Ozone loss rates in the Arctic stratosphere in the winter 1991/92: Model calculations compared with Match results

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Abstract. We present box model calculations of ozone loss rates corresponding to the results of the Match experiment 1991/92. The Match technique infers chemical ozone depletion from an analysis of pairs of balloon soundings that measure ozone in the same airparcel at different points of a calculated trajectory. It allows a quantitative comparison with model results because the exposure of the observed airmasses to sunlight is well known. The model significantly underestimates the loss rates inferred for January to mid-February. Extensive sensitivity studies show that the discrepancy between model and Match results cannot be explained by the known uncertainties in the model parameters.

Introduction

In recent years substantial chemical ozone depletion has been observed in the Arctic polar vortex [e.g. *Waters et al.*, 1993; *Manney et al.*, 1996; *Müller et al.*, 1996]. It is now widely accepted that this ozone loss is qualitatively understood in terms of halogen-catalyzed chemistry. Nevertheless, recent studies indicate that current models underestimate the observed ozone depletion [*Goutail et al.*, 1998; *Hansen et al.*, 1997; *Woyke et al.*, 1997]. *Edouard et al.* [1996] proposed that the limited spatial resolution of 3D models could account for the discrepancy between observed and simulated ozone loss. However, box models are not affected in this way and may even overestimate ozone loss rates by failing to account for mixing processes. Here, we present a box model study that quantitatively tests the current understanding of chemical ozone destruction.

The ozone loss in an airparcel strongly depends on its exposure to sunlight and, in particular under twilight conditions, the precise value of the solar zenith angle (Fig. 1). Therefore, a quantitative comparison of simulated ozone loss with observations requires a detailed knowledge of these quantities. Such data are available from the Match analyses [*von der Gathen et al.*, 1995], where trajectory calculations are used to identify pairs of balloon soundings that measure ozone in the same airmass at two different times and locations. As the uncertainties connected with such a single "match" ($\approx 10\%$) are of the same order as the ozone change occuring over a few days, the chemically induced ozone loss

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must be deduced from a statistical analysis of many matches.

The first Match analysis was carried out for the winter 1991/92 employing ≈ 1200 ozonesondes launched from 26 stations [*Rex et al.*, 1998]. A suitably initialized photochemical box model was time integrated along each trajectory of the 1991/92 Match analysis in the potential temperature range 465-485K. In the following we compare the simulated ozone loss rates with the corresponding Match results.

Model Description and Initialization

The photochemical box model used here [*Müller et al.*, 1994] includes a comprehensive set of gas phase and heterogeneous reactions for stratospheric chemistry, employing recommended kinetic parameters [*DeMore et al.*, 1997]. The reaction channel $OH + ClO \rightarrow HCl + O_2$ was included with a temperature dependent branching ratio of about 6% [*Lipson et al.*, 1997]. The photolysis rates are derived from a spherical geometry scheme [*Lary and Pyle*, 1991]. Heterogeneous chemistry includes 11 reactions on NAT and ice, 3 reactions on SAT, and 8 reactions on $H_2SO_4/HNO_3/H_2O$ solutions [*Carslaw et al.*, 1995], including the key bromine reactions [*Lary et al.*, 1996]. We assume that NAT particles form either from the liquid aerosols or on SAT at a supersaturation with respect to NAT of 10, equivalent to about 3K supercooling, consistent with observations in the Arctic vortex [*Schlager et al.*, 1990; *Dye et al.*, 1992]. Evaporating NAT crystals are assumed to release SAT particles.

To derive ozone loss rates corresponding to the Match results the change in the ozone mixing ratio has to be simulated along each trajectory of the Match dataset. The 1991/92 Match analysis is based on 10 day backward trajectories [*Knudsen and Carver*, 1994] ending at the locations of the ozonesonde stations. Although the first ozone measurement is located near some point along the trajectory, we calculated the chemical evolution over the whole 10 day period, allowing the model to adapt to the photochemical conditions along the trajectory before the first measurement of the Match pair is reached. We derived initialization values for these model runs from simulations of the chemical evolution throughout the winter along three idealized trajectories (Fig. 2). These trajectories were chosen to descend from different altitudes, with a maximum distance of $\approx 50K$ in potential temperature (Θ), so that for the period of interest results representative of the Θ range 465-485K can be obtained by linear interpolation in Θ. These initial values are broadly consistent with HALOE, CLAES, MLS, and MIPAS observations inside the polar vortex [*Müller et al.*, 1996; *Douglass et al.*, 1995; *von Clarmann et al.*, 1993]. The initialization for each Match trajectory and the simulated and observed ozone mixing ratios are available as supplementary material.
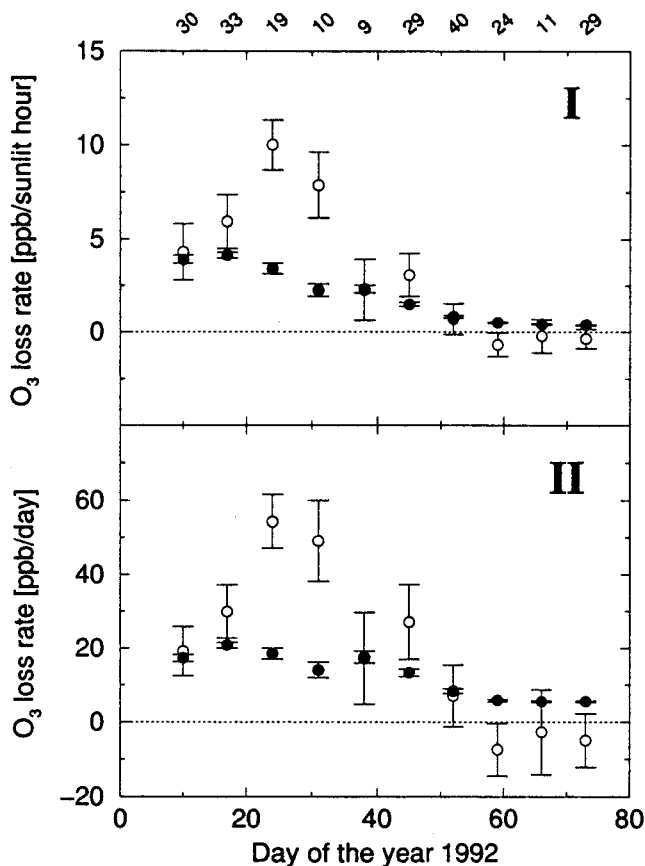
Figure 3. Comparison between ozone loss rates inferred by the Match analysis [Rex et al., 1998] (open circles) and ozone loss rat es analogously inferred from model simulations along the trajectories of the Match dataset (filled circles). I: Ozone loss per sunlit time. II: Ozone loss per day. The ozone loss rates result from linear regressions over all matches in the potential temperature range 465-485K, inside the polar vortex classified into time intervals of ±7 days. The number of matches contributing to each point is specified above panel I. The error bars denote the 1σ uncertainty of the linear regressions.

Finally, we investigated the influence of uncertainties in the laboratory data describing the kinetics of the ClO dimer and the ClO-BrO cycle. Additionally we doubled all photolysis rates to examine the effect of errors of the actinic flux calculated by the photolysis code. The ozone loss rates inferred by the Match experiment cannot be reproduced on the basis of plausible assumptions on the errors of the ki-
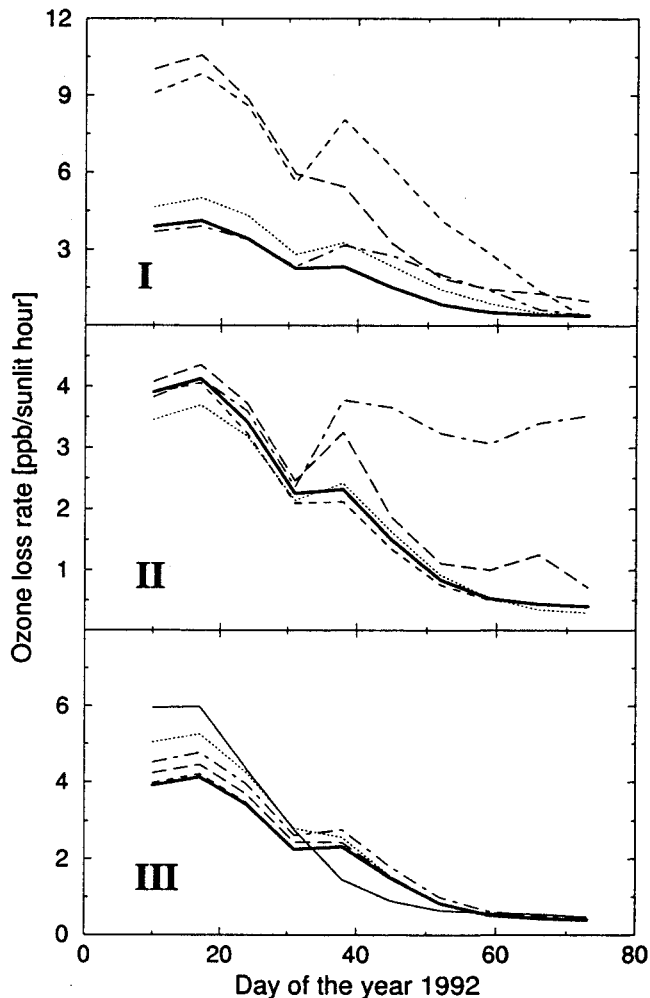

Figure 4. Results of the sensitivity studies. In all panels the reference case is plotted as thick solid line. I: Initialization based on idealized trajectories without latitude oscillation (dot dashed line), initialization of the idealized trajectories with 3.6 ppb Cl_y (dotted line), 8 ppb Cl_y (dashed line), and 100 ppt Br_y (long dashed line); II: model runs assuming SAT formation at equilibrium (dotted line), and model runs assuming only liquid aerosol (dashed line), model runs along Match trajectories with temperatures reduced by 5K (long dashed line), and results obtained omitting the chlorine deactivating reactions for the model runs along the Match trajectories (dot dashed line); III: model runs with doubled Cl_2O_2 photolysis rate (dotted line), rate constant for Cl_2O_2 formation corresponding to the upper limits given by DeMore et al. [1997] (dashed line), doubled BrCl pho tolysis rate (long dashed line), rate constants for the reactions ClO + BrO $\rightarrow$ BrCl + O_2 / Br + ClOO corresponding to the upper limit given in [DeMore et al., 1997] (dot dashed line), and with all photolysis rates doubled (solid line).
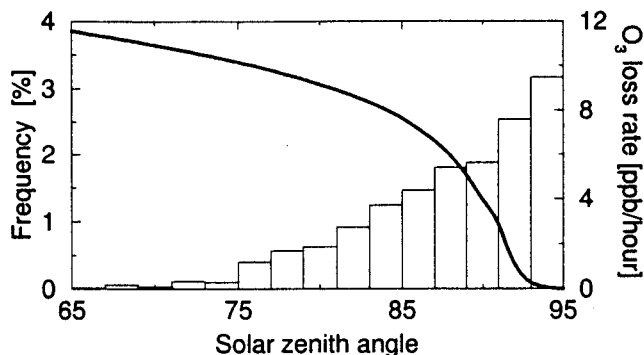
1 ppb HCl does not get activated. Such values are clearly unrealistic.

Next the question arises whether the model underestimates the degree of chlorine activation. The model runs along the idealized trajectories result in complete chlorine activation near day 20 (Fig. 2). Therefore during the period of maximum ozone loss our initialization procedure can only overestimate the fraction of chlorine activated. Model runs exploring various formation mechanisms of aerosol particles, like complete freezing of the sulfate aerosol at the SAT equilibrium temperature or, in contrast, no formation of crystalline aerosols at all, show that the degree of activation depends only weakly on the details of the heterogeneous chemistry. Another source of error influencing the chlorine activation as well as the efficiency of the ozone loss cycles are the temperatures along the Match trajectories. However, even 5K reduction of the temperatures only slightly enhances the ozone loss in January. Furthermore, results obtained neglecting the HCl and ClONO$_2$ formation reactions exclude that an overestimation of the chlorine deactivation causes the deviation from the Match results.

Figure 1. Zenith angle dependence of the equilibrium ozone loss rate modeled for 20 Jan. and a temperature of 200K on the 475K level (solid line) compared to the frequency of occurrence of solar zenith angles along the trajectories connecting the Match measurements in the period between day 3 and day 45 (histogram) of the year 1992.

To construct the idealized trajectories the diabatic descent of vortex air was estimated from balloon-borne N_2O observations [*Bauer et al.*, 1994]. We derived the average and minimum vortex temperatures on the resulting levels from UKMO analysis data and assumed a sinusoidal temperature oscillation around the average temperature with an amplitude equal to the difference between average and minimum temperature. The airparcels were assumed to oscillate around 70°N with an amplitude increasing from 5° to 15° towards 5 Jan., in approximate accordance with the vortex dynamics of the 1991/92 winter.

The chemical composition of these idealized airparcels was initialized on 15 Dec. as follows: The CH_4 amount was derived from a correlation with N_2O [*Müller et al.*, 1996]. The O_3, HCl, and H_2O mixing ratios were interpolated to these CH_4 levels from a HALOE (V18) measurement inside the vortex on 4 Dec. 91 [*Müller et al.*, 1996]. The $ClONO_2$ mixing ratio is estimated as the difference between the Cl_y amount [*Schmidt et al.*, 1994] and the HALOE HCl mixing ratio. We assumed a Br_y mixing ratio of 20 ppt, which approximately corresponds to the source gas concentration in the troposphere [*WMO*, 1995] and thus can be considered as an upper limit. The amount of NO_y was derived from a correlation with N_2O [*Kondo et al.*, 1994] and was partitioned according to results of the Mainz photochemical 2D model (J.-U. Grooß, pers. comm., 1997). The aerosol surface area was deduced from observations of *Deshler* [1994]. does not get activated. Such values are clearly unrealistic.

Results and Sensitivity Studies

To follow the Match evaluation procedure, we determined the ozone change calculated by the model between the times of the two ozone soundings for each individual Match trajectory. A linear regression between ozone decrease and the time of exposure to direct sunlight of all matches in a 14 day interval yields the average ozone loss per sunlit time for that period (Fig. 3). Multiplying these loss rates with the vortex-averaged sunlit time per day gives the mean ozone loss per day (compare *Rex et al.* [1998]).

The model is able to reproduce the ozone loss rates inferred by the Match analysis from mid-February to March but strongly underestimates the ozone loss rates towards the

end of January (Fig. 3), a period that contributes a large fraction of the overall ozone depletion integrated over the winter.

We carried out extensive sensitivity studies to investigate whether the discrepancy between model and Match results could be caused by uncertainties in model parameters (Fig. 4). One possible source of error is the initialization. Model runs with an initialization based on idealized trajectories without latitude oscillations demonstrate that the ozone loss modeled along the January Match trajectories only weakly depends on the detailed course of the idealized trajectories. The available amount of NO_y impacts the ozone loss rates during the period of chlorine deactivation, but only the amounts of Cl_y and Br_y strongly influence the peak ozone loss rates reached in early winter. While our initialization procedure yields Cl_y values slightly below 3 ppb, additional model runs were carried out assuming 3.6 ppb Cl_y. This corresponds to the tropospheric mixing ratio of organic chlorine in 1991 [*Schmidt et al.*, 1994] and can therefore be considered as an upper limit. However, towards the end of January the model still underestimates the Match results by more than a factor of two. To reach the maximum ozone loss rates inferred by the Match analysis for example a Br_y mixing ratio of 100 ppt or a Cl_y mixing ratio of 8 ppb would be necessary where in the latter case approximately
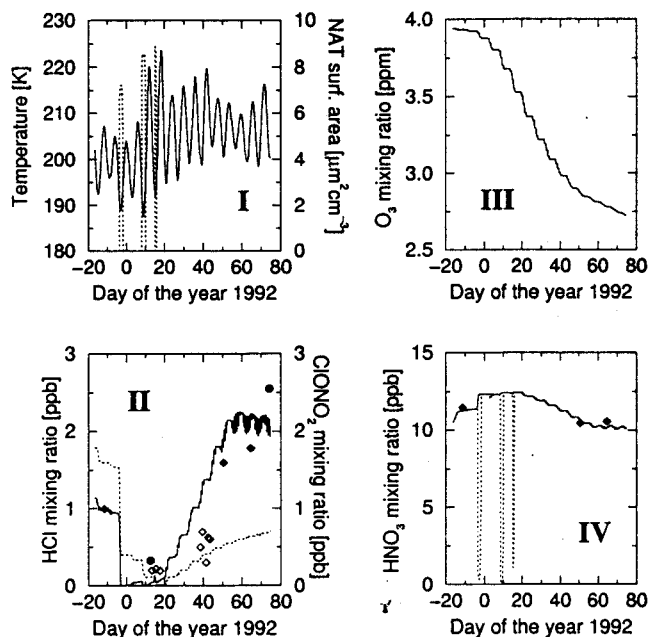

Figure 2. Results of one of the model runs along idealized trajectories (descending from 554K on 15 Dec. to 466K on 15 Mar.) yielding initialization values for model runs along the trajectories of the Match dataset . I: Temperature (solid line) and NAT surface area (dotted line). II: $ClONO_2$ (solid line) and HCl (dotted line) mixing ratios. Additionally results interpolated from HALOE (V18) HCl (open diamonds) and MIPAS $ClONO_2$ measurements (circles) as well as the vortex average of CLAES $ClONO_2$ observations (filled diamonds) are shown. III: O_3 mixing ratio. IV: Gasphase (dotted line) and total (solid line) HNO_3 mixing ratio together with the vortex average of CLAES (V8) observations (filled diamonds).

netics of the ozone loss cycles. For example, to reach loss rates of the order of 9 ppb per sunlit hour, the Cl_2O_2 formation and its photolysis would have to proceed four times faster than in the current model. In summary, even the combined effect of the known model errors does not explain the difference between the modeled ozone loss rates and the corresponding Match results.

Conclusions

The ozone loss rates determined by the Match analysis for the period from January to mid-February 1992 are significantly underestimated by our model. In the model, inorganic chlorine is activated to a high degree during this period. Therefore neither enhanced chlorine activation, for example due to mountain-induced gravity waves as suggested by *Carslaw et al.* [1998], nor a slower deactivation can improve the agreement of the simulated ozone loss rates and the Match results. Furthermore, model runs with upper limits of the Cl_y and Br_y amount exclude that the discrepancy between model and Match results can be attributed to a lack of active chlorine or bromine participating in the known ozone loss cycles. Finally we showed that the discrepancies cannot be explained by reasonable errors in the rate constants and photolysis rates determining the efficiency of the ozone loss cycles.

The degree of ozone loss deduced with the Match technique for the winter 1991/92 can therefore not be explained within the known uncertainties of current photochemical models. Possible systematic errors of the Match analysis not represented by the error bars in Fig. 3 have been discussed in detail by *Rex et al.* [1998]. For example overestimated rates of diabatic cooling would lead to an overestimate of the ozone loss rates. But even if diabatic cooling is neglected completely, the inferred ozone loss rates exceed 40 ppb/day. The maximum distance of the ozonesondes to the trajectory allowed for a match does not influence the inferred ozone loss rates systematically. Moreover, ozone depletion of comparable magnitude has been inferred with independent techniques [*Müller et al.*, 1996]. Thus errors in the Match analysis are unlikely to explain the large deviation from the model results. Therefore our results indicate that some process not represented adequately in current models might lead to additional ozone loss.

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