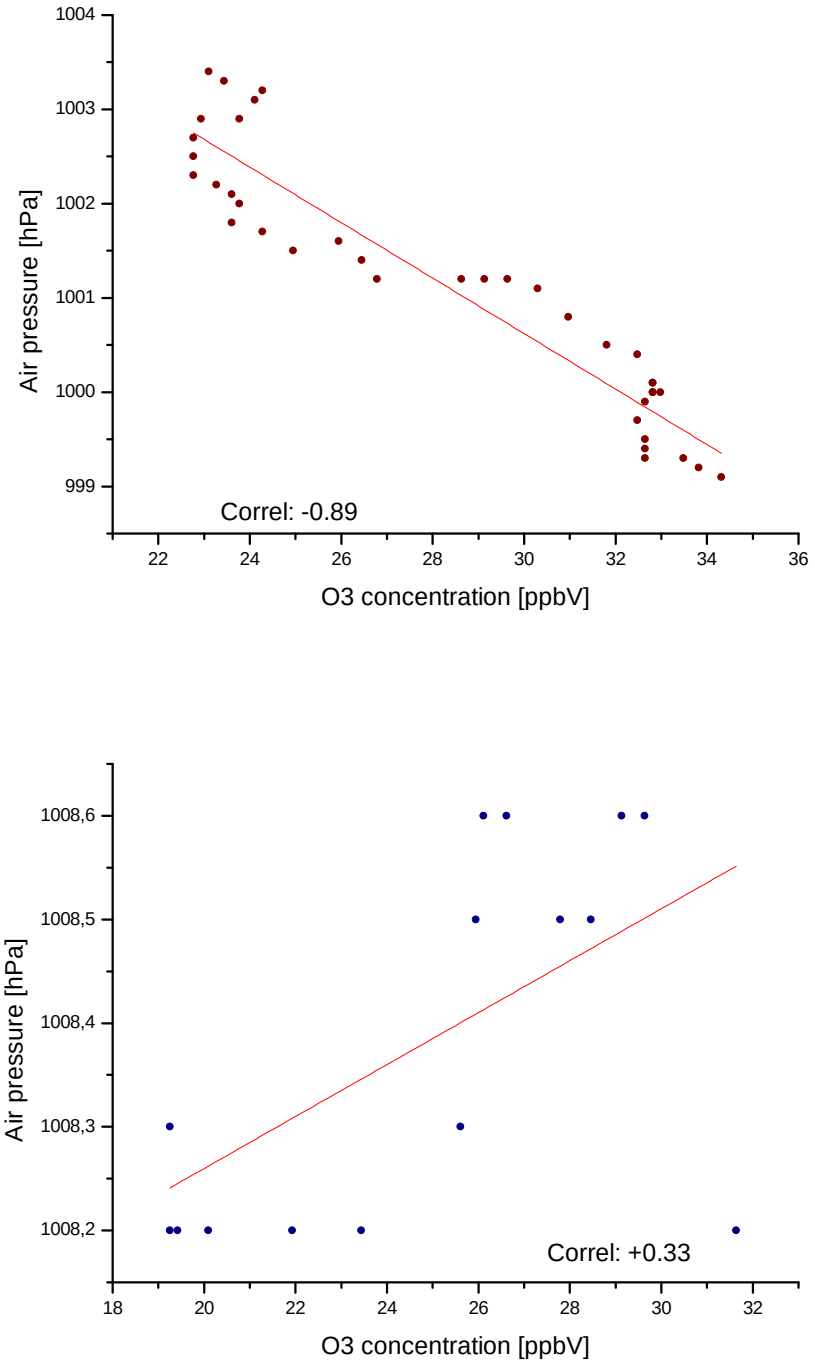


Figure 5.5: *Correlation between the air pressure and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE3.*

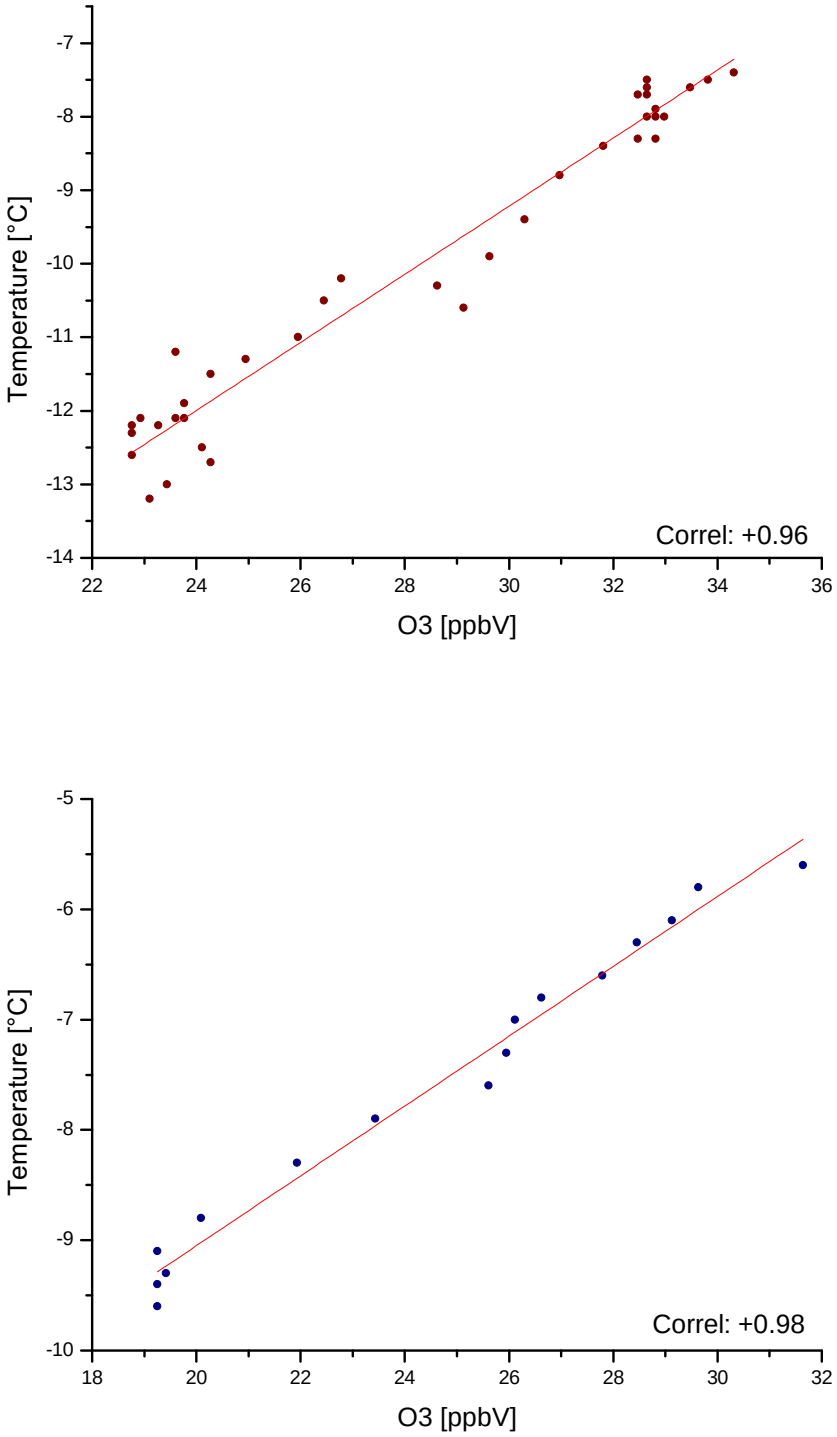


Figure 5.6: *Correlation between the air temperature and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE3.*

5.3.4 ODE4

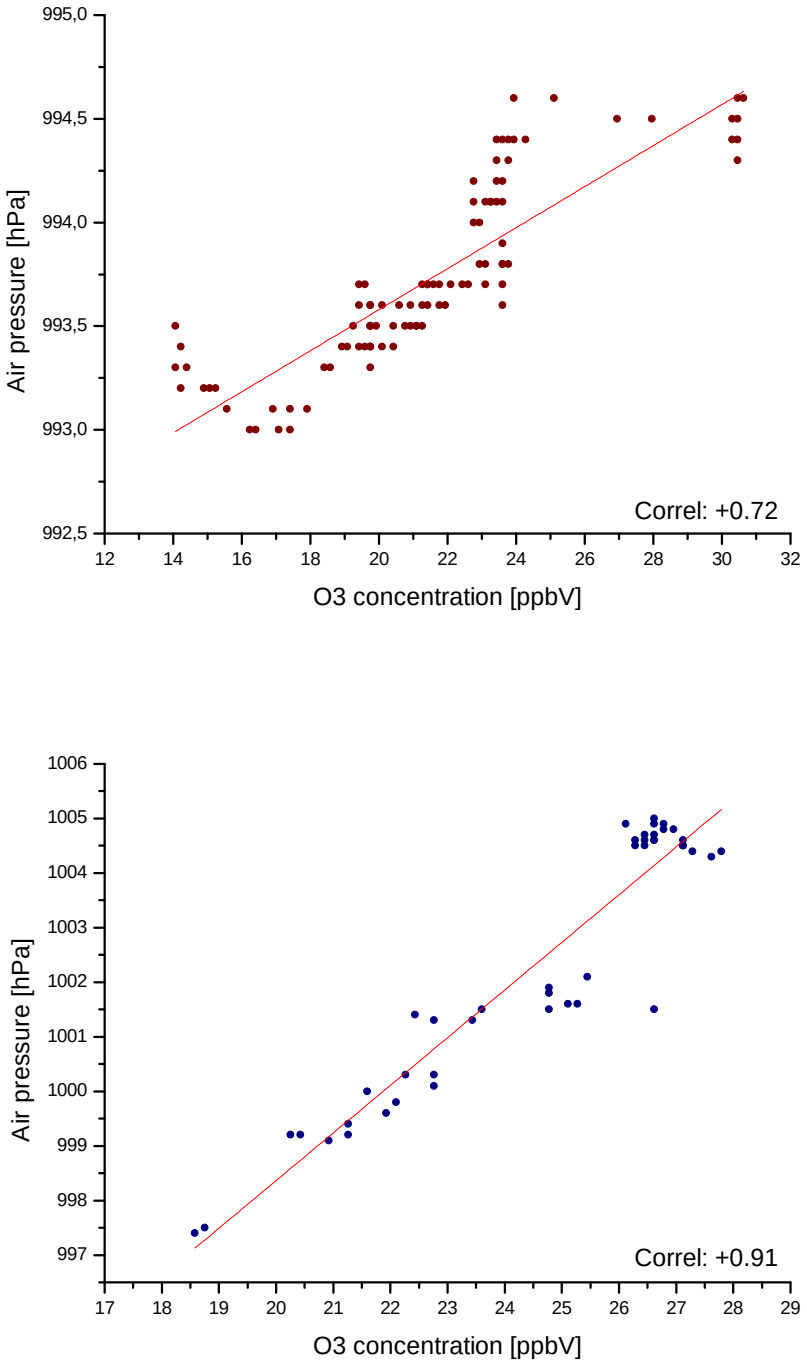
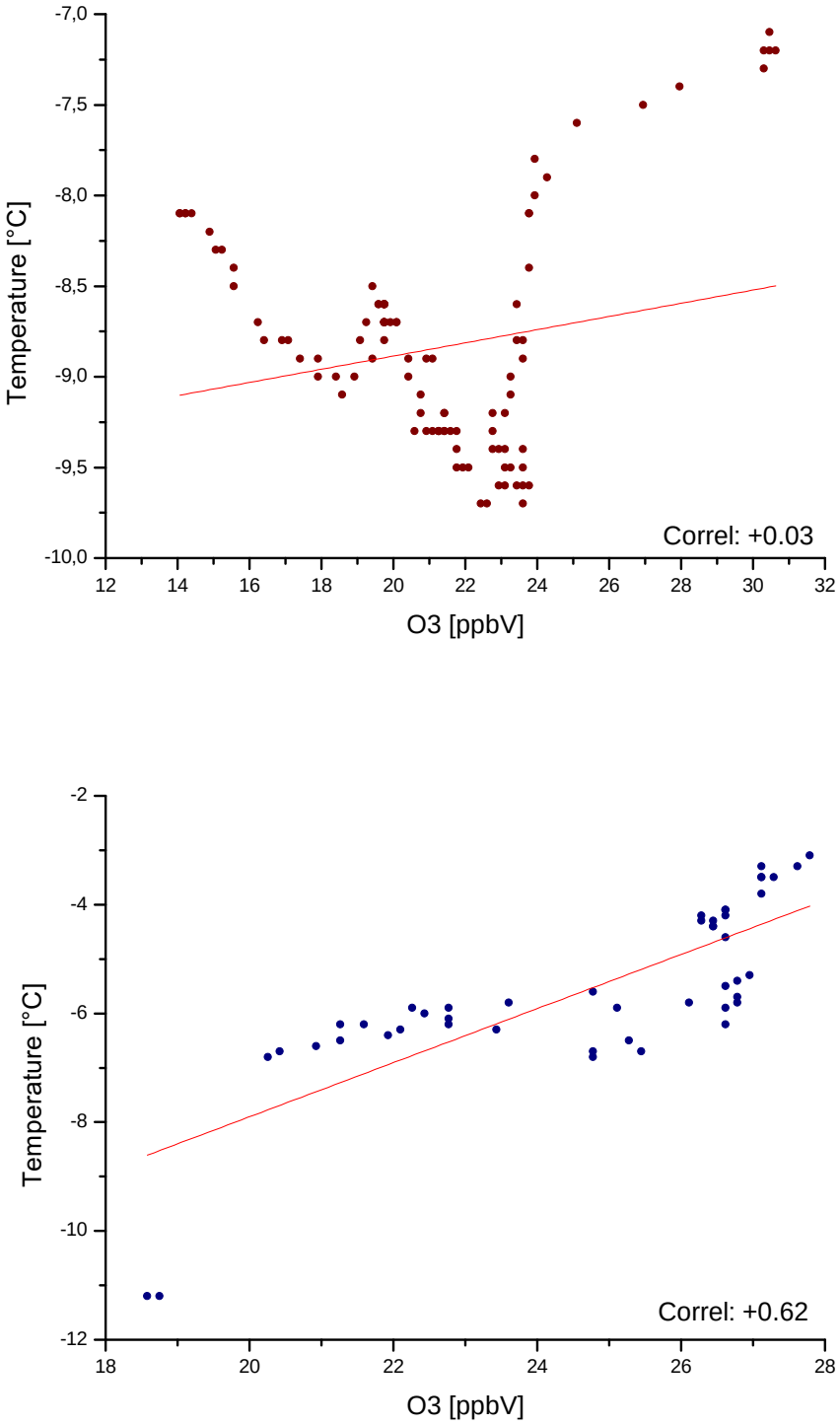


Figure 5.7: *Correlation between the air pressure and the ozone concentration during the drop (top) and the increase (bottom) of the ozone concentration during ODE4.*



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