Important contributions of sea-salt aerosols to atmospheric bromine cycle in the Antarctic coasts

Keiichiro Hara1, Kazuo Osada2, Masanori Yabuki3, Hisahiro Takashima1, Nicolas Theys4 & Takashi Yamanouchi5

Polar sunrise activates reactive bromine (BrOx) cycle on the Antarctic coasts. BrOx chemistry relates to depletion of O3 and Hg in polar regions. Earlier studies have indicated “blowing snow” as a source of atmospheric BrOx. However, surface O3 depletion and BrO enhancement occurs rarely under blowing snow conditions at Syowa Station, Antarctica. Therefore, trigger processes for BrOx activation other than the heterogeneous reactions on blowing snow particles must be considered. Results of this study show that enhancement of sea-salt aerosols (SSA) and heterogeneous reactions on SSA are the main key processes for atmospheric BrOx cycle activation. Blowing snow had Br− enrichment, in contrast to strong Br− depletion in SSA. In-situ aerosol measurements and satellite BrO measurements demonstrated clearly that a BrO plume appeared simultaneously in SSA enhancement near the surface. Results show that surface O3 depletion at Syowa Station occurred in aerosol enhancement because of SSA dispersion during the polar sunrise. Amounts of depleted Br− from SSA were matched well to the tropospheric vertical column density of BrO and BrOx concentrations found in earlier work. Our results indicate that SSA enhancement by strong winds engenders activation of atmospheric BrOx cycles via heterogeneous reactions on SSA.

The reactive bromine (BrOx) cycle is activated in polar regions during the polar sunrise1–3. The atmospheric BrOx cycle relates to atmospheric chemistry such as depletion of O3 (R1) and Hg, and oxidation of dimethylsulfide4,5.

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \quad \text{(R1)}
\]

Results of earlier studies have shown that BrOx origins are heterogeneous reactions (R2–3) occurring on the surfaces of blowing snow, sea-salt aerosols (SSA), frost flowers, and surface snow6–9 and subsequent photolysis of Br2 and BrCl (R4–5).

\[
\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \quad \text{(R2)}
\]

\[
\text{HOBr} + \text{Cl}^- + \text{H}^+ \rightarrow \text{BrCl} + \text{H}_2\text{O} \quad \text{(R3)}
\]

\[
\text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2\text{Cl}^- \quad \text{(R4)}
\]

\[
\text{Br}_2\text{Cl}^- \rightarrow \text{Br}_2 + \text{Cl}^- \quad \text{(R5)}
\]

Satellite measurements showed high BrO concentrations over sea-ice with the appearance of frost flowers8. Additionally, high BrOx plumes in the Antarctic coasts were found to originate from sea-ice zones2,10. Model studies presented the contribution of blowing snow as a BrOx source in polar regions1,6. The lifetime of blowing snow, however, is too short because of efficient dry deposition. Although reactions of R2 and R3 require acidity for the
release of Br$_2$ and BrCl as a trigger of the atmospheric BrO$_x$ cycle, blowing snow has higher pH. In contrast to large amounts of acidic species supplied from anthropogenic processes in the Arctic\cite{11}, the source strength of anthropogenic acidic species is less in the Antarctic Circle. Therefore, acidity/alkalinity in the surface snow with high salinity is likely to be different in Antarctica and the Arctic. To elucidate this discrepancy, we explore the origins of atmospheric BrO$_x$ based on simultaneous measurements of aerosols and blowing snow at Syowa Station, Antarctica.

**Results and Discussion**

**Short-term features of aerosol number density and BrO.** Blowing snow appeared on 27 September 2005 at Syowa under strong wind conditions (Fig. 1). Aerosol number concentrations increased concomitantly with the occurrence of blowing snow. Here, we designate ice particles with with $D_p$ (diameter) $> 10\mu m$ and particles dominantly containing sea-salts with $D_p < 10\mu m$ respectively as blowing snow particles and sea-salt aerosols (SSA). Air masses around Lützow-Holm Bay passed through the boundary layer over sea-ice during the prior 5 days (Fig. S1). Previous investigations\cite{2,6} pointed out that blowing snow acts as a source of BrO$_x$. However, satellite measurements showed that the tropospheric vertical column density of BrO (VCDBrO) was not markedly elevated on 27 September. Although some likelihood exists that cloud cover disturbed satellite BrO measurement near the surface, the surface O$_3$ concentration dropped slightly under storm conditions on 27 September. Considering that O$_3$ can be depleted by the reaction (R1) during polar sunrise, slight O$_3$ depletion implies low BrO concentration near the surface. The wind speed dropped suddenly around 00UT on 28 September 2005. Blowing snow disappeared on 28 September 2005 because of the sudden decline of the cyclone, reduction of release of blowing snow particles, and the rapid deposition of blowing snow particles. Aerosol-enhanced conditions (AECs) with higher number concentrations in fine and coarse modes and without blowing snow (i.e., Antarctic haze\cite{12}) persisted after the storm condition. Similarly, the O$_3$ concentration dropped to 13.7 ppb. VCDBrO was enhanced to the order of $10^{14}$ mole cm$^{-2}$ near Syowa. The BrO-enhanced area overlapped the area with wind speed of less than 10 m s$^{-1}$. This condition persisted until 29 September 2005. The aerosol and O$_3$ concentrations recovered simultaneously to their respective background levels on 30 September, when an air mass came from the free troposphere over the continent (Fig. S1). Background aerosol number concentrations in September were 200–300 cm$^{-3}$ in CN, 2–3 cm$^{-3}$ in $D_p > 0.3\mu m$, and 0.1–0.2 cm$^{-3}$ in $D_p > 1.0\mu m$\cite{13}. This relation suggests strongly that BrO enhancement and O$_3$ depletion are related to AECs rather than to appearance of blowing snow at the Antarctic coasts.
Chemical constituents of blowing snow and aerosols on 27–29 September 2005. Major constituents of blowing snow and aerosols in the case on 27–29 September 2005 are sea-salts (Fig. 2). Lower molar ratios of \( \text{SO}_4^{2-}/\text{Na}^+ \) by sea-salt fractionation on sea-ice\(^{14,15} \) constitute direct evidence that sea-salts in blowing snow and aerosols originated from sea-ice. The aerosol number concentrations in the storm and AECs were much higher relative to the background levels at Syowa (Fig. 1). Therefore, SSA on 28–29 September was likely released from sea-ice area through erosion of saline snow\(^{16} \) on sea-ice by strong winds and by sublimation of snow particles\(^{16–18} \).

Data show that Br\(^-\) was enriched in blowing snow, whereas Br\(^-\)/Na\(^+\) in aerosols was lower than seawater ratio (SWR), particularly in ultrafine – fine modes (Fig. 2). Br\(^-\) was depleted also from SSA in coarse mode on 28 September. Although Br\(^-\) release from sea-salts can be promoted in acidic conditions\(^1,3,19 \), pH tended to increase with conductivity corresponding to sea-salt concentrations (Fig. S2). Comparison between air mass origins and the conductivity of blowing snow samples shows no clear differences (Fig. S3) because air masses in most cases flowed over sea-ice area in Lützow-Holm Bay immediately before approaching Syowa Station. When sea-ice in the Ongul Strait was broken and flowed twice in winter 2004, Syowa Station was ca. 2 km distant from seasonal sea-ice. Although multi-year sea-ice with age of 2–3 years and thickness of 56–110 cm were present in the Ongul Strait in 2005–2006, snow on the sea-ice in the strait often high salinity because of the migration of seawater through cracks during the winter. Therefore, blowing snow particles might be released from snow on sea-ice in Lützow-Holm Bay through erosion in strong winds, as suggested by earlier work\(^16 \). Conductivity and sea-salt concentrations of blowing snow samples can be altered by mixing of snowfall particles during sampling and dilution by snowfall deposition onto the sea-ice/snow surface (before release to the atmosphere). However, it is difficult to divide pH between blowing snow particles and snowfall particles in our sampling procedures because blowing snow and snowfall occurred simultaneously in storm conditions. Because of snowfall mixing during sampling, the ambient pH of blowing snow particles is expected to be higher than the pH in blowing snow samples (Supplementary). Therefore, Br\(^-\) release might be reduced in blowing snow with higher pH comparing to SSA. By contrast, SSA have longer residence time and larger surface area relative to volumes. In general, the larger relative surface area in smaller particles can enhance heterogeneous reactions. Consequently, many BrO\(_3\) can be released from SSA through heterogeneous reactions and can be converted in the atmosphere through heterogeneous reactions (R2–5)\(^{14} \). Considering Br\(^-\) enrichment in blowing snow and strong Br\(^-\) depletion in SSA during AECs, we anticipate that SSA dispersion and then Br\(^-\) depletion in SSA through the heterogeneous reactions play important roles in the atmospheric BrO\(_3\) cycle in the case of 27–30 September 2005.

Relation between AECs and surface \( \text{O}_3 \). Satellite BrO measurements are difficult to take at Syowa during June through early September because of the low elevation angle of sunlight. Therefore, some other proxy is needed to elucidate the relation between BrO\(_3\) cycles and SSA during the polar sunrise. Considering that BrO\(_3\) destroys surface \( \text{O}_3 \) by R1, we attempt to identify BrO\(_3\) enhancement by the occurrence of low \( \text{O}_3 \) episodes (LOEs). Here, we define LOEs as cases of \( \text{O}_3 \) depletion amounts (\( \Delta \text{O}_3 \)) larger than 10 ppb relative to the background levels, except for local contamination. Although aerosol concentrations increased with the occurrence of blowing snow (Fig. 1), \( \Delta \text{O}_3 \) in the storm conditions was 5.6 ± 2.9 ppb on average. Aerosol data during the LOEs (Fig. 3) did not include data with blowing snow. Therefore, this comparison implies that LOEs occurred considerably more often in times of high aerosol concentrations (Fig. 3a). Furthermore, major aerosol constituents in ultrafine (\( D_p < 0.2 \mu m \)) – fine (\( D_p = 0.2–2.0 \mu m \)) – coarse (\( D_p > 2.0 \mu m \)) modes were sea-salts that had originated from sea-ice areas, particularly in AECs\(^{11,20} \). Therefore, LOEs and BrO enhancement at Syowa might be linked closely.
to SSA enhancement. Actually, AECs appeared in May–December (frequently in June–October) at Syowa. During the polar night, surface O3 dropped only slightly in AECs (Fig. 3b). This result is likely attributable to low BrOx concentrations in the atmosphere by reduction of the following photochemical reactions during times of less solar radiation, in spite of a large dispersion of SSA.

\[
\begin{align*}
\text{Br}_2 + \text{hv} & \rightarrow 2\text{Br} \\
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr} + \text{O}_2
\end{align*}
\]

(R6) (R7)

Data show that \(\Delta O_3\) tended to increase from early polar sunrise (July) through August. In August, the largest \(\Delta O_3\) reached 34 ppb, corresponding to nearly complete O3 depletion at Syowa. Although larger \(\Delta O_3\) continued into September, \(\Delta O_3\) began to decrease gradually after October when sea-ice starts melting off Syowa. Consequently, LOE, AEC, and BrO enhancement might occur simultaneously in July–October.

**Seasonal variation of constituents of blowing snow and aerosols.** Molar ratios of \(\text{SO}_4^{2-}/\text{Na}^+\) in blowing snow and aerosols were lower than SWR in April–October (Fig. 4) because of sea-salt fractionation on sea-ice\(^{14,15}\). Additionally, \(\text{SO}_4^{2-}/\text{Na}^+\) ratios in blowing snow matched those in aerosols well. The daily minimum of air temperature at Syowa Station dropped to temperature for mirabilite precipitation (ca. \(-8^\circ C\)) in mid-February and March. Although mirabilite is expected to be precipitated on new sea-ice in mid-February and March, high nss-\(\text{SO}_4^{2-}\) concentrations might mask evidence of \(\text{SO}_4^{2-}\) depletion in aerosols and blowing snow. Therefore, sea-salts in blowing snow and aerosols were likely to be supplied from sea-ice areas by strong winds. \(\text{Br}^-/\text{Na}^+\) ratios can be changed by (1) Br\(^-\) enrichment by sea-salt fractionation, (2) Br\(^-\) loss by heterogeneous reactions, and (3) uptake/deposition of BrO\(_x\) generated via bromine depletion in sea-salts and oxidation of short-lived bromocarbons such as CHBr3. Because mirabilite (\(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}\); below \(-8^\circ C\)) and hydrohalite (\(\text{NaCl} \cdot 2\text{H}_2\text{O}\); below \(-22^\circ C\)) are precipitated in/on sea-ice\(^{15}\), \(\text{Br}^-/\text{Na}^+\) ratios increase gradually with sea-salt fractionation. Assuming only the occurrence of mirabilite precipitation, \(\text{Br}^-/\text{Na}^+\) ratios changed from seawater ratio (0.0017) to 0.0020 (Supplementary), which was lower than the ambient ratios found for blowing snow. During our measurements, air temperature dropped to \(-37^\circ C\) at Syowa. When temperature near the snow and sea-ice surface reach to \(-25--26^\circ C\), the Br\(^-\)/Na\(^+\) ratios can elevate to 0.004–0.005 by hydrohalite precipitation (Fig. S8). This coincidence implies strongly that sea-salt fractionation engendered Br\(^-\) enrichment (high Br\(^-\)/Na\(^+\) ratios). Indeed, earlier studies\(^{21,25}\) have found substantial contributions of sea-salt bromines in the Antarctic troposphere. Uptake/deposition of BrO\(_x\) can modify Br\(^-\)/Na\(^+\) ratios in the surface snow, blowing snow, and snowfall. BrO\(_x\) concentrations were minimal in winter and increased in spring–autumn at Dumont d’Uville Station, Antarctica\(^{23}\). However, our estimation (Supplementary) showed that ambient BrO\(_x\) concentrations were too low to make an important contribution to Br\(^-\)/Na\(^+\) ratios in blowing snow. In addition, the relation between Na\(^+\) and Br\(^-\)/Na\(^+\) ratios in blowing snow and snowfall shows larger variation of Br\(^-\)/Na\(^+\) ratios in snowfall samples with lower Na\(^+\) concentrations and correlation (\(R^2 = 0.48\)) in blowing snow with high Na\(^+\) concentrations (Supplementary). Because of the correlation and high Na\(^+\) concentrations in blowing snow, the impact of BrO\(_x\) uptake/deposition on Br\(^-\)/Na\(^+\) ratios in blowing snow might be small or slight during winter–spring. Consequently, we conclude that sea-salt fractionation promotes dominant to high Br\(^-\)/Na\(^+\) ratios in blowing snow.

Furthermore, Br\(^-\)/Na\(^+\) ratios in both blowing snow and aerosols showed a maximum level during May–July, except in the winter of 2004, when fast sea-ice in front of Syowa broke and flowed in March and August. In
contrast to strong Br$^-$ enrichment in blowing snow, Br$^-$/Na$^+$ ratios in aerosols decreased to become lower than SWR throughout the year, particularly after early July. These seasonal features of Br$^-$/Na$^+$ ratios in aerosols were consistent with those at Dumont d’Uville Station, Antarctica\textsuperscript{23}. The heterogeneous reactions (R2–5) might drive the Br$^-$ release from SSA. Considering the marked Br$^-$ enrichment that is found in blowing snow (Figs 2 and 4), Br$^-$ might be enriched in SSA at the moment of release from the sea-ice area. Consequently, efficient Br$^-$ depletion from SSA might be promoted immediately after SSA release into the atmosphere. Therefore, a large amount of BrO$\times$ can be released from SSA via heterogeneous reactions.

Estimation of BrO$\times$ released from SSA. Previous works\textsuperscript{2,6,9} estimated a dominant contribution of sea-ice-origin SSA and blowing snow to BrO$\times$. The Br$^-$ enrichment in blowing snow and strong Br$^-$ depletion in SSA were not considered in those estimations. For that reason, the SSA contribution to atmospheric BrO$\times$ might be underestimated. To estimate the release amounts of BrO$\times$ from SSA, we assumed the following initial conditions.

1. Initial molar ratios of Br$^-$/Na$^+$ in SSA:
   
   \[
   \text{Br}^-/\text{Na}^+ = 0.0050 \quad \text{(maximum ratio of blowing snow during the winter), and} \\
   \text{Br}^-/\text{Na}^+ \text{ ratios of blowing snow in each case.}
   \]

2. Br$^-$/Na$^+$ ratios in SSA; ambient ratios and complete Br$^-$ loss from SSA.

3. Molecular weight of sea-salts: 62.288 g mol$^{-1}$, as estimated from SWR\textsuperscript{24}.

Because of assumption\textsuperscript{3}, the estimated value in the complete Br$^-$ loss is equivalent to the upper limit of the BrO$\times$ release from SSA. Data show that Na$^+$ concentrations were 50–255 nmol m$^{-3}$ (3.2–15.9 µg m$^{-3}$ in SSA mass concentration) during AECs (Fig. S9). Aerosol particles were measured and collected in the observatory after passage through the air inlet and tubes. Therefore, the aerosol concentrations can be underestimated particularly in particles larger than 5 µm. From comparison of aerosol number concentrations measured in and outside

**Figure 4.** Seasonal features of air temperature, solar radiation, molar ratios of SO$_4^{2-}$/Na$^+$, Cl$^-$/Na$^+$, Br$^-$/Na$^+$, and Mg$^{2+}$/Na$^+$ in blowing snow and aerosols at Syowa Station, Antarctica. The blue line in (a) shows temperatures for mirabilite precipitation. Gray lines in (b–d) show bulk seawater ratios.
Furthermore, water-soluble aerosol constituents were determined using ion chromatography after extraction using silica gel columns (DX-120; Dionex Corp.). All samples were moved to 14 ml polypropylene vials with an airtight cap immediately after sampling. They were subsequently diluted 102–103 times using ultrapure water in reference to their conductivity. Sample solutions were filtered using a disposable filter (0.45 μm pore, DISMIC-13HP; Advantec MFS Inc.) before analysis. Then, water-soluble constituents in blowing snow and snowfall were determined using ion chromatography (DX-120; Dionex Corp.).

Sample analysis of blowing snow and aerosols. Samples of blowing snow and snowfall were melted at room temperature (ca. 20 °C). Because of the high concentrations of blowing snow samples, the samples were diluted 108–109 times using ultrapure water in reference to their conductivity. Sample solutions were filtered using disposable filters (0.45 μm pore, DISMIC-13HP; Advantec MFS Inc.) before analysis. Then, water-soluble constituents in blowing snow and snowfall were determined using ion chromatography (DX-120; Dionex Corp.). Furthermore, water-soluble aerosol constituents were determined using ion chromatography after extraction using 14 ml of ultrapure water. Analytical procedures and conditions were set as described for our previous work.6,27.
Measurements of aerosol number concentrations and size distributions. Aerosol number concentrations and size distributions were monitored using an optical particle counter (OPC: TD-100; Sigma Tech.) and a condensation particle counter (CPC: 3010; TSI Inc.) at Syowa Station, Antarctica from February, 1996. Measured size ranges were \(D_p (\text{diameter}) > 0.3, >0.5, >1.0, >2.0, >3.0, \text{and} >5.0 \mu \text{m} \) in OPC. Using the CPC, we measured the aerosol number concentrations of condensation nuclei with sizes larger than 10 nm diameter. After OPC and CPC were installed at the atmospheric observatory in February, 1996–January, 2004, they were operated in the clean air observatory from February, 2004. Details of OPC specifications were presented in an earlier report. Locally contaminated data were filtered by standard deviation in 10-min averages with wind data, as described for our earlier work.

Ozone measurements. Monitoring of surface \(O_3\) was conducted using a UV photometer (Model 1100; Tokyo Dylec Corp.) at Syowa Station, Antarctica since February, 1997 by the Japan Meteorological Agency. From February, 1997 through January, 2007, \(O_3\) concentrations were measured at the meteorological observatory. \(O_3\) measurements were made at a clean air observatory from February, 2007. Similar to aerosol data screening, locally contaminated data were filtered by standard deviation in reference to 10-min average and wind data.

Tropospheric BrO from satellites. Tropospheric BrO vertical column densities (VCDs) from SCIAMACHY onboard ENVISAT were retrieved during 2004–2006 using the algorithm developed by the Belgian Institute for Space Aeronomy (IASB-BIRA).

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Acknowledgements
We thank the members of the 45th–47th Japanese Antarctic Research Expedition for assistance with aerosol measurements at Syowa Station. This study was supported financially by the “Observation project of global atmospheric change in the Antarctic” for JARE 43–47. This work was also supported by a Grant-in Aid (No. 16253001, PI: T. Yamanouchi, No. 15310013, PI: K. Osada, and No. 22310013, PI: K. Hara) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for providing the HYSPLIT transport and dispersion model and READY website used for this research (http://www.arl.noaa.gov/ready.html).

Author Contributions
K.H., K.O. and T.Y designed the experiments, which were conducted by K.O., K.H., and M.Y. K.H. wrote the manuscript and conducted sample analysis. K.O., K.H. and M.Y. took winter samples of blowing snow and aerosols at Syowa Station. H.T. and N.T. contributed to BrO analysis and discussion of BrO distributions. All authors reviewed and commented on the paper.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-32287-4.

Competing Interests: The authors declare no competing interests.

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