JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D12, PAGES 15,175–15,184, JUNE 27, 2000

Ozone loss rates in the Arctic stratosphere in the winter 1994/1995: Model simulations underestimate results of the Match analysis

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Abstract. We present box model simulations of ozone loss rates in the Arctic lower stratosphere for the winter 1994/1995. The ozone loss was simulated along each of the trajectories of the Match data set for 1994/1995 to conduct a quantitative comparison with the Match results. The simulated ozone loss rates reach their maximum value of $\approx$ 4 ppb per sunlit hour at the end of January. For this period and for potential temperatures below 475 K the model results are in good agreement with the Match results, but for potential temperatures above 475 K the model underestimates the ozone loss rate by up to a factor of 2. This difference cannot be explained by known uncertainties of the model. Enhanced ozone loss has also been observed in March 1995 for potential temperatures below 475 K. These loss rates are also substantially underestimated by the model, but are within the range of the model uncertainties. In particular, the ozone loss rates simulated for March 1995 strongly depend on the extent of denitrification.

1. Introduction

In the past decade, evidence for substantial ozone depletion in the Arctic lower stratosphere has been reported [e.g., *Browell et al.*, 1993; *Waters et al.*, 1993; *Manney et al.*, 1994; *Donovan et al.*, 1995; *Andersen*, 1999]. These observations have raised questions about the role of the coupling of chemistry and dynamics in Arctic ozone depletion and have underlined the necessity of quantitative estimates of the chemically induced ozone loss [e.g., *Solomon*, 1999]. Recently, various techniques have been developed to isolate the chemically induced ozone depletion from dynamical effects [*Manney et al.*, 1995; *von der Gathen et al.*, 1995; *Müller et al.*, 1996; *Deniel et al.*, 1998; *Knudsen et al.*, 1998; *Goutail et al.*, 1999; *Rex et al.*, 1999; *Lucic et al.*, 1999]. Attempts have been made to reproduce these observed chemical ozone losses in model simulations. However, several independent studies indicate that both box models and three-dimensional chemical transport models underestimate the ozone loss for the Arctic winter derived by such methods [*Hansen et al.*, 1997; *Deniel et al.*, 1998; *Goutail et al.*, 1999; *Woyke et al.*, 1999].

In particular, a comparison of ozone loss rates derived with the Match method for the winter 1991/1992 [*Rex et al.*, 1998] with corresponding box model results revealed that the model simulations significantly underestimate the early winter ozone loss [*Becker et al.*, 1998]. The Match technique determines the chemical ozone loss from a statistical analysis of pairs of ozone sonde measurements (so-called "matches"), which took place at two different points along a calculated air mass trajectory [*von der Gathen et al.*, 1995]. The relatively small number of matches in the winter 1991/1992 meant that a time-dependent comparison of Match and model results could only be carried out on the 475 K potential temperature level. In the winter 1994/1995 the coordination of more than 1000 ozone sonde launches lead to a larger number of matches, allowing the determination of time-dependent ozone loss rates over a wide height range [*Rex et al.*, 1999].

Here we present ozone loss rates simulated along the trajectories of the Match analysis for the winter 1994/1995, analogously to our box model study carried out for the winter 1991/1992 [*Becker et al.*, 1998]. The ozone change is simulated along each trajectory of the Match data set of 1994/1995 and evaluated in the same way as the Match ozone sonde measurements. This procedure allows a quantitative comparison of the model results with the Match deduced ozone loss rates.

The winter 1994/1995 was characterized by a strong polar vortex with temperatures below the equilibrium temperature of nitric acid trihydrate (NAT) occurring as early as mid December [*Naujokat and Pawson*, 1996]. A minor warming from mid January till mid February lead to an increase of vortex temperatures, but in March 1995 the minimum tem-

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Paper number 2000JD900056.
0148-0227/00/2000JD900056$09.00

peratures fell below the NAT equilibrium temperature again. The Arctic winter 1994/1995 was exceptionally cold [*Naujokat and Pawson*, 1996], and consequently strong ozone depletion has been observed [*Donovan et al.*, 1995; *Manney et al.*, 1996b; *Müller et al.*, 1996; *Goutail et al.*, 1999; *Rex et al.*, 1999].

The current consensus is that the Arctic ozone loss can be explained exclusively by halogen-catalyzed ozone destruction cycles [*Solomon*, 1990; *Anderson et al.*, 1991; *Solomon*, 1999]: In the polar winter, temperatures below ≈ 195 K allow the formation of polar stratospheric clouds (PSC). Heterogeneous reactions on PSC particles, especially $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$, convert the chlorine in the reservoir species HCl and $ClONO_2$ into Cl_2. With the return of sunlight, Cl_2 is rapidly photolyzed, and chlorine radicals are formed. In the lower stratosphere, ozone is destroyed mainly by the ClO-dimer cycle [*Molina and Molina*, 1987] and the BrO-ClO-cycle [*McElroy et al.*, 1986]. Additionally, the ClO-O cycle [*Molina and Rowland*, 1974] is of increasing importance at greater altitudes. In the present study we find significant differences between the ozone loss rates derived by the Match analysis for early winter and the corresponding model results much like for the winter 1991/1992 [*Becker et al.*, 1998]. Therefore the question arises whether the currently known ozone loss mechanisms may not be sufficient to explain the observed ozone loss.

The ozone loss terminates in spring, as chlorine is deactivated through reformation of $ClONO_2$ and HCl. In the Arctic, usually the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ is the dominant pathway for chlorine deactivation [*Müller et al.*, 1994; *Douglass et al.*, 1995]. The main source of NO_x is either the photolysis or the reaction with OH of HNO_3. Thus one might expect that denitrification of the vortex air masses by sedimentation of PSC particles should strongly influence the springtime ozone loss. In contrast, *Portmann et al.* [1996] concluded from two-dimensional (2-D) model simulations that denitrification has only moderate influence on the Antarctic and probably also the Arctic ozone loss. The results presented here show that under the conditions of the Arctic winter 1994/1995 the ozone loss rates simulated for the period from mid February to March are extremely sensitive to the assumed extent of denitrification. This conclusion agrees with the recent results of *Waibel et al.* [1999] for the winter 1994/1995 and supports the conclusion of *Rex et al.* [1997] that denitrification was important for the ozone loss in the Arctic winter 1995/1996.

2. Method

2.1. Model Description

The photochemical box model used in this study [*Müller et al.*, 1994; *Becker et al.*, 1998] includes a comprehensive set of gas phase and heterogeneous reactions relevant to the stratosphere. Kinetic parameters follow the recommendations of *DeMore et al.* [1997]. Additionally, the reaction channel $OH + ClO \rightarrow HCl + O_2$ is taken into account with a temperature-dependent branching ratio of about 6% [*Lipson et al.*, 1997]. The photolysis rates are calculated with an updated version [*Becker et al.*, 2000] of the spherical geometry scheme of *Lary and Pyle* [1991]. The model includes heterogeneous reactions on NAT, ice, sulphuric acid tetrahydrate (SAT) and liquid $H_2SO_4/HNO_3/H_2O$ solutions [*Carslaw et al.*, 1995, 1997]. NAT particles are assumed to form either from liquid aerosol particles or on SAT at a supersaturation with respect to NAT of 10, equivalent to about 3 K supercooling, consistent with observations in the Arctic vortex [*Schlager et al.*, 1990; *Dye et al.*, 1992]. The residual particles, which remain after NAT evaporation, are assumed to consist of SAT.

2.2 Simulation of the Match Analysis

As the ozone loss rate simulated along a specific trajectory strongly depends on the exact course of the solar zenith angle [e.g., *Becker et al.*, 1998], we simulate the ozone chemistry along each trajectory of the Match 1994/1995 data set to conduct a quantitative comparison with the Match results. The original Match trajectories, based on the meteorological analysis of the European Centre for Medium-Range Weather Forecasts (ECMWF) start at the position of the first ozone measurement of the respective match. These trajectories were extended 5 days backward to allow the model to better adapt to the photochemical conditions along the trajectories. To account for the bias of the ECMWF analysis temperatures close to the NAT formation temperature [*Knudsen*, 1996], the temperatures along the Match trajectories were reduced by 2 K. Sensitivity studies were performed with the unaltered temperatures. In the following, the extended and temperature adjusted trajectories are referred to as Match trajectories.

The ozone change simulated along each individual Match trajectory for the period between the two ozone sonde measurements is evaluated analogously to the Match ozone observations: A linear regression between ozone decrease and the time of exposure to direct sunlight of all matches within the time and height interval of interest yields the average ozone loss per sunlit time. Multiplying these loss rates with the vortex-averaged sunlit time per day gives the mean ozone loss per day [cf. *Rex et al.*, 1999].

2.3 Initialization

Similar as in our study on the winter 1991/1992 [*Becker et al.*, 1998], initial chemical species mixing ratios for the simulations along the Match trajectories were derived from simulations of the chemical evolution throughout the whole winter along idealized trajectories, representative for vortex air in the lower stratosphere (Table 1). Diabatic descent rates were estimated from the decrease of potential temperature of isolevels of the mixing ratios of CH_4 (from HALOE) and N_2O (from whole air sampler observations (A. Engel, personal communication, 1996)) over the winter, assuming no mixing with extravortex air takes place. The N_2O data were converted to equivalent CH_4 values using the CH_4/N_2O correlation of *Engel et al.* [1996]. The highest trajectory was started at the highest possible altitude for which observations were available for the chemical initialization (see be-

Table 1. Initialization of the Idealized Trajectories

Θ_s, K	Θ_e, K	N_2O, ppb	CH_4, ppm	O_3, ppm	Cl_y, ppb	HCl, ppb	$ClONO_2$, ppb	Br_y, ppt	NO_y, ppb	HNO_3, ppb	N_2O_5, ppb	H_2O, ppm	NO_y^{Feb}, ppb
386	368	270	1.55	0.57	1.15	0.34	0.81	6.5	3.3	2.43	0.003	4.41	4.3
419	379	210	1.32	1.16	2.12	0.79	1.33	12.8	7.0	5.53	0.006	4.05	5.5
446	390	180	1.20	1.85	2.50	1.19	1.31	14.7	9.1	7.58	0.01	4.46	5.9
477	401	150	1.09	2.69	2.81	1.44	1.37	15.7	11.3	9.61	0.03	4.83	6.5
512	417	120	0.98	3.15	3.05	1.62	1.43	15.9	13.3	11.32	0.08	4.93	5.3
567	438	90	0.86	3.61	3.22	1.83	1.39	15.9	15.2	12.48	0.45	5.10	5.0
620	462	60	0.75	3.89	3.32	2.02	1.30	15.9	16.5	11.26	1.72	5.36	7.4
645	472	45	0.69	3.97	3.35	2.17	1.18	15.9	16.8	9.74	2.47	5.49	8.7
659	485	30	0.63	4.01	3.36	2.20	1.16	15.9	16.2	8.51	2.76	5.65	10.3

Trajectories are starting on December 15, 1994, on the isentropic level Θ_s and are ending on March 31, 1995, on level Θ_e. In column NO_y^{Feb}, the NO_y profile measured on February 11, 1995, by *Sugita et al.* [1998] is shown; these data were used to determine the assumed rate of denitrification (see text).

low). Nine idealized trajectories were staggered to allow a sufficient vertical resolution in the altitude region of interest (Table 1).

The temperature along the idealized trajectories was assumed to oscillate around the vortex averaged temperature of the U.K. Meteorological Office (UKMO) analysis, with an amplitude reaching the vortex minimum of the UKMO temperature on the potential temperature levels reached by the trajectories at the end of the integration (Plate 1). The latitude of the idealized air parcel was assumed to oscillate simultaneously around 70° N. Corresponding to the dynamical evolution of the vortex, the amplitude of the latitude oscillation was chosen to be 10° before January 20 and from February 12 until February 26, up to 20° between January 20 and February 12, and 5° after February 26.

The chemical composition of the idealized air masses was initialized employing observations available for the Arctic vortex in 1994/1995 as much as possible: The O_3, HCl, and H_2O mixing ratios were interpolated to the respective methane levels from four HALOE (V18) profiles, measured inside the polar vortex between November 19 and 22, 1994 [*Müller et al.*, 1996]. The total amount of inorganic chlorine (Cl_y), inorganic bromine (Br_y), and reactive nitrogen (NO_y) was deduced from the correlation with N_2O (see *Woyke et al.* [1999], *Wamsley et al.* [1998], and *Sugita et al.* [1998] respectively). The fraction of Cl_y remaining after the subtraction of HCl was initialized as $ClONO_2$. The NO_y partitioning corresponds to results of the Mainz photochemical 2-D model (J.-U. Grooß, personal communication, 1997). The sulfate aerosol surface areas approximate the observations of *Deshler and Oltmans* [1998]. The specific values employed are listed in Table 1 for all nine idealized trajectories.

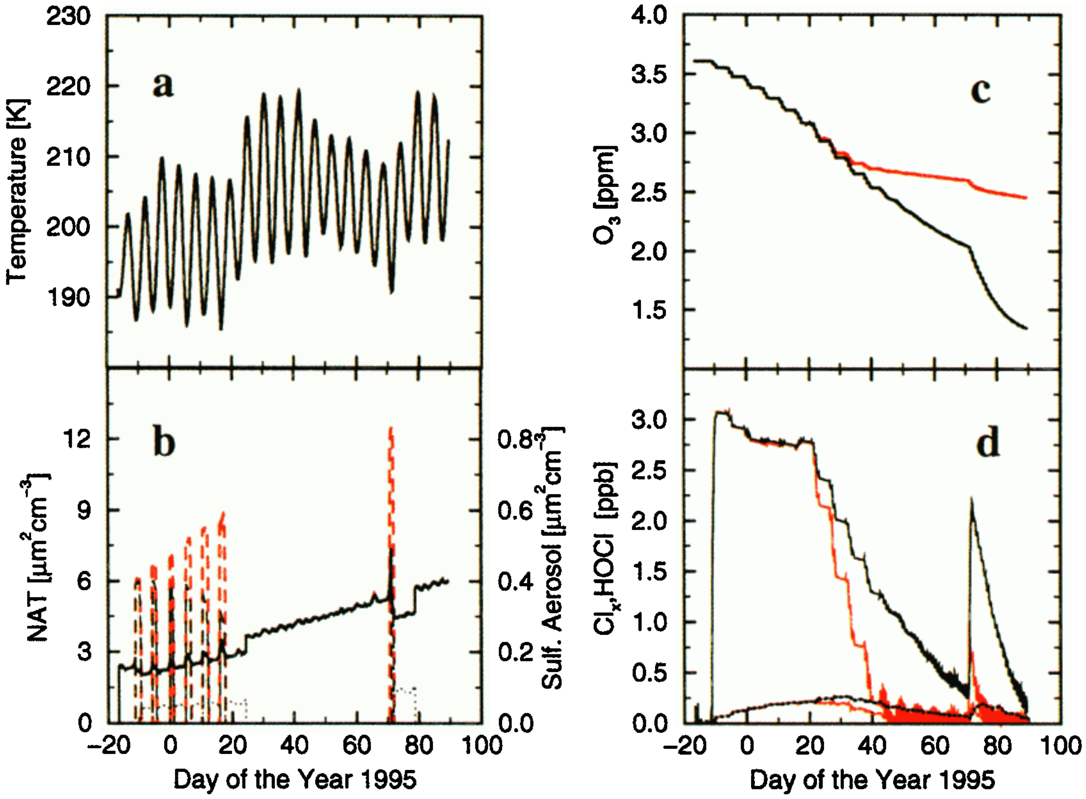
Several measurements indicate that substantial denitrification occurred during early winter 1994/1995 in the Arctic [*Fischer et al.*, 1997; *Arnold et al.*, 1998; *Sugita et al.*, 1998; *Waibel et al.*, 1999]. To account for denitrification, we assumed a linear decrease of the HNO_3-mixing ratio whenever NAT particles exist. The rate of HNO_3 decrease was adapted to reproduce an NO_y profile measured on February 11, 1995, by *Sugita et al.* [1998] (Table 1). Without denitrification the chlorine deactivation proceeds faster (Plate 1). Moreover, in this case the steady degradation of HNO_3 causes a buildup of N_2O_5 after the chlorine deactivation is completed, and NO_x is no longer consumed by the reaction of NO_2 with ClO. In this case any chlorine reactivated during the cold period in March is immediately converted into $ClONO_2$, since N_2O_5 acts as a NO_x reservoir. Note that because the denitrification takes place before the chlorine deactivation sets in, its exact timing has no significant influence on the simulated ozone loss.

The results calculated for the idealized trajectories agree well with observations of $ClONO_2$ and HNO_3 inside the polar vortex if denitrification is taken into account, while the simulations without denitrification overestimate the observed $ClONO_2$ and HNO_3 mixing ratios (Plate 1 and Figure 1) substantially.

3. Results

3.1. Simulated Ozone Loss Rates

Figure 2 compares the ozone loss rates derived from simulations along the Match trajectories with the corresponding Match results on the four potential temperature intervalls between 440 K and 490 K, where the statistical errors of the Match results are smallest. The simulated ozone loss rate over the whole height range accessible with our initialization method is compared with the corresponding Match results in Plate 2. Two periods of enhanced ozone loss rates can be distinguished. Consistent with the Match analysis, the model predicts the maximum ozone loss per sunlit time for end of January. For potential temperatures below 475 K, the simulated ozone loss rates agree well with the Match results. However, for potential temperatures above 475 K, the model underestimates the early winter ozone loss by up to a factor of 2. Similar discrepancies between Match and model results have been found for late January and early Febru-



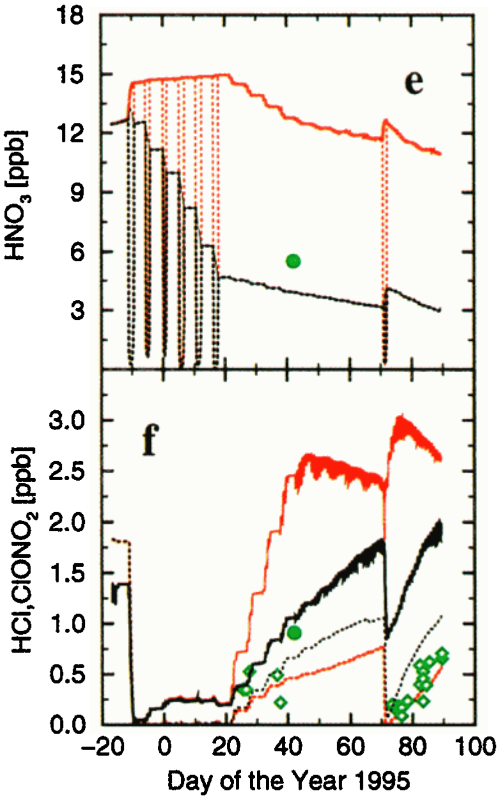


Plate 1. Results of the simulations along the sixth idealized trajectory (descending from 567 K to 438 K) with denitrification (black lines) and without denitrification (red lines). (a) Temperature. (b) NAT surface area (left axis, dashed line), SAT, and liquid sulfate aerosol surface area (right axis, dotted and solid line). (c) Ozone mixing ratio. (d) Active chlorine (solid line) and HOCl (dotted line) mixing ratio. (e) Total (solid line) and gas phase (dotted line) HNO_3 mixing ratio. (f) $ClONO_2$(solid line) and HCl (dotted line) mixing ratio. The green solid circle represents in Plate 1e a MIPAS HNO_3 measurement and in Plate 1f represents a MIPAS $ClONO_2$ measurement [*von Clarmann et al.*, 1997]. Green diamonds represent HALOE HCl measurements inside the polar vortex [*Müller et al.*, 1996].

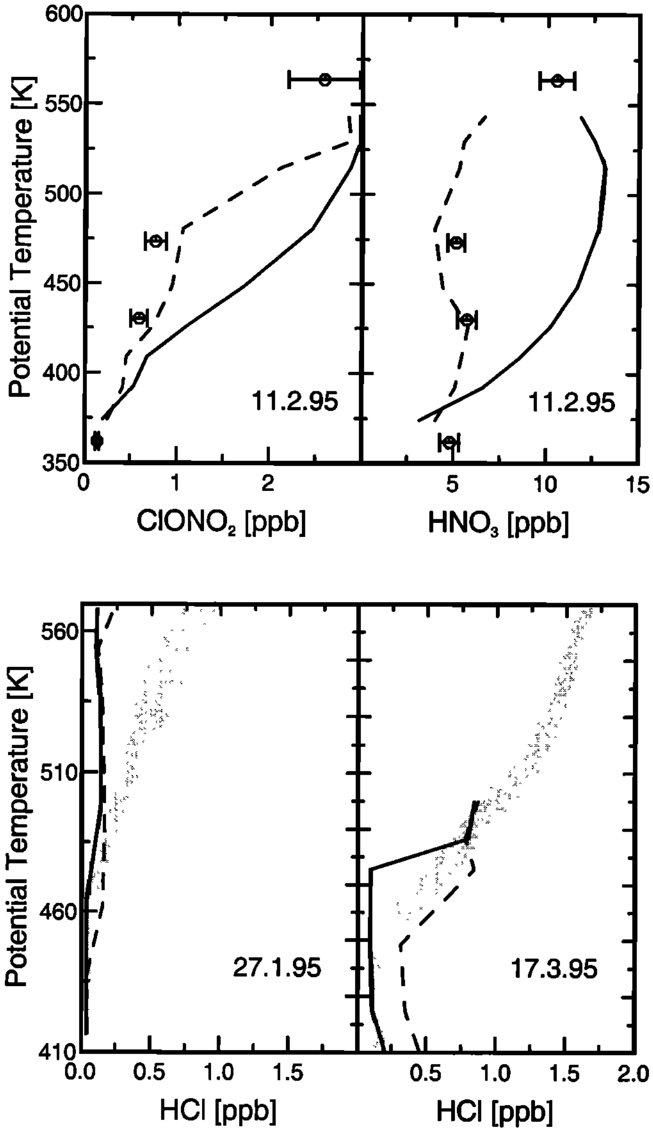


Figure 1. Profiles deduced from the simulations along idealized trajectories with denitrification (dashed line) and without denitrification (solid line) in comparison with observations. (top) HNO_3 and $ClONO_2$ profile measured by the MIPAS instrument on February 11, 1995 [*von Clarmann et al.*, 1997]. (bottom) Range of HCl profiles measured by the HALOE instrument between January 26 and 28, 1995 (three profiles) and between March 15 and 18, 1995 (six profiles) [*Müller et al.*, 1996].

ary 1992 [*Becker et al.*, 1998]. Also I. Kilbane-Dawe et al. (A comparison of Match and 3-D model ozone loss rates in the arctic polar vortex during the winters of 1994/1995 and 1995/1996, submitted to Journal of Atmospheric Chemistry, 2000) found discrepancies between the ozone loss rates of the Match data set for the winters 1994/1995 and 1995/1996 and simulations employing a three-dimensional chemical transport model. During January 1995 the model (available) chlorine for potential temperatures <500 K is nearly completely activated (Plate 1) so that at this time the extent of denitrification has little influence on the simulated ozone loss. However, the timing of chlorine deactivation later in winter is determined by the extent of denitrification assumed in the model simulations; ozone destruction continues for approximately 2 weeks longer if denitrification is taken into account.

Enhanced ozone loss rates have also been observed during a cold period in March. Owing to the longer sunlit time per day, this period contributes up to 50 % of the integrated ozone loss in an airparcel according to the Match results. During this period typical Match trajectories reach minimum temperatures close to the NAT equilibrium temperature. Thus chlorine reactivation takes place on liquid aerosol slightly above the NAT formation temperature and for some trajectories also on NAT particles. The temperatures at isentropic levels above ≈ 450 K do not allow significant chlorine reactivation in the model. If denitrification is neglected, the ozone loss rates are only slightly enhanced. The ozone loss rates the model yields with denitrification are approximately twice as high as without denitrification.

This result does not agree with the conclusions of *Portmann et al.* [1996] based on two-dimensional model simulations of the Antarctic winter. They proposed that denitrification might not be necessary to reach an ozone loss in the Arctic which is comparable to the one observed in the Antarctic. The different behavior in our simulations is probably caused by the different relative importance of HCl and $ClONO_2$. In our calculations for the Arctic winter 1994/1995, the available chlorine is practically completely activated and during chlorine deactivation predominatly $ClONO_2$ (Plate 1) is reformed. In contrast, in the simulations of *Portmann et al.* [1996] HCl is most of the time the dominant chlorine reservoir. In the latter case, additional $ClONO_2$ reacts heterogeneously with HCl and thus leads to additional active chlorine instead to a chlorine deactivation. Furthermore, due to the lower temperatures in the Antarctic vortex, the heterogeneous reaction of $ClONO_2$ with H_2O is more efficient and counteracts the reformation of $ClONO_2$, as long as the air masses are not dehydrated to a large extent.

Even if denitrification is considered in our simulations, however, the model still underestimates the ozone loss rates during March. The following section investigates, whether the differences between Match deduced ozone loss rates and simulated ozone loss can be attributed to uncertainties of model parameters.

3.2. Sensitivity Studies

In the following, we focus on the altitude regions and time periods where the largest differences between Match and model results occur: The ozone loss periods in early winter at 490 K and in March at 440 K. As the reference case, we employ the simulations with denitrification.

3.2.1. Results for 490 K. Earlier we have demonstrated that uncertainties of the relevant rate constants and photolysis rates, of the Cl_y and of Br_y mixing ratios, and the details of the heterogeneous chemistry cannot explain the difference between the Match results and the corresponding simulated ozone loss rates for early winter 1991/1992 on the 475 K

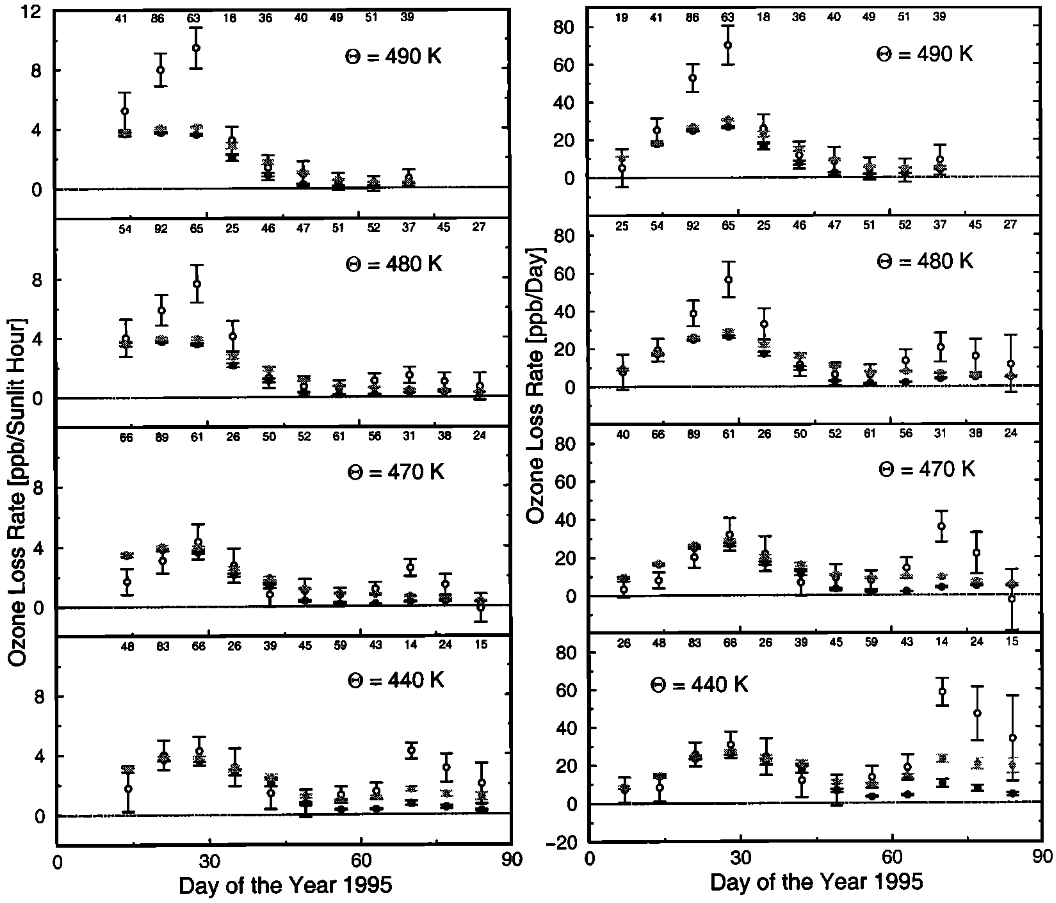


Figure 2. Time dependence of (left) the ozone loss per sunlit hour and (right) the ozone loss per day for various potential temperatures. Results of the Match analysis (open circles) [*Rex et al.*, 1999] in comparison with model results obtained with denitrification (solid grey circles) or without denitrification (solid black circles). Each point was deduced from Matches inside a ±7 day time interval and a ±10 K potential temperature interval. The number of matches contributing to each point is specified at the upper edge of each panel. The error bars correspond to the 1 σ uncertainty of the linear regression.

level [*Becker et al.*, 1998]. This conclusion can be transferred to the situation in early winter 1994/1995. Plate 3a, summarizes the sensitivity of the simulated ozone loss rates to variations of the kinetic parameters that determine the efficiency of the ozone loss cycles relevant for the 490 K level. While some enhancement of the ozone loss rates can be achieved in this way, the observed loss rates above 6 ppb per sunlit hour are not reproduced.

To validate our initialization procedure based on idealized trajectories, we investigated the sensitivity of the model results to the backward extension of the Match trajectories. Match trajectories extended an additional 10 days backward yield somewhat lower ozone loss rates (green line in Plate 3b), thus our initialization may slightly overestimate the degree of chlorine activation. This is not surprising, as the available chlorine in the simulations along the idealized trajectories is almost completely activated during early winter (Plate 1). Thus uncertainties in the initialization are unlikely to be responsible for the underestimate of the observed ozone loss rates. Additionally, we carried out simulations where the major deactivation reactions ($ClO + NO_2$, $CH_4 + Cl$, $ClO + OH$) have been omitted. The results (violet line in Plate 3b) show that the discrepancies between Match and model results cannot be explained by chlorine deactivation occurring too rapidly in the simulations along the Match trajectories.

Plate 3 further demonstrates that the simulated ozone loss rates for 490 K change by no more than 0.15 ppb per sunlit hour, if the 2 K temperature correction is omitted or replaced by short-term temperature reductions of 10 K (red and blue line in Plate 3b). This last case was introduced to estimate the possible influence of mesoscale temperature fluctuations as induced by orographic gravity waves. Temperatures are reduced, typically for 1 or 2 hours, by 10 K whenever the trajectory is located between 338° and 342° longitude, corresponding to the lee side of Greenland. In summary, the ozone loss rates deduced by the Match analysis for end of January on the 490 K level cannot be explained within the framework of the currently accepted chemistry.

3.2.2. Results for 440 K. The early winter results show that at this altitude simulated ozone loss rates of the order of 4 ppb per sunlit hour, as they are observed in March 1995, are possible, if most of the available chlorine is activated. Thus our sensitivity studies for March 1995 on the 440 K

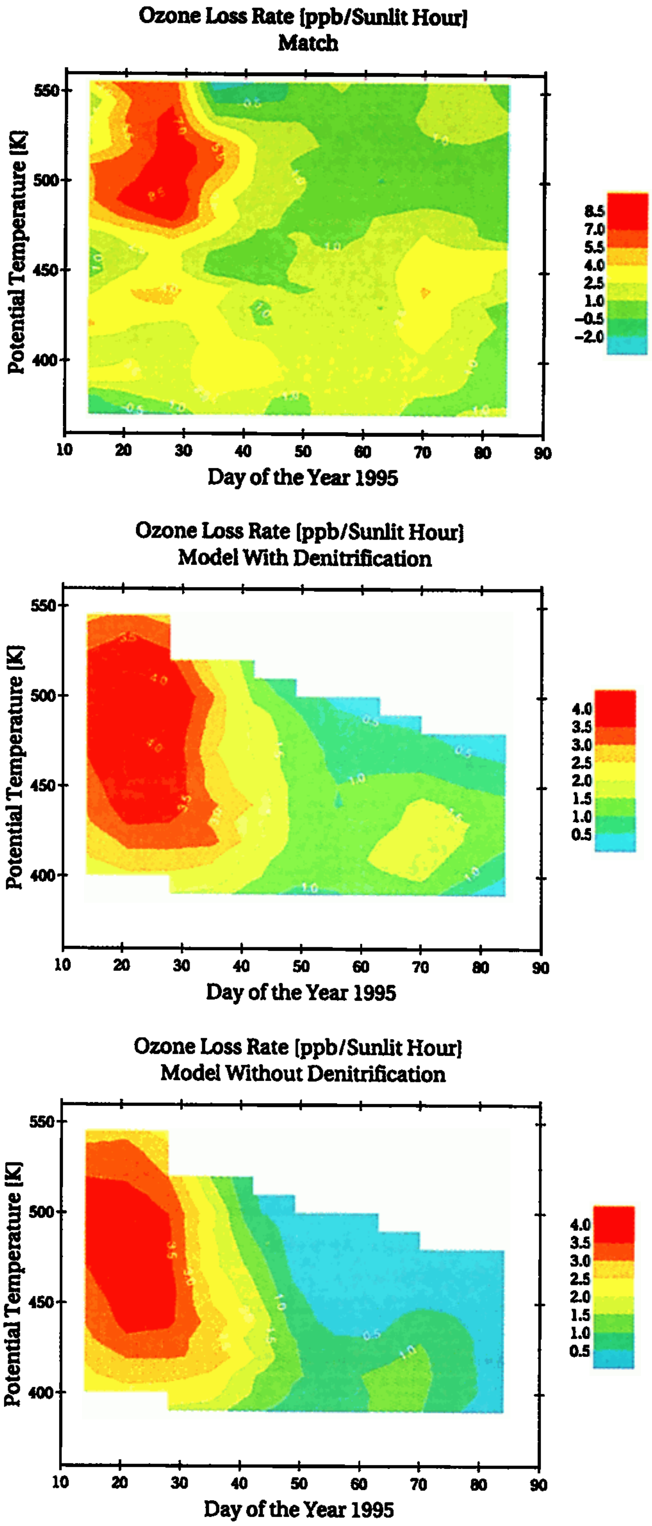


Plate 2. Height and time dependence of the ozone loss per sunlit hour. The loss rates were deduced by linear regression over matches in time intervals of ±7 days and potential temperature intervals of ±10 K. Potential temperature intervals of ±15 K were used for Match results above 530 K. Note that the top panel has a different color scale.

level mainly focus on the question, whether the model underestimates the degree of chlorine activation during that period.

Typical Match trajectories for March 1995 reach minimum temperatures close to the NAT point. Thus the simulated chlorine activation and consequently the simulated ozone loss rates vary strongly with the temperature along the Match trajectories. If the analysis temperatures are used without correction (red line in Plate 3d), hardly any reactivation takes place. If, on the other hand, temperatures are reduced by 3 K instead of 2 K (violet line in Plate 3d), the ozone loss rate is enhanced by up to 30%. Like on the 490 K, level short time temperature fluctuations of 10 K have nearly the same effect as a constant temperature reduction of 2 K.

As the heterogeneous processing partly takes place on liquid aerosol at temperatures slightly above the NAT formation temperature, the ozone loss rates are also sensitive to changes in the surface area of the sulfate aerosol. Simulations with doubled aerosol surface area yield up to 30% higher ozone loss rates (red line in Plate 3c).

Furthermore, the $ClONO_2/HCl$ ratio at the beginning of March impacts the simulated ozone loss rates. As the chlorine reactivation mainly takes place through heterogeneous reaction of $ClONO_2$ with HCl, any $ClONO_2$ surplus does not get activated. Thus, for example, the consideration of the additional HCl production through the reaction channel $ClO + HO_2 \rightarrow HCl + O_3$ [*Finkbeiner et al.*, 1995] leads to ozone loss rates enhanced by ≈ 20% in March (green line in Plate 3c).

The reaction probabilities of the heterogeneous reactions as well as the NAT formation temperature depend on the water vapor mixing ratio. One might speculate that besides denitrification, also dehydration took place in the 1994/1995 winter. If we assume a strong dehydration to ≈ 3 ppm H_2O, no significant reactivation takes place (blue line in Plate 3c). Thus our conclusion that the simulated ozone loss rates strongly depend on the assumed denitrification is only valid if no substantial dehydration took place simultaneously. However, balloon-borne H_2O measurements in the Arctic in 1994/1995 [*Ovarlez and Ovarlez*, 1996] do not show a clear signal of dehydration. Further, the model study of *Waibel et al.* [1999] on the winter 1994/1995 offers an explanation for the observed denitrification in the Arctic with only moderate concurrent dehydration occurring.

In summary, the ozone loss simulated for March 1995 is very sensitive to model assumptions that influence the efficiency of the chlorine activation. These assumptions cannot be constrained with certainty by observations. Thus we cannot rule out the possibility that the difference between Match and model results for this period is due to model uncertainties. For example, the simulated ozone loss rates almost correspond to the Match results if a 3 K temperature reduction is combined with a doubled sulfate aerosol surface area and an additional reaction channel $ClO + HO_2 \rightarrow HCl + O_3$ with a 3% branching ratio (violet line in Plate 3c).

4. Summary

We have presented box model simulations of ozone loss rates in the Arctic winter 1994/1995 that correspond to the results of the Match analysis. Enhanced ozone loss was found in the model as well as in the Match analysis in early winter, with the maximum loss rates occurring at the end

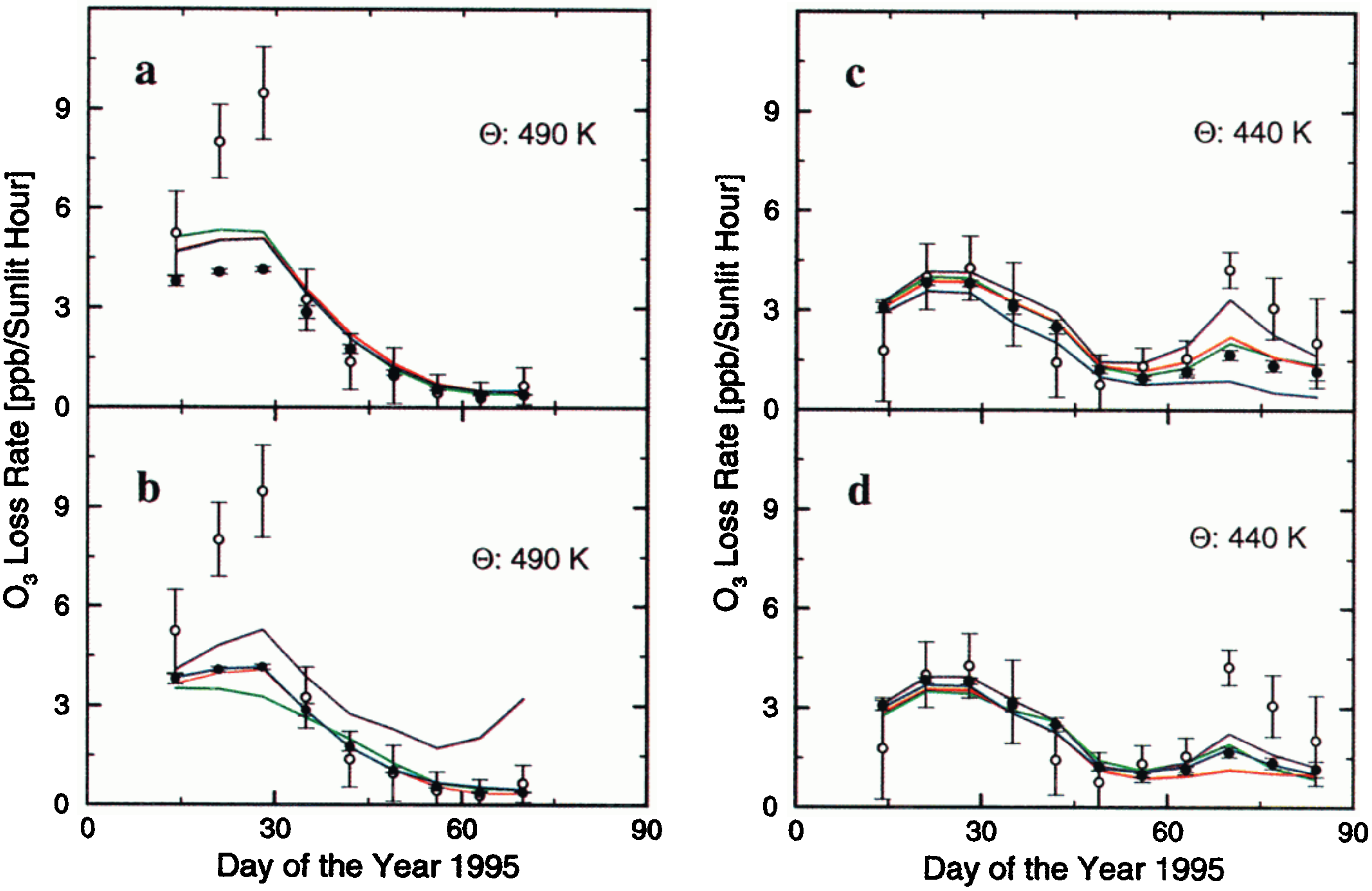


Plate 3. Sensitivity studies. The solid circles correspond the reference case, and the open circles correspond to the Match results. (a) Results for 490 K: Simulations with doubled Cl_2O_2 photolysis rate and Cl_2O_2 formation rate constant chosen as the upper limit of the uncertainties according to *DeMore et al.* [1997] (green line), simulations with doubled BrCl photolysis rate and rate constants of the reactions $ClO + BrO \rightarrow BrCl + O_2$ / $Br + ClOO$ chosen as the upper limit of the uncertainties according to *DeMore et al.* [1997] (red line), simulations with O_3 photolysis rate doubled and rate constant of the reaction $ClO + O \rightarrow Cl + O_2$ chosen as the upper limit of the uncertainties according to *DeMore et al.* [1997] (blue line). (b) Further results for 490 K: Simulations along Match trajectories expanded an additional 10 days backward (green line), along Match trajectories without temperature correction (red line), with short-term temperature fluctuations of 10 K instead of a constant temperature correction (blue line), and simulations without chlorine deactivating reactions (violet line). (c) Results for 440 K: with an additional reaction channel $HO_2 + ClO \rightarrow HCl + O_3$ [*Finkbeiner et al.*, 1995] with as 3% branching ratio (green line), with doubled background aerosol surface area (red line), with dehydration to ≈ 3 ppm H_2O (blue line), and with a combination of the reaction channel $HO_2 + ClO \rightarrow HCl + O_3$, dehydration and a temperature reduction of 3 K (violet line). (d) Further results for 440 K: like Plate 3b, except simulations along Match trajectories with a temperature correction of −3 K (violet line).

of January, and during a cold period in mid March. The model substantially underestimates the ozone loss rates in both periods. The differences between the ozone loss rates simulated for early winter 1994/1995 and the corresponding Match results vary strongly with height: Match and model results in January agree well for potential temperatures below 475 K, but for potential temperatures above 475 K the model underestimates the ozone loss by up to a factor of 2.

Sensitivity studies were carried out to investigate the significance of these differences. The early winter differences cannot be explained by uncertainties of the model parameters. The ozone loss rates simulated for March strongly depend on the assumed extent of dehydration, the exact temperatures along the Match trajectories, the sulfate aerosol surface area, and assumptions on possible additional HCl production channels. For the conditions of the Arctic winter 1994/1995, in particular denitrification played an important role for the enhanced ozone loss in March. Thus, while substantial, the differences between the simulated ozone loss and the Match results for March are not necessarily significant.

Independent techniques have been used to estimate the chemically induced ozone loss in the winter 1994/1995 [*Manney et al.*, 1996a; *Müller et al.*, 1996; *Deniel et al.*, 1998;

Goutail et al., 1999; *Woyke et al.*, 1999]. The results of those studies are consistent with the Match results, giving no reason to question the validity of the Match analysis. Further, independent model studies [*Deniel et al.*, 1998; *Goutail et al.*, 1999; *Woyke et al.*, 1999] likewise found large discrepancies between simulated ozone loss and ozone loss deduced from observations. Moreover, an intercomparison of a variety of chemical models confirms that the differences between early winter Match results for 1994/1995 and the corresponding model results cannot be explained by specific errors of the particular model used here (M. Krämer, personal communication, 1999).

The difference between the ozone loss rates simulated for early winter 1991/1992 and 1994/1995 and the corresponding Match results remains an open question. Apparently, the currently known ozone loss mechanisms are not sufficient to explain the observed ozone losses in the Arctic.

Acknowledgments. We thank the U.K. Meteorological Office and the European Centre for Medium-Range Weather Forecasts (ECMWF) for providing their meteorological analyses, J. M. Russell III and the HALOE team for providing HALOE data, A. Engel for the whole air sampler N_2O data, and J.-U. Grooß for 2-D model results. This work was partly supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie.

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(Received August 10, 1999; revised January 13, 2000;
accepted January 18, 2000.)