A-10 A Study on Elucidating Mechanisms of Polar Ozone Depletion Using Satellite Remote Sensing Data

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1. Introduction

After the discovery of the ozone hole in the Antarctica1), several studies have been conducted in order to study the chemical/physical mechanisms of ozone depletion2). As a result, it was revealed that stratospheric ozone depletion is the result of catalytic chemistry involving man-made chlorofluorocarbons, which is most evident in each austral spring in Antarctica, where about half of the total ozone column is depleted each September, forming the Antarctic ozone hole. Measurements of large amounts of chlorine monoxide (ClO), a key ozone destruction catalyst, are among the fingerprints showing that human releases of chlorofluorocarbons are the primary cause of this change3). Enhanced ozone depletion in the Antarctic and Arctic regions is linked to heterogeneous chlorine chemistry that occurs on the surfaces of polar stratospheric clouds (PSCs) at cold temperature. Further, large PSC particles fall with a speed of >1 km/day, depleting available nitric acid. This is called as irreversible denitrification that facilitates ozone destruction. As human use of chlorofluorocarbons continues to decrease, these changes throughout the ozone layer are expected to gradually reverse during the twenty-first century. However, comprehensive and quantitative understanding of the ozone-depletion mechanisms, including the PSCs and denitrification processes, has not yet been done.

2. Research Objective

In order to contribute to the global monitoring of the ozone layer, the Ministry of the Environment decided to develop and launch a satellite sensor called the Improved Limb Atmospheric Spectrometer (ILAS) and its successor ILAS-II. ILAS onboard the Advanced Earth Observing Satellite (ADEOS) was successfully launched on 17 August 1996, and made continuous measurements of ozone and its related gas species from November 1996 to June 1997. ILAS-II onboard the ADEOS-II was launched on 14 December 2002, and made continuous measurements from April to October 2003.

The purpose of this study is to contribute the further understanding of the chemical/physical mechanisms of the ozone depletion in the stratosphere. In order to achieve the purpose, we have conduct the study with five sub-themes as follows: 1) A research on improving retrieval algorithms for vertical profiles of atmospheric parameters from remotely sensed spectral data from ILAS/ILAS-II. 2) A research on validating satellite data with ground-based, balloon, and other satellites data. 3) A research on elucidating polar ozone depletion using ILAS/ILAS-II satellite data. 4) A research on quantifying chemical ozone destruction using chemical transport model. 5) Comparison of ILAS-II and ground-based FTIR measurements of ozone (O_3), nitric acid (HNO_3), nitrous oxide (N_2O), and methane (CH_4) over Kiruna, Sweden. Hereafter, research method, results, and discussion are described for each sub-theme. Conclusions of this study are mentioned finally.

3. Research Method

(1) Sub-theme-1

Until now, we have been developing a technique to distinguish gas and aerosol absorption from the total absorption measurements from ILAS and ILAS-II infrared spectrometers. In this study, we have successfully developed the method based on a "aerosol physical model". Using this newly-developed method, we assessed the quality of retrieved gas profiles for all of the ILAS occultation events (about 6000 scenes). Especially, the conventional method has difficulties in retrieving gas profiles in a scene with highly aerosol loading like PSC. Therefore, we compared separately for PSC scenes and non-PSC (background) scenes with both methods. We have also examined a positive bias in the methane data in the winter seasons, using the newest absorption cross-section data for gas (HITRAN 2004 database).

(2) Sub-theme-2

1) For solar absorption spectrum taken by a ground-based FTIR (Fourier Transform Infrared spectrometer) at Poker Flat, Alaska, precise error analysis has been done for observation and retrieval of stratospheric trace gases. Resulted errors of stratospheric partial column amount were in the range of 3-20 %. On the basis of this consideration comparative and correlative analyses of the FTIR and satellite data were conducted, of which the results showed consistent comparison between the ILAS-II and the Alaska FTIR data.

2) The instrumental line shape (ILS) is very important for the height retrieval from ground-based solar spectra because the profile information of trace species comes from pressure broadening of the absorption line. Uncertainty of the ILS causes uncertainty of the retrieved profile. We adjusted the optics of the FTIR at Tsukuba to improve the ILS, then the precision of the height retrieval. Temporal variations of some trace species were investigated from the solar spectra observed at Tsukuba.

3) By using GPS radio occultation (RO) temperature profiles with the German CHAMP satellite, having good height resolution and measurement accuracy comparable to a radiosonde, we studied the climatological behavior of atmospheric gravity waves in the lower stratosphere in

both the Arctic and Antarctic regions between May 2001 and December 2005. From the temperature (T) profiles we analyzed temperature fluctuations, T' with vertical wave length shorter than 7 km and then determined the wave potential energy (Ep) at 12-33 km every one month in a cell with 20°×10° in longitude and latitude.

4) Simultaneous observations with balloon borne Optical Particle Counter and lidar were performed at Ny-Aalesund, Spits-Bergen in winters of 2002/03, 2003/04, 2004/05 and 2005/06, and in autumn of 2005.

(3) Sub-theme-3

1) We assessed the quality of ILAS-II Version 1.4 (V1.4) data of ozone, HNO_3), N_2O, CH_4, and aerosol extinction coefficient (AEC) at 780 nm. To do this, we used coincident satellite data and a few balloon data. With this assessed data set, several chemical/dynamical processes in the Antarctic vortex in 2003 were examined below 2) to 6).

2) To evaluate the frequency of the PSC occurrence, AEC data are analyzed with temperature, HNO_3, and water vapor data. This study also used T(NAT) (Nitric Acid Trihydrate (NAT) saturation temperature) as a reference for the existence of PSC.

3) To examine the degree of irreversible denitrification within a short-time, variations in HNO_3 and AEC data coupled with air-mass trajectories are calculated. If the measurements A and B are both on the one same trajectory, this forms one match pair, and it is called as the Match technique. This technique is used for seeing the net chemical or micro-physical variations.

4) To deduce the net chemical ozone destruction and its rates, ozone and N_2O as a dynamical tracer are used. The tracer correlation method is introduced in this analysis. First, the ozone-N_2O correlation in the beginning of May was established and used for the reference. Then, such correlations between June and October are taken for each 10-day period bin. The deviation in the ozone axis from the reference correlation is amounted to the net chemical changes in ozone. The daily-averaged deviation for several altitude ranges are calculated to show the amount of total destruction of ozone. The difference in ozone between a day and the one day former gives an ozone destruction rate per day.

5) To examine the meridional circulation in the middle atmosphere we analyzed methane distributions in the southern hemisphere stratosphere and mesosphere at high latitudes by complementary use of the ILAS and ILAS-II observations. Though the ILAS and ILAS-II operated in different periods, we can obtain almost one year cycle data at high latitudes of the southern hemisphere where the horizontal mixing is supposed to be small and the vertical displacement of minor species can be regarded as an indication of the vertical velocity.

6) To examine time evolutions of the inorganic chlorine species in the 1997 Arctic winter, we used the ILAS chlorine nitrate ($ClONO_2$) data of which the quality was evaluated (for ILAS-II data, it is not evaluated yet). First, the PSC event was extracted according to the conventional method. Next, the amount of the total inorganic chlorine (Cly) was deduced from N_2O data using the well-known and tight correlation between Cly and N_2O in the lower stratosphere.

Then, $ClONO_2$/Cly ratios were analyzed with a merit of excluding any dynamical changes in Cly. Further, we investigated the cause of variations in the $ClONO_2$/Cly ratio by using NO_2 data that are strongly related to $ClONO_2$ from a view of photochemistry.

(4) Sub-theme-4

Time Threshold Diagnostics (TTD) is a method developed by Sugata$^{4)}$ to quantify the air parcel transport from one side of a boundary across to the other with time scales longer than a specified time threshold. In this method, by calculating the trajectories of the air parcels distributed in the space, an air parcel that has been on one side of the boundary for longer than the time threshold, crosses it, and then remains on the other side longer than the time threshold is considered to have been transported from one side to the other across the boundary (see Sugata$^{4)}$ for details). In this study, we applied this method to the polar vortex boundary, setting the time threshold to 7 days.

The CCSR/NIES chemical transport model calculations with T42 resolution (2.8° by 2.8°) were executed from November 21, 1996, to June 1, 1997. The main target of this study is a variation of seasonal time scale after January 1, 1997. Three numerical experiments were made:

・Experiment 1: The chemistry was switched on in all the horizontal regions of the CTM.

・Experiment 2: The chemistry was switched on inside the Arctic polar vortex boundary, while the ozone chemistry was switched off outside the boundary.

・Experiment 3: The ozone chemistry was switched off in all the horizontal regions.

(5) Sub-theme-5

Ground-based FTIR measurements were taken at Kiruna (northern Sweden, 68ºN, 20ºE) as part of ILAS-II validation. These ground-based observations of vertical profiles of O_3, HNO_3, N_2O, and CH_4 were compared to ILAS-II measurements processed by the V1.4 retrieval algorithm. Nineteen coincident FTIR and ILAS-II observations were determined and analyzed. Average relative differences were within 10 to 15 % for all four gases. O_3, N_2O, and CH_4 had a negative bias of ILAS-II measurements relative to the FTIR measurements. The bias of ILAS-II measurements relative to the FTIR measurements was positive for HNO_3.

4. Results and discussion

(1) Sub-theme-1

To examine the newly-developed method to distinguish the gas and aerosol absorption precisely, we first looked vertical profiles of several gases in the presence of PSC. As a result, apparent abnormal positive/negative biases in these gas profiles seen from the conventional method were significantly suppressed by using the new method. Next, we assessed the whole of the ILAS-observed profiles (6000 scenes) retrieved with the new method. Absolute differences between the new and conventional methods were not significant for ozone and nitric acid for which the strong absorption was seen, even for the PSC cases. For water vapor and methane, a significant update was seen for the PSC cases. A 1.8 ppmv difference at the maximum between the two was found for water vapor, and a 0.8 ppmv difference was found for methane. For nitrous oxide, chlorine nitrate, and CFC-12 were changed for better ways, respectively. Methane data retrieved by using the HITRAN 2004 spectroscopic database suppress the positive bias depending on the amount of nitric acid. In total, using the new gas-aerosol separation method and the recent spectroscopic database, we found significant progress in the gas profile retrievals. But, some issues still exist; one is a negative bias (amount to 5-10%) in nitrous oxide data below 15 km, the other is a positive bias (15-10%) in methane data in the winter season. Nevertheless, the latest ILAS data product gives a better quality compared to the former data product. We have been also processed the ILAS-II data with the completely identical retrieval program as was developed for the ILAS data.

(2) Sub-theme-2

1) A comparative study is conducted between ILAS-II V1.4 data product and FTIR observation at Poker Flat, Alaska (65°N). The results showed the difference is less than 20% for the O_3 total column amount and vertical profiles, and is less than 10% for HNO_3 above the 17-km altitude. The detailed error analysis of FTIR data showed the error less than 20% so the differences between ILAS-II and O_3/HNO_3 FTIR data were within the FTIR measurement error. For examining statistical error, time series of the trace gas amounts is derived to show seasonal and year-to-year variations.

2) The ILS of Tsukuba FTIR was measured using HBr gas cell and analyzed with LINEFIT9. The optics was adjusted with some methods and the ILS was measured each time and compared. The SFIT program was applied to derive the vertical column densities of HCl, HF, O_3, HNO_3, N_2O, and CO from the solar spectra observed at Tsukuba, Japan since December 1998. After some adjustment of the position of the first aperture and focus, the instrumental line shape becomes much better and the results of the height retrieval for ozone also become better. HCl column increased from 1999 to 2001 and decreased after 2003. HF column increased from 1999 to 2002 and the increase seems to be stopped after 2003. It is indicated that the effect of the decrease of the CFCs can be find in Cly and Fy in the stratosphere.

3) Deriving the gravity wave potential energy (Ep) at 12-33 km from CHAMP-satellite GPS occultation, Ep in the Arctic region shows a clear annual variation with maximum in winter (December-February), which is consistent with the seasonal cycle of the planetary wave activity. In the Antarctic region, Ep gradually increases from July to September and reaches maximum in spring (September-October) before decreasing rapidly. Time derivative (monthly) of the polar night jet magnitude correlates well with Ep. We also confirmed similarity in the horizontal distribution of Ep and the polar night jet. These results suggest that the unbalanced flow due to the distortion of the polar vortex can excite gravity waves through geostrophic adjustment, in addition, the Ep enhancement is related to the active planetary wave breaking and the decay of the polar vortex.

4) Balloon-borne observations with lidar experiments at Ny-Aalesund suggest that fine aerosol until 0.056 micron in radius affect visible optical property, not only for background

aerosol layer but also for liquid phase PSCs layer. Visible extinction coefficient is basic aerosol data for ILAS and ILAS-II. Consideration for variations in such small size range is also important understand stratospheric aerosol phenomena based on ILAS and ILAS-II measurements. Size distributions with radius from 0.056 to 0.6 μm for background aerosol layer show small variation in 2002/03 and 2003/04. However, they show some enhancements regionally, temporally, or in limited size range. Aerosol enhancement associated with sudden warming of stratosphere in 2006 show different feature with those observed in 2004. Long term variations of stratospheric aerosol show that perturbations by Pinatubo eruption continue until 2000, especially in large size range. This study show that these interesting phenomenon will be observed by satellite borne sensor.

(3) Sub-theme-3

1) The comparative results show that the accuracy in ozone, HNO_3, N_2O, CH_4, and AEC data are all estimated to be within 10-20 %. Using the quality evaluated V1.4 data set, the below-mentioned quantitative analyses were done.

2) PSC was first observed with ILAS-II at the end of May, and observed most frequently in August/September as temperatures cooled. At approximately 20 km late in the PSC season, however, PSC was less likely to occur, despite cold temperatures. The probability of PSC occurrence and the probability of temperatures colder than T(NAT) were well correlated below 20 km throughout the winter. In contrast, PSC frequency at 22 km from late August to early September was low even when temperatures were sufficiently colder than T(NAT).

3) The difference in HNO_3 between the initial and the final times of the one match trajectory is plotted versus the ratio of AEC at the initial and final times. In June at 20 km, the magnitude of HNO_3 difference is well anti-correlated with that of AEC ratio. It means that gas-phase HNO_3 is depleted as a result of an uptake in the PSC particle, and conversely, AEC value enhances as a result of the HNO_3 uptake. In August where temperature cooled further, the HNO_3 value has already depleted to within 2 ppbv at the initial time of trajectories, with a small values of AEC. The expected HNO_3 value in August is calculated as 12 ppbv, revealing a significant denitrification (up to 10 ppbv).

4) As a result of the tracer correlation method, we found that the ozone value of 2.5 ppmv in June decreased to almost zero in the end of September at altitudes of 15-17 km. At 21-22 km, the ozone value of 3.0 ppmv decreased to 1.0 ppmv. In these altitudes, a significant change in ozone was found in September, amounting 90 ppbv per day of the ozone destruction rate at the maximum. Such a degree of the destruction rate is in good agreement with rates reported previously, suggesting a sort of the maximum ozone destruction rate in the observational stand point.

5) In a time-height cross section of methane we observed clear downward progression of isolines with a speed of 1.4 km/month when we pay attention to the 0.6 ppmv line located in the middle stratosphere. This is consistent with the previous works as reported by Schoeberl et al.5) and Kawamoto and Shiotani6). In the upper stratosphere we found a methane maximum

moving faster than those isolines in the middle stratosphere. The maximum in the lower mesosphere or the minimum around the stratopause is also confirmed by the HALOE observations. On the basis of climatological outputs from the global circulation model with chemistry (WACCM: Whole-Atmosphere Community Climate Model) we found that the minimum methane concentration is due to its oxidation.

6) We analyzed the time evolutions of $ClONO_2$/Cly ratio at 475, 550, and 625 K levels separately for inside the vortex, boundary of it, and outside it. Further, we separated in time with Period-1 (15 Jan. - 10 Feb.), Period-2 (11 Feb. - 10 Mar.), and Period-3 (11 Mar. - 30 Apr.). In Period-1, the amount of $ClONO_2$ inside the vortex is lower than that outside the vortex at the 475 K level, suggesting the chlorine activation by PSCs. In Period-2, the amount of $ClONO_2$ inside the vortex is higher than that outside the vortex at the all levels, suggesting the deactivation process by which $ClONO_2$ forms. In Period-3, the amount of $ClONO_2$ at the vortex boundary is apparently lower than that inside the vortex, suggesting an earlier decrease of $ClONO_2$ at the vortex boundary. The cause of these variations would be due to temperature, aerosol surface area, insolation, and the amount of NO_2. For inside the vortex, $ClONO_2$ decreases at temperature below 195 K. It is ambiguous that the relation between $ClONO_2$ and aerosol extinction coefficient at 780 nm data. $ClONO_2$ decreases in the latter half of March when solar insolation increases. The relation between $ClONO_2$ and NO_2 is first presented from this continuous measurement, and the decrease of $ClONO_2$ is almost equivalent to the increase of NO_2 inside the vortex in March-April 1997.

(4) Sub-theme-4

The TTD analysis shows that there were 4 large outflow events of the Arctic polar vortex air toward the outside in the period Jan. 1 – April 30, 1997. In spite of the fact that the 1997 Arctic polar vortex was unusually stable, the analysis of the Antarctic vortex in the same year indicates that the Antarctic polar vortex was much more stable than the 1997 Arctic vortex.

A CTM calculation with a polar chemical ozone tracer shows that the effect on the ozone concentration outside the polar vortex near the vortex boundary in the equivalent latitude band of 55°-65°N and 450 K is 0.3 ppmv (15-20% of the ozone concentration at this height) and that on the total ozone is 12-15 DU (3-4% of the total ozone) by the end of April just before the final vortex breakup.

The degree of isolation of the polar vortex is determined by the downward advection in the vortex and horizontal mixing between inside and outside the vortex. The TTD analysis indicates that the air mass exchange due to the horizontal mixing is one order smaller than that due to the downward advection. The analysis also indicates that with the downward motion of 1.6 km/month, it is impossible for the vortex air to be completely replaced by the air from the outside by the end of the polar vortex breakup. This implies that the Arctic vortex 1997 does not necessarily behave as “Flowing Processor” of ozone destruction during the existence. In the vicinity of the polar vortex, however, the ozone concentration decreases due to the polar ozone depletion, showing that the Arctic vortex has a role of “Flowing Processor”. On the other hand, the Arctic polar vortex 1997 behaves as “Containment Vessel” when it breaks up, distributing the ozone depleted air into the surrounding air. All these results suggest that the Arctic polar vortex is not a perfect “Flowing Processor” but also an imperfect “Flowing Processor” and a partly “Containment Vessel”.

(5) Sub-theme-5

Vertical VMR profiles of O_3, HNO_3, N_2O, and CH_4 were measured by a ground-based Fourier spectrometer at Kiruna and compared to profiles derived from ILAS-II measurements on 19 different days. The resolution of the ILAS-II measurement profiles was degraded to the FTIR resolution to compare the measurements. Differences were between 10 and 15 % for all four gases. The VMR profiles of O_3, N_2O, and CH_4 were smaller for ILAS-II compared with the FTIR data; only for HNO_3 was the bias positive.

Other previous independent comparisons7), 8), 9) showed that the FTIR results are well-established to be able to validate satellite data. Differences in measurement time and location were constrained to less than 12 hours and 500 km. These criteria yielded 19 coincident measurements. A larger number of coincidences could have decreased differences and made the statistical results more robust. Some of the differences between the FTIR and ILAS-II could have arisen from the local and spatial differences of the measurements, although there is no large variability in space and time expected for the four gases, especially in September and October, where most of the coincidences are found. Another reason might be that the spectroscopic windows used by FTIR and ILAS-II were different.

5. Conclusions

We developed a method for retrieving gas and aerosol component precisely from the broadband (0.1 micron resolution) infrared spectrometer, like ILAS and ILAS-II, for the first time. For validating the retrieved gas profiles from the ILAS and ILAS-II data, observations of trace gases, temperature, and aerosols/PSCs (amount and size distribution) were conducted and their data retrieval techniques were studied for quantitative comparison/validation, with FTIR in Alaska, LEO-satellite GPS occultation, and balloon-borne particle counters, respectively, as well as use of ozonesondes campaign at Fairbanks, Alaska. Precise error analysis of FTIR data processing, and instrumental biases were studied. It was shown that O_3 and HNO_3 observed with ILAS-II and Alaska FTIR agreed within 20 % error. Balloon aerosol observations suggested that small particles with sizes down to 0.056 microns are important in precise estimation of ILAS and ILAS-II extinction. GPS occultation clarified couplings between atmospheric gravity waves and planetary waves/polar vortices, showing the technique was a strong tool to depict polar stratospheric temperature disturbances. Finally, the retrieved gas profiles from the ILAS and ILAS-II data were comprehensively validated to be able to use for polar stratospheric researches.

Using these established datasets, we obtained scientific results of several quantitative analyses in the 2003 Antarctic stratosphere and the 1997 Arctic stratosphere. First, we successfully derived the frequency of the polar stratospheric clouds (PSCs) in the Antarctic winter. Especially at 20 km altitude, the frequency was as high as 80% in the beginning of August, suggesting that this high frequency contributed to the chlorine activation through heterogeneous reactions on PSC particles. Second, from the short time variations of nitric acid and aerosol extinction coefficient data, quite distinct features between June and August were found. In June, the temporary denitrification was found, while in August the significant irreversible denitrification up to 10 ppbv of nitric acid depletion was found. Third, in conjunction to such a winter circumstance that could occur a large ozone hole in the 2003 Antarctic, we have also found significant ozone destruction and its loss rate. Especially at 21 km, ozone values decreased to zero in the end of September from 3 ppmv in the beginning of winter. The ozone loss rate was also as high as 80-90 ppbv/day in September which is identical to the largest record reported before. Forth, for dynamical processes, we found descent of air from mesosphere to stratosphere from summer to winter in the 2003 Antarctic using the methane data. Fifth, using the ILAS $ClONO_2$ data, we also found complicated features of chlorine partitioning in the 1997 Arctic. Especially, a good anti-correlation between $ClONO_2$ and NO_2 was found in March-April for the first time. Finally, we clearly showed that the degree of isolation of the 1997 Arctic vortex using the time-threshold diagnostics, the CCSR/NIES chemical transport model experiment, and ILAS data. The impact of the vortex air in which ozone was chemically depleted to air outside the vortex was quantitatively estimated. This new approach was first applied to study of airmass transport between the vortex.

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