

## Chlorine in the stratosphere

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### RESUMEN

Este artículo reseña varios aspectos de los compuestos clorados presentes en la estratosfera, que incluyen tanto su papel como agentes químicos como su función de trazadores de los procesos dinámicos. En la estratosfera, el cloro reactivo se libera a partir de los clorofluorocarbonos y otros gases orgánicos que contienen cloro. La mayor parte del cloro reactivo se convierte en compuestos inertes que almacenan cloro, como  $\text{ClONO}_2$  y  $\text{HCl}$ . La reactivación del cloro estratosférico ocurre principalmente por reacciones heterogéneas en vórtices polares invernales, en combinación con la luz solar. Los ciclos catalíticos de  $\text{Cl}$ ,  $\text{ClO}$ ,  $\text{BrO}$ ,  $\text{Cl}_2\text{O}_2$ ,  $\text{ClO}_2$  y otros compuestos como  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{OH}$  y  $\text{HO}_2$  destruyen el oxígeno impar (ozono y oxígeno atómico) de la atmósfera. El ciclo del dímero de  $\text{ClO}$  es particularmente importante en la formación del agujero de ozono, mientras que en latitudes medias el  $\text{HOCl}$  tiene alguna relevancia. También los eventos de protones solares pueden alterar la química del cloro estratosférico, aunque su efecto de activación o desactivación depende de las condiciones de iluminación. La vida media atmosférica de los clorofluorocarbonos determina la disponibilidad de las sustancias que destruyen el ozono en la estratosfera y depende de la circulación de Brewer-Dobson, que a su vez establece a qué altitudes y por cuánto tiempo está expuesta una porción de aire a la fotoquímica. Por su parte, los gases orgánicos clorados pueden usarse como trazadores para estimar la edad del aire estratosférico y así examinar la circulación de Brewer-Dobson. El uso de métodos complementarios de medición ha sido esencial para ampliar nuestros conocimientos sobre los compuestos clorados en la estratosfera. El  $\text{ClO}$  se mide principalmente con métodos de percepción remota en las regiones del infrarrojo y de microondas. Las bandas del infrarrojo lejano son ideales para medir el  $\text{HOCl}$ , pero también se encuentra información sustancial en las regiones de microondas y del infrarrojo medio. El  $\text{ClONO}_2$  se mide sólo en el infrarrojo térmico, en tanto que el  $\text{HCl}$  se puede observar en las regiones de microondas y del infrarrojo lejano y medio. Sin embargo, las bandas del  $\text{HCl}$  en el infrarrojo medio se encuentran en longitudes de onda en que la radiación de cuerpo negro a temperaturas terrestres es tan baja que el  $\text{HCl}$  sólo se puede detectar mediante la técnica de absorción solar. Los clorofluorocarbonos se miden con mayor exactitud utilizando métodos de muestreo *in situ*, aunque para lograr una cobertura global se requieren mediciones en el infrarrojo térmico realizadas desde satélites. En términos epistemológicos, la investigación de la química de la estratosfera y el papel específico de los compuestos clorados se ha basado en distintos conceptos científicos como el razonamiento deductivo, el falsacionismo, el razonamiento abductivo y la llamada “solución de enigmas dentro de la ciencia normal”. Sin embargo, la concepción estructuralista de la visión no enunciativa de las teorías es probablemente la que mejor se aplica a la investigación de la química del cloro en la estratosfera.

### ABSTRACT

This paper reviews the various aspects of chlorine compounds in the stratosphere, both their roles as reactants and as tracers of dynamical processes. In the stratosphere, reactive chlorine is released from chlorofluorocarbons and other chlorine-containing organic source gases. To a large extent reactive chlorine is then sequestered in reservoir species  $\text{ClONO}_2$  and  $\text{HCl}$ . Re-activation of chlorine happens predominantly in polar winter vortices by heterogeneous reaction in combination with sunlight. Catalytic cycles involving  $\text{Cl}$ ,  $\text{ClO}$ ,  $\text{BrO}$ ,  $\text{Cl}_2\text{O}_2$ ,  $\text{ClO}_2$  and others like  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{OH}$ , and  $\text{HO}_2$  remove odd oxygen (ozone and atomic oxygen) from the atmosphere. Under an ozone hole condition, the  $\text{ClO}$  dimer cycle is particularly important,

while in mid-latitudes the short-lived reservoir HOCl has some importance. Solar proton events can also affect stratospheric chlorine chemistry, but whether solar protons effectively activate or deactivate chlorine was shown to depend on illumination conditions. The lifetime of chlorofluorocarbons has an impact on the availability of ozone destructing substances in the stratosphere and depends on the Brewer-Dobson circulation which controls at which altitudes and how long an air parcel is exposed to photochemistry. In turn, the chlorine-containing source gases can be used as tracers to constrain the age of stratospheric air and thus to diagnose the Brewer-Dobson circulation. The use of complementary measurement systems was essential to extend our knowledge on chlorine-containing compounds in the stratosphere. ClO is best measured by remote sensing in its rotational bands in the far infrared and microwave region. For HOCl the far infrared bands are ideal, but some substantial information was also gained with microwave and mid-infrared measurements. ClONO<sub>2</sub> is only measured in the thermal infrared, while HCl has a measurable signal in the microwave, far infrared and mid-infrared regions. The mid-infrared HCl lines, however, are situated at wavelengths where blackbody emission at terrestrial temperatures is so low that infrared measurements of HCl are possible only in solar absorption geometry, but not in thermal emission. Chlorine source gases are most accurately measured by air sampling techniques, while global coverage can only be achieved by satellite-borne thermal infrared measurements. In epistemological terms, research on stratospheric chemistry and particularly the role of chlorine compounds used various scientific concepts from deductive reasoning, falsificationism, abductive reasoning and so-called “puzzle-solving within normal science”. The structuralist theory of science with the concept of non-statement view of theories, however, seems to be best applicable to stratospheric chlorine research of the recent decades.

**Keywords:** Stratosphere, chlorine.

## 1. Introduction

Stratospheric chlorine has been a scientific topic since the famous work of Molina and Rowland (1974), who proposed that atomic chlorine released from chlorofluorocarbons in the stratosphere would lead to the catalytic destruction of the ozone layer. Stratospheric ozone theory has been considerably expanded since then and the role of the various chlorine compounds involved has been assessed by a large number of theoretical and empirical studies. However, the importance of the initial hypothesis on the role of anthropogenic chlorine in stratospheric ozone was rewarded by the 1995 Nobel Prize in Chemistry presented to M. J. Molina, F. S. Rowland, and P. J. Crutzen for investigating the role of nitrogen species in ozone destruction. While there are numerous papers (e.g., McElroy and Salawitch, 1989; Solomon, 1990; Molina, 1996) as well as textbooks (e.g., Brasseur and Solomon, 2005) where stratospheric chemistry is thoroughly described, this paper aims at reviewing the cross-fertilization of modeling, atmospheric composition measurements, as well as laboratory studies, and shows how rigorous testing of hypotheses has led to a steady refinement of our knowledge on stratospheric chlorine chemistry. Thus, some attention is also paid to the concepts of growth of knowledge.

### 1.1 Pre-paradigmatic science: The sources of stratospheric chlorine

Long-lived chlorine-containing organic gases are released on the Earth's surface. These include methyl chloride (also called chloromethane, CH<sub>3</sub>Cl), chlorofluorocarbons (CFCs), chlorocarbons and hydrochlorofluorocarbons (HCFCs) (Lovelock, 1977). Methyl chloride is the only relevant natural source of stratospheric chlorine. While having minor anthropogenic sources (Lovelock, 1975; Singh *et al.*, 1979), it is mainly produced biologically by fungal species (Harper, 1985, and references therein), salt marsh plants (Ni and Hagar, 1999) and on algae (Laternus, 2001). Khalil *et al.* (1999), however, suggest that oceans account for only 12% of methyl chloride emissions, while soils contribute the major part. CFCs were invented in the 1930s, are produced only anthropogenically and are used mainly as refrigerants and propellants (Molina, 1996). The only chlorocarbon of relevance in the atmosphere is carbon tetrachloride (CCl<sub>4</sub>). The most abundant HCFC in the atmosphere is HCFC-22. It has been used as refrigerant, particularly after the ban of the widely used CFCs under the Montreal Protocol. These gases are uplifted into the stratosphere, and, being rather inert in the troposphere and lower stratosphere, they survive the transport into the middle stratosphere. Since these gases are

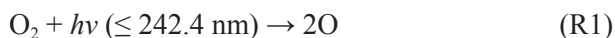
the source of stratospheric chlorine, they are called 'chlorine source gases'. The most abundant chlorine source gases are CH<sub>3</sub>Cl (methyl chloride), CF<sub>2</sub>Cl<sub>2</sub> (CFC-12), CCl<sub>3</sub>F (CFC-11), CHF<sub>2</sub>Cl (HCFC-22), CH<sub>3</sub>CCl<sub>4</sub> (methyl chloroform), CCl<sub>4</sub> (CFC-10, carbon tetrachloride) and CF<sub>2</sub>ClCFCl<sub>2</sub> (CFC-113) (Montzka *et al.*, 1996a). Long lifetimes and thus accumulation of halogenated hydrocarbons have already been published by Lovelock *et al.* (1973).

One might also suspect that naturally produced HCl contributes to the stratospheric ozone budget (*c.f.* Stolarski and Cicerone, 1974), but tropospheric HCl is efficiently washed out before it can enter the stratosphere, and even the fast injection into the stratosphere by volcanic explosions has little effect on the stratospheric chlorine budget because the water contained in the volcano plumes leads to immediate washout (Brasseur, 1992; Mankin *et al.*, 1992; Wallace and Livingston, 1992; Tabazadeh and Turco, 1993; McCormick *et al.*, 1995). Some local HCl column increase by up to 40% in volcano plumes, however, has been observed by Coffey (1996) by means of infrared solar absorption spectroscopy.

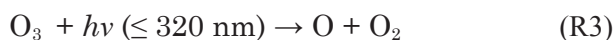
Particularly in its early phase, prior to 1974, research on halogenated hydrocarbons in the atmosphere was 'pre-paradigmatic' in the sense of Kuhn (1962, 2001). Atmospheric chlorine compounds were not a topic in themselves. Being inert in the troposphere, they were not associated with any environmental problem. Instead, their importance was their role as tracers of air motion (*e.g.*, Lovelock, 1971; Su and Goldberg, 1973; Lovelock *et al.*, 1973).

### 1.2 The setting of a paradigm: The catalytic destruction of ozone

Ozone in the stratosphere is formed by photolysis of molecular oxygen and subsequent recombination of a fraction of the released oxygen atoms with molecular oxygen in a three-body reaction (Chapman, 1930).



where M is a third body for non-reactive quenching. Reaction R2 is in a fast equilibrium with photolytic destruction of ozone:



Another loss reaction is



In equilibrium conditions ozone concentration thus depends on illumination, temperature and pressure. Ozone is most abundant at 15-25 km altitude in terms of number density (35 km in terms of mixing ratio) (Brasseur and Solomon, 2005). Above, the decrease of air density and thus the decrease of the number density of molecular oxygen leads to a decreasing efficiency of reactions R1 and R2, while sink reaction R4 is more efficient. Below the maximum, there is not sufficient ultra-violet radiation of wavelengths below 242.4 nm for photolysis of O<sub>2</sub>. The fast equilibrium between ozone and atomic oxygen turns any other reaction transforming one 'odd oxygen' (ozone or atomic oxygen) into another meaningless for the ozone budget. In contrast, any reaction transforming any odd oxygen into molecular oxygen, like R4, is an effective ozone sink.

Odd oxygen is efficiently removed by catalytic cycles. The first catalytic cycle was proposed by Hampson (1964), involving hydrogen chemistry as suggested by Bates and Nicolet (1950). In 1970 Crutzen proposed a catalytic cycle involving NO and NO<sub>2</sub>. These ozone loss paths considerably improved the quantitative understanding of stratospheric ozone. Stolarski and Cicerone (1974) were the first to suggest catalytic cycles involving chlorine compounds; interestingly, they already mentioned the possibility of heterogeneous reactions which are discussed in the next section. They considered volcanic eruptions, solid fuel rockets, and other tropospheric sources of chlorine compounds that, as we know today, are not stable enough to survive transport into the stratosphere or, like HCl, are efficiently washed out. About the same time, Molina and Rowland (1974) identified halogenated hydrocarbons as an efficient source of stratospheric chlorine and postulated catalytic ozone destruction.

The catalytic cycle



destroys two odd oxygens to form two oxygen molecules without changing the reactive chlorine budget. The expectation of the ozone layer which shields life on Earth from harmful solar ultraviolet radiation being destroyed triggered the interest of researchers in stratospheric chemistry, and also the readiness of politicians to spend money on such research. Public awareness that environmental problems are not limited to the biosphere and troposphere had already been raised since Johnston (1971) warned about the possible reduction of the ozone layer through a catalytic cycle involving nitrogen oxides from supersonic aircraft exhaust. Numerous experiments to measure stratospheric composition were designed and performed subsequently, and the chemistry of the stratosphere has become a research topic in its own right.

The first signs of catalytic ozone loss were expected for mid-latitudes above 30 to 40 km (Crutzen, 1974; Crutzen *et al.*, 1978), an altitude which contributes little to the total ozone column (Solomon, 1990). Even a self-healing process was identified, where ultraviolet radiation was better transmitted through the ozone-depleted upper atmospheric layers, leading to more atomic oxygen (reaction R2), and thus more efficient ozone formation below (World Meteorological Organization, 1985).

The paradigm of stratospheric ozone chemistry was set. According to Kuhn (1962, 2001), a paradigm is something like an established theoretical system which is largely agreed on by the scientific community and, *e.g.*, included in textbooks, taught at universities and thus part of the education of young scientists. The exact definition of the term ‘paradigm,’ however, is somewhat ambiguous. Masterman (1970) has identified 21 different definitions in the work of Kuhn, and there may be more. At least four of these definitions fit well within the fluorocarbon ozone theory already in the early 1980s.

After the discovery of enormous ozone losses in the Antarctic (see below), in 1987 the Montreal Protocol was agreed to limit emissions of ozone depleting substances in order to protect the ozone layer (see the United Nations Environment Programme for the Montreal Protocol and its amendments). In consequence, a decrease in the growth rates of CFC-11 and CFC-12 was observed since about 1989 (Elkins *et al.*, 1993), but substitutes like HCFC-23, HCFC-134a, HCFC-141a/b, and HCFC-142b gained increasing importance (Schauffler *et al.*, 1995; Oram *et al.*, 1996,

1998; Montzka *et al.*, 1994, 1996b; O’Doherty *et al.*, 2004). The threat of the possible loss of the ozone layer led to the monitoring of CFCs on ground since the mid/late 1970s by gas chromatographic methods (*e.g.*, Cunnold *et al.*, 1994), which have been used routinely to monitor these species in the troposphere (*e.g.*, Simmonds *et al.*, 1998; Montzka *et al.*, 2009; Elkins *et al.*, 2012). Long-term trends of organic chlorine using ground based Fourier transform infrared spectroscopic measurements were analyzed by Irion *et al.* (1994) and Rinsland *et al.* (2005c, b, 2010). All the more recent ones of these measurements confirm a decline of atmospheric chlorine loading as a result of the Montreal Protocol and its amendments.

## 2. Corroboration and falsification: Stratospheric trace gas measurements

From a fallibilist viewpoint, the final proof of the validity of a hypothesis by means of evidence is generally impossible. Inductive generalizations of examples are nonconclusive (Hume, 1748). The falsificationist approach of critical rationalism as propagated by Popper (1934, 2005a, b), even in the context of empirical science, does not require a new theory to be built upon evidence but to make testable, *i.e.* possibly falsifiable, predictions. The more falsification attempts fail, the better the hypothesis is corroborated. The Popperian demarcation between science and metaphysics is that metaphysical hypotheses make no falsifiable predictions.

The hypothesis of Molina and Rowland (1974) was inferred by deduction from known accepted theories. While challenged by some representatives of the industry as unscientific (*c.f.*, *e.g.*, Taubes, 1993), this hypothesis made a number of potentially falsifiable predictions and thus is a prime example of a scientific hypothesis according to the Popperian demarcation. The main empirically testable (and, in Popper’s terminology, falsifiable) partial hypotheses were (a) CFCs can be observed in the stratosphere, and their vertical distribution is consistent with their photochemical decomposition at higher altitudes, (b) existence of Cl or ClO in the stratosphere, and (c) actual ozone depletion. A negative test of any of these sub-hypotheses, which follow from the main hypothesis would act as falsification of the main hypothesis (*modus tollens*), while the main hypothesis would be corroborated by positive tests.



### 2.1 Halogenated hydrocarbons in the stratosphere

Fabian (1986) summarizes early profile measurements, obtained by balloon-borne air sampling and subsequent gas-chromatographic laboratory analysis. The first stratospheric methyl chloride measurements were obtained in 1975 by Singh *et al.* (1979) and Robinson *et al.* (1977). CFC-11 and CFC-12 and  $\text{CCl}_4$  profiles extending into the stratosphere were measured as early as 1974 by Lovelock (1974), Heidt *et al.* (1975) and Krey *et al.* (1976). The first methyl chloroform measurements in the stratosphere were obtained in 1976 by Singh *et al.* (1977), and measurements of stratospheric HCFC-22 have been obtained since 1980 (Leifer *et al.*, 1981). All these measurements have confirmed the existence of these species in the stratosphere. Furthermore, the mixing ratios of all these gases were found to decrease with altitude, corroborating the hypothesis of photochemical decomposition in the stratosphere. Total chlorine measurements by a collection system were made by Berg *et al.* (1980). These *in situ* measurements were later complemented by remotely sensed profiles.

The first remote measurements of halogenated hydrocarbons in the stratosphere were obtained using infrared solar absorption spectroscopy from balloon-platforms (Murcray *et al.*, 1975; Williams *et al.*, 1976b; Goldman *et al.*, 1981). These were soon complemented by infrared atmospheric limb emission measurements, which are independent of a solar background signal (Brasunas *et al.*, 1986; Kunde *et al.*, 1987; von Clarmann *et al.*, 1993b, 1995). These measurements take advantage of the pronounced vibrational-rotational bands of CFCs in the infrared. In support of these spectroscopic measurements, the spectroscopic data needed to analyze the remote measurements were provided first by statistical band model analysis (Goldman *et al.*, 1976), and later by laboratory-obtained measurements (*e.g.*, Massie *et al.*, 1985, 1991; Massie and Goldman, 1992; Varanasi, 1992a, b; Varanasi and Nemtchinov, 1994). Contrary to most other species whose radiance spectra are calculated under consideration of individual rotational/vibrational transitions, the lines of CFCs are so densely spaced that temperature and pressure-dependent absorption cross-section spectra are interpolated directly to the actual atmospheric conditions.

The first organic chlorine measurements from space were obtained in solar occultation with the

Atmospheric Trace Molecule Spectroscopy experiment (ATMOS) (Park *et al.*, 1986; Zander *et al.*, 1987a, 1992, 1994; Rinsland *et al.*, 1989; Gunson *et al.*, 1994). Nearly two decades later, the Fourier Transform Spectrometer used in the Atmospheric Chemistry Experiment (ACE-FTS) measured organic chlorine also in solar occultation (Rinsland *et al.*, 2005a; Nassar *et al.*, 2006; Mahieu *et al.*, 2008; Brown *et al.*, 2011). With ACE-FTS even the lower concentrated CFC substitutes CFC-113, HCFC-142b, and HCFC-23 could be measured (Dufour *et al.*, 2005; Rinsland *et al.*, 2009; Harrison *et al.*, 2012). Also the Improved Limb Atmospheric Spectrometer (ILAS) on the Japanese ADEOS satellite measured CFC-12 (Khosrawi *et al.*, 2004).

Space-borne limb emission observations of CFCs were performed from the Upper Atmosphere Research Satellite (UARS) with the Cryogenic Limb Array Etalon Spectrometer (CLAES) (Roche *et al.*, 1993b; Nightingale *et al.*, 1996), with the Cryogenic Infrared Radiance Instrumentation for Shuttle from a space shuttle (Bingham *et al.*, 1997), with the Cryogenic Infrared spectrometers and Telescopes (CRISTA) (Spang *et al.*, 1997), and with the High Resolution Dynamics Limb Sounder (HIRDLS) instrument onboard NASA's Earth Observing System (EOS) Aura satellite (Khosravi *et al.*, 2009), and finally with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) (Hoffmann *et al.*, 2008; Moore and Remedios, 2008; Kellmann *et al.*, 2012). While infrared emission instruments are generally less sensitive than occultation measurements, they provide better coverage and allow also night-time measurements. CFC-11 and CFC-12 distributions over altitude and latitude are shown in Figures 1 and 2, respectively. MIPAS measurements have been selected as an example. Figures 3 and 4 show CFC-11 volume mixing ratios at 14 km altitude and CFC-12 volume mixing ratios at 20 km altitude, respectively, represented over time and latitude. The decadal decline is seen best at tropical latitudes.

Also the intermediate products of CFC-decomposition were measured remotely:  $\text{COCl}_2$  was first measured by solar occultation spectroscopy. Measurements from stratospheric balloon platforms were reported by Toon *et al.* (2001), while first space-borne measurements were obtained with ACE-FTS (Fu *et al.*, 2007).  $\text{COCl}_2$  is also seen in limb emission, and it is a byproduct of the MIPAS CFC-11 retrieval

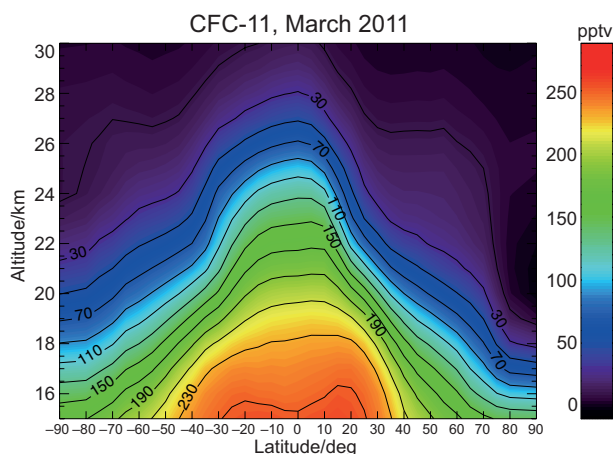


Fig. 1. CFC-11 in March 2011 over altitude and latitude. This monthly mean distribution has been calculated on the basis of MIPAS measurements (Kellmann *et al.*, 2012). In the lower tropical atmosphere mixing ratios are largest, because air has not yet been exposed to hard ultraviolet radiation for a long time. Following the stratospheric circulation, mixing ratios decrease with altitude and latitude, reflecting loss by photolysis. Particularly low mixing ratios over the North Pole are caused by subsidence of CFC-poor air from high altitudes.

(Kellmann *et al.*, 2012). Also COClF was measured by ACE-FTS (Rinsland *et al.*, 2007; Fu *et al.*, 2009). The detection of  $\text{COCl}_2$  was particularly important since its band is situated at the same spectral position as the  $\nu_4$  band of CFC-11, and not treating  $\text{COCl}_2$  correctly in the retrieval will trigger errors in CFC-11.

All these organic chlorine measurements in the

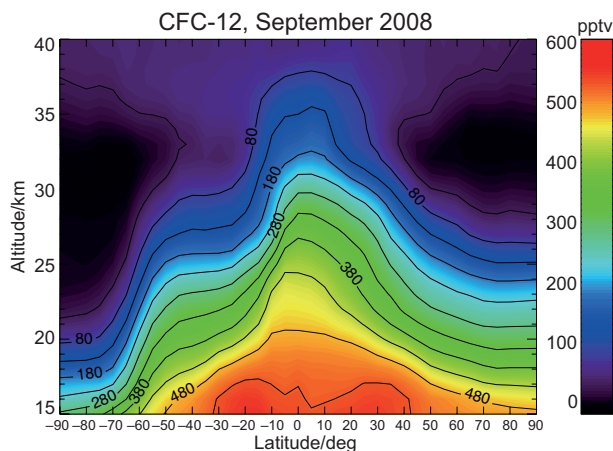


Fig. 2. CFC-12 in September 2008 over altitude and latitude from MIPAS. For details, see caption for Figure 1. Large latitudinal gradients at about 20 and 60° S indicate the subtropical mixing barrier and the boundary of the polar vortex.

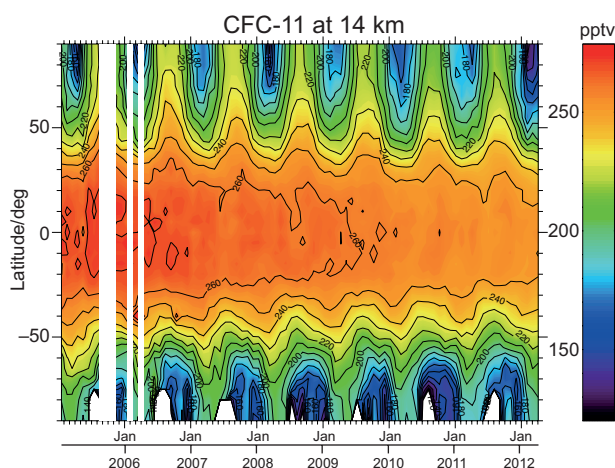


Fig. 3. Monthly mean volume mixing ratios of CFC-11 at 14 km altitude over latitude and time as measured by MIPAS (Kellmann *et al.*, 2012). The decadal decline of these gases is most visible in the tropics. Very low values during local polar winters are due to the air subsided from higher altitudes. White areas represent data gaps due to interrupted instrument operation (late 2005/early 2006), or when the measured spectra could not be analyzed because they were contaminated by the PSC signal.

stratosphere were in agreement with the fluorocarbon ozone theory in a sense that (a) CFCs indeed existed in the stratosphere, (b) were decomposed there as anticipated, and (c) their mixing ratios followed the tropospheric time series with some time lag to be explained by transport times from the troposphere to the stratosphere. Penkett *et al.* (1980) found that methyl chloride concentrations fall off with altitude due to reaction with hydroxyl radicals; these authors

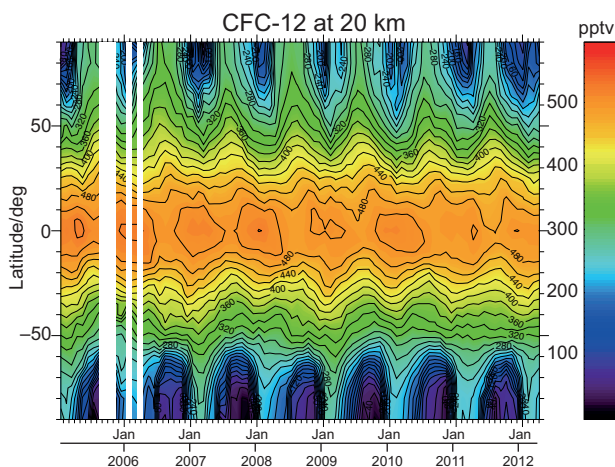


Fig. 4. Monthly mean volume mixing ratios of CFC-12 at 20 km altitude over latitude and time as measured by MIPAS. For further details, see caption for Figure 3.

thus concluded that chlorine of anthropogenic origin is predominant in the stratosphere. Russell III *et al.* (1996) found that stratospheric increases of HCl measured with the Halogen Occultation Experiment between 1991 and 1995 agreed well with the CFC-trend between 1995 and 1992 in the troposphere, which strongly corroborated the hypothesis of CFCs being the dominant source of chlorine in the stratosphere. The time lag between the tropospheric and stratospheric measurements again reflected the transport times.

## 2.2 CIO measurements in the stratosphere

The chlorofluorocarbon ozone theory predicted the existence of ClO in the stratosphere. According to model calculations by Crutzen (1974) and Crutzen *et al.* (1978) maximum ClO concentrations were expected at about 40 km altitude. Balloon-borne *in situ* measurements by Anderson *et al.* (1977, 1980) using *in situ* resonance fluorescence confirmed a layer of large ClO abundances between 30 and 40 km. Menzies (1979) measured stratospheric ClO by balloon-borne solar absorption infrared spectroscopy and found peak mixing ratios near 34 km altitude. The rotational lines of the ClO molecule were used by Waters *et al.* (1981) for measurements of limb microwave emissions. Retrieved ClO abundances were also found in agreement with theoretical predictions. Microwave spectroscopy was also used to obtain ground-based measurements of stratospheric ClO (Parrish *et al.*, 1981). The microwave limb emission technique was also used for the first global measurements of stratospheric ClO, which were provided by the Microwave Limb Sounder on the Upper Atmospheric Research Satellite (Waters *et al.*, 1993). Later satellite ClO measurements were provided by the Millimeter-wave Atmospheric Sounder (MAS) on the Space Shuttle (Aellig *et al.*, 1996), MIPAS on Evisat (Glatthor *et al.*, 2004; von Clarmann *et al.*, 2009b), the Sub-Millimeter Radiometer (SMR) on the Odin satellite (Urban *et al.*, 2004, 2005), the Microwave Limb Sounder on the Aura satellite (Santee *et al.*, 2008a) and the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES) on the International Space Station (ISS) (Sato *et al.*, 2012). Today, stratospheric ClO is monitored regularly from the ground from multiple stations, many associated to the Network for Detection of Atmospheric Composition Change (NDACC), *e.g.*, from Ny Alesund, Spitsbergen (Raffalski *et al.*, 1998), Mauna Kea, Hawaii (*e.g.*, Solomon *et al.*, 1984; Nedoluha *et al.*, 2011), Scott

Base (Antarctic) (Solomon *et al.*, 2000), and Thule, Greenland (de Zafra *et al.*, 1994). Further ground-based ClO measurements were performed on campaign basis, *e.g.*, at the McMurdo station, Antarctica (de Zafra *et al.*, 1989). These measurements are complemented by airborne measurements (*e.g.*, Crewell *et al.*, 1994; Wehr *et al.*, 1995) and balloon-borne measurements (*e.g.*, Stachnik *et al.*, 1992, 1999; de Lange *et al.*, 2012). For remote measurements of ClO, sub-millimeter and microwave measurements are the method of choice. Infrared ClO measurements are much less sensitive and the ClO transitions are largely overlapped by the signal of other infrared emitters/absorbers, but when other measurements are lacking, they still are useful. First steps towards infrared detection of ClO were undertaken by Rinsland and Goldman (1992) who searched for suitable lines in the infrared region and cleared the way for the MIPAS measurements mentioned above.

Already the earliest of these ClO measurements corroborated the chlorofluorocarbon theory of ozone destruction. The only open question remained if this reactive chlorine indeed led to long-term ozone depletion. Ozone time series available at the time were too short to significantly identify a negative trend of upper stratospheric ozone concentrations, given the large natural variability of ozone (Molina, 1996).

## 3. Refinement of the hypotheses: Chlorine reservoirs

Chlorine released from organic chlorine source species is not fully available as Cl or ClO, but forms so-called reservoir species that are much less reactive than radicals. This leads to a reduced efficiency of the catalytic chlorine cycle. The main chlorine reservoirs are HCl, ClONO<sub>2</sub>, and HOCl.

### 3.1 HCl

Atomic chlorine was found to react with methane to produce HCl, as already established by Stolarski and Cicerone (1974), who suggested the catalytic chlorine cycle for the first time.



Further reactions removing atomic chlorine yielding HCl involve H<sub>2</sub>, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and CH<sub>2</sub>O (Brasseur and Solomon, 2005). Its role as a temporary sink



of reactive chlorine has been discussed by Molina and Rowland (1974), Crutzen (1974), and Wofsy *et al.* (1975). Gas phase chlorine reactivation from its chemical reservoir is generally slow.

The first measurements of stratospheric HCl based on air-sampling by means of balloon or aircraft platforms were reported by Lazrus *et al.* (1975, 1976). Spectroscopic measurements by infrared solar absorption technique from the ground and aircrafts has been used by Farmer *et al.* (1976) and Mankin and Coffey (1983), and from stratospheric balloons by Williams *et al.* (1976a), Ackerman *et al.* (1976), and Raper *et al.* (1977). Eyre and Roscoe (1977) used a balloon-borne pressure modulator infrared radiometer; Chance *et al.* (1980) used far infrared spectroscopy, while Stachnik *et al.* (1992) used microwave emission radiometry. Farmer *et al.* (1990) have compared HCl measurements from six infrared solar occultation instruments and two far-infrared limb emission instruments, mounted on a balloon platform. More recent balloon-borne limb emission measurements have been performed with the Terahertz and Submillimeter Limb Sounder (TELIS) (de Lange *et al.*, 2012). Balloon-borne *in situ* spectroscopic techniques were employed by May and Webster (1989), Scott *et al.* (1999), and Moreau *et al.* (2005).

High resolution infrared solar occultation spectroscopy was employed by the ATMOS instrument (Raper *et al.*, 1987; Zander *et al.*, 1996) and the GRILLE spectrometer (Achard *et al.*, 1997). The Halogen Occultation Experiment (HALOE) on UARS provided HCl profiles for more than 14 years from 1991 to 2005 (Russell III *et al.*, 1993a; Webster *et al.*, 1994; Groöb and Russell III, 2005). The ACE-FTS instrument has measured HCl from 2004 (Bernath *et al.*, 2005; Mahieu *et al.*, 2008) and remains operational to date. Beyond infrared occultation, HCl is also measured in sub-millimeter and microwave regions, particularly by the MLS instruments on the UARS (Waters *et al.*, 1993) and Aura (Froidevaux *et al.*, 2008) satellites, by SMR on ODIN (Murtagh *et al.*, 2002), and by SMILES on the ISS (Kikuchi *et al.*, 2010). In this context, it should be mentioned that the HCl lines in the infrared spectrum are in the high-wavenumber part of the spectrum, where the values of the Planck function at terrestrial temperatures are so low that emission sounding is not possible. This explains

why, *e.g.*, MIPAS does not have HCl among its target gases.

Ground-based high-resolution spectroscopy at first provided total zenith column amounts of HCl only (Goldman *et al.*, 1986, 1987; Zander *et al.*, 1987b; Rinsland *et al.*, 1991; Wallace and Livingston, 1991), and an *ad hoc* hypothesis of a constant fraction of tropospheric HCl was used at the time. The first attempts to retrieve altitude-dependent information from ground-based infrared solar absorption measurements of varying solar zenith angle were made by Marché *et al.* (1980). Another approach, exploiting the spectral line shape containing some altitude information via pressure broadening of the line, was proposed by Stiller *et al.* (1995). The latter approach, however, only became widely accepted after higher resolving spectrometers became standard (see Hase *et al.*, 2004 for methodology). Stratospheric HCl time series were soon found to correlate well with tropospheric time series of CFCs when considering a transport-induced time-lag. This further corroborated the hypothesis of anthropogenic sources of stratospheric HCl.

Today, HCl profiles are routinely measured from the ground using high-resolution Fourier transform infrared solar absorption spectroscopy, particularly as part of the NDACC monitoring activities (*e.g.*, Kohlhepp *et al.*, 2012). HCl is measured routinely at various NDACC stations located in different latitudes around the world (*cf.* <http://www.ndsc.ncep.noaa.gov>). A major topic of current research with respect to HCl is the analysis of time series in order to identify a response of the trend of stratospheric chlorine reservoirs to the Montreal Protocol. Both ground-based and satellite data sets contribute to this research (*e.g.*, Rinsland *et al.*, 2003; Lary and Aulov, 2008; Kohlhepp *et al.*, 2012). As expected, there is now a decline in stratospheric HCl concentrations. Another application of such ground-based measurements besides monitoring is the validation of satellite data (*e.g.*, Mahieu *et al.*, 2008).

### 3.2 ClONO<sub>2</sub>

The species NO<sub>3</sub>Cl was first discovered by Martin and Jacobson in 1955, and called nitroxyl chloride (Martin and Jacobsen, 1955; Martin, 1958). In the literature on atmospheric sciences, this species is usually written ClONO<sub>2</sub> and called ‘chlorine nitrate’. It is a reservoir of both reactive chlorine and nitrogen



that is formed by a three-body reaction of ClO, NO<sub>2</sub>, and a third body M (Rowland *et al.*, 1976).



Chlorine nitrate is broken down by photolysis but also through reaction with atomic oxygen, atomic chlorine, or OH. All these mechanisms depend somehow on sunlight, either directly, as in the case of photolysis, or indirectly, because the reactants have a diurnal cycle themselves and are more abundant in the sunlit atmosphere. Solomon *et al.* (1984) have analyzed the diurnal cycle of stratospheric ClO and attributed it to the diurnal cycle of ClONO<sub>2</sub>. Besides its role as a temporary reservoir of chlorine, ClONO<sub>2</sub> is also involved in a reaction cycle that removes ozone (Brasseur and Solomon, 2005, p. 407).

The only remote sensing technique by which ClONO<sub>2</sub> is measured is mid infrared spectrometry. The first observation of ClONO<sub>2</sub> in the atmosphere was published in 1977 by balloon-borne solar occultation spectrometry (Murcray *et al.*, 1977), but this time only upper limits could be inferred from measurements in the Q branch region of the ClONO<sub>2</sub>  $\nu_4$  band near 780 cm<sup>-1</sup>. The authors concluded that it could not be ruled out that ClONO<sub>2</sub> was actually formed in the atmosphere as a temporary chlorine reservoir. A more robust measurement in a different part of the infrared spectrum (near 1292 cm<sup>-1</sup>) was published by the same group in 1979 (Murcray *et al.*, 1979) and yielded an altitude resolved profile. Multiple studies on ClONO<sub>2</sub> spectroscopic data have been carried out since then in order to improve the robustness of the retrievals (Ballard *et al.*, 1988; Birk and Wagner, 2000). Later, balloon-borne solar occultation measurements of ClONO<sub>2</sub> were reported (Rinsland *et al.*, 1985; Payan *et al.*, 1998; Toon *et al.*, 1999), as well as airborne solar absorption spectrometry (Mankin and Coffey, 1989; Mankin *et al.*, 1990; Toon *et al.*, 1992). The first nighttime profile measurements of ClONO<sub>2</sub> were made by limb infrared emission spectroscopy from a balloon-borne platform (von Clarmann *et al.*, 1993a; Johnson *et al.*, 1996). Infrared emission measurements of ClONO<sub>2</sub> column densities from an aircraft were reported by Blom *et al.* (1995) and Glatthor *et al.* (1998).

Space-borne measurements of ClONO<sub>2</sub> were obtained with the ATMOS instrument in solar occultation (Zander *et al.*, 1986; Rinsland *et al.*, 1994) and later with ILAS (Hayashida *et al.*, 2007) and

ACE-FTS (Wolff *et al.*, 2008). Being an emission sounder independent from sunlight, CLAES obtained the first global ClONO<sub>2</sub> measurements covering also the dark part of the atmosphere (Roche *et al.*, 1993a, 1994). Also the CRISTA instrument measured ClONO<sub>2</sub> (Riese *et al.*, 1997, 1999). The first long-term space borne measurements of this reservoir gas, covering also polar night regions, were obtained with MIPAS on Envisat (Höpfner *et al.*, 2004). The MIPAS instrument ceased to operate in its original high spectral resolution measurement mode in 2004, but resumed operation at reduced spectral resolution in 2005, under which ClONO<sub>2</sub> could still be measured (von Clarmann *et al.*, 2009b). The only known *in situ* technique to measure ClONO<sub>2</sub> is thermal dissociation/resonance fluorescence ([http://airbornescience.nasa.gov/instrument/ClONO<sub>2</sub>](http://airbornescience.nasa.gov/instrument/ClONO2), accessed on 27 March 2013).

Ground-based measurements of stratospheric ClONO<sub>2</sub> are exclusively obtained with high resolution Fourier transform infrared spectrometry. Zander and Demoulin (1988) for the first time identified ClONO<sub>2</sub> in ground-based infrared spectra taken from the Jungfraujoch station in the Swiss Alps. Today, within the NDACC activities, this species is monitored on a regular basis from FTIR measurement stations already mentioned in the context of HCl monitoring (see above) (*e.g.*, Reisinger *et al.*, 1995; Rinsland *et al.*, 2003; Kohlhepp *et al.*, 2011). As with HCl, one of the main scientific questions is how the time series reflect the decrease of CFCs after the Montreal Protocol. Negative trends have actually been determined, and the observed decrease of ClONO<sub>2</sub> was observed to be stronger than that of HCl. This difference was observed to be latitude-dependent (Kohlhepp *et al.*, 2012).

### 3.3 HOCl

HOCl is the chlorine reservoir with the shortest lifetime, and it links stratospheric chlorine chemistry with odd hydrogen chemistry.



HOCl is also involved in a catalytic ozone destruction cycle (Daniel *et al.*, 1999; Millard *et al.*, 2002). Before 2002, only a limited number of HOCl measurements were available. HOCl was measured by infrared solar absorption techniques from bal-

loon-, space-, and airborne platforms (Larsen *et al.*, 1985; Raper *et al.*, 1987; Toon and Farmer, 1989; Toon *et al.*, 1992), by balloon-borne far infrared limb emission (Chance *et al.*, 1989; Traub *et al.*, 1990; Johnson *et al.*, 1995), as well as balloon-borne infrared limb emission (von Clarmann *et al.*, 1997). MIPAS onboard Envisat provided the first global HOCl data set (von Clarmann *et al.*, 2006, 2012). The latter data set covers more than a full annual cycle. Further global HOCl measurements have been provided by the Microwave Limb Sounder (MLS) (Cofield and Stek, 2006) and SMILES (Kasai *et al.*, 2009; Kikuchi *et al.*, 2010; Baron *et al.*, 2011). The best choice for remote measurement of HOCl are its rotational lines in the sub-millimeter spectral region as they are nicely separated, while the mid-infrared spectral lines are largely masked by interfering species and the sensitivity is inferior in the mid-infrared region; however, infrared HOCl measurements still turned out to be useful. The SPIRALE instrument is an *in situ* instrument using IR absorption by tunable diode lasers and also has HOCl on its target gas list (Moreau *et al.*, 2005).

Kovalenko *et al.* (2007) reported discrepancies between measured and modeled HOCl abundances, and suggested that reaction rate coefficients for HOCl formation from ClO and HO<sub>2</sub> as published by Stimpfle *et al.* (1979) might be more appropriate than the JPL-2006 recommendation valid at the time (Sander *et al.*, 2006). On the basis of MIPAS measurements, von Clarmann *et al.* (2009a) came to the same conclusion, and this view eventually influenced the Assessment Report of the World Meteorological Organization (2011). Since then, the JPL recommendation was updated (Sander *et al.*, 2010), and von Clarmann *et al.* (2012) confirmed that model calculations on the basis of the most recent JPL recommendation led, on a global scale, to the best agreement with MIPAS measurements, even better than model calculations based on Stimpfle *et al.* (1979) rate coefficients. This, however, seems not to be conclusive, and to date research continues on which set of rate constant best reproduces the diurnal cycle of HOCl as measured by SMILES (Khosravi *et al.*, 2012; Kuribayashi *et al.*, 2013).

Figure 5 shows a monthly zonal mean HOCl volume mixing ratios represented as a function of altitude and latitude for September 2003. The local time of the measurements taken with MIPAS on En-

visat in a sun-synchronous orbit was around 22:00. The altitude of the maxima in the middle/upper stratosphere depends on local time: The maximum is found at higher altitudes during nighttime than during daytime. The morphology of the HOCl distribution and its temporal variation is a combined effect of photolysis, temperature and availability particularly of ClO, HO<sub>2</sub>, and OH, which in themselves show pronounced diurnal variation. Largest mixing ratios are typically found in the mid-latitudes in the local summer hemisphere, and coincide with the maxima of ClO.

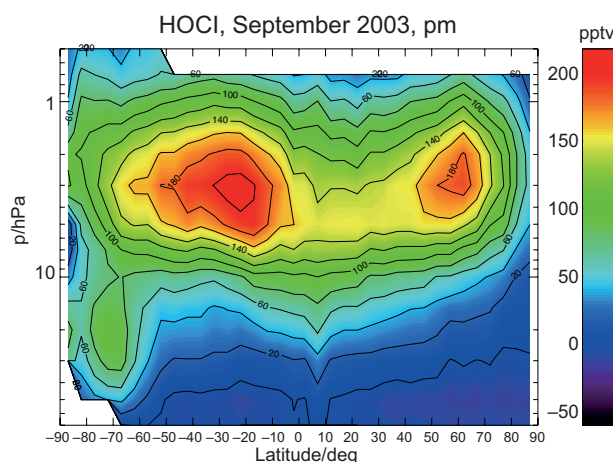


Fig. 5. Zonal mean HOCl distribution for September 2003 based on MIPAS measurements. The local times of the measurements were about 22:00 LT.

#### 4. The scientific revolution: the Antarctic ozone hole

In 1985, the Antarctic ozone hole was detected by Farman *et al.* (1985), after Chubachi (1984) had presented measurements of very low ozone over the Antarctic station Syowa. The occurrence of the ozone hole at these low altitudes in the South Pole was puzzling. Although Farman *et al.* (1985) found an anticorrelation of ozone and chlorine, no conclusive explanation was readily available to explain why (a) the dramatic ozone loss was found in the Antarctic spring, while models predicted largest ozone loss in mid-latitudes; (b) why the ozone loss was largest in the lower stratosphere, while most free chlorine was expected in the middle/upper stratosphere; (c) why this dramatic ozone loss was limited to polar spring, while no such annual cycle was known for the

reactants; and (d) why ozone loss was so dramatic, while theory predicted a long-term ozone loss of a low percent only. This situation, when some given evidence can by no means be explained within the current paradigm, is a Kuhnian 'scientific crisis'.

Solomon (1990) and Brasseur and Solomon (2005) summarize several early hypotheses to solve this puzzle; however, they were all refuted by counterevidence and eventually rejected. These hypotheses included catalytic ozone destruction by subsided  $\text{NO}_x$  generated in the mesosphere due to solar activity (Callis and Natarajan, 1986). While the basic mechanisms claimed by these authors—solar influence of meso-spheric  $\text{NO}_x$  and subsidence of mesospheric air into the stratosphere—were later confirmed (*c.f.* Section 7), this hypothesis was in conflict even with the  $\text{NO}_x$  measurements available at the time it was published: It had been shown that at the altitudes of ozone loss there was not nearly enough  $\text{NO}_x$  to explain the ozone hole by the catalytic  $\text{NO}_x$ -cycle. On the contrary, less and not more  $\text{NO}_x$  was found in the ozone hole region (Noxon, 1978; McKenzie and Johnston, 1984). Further counterevidence against the solar cycle theory was provided by low  $\text{NO}_x$  measurements by Mount *et al.* (1987), Farmer *et al.* (1987), Coffey *et al.* (1989), Fahey *et al.* (1989), and Heidt *et al.* (1989).

Another hypothesis to explain the ozone hole suggested the upward motion of air due to radiative heating in Austral spring which would uplift ozone-poor air and thus lead to low ozone values where normally the maximum ozone mixing ratios were expected (Tung *et al.*, 1986). This uplifting of air would, however, imply increased column amounts of tropospheric source gases like  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , or CFCs. The contrary has also been observed (Parrish *et al.*, 1988; Goldman *et al.*, 1988; Loewenstein *et al.*, 1989; Toon *et al.*, 1989a, b). All these measurements indicated strong subsidence rather than upwelling, and this hypothesis was thus also refuted. Low CFC mixing ratios in the lower stratosphere during the polar winter, indicating subsidence rather than upwelling, are also seen in Figures 3 and 4.

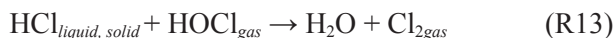
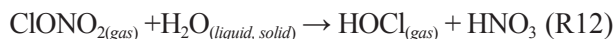
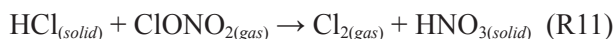
The currently accepted explanation of the ozone hole requires interaction of several processes that are all characteristic of the Antarctic polar winter stratosphere and lead us back to the title species of this paper, *i.e.*, chlorine. These processes are (a) subsidence of air from higher altitudes, supplying lower

altitudes with large amounts of inorganic chlorine; (b) heterogeneous chlorine activation, typically on polar stratospheric cloud surfaces; this often goes along with denitrification, which prevents reactive chlorine from reacting with  $\text{NO}_2$  to form  $\text{ClONO}_2$ ; (c) reappearance of sunlight to photolyze the immediate products of the heterogeneous reactions,  $\text{Cl}_2$ , and  $\text{HOCl}$ , to give reactive chlorine; and (d) catalytic ozone destruction involving the chlorine monoxide dimer or by a coupled bromine/chlorine cycle. Both these catalytic cycles are particularly efficient at higher pressures and do not require atomic oxygen. These hypotheses explained the occurrence of the ozone hole over the Antarctic, the altitude region, and why the ozone hole was observed only since the chlorine loading of the stratosphere reached a certain level. For all these processes the stable Antarctic polar vortex, the boundaries of which form a mixing barrier (*c.f.* Fig. 2), serves as an efficient reactor, preventing the supply of warmer air or dilution effects.

(a) *Subsidence of air from higher altitudes.* The typical fractionation of stratospheric chlorine is such that the organic source gases dominate at lower altitudes, while inorganic chlorine is more abundant at higher altitudes. Only the latter is harmful to ozone. Subsidence in the polar winter vortex by radiative cooling and as part of the wintertime circulation brings large amounts of inorganic chlorine down to altitudes where the ozone hole happens. Evidence of subsidence has already been discussed above as a counter-argument to the theory of upwelling air causing low ozone concentrations. The predominating chlorine at the beginning of the polar winter is  $\text{HCl}$  (Santee *et al.*, 2008b). A clear signal of subsided air in the Antarctic stratosphere, appearing as low mixing ratios of CFCs, is seen in Figures 2-4.

(b) *Heterogeneous chlorine activation.* On polar stratospheric clouds, which exist only in the particularly cold polar winter vortices, the inorganic chlorine, available in large amounts but only in the form of reservoir species like  $\text{HCl}$  or  $\text{ClONO}_2$ , could be reactivated by heterogeneous reactions. The first observations of stratospheric clouds were presented by Stormer (1929, 1932) as side effects of aurora borealis observations, and their altitude was estimated at 21-25 km. The first satellite-borne measurements were obtained with the Stratospheric Aerosol Measurement II (SAM-II) aboard the Nimbus-7 spacecraft (McCormick *et al.*, 1982). The need of heterogeneous

processes on cloud surfaces to explain the dramatic Antarctic spring ozone loss was first mentioned by Solomon *et al.* (1986). Exposure of an air parcel to cold temperatures was found essential for chlorine activation. Typical heterogeneous reactions for chlorine activation are



or



(Solomon, 1990; Brasseur and Solomon, 2005). Since no studies on the efficiencies of these heterogeneous reactions were initially available, heterogeneous chlorine activation was challenged as speculative by Crutzen and Arnold (1986). However, in the Antarctic winter stratosphere much lower concentrations than elsewhere of  $\text{ClONO}_2$  and  $\text{HCl}$  were indeed found, supporting the hypothesis that these reservoirs were “held in condensed form, *e.g.*, PSCs or some other unidentified molecular form” (Farmer *et al.*, 1987). Further measurements of reduced chlorine reservoirs were obtained by Coffey *et al.* (1989) and Toon *et al.* (1989a). Changing  $\text{HCl}$  vertical column amounts, however, do not unambiguously hint at heterogeneous processing because also upwelling or subsidence of air will affect the  $\text{HCl}$  vertical column amounts. Usually the ratio  $\text{HCl}/\text{HF}$  is used as an indicator for heterogeneous processing and chlorine activation to distinguish chemical from dynamical effects. In agreement with measurements of reduced  $\text{HCl}$ , large values of  $\text{ClO}$  were actually measured (de Zafra *et al.*, 1987; Solomon *et al.*, 1987a; Brune *et al.*, 1989). Further support of the hypothesis on the importance of heterogeneous chemistry was provided by model calculations which reproduced measured  $\text{ClO}$  amounts and ozone reductions reasonably well when heterogeneous chlorine activation was considered (Jones *et al.*, 1989) but not without these (Garcia and Solomon, 1983). Also laboratory studies on the efficiency of the heterogeneous reactions supported this hypothesis (Leu, 1988; Tolbert *et al.*, 1988). A refined view on heterogeneous chemistry was later

published by Turco *et al.* (1989), who distinguished between different PSC types (nitric acid haze, ice clouds, and lee wave clouds). In the following years heterogeneous chlorine activation was confirmed by many experiments, *e.g.*, CLAES (Roche *et al.*, 1993a), UARS-MLS (Waters *et al.*, 1993; Geller *et al.*, 1995), AURA-MLS (Santee *et al.*, 2008b), HALOE (Russell III *et al.*, 1993b; Geller *et al.*, 1995; Mickley *et al.*, 1997), ACE-FTS (Dufour *et al.*, 2006b; Santee *et al.*, 2008b), ILAS (Nakajima *et al.*, 2006), MIPAS-Envisat (Höpfner *et al.*, 2004; von Clarmann *et al.*, 2009b), and SMILES (Sugita *et al.*, 2012). Since the discovery of the importance of heterogeneous chlorine activation and the role of polar stratospheric clouds, the characterization of various types of these clouds has become a research field in itself that is beyond the scope of this overview. In the polar vortices  $\text{HOCl}$  has heterogeneous sources and sinks, and thus can contribute to the polar chlorine chemistry (Abbatt and Molina, 1992; Crutzen *et al.*, 1992; Hanson and Ravishankara, 1992; Prather, 1992b). However, it was found not to be primarily produced by a heterogeneous reaction but by a reaction of heterogeneously generated  $\text{ClO}$  and  $\text{HO}_2$  (von Clarmann *et al.*, 2009a). The lower stratospheric Antarctic enhancement seen in Figure 5 (green tongue in the left lower corner of the figure) occurred after the formation of  $\text{ClO}$  and not immediately during the period of heterogeneous processing.

PSC-particles can remove  $\text{HNO}_3$  from the atmosphere and thus lead to lower  $\text{NO}_x$  concentrations (McElroy *et al.*, 1986a). The growth of PSC particles by condensation can make them large enough for sedimentation (Toon *et al.*, 1986). If these sedimenting cloud particles contain  $\text{HNO}_3$  they will lead to the irreversible removal of nitrogen compounds from the altitude layer where condensation happens (Salawitch *et al.*, 1988). This denitrification enhances the efficiency of chlorine chemistry because  $\text{NO}_2$  is missing for the reformation of  $\text{ClONO}_2$  after the chlorine activation. Denitrification has indeed been observed by Fahey *et al.* (1990), Toon *et al.* (1990), and Deshler *et al.* (1991). Denitrification and the depth of the ozone hole, however, are not necessarily correlated (Santee *et al.*, 1998; Brasseur and Solomon, 2005). Early winter denitrification also dehydrates the stratosphere, preventing sustained heterogeneous chlorine reactivation in spring (Portmann *et al.*, 1996; Chipperfield and Pyle, 1998). Tabazadeh *et al.* (2001)

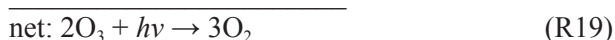
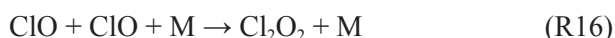
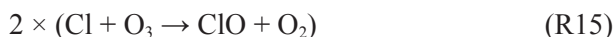


concluded that the vertical extent of the denitrified layer is critical for major column ozone loss, and Fahey *et al.* (1990) argued that ozone destruction is most efficient in the case of large denitrification going along with little dehydration, and concluded that selective growth and sedimentation of the PSC particles rich in nitric acid is essential.

At the end of the polar winter/spring ozone depletion terminates because of deactivation by reformation of the reservoir HCl (Santee *et al.*, 2008b). The deactivation path via ClONO<sub>2</sub> is usually not efficient in the Antarctic spring due to the lack of NO<sub>2</sub> in denitrified air.

(c) *Reappearance of sunlight.* The immediate products of the heterogeneous reactions described above are Cl<sub>2</sub> and HOCl, but the availability of sunlight in polar spring photolysis yields atomic chlorine for catalytic ozone destruction. This explains why the ozone hole is observed in the polar spring but not in the polar winter. MLS/UARS measured largest lower stratospheric ClO concentrations in sunlit regions of air which had encountered heterogeneous processing by polar stratospheric clouds (Yudin *et al.*, 1997). Since sunlight is essential for large ozone loss, the severity of an ozone hole depends largely on how long heterogeneous chlorine activation still competes with the reformation of reservoirs in spring when enough sunlight is available for keeping the catalytic cycles going.

(d) *The chlorine monoxide dimer cycle.* The ClO catalytic cycle (R5-R7) is not efficient at low altitudes where the ozone hole is observed since it requires the presence of atomic oxygen (Salawitch *et al.*, 1993; Molina, 1996). Instead, the particular catalytic cycle relevant for polar ozone hole chemistry is the ClO dimer cycle (Molina and Molina, 1987; Barrett *et al.*, 1988; Cox and Hayman, 1988; Anderson *et al.*, 1989a).



Such reaction cycles involving termolecular reactions with a third body M are more efficient at higher pressures, which is in agreement with the ozone hole being a lower stratospheric phenomenon. Furthermore, contrary to the catalytic cycle R5-R7, the dimer catalytic cycle does not depend on the availability of atomic oxygen, which is not very abundant at polar winter/spring conditions and in low altitudes. The contribution of this catalytic cycle to Antarctic ozone destruction was estimated at 75% (Anderson *et al.*, 1991). Similar characteristics —particularly independence of atomic oxygen— apply to the coupled catalytic cycle involving also Br and BrO, first suggested by McElroy *et al.* (1986b).



The importance of the bromine cycle is highlighted by Barrett *et al.* (1988), who estimated it to account for 5-15% of the ozone loss rate.

Solomon (1990) argues that excessive ozone destruction requires mixing ratios of ClO of the order of 1 ppbv, which would go along with accordingly decreased mixing ratios of the chlorine reservoirs. Again falsifiable predictions were available which led to testing the hypothesis by extensive measurement campaigns in 1986/87 that strongly corroborated this hypothesis: de Zafra *et al.* (1987) and Solomon *et al.* (1987a) measured Antarctic lower stratospheric ClO abundances high enough to be consistent with the dimer cycle. Figure 6 shows the ClO distribution as measured by MIPAS in September 2011. Large mixing ratios, exceeding 1 ppbv are found in the Antarctic lower stratosphere. Figure 7 shows that Antarctic winter chlorine activation is a regular feature, although the intensity varies slightly from year to year.

The first stratospheric measurements of the ClO dimer itself were only obtained in 2004 by Stimpfle *et al.* (2004), using a thermal dissociation technique involving chemical conversion vacuum UV resonance

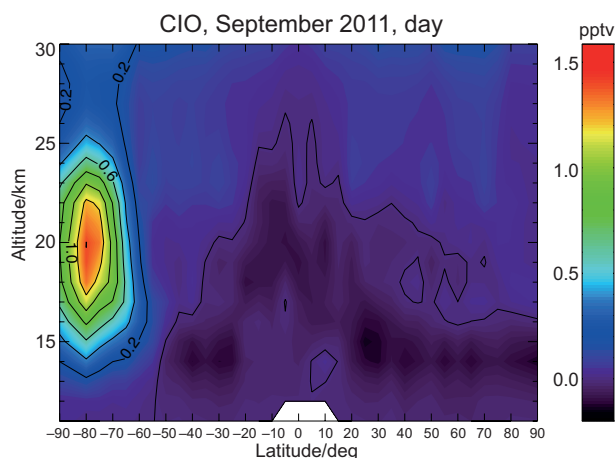


Fig. 6. Monthly mean daytime CIO distribution for September 2011 based on MIPAS measurements. Large mixing ratios, exceeding 1 ppbv are seen in the Antarctic lower stratosphere.

fluorescence. Another indirect indicator of CIO dimer chemistry or coupled BrO/CIO chemistry is the existence of OCIO, formed by the reaction of two CIO molecules or by BrO and CIO. OCIO was measured by Solomon *et al.* (1987b), Sanders *et al.* (1989, 1993), and Solomon *et al.* (1990) with solar and lunar visible and near ultraviolet absorption spectroscopy; by Wahner *et al.* (1989) with near UV solar absorption spectroscopy; and by Kreher *et al.* (1996) using ground-based visible and near infrared spectroscopy. More recently, satellite observations of OCIO became available; these include the nadir looking UV-visible instruments GOME on the ERS-2 satellite (Wagner *et al.*, 2001) and OMI on NASA's Aura satellite (Levelt *et al.*, 2006), stellar occultation with the GOMOS on Envisat (Tetard *et al.*, 2009; Fussen *et al.*, 2006) as well as limb scatter measurements by SCIAMACHY on Envisat (Kühl *et al.*, 2008) and OSIRIS on the Odin satellite (Krecl *et al.*, 2006). Since OCIO is rapidly photolyzed, it can be measured only during low sun.

Salawitch *et al.* (1988) found that the concentrations of halogen gases before 1970 were too low to cause major ozone loss, even if thermal conditions were favorable. Spatial and temporal anticorrelations between CIO and ozone in the Antarctic vortex corroborated the hypothesis that activated chlorine is indeed responsible for the ozone hole (Anderson *et al.*, 1989b).

The formation of the hypothesis involving steps *a-d* was abductive in the sense that it solved the puzzle

in a way that facts which had been surprising before this hypothesis was available became expectable and predictable; in other words, the observed facts could be deduced from the postulated mechanism (*c.f.*, *e.g.*, Peirce, 1931). The fact that many of the processes involved were first predicted on the basis of theoretical considerations and later confirmed or refuted by experimental evidence, not vice versa, is in agreement with the logic of scientific discovery as characterized by Popper (1934, 2005a, b). While scientific knowledge is always conjectural, the hypothesis of ozone destruction by reactive chlorine brought into the stratosphere via CFCs is now extremely well corroborated by empirical evidence. Whether the explanation of the ozone hole is a scientific revolution in the sense of Kuhn (1962, 2001) can, however, be challenged. The explanation of the ozone hole was undoubtedly a major breakthrough in atmospheric chemistry, but still the growth of knowledge was accumulative in the sense that the hard core of the old theory had not to be rejected, it only needed to be extended by amendments, *i.e.* heterogeneous reactions and further catalytic cycles. No incommensurability between the old and the new theory was encountered. Scientists associated with the old paradigm did not dogmatically defend it, but contributed significantly to its refinement. All of the above indicates that this scientific breakthrough was not a scientific revolution in the Kuhnian sense. However, it would certainly be odd to call this breakthrough 'normal science' as opposed to 'extraordinary science' in Kuhnian terminology. This example shows that the Kuhnian view on the scientific growth of knowledge is, at least in some cases, questionable.

Even when the chemistry and dynamics of the ozone hole were well understood, the Antarctic stratosphere remained thoroughly monitored. Some Austral polar winters stood out in particular: The eruption of the Mount Pinatubo volcano in June 1991 injected huge amounts of sulfur compounds into the stratosphere. Solomon *et al.* (1993) postulated that similar reactions as those on PSCs may take place on the surface of liquid sulfuric acid aerosols. Indeed, the authors measured huge amounts of CIO as early as in the austral autumn of 1992, prior to the PSC season. Laboratory studies on the uptake of  $\text{ClONO}_2$  onto sulfuric acid by Hanson and Ravishankara (1994) confirm the relevance of sulfuric acid aerosols, particularly when polar stratospheric clouds

are not formed despite it being cold enough. This type of heterogeneous reactions causes considerable chlorine activation not only under conditions of extreme aerosol loadings due to volcanoes. Significant chlorine activation can also happen on background aerosol (Hanson *et al.*, 1994). The role of chlorine activation on sulfate aerosol polar in vortices is further discussed in Section 5.1.

For the first time since the availability of observations, the Antarctic polar vortex in 2002 encountered enhanced wave activity, which led to displacement and finally a split of the vortex (Newman and Nash, 2005). OCIO measurements with the Global Ozone Monitoring Experiment (GOME) indicated that chlorine activation was similar to the preceding years until the early major warming event registered on September 26. This atypical dynamics had several consequences: The less stable vortex had a much more permeable boundary, leading to dilution of the vortex air by mixing with mid-latitudinal air (Glatthor *et al.*, 2005), and chlorine was deactivated very early (Grooß *et al.*, 2005). Further, due to vortex displacement, vortex air was moved to sunlit areas. This led, *e.g.*, to the generation of large amounts of HOCl, because sunlight triggered HO<sub>x</sub> chemistry in a polar winter air mass which was, due to subsidence, rich in inorganic chlorine (von Clarmann *et al.*, 2009a) (*c.f.* the green tongue in the left lower corner of Fig. 5).

Lowest ozone amounts to date were measured in the Antarctic winter stratosphere in 1994, as reported by the NASA Ozone Watch website (<http://ozonewatch.gsfc.nasa.gov/>), while the largest ozone hole in terms of area covered by ozone column amounts below 220 Dobson units happened in 2006. Figure 7 shows that chlorine activation in this particular winter was more pronounced and it extended over a wider altitude range compared to other winters. In response to the Montreal Protocol and related reduced emissions of CFCs, the Antarctic ozone holes stopped to grow in depth and size. First signs of recovery have been reported but due to the superimposed large natural variability it is hard to identify significant trends and unambiguously assign them to reduced chlorine loading of the stratosphere. Weatherhead and Andersen (2006), the World Meteorological Organization (2011), and Salby *et al.* (2011) have subtracted the component of Antarctic ozone variation caused by the dynamical variability and see a positive ozone trend over 10 years in the residual ozone signal which they attribute to CFC reduction.

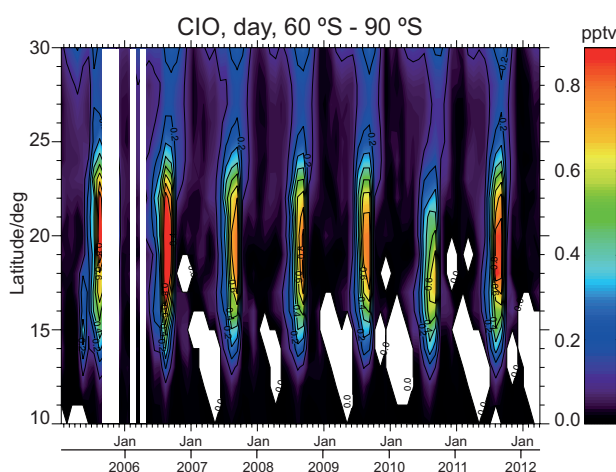


Fig. 7. Temporal development of ClO distribution in the Antarctic (60–90° S.) stratosphere. White stripes are due to missing data, while other white areas represent unrealistic negative data due to a low bias in MIPAS lower stratospheric ClO.

## 5. Normal science after the paradigm shift

With the basic principles of the ozone hole understood, the “normal science within the paradigm” (Kuhn, 1962, 2001) began, including more and better measurements of the abundances of relevant atmospheric constituents, better determination of the rate constants of the reactions involved, and application of the lessons learned to other regions and times. No further paradigm shifts have taken place since then, although an anomaly nearly led to a temporary scientific crisis (*c.f.* Section 6).

### 5.1 The Arctic

After the discovery of the Antarctic ozone hole the obvious question was if and to what extent a similar disastrous ozone loss could take place in the Arctic. Due to larger wave activity in the Northern Hemisphere, the Arctic polar vortex is often displaced from the pole, distorted in shape, and shows a much more permeable boundary than its Antarctic counterpart. Parts of the Arctic polar vortex wander through sunlit areas early in the year. In consequence, the Arctic vortex is generally warmer than the Antarctic vortex. Also, earlier stratospheric warming events interrupt periods of heterogeneous chlorine activation in spring. The latter is particularly crucial, because major ozone loss depends on heterogeneous chlorine activation in springtime sunlit conditions.

The strong subsidence, bringing down large amounts of inorganic chlorine, was observed also



in Arctic polar winters (Schmidt *et al.*, 1991, 1994; Toon *et al.*, 1994; von Clarmann *et al.*, 1995; Rinsland *et al.*, 1999). In the Arctic winter vortex, temperatures low enough to allow for the formation of polar stratospheric clouds are reached less frequently than in the Antarctic, and the PSC areas cover smaller regions; PSCs were nevertheless also observed there (*e.g.*, Hofmann *et al.*, 1989). Heterogeneous chemistry was also found to take place in the Arctic winter. Measurements of activated chlorine in Arctic winter vortices include airborne *in situ* techniques (Brune *et al.*, 1990; King *et al.*, 1991; Webster *et al.*, 1993b), ground-based microwave measurements (de Zafra *et al.*, 1994; Shindell *et al.*, 1994; Raffalski *et al.*, 1998; Nagar *et al.*, 1999; Ruhnke *et al.*, 1999; Klein *et al.*, 2000), airborne sub-millimeter measurements (Crewell *et al.*, 1994, 1995; Wehr *et al.*, 1995), UARS MLS (Schoeberl *et al.*, 1993; Waters *et al.*, 1993, 1995; MacKenzie *et al.*, 1996; Santee *et al.*, 1996b), infrared limb emission with MIPAS (Glatthor *et al.*, 2004; von Clarmann *et al.*, 2009b), for ClO; and lunar occultation (Solomon *et al.*, 1988; Fiedler *et al.*, 1993; Riviere *et al.*, 2004), ground-based differential optical absorption spectroscopy (DOAS) (Perner *et al.*, 1991, 1994; Fiedler *et al.*, 1993; Gil *et al.*, 1996), airborne DOAS (Brandtjen *et al.*, 1994; Pfeilsticker *et al.*, 1997), balloon-borne UV-visible spectrometry (Pommereau and Piquard, 1994; Renard *et al.*, 1997), for OClO, just to name a few. Satellite observations of OClO have already been listed in Section 4 and include GOME (Wagner *et al.*, 2001), OMI (Levelt *et al.*, 2006), GOMOS (Fussen *et al.*, 2006; Tetard *et al.*, 2009), SCIAMACHY (Kühl *et al.*, 2008) and OSIRIS (Krecl *et al.*, 2006).

Manney *et al.* (1994), *e.g.*, report ClO observations indicating that nearly all available inorganic chlorine was activated in the winter 1992/93. Indirect evidence of chlorine activation is implied by the reduction of HCl and/or ClONO<sub>2</sub> reservoirs. Such measurements are available from ground-based solar absorption infrared spectroscopy (Adrian *et al.*, 1994; Notholt *et al.*, 1994, 1995; Blumenstock *et al.*, 1997), balloon-borne infrared limb emission spectroscopy with MIPAS-B (von Clarmann *et al.*, 1993a), airborne infrared solar absorption spectroscopy (Toon *et al.*, 1992), air-borne infrared emission spectroscopy with MIPAS-FT (Glatthor *et al.*, 1998), multiple instruments on UARS (Roche *et al.*, 1994; Dessler

*et al.*, 1995), spaceborne infrared solar occultation measurements with ILAS (Hayashida *et al.*, 2007) and ACE-FTS (Dufour *et al.*, 2006a), as well as *in situ* techniques (Lelieveld *et al.*, 1999). Significant areas of activated air were found even in the Arctic polar vortex (MacKenzie *et al.*, 1994; Santee *et al.*, 2003). Generally smaller ClO mixing ratios than in the Antarctic (compare Figures 7 and 8) suggest that the efficiency of the ClO dimer cycle may be smaller, and that the catalytic bromine cycle plays a particular role in the Arctic (Toohey *et al.*, 1990).

Figure 8 shows the temporal development of ClO in the Arctic based on MIPAS measurements. While less pronounced than in the Antarctic, chlorine activation is a regular phenomenon also in the Arctic. The year-to-year variation is considerable.

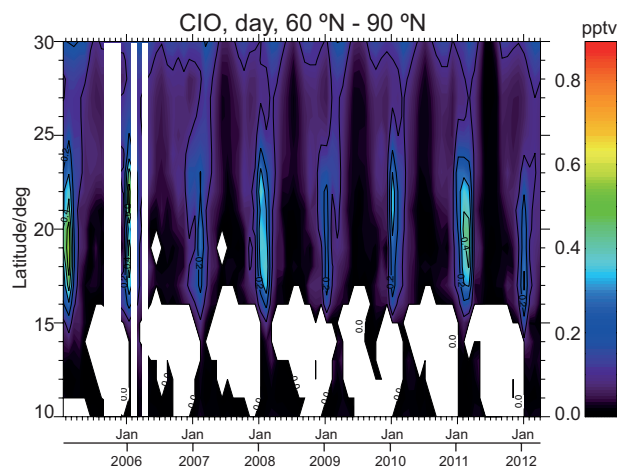


Fig. 8. Temporal development of ClO distribution in the Arctic (60°N-90°N) stratosphere. White stripes are due to missing data, while other white areas in the plot represent unrealistic negative data due to a low bias in MIPAS lower stratospheric ClO.

Denitrification also occurs in Arctic winters (Fahey *et al.*, 1990), but typically to a much smaller extent than in the Antarctic. Gao *et al.* (2001) have highlighted the importance of denitrification for Arctic ozone depletion; Höpfner *et al.* (1996) observed the removal of gaseous HNO<sub>3</sub> in the Arctic vortex in 1992 by airborne infrared emission spectroscopy. Moderate large-scale denitrification was observed in the polar Arctic spring 2000 by UARS MLS (Santee *et al.*, 2000), while Popp *et al.* (2001) report strong denitrification, inferred from *in situ* measurements. Kondo *et al.* (2000) have seen a denitrification signal



from ILAS gas and aerosol data. ATMOS measurements indicate denitrification, but no significant dehydration in the Arctic winter 1992/93 (Rinsland *et al.*, 1999). Even without extensive denitrification, over 90% of the inorganic chlorine was observed to be converted to active forms in January/February 1989 (Toon *et al.*, 1992).

Figure 9 shows the temporal development of  $\text{ClONO}_2$  at 20 km altitude as measured by MIPAS. The latitude coverage of large mixing ratios is generally larger in the Antarctic. Polar winter minima of  $\text{ClONO}_2$  indicate chlorine activation. The low- $\text{ClONO}_2$  areas extend over a wider latitude range and a longer time span in the Antarctic than in the Arctic. The largest  $\text{ClONO}_2$  mixing ratios are generally seen in polar spring and reflect chlorine deactivation. This is much more pronounced in the Arctic than in the Antarctic where denitrification makes chlorine deactivation via  $\text{ClONO}_2$  formation comparatively inefficient.

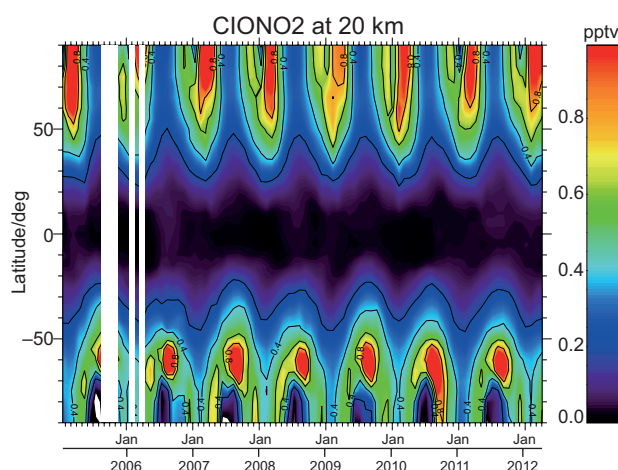


Fig. 9. The temporal development of  $\text{ClONO}_2$  at 20 km, based on MIPAS monthly mean mixing ratios. White stripes represent data gaps due to missing measurements.

Arctic ozone depletion terminates as a consequence of warming events when PSCs are no longer present and chlorine is deactivated by reservoir formation. With increasing illumination in Arctic spring,  $\text{HNO}_3$  is photolyzed, giving rise to  $\text{NO}_2$  (Webster *et al.*, 1993a). In the Arctic enough  $\text{NO}_2$  typically remains available towards the end of the polar winter and huge amounts of  $\text{ClONO}_2$  are formed (von Clarmann *et al.*, 1993a, 1997; Roche *et al.*, 1994; Blom *et al.*, 1995). At the same time  $\text{ClO}$  concentrations are shown to decline and ozone loss ceases (Salawitch *et al.*, 1993; Toohey

*et al.*, 1993). Contrary to Antarctic vortices, the leading chlorine deactivation path is, due to the availability of  $\text{NO}_2$ ,  $\text{ClONO}_2$  formation which in some winters largely exceeds  $\text{HCl}$  formation (Adrian *et al.*, 1994; Douglass *et al.*, 1995; Rinsland *et al.*, 1995; Santee *et al.*, 1996a, 2008b; Payan *et al.*, 1998). Due to the dependence of the  $\text{ClONO}_2$  formation on  $\text{HNO}_3$  photolysis,  $\text{ClONO}_2$  maxima are found in a collar near the edge of the vortex, while chlorine remains activated for a longer time when closer to the core of the vortex (*e.g.*, Toon *et al.*, 1992). Figure 10 shows MIPAS measurements of  $\text{ClONO}_2$  over the Arctic at 18 km altitude in March 2011. The ‘collar’ of enhanced values is clearly visible.

Some Arctic winters stand out due to particular events: The Arctic winter of 1991/1992 was characterized by a large aerosol loading as a result of the Mount Pinatubo eruption (*e.g.*, Browell *et al.*, 1993). The effect of volcanic eruptions on ozone by the excess sulfate aerosol serving as a medium for heterogeneous chlorine activation was heavily debated (*e.g.*, Brasseur, 1992; Prather, 1992a; Toon *et al.*, 1993; Wilson *et al.*, 1993; Dessler *et al.*, 1993). Borrmann *et al.* (1997) have investigated if chlorine activation can also be accelerated by heterogeneous reactions on volcanic cloud droplets, but found that these could not compete with reactions on PSC surfaces. Cox *et al.* (1994) found that  $\text{HCl}$  dissolution and  $\text{ClONO}_2$  hydrolysis on sulfuric acid could have appreciable rates at temperatures below 190 K and large aerosol loading. While the role of sulfate aerosols for chlorine activation in polar vortices remains debatable, it seems to be important for mid-latitudinal ozone chemistry (see Section 5.2).

The largest Arctic polar ozone depletion at the time of writing occurred in spring 2011. Some authors even claimed that this was an ozone hole as known from the Antarctic (Manney *et al.*, 2011), although this view was not entirely shared by all scientists (Sinnhuber *et al.*, 2011). The polar vortex of that particular year was exceptionally cold and stable, and its boundary had little permeability (Isaksen *et al.*, 2012). Chlorine activation was particularly strong (*c.f.* Fig 8). During February and March, 30–55% of the observed ozone destruction was attributed to the  $\text{ClO}$  dimer cycle, and 30–35% to the combined  $\text{ClO}$ – $\text{BrO}$  cycle (Kuttippurath *et al.*, 2012). While in response to the Montreal Protocol there is a decline in stratospheric chlorine loading, climate change, following the cooling of the stratosphere, can over-

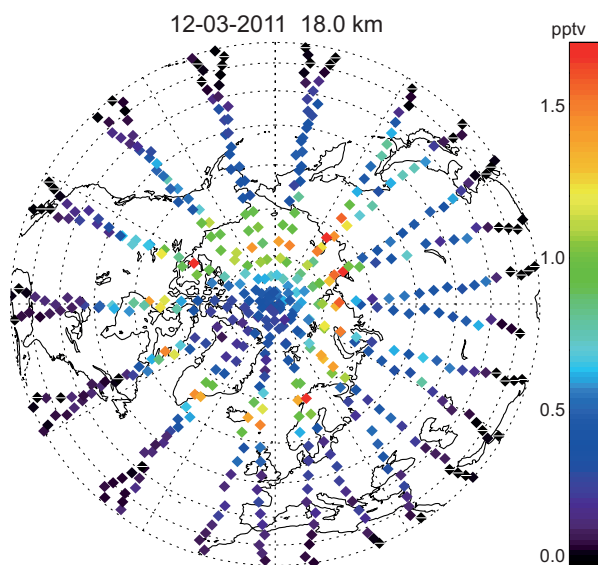


Fig. 10. Chlorine nitrate measurements by MIPAS over the Arctic at 18 km altitude on 12 March 2011. The ‘collar’ of large mixing ratios surrounds the core area of the polar vortex where  $\text{ClONO}_2$  values are lower.

compensate the reduced chlorine loading of the stratosphere. This effect had already been predicted by Austin *et al.* (1992) and Shindell *et al.* (1998), and the most recent measurements corroborate their hypothesis. This is in agreement with observations of ‘atypically cold’ Arctic winters along with large chlorine activation during the 1990s by Santee *et al.* (2003) and the finding that “cold winters are getting colder” (Rex *et al.*, 2006). Sinnhuber *et al.* (2011), whose model reproduces the MIPAS measurements of all involved constituents during the Arctic winter of 2011 remarkably well, studied the sensitivity of ozone chemistry to a further cooling of the stratosphere and found that a reduction of stratospheric temperatures by 1 K would cause an additional ozone loss of 18–25 Dobson units and would outweigh a decrease of stratospheric halogen loading by 10%.

### 5.2 Middle and low latitudes

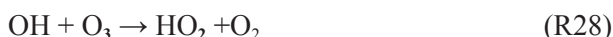
While outside polar vortices no polar stratospheric clouds exist, other media are discussed to provide liquid or solid surfaces for heterogeneous chlorine activation. One of them is sulfate aerosol. It is important both in the context of nitrogen and chlorine chemistry (Brasseur and Solomon, 2005). Also for the investigation of the role of sulfate aerosols on mid-latitude stratospheric chemistry, the Pinatubo aerosol cloud provided an ideal test case (McCormick *et al.*,

1995). Indeed, reduced ozone concentrations were found after the eruption in the tropical stratosphere (Grant *et al.*, 1992) and globally (Randel *et al.*, 1995). Weaver *et al.* (1993) found no correlation between the magnitude of ozone changes and aerosol surface area density, but Hofmann *et al.* (1994) could assign low ozone measurements to backward trajectories from high latitudes where more efficient heterogeneous processing was expected in the colder atmosphere, because the probability of reaction R12 increases exponentially with decreasing temperature (Robinson *et al.*, 1997). Enhanced ClO concentrations were indeed measured along the increased aerosol loading (Avallone *et al.*, 1993; Wilson *et al.*, 1993). Increased chlorine activation, however, is partly counterbalanced by removal of active nitrogen, and Fahey *et al.* (1993) and Kinnison *et al.* (1994) found that after the Mount Pinatubo eruption, the chlorine catalytic cycle became the second most important ozone-controlling process after the  $\text{HO}_x$  catalytic cycle in the lower stratosphere. Chlorine and nitrogen chemistry interact in the sense that the sequestering of  $\text{HNO}_3$  reduces the availability of  $\text{NO}_2$  necessary for chlorine deactivation, similar as in polar vortices, and *in situ* measurements by Webster *et al.* (1998) indicate an increase of HCl during the decay of the Mount Pinatubo aerosol loading, hinting at enhanced chlorine activation during the period of high aerosol loading. Tie and Brasseur (1996) concluded that in situations of low chlorine loading of the stratosphere volcanic aerosol reduces ozone depletion via the removal of reactive nitrogen, while under high chlorine loading this aerosol enhances ozone destruction via chlorine activation and de-acceleration of  $\text{ClONO}_2$  formation. Kawa *et al.* (1997) found that chlorine activation depends strongly on the exposure of the aerosol-loaded air to temperatures below 195 K, and Pitari *et al.* (1991) highlight the relevance of chlorine activation on sulfate aerosols also for non-polar latitudes. Anderson *et al.* (2012) have shown that non-polar chlorine activation is very sensitive to water convectively injected into the stratosphere. The issue of heterogeneous chemistry on sulfate aerosol will gain further importance as a side effect of climate engineering, where release of sulfur into the lower stratosphere is discussed to shield Earth from solar radiation in order to fight global warming (Tilmes *et al.*, 2008).

A further link of chlorine activation and climate change is the relation of ClO with  $\text{CH}_4$ . The reaction

of atomic chlorine with methane sequesters active chlorine in the HCl reservoir (Siskind *et al.*, 1998). Thus, an anticorrelation of active chlorine and methane is expected and has indeed been observed in the upper stratosphere by Froidevaux *et al.* (2000), using UARS-MLS ClO and UARS-HALOE methane.

An important issue in mid-latitudinal ozone destruction is, besides the relevance of catalytic cycles involving ClONO<sub>2</sub> or bromine compounds, the larger relative importance of the HOCl catalytic cycle (Daniel *et al.*, 1999; Millard *et al.*, 2002):



This ozone destruction cycle does not need atomic oxygen and its rate is, contrary to the ClO dimer cycle, only linear in the concentration of ClO. Thus it is particularly important for mid-latitude stratospheric ozone chemistry. It contributes about 7% to ozone loss in the lower stratosphere outside the tropics (Lee *et al.*, 2002) and its rate-limiting step is reaction R26 (Kuribayashi *et al.*, 2013). Uncertainties of related rate constants have already been discussed in Section 3.3.

The theoretical framework involving chemistry, dynamics and thermodynamics was strongly corroborated and refined in quantitative terms for seasonal cycles. The atmosphere does not allow laboratory-like experiments where the atmospheric parameters can be intentionally scanned through in any controlled manner like independent variables to test the theory in its entire range of definition, but natural variability helps here. Meanwhile there is a wealth of literature (*e.g.*, Dufour *et al.*, 2006b, just to name one) where the current theoretical framework is increasingly corroborated and refined in quantitative terms for a wide variety of atmospheric conditions, by, in Kuhnian terminology, ‘normal science’. Minor anomalies often seem to hint rather at problems in the implementation of theories in models than deficiencies in the theory itself.

## 6. Another scientific crisis: The chlorine monoxide dimer cycle

The importance of the ClO dimer cycle for polar winter ozone depletion has already been highlighted in Section 4. Stratospheric ozone chemistry seemed to be well understood both in qualitative and quantitative terms, although uncertainties in the Cl<sub>2</sub>O<sub>2</sub> photolysis had long been identified as the major source of uncertainty in the quantitative understanding of polar ozone chemistry (Solomon, 1988). Another source of uncertainty was the equilibrium constant of the thermal dimer formation/decomposition (von Hobe *et al.*, 2006). The latter is particularly important, since thermal decomposition of the dimer yields ClO molecules, while only photolysis of the dimer yields the atomic Cl necessary for catalytic ozone destruction in the absence of atomic oxygen. All these uncertainties have led to a number of dedicated studies (*e.g.*, Berthet *et al.*, 2005; Bröske and Zabel, 2006; Frieler *et al.*, 2006). In spite of all reported uncertainties, however, excellent agreement between model calculations and ClO measurements was found (Solomon *et al.*, 2002).

In 2007, Pope and colleagues published a revised version of the Cl<sub>2</sub>O<sub>2</sub> ultraviolet photolysis rate, which predicted Cl<sub>2</sub>O<sub>2</sub> to be much more stable under stratospheric sunlit conditions than originally expected (*c.f.*, *e.g.*, Sander *et al.*, 2006). The new data were said to “threaten to shatter established theories of ozone chemistry” by Schiermeier (2007), who cites Markus Rex saying: “If the measurements are correct we can basically no longer say that we understand how ozone holes come into being”. Sixty per cent of ozone destruction at the poles then would be due to an unknown mechanism. This result triggered a wide range of activities, including new laboratory studies, installation of a new SPARC initiative (Kurylo and Sinnhuber, 2009), and the RECONCILE research project funded by the European Commission (von Hobe *et al.*, 2012). Subsequent analyses of MLS data, however, confirmed the old kinetic data and suggested that the error margins of the old photolysis data were overestimated by a factor of two (Kawa *et al.*, 2009). Schofield *et al.* (2008) challenged the then recommended thermal equilibrium constant, but found no combination of kinetic parameters in agreement with both their self-match measurements and the new photolysis data by Pope *et al.* (2007). Balloon-borne infrared emission measurements of



the ClO dimer along with ClO and ClONO<sub>2</sub> also confirmed the established chlorine chemistry (Wetzel *et al.*, 2010). The latter were the first remote measurements of the ClO dimer, obtained with mid-infrared emission spectroscopy. New laboratory experiments were carried out (*e.g.*, Papanastasiou *et al.*, 2009), none reproducing the photolysis rates by Pope *et al.* (2007). Instead, the older work by Burkholder *et al.* (1990) was largely confirmed in tendency. In their overview paper, von Hobe *et al.* (2012) summarize the results of this reassessment: “No evidence has been found that would support the existence of yet unknown chemical mechanisms making a significant contribution to polar ozone loss”.

Kuhn (1962, 2001) suspects that paradigms are defended in tendency even in case of anomalies — and the new UV cross-sections published by Pope *et al.* (2007) certainly were an anomaly in the Kuhnian sense. However, subsequent activities, including the installation of a dedicated SPARC initiative and the RECONCILE campaign, suggest that a major segment of the community was alarmed and suspected a scientific crisis. The large number of activities and people involved seem to refute the Kuhnian hypothesis: It appears that there is not so much a tendency to ignore an anomaly or to defend a paradigm by *ad hoc* auxiliary hypotheses, but rather to get on the bandwagon if there seems to be a ghost of a chance to be part of a scientific revolution.

## 7. The non-statement view: Chlorine chemistry during solar proton events

The non-statement view is a structuralist concept of theory of science where theories are not considered as universal statements that are corroborated or falsified, but are understood to be composed of a hard core theoretical framework and a number of intended applications (Sneed, 1971; see also Stegmüller, 1973). Empirical counterevidence does not lead to the rejection of the hard core of the theory, but simply removes this particular application from the list of valid applications. The theory of subsiding NO<sub>x</sub>-rich air from higher altitudes as postulated by Callis and Natarajan (1986) is a typical example: Mesospheric air is clearly affected by the solar cycle (McPeters, 1989), and there is evidence of subsidence (*e.g.*, Callis *et al.*, 1996). This theory just failed to explain the ozone hole (*c.f.* Section 4).

Although primarily being a NO<sub>x</sub> issue, solar

impact is also relevant to chlorine chemistry. Solar proton events (SPEs) have long been known to be a source of upper stratospheric nitrogen oxides (Jackman *et al.*, 1990). Solomon and Crutzen (1981) found that the inclusion of ClO<sub>x</sub> chemistry is important to quantify SPE induced ozone chemistry. Jackman *et al.* (2000) stated that the interaction of NO<sub>x</sub> chemistry with halogen chemistry leads to chlorine deactivation via ClONO<sub>2</sub> formation, resulting in reduced ozone destruction. The first empirical evidence of solar proton induced perturbed chlorine chemistry was found by von Clarmann *et al.* (2005) in MIPAS data. After the SPE around Halloween 2003, ClO averaged over the polar cap, the major parts of which were still illuminated, was reported by these authors to increase after the proton forcing, except for regions poleward of 70° N, where the polar vortex was dark. In these regions a ClO decrease was observed (Funke *et al.*, 2011). The sudden increase of HOCl during this SPE, which also was observed with MIPAS data, did not only confirm SPE-induced chlorine activation but also was the first experimental evidence of accelerated HO<sub>x</sub> chemistry during an SPE.

Damiani *et al.* (2012) found a negative response of ClO to the January 2005 SPE, when the polar cap stratosphere was still in the dark. This is in agreement with the dependence on illumination found for the SPE in the year 2003. During the SPE in 2012, however, the observed ClO variation was well within day-to-day variability of the vortex averages. The fact that no significant change in ClO was observed is attributed to the considerably smaller ionization rates during the solar storm in 2012 (von Clarmann *et al.*, 2013).

In summary, there is evidence of solar effects on stratospheric chlorine. No experimental evidence, however, has been found that there would be any major or sustained impact on stratospheric ozone. Sustained ozone changes related to energetic particles and ionization seem to be largely dominated by NO<sub>x</sub> chemistry.

## 8. The greenhouse potential of chlorine compounds

Every molecule with transitions in the infrared can contribute to the greenhouse warming of the lower atmosphere. While CO<sub>2</sub> is in the main focus of anthropogenic greenhouse warming since Arrhenius (1896), CH<sub>4</sub>, N<sub>2</sub>O and CFCs also contribute to this effect (Ramanathan, 1975; Lacis *et al.*, 1981). The



large number of vibrational-rotational transitions of CFCs which lead to dense spectra with little structure, their position in the window region of the infrared spectrum of the atmosphere, and their absolute band strengths make these gases efficient infrared absorbers (Shine, 1991). This, along with their long lifetimes, makes CFCs efficient greenhouse gases. Their global warming potential is, depending on the particular species and the time horizon considered, about  $10^3$ . This means that the radiative forcing impact of the emission of 1 kg of CFC-11 can be up to a factor of 2860 larger than that of 1 kg  $\text{CO}_2$ , for a time horizon of five years. For longer time horizons, the global warming potential is not that large, because the lifetime of CFC-11 is shorter than that of  $\text{CO}_2$  (Daniel *et al.*, 1995). Hansen *et al.* (1989) estimated the contribution of CFCs to the total greenhouse forcing in the 1980s at 25%. As a consequence, their emissions are analyzed (Manning *et al.*, 2003; Hurst *et al.*, 2006; Liang *et al.*, 2008) and these species are monitored and analyzed for possible trends on a regular basis (*e.g.*, Gardiner *et al.*, 2008; Montzka *et al.*, 2009). Additionally, some of the less abundant chlorine source gases have large global warming potentials. HCFC-245fa, *e.g.*, has a global warming potential of up to 2400 relative to  $\text{CO}_2$  (Ko *et al.*, 1999).

Beyond the direct radiative forcing of CFCs and HCFCs, also ozone perturbations—induced by the released chlorine atoms—are relevant for the radiative budget of the Earth (Morgenstern *et al.*, 2008). Thus, the Montreal Protocol has not only started to cure the ozone layer but has also avoided a severe additional change in the surface climate (Garcia *et al.*, 2012).

## 9. A holistic view: Lifetimes of chlorine source gases and the Brewer-Dobson circulation

In a holistic view, a hypothesis cannot be tested in any isolated manner. Any empirical test requires auxiliary hypotheses. Without these, on the basis of the isolated hypothesis alone, no prediction can be made. This view traces back to Pierre Maurice Marie Duhem (1861–1916) and Willard Van Orman Quine (1908–2000) and was, according to Stegmüller (1973), for the first time named ‘Duhem-Quine-thesis’ by Lakatos (1970). The problem of the lifetimes of CFCs in a changing stratosphere can be seen from this perspective.

The links between the lifetimes of chlorine source gases and the Brewer-Dobson circulation are two-fold. On one hand, the Brewer-Dobson circulation

affects the lifetimes; on the other, tracers of different lifetimes help to constrain the intensity of the Brewer-Dobson circulation.

Increasing abundances of greenhouse gases cause the warming of the troposphere and the cooling of the stratosphere (IPCC, 2007). From this, a change of stratospheric circulation is expected (Butchart *et al.*, 2006). Models predict the Brewer-Dobson circulation to intensify (Austin and Li, 2006; Austin *et al.*, 2007; Garcia and Randel, 2008; McLandress and Shepherd, 2009; Oman *et al.*, 2009; SPARC CCMVal, 2010), while mid-latitudinal stratospheric mean age of air measurements seem to suggest a constant age of air over 30 years, which is claimed not to be consistent with an intensified Brewer-Dobson circulation (Engel *et al.*, 2009). Global mean age of stratospheric air trends inferred from MIPAS  $\text{SF}_6$  measurements by Stiller *et al.* (2012) show large variability with latitude and altitude instead of a simple sign for accelerated circulation. CFC measurements by Kellmann *et al.* (2012) confirm that the measured trends cannot be explained by age-corrected emission rates but hint at changes in stratospheric circulation or mixing patterns. A changing Brewer-Dobson circulation has substantial feedbacks on chlorofluorocarbon lifetimes, because the times during which the molecules are exposed to certain altitude and latitude specific actinic fluxes differ (Butchart and Scaife, 2001; Douglass *et al.*, 2008). In consequence, the lifetimes of chlorine source gases have indeed become a scientific issue in themselves. It is postulated that some of these current lifetimes are considerably underestimated (Ko *et al.*, 2012). Douglass *et al.* (2008) have shown that realistic age of air in models is inconsistent with current lifetime estimates. Evidence is emerging that lifetimes are longer than reported in past assessments. For a known intensity of the Brewer-Dobson circulation, which here serves as an auxiliary hypothesis, the lifetimes can be estimated from global CFC measurements.

Besides their lifetimes, chlorine source gases also play a role as a diagnostic tool for the Brewer-Dobson circulation. The usual diagnostic for the intensity of the Brewer-Dobson circulation is the age of stratospheric air (Li and Waugh, 1999; Waugh and Hall, 2002), which is the time lag from the transition of an air parcel into the stratosphere until the date when the air parcel is sounded elsewhere in the stratosphere. However, the age of an air parcel is an ambiguous figure because, as a result of mixing, the air parcel is

composed of air of different ages. Instead, the mean age of the air parcel is used to diagnose the Brewer-Dobson circulation and the relative weights of the different ages contributing to the mean age are called “age spectrum”. For any tracer with no strictly linear growth of abundance in the troposphere, knowledge of the age spectrum is a prerequisite to determine the mean age of an air parcel. As a consequence, inference of the mean age from measurements of inert tracers with monotonically nonlinearly increasing tropospheric mixing ratios like  $\text{SF}_6$  also requires consideration of the age spectrum, which, in itself, is age-dependent (*e.g.*, Andrews *et al.*, 1999). Often, the age spectrum is parameterized using a Green’s function approximated by a Wald (inverse Gaussian) distribution. This approximation, however, is strictly speaking only valid for one-dimensional mixing processes (Waugh and Hall, 2002). The width parameter is another uncertainty (Hall and Plumb, 1994; Volk *et al.*, 1997; Waugh *et al.*, 1997). Schoeberl *et al.* (2005) have proposed to use long-lived non-inert tracers of different known lifetimes like chlorofluorocarbons to directly infer the age spectrum from measurements. Here, the knowledge of lifetimes is an auxiliary hypothesis to diagnose the Brewer-Dobson circulation.

However, neither the lifetimes of the CFCs nor the intensity of the Brewer Dobson circulation are exactly known. Due to the mutual impact of the estimated lifetimes and the estimated intensity of the Brewer Dobson circulation, quantifying both these unknown quantities in a self-consistent manner is a challenge. Both the strategies discussed above, each aiming at a solution for different research problems, are approximations to the solution of the coupled problem. Coming back to the Duhem-Quine thesis, we see that the lifetimes of CFCs cannot be assessed without auxiliary assumptions on the Brewer-Dobson circulation. In turn, the latter can best be diagnosed with auxiliary assumptions on the lifetimes on observed tracers available. A holistic approach to this coupled problem involving simultaneous multi-parameter analysis will probably lead to the most robust results.

## 10. Critical summary and discussion

Long-lived, organic, predominantly anthropogenic source gases like CFCs survive transport into the stratosphere where they are photolyzed. Resulting reactive chlorine can destroy ozone, but it is sequestered into the reservoir gases  $\text{HCl}$ ,  $\text{ClONO}_2$ , and

$\text{HOCl}$ . Major chlorine-induced ozone loss depends on the reactivation of chlorine that can be caused by heterogeneous reaction on polar stratospheric cloud particles, volcanic or background aerosol, or triggered by solar proton events. In response to the Montreal Protocol, the stratospheric chlorine loading has started to reduce, but stratospheric ozone abundances depend on a couple of further mechanisms which are all interlinked. These include:

- (1) Global warming goes along with the cooling of the stratosphere. In a cooler environment polar stratospheric clouds are more frequent, and also heterogeneous chlorine activation on sulfuric acid aerosols is far more efficient in a cooler atmosphere.
- (2) Atmospheric dynamics rules polar vortex dynamics and thus determines the thermodynamic conditions, which constrain heterogeneous chlorine activation. Atmospheric dynamics are coupled with climate change.
- (3) Atmospheric circulation may change in response to greenhouse warming. Since this circulation distributes the ozone destructing chlorine species in the stratosphere, this effect is also coupled with ozone loss.
- (4) Changes in stratospheric humidity, which depend on the thermodynamic and dynamical conditions at the tropical tropopause, will affect ozone chemistry.
- (5) Other trace gases with variable stratospheric abundances, like methane, interact with chlorine chemistry. The use of chlorine source gases as tracers of transport and mixing processes depends on the lifetime of these species, but in turn the determination of tracer lifetimes requires knowledge of the circulation.

While our understanding of the individual processes with respect to stratospheric chlorine seems pretty mature after about 40 years of related research, it is the coupling processes and process interactions which may be the main challenge in the future.

Besides the issues related to atmospheric sciences, stratospheric chlorine is also an interesting object with respect to the concepts of growth of knowledge. It appears that in climate research scientific revolutions do not go along with the refutation of and old paradigm as claimed by Kuhn (1962, 2001) (*also c.f.* Watkins, 1970). Instead, a scientific revolution can leave the main contents of the existing paradigm intact, but identify processes which are compatible with the old paradigm while their relevance was hitherto underestimated or even ignored (*e.g.*, the ozone hole, which *prima facie* was counter-inductive with respect to the CFC ozone theory). Without distorting

history, the characteristics of scientific revolutions as described by Kuhn seem not to be applicable to the discontinuities of knowledge in climate research, but the latter are still far beyond the Kuhnian ‘normal science’ (e.g., explanation of the ozone hole by heterogeneous chlorine activation and the ClO catalytic cycle). The view of Popper (1934, 1963, 2005a, b, 2009, ) that a new hypothesis includes the old one as a special case but is applicable to a wider class of cases is better supported by the development of the theoretical framework of stratospheric chemistry and dynamics.

The falsificationist approach suggested by Popper (1934, 1963, 2005a, b, 2009) claims that a positive proof of any scientific hypothesis is impossible because evidence can be provided only by examples, their generalization would be inductive, and induction in its traditional sense is not conclusive (Hume, 1748). Instead, a hypothesis can be maintained until falsified, *i.e.*, until a prediction made by this hypothesis clashes with evidence (*modus tollens*). Poppers falsificationism has proven to be applicable not only to a Kuhnian paradigm shift but also within the Kuhnian puzzle solving process in the context of ‘normal science’. In this abductive process tentative but finally erroneous explanations of by then unexplained phenomena are refuted by counterevidence. Examples are the solar cycle and the upwelling air explanations of the ozone hole. For the general theoretical framework (or ‘research program’ in Lakatos terminology) the so-called ‘methodical’ or ‘sophisticated’ falsificationism was the concept best fitting to the history of discoveries: The discovery of a result in some conflict with the theory does not lead to the refutation of the full theoretical framework theory, but to the refinement of the hypothesis, occasionally involving auxiliary hypotheses that, in agreement with Feyerabend (1970, 1983) can be useful, even if *ad hoc* in the first place. The Sneed’s structuralist ‘non-statement view of theories’ distinguishes between a theory and a proposition. A proposition is a theoretical framework and an intended application. Counterevidence refutes only the particular application, but not the theoretical framework. This view is to some degree compatible with Lakatos (1970) approach of sophisticated falsification, and seems to best reflect how the growth of knowledge in atmospheric chlorine chemistry has actually been achieved.

All scientific knowledge is and remains conjectural knowledge. Even the assignment of a probability to a deductive conclusion is denied by Popper and Miller (1983), but considered possible by Carnap and Stegmüller (1959). The vast majority of papers discussed in this overview article are in agreement with the conjectural concept of knowledge: In many places it is stated that a hypothesis is “supported” or “corroborated” by observations, while the author of these lines has not detected any claim that observations would prove a hypothesis.

Normal science, *i.e.*, science not aiming at a paradigm shift, a scientific revolution, or a refutation of the axioms upon which an established theory is built, seems to be underrated by Popper (1970). Normal science leads to more elaborated, more quantitative theories, and thus enhances the testability of the theories and extends the applicability of the theoretical framework. Normal science does not necessarily hint at a dogmatic or less than extraordinary researcher, but science may stay on the Kuhnian ‘normal level’ simply because the basic axioms happen not to cause major anomalies. The Kuhnian concept of ‘normal science’ contrasting to ‘extraordinary science’ is not well supported by the history of research on chlorine in the stratosphere.

Satellite missions launched after the detection of the ozone hole show the importance of keeping an eye on possible serendipity already during mission planning. While the public awareness of the ozone hole problem has certainly helped to implement missions like AURA, ENVISAT, SCISAT-ACE, ODIN, etc., the mission preparation took quite some time (from 1988 to 2002 in the case of ENVISAT, from the proposal of the MIPAS instrument to the launching of the satellite) and a major part of the target questions of the mission had already been solved at the date of launch. ACE, *e.g.*, although its orbit was optimized for measurements over northern latitudes, considerably contributed with its FTS-instrument to tropical biomass burning research, and, similarly, MIPAS on Envisat tackled a lot of scientific questions beyond stratospheric ozone research which was the topic of the day when the proposal was selected. The concept of the latter instruments, being Fourier transform spectrometers with the ability to measure multiple species, benefited serendipity in a sense that the measurements were applicable to a wider range of scientific topics than anticipated.

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