

# SCIENTIFIC REPORTS

OPEN

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

Keiichiro Hara<sup>1</sup>, Kazuo Osada<sup>2</sup>, Masanori Yabuki<sup>3</sup>, Hisahiro Takashima<sup>1</sup>, Nicolas Theys<sup>4</sup> & Takashi Yamanouchi<sup>5</sup>

Received: 8 March 2018

Accepted: 5 September 2018

Published online: 14 September 2018

Polar sunrise activates reactive bromine ( $\text{BrO}_x$ ) cycle on the Antarctic coasts.  $\text{BrO}_x$  chemistry relates to depletion of  $\text{O}_3$  and Hg in polar regions. Earlier studies have indicated “blowing snow” as a source of atmospheric  $\text{BrO}_x$ . However, surface  $\text{O}_3$  depletion and BrO enhancement occurs rarely under blowing snow conditions at Syowa Station, Antarctica. Therefore, trigger processes for  $\text{BrO}_x$  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  $\text{BrO}_x$  cycle activation. Blowing snow had  $\text{Br}^-$  enrichment, in contrast to strong  $\text{Br}^-$  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  $\text{O}_3$  depletion at Syowa Station occurred in aerosol enhancement because of SSA dispersion during the polar sunrise. Amounts of depleted  $\text{Br}^-$  from SSA were matched well to the tropospheric vertical column density of BrO and  $\text{BrO}_x$  concentrations found in earlier work. Our results indicate that SSA enhancement by strong winds engenders activation of atmospheric  $\text{BrO}_x$  cycles via heterogeneous reactions on SSA.

The reactive bromine ( $\text{BrO}_x$ ) cycle is activated in polar regions during the polar sunrise<sup>1–3</sup>. The atmospheric  $\text{BrO}_x$  cycle relates to atmospheric chemistry such as depletion of  $\text{O}_3$  (R1) and Hg, and oxidation of dimethylsulfide<sup>1,2,4,5</sup>.

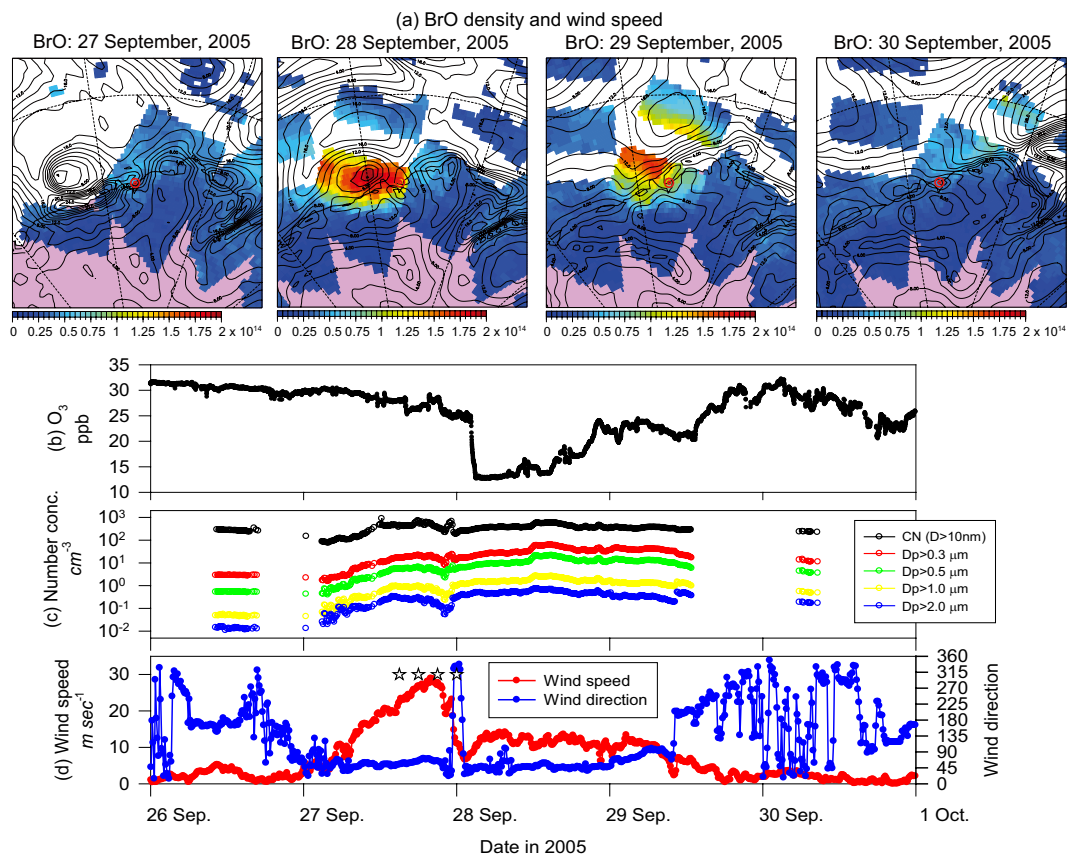


Results of earlier studies have shown that  $\text{BrO}_x$  origins are heterogeneous reactions (R2–3) occurring on the surfaces of blowing snow, sea-salt aerosols (SSA), frost flowers, and surface snow<sup>6–9</sup> and subsequent photolysis of  $\text{Br}_2$  and  $\text{BrCl}$  (R4–5).



Satellite measurements showed high BrO concentrations over sea-ice with the appearance of frost flowers<sup>8</sup>. Additionally, high  $\text{BrO}_x$  plumes in the Antarctic coasts were found to originate from sea-ice zones<sup>2,10</sup>. Model studies presented the contribution of blowing snow as a  $\text{BrO}_x$  source in polar regions<sup>2,6</sup>. The lifetime of blowing snow, however, is too short because of efficient dry deposition. Although reactions of R2 and R3 require acidity for the

<sup>1</sup>Department of Earth System Science, Faculty of Science, Fukuoka University, Fukuoka, Japan. <sup>2</sup>Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan. <sup>3</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto, Japan. <sup>4</sup>Belgian Institute for Space Aeronomy, Brussels, Belgium. <sup>5</sup>National Institute of Polar Research, Tokyo, Japan. Correspondence and requests for materials should be addressed to K.H. (email: [harakei@fukuoka-u.ac.jp](mailto:harakei@fukuoka-u.ac.jp))

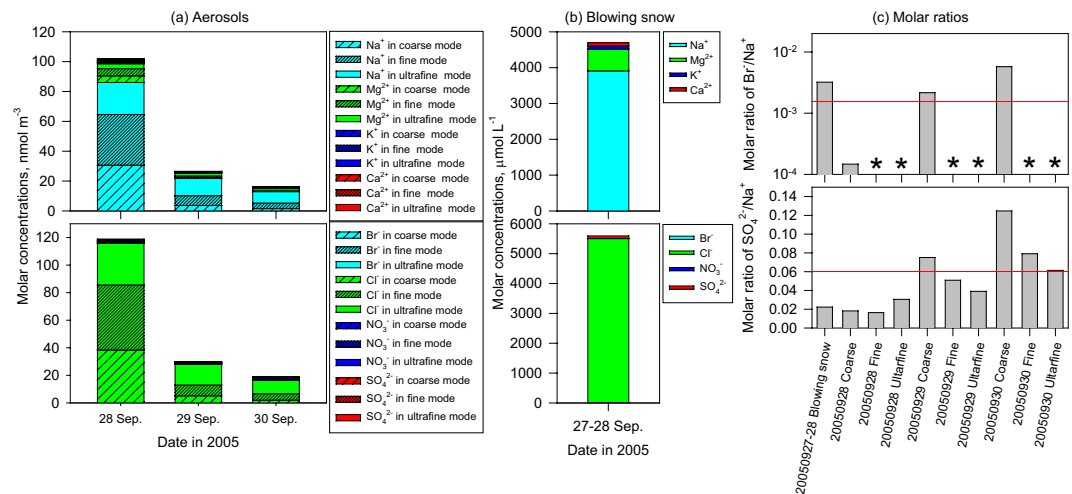


**Figure 1.** BrO mapping around Lützow-Holm Bay on 27–30 September 2005 and short-term features of the concentrations of surface  $\text{O}_3$ , condensation nuclei, and aerosol particles larger than  $0.3 \mu\text{m}$  and  $1 \mu\text{m}$ , wind directions and wind speed at Syowa Station, Antarctica on 26–30 September 2005. Unit of BrO density is mole  $\text{cm}^{-2}$ . Thick lines in BrO maps are wind speeds at 925 hPa in the ERA-interim. Stars in (d) show the occurrence of blowing snow observed visually every 3 hr by us and by members of the Japanese Meteorological Agency.

release of  $\text{Br}_2$  and  $\text{BrCl}$  as a trigger of the atmospheric  $\text{BrO}_x$  cycle, blowing snow has higher pH. In contrast to large amounts of acidic species supplied from anthropogenic processes in the Arctic<sup>11</sup>, 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  $\text{BrO}_x$  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 as a cyclone approached (Fig. 1). Aerosol number concentrations increased concomitantly with the occurrence of blowing snow. Here, we designate ice particles with  $D_p$  (diameter)  $> 10 \mu\text{m}$  and particles dominantly containing sea-salts with  $D_p < 10 \mu\text{m}$  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<sup>2,6</sup> pointed out that blowing snow acts as a source of  $\text{BrO}_x$ . However, satellite measurements showed that the tropospheric vertical column density of BrO ( $\text{VCD}_{\text{BrO}}$ ) was not markedly elevated on 27 September. Although some likelihood exists that cloud cover disturbed satellite BrO measurement near the surface, the surface  $\text{O}_3$  concentration dropped slightly under storm conditions on 27 September. Considering that  $\text{O}_3$  can be depleted by the reaction (R1) during polar sunrise, slight  $\text{O}_3$  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<sup>12</sup>) persisted after the storm condition. Simultaneously, the  $\text{O}_3$  concentration dropped to 13.7 ppb.  $\text{VCD}_{\text{BrO}}$  was enhanced to the order of  $10^{14}$  mole  $\text{cm}^{-2}$  near Syowa. The BrO-enhanced area overlapped the area with wind speed of less than  $10 \text{ m s}^{-1}$ . This condition persisted until 29 September 2005. The aerosol and  $\text{O}_3$  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  $200\text{--}300 \text{ cm}^{-3}$  in CN,  $2\text{--}3 \text{ cm}^{-3}$  in  $D_p > 0.3 \mu\text{m}$ , and  $0.1\text{--}0.2 \text{ cm}^{-3}$  in  $D_p > 1.0 \mu\text{m}$ <sup>13</sup>. This relation suggests strongly that BrO enhancement and  $\text{O}_3$  depletion are related to AECs rather than to appearance of blowing snow at the Antarctic coasts.

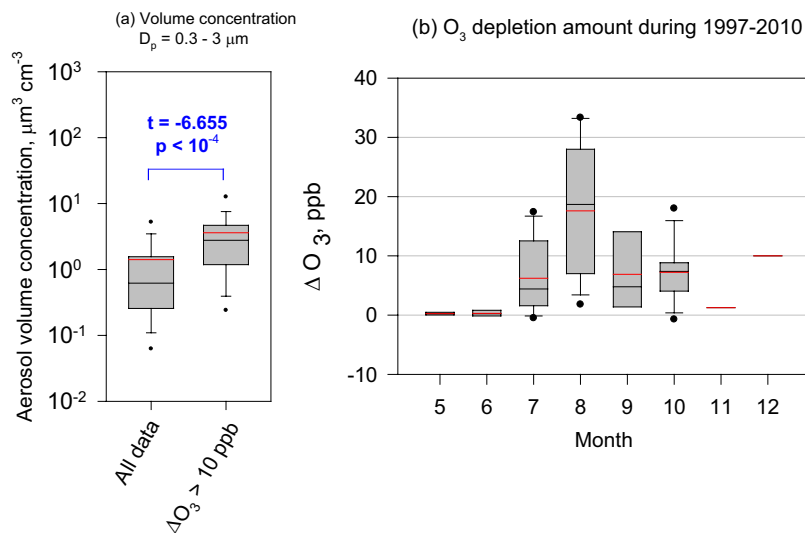


**Figure 2.** Molar concentrations of (a) aerosols on 28–30 September 2005, (b) blowing snow taken on 27–28 September 2005, and (c) molar ratios of  $\text{SO}_4^{2-}/\text{Na}^+$  in blowing snow and aerosols during 28–30 September. Coarse, fine, and ultrafine modes respectively have ranges of  $D_p > 2\ \mu\text{m}$ ,  $D_p = 0.2\text{--}2\ \mu\text{m}$ , and  $D_p < 0.2\ \mu\text{m}$ . Red lines and asterisks in (c), respectively represent bulk seawater ratios and data with  $\text{Br}^-$  concentrations below the detection limit.

**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<sup>14,15</sup> 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<sup>16</sup> on sea-ice by strong winds and by sublimation of snow particles<sup>16–18</sup>.

Data show that  $\text{Br}^-$  was enriched in blowing snow, whereas  $\text{Br}^-/\text{Na}^+$  in aerosols was lower than seawater ratio (SWR), particularly in ultrafine – fine modes (Fig. 2).  $\text{Br}^-$  was depleted also from SSA in coarse mode on 28 September. Although  $\text{Br}^-$  release from sea-salts can be promoted in acidic conditions<sup>1,3,19</sup>, 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 Lützw-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 Lützw-Holm Bay through erosion in strong winds, as suggested by earlier work<sup>16</sup>. 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,  $\text{Br}^-$  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  $\text{BrO}_x$  can be released from SSA through heterogeneous reactions and can be converted in the atmosphere through heterogeneous reactions (R2–5)<sup>1,4</sup>. Considering  $\text{Br}^-$  enrichment in blowing snow and strong  $\text{Br}^-$  depletion in SSA during AECs, we anticipate that SSA dispersion and then  $\text{Br}^-$  depletion in SSA through the heterogeneous reactions play important roles in the atmospheric  $\text{BrO}_x$  cycle in the case of 27–30 September 2005.

**Relation between AECs and surface  $\text{O}_3$ .** Satellite  $\text{BrO}$  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  $\text{BrO}_x$  cycles and SSA during the polar sunrise. Considering that  $\text{BrO}_x$  destroys surface  $\text{O}_3$  by R1, we attempt to identify  $\text{BrO}$  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  $5.6 \pm 2.9$  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 ( $D_p < 0.2\ \mu\text{m}$ ) – fine ( $D_p = 0.2\text{--}2.0\ \mu\text{m}$ ) – coarse ( $D_p > 2.0\ \mu\text{m}$ ) modes were sea-salts that had originated from sea-ice areas, particularly in AECs<sup>11,20</sup>. Therefore, LOEs and  $\text{BrO}$  enhancement at Syowa might be linked closely



**Figure 3.** (a) Aerosol volume concentrations of the whole period (1997–2011) and surface ozone depletion ( $\Delta O_3 > 10$  ppb), with (b) seasonal features of  $\Delta O_3$  in aerosol enhancement at Syowa Station during 1997–2011 (see Table S1). In Fig. 3a, “t” and “p” respectively denote *t*-values and *p*-values of *t*-tests. Degrees of freedom for the *t*-test were 148,180.

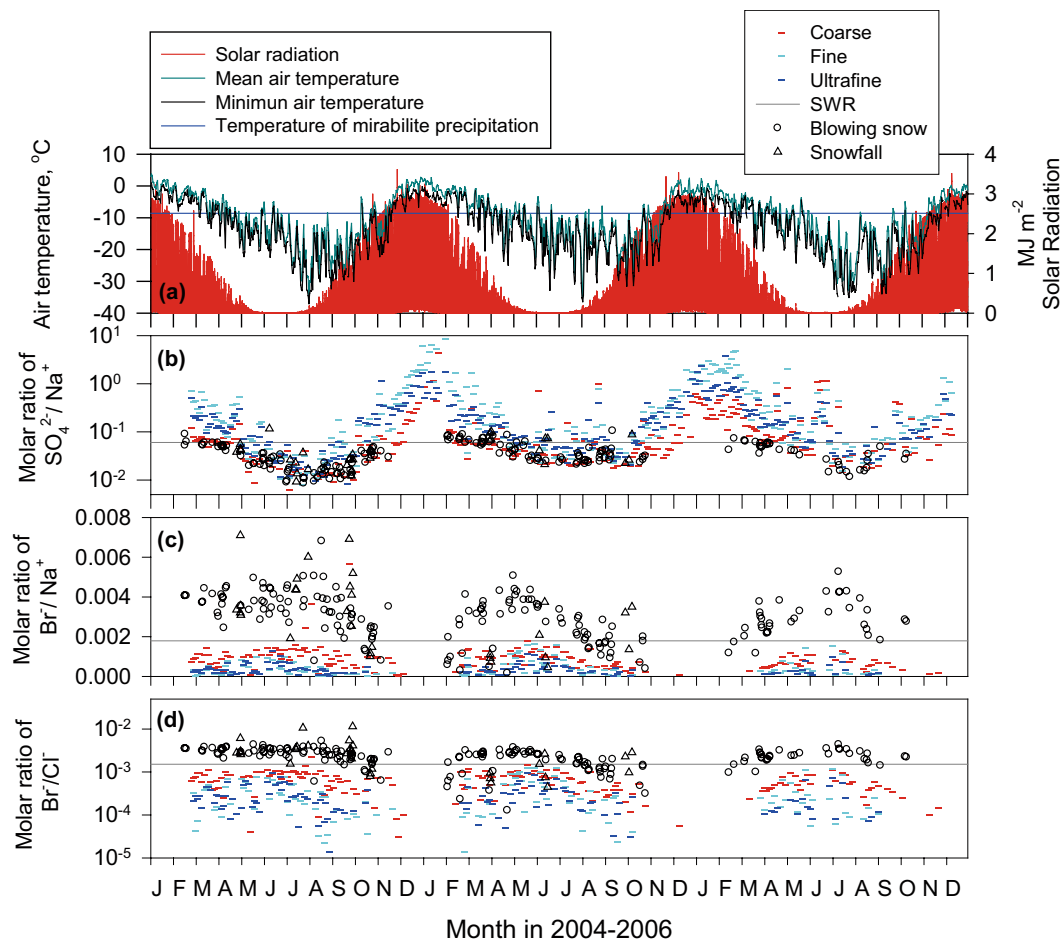
to SSA enhancement. Actually, AECs appeared in May–December (frequently in June–October) at Syowa. During the polar night, surface  $O_3$  dropped only slightly in AECs (Fig. 3b). This result is likely attributable to low  $BrO_x$  concentrations in the atmosphere by reduction of the following photochemical reactions during times of less solar radiation, in spite of a large dispersion of SSA.



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  $O_3$  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  $SO_4^{2-}/Na^+$  in blowing snow and aerosols were lower than SWR in April–October (Fig. 4) because of sea-salt fractionation on sea-ice<sup>14,15</sup>. Additionally,  $SO_4^{2-}/Na^+$  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- $SO_4^{2-}$  concentrations might mask evidence of  $SO_4^{2-}$  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.  $Br^-/Na^+$  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  $CHBr_3$ . Because mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ; below  $-8^\circ C$ ) and hydrohalite ( $NaCl \cdot 2H_2O$ ; below  $-22^\circ C$ ) are precipitated in/on sea-ice<sup>15</sup>,  $Br^-/Na^+$  ratios increase gradually with sea-salt fractionation. Assuming only the occurrence of mirabilite precipitation,  $Br^-/Na^+$  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<sup>21,22</sup> 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<sup>23</sup>. 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



**Figure 4.** Seasonal features of air temperature, solar radiation, molar ratios of  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{Cl}^-/\text{Na}^+$ ,  $\text{Br}^-/\text{Na}^+$ , and  $\text{Mg}^{2+}/\text{Na}^+$  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.

contrast to strong  $\text{Br}^-$  enrichment in blowing snow,  $\text{Br}^-/\text{Na}^+$  ratios in aerosols decreased to become lower than SWR throughout the year, particularly after early July. These seasonal features of  $\text{Br}^-/\text{Na}^+$  ratios in aerosols were consistent with those at Dumont d'Uville Station, Antarctica<sup>23</sup>. The heterogeneous reactions (R2–5) might drive the  $\text{Br}^-$  release from SSA. Considering the marked  $\text{Br}^-$  enrichment that is found in blowing snow (Figs 2 and 4),  $\text{Br}^-$  might be enriched in SSA at the moment of release from the sea-ice area. Consequently, efficient  $\text{Br}^-$  depletion from SSA might be promoted immediately after SSA release into the atmosphere. Therefore, a large amount of  $\text{BrO}_x$  can be released from SSA via heterogeneous reactions.

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

- (1) Initial molar ratios of  $\text{Br}^-/\text{Na}^+$  in SSA:

$\text{Br}^-/\text{Na}^+ = 0.0050$  (maximum ratio of blowing snow during the winter), and  $\text{Br}^-/\text{Na}^+$  ratios of blowing snow in each case.

- (2)  $\text{Br}^-/\text{Na}^+$  ratios in SSA; ambient ratios and complete  $\text{Br}^-$  loss from SSA.
- (3) Molecular weight of sea-salts:  $62.288 \text{ g mol}^{-1}$ , as estimated from SWR<sup>24</sup>.

Because of assumption<sup>2</sup>, the estimated value in the complete  $\text{Br}^-$  loss is equivalent to the upper limit of the  $\text{BrO}_x$  release from SSA. Data show that  $\text{Na}^+$  concentrations were  $50\text{--}255 \text{ nmol m}^{-3}$  ( $3.2\text{--}15.9 \mu\text{g m}^{-3}$  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  $5 \mu\text{m}$ . From comparison of aerosol number concentrations measured in and outside

the observatory, the underestimated mass concentrations in aerosol samples were estimated as 5–20  $\mu\text{g m}^{-3}$  depending on the aerosol number concentrations (Supplementary). Therefore, we assumed SSA mass concentrations in  $D \leq 10 \mu\text{m}$  of 7.9–46.4  $\mu\text{g m}^{-3}$  in AECs (Table S2). In this range, the released  $\text{BrO}_x$  amounts can be estimated as 9–56 pptv ( $\text{Br}^-/\text{Na}^+ = 0.0032$ ) and 12–70 pptv ( $\text{Br}^-/\text{Na}^+ = 0.0050$ ) in the case of complete  $\text{Br}^-$  release from SSA (Fig. S12). The estimated levels were consistent with the sum concentrations of  $\text{BrO}_x$  ( $\text{Br}_2$ ,  $\text{BrCl}$ , and  $\text{BrO}$ ) measured at Halley<sup>10,25</sup>. The major  $\text{BrO}_x$  species are  $\text{Br}_2$  and  $\text{BrO}$ , which can be mutually converted after photolysis and reaction with  $\text{O}_3$  under UV radiation.  $\text{VCD}_{\text{BrO}}$  depends on the aerosol enhanced layer thickness. The aerosol thickness of the enhanced layer was 2–4 km over Syowa Station<sup>26</sup>. Moreover, vertical profiles of potential temperature imply that the thickness reached 3 km on 28–29 September 2005 (Fig. S13). In the case of SSA mass concentrations (12  $\mu\text{g m}^{-3}$ ) and the thickness (3 km) on 28 September 2005, ambient amounts of  $\text{BrO}_x$  can be estimated as  $1.2 \times 10^{14}$  mole  $\text{cm}^{-2}$  ( $\text{Br}^-/\text{Na}^+ = 0.0032$ ) and  $1.7 \times 10^{14}$  mole  $\text{cm}^{-2}$  ( $\text{Br}^-/\text{Na}^+ = 0.0050$ ). These values were well matched to the observed  $\text{VCD}_{\text{BrO}}$  ( $1 \times 10^{14}$  mole  $\text{cm}^{-2}$ ) on 28–29 September 2004 by SCIAMACHY around Syowa. Similarly,  $\text{BrO}_x$  amounts in the other AECs in 2004–2006<sup>12</sup> (Table S2) can be estimated as  $6.9 \times 10^{13}$ – $1.7 \times 10^{14}$  mole  $\text{cm}^{-2}$  using ambient  $\text{Br}^-/\text{Na}^+$  ratios of blowing snow and aerosols. These values were similar to the  $\text{BrO}_x$  concentrations at Halley<sup>10,25</sup>. Therefore, the agreement suggests that the  $\text{BrO}_x$  release from SSA has a greater contribution than that suggested by earlier studies<sup>9</sup>. Furthermore, higher  $\text{Br}^-/\text{Na}^+$  ratios of blowing snow are likely to enhance activation of  $\text{BrO}_x$  cycles and  $\text{O}_3$  depletion in August at Syowa. Considering pH in blowing snow and the weaker anthropogenic impact leading to low concentrations of acidic species in the Antarctica, heterogeneous reactions on SSA after dispersion to the atmosphere were likely to be necessary processes for the atmospheric  $\text{BrO}_x$  cycle at the Antarctic coasts. Consequently, our results provide direct evidence that SSA dispersion from sea-ice by strong winds and the heterogeneous reactions on SSA play crucially important roles as the initial step to activate atmospheric  $\text{BrO}_x$  cycles at the Antarctic coasts during the polar sunrise.

Atmospheric sea-salt and halogen chemistry are important processes affecting atmospheric sea-salt and  $\text{BrO}_x$  cycles, which are associated closely with  $\text{O}_3$  and Hg depletion, and with DMS oxidation. Results show that SSA can be dispersed not only to the boundary layer but also to the free troposphere, at approx. 4 km altitude<sup>26</sup>. The SSA dispersion engenders modification of the atmospheric chemistry such as oxidation capacity related to  $\text{O}_3$  and  $\text{BrO}$  in the Antarctic free troposphere during the polar sunrise. Furthermore, multi-year sea-ice cover declines gradually with climate change (global warming), particularly in the Arctic. Actually,  $\text{Br}^-$  enrichment proceeds on one-year sea-ice by sea-salt fractionation<sup>16</sup>. Therefore, atmospheric sea-salt and  $\text{BrO}_x$  cycles are expected to change in polar regions through the complex linkage of ocean, sea-ice/snow, and the atmosphere.

## Methods and Analysis

**Sampling of blowing snow and snowfall.** Pre-cleaned polypropylene cuboid bottles (500 ml) were used for sampling of blowing snow. The bottle was turned perpendicularly and set on a balustrade (ca. 3 m above ground/snow surface) of the atmospheric observatory, facing the wind direction in conditions of blowing snow and strong winds. Using our blowing snow sampling procedure, we were unable to segregate blowing snow particles and snowfall particles. Winds from clean air sectors accompanied the blowing snow at Syowa Station. Therefore, local contamination was not mixed in the samples. Snowfall was collected in pre-cleaned polyethylene bags fixed in a plastic container on the roof of the atmospheric observatory under calm wind conditions with snowfall and without blowing snow. Our measurements taken in 2004–2006 were of 180 and 33 samples of blowing snow and snowfall (78, 67, and 35 samples of blowing snow in 2004, 2005, and 2006; 22, 11, and 0 samples of snowfall in 2004, 2005, and 2006). Blowing snow and storm events occurred a few times a week during March–October at Syowa Station in 2004–2006. Therefore, blowing snow samples were taken in most blowing snow events at Syowa Station during our measurements. Weather conditions were usually stable from November until mid-February at Syowa Station. Therefore, blowing snow samples could not be collected in this study in November – mid-February. Both samples were melted in the observatory immediately after sampling, and were transferred to 14 ml polypropylene vials with an airtight cap. They were kept in the freezer until analysis at our laboratory in Japan. Using surplus solutions, pH and conductivity were measured using a portable pH meter (B-212; Horiba Ltd.) and a conductivity meter (B-173; Horiba Ltd.) at the Syowa Station observatory.

**Sampling of aerosols.** Routine size-segregated aerosol samples were collected for 2–3 days using a mid-volume-impactor (MVI) and a back-up filter holder. Cut-off diameters were 2 and 0.2  $\mu\text{m}$ . A Nuclepore filter (25 mm $\phi$ , 110606; Whatman plc.) and PTFE filter (47 mm $\phi$ , J100047A; Advantec MFS Inc.) were used respectively as sample substrates for MVI and back-up filtering. Along with the routine sampling, additional aerosol sampling was made daily in the aerosol enhanced conditions using the same MVI system. To avoid local contamination from the main area of Syowa Station, aerosol sampling was done only in winds from the clean air sector using a wind selector at the clean air observatory ca. 400 m distant from the main area. Aerosol samples (filters) were moved to 14 ml polypropylene vials with an airtight cap immediately after sampling. They were subsequently kept in a freezer until analysis in Japan.

**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  $10^2$ – $10^3$  times using ultrapure water in reference to their conductivity. Sample solutions were filtered using disposable filters (0.45  $\mu\text{m}$  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<sup>12,27</sup>.

**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  $D_p$  (diameter)  $>0.3$ ,  $>0.5$ ,  $>1.0$ ,  $>2.0$ ,  $>3.0$ , 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<sup>13</sup>. Locally contaminated data were filtered by standard deviation in 10-min averages with wind data, as described for our earlier work<sup>12</sup>.

**Ozone measurements.** Monitoring of surface  $\text{O}_3$  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,  $\text{O}_3$  concentrations were measured at the meteorological observatory.  $\text{O}_3$  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)<sup>28</sup>.

## References

1. Simpson, W. R. *et al.* Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys.* **7**, 4375–4418 (2007).
2. Jones, A. *et al.* BrO, blizzards, and drivers of polar tropospheric ozone depletion events. *Atmos. Chem. and Phys.* **9**, 4639–4652 (2009).
3. Abbatt, J. P. D. *et al.* Halogen activation via interactions with environmental ice and snow in the polar lower troposphere and other regions. *Atmos. Chem. Phys.* **12**, 6237–6271 (2012).
4. Saiz-Lopez, A. *et al.* On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for  $\text{O}_3$ ,  $\text{HO}_x$ ,  $\text{NO}_x$  and the Hg lifetime. *Atmos. Chem. Phys.* **8**, 887–900 (2008).
5. Read, K. *et al.* DMS and MSA measurements in the Antarctic Boundary Layer: impact of BrO on MSA production. *Atmos. Chem. Phys.* **8**, 2985–2997 (2008).
6. Yang, X., Pyle, J. A., Cox, R. A., Theys, N. & Van Roozendaal, M. V. Snow-sourced bromine and its implications for polar tropospheric ozone. *Atmos. Chem. Phys.* **10**, 7763–7773 (2010).
7. Kaleschke, L. *et al.* Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. *Geophys. Res. Lett.* **31**, L16114, <https://doi.org/10.1029/2004GL020655>, (2004).
8. Burd, J., Peterson, P., Nghiem, S., Perovich, D. & Simpson, W. Snowmelt onset hinders bromine monoxide heterogeneous recycling in the Arctic. *J. Geophys. Res.* <https://doi.org/10.1002/2017JD026906> (2017).
9. Yang, X., Pyle, J. & Cox, R. Sea salt aerosol production and bromine release: Role of snow on sea ice. *Geophys. Res. Lett.* **35**, L16815, <https://doi.org/10.1029/2008GL034536> (2008).
10. Buys *et al.* High temporal resolution  $\text{Br}_2$ ,  $\text{BrCl}$  and BrO observations in coastal Antarctica. *Atmos. Chem. and Phys.* **13**, 1329–1343 (2013).
11. Quinn, P. *et al.* Arctic haze: current trends and knowledge gaps. *Tellus* **59B**, 99–114, <https://doi.org/10.1111/j.1600-0889.2006.00238.x>, (2007).
12. Hara, K. *et al.* Haze episodes at Syowa Station, coastal Antarctica: Where did they come from? *J. Geophys. Res.* **115**, D14205, <https://doi.org/10.1029/2009JD012582> (2010).
13. Hayashi, M. *et al.* Monitoring of aerosol concentration at Syowa Station, *Antarctic Record*, **54**, 474–486 (in Japanese with English abstract) (2010).
14. Wagenbach, D. *et al.* Sea salt aerosol in coastal Antarctic regions. *J. Geophys. Res.: Atmospheres* **103**, 10961–10974 (1998).
15. Hara, K., Osada, K., Yabuki, M. & Yamanouchi, T. Seasonal variation of fractionated sea-salt particles on the Antarctic coast. *Geophys. Res. Lett.* **39**, L18801, <https://doi.org/10.1029/2012GL052761> (2012).
16. Hara, K., Matoba, S., Hirabayashi, M. & Yamasaki, T. Frost flowers and sea-salt aerosols over seasonal sea-ice areas in north-western Greenland during winter–spring. *Atmos. Chem. Phys.* **17**, 8577–8598 (2017).
17. Osada, K. *et al.* Sulfate depletion in snow over sea ice near Syowa station, Antarctica in relation to the origin of sulfate depleted sea-salt aerosol particles in winter. *Polar Meteorol. Glaciol.* **15**, 21–31 (2001).
18. Rhodes, R., Yang, X., Wolff, E., McConnell, J. & Frey, M. Sea ice as a source of sea salt aerosol to Greenland ice cores: a model-based study. *Atmos. Chem. Phys.* **17**(15), 9417–9433, <https://doi.org/10.5194/acp-17-9417-2017> (2017).
19. Kalnajs, L. & Avallone, L. Frost flower influence on springtime boundary-layer ozone depletion events and atmospheric bromine levels. *Geophys. Res. Lett.* **33**, L10810, <https://doi.org/10.1029/2006GL025809> (2006).
20. Hara, K. *et al.* Seasonal features of ultrafine particle volatility in the coastal Antarctic troposphere. *Atmos. Chem. Phys.* <https://doi.org/10.5194/acp-11-9803-2011> (2011).
21. Yang, X. *et al.* Tropospheric bromine chemistry and its impacts on ozone: A model study, *J. Geophys. Res.* **110** (D23), <https://doi.org/10.1029/2005jd006244>, (2005).
22. Parrella, J. P. *et al.* Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury, *Atmos. Chem. and Phys.* **12** (15), <https://doi.org/10.5194/acp-12-6723-2012> (2012).
23. Legrand, M., Yang, X., Preunkert, S. & Theys, N. Year-round records of sea salt, gaseous, and particulate inorganic bromine in the atmospheric boundary layer at coastal (Dumont d’Urville) and central (Concordia) East Antarctic sites. *J. Geophys. Res.* **121**, 997–1023 (2016).
24. Millero, F., Feistel, R., Wright, D. & McDougall, T. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep Sea Res. Part I: Oceanographic Research Papers* **55**, 50–72 (2008).
25. Saiz-Lopez, A. *et al.* Boundary layer halogens in coastal Antarctica. *Science* **317**, 348–351 (2007).
26. Hara, K., Hayashi, M., Yabuki, M., Shiobara, M. & Nishita-Hara, C. Simultaneous aerosol measurements of unusual aerosol enhancement in the troposphere over Syowa Station, Antarctica. *Atmos. Chem. Phys.* **14**, 4169–4183 (2014).
27. Hara, K. *et al.* Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations. *J. Geophys. Res.* **109**, D20208, <https://doi.org/10.1029/2004JD004713>, (2004).
28. Theys, N. *et al.* Global observations of tropospheric BrO columns using GOME-2 satellite data. *Atmos. Chem. Phys.* **11**, 1791–1811, <https://doi.org/10.5194/acp-11-1791-2011> (2011).

## 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. 15310012, 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.

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018