Atmos. Chem. Phys., 9, 4545–4557, 2009
www.atmos-chem-phys.net/9/4545/2009/

Atmospheric Chemistry and Physics

Ozone in the boundary layer air over the Arctic Ocean: measurements during the TARA transpolar drift 2006–2008

J. W. Bottenheim[1], **S. Netcheva**[1], **S. Morin**[2,*], **and S. V. Nghiem**[3]

[1]Environment Canada, 4905 Dufferin Street, Toronto, ON M3H 5T4, Canada
[2]LGGE, CNRS – UJF Grenoble, 38400 St. Martin d'Hères, France
[3]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA
[*]now at: CEN, CNRM/GAME, Météo-France – CNRS, 38400 St. Martin d'Hères, France

Received: 3 March 2009 – Published in Atmos. Chem. Phys. Discuss.: 31 March 2009
Revised: 6 July 2009 – Accepted: 8 July 2009 – Published: 15 July 2009

Abstract. A full year of measurements of surface ozone over the Arctic Ocean far removed from land is presented (81° N–88° N latitude). The data were obtained during the drift of the French schooner TARA between September 2006 and January 2008, while frozen in the Arctic Ocean. The data confirm that long periods of virtually total absence of ozone occur in the spring (mid March to mid June) after Polar sunrise. At other times of the year, ozone concentrations are comparable to other oceanic observations with winter mole fractions of ca. 30–40 nmol mol^{-1} and summer minima of ca. 20 nmol mol^{-1}. Contrary to earlier observations from ozone sonde data obtained at Arctic coastal observatories, the ambient temperature was well above −20°C during most ODEs (ozone depletion episodes). Backwards trajectory calculations suggest that during these ODEs the air had previously been in contact with the frozen ocean surface for several days and originated largely from the Siberian coast where several large open flaw leads and polynyas developed in the spring of 2007.

1 Introduction

Marine boundary layer ozone depletion in the Arctic following Polar sunrise was first reported in the 1980s (Oltmans, 1981; Oltmans and Komhyr, 1986; Barrie et al., 1989; Bottenheim et al., 1986). Ozone can be destroyed by reaction with bromine atoms (Br) leading to the production of a bromine-monoxide (BrO) molecule, as first proposed by Barrie et al. (1988):

$$O_3 + Br \rightarrow BrO + O_2 \quad \text{(R1)}$$

Reaction (R1) is an efficient ozone destruction process provided that there is ample supply of Br atoms, and the BrO molecule can be recycled into atomic Br. In Polar regions the Br atoms are believed to be produced by chemical activation of seasalt bromide, while recycling is aided by surface mediated chemical interactions causing the so-called bromine explosion (for a recent review see Simpson et al., 2007). The presence of BrO during an ozone depletion event in the Arctic was confirmed by Hausmann and Platt (1994). Since this depends on Reaction (R1) it can be considered a marker for the occurrence of ozone depletion chemistry. Based on this fact, and with the advent of the GOME satellite measurements of BrO that have shown widespread areas where tropospheric BrO levels exceed anticipated background values (Richter et al., 1998; Wagner and Platt, 1998), it is believed that the surface ozone depletion is an Arctic-wide phenomenon. While it is clear that the Arctic ozone depletion in the boundary layer originates from chemical interactions at the surface, actual in-situ observations have been limited to those obtained at coastal sites (Simpson et al., 2007), or campaigns of short duration such as on ice islands near the coast (Hopper et al., 1994, 1998; Morin et al., 2005), from aircraft (Sheridan et al., 1993; Leaitch et al., 1994; Jaeschke et al., 1999; Ridley et al., 2003) or icebreakers (Jacobi et al., 2006).

Correspondence to: J. W. Bottenheim
(jan.bottenheim@ec.gc.ca)

Published by Copernicus Publications on behalf of the European Geosciences Union.

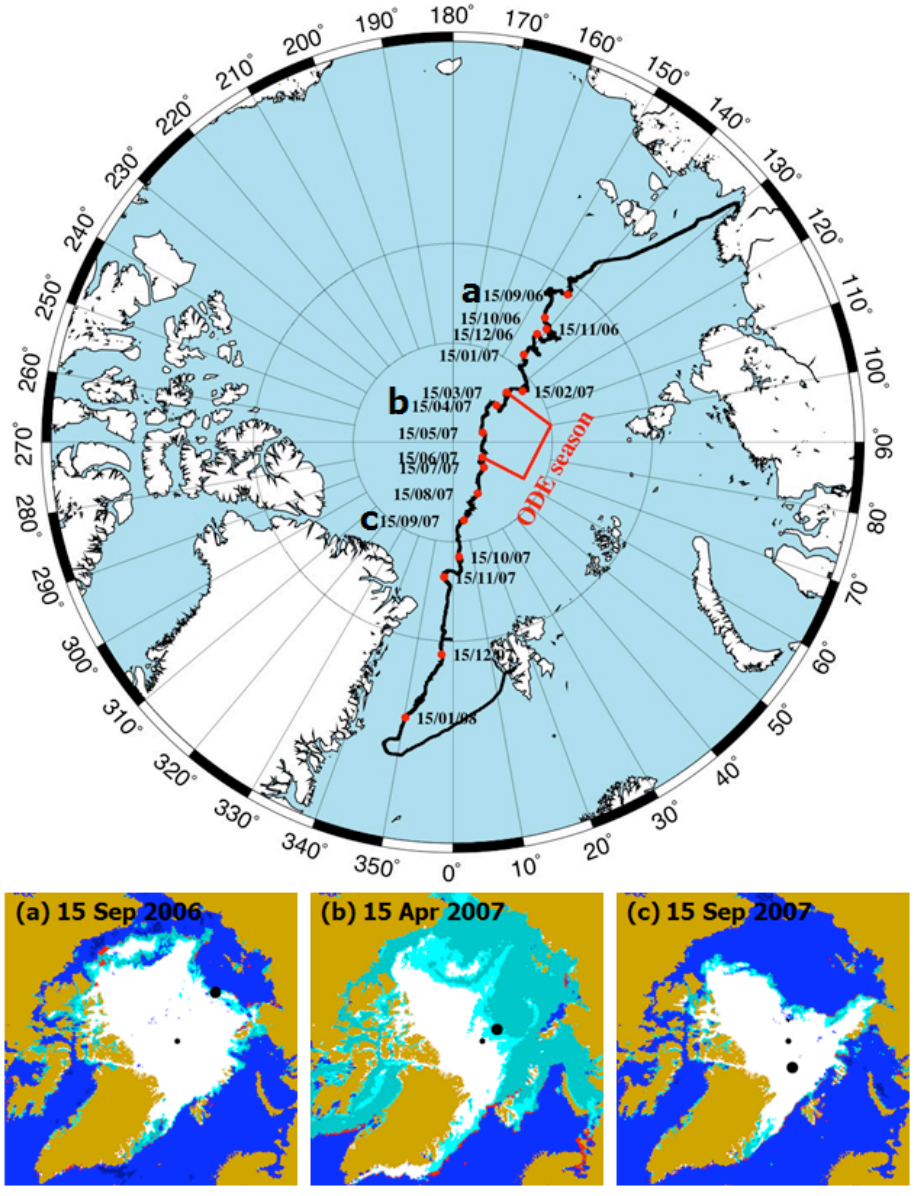

Fig. 1. Track of the TARA drift (September 2006–January 2008). Top panel: TARA drift track across the Arctic Ocean with the time period of ODE season marked in red and locations a, b, and c corresponding to the time of the three QuikSCAT sea ice maps below. Bottom panels: QuikSCAT sea ice maps for 15 September 2006 **(a)**, 15 April 2007 **(b)**, and 15 September 2007 **(c)**. The colors are brown for land, blue for open water, cyan for first year ice, turquoise for mixed ice, and white for multi-year ice. In each map, the small black dot marks the North Pole and the large black dot represents the TARA location. Note that TARA was near the multi-year ice edge on 15 September 2006, and TARA was also located near the multi-year ice edge, which had migrated close to the North Pole by 15 April 2007, indicating the rapid advection of the multi-year ice pack along the Transpolar Drift Stream. This rapid evacuation of multi-year sea ice toward the West Arctic left a vast region in the East Arctic for first-year sea ice to form behind TARA.

TARA is a privately owned French polar schooner that was specifically built to withstand a journey to the North Pole and resist the forces of the Arctic Ocean ice. During 2006–2008 she drifted frozen in the Arctic Ocean ice, recreating the Nansen expedition of 1893–1895 (http://arctic.taraexpeditions.org). For this purpose TARA sailed in the summer of 2006 from its home port in Lorient, France, to Tiksi, a small town at the mouth of the Lena River in Siberia, Russia, and then headed north. Aided by the Russian Icebreaker the Kapitan Dranytsin TARA reached an ice floe at 80° N/143° E where it let itself freeze in the ice. The subsequent drift lasted about 16 months before TARA was released in the North Greenland Sea in late January 2008 (see Fig. 1).

During this expedition the crew on board of TARA undertook several experiments investigating the physical and chemical state of the environment at its location in the Arctic Ocean ice as part of the European Union project DAMOCLES (http://www.damocles-eu.org). Included was the installation and operation of a commercial ozone monitor. As a result, the TARA expedition has provided for the first time a full year of observations of the O_3 concentration over the frozen Arctic Ocean surface hundreds of kilometers from land.

2 Experimental

The ozone monitor used during the TARA expedition was a Thermo Electron Industries Model 049 ozone monitor (TEI049) which is based on UV absorption spectroscopy. The operation of the instrument, as well as data collection was 100% controlled by a Campbell Scientific Model CS21X data logger, and the results were transferred daily to an onboard laptop computer. The CS21X was programmed to collect raw data at a 10 s interval, and to compute a five minute average of these data. The 5-min averages were frequently transmitted via satellite communication eventually to Toronto to permit status control during the drift.

The TEI049 did not have extensive electronic processor control. Hence to be able to fully assess the operation of the instrument after the expedition several parameters indicating its operational status were continually logged. These included the temperature and sample pressure of the absorption cells. The sample flow through the instrument, which is controlled by glass capillaries, was logged by installing small electronic flow meters in the flow path following the absorption cells but before the capillaries. An additional pressure sensor determined the vacuum produced after the flow controlling capillaries to gauge sampling pump performance.

Once a day, a zero reading was collected by sampling ambient air for 30 min via an ozone removing filter (MSA type N gas mask canister); every fifth day, the zero air was internally photolyzed to produce a span sample containing ozone at approx. 60 nmol mol^{-1}. However, this procedure was subsequently found to be unreliable and the readings could only be used to confirm that the instrument was operating properly (i.e. responding to the presence of ozone). Rather, the instrument was calibrated against a National Institute of Standards and Technology (NIST) traceable standard before and after the expedition. It was planned to perform an additional calibration midway during the drift but due to logistical problems this calibration did not materialize, and no additional calibrations during the expedition were attainable. The results from the pre and post calibrations showed a 18% drift in the slope of the calibration and negligible drift in the zero. It is debatable whether this drift had occurred linearly over time and the daily zero/span data were not reliable to assess this fact. Therefore, the mean of the two calibration slopes was used to adjust the raw data.

The TEI049 and CS21X were installed in a storage compartment at the aft of the vessel, approximately 10 m behind the communications room where the laptop computer was placed. This storage compartment was not heated and hence was expected to experience variable, and on occasion quite low ambient temperatures. Therefore, a thermocouple was installed to control the power to the cooling fan of the TEI049 and the fan was programmed to operate only when the ambient temperature inside the instrument casing was higher than +20°C. Prior to installation of the thus modified instrument, its operation at low ambient temperatures was inspected in a cold room and found to be acceptable down to −15°C, well below the official instrument specifications. During the drift the temperature in the storage compartment rarely dropped below −10°C; data collected at lower temperature were deleted from consideration. Ambient air was sampled via a weekly changed Teflon intake filter (47 mm diameter, 5 μm pore size) and approx. 10m of 3/8″ ID PFA Teflon tubing. The filter was mounted in a PFA filter holder housed in a stainless steel hood (to protect against inclement weather) which was mounted at the back railing of the vessel.

While one objective of the expedition was to use as much as feasible green energy, it was unavoidable to operate a diesel power generator for several hours per day to produce electrical energy, especially during the cold, dark winter. The exhaust of the generator was not in close proximity to the air intake for the ozone instrument, but nevertheless some impact was anticipated, especially under conditions of low local wind speed. For this reason all data collected during the actual operation of the diesel generators were filtered from the final data set. Filtered data are indicated in light grey in Fig. 2.

In order to obtain insight into the origin and destination of the air mass that was measured during the campaign, daily trajectories were calculated with the Environment Canada 3-D trajectory model which is similar to the well known Hysplit model (Draxler and Hess, 1998). The calculations started for each day at 12:00 UTC and an altitude of 10 and 500 m above sea level, and were calculated for a 10 day period backwards as well as forwards from the (variable) location of TARA.

3 Results

Figure 2 shows a one year record of ozone measurements made on board of TARA. It has to be realized that these measurements were not obtained at one fixed location, but rather during the drift of TARA shown in Fig. 1. However, they were all obtained at a location higher than 80° N latitude and hence represent a full year of observations of surface layer air over the frozen Arctic Ocean. The red curve is a smoothed curve of the 5 min averaged valid observations as discussed

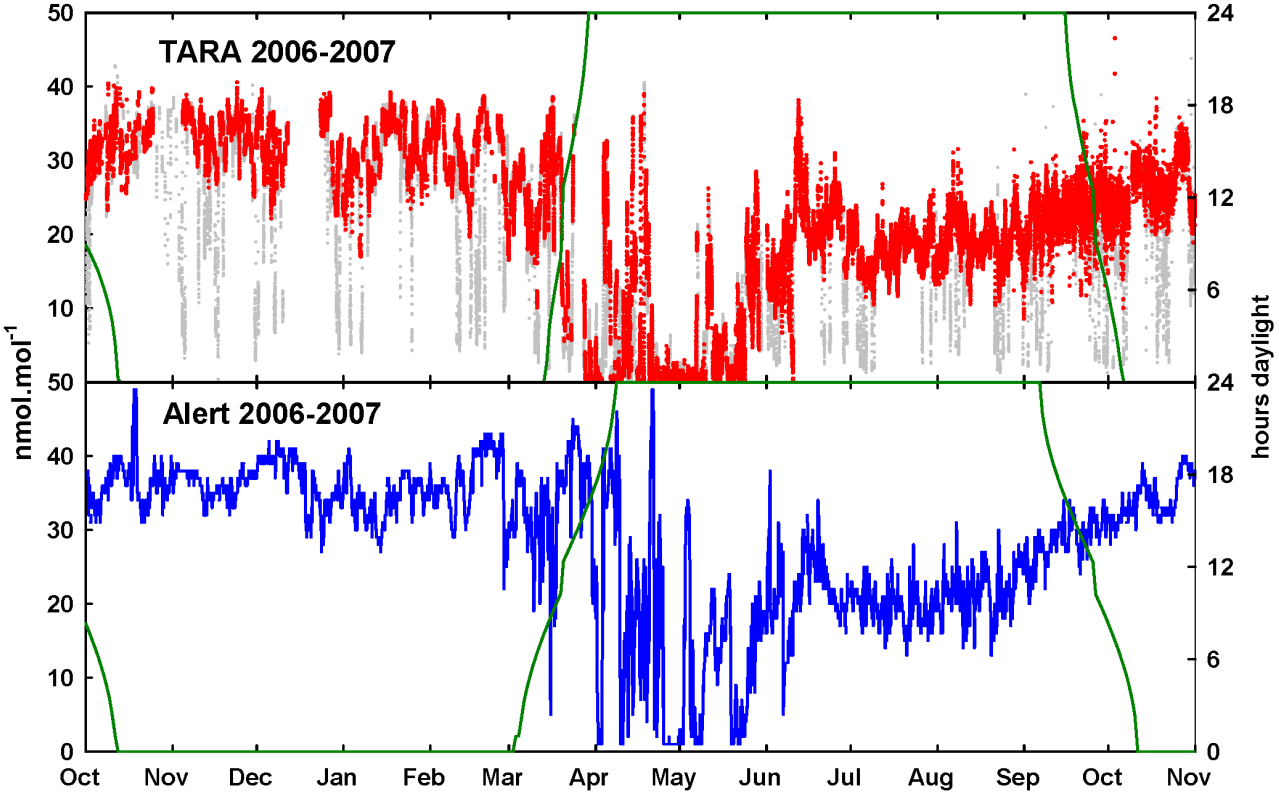

Fig. 2. One year of ozone measurements observed over the Arctic Ocean (TARA) and a coastal observatory (Alert, NU). Top panel: TARA data: red – observations (smoothed) when the power generators were off; grey – observations when a power generator was on; green – hours of daylight. Bottom panel: blue: Alert data, hourly averaged; green – hours from sunrise to sunset.

above; the curve in light grey shows measurements filtered from consideration since the diesel power generator was operating during that time. The data were smoothed since even the 5 min record was often quite noisy with an amplitude occasionally as large as 5–10 nmol mol^{-1}. Closer inspection of the full data record indicates that this noise was probably caused by fluctuations in the electrical power at the times that the diesel generator was not in operation. When the generator was operating, the noise decreased to less than 2 nmol mol^{-1} (but as mentioned, these data were filtered from the final record).

Figure 2 shows an annual pattern that is to a large extent similar to observations at Arctic coastal observatories (Alert, Barrow and Ny Ålesund, see Helmig et al., 2007); for comparison purposes we include concurrent observations at Alert. The similarity between the TARA and Alert data is striking. At both locations, typical wintertime ozone mole fractions (October 2006 to March 2007) ranged between 30 and 40 nmol mol^{-1}. During summer (mid-June to mid September 2007), ozone levels were lower than in winter, with average values on the order of 15–20 nmol mol^{-1}. Sunset (24 h darkness) took place in early October, and this month represents the transition between generally low mole fractions in summer and higher ozone levels in winter. Thus, the seasonal trend of ozone levels in the middle of the Arctic Ocean appears consistent with coastal records for winter, summer and fall.

In Fig. 3 we present a closer look at the spring data for 2007. We have included the concurrent observations at the coastal observatories Alert, Zeppelin Fjellet and Barrow. At this time of year there is more of a contrast between coastal sites and the central Arctic (TARA). With the exception of two episodes at 7 and 11 May the ozone mole fraction was consistently below 5 nmol mol^{-1} between 21 April and 25 May, and in fact for a period of 20 days continuously below detection limit. Remarkably, at TARA the "ozone depletion season" (as defined in the next section) appeared to start quite abruptly around mid March, close to equinox, continuing into early June. Coincidentally, at this period in the drift TARA was at its closest to the North Pole (North latitude/East longitude at 86.3/133.0, 87.1/130.6, 88.4/108.4 and 88.3/63.2 on 15 March, 15 April, 15 May and 15 June, respectively). Consequently, these data were not only obtained exclusively over the frozen Arctic Ocean, but also represent geographically the most Northerly observations to date. In Fig. 3 we have added the actual 5 min data as open circles.

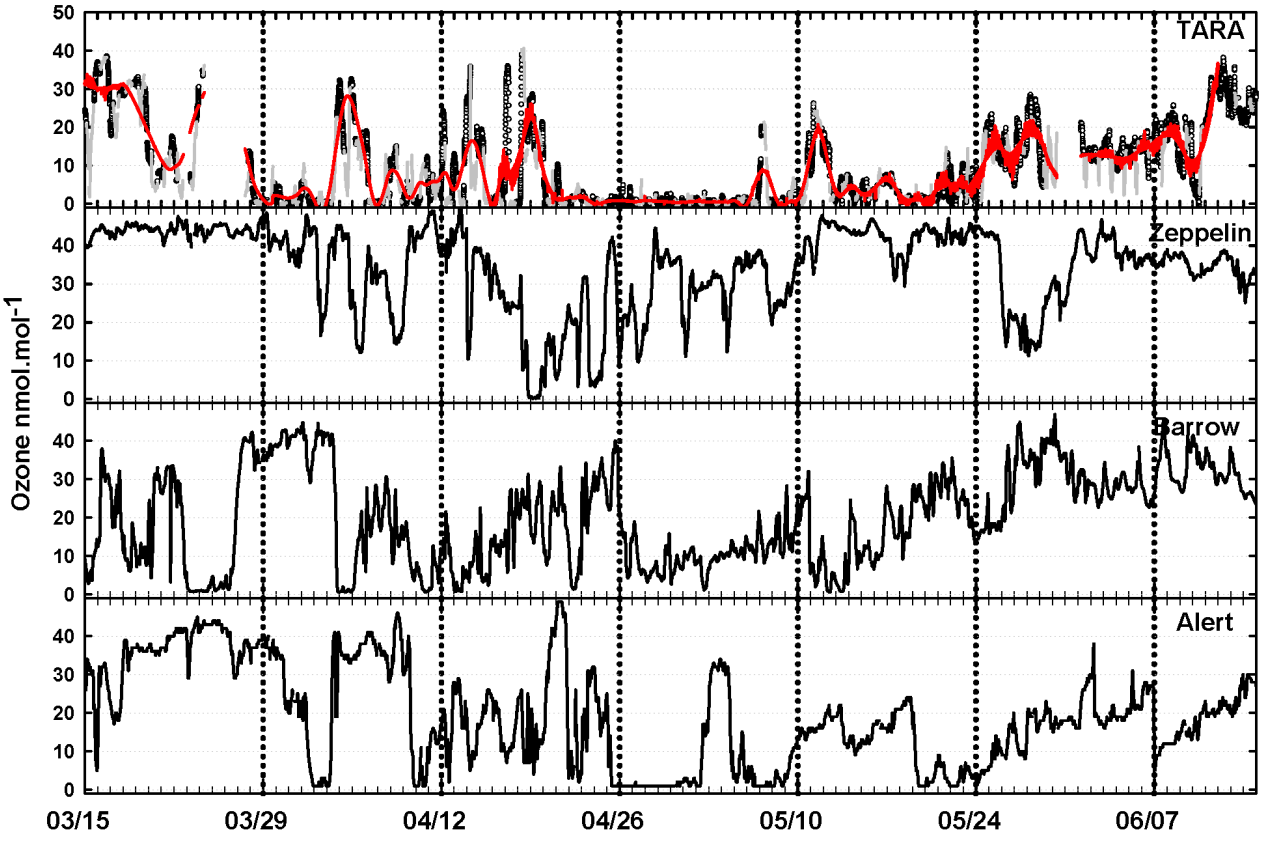

Fig. 3. Ozone observations during the "ozone depletion season" (15 March–15 June 2007). Top panel **(A)**: TARA: red – observations (smoothed) when the power generators were off; black circles: 5 min averaged data when the power generators were off; grey circles: 5 min averaged data when a power generator was operating. Second panel **(B)**; 30 min averaged data at Zeppelin Fjellet (Ny Ålesund) Third panel **(C)**: 30 min averaged data at Barrow (AK) Bottom panel **(D)**: hourly averaged data at Alert (Nu).

As observed, the ozone values drop quite rapidly with the advent of sunlight. There are occasional short periods when the ozone mole fraction increases almost to normal background levels of 30–40 nmol mol^{-1}, but the prevailing levels are close to zero. While the detection limit of the TEI049 is nominally 0.5–1 nmol mol^{-1}, it is not possible to obtain an accurate number in this case, given the noise in the actual signal. Figure 4a–c show concurrent meteorological observations, temperature, wind speed and wind direction, as measured from a 10 m tower. Figure 4c also includes summary information from daily back trajectories, where each entry pertains to the history of an air parcel arriving at TARA on the date indicated.

4 Discussion

The TARA ozone data confirm what has been long postulated based on long term ozone measurements at coastal Arctic observatories on land. During the winter, summer and fall, ozone in the surface boundary layer over the frozen Arctic Ocean appears to be no different from any other Northern hemispheric background location. Occasional decreases in ozone of ca. 5–10 nmol mol^{-1} from the long time running mean were observed at TARA throughout the year, especially in the winter. Such episodes are also observed at the Arctic coastal observatories. They are due to rapid transport of polluted air masses from mid latitude regions (Worthy et al., 1994; Harris et al., 2000). In fact, occasionally at the Alert observatory, an increase in the gaseous mercury concentration has been observed during such episodes which excludes halogen chemistry as the cause for the decrease in ozone (Bottenheim and Steffen, unpublished results, 2003).

However, in the spring, there is a large deficit in ozone in comparison with any other Northern hemispheric location, and we focus next on the TARA data for this period. Several environmental conditions appear necessary for Arctic ozone depletion in the (marine) boundary layer to occur. Although many details are still subject of ongoing debate, they can be summarized as follows:

1. Presence of bromine atoms, predominantly produced from sea salt bromide ions.

2. Presence of sunlight. This condition derives from the fact that Br atoms have to be produced from reactions such as

$$Br_2 + h\nu \rightarrow 2Br \quad \text{(R2)}$$

3. Presence of a suitable surface for stimulating the so-called "bromine explosion" (Platt and Lehrer, 1996; Wennberg, 1999), translating into ice and snow surfaces highly concentrated in sea salt, such as ice covered by frost flowers. Whether the presence of frost flowers is a necessary condition is a hotly debated topic (e.g. Rankin et al., 2002; Kaleschke et al., 2004; Domine et al., 2005; Simpson et al., 2005; Piot and von Glasow, 2008).

4. Low temperatures (Tarasick and Bottenheim, 2002).

5. Presence of a strong stably stratified boundary layer (Lehrer et al., 2004; Anderson and Neff, 2008).

For an extensive review of these aspects we refer to Simpson et al. (2007).

4.1 The ozone depletion season in 2007 as observed from TARA

A generally accepted definition of what constitutes an "ozone depletion episode" does not exist. A working definition of a "severe ozone depletion episode" was proposed by Ridley et al. (2003), subsequently adopted by Piot and von Glasow (2008). In this paper we will follow their suggestion and define the "ozone depletion season" as the period of the year when severe ozone depletions are observed, with "severe" implying ozone mole fractions below 5 nmol mol^{-1} (or 80% depleted from normal, ca. 40 nmol mol^{-1} in spring), and with a transition period where ozone is between 5–20 nmol mol^{-1} (>50% deviation from normal). The TARA dataset can be roughly divided into three periods and we investigate these periods in turn. We refer the reader to Figs. 3 and 4 for the details described in the text.

4.1.1 21 March–21 April

As can be seen in Fig. 4, the first rays of sunlight after the dark (24 h absence of sun light) winter appeared at TARA on 14 March, and by 29 March there was 24-h sunlight. The late date of polar sunrise was due to the fact that at this time TARA was at almost 87° N. Within a week of sunrise the first ozone depletion episode, with a decrease of the ozone mole fraction to almost 5 nmol mol^{-1} was registered on 20 March, marking the onset of the ozone depletion season. This episode lasted about two days and terminated when both ambient temperature and wind speed increased drastically (to −8°C and 12 m s^{-1}, respectively), and the air mass origin veered towards the South, all indicative of a change in synoptic weather patterns. Due to power problems for the next several days there are no ozone data available between 24–29 March, when a once again an ODE is in progress, lasting to approximately 4 April.

It is tempting to suggest that it was not a coincidence that these first depletions were occurring locally when the first rays of sunlight appeared. On 21 March there was already 12 h sunlight, the local wind speed was almost zero, the temperature was ca. −30°C and the air mass origin was from the North (i.e. from the North Pole and beyond to the Canadian Arctic). Trajectory data suggest that an air parcel arriving at 10 m a.s.l. had been close to the surface (arbitrarily defined as less than 200 m a.s.l.) for about 3 days, a relatively short but sufficient period of time for rapid ozone depletion chemistry in a shallow boundary layer (Hopper et al., 1994; Lehrer et al., 2004). Since we have no additional chemical information, it is not possible to be certain about local production. We note that the conditions during this first episode were somewhat unusual in comparison with subsequent observations (temperature at −30°C, origin from the North).

Note that the ambient temperature decreased rapidly on 25 March, as did the wind speed. The absence of ozone data until 29 March does not permit us to be specific, but we speculate that the second ODE was in fact a continuation of the first ODE. In the discussion that follows a recurring pattern during the spring will be clear: an ODE is interrupted for a short time by an (often large) increase in temperature, wind speed and ozone mole fraction, with the latter frequently increasing to "normal" background levels for this time of year, ∼40 nmol mol^{-1}. We interpret these events as due to a change in synoptic weather patterns causing a temporary breakdown of the strong surface boundary layer driven by local turbulence. As a result warmer air that had not been in contact with the surface and hence was not depleted of ozone is mixed down to the surface.

Between 4 and 21 April, the weather conditions were quite variable. Ambient temperature fluctuated often by as much as 10°C on one day, rising from ca. −25°C to −15°C. Similarly, there was a large variation in the local wind speed (e.g. 5, 14 and 19 April). Concurrently, the ozone mole fraction fluctuated between almost zero to at least 30 nmol mol^{-1}. Trajectory data do not indicate a major change in air mass origin, but suggest that the air mass observed generally remained below 200 m a.s.l. for at least 4 days. Since at this time there was already 24 h of sunlight, these variations are much larger than could be expected from a day-night effect. Instead, these events are almost certainly similar to what was deduced above, except that the synoptic changes are frequent.

4.1.2 21 April–23 May

The period of frequent intrusions by air from above the surface boundary layer came to an end on 21 April when the

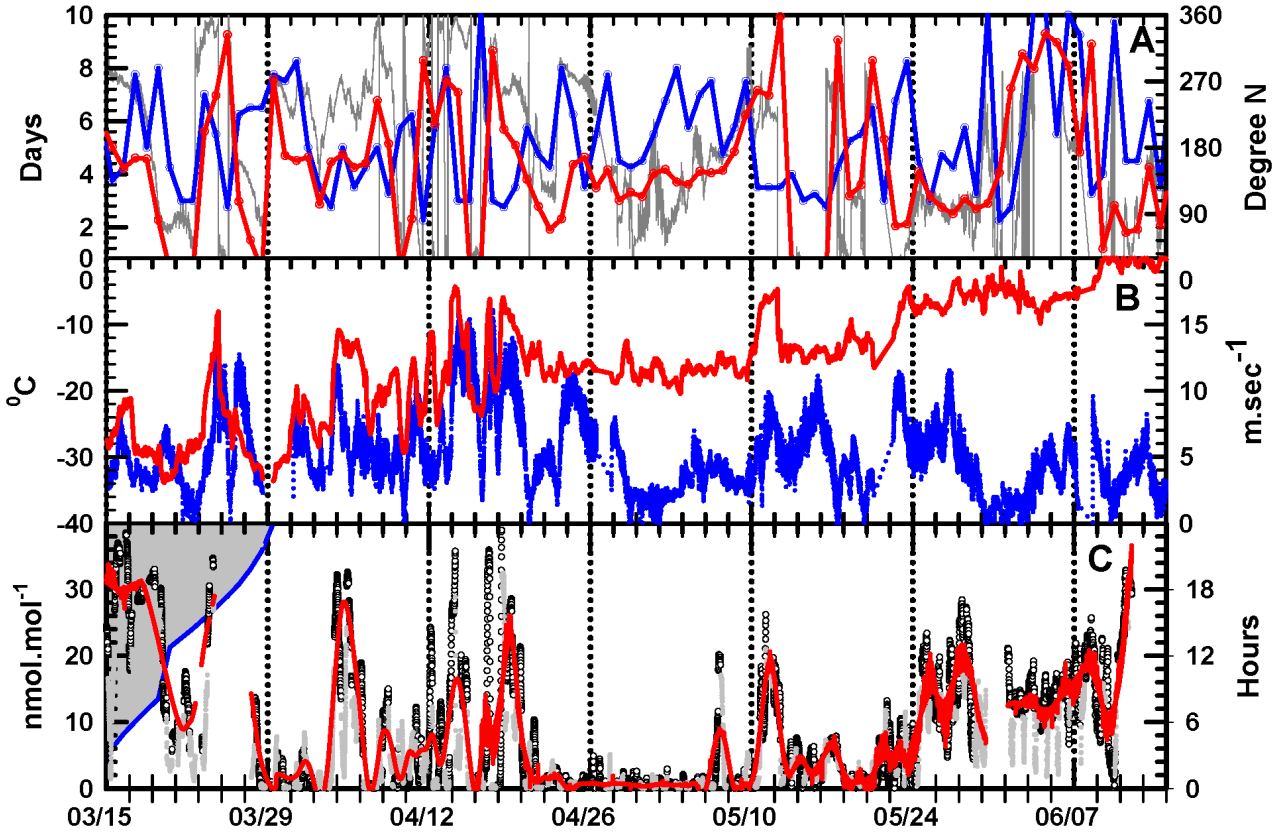

Fig. 4. TARA observations during the "ozone depletion season" (15 March–15 June 2007). Top panel **(A)**: grey – wind direction at 10 m, blue – number of days back trajectory was below 200 m; red – bearing of back trajectory at 10 m over 1 day. Middle panel **(B)**: blue – wind speed at 10 m; red – temperature at 10 m. Bottom panel **(C)**: red – ozone smoothed; black circles – 5 min averaged ozone, generator off; grey circles – 5 min averaged ozone, generator on; blue – hours of daylight.

longest uninterrupted total ozone depletion period started. The wind speed was quite variable ranging from greater than 10 m s^{-1} on 24 April to below 2 m s^{-1} in early May without any indication of a variation in the ozone mole fraction. Temperature was remarkably constant, slowly increasing from −17°C on 21 April to −13°C on 24 May (Vihma et al., 2008). Trajectory data suggest an average contact with the surface of at least the last 3 days before reaching TARA, and the origin is mostly from the South.

Hopper and Hart (1994) in their analysis of the synoptic meteorological conditions in the Canadian Arctic during the Polar Sunrise experiment 1992 noted frequent short-term variability in the winter patterns that started to decrease significantly after Polar Sunrise. Similarly Worthy et al. (1994) indicated that short term variability in greenhouse gases such as CO_2 markedly decreased at that time. We believe that a similar increase in atmospheric stability created the conditions for the prolonged ODE observed from TARA at this time. Only three short episodes of increasing ozone are noticeable on 7, 11 and 17 May. As before the episodes on 11 and 17 May occurred during periods of increasing wind speed and an air mass origin from the Northwest. The 11 May episode which had the largest increase in ozone was also accompanied by a sudden increase in ambient temperature. The meteorological data do not hint at an explanation for the 7 May episode.

4.1.3 23 May–11 June

This period represents the transition period between the ozone depletion season and a return to normal hemispheric background levels of ozone. During this time ozone mole fractions varied between 10–20 nmol mol^{-1}, until on 11 June ozone increased to 30 nmol mol^{-1} and no further ozone depletions were observed. Wind speed and air mass origin are not much different from previous days but the ambient temperature increased on 24 May to well above −10°C, stabilizing to at about −6°C, and then further increasing to about 0°C on 11 June.

4.2 ODEs and the ambient temperature

Tarasick and Bottenheim (2002) observed that ozone depletions, recorded by ozone sondes at Arctic coastal observatories, appeared to be predominantly associated with ambient temperatures below −20°C. They hypothesized that this threshold is linked to thermodynamics. Low temperatures may be required to modify the chemical properties of reactive surfaces in a manner able to speed up halogen activation. This includes increased bromide/chloride ratio in seawater-derived media due to precipitation of $NaCl \cdot 2H_2O$ below −22°C (Koop et al., 2000; Morin et al., 2008), the temperature dependence of the $BrCl+Br^- \rightleftharpoons Br_2Cl^-$ reaction (Sander et al., 2006) and potential reduction in alkalinity of the surface due to carbonate precipitation (Sander et al., 2006; Piot and von Glasow, 2008) although Morin et al. (2008) have shown that this issue requires further investigations.

Our analysis of the TARA data during the ODE season showed qualitatively a good correlation with ozone depletion: often the temperature increased substantially during a temporary recovery of ozone. We do not have vertical profile data, but proposed above that these observations are indicative of a temporary break-up of the lower boundary layer which is usually only a few hundred meters deep (e.g. Bottenheim et al., 2002). In agreement with the observations of Tarasick and Bottenheim (2002) the ambient temperature during the first period described above was below −20°C. Several recent studies reported similarly low ambient temperatures during ODEs (e.g. Bottenheim et al., unpublished results, 2009). Remarkably, during the most persistent period of virtually complete absence of ozone the ambient temperature was well above −20°C. Even more interestingly, during the final transition period when the ozone mole fraction was ca. 10–20 nmol mol^{-1} the ambient temperature was as high as −6°C. Such temperatures would appear to rule out locally efficient bromine explosions. We note that Piot and von Glasow (2008) in their modeling study did not find such a marked temperature dependence either. Clearly more research is required to resolve this issue.

4.3 Origin of the observed air masses

Back trajectory calculations are traditionally used to try and gain insight into the origin of the sampled air at surface locations. However, one might question the veracity of such data, and we certainly would not want to overstate their use, especially after the first couple of days (Kahl, 1993). This pertains in particular to the TARA data where the calculations have to rely exclusively on meteorological objective analysis data. According to the trajectory data air parcels had traveled at a rate of approximately 300–400 km day^{-1} or about 3–4 m s^{-1} before reaching TARA. It is encouraging to note that this number is generally in good agreement with the locally observed wind speed. Furthermore, a cursory inspection of Fig. 4 shows reasonably good agreement between the origin of the observed air mass as suggested by the trajectories and the local wind direction. We therefore feel confident that the trajectories qualitatively give good insight into the recent past of the air observed at TARA. Figure 5 shows 3-day back trajectories during the ozone depletion season on days that the 24 h average ozone mole fraction was below 5 nmol mol^{-1} at TARA. A three day limit was imposed since inspection of Fig. 4a suggests that the air was continually below 200 m and hence most likely in contact with the surface. This would imply sufficient time to permit development of the bromine explosion and hence ozone depletion to occur (Hopper et al., 1994). It can be seen that air containing the lowest ozone mole fractions (below 1 nmol mol^{-1}) at TARA originated predominantly from the East Siberian Sea region. This preference appears to diminish for days that the ozone mole fraction was higher than 1 nmol mol^{-1} at TARA.

4.4 Satellite observations during spring 2007

We inspect satellite data to explore whether they can shed more light on conditions that preceded the observed ozone depleted air. In particular we wish to ascertain whether conditions 1., presence of bromine atoms, and 3., presence of suitable surface conditions were fulfilled.

Reaction (R1) is the exclusive chemical route towards the production of BrO, and hence BrO can conveniently be used as proxy to determine the presence of Br atoms. We therefore consulted the daily distribution of BrO over the Arctic derived from SCIAMACHY data, available on the internet at (http://www-iup.physik.uni-bremen.de/doas/scia_data_browser.htm). These SCIAMACHY images are believed to represent the tropospheric column of BrO and hence it is somewhat debatable whether they are a true representation of BrO at the surface (see e.g. McElroy et al., 1999; Hönninger and Platt, 2002; Morin et al., 2005). Furthermore, the original satellite information covers the whole atmosphere. Therefore, in order to extract tropospheric column information stratospheric BrO absorption has to be subtracted, and the validity of the applied procedures is currently under discussion (D. W. Tarasick, personal communication, 2009). In view of these uncertainties, we feel that an in-depth comparison of SCIAMACHY data with TARA data may not be warranted at this time. Figure 6 shows the monthly average BrO tropospheric column for April 2007. As can be seen the satellite data indicate the presence of BrO clouds with vertical column densities of ca. 1.0×10^{14} molec cm^{-2} over the East Siberian Sea. This is the same region from where the air with the lowest ozone mole fraction originated according to the trajectory calculations Note also that the trajectory data indicate that the air with higher mole fractions of ozone appear to originate from areas with less BrO column densities. We conclude that the SCIAMACHY data lend qualitative support to the trajectory data, and suggest that required condition of presence of BrO was fulfilled.

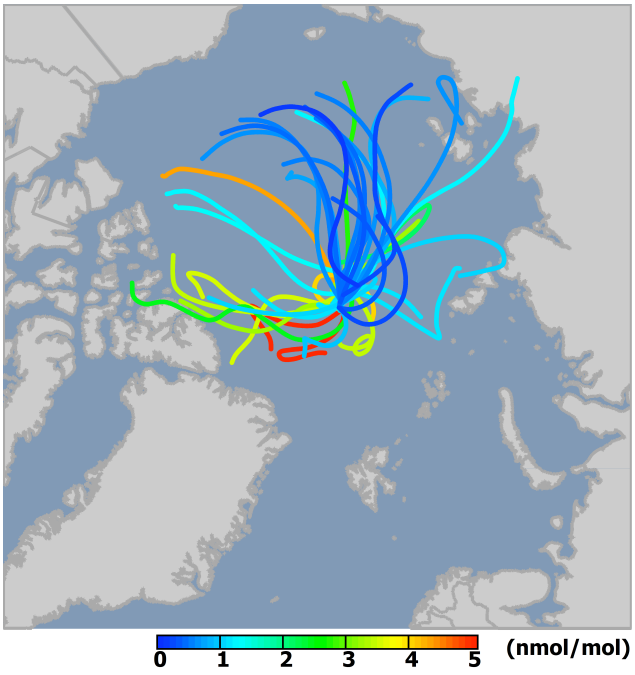

Fig. 5. Three day back trajectories of the observed air during the "ozone depletion season" (15 March–15 June 2007), when ozone was observed to be less than 5 nmol mol^{-1} at TARA.

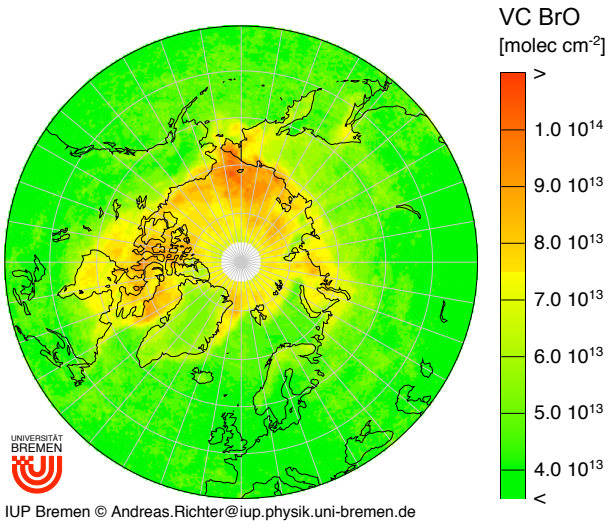

Fig. 6. Average vertical column density of BrO over the Arctic for April 2007, as derived from SCIAMACHY observations. From http://www-iup.physik.uni-bremen.de/doas/scia_data_browser.htm, courtesy A. Richter, University of Bremen.

The ice surface conditions were probed using sea ice maps derived from QuikSCAT satellite scatterometer data (Nghiem et al., 2005, 2006; Nghiem and Neumann, 2007). These maps show an immense region of first year ice on the Russian side of the Arctic Ocean during the spring of 2007. In 2007, the acceleration of the Transpolar Drift (TD), known as the "Polar Express", excessively transported sea ice toward the Atlantic sector and finally out of the Arctic across Fram Strait, leaving the Russian side dominated by first year ice (Nghiem et al., 2007). The TD acceleration was actually verified by none other than the drift of TARA itself (Gascard et al., 2008; Rampal et al., 2009). These conditions suggest that there was an abundance of leads, polynyas, recently refrozen surfaces, thin ice, and frost flowers. Notable events can be seen in these maps:

1. 10 April (Fig. 7a): an elongated feature of open water opened up in the Laptev Sea along the east of the Taymyr Peninsula and stretched to the north all the way to the northernmost tip of the North Land.

2. 18 April (Fig. 7b): the open water feature started on 10 April became a vast polynya, more than 260 km at the largest east-west extent and about 590 km in the north-south direction. This vast polynya underwent a severe sea state by gale-force winds (17–20 m s^{-1} in the Beaufort scale) that sprayed seawater on the snow cover on sea ice in the vicinity and it became a source of salty snow. Several small polynyas were also detected in the Laptev Sea to north of the Russian coast between the Taymyr Peninsula and the Lena River basin.

3. 22 April (Fig. 7c): the vast polynya had been refrozen where the satellite scatterometer recorded very high backscatter, even as high as or higher than backscatter of multi-year ice), indicating the formation of a large region of frost flowers in the gigantic polynya.

4. 26 April (Fig. 7d): the backscatter in the polynya reduced somewhat but still remained high (as high as backscatter of mixed ice), indicating the frost flowers had been proceeding into the decaying phase.

5. 2 May (Fig. 7e): the backscatter in the polynya further reduced to the level of backscatter of first year ice. The increase and then decrease of backscatter in the vast polynya is the classic telltale of the frost flower formation and evolution process (Nghiem et al., 1997). The backscatter change corresponding to frost flower formation is observable with the low-resolution QuikSCAT data in this case thanks to the enormous size of the polynya (84 200 km^2), slightly larger than the area of Lake Superior (82 400 km^2), which is the largest one of the Great Lakes between United States and Canada.

6. 20 May (Fig. 7f): another vast polynya was well developed in the Laptev Sea from a series of separated polynyas, located to the east of the Taymyr Peninsula, which started to develop on 2 May as seen in Fig. 7e. The high backscatter area to the south of this polynya was caused by larger ice scatterers formed from refrozen ice that underwent a melt event started around

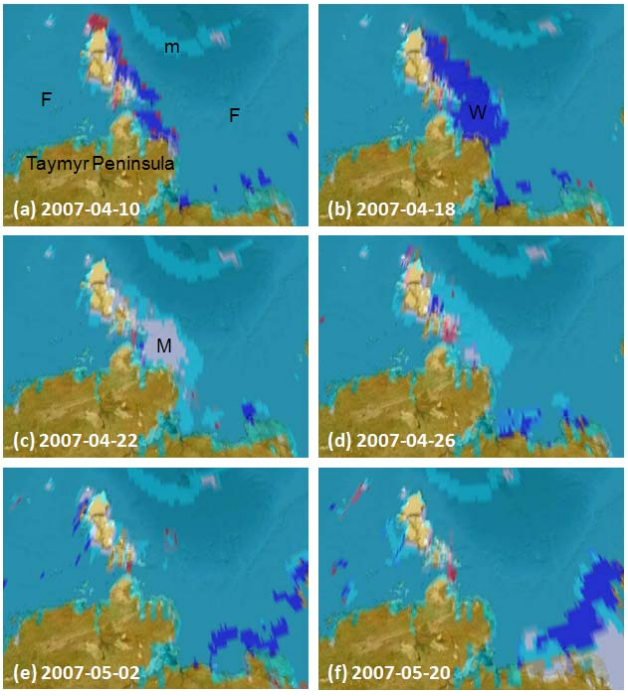

Fig. 7. QuikSCAT observations of sea ice in April and May 2007. The color code is: brown for land, blue for open water (W), different shade of cyan for first year ice (F), turquoise for mixed ice (m), and gray for area with backscatter as high as that of multi-year ice (M). In area M, the backscatter levels with the horizontal polarization in ascending passes are: −10.8 dB on 22 April (in the backscatter range of multi-year ice), −12.2 dB on 26 April (in the backscatter range of mixed ice), and −14.5 dB on 2 May (in the backscatter range of first year ice). The results show the development of a vast polynya along the east coast of the North Land in the north of the Taymyr Peninsula in April and another extensive polynya to the east of the Taymyr Peninsula in May. On 18 April **(b)**, the vast polynya had a backscatter level as high as −12.3 dB, consistent with the prevailing gale-force winds.

11 and 12 May, corresponding to the sudden warming episode with a sharp increase in air temperature and a concurrent ozone rebound as presented earlier.

In summary, this analysis shows that the conditions were highly favorable for the occurrence of bromine explosions and hence fast ozone depletion (Simpson et al., 2007). The timing of the development of the two vast polynyas in April-early May and in late May coincides well with the two major ozone depletion episodes as seen in Fig. 3. Also noted is the curving feature of mixed ice (marked by "m" in Fig. 7a) at the top of each ice map in Fig. 7, which was a remnant of older sea ice that survived the 2006 summer. This feature drifted northward along the direction of the Transpolar Drift Stream in the upstream of the TARA. It is interesting to note that this potential area of origin for the ozone depletion is in reasonable agreement with the so-called "cold spot" area derived from a climatology of 9 years of ozone and concurrent trajectory data from the three main Arctic observatories, in particular Alert and Zeppelin Fjellet (Bottenheim and Chan, 2006).

4.5 How widespread is ozone depletion in the Arctic troposphere?

Bottenheim and Chan (2006) performed a long-term climatology of ozone depletion measurements at Alert, Barrow and Zeppelin Fjellet. Their results raised the possibility that since the time required for an air parcel to travel from source to receptor point was on average about 5–6 days, the ozone depletion process might not necessarily be fast. The TARA data do not agree with this scenario. Rather, they reinforce the alternate scenario that extensive air masses devoid of ozone are roaming the Arctic Ocean. Paraphrasing Hopper et al. (1994, 1998), the norm of the Arctic Ocean surface air is complete absence of ozone, which is occasionally interrupted by short episodes during which increased turbulence leads to the breakup of the surface inversion bringing ozone containing air to the surface Such a scenario is a different view to interpret the TARA data, in particular the extended period of virtually no ozone in the surface air. As we have discussed above, there was a preference for the air observed to originate from the South to Southeast, an area where surface conditions appears to have been favorable for depletion chemistry. However, this was not uniformly the case, and furthermore wind speeds and in particular the local ambient temperature were not at levels that are believed to be conducive towards local ozone depletion chemistry. This contradiction would be explained by the hypothesis of Hopper et al. (1994, 1998): TARA was surrounded by large areas of ozone depleted air in a shallow surface boundary layer, strongly decoupled from overlying layers of air containing "normal" levels of ozone.

5 Summary and conclusion

The TARA expedition to the Arctic in 2006–2008 has for the first time provided a year-long record of ozone mole fractions in the surface boundary layer air over the frozen Arctic Ocean. It has confirmed the occurrence of large periods of substantial to total depletion of ozone in the spring after Polar sunrise, long predicted to be the case as derived from remote sensing of BrO. The seasonal cycle was very similar to long term observations at Arctic Ocean coastal observatories, but with more prolonged periods of total depletion. Occasional reappearance of ozone was usually associated with a rise in ambient temperature, suggesting mixing downwards of warmer, ozone containing air from above the surface inversion. Severe ozone depletion was only observed when the temperature returned to levels well below −10°C.

Five conditions were listed that have been associated previously as requirements for the occurrence of an ODE. Summarizing TARA relevant observations:

1. SCIAMACHY satellite data indicate the presence of bromine atoms over large regions upwind to the TARA location.
2. ODEs did not start until after polar sunrise.
3. Quikscat satellite data show large areas of first year ice containing leads, polynyas and frost flowers upwind.
4. Low temperatures were experienced at the first part of the ODE season; however, for much of the time it was warmer than would have been expected based on previous observations.
5. The longest ODE (21 April–23 May) occurred under very quiet atmospheric conditions.

Except for ambient temperatures below −20°C, the TARA data conform to all these preconditions. With the data in hand, it is not possible to distinguish whether locally a depletion process was taking place. However, a combination of back trajectory calculations and remote sensing data suggested that frequently favorable conditions for a bromine explosion and hence ozone depletion existed upwind of TARA. If indeed this area was the genesis of the ozone depletion, then the process would have to be fast, as is generally believed to be the case (Hausmann and Platt, 1994). This reinforces the hypothesis that Arctic Ocean surface air will predominantly contain unusually low levels of ozone in the spring (Hopper et al., 1994, 1998). The collection of long term surface data over more areas of the Arctic Ocean, in particular in the spring is required to verify the concept of a largely ozone free surface air during Arctic spring.

In the near future the Arctic Ocean will be covered in the spring largely with first year ice, facilitating the formation of leads and polynyas and thus enhancing the out flux of sea salts. This appears to be the likely surface for producing Br and hence leading to ozone depletion, and if anything this would then further reinforce the absence of measurable levels of ozone over the frozen Arctic Ocean in the spring. We note that a substantial increase in temperature might eventually counteract this effect. For instance, if frost flowers growth is essential for driving the bromine explosion and hence ozone depletion chemistry, then a decreasing frost flower growth and hence salt flux could impede the efficiency of the bromine explosion effect.

Finally, implications should be expected from the absence of ozone in the surface boundary layer over the frozen Arctic Oceans in the spring. We have no vertical profile information at this time, but it seems safe to assume that the depth of the boundary layer was at most a few hundred meters, and probably much less. Large-scale radiative effects are therefore not likely. However, the oxidizing capacity of the surface air will not be driven by ozone chemistry, and surface exchange processes as well as the underlying ocean including the marine biology may well be impacted. Nothing is known about such effects at this time.

Acknowledgements. The TARA expedition was made possible by several sponsors, but primarily by the company “agnès b” and its owner, E. Bourgois. We thank the TARA team, in particular logistics coordinator R. Troublé, science coordinator C. de Marliave, expedition leader G. Redvers, and the DAMOCLES scientists who kept our instrument running and sent us regular updates, in particular M. Weber and H. Le Goff. DAMOCLES is a project financed by the European Commission in the 6th Framework Programme for Research and Development (project no. 018509). We thank Jaak Jaagus, Timo Palo and Erko Jakobson (University of Tartu) for providing meteorological data, Elton Chan (Environment Canada) for assistance with Fig. 5, and Andreas Richter (University of Bremen) for providing Fig. 6. The ozone measurement project was part of the OASIS-CANADA program (Ocean Atmosphere Sea Ice and Snow interactions in Polar regions), supported by the Canadian Federal Program Office for the International Polar Year (project #MD-065) The research carried out at the Jet Propulsion Laboratory, California Institute of Technology, was supported by the National Aeronautics and Space Administration (NASA) Cryospheric Sciences Program.

References

Anderson, P. S. and Neff, W. D.: Boundary layer physics over snow and ice, Atmos. Chem. Phys., 8, 3563–3582, 2008, http://www.atmos-chem-phys.net/8/3563/2008/.

Barrie, L. A., Bottenheim, J. W., Rasmussen, R. A., Schnell, R. C., and Crutzen, P. J.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic troposphere, Nature, 334, 138–141, 1988.

Barrie, L. A., den Hartog, G., Bottenheim, J. W., and Landsberger, S. J.: Anthropogenic aerosols and gases in the lower troposphere at Alert, Canada in April 1986, J. Atmos. Chem., 9, 101–127, 1989.

Bottenheim, J. W. and Chan, E.: A trajectory study into the origin of spring time Arctic boundary layer ozone depletion, J. Geophys. Res., 111, D19301, doi:10.1029/2006JD007055, 2006.

Bottenheim, J. W., Gallant, A. J., and Brice, K. A.: Measurements of NO_y species and O_3 at 82° N latitude, J. Geophys. Res., 13, 113–116, 1986.

Bottenheim, J. W., Fuentes, J. D., Tarasick, D. W., and Anlauf, K. G.: Ozone in the Arctic lower troposphere during winter and spring 2000 (ALERT2000), Atmos. Environ., 36, 2535–2544, 2002.

Domine, F., Taillandier, A.-S., Simpson, W. R., and Severin, K.: Specific surface area, density and microstructure of frost flowers, Geophys. Res. Lett., 32, L13502, doi:10.1029/2005GL023245, 2005.

Draxler, R. R. and Hess, G. D.: An overview of the HYSPLIT 4 modeling system for trajectories, dispersion and deposition, Austr. Meteorolog. Mag., 47, 295–308, 1998.

Gascard, J.-C., Festy, J., Le Goff, H., et al.: Exploring Arctic transpolar drift during dramatic sea ice retreat, EOS Trans. AGU, 89(3), 21–22, doi:10.1029/2008EO030001, 2008.

Harris, J. M., Dlugokencky, E. J., Oltmans, S. J., Tans, P. P., Conway, T. J., Novelli, P. C., Thoning, K. W., and Kahl, J. D. W.: An interpretation of trace gas correlations during Barrow, Alaska, winter dark periods, 1986–1997, J. Geophys. Res., 105(D13), 17267–17278, 2000.

Hausmann, M. and Platt, U.: Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, J. Geophys. Res., 99, 25399 – 25413, 1994.

Helmig, D., Oltmans, S. J., Morse, T. O., and Dibb, J. E.: What is causing high ozone at Summit, Greenland?, Atmos. Environ., 41, 5031–5043, doi:10.1016/j.atmosenv.2006.05.084, 2007.

Hönninger, G. and Platt, U.: Observation of BrO and its vertical distribution during surface ozone depletion at Alert, Atmos. Environ., 36, 2481–2489, 2002.

Hopper, J. F. and Hart, W.: Meteorological aspects of the 1992 Polar Sunrise Experiment, J. Geophys. Res., 99, 25315–25328, 1994.

Hopper, J. F., Peters, B., Yokouchi, Y., Niki, H., Jobson, B. T., Shepson, P. B., and Muthuramu, K.: Chemical and meteorological observations at ice camp SWAN during Polar Sunrise Experiment 1992, J. Geophys. Res., 99, 25489–25498, 1994.

Hopper, J. F., Barrie, L. A., Silis, A., Hart, W., Gallant, A. J., and Dryfhout, H.: Ozone and meteorology during the 1994 Polar Sunrise Experiment, J. Geophys. Res., 103, 1481–1492, 1998.

Jacobi, H. W., Kaleschke, L., Richter, A., Rozanov, A., and Burrows, J. P.: Observation of fast ozone loss over frost flowers in the marginal ice zone of the Arctic Ocean, J. Geophys. Res., 111, D15309, doi:10.1029/2005JD006715, 2006.

Jaeschke, W., Salkowski, T., Dierssen, J. P., Trümach, J. V., Krischke, U., and Günther, A.: Measurements of trace substances in the Arctic troposphere as potential precursors and constituents of Arctic haze, J. Atmos. Chem., 34, 291–319, 1999.

Kahl, J. D. W.: A cautionary note on the use of air trajectories in interpreting atmospheric chemistry measurements, Atmos. Environ., 27A, 3037–3038, 1993.

Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A. M., Roscoe, H. K., Hollwedel, J., Wagner, T., and Jacobi, H.-W.: Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry, Geophys. Res. Lett., 31, L16114, doi:10.1029/2004GL020655, 2004.

Koop, T., Kapilashrami, A., Molina, L. T., and Molina, M. J.: Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer, J. Geophys. Res., 105, 26393–26 402, 2000.

Leaitch, W., Barrie, L., Bottenheim, J. W., Li, S., Shepson, P. B., Muthuramu, K., and Yokouchi, Y.: Airborne observations related to ozone depletion at polar sunrise, J. Geophys. Res., 99(D12), 25499–25517, 1994.

Lehrer, E., Hönninger, G., and Platt, U.: A one dimensional model study of the mechanism of halogen liberation and vertical transport in the polar troposphere, Atmos. Chem. Phys., 4, 2427–2440, 2004,
http://www.atmos-chem-phys.net/4/2427/2004/.

McElroy, C. T., McLinden, C. A., and McConnell, J. C.: Evidence for bromine monoxide in the free troposphere during the Arctic polar sunrise, Nature, 397, 338–341, 1999.

Morin, S., Hönninger, G., Staebler, R. M., and Bottenheim, J. W.: A high time resolution study of boundary layer ozone chemistry and dynamics over the Arctic Ocean near Alert, Nunavut, Geophys. Res. Lett., 32, L08809, doi:10.1029/2004GL022098, 2005.

Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., and Savarino, J.: Precipitation of salts in freezing seawater and ozone depletion events: a status report, Atmos. Chem. Phys., 8, 7317–7324, 2008,
http://www.atmos-chem-phys.net/8/7317/2008/.

Nghiem, S. V. and Neumann, G.: McGraw-Hill Yearbook of Science and Technology, chap. Arctic Sea-Ice Monitoring, McGraw-Hill, New York, 12–15, 2007.

Nghiem, S. V., Martin, S., Perovich, D. K., Kwok, R., Drucker, R., and Grow, A. J.: A laboratory study of the effect of frost flowers on C band radar backscatter from sea ice, J. Geophys. Res., 102, 3357–3370, 1997.

Nghiem, S. V., van Woert, M. L., and Neumann, G.: Rapid formation of a sea ice barrier east of Svalbard, J. Geophys. Res., 110, C11013, doi:10.1029/2004JC002654, 2005.

Nghiem, S. V., Chao, Y., Neumann, G., Li, P., Perovich, D. K., Street, T., and Clemente-Colón, P.: Depletion of perennial sea ice in the East Arctic Ocean, Geophys. Res. Lett., 33, L17501, doi:10.1029/2006GL027198, 2006.

Nghiem, S. V., Rigor, I. G., Perovich, D. K., Clemente-Colón, P., Weatherly, J. W., and Neumann, G.: Rapid reduction of Arctic perennial sea ice, Geophys. Res. Lett., 34, L19504, doi:10.1029/2007GL031138, 2007.

Oltmans, S. J.: Surface ozone measurements in clean air, J. Geophys. Res., 86, 1174–1180, 1981.

Oltmans, S. J. and Komhyr, W. D.: Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climate Change baseline observatories, J. Geophys. Res., 91, 5229–5236, 1986.

Piot, M. and von Glasow, R.: The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events, Atmos. Chem. Phys., 8, 2437–2467, 2008,
http://www.atmos-chem-phys.net/8/2437/2008/.

Platt, U. and Lehrer, E.: Arctic tropospheric Ozone Chemistry, ARCTOC., Tech. rep., Final Report of the EU-Project No EV5V-CT93-0318, 1996.

Rampal, P., Weiss, J., and Marsan, D.: Positive trend in the mean speed and deformation rate of Arctic sea ice, 1979–2007, J. Geophys. Res., 114, C05013, doi:10.1029/2008JC005066, 2009.

Rankin, A. M., Wolff, E. W., and Martin, S.: Frost flowers : Implications for tropospheric chemistry and ice core interpretation, J. Geophys. Res., 107, 4683, doi:10.1029/2002JD002492, 2002.

Richter, A., Wittrock, F., Eisinger, M., and Burrows, J. P.: GOME observations of tropospheric BrO in northern hemispheric spring and summer 1997, Geophys. Res. Lett., 25, 2683–2686, 1998.

Ridley, B. A., Atlas, E. L., Montzka, D. D., et al.: Ozone depletion events observed in the high latitude surface layer during the TOPSE aircraft program, J. Geophys. Res., 108, D8356, doi:10.1029/2001JD001507, 2003.

Sander, R., Burrows, J., and Kaleschke, L.: Carbonate precipitation in brine – a potential trigger for tropospheric ozone depletion events, Atmos. Chem. Phys., 6, 4653–4658, 2006,
http://www.atmos-chem-phys.net/6/4653/2006/.

Sheridan, P. J., Schnell, R. C., Zoller, W. H., Carlson, N. D., Rasmussen, R. A., Harris, J. M., and Sievering, H.: Composition of Br-containing aerosols and gases related to boundary layer destruction in the Arctic, Atmos. Environ., 27A, 2839–2849, 1993.

Simpson, W. R., Alvarez-Aviles, L., Douglas, T. A., Sturm, M.,

and Domine, F.: Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime, Geophys. Res. Lett., 32, L04811, doi:10.1029/2004GL021748, 2005.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Frieß, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, Atmos. Chem. Phys., 7, 4375–4418, 2007, http://www.atmos-chem-phys.net/7/4375/2007/.

Tarasick, D. W. and Bottenheim, J. W.: Surface ozone depletion episodes in the Arctic and Antarctic from historical ozonesonde records, Atmos. Chem. Phys., 2, 197–205, 2002, http://www.atmos-chem-phys.net/2/197/2002/.

Vihma, T., Jaagus, J., Jakobson, E., and Palo, T.: Meteorological conditions in the Arctic Ocean in spring and summer as recorded on the drifting ice station Tara, Geophys. Res. Lett., 35, L18706, doi:10.1029/2008GL034681, 2008.

Wagner, T. and Platt, U.: Satellite mapping of enhanced BrO concentrations in the troposphere, Nature, 395, 486–490, 1998.

Wennberg, P.: Bromine explosion, Nature, 397, 299–301, 1999.

Worthy, D. E. J., Trivett, N. B. A., Hopper, J. F., Bottenheim, J. W., and Levin, I.: Analysis of long-range transport events at Alert, Northwest Territories, during the Polar Sunrise Experiment, J. Geophys. Res., 99, 25379–25390, 1994.