



## Spring and summertime diurnal surface ozone fluxes over the polar snow at Summit, Greenland

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[1] Continuous surface-layer ozone flux measurements over the polar, year-round snowpack at Summit, Greenland, resulted in deposition velocities ( $v_d$ ) that were smaller than most previous assumptions and model inputs. Substantial seasonal differences were seen in the ozone  $v_d$  behavior. Spring, daytime ozone  $v_d$  values showed low variability and were consistently  $\leq 0.01$  cm s<sup>-1</sup>. During summer, ozone fluxes displayed distinct diurnal cycles, and evidence for regular occurrences of bi-directional behavior. Summer, daytime  $v_d$  ranged between  $\sim 0.01$  to 0.07 cm s<sup>-1</sup>. Maximum summertime downward fluxes (ozone deposition) coincided with the hours of maximum solar radiation, i.e., noon–afternoon. During summer nighttime hours upward ozone fluxes were observed. These upward fluxes were interpreted as ozone production in a shallow layer near and above the snow surface with resulting upward ozone fluxes out of the shallow surface layer. Comparisons with published observations from temperate, midlatitude sites suggest different controls and behavior of ozone fluxes, and that ozone fluxes over snow depend on a myriad of parameters, including solar irradiance, snow chemical and physical properties, snowpack depth, and the type of substrate underneath the snow. **Citation:** Helmig, D., L. D. Cohen, F. Bocquet, S. Oltmans, A. Grachev, and W. Neff (2009), Spring and summertime diurnal surface ozone fluxes over the polar snow at Summit, Greenland, *Geophys. Res. Lett.*, 36, L08809, doi:10.1029/2008GL036549.

### 1. Introduction

[2] Recent work at Summit, Greenland, and other polar sites has illustrated that chemical reactions in the snow constitute both sources and sinks for reactive trace gases in the polar boundary layer [Grannas *et al.*, 2007, and references therein]. In combination with the unique (i.e., abundance of high stability) boundary layer conditions, snowpack emissions can significantly influence the atmospheric chemistry over snow [Neff *et al.*, 2008]. Ozone chemistry is of particular interest as it greatly influences the oxidation chemistry of the atmosphere. Ozone depletion

events during polar sunrise have triggered extensive polar research. These studies have revealed the importance of halogen-induced, catalytic ozone destruction chemistry; however, this process appears to be restricted to coastal and sea ice regions, where the ocean can provide the necessary halogen source to engage in this chemistry.

[3] Remarkably, previously published literature with studies from continental environments show that ozone fluxes over snow, expressed as ozone deposition velocity (ozone  $v_d$ ), can vary over a wide range, i.e., from  $\sim -3$  to 2 cm s<sup>-1</sup>. The literature includes several reports with upward ozone fluxes, interpreted as ozone coming out of seasonal, midlatitude snow [Galbally and Allison, 1972; Zeller and Hehn, 1996; Zeller, 2000]. Later research has questioned if these data are representative for year-round snow conditions, and it has been pointed out that smaller ozone  $v_d$  values are expected over the extensive snow-covered polar areas [Helmig *et al.*, 2007a]. Small changes in ozone deposition can have a significant impact on high-latitude ambient ozone concentrations as in the absence of photochemical processes during the dark winter months, ozone deposition to the snow surface is an important sink term in the polar ozone budget. Chemical reaction mechanisms determining the ozone surface sink remain elusive, with suggested reactions including quasi-liquid layer chemistry, reactions with nitrogen oxides (NO<sub>x</sub>), halogens, organic matter, particulate matter from deposited aerosols, biological material, or a combination of these [Peterson and Honrath, 2001; Albert *et al.*, 2002; Bocquet, 2007]. Experiments in this study address the ambiguity in the polar ozone flux behavior by providing measurements of ozone fluxes for five weeks in the spring, and seven weeks in the summer at a polar, snow-covered site.

### 2. Instrumentation and Methods

[4] This study was conducted at Summit, Greenland (72°34'N, 38°29'W; 3208 m asl), June 29–August 14, 2004 (day of year (DOY) 180–226), and March 21–April 28, 2005 (DOY 80–118) at the ‘Science Trench’,  $\sim 250$  m in the predominant upwind direction from other camp structures. The facility consisted of a 12 m-flux tower with a below-surface laboratory. The fetch in all directions was flat, homogeneous, dry polar snow. Considerable effort was directed towards improving and defining the precision of the contributing gradient measurements to allow for a highly sensitive ozone flux determination. Another emphasis was to allow for redundancy of measurements for quality control. Tower gradients of temperature, wind speed, and ozone were measured at  $\sim 0.75$  m, 2.0 m, and 9.3 m during 2004.

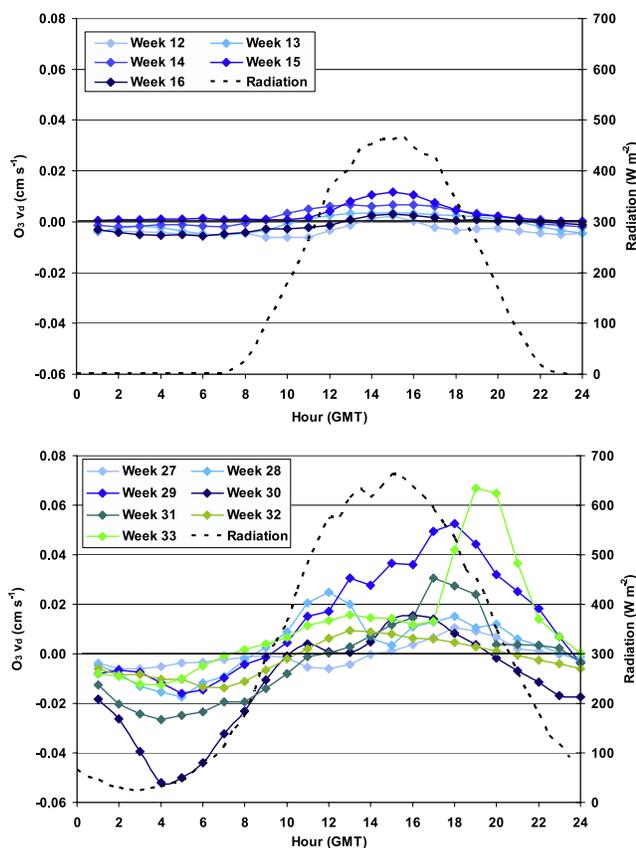
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**Figure 1.** Weekly median, smoothed, hourly values of the ozone exchange velocity (expressed as ozone deposition velocity values,  $v_d$ ) (top) for the spring period, March 21–April 28, 2005, and (bottom) for the summer experiment, June 29–August 14, 2004. The graphs also show the median diurnal incoming solar radiation, derived from the actual measurements during the summer 2004 experiment. For spring 2005, radiation data for DOY 89–104 in the prior year are shown as a surrogate (reflecting the middle portion of the spring period).

In 2005, ozone was measured at 0.30 m and 7.3 m. Actual measurement heights changed over the course of the experiment due to snow accumulation and were corrected using data from a surface distance sensor (Model SR50, Campbell Scientific Instruments). Air temperature gradients were measured with aspirated E-type thermocouples (Model 43408, R.M. Young Co., U.S.A.), wind speed gradients with cup anemometers (Model 010C, Met One Instruments, U.S.A.), incoming solar radiation with a pyranometer (LI200X, Campbell) at  $\sim 1.4$  m height above the surface. Ozone was monitored continuously by sampling air through 18 m-long, 0.39 cm i.d. PFA sampling lines equipped with a PFA inlet funnel/filter, and with three dedicated, commercial UV absorption monitors (Model 49C, Thermo Electron Corporation, Franklin, MA). The acquisition sequence of these monitors was modified to yield a 2.3-times longer signal integration time and an improved precision of 0.05–0.10 ppbv ( $1\sigma$ ) for 1-min data. Inlets were brought to the same height twice daily for 30 min to track and correct

instrument offsets. Using this protocol, the uncertainty for ozone differences (over respective gradient intervals) was reduced to 0.07–0.09 ppbv for 30-min data averages. Atmospheric turbulence was measured with a sonic anemometer (CSAT-3, Campbell Scientific) at 2 m height.

[5] Data were quality-controlled, filtered, and processed according to the following criteria: Measurements with the winds from the station (NW-NE) sector were eliminated. Occasional riming on the sensor heads and temperatures below  $-35^\circ\text{C}$  (spring period only) resulted in low-quality turbulence data which were removed. Flux analyses were done on 30-min data blocks, and data which did not follow Monin-Obukhov (MO) similarity theory turbulence statistics (i.e., based on the behavior in their frequency spectra [Kaimal and Finnigan, 1994]) were rejected. This filter in essence also removed periods that were disturbed by intermittent non-stationary conditions [Cullen *et al.*, 2007]. Sensible heat fluxes and boundary layer parameters were calculated from concurrent profile gradient and eddy-covariance measurements and were evaluated for identification of the best approach for the chemical flux determination. When flux gradient profile calculations (9.3 m–2.0 m, and 2.0 m–0.75 m) were compared with results from the sonic anemometer, profile gradient heat fluxes from the higher gradient showed a larger variability and deviation. Hence, it was suspected that the 9.3-m measurements were frequently not within the constant flux layer; therefore ozone fluxes were calculated using only the lower gradient interval. Furthermore, while profile gradient sensible heat fluxes agreed reasonably well with the eddy covariance measurements during night (average difference of 26%), the gradient heat fluxes appeared to be overestimated during the day, which suggested that the accuracy of the temperature gradient measurements was inadequate. Consequently, ozone fluxes were calculated using a modified gradient method, which used sonic anemometer derived turbulence parameters and the ozone gradients. Data were filtered for near-neutral stability conditions (i.e., data outside the range of gradient Richardson number ( $Ri$ )  $-0.1 < Ri < 0.15$  were eliminated), to minimize the error introduced by the stability term. After applying all filters, 1043 and 760  $\frac{1}{2}$ -hour runs remained for the 2004 summer, and 2005 spring experiments, respectively. Ozone fluxes ( $F_{O_3}$ ) were converted into deposition velocity values ( $v_d = -F_{O_3}/[O_3]$ ), as this parameter is concentration-independent and most commonly reported in the literature. Note that the sign of  $v_d$  is opposite to the flux, so that positive deposition velocities indicate deposition to snow. We chose to use the term ‘exchange velocity’ and ‘upward exchange velocity’ to avoid the nomenclature of negative velocity. Data from the same  $\frac{1}{2}$ -h time interval over one-week periods were averaged. Then, these  $\frac{1}{2}$ -h data were averaged to 1-h means and their 3-point running means were calculated to better discern the diurnal flux dependence from the day-to-day variability. Please note that due to the data filtering there will be a variable number of data points that were considered for calculating these averaged values. Further details on the instrumentation, measurement protocols, and data processing are provided in the auxiliary material, and by Cohen [2006], Cohen *et al.* [2007], Bocquet [2007], and F. Bocquet *et al.* (Evaluation of the flux gradient

technique for measurement of small ozone surface fluxes at Summit, Greenland, manuscript in preparation, 2009).<sup>1</sup>

### 3. Results and Discussion

#### 3.1. Ozone Surface Exchanges

[6] The median hourly ozone exchange velocity diurnal profiles for the spring period 2005 are shown in Figure 1 (top); these ozone  $v_d$  data range from  $-0.01$  to  $0.01$   $\text{cm s}^{-1}$ . (Graphs with weekly hourly data with standard deviation (representing the day-to-day variability) are presented in the auxiliary material.) The ozone  $v_d$  diurnal profiles for seven summer weeks from June 29 to August 14, 2004, resulted in a range of ozone  $v_d$  values from  $-0.05$  to  $0.07$   $\text{cm s}^{-1}$  (Figure 1, bottom). Both of these seasonal data ranges are low compared to ozone  $v_d$  exchange values seen in most other landscapes. The magnitude of these experimentally-determined ozone exchange velocities is in agreement with our recent model sensitivity study, which concluded that for polar snow, ozone  $v_d$  should be less than  $0.01$   $\text{cm s}^{-1}$  during January, and that only a narrow subset of the wide range of reported snow deposition values could be deemed representative for polar conditions [Helmig *et al.*, 2007a]. The Summit experimental data are further evidence that the ozone exchange velocity over polar snow is within this range of comparatively small values. Similarly low exchange velocities of  $0.01$ – $0.12$   $\text{cm s}^{-1}$  have only been seen over the oceans. Over land, in particular over vegetation, ozone fluxes are largely determined by stomatal uptake, with resulting values up to  $1.5$   $\text{cm s}^{-1}$  during noontime hours [Wesely and Hicks, 2000].

#### 3.2. Diurnal and Seasonal Behavior

[7] While the seasonal data sets show a considerable degree of variability among the weekly averages, a regular diurnal behavior and a distinct difference between these two measurement periods is evident. The summer data show an overall higher variability in the weekly data. Nonetheless, a consistent pattern observed is that ozone exchange velocities are mostly negative during the  $\sim 00$ – $10$  hours, increase steadily during the morning hours, and turn positive between  $\sim 11$ – $23$  hours, with maximum values occurring during mid-afternoon. Averaged irradiance data were included in Figure 1 to illustrate the relationship between the ozone flux and the incoming solar radiation cycle. During the summer months the sun does not set at Summit's  $72^\circ$  latitude, however, solar cycles are still quite prominent with a  $\sim 14$ -fold difference in daytime-nighttime solar irradiance. The data in Figure 1 show that the minima and maxima in the ozone exchange velocity occur close to the times of solar minima and maxima, respectively, although on average possibly shifted towards 2–3 h later time. A similar shift can be discerned from a comparison of the ozone fluxes with the sensible heat flux (Figure S5), where both the onset and end of negative ozone deposition fluxes appear to lag 2–3 h behind the heat flux. This behavior suggests that the ozone exchange is closely linked to the diurnal solar irradiance cycle. However, the delay between the sensible heat and the ozone fluxes hints towards different processes that

are governing these fluxes. The sensible heat flux is determined by the heating and cooling of the snow surface by incident solar radiation and air mass changes. During the summer period, the onset of positive heat flux occurs when the snow surface warms up above the air temperature, which is  $\sim 4$ – $5$  h after the “nighttime” minimum in solar irradiance. As it takes another 2–3 h before ozone deposition fluxes show a response (i.e., turn negative), it can be concluded that the ozone surface sink requires this much more time to become effective. This delay possibly has a contribution from the required transport time to exchange ozone-depleted air between the snowpack (i.e., the depth where ozone destruction occurs, see discussion below) and the snow surface.

[8] An overall more consistent ozone exchange velocity was found during the spring (Figure 1, top), when higher minima and lower maxima in the diurnal ozone exchange velocity result in a much smaller diurnal amplitude. Nonetheless, a similar diurnal behavior can be discerned, with smaller, negative ozone exchange velocity values occurring during “night” and the early morning hours, and positive  $v_d$  values during the late morning–mid afternoon hours. Again, this behavior mirrors the solar irradiance cycle. During this period in April solar irradiance dropped to  $<1$   $\text{W m}^{-2}$  for  $\sim 7$  h during the night. It is noteworthy that while there is a clear dependency of the ozone exchange signal on the solar irradiance cycle, this relationship does not appear to be linear. While the integrated 24-hour solar irradiance approximately doubled from spring to summer, the amplitude of the ozone exchange signal increased by a factor of 5–10.

#### 3.3. Relationship Between Ozone Surface Fluxes and Ozone in the Snowpack

[9] Two other experiments [Peterson and Honrath, 2001; Helmig *et al.*, 2007b] have provided ozone measurements at different depths in interstitial air in the Summit snowpack. These measurements have found distinct diurnal concentration cycles, with lowest ozone levels occurring a few hours after the time of maximum solar irradiance (noon–afternoon). Most of the ozone depletion occurred in the first 30 cm below the snow surface. The ozone gradient (above the surface–below the surface) also had a clear seasonal signal, with lower ozone gradients observed during early spring than during mid-summer [Helmig *et al.*, 2007b]. The latter study argued that solar irradiance appeared to be the most obvious indicator for the observed ozone cycles.

[10] The exchange rate of air above the surface with air inside the permeable snowpack depends on multiple conditions including snow physical parameters, advection caused by wind pumping, convection, and diffusivity [Domine *et al.*, 2008, and references therein]. At Summit, the combined effect of these processes yields rather similar gas exchange rates throughout the day and season (M. Albert, personal communication, 2006). Consequently, it was postulated that the concentration changes in the snowpack should reflect the ozone depletion rate in the snowpack, and that this ozone depletion should be a determining sink for ozone surface fluxes [Helmig *et al.*, 2007b]. The comparison of the ozone exchange rates measured in this study with the previously reported snowpack measurements provide new evidence supporting this hypothesis, as it indicates that ozone

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008GL036549.

surface fluxes, both in their diurnal and seasonal signal, are connected to the ozone concentration changes seen in the snowpack.

[11] As mentioned in the introduction section, several previous studies have investigated possible chemical mechanisms contributing towards the ozone destruction in the snow. Combined, the previously reported ozone snowpack measurements and these new surface flux data unanimously support a photochemical mechanism. There were no measurements of potential ozone reactants conducted in the context of this study for further elaboration of the previous literature. The observed ozone behavior provides a strong motivation for future continuous diurnal and seasonal snowpack measurements of chemical species such as  $\text{NO}_x$ , volatile organic compounds, halogens, and complex organic material, as measurements of these species are anticipated to provide new insight into the chemistry and fluxes of ozone inside and above the snowpack.

### 3.4. Ozone Production Above the Snow Surface

[12] Occurrences of negative ozone exchange velocities are caused by ozone levels being higher in air collected from the nearest-to-the surface inlet level than at the  $\sim 2\text{-m}$  height. This condition will cause upward ozone fluxes during those times. Albeit the absolute values for these upward fluxes are small (relative to downward daytime fluxes), conditions with negative exchange velocities are encountered consistently during twilight/high solar zenith angle times (summer nights). Interstitial air measurements showed that during most ( $>99\%$ ) times, ozone levels in the snow were less or equal to ambient levels [Helmig *et al.*, 2007b] (with the exception being periods with rapid drop in ambient ozone, causing ozone from within the snow flowing upward, re-equilibrating with above-surface air), and there was no evidence for ozone being produced in the snow. Tethered balloon vertical profile measurements [Helmig *et al.*, 2002] did not provide evidence of significant ozone production in the surface layer at Summit, although it should be noted that very few nighttime profiles were conducted and that these ozonesonde measurements lacked the necessary sensitivity to discern ozone gradients  $<0.1$  ppbv  $\text{m}^{-1}$ . Therefore, the higher sensitivity ozone flux experiments reported in this study provide the first evidence that small, negative ozone gradients, resulting in positive (upward) ozone fluxes can be encountered at Summit. Such situations typically occurred when solar irradiance was low (below  $\sim 100$   $\text{W m}^{-2}$ ), which often coincides with times of increased atmospheric stability. We conclude that during these twilight conditions, while ozone depletion in the snow had ceased, photochemical ozone formation just above the snow surface exceeded surface deposition rates, resulting in upward ozone flux out of the surface layer. Since the snowpack measurements showed that ozone remains at lower levels inside the snow than above the surface, there must be a bi-directional flux behavior, with ozone transport both upward and downward (into the snow) from the surface layer. New experiments with multiple height, concurrent  $\text{NO}_x$  and ozone profile measurements are currently in progress to further investigate this hypothesis.

[13] Other previous studies have provided explanation for ozone production in the polar environment. Polar, sunlit snow has been found to be a source of  $\text{NO}_x$  (from photolysis

of nitrate in the snow) [Honrath *et al.*, 1999; Jones *et al.*, 2000], resulting in  $\text{NO}_x$  emissions out of the snow [Honrath *et al.*, 2002], and significant  $\text{NO}_x$  concentration enhancements in the shallow surface layer. This phenomenon, together with an active radical photochemistry above the polar snowpack, can lead to conditions of ozone production, and increased ozone concentrations in the surface layer, a situation that so far has only been observed at South Pole [Crawford *et al.*, 2001; Davis *et al.*, 2008; Helmig *et al.*, 2008]. Davis *et al.* [2004] presented arguments for a less pronounced concentration buildup and surface layer photochemistry at Summit (than at South Pole). Nonetheless, our new ozone flux data from Summit provide evidence that ozone production chemistry over snow does not only occur at South Pole, but possibly, albeit at lower rates, extends to other areas in the polar environment.

### 3.5. Net Ozone Flux

[14] Please remember that numerous data filters had to be applied for the gradient flux data analysis. Consequently, the relative contribution of certain flux conditions over others was likely biased, as this method basically eliminated all situations with moderately to highly stable, and highly unstable atmospheric conditions from the data set. Therefore, these results are not unequivocal enough to gauge if, integrated over a longer period of time, the Summit snowpack is a net sink or source of ozone. However, the more complete (i.e., with fewer data eliminated by data filters) ozone gradient data allow further insight into this question. Helmig *et al.* [2007b, Figure 10] show the distribution of all 10 m–0.5 m 30-min ozone gradients for the 2005 summer. The data in this figure illustrate that there were more frequent occurrences of positive ozone gradients, and that positive gradients overall had higher absolute values than negative gradients. Furthermore, since positive gradients were more frequently observed during daytime hours, when sensible heat fluxes and the vertical transfer velocity typically are highest [Cullen and Steffen, 2001; Cohen *et al.*, 2007, Figure 6], it can be concluded that overall significantly more ozone was moving downward (i.e. deposition) than upward. Please note that these conclusions are only valid for the height layer of the atmosphere that was probed in these experiments. As the ozone production rate is dependent on precursors and their vertical concentration gradient, ozone fluxes will change with height (flux divergence). Any conclusions about the downward-upward distribution of fluxes need to be considered within that context.

## 4. Summary and Conclusions

[15] Ozone fluxes over the polar snow at Summit are small compared to the body of data from midlatitude sites with seasonal snow cover. Springtime ozone  $v_d$  were  $\leq 0.01$   $\text{cm s}^{-1}$ , and summertime ozone  $v_d$  fell within the range of  $-0.05$  to  $0.07$   $\text{cm s}^{-1}$ . Ozone fluxes displayed a diurnal and seasonal variability that appears to be determined by the solar irradiance cycle. For modeling of ozone surface uptake in snow-covered polar regions, we recommend consideration of these lower values, as well as the observed ozone  $v_d$  diurnal and season variability, rather than

using a constant  $v_d$  description as is currently done in most atmosphere-climate models.

[16] The combination of snowpack emissions of reactive trace gases, solar irradiance, and reduced turbulence, causes situations with ozone production above the snow surface and upward fluxes. In order to achieve a more quantitative assessment of the ozone budget and fluxes into and out of the polar surface layer, new experiments are needed with, preferably, concurrent multiple height concentration and ozone flux measurements, mixed boundary-layer mixing height observations, measurements of ozone snowpack reactants (e.g., nitrogen oxides, halogens, organic species), and input of these data in a surface exchange–atmospheric chemistry model.

[17] Concentrations of inorganic and organic trace constituents are typically higher in midlatitude, seasonal snow than in the year-round snow in the remote polar regions. Recent research has also shown that gas exchange between the soil and the snowpack can result in much higher interstitial trace gas levels than present in polar snow, e.g., up to 25 ppbv of  $\text{NO}_x$  have been reported at a Rocky Mountain site [Helmig et al., 2009]. As this research has shown that ozone fluxes are dependent on snow photochemistry, most likely involving secondary snow constituents, these large differences in snow chemical impurities and interstitial gas concentrations point towards different controls and magnitude of ozone exchanges in these different environments. These findings provide some new arguments for interpreting the high variability, and reports of upward ozone fluxes in the literature. It is becoming increasingly evident that ozone fluxes over snow depend on a myriad of parameters. Consequently, this research suggests to explicitly differentiating ozone exchange processes depending on snow chemical and physical properties, snowpack depth, and type of substrate underneath the snow, and further experimental work is needed for better quantification of these dependencies.

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