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Evidence for the effectiveness of the Montreal Protocol to protect the ozone layer

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Abstract

The release of man-made ozone depleting substances (ODS, including chlorofluorocarbons and halons) into the atmosphere has lead to a near-linear increase in stratospheric halogen loading since the early 1970s, which started to level off after the mid-1990s and then to decline, in response to the ban of many ODSs by the Montreal Protocol (1987). We developed a multiple linear regression model to test whether this has already a measurable effect on total ozone values observed by the global network of ground-based instruments. The model includes explanatory variables describing the influence of various modes of dynamical variability and of volcanic eruptions. In order to describe the anthropogenic influence a first version of the model contains a linear trend (LT) term, whereas a second version contains a term describing the evolution of equivalent effective stratospheric chlorine (EESC). By comparing the explained variance of these two models we evaluated which of the two terms better describes the observed ozone evolution. For a significant majority of the stations, the EESC proxy fits the long term ozone evolution better than the linear trend term. Therefore, we conclude that the Montreal Protocol has started to show measurable effects on the ozone layer about twenty years after it became legally binding.

1 Introduction

Stratospheric ozone depletion by chlorine radicals was first discussed by Stolarski and Cicerone (1974) and Molina and Rowland (1974). The latter also discovered that man made chlorofluorocarbons (CFCs) act as a source for stratospheric chlorine. The full extent of anthropogenic ozone destruction became evident when the Antarctic ozone hole was discovered (Farman et al., 1985), which was subsequently explained as caused by ozone depleting substances (ODS) including CFCs and halons and a complex chemistry involving heterogeneous reactions on the cold surfaces of polar stratospheric clouds and aerosols (e.g., Solomon et al., 1987; Peter, 1997; Solomon, 1999).

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At northern mid-latitudes, significant negative trends in wintertime total ozone were first documented by the International Ozone Trends Panel (WMO, 1989). Many further studies confirmed a significant decrease in the thickness of the extratropical ozone layer (e.g., Staehelin et al., 2001, 2002).

An efficient reduction of the global anthropogenic emissions of ODS was reached by the Montreal Protocol (1987) and its subsequent Amendments (WMO, 2007). This was confirmed by long-term measurements of selected CFCs at remote ground stations (Montzka et al., 1996) as well as by balloon-borne measurements in the stratosphere (Engel et al., 2002). The successful implementation of the Montreal Protocol (e.g., WMO, 2007) launched a discussion on ozone recovery in the second half of this century and a potential subsequent super-recovery by greenhouse gas-induced cooling of the upper stratosphere and an predicted increase in the Brewer-Dobson circulation as a result of climate change (e.g., Butchart and Scaife, 2001; Newchurch et al., 2003; Krizan et al., 2005; Austin and Wilson, 2006; Butchart et al., 2006; Eyring et al., 2007; Harris et al., 2008; Shepherd, 2008; Hegglin and Shepherd, 2009; Li et al., 2009; McLandress and Shepherd, 2009; Waugh et al., 2009). However, results of numerical simulations published by Hegglin and Shepherd (2009) predicted remarkable differences in the evolution of the ozone layer in the Northern and the Southern Hemisphere within the current century.

Depending on their physico-chemical properties individual ODS have different potentials to deplete stratospheric ozone. Equivalent Effective Stratospheric Chlorine (EESC) is a convenient quantity to characterize the ozone depletion potentials of halogens (chlorine and bromine) taking into account the temporal evolution of the emissions of the individual species, their transport into the stratosphere and their atmospheric lifetimes (WMO, 2007). Since air is transported from the tropical troposphere into the stratosphere, and then takes a few years from the tropical entry point before reaching high latitudes (Newman et al., 2006), an additional lag of 2.5 years applies when using EESC to describe the polar latitudes. Between the early 1970s and the mid-1990s EESC increased in an almost linear way (see Fig. 1). EESC peaked in 1997,

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several years after the peak in emissions, due to the long transport time to reach the ozone layer and the long atmospheric lifetimes of ODS. This was confirmed by ground based Fourier Transform Infrared Reflectance (FTIR) measurements at Jungfraujoch (Switzerland) of column amounts of the stratospheric reservoir species hydrogen chloride (HCl), which is formed by the reaction of methane (CH_4) with chlorine radicals released by the stratospheric photolysis of CFCs (black line in Fig. 1) (Rinsland et al., 2003). These findings suggest that the slow recovery of the ozone layer over mid-latitudes may have started at the earliest in the late 1990s.

The bulk of stratospheric ozone resides in the lower and middle stratosphere. At these altitudes extra-tropical ozone is highly variable and therefore the effect of the Montreal Protocol on total ozone is much more difficult to identify than in the upper stratosphere (e.g., Weatherhead et al., 2000). Reinsel and colleagues (2002) estimated that detection of the first stage of recovery (defined as a deviation from a linear increase) requires about 7–8 years of total ozone observations since the onset of the recovery. Recent studies provide growing evidence that a weakening or reversal of negative trends may already be detectable (Newchurch et al., 2003; Guillas et al., 2004; Steinbrecht et al., 2004; Reinsel et al., 2005; Yang et al., 2005; Brunner et al., 2006; Weatherhead and Anderson, 2006; Yang et al., 2006; WMO, 2007; Harris et al., 2008). Increases in total ozone since the early 1990s have been observed at many sites in northern mid-latitudes, but the attribution of this increase to changes in EESC is a difficult task (Yang et al., 2006) because several factors may have contributed to an apparent flattening or reversal in ozone tendencies, including: (i) changes in synoptic scale meteorological variability and long-term climate variability (e.g., Hood and Zaff, 1995; Steinbrecht et al., 1998; Appenzeller et al., 2000; Thompson an Wallace, 2000; Orsolini and Doblas-Reyes, 2003; Brönnimann and Hood, 2003; Shepherd et al., 2008; Rieder et al., 2010); (ii) the large volcanic eruption of Mount Pinatubo in 1991 leading to record low values in the following two years (e.g., Gleason et al., 1993; Rosenfield et al., 1997; Robock, 2000; Yang et al., 2005; Brunner et al., 2006; WMO, 2007); (iii) the maximum in solar activity in 2001 (Steinbrecht et al., 2004), and (iv) particularly cold

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winters with enhanced polar ozone loss in the Arctic during the mid 1990s and in the Antarctic in 2006 with one of the largest austral ozone holes ever (WMO, 2006).

Numerical simulations have been performed in order to describe in a quantitative way the effect of anthropogenic emissions of ODS on the stratospheric ozone layer. During the last decade a number of three dimensional models have been developed aiming at describing the complex interactions of stratospheric chemistry and transport allowing climatic changes to be taken into account (e.g., WMO, 2007). However, the validation of these models regarding their capability to adequately describe all relevant processes and hence to reliably predict the evolution of stratospheric ozone remains a challenging task (Eyring et al., 2007).

Here we use a statistical test as a complementary method to provide evidence for the effectiveness of the Montreal Protocol. The basic concept of the approach is simple: We test whether the temporal evolution of total ozone measurements can be better described by a linear trend (LT, starting on 1 January 1970, as expected without the regulation by the Montreal Protocol), or by the evolution of EESC (including the regulation; see Fig. 1). The test itself is a binomial test with a probability of 50% (also known as sign-test). The decision between LT and EESC is based on the comparison of the variances (R^2) produced by the two versions of the regression model. The model includes additional explanatory variables describing other (natural) influences, which have been previously selected by backward elimination methods. Section 2 contains the description of the statistical methods and the total ozone measurements, Sect. 3 describes the results and the discussion and Sect. 4 draws the conclusions.

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2 Methods and measurements

2.1 Multiple linear regression models and selection of explanatory variables

We used the following multiple regression modelling approach, which describes the explained variance (R^2)

$$\mathrm{TOZ} = M + b_1 \cdot \mathrm{Trend} + \sum_{j=2}^{m} b_j \cdot X_j + \varepsilon \,, \quad (1)$$

where "TOZ" is the measured total ozone monthly mean value, M is the seasonal variation of total ozone described by individual values for each month, "Trend" is either EESC or LT, b_1 the trend coefficient, X_j are other explanatory variables and b_j their respective coefficients (see Table 1 and text below). The residual errors are described by ε. The autocorrelation (in time) is not taken into account in either versions (using EESC or LT). However, autocorrelation is expected to not affect the results of our comparative analysis, as it should affect both versions in the same way.

The most suitable explanatory variables (describing most of the variance) are selected by backward elimination (for a detailed description see Mäder et al., 2007). We first selected the explanatory variables for individual stations. We start with a multiple linear regression model including 44 potentially relevant explanatory variables. The significance (p value) of the coefficients is used to eliminate the least important term in the model. With the resulting reduction in variables the step is repeated iteratively until no explanatory variable is left. The sequence of elimination defines a ranking of the variables separately for each station.

In a second step the backward elimination process is applied to latitude belts. Using average ranks of the variables across all stations of a latitude belts, the variable with the lowest explanatory skill (highest mean rank over all ranking tables of the current belt) is then determined and removed. By repeating this step, a ranking table optimized over all stations of a latitude belt is generated. Each version of the model with a selection

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of variables is based on this ranking table, and the number of variables in the model is determined by the number of significant variables and the explained variance (R^2) as described in Mäder et al. (2007). If not already present, a term for the trend was added.

In the next step, we test, based on R^2, whether the temporal evolution of the individual stations is better fitted by EESC or by the linear trend LT. Then we calculate, using the sign-test, for the different latitude belts if a significant part of the stations show the same preference. This approach with two comparable proxies for the anthropogenic influence is only qualitative in nature, but it is robust and avoids the selection of a fixed point in time for the turnaround (Percival and Rothrock, 2005) as was done in other studies (Reinsel et al., 2002; Newchurch et al., 2003; Reinsel et al., 2005; Yang et al., 2005; Weatherhead and Anderson, 2006; Yang et al., 2006).

2.2 Spatial correlation

Since the distances between some of the ground-based stations are small, their preference for either EESC or LT may not be independent because of spatial correlations of the measurements. Therefore, we tested the spatial correlation of our results as expressed by the following transformed difference T between the proportions of explained variance:

$$T = \text{sign}\left(R^2_{\text{EESC}} - R^2_{\text{LT}}\right) \cdot \sqrt{\left|R^2_{\text{EESC}} - R^2_{\text{LT}}\right|} \quad (2)$$

where R^2_{EESC} and R^2_{LT} are the explained variances of the model using either EESC or LT. We used the square root transformation since a normal distribution is an important requirement for spatial analysis and the distribution of T is, in contrast to the simple difference, very close to it. For the calculation of the spatial correlation of T we used the estimator by Cressie and Hawkins (1980). The semivariance $s_{C(h)}$ for a given class $C(h)$ of distances around h between two stations (typically about 10 to 30 classes are

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used) is defined as

$$s_{C(h)} = \frac{\left(\frac{1}{n_{C(h)}} \sum_{(i,j)\in h} \sqrt{|T_i - T_j|}\right)^4}{0.914 + \frac{0.988}{n_{C(h)}}} \tag{3}$$

where $n_{C(h)}$ is the number of pairs of stations in this distance class. Graphs of $s_{C(h)}$ versus h show the structure of the spatial correlation. In case of significant spatial correlations, $s_{C(h)}$ increases with h. Often the increase is restricted to short distances and $s_{C(h)}$ remains constant above a certain distance called *range*. Above this range, the individual stations are no longer correlated (Cressie, 1993). In our analysis, we calculated the spatial correlation separately for the northern, southern and tropical latitude belt as well as for all stations together (see Sect. 3.1).

2.3 Total ozone measurements used in this study

For the ozone time series we used the ground based stations provided by WOUDC (World Ozone and Ultraviolet Data Centre, Toronto, www.woudc.org, measurements up to March 2007 as available in May 2007) with sufficiently long time series (at least 120 monthly mean values and measurements beyond the year 2000). Available series are different in length. Data before 1948 were not used, since the relevant proxies are not available for the time before 1948. However, this restriction affected only a few stations as most ozone time series started later. Ground based measurements were selected because at many stations, observation started in the 1960s or early 1970s, allowing to better fit the individual coefficients of the model (especially for slowly varying processes) than would be possible for satellite observations available since 1979. Data quality of ground based total ozone measurements is expected to be ensured by comparison with standard instruments. However, some total ozone records reported at WOUDC contain discontinuities partially because of technical problems (Fioletov et al., 2008). Parts of the records of stations showing obvious discontinuities were excluded

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after visual inspection. Under the assumption that data quality problems of individual stations are random, the conclusions drawn here will remain valid, and any further attempt to homogenize, improve or select certain data is inevitably connected with other problems or biases.

Totally 116 stations with 34 923 monthly total ozone values were used, which corresponds to typically 23.5 years of data per station.

3 Results and discussion

3.1 Selected explanatory variables and spatial correlation

The explanatory variables X_j were selected by backward elimination (see Sect. 2.1), starting with a large set of different time series of possible variables. Table 1 shows the result and gives a short description of the selected variables. The variable of equivalent latitude (EL) was developed to describe the effect of dynamics on column ozone (Wohltmann et al., 2005). It is based on the equivalent latitude fields of potential vorticity vertically integrated using a climatological ozone profile. The EL was selected in all bands except at the South Polar sites. It is known that changes in atmospheric dynamics contributed significantly to the past evolution of stratospheric ozone at different sites (e.g., Labitzke and van Loon, 1999; Chipperfield and Jones 1999; Appenzeller et al., 2000; Hadjinicolaou et al., 2002; Orsolini and Doblas-Reyes, 2003; Harris et al., 2008) and it is well know that the increase in total ozone found at northern mid-latitudes in the 1990s (Hood and Soukharev, 2005; Harris et al., 2008) is attributable to a large extent to changes in dynamics. The inclusion of EL in the model gives some confidence that the main results of the study are not confused by changes in dynamics, since changes in transport are believed to be the main driver for the long-term evolution of the ozone shield besides ODS.

A large perturbation of stratospheric ozone was caused by the eruption of Mount Pinatubo in 1991 close to the maximum of EESC. Since large volcanic eruptions lead

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to lower total ozone values in the subsequent years (e.g., Randel et al., 1995; Hadjinicolaou et al., 1997), this may lead to a preference for EESC over the linear trend. Based on the backward elimination procedure the variable SAD (vertically integrated stratospheric aerosol surface area density) representing the effect of volcanic eruptions was identified as an essential variable in the two northern latitude belts. On the Southern Hemisphere the influence of the past volcanic eruptions (e.g., Gunung Agung, 1963; El Chichón, 1982; Mt. Pinatubo, 1991) on column ozone could not be identified in similar strength as in the Northern Hemisphere. This hemispheric difference in the effect of volcanic eruptions was explained by Robock et al. (2007) as the combination of the difference in land mass at the latitude of the jet stream and the stronger polar vortex in the Southern Hemisphere. The inclusion of SAD in the model distinctively reduces the residuals for the corresponding time period. Thus, in contrast to other studies (Reinsel et al., 2002; Yang et al., 2006) we apply the regression model including SAD to the complete ozone time series instead of removing a couple of years following the eruption of Mount Pinatubo.

In earlier WMO assessments the Quasi Biennial Oscillation (QBO) and the eleven year solar cycle were used as explanatory variables in order to remove long-term variability in statistical trend models. They were not selected as important proxies for the long-term ozone evolution in our model selection procedure (comp. Mäder et al., 2007). Possibly some of the variability caused by QBO is captured by EL. The solar cycle is nevertheless included as explanatory variable in the sensitivity analysis presented in Sect. 3.2.

To illustrate the model performance one sample station for the Northern mid-latitude (Hohenpeissenberg, Germany) and the Northern Polar belt (Resolute, Canada) is analyzed (see supplementary material).

Ground-based total ozone measurements are unevenly distributed over the globe, a substantial part of the monitoring sites being located in Europe. In case of spatial correlations the basic approach of the study would need a modification. As shown in Fig. 2 spatial correlation is only visible if all belts are used together (bottom right;

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global). But for the single belts no increase in $s_{C(h)}$ even for small distances is visible, but rather, $s_{C(h)}$ appears to stay constant (this situation is called a *pure-nugget-model* and implies uncorrelated random deviations). Therefore we may assume that spatial correlation does not reduce the multitude of pieces of independent information in our test, as long as we analyze the three latitude belts separately.

3.2 Long-term ozone evolution: linear trend vs. EESC

After selection of the explanatory variables for each latitudinal belt a test was used to study whether the measurements of the individual sites rather follow a linear trend or the time evolution of EESC (see also introduction). The trend term was estimated for every calendar season separately and a binomial test was used to test whether the stations in a given latitude belt showed a significant preference for one of two the models. The use of this test is justified because no spatial correlation was found (see Sect. 3.1). The two northern latitude belts show a clear preference for EESC to describe the measured ozone evolution (see Fig. 3). The results are significant at the 5% level (which corresponds to a 95% confidence interval) individually as well as together. In the tropical latitude belt EESC and LT are nearly balanced. This result can be explained by the small trends compared to the high variation of total ozone. In the two southern latitude belts EESC is again preferred. The result of the southern mid-latitudes is not significant, probably because of the small number of stations, whereas both southern latitude belts together show a significant result. However, note that the results of the South Polar latitudes should be ignored, since the amount of polar ozone depletion over Antarctica (ozone hole condition) is presently determined by dynamical factors, whereas ODS concentrations are still high enough not to be a limiting factor. In contrast, the situation in the Arctic is less dynamically driven (e.g., Solomon, 2007) and thus more strongly influenced by the present ODS levels which justifies including the results for this region.

In our analysis the last years are expected to be most relevant because the difference between EESC and LT increases with time (Fig. 1). To test the expected change in time,

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we repeated our analysis for different time windows. Figure 4 shows that the number of ozone series following EESC rather than LT increases with time, which supports the results.

In order to test the robustness of the results we performed a number of sensitivity studies (see Table 2). The last solar cycle which peaked in the year 2001 most likely contributed to the observed ozone increase in the uppermost stratosphere since the mid 1990s and hence to the apparent turnaround in total ozone (Steinbrecht et al., 2004; Dameris et al., 2006). Based on our elimination process, solar flux, described by the solar flux intensity at 10.7 cm, is not one of the most important influence factors for total ozone (Mäder et al., 2007). Consequently, inclusion of solar flux in the equations does not affect our results significantly (see Table 2). In a recent study, Newman et al. (2007) postulated a new formulation to calculate EESC which includes an age-of-air dependent fractional release of ODS and an age-of-air spectrum. The replacement of the EESC time series used by WMO/UNEP (WMO, 2007) by two different time series taken from Newman et al. (2007) does not change our results strongly (see Table 2). (The two EESC variations were downloaded from the NASA Goddard website at http://code916.gsfc.nasa.gov/Data_services/automailer/index.html. The following parameters were used: WMO-Scenario: A1; Mean of age-of-air: 5.5 and 3.0 years; Width of Age-of-Air Spectrum: 1.5 years; Use Inorganic: yes; EESC with α: 60.) The robustness of the results was to be expected, since the different versions of EESC are nearly identical up to linear transformations, and such alterations do not affect the significance of a variable in multiple linear regression.

4 Conclusions

In the late 1970s and the 1980s, i.e. since the paper of Molina and Rowland (1974), the search for a significant downward trend of total ozone measurements was an important research topic in the debate whether it was justified to limit man made ODS emissions. Statistical models were developed in which natural variability was removed by using the

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explanatory variables of Quasi Biennial Oscillation and the eleven year solar cycle. Significant downward trends were first published in the Ozone Trend Panel report in 1989 (WMO, 1989) for northern mid-latitudes (where a large part of the population lives). This was viewed as evidence that the stratospheric ozone layer had been diminished by man made emissions of ODS. The Montreal Protocol (1987, including its enforcements in the subsequent years) has proved to be very effective to limit ODS emissions. More than twenty years later, the documentation of the beneficial effect of the Montreal protocol to protect the ozone layer is still not a simple task. One approach to this problem has been the use of 2- and 3-dimensional numerical models to describe the effect of reductions of ODS on the ozone layer. However, because of the complex interactions between transport and chemical processes (including e.g. heterogeneous processes on polar stratospheric clouds) and the limited computer resources such models need simplifications. Moreover, the validation against observations revealed largely varying degrees of success of the individual state-of-the-art models with respect to the reproduction of individual processes including the observed ozone evolution (Eyring et al., 2007; WMO, 2007). Because of this large model spread the results concerning the effect of changes in man-made ODS emissions versus changes in dynamics remained controversial.

A complementary approach to describing the effect of changes in the column ozone is the use of statistical modelling. The results of such an approach, however, do not provide direct causal relationship and only allow a sound interpretation if the used proxies are directly linked to the determining processes, which is generally difficult to prove. The proxies EL, T50 and PV470 identified by the elimination procedure, for example, are not readily attributable to a specific dynamical process but rather represent the combined effect of several processes including wave activity at different levels, the residual circulation, and the quasi-biennial oscillation. The effect of man made ODS emissions on chemical ozone depletion, on the other hand, is more directly represented by the parameter EESC.

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The aim of the study is not to provide reliable quantitative numbers concerning the attribution of ozone layer changes to chemical depletion or dynamics. The goal is rather to proof the effectiveness of the Montreal Protocol for the protection of the ozone layer. For this we compared two statistical ways to model the temporal evolution of the ozone layer, a linear upward trend (as a surrogate of the time evolution of the ozone layer without a Montreal Protocol) and the temporal evolution attributable to the observed evolution of ODS following the Montreal protocol (EESC). We argue that the dynamical proxies, in particular EL, can represent dynamical changes in a sufficient way not to confuse the discrimination between a linear trend and an EESC trend. Note that our results have to be viewed as qualitative analysis. However, because of their robustness we regard our results as clear and unprecedented evidence for the effectiveness of the Montreal Protocol for the protection of the ozone shield, proving the success of international cooperation between science, economy and politics.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/10/19005/2010/ acpd-10-19005-2010-supplement.pdf.

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Table 1. Optimized versions of the regression model for total ozone (TOZ) of the five latitude belts (see Mäder et al., 2007). The explanatory variables are sorted according to their rank determined in the model selection procedure. If not already included, a seasonal trend term (seas:Trend) was added for this study. The variable M (=month) represents the residual seasonal cycle; EL, the equivalent latitude proxy; Trend is either EESC or LT; T_X, the temperature at pressure level X; PV_{470}, the potential vorticity at potential temperature level 470; SAD, the vertically integrated aerosol surface area density (describing the influence of volcanic eruptions); V_{PSC}, the cumulative volume of polar stratospheric clouds (describing polar ozone depletion); QBO_{30} the quasi biennial oscillation at pressure level 30 hPa. M is represented by 12 values. The notation seas:Trend indicates that different coefficients for Trend are estimated for each of the seasons (4 values). The other variables are characterized by a single (annual-mean) coefficient.

Latitude belt	Optimized version of regression model
North Polar (NP): 11 stations north of 62° N	TOZ∼EL+M+seas : Trend+V_{PSC}+T_{50}+SAD
Northern Mid-latitude (NM): 65 stations 33° N–62° N	TOZ∼EL+M+T_{10}+seas : Trend+SAD
Tropical (TR): 27 stations 30° S–33° N	TOZ∼EL+M+seas : Trend
Southern Mid-latitude (SM): 7 stations 60° S–30° S	TOZ∼EL+T_{50}+QBO_{30}+M+seas : Trend
South Polar (SP): 6 stations south of 60° S	TOZ∼PV_{470}+seas : Trend+EL+M+T_{50}

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Table 2. Number of stations preferring EESC over LT in different versions of the basic model. The column *Standard* corresponds to the main results of the paper. The column *All data* includes also the as “dubious” classified data from WOUDC (see Sect. 2). The fifth column refers to Sect. 3.2 on the influence of the solar cycle with solar flux at 10.7 cm as additional proxy. The last two columns represent the results if the new formulation for EESC by Newman et al. (2007) with an age-of-air of 5.5 and 3.0 years, respectively is used (see Sect. 3.2).

Region	Number of stations	Standard	All data	Solar Cycle	EESC with age-of-air of	
					5.5 years	3.0 years
NP	11	9	9	9	10	9
NM	65	54	52	46	50	46
TR	27	15	11	16	16	15
SM	7	5	6	5	5	5
SP	6	6	6	6	5	6

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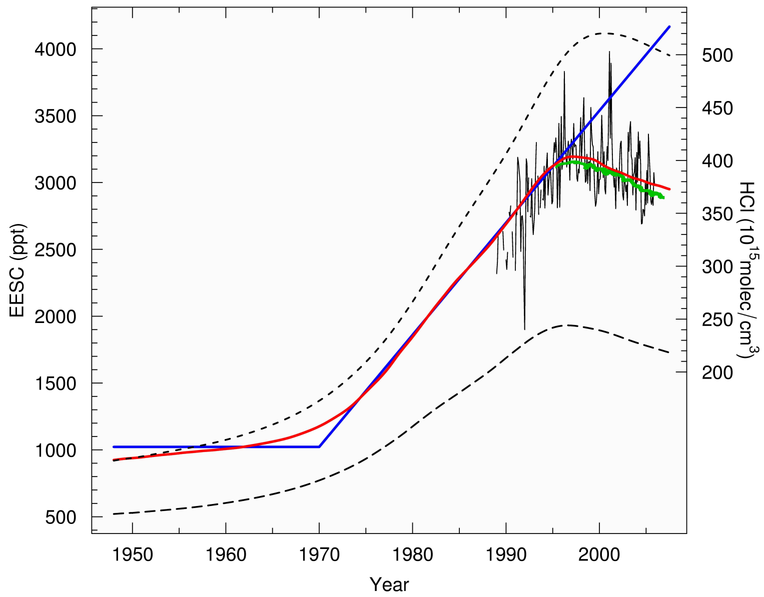

Fig. 1. Left axis: Time series of Equivalent Effective Stratospheric Chlorine (EESC, provided by the European Environment Agency, EEA) for extra-polar latitudes (red line) and linear trend (LT) as used in many previous studies (blue line). Right axis: time series of ground-based HCl columns measured at Jungfraujoch (Switzerland, 3580 m a.s.l., black solid line) and the averaged observation as reported by WMO (2007, green line). For polar stations the same EESC and LT curves are used, but applying an additional time lag of 2.5 years (Newman et al., 2006). The two black dashed curves show EESC based on a new formulation by Newman et al. (2007) using 5.5 (upper curve) and 3.0 years (lower curve) as mean age-of-air values.

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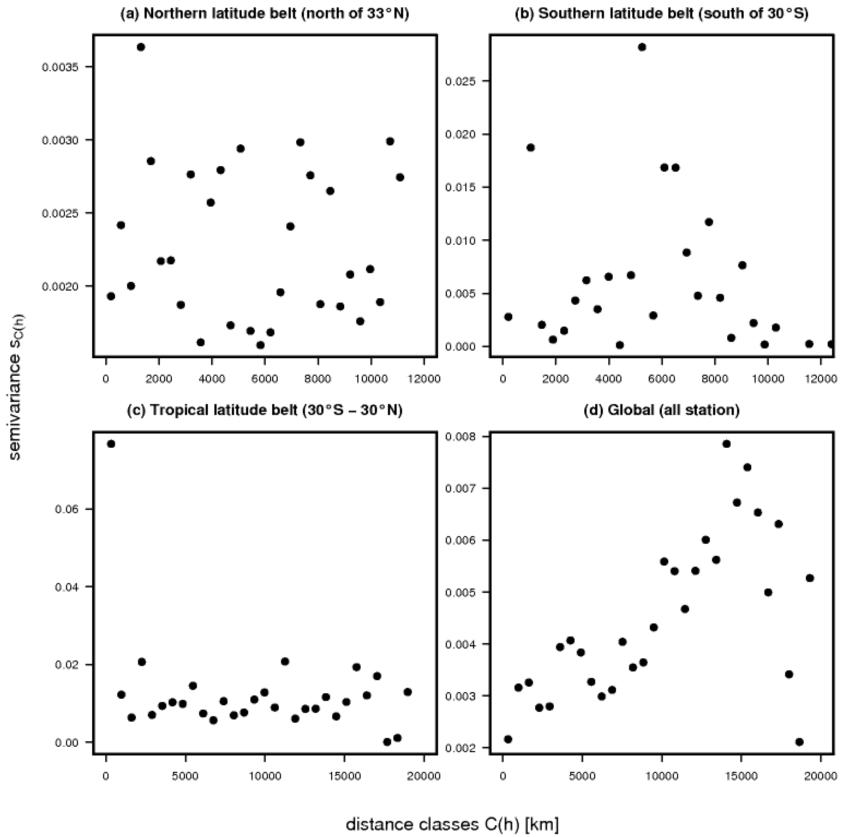

Fig. 2. Spatial variograms for the **(a)** northern, **(b)** southern, **(c)** tropical latitude belts and for **(d)** all stations together. In contrast to panel d, panel a to c do not show an increase of semivariance. As consequence, for the three latitude belts (a–c), used each apart, the number of stations can be used without corrections for the sign-test. But this is not the case for the situation in panel d where all the three other belts are used together.

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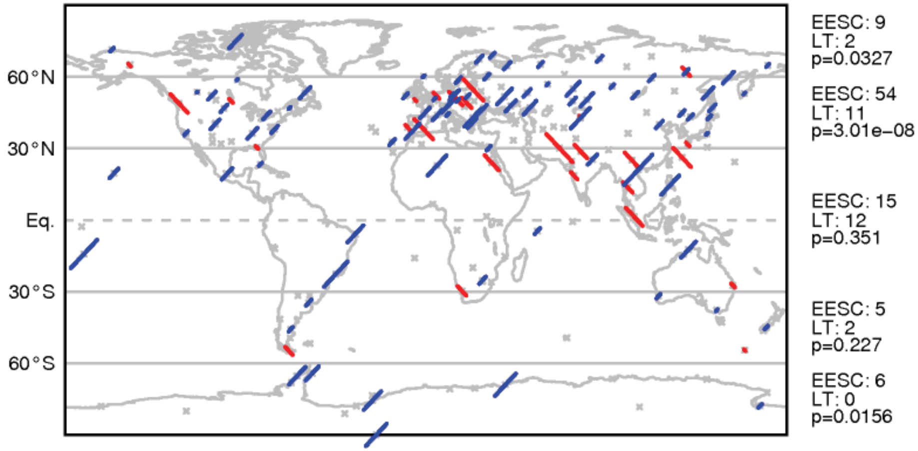

Fig. 3. Map of ground based stations used in this study. Stations preferring *EESC* over linear trend (see text and Fig. 1) are represented by blue lines and a positive slope, others with red lines and a negative slope. The length of the lines represents the absolute value of the test statistic T. For each latitude belt, the numbers of stations preferring EESC or LT are given on the right-hand side together with the p-value of the binomial test.

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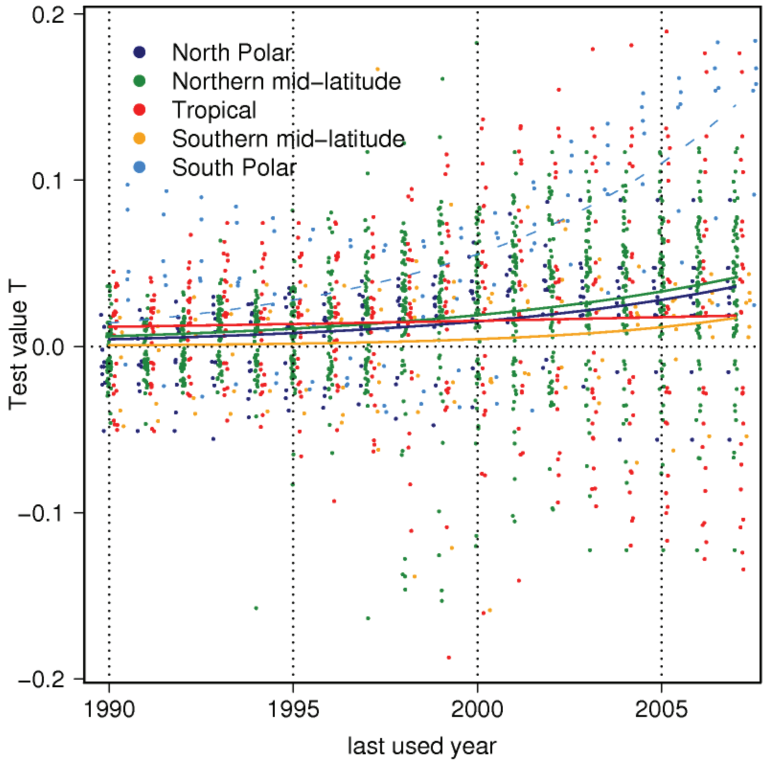

Fig. 4. Evolution of the test value T with increasing time window. Single points represent the T (test value of preference of EESC over LT, see Eq. 2) values for each station for an upper bound of the time window given by the value on the x-abscissa. The points are jittered horizontally for better visibility. Solid lines represent the different latitude belts and are calculated by fitting a simple exponential model. The coefficients for the southern mid-latitudes and the tropical latitude belt are not significant, in contrast to the others. The results from the Southern polar region show that the region is still saturated with ODS and therefore, a linear response to the ODS concentration is not observed.

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