Match campaigns to measure stratospheric ozone loss—a key contribution to International Polar Year 2007-2008

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International Polar Year 2007-2008

The year 2007 marks an important event in geosciences—the 125th anniversary of the first International Polar Year (IPY) 1882-1883. The activities started during the first IPY and its follow-ups in 1932-1933, in particular the International Geophysical Year 1957-1958, laid the ground for many important elements of our current understanding of the Earth system. To add to this tremendous success and to build up momentum to another ground-breaking research activity, the international community of geoscientists established IPY 2007-2008.

The focus on the polar regions demonstrates the general notion that we have made significant progress in observing and understanding the Earth system but that our understanding of many processes in the polar regions is still limited by the sparse amount of data available. An impressive spectrum of activities during IPY will address all aspects of polar research from oceanography, physics of the solid earth, and the cryosphere to the atmosphere (http://www.ipy.org).

Key elements of atmospheric research during IPY are studies addressing stratospheric polar ozone depletion—one of the strongest anthropogenic signals in the global climate system. One of the largest research activities in the polar stratosphere during IPY is the Match activity.

Destruction of the ozone layer in the polar environment

The ozone layer is an important component of the global environmental system. The absorption of harmful solar ultraviolet (UV) radiation in the ozone layer protects the biosphere and heats the stratosphere. Thus, changes in the atmospheric circulation and in the emission of anthropogenic substances that affect the abundance of ozone in the atmosphere have direct effects on the global climate system. A detailed understanding of the processes that regulate the distribution of ozone in the atmosphere is fundamental for reliable climate predictions and for estimating future UV levels at the surface—an important parameter for the biosphere.

Since the 1960s and 1970s, humankind has emitted large quantities of chlorofluorocarbons (CFCs) and bromine-containing compounds (halons) into the atmosphere. In the troposphere, these substances are extremely stable and poorly reactive and reach a local atmospheric lifetime of centuries. However, from the troposphere, they ascend slowly into the stratosphere, where they break down due to the presence of highly energetic short-wave UV radiation above the ozone layer.

The breakdown of CFCs and halons releases chlorine and bromine radicals, which destroy ozone very efficiently. The ozone destruction cycles involve a group of so-called active chlorine compounds "ClO_x" (chlorine (Cl), chlorine monoxide (ClO) and dichlorine peroxide (Cl_2O_2). Fortunately, by rapid reactions of these species with other trace species in the stratosphere, the ClO_x species are tied into the inactive reservoir species chlorine nitrate ($ClONO_2$) and hydrogen chloride (HCl), which hardly damage the ozone layer. As a consequence the stratospheric abundance of ClO_x is usually very small.

At the current stratospheric concentrations of total bromine in the stratosphere, the bromine radicals are only efficient in destroying ozone, if ClO_x is present at considerable concentrations. Hence, the effect of the CFC and halon emissions on stratospheric ozone is very limited in mid- and tropical latitudes. Here, significant ozone depletion is limited to the highest reaches of the ozone layer, where UV radiation is sufficiently intense to trigger reactions

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that release significant amounts of chlorine radicals from the longer-lived reservoir species.

The situation is different in the polar region. Inside the polar vortex—an isolated low-pressure system which forms each winter in the polar stratosphere—temperatures drop significantly. At temperatures below approximately –78°C, polar stratospheric clouds (PSCs) can form (Figure 1). At the surface of PSC particles, heterogeneous chemical reactions take place, which can completely convert the harmless chlorine reservoir compounds back into ClO_x within a few hours. During the following polar spring, ClO_x then destroy ozone in a catalytic cycle that requires the presence of sunlight. The presence of bromine radicals allows a second catalytic cycle to occur that, overall, makes the ozone-depletion process even more efficient. For more than two decades, these processes have led to the seasonal occurrence of the ozone hole over the Antarctic almost every spring (e.g. WMO, 2007).

In comparison with the Antarctic, the meteorological conditions in the Arctic winter stratosphere are substantially more variable and the temperatures are usually considerably higher, leading to a less frequent and less widespread formation of polar stratospheric clouds. In the early 1990s, it was unclear whether comparable chemical processes that were known from the Antarctic would lead to ozone destruction in the Arctic stratosphere. For dynamical reasons, the ozone field in the Arctic is very different from the Antarctic and the signatures of chemical ozone depletion are hard to detect.

Several methods have been developed to identify and quantify ozone losses in the variable Arctic environment. These include the Match method, which was developed to measure precisely the rate of chemical loss of ozone in the polar stratosphere. Since the early 1990s, anthropogenic chemical loss of ozone was clearly detected in a number of cold Arctic winters. Detailed comparisons of measured ozone loss rates and model results show the large uncertainty of our quantitative understanding of the ozone loss process and the critical role of large uncertainties in key kinetic parameters that are needed to calculate chemical ozone loss rates with a chemical model. To advance our quantitative understanding of the ozone loss process and to provide a better basis for model-based predictions of the future of the ozone layer, an additional Match campaign is currently taking place in the Antarctic within the frame of IPY.

Figure 1 — Polar stratospheric clouds

Quantifying anthropogenic ozone loss—the Match method

The ozone abundance above an individual polar station changes constantly, owing to variable transport processes. Such dynamically caused fluctuations mask anthropogenic chemical loss and have to be separated from any chemical ozone loss signal. Instead of observing time series of ozone at fixed locations (i.e. in a Eulerian sense), the Match approach is based on Lagrangian measurements. The basic idea is to perform repeated measurements in individual air masses as they drift across the polar cap and sometimes approach one of many ozonesonde stations located in the polar regions.

The principle advantage of this procedure is that the advection terms which dominate ozone changes in the Eulerian framework disappear in the Lagrangian formulation of the continuity equation. The impact of diffusion terms in the continuity equation can also be limited by careful selection of the observed air masses based on properties of the flow. Hence, changes in the concentration of ozone during the interval between two measurements can be attributed to a chemical depletion. By a statistical analysis of a large number of such pairs of measurements, it is possible to observe anthropogenic chemical ozone depletion directly and to measure chemical ozone loss rates *in situ*.

In the Match approach, the measurements are performed using ozonesondes launched at many polar and sub-polar stations. To identify "Match events"—situations where individual air masses are usually probed twice at different stations—trajectories are calculated, based on data of the European Centre for

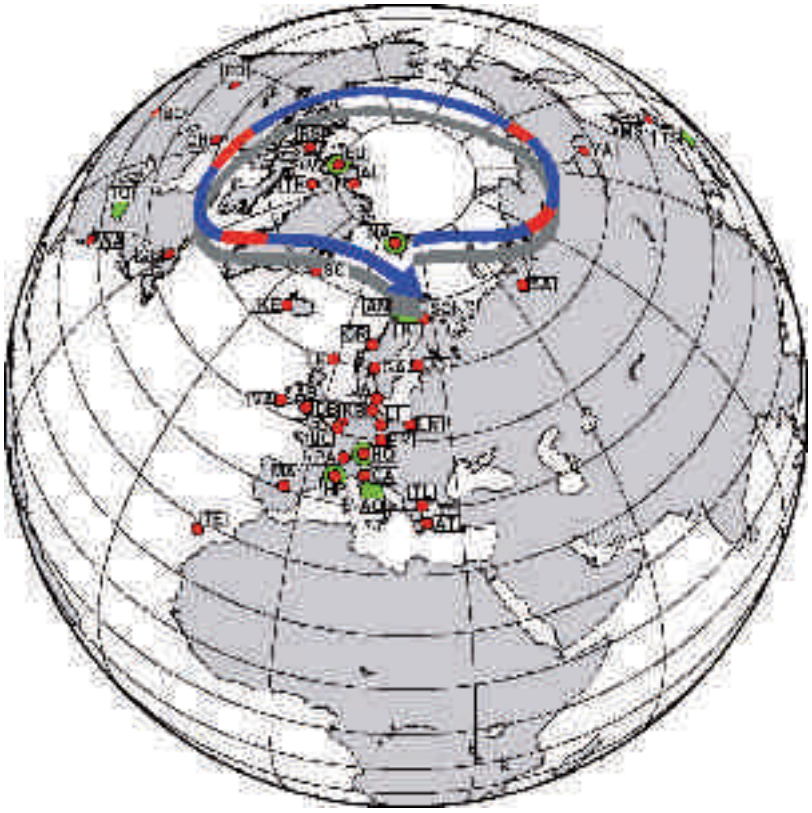

Figure 2 — Illustration of the Match approach: red dots denote ozonesonde stations; the blue line shows an example trajectory with sunlit parts in red.

Medium-Range Weather Forecasts (Figure 2). For the 1991/1992 Arctic winter, the Match events were identified after some 1 200 ozonesondes were launched during the winter without real-time coordination (Rex, 1993; von der Gathen *et al.*, 1995). Since the winter of 1994/1995, Match events have been produced by triggering several hundred ozone soundings per winter in real-time coordination.

During a Match experiment, 300 to 600 ozonesondes are typically launched at about 30 stations in the northern hemisphere or at nine stations in the Antarctic. Data from satellites are also used. Because of large vertical shear in the flow, however, this is limited to satellite sensors that can provide high vertical resolution data (1-1.5 km or better. Data from the Polar Ozone and Aerosol Measurement missions, the Improved Limb Atmospheric Spectrometer and the SAGE (Stratospheric Aerosol and Gas Experiment) satellites have been successfully used. Match campaigns have taken place in 10 Arctic winters and one Antarctic winter (2003), not counting the second Antarctic Match campaign in the southern hemisphere that is currently underway.

A number of important steps in ozone research rely on the Match approach. Match found, for the first time, unambiguous evidence of anthropogenic chemical ozone loss in the Arctic stratosphere. Further, based on Match *in situ* data, it was shown that sunlight is indeed needed for the ozone loss process, which confirms an important element of our theoretical understanding of the process. It was also demonstrated that denitrification has the potential to worsen ozone loss in the Arctic if a winter is particularly cold (Rex *et al.*, 1997). Previously, this effect was known only in the Antarctic stratosphere. Multi-annual data from the Match campaigns allowed the sensitivity of Arctic ozone loss on changes in climate—a key parameter for future projections of polar ozone loss in the changing atmosphere—to be established.

It was decided to continue the Match activity based on two results of research over the past decade. First, the conditions in the air masses sampled by Match are well characterized, hence the products are particularly well suited for detailed comparisons with highly constrained model calculations. This allows a close inspection of the degree of our theoretical understanding of the ozone loss process. Recently, large uncertainties in our theoretical understanding of the kinetics of the relevant chemical processes became apparent. Continued Match measurements can help to provide a better observational basis for reducing these uncertainties.

Second, although warm and cold Arctic stratospheric winters are driven by internal variability of the climate system, a tendency that the cold Arctic winters became significantly colder over the past 40 years has been observed. This change in climate conditions in the Arctic stratosphere has contributed to large Arctic ozone losses since the mid-1990s. It is unclear whether the trend will continue in the future and what the effect on Arctic ozone might be. These two issues are discussed in more detail below.

Quantitative understanding of the chemical ozone loss process

A quantitatively correct theoretical understanding of observed ozone loss rates is indispensable for a reliable forecast of the stratospheric ozone distribution in a world of increasing greenhouse-gas concentrations and declining halogen loading. Models of different degrees of complexity have been developed to calculate ozone loss rates for the air masses probed during the Match campaigns. The most robust statements about the status of our present understanding come from model runs in which

the degree of chlorine activation is externally specified. This model set-up allows the calculation of robust upper limits of possible ozone loss rates based on our current theoretical understanding of the chemistry. It turns out that, based on standard assumptions, the calculated upper limits are consistently about 20 per cent smaller that the observed ozone loss rates in cold Arctic Januaries (Rex *et al.*, 2004).

One key assumption common to all models concerns the total amount of bromine species in the stratosphere. For a long time, it was assumed that only long-lived bromine species such as methyl bromide and halons were able to reach the stratosphere. Recent observations of bromine, however, suggest that a larger amount of bromine is present in the stratosphere than can be explained by long-lived bromine species alone. This indicates that a fraction of very short-lived bromine species is also able to reach the stratosphere. Increasing the level of stratospheric bromine explains about half the discrepancies between calculated upper limits of ozone loss rates and observations.

The model calculations are based on kinetic parameters which are recommended by a panel of laboratory chemists about every four years. From observations of the balance between ClO and chlorine peroxide (ClOOCl) in the stratosphere, however, it was deduced that the photolysis rate of ClOOCl is larger (about 150 per cent) than the currently recommended value (Stimpfle *et al.*, 2004). This value, deduced from *in situ* observations, is still within the uncertainty estimate of the recommended value. Using the larger value, the computed ozone loss rate in the model increases further, eliminating most of the remaining discrepancies (Frieler *et al.*, 2006; WMO, 2007). These results triggered new laboratory measurements of the photolysis cross-sections of ClOOCl (Pope *et al.*, 2007). Interestingly, the new and much improved measurements report values nearly an order of magnitude smaller than the cross-sections that are derived from *in situ* measurements and result in good reproduction of observed ozone loss rates. Based on the Pope *et al.* (2007) cross-sections, our understanding of the polar ozone loss process would completely fall apart—a fact that highlights the huge uncertainties that are still present in our theoretical understanding of one of the most important anthropogenic processes in the global atmosphere.

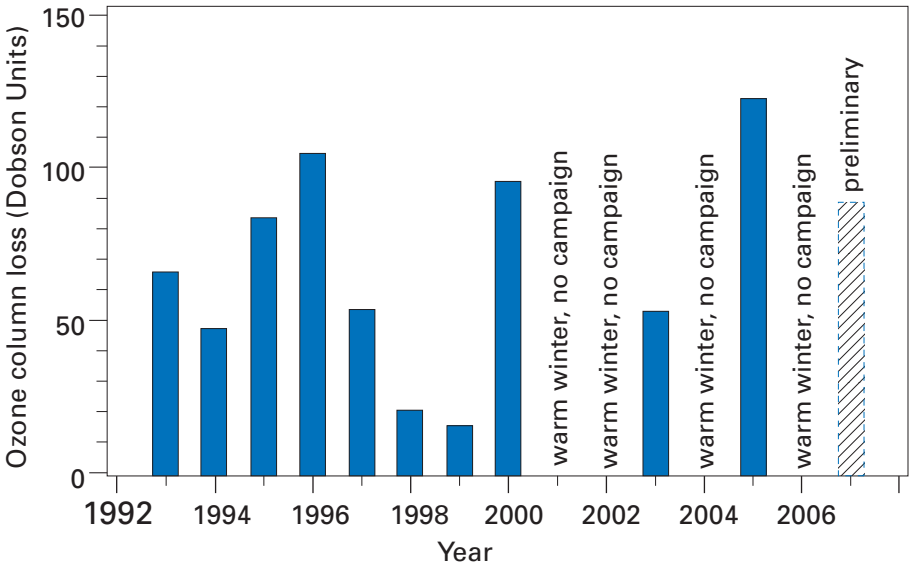

Figure 3 — Variation of total ozone losses since the early 1990s

Ozone loss and climate change

Figure 3 illustrates the interannual variation of chemical ozone losses in the Arctic since the beginning of the 1990s. The pronounced year-to-year variability is much larger than the impact of the gradual change of the chlorine and halogen loading during this time period. Rather, due to the important role of the heterogeneous reactions on polar stratospheric clouds, ozone loss variability is mainly driven by the pronounced variability of the meteorological conditions. This is demonstrated in Figure 4, where ozone losses are shown versus V_{PSC}. (V_{PSC} is a purely temperature-based parameter, which, essentially, gives the winter average volume when the temperatures were below the polar stratospheric cloud formation threshold.)

From the slope of the compact empirical relation between ozone loss and V_{PSC} shown in Figure 4 the sensitivity of Arctic ozone loss on potential climate change in the Arctic stratosphere can be derived. For the current halogen loading, it turns out that approximately 15 Dobson Units of additional ozone loss per Kelvin cooling of the Arctic stratosphere can be expected. Figure 4 also gives a comparison of the observational data with a model based on standard assumptions of the WMO Ozone Assessment 2002. This model underestimated the climate sensitivity of Arctic ozone loss by a factor of about three. The model improvements described above result in a substantial improvement of the model's ability to reproduce the observed climate sensitivity and hence an improved forecast ability.

Figure 5 shows the development of the parameter V_{PSC} over the past four decades (Rex *et al.*, 2006; WMO, 2007). The warm winters which define the lower envelope of the variability show only small changes. The risk of large ozone losses in the Arctic or even the formation of an Arctic ozone hole, however, depends on the future development of the conditions in the cold winters—the

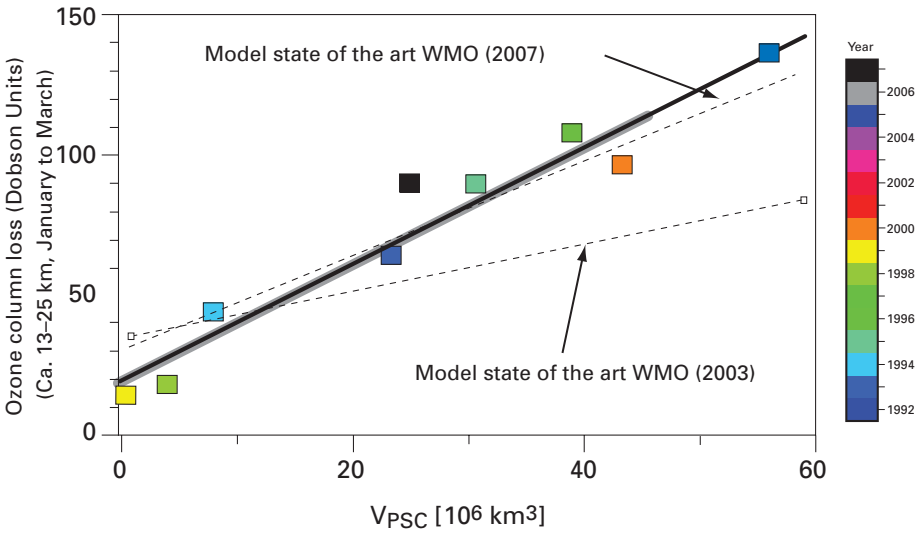

Figure 4 — Relation between total ozone loss and V_{PSC} (temperature-based parameter, giving the winter average volume, in which temperatures were below the threshold for the formation of polar stratospheric clouds (PSC)). The value for the year 2007 (black symbol) is based on preliminary data.

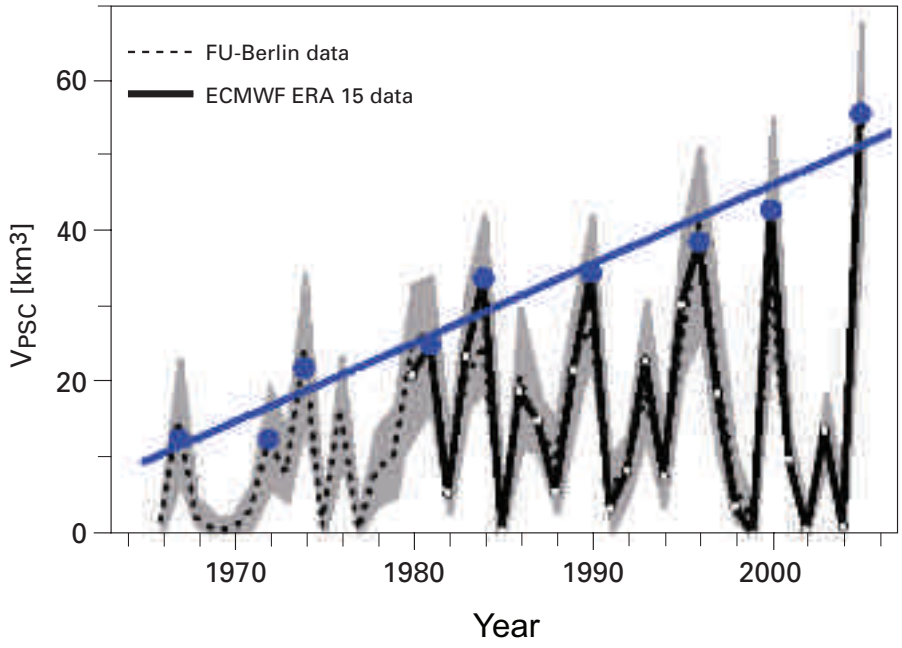

Figure 5 — Long-term evolution of V_{PSC} over the past four decades

upper envelope of the variability. The cold winters show a significant tendency to have become colder over the last four decades. The probability for the coincidental occurrence of such a trend in a random time series is smaller than 10^{-6} (Rex *et al.*, 2006). There are two possible explanations: first, the trend is forced externally, e.g. by the increasing greenhouse-gas concentration in the atmosphere; or, second, it is due to long-term internal variability of the climate system on a decadal time-scale. Indeed, increasing levels of greenhouse gases tend to cool the stratosphere but the observed cooling during the cold winters is much larger than can be understood easily and would require the existence of a dynamic feedback mechanism. Investigations of possible feedback mechanisms and the role of decadal scale internal variability of the Arctic stratosphere are necessary and require global 3D-model studies. A better understanding of the reasons for the observed past trend is essential before the probability of its continuing in the future can be assessed.

Large ozone losses in some of the recent Arctic winters were a result of the long-term changes in the distribution of V_{PSC} and, thus, a result of the long-term change in climate conditions in the Arctic winter stratosphere. Such large ozone losses would not have occurred were the meteorological conditions of the 1960s still present, even for today's high halogen load. Hence, a reliable prediction of the ozone distribution in the Arctic stratosphere for the coming decades requires a better understanding of the reasons for these meteorological changes.

Observations during International Polar Year will help to address the issues described above. The concerted action by innumerable scientists from all over the world to better explore the Arctic environment in all its aspects is an exciting enterprise and an unprecedented opportunity to improve our understanding of many aspects of these harsh but extremely beautiful and interesting parts of our planet.

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