

# The Potential Impact of the Reaction $\text{OH} + \text{ClO} \longrightarrow \text{HCl} + \text{O}_2$ on Polar Ozone Photochemistry

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**Abstract.** We call attention to the likely importance of the potential reaction  $\text{OH} + \text{ClO} \longrightarrow \text{HCl} + \text{O}_2$ . It may only be a minor channel for the reaction of OH with ClO, which is often ignored in models, but if it occurs it considerably increases the rate of recovery of HCl after an air parcel has encountered a polar stratospheric cloud (PSC). The net effect of this reaction on the ozone concentration depends on the relative HCl concentration and whether the air parcel is in a PSC. When an air parcel is in a PSC and the HCl concentration is less than the sum of the HOCl and ClONO<sub>2</sub> concentrations, heterogeneous ClO<sub>x</sub> production is rate limited by the production of HCl. Under these conditions the reaction allows HCl to be reprocessed more rapidly by the heterogeneous reactions of HCl with HOCl and ClONO<sub>2</sub>. This allows high ClO<sub>x</sub> concentration to be maintained for longer, and at a slightly higher level, than would otherwise be possible which in turn leads to more ozone depletion. When there are PSCs but HCl is in excess, or outside of the PSC regions (i.e. during the recovery phase), the reaction will always reduce the ClO/HCl ratio and hence slightly reduce the ozone loss.

**Key words:** ClO, HCl, ozone loss.

## 1. Introduction

This paper considers the importance of the potential reaction



on the partitioning of reactive chlorine, and on the associated ozone loss, in the lower stratosphere. Reaction (1) is speculative and so is usually neglected in numerical models as it is only a minor channel of the OH + ClO reaction. Kinetic studies of this reaction are described by Leu and Lin (1979), Burrows & Cox (1981), Ravishankara *et al.* (1983), Hills and Howard (1984) and Poulet *et al.* (1986) which were reviewed by Atkinson *et al.* (1992) and DeMore *et al.* (1992)). The latest study gives an upper limit of 14% for the branching ratio to give HCl + O<sub>2</sub> as products, but the uncertainties in all the studies do allow for the possibility that the HCl yield is zero.

Toumi and Bekki (1993) found that including reaction (1) in a two-dimensional radiative-chemical-transport model brought the model into better agreement with observations of the ClO/HCl ratio in the upper stratosphere. In addition, the observed trend of upper stratospheric ozone was in good agreement with the model when reaction (1) was included whereas it was not when it was omitted. They also found that it was the main sink for OH in regions of elevated ClO and low ozone. McElroy and Salawitch (1989), Natarajan and Callis (1990) and Chandra *et al.* (1993) also concluded that chlorine chemistry is better modelled when 8–10% of reaction (1) yields HCl. Since these various studies have already considered different branching ratios this study will focus on a different aspect which was not previously considered, namely, situations when heterogeneous production of ClO<sub>x</sub> is rate limited by HCl formation in the lower stratosphere. The branching ratio used in this study is 8% based on the recommendations of the modelling studies just mentioned.

We investigate the effect of this reaction in the lower stratosphere using two different models, a box model (*AutoChem*) and a two-dimensional isentropic model (*SLIMCAT*). In the box model two different idealised test cases are considered. Both cases highlight that the effect of this reaction on the ozone loss depends on the HCl concentration. The single layer isentropic chemical transport model (*SLIMCAT*) was used to study the effect of reaction (1) during the particularly cold stratospheric winter of 1992/93.

## 2. Model Descriptions

The two models that we have used in this study, *AutoChem* and *SLIMCAT*, are separate models. Both have a comprehensive stratospheric reaction scheme, with the *AutoChem* reaction scheme being more detailed as it is used for sensitivity simulations. The *SLIMCAT* chemistry scheme is designed for efficient use in multidimensional models.

The box model used for the idealised simulations is a new model called *AutoChem* described in more detail in the appendix. The version of the box model used here contains a total of 62 species. No family or photochemical equilibrium assumptions are made. 60 species are integrated separately with a 15 minute timestep. The box model contains a total of 266 reactions, 169 bimolecular reactions, 37 trimolecular reactions, 47 photochemical reactions and 13 heterogeneous reactions. The rate constants for the reactions were taken from Atkinson *et al.* (1992) and DeMore *et al.* (1992). The box model simulations, which are all at 75 mb, use a sulphate aerosol surface area of  $1 \mu\text{m}^2/\text{cm}^3$ , which is typical of a background aerosol distribution.

In this study we have also used a single layer isentropic model (*SLIMCAT*). This is a 2D (latitude-longitude) version of the *TOMCAT* 3D off-line transport model described by Chipperfield *et al.* (1993, 1994a, b, c). The isentropic model advects tracers on surfaces of constant potential temperature ( $\theta$ ) and is forced using the

winds and temperatures from the 6-hourly analyses of the European Centre for Medium Range Weather Forecasts (ECMWF). For the numerical simulations presented here the model was used on the 475 K  $\theta$  surface. The analysed fields were used in the spectral truncation of T21. The model grid itself was  $5.6^\circ \times 5.6^\circ$ . The analysed fields of temperature and horizontal wind are interpolated from the ECMWF model levels (which are isobaric above 70 hPa) onto the required  $\theta$  surface. The model ignores vertical (diabatic) motion. This is an approximation although in the lower stratosphere diabatic heating rates are small. Furthermore, in this study the model is used to investigate the effect of including reaction (1) by comparing the difference between two simulations which will reduce the effect of the isentropic approximation. *SLIMCAT* has an identical chemistry scheme to the *TOMCAT* 3D model and includes a detailed description of stratospheric chemistry of the  $\text{O}_x$ ,  $\text{NO}_y$ ,  $\text{ClO}_y$ ,  $\text{BrO}_y$  and  $\text{HO}_x$  families and a treatment of heterogeneous chemistry on polar stratospheric clouds (PSCs) and sulphate aerosols. The PSC scheme was described in Chipperfield *et al.* (1993, 1994a). The treatment of heterogeneous reactions on sulphate aerosols was described in Chipperfield *et al.* (1994b). The distribution of sulphate aerosol surface area density was specified at  $1 \mu\text{m}^2/\text{cm}^3$  as in the *AutoChem* box model above.

In both models the surface area of the PSC particles is calculated from the amount of condensed species by using a specified particle radius. For type I PSCs the model temperature and mixing ratios of  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  are used, together with the algorithm of Hanson and Mauersberger (1988), to predict when these PSCs are thermodynamically possible and the resultant equilibrium gas phase mixing ratio of  $\text{HNO}_3$ . The balance of the model  $\text{HNO}_3$  is put into the condensed phase. The particles of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  (nitric acid trihydrate – NAT) are assumed to have a radius of  $1 \mu\text{m}$ , which is used in the calculation of the available surface area. A similar procedure is used for type II PSCs (see Chipperfield *et al.*, 1993).

### 3. Results

To investigate the role of reaction (1) some idealised simulations were performed in the box model. Then, to give a more general perspective, the reaction was also included in two *SLIMCAT* simulations. All of the simulations point to the same conclusion: reaction (1) may be important and the effect it has depends critically on the HCl concentration.

#### 3.1. REPEATED EXPOSURE TO PSCS

The calculations presented in this section are intended to crudely simulate an air parcel in the Arctic lower stratosphere from autumn to spring and will be referred to as test case A. The initial conditions for this simulation are shown in Table I. Figure 1 shows the time evolution of the temperature and solar zenith angle for the 100 day simulation. In the initial and final period no PSCs are encountered, but

TABLE I. The initial conditions (v.m.r.) used test case A

Aerosol data	$1.0 \mu\text{m}^2/\text{cm}^3$	$\phi$	$60^\circ \text{ N}$	P	75 mb
O <sub>3</sub>	$2.5 \times 10^{-6}$	HNO <sub>3</sub>	$8.0 \times 10^{-9}$	NO	$1.0 \times 10^{-9}$
NO <sub>2</sub>	$1.0 \times 10^{-9}$	N <sub>2</sub> O <sub>5</sub>	$1.0 \times 10^{-9}$	ClO	$0.1 \times 10^{-9}$
HCl	$2.0 \times 10^{-9}$	ClONO <sub>2</sub>	$1.0 \times 10^{-9}$	HOCl	$0.1 \times 10^{-9}$
BrO	$7.0 \times 10^{-12}$	BrONO <sub>2</sub>	$7.0 \times 10^{-12}$	N <sub>2</sub> O	$0.15 \times 10^{-6}$
CH <sub>4</sub>	$1.5 \times 10^{-6}$	CO	$10 \times 10^{-9}$	CO <sub>2</sub>	$345 \times 10^{-6}$
H <sub>2</sub>	$0.56 \times 10^{-6}$	H <sub>2</sub> O	$4.5 \times 10^{-6}$	H <sub>2</sub> O <sub>2</sub>	$1.0 \times 10^{-12}$

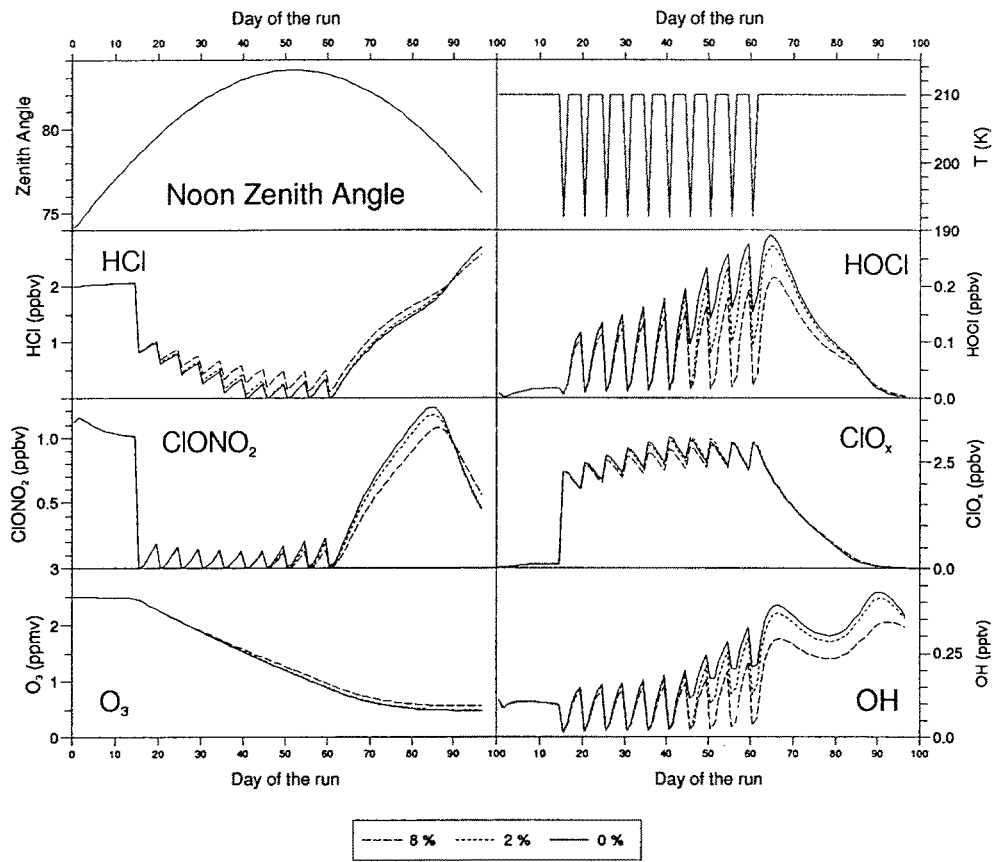


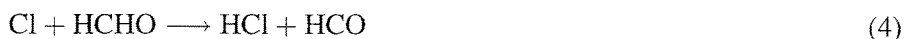
Fig. 1. Case A: Repeated exposure to PSCs. Noon values, the effect of including reaction (1) as a 2% and 8% channel on the partitioning of reactive chlorine.

during the coldest part of the winter several PSCs are encountered at an interval of four days, with one day being spent in the PSC. This time interval was used as it typically takes an air parcel between four and six days to circulate in the polar vortex once.

Let us now examine the main reactions which affect the HCl concentration, the rate at which HCl is converted into  $\text{ClO}_x$  ( $= \text{Cl} + \text{ClO} + 2\text{Cl}_2\text{O}_2$ ) and the rate at which it recovers. The relative importance of the various HCl production channels varies considerably depending whether an air parcel is currently in a PSC and whether it has encountered one in the last month or so. Before a PSC has been encountered by an air parcel most of the HCl production is due to the reaction



with a small contribution due to each of the following reactions



When a PSC is encountered the HCl and  $\text{ClONO}_2$  concentrations fall whereas the  $\text{ClO}_x$  concentration increases. The absolute rate of HCl production due to  $\text{Cl} + \text{CH}_4$  increases due to an increase in the Cl concentration. However, as the concentrations of ClO is enhanced when a PSC is encountered, the proportion of the total production of HCl due to reaction (1) jumps from about 1% to between 10% and 60% depending on the amount of OH and ClO present.

When an air parcel is not in a PSC the main effect of including reaction (1) is an enhancement of the HCl concentrations at the expense of  $\text{ClO}_x$ . The HOCl and  $\text{ClONO}_2$  concentrations remain virtually unchanged. However, when the HCl concentration becomes less than the sum of the HOCl and  $\text{ClONO}_2$  concentrations reaction (1) starts to play an important role (Figure 1). This is because the further production of  $\text{ClO}_x$  by the heterogeneous reactions



is now rate limited by the gas phase formation of HCl. Therefore, as under these circumstances reaction (1) is an important source of HCl, more HOCl and  $\text{ClONO}_2$  can be converted into  $\text{ClO}_x$ . Consequently, while the air parcel continues to encounter PSCs the  $\text{ClONO}_2$  concentration is reduced (in this case by a factor of between 1 and 0.1 relative to the simulation without reaction (1)) as is the HOCl concentration (in this case by a factor of between 1 and 0.1 relative to the simulation without reaction (1)). It is interesting that the HOCl concentration is reduced by such a large amount as there has been no observational evidence to date of the very high HOCl concentrations sometimes predicted by numerical models (e.g. the solid line in Figure 1). The measurements of Toon *et al.* (1992) made insight the polar vortex during January gave an upper limit to the HOCl column of  $0.2 \times 10^{15}$

molecules/cm<sup>2</sup> and a total ClO<sub>y</sub> column of  $9.2 \times 10^{15}$  molecules/cm<sup>2</sup> showing that only a relatively small fraction of ClO<sub>y</sub> was in the form of HOCl.

As observed (for example *von Clarmann et al.* (1993)), when PSC processing has finished the main recovery is still initially into ClONO<sub>2</sub>, with the ClONO<sub>2</sub> concentration peaking approximately 20 days after the last cloud was encountered. As time progresses, at about 40 days after the last PSC was encountered, the ClONO<sub>2</sub> concentration decreases and HCl again becomes the main ClO<sub>y</sub> (total inorganic chlorine) reservoir. Chlorine driven ozone depletion can continue until the conversion is complete (*Toumi et al.* (1993)). When reaction (1) is included this recovery of HCl starts earlier and reaches completion more rapidly.

Sunlight is required to produce OH for reaction (1) to be important. When an air parcel is in sunlight, the main effects of including the reaction on the partitioning of ClO<sub>y</sub> in this simulation were:

1. Higher and more sustained ClO<sub>x</sub> concentrations when the HCl concentration is less than the sum of the HOCl and ClONO<sub>2</sub> concentrations. In test case A up to 0.3 ppbv more ClO<sub>x</sub> was formed. Hence more ozone depletion during periods when the HCl concentration is negligible.
2. Faster production of HCl and hence a quicker recovery of HCl concentrations after PSCs have evaporated.
3. A more rapid decay of ClO<sub>x</sub> after PSCs have evaporated. Hence slightly less ozone depletion during periods when there are no PSCs.
4. When HCl concentrations are low during processing, lower HOCl concentrations, by a factor of between 1 and 0.1 relative to the simulation without reaction (1), due to more HCl being available for the heterogeneous reaction of HOCl with HCl.
5. When HCl concentrations are low during processing, lower ClONO<sub>2</sub> concentrations, by a factor of between 1 and 0.1 relative to the simulation without reaction (1), due to more HCl being available for the heterogeneous reaction of ClONO<sub>2</sub> with HCl.

It is therefore clear that even though reaction (1) is not normally considered in models, it is a possible minor channel for the reaction OH + ClO which is important as far as the partitioning of ClO<sub>y</sub>, and hence ozone depletion, is concerned. Figure 1 shows that even when a branching ratio of only 2% is assumed the reaction still has an effect albeit much less than when 8% is used.

It is worth noting that the production of HCl due to



is between 2% and 15% depending on the time of day and the degree of processing (see also *Austin et al.*, 1992). Consequently, models which do not include HCHO (formaldehyde) will typically underestimate the HCl production by this amount. The increase in the HCHO concentration is a consequence of more Cl which oxidises CH<sub>4</sub> to CH<sub>3</sub>, which in turn gives more HCHO. Also, if the reaction



occurs, and it is assumed that the branching ratio is the upper limit value of 0.3% (see DeMore *et al.* (1992) and the references therein for a discussion of the kinetics of this reaction) then the reaction will contribute between 1% and 10% to the production of HCl depending on the time of day and the degree of processing.

When reaction (1) is included as an 8% channel the OH concentration was reduced in this simulation by a factor of between 0.2 and 1 because reaction (1) is a sink for OH (up to  $\approx 4\%$  of the loss of OH during this stimulation) and, in addition, there is less OH production due to the photolysis of HOCl as the HOCl concentration has also dropped.

In summary, when no PSC has been encountered the main production of HCl is due to  $\text{Cl} + \text{CH}_4$ . When an air parcel encounters a PSC (giving high  $\text{ClO}_x$  and low HCl and  $\text{ClONO}_2$ ) the relative importance of  $\text{Cl} + \text{CH}_4$  drops and reaction (1), becomes an important source of HCl.

The partitioning of  $\text{ClO}_y$  before a PSC is entered will determine how quickly, if at all, the HCl concentration will become negligible. In the case just considered (test case A) the HCl concentration was greater than the  $\text{ClONO}_2$  concentration as it was assumed that there had been no previous processing of that air parcel by PSCs. However,  $\text{ClONO}_2$  could be the dominant  $\text{ClO}_y$  reservoir (e.g. Webster *et al.* (1993)), this can occur if, for example, PSCs had been previously encountered. Consequently, as reaction (1) becomes important when the HCl concentration is less than the sum of the HOCl and  $\text{ClONO}_2$  concentrations, the relative partitioning of  $\text{ClO}_y$  before a PSC is entered will determine if and when this reaction plays a role.

To illustrate this figure 2 shows the effect of repeating the simulations just described but with the concentrations of HCl and  $\text{ClONO}_2$  interchanged (test case B). Examining Figure 2 shows that reaction (1) now has a more noticeable effect from the time the first PSC in the simulation is encountered. This is because the HCl becomes negligible after the first PSC is encountered. As a result, in this simulation including reaction (1) more noticeably enhances the  $\text{ClO}_x$  concentration, so that more ozone is depleted. In this simulation reaction (1) has had a much more noticeable effect on the HOCl and OH concentrations, both concentrations have been reduced markedly during the periods of PSC processing.

In test case B shown in Figure 2 more ozone depletion occurs when reaction (1) is included whereas in test case A shown in Figure 1 there was less ozone depletion when reaction (1) was included. This emphasises that reaction (1) increases  $\text{ClO}_x$  levels, and hence ozone depletion, under quite specific circumstances, which are:

1. The presence of sunlight to produce OH.
2. The HCl concentration is less than the sum of the HOCl and  $\text{ClONO}_2$  concentrations before a PSC is entered, i.e. heterogeneous  $\text{ClO}_x$  production is rate limited by HCl formation.

When this is not the case including reaction (1) slightly increases the HCl concentration at the expense of  $\text{ClO}_x$  and hence slightly reduces the ozone depletion which occurs.

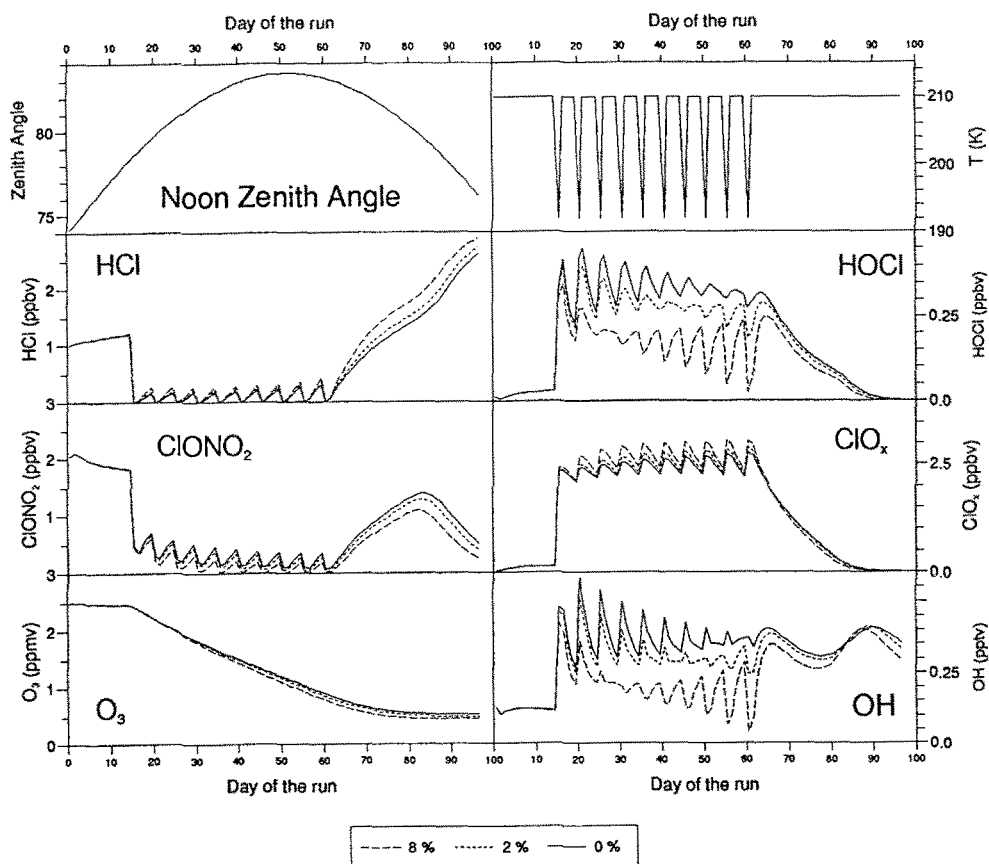


Fig. 2. Case B: The same as test case A but with the HCl and ClONO<sub>2</sub> concentrations interchanged

However, when these criterion do apply, it is a very important reaction which affects both the partitioning of reactive chlorine and the concentration of OH. As shall be seen in the next section, in the northern hemisphere these circumstances are most likely to be encountered by air within the edge of the polar vortex during mid-winter and within the vortex itself during late winter as more sunlight reaches high latitudes. During a cold stratospheric winter, this air will typically encounter several PSCs which will reduce the HCl concentrations. The air parcels are also likely to have excursions to lower sunlit latitudes where OH is present. In the southern hemisphere this reaction is likely to be important during late winter and early spring while the vortex is still intact but sunlight has returned.

### 3.2. THE ARCTIC WINTER OF 1992/93

Relative to the interannual variability observed in the northern hemisphere lower stratospheric temperatures the winter of 1992/93 can be classed as long and cold.



PSCs were present in the lower stratosphere from early December 1992 until late February 1993 (e.g. see Chipperfield, 1994). During January the vortex was centred on the pole but during February distortions to the vortex ensured that air parcels travelling around its edge made excursions to sunlit latitudes. Therefore, both of the criteria already determined above for reaction (1) to be important were satisfied during this time. Due to their idealised nature, stationary box simulations (like those considered above) can overestimate the effect of a given process. For this reason, this subsection considers the results of model simulations which used the meteorological analyses of temperature and wind prepared by the ECMWF in the SLIMCAT model. It should be mentioned that the TOMCAT model has already had considerable success in reproducing a variety of observations (Chipperfield *et al.* (1993, 1994a, b, c)) and offline models forced by meteorological analyses are powerful tools for studying atmospheric chemistry.

Two SLIMCAT runs were performed. Experiment SC1 assumed an 8% channel for reaction (1) while simulations SC2 did not include the reaction. In both simulations the model was integrated from 1 January 1993 until 3 March 1993. To illustrate the effect of reaction (1) we will show results on 21 February 1993. This day is towards the end of the period of occurrence of PSCs. Figure 3 shows the potential vorticity (PV) field at 475 K on this day. The polar vortex is distorted and has been displaced towards northern Europe. Also shown is the area enclosed by the 193 K temperature contour which indicates the approximate region where PSCs can form. Figure 4 shows the results of the simulation SC1 which included reaction (1) on the 21 February 1993. Figure 5 shows the differences between simulations SC1 and SC2 for the same day (i.e. with-without). This day was chosen as the effect of including reaction (1) is clearly evident in all of the  $\text{ClO}_y$  species. For most of January, and into February, PSCs were present on the 475 K surface. On 21 February the vortex contained very low amounts of HCl due to PSC processing (Figure 4(a)) with a large area less than 0.1 ppbv. In late February the air within the vortex experiences much more sunlight than earlier in the winter (due both to the increased distortion of the vortex and the receding polar night terminator) and the effect of reaction (1) can be clearly seen. Examining Figures 4(a) and 5(a) together shows that in the centre of the vortex including reaction (1) has allowed the HCl concentrations to recover more quickly. In run SC1 there is up to 0.14 ppbv more HCl. Indeed, comparison of Figures 4(a) and 5(a) shows that essentially all of the HCl inside the polar vortex in simulation SC1 is due to reaction (1). Figure 5(a) shows that the largest increase in HCl has occurred in the region of the vortex near the pole. On this day the region of the vortex situated over northern Europe is still experiencing PSCs and the region of zero difference to the north of Scotland is immediately downwind of the PSCs region (Figure 3). In both SC1 and SC2 the HCl is effectively zero due to this PSC processing.

The highest levels of  $\text{ClO}_x$  occur within the vortex where it has been produced heterogeneously. In general the regions of high  $\text{ClO}_x$  correspond to the regions of low HCl discussed above. On February 21 the model simulation SC1 has up to 1.3

PV on the 475 K isentropic surface  
ECMWF analysis for 21/2/1993 Time:12.00

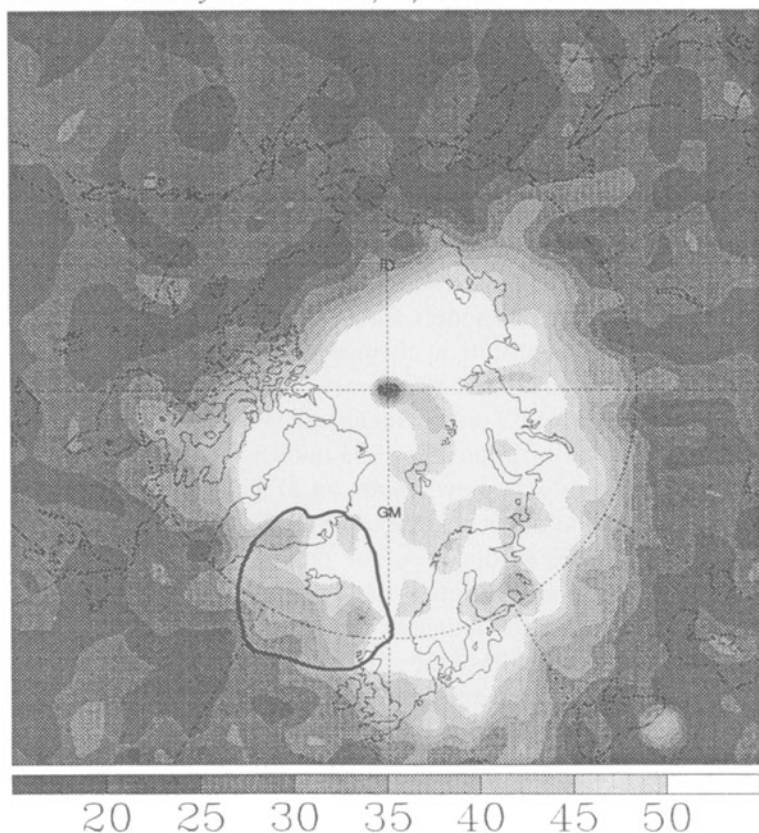
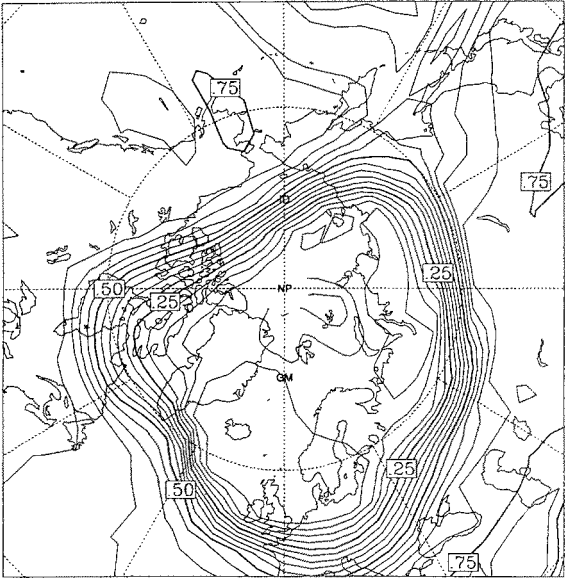


Fig. 3. Potential vorticity ( $\times 10^{-6} \text{ K m}^2 \text{ s}^{-1} \text{ Kg}^{-1}$ ) for the 21 February 1992 on the 475 K isentropic level from the ECMWF analyses. The solid line is the 193 K temperature contour.

ppbv  $\text{ClO}_x$  inside the polar vortex (Figure 4(b)). Figure 5(b) shows that including reaction (1) has increased  $\text{ClO}_x$  inside the polar vortex by up to 0.3 ppbv. Under these conditions of low HCl further  $\text{ClO}_x$  production is limited by the rate at which HCl can be formed. The inclusion of reaction (1) in run SC1 increases the rate of recovery of HCl which in turn permits more  $\text{ClO}_x$  production in the subsequent PSC events. This can be seen between Scandinavia and Iceland, downwind of the current PSC event, where the largest increase is present.

In the SLIMCAT simulations the highest levels of HOCl occur within the vortex where it has been produced heterogeneously by the reaction  $\text{H}_2\text{O} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{HNO}_3$ . In simulation SC1 there is up to 0.25 ppbv of HOCl inside the vortex (Figure 4(c)). Figure 5(a) shows that when reaction (1) is included there is more HCl present within the vortex and this can react heterogeneously with any HOCl present. Consequently, there is also lower HOCl in run SC1 compared

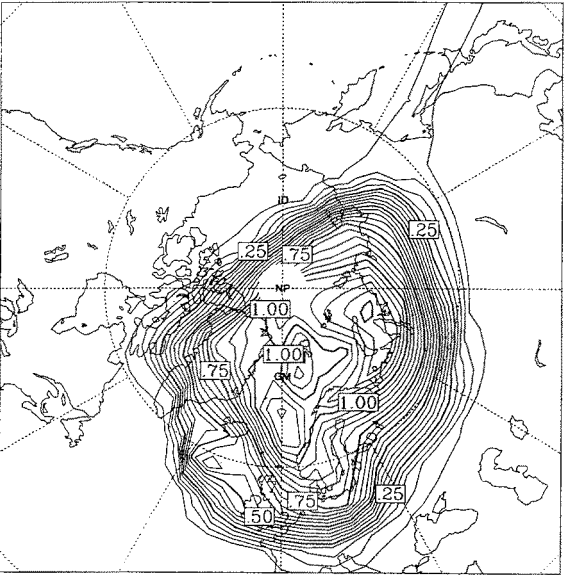
HCl (ppbv) on the 475 K isentropic surface  
SLIMCAT Experiment 1 for 21/2/1993 Time:6.00



CONTOUR FROM .05 TO 1.4 BY .05

Fig. 4a.

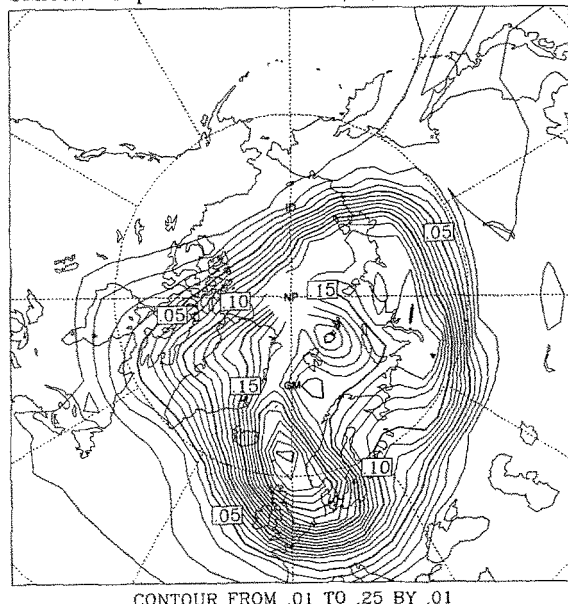
ClOx (ppbv) on the 475 K isentropic surface  
SLIMCAT Experiment 1 for 21/2/1993 Time:6.00



CONTOUR FROM .05 TO 1.25 BY .05

Fig. 4b.

HOCl (ppbv) on the 475 K isentropic surface  
SLIMCAT Experiment 1 for 21/2/1993 Time:6.00



CONTOUR FROM .01 TO .25 BY .01

Fig. 4c.

to SC2 (Figure 5(c)). For this particular day including reaction (1) has lead to a reduction of HOCl within the vortex of up to 0.05 ppbv (up to  $\approx 24\%$ ).

Figure 4(d) shows the distribution of  $\text{ClONO}_2$  from run SC1 on 21 February. At this stage of the winter the recovery phase is underway and  $\text{ClO}_x$  is being deactivated. The largest mixing ratio of  $\text{ClONO}_2$  within the vortex is 1.4 ppbv. The inclusion of reaction (1) has reduced  $\text{ClONO}_2$  by up to 0.28 ppbv (Figure 5(d)). The largest reduction coincides with the region of recent PSC processing where larger HCl in run SC1 has permitted the processing of more  $\text{ClONO}_2$  (see above).

By 21 February 1993 PSCs had been present in the Arctic lower stratosphere almost continuously for over two months. The enhanced heterogeneous production of  $\text{ClO}_x$  in regions of very low HCl concentrations which resulted from including reaction (1) has lead to slightly more ozone destruction in these regions. This is most noticeable in the vortex edge, where the air parcels do experience some sunlight during their intermittent excursions to lower latitudes as the vortex is distorted and displaced. In the vortex edge the additional decrease in ozone since the start of the model integration due to including the reaction is up to 0.016 ppmv ( $\approx 0.8\%$ ). By the end of February this additional loss had increased to 1%.

Conversely, in regions where there are no PSCs, reaction (1) leads to slightly less  $\text{ClO}_x$  by simply converting ClO to HCl. Therefore, the ozone destruction in these regions is less than when the reaction is included. The increase in ozone at midlatitudes between simulations SC1 and SC2 is very small (around  $\approx 0.1\%$ ).

ClONO<sub>2</sub> (ppbv) on the 475 K isentropic surface  
SLIMCAT Experiment 1 for 21/2/1993 Time:6.00

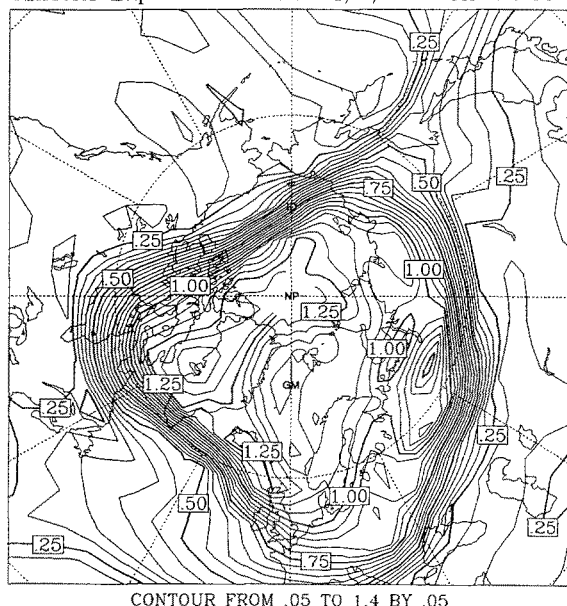


Fig. 4d.

Fig. 4. Results from the SLIMCAT model run SC1 for the 21 February 1993 on the 475 K isentropic level when reaction (1) is included. (a) HCl mixing ratio (ppbv), (b)  $\text{ClO}_x$  mixing ratio (ppbv), (c) HOCl mixing ratio (ppbv), (d)  $\text{ClONO}_2$  mixing ratio (ppbv)

This is in agreement with the box model simulations and reflects the importance of the  $\text{ClO}_x$  cycles for ozone loss in the low stratosphere. A much larger effect will occur where the  $\text{ClO}_x$  cycles are more important at around 40 km (see Toumi and Bekki (1993)).

#### 4. Summary

We have investigated the possible importance of the reaction  $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$  on the chemistry of the polar lower stratosphere using two numerical models. Although this may only be a minor channel of the  $\text{OH} + \text{ClO}$  reaction, our model results show it may be important in determining the partitioning of  $\text{ClO}_y$  during and immediately after PSC events. Assuming that this minor channel does indeed occur, it will be important if sunlight is present to produce OH and if, before a PSC is entered, the HCl concentration is less than the sum of the  $\text{ClONO}_2$  and HOCl concentrations. Under these conditions it becomes a major source of HCl and allows further heterogeneous production of  $\text{ClO}_x$  to take place. As a result of this the concentration of  $\text{ClO}_x$  can be maintained at a higher level, and for longer, while the PSC persist. This also results in considerably lower HOCl and

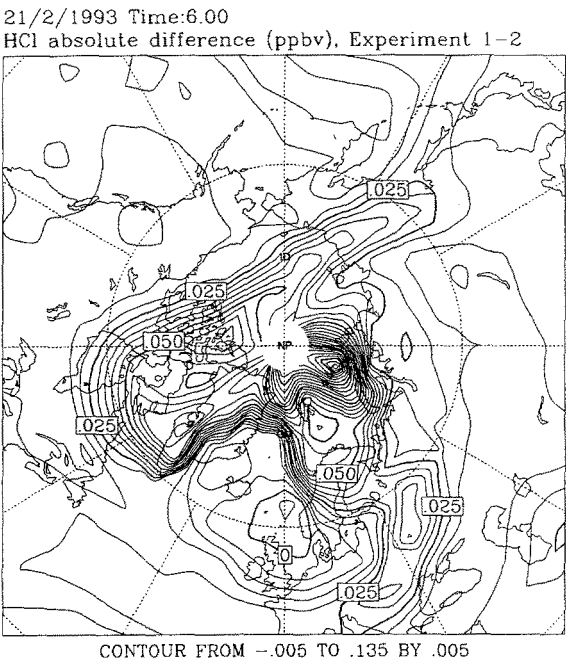


Fig. 5a.

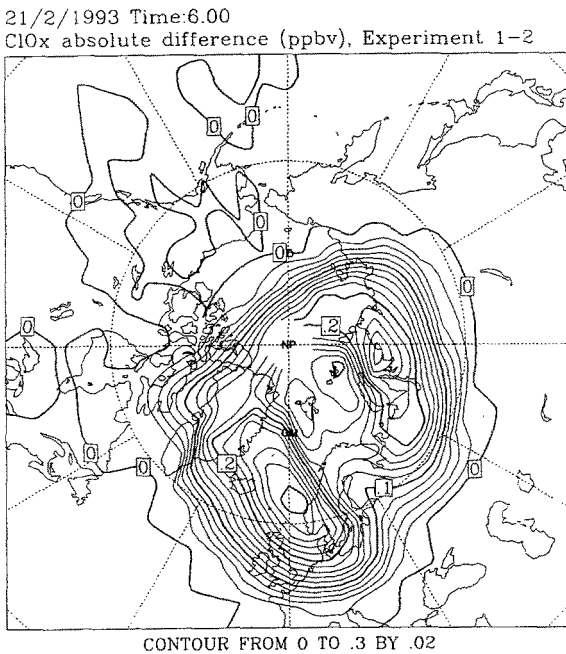
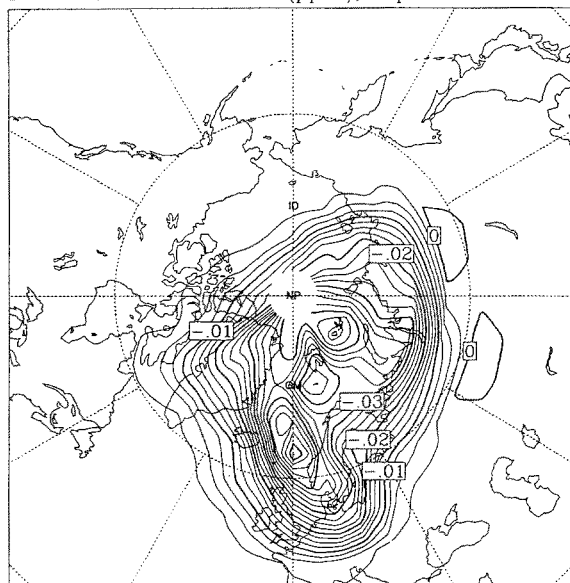


Fig. 5b.

21/2/1993 Time:6.00

HOCl absolute difference (ppbv), Experiment 1-2

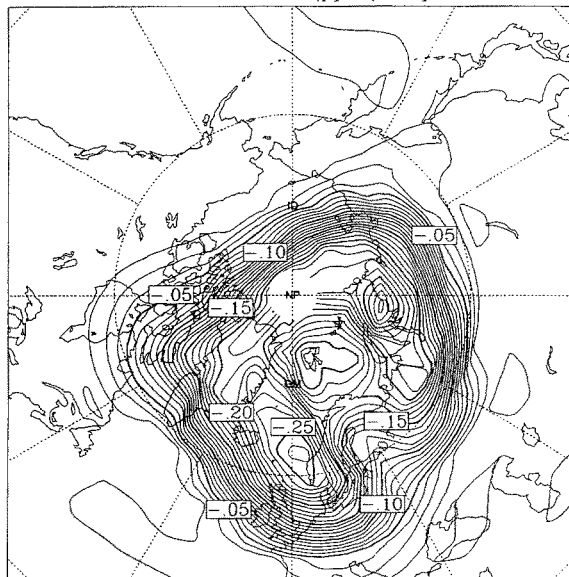


CONTOUR FROM -0.0525 TO 0 BY .0025

Fig. 5c.

21/2/1993 Time:6.00

ClONO2 absolute difference (ppbv), Experiment 1-2



CONTOUR FROM -0.28 TO -0.01 BY .01

Fig. 5d.

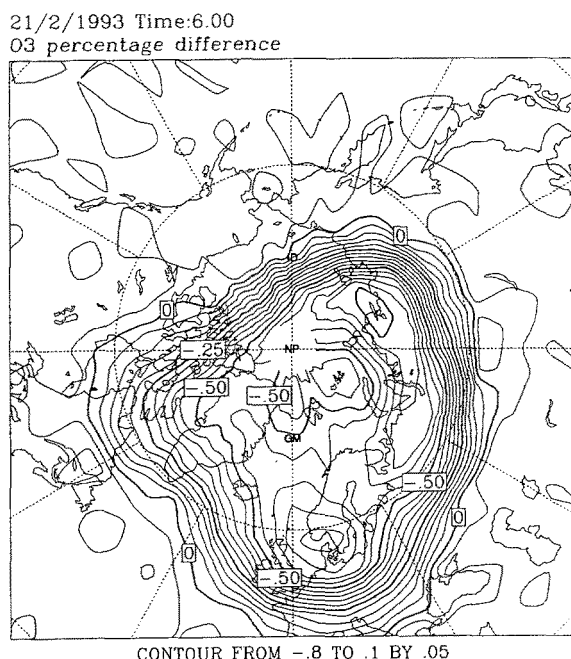


Fig. 5c.

Fig. 5. The difference in concentrations between *SLIMCAT* model run SC1 which included reaction (1) and run SC2 which did not (with-without) for 21 February 1993 (i.e. after 50 days of integration). (a) Difference in HCl (ppbv), (b) difference in  $\text{ClO}_x$  (ppbv), (c) difference in HOCl (ppbv), (d) difference in  $\text{ClONO}_2$  (ppbv) and (e)  $\text{O}_3$  percentage difference.

$\text{ClONO}_2$  concentrations while PSCs are present. Once the PSCs have evaporated the decline of  $\text{ClO}_x$  is more rapid. As confirmed by observations,  $\text{ClONO}_2$  is the main reservoir in the period immediately after all the PSCs have evaporated followed by a conversion of the  $\text{ClO}_x$  to HCl which happens faster when the reaction  $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$  is included.

The effect of including the reaction on the calculated ozone depletion depends entirely on the HCl concentration. When the HCl concentration is less than the sum of the HOCl and  $\text{ClONO}_2$  concentrations heterogeneous production of  $\text{ClO}_x$  is rate limited by HCl formation, so under these conditions including the reaction enhances the  $\text{ClO}_x$  and hence the ozone depletion. Under conditions when only gas phase chemistry operates the reaction is not so important in the lower stratosphere and converts a small amount of the  $\text{ClO}_x$  present into HCl, slightly reducing the  $\text{ClO}/\text{HCl}$  ratio (see also Toumi and Bekki (1993)). Under these conditions, including the reaction slightly reduces the ozone depletion.



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## Appendix

### A AutoChem description

The box model used in this study is a new model called AutoChem. This model automates the process of writing numerical chemical models. Given a list of required species and a set of reaction databases for bimolecular, trimolecular, photochemical and heterogeneous reactions the programme automatically writes the fortran code to calculate the time derivatives and jacobian matrix required by the numerical time integration code. It also writes all the required service subroutines to calculate reaction rates, as well as generating a LaTeX file which contains a model summary and reaction table. This enables new reaction schemes to be used, containing different chemical species and/or rates without the user having to write any fortran code. The user has control over which reactions are included, for example, whether reactants and products have to be included in the model, just reactants or just products. Reactions which are just upper limit estimates, with unknown products of the required species, or reactions which are endothermic by more than a given amount can be automatically excluded if required. As a result, new or novel processes can be examined quickly and easily enabling the emphasis to be on the science not the programming. An automatic analysis procedure is also included which calculates production and loss timescales, the contribution of each reaction in a rate of change expression to the overall rate of change, and the relative partitioning between any number of user defined species.

The version of the box model used here contains a total of 62 species. No family or photochemical equilibrium assumptions are made. 60 species are integrated separately with a 15 minute timestep, namely:  $\text{O}(^1\text{D})$ ,  $\text{O}(^3\text{P})$ ,  $\text{O}_3$ , N, NO,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ , HNO, HONO,  $\text{HNO}_3$ ,  $\text{HNO}_3(\text{s})$ ,  $\text{HO}_2\text{NO}_2$ , Cl,  $\text{Cl}_2$ , ClO, ClOO, OClO,  $\text{Cl}_2\text{O}_2$ ,  $\text{Cl}_2\text{O}_3$ , ClNO, ClNO<sub>2</sub>, ClONO, ClONO<sub>2</sub>, ClCo,  $\text{ClCO}_3$ , HCOCi, HCl,  $\text{HCl}(\text{s})$ , HOCl, H, OH,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_3\text{O}_2\text{NO}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_3\text{O}$ , HCHO, HCO, Br,  $\text{Br}_2$ , BrO,  $\text{BrONO}_2$ , BrONO, HBr, HOBr, BrCl,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}(\text{s})$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , CN, NCO, HCN. The model contains a total of 266 reactions, 169 bimolecular reactions, 37 trimolecular reactions, 47 photochemical reactions and 13 heterogeneous reactions. The rate constants for the reactions were taken from Atkinson *et al.* (1992) and DeMore *et al.* (1992).

The time integration scheme is an adaptive timestep Burlisch-Stoer (1980) scheme specifically designed for integration of stiff systems after Press *et al.*

(1992). The time integration package is as accurate as the often used Gear package but faster. Photolysis rates are calculated using full spherical geometry and multiple scattering as described by Lary and Pyle (1992a, b) after Meier *et al.* (1983), Nicolet *et al.* (1983) and Anderson (1983). The model has also been used to perform for the first time 4D variational analysis of chemical species (Fisher and Lary (1994)).

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