

## Chapter 2

### The role of halogen species in atmospheric ozone chemistry

Due to anthropogenic emissions of chlorofluorocarbons (CFCs) and other halogen source gases mankind has significantly changed the atmospheric concentration of halogen compounds during the last three or four decades. For the current atmospheric composition the major fraction of the chlorine loading and also a large fraction of the bromine loading is of anthropogenic origin. In light of the strong anthropogenic influence on the Earth's atmosphere it is obvious that the knowledge of atmospheric bromine and chlorine chemistry and in particular their effect on atmospheric ozone is crucial in predicting future properties of (human) life on our planet. This includes on one hand the determination of the sources and sinks of atmospheric halogen compounds and on the other hand the understanding of the partitioning of the halogen species into the different chemical compounds.

In this chapter the importance of halogen compounds for atmospheric chemistry is discussed. The first section gives an overview about ozone chemistry, the second section deals with the atmospheric halogen budget and the third section with fundamental chemical properties of halogen species. In particular the influence of halogen chemistry on the atmospheric O<sub>3</sub> concentrations and on the oxidation capacity of the atmosphere is discussed. In section 2.4. and 2.5. specific aspects of the halogen chemistry for the stratosphere and the troposphere are elucidated, respectively.

#### 2.1 Atmospheric Ozone

Ozone is present in both the stratosphere and the troposphere with the main bulk located in the stratosphere. This so called ozone layer was a fundamental prerequisite for the evolution of life outside the oceans, because it absorbs the harmful solar ultraviolet radiation.

Ozone in the troposphere is roughly about 10% of the total atmospheric abundance. Due to industrial processes and in particular car traffic, tropospheric ozone levels have grown in the last decades up to about two to three times the natural concentrations. Enhanced ozone in the troposphere is affecting human health, in particular during smog episodes when tropospheric ozone concentrations go far beyond natural values.

Since the sources and sinks of ozone are different for the stratosphere and the troposphere, in the following sections both atmospheric layers will be described separately.

##### 2.1.1 Ozone in the stratosphere

A photochemical theory for formation and destruction of stratospheric ozone based on oxygen-only chemistry was first proposed by Chapman [1930].



One important finding was that ozone and atomic oxygen rapidly interchange with one and another (reactions 2.2 to 2.6), while the sum of the two is linked to much slower chemical processes (reaction 2.7). This led to the concept in treating ozone and atomic oxygen together as ‘odd oxygen’ distinct from the much longer lived ‘even oxygen’.

According to the above reaction scheme the shape of the stratospheric ozone profile is qualitatively well described. However, the magnitude of the ozone concentration is overestimated by about a factor of two (Figure 2.1).

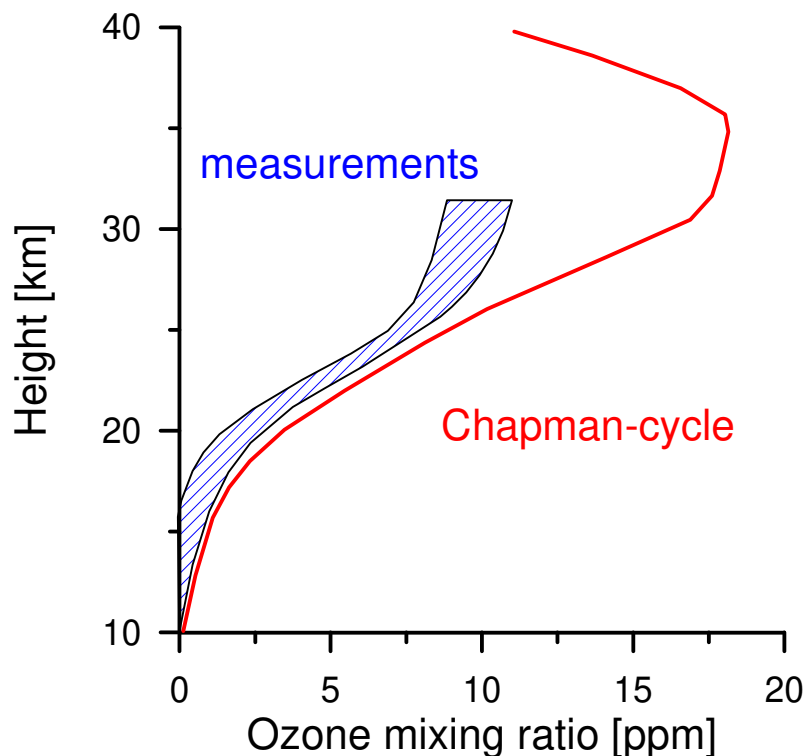
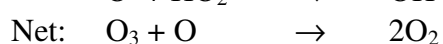
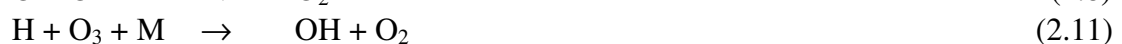
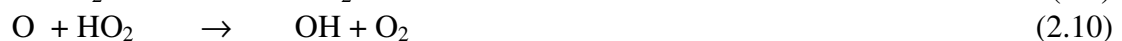
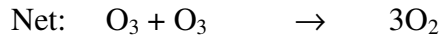


Figure 2.1. Comparison of measured ozone profiles and modelled ones taking into account only the reactions of the Chapman-cycle (adapted from Röth [1994]).

This raised the question whether there are destruction mechanisms in addition to reaction (2.3) and (2.4). Such mechanisms were indeed found during the following years. The first set of catalytic ozone destruction cycles involves hydrogen species [Bates and Nicholet, 1950; Hampson, 1964]:

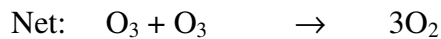




OH is formed by



Further ozone destruction cycles involve nitrogen species [Crutzen, 1970; Johnston, 1971]:



NO is mainly formed by



Another ozone destruction cycle involves chlorine species [Stolarski and Cicerone, 1974; Molina and Rowland, 1974]. It will be described in detail in section 2.4. Under unperturbed stratospheric chemical conditions the chlorine catalytic destruction cycle is of less importance compared to those of hydrogen and nitrogen species. Figure 2.2 summarises the contributions of the different ozone destruction cycles for the stratosphere.

Taking into account the above mentioned catalytic ozone destruction cycles the measured stratospheric ozone profiles could finally be well described. However, it also became clear that due to anthropogenic emissions of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , and in particular the direct emission of NO and  $\text{NO}_2$  by aircrafts, the atmospheric ozone content might be largely influenced. While the study of possible ozone depletion due to hydrogen and nitrogen species remains an important area of research [Johnston, 1992] it turned out that in particular the increase of the atmospheric halogen loading due to anthropogenic emissions has a dominant impact on the ozone concentration. The role of halogen species on stratospheric ozone will be described in detail in section 2.4.

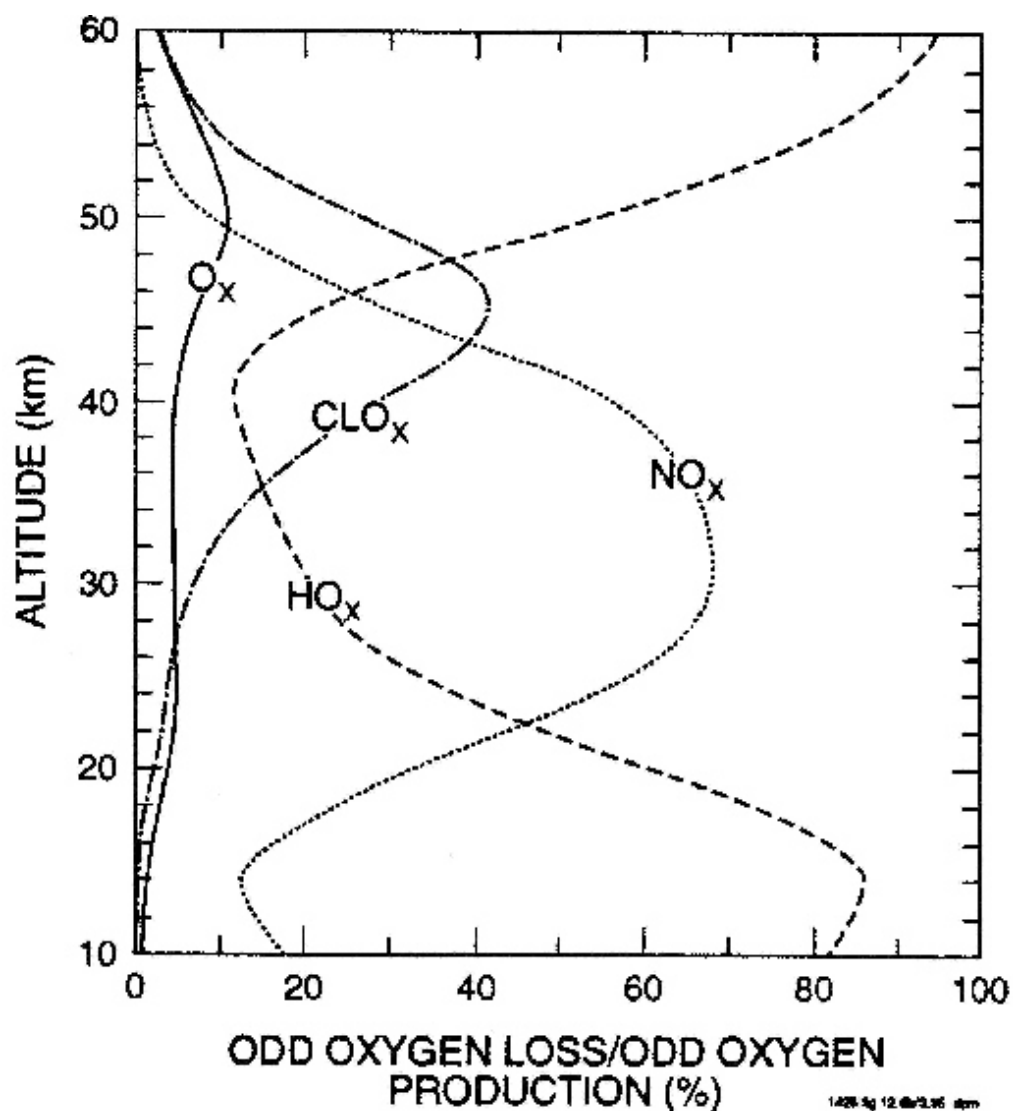
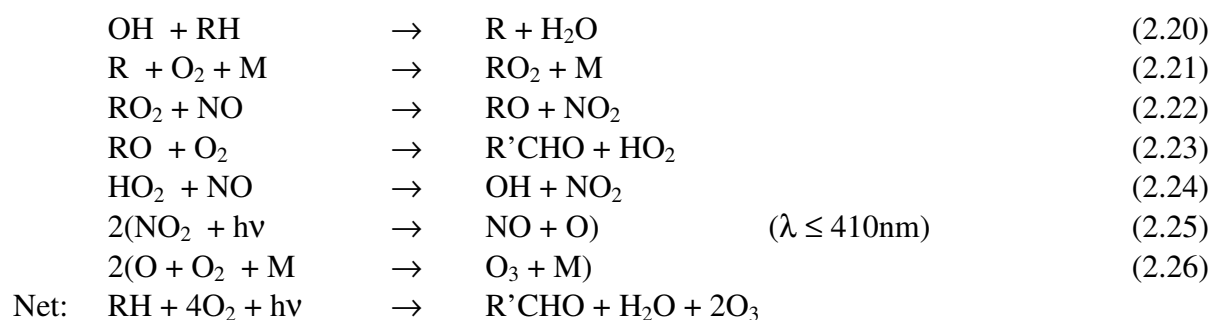


Figure 2.2 Calculated ratio of the odd oxygen loss rate due to the  $O_x$ ,  $HO_x$ ,  $NO_x$  and  $ClO_x$  destruction cycles to the odd oxygen production rate [Brasseur, 1995].

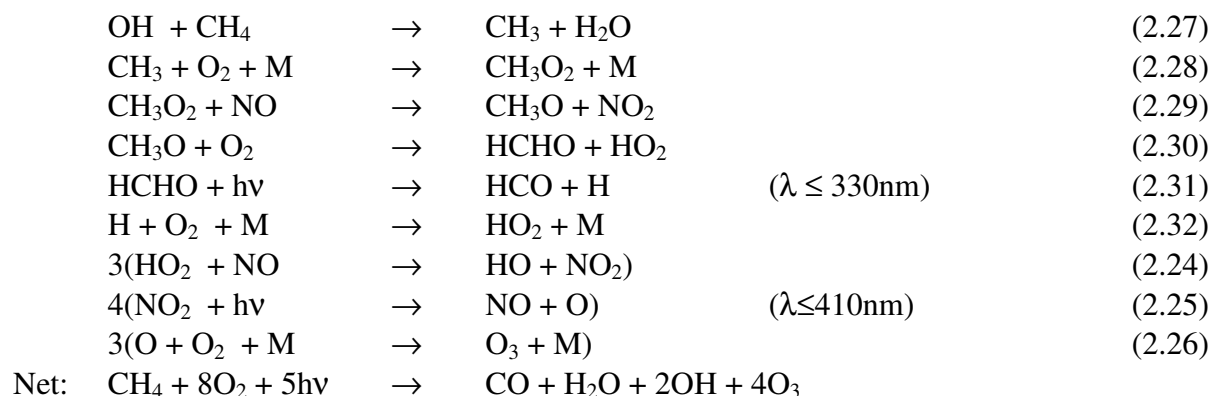
### 2.1.2 Ozone in the troposphere

In contrast to the stratosphere, ozone production via reaction 2.1. is negligible in the troposphere because the short-wave solar radiation required ( $\lambda \leq 240\text{nm}$ ) is already absorbed at higher altitudes. Thus in the beginning of the 20th century all ozone in the troposphere was believed to be of stratospheric origin. In the mid 1940, however, it became obvious that production of ozone was also taking place in the troposphere. After heavy damage had repeatedly occurred to vegetable crops in the Los Angeles area, it was shown that plant damage can be produced by ozone. In the early 1950's, Haagen-Smit et al. [1952] proposed that ozone could be formed as a result of photochemical reactions involving nitrogen species and reactive non-methane hydrocarbons, NMHC, present in automobile exhaust (like ethylene, butane, etc.). Since there are several hundreds of different hydrocarbons emitted by automobiles, the photochemistry involved is very complex. However, extensive research has indicated that the following reaction scheme is responsible for the production of ozone in the polluted troposphere (RH is used as abbreviation for NMHC) :



The carbonyl compounds can undergo further photochemical reactions which will result in additional production of organic and hydrogen radicals, and in turn produce more ozone. NMHC and  $\text{NO}_x$  (reactive nitrogen species  $\text{NO}_x$ :  $\text{NO}$  and  $\text{NO}_2$ ) are called ozone precursors. In the above reaction scheme, NMHCs are consumed while  $\text{NO}_x$  acts as a catalyst.

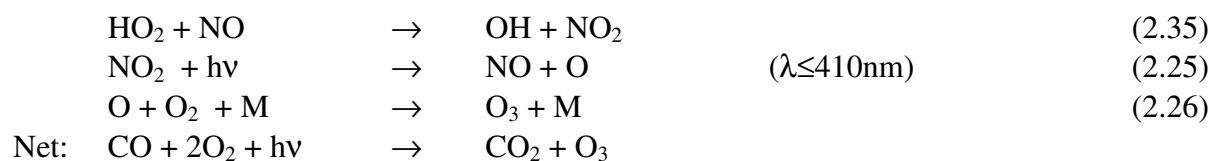
In the free troposphere and the remote oceanic boundary layer, NMHC concentrations are relatively small. Under such conditions the ozone production is dominated by oxidation of  $\text{CO}$  and  $\text{CH}_4$  instead of NMHC [Crutzen, 1974]. The reaction schemes are similar to those of NMHC:



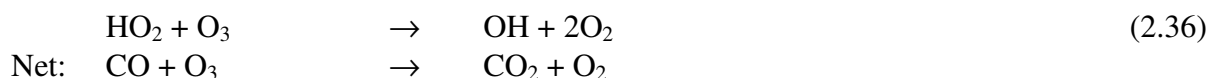
For each molecule of  $\text{CH}_4$  which is oxidised to  $\text{CO}$  four ozone molecules and two  $\text{OH}$  radicals are produced. The carbon monoxide produced by the methane reaction or emitted directly from fossil fuel combustion can then itself interact with the hydroxyl radical.



The following reactions depend on the  $\text{NO}_x$  concentrations. For high  $\text{NO}_x$  concentrations (mixing ratios above about 5 - 10 ppt), they lead to ozone production:



For low  $\text{NO}_x$  concentrations (mixing ratios below about 5 - 10 ppt) ozone destruction occurs:



In 1971, a fundamental aspect of the atmosphere's reactivity was discovered [Levy, 1971]: The photochemical production of the hydroxyl radical by ozone photolysis:



This observation was crucial because it was known that the hydroxyl radical was capable of reacting with a large number of molecules. Thus via OH-radical production, ozone is largely influencing the oxidation capacity of the atmosphere. The fundamental importance of the oxidation by the OH radical is that it thus can convert non-soluble compounds into highly soluble ones which are removed from the atmosphere very efficiently by wet deposition.

## 2.2 Sources and sinks of atmospheric halogen species

The main fraction of natural and anthropogenic halogen source gases is believed to be emitted in the form of (partly) halogenated organic compounds. Natural emitted species contain partly halogenated compounds which are readily converted into inorganic species and then removed from the atmosphere. Natural sources of halogen compounds are mainly the oceans and (the natural part of) biomass burning. Before the 1990's, anthropogenic emitted species were mainly completely halogenated compounds, the so called chlorofluorocarbons (CFCs) and halons, bromine containing species, which have been continuously replaced by hydrochlorofluorocarbons (HCFCs) after the Montreal protocol and the succeeding amendments.

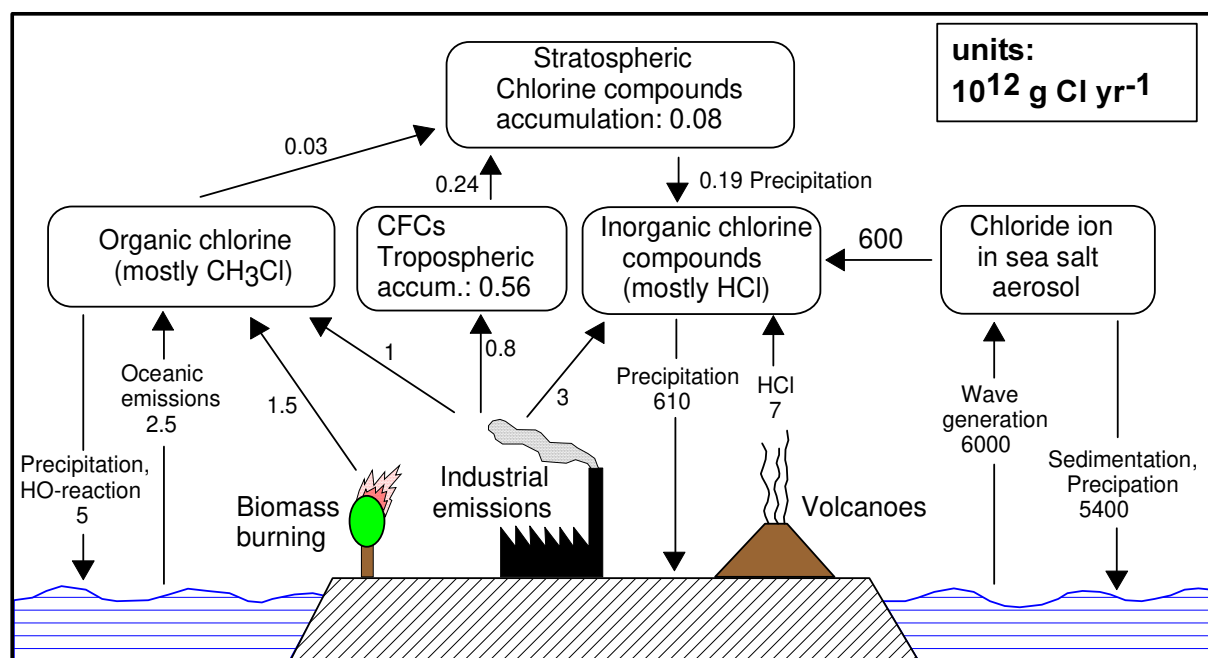


Figure 2.3 Global atmospheric chlorine cycle (adapted from Graedel and Crutzen [1993]).

During the last decade it was found that bromine and chlorine species can also be emitted into the atmosphere as inorganic compounds by autocatalytic release from sea-salt spray during polar spring [Tang and McConnel, 1996; Vogt et al., 1996; Platt and Lehrer, 1997]. Also, high concentrations of BrO have been detected above the dead sea valley [Hebestreit et al., 1999]. Another source of inorganic halogen emissions are volcanoes, but the magnitude of these emissions is very uncertain. An overview about the atmospheric chlorine cycle is given in Figure 2.3.

The origin and fate of the different atmospheric halogen sources are described in more detail in the following subsections.

### 2.2.1 Stratospheric halogen compounds, the importance of CFCs and halons

CFCs and halons are very stable in the troposphere and are thus transported into the stratosphere where they are photolysed or destroyed via reaction with O<sup>1</sup>D.

Today about 85% of the stratospheric chlorine loading and about 52% of the stratospheric bromine loading are due to anthropogenic sources [Schauffler et al., 1993, Wamsley et al., 1998]. Despite of the strong emission rates of CFCs during the last few decades, the large contribution to the total atmospheric halogen loading results in particular from the long atmospheric lifetimes compared to those of the natural source gases.

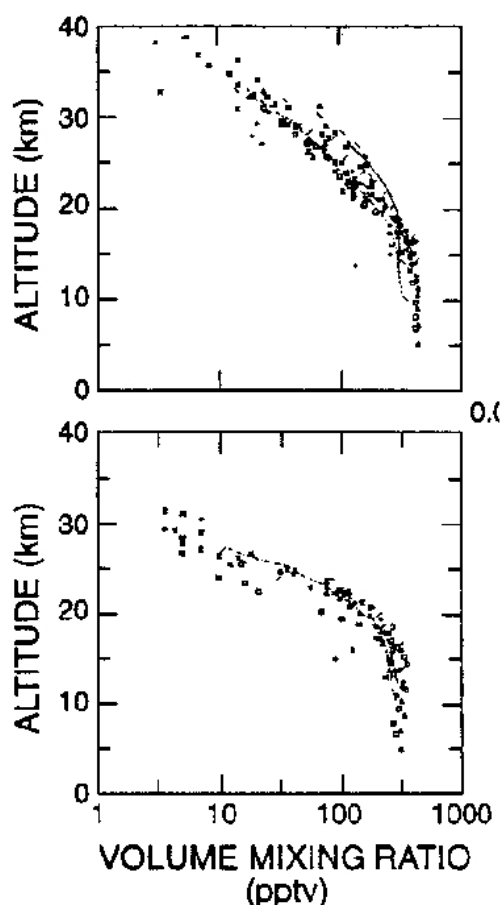


Figure 2.4 Altitude profiles of CFC-11 (bottom) and CFC-12 (top) [NASA, 1994].

In the mid 1970's, Molina and Rowland [1974] and Rowland and Molina [1975] pointed out that the CFCs released from anthropogenic sources have very long atmospheric residence times. In contrast to the halogen compounds emitted from natural sources they are not removed by dry or wet deposition and, additionally, they are very stable with respect to photolysis or chemical destruction within the troposphere (see Figure 2.4). Removal of the CFCs from the atmosphere thus includes in a first step the transport from the troposphere to the stratosphere where they are photochemically converted into reactive compounds (see Fig. 2.4) and in a second step the deposition of these compounds after their return back into the troposphere. For example, chlorine species are mainly removed from the atmosphere in the form of HCl which is highly soluble in water and can be efficiently removed by wet deposition. To assess the time scales on which these processes occur one has to consider the partitioning of the atmospheric mass (about 90% in the troposphere and about 10% in the stratosphere) and the time needed for the exchange of air between the stratosphere and the troposphere (of about five years). The circulation responsible for this exchange is often referred to as Dobson-Brewer-circulation [Dobson, 1930; Brewer, 1949; Andrews et al, 1987; Holton, 1995], see Fig. 2.5.

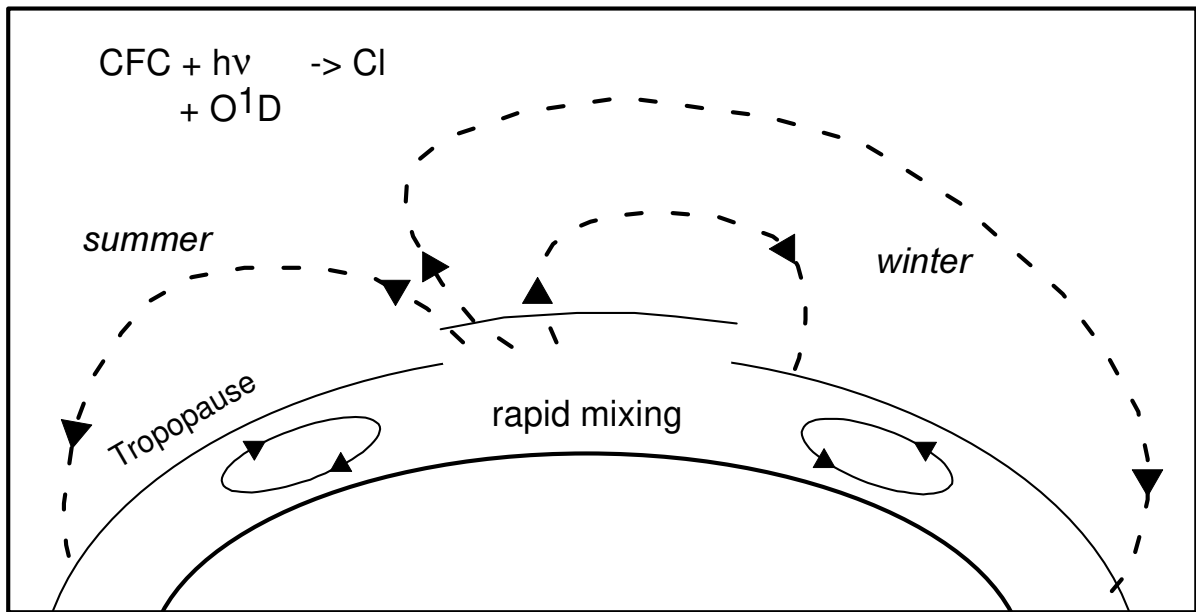


Figure 2.5 Schematic diagram of the Brewer-Dobson Circulation (adapted from Solomon et al. [1998]). Because the stratosphere contains only about 10% of the total atmosphere, the circulation must turn over many times to destroy all of the CFCs present, resulting in a long atmospheric live time of these species.

To remove CFCs from the atmosphere air has to cycle through the Dobson-Brewer circulation at least about ten times. Depending on the photochemical destruction rate of CFCs in the stratosphere a wide range of total lifetimes results for the different CFCs (see Table 2.1). In the case of CFC-11, this leads to a lifetime of about 50 years, for CFC-115 of about 500 years. As an example for the anthropogenically induced increase of CFCs, Figure 2.6 shows the evolution of CFC-11. An increase can also be seen by the measurements of ClO in the stratosphere (Figure 2.7).

After the Montreal protocol (1987) and the amendments of Copenhagen (1989) and London (1992) the production of CFCs was limited and finally stopped. And, in fact, the concentrations of CFCs in the troposphere have already reached their maximum values (see e.g. Figure 2.6). CFCs have been succeedingly replaced by partly halogenated substitutes, the

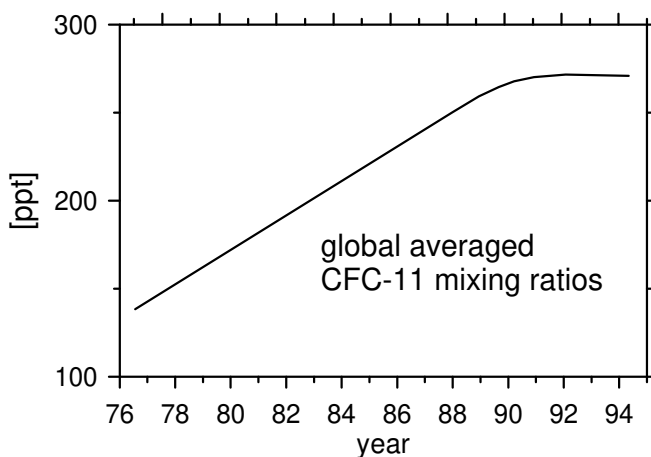


Figure 2.6 Global averaged increase of CFC-11 (adapted from IPCC [1996]).

HCFCs. These compounds are less stable than CFCs and halons and thus have shorter atmospheric lifetimes (see Table 2.1). However, it will take several decades until the stratospheric chlorine loading will return to pre ozone hole levels. Figure 2.8 provides an overview about the evolution of the atmospheric chlorine loading under different emission constraints until the year 2080. It should be noted that the recovery of the ozone hole might be further delayed due to stratospheric temperature changes as a consequence of the release of greenhouse gases.



Species	trivial name	Stratospheric lifetime [years]	Tropospheric lifetime [years]
<b>CFCs</b>			
CFCl <sub>3</sub>	CFC-11	55	∞
CF <sub>2</sub> Cl <sub>2</sub>	CFC-12	116	∞
CClF <sub>3</sub>	CFC-13	640	∞
CF <sub>2</sub> ClCFCl <sub>2</sub>	CFC-113	110	∞
CF <sub>2</sub> ClCF <sub>2</sub> Cl	CFC-114	220	∞
CF <sub>3</sub> ClF <sub>2</sub> Cl	CFC-115	550	∞
<b>HCFCs</b>			
CHF <sub>2</sub> Cl	HCFC-22	240	17
CF <sub>3</sub> CHCl <sub>2</sub>	HCFC-123	47	2
CF <sub>3</sub> CHFCl	HCFC-124	129	7
CH <sub>3</sub> CFCl <sub>2</sub>	HCFC-141b	76	13
CH <sub>3</sub> CF <sub>2</sub> Cl	HCFC-142b	215	25
CF <sub>3</sub> CF <sub>2</sub> CHCl <sub>2</sub>	HCFC-225ea	120	3
CF <sub>2</sub> ClCF <sub>2</sub> CHClF	HCFC-225cb	120	9
CH <sub>2</sub> FCI	HCFC-31	1.5	
<b>HFCs</b>			
CH <sub>2</sub> F <sub>2</sub>	HFC-32	7	
CF <sub>3</sub> CF <sub>2</sub> H	HFC-125	40	400
CF <sub>3</sub> CFH <sub>2</sub>	HFC-134a	16	210
CF <sub>3</sub> CH <sub>3</sub>	HFC-143a	70	
CH <sub>3</sub> F	HFC-41	4	
CH <sub>3</sub> CHF <sub>2</sub>	HFC-152a	1.7	62
CH <sub>2</sub> FCH <sub>2</sub> F	HFC-152	0.4	
<b>halons</b>			
CF <sub>3</sub> Br	H-1301	77	∞
CF <sub>2</sub> ClBr	H-1211	11	2.3
CF <sub>2</sub> Br <sub>2</sub>	H-1202		3.3
CF <sub>2</sub> BrCF <sub>2</sub> Br	H-2402	20	3.4
CF <sub>2</sub> HBr	H-1201		5
CF <sub>3</sub> CHFBBr	H-2401		2.8
CF <sub>3</sub> CHClBr	H-2311		0.8
<b>other</b>			
<b>halo carbons</b>			
CH <sub>3</sub> Br	methyl bromide		1.6
CH <sub>2</sub> Br <sub>2</sub>	dibromomethane		0.2
CHBr <sub>3</sub>	bromoform		0.03 - 0.1
CH <sub>2</sub> BrCl	bromochloro-methane		<1
CHBr <sub>2</sub> Cl	dibromochloro-methane		0.4
CHBrCl <sub>2</sub>	bromodichloro-methane		0.4
CH <sub>2</sub> BrCH <sub>2</sub> Br	1,2-dibromoethane		0.4
CCl <sub>4</sub>	carbon tetrachloride	47	∞
CHCl <sub>3</sub>	chloroform	0.55	
CH <sub>3</sub> CCl <sub>3</sub>	methyl chloroform	6	7

Table 2.1 Lifetimes of halogen compounds in the atmosphere [Schauffler et al., 1993; Wamsley et al., 1998; Brasseur, 1995].

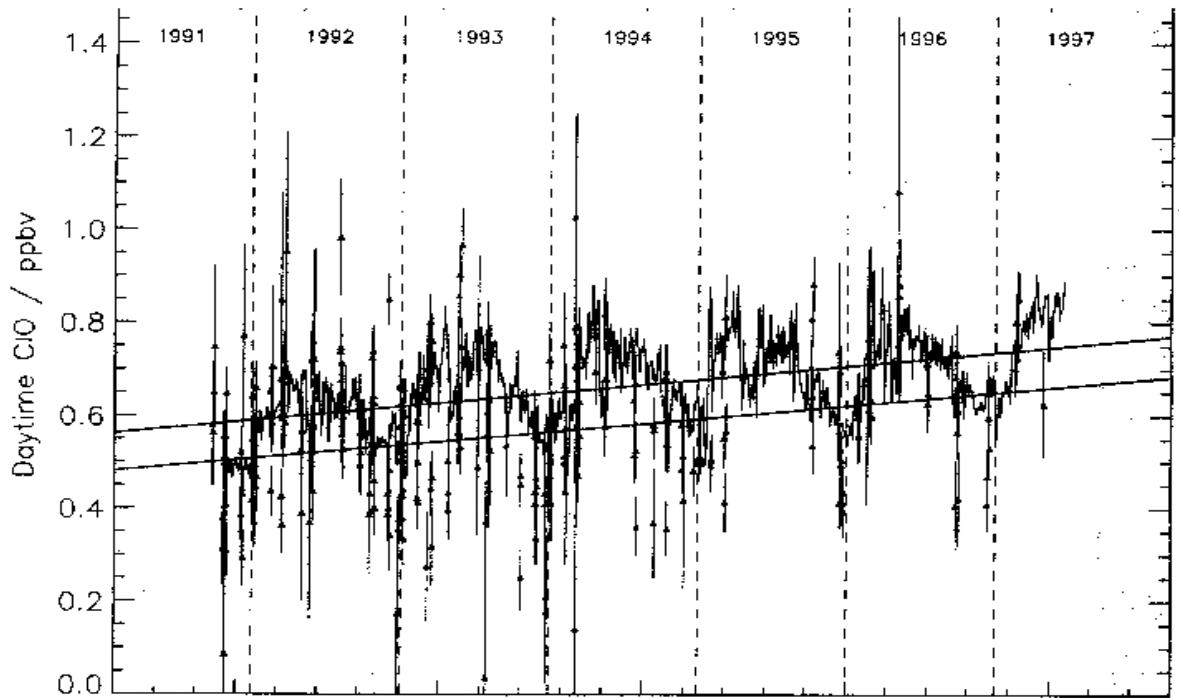


Figure 2.7 Temporal evolution of daytime ClO as measured by MLS (triangles) and modelled by SLIMCAT (solid line) at 4.6 hPa (~36 km). The straight lines represent the linear trend fitted to the two data sets [Ricaud et al., 1997].

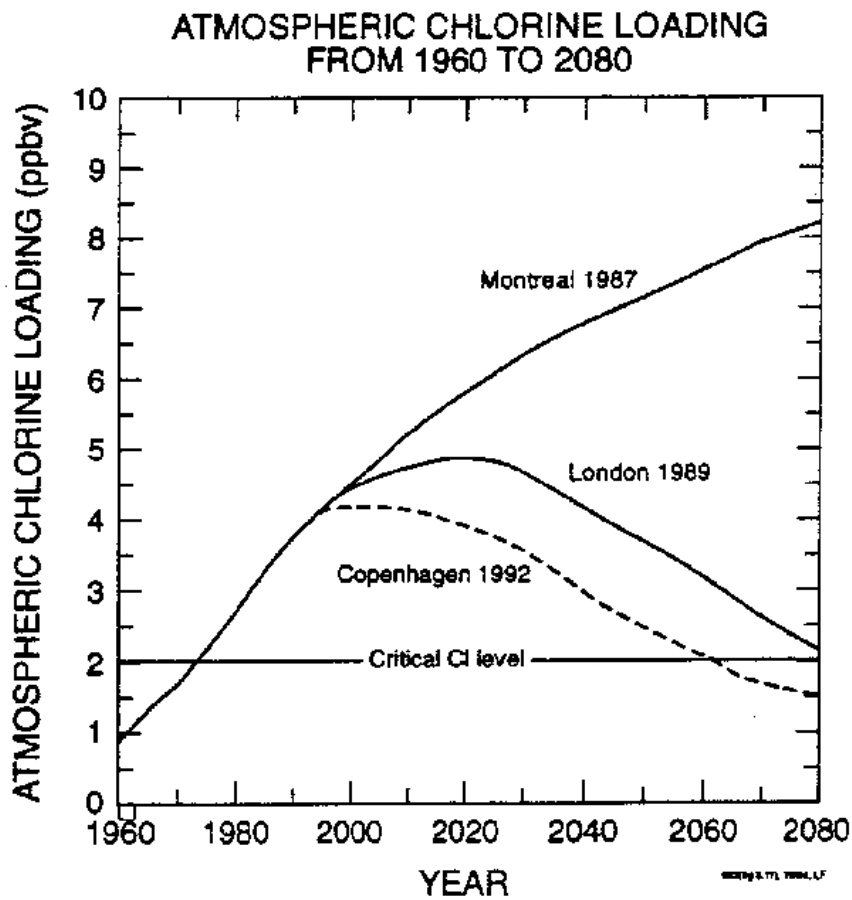


Figure 2.8 Predicted future atmospheric burden of chlorine (adapted from Brasseur [1995]).

## 2.2.2 Tropospheric halogen compounds

Partly halogenated organic compounds are less stable compared to CFCs and halons and are destroyed already in the troposphere (see Table 2.1). Thus they can provide a source of reactive halogen compounds in the troposphere. Under certain conditions reactive halogen compounds can also be directly released in the troposphere. However, in contrast to the stratosphere reactive halogen compounds are removed very efficiently from the troposphere by wet and dry deposition. Both sources for the release of reactive halogen compounds in the troposphere are described in the following subsections.

### 2.2.2.1 Emissions of partly halogenated halocarbons

The halocarbon compounds emitted from natural sources contain mainly halogenated methane species, from which methylchloride, methylbromide, and methyl iodide are the most abundant. Minor contributions of the atmospheric methylchloride and methylbromide are also due to anthropogenic sources. Several other halocarbon compounds are also emitted to the troposphere, but only methylchloride and methylbromide are stable enough to contribute significantly to the stratospheric halogen loading. It should be noted that currently it is speculated that also the shorter lived natural source gases might enter the stratosphere in considerable amounts under specific conditions like heavy thunderstorm clouds [Dvortsov et al., 1999]. These species might also be a possible source of significant amounts of reactive halogen compounds (e.g. about 1 to 2 ppt BrO) in the free troposphere [Dvortsov et al., 1999; Wagner et al., 1999a; Pfeilsticker et al., 1999; Van Roozendaal et al., 1999a; Platt et al., 1999]

Species	trivial name	mixing ratio at tropopause [ppt]	contribution to total Cl at tropopause [%]	mixing ratio in the lower stratosphere [ppt]	contribution to total Cl in lower stratosphere [%]
CFCl <sub>3</sub>	CFC-11	264	22.6	236	22.4
CF <sub>2</sub> Cl <sub>2</sub>	CFC-12	494	28.2	465	29.5
CF <sub>2</sub> ClCFCl <sub>2</sub>	CFC-113	74.6	6.4	67.9	6.5
CF <sub>2</sub> ClCF <sub>2</sub> Cl	CFC-114	16.4	1.0	15.3	1.0
CF <sub>3</sub> ClF <sub>2</sub> Cl	CFC-115	4.4	0.1	3.7	0.1
CHF <sub>2</sub> Cl	HCFC-22	96	2.8	92	2.9
CH <sub>3</sub> CF <sub>2</sub> Cl	HCFC-142b	2.8	0.1	2.1	0.1
CH <sub>3</sub> Cl	methyl chloride	531	15.1	469	14.9
CH <sub>2</sub> Cl <sub>2</sub>		14.9	0.9	15.3	1.0
CHCl <sub>3</sub>		3.13	0.3	1.7	0.2
CH <sub>3</sub> CCl <sub>3</sub>	methyl chloroform	117	10.0	100	9.5
CCl <sub>4</sub>	carbon tetrachloride	109	12.4	98	12.4

Table 2.2. Chlorine compounds at the tropopause region and in the lower stratosphere [Schauffler et al., 1993; Wamsley et al., 1998; *Brasseur, 1995*].

Species	trivial name	mixing ratio at tropopause [ppt]	contribution to total Br at tropopause [%]	mixing ratio in the lower stratosphere [ppt]	contribution to total Br in lower stratosphere [%]
CF <sub>3</sub> Br	H-1301	2.77	13.1	2.64	14.9
CF <sub>2</sub> ClBr	H-1211	2.58	12.3	2.2	12.4
CF <sub>2</sub> BrCF <sub>2</sub> Br	H-2402	1.41	13.4	1.27	14.3
CHBr <sub>3</sub>		0.5			
CHCl <sub>2</sub> Br		0.02			
CH <sub>2</sub> ClBr		0.12			
CH <sub>2</sub> Br <sub>2</sub>		0.72	6.8	0.23	2.6
CH <sub>3</sub> Br	methyl bromide	11.44	54.4	9.91	55.8

Table 2.3. Bromine compounds at the tropopause region and in the lower stratosphere [Schauffler et al., 1993; Wamsley et al., 1998; *Brasseur, 1995*].

There are no known natural sources of fluorine. All iodine compounds from natural sources are believed to have very short atmospheric lifetimes and to exist in substantial amounts in the troposphere [Alicke et al., 1999] and not in the stratosphere [Pundt et al., 1998a]. However, it should be noted that already very small concentrations of reactive iodine species could have a significant impact on ozone chemistry due to their high reactivity [Solomon et al., 1994; 1998]. Table 2.2 and 2.3 summarise the anthropogenic as well as natural sources of halo carbons.

#### 2.2.2.2 Release of reactive bromine from sea salt during polar spring.

The ocean provides an enormous reservoir of halogen species. Due to wave activities sea salt spray is continuously emitted into the atmosphere, but is nearly almost deposited again into the ocean. However, under certain conditions there exist very efficient mechanisms to release reactive bromine and probably also chlorine compounds into the gas phase (see section 2.5). Reactive halogen species released from sea salt can thus play an important role for the chemistry in the boundary layer and probably also in the free troposphere. High concentrations of BrO have for example been measured during episodes of sudden total ozone depletion in the polar boundary layer during polar spring [Bottenheim et al., 1986; Barrie et al., 1988; Solberg et al., 1996; Wessel, 1996; Kreher et al., 1997; Platt and Lehrer, 1996]. This phenomenon was first discovered in the northern hemisphere and it was speculated that it might be caused by anthropogenic pollution [Shaw, 1995]. However, in recent years, it was also discovered in the Antarctic; thus it is expected to be a natural phenomenon [Wessel, 1996; Kreher et al., 1997; Wagner and Platt, 1998].

Several theories have been proposed for the release mechanism of bromine (and probably also chlorine-) species from the sea salt:

a) The release of HBr from sea-salt Br<sup>-</sup> by strong acids [Mozurkewich, 1995].

b) The release of HBr, BrNO or BrONO<sub>2</sub> from sea-salt Br<sup>-</sup> by N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> [Finnlayson-Pitts et al., 1990].

c) Autocatalytic release of Br<sub>2</sub> (or BrCl in the presence of Cl) [Tang and McConnel, 1996].

During the last two years strong evidence was found that the autocatalytic release from sea-salt spray is the most appropriate mechanism [Tuckermann et al., 1997; Wagner and Platt, 1998] for the release of halogen species. Current research focuses mainly on the quantification of the amounts of halogen species released and the dependence of such episodes on latitude and season. Further questions are whether these halogen sources might be also important for the free troposphere and whether there are similarly effective release mechanisms also at other latitudes. High BrO concentrations have e.g. been measured in the dead sea valley in coincidence with the depletion of tropospheric ozone [Hebestreit et al., 1999]. These aspects will be discussed in more detail in section 2.5.

There are also volcanic sources of inorganic halogen species. Large amounts of HCl are known to be emitted from volcanoes. Nevertheless, only small amounts (about 0.1 to 0.2 ppb) of HCl reach the stratosphere [Schauffler et al., 1993].

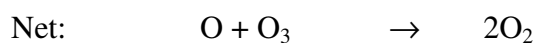
### 2.3 Fundamental schemes of atmospheric halogen chemistry

Current atmospheric research includes halogen compounds belonging to four different ‘families’: fluorine, chlorine, bromine and iodine species. In general the atmospheric reactivities, and in particular the atmospheric photolysis rates, increase from fluorine to iodine species. In consequence, the atmospheric lifetimes of the species belonging to the different families and their importance for atmospheric chemistry vary significantly. While in the troposphere chlorine, bromine and iodine are believed to be important for the chemistry, in the stratosphere only chlorine and bromine seem to have a significant influence. Fluorine species are rapidly converted to photochemical stable HF and thus have only negligible influence on the chemistry of the troposphere and stratosphere [Rowland and Molina, 1975; Stolarsky and Rundel, 1975; Sze, 1987].

In general, halogen species (and also those of other chemical ‘families’) are divided into ‘source gases’ (mostly organic compounds), and reactive species. The latter are of the form X, XO, HOX, HX, XONO<sub>2</sub>, where X refers to F, Cl, Br, or I; the reactive species are usually denoted as X<sub>y</sub>. Furthermore, the halogen radicals X and XO are referred to as active compounds or X<sub>x</sub>. The great importance of halogen compounds results from the direct coupling of these active compounds to the atmospheric O<sub>3</sub> chemistry.

To date the emission rates (anthropogenic as well as natural) of the halogen source gases and the liberation processes of reactive compounds are not fully understood and are subject of intense scientific research. However, once in its active forms the catalytic reactions of halogen radicals which destroy ozone are quite simple.

The following reaction scheme illustrates the fundamental halogen catalysed O<sub>3</sub> destruction cycle (with X = Cl, Br, I).



The efficiency of reaction 2.40 depends on the atmospheric concentration of oxygen atoms which increases with altitude due to the dependence of reaction 2.1 on the solar UV flux.

Thus for unperturbed atmospheric conditions the only important halogen catalysed ozone destruction is thought to take place at high altitudes (about 40 km) with  $X = Cl$  (see Figure 2.2).

However, a variety of chemical reactions involving different atmospheric species could also recycle  $XO\bullet$  to  $X\bullet$ . The importance of each of these recycling reactions depends on the halogen family and on the atmospheric conditions (in particular on the altitude). Some of them have just become important because of the anthropogenic increase of the atmospheric chlorine and bromine concentrations. These chemical reactions which can also close the catalytic cycle described above (as alternative to reaction 2.40) will be discussed in sections 2.4 and 2.5.

## 2.4 Halogen chemistry of the stratosphere

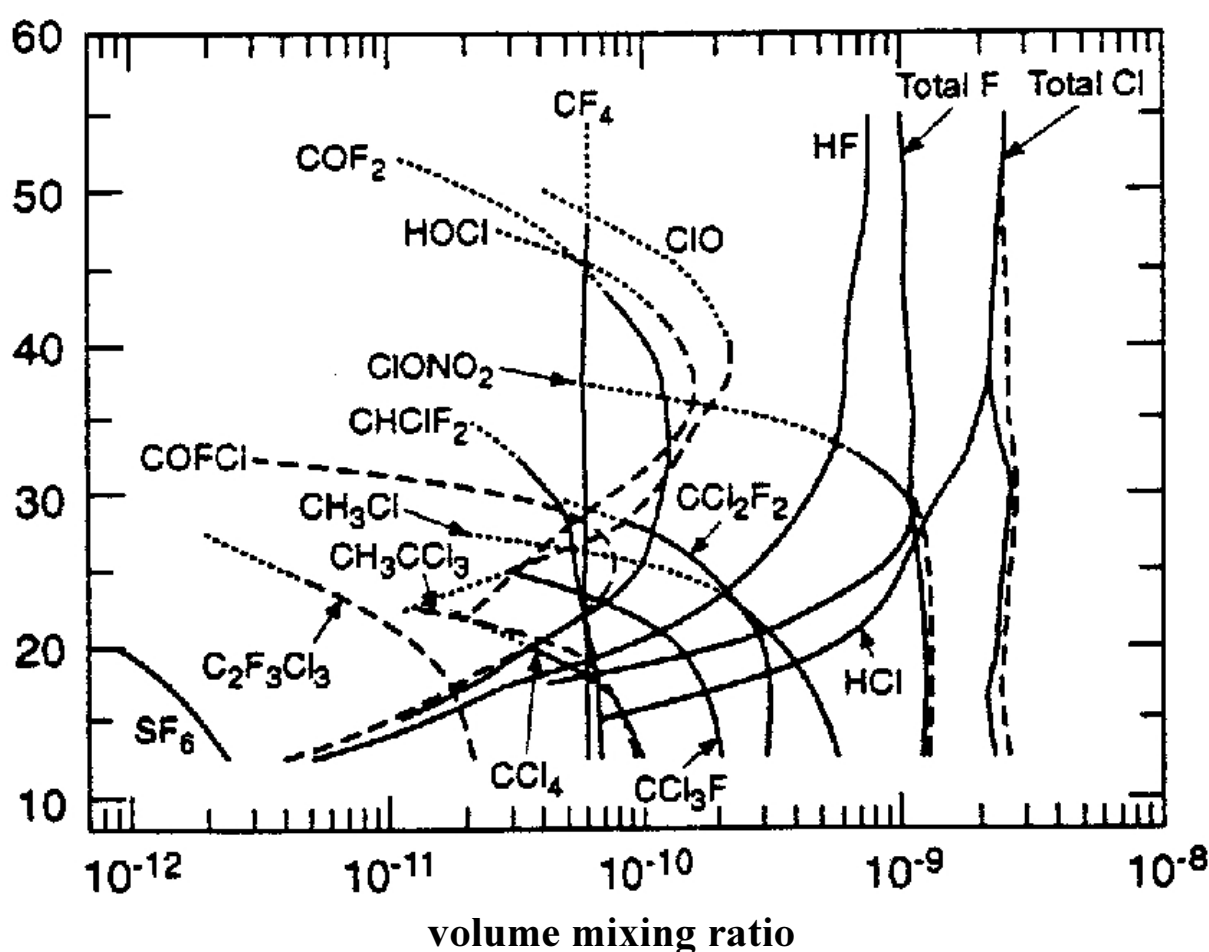
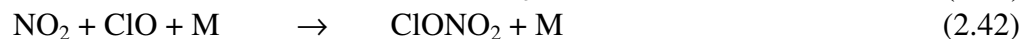
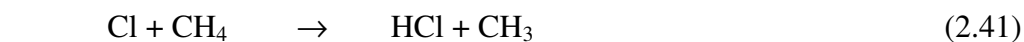


Figure 2.9 Stratospheric altitude profiles of chlorine and fluorine species near  $30^\circ N$  for springtime [Zander et al., 1992].

As pointed out in section 2.3 only chlorine and bromine species are believed to play a major role in the chemistry of the stratosphere. After the photochemical destruction of the halo carbons which have entered the stratosphere (mainly CFCs, halons, methylchloride and methylbromide) a complex set of reactions takes place leading to the partitioning among a number of inorganic halogen species ( $Cl_y$  and  $Br_y$ ). The active species then take part in ozone destruction cycles. It is important to note that under normal (non ozone hole) conditions only a

few percent of stratospheric chlorine is present in its active form while the main fraction exists as so called reservoir species HCl and ClONO<sub>2</sub> (see Figure 2.9). These reservoir gases are formed via:



For unperturbed atmospheric conditions the chlorine catalysed ozone destruction is mainly important at an altitude between about 40 and 50 km (see Fig. 2.2).

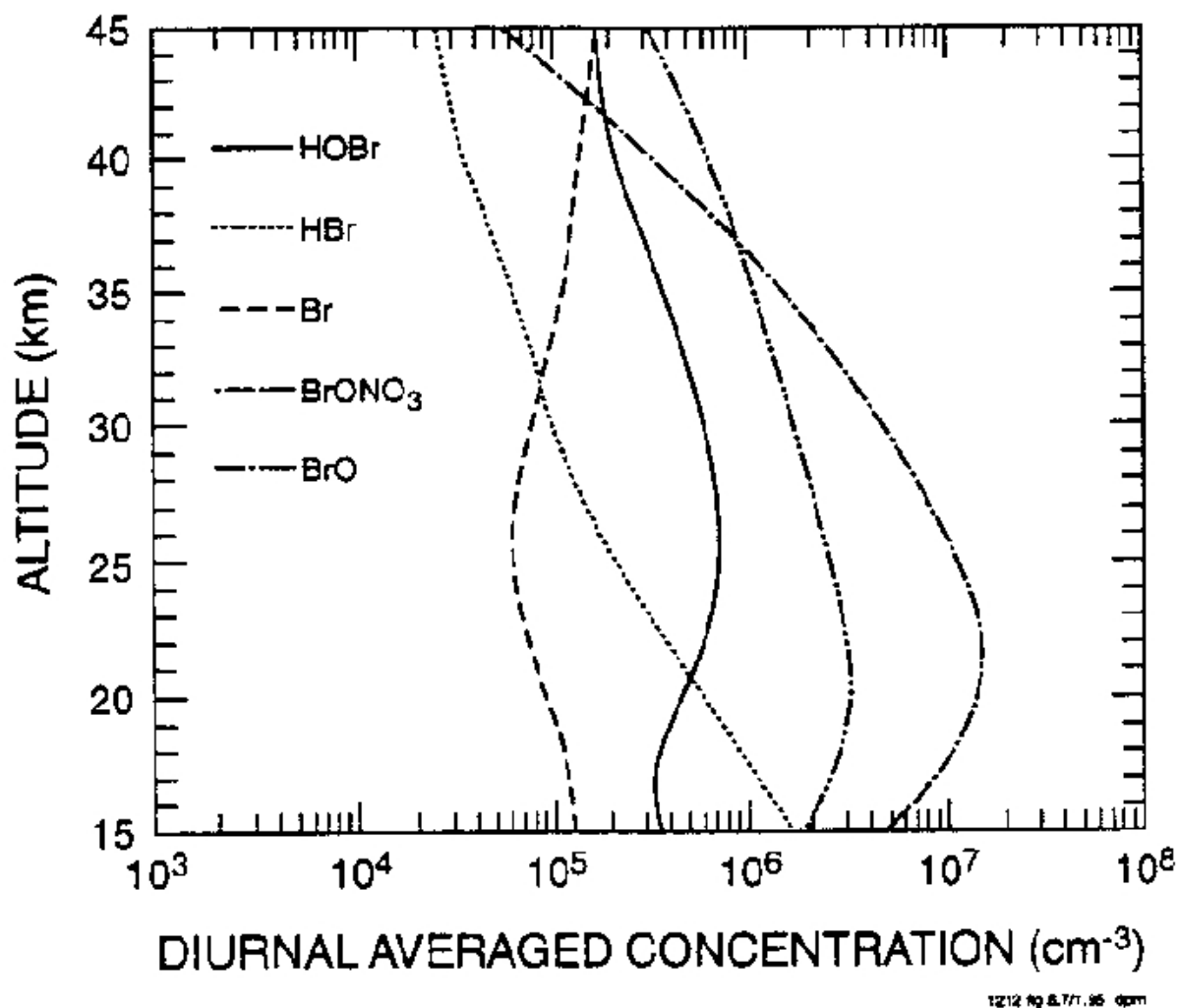


Figure 2.10 Stratospheric altitude profiles of inorganic bromine species (from Poulet et al. [1992]).

Bromine species are less abundant by about two orders of magnitude compared to chlorine. However, on a molecule to molecule comparison the ozone depletion potential of bromine is much larger than that of chlorine because the reaction rates of bromine compounds are higher and a much larger fraction (about 50%) is present in the active forms. In particular, Br atoms do not react with methane to form HBr as is the case for Cl atoms (reaction 2.41). The partitioning of bromine species in the stratosphere is illustrated in Fig. 2.10.

The following sub-sections describe the stratospheric halogen chemistry first for ‘normal’ atmospheric conditions. These conditions are representative for most of the latitudes and seasons and the stratospheric chlorine exists mainly as reservoir species. The second section describes the halogen catalysed ozone destruction which occurs under ‘ozone hole’ conditions when due to cold atmospheric temperatures heterogeneous reactions are possible which lead to a very effective activation of stratospheric chlorine species.

#### 2.4.1 Stratospheric halogen chemistry under ‘non-ozone hole’ conditions

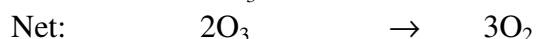
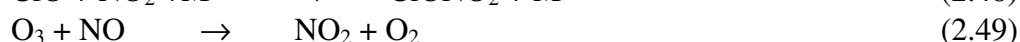
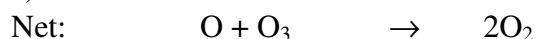
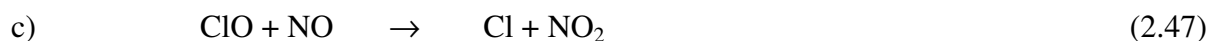
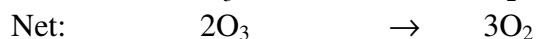
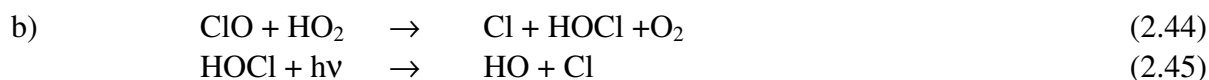
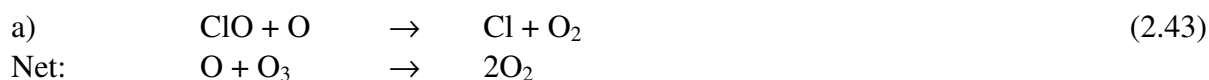
Halogen catalysed ozone destruction is initiated by the reaction:



with X = Cl and Br.

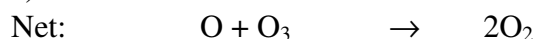
Under normal atmospheric conditions the cycle is closed by the reactions of XO with several reactants.

For chlorine the following cycles are important:

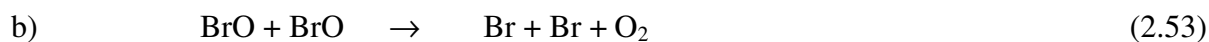


As pointed out before these ozone destruction cycles involving active chlorine species are of importance under normal atmospheric conditions only in the altitude range of 30 to 40 km. However, this situation changes dramatically under ‘ozone hole’ conditions when a strongly enhanced fraction of stratospheric chlorine exists in its active forms (see section 2.4.2).

For bromine the following cycles occur:







The BrO-BrO self reaction leads also to the products  $\text{Br}_2 + \text{O}_2$ .  $\text{Br}_2$  can be photolysed to  $2\text{Br}$  which also closes the cycle.



The BrO-ClO reaction also leads to the products



$\text{BrCl}$  can be photolysed to  $\text{Br} + \text{Cl}$  which also closes the cycle. In contrast, the  $\text{OCIO}$  channel does not destroy ozone.  $\text{OCIO}$  is photolysed to  $\text{ClO} + \text{O}$ ; the oxygen reforms one ozone molecule.

It is important to note here that  $\text{OCIO}$  shows characteristic absorption features in the UV spectral range which can be detected in atmospheric absorption spectra when the stratospheric chemistry is disturbed under ozone hole conditions [Solomon et al., 1987a; Schiller et al., 1990; Pommereau and Piquard, 1994; Erle et al., 1998; Wagner et al., 1999a,b]. Since the stratospheric  $\text{BrO}$  concentration varies only slightly  $\text{OCIO}$  measurements can be used as an indicator for stratospheric chlorine activation (see section 7).

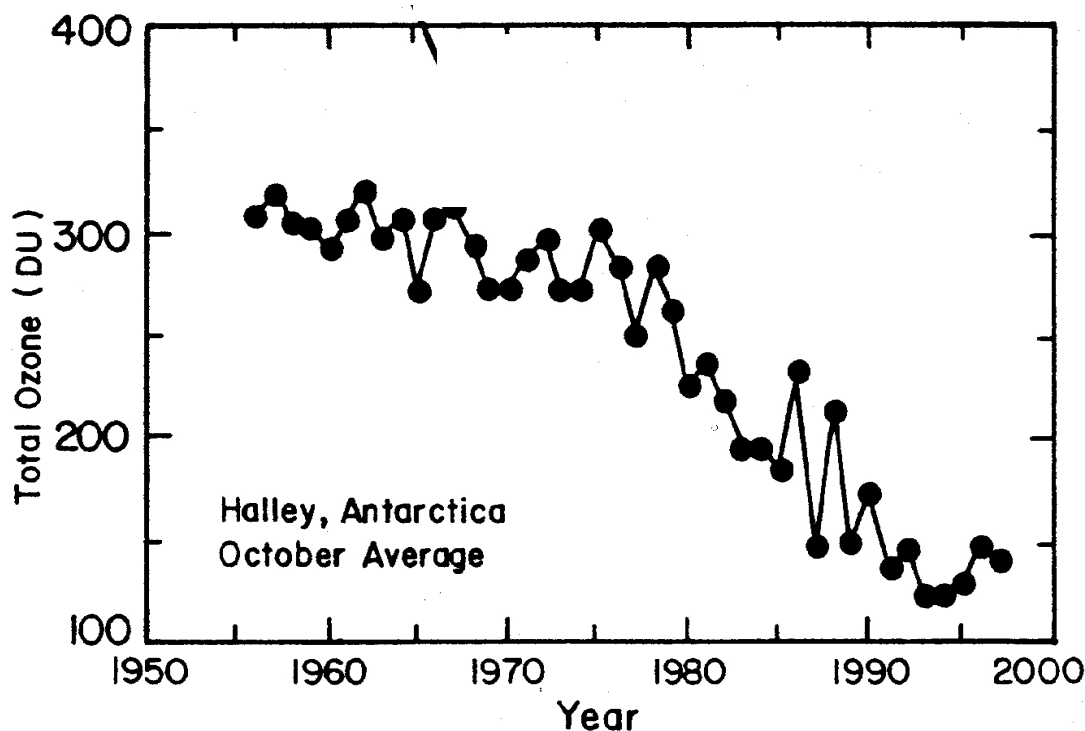


Figure 2.11 Observations of total ozone at Halley, Antarctica [Farman et al., 1986; Jones and Shanklin, 1995] (adapted from Solomon [1998]).

While under normal stratospheric conditions the pure bromine catalysed ozone destruction cycle is negligible compared to the hydrogen, nitrogen and chlorine catalysed destruction cycles, due to the coupling with the chlorine cycle via reaction 2.50 the efficiency of atmospheric bromine to destroy ozone is strongly enhanced. Via this coupling especially the increase of the atmospheric bromine concentration has a comparably large impact, which can be further enhanced under ‘ozone hole’ conditions.

#### 2.4.2 Stratospheric halogen chemistry under ‘ozone hole’ conditions

During the 1970’s it was expected that ozone depletion caused by the increase of halogen compounds in the atmosphere would be in the range of about several percent and might become observable sometime in the 21st century (see e.g. Wuebbles et al., [1983]). This estimate was derived by calculating the ozone destruction according to the above listed catalytic cycles based only on gas-phase chemistry. In the scope of this estimates the strong ozone depletion found during the Antarctic spring in the mid 1980s [Farman et al., 1985] was totally unexpected. Total atmospheric ozone columns fell far below 200 DU, which is only about 50% of the values observed in previous years (see Figure 2.11). This decrease continued during the following years and especially the ozone concentrations at altitudes where usually the maximum of the ozone layer resides were nearly completely destroyed (Fig. 2.12).

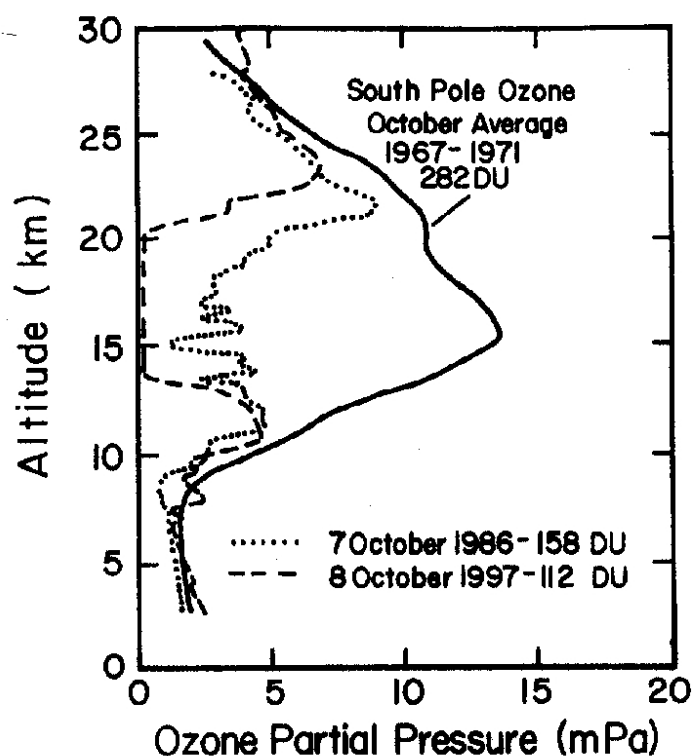


Figure 2.12 Comparison of Ozone profiles at the South Pole for the month of October in different years. The ozone concentrations of the late 1960s and early 1970 are much higher than those of 1986 and 1997 [Solomon, 1998].

Such a strong ozone destruction succeeded the expected destruction rates by far and the need for an explanation stimulated the scientific discussion. The first suggestions included a large variety of different mechanisms like dynamically upward motion of tropospheric air lower in ozone or high solar activity enhancing atmospheric nitrogen oxides. While these theories soon

proved to be in conflict with observations (a review is given by Solomon [1988]) it turned out that heterogeneous reactions occurring on polar stratospheric clouds during the polar night were responsible for the observed strong ozone destruction. Such PSCs are expected to have occurred naturally also in previous times, they were observed e.g. by Robert Scott in 1911 [Scott, 1996]. However, as will be discussed below only due to the strongly enhanced stratospheric chlorine concentrations they could dramatically increase their destructive power. The different mechanisms which lead to the activation of chlorine species under the conditions of the polar night will be shortly summarised in the following paragraph (see also Figure 2.13).

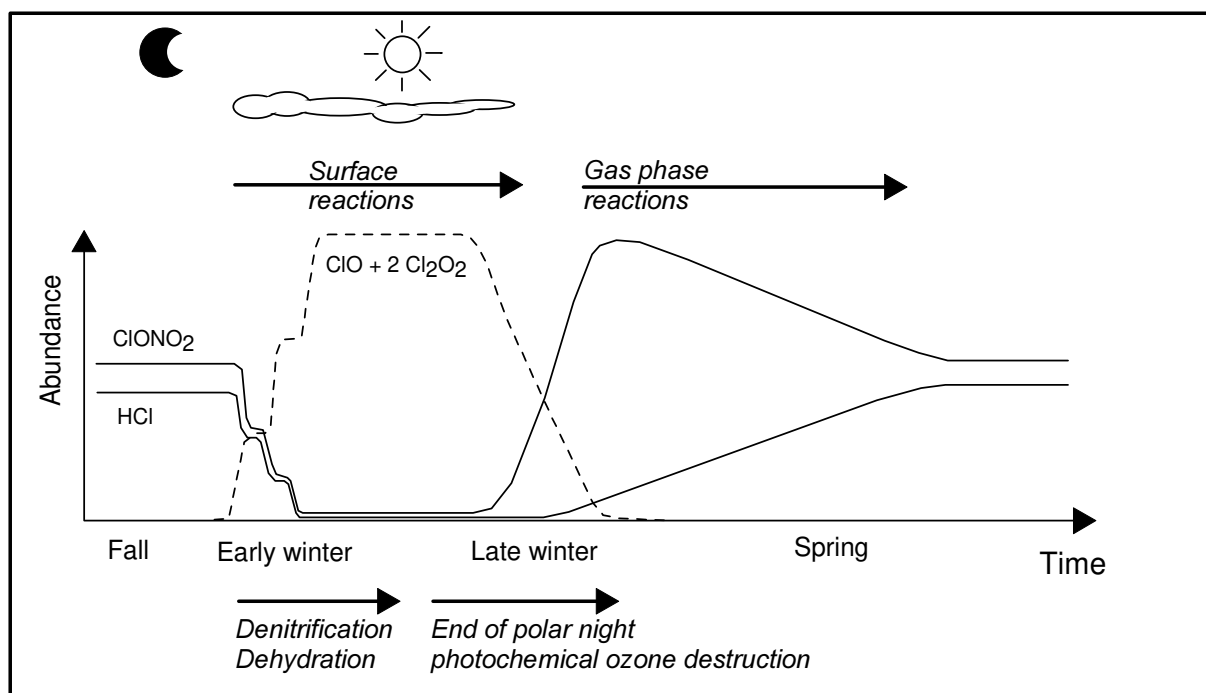
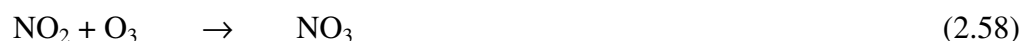


Figure 2.13 Schematic drawing of the dynamic and photochemical evolution of the stratosphere during polar winter/spring.

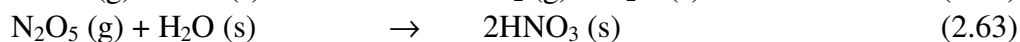
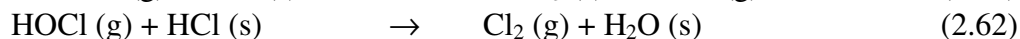
The lack of solar heating in the winter leads to very cold temperatures in polar regions. Because of the generally strong descent of cold air and the rotation of the Earth, a pronounced circumpolar wind field is established each winter. The region of strong winds is characterised by high values of potential vorticity and confines an area which is referred to as polar vortex. The large gradient in potential vorticity at the edge of the polar vortex acts as an effective barrier to horizontal transport. Thus the winter polar vortices in both hemispheres constitute confined regions with conditions very different from the conditions usually found in the Earth's atmosphere.

Under these conditions the stratospheric chemistry changes substantially: In the darkness of the polar night  $\text{NO}_x$  is converted into  $\text{N}_2\text{O}_5$



$\text{N}_2\text{O}_5$  is then converted into  $\text{HNO}_3$  (see below); these processes are referred to as denoxification.

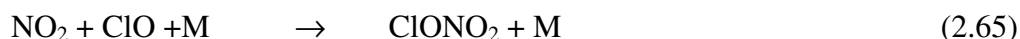
The cold vortex temperatures are the prerequisite for the formation of polar stratospheric clouds (PSCs). Reactions not possible in the gas phase occur on the surfaces of those PSC particles:



(s) and (g) indicate reactants in the solid or gas phase.

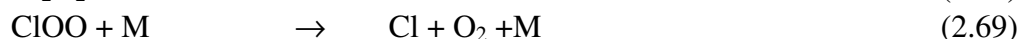
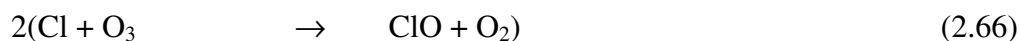
Two main effects are the consequence of these heterogeneous reactions: the release of active chlorine from its reservoirs and the removal of  $\text{NO}_x$ . The composition and physical state of PSCs is still an important subject of ongoing scientific discussion (see below).

When the PSC particles grow to large particles they can be removed from the stratosphere by sedimentation. In such cases nitrogen oxides and  $\text{H}_2\text{O}$  are removed irreversibly from the stratosphere. These processes are referred to as denitrification and dehydration, respectively [Waibel et al., 1999]. The denoxification and in a more persistent manner the denitrification of the stratosphere are the basis for an effective chlorine activation since reactions which convert the active chlorine compounds into the reservoir species are suppressed for small  $\text{NO}_x$  concentrations:



When the chlorine species are in their active forms at the end of the polar night the stratosphere is prepared for the photochemical ozone depletion which occurs when the sun rises.

PSCs have been present in both polar regions long before the discovery of the ozone hole (see e.g. Scott [1996]). Accordingly, chlorine activation can be expected to have occurred already in previous polar winters. While during the last decades the concentration of active chlorine species increased steadily due to the anthropogenic emissions of CFCs, the very sudden appearance of the ozone hole indicates that non-linear processes should play a major role in the observed ozone depletion. Such a non-linear mechanism is provided by a catalytic ozone destruction cycle including the ClO-ClO self reaction as the rate determining step [Molina and Molina, 1987]:



The ozone destruction rate of this cycle depends on the square of the ClO concentration thus making it very efficient for chlorine activated stratospheric air masses. This ClO-dimer-cycle is responsible for the majority (about 70 to 80%) of the ozone depletion during perturbed stratospheric conditions. The other cycle which significantly contributes to ozone depletion during ozone hole conditions is the combined bromine-chlorine cycle (reactions 2.55 - 2.57), the so called ClO/BrO cycle [McElroy, 1986]. Depending on the temperature this cycle is

responsible for about 16 to 28% of the total ozone loss [Anderson et al., 1989]. The ClO/O cycle (reactions 2.39; 2.40/2.43) contributes for about 5% [Anderson et al., 1989; Solomon, 1990] of the observed ozone depletion. In Fig. 2.13 the dynamic and photochemical evolution of the stratosphere during polar fall/winter/spring is displayed.

### 2.4.3 Open questions of stratospheric halogen chemistry

Today it is believed that all fundamental processes leading to the ozone destruction under ozone hole and 'normal' atmospheric conditions are understood. Nevertheless, several aspects still remain unclear, at least to a certain degree. They include in particular atmospheric dynamics, formation of PSCs and heterogeneous chemistry. They are of particular interest with respect to major foci of today's stratospheric ozone research:

A) The quantitative understanding and prediction of the ozone depletion during the Arctic winter/spring.

B) The investigation of ozone trends at mid-latitudes (see Figure 2.14).

Progress in understanding of both fields of stratospheric ozone chemistry requires further research regarding three major aspects described in the following three sections.

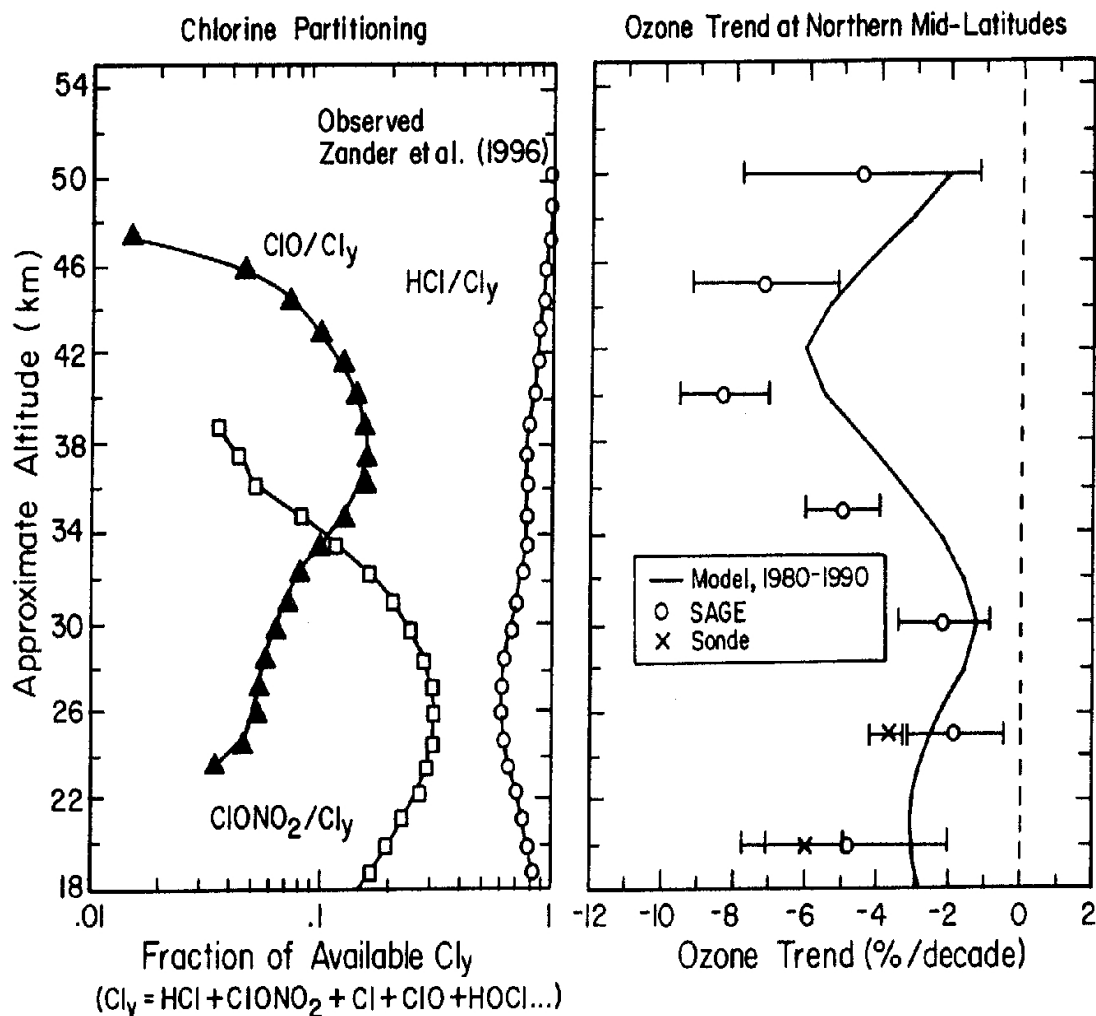


Figure 2.14 left: Observation of chlorine partitioning as a function of altitude [Zander et al., 1996]. Right: Observed vertical profiles of the ozone trend at northern mid-latitudes [SPARC, 1998] together with a current model estimate from Solomon et al. [1997].

### 2.4.3.1 Influence of dynamic processes on ozone destruction

One important prerequisite for the strong ozone depletion under Antarctic ozone hole conditions is the effective isolation of in-vortex air from air masses outside. Such high transport barriers are established for the Antarctic polar vortex due to the rotational symmetry of the Antarctic topography. To the contrary, in the northern hemisphere the development of a comparably stable vortex is prevented by the different land/water distribution and several topographic barriers in meridional orientation like the Scandinavian mountains. Planetary waves induced by such barriers reach into the stratosphere causing the Arctic polar vortex often to be deformed and displaced from the pole. Due to these instabilities the stratospheric temperatures during the polar night are on average about 10 K higher (Figure 2.15) compared to the southern hemisphere leading to less frequent formation of PSCs (see Figure 2.16). However, the rate of air transport through the vortex boundary is still uncertain. The transport of chlorine activated air into mid-latitudes might be responsible for enhanced in-situ ozone depletion in those regions which is very important with respect to the increase of the solar UV flux at mid-latitudes. The decrease of ozone at mid-latitudes can also be caused by the exchange of ozone depleted air from inside the polar vortex. On the other hand, the transport of air rich in  $\text{NO}_x$  from outside to the inside of the polar vortex could reduce the halogen induced ozone depletion via reaction 2.65. While up to now several mechanisms for the transport of air masses across the vortex edge have been discovered like the splitting of the polar vortex or the separation of so called filaments or laminae from the vortex edge the quantitative understanding remains rather poor.

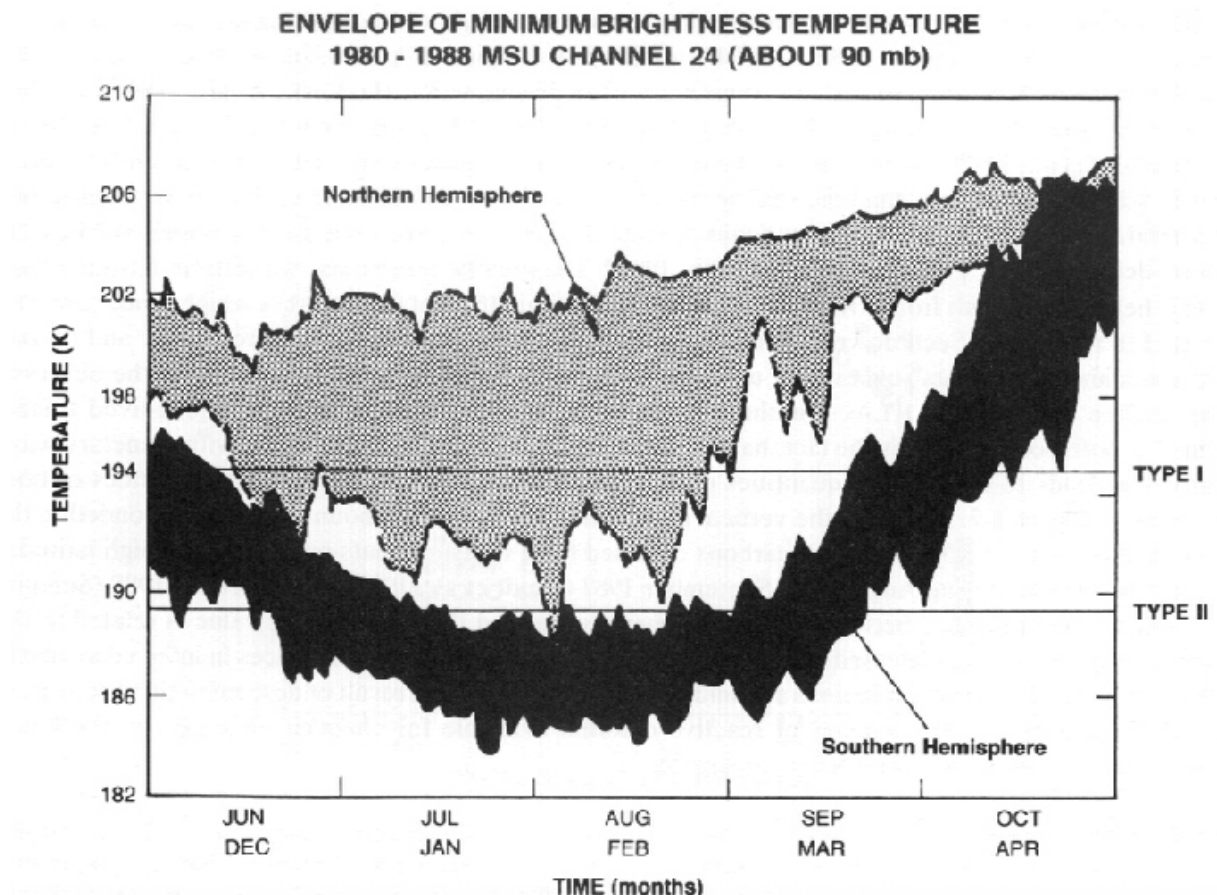


Figure 2.15 Envelope of minimum temperature 1980-1988 at about 90 mb from MSU measurements [WMO 1991].

A second major question concerns the formation of PSCs in adiabatically cooled air of lee waves caused by mountains or frontal zones in the troposphere [Carlaw et al., 1998; Schreiner et al., 1999]. Most recent studies suggest that a large amount of Arctic stratospheric air might be processed by PSCs which can form under such conditions. This is of considerable importance since the frequency of these PSCs is underestimated by synoptic temperature analysis. Figure 2.16 compares the frequency of PSC observations in both hemispheres.

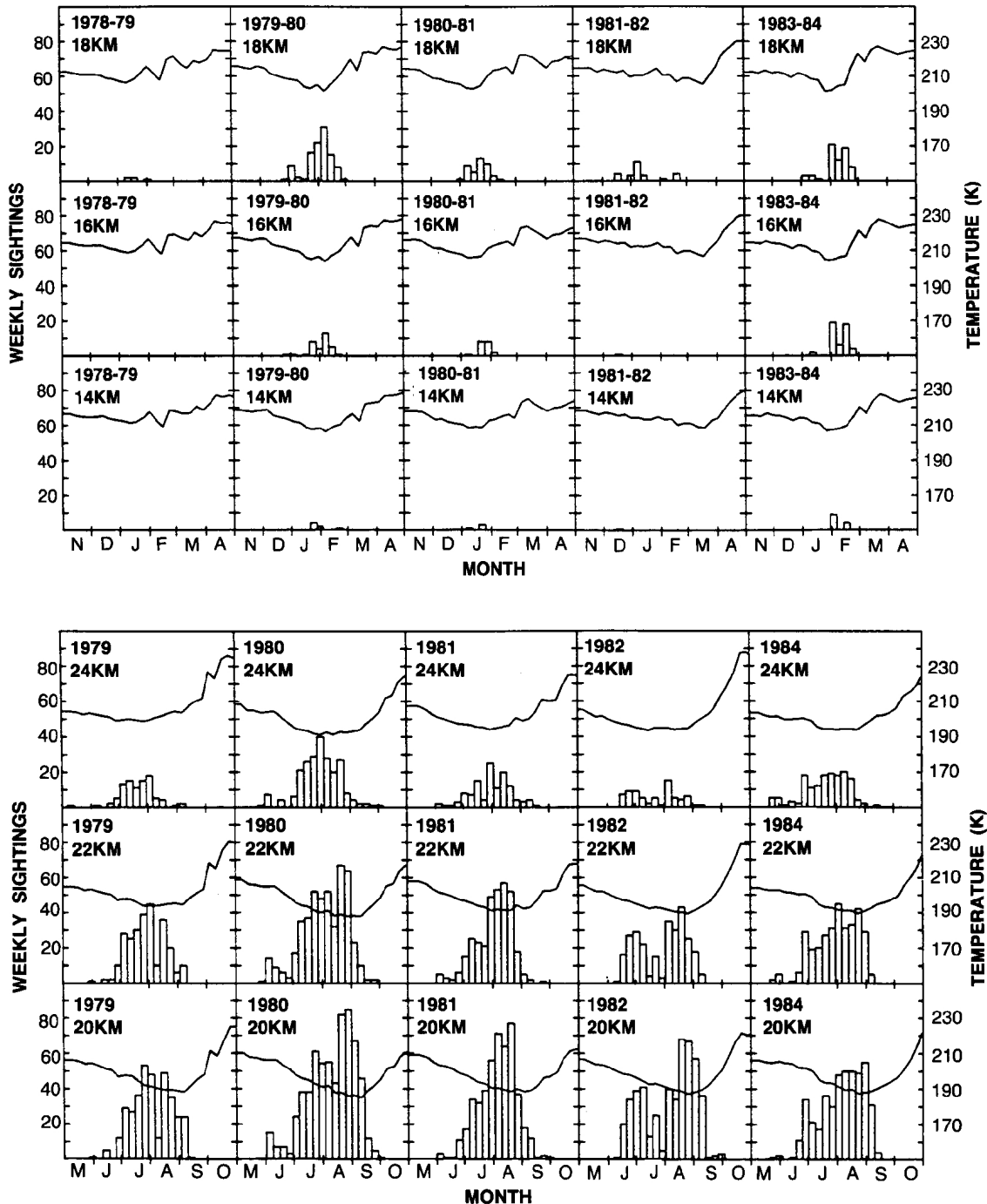


Figure 2.16 Frequency of PSC observations from satellite in the northern (top) and southern (bottom) hemisphere [WMO 1991].

### 2.4.3.2 PSC formation

During the first years after the discovery of the ozone hole the theories of PSC formation included two major types of PSCs [Toon et al., 1986; Crutzen and Arnold, 1986]:

A) Type 1 PSC particles, composed of solid nitric acid trihydrate (NAT). Such PSC can condense at temperatures well above the frost point (typically at about 195 K around 18 km). McElroy et al. [1986] also considered the possibility of nitric acid/water particles, suggesting that nitric acid monohydrate (NAM) was likely to form.

B) When temperatures fall below the frost point (about 188K) water vapour can condense on type 1 PSC particles and thus form type 2 PSCs. These PSC particles grow rapidly and can leave the stratosphere by sedimentation.

Toon et al. [1990] were the first to present evidence that PSCs may be composed not only of solid but also of liquid particles, drawing upon LIDAR measurements by Browell et al. [1990]. From these and other LIDAR measurements [Beyerle et al., 1994; Adriani et al., 1995; Steffanutti et al., 1995; Gobbi et al., 1998] high backscatter ratios (indicating the presence of clouds) were observed while the depolarisation values showed both, high and also very low values. Small values correspond to scattering by spherical particles indicating liquid phase PSCs. These observations caused a subdivision of type 1 PSCs into type 1a (depolarising solid) and type 1b (non-depolarising liquid).

Further shortcomings were discovered by satellite and in-situ measurements demonstrating that the detailed relationship of type 1 PSC formation to temperature are often difficult to reconcile with NAT thermodynamics [Kawa et al., 1990; Rosen et al., 1989; Arnold et al., 1992; Dye et al., 1996; Del Negro et al., 1997; Santee et al., 1998a]. Toon and Tolbert [1995] further showed that infrared spectra of type 1 PSCs observed over Antarctica were inconsistent with those expected for NAT. Observations by Dye et al. [1992] and their analysis by Carslaw et al. [1994], Drdla et al. [1994] and Tabzadeh et al. [1994] have demonstrated that some PSCs are probably composed of supercooled ternary liquid solutions of  $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ . The observations showed a monotonous growth in particle volume with decreasing temperature rather than a 'step-function' as expected at the stability point for NAT. These findings were confirmed by laboratory studies which showed that realistic solutions and particles containing  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{HNO}_3$  remain liquid even at very cold temperatures, as low as 188K [Beyer et al., 1994; Koop et al., 1995; Anthony et al., 1997; Clapp et al., 1997; Bertram and Sloan, 1998].

The current understanding of PSCs includes liquid and solid type 1 PSCs above the frost point and solid type 2 PSCs below. However, the mechanisms whereby solid type 1 PSCs can be formed above the frost point are still not clear. In particular it has been hypothesised that temperature histories as well as local temperatures are likely to be important in determining if and when freezing occurs [Tabzadeh et al., 1996; Santee et al., 1998a; Larsen et al., 1997].

Laboratory studies have shown that water ice, NAT, and ternary solutions are all effective in heterogeneously activating chlorine, but with different efficiencies and different dependencies on temperature, water vapour abundance, and pressure [Carslaw et al., 1997b; JPL, 1997]. But in spite of these differences and uncertainties concerning the reactivities of various surfaces, it is thought that rather effective chlorine activating reactions can occur irrespective of particle phase below about 198 K at 20 km and below about 200 - 210 K at 12 - 14 km. It can be concluded that the details of the reactivities and the microphysics which control particle surface areas are not critical to the formation of the ozone hole [Portman et al., 1996; Carslaw et al., 1997a]. They are likely to be more important at regions where temperatures are not extremely cold.



### 2.4.3.3 Heterogeneous reactions

In section 2.4.2. we have introduced the fundamental heterogeneous reactions occurring on PSCs during polar winter (reactions 2.60 - 2.64). Recently, it turned out that additional heterogeneous reactions also have to be considered, at least for specific atmospheric conditions. For example it was discovered that even at the surface of the stratospheric background aerosol chlorine activation can occur [Solomon et al., 1993; Waschewsky and Abbatt, 1998; Erle et al., 1999]. In particular, heterogeneous reactions including bromine species can have significant influence on chlorine activation via the reactions:



Also the hydrolysis of  $\text{N}_2\text{O}_5$  (reaction 2.63) and of  $\text{ClONO}_2$  (reaction 2.61) occur on sulphate aerosols. As a consequence the  $\text{NO}_x/\text{HNO}_3$  ratio decreases while the  $\text{Cl}_x/\text{ClONO}_2$  ratio increases compared to pure gas phase chemistry.

These recent studies have two major consequences: First, heterogeneous chemistry on sulphate aerosols seems to be the most likely cause for the observed mid-latitude ozone loss of about 5 to 10 % per decade [Stolarsky et al., 1991; McPeters et al., 1996a; b; Harris et al., 1997; Staehelin et al., 1998c] which can not be explained by pure gas phase chemistry (see also Figure 2.14). Second, the chlorine activation in polar regions is expected to continue even when  $\text{NO}_x$  concentrations are already increasing during spring, because heterogeneous chemistry on aerosols can continue after the evaporation of the PSCs.

## 2.5 Halogen chemistry of the troposphere

Stratospheric and tropospheric halogen chemistry differ in two major ways: First, the UV radiation necessary for the destruction of the stable (i.e. fully halogenated) halo carbons, in particular the CFCs does not penetrate into the troposphere; thus these compounds can not be a source of reactive halogen compounds in the troposphere. Second, the convectionally driven tropospheric circulation including, in particular, large amounts of water vapour leads to an effective removal of soluble halogen compounds from the atmosphere by wet deposition. In consequence, the tropospheric sources and sinks as well as the chemical partitioning are quite different from those in the stratosphere (see also section 2.4).

In particular it is generally thought that reactive halogen compounds can have only small tropospheric lifetimes and the resulting small abundances are of negligible importance for the chemistry of the troposphere.

The first prominent exception of this general picture was found during the 1980's. Barrie et al. [1988] discovered that enhanced tropospheric bromine levels are very likely the cause for the very efficient ozone destruction observed during Arctic spring (Figure 2.17). Later on, it was shown by several groups that in particular enhanced  $\text{BrO}$  concentrations are present during such episodes of tropospheric ozone depletion [Hausmann and Platt, 1994; Platt and Lehrer, 1996; Kreher et al., 1997; Tuckermann et al., 1997].

When enhanced levels of reactive bromine (and chlorine) species are present ozone can be destroyed via reaction 2.39. However, due to the low concentration of oxygen atoms in the troposphere the main recycling paths for  $\text{ClO}$  and  $\text{BrO}$  are different from those in the stratosphere. The most important ozone destruction cycle involves the self reaction of the  $\text{BrO}$  radical (reactions 2.53 - 2.54). In the presence of chlorine atoms  $\text{BrO}$  can also be recycled via

reaction with ClO [LeBras and Platt, 1995] (reactions 2.55 - 2.57). A third cycle includes the reaction of BrO with HO<sub>2</sub> [Barrie et al., 1988; Sander and Crutzen, 1995].

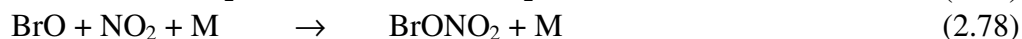
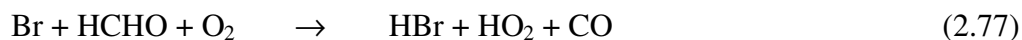


Solomon [1994] pointed out that also the reaction with IO could be of significant importance even if the IO concentrations are small because of the fast reaction.



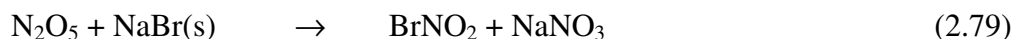
The efficiency of this cycle is about 20 times that of the BrO self reaction (reactions 2.53-2.54).

The above mentioned tropospheric ozone destruction cycles are well suited to describe the observed high ozone destruction rates during polar spring. However, for a long time it remained unclear how the high concentrations of reactive bromine could have been liberated in the gas phase. In addition, it turned out that very efficient recycling reactions are needed to compete with reactions transforming the reactive species into reservoir compounds like HBr and BrONO<sub>2</sub>.

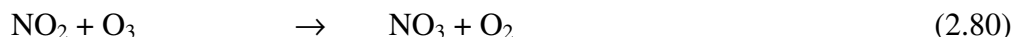


While the degradation of partly halogenated organic compounds (like CH<sub>3</sub>Br) is too slow to provide the observed high production rates of reactive bromine compounds it turned out that the release from sea salt aerosols would be the most probable mechanism [Tang and McConnell, 1996; Vogt et al., 1996]. The satellite observations of enhanced tropospheric BrO concentrations in both polar regions performed during this thesis strongly confirmed this theory [Wagner and Platt, 1998; Richter et al., 1998] (see also section 6.3).

A first suggestion was that an initial bromine concentration is released from sea salt (via heterogeneous reaction with Nitrogen oxides:

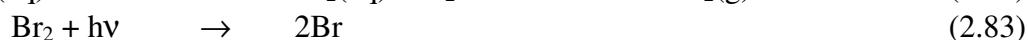
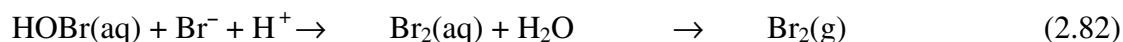


N<sub>2</sub>O<sub>5</sub> is formed via:



Even at high NO<sub>2</sub> concentrations (for polar tropospheric conditions) as for example 50 ppt these reactions are too slow to provide the high BrO concentrations observed in the polar troposphere. However, the released reactive bromine compounds could serve as an initial step for an autocatalytic amplification of the bromine concentrations (Also the degradation of halogenated organic compounds might contribute).

Via reaction with HO<sub>2</sub> (reaction 2.72) BrO forms HOBr, which is highly soluble in water (in particular also in aerosol particles). There it can react with Br<sup>-</sup> ions:



As a result of these reactions Br<sub>2</sub> is released again to the gas phase. In total for one Br-atom entering the aerosol two atoms are released to the gas phase. This leads to an exponential growth of the reactive bromine concentrations - as long as at >50% of the released Br-atoms react to HOBr. Tang and McConnell [1996] showed that within 1.5 days about 100 ppt BrO could be released from the sea salt aerosol by this mechanism. Vogt et al. [1996] extended the reaction scheme to chlorine compounds:



Up to now high tropospheric BrO concentrations have mainly been detected during polar spring. McConnell and Henderson [1993] suggested that a prerequisite for the release of reactive halogen compounds could be the appearance of ice surfaces on which sea salt aerosol deposits.

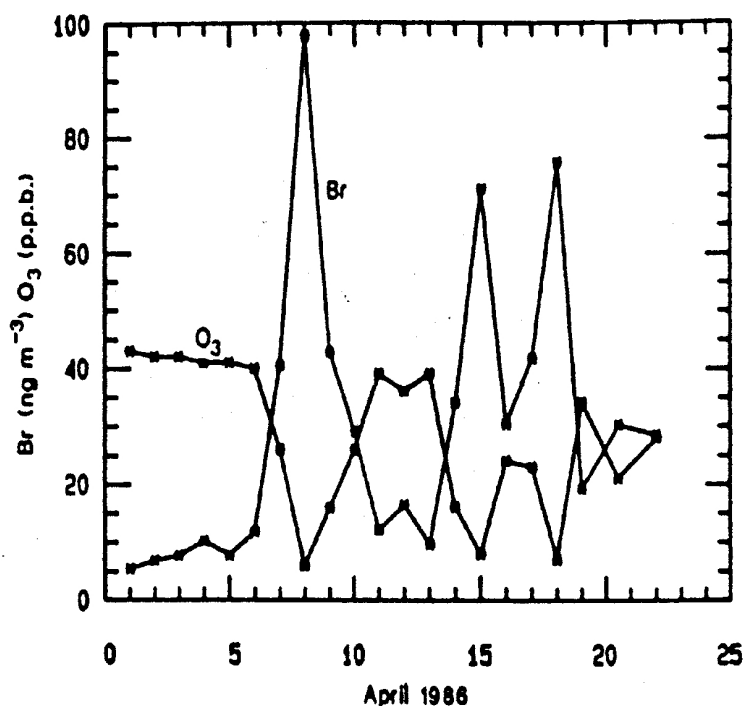


Figure 2.17 Anticorrelation of tropospheric ozone and filterable bromine at Alert (Canada), April 1986 [Barrie et al., 1988].

### 2.5.1 Open questions of tropospheric halogen chemistry

The picture of tropospheric halogen chemistry changed dramatically during the last years. Its importance first became obvious due to ozone depletion events in the Arctic spring; later similar observations were made also in the Antarctic [Kreher et al., 1997; Wagner and Platt,

1998]. While to date powerful mechanisms for the release of high BrO concentrations under these conditions are understood many aspects still remain unclear (like the dependence of the BrO events from the latitude, from geographical conditions as well as from the solar zenith angle).

Another interesting question is to search for enhanced levels of reactive halogens in other regions of the Earth. Only recently enhanced BrO concentrations were found in the dead sea valley [Hebestreit et al., 1999]. Due to the different conditions (no sea ice) the release mechanisms for these BrO observations, can be expected to be different in detail. However, similar to the conditions for frozen sea water at the dead sea also a large enrichment of bromine species is present.

Most recent measurements from Alicke et al. [1999] showed also high concentrations of IO in mid-latitude coastal regions. These observations focus the scientific interest onto the role of iodine compounds (e.g. during ozone depletion events in polar regions) which still is only very poorly known.

Another very interesting branch of the current research regards the possible presence of reactive bromine species in the free troposphere outside polar regions. First hints were presented from a comparison of the pure stratospheric column of BrO measured from balloons with the total atmospheric column determined from ground based and satellite measurements [Pundt, 1997; Wagner et al., 1998b] suggesting a BrO mixing ratio of about 1 to 2 ppt. Meanwhile there have been found several further indications including also modelling studies [Dvortsov et al., 1999; Waschewsky and Abbatt, 1998; Friess et al., 1999; Platt et al., 1999]. For assumed mixing ratios of 1 to 2 ppt tropospheric BrO can lead to several important effects: It can significantly affect the ozone concentration and thus the oxidising capacity of the troposphere. Additionally it changes the partitioning of  $\text{NO}_2/\text{NO}$  and  $\text{HO}_2/\text{OH}$ . BrO in the free troposphere can also liberate reactive chlorine species via reactions 2.84 and 2.85.