

Chlorine chemistry and the potential for ozone depletion in the arctic stratosphere in the winter of 1991/92

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Abstract. We present an analysis of chlorine chemistry in the Arctic stratosphere during the winter of 1991/92 and assess its potential implications for ozone depletion. In accordance with observations of total organic chlorine, ClONO₂ and HCl, box model results indicate the following: (1) An almost complete activation of chlorine during the cold winter period. (2) A possible contribution from the heterogeneous reaction HOCl + HCl and the gas-phase reaction CH₃O₂ + ClO to the complete conversion of HCl to active chlorine. (3) A strong buildup of ClONO₂ following PSC disappearance which remains the main chlorine reservoir for about a month, after which HCl becomes dominant. (4) Appreciable chemical ozone loss in the lower stratosphere inside the polar vortex is conceivable for the winter of 1991/92.

Introduction

One objective of the European Arctic Stratospheric Ozone Experiment (EASOE) was to provide a wide spatial and temporal coverage of measurements of chemical species in the polar stratosphere. Here, we use several of these measurements in an attempt to provide a synoptic view of the chemical evolution of chlorine and nitrogen species in the Arctic lower stratosphere during the winter of 1991/92.

Ground-based observations of total column ClONO₂ over the entire winter [Adrian *et al.*, 1994], along with balloon-borne observations of ClONO₂ inside the vortex on January 13, 1992 and March 14, 1992 [v. Clarmann *et al.*, 1993; Oelhaf *et al.*, 1994], indicate a sizable conversion of this species to active chlorine during the coldest period from the end of December to the end of January, followed by an almost complete transformation of the available chlorine to ClONO₂ during the beginning March. Moreover, ground-based observations of very low column densities of HCl during the winter and spring of 1992 [Adrian *et al.*, 1994; Bell *et al.*, 1994] suggest a substantial conversion of HCl to active chlorine.

In order to analyze the mechanisms responsible for the exceptional, unprecedented observations of chlorine species we conducted chemical box model calculations for air parcels representative of the conditions in the Arctic vortex in 1991/92. Encouraged by the ability of our model to repro-

duce the principal features the disturbed chlorine chemistry in accordance with the observations, we further investigated the potential consequences of the simulated high levels of active chlorine for ozone loss.

Model description

We use a chemical box model [Crutzen *et al.*, 1992] including a complete set of gas-phase and heterogeneous reactions, the latter both on liquid sulfuric acid and nitric acid trihydrate (NAT) surfaces (Table 1). In the model, NAT particles form at 3 K supercooling, as indicated by observations in the Arctic [Schlager *et al.*, 1990; Dye *et al.*, 1992]. For the computation of the photolysis rates, a scheme was adopted that accurately describes photolysis at large solar zenith angles [Lary and Pyle, 1991] and includes the temperature depen-

Table 1. Reactions important to this work

	Reaction	γ
H1	N ₂ O ₅ + H ₂ O → 2HNO ₃	0.0006
H2	ClONO ₂ + H ₂ O → HOCl + HNO ₃	0.006
H3	ClONO ₂ + HCl → Cl ₂ + HNO ₃	0.3
H4	HOCl + HCl → Cl ₂ + H ₂ O	0.1
H5	N ₂ O ₅ + HCl → ClONO ₂ + HNO ₃	0.003
		Rate const.
R1	Cl + CH ₄ → HCl + CH ₃	1.0(-14)
R2	ClO + NO ₂ + M → ClONO ₂ + M	1.6(-12)
R3	ClO + HO ₂ → HOCl + O ₂	1.6(-11)
R4	Cl + O ₃ → ClO + O ₂	7.9(-12)
R5	ClO + NO → Cl + NO ₂	2.7(-11)
R6	ClO + O → Cl + O ₂	4.3(-11)
R7	HNO ₃ + hν → NO ₂ + OH	4.7(-8)
R8	HNO ₃ + OH → NO ₃ + H ₂ O	5.4(-13)
R9	ClONO ₂ + hν → Cl + NO ₃	1.8(-5)
R10	ClO + CH ₃ O ₂ → Cl + prod.	1.0(-12)
R11	ClO + ClO + M → Cl ₂ O ₂ + M	2.7(-13)
R12	Cl ₂ O ₂ + M → ClO + ClO + M	3.9(-5)
R13	Cl ₂ O ₂ + hν → ClOO + Cl	7.1(-4)
R14	ClO + BrO → Cl + Br + O ₂	8.7(-12)

For the heterogeneous reactions H1-H5, reaction probabilities γ for NAT [DeMore *et al.*, 1992] are listed. On sulfuric acid (with weight percentage W) only H1 ($\gamma = 0.1$) and H2 ($\gamma = 10^{1.86-0.0747 \cdot W}$) were included [Hanson and Ravishankara, 1991]. For the gas-phase reactions R1-R14, rate constants (in cm³ s⁻¹ molec⁻¹; except R12 in s⁻¹) [DeMore *et al.*, 1992] for 100 mbar and 200 K and photolysis rates (in s⁻¹) for 85° zenith angle are given.

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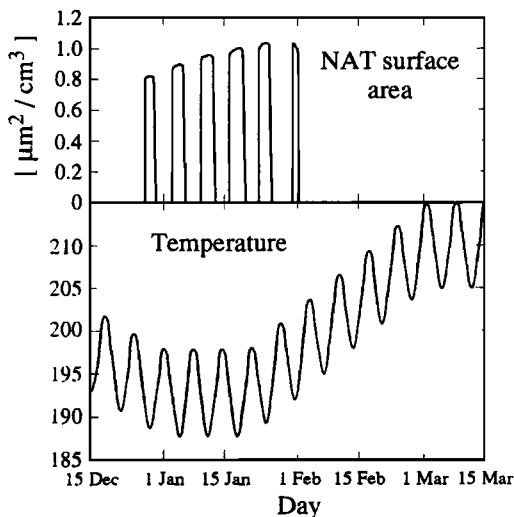


Figure 1. The adopted temperature history and the NAT surface area (in $\mu\text{m}^2/\text{cm}^3$) over the model period December 15, 1991 to March 15, 1992.

dence of the UV-cross sections for HNO_3 [Burkholder *et al.*, 1993]. We use one quarter of the recommended upper limit [DeMore *et al.*, 1992] as reaction rate for R10. A rate of this order has recently been substantiated by measurements which further disclosed CH_3OCl as a product of R10 [Helleis *et al.*, 1993].

The temperature history (Fig. 1), of the air parcels inside the polar vortex in the lower stratosphere during the winter of 1991/92 was estimated from observations [Naujokat and Labitzke, 1993; Waters *et al.*, 1993]. Further, to simulate the diabatic descent in the vortex indicated by observations of inert tracers [Schmidt *et al.*, 1993], they are assumed to sink from 550K to 450K (22–17km) over the model period. Some simulations have also been performed for different height levels to estimate total column amounts. The air parcels are either constrained to constant latitude (58°N – 78°N), or sinusoidal variations in latitude ($68^\circ \pm 10^\circ\text{N}$) were prescribed. In accordance with meteorological observations, the cooling episodes and the southward excursions are assumed to take place over northern Europe.

There are some limitations in using a box model in this, highly idealized way, and, consequently, a detailed, quantitative comparison with measurements is not attempted. Nonetheless, since the model assumptions are representative of the situation inside the polar vortex in the winter 1991/92, some conclusions about the chemical mechanisms at work may be drawn on account of the model results.

Model results and observations

Chlorine and nitrogen species. In the model, NAT particles exist from the end of December to the end of January (Fig. 1) in accordance with estimates based on a thorough meteorological analysis [Newman *et al.*, 1993] and lidar measurements [Stein *et al.*, 1993]. The surfaces of these particles catalyze the heterogeneous reactions H3–H5 that activate HCl. While H5 is unlikely to be very effective due to prior removal of N_2O_5 by reaction on sulfate aerosol particles via H1, reactions H3 and H4 proceed rapidly, effectively titrating

the available ClONO_2 and HOCl against HCl on a timescale of hours (Fig. 2). The further depletion in HCl is much slower and is controlled by the supply of reaction partners for HCl. The most important partner under sunlight conditions and when PSCs exist is HOCl produced via R3. Further, whenever PSCs evaporate during warm periods (Fig. 1), HNO_3 is released into the gas-phase and ClONO_2 recovers via R2 (Fig. 2), thereby using up the NO_x produced by R7 and R8. Thus, NO_2 concentrations remain low. Similarly, in PSC-free periods, HOCl builds up via reaction R3 (Fig. 3). With the PSCs reappearing during cold periods, HCl is removed via H3 and H4 with ClONO_2 and HOCl being about equally important. Since the buildup of HCl during the warm periods is much slower than that of HOCl and ClONO_2 (see below), the recurrent evaporation of PSCs thus enhances the depletion of HCl. In the model, HCl is severely depleted in the lower stratosphere, a finding supported by the very low column amounts of HCl measured at the end of January. The ClONO_2 concentrations remain extremely low in the model throughout the period when PSCs exist, in good accordance with the balloon-borne observation on January 13.

After the last PSCs disappear in the model simulation, the active chlorine is almost completely converted to ClONO_2

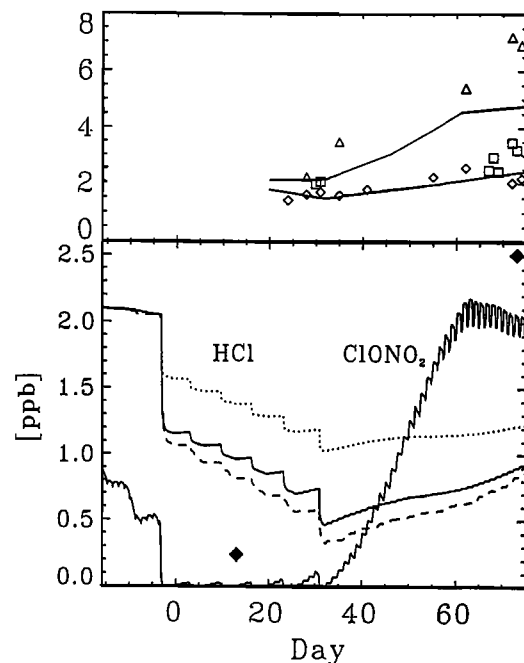


Figure 2. The main chlorine reservoirs over the model period: Upper panel shows the FTIR observations of stratospheric HCl column amounts over Kiruna (diamonds) and Greenland (squares) and ClONO_2 total column amount over Kiruna (triangles) (see Adrian *et al.* [1994] for details); also column densities of HCl (thick solid line) and ClONO_2 (thin solid line) derived from the model results are shown (all in 10^{15} cm^{-2}). Lower panel shows HCl and ClONO_2 mixing ratio in the lower stratosphere from the model results (at 68°N), dotted line shows simulated HCl neglecting reactions H4 and R10, dashed line the results allowing excursions in latitude. Diamonds in the lower panel indicate the mixing ratios of ClONO_2 on March 14, 1992, (about 17 km height) and on January 13, 1992, (about 18 km height), both observed by MIPAS-B.

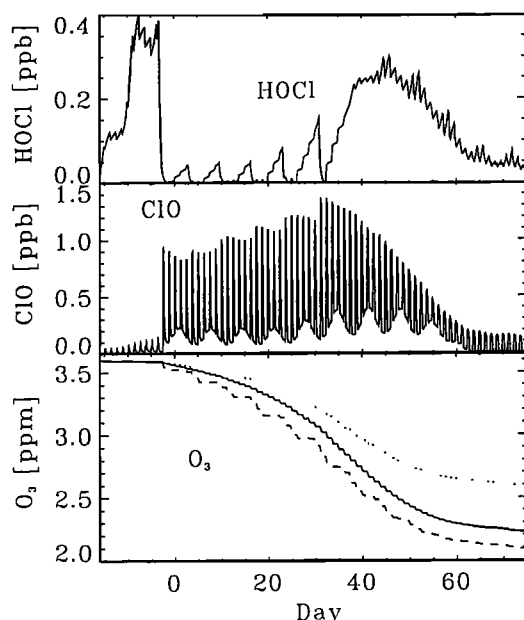


Figure 3. The mixing ratios of HOCl, ClO and ozone in the lower stratosphere (at 68°N) over the model period. Dotted line in lower panel indicates ozone simulated neglecting reactions H4 and R10, dashed line the results allowing excursions in latitude.

via R2; the recovery of HCl via R1 is much slower (Fig. 2). This pattern is clearly borne out by measurements which show (in agreement with the model) extremely high column amounts of ClONO₂, yet only a slow recovery of HCl towards the end of winter (Fig. 2). It is further corroborated by the balloon-borne observation on March 14 which shows very high mixing ratios of ClONO₂ in the lower stratosphere.

The reason for the preferred production of ClONO₂ over HCl can be explained by the relative effectiveness of reactions R1 and R2 for the removal of active chlorine:

$$\alpha = \frac{d[\text{HCl}]/dt}{d[\text{ClONO}_2]/dt} = \frac{k_1[\text{CH}_4][\text{Cl}]}{k_2[\text{NO}_2][\text{ClO}]} \approx \frac{k_1[\text{CH}_4]k_5[\text{NO}]}{k_2[\text{NO}_2]k_4[\text{O}_3]}$$

Assuming NO/NO₂ ≈ 1 and mixing ratios of O₃ and CH₄ in the ppmv range, α ≈ 10⁻², and thus practically all the active chlorine will initially be converted into ClONO₂. The rate of increase in ClONO₂, and thus the rate of chlorine deactivation, is controlled by the rate of release of NO₂ from the HNO₃ via R7 and R8 after the evaporation of NAT.

The activation of chlorine is further reflected in the high mixing ratios of ClO indicated by the model results (Fig. 3). The simulated temporal variation of ClO is consistent with aircraft [Crewell *et al.*, 1994] and satellite observations [Waters *et al.*, 1993].

Ozone. Previous modeling studies of Arctic ozone depletion [McKenna *et al.*, 1990; Brune *et al.*, 1991; Chipperfield *et al.*, 1993] have simulated significant ozone loss for the lower stratosphere for February 1989 and 1990. Here, we focus on the entire winter of 1991/92. Our model results representative of the polar vortex (78°N–68°N, corresponding to a total of 300–670 hours of sunlight over the model period) show an integral ozone destruction of 15%–38% in the air parcel (Table 2) in accordance with observed ozone loss rates for the period from mid January to mid February 1992

[Proffitt *et al.*, 1993]. The results of model runs performed for vortex conditions at lower latitudes (58°N and 63°N, Table 2) as a sensitivity study, are consistent with the finding of Brune *et al.* [1991] that the amount of ozone depletion strongly increases with decreasing latitude. To demonstrate the sensitivity of ozone depletion to the duration of PSC existence, model runs were performed for an unrealistically short (10 days) and long (50 days) PSC periods by shifting temperatures up and down by 3 K (Table 2). However, in 1992, possibly also unprocessed air masses existed in the vortex [Newman *et al.*, 1993], for which the present analysis is not applicable.

Furthermore, the suggestion by Crutzen *et al.* [1992], that a cycle involving R10 and H4, could be of relevance to Antarctic ozone depletion is extended here to the Arctic (Table 2, Figs. 2 and 3). For the Arctic high latitude ozone loss, this cycle may be of comparable importance as the BrO-ClO cycle (Table 2). Since it is strongly dependent on solar illumination [Crutzen *et al.*, 1992], it is triggered earlier during southward excursions if variations in latitude are considered, so that in this case, the HCl activation, and thus the ozone depletion, is slightly stronger (Table 2, Figs. 2,3).

In a study for the 1991/92 Arctic vortex [Salawitch *et al.*, 1993], the model was initialized with more ClONO₂ than HCl based on in-situ measurements of HCl [Webster *et al.*, 1993]. Under these circumstances, the complete activation of HCl proceeds via H3 and requires no further explanation. Thus, the impact of H4 and R10 would be reduced. Further, if H2 does not occur in the stratosphere, as suggested by Webster *et al.* [1993], the inorganic chlorine reservoir would not be activated completely since any ClONO₂ in excess of HCl would remain unprocessed; consequently, less ozone depletion than for the initialization with excess HCl employed here is simulated [Salawitch *et al.*, 1993]. In contrast to this view, the ClONO₂ profile measured on January 13, 1992 [v. Clarmann *et al.*, 1993; Oelhaf *et al.*, 1994] indicates that only very little ClONO₂ is present in the lower stratosphere during the coldest period of the winter 1992.

Conclusions

Measurements and model results discussed here yield a consistent picture. Specifically, the activation of chlorine

Table 2. Ozone depletion in percent

lat.	<i>T</i> – 3K	<i>T</i>	<i>T</i> + 3K	<i>A</i>	<i>B</i>
58°N	81	60	39	64	45
63°N	70	56	33	49	42
68°N	49	38	23	28	27
73°N	27	23	18	13	15
78°N	17	15	14	7	9
68° ± 10°N	53	42	24	29	30

Ozone depletion simulated in the model from 15.12.91 to 15.3.92 for temperature *T* (as in Fig. 1) and with the temperature history shifted upward (*T* + 3K) and downward (*T* – 3K) by three Kelvin. Further, results are shown from model runs neglecting *A*: Reactions H4 and R10 and *B*: neglecting bromine chemistry.

during the cold winter period, reflected in balloon-borne measurements of little ClONO₂ [v. Clarmann et al., 1993; Oelhaf et al., 1994], aircraft measurements of high concentrations of ClO, low levels of HCl [Crewell et al., 1994] and large column amounts of OClO [Brandtjen et al., 1994] and ground-based observations of low column amounts of HCl and ClONO₂ inside the polar vortex [Adrian et al., 1994; Bell et al., 1994] is matched by the model results. After the final disappearance of the PSCs, the model shows high column amounts of ClONO₂ and an almost complete conversion of active chlorine to ClONO₂ (Fig. 2), which remains the dominant inorganic chlorine compound for more than a month, all in accordance with the observations.

Our model results show that reactions H4 and R10, hitherto omitted in model studies of Arctic ozone loss, may possess a substantial impact on halogen-catalyzed ozone destruction (Table 2). The simulations performed for conditions representative of the lower stratosphere inside the polar vortex for the Arctic winter of 1991/92 indicate, in accordance with observations [Proffitt et al., 1993], that considerable chemical ozone loss may have taken place.

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