

Arctic “ozone hole” in a cold volcanic stratosphere

A. Tabazadeh^{*†}, K. Drdla^{*}, M. R. Schoeberl[‡], P. Hamill[§], and O. B. Toon[¶]

^{*}National Aeronautics and Space Administration Ames Research Center, Earth Science Division, MS: 245-4, Moffett Field, CA 94035; [‡]National Aeronautics and Space Administration Goddard Space Flight Center, Greenbelt, MD 20771; [§]Department of Physics, San Jose State University, San Jose, CA 95192; and [¶]Laboratory for Atmospheric and Space Physics, Program in Atmospheric and Oceanic Science, University of Colorado, Boulder, CO 80309

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Optical depth records indicate that volcanic aerosols from major eruptions often produce clouds that have greater surface area than typical Arctic polar stratospheric clouds (PSCs). A trajectory cloud-chemistry model is used to study how volcanic aerosols could affect springtime Arctic ozone loss processes, such as chlorine activation and denitrification, in a cold winter within the current range of natural variability. Several studies indicate that severe denitrification can increase Arctic ozone loss by up to 30%. We show large PSC particles that cause denitrification in a nonvolcanic stratosphere cannot efficiently form in a volcanic environment. However, volcanic aerosols, when present at low altitudes, where Arctic PSCs cannot form, can extend the vertical range of chemical ozone loss in the lower stratosphere. Chemical processing on volcanic aerosols over a 10-km altitude range could increase the current levels of springtime column ozone loss by up to 70% independent of denitrification. Climate models predict that the lower stratosphere is cooling as a result of greenhouse gas built-up in the troposphere. The magnitude of column ozone loss calculated here for the 1999–2000 Arctic winter, in an assumed volcanic state, is similar to that projected for a colder future nonvolcanic stratosphere in the 2010 decade.

Eruptions with a volcanic explosivity index (VEI) of 4 or higher produce significant stratospheric injections (1, 2). Sulfur dioxide (2), the most important atmospheric component of volcanic emissions, is converted into sulfate aerosols after injection into the stratosphere. More than 100 eruptions with VEIs ≥ 4 are thought to have occurred in the past 500 years (1). However, only about half of all large eruptions are sulfur-rich (2, 3). Both the 1982 El Chichon (VEI = 4) (4) and 1991 Mt. Pinatubo (VEI = 5) (5) eruptions were sulfur-rich, producing volcanic clouds in the stratosphere that lasted for a number of years (6). On the other hand, the relatively sulfur-poor eruption of Mt. St. Helens (VEI = 5) (2, 7) in 1980 contributed very little sulfate mass to the stratospheric aerosol layer (6). The fact that Mt. St. Helens' plume was emitted at an angle also reduced the amount of possible stratospheric injections by this volcano. Nevertheless, large sulfate-rich eruptions are common (6). Therefore, it is important to understand to what extent these eruptions could affect the Arctic ozone layer in the next 30 years or so, while anthropogenic chlorine levels are still sufficiently high [≈ 3 parts per billion in volume (ppbv)] to cause severe ozone depletion (8, 9).

Model simulations (10) have shown that the early rapid growth of the Antarctic “ozone hole” in the early 1980s may have been influenced (in part) by a number of large volcanic eruptions. The goal of this study is to explore how a large eruption could affect Arctic ozone loss processes, such as chlorine activation and denitrification, in a cold year within the current range of natural variability. It is projected that the Arctic climate may be colder in the future as a result of greenhouse gas emissions and their buildup in the lower troposphere (8). Thus, we also investigate how a possible large eruption could affect ozone loss in a colder Arctic climate.

Volcanic Aerosol Effects

Volcanic aerosols at cold polar temperatures are just as efficient as polar stratospheric clouds (PSCs) in activating chlorine spe-

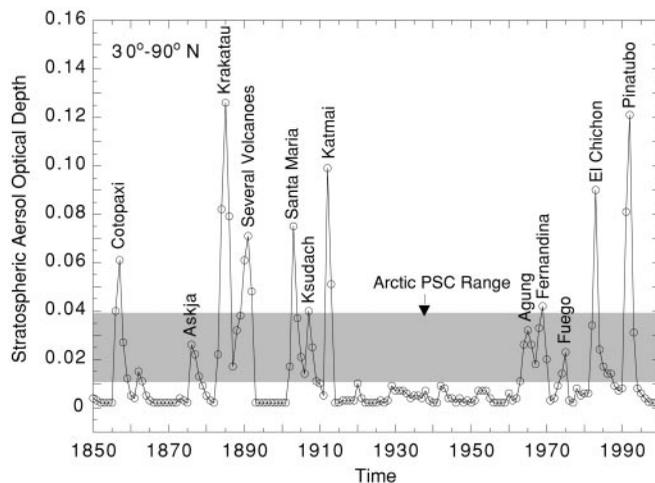


Fig. 1. The stratospheric aerosol optical depth (at $\lambda = 0.55 \mu\text{m}$) over time in the last 150 years (the data shown are taken from table 1 in ref. 6). Also shown are calculated PSC optical depths based on Stratospheric Aerosol Measurement (SAM) II aerosol extinction profiles (at $1 \mu\text{m}$) in the Arctic (28). The Arctic PSC optical depth range shown is derived from vertical extinction profiles in the Arctic when temperature profiles are (well) below the condensation point of PSCs over at least a 4-km altitude range.

cies that catalytically destroy ozone molecules (9, 10). The advantage of volcanic aerosols over PSCs (particularly in the Arctic) is that they can activate substantial amounts of chlorine at warmer temperatures ($\approx 200 \text{ K}$), mainly because they are composed of sulfate aerosols that do not evaporate above the condensation point of PSCs [typically 195 K at ≈ 50 millibar (mbar; $1 \text{ mbar} = 10^2 \text{ Pa}$)]. Also, volcanic aerosols can increase the magnitude of chlorine activation below about 17 km, where PSCs typically cannot persist in the Arctic. Thus, volcanic aerosols can extend the vertical (altitudes $< 17 \text{ km}$) and horizontal (areas with temperatures $> 195 \text{ K}$) range of chlorine activation in the Arctic stratosphere.

Unlike the Antarctic (where it is cold every winter), the wintertime Arctic climate in the stratosphere is highly variable (8, 11, 12). Some Arctic winters are cold and others are warm. There is no quantitative way of determining ahead of time which winters in the future will be cold. Observational data (9, 11) indicate that significant ozone loss in the Arctic occurs only in cold winters, and volcanoes can substantially increase this loss by enhancing the spatial scales over which ozone molecules can get destroyed in the stratosphere.

Recent sulfur-rich volcanic eruptions have not greatly affected springtime Arctic ozone loss for several reasons. After the eruption of El Chichon in 1982, the anthropogenic chlorine

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Abbreviations: VEI, volcanic explosivity index; ppbv, parts per billion in volume; PSC, polar stratospheric cloud; NAD, nitric acid dihydrate; NAT, nitric acid trihydrate; STS, ternary supercooled solution; DU, Dobson units; SAOD, stratospheric aerosol optical depth.

[†]To whom reprint requests should be addressed. E-mail: atabazadeh@mail.arc.nasa.gov.

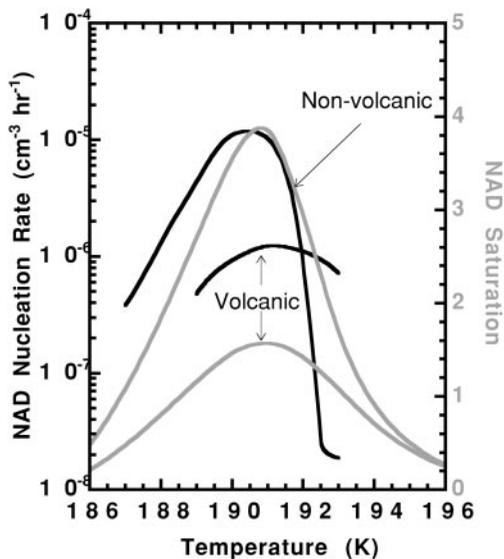


Fig. 2. Modeled variations in the NAD saturation ratio and nucleation rate as a function of temperature at 50 mbar. Calculations for a nonvolcanic atmosphere were performed at 50 mbar (≈ 20 km) for HNO_3 , H_2O , and H_2SO_4 mixing ratios of 10 ppbv, 5 ppmv and 0.17 ppbv, respectively. For volcanic calculations, the sulfate volume mixing ratio was increased to 20 ppbv (29).

levels in the stratosphere were not yet sufficient (8) to cause large ozone depletion in the relatively warm (≈ 10 K warmer than the Antarctic) Arctic stratosphere. After the 1991 Mt. Pinatubo eruption, chlorine levels were large enough to lead to substantial ozone depletion in the Arctic. In fact, the March column ozone abundances (averaged from 63° to 90° N latitude; ref. 11) from 1990 to 1996 are lowest in 1993, despite the fact this winter was not the coldest or most persistent Arctic winter in the early to mid 1990s (12). Polar projection maps of total average column ozone abundance in March 1993 show a moderate ozone loss over a wide area around the north pole (consistent with the hemispheric distribution of volcanic particles), whereas the larger ozone losses in the colder nonvolcanic 1996 winter are confined to a relatively small area to the east of the north pole (consistent with the localized PSC distributions in a nonvolcanic year) (11). Thus, volcanoes have the potential to significantly increase the areal coverage of ozone loss in the Arctic. In 1993 the lack of Arctic vortex persistence into early spring (12) may have prevented Pinatubo aerosols from causing more ozone destruction during this year. Below, we estimate how much possible column ozone loss can occur inside a cold and stable Arctic vortex in a volcanic year.

In Fig. 1, the change in the stratospheric aerosol optical depth (SAOD) over time is shown for the last 150 years (6). The SAOD increases by a factor of about 10 to 100 after major volcanic eruptions. SAODs in a volcanic year (and a few years after each

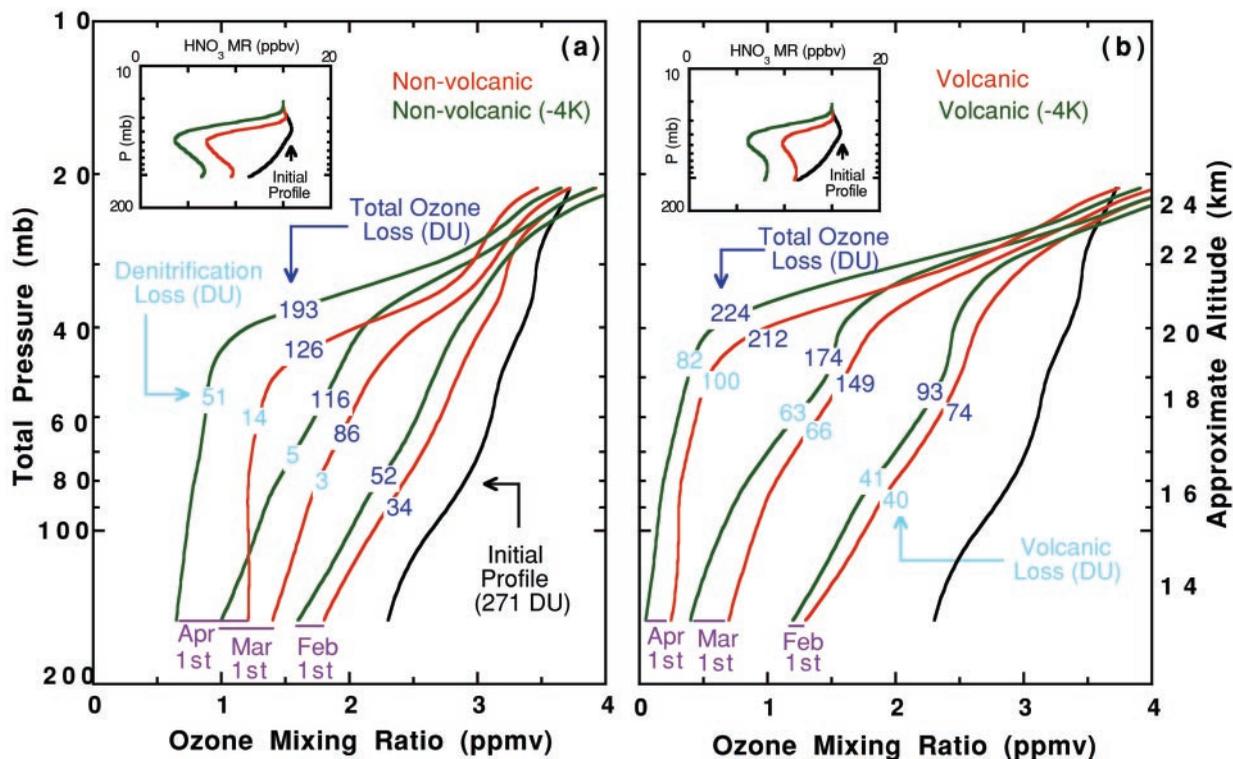


Fig. 3. Vortex-averaged computed denitrification fields (*insets*) and column ozone profiles in Dobson units (DU) for temperatures corresponding to the 1999–2000 Arctic winter and a winter that is 4 K colder (a). One DU is equal to 2.7×10^{16} ozone molecules in a 1-cm^2 column that is extended from the surface up to the top of the atmosphere (≈ 100 km high). A typical ozone column overhead contains roughly 300 DU of ozone molecules. (b) Ozone losses for the same temperatures as in a but with volcanic aerosols included. We increased sulfate volume mixing ratio (29) in the model from 0.17 ppbv (nonvolcanic) to 20 ppbv (volcanic) to account for volcanic aerosol effects on ozone. We used the Integrated MicroPhysics and Aerosol Chemistry on Trajectories (IMPACT) model in a quasi-three-dimensional mode (15, 16) to obtain the results shown. Nearly 3,000 initial points were distributed evenly (in both horizontal and vertical directions) inside the Arctic vortex on Jan. 15, 2000 between ≈ 450 and 700 K surface. Forward and backward diabatic trajectories were run from each initialized point (based on the United Kingdom Meteorological Office data set) to obtain roughly 3,000 winter-long air parcel temperature and position histories. See refs. 20 and 21 for initialization of the ozone, HNO_3 , and other reactive gas phase profiles in the beginning of the winter. Results shown are the average values calculated for all trajectories located in the vortex. Total column ozone losses and those attributed to denitrification, and additional chemical processing on volcanic aerosols are also marked for nonvolcanic (a) and volcanic (b) cases, respectively. We assumed that all NAD particles convert to NAT immediately after nucleation. For volcanic conditions, denitrification had no appreciable effect on the total column ozone loss.

eruption) are similar (or larger) in magnitude to optical depths of typical Arctic PSCs. Stratospheric variations in aerosol optical depth can significantly affect heterogeneous chemistry that leads to ozone depletion because particle surface areas are directly proportional to the optical depth. Below we consider how the continuous presence of volcanic cloudy-like conditions in the Arctic can affect springtime ozone loss processes (13–18) in a cold year such as the winter of 1999–2000.

Model Simulations

Recently, we have shown (13) that the observed large PSC particles (14) that cause denitrification in a nonvolcanic atmosphere most likely form by homogeneous nucleation of nitric acid dihydrate (NAD) crystals (19) in the ubiquitous ternary supercooled solution (STS) droplets of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ in the stratosphere. Nucleated NAD crystals may later transform into the more stable nitric acid trihydrate (NAT) phase, causing more denitrification (13). In Fig. 2 temperature variations in NAD saturation and nucleation rates are shown for both nonvolcanic and volcanic conditions. Fig. 2 shows that the sulfate-rich composition (see figure 10 in ref. 20) of STS droplets in a volcanic year limits the magnitude of NAD saturation, S (≈ 1), which causes NAD particle production rates to drop by almost a factor of 10 (13). Note that for temperatures above 192 K, NAD nucleation rates under volcanic conditions are faster than those calculated for a nonvolcanic state (because of higher levels of aerosol volume). However, NAD freezing rates are too slow at temperatures above 192 K to cause significant denitrification (13). Below we use a microphysics model to investigate how the change in NAD particle production rates will affect the denitrification process under volcanic conditions.

We used a coupled chemistry–microphysics trajectory model (15, 16) to evaluate the effects of volcanic perturbations on Arctic ozone loss processes under current and possible future colder conditions (13, 17, 18, 21). In Fig. 3 vortex-averaged denitrification fields (*Insets*) are shown for the winter of 1999–2000 for four cases. As shown (13, 17, 18), denitrification is enhanced in a colder (by 4 K) nonvolcanic atmosphere. Most of the denitrification in a nonvolcanic atmosphere is caused by sedimentation of large NAD (or NAT) particles (13). In a volcanic atmosphere, denitrification fields are lower by about 30–60% in magnitude as compared with nonvolcanic values. Also, over 70% of denitrification in a volcanic year occurs by sedimentation of relatively large STS particles. Thus the narrow temperature range of NAD particle stability (NAD is stable when $S > 1$, Fig. 2) in a volcanic year limits the effectiveness of large NAD (or NAT) particles to cause substantial denitrification. A number of observational data sets (22–24), after the eruption of Mt. Pinatubo indicate that PSCs tend to remain in the STS form in a volcanic cloud, supporting the results of our calculations that it is more difficult for NAD particles to efficiently form, grow, and denitrify the atmosphere in a volcanic year.

In Fig. 3, simulations of the vortex-averaged cumulative changes in the total column ozone caused by both denitrification and volcanic aerosol effects are shown over 3 months for temperatures that occurred in the winter of 1999–2000. For all cases, denitrification has little effect on the total column ozone loss through March 1. The total column ozone losses for volcanic cases are higher by a factor of about 2 in mid (February 1) and late (March 1) winter compared with nonvolcanic values. If the vortex persists into early spring (April 1), then substantial ozone losses, reaching Antarctic values (8–10), could occur in either a colder (by 4 K) nonvolcanic stratosphere or any of the two volcanic scenarios. Potentially, a denitrified Arctic stratosphere in early spring is primed for ozone destruction because reactive nitrogen that can mediate ozone loss (by sequestering active chlorine) has been removed from the stratosphere. In fact, a

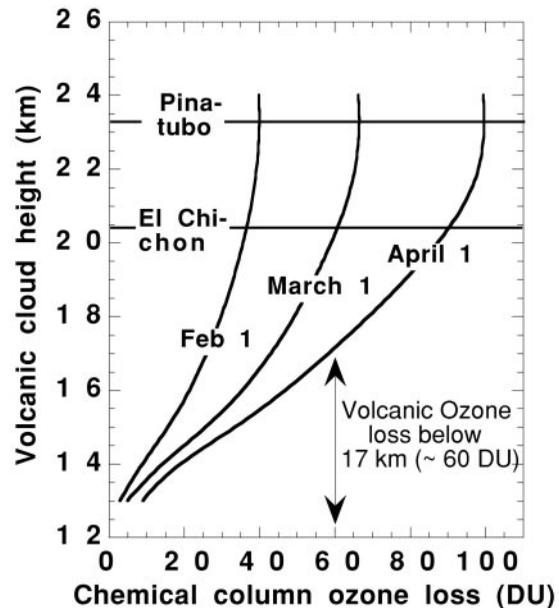


Fig. 4. The difference in the total column ozone loss between a volcanic and a nonvolcanic year. The lines are obtained by subtracting the volcanic profiles (red lines in Fig. 3b) from the nonvolcanic profiles (red lines in Fig. 3a) in Fig. 3. Also shown are the observed top heights of the volcanic aerosol plume in January (after the eruption year of each volcano) based on the Stratospheric Aerosol Measurement (SAM) II (used for El Chichon) and Stratospheric Aerosol and Gas Experiment (SAGE) II (used for Mt. Pinatubo) data. The marked peak height of the volcanic aerosol layer is obtained by subtracting the averaged volcanic aerosol extinction profile from the average nonvolcanic extinction profile during quiescent years. Because both the SAM II and the SAGE II data were limited to latitudes below about 70° N, we ran a trajectory plume dispersal model (30) (initialized on 5/3/1999 and 6/15/1999 at the El Chichon and Mt. Pinatubo locations, respectively) to investigate the extent of volcanic plume dispersal inside the Arctic region. Results from trajectory simulations indicate that within 3 months of each simulated eruption, volcanic material would have been widely distributed in the Arctic region in 1999, reaching latitudes as far as the north pole.

number of studies have shown that massive denitrification in the Arctic can increase ozone loss by about 30% in a nonvolcanic stratosphere (17, 18), which is in accord with the results shown in Fig. 3. However, denitrification effects on ozone become insignificant in a volcanic stratosphere because the constant presence of cloudy-like conditions provides an Antarctic-like environment, where denitrification has also been shown to have a negligible effect on ozone loss (10). Overall, higher aerosol abundances in volcanic scenarios lead to greater ozone loss because modeled active chlorine column concentrations (not shown) are higher by about 30% (throughout midwinter to early spring) and persist at elevated values for longer periods than those calculated for nonvolcanic scenarios.

Fig. 4 shows the altitude dependence of the difference in column ozone loss between a nonvolcanic and a volcanic year. As shown in Fig. 4, high-latitude volcanic clouds extended to high altitudes after two major recent eruptions. Also, volcanic aerosols extend all the way to the tropopause level, where PSCs are generally not found in the warm Arctic lower stratosphere. It is interesting to note that about 60 Dobson units (DU; Fig. 4) of the total ozone loss attributed to volcanic aerosols (≈ 100 DU, Fig. 3b) occurs at altitudes below about 17 km where typical Arctic PSCs cannot persist for a long time. In fact, nearly one-third of the total column ozone depletion is caused by volcanic aerosol effects at altitudes below about 17 km [60 DU (Fig. 4)/212 DU total loss (Fig. 3)]. Similar analysis of measured vertical ozone profiles in the Antarctic show that Pinatubo

aerosols augmented ozone depletion in 1992 and 1993 by causing additional ozone loss in the 10- to 12-km altitude range, where it is often too warm for PSCs to form over the south pole (25, 26).

Atmospheric Implications

Over the last few years (13, 17, 18, 21) a number of studies have drawn attention to the possible effects of climate change on Arctic ozone depletion. In sum, the warming of the Earth's surface because of anthropogenic greenhouse gases (8, 21) in the lower troposphere is leading to a cooling in the stratosphere. This cooling can increase the spatial and temporal extent of PSC activity in the north. Colder, longer-lasting conditions can lead to massive Arctic denitrification (13, 17, 18) with important implications for ozone loss in the 2010 decade time frame (21). Here we show that severe ozone loss can occur now (in this decade) in a volcanic year with a climate similar to the cold Arctic winters of the 1990s with a moderately stable vortex that persists into early spring. For instance, Fig. 3 shows that the total column ozone loss in the early spring of 2000 could have been up to 70% [212 DU loss (Fig. 3b)/126 DU loss (Fig. 3a)] higher if volcanic aerosols were present inside the Arctic vortex. In addition, there is very little change in the total column ozone loss between a volcanic atmosphere with 1999–2000 temperatures (212 DU) and one in which 1999–2000 temperatures are lowered by 4 K (224 DU). Thus, volcanic aerosol effects on Arctic ozone are relatively insensitive to temperature and a strong volcano can cause large ozone depletion in a cold winter within the current range of the observed (12, 27) variability.

Our calculations indicate that springtime Arctic column ozone loss during a cold volcanic year could approach values measured

inside the Antarctic “ozone hole” (8–10). Fig. 1 shows that during the past 150 years, 9 volcanic eruptions have produced clouds that were optically thicker than Arctic PSCs, and 13 eruptions produced clouds that were as thick as Arctic PSCs. Volcanic clouds from each eruption tend to last longer than a year. Fully 47 years in the last 150 have had volcanic clouds as optically thick as PSCs, whereas 13 years have had clouds much thicker than PSCs. There has been only one long time period (1915–1963) without any significant presence of volcanic clouds (Fig. 1). Given that half of the Arctic winters were cold in the last decade (12, 27), the yearly probability for the occurrence of a cold volcanic year is about 15% [50% probability for a cold Arctic year \times 31% (47/150) probability for a volcanic cloudy year]. Hence, it is possible for \approx 5 Arctic winters in the next three decades to be cold and volcanic. Therefore, a volcanic “ozone hole” is likely to occur in the Arctic during the next few decades before chlorine recovers to its preindustrial levels (8, 21). If a period of high volcanic activity (1883–1893 or 1902–1912, Fig. 1) coincides with a period of cold Arctic winters (like 1994–1995 to 1996–1997, ref. 27), then a springtime Arctic “ozone hole” may reappear for a number of consecutive years, resembling the pattern seen in the Antarctic every Spring since 1980s (8). Thus, understanding and monitoring the effects of large volcanic eruptions on ozone are essential for devising mitigation strategies to deal with possible severe ozone depletion scenarios in the Arctic region over the next few decades.

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