Developing the ACE Stratospheric Chlorine Inventory

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ABSTRACT

The development of a stratospheric chlorine inventory utilizing ACE-FTS observations of numerous chlorine-containing gases was a significant scientific contribution from the early years of the ACE mission. Although this chlorine inventory has already been presented as a peer-reviewed publication, this chapter discusses the rationale for initiating this effort, some challenges encountered, the final results and some more recent related developments.

1. INTRODUCTION

In September 2000, I began graduate work on ACE under the supervision of Professor Peter Bernath in the Department of Chemistry at the University of Waterloo. At my first ACE science team meeting that October, I quickly got a sense of what an important project the ACE mission would be for Canada and for atmospheric science overall. From reading the scientific literature, I also recognized the impressive research that resulted from just a few days of ATMOS observations from four space shuttle missions, yet ACE would employ a similar approach from a small satellite that could yield multiple years of data. Since the primary objective of ACE was to obtain a better understanding of the chemical and physical processes related to ozone depletion, one paper that seemed particularly relevant to me was the ATMOS stratospheric chlorine budget for 1994 (Zander et al., 1996). The increase in stratospheric chlorine-containing gases was the largest anthropogenic contributor to ozone depletion and ATMOS was unique in its ability to measure stratospheric profiles of many of these gases. Supplementing the measured profiles with data from other sources (models or other measurements) gave a budget or inventory of chlorine-containing gases and a profile of total stratospheric chlorine (Cl_{TOT}) for the northern midlatitudes in November 1994. However, it was difficult to say how the present stratospheric chlorine inventory differed since the Montreal Protocol

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on Substances that Deplete the Ozone Layer had been adopted in 1987 and subsequently strengthened with numerous amendments (London, Vienna, Copenhagen, Montreal). The goal of the international community via the Montreal Protocol and amendments was to control the emission of ozone depleting substances, so that they their stratospheric concentrations would decline, thus allowing stratospheric ozone to recover to natural levels. Emerging evidence from ground-based measurements (Montzka et al., 1996; Prinn et al., 2000), balloon measurements (Sen et al., 1999) and stratospheric HCl measured by the satellite-borne HALOE (Anderson et al., 2000), suggested that atmospheric chlorine might actually be stabilizing or declining, but if ACE could provide a detailed stratospheric chlorine inventory for different regions of the world over a longer time frame, this would give a more complete picture than ever before, so I was determined to make this a major focus of my research.

2. COMPONENT CHLORINE SPECIES

Leading up to the ACE launch, I contributed to the mission in various ways, such as developing an automated system for a priori temperature and pressure profiles for ACE retrievals and participating in pre-launch instrument testing conducted at the Instrument Calibration Facility at the University of Toronto (Nassar et al., 2003). Finally, on August 12, 2003, ACE successfully launched from Vandenberg Air Force Base using a Pegasus-XL rocket. In early 2004, ACE-FTS spectra arrived and Chris Boone began to test his retrievals (Boone et al., 2005), while I looked at the results for some species, by plotting the profiles, taking averages, identifying outliers, etc. to assist him in retrieval development.

With the retrieval of the first few chlorine species HCl, $ClONO_2$, CH_3Cl, CCl_4, CCl_2F_2 (CFC-12), CCl_3F (CFC-11) and $CHClF_2$ (HCFC-22), the chlorine budget began to take shape and attempts to calculate Cl_{TOT} were made by taking the sum of organic chlorine (CCl_y) and inorganic chlorine (Cl_y) species according to the following:

$$CCl_y = 4[CCl_4] + 3[CCl_3F] + 2[CCl_2F_2] + [CH_3Cl] + [CHClF_2] + 3[CCl_2FCClF_2] + [CH_3CClF_2] + 3[\mathit{CH_3CCl_3}] + \textit{minor species}$$

$$Cl_y = [HCl] + [ClONO_2] + [COClF] + [\mathit{ClO}] + 2[\mathit{ClOOCl}] + [\mathit{HOCl}] + 2[\mathit{COCl_2}]$$

$$Cl_{TOT} = CCl_y + Cl_y$$

Unfortunately, the differing altitude ranges of retrieved profiles for each species and those requiring data from other sources (italicized above) meant

there was still much additional work to be done. Continual refinements to the retrievals were implemented, in many cases extending the altitude ranges with different sets of microwindows. In addition, COClF was retrieved from ACE-FTS spectra (Rinsland et al., 2007) as well as the first space-borne measurements of Cl_2FCClF_2 (CFC-113) and CH_3CClF_2 (HCFC-142b) (Dufour et al., 2005). Efforts to retrieve ClO resulted in partial success, with retrieval only possible during periods of lower stratospheric ClO enhancement at southern high latitudes. Data for chlorine species that could not be retrieved from ACE observations at that time were acquired such as upper stratospheric ClO from Odin-SMR (Urban et al., 2005; Berthet et al., 2005), HOCl from MIPAS on ENVISAT (von Clarmann et al., 2006), $COCl_2$ from MkIV balloon measurements (Toon et al., 2001), CH_3CCl_3 and numerous minor species from the SOLVE aircraft campaigns (Schauffler et al., 2003) and ClO-OCl (ClO dimer) concentrations were calculated from ClO (Stimpfle et al., 2004).

3. A COMPRENSHIVE CHLORINE INVENTORY

The ACE-FTS retrieved chlorine species for one full year were supplemented with these other data to yield a comprehensive chlorine inventory with calculated Cl_{TOT} profiles for 5 latitude zones: northern high latitudes (60-82°N), northern midlatitudes (30-60°N), tropics (30°S-30°N), southern midlatitudes (30-60°S) and southern high latitudes (60-82°S) (Nassar et al. 2006a), which was followed by a fluorine inventory using a similar approach shortly after (Nassar et al., 2006b).

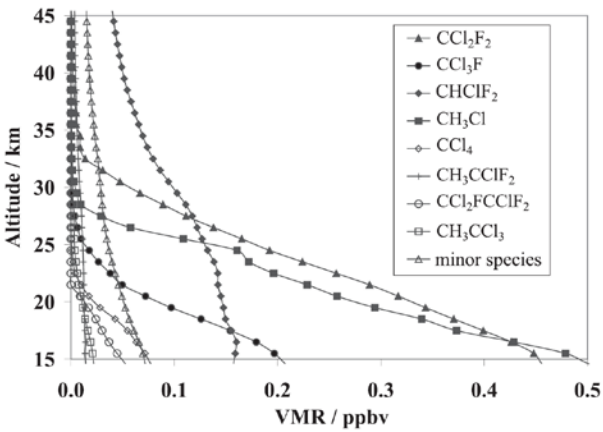

***Figure 1**. Average southern midlatitude organic chlorine profiles in 2004.*

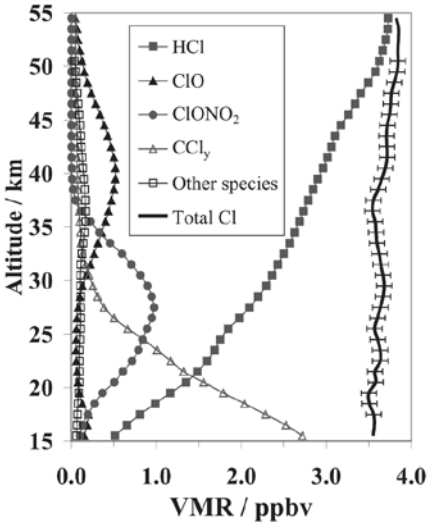

***Figure 2**. Stratospheric chlorine inventory for the northern midlatitudes in 2004. Error bars indicate the 1σ precision on Cl_{TOT} for 17.5-50.5 km.*

The northern and southern midlatitude mean Cl_{TOT} profiles were relatively flat with a mean value of 3.65±0.09 ppb and slope of 0.007±0.001 ppb/km. There were slightly lower values of Cl_{TOT} in the tropics and slightly higher values at high latitudes (see Table 1), a pattern of latitudinal variation and slopes that confirmed the beginning of a decline in global stratospheric chlorine, consistent with current knowledge of atmospheric circulation patterns and tropospheric measurements (Prinn et al., 2000).

Table 1. Mean total chlorine and the slope (with 1σ precision) for 17.5 - 50.5 km altitude in five latitude zones.

Zone	***Mean Cl_{TOT}, ppb***	***Slope, ppb/km***
Northern high latitudes (60-82°N)	3.74 ± 0.12	0.010 ± 0.001
Northern midlatitudes (30-60°N)	3.65 ± 0.09	0.007 ± 0.001
Tropics (30°S-30°N)	3.62 ± 0.11	0.009 ± 0.001
Southern midlatitudes (30-60°S)	3.65 ± 0.09	0.007 ± 0.001
Southern high latitudes (60-82°S)	3.71 ± 0.16	0.014 ± 0.001

The key results of the chlorine inventory work were included in Chapter 1 of the World Meteorological Organization (WMO) Scientific Assessment of

Ozone Depletion: 2006 (Clerbaux et al., 2007). These WMO reports occur every 4 years and serve as the primary scientific document for international policy regarding protection of the ozone layer. The chlorine inventory results provided new evidence of the effectiveness of the Montreal Protocol at reducing the atmospheric chlorine burden. Although by the time of publication, multiple other methods had already demonstrated a decline in the atmospheric burden of many ozone depleting gases, the ACE chlorine inventory reinforced those findings by an independent method. Together the collection of papers using multiple approaches to demonstrate a decline in ozone depleting substances has firmly established the effectiveness of the Montreal Protocol, which is often regarded as the most successful global environmental treaty to date.

After my PhD, my scientific focus shifted to the troposphere, greenhouse gases and other satellites, but I remain involved with ACE. Fortunately, much ACE chlorine-related work has continued with developments such as validation of important chlorine species (Mahieu et al., 2008; Froidevaux et al., 2008), global retrievals $COCl_2$ and COClF (Fu et al., 2007; 2009), studies of chlorine partitioning (Dufour et al., 2006; Santee et al., 2008), as well as multi-year analyses of trends in HCl (Froidevaux et al., 2006; Lary et al., 2007; Lary & Aulov, 2008) and many other chlorine and fluorine species (Rinsland et al., 2005; Brown et al., 2011).

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