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GEOPHYSICAL RESEARCH LETTERS, VOL. 21, NO. 13, PAGES 1371-1374, JUNE 22, 1994

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Abstract. Daily ground-based NO_2 column measurements have been conducted with UV-visible SAOZ diode-array spectrometers at Sodankyla in northern Finland since January 1990 and at 3 additional stations during EASOE. Inspection of the data indicates: a total NO_2 reduction by 30% by the Pinatubo aerosol in spring and summer 1992 compared to the previous years; a poor correlation in winter with potential vorticity indicative of motion of the vortex and of advection of air from mid-latitude, frequent during EASOE; an absence of significant global denitrification by sedimentation of nitric acid on PSC particles inside the vortex; and a high correlation between total NO_2 and 30 - 50 hPa temperature. The latter is unexpected in winter 1991-92, since most of NOx ($NO + NO_2 + ClONO_2 + 2N_2O_5$) at the altitude of the aerosol layer should have been converted into liquid nitric acid. This is expected to revert only slowly to NOx at high latitude in winter. The correlation suggests a temperature dependent saturation of the aerosol water / sulfuric acid droplets and / or a temperature dependent mechanism of restitution of NOx to the gas phase.

Introduction

Because of its ability to convert ClO into $ClONO_2$ in the stratosphere, that is to convert active chlorine compounds and thus to inhibit ozone destruction, NO_2 is one of the key parameters in the polar ozone depletion issue. However, its amount and variation in polar regions depend on many parameters: 1) dynamics, because of a possible advection of NOx species from other latitudes, 2) duration of the day, because of the photolysis of the NOx reservoirs and of the radicals themselves, 3) microphysics and heterogeneous chemistry on PSC, because of a possible removal of NOx from the stratosphere by sedimentation, 4) temperature, because of the dependence of all the above parameters to temperature and 5) volcanic aerosols in 1991 - 92 after the eruption of Mount Pinatubo, which are able to convert NOx into HNO_3 in the lower stratosphere, and then to deplete their concentration.

In order to investigate the influence of the above parameters on NO_2 column variations, ground-based UV-visible spectrometers were installed in the Arctic region at the latitude of the polar circle.

After first tests on a campaign basis begun in 1988 (Pommereau and Goutail, 1988), a SAOZ diode-array spectrometer, able to measure NO_2 columns from the ground twice a day at twilight, was installed permanently at Sodankyla in northern Finland (67°20 N, 26°E) in January 1990. For the purpose of EASOE, the above observations were reinforced by the deployment of 3 additional similar instruments at Scoresbysund in Greenland (71°N, 21°W), on-board the Norwegian weather ship Polarfront in station in the northern Atlantic (66°N, 02°E) and on the other side of the hemisphere, at Zhigansk (66°40, 123°E) in eastern Siberia. The data available from Sodankyla since 1990 and Zhigansk in winter 1991-92, will be used together with meteorological information from ECMWF, to investigate the relationship between NO_2 columns and dynamical and photochemical parameters.

Measurements

SAOZ is a 300 - 600 nm, 0.65 nm FWHM resolution, 512 elements diode array spectrometer looking at sunlight scattered by the atmosphere at zenith (Pommereau and Goutail, 1988). Measurements are performed every 5 minutes from sunrise until sunset. The data analyzed in real time are transmitted by satellite collection (ARGOS) for operational purpose and recorded onto diskettes sent by mail for further analysis. Results presented below are those of the reanalysis.

Nitrogen dioxide is measured by a differential absorption method in the visible bands between 412 and 515 nm, on 17 narrow features (1 - 5 nm large) simultaneously. Slant columns are determined after removal of the signatures of other absorbers(O_3, O_4, H_2O) present in the spectra, by an iterative procedure.

In order to retrieve the constituent vertical total column, slant columns are divided by an air mass factor (AMF) which corresponds to the enhancement of slant optical path compared to the vertical. AMFs are calculated with a simple scattering model with NO_2 profiles measured from balloon at mid latitude. AMF is postulated identical at sunset and sunrise and not to vary during the year. Its value is 17.7 at 90° SZA and 440 nm.

Each twilight vertical column results from an average of about 5 measurements performed between 86° and 91°. The precision (one standard deviation) of the vertical column estimated from the spectral least squares fit on the 17 NO_2

Paper number 93GL01783
0094-8534/94/93GL-01783$03.00

bands and for an average of 5 measurements during twilight, is of $1*10^{14}$ mol. cm^{-2}. Uncertainties of absolute cross-sections introduce a systematic error of 15%. The ones of AMF, not included above, will be discussed later. Recent intercomparison with totally different instrument / resolution / sampling / software / field of view in the frame of the Network for Detection of Stratospheric Changes (NDSC), have shown discrepancies not exceeding 2 10^{14} mol.cm^{-2} when converted into vertical columns, that is consistent with the above figure. Tropospheric pollution can also contribute. Large NO_2 column increases occur sometimes mostly in northern Scandinavia (Pommereau and Goutail, 1988) but never in Siberia. They are caused by a combination of surface pollution and multiple scattering enhancement. The largest are easy to detect and remove by looking at simultaneous spikes in O_4 absorption. However, small ones can still be present in the data set of Sodankyla.

Experimental data

Three years of permanent observations at Sodankyla in Finland are displayed in figure 1: morning and evening NO_2 vertical columns from which the largest polluted days have been removed in panel (a); difference between evening and morning in panel (b); temperature at 50 hPa measured by radio-sounding in panel (c).

An enlargement of the above observations at Sodankyla in winter 1991-92 together with those conducted at the same latitude, except on the other side of the hemisphere at Zhigansk, is shown in figure 2. Panel (a): morning and evening columns; panel (b) diurnal variation; panel (c) temperature at 10, 30 and 50 hPa from ECMWF; panel (d) potential vorticities (PV) at 475 K (approx. 20 km), 550 K (approx. 22 km) and 700 K (approx. 27 km), indicative of the motion of the vortex (high PV inside). NO_2 columns resulting from integration of vertical profiles measured from balloons above Sodankyla by solar occultation with a similar UV-vis spectrometer (Pommereau and Piquard, this issue), are also shown in panel (a): open circles for morning flights and close circles for the evening. Measurements at the two other European Arctic stations are not shown because of lack of space. They are very similar to the ones of Sodankyla.

Figure 1 demonstrates the large NO_2 seasonal variation at polar circle (maximum in summer, minimum in winter) and the semi-annual cycle of the amplitude of the diurnal variation, because of the absence of N_2O_5 photolysis during winter and of the inhibition of N_2O_5 formation during the polar day in summer. Compared to 1990 and 1991, the summer column maximum is reduced by 30% in 1992, as well as the spring amplitude of the diurnal cycle at similar temperature. This is attributed to volcanic aerosol from Mount Pinatubo which arrived first in September 1991 above Sodankyla, deepened progressively until January 1992 (Sarkissian et al., this issue) and deepened again after the vortex moved away from the European Arctic (Kastad et al., this issue). At smaller time scale, spikes related to tropospheric pollution are often present in Scandinavia but not in Siberia. Large variations persistent for a few days or weeks also appear very similar to the ones reported by Noxon (1979) and known as Noxon's "cliff". They correlate apparently to stratospheric temperature variation (end 1990).

Figure 2 demonstrates that balloon and ground-based NO_2 columns at Sodankyla are consistent, but at one occasion on January 30. Both instruments and their spectral analysis being identical, systematic errors are common. An AMF of 17.7 at 90°SZA is then consistent in winter.

The large difference between Sodankyla, located in the cold stratosphere of the European Arctic, and Zhigansk, in the warm stratosphere of the Siberian Arctic, is striking in figure 2. The quality of the data was checked carefully by looking at the complete diurnal cycles at high sun at noon at spring. There is no doubt: on average in winter, the NO_2 column is larger by a factor of 3 at Zhigansk. The reality of this effect is confirmed by the diurnal variation, small until early February at Sodankyla and already present from January 10, at Zhigansk. This indicates that not only total NO_2 but also N_2O_5 was larger above the eastern side of the Northern hemisphere in winter, in and outside the vortex.

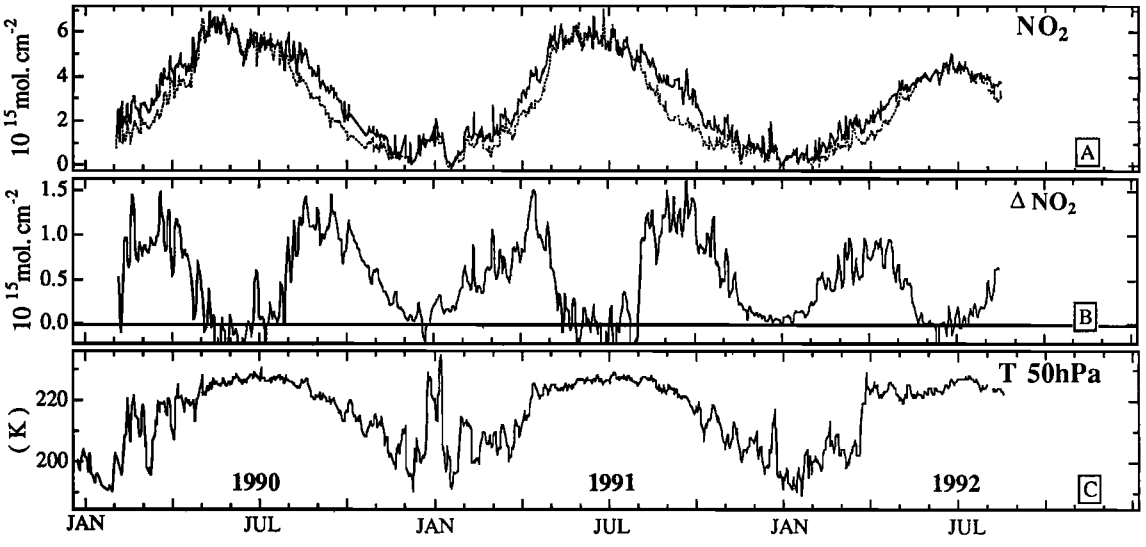

Fig 1. Three years observations at Sodankyla in northern Finland. Panel (A): NO_2 vertical columns measured twice a day, on the morning (····· lower curve) and the evening (— upper curve). Panel (B): difference between evening and morning (proportional to 2 times ΔN_2O_5). Panel (C): temperature from daily radio-soundings at the same station.

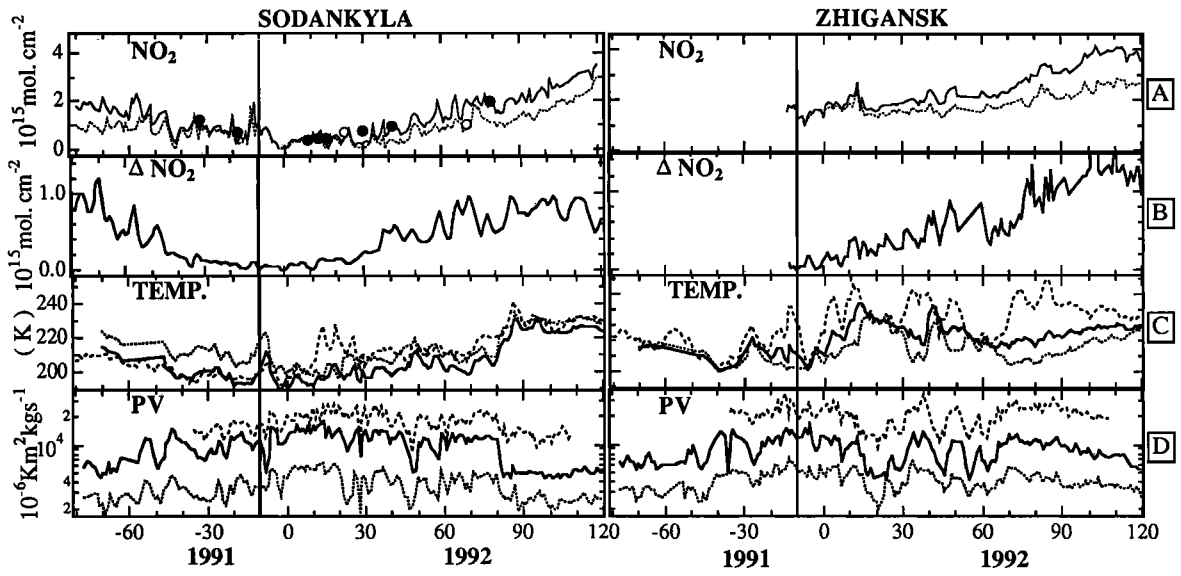

Fig 2. Measurements conducted during EASOE from October 1991 until April 1992 at Sodankyla (left) and Zhigansk in eastern Siberia (right) The vertical bar indicates the date of the solstice (21 December). Panel (A): morning (·····) and evening (——) NO_2 columns; Panel (B) evening-morning difference; Panel (C) temperature at 10 hPa (– – –) , 30 hPa (——) and 50 hPa (– · –) from ECMWF; Panel (D) potential vorticity (PV) at 700 K (– – –), 550 K (——) and 475 K (·····) in logarithmic ordinate.

The same is true also at spring in April, but in that case there is an explanation. By the end of March, the vortex moved rapidly away from the European Arctic toward Siberia and the aerosol layer extended in both density (x2) and altitude (up to 25 km) at Sodankyla (Kastad et al., this issue). In contrast, Zhigansk remained inside the vortex, up to the end of April. The difference in NO_2 columns between the 2 stations at Spring can thus be related to a difference in aerosol loading.

In winter and spring, NO_2 variations do not correlate with PV indicative of the motion of the vortex as observed at our station of Dumont d'Urville in Antarctica. There is no apparent difference between the inside and the outside, except after the final warming as said above. Zhigansk and Sodankyla both experienced the vortex and the outside during the winter. There is no NO_2 signature which would correspond to an advection of air from mid-latitude marked by low PV, e.g. during the second half of January above Sodankyla and which resulted in the lowest ozone columns recorded during the winter.

The 30-50 hPa temperatures seem to correlate best with the NO_2 variations, but not the 10 hPa one: a warming at this uppermost level in mid January at Sodankyla had no consequence on NO_2. The lowest NO_2 column ever recorded during the campaign was the one observed on 29 December at Sodankyla on the coldest day, where PSC, an ozone minihole and a temperature minimum as low as -92°C at 23 km were reported (Sarkissian et al., this issue). Warming at 30 and 50 hPa in winter are accompanied by NO_2 increases (e.g. end of 1990, 18-24 December 1991 at Sodankyla at the solstice when the sun remained below the horizon at noon, or 9-13 January at Zhigansk). Finally, similar NO_2 columns are observed at Zhigansk and Sodankyla at similar 30-50 hPa temperatures at the same date and thus same illumination. This occurred twice: on December 22-23, 1991 (about $1 * 10^{15}$ mol. cm^{-2} at around 205 K at the two stations) and on March 10 - 20, 1992 (about $2 * 10^{15}$ mol. cm^{-2} around 220 K). Most of the observed NO_2 (and N_2O_5) variations at a given station or between the two stations in winter, appear then to correlate best with temperature variations of the lower stratosphere.

Discussion

AMF factors. AMF used to convert slant into vertical columns, are derived from calculations assuming an NO_2 vertical distribution similar to that of mid latitude. New calculations with actual arctic NO_2 profiles measured from balloons, show that the current AMF might be sometimes overestimated in winter. This is demonstrated by the comparison between ground-based and balloon integrated total columns shown in figure 2. In winter, the weaker NO_2 layer at high altitude makes the lower stratosphere contribute relatively more. The largest difference occured on January 30, 1992 in presence of an NO_2 layer around 15 km (Pommereau and Piquard, this issue).

Another concern is the consequence of volcanic aerosol on retrieved NO_2 columns. For interpreting their observations in New Zealand in 1992, Johnston et al. (1992) have assumed a conservative possible AMF reduction of 20% because of the increased altitude of the scattering height at twilight. Single scattering calculations with actual NO_2 and aerosol optical thickness measured with SAOZ balloons, indicate an AMF reduction of few percent. Multiple scattering calculations by a Monte-Carlo method (Perliski and Solomon, 1992) concluded also to a very small contribution. The comparison of balloon and ground based total columns, this after, confirm. The consequence of the Pinatubo aerosol layer on NO_2 AMF at 440 nm and 90° SZA is not detectable, at least before the arrival of the thicker and higher altitude cloud, after the final warming.

Heterogeneous conversion of NOx onto volcanic aerosol. A 40% apparent reduction of NO_2 columns above New Zealand in austral winter and spring 1991 was reported by

Johnston et al., (1992). Here we report 30% at spring after the final warming and in summer and a negligible effect in winter in the Arctic. Because of the small contribution of the AMF reduction as said above and also of the small effect of additional sunlight attenuation (Perliski and Solomon, 1992), most of this is thought to be the consequence of an heterogeneous conversion of NOx into HNO_3 on sulfate aerosol (Lateltin et al., this issue). The difference between the two hemispheres could relate to the denser and higher aerosol cloud in the South (Johnston et al., 1992).

Relation between NO_2 columns and stratospheric transport. After Noxon, (1979), it was generally assumed that most of the observed NO_2 day to day fluctuations in winter were related to advection of air which had been previously more (south) or less (north) exposed to sunlight and that a fast transition between the two regimes explains the "cliff" which was sometimes reported. Inspection of the relation between PV at any level and NO_2 in figure 2, does not support this idea at least for 1991-92. Advection from lower latitude marked by low PV episodes at all levels, are not correlated with larger NO_2 columns. However, this might be due in 1991-92 to the large denoxification by aerosol at mid latitude which would result in a weaker latitudinal NOx gradient.

Denitrification. Inside the Antarctic vortex, NOx species are removed from the stratosphere by heterogeneous conversion into HNO_3 onto PSC particles, which are then sedimented (Mount et al, 1987). Lower NO_2 columns as well as smaller diurnal variations indicative of a reduction of N_2O_5 and thus of total NOx, is a common feature when the vortex approaches our station at Dumont d'Urville in Antarctica at spring. Nothing similar was observed during EASOE in the Arctic. Therefore it can be concluded that nothing special - denitrification or larger denoxification - happened inside the vortex in the Arctic in winter 1991-92.

NO_2 - Temperature relation. NO_2 columns variations are found to correlate the closest with 30-50 hPa temperatures in winter. Such correlation was already reported in the Arctic winter 1988, which was then partly understood only from gas phase chemistry considerations (Pommereau and Goutail, 1988). In 1991-92, volcanic aerosol surfaces were large enough to convert most of NOx up to 22-24 km into HNO_3 in the liquid droplets within a few days (Lateltin et al., this issue). The question is then to understand the presence of larger NO_2 columns at warm temperature. This would suggest a temperature dependent saturation of water / sulfuric acid droplets and a larger HNO_3 photolysis rate or a temperature dependent mechanism of restitution of NOx to the gas phase. Because of the absence of denitrification and of the strong adiabatic warming at each circling around the vortex, such NOx release at warm temperature, would have been able to prevent an ozone depletion in winter 1991-92.

Acknowledgements. This work was supported by European Economic Community in the frame of the EASOE campaign (Grants STEP-0013 and STEP-0141), by the French Programme Atmosphère Moyenne (PAMOY) and the Russian Federation Committee for Hydrometeorology, which are gratefully acknowledged.

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(Received: December 4, 1992; Revised: February 17, 1993; Accepted: June 30, 1993)