



## Discussion

## Do cosmic-ray-driven electron-induced reactions impact stratospheric ozone depletion and global climate change?

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## ABSTRACT

Recently, the cosmic-ray-driven electron-induced reaction mechanism (CRE) was introduced to explain polar ozone depletion and surface temperature change. It was proposed that the dissociation of chlorofluorocarbons (CFCs) on ice surfaces of polar stratospheric clouds plays the dominant role in forming the ozone hole. Efforts have been made to predict polar ozone loss in future years. It was further proposed that CFCs and cosmic-ray-driven ozone depletion may control global surface temperatures. These assertions challenge the fundamental understanding of Antarctic stratospheric ozone loss and global warming. Here we show that these arguments based on the CRE mechanism are inconclusive. First, correlations of satellite data of CFC-12, N<sub>2</sub>O and CH<sub>4</sub> from ACE-FTS show no evidence of significant loss of CFC-12 as predicted by the CRE mechanism. Second, conclusions drawn about a possible CRE impact on the atmosphere, based on correlations of different observed atmospheric parameters, do not have a physical basis. Finally, predictions on the future development of the atmosphere based on these correlations are not reliable for either the ozone hole or global surface temperatures.

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## 1. Introduction

The Antarctic ozone hole is one of the most striking examples of the impact of human activities on the atmosphere. In 1985, when the ozone hole was discovered (Farman et al., 1985) all the major physico-chemical mechanisms responsible for its occurrence were unknown and a number of competing theories were put forward to explain the phenomenon (Solomon, 1999). Today, however, the fundamental mechanisms causing the ozone hole are understood and man-made halogen compounds have been identified as the ultimate cause of stratospheric ozone loss (e.g., Solomon, 1999; Müller, 2009; WMO, 2011).

Briefly, Antarctic ozone loss is caused by a chain of events starting in autumn with cooling of the polar stratosphere and formation of the polar vortex. The polar vortex is a strong stratospheric wind jet that isolates the polar air mass from mid-latitudes. In winter, when stratospheric temperatures are low enough, polar stratospheric clouds (PSCs) form, which consist of water ice, nitric acid hydrates and supercooled liquid ternary HSO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O droplets (Peter, 1997). The PSCs and cold binary sulfate particles provide surfaces allowing heterogeneous reactions to occur which convert chlorine from so-called reservoir species (mostly HCl and

ClONO<sub>2</sub>) into an active, ozone destroying form (Solomon et al., 1986; Peter, 1997; Solomon, 1999). Ozone destruction occurs in catalytic cycles, in the Antarctic stratosphere mainly through a cycle involving chlorine peroxide (ClOOCl) (Molina and Molina, 1987; Solomon, 1999; von Hobe et al., 2007). Ozone destruction stops in spring either after temperatures rise above the threshold temperature for efficient heterogeneous chlorine activation ( $\approx 195\text{K}$ ) and the halogen reservoir species reform (e.g., Douglass et al., 1995; Grooß et al., 1997), or when extremely low mixing ratios of ozone are reached (Solomon et al., 2005, 2007a).

Recently, a mechanism was proposed to explain of the ozone hole that claimed to be “drastically different” from the established mechanism outlined above, namely the cosmic-ray-driven electron-induced reaction mechanism (denoted as the “CRE” hereafter), which is based on the cosmic-ray-driven electron-induced reaction of halogenated molecules adsorbed on ice surfaces Lu (2010a), and references therein). There has been some debate on these issues previously (Lu and Sanche, 2001a, 2002; Harris et al., 2002a; Patra and Santhanam, 2002; Müller, 2003; Müller, 2008; Wang et al., 2008; Lu, 2009; Müller and Grooß, 2009; Alvarez-Madrigo, 2010), but a new analysis by Lu (2010a) goes significantly beyond earlier conclusions. In particular, he states that “...the observed satellite data have demonstrated that the CRE mechanism plays the dominant role in forming the ozone hole in the spring polar stratosphere” and that “these observed data point to the possibility that the global warming observed in the late 20th century was

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dominantly caused by chlorofluorocarbons (CFCs), modulated by CRE-driven ozone depletion”. Based on the latter conclusion, it is discussed that “global cooling may have started in 2002”. These assertions challenge the fundamental understanding of polar ozone loss and global climate change.

The CRE mechanism is based on the physical chemistry of solvated electrons in water and other polar media and of the dissociative electron attachment (DEA) caused by these low-energy electrons. We neither question the findings from laboratory experiments on bulk and interface solvated electrons in water (e.g., Siefertmann et al., 2010) nor those on the occurrence of DEA on ice surfaces for a variety of compounds (including CFCs) (Arumainayagam et al., 2010; Lu, 2010a). However, we question the conclusions reported by Lu (2010a) on atmospheric processes.

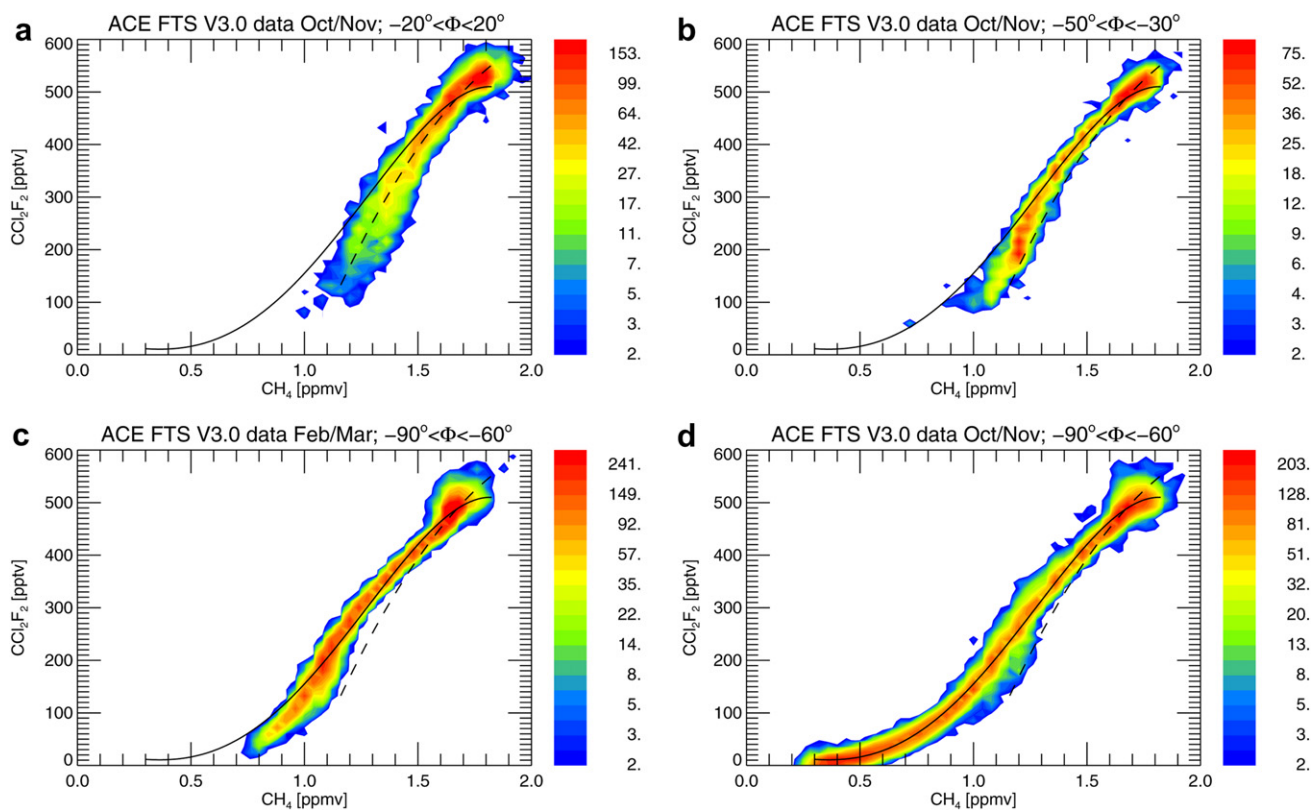
Here, we scrutinise the new theories and concepts put forward by Lu (2010a), in particular regarding the prediction of the future development of the ozone hole and the prediction of a global cooling until the year 2050. We find that the predictions of the future development of the ozone hole based on the CRE mechanism are not reliable and that the prediction of global cooling until 2050 is incorrect.

## 2. Analysis of CFC, N<sub>2</sub>O, and CH<sub>4</sub> observations

Very compact correlations are reported in the literature between observations of long-lived tracers like CH<sub>4</sub> and N<sub>2</sub>O and CFCs (e.g., Michelsen et al., 1998; Müller et al., 2001). The reason for these compact relations is that all these tracer gases are well mixed in the troposphere and have long lifetimes and similar photochemical sinks in the stratosphere (Plumb, 2007). As an example, we show correlations observed from the satellite

experiment ACE-FTS (Walker et al., 2005). Fig. 1 shows the correlation of CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) data with CH<sub>4</sub> for tropical and middle latitudes (top panels) and the polar correlation for the beginning and end of the polar winter. From the tropical data, the photolytic decomposition of both species with increasing altitude can be seen in the up-welling branch of the Brewer–Dobson circulation (Brewer, 1949; Holton et al., 1995). For mixing ratios below about 1 ppmv of CH<sub>4</sub> the CFC-12 in the tropics seems to be mostly dissociated. The tracer–tracer correlation changes due to mixing when air masses exhibiting different locations in the correlation space are mixed (Plumb, 2007; Müller et al., 2005, 2007) and transported poleward. However, no significant change of the tracer correlation is observed over the Antarctic winter and spring, when PSCs are ubiquitous in the Antarctic polar vortex (Michelsen et al., 1998; Müller et al., 2001) (Fig. 1, panels c and d). Such behaviour is in clear contrast to the predictions of DEA-induced loss of CFC-12 on PSC surfaces.

Müller and Grooß (2009) used the year-to-year deviation from the polar tracer correlation of ACE-FTS N<sub>2</sub>O and CFC-12 to demonstrate that a decomposition of CFC-12 by the DEA mechanism cannot be significant. Otherwise it would be visible as a CFC sink correlated with the cosmic ray intensity, which is not observed. Lu (2010a) puts forward the argument that also N<sub>2</sub>O or ClONO<sub>2</sub> may be decomposed by DEA like the CFCs. In contrast, CH<sub>4</sub> would not be expected to be affected by DEA. A DEA-induced decomposition of N<sub>2</sub>O or ClONO<sub>2</sub> is speculative, since the DEA mechanism for stratospherically relevant species has only been demonstrated in the laboratory for CFC-11, CFC-12, and HCl (Lu and Sanche, 2001a,b; Lu, 2010a). To our knowledge, there is currently no laboratory measurement available where DEA cross-sections have been measured for N<sub>2</sub>O and ClONO<sub>2</sub>.



**Fig. 1.** CFC-12/CH<sub>4</sub> correlation for different latitude regions from ACE-FTS (data version 3.0). Panel a shows tropical latitudes, panel b shows mid-latitudes, panel c shows Southern polar latitudes in February and March, and panel d shows Southern polar latitudes in October and November. The number of observations per bin are shown. For better comparison, a polynomial fit to the data of panel a and d is shown in all plots as a black dashed and solid line, respectively. No data are displayed above about 28 km where the CFC-12 concentration is below the detection limit of the ACE-FTS retrieval.

If there was a significant decomposition of both CFCs and  $N_2O$  on ice PSCs, it would in principle be possible that the  $N_2O$ –CFC-12 correlation could remain unchanged even when DEA-induced loss of CFCs occurred. However, if the arguments of Lu (2010a) were true that cosmic rays are a sink for  $N_2O$  but not for  $CH_4$ , this process should be visible as a signature in the  $N_2O$ – $CH_4$  correlation. This is not observed (Michelsen et al., 1998). Likewise, the ACE-FTS measurements of CFC-12 and  $CH_4$  in the Antarctic stratosphere in winter and spring (Fig. 1) show no signature of a chemical loss of CFC-12 for a given  $CH_4$  mixing ratio. Figure 19 of Lu (2010a) shows a comparison of HALOE  $CH_4$  and CLAES CFC-12. Here it is important that this comparison is based on measurements of the two tracers that are observed in comparable air masses. However, these two instruments have different viewing geometries and therefore different latitudinal coverage. Moreover, the HALOE and CLAES data shown by Lu (2010a) represent different years (1992–1998 versus 1992). Therefore the figures generated from the two data sets are not directly comparable. Fig. 2 shows a comparable latitude–altitude cross section based on ACE-FTS data for  $CH_4$ ,  $N_2O$  and CFC-12. The underlying data are observed at the exact same locations and, indeed, they show very similar structure. For all three species, the decline in polar latitudes between March and September is caused by the diabatic descent in the polar vortex (Plumb, 2007). The contour levels at 20 km altitude in March of all three species have descended to about 17 km in September. Visible are also the global structures caused by the ascent of the air in the tropics and by photolytical decomposition of the three species with increasing altitude according to their different lifetimes. From these data, no obvious evidence of any significant sink of CFC or  $N_2O$  in addition to the established photochemical loss processes can be found.

### 3. Conclusions for stratospheric ozone and global climate

In Section 2, we have shown that the CRE effect does not significantly contribute to the dissociation of CFC-12 in the stratosphere. Similar analyses have been made for CFC-11 (not shown). However, even if the CRE effect did contribute significantly to CFC

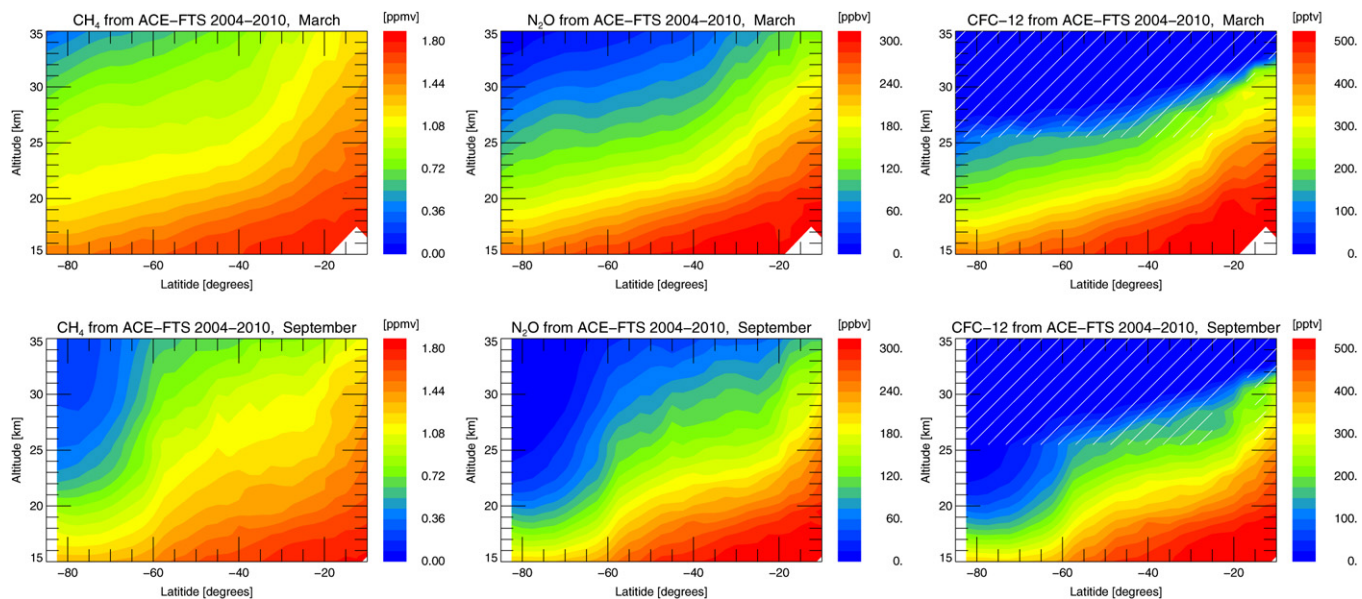
dissociation, the analyses of Lu (2010a) and the conclusions on the future development of stratospheric ozone and global climate would also be problematic as explained below.

First, it should be noted that the scientific findings about stratospheric ozone depletion outlined in the introduction are supported by strong evidence based on a combination of laboratory work, field measurements and atmospheric modelling (WMO, 2011). In contrast, many assumptions presented by Lu (2010a) are based only on correlations of two parameters. These correlations, however, can only give an indication of a cause-and-effect chain. They are no proof of a theory. Below, we discuss in detail different aspects of the CRE mechanism proposed by Lu (2010a) as the causes for the correlations shown based on the current state of scientific knowledge.

#### 3.1. The vertical extent of polar ozone depletion

Lu (2010a) repeats an argument previously made and debated (Lu and Sanche, 2001a; Wang et al., 2008; Lu, 2009; Müller and Grooß, 2009), namely, that “the ozone hole is exactly located in the polar stratosphere at  $\sim 18$  km, where the rate of ionisation for cosmic rays producing electrons shows a maximum”. However, the current understanding is that the vertical extent of the ozone loss in the ozone hole is determined by the temperature structure of the polar stratosphere. Heterogeneous chlorine activation as a prerequisite for ozone depletion occurs at low temperatures on different stratospheric particles, PSCs (consisting of water ice, nitric acid hydrates and supercooled liquid ternary  $H_2SO_4/HNO_3/H_2O$  particles) or on liquid binary  $H_2SO_4/H_2O$  particles (e.g., Solomon, 1999; Hofmann and Solomon, 1989; Cox et al., 1994; Ravishankara and Hanson, 1996; Peter, 1997; Pitts et al., 2009; Drdla and Müller, 2010; WMO, 2011).

The onset of chlorine activation occurs when temperatures fall below about 195K, which is still well above the temperature at which ice particles (on which the CRE mechanism focuses) form in the stratosphere. In Arctic winter, when the occurrence of ice PSCs is rare (Pitts et al., 2010), ozone depletion has also been reported (e.g. Harris et al., 2002b; Rex et al., 2002; Tilmes et al., 2004; WMO,



**Fig. 2.** Satellite-based observations of  $CH_4$ ,  $N_2O$  and CFC-12 by ACE-FTS (data version 3.0) as a function of latitude and altitude. The top row shows data averaged for the period from 22 February to 31 March for the years 2004–2010, while the bottom row corresponds to the period from 1 September–11 October. Note that the white hatched area indicates the altitudes where CFC-12 retrieval of ACE-FTS is below its detection limit. The plots were composed from 4819 individual profiles. Less than 2% of the profiles were omitted, namely those with known convergence problems in the  $N_2O$  retrieval reported by the ACE-FTS science team.

2011), which cannot be explained by the CRE mechanism. The coincidence that the CR-induced ionisation rate peaks in about the same altitude region where temperatures are low enough for heterogeneous chlorine activation cannot be interpreted as evidence that cosmic rays are the cause of the ozone depletion and does not support the CRE mechanism.

### 3.2. Quantitative understanding of polar ozone and predictions of the future of the ozone hole

A point made by Lu (2010a) is that based on the proposed CRE mechanism “...quantitative predictions of the Antarctic ozone hole in the future are given”. The analysis by Lu (2010a) expands earlier work (Lu, 2009), where a linear fit between total ozone measurements and CR activity was used to predict the mean total Antarctic ozone in spring. For example, for October 2008, a value of 187 Dobson units was predicted (Lu, 2009). In the CRE mechanism put forward by Lu (2010a), the linear dependence of polar ozone on CR activity is replaced by a quadratic dependence and equivalent effective stratospheric chlorine (EESC), a measure of stratospheric halogen loading (Newman et al., 2007), is introduced as an explanatory variable to allow fits to be made over longer time periods. This fit to EESC and the 11-year solar cycle-based CR modulation (Fig. 20c of Lu, 2010a) is not able to reproduce the ozone data, e.g. around 1990. This is expected since the fit is not based on the mechanisms responsible for ozone depletion and therefore is not suited for making predictions. The use of cosmic ray intensity as a predictor of the future development of the ozone hole has been criticised before by the argument that no strong correlation between Antarctic ozone levels and CR intensity is observed (Müller and Grooß, 2009).

Of course, the expected ozone recovery will be closely linked to EESC (WMO, 2011) and EESC has been used as a predictive parameter to estimate the time at which the Antarctic ozone hole will recover from the depletion by man-made halocarbons (Newman et al., 2006). However, inter-annual variability of the atmosphere prevents accurate predictions for a particular year from simulations. Furthermore, climate-change-driven changes in the stratosphere, e.g., in stratospheric temperatures and in stratospheric circulation, will have an important impact on future stratospheric ozone levels (e.g., IPCC/TEAP, 2005; WMO, 2011).

Moreover, regarding the future trend of the ozone hole, self-contradictory statements are made by Lu (2010a). On the one hand, quantitative predictions are reported, for example: “...the CRE model will predict the three-month (October–December) average zonal mean total O<sub>3</sub> values over Antarctica (60–90°S) in 2009 to be 219 ± 5 DU”. On the other hand, Lu (2010a) states: “Although atmospheric dynamics and meteorological conditions could cause large total O<sub>3</sub> fluctuations from year to year [...], a long-term trend of the polar O<sub>3</sub> loss is predictable”. The latter statement implies that accurate predictions for a particular year based on Eq. 8 of Lu (2010a) are not possible, but nonetheless such predictions are reported.

Also, as pointed out earlier (Müller and Grooß, 2009), the absolute value of the ozone column average is not correctly calculated by Lu (2009). This is also the case for the ozone averages reported by Lu (2010a). The “October average zonal mean total O<sub>3</sub>” over Antarctica (60–90°S) in 2006 derived from OMI data should be 211 DU, not 181 DU as stated in the first paragraph of Section 7 of Lu (2010a). Therefore, predictions of future polar total ozone values based on Eqs. 7 and 8 of Lu (2010a) cannot be considered meaningful.

### 3.3. Simulations of the ozone hole in numerical models

Lu (2010a) also implicitly criticises the ozone simulations of chemistry-climate models (CCMs). There are known problems with

the polar ozone simulations of CCMs (Eyring et al., 2006) that have been gradually improved recently and great efforts are being invested in validating and improving the performance of models in predicting ozone depletion (Austin et al., 2010; Eyring et al., 2010). Chemistry-climate models, results from which are displayed in Fig. 15b of Lu (2010a), do not use observed temperatures and winds and can therefore only calculate temperatures and ozone in a climatological sense. Therefore, statements about particular years of CCM results (as in the caption of Fig. 15b of (Lu, 2010a) are not meaningful. Chemistry transport models (CTMs), in which simulations are based on observed temperatures and winds, allow the observed ozone to be reproduced much better (e.g., Chipperfield, 2003; Grooß and Müller, 2007).

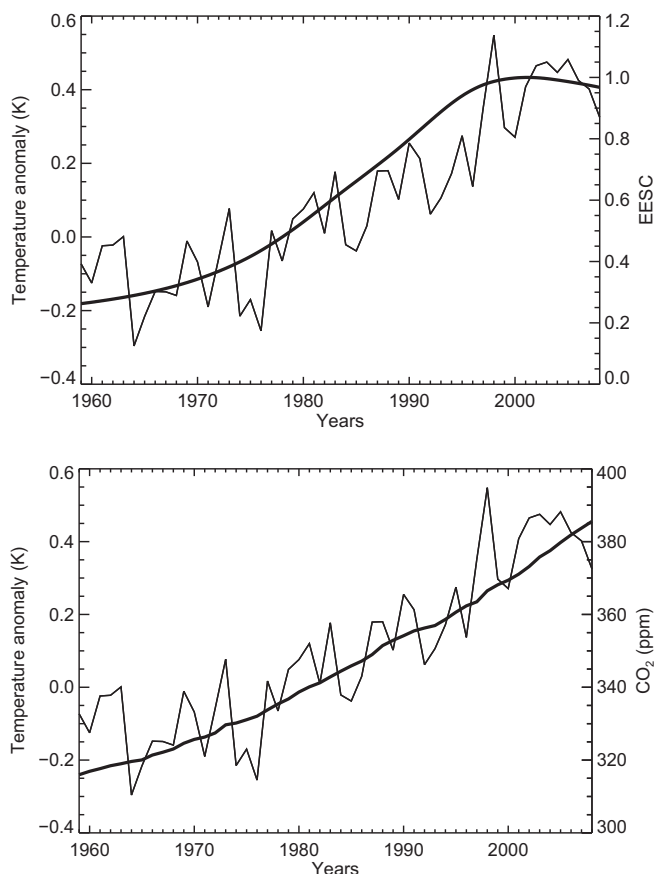
### 3.4. Temperature–ozone correlation

Lu (2010a) further reports a correlation between total ozone measurements and temperatures in the lower stratosphere (100 hPa) at Halley Research Station. In general, the correlation of total ozone and temperature and pressure in the lower stratosphere has been known for a long time. Low stratospheric ozone columns are associated with anti-cyclonic circulation, low stratospheric temperatures and a high tropopause (Dobson, 1963).

Further, because of the fact that ozone is an important absorber of atmospheric radiation, both at ultraviolet and at infrared wavelengths, a cooling of the Antarctic stratosphere caused by the occurrence of the ozone hole is expected. Indeed, (Jones and Shanklin, 1995) already pointed out the strong temperature response caused by the Antarctic ozone depletion in observations at Halley; they find that by 1995 a signal of ozone loss is apparent in the spring and summer temperature records, with temperatures at the 100 hPa level consistently close to, or lower than, the historical (1957–72) minimum for the period October to January. Similarly, Randel et al. (2009) report cooling trends in the Antarctic lower stratosphere during spring and summer for the period 1970–2007 associated with the development of the Antarctic ozone hole, which are substantially greater than those observed globally. Thus, the correlations between temperature and ozone column shown in Fig. 17 and 18 of Lu (2010a) are caused by the radiative effect of the reduced ozone concentrations in the ozone hole. The impact of the solar cycle on stratospheric temperatures has also been investigated, the maximum effect is in the order of a 1K response amplitude located in the tropical upper stratosphere (Ramaswamy et al., 2001; Randel et al., 2009).

### 3.5. Chlorofluorocarbons and climate change

Lu (2010a) further extends the analysis to surface temperatures. He reports that a time series of the surface temperature is correlated with EESC. This is the case to a certain extent as both chlorine source gases and CO<sub>2</sub> concentrations over the last century had a similar increase (however, the onset of CFC increase is somewhat later). In order to illustrate how easily different conclusions may be derived from correlations such as those shown in Fig. 21 of Lu (2010a), we show in Fig. 3 the relation between surface temperatures and stratospheric halogen loading (left panel) as well as surface temperatures and atmospheric CO<sub>2</sub> concentrations (right panel). The inspection of this figure (in the same way as Fig. 21 of Lu (2010a) is interpreted) could suggest that surface temperatures are equally well (or perhaps better) correlated with CO<sub>2</sub> concentrations than with EESC. Clearly, this should not be considered as a proof that CO<sub>2</sub> increases cause an increase in surface temperatures. In the same way, showing a correlation between EESC and surface temperatures in Fig. 21 of Lu (2010a) does not prove that EESC is the cause of the observed global warming.



**Fig. 3.** Time series of temperature anomalies (thin lines) and stratospheric chlorine loading (top, thick line) and carbon dioxide (bottom, thick line). Shown are combined land and marine temperature anomalies from the Hadley Centre (HadCRUT3, see <http://www.cru.uea.ac.uk/cru/data/temperature/>). The equivalent effective stratospheric chlorine (EESC), a measure of the stratospheric halogen loading after (Newman et al. (2007) assuming an age of air of 5.5 years (age of air spectrum width is 2.75 years and bromine scaling factor is 60). EESC is normalised to its peak value in the year 2001. The yearly average atmospheric carbon dioxide data (in mole fraction, ppm) are taken from the measurements of the NOAA Earth System Research Laboratory at Mauna Loa Observatory, Hawaii Keeling et al. (1976), see also [www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)).

Instead, the globally averaged surface temperatures are controlled by a combination of multiple effects, most prominently the increase in emissions of CO<sub>2</sub> and other greenhouse gases, but also changes in sulfate aerosol, cloud cover, the El Niño southern oscillation (ENSO) index and solar activity (see e.g., Solomon et al., 2007b).

In a more recent publication, Lu (2010b) continues these arguments by showing correlations between CO<sub>2</sub>, halocarbons and global surface temperature anomalies. He argues that CFCs show a larger greenhouse effect than CO<sub>2</sub> on the basis of a simplified radiation model calculation, looking at transmitted radiation at the surface and claims that the CO<sub>2</sub> lines would be saturated, which would represent a process not considered in the analyses reported in the IPCC report (Solomon et al., 2007b). This argument was already rebutted by Plass (1956) on the basis of the fundamentals of atmospheric radiation processes, arguments which are still valid although the state of radiation modelling has been greatly advanced since then (Plass et al., 2010). Briefly, the CO<sub>2</sub> lines in the centre of the absorption at the surface are indeed saturated but this is not the case in the wings of the lines nor at higher altitudes. The additional proposed CO<sub>2</sub> emissions indeed cause the major part of radiative forcing as it was extensively shown in the latest IPCC report (Solomon et al., 2007b).

Lu (2010a) further points to the recent drop in surface temperatures since about the year 2000. It has been shown that the climate over the 21st century may include periods of about a decade where the globally averaged surface air temperature shows no trend or even slight cooling in the presence of longer-term warming (Easterling and Wehner, 2009). A plausible explanation for the recent decrease of surface temperatures is a combination of low El Niño index, low solar activity, and the Kasatochi volcano eruption in 2008 (Schönwiese et al., 2010). Further, Solomon et al. (2010) find that because stratospheric water vapour concentrations decreased by about 10% after the year 2000 the rate of increase in global surface temperature over 2000–2009 slowed down by about 25% compared to what would have occurred due to increases in carbon dioxide and other greenhouse gases alone. While the details of these issues are still being debated, all known projections show that the trend of global warming will continue as long as CO<sub>2</sub> increases in the atmosphere (Solomon et al., 2007b). Indeed, because the recovery of the atmosphere from an anthropogenic CO<sub>2</sub> perturbation will take place on time scales of centuries or longer, the climate change that takes place due to anthropogenic CO<sub>2</sub> increases will be largely irreversible for 1000 years after emissions have stopped (Archer and Brovkin, 2008; Solomon et al., 2009).

#### 4. Conclusions

By analysing the ACE-FTS data, we demonstrated that there cannot be significant CFC decomposition besides photolytic decomposition in the stratosphere by the proposed CRE effect (Lu, 2010a). We further demonstrated that the methods of analysing ozone and global temperature data used by Lu (2010a) which are based solely on correlations of parameters, are not conclusive to explain the complex processes both of ozone depletion and surface temperature development. Thus, meaningful predictions based on the correlation of EESC and temperature anomalies cannot be drawn. The strong conclusions for climate models put forward by Lu (2010a) do not have a physical basis. The finding of the IPCC that “most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed rises in anthropogenic greenhouse gas concentrations” (Solomon et al., 2007b) remains unchallenged by the analysis of Lu (2010a).

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