Ozone depletion in the interstitial air of the seasonal snowpack in northern Japan

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ABSTRACT

To examine the behaviour of ozone (O_3) in the seasonal snowpack, measurements were taken of O_3 and CO_2 in the interstitial air on Rishiri Island, which is located in northern Japan, during the 2010/11 winter season. Exhibiting variation on timescales ranging from several minutes to several days, the atmospheric O_3 in the surface air generally increased from December (38 ppb) to April (52 ppb). The ozone mixing ratio sharply decreased below the snow surface. Whereas the CO_2 data in the interstitial air indicated that a rapid exchange between the snow and the atmosphere occurred intermittently, the O_3 mixing ratio remained low and constant (< 5 ppb) in the snowpack interior. The vertical profile of the O_3 mixing ratio indicates that the e-folding lifetime of the O_3 loss reaction was 5.0 ± 2.3 minutes during the day and 10.0 ± 6.3 minutes at night, suggesting photochemical O_3 depletion occurred during the daytime. Kinetic experiments using ambient (maritime) air and snow indicate that the photochemical O_3 loss is proportional to the solar radiation and that the O_3 loss rate decreases as dawn approaches during the night. The result of the kinetic experiments using artificial O_3 in the pure air and snow suggests the important role of gaseous species in the ambient air towards O_3 depletion.

Keywords: ozone, carbon dioxide, snowpack, photochemical reaction

To access the supplementary material to this article, please see Supplementary files under 'Article Tools'.

1. Introduction

Recent studies on snowpack processes and atmosphere-snow gas exchange have revealed their substantial impact on the chemical composition of the lower troposphere (Dominé and Shepson, 2002; Grannas et al., 2007; Helmig et al., 2007a). One notable scientific issue in this field is the periodic ozone (O_3) depletion events occurring during polar sunrise, which were initially reported in the 1980s. Studies on the rapid and episodic removal of O_3 in coastal regions have highlighted the role of halogen photochemistry in affecting polar atmospheric chemistry (Barrie et al., 1988; Oltmans et al., 1989; Fan and Jacob, 1992). Since then, extensive research into O_3 depletion events has been performed, such as how and to what extent reactive Br is

produced during sea-ice formation and from sea-salt deposition on ice (see, e.g., Simpson et al., 2007).

In areas far from the coast, other interesting chemical reactions are also found in the snowpack, such as photo-denitrification processes affecting levels of oxidised nitrogen species and HONO in the interstitial air and surface layer (Honrath et al., 1999). This raised the question of how active nitrogen oxide chemistry in the snowpack affects the loss or production of O_3 in the snowpack and overlying atmosphere (Grannas et al., 2007). Peterson and Honrath (2001) found that at Summit, in Greenland (72°34′N, 38°29′W, 3212 m asl), the reactions with NO and NO_2 can only account for 6% of the observed O_3 loss rate; they suggested catalytic O_3 destruction by bromine explains the high rate of O_3 destruction.

Low O_3 mixing ratios in the snowpack throughout the day have been reported at Alert, Canada (82°32′N, 62°43′W, 10 m asl; Albert et al., 2002), and Barrow, USA (71°19′N, 156°40′W, 8 m asl; Helmig et al., 2012). In describing the role of the photochemical process of O_3

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destruction, Albert et al. (2002) discussed a dark destruction mechanism that involved catalytic removal by black carbon and reactions with humic and fulvic acids. At Summit, up to 90% of the atmospheric O_3 was preserved in the bulk of the snowpack under low irradiance levels, and the O_3 loss rates increased significantly with increasing solar irradiance (Helmig et al., 2007b). Bocquet et al. (2007) investigated the O_3 mixing ratio of interstitial air in the seasonal snowpack at a subalpine forest site at Niwot Ridge, USA (40°02′N, 105°33′W, 3050 m asl), during January–June 2004. They reported decreases in the O_3 mixing ratio to less than 10% of the ambient air levels (15–80 ppb) within the first 10–20 cm beneath the surface. This pattern appeared to be independent of solar radiation cycles.

During the 2007 winter season, we found a negative correlation between atmospheric O_3 and CO_2 on Rishiri Island, Japan, on time scales ranging from several minutes to a few days (Inoue et al., 2008). It is known that at high latitudes and altitudes, CO_2 emissions from soils during periods of snow cover are an important component of an ecosystem's carbon budget. Emissions during the snow-covered period can account for as much as 10–50% of total annual soil respiration (Schindlbacher et al., 2007, and references therein). Helmig et al. (2007a), who reviewed studies on the dry deposition of O_3 in snow-covered areas, reported that most studies found O_3 deposition onto the snow surface, and only a few reported an efflux of O_3 from the snow surface. On Rishiri Island, the negative correlation between atmospheric O_3 and CO_2 suggests the occurrence of dry deposition of O_3 together with emissions of CO_2 produced by soil respiration, in addition to the effect of anthropogenic pollutants.

However, the chemical reactions leading to O_3 depletion in the interstitial air of the seasonal snowpack at mid-latitudes under daytime and nighttime conditions are not well understood. Comparing data obtained at mid-latitudes with results from high latitudes and altitudes will allow us to examine the processes involved in the loss of O_3 and in the snowpack-air gas exchange. In this study, measurements were taken of the O_3 and CO_2 in the interstitial air of the seasonal snowpack on Rishiri Island, at the northern tip of Japan, during the period from December 2010 to April 2011. We assumed that CO_2 is a conservative tracer, and we therefore used CO_2 measurements to evaluate O_3 losses due to chemical reactions in the interstitial air. In addition, chemical kinetic experiments were conducted to investigate the O_3 loss processes in Sapporo and on Rishiri Island during the 2010/11 winter season. We will discuss the O_3 loss in the seasonal snowpack during the day and at night based on our observations and the chemical kinetic experiments.

2. Observations

2.1. Site

We installed a system for measuring O_3 and CO_2 in the interstitial air of the snowpack and overlying air at the Rishiri Observatory (RIO; 45°07′N, 141°12′E, 40 m asl) on Rishiri Island (Fig. 1). The island has an area of 182 km^2, and at the centre is Mt. Rishiri (1721 m), a Quaternary stratovolcano. Approximately 5500 residents live in the few principal districts on the island. The RIO is situated on a slightly sloped area at the southern foot of Mt. Rishiri, 400 m away from the main road. Approximately 750 residents live in the coastal area, 2 km from the observatory. In the lower region of the volcanic slope there is a deciduous broadleaf forest, whereas in the upper area, conifers such as Yezo spruce (*Picea jezoensis*) and Todo fir (*Picea glehnii*) dominate (Haruki et al., 2004). On the gentle slope above the main road, Todo firs are present, having been planted 40 yr earlier; the canopy height is 3–4 m at present. The floor vegetation is mostly evergreen Sasa bamboo (*Sasa senanensis*, *Sasa kurilensis*). A tower (200 cm high) for measuring O_3 and CO_2 in the interstitial air of the seasonal snowpack was built in an open space approximately 5 m south of the RIO.

2.2. Atmospheric O_3 and CO_2

The analytical methods used herein have been reported in earlier publications (Tanimoto et al., 2000; Inoue et al., 2008; Inoue and Zhu, 2013); therefore, only a short description is provided here. We mounted an air intake 1.5 m above the roof of the observatory (5 m above the ground). Using a blower, air samples were drawn from the intake to a Pyrex glass manifold in the observatory through a Teflon tube (25 mm o.d., 22 mm i.d.). Sample air for the measurement of atmospheric O_3 was continuously pumped at a rate of 2 dm^3 min^{-1} through a 6.35 mm Teflon tube connected to the glass manifold.

Atmospheric O_3 was measured using a UV absorption analyser (O_3 analyser, Model 1015, Dylec Inc., Ibaraki, Japan). The output voltage was digitised via an analogue-to-digital control unit (FA-M3R, Yokogawa Electric Corp., Tokyo, Japan). The O_3 analyser was calibrated prior to its usage at the RIO using an O_3 primary standard (49PS, Thermo Fisher Scientific, Inc., Georgia, USA). The detection limit of the O_3 measurement was 1 ppb, and the overall uncertainty was estimated to be 5% at a mixing ratio of 20 ppb (Tanimoto et al., 2000).

Atmospheric CO_2 was measured using a non-dispersive infrared gas (NDIR) analyser (LI 6262, LI-COR Inc., Nebraska, USA), a sampling unit and four working reference gases (Supplementary files).
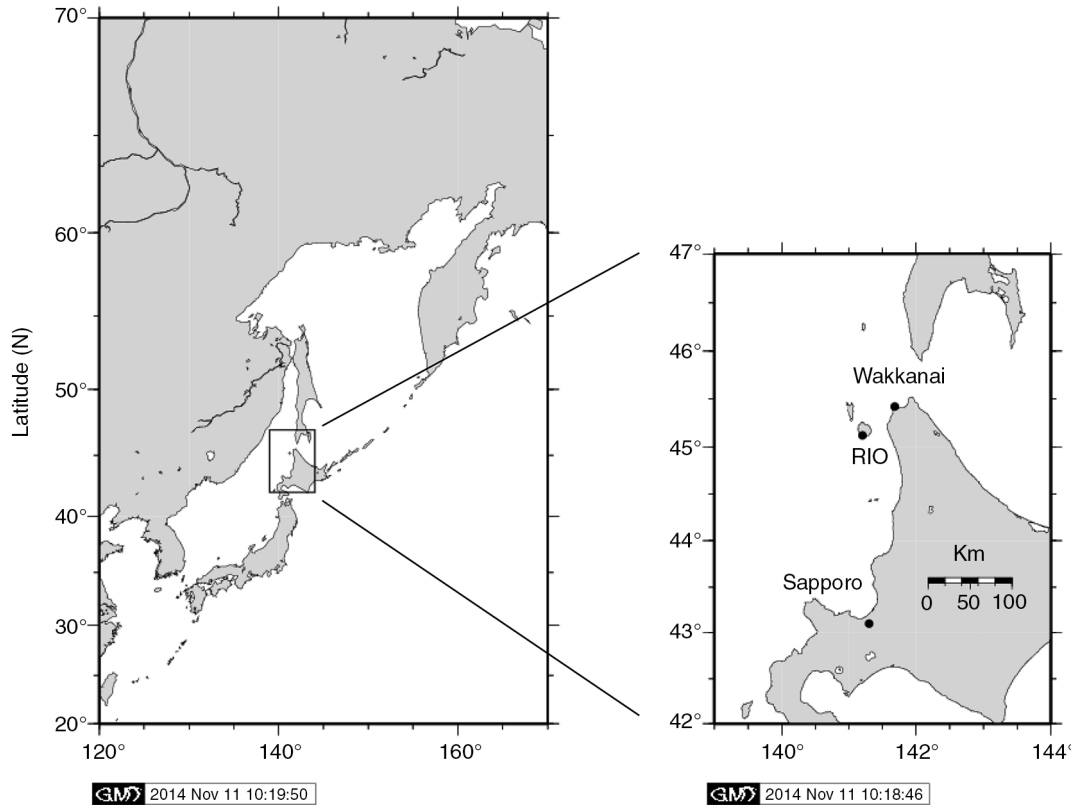
Fig. 1. The observation site for measurements of O_3 and CO_2 mixing ratios in the interstitial air of the seasonal snowpack on Rishiri Island (RIO). Chemical kinetic experiments were conducted at the RIO and on the campus of Hokkaido University, Sapporo.

2.3. O_3 and CO_2 in the interstitial air of the seasonal snowpack

A tower with horizontal bars (Seok et al., 2009) was installed in the middle of December 2010, prior to snow accumulation. Figure 2 shows a schematic diagram representing the system for taking measurements of the O_3 and CO_2 in the interstitial air at five heights (10, 30, 60, 90, 120 cm) above the ground. Except for the inlet 5 m above the ground (Section 2.2), the adjacent horizontal bars were fixed by alternating them 90° each time. A filter consisting
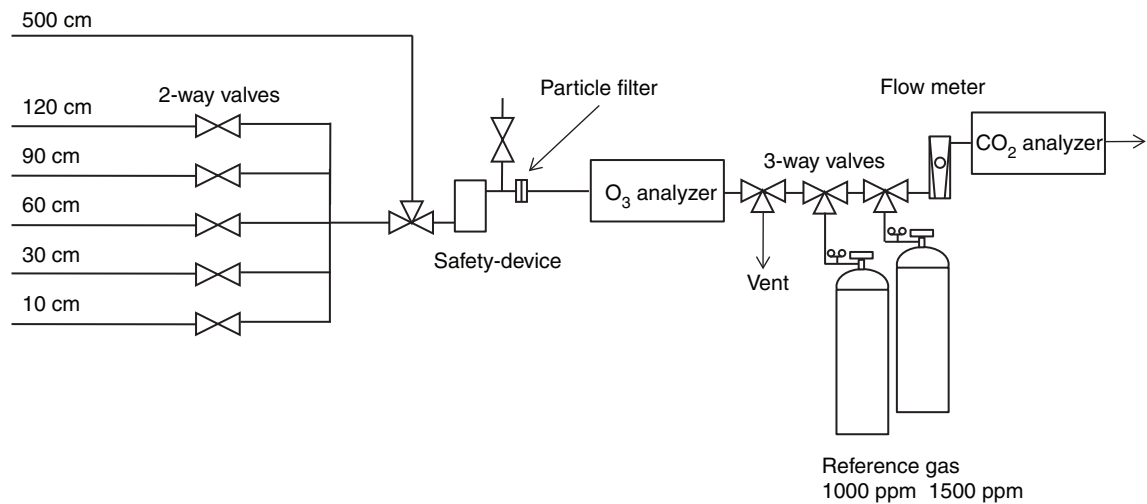

Fig. 2. A schematic diagram of the system used for taking the measurements of the O_3 and CO_2 mixing ratios in the interstitial air of the seasonal snowpack on Rishiri Island during the winter of 2010/11.

of hydrophobic polytetrafluoroethylene (diameter 25 mm, pore size 0.2 μm, PTFE) (Acropak, Pall Corp., Michigan, USA) was fitted at each end of the horizontal bar. Gas analysers and a data acquisition unit were located in an experimental room at the RIO. Sample air at heights between 120 and 0 cm was introduced into the O_3 analyser (1015, Dylec) using a small internal pump and, sequentially, into the CO_2 probe (GMP343, Vaisala, Helsinki, Finland) through the 6.35 mm Teflon tube (10 m in length), which flowed at a rate of 2 dm^3 min^{-1} for 5 minutes every 2 hours. It is desirable to analyse the O_3 and CO_2 mixing ratios from small volumes of sample air because drawing interstitial air from within the snowpack disturbs the natural transport of air in the snowpack. We sampled approximately 10 dm^3 of interstitial air from the paired inlets for our measurements. The mean flow rate was expected to be 1 dm^3 min^{-1} for each inlet, thus 5 dm^3 of interstitial air was sampled for each inlet. Assuming a spherical volume and a snow density of 300 kg m^{-3}, the affected radius surrounding each inlet is approximately 12 cm. There is no overlap within this radius because all of the sampling inlets were at least 60 cm apart. Bowling et al. (2009) estimated the time required for the re-establishment of the CO_2 gradient using the equation $t = d^2/4D_C$. The diffusion time t for a given distance d has a relationship with the diffusion coefficient of CO_2 in the snowpack D_C. According to our estimation of D_C (0.063–0.114 cm^2 s^{-1}) and calculation of the diffusion distance d (the sampling diameter, 24 cm), the diffusion time t was 38 minutes (Zhu et al., 2014), which is shorter than our sampling interval of 120 minutes. The output voltage of the analysers remained comparatively constant during the 5 minutes interval, except for the CO_2 measurements in the first 1–2 minutes following a change in sampling height. These observations indicate that the O_3 and CO_2 mixing ratios used in this study were representative for the given inlet height. During the remaining time when measurements between 10 and 120 cm above the ground were not being taken (95 minutes), sample air from a height of 5 m was introduced into the analysers.

Although we attached a hydrophobic Teflon filter to each inlet, we were afraid that meltwater would penetrate farther into the automated system than expected. Therefore, we installed a safety device (Fig. 2) in order to prevent the system from being damaged by meltwater. When air in the experimental room was introduced into the CO_2 and O_3 analysers by opening the two-way valve between the safety device and the particle filter, the analysers were not affected because the interstitial air flow had been stopped.

2.4. Ancillary data

The temperature was measured at five heights (10, 30, 60, 90, 120 cm) above the ground and at 0 and 10 cm below the soil surface using type-T thermocouples and recorded on a data logger (GL220, Graphtec Corp., Yokohama, Japan) at 5-minute intervals from December 2010 to April 2011. In early April, temperatures from 2 to 6°C were recorded below 30 cm in the seasonal snowpack (O_3 data showed that air intakes at 10 and 30 cm were within the snowpack). These temperature data were omitted. Every 3 hours pictures were taken of the snow scale, standing approximately 3 m from the snow tower, and the snow depth was determined. The snow depth at the inlets seemed to be a few centimetres thicker than that at the snow scale. However, in this work, we will report the snow depth determined by the snow scale. The snowpack development during the 2010/11 winter season was slightly less than that during 2009/10, in which the maximum snow depth reached up to 125 cm and was significantly thinner than that in 2011/12 (200 cm).

Meteorological data were obtained at the weather observatories in Kutsukata (42°25′N, 141°41′E, 14 m asl) on Rishiri Island, Wakkanai (45°25′N, 141°41′E, 2.8 m asl), and Sapporo (43°04′N, 141°20′E, 17.5 m asl). Our observation site within the campus of Hokkaido University (HU) is located 2 km away from the weather station in Sapporo and approximately 15 km from the coast. In Sapporo, prevailing winds blew from the northwest during the winter season (Monthly Report of JMA, 2013), implying a maritime air origin.

Atmospheric NO and NO_2 have been monitored at the N19 station approximately 1.2 km north from the main building of the Graduate School of Environmental Science (GSES), Hokkaido University. Hourly data of the atmospheric NO and NO_2 were used in this work.

2.5. O_3 loss experiment in an acryl vessel

To investigate the O_3 depletion within the snow, chemical kinetic experiments were conducted during the 2010/11 and 2011/12 winter season using an acryl-cylindrical snow chamber (inner diameter 13.4 cm, length 31 cm, volume 4.4 dm^3) with flanges (outer diameter 20 cm) at both ends. Plastic nuts and bolts secured the flange on each end of the acryl chamber to flanges of the same size on the ends of the Teflon tubes (outer diameter 6.5 mm). A silicone rubber O-ring coated with Teflon (inner diameter, 15 cm; cord diameter, 5 mm) was installed between the surfaces of each pair of flanges as a seal to prevent sample air from escaping. Before the experiment, the inside of the chamber was flushed with filtered ambient air (0.2 μm), while the O_3 mixing ratio was continuously monitored by the O_3 analyser (Dylec 1050) installed in an experimental room. By passing the filtered ambient air through the chamber for at least several hours, we examined the O_3 destruction in the chamber without snow. The O_3 mixing ratio decreased

by 2 ± 2 ppb after passing through the acryl chamber. Taking into account the variability in the O_3 loss for the blank experiment, we discuss only the variations that were larger than 10% for the O_3 mixing ratio in the ambient air in this work.

Following the instructions of the Japanese Society of Snow and Ice (Matoba, 2010), we have collected snow samples from the experimental field to conduct O_3 loss experiments. After putting on polyethylene gloves, snow samples were collected from a snow pit wall using a Teflon tool and carefully placed in the acryl cylinder. In this kinetic experiment, we used snow from at least a few days after the snowfall. A few meters away from the RIO and from the main building of the GSES (43°04′N, 141.21′E, 19 m asl), HU, we mounted two air intakes attached to the hydrophobic PTFE filter, both at 100 cm above the snow surface. Ambient air or sample air (via the acryl chamber) was introduced into the O_3 analyser at a flow rate of $2\ dm^3\ min^{-1}$ through a Teflon tube (outer diameter 6.35 mm) alternately from each inlet. The acryl chamber was placed in a snow pit prepared in a shaded area of the GSES building. The total length of the Teflon tube was the same for both the ambient air and the sample air via the acryl chamber (5.5 m). Using a snow density of 322 kg m^{-3} in the acryl chamber measured before the kinetic experiment during 15–19 March 2011 (Section 3.3), the residence time of the sample air in the chamber was estimated to be 1.6 minutes.

Ozone in pure dry air, produced by an O_3 generator which uses irradiation with 185-nm UV light from a low-pressure mercury lamp (Hamamatsu Photonics K. K.,

Hamamatsu, Japan) and pure air from a gas cylinder ($CO_2 < 50$ ppb, $CO < 20$ ppb, $CH_4 < 20$ ppb, $NO_x < 10$ ppb, $SO_2 < 5$ ppb, dew point $\leq 80°C$, Nissan Tanaka, Saitama, Japan), was used to examine the effects of natural gases/aerosols on the O_3 loss in the acryl chamber. Pure dry air in the gas cylinder was introduced into the O_3 generator at a flow rate of 2.5 dm^3 min^{-1}, and an aliquot of air (2 dm^3 min^{-1}) was pumped into the O_3 analyser, either directly or through the snow in the acryl chamber. A portion of air (0.5 dm^3 min^{-1}) was vented off through a column packed with granular charcoal. The acryl chamber was placed in the snow pit near the GSES.

3. Results and discussion

3.1. Snow depth and temperature

During the 2010/11 winter season, a snowpack at the RIO developed rapidly in early January and remained relatively constant until the middle of March, except for an addition in late February (Fig. 3). The seasonal snow cover reached its maximum in late February with a depth of 105 cm. After the middle of March, the snow depth decreased rapidly and the snow had melted completely by the middle of April.

During the period of snow cover, the daily mean air temperature (120 cm) was $-1.8°C$, with a minimum of $-11.3°C$ on 7 January and a maximum of 6.9°C on 6 April. The mean air temperature was 4.3°C during the rapid melting of snow in early April. Within the bulk of the snow, the temperature remained constant (approximately 0°C) except in early January. After the rapid accumulation
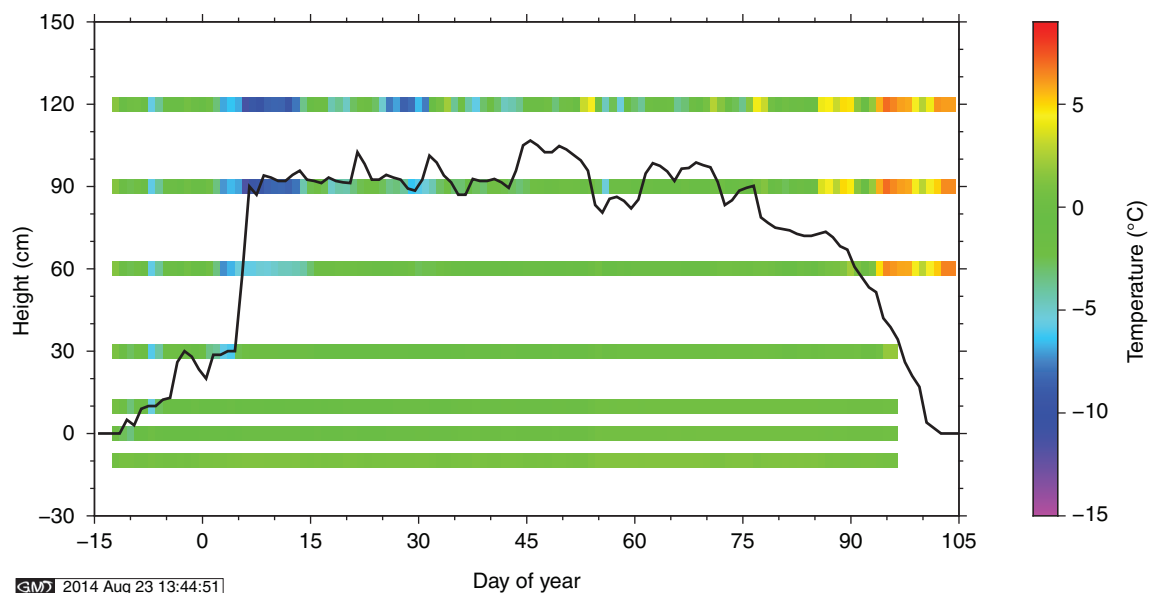

Fig. 3. A colour plot of the temperatures at -10, 0, 10, 30, 60, 90 and 120 cm above the ground. The solid line shows the snow depth and the horizontal axis the days of the year in 2011. Negative values indicate days prior to 1 January 2011.

of snow during 7–15 January, the temperature at 60 and 90 cm above the ground ranged from -9.6 to $-4.2°C$. Over the same period, the temperature at the soil surface was close to $0°C$ because of the thermal insulation of the snowpack.

3.2. O_3 mixing ratio in the interstitial air

Figure 4 illustrates the temporal variations in O_3 in and above the seasonal snowpack at the RIO during the period from December 2010 to April 2011. The atmospheric O_3 at 5 m above the ground increased from December (38 ppb) to April (52 ppb) while showing variation on time scales that corresponded to synoptic scale phenomena (Zhu et al., 2012). Within the bulk of the snow, the O_3 mixing ratio was continuously low ($<10\%$ of the ambient air) throughout the day, a pattern that is the same as that found in the seasonal snowpack at Alert (Albert et al., 2002) and Niwot Ridge (Bocquet et al., 2007), but different from that at Summit (Helmig et al., 2007a).

In the interior of the seasonal snowpack, the CO_2 mixing ratio generally decreased along with distance from the

ground and varied largely from day to day (Fig. 5). Because snow acts as a thermal insulator for soil due to the large amount of interstitial air, the soil temperature remained relatively high compared with that of the overlying air. Water is continuously supplied from snow melting at the soil surface. Environments of subnival soil allow micro-organisms to produce CO_2 through the mineralisation of organic matter beneath the snow cover. As discussed by Zhu et al. (2014), a significant decrease in the CO_2 mixing ratio occurred intermittently, which indicates exchanges of air in the snowpack with the overlying air. For example, the CO_2 mixing ratio at 30 cm above the ground decreased to a level lower than 500 ppm from 1000 ppm in the afternoon of 6 February 2011. During this period, the O_3 mixing ratio in the snow interior remained constant (Fig. 4).

To investigate the diurnal variation below the snow surface, the O_3 mixing ratio during the period from 15 January to 14 February 2011, in which the snow depth remained relatively constant (93 cm), was plotted against the local time ($=$ Japan Standard Time, JST) in Fig. 6. Between 15 January and 14 February, the O_3 mixing ratio in the snowpack between 10 and 60 cm above ground level
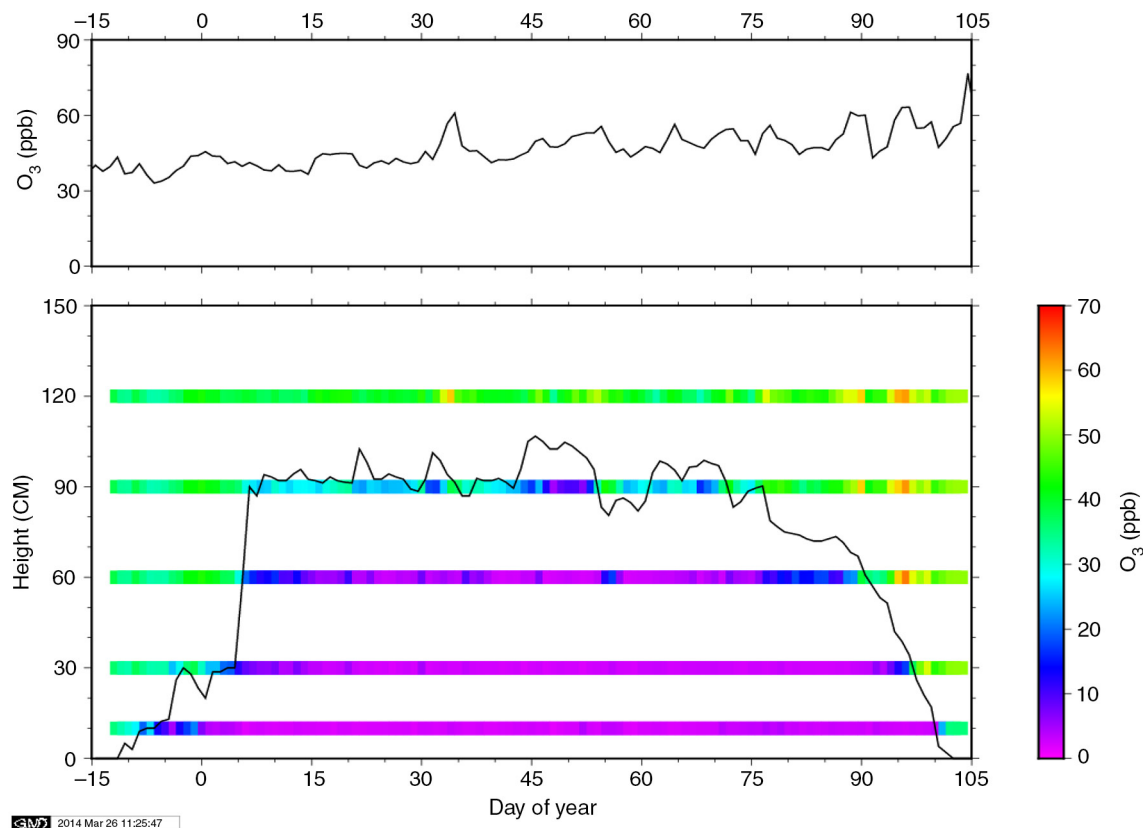

Fig. 4. A colour plot of the O_3 mixing ratio at 10, 30, 60, 90 and 120 cm above the ground (lower panel) and 500 cm above the ground (upper panel). In the lower panel, the solid line shows the snow depth and the horizontal axis the day of the year in 2011. Negative values indicate days prior to 1 January 2011.
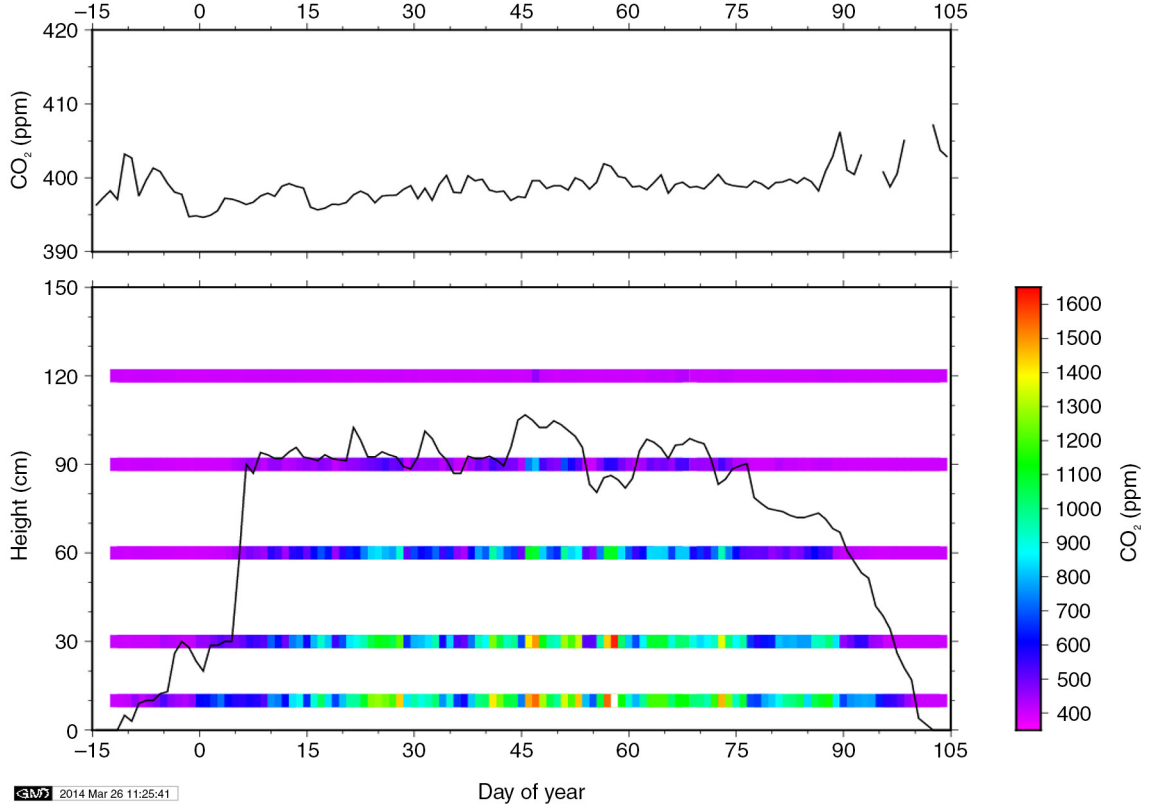
Fig. 5. A similar plot as that in Fig. 4 except for the CO_2 mixing ratio.

remained constant and low. At 90 cm above ground, a few centimetres below the snow surface, O_3 mixing ratio varied slightly, reaching its maximum during the night and minimum in the day; this pattern differs from that at 120 cm.
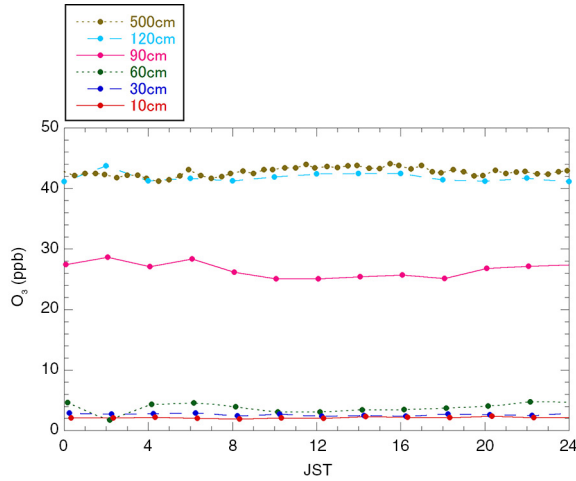

Fig. 6. Diurnal variations in the O_3 mixing ratio in the interstitial air of the seasonal snowpack and overlying air on Rishiri Island. Solid circles at each height show the median value of 5-minute averages during the period from 15 January to 14 February 2011.

Figure 7 illustrates the relationship between O_3 and CO_2 in the interstitial air during the period 18–23 February, a few days after the rapid accumulation of snow. During this period, the snow depth (103 cm) was relatively constant and thicker than 90 cm. In the snowpack, CO_2 can be assumed to be conserved and controlled by simple physical mixing in the snowpack. Therefore, we can calculate the fraction of ambient air relative to the total volume of interstitial air by using CO_2 data measured at 10 and 120 cm above the ground [eqs. (1) and (2)].

$$f_{amb} + f_{10cm} = 1 \qquad (1)$$
$$f_{amb} \times C_{amb} + f_{10cm} \times C_{10cm} = C_i \qquad (2)$$

where f_{amb} is the fraction of ambient air at 120 cm above the ground relative to the total volume of interstitial air and f_{10cm} is the fraction of air at 10 cm above the ground. C_{amb} and C_{10cm} are the CO_2 mixing ratios at 120 and 10 cm above the ground, respectively, and C_i is the mixing ratio of CO_2 at i cm above the ground. If O_3 is conserved in the interstitial air, then f_{amb} calculated by using O_3 data should be the same as that calculated by using the CO_2 data, and a straight line should connect the two measurement points at 10 and 120 cm (solid line in Fig. 7). The O_3 data plotted below the conservative mixing line (dotted line) indicate the removal of O_3 in the interstitial air. It is clear that O_3
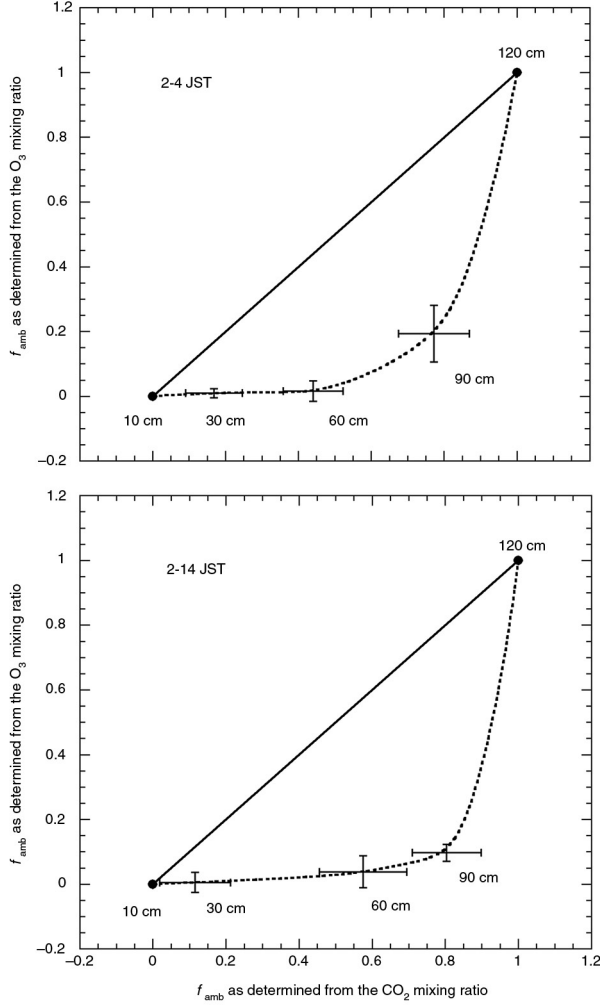
Fig. 7. The mean fraction of ambient air to the total volume of interstitial air (f_{amb}, fraction of snowpack air derived from ambient air) as determined from the O_3 mixing ratio in relation to the mean fraction as determined from the CO_2 mixing ratio at 2–4 JST (top) and 12–14 JST (bottom) during the period from 18–23 February 2011. The error bar at each height shows the standard deviation of the mean.

decreases sharply close to the surface. Whereas the fraction (expressed as percent) of ambient air (as determined from the CO_2 mixing ratio) was approximately 80% at 90 cm, the O_3 level reached approximately 10% around noon (12–14 JST) and 20% before dawn (2–4 JST). Both during the day and at night, the O_3 mixing ratio in the interstitial air significantly dropped compared with the single mixing line, suggesting several processes for the depletion of O_3 in the interstitial air – O_3 loss by photochemical reactions, as well as chemical reactions in the seasonal snowpack at night.

3.3. O_3 loss rate

Figure 8 illustrates the vertical profiles of O_3 loss expressed as a ratio (%) of the O_3 mixing ratio between the interstitial
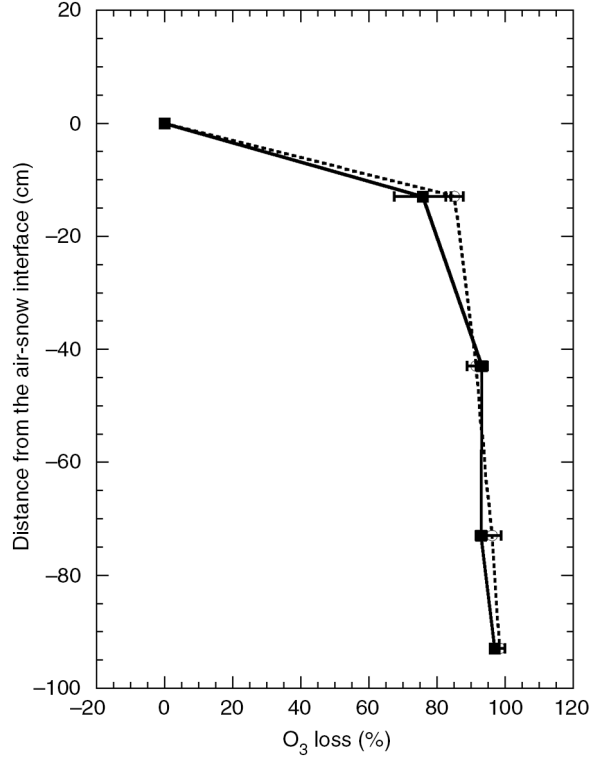

Fig. 8. O_3 depletion in the seasonal snowpack relative to the O_3 mixing ratio in the ambient air above the snow surface from 18 February to 23 February 2011. The atmospheric O_3 mixing ratio at 120 cm was assumed to be equal to that at the snow surface (0 cm). The dotted line with open circles shows O_3 depletion during the day (12–14 JST), and the solid line with solid squares at night (2–4 JST).

air and surface air during 18–23 February 2011, as the aforementioned O_3 data are suggestive of rapid O_3 loss during the downward transport of ambient air by diffusion. Assuming a one-dimensional diffusive flux and that O_3 reaction is a first-order loss process, variations in the O_3 mixing ratio in the interstitial air can be written as follows:

$$\frac{d[O_3]}{dt} = \frac{d}{dz}\left(W_P K_{eff}\frac{d[O_3]}{dz}\right) - k[O_3] \qquad (3)$$

where $[O_3]$ represents the O_3 concentration (mol m^{-3}) in the interstitial air, z represents the depth (m) from the snow surface, k is the rate constant (s^{-1}), W_p is the correction factor for wind pumping and K_{eff} is the effective diffusion constant (m^2 s^{-1}) of O_3 through the snowpack. We estimated K_{eff} for the O_3 molecule at the RIO site using eq. (4), which was used for CO_2 molecules through the snowpack (Sullivan et al., 2008; Zhu et al., 2014),

$$K_{eff} = \theta\tau D_{O_3}\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)^{1.823} \qquad (4)$$

where θ is the snowpack porosity (estimated as $1 - \rho_{snow}/\rho_{ice}$, ρ_{snow} for the snow density and ρ_{ice} for the ice density, 973 kg m^{-3}) and τ is the snowpack tortuosity (estimated as $\theta^{1/3}$). In this work, we used the bulk snow density (290 kg m^{-3}) to evaluate the snowpack porosity and the tortuosity was measured at the RIO on 23 February 2014. D_{O_3} is the diffusion coefficient for O_3 in the air at a standard temperature (T_0, K) and pressure (P_0, hPa). T is the temperature in the snowpack, and P is the barometric pressure. The diffusion coefficient for O_3 in the air was estimated to be 0.11×10^{-4} m^2 s^{-1} at 273.15 K and 1013 hPa, using an equation by Laisk et al. (1989).

A number of studies have indicated a possibly large potential error when trace gas flux through the snowpack is estimated using molecular diffusion because this method does not include the effect of wind pumping (Seok et al., 2009; Zhu et al., 2014). Seok et al. (2009) examined the relationship between the CO_2 flux and wind speed, and reported that the actual gas fluxes were most likely 57% higher than the fluxes calculated by Fick's first law of diffusion. During the snow season, Zhu et al. (2014) estimated that the actual CO_2 flux was approximately 48% larger than the flux calculated by the diffusion method on Rishiri Island over the same period of the present observation. If the wind pumping effect can be expressed by multiplying a factor W_p by the flux based on the diffusion method, variations in the O_3 concentration can be written using eq. (3). In this work, we used a W_p of 1.48.

As a first step for understanding the time scale of the O_3 loss reaction, we applied eq. (3) to the average vertical profile of the ozone loss, meaning a constant O_3 concentration with time ($\frac{d[O_3]}{dt} = 0$). Equation (3) can be integrated as:

$$[O_3] = [O_3]_0 \exp\left(-\sqrt{\frac{k}{W_P K_{eff}}} z\right) \qquad (5)$$

where subscript 0 refers to the O_3 concentration at the snow surface. Below 43 cm from the snow surface (60 cm above the ground), O_3 did not remain long enough to evaluate the lifetime of the O_3 loss reaction. Using the values of $[O_3]/[O_3]_0$, W_p, K_{eff}, and z in eq. (5), only the O_3 loss data at 13 cm below the snow surface (90 cm above the ground) allows us to estimate the e-folding lifetime ($1/k$) of the O_3 loss reaction as 5.0 ± 2.3 minutes during the day and 10.0 ± 6.3 minutes at night. Albert et al. (2002) performed a chemical kinetic experiment involving ambient air flowing at a rate of 2 dm^3 min^{-1} through a quartz cylindrical chamber (23.5 dm^3). At Alert, the e-folding lifetime of O_3 was estimated to be 18 minutes under irradiated conditions and 55 minutes under dark conditions. To examine the O_3 loss rate near the snow surface, it is necessary to measure the O_3 mixing ratio at intervals of a few

centimetres without disturbing the interstitial air near the surface.

3.4. O_3 loss in an acryl chamber

To investigate the reactions taking place in the seasonal snowpack, we conducted chemical kinetic experiments using the acryl chamber at the Sapporo and Rishiri localities. Figure 9 shows an example of the time series for the O_3 mixing ratio in the ambient air at Sapporo and the O_3 loss (R_{O_3}), defined by the ratio of the O_3 mixing ratio before the inlet (O_3^{in}) of the acryl chamber and the O_3 decrease between the inlet and outlet ($O_3^{in} - O_3^{out}$):

$$R_{O_3} = \left(\frac{O_3^{in} - O_3^{out}}{O_3^{in}}\right) \times 100 \qquad (6)$$

During the period 15–19 March 2011, the atmospheric O_3 mixing ratio ranged from 8 to 65 ppb with a mean value of 40 ppb (Fig. 9). The R_{O_3} showed clear diurnal variation regardless of any variation in the atmospheric O_3 mixing ratio. O_3 loss began to increase significantly immediately after sunrise and reached its maximum at approximately noon. After sunset, the efficiency of O_3 loss decreased gradually and monotonically towards dawn. Except for 18 March, the atmospheric NO measured approximately 1.2 km from our observation site showed a pattern that decreased from daytime toward midnight and reached to a level lower than 5 ppb. From 18 JST to 24 JST on 18 March, increases in NO and NO_2 and decreases in O_3 occurred almost simultaneously, while R_{O_3} remained fairly constant. At the RIO, we conducted the O_3 loss experiment on 23 and 24 February 2011; rain fell in the early morning on 24 February. The O_3 loss showed a pattern (Supplementary Fig. 2) similar to that of the kinetic experiment in Sapporo from 15–19 March 2011, suggesting the photochemical reaction process occurred even at a lower solar radiation.

The experiment for which the ozone generator was used did not show any clear diurnal variation in R_{O_3}, although a small hump occurred around noon, which can probably be caused by the photochemical O_3 loss (Fig. 10). The R_{O_3} remained at a generally lower level even during daytime and nighttime, which showed a different pattern from the kinetic experiment during 15–19 March 2011. It is clear that some gaseous substance in the ambient air plays an important role in the photochemical reaction on the snow surface. The kinetic experiment shown in Fig. 10 indicates that solar radiation is sufficient to decompose the O_3 in the acryl chamber if ambient air and snow are used.

Compared with the experiments at Alert, the O_3 loss found in the kinetic experiment during 15–19 March 2011 was more rapid both during the day and at night in Sapporo, where the e-folding lifetime was calculated to be
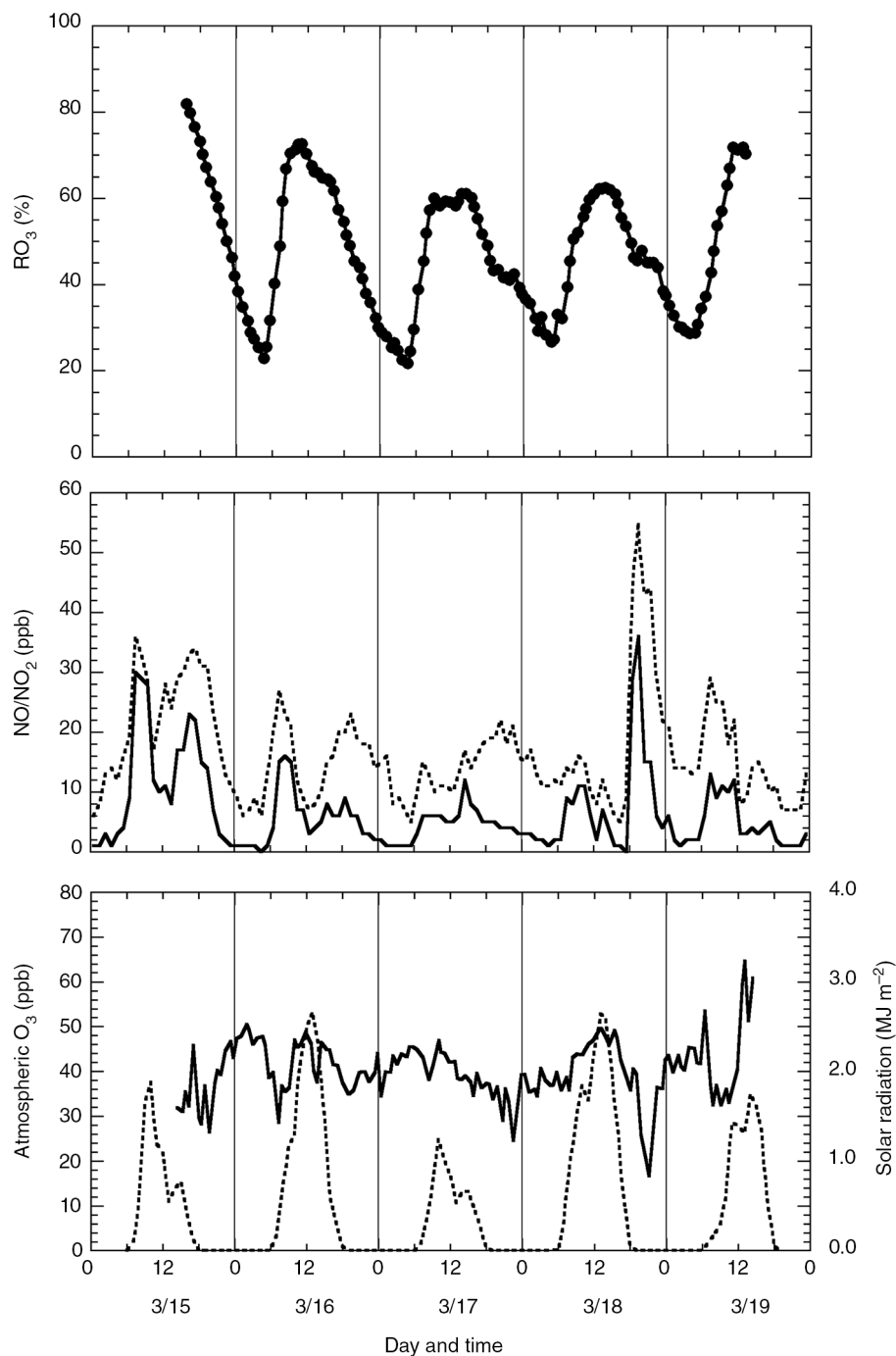
Fig. 9. Kinetic experiment of O_3 loss in the acryl chamber filled with snow during 15–19 March 2011. In the lower panel, the solid line shows the ozone mixing ratio in the filtered ambient air used for the experiment, and the dotted line shows the solar radiation at the Sapporo weather observatory, 2 km away from the experimental site at HU. In the middle panel, the solid line shows the atmospheric NO measured at the N19 station operated by Sapporo, 1.2 km away from our site, and dashed line NO_2 which was estimated by subtracting NO from NO_X. In the upper panel, the solid circles show the five-point moving averages.

1.3–1.7 minutes for the maximum ozone loss rate during the day and 4.5–7.2 minutes for the minimum ozone loss rate before dawn. The kinetic experiment gave lifetimes

shorter than those of the observations on Rishiri Island. The ratio of the surface area to the volume of the acryl chamber is larger than that of the tower observation, which
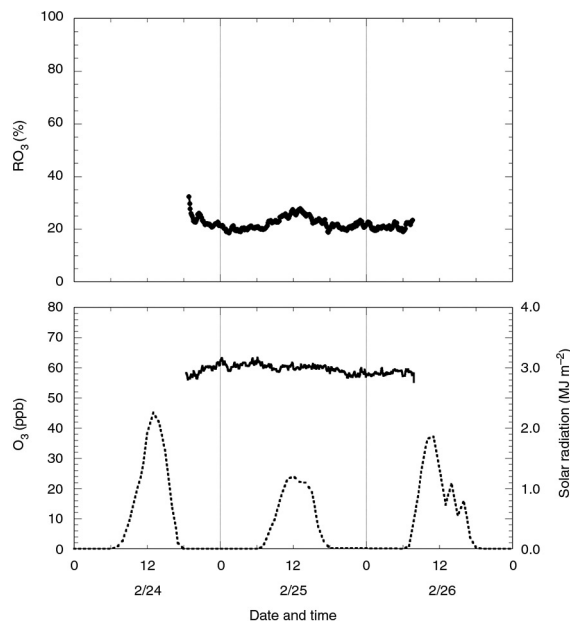
Fig. 10. Kinetic experiment of O_3 loss in the acryl chamber filled with snow during 24–26 February 2012. In the lower panel, the solid line shows the O_3 concentration produced by the O_3 generator and the pure air in the cylinder, and the dashed line the solar radiation at Sapporo weather observatory. In the upper panel, the solid circles show the five-point moving averages.

will result in rapid O_3 loss by photochemical reaction. Additionally, because we conducted the kinetic experiment in Sapporo, the concentrations of the chemical ingredients related to O_3 depletion are most likely different from those of Rishiri. Both our field observations and kinetic experiments show that even the reaction rate before dawn (at night) is higher than that of Alert under irradiated conditions.

To explain the O_3 loss during the night, Albert et al. (2002) suggested the involvement of crustal materials, black carbon emitted from anthropogenic sources, or humic and fluvic acids deposited in the snowpack. Bocquet et al. (2007) indicated the importance of NO production via nitrification and de-nitrification processes in the subnival soil during nighttime O_3 depletion in the interstitial air at Niwot Ridge.

It is clear that the reactant that is involved in the nighttime reaction was not consumed during the experiment because the nighttime reaction exhibited almost the same R_{O_3} value after sunset every day. The R_{O_3} decreased from 70 to 30% from sunset to dawn. These results indicate that the chemical substance involved in the nighttime loss decreased during the night but subsequently increased prior to the next sunset, either in the ambient air or on the snow surface in the acryl chamber. In the former case, the chemical substance must have a relatively short lifetime

(a few to several hours) that decreases with time because a chemical substance with a lifetime longer than a day would accumulate in the nocturnal boundary layer during the night; therefore, increases in R_{O_3} would be expected during the night. If chemical substances that deposit on the wet snow surface were related to the O_3 loss reaction at night, they should be in the sample air as gas (or fine particles <0.2 μm). For example, organic compounds that have hydrophilic functional groups, black carbon (<0.2 μm) and halogenated species (e.g. Br^- and I^-) produced from alkyl halides could contribute to the O_3 depletion in the seasonal snowpack at night. NO_X, which is known as an important gas for O_3 dynamics in the interstitial air (Grannas et al., 2007), increased in the ambient air during nighttime on 18 March. However, R_{O_3} did not change much, which suggests the minor role of NO_X in the O_3 depletion in the acryl chamber.

During daytime, the natural logarithm of the ratio between the O_3 mixing ratios before and after the acryl chamber correlated well with the solar radiation observed at the Sapporo weather observatory. The relationship between solar radiation and $-\log_e(O_3^{out}/O_3^{in})$ resulted in a correlation coefficient of 0.44 on 16 March ($p < 0.5$), 0.75 on 17 March ($p < 0.05$), 0.83 on 18 March ($p < 0.01$) and 0.87 on 19 March ($p < 0.05$), while the slope of the linear relationship varied day-to-day. These results suggest day-to-day variations in the chemical substances in the ambient/ interstitial air related to the photochemical O_3 loss reaction.

During the day, halogen (bromine and iodine) chemistry and NO_X are supposed to be chemical substances related to O_3 loss through a photochemical reaction. Honrath et al. (1999) reported that the NO_X ($NO + NO_2$) mixing ratio within the interstitial air of the seasonal snowpack at Summit was a factor of 3 to >10 times higher than that in ambient air. At mid-latitudes, significant increases in the NO_X mixing ratio were also observed in synthetic and ambient air passed through a sunlit chamber filled with natural or artificially created snow added to NO_3^- (Honrath et al., 2000). Laboratory and field experiments indicate that the NO_X production in snow approximates that expected from the aqueous photolysis of NO_3^-, as reviewed by Grannas et al. (2007). However, at Summit the reactions with NO and NO_2 can only account for 6% of the observed O_3 loss rate (Peterson and Honrath, 2001). Catalytic O_3 destruction by bromine was suggested to explain the high rate of O_3 destruction.

Halogen chemistry is believed to play a central role in the depletion of surface O_3 in the Arctic at polar sunrise (Barrie et al., 1988; Fan and Jacob, 1992), and a similar chemistry is anticipated at mid-latitudes (Sander and Crutzen, 1996; Vogt et al., 1996). A bromine atom released from photolysable species such as molecular bromine during daytime is

suggested to destroy ozone through a gas-phase catalytic cycle shown below:

$$O_3 + Br \rightarrow BrO + O_2 \tag{7}$$

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{8}$$

$$HOBr + h\nu \rightarrow Br + OH \tag{9}$$
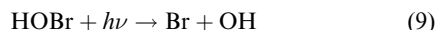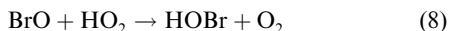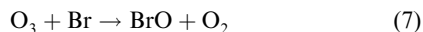
The photolysable bromine species are reportedly produced via heterogeneous reactions between gaseous molecules and a bromide ion (Br^-), which is most often derived from sea salt and is present in solution or on ice surfaces (Simpson et al., 2007). Pratt et al. (2013) investigated the photochemical production of molecular bromine in snow and ice at Barrow, which led to the bromine explosion in the interstitial air in the snowpack. In this work, the kinetic experiment was conducted using the artificial O_3 and natural snow (Fig. 10), which did not clearly show O_3 depletion in the daytime, while solar radiation was enough to cause O_3 loss through photochemical reaction(s). If the photochemical O_3 loss in our kinetic experiment using ambient air and natural snow is caused by a reaction involving bromine species, then the main source of the reactive bromine originated from the gaseous ones in the environment. On Rishiri Island, Kanaya et al. (2002) reported the mixing ratio of atmospheric alkyl iodides (CH_2I_2, CH_3I, C_2H_5I, etc.) up to the order of a few ppt in June 2001. Saiz-Lopez and Plane (2004) reported that in mid-latitudinal coastal regions I_2, most likely emitted from macro-algae during low tide, is the main source for iodine atoms. These results suggest the possible contribution of iodine chemistry [replacing Br in eqs. (7–9)] to the O_3 depletion (Simpson et al., 2007) in the seasonal snowpack in mid-latitudinal coastal regions along with bromine chemistry.

The results of the kinetic experiment suggest a lasting O_3 depletion mechanism in the natural seasonal snowpack, but at the moment we cannot quantitatively discuss the O_3 depletion mechanism during the day and at night. To examine O_3 loss processes at mid-latitudes, it is necessary to measure O_3 and some other chemical substances near the snow surface, and experiments examining the wavelength dependence of O_3 depletion or adding chemical compounds such as sodium bromide to the snow/ice, amongst others, are needed on the condition that meteorological parameters are controlled.

4. Conclusion

The O_3 mixing ratio in the interstitial air of the seasonal snowpack on Rishiri Island in the Sea of Japan decreased significantly near the surface during the study period, especially during the day. In the bulk of the snowpack, the O_3 mixing ratios remained low and constant ($<10\%$ of the ambient air) both during the day and at night, a pattern similar to that found at Alert and Niwot Ridge but different from the pattern at Summit.

The kinetic experiment conducted in Sapporo in which snow and filtered ambient air ($<0.20\ \mu m$) were used clearly showed that daytime photochemical reactions, as well as nighttime reactions, caused O_3 losses. The reaction rate at night decreased gradually and monotonically from sunset until dawn. In contrast, in the kinetic experiment in which an O_3 generator and snow were used, the O_3 loss rate was relatively low and constant both in the daytime and at night. This result suggests that gaseous species in the ambient air play an important role in the O_3 depletion in the acryl chamber. In the context of this study, we infer that the gaseous species are halogen (bromine and iodine) species produced from alkyl halides. The role of iodine species in the O_3 loss should be clarified by taking into account differences in proximity to the coast and between mid- and high-latitude sites. In addition to halogen species, organic compounds with hydrophilic functional groups and black carbon ($<0.2\ \mu m$) might contribute to nighttime O_3 losses.

Our study, which was conducted in mid-latitude coastal and seasonal snowpack areas, showed that O_3 was rapidly depleted in the interstitial air of the snowpack. This differs from results obtained in polar regions with year-round snow. The different result in mid-latitude regions might be attributable to the presence of reactive species specific to coastal regions or to anthropogenic species. Further investigations to better understand O_3 loss mechanisms in the seasonal snowpack, which are likely to be affected by a warming climate, are warranted to improve predictions of future changes in O_3 chemistry.

5. Acknowledgements

References

Albert, M. R., Grannas, A. M., Bottenheim, J. W., Shepson, P. B. and Perron, F. E. 2002. Processes and properties of snow-air transfer in the high arctic with application to interstitial ozone at Alert, Canada. *Atmos. Environ.* **36**, 2779–2787.

Barrie, L. A., Bottenheim, J. W., Rasmussen, R. A., Schnell, R. C. and Crutzen, P. J. 1988. Ozone destruction and photochemical

reactions at polar sunrise in the lower Arctic troposphere. *Nature*. **334**, 138–141.

Bocquet, F., Helmig, D. and Oltmans, S. J. 2007. Ozone in interstitial air of mid-latitude, seasonal snowpack at Niwot Ridge, Colorado. *Arct. Antarct. Alp. Res.* **39**, 375–387.

Bowling, D. R., Massman, W. J., Schaeffer, S. M., Burns, S. P., Monson, R. K. and co-authors. 2009. Biological and physical influences on the carbon isotope content of CO_2 in a subalpine forest snowpack, Niwot Ridge, Colorado. *Biogeochem.* **95**, 37–59.

Dominé, F. and Shepson, P. B. 2002. Air-snow interactions and atmospheric chemistry. *Science*. **297**, 1506–1510.

Fan, S.-M. and Jacob, D. J. 1992. Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols. *Nature*. **359**, 522–524.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C. and co-authors. 2007. An overview of snow photochemistry: evidence, mechanisms and impacts. *Atmos. Chem. Phys.* **7**, 4329–4373.

Haruki, M., Fujiwara, A., Matuda, K., Natsume, S., Yajima, T. and co-authors. 2004. Forest vegetation in Rishiri and Rebun Islands northern Hokkaido, Japan. *Rishiri Kenkyu*. **23**, 57–91. In Japanese with English abstract.

Helmig, D., Bocquet, F., Cohen, L. and Oltmans, S. J. 2007b. Ozone uptake to the polar snowpack at Summit, Greenland. *Atmos. Environ.* **41**, 5061–5076.

Helmig, D., Boylan, P., Johnson, B., Oltmans, S., Fairall, C. and co-authors. 2012. Ozone dynamics and snow-atmosphere exchanges during ozone depletion events at Barrow, Alaska. *J. Geophys. Res.* **117**, D20303.

Helmig, D., Ganzeveld, L., Butler, T. and Oltmans, S. J. 2007a. The role of ozone atmosphere-snow gas exchange on polar, boundary-layer tropospheric ozone – a review and sensitivity analysis. *Atmos. Chem. Phys.* **7**, 15–30.

Honrath, R. E., Peterson, M. C., Dziobak, M. P., Dibb, J. E., Arsenault, M. A. and co-authors. 2000. Release of NO_X from sunlight-irradiated midlatitude snow. *Geophys. Res. Lett.* **27**, 2237–2240.

Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B. and co-authors. 1999. Evidence of NO_X production within or upon ice particles in the Greenland snowpack. *Geophys. Res. Lett.* **26**, 695–698.

Inoue, H. Y., Fukazawa, Y., Tanimoto, H., Matsueda, H., Sawa, Y. and co-authors. 2008. Atmospheric CO_2 and O_3 observed on Rishiri Island from December 2006 to March 2007. *Pap. Meteorol. Geophys.* **59**, 31–38.

Inoue, H. Y. and Zhu, C. 2013. Ecosystem respiration derived from ^{222}Rn measurements on Rishiri Island, Japan. *Biogeochem.* **115**, 185–194.

Kanaya, Y., Yokouchi, Y., Matsumoto, J., Nakamura, K., Kato, S. and co-authors. 2002. Implications of iodine chemistry for daytime HO_2 levels at Rishiri Island. *Geophys. Res. Lett.* **29**, 1212.

Laisk, A., Kull, O. and Moldau, H. 1989. Ozone concentration in leaf intercellular air spaces is close to zero. *Plant Physiol.* **90**, 1163–1167.

Matoba, S. 2010. Guidebook for snowpack observation, The Japanese Society of Snow and Ice, Asakura Shoten, Tokyo, Japan, pp. 1–136 (in Japanese).

Monthly Report of JMA, 2013. Japan Meteorological Agency/ Japan Meteorological Business Support Center, Tokyo, Japan (Data are stored on CD).

Oltmans, S. J., Schnell, R. C., Sheridan, P. J., Peterson, R. E., Li, S. M. and co-authors. 1989. Seasonal surface ozone and filterable bromine relationship in the high Arctic. *Atmos. Environ.* **23**, 2431–2441.

Peterson, M. and Honrath, R. E. 2001. Observations of rapid photochemical destruction of Ozone in snowpack interstitial air. *Geophys. Res. Lett.* **28**, 511–514.

Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pöhler, D. and co-authors. 2013. Photochemical production of molecular bromine in Arctic surface snowpacks. *Nature Geosci.* **6**, 351–356.

Saiz-Lopez, A. and Plane, M. C. 2004. Novel iodine chemistry in the marine boundary layer. *Geophys. Res. Lett.* **31**, L04112.

Sander, R. and Crutzen, P. J. 1996. Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J. Geophys. Res.* **101**, 9121–9138.

Schindlbacher, A., Zechmeister-Boltenstern, S., Glatzel, G. and Jandl, R. 2007. Winter soil respiration from Austrian mountain forest. *Agr. Forest Meteorol.* **146**, 205–215.

Seok, B., Helmig, D., Williams, M. W., Liptzin, D., Chowanski, K. and co-authors. 2009. An automated system for continuous measurements of trace gas fluxes through snow: an evaluation of the gas diffusion method at a subalpine forest site, Niwot Ridge, Colorado. *Biogeochemistry*. **95**, 95–113.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P. and co-authors. 2007. Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys.* **7**, 4375–4418.

Sullivan, P. F., Welker, J. M., Arens, S. J. T. and Sveinbjörnsson, B. 2008. Continuous estimates of CO_2 efflux from arctic and boreal soils during the snow-covered season in Alaska. *J. Geophys. Res.* **113**, G04009.

Tanimoto, H., Kajii, Y., Hirokawa, J., Akimoto, H. and Minko, N. P. 2000. The atmospheric impact of boreal forest fires in far eastern Siberia on the seasonal variation of carbon monoxide: observations at Rishiri, A northern remote island in Japan. *Geophys. Res. Lett.* **27**, 4073–4076.

Vogt, R., Crutzen, P. J. and Sander, R. 1996. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature*. **383**, 327–330.

Zhu, C., Inoue, H. Y., Matsueda, H., Sawa, Y., Niwa, Y. and co-authors. 2012. Influence of Asian outflow on Rishiri Island, northernmost Japan: application of radon as a tracer for characterizing fetch regions and evaluating a global 3D model. *Atmos. Environ.* **50**, 174–181.

Zhu, C., Nakayama, M. and Inoue, H. Y. 2014. Continuous measurement of CO_2 flux through the snowpack in a dwarf bamboo ecosystem on Rishiri Island, Hokkaido, Japan. *Polar Sci.* **8**, 218–231.