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A high time resolution study of boundary layer ozone chemistry and dynamics over the Arctic Ocean near Alert, Nunavut

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[1] During the field campaign “Out On The Ice” (OOTI) in the spring of 2004 at Alert, Nunavut ($N82^{\circ}30'$, $W62^{\circ}19'$) an event occurred where surface ozone (O_3) and reactive bromine species in the boundary layer showed dramatic changes on a timescale of minutes and a spatial scale of a few kilometers. In apparent direct response to changes in surface wind speed and direction, surface O_3 mole fractions of >30 $\text{nmol}\cdot\text{mol}^{-1}$ replaced stable, O_3 depleted boundary layer conditions for about 5 hours. High time resolved (seconds to minutes) chemical and meteorological observations on the ice and on land, as well as synoptic weather maps and routine radiosonde data are used to constrain the unfolding of the event. It is hypothesized that the bromine oxide (BrO) distribution in the troposphere over the frozen ocean features a maximum in a narrow transition layer that separates the boundary layer from free tropospheric air above. **Citation:** Morin, S., G. Hönninger, R. M. Staebler, and J. W. Bottenheim (2005), 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.

1. Introduction

[2] It is now well known that surface O_3 in the coastal Arctic troposphere frequently shows episodes of drastically reduced mole fractions, the so-called ozone depletion events (ODE). ODEs occur every year during the polar sunrise period [Tarasick and Bottenheim, 2002]. O_3 data obtained since 1985 at the Global Atmospheric Watch (GAW) station situated 6 km south of Canadian Forces Station (CFS) Alert often shows that in a matter of a few hours the O_3 mole fraction can decrease from its mean background value, around 40 $\text{nmol}\cdot\text{mol}^{-1}$, to values as low as 1 $\text{nmol}\cdot\text{mol}^{-1}$ and below, and remain at this level for days [Bottenheim *et al.*, 2002a]. The complex mechanisms of O_3 removal have been studied for several years. Laboratory, field and modelling studies have confirmed the hypothesis that O_3 is removed through catalytic reaction cycles involving bromine atoms. The origin of these bromine atoms is believed to be primarily activation of bromide ions in sea-salt, involving heterogeneous chemical processes on aerosols and the surface snowpack [Barrie *et al.*, 1988; Fan and

Jacob, 1992; Hausmann and Platt, 1994; Vogt *et al.*, 1996; Fickert *et al.*, 1999; Michalowski *et al.*, 2000]. Atmospheric circulation explains much of the variance in the O_3 mole fraction, as has been shown by several trajectory studies [Worthy *et al.*, 1994; Bottenheim *et al.*, 2002b]. For instance, at Alert air masses originating from the south generally contain background levels of O_3 , while northerly flow from the sea ice covered Arctic Ocean is frequently linked to O_3 depletion chemistry [Hopper *et al.*, 1998]. Variability in the regional meteorological pattern influences the long-range advection of the air mass that is sampled and, as a result, the mesoscale pattern of its O_3 content. In this paper we present and discuss data collected during the OOTI 2004 campaign. We show that dynamic conditions of the boundary layer near the shore induce large temporal and spatial variations of the O_3 content on time scales of minutes, and hypothesize that this has implications for the lower tropospheric distribution of BrO.

2. Experimental

2.1. Measurement Sites

[3] Measurements were performed simultaneously on land and on the frozen ocean. On land data were collected at the Special Studies Trailer (SST) and the GAW observatory which are located on a plateau ca. 190 m above sea level (ASL) and ca. 6 km to the SSW of CFS Alert, the main base at the coast of Northern Ellesmere Island. The Alert weather station, site of twice daily radiosonde launches, is located at CFS Alert at 60 m ASL. The OOTI site on the Arctic Ocean sea ice was ca. 5 km off the coast to the NNW of CFS Alert. This site was surrounded by a few pressure ridges at distances of a few 100 m, typically ranging from 1–3 m in height. The ice surface was motionless during the experiment, and covered by wind-packed snow from winter 2003–2004. Most instrumentation at this site was housed in a mobile package that could be easily transported by sled, and featured fully automated, battery powered equipment.

2.2. Instrumentation

[4] On land, surface O_3 was measured at the SST site with a UV absorption instrument (model TEI 49-C, Thermo Environmental Instruments, Inc., Franklin MA, USA), calibrated against standards traceable to the National Institute of Standards and Technology (NIST). At the OOTI site O_3 measurements were performed at 1 m above the surface by another UV absorption based monitor (model 202, 2B Technologies, Golden CO, USA). This monitor was calibrated with an O_3 generator against a TEI 49 instrument over a wide range of O_3 mole fractions (0 – 100 $\text{nmol}\cdot\text{mol}^{-1}$, $r_{O_3,TEI49}(ppb) = 0.907 \cdot r_{O_3,2B202}(ppb) + 2.2$, $R^2 = 0.9943$). This calibration was adjusted at the beginning of the field study against the TEI 49 instrument at the SST. The baseline

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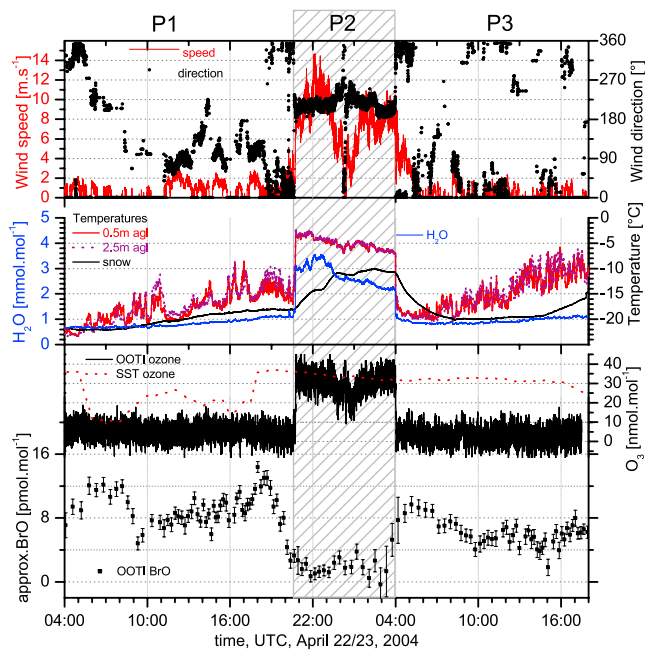


Figure 1. Boundary layer meteorological and chemistry data collected at the SST and the OOTI sites on April 22/23, 2004. BrO mole fractions are approximate due to uncertainties in the vertical profile.

stability was frequently checked using a zero-ozone cartridge. BrO including vertical distribution was monitored at the OOTI site by the MAXDOAS technique (MiniMAXDOAS, Hoffmann Messtechnik, Rauenberg, Germany) [Hönninger *et al.*, 2004]. Spectra were recorded at 2°, 5°, 10°, 20° and 90° elevation angle above the horizon, to derive BrO vertical profile information and average mole fractions. Derived BrO differential slant column densities are accurate to ~5%, however, the determination of profile information necessary to convert slant columns to mole fractions carries an uncertainty of ~50%. The viewing direction of the MAXDOAS was towards the north, therefore the instrument averaged over an airmass ranging from the measurement location to 10–15 km north of the site. Meteorological variables were measured at the GAW and OOTI sites. At the latter location, temperature was measured at 0.5 and 2.5 m on the meteorological mast over the ocean and in the snow 3 cm below the surface, with radiation-shielded thermocouples. Humidity and temperature at 1.5 m were monitored with a sensor (model HMP-35C RH/T, Vaisala, Helsinki, Finland) fixed on the mast. OOTI wind was measured at 3 m height with a propeller anemometer (model 05103-10, RM-Young, Traverse City MI, USA). Sonic anemometers (CSAT-3, Campbell Scientific, Logan UT, USA) measured the turbulent wind components at 10 Hz at the SST (1.5 m above ground) and OOTI site (2.0 m above ground).

3. Results

[5] Data relevant for discussion in this paper are presented in Figure 1. These data comprise the period from April 21 to 23, during which three very distinct regimes were observed. For the OOTI site, O₃ is shown at 10 s resolution and the meteorological data are at 1 sec resolution, while O₃ data at

the SST are 30 min averaged values. The MAXDOAS time resolution for the period discussed here varied with light intensity between 40 min (midnight) and 10 min (noon). The three periods labelled P1–P3 were characterized by distinctly different meteorological conditions. However, the sky remained clear for most of the time, including the high wind regime (P2), thus permitting direct comparison for the MAXDOAS data during the three periods (no aerosol perturbation). During P1, weather conditions over the ocean were calm, with a wind speed below 2 m.s⁻¹, and very low levels of O₃ at the surface (<5 nmol.mol⁻¹). Temperatures ranged between -20 and -15°C, and the water mole fraction was about 1 mmol.mol⁻¹. Previous measurements suggest that under these conditions the bulk of the BrO is present in a surface layer of ca. 500 m [Hönninger and Platt, 2002; Hönninger *et al.*, 2004]. P2 is characterized by a high wind speed at the surface of the ocean (>8 m.s⁻¹) with a steady wind direction (from 215° true), and “normal” background O₃, reaching >30 nmol.mol⁻¹ during most of the time. The ambient temperature was much higher than during P1, reaching -3°C at the beginning of the event. During P2 the MAXDOAS shows very low BrO in the lower troposphere. Finally, conditions during P3 were similar to P1. Changes between the three periods were very abrupt, as can be seen in Figure 2. During the P1–P2 transition, the wind and the temperature picked up in a matter of a few minutes, and this correlated directly with dramatic changes in the surface O₃ mole fraction. The high wind episode ended as dramatically as it had started, with air temperature and humidity dropping in less than one minute, O₃ in approximately three minutes, the wind speed in about 1 hour, and snow temperature in about 2 hours to levels similar to period P1.

4. Discussion

[6] We present a conceptual model to interpret the field data, based on spatial, dynamic and chemical considerations. The use of a wide range of surface data from the two sites and standard radiosonde measurements from the weather station at Alert allows us to derive a plausible

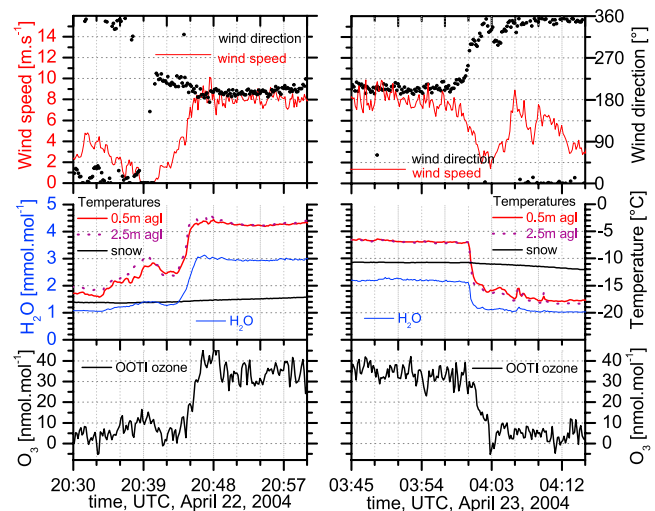


Figure 2. Close-up on the onset and end of the wind episode over the Arctic ocean.

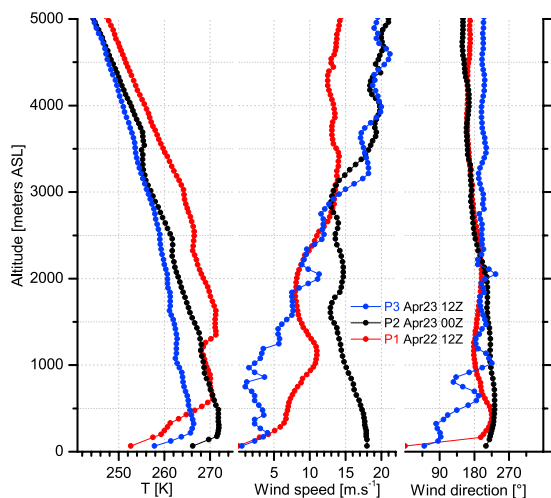


Figure 3. Temperature and wind data recorded during three radiosonde ascents, during P1 (red), P2 (black) and P3 (blue).

spatial distribution of air masses over the coast, and its evolution during this event.

4.1. Spatial Characteristics

[7] The event can be described at two different temporal and spatial scales. At the spatial scale of Alert, this was a highly localized event: less than 10 km separated the two sites and yet this was sufficient to observe very different conditions over a time span of minutes. The local geography of Northern Ellesmere Island with mountain ranges well over 1000 m in height to the south of Alert often induces a katabatic flow towards the ocean transporting primarily entrained free tropospheric air, characterized by the typical signature of O₃ levels near 40 nmol.mol⁻¹ and little BrO in the spring. During P1, free tropospheric winds were essentially decoupled from the stable and calm surface layer (Figure 3). The surface air was much colder and dryer than the free tropospheric airmass above, and was depleted of O₃ but enriched in BrO. At the synoptic scale, inspection of weather maps covering the Arctic for the period April 22–24 show that a transition occurred, with a weakening high-pressure center over Northern Greenland, and the simultaneous appearance of a low-pressure center above the North Pole. The data for April 23 00h UTC indicate that at that time both centers existed, supporting a strong geostrophic flow from the south-west over Alert. A plausible scenario is therefore that the temporary strengthening of the synoptic flow enhanced the katabatic flow so that it carried enough kinetic energy to erode the stable air mass over the ocean during the P1–P2 transition. This picture is confirmed by the 12 hourly radiosonde data that show a continuous wind profile only at this time over Alert with the greatest wind speed observed at the surface (see Figure 3). 12 hours later the synoptic flow had sufficiently weakened so that the local conditions near Alert had reverted to the previous conditions.

4.2. Boundary Layer Stability

[8] Dynamic characteristics of the air column above both sites argue in favor of an instability of the marine boundary

layer caused by the interaction between the two air masses described before. In P1, the surface layer displayed a strong stable stratification; the radiosonde profiles indicate a potential temperature increase of +10 K in the first 200 m. Such a temperature inversion can only be eroded if the kinetic energy of the flow aloft can overcome the potential energy stored in the stable surface layer. The calculation of the critical Richardson number [Stull, 1988, p. 176] suggests that a wind speed of about 18 m.s⁻¹ at 200 m is required to overcome the 0.05 K.m⁻¹ stratification observed in the lowest 200 m earlier on April 22. The radiosonde ascent at April 23, 00h UTC shows that this threshold level was indeed reached (see Figure 3). Wind direction data from the radiosondes are further evidence for this picture. Data for April 22, 12h UTC and April 23, 12h UTC show that the very light winds in the shallow surface layer came from close to 0° (North), while above this layer the wind direction was close to 200°. In contrast with these observations, the April 23, 00h UTC release showed that the wind direction now was close to 200° right down to the surface. We conclude that increasing wind speed in the upper layer caused intense shearing between 200 and 300 m, which eventually led to the erosion of the surface inversion.

4.3. Spatial Extent of the Event as Constrained by O₃ and BrO Data

[9] Figure 4 shows a schematic representation of the unfolding of the event. As discussed before, the flow was constrained by the local topography, with the SST site (inland and at 190 m ASL) being subjected to the turbulent flow touching the ground several hours earlier than at the OOTI site (sonic anemometer data at the SST, data not shown). Comparison of the data for O₃ at the two sites

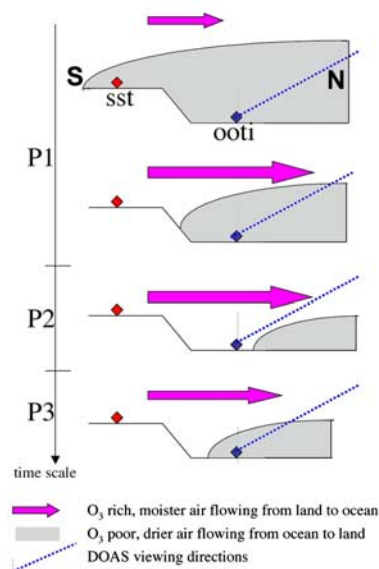


Figure 4. Schematic South-North cross section from the SST and OOTI measurement sites. The sketched wind patterns and airmass boundaries show the conceptual 2D picture of the unfolding of the wind episode supported by our surface measurements and the radiosonde data.

indicates that the upper air flow reached the ocean surface 3 hours later. During P1 and P3 the MAXDOAS measurements suggest that BrO resides in a shallow layer less than 500 m deep. The changes P1–P2 and P2–P3 as measured at the OOTI site are very abrupt, and very little mixing between airmasses appears to have taken place. However, note that the BrO mole fraction inferred from MAXDOAS at the OOTI site looking northward does increase before the airmass change is recorded at the surface, because MAXDOAS is sensitive to the whole vertical extent of the boundary layer where the temperature inversion breaks up from the top. This starts around 18h UTC as inferred from the SST data. A similar pattern can be seen during the transition P2–P3, where the MAXDOAS already probes the approaching airmass several minutes prior to its arrival at the measurement site. The observation of distinct maxima in the BrO mole fraction during the transition periods indicates active chemistry in the zone between the cold surface air containing reactive bromine and warmer air rich in O₃ aloft. In this zone reactive bromine coexists with O₃ resulting in an increase in the $\frac{[BrO]}{[Br]}$ ratio (R_{BrO_x}). Neglecting formaldehyde and olefin reaction with Br atoms as well as the BrO + NO reaction, this ratio can be calculated using the following approximation:

$$R_{BrO_x} = \frac{k_{Br+O_3}[O_3]}{J_{BrO} + 2k_{BrO+BrO}[BrO]} \quad (1)$$

During P1 and P3 $R_{BrO_x} \cong 4$ over the ocean, which implies that 80% of BrO_x was present as BrO in the surface layer, 20% as Br atoms. During the transition P1–P2, with the O₃ mole fraction reaching 30 nmol.mol⁻¹, and constant Br + BrO in the contact zone, R_{BrO_x} reaches 25, suggesting an almost total Br to BrO conversion through the fast reaction of Br atoms with O₃. This conversion resulted in a net increase of BrO of the order of 25 to 30%, as was observed by the MAXDOAS at the onset and the end of the surface event over the ocean.

5. Implications

[10] Atmospheric dynamics plays a major role in influencing the variability of surface O₃ concentrations in the Arctic. Our measurements with unprecedented time resolution on the Arctic Ocean give a graphic illustration of how this can lead to sudden drastic changes in atmospheric physical and chemical variables. We deduced that a combination of katabatic winds, and a change in the synoptic weather pattern created the conditions for the rapid change that we observed. While the coastal location undoubtedly is responsible for the high rate of change, the narrow size of the transition zone enriched in BrO, and sharp contrast between the two air masses may well be a more general feature. The marine boundary layer over the Arctic ocean in the spring is usually in the order of a few 100m, subject to strong temperature inversions, and devoid of ozone [Hopper *et al.*, 1998]. Similarly to what we observed during the high wind episode in the horizontal dimension at the surface, it should be separated from the free troposphere above by a narrow transition layer. It is then conceivable that analogous to the time series profile

of BrO we observed at the surface, spatially the vertical BrO profile exhibits a local maximum at the top of the boundary layer due to efficient Br to BrO conversion in the transition layer.

[11] The surface observations at the OOTI site also have some relevance for understanding the onset of the ozone depletion process itself. During the transition P2–P3 the temperature dropped in about 1 minute, while the O₃ mole fraction dropped in 3 minutes. In contrast, the decrease in snow temperature took about an hour, resulting in positive heat fluxes (based on direct measurements with the sonic anemometer; data not shown), and therefore a convective surface layer conducive to efficient mixing. Large vertical gradients could therefore be present in the lowest meter above the sea ice/snow pack surface featuring unusually high reactive bromine levels originating from the snow pack and causing very rapid ozone destruction. However, spatially confined, active surface chemistry would not be detected as such by instrumentation that requires long path lengths like ground-based or satellite DOAS. Similarly to our hypothesis of an enriched BrO transition layer between the marine boundary layer and the free troposphere above, local in situ measurements [e.g., Avallone *et al.* 2003] are required to verify these hypotheses.

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