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First investigations of IO, BrO, and NO₂ summer atmospheric levels at a coastal East Antarctic site using mode-locked cavity enhanced absorption spectroscopy

Roberto Grilli,¹ Michel Legrand,² Alexandre Kukui,^{3,4} Guillaume Méjean,¹ Suzanne Preunkert,² and Daniele Romanini¹

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[1] IO, BrO, and NO₂ were measured for the first time at Dumont d'Urville (East Antarctic coast) during summer 2011/2012 by using a near-UV-Visible laser spectrometer based on mode-locked cavity-enhanced absorption spectroscopy. IO mixing ratios ranged from the 2σ detection limit (0.04 pptv) up to 0.15 pptv. BrO remained close or below the detection limit (2 pptv) of the instrument. Daily averaged NO₂ values ranged between the detection limit (10 pptv) and 60 pptv being far higher than levels of a few pptv commonly observed in the remote marine boundary layer. Data are discussed and compared with those available for another coastal Antarctic station (Halley, West Antarctica). It is shown that the oxidative capacity of the atmospheric boundary layer at coastal Antarctic sites is quite different in nature from West to East Antarctica, with the halogen chemistry being promoted at West and the OH chemistry at East. **Citation:** Grilli, R., M. Legrand, A. Kukui, G. Méjean, S. Preunkert, and D. Romanini (2013), First investigations of IO, BrO, and NO₂ summer atmospheric levels at a coastal East Antarctic site using mode-locked cavity enhanced absorption spectroscopy, *Geophys. Res. Lett.*, 40, 791–796, doi:10.1002/grl.50154.

1. Introduction

[2] Valuable paleo-climate information can be derived from studies of chemical compounds preserved in polar ice cores (see *Legrand and Mayewski* [1997] for a review). For instance, sulfur, one of the critical species for which an overall understanding of the biogeochemical cycle is needed for climate change studies [*Charlson et al.*, 1987], is a key component of aerosol archived in polar ice. Motivated by a possible atmosphere/ocean sulfur link, numerous ice core studies focused on past change of methanesulfonate and sulfate, two aerosol species produced by the oxidation of dimethylsulfide (DMS) emitted in summer by marine biota

[*Legrand, 1997*]. The lack of knowledge of the atmospheric behavior of DMS under Antarctic summer conditions also stimulated studies of the atmospheric DMS cycle including dimethylsulfoxide, SO₂, sulfate, and methanesulfonate measurements. These were carried out at coastal Antarctic sites like Dumont d'Urville (DDU) [*Jourdain and Legrand, 2001*] and Palmer [*Berresheim and Eisele, 1998*]. The most efficient atmospheric oxidants of DMS are OH, BrO, and NO₃ whereas others like Cl, IO, and O₃ are less efficient (see *Barnes et al.* [2006] for a review). In summer only OH and BrO may efficiently compete in oxidizing the DMS. At Palmer, and for the first time in Antarctica, OH radicals were measured indicating a mean 24 h concentration of 1.1×10^5 radicals cm⁻³ [*Jefferson et al.*, 1998] in February. More recently, measurements of BrO made at Halley by *Saiz-Lopez et al.* [2007] indicate a mean level of 3 pptv during January–March. Such high BrO levels in summer make the BrO reaction with DMS producing dimethylsulfoxide four times faster than the one with OH (addition pathway) [*Read et al.*, 2008] whose levels reach 4×10^5 radicals cm⁻³ at that site [*Bloss et al.*, 2007].

[3] At DDU, with a 24 h mean value of 2×10^6 molecule cm⁻³, the OH levels observed at this site from December 2010 to January 2011 by *Kukui et al.* [2012] are the highest ever measured in coastal Antarctica. However, because neither NO_x nor halogen oxides, including BrO, were documented at this site, additional studies of these compounds are needed to better constrain the OH budget at that site. This paper reports on the first measurements of IO, BrO, and NO₂ made during the summer of 2011/2012 at DDU by deploying a new laser instrument based on mode-locked cavity enhanced absorption spectroscopy. Data are discussed in relation with the oxidizing properties of the atmosphere at the East Antarctic coast.

2. Method

[4] Field measurements of BrO, IO, and NO₂ were performed using a compact near-UV-Visible frequency comb spectrometer based on mode-locked cavity-enhanced absorption spectroscopy (ML-CEAS) [*Gherman and Romanini, 2002*]. Details on the instrument are given in *Grilli et al.* [2012a]. Briefly, a frequency-doubled, spectrally broad (a few nanometers) beam from a commercial femtosecond laser (100–250 fs, 80 MHz, Chameleon Ultra II from Coherent, Inc.) tuned at 338 or at 436 nm is injected into one of two 90 cm long high-finesse cavities (effective optical path lengths of 1.8 and 10 km at 338 and 436 nm, respectively). The transmitted radiation is analyzed by a high-resolution

¹UJF - Grenoble 1 / CNRS, LIPhy UMR 5588, Grenoble, France.

²UJF - Grenoble 1 / CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) UMR 5183, Grenoble, France.

³Laboratoire des Atmosphères, Milieux, Observations Spatiales (LATMOS), Paris, France.

⁴Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E) UMR-CNRS 6115, Orléans, France.

Corresponding author: M. Legrand, Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS-Université Joseph Fourier Grenoble, 54 Rue Molières, BP 96, Saint Martin d'Hères, 38402, France. (legrand@lgge.obs.ujf-grenoble.fr)

(0.37 cm⁻¹) spectrograph composed of an echelle grating and a blue-enhanced CCD camera. The instrument fits on a 120 × 60 cm² breadboard for a total weight of about 200 kg including the laser controllers (100 kg).

[5] For all inlet gas lines we used perfluoroalkoxy (PFA), which was found to be the best material to efficiently deliver the highly reactive IO and BrO radicals into the cavity. First, performing laboratory experiments with different tube materials, *Grilli et al.* [2012b] have reported no detectable losses of BrO at the level of 50 pptv when using PFA tubes. Second, during a field campaign conducted in June 2011 with the same instrument at the Station Biologique de Roscoff (see details in *Grilli et al.* [2012a]), no change of IO that was present at a mixing ratio close to 2 pptv was observed when the inlet tube length was increased from 2 to 7 m. A diaphragm pump is connected to the cavity exit to provide an airflow rate inside the cell of 800 cm³ per min through an adjustable flow restriction valve. The ambient air is sampled through a 5 m long (6 mm diameter) PFA tube with the inlet being protected against drifting snow with a specially designed glass piece. A filtered air system, free of NO₂, IO, and BrO, is also connected to the main gas line in order to replace the outdoor sample when reference spectra and ring-down events (photon life time inside the cavity, τ_0) are acquired. The measurement of τ_0 is essential to calculate the effective absorption path length used to convert the acquired spectra in absorption units. This represents the only calibration needed for the ML-CEAS technique. Being a direct absorption technique the ML-CEAS, in principle, does not require calibration standards, while the systematic uncertainty is mainly related to the uncertainty of the path length (determined from τ_0 with an estimated error of less than 1%) and the accuracy of the used absorption cross-sections available in literature for IO and BrO (~10%) [*Newman et al.*, 1998; *Wilmouth et al.*, 1999].

[6] It should be noted that during measurement, radicals are dissociated by the UV-Visible radiation; however, because the measured concentrations were found to be independent to the laser power, this effect appears to be of minor importance [*Grilli et al.*, 2012a]. The residence time of sampled air within the inlet line and the cavity is about 20 s and in absence of solar UV radiation the perturbation of photo stationary state ratio between NO and NO₂ may result in an overestimation of NO₂ via its production by the reaction of ozone with NO. Assuming a rate constant of 1.23×10^{-14} molecule⁻¹ s⁻¹ at 0°C for the reaction of NO with O₃ [*Sander et al.*, 2011] and a typically ozone mixing ratio of 20 ppbv at DDU in January [*Legrand et al.*, 2009; *Preunkert et al.*, 2012], we calculate an NO₂ overestimation up to 5 pptv when ambient air NO levels reach 35 pptv in the early afternoon (see section 7).

[7] The broadband spectra are averaged over 1 min at 338 nm for detection of BrO or 5 min at 436 nm for detection of IO and NO₂. The ratio between the spectra in the absence and in the presence of the absorption features are converted in unit of absorption and fitted by a multicomponent fit routine, where the reference cross-sections are used as components and a fifth degree polynomial is used to take into account for laser frequency drift and laser instabilities during acquisitions. The resulting detection limits (taken as 2 σ) of 2, 0.04, and 10 pptv are estimated for BrO, IO, and NO₂, respectively.

3. The Dumont d'Urville Site

[8] IO and NO₂ measurements were conducted quasi-continuously from 31 December 2011 to 19 January 2012, and over a few pairs of days (25–26 and 28–29 January, 5–6 February). Furthermore, tests for the presence of BrO were performed from 31 January in the afternoon to 3 February at noon.

[9] The site of Dumont d'Urville (66°40'S, 140°01'E, 40 m above the sea level) is settled on a small island (0.3 km²). Thus, considering the prevailing southeastern (120°E to 160°E) surface wind direction, measurements were carried out at “iono site” located at the southern headland of the island where the influence of station activities is minimized. As shown by *Preunkert et al.* [2012] on the basis of CO measurements, the “iono site” may be occasionally influenced by station activities but generally for less than 1 h. That occurs when wind is either very weak or blowing from the station (north to northeastern direction). The impact of station activities (combustion) on NO₂ measurements is examined in section 4.

[10] The climate at DDU is characterized by three different situations with air masses coming from either inland Antarctica, or coastal Antarctica, or offshore ocean. To characterize the origin of sampled air masses, 3 days backward-trajectories were computed using the HYbrid Single-Particle Lagrangian Integrated Trajectory model (R.R. Draxler and G.D. Rolph, NOAA Air Resources Laboratory, Silver Spring, Maryland, 2003, available at <http://www.arl.noaa.gov/ready/hysplit4.html>). The model was run in a backward mode for three levels (at 0, 250, and 500 m above sea level). For each backward trajectory, the fractions of air mass residence times over the Antarctic continent (i.e., latitudes > 70°S), over the open sea (latitudes < 67°S), and along the coast (67°S < latitudes < 70°S) were calculated.

4. Contaminations by Station Activities

[11] The pollution plume related to DDU station activities (combustion) that occasionally reached the “iono site” is clearly detected in the NO₂ record (Figure 1). Over the reported period, wind conditions often changed from moderate to high wind speed blowing from the continent (10 and 12 January, respectively) to very low wind blowing from the station sector (from 60°W to 60°E, for instance early morning 11, 13, and 14 January). The effect of changes in wind direction is clearly detected in the NO₂ record with huge increases (300 to 1500 pptv) over a few tens of minutes. As seen in Figure 1c, where all 15 min averaged NO₂ data are reported as a function of wind speed, contamination can be suspected mainly when wind speed dropped to less than 2 m s⁻¹. To discard the impact of combustion on the NO₂ record, 15 min data obtained under low wind speed conditions (< 2 m s⁻¹) and/or when the wind was blowing from 60°W to 60°E were scrutinized and, if obviously impacted by station activities, were discarded from the data set. The filtered NO₂ mixing ratios were then one hour averaged (Figure 2).

5. Halogen Oxides

[12] BrO levels (not shown) remained close or below detection limit (2 pptv) of the instrument, being at least two times lower than the Halley levels in summer (3 pptv,

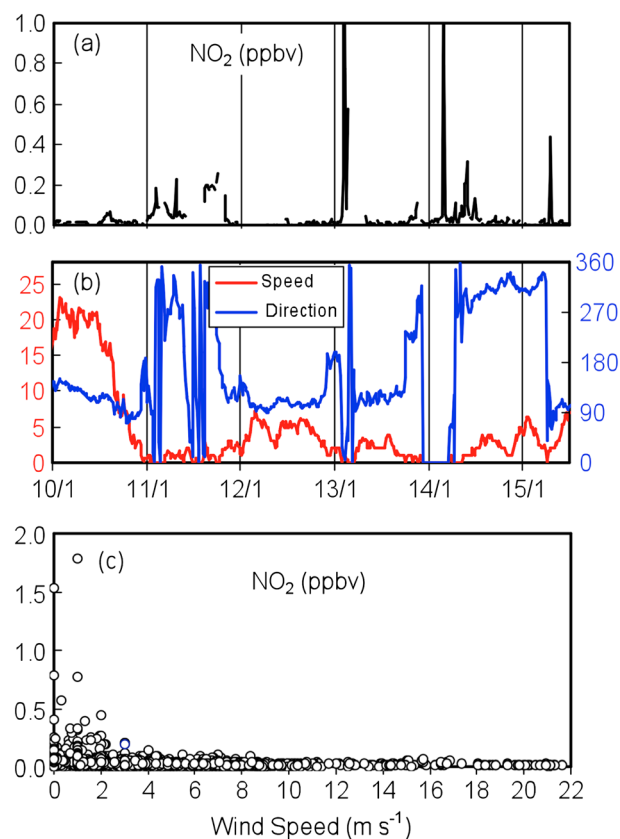


Figure 1. (a) and (b) The 15 min mean NO₂ mixing ratios recorded at DDU (iono site) along with wind conditions from 10 to 15 January 2012. (c) NO₂ mixing ratio (15 min averages) versus wind speed. The detection limit for NO₂ is 10 pptv (2σ).

Saiz-Lopez et al. [2007]). Spatial and temporal variability of the tropospheric BrO columns show that regions with enhanced columns exhibit an excellent correlation with the areas of sea ice, located along the coast line of Antarctica [*Theys et al.*, 2011]. Though limited to 4 days, the observation of rather low BrO mixing ratios at DDU is thus consistent with a quasi-absence of sea ice offshore the site in January (data available at <http://www.esrl.noaa.gov/psd>).

[13] IO mixing ratios at DDU ranged most of the time from the detection limit (0.04 pptv) up to 0.15 pptv (Figure 2). These values are more than one order of magnitude lower than those observed at Halley in summer (3 pptv, *Saiz-Lopez et al.* [2007]) where high mixing ratios of both IO and BrO were observed in air masses having been over sea ice within the previous 24 h. Even when air masses arriving at DDU had been in contact with the ocean (from 12 to 15 January for instance, Figure 2), IO mixing ratios remained very low. Although the common link of the two species with sea ice is not fully understood, as for BrO, the IO levels are consistently lower at DDU than at Halley in relation with far less abundant sea ice in the Indian (DDU) than in the Atlantic (Halley) sector (data available at <http://www.esrl.noaa.gov/psd>).

6. NO₂ Mixing Ratio Versus Air Mass Origins

[14] Hourly mean NO₂ mixing ratios rarely exceeded 50 pptv and daily means ranged from 10 to 60 pptv with an overall daily mean of 20 ± 13 pptv. That is at least

three times higher than values reported for the coastal site of Halley in January 2005 (5 to 7 pptv, *Bauguitte et al.* [2012]).

[15] The observed NO₂ levels appear to be highly dependent on the origin of sampled air masses. Indeed, during the first week of January, air masses were coming from inland Antarctica (Figure 2). The continental character of air masses then decreased with enhanced coastal contribution and a few sporadic marine inputs until 10 January. Over these 11 days, highest NO₂ daily means close to 45 ± 12 pptv were observed when air masses came from the continent and under high solar radiations (31 December, 1 and 7 January), other values remaining close to 20 pptv. On 9 January a low-pressure system approached the Antarctic coast and during the following week, air masses were characterized by significant marine input with snowfall events, particularly on 15 January with a pure marine contribution. From 10 to 18 January hourly mean NO₂ mixing ratios remained below 25 pptv and the daily means reached a minimum close or below the detection limit on 12 and 15 January. For the remaining 7 days of sampling, air masses were mostly of continental origin and daily mean NO₂ mixing ratios of 10 to 31 pptv were observed, which were lower than at the beginning of January. From these observations it can be concluded that, except when a pure marine air mass was sampled, NO₂ mixing ratio at DDU largely exceeded the ones (5–7 pptv) observed at Halley, with higher values in air masses originating from inland Antarctica. The high values of NO₂ in inland Antarctic air masses are likely related NO_x emissions following the photolysis of nitrates present in snow over the Antarctic plateau [*Davis et al.*, 2008].

[16] The NO₂ mixing ratios exhibit a diurnal cycle with an early morning minimum close to 10 pptv between 05:00 and 08:00 (local time) and a wide maximum of 25–30 pptv between 13:00 and 23:00 (Figure 3). This diurnal variation characterized by an early morning minimum is qualitatively consistent with observations made in previous Antarctic studies (see the pioneer study from *Jones et al.* [2000] at Neumayer for instance). Note however that NO₂ levels already reached high values in the early afternoon, a feature that was not seen at Halley by *Bauguitte et al.* [2012] who found a regular increase from 2.5 pptv between 05:00 and 08:00, 7 pptv in the early afternoon up to 10 pptv around 19:00–21:00. As discussed in section 2, an overestimation of the NO₂ level up to 5 pptv when the ambient air NO level reaches 35 pptv in the early afternoon (see section 7) is possible and may partly account for the rapid increase of NO₂ between 12:00 and 15:00 detected at DDU and not at Halley.

[17] In their detailed discussions of the NO_x chemistry at Halley, *Bauguitte et al.* [2012] found that the photolysis of nitrate present in snow covered areas surrounding the site acts as a source of NO_x and the halogen chemistry controls the lifetime of NO₂. DDU is not directly located on a snow-covered surface and the nearby inland Antarctic region where snow accumulates is located 20 km from DDU [*Agosta et al.*, 2011]. Nevertheless, in spite of this difference in the proximity of snow covered area around the site, given the low halogen oxides levels at DDU (section 5), the factor controlling the lifetime of NO₂ would be different at Halley and DDU. Calculations suggest that with OH levels reaching 3.5×10^6 radicals cm⁻³ at noon [*Kukui et al.*, 2012] (instead of 7×10^5 radicals cm⁻³ at Halley, *Bloss et al.* [2007]), the

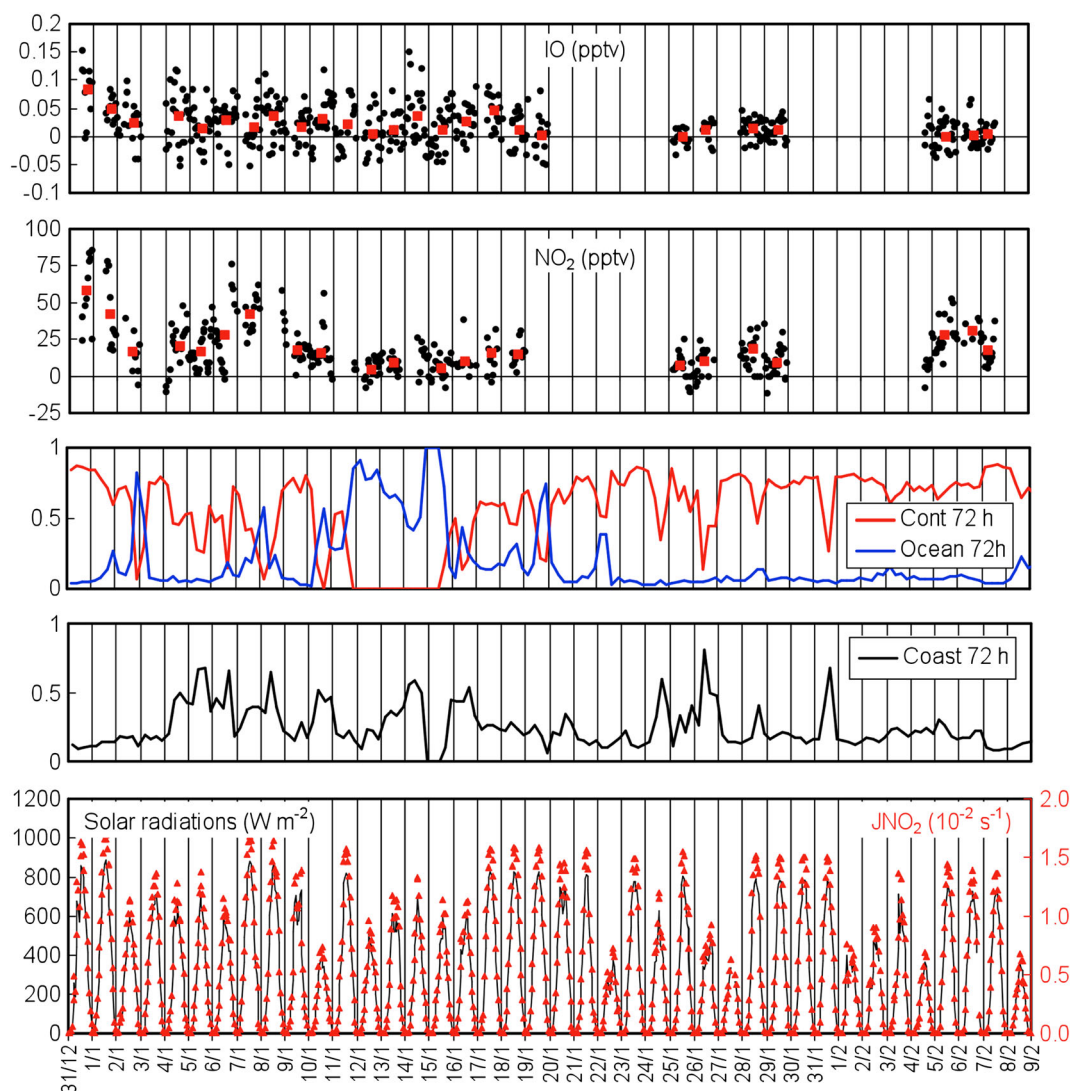


Figure 2. IO and NO₂ mixing ratios at DDU in January/February 2012 versus the origin of sampled air masses and sunlight conditions. Detection limits are 0.04 and 10 pptv (2σ), respectively. Black and red points (top) refer to 1 h averages and daily means, respectively. The fraction of residence times (middle) over the Antarctic continent, the ocean, and along the coast are denoted Cont 72 h, Ocean 72 h, and Coast 72 h, respectively (see section 3). The solid line and red triangles (bottom) refer to solar radiations and estimated NO₂ photolysis rate (JNO_2). Following *Kukui et al.* [2012] the values of JNO_2 were estimated using total global irradiance routinely measured at DDU together with the Tropospheric Ultraviolet and Visible radiation model (version 5.0, *Madronich* [1993]).

production of HNO₃ appears to be a significant sink of NO₂ with the NO_x lifetime approaching 10 h.

7. Implications for the Oxidizing Properties of the Atmosphere at the East Antarctic Coast

[18] As discussed by *Kukui et al.* [2012], with a 24 h average value of 2×10^6 radicals cm⁻³, the OH levels at DDU in summer 2010/2011 were about five times higher than those observed at other coastal sites of Halley [*Bloss et al.*, 2007] and Palmer [*Jefferson et al.*, 1998]). At remote areas the major atmospheric source of OH is the photolysis of ozone followed by the reaction of O(¹D) with water vapor. Based on steady state calculations accounting for major radical sources and sinks for which relevant chemical measurements were made (including O₃, H₂O₂, CH₃OOH,

HCHO, and CO) *Kukui et al.* [2012] showed however that the 24 h average OH level at DDU would be about 7×10^5 molecule cm⁻³ if only the O₃ photolysis source is considered. This suggested that a HO₂ to OH conversion mechanism (reactions with halogen oxides or NO) is needed to explain the observations at DDU. Although neither halogen oxides nor NO data were measured during the 2010/2011 campaign, it has been concluded on the basis of sensitivity of the steady state calculations to NO_x level that some conversion mechanism of RO₂ to OH equivalent to an NO level of 20–50 pptv is needed to explain the OH measurements.

[19] In contrast to these previous calculations, here the steady state OH concentrations were estimated using the NO diurnal cycle derived from the NO₂ measurements. The NO mixing ratios were calculated assuming steady state

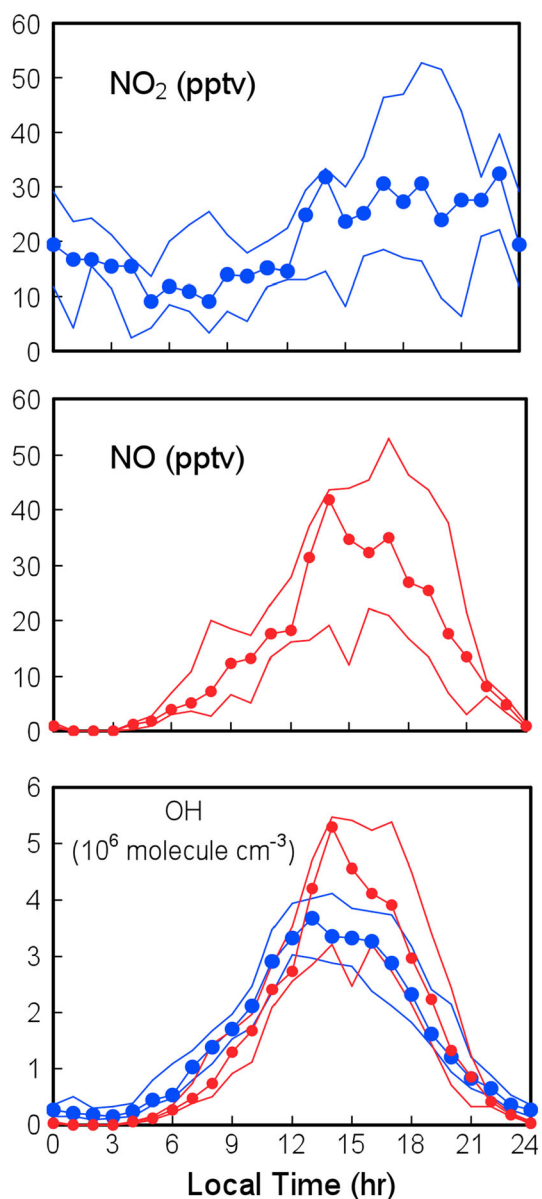


Figure 3. (top) The diurnal cycle of observed NO₂ mixing ratio, (middle) estimated NO mixing ratio, and (bottom) measured (blue) and calculated (red) OH concentration (see section 7). The points and lines correspond to median and first and third quartiles, respectively. Calculations were made discarding days over which the marine fraction became important.

conditions for NO_x and accounting for the photolysis of NO₂ and the reactions of NO with O₃ and RO₂. The NO was calculated according to the equation (1) using median values of O₃, RO₂, and JNO₂ measured during 2010/2011 campaign and NO₂, IO, and BrO data obtained in this work during summer 2011/2012. As discussed by Kukui *et al.* [2012], we have assumed that under conditions encountered at DDU the peroxy radicals are represented in similar proportions by HO₂ and CH₃O₂. For calculations, the reaction rate coefficients were taken from Sander *et al.* [2011].

$$[\text{NO}] = ([\text{NO}_2] \times \text{JNO}_2) / (k_{\text{O}_3}[\text{O}_3] + 0.5(k_{\text{HO}_2} + k_{\text{RO}_2})[\text{RO}_2] + k_{\text{IO}}[\text{IO}] + k_{\text{BrO}}[\text{BrO}]) \quad (1)$$

[20] The characteristic time to reach photo stationary NO mixing ratios is determined by the sum of NO_x interconversion rates. For a typical ozone level of 20 ppbv at DDU, this time ranges from 3 min at night to about 40 s at noon. The validity of the steady state approach used for the NO estimation is based on the assumption (see section 6) that NO_x is not emitted in the immediate vicinity of the site. With a typical wind speed of 5 m s⁻¹, at least 1 h is needed for an air mass having been in contact with inland surface snow (located at least 20 km from DDU) to reach the site.

[21] In contrast to conditions encountered at Halley where the reaction of NO with RO₂ is negligible with respect to those with O₃ and XO, at DDU the reaction of NO with O₃ as well as with RO₂ are faster, whereas the reactions with XO represent less than 5% of the total loss of NO in equation (1). Over the entire NO₂ sampling period, an overall mean daily NO mixing ratio of 13 ± 13 pptv is calculated. Higher daily mean NO mixing ratios are calculated for the beginning of the period that was characterized by air masses with a strong continental character (42 ± 14 pptv) over 31 December, 1 and 7 January.

[22] As shown in Figure 3, the calculated and measured OH concentration levels are quite similar, which supports the previously proposed mechanism with RO₂ to OH conversion in reactions with NO. The shift of ~2 h seen between calculated and measured OH concentrations may be to some extent related to the possible overestimation of NO₂ in the early afternoon discussed in section 2. Furthermore, it should be kept in mind that the NO₂ measurements were performed not at the same time as OH and other parameters used in the calculations.

[23] Thus, it appears that the oxidative capacity of the atmospheric boundary layer at coastal Antarctic sites in summer is quite different in nature from West to East Antarctica. The halogen chemistry is promoted by the larger sea-ice coverage in the Western part of Antarctica compared to the Eastern part. Conversely, the OH chemistry is strengthened in East Antarctica in relation with continental air masses bringing ozone, as already shown by Legrand *et al.* [2009], but also of NO_x released from the snowpack of the Antarctic plateau. The more frequent exports of air masses from inland Antarctic plateau to the east coast than to the west coast are due to a large difference of the topography at the two Antarctic regions [König-Langlo *et al.*, 1998]. These differences may impact for instance the DMS chemistry. As calculated by Read *et al.* [2008] the 3 pptv of BrO observed at Halley make this radical the most efficient oxidant of DMS (lifetime of 0.4 days against 1.5 days with OH). At DDU the situation is reversed with a lifetime of DMS of 0.3 days with respect to the OH addition pathway reaction against more than 1.2 days considering an upper limit of 1 pptv of BrO.

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