A comparison of measurements from ATMOS and instruments aboard the I:R-2 aircraft: I halogenated gases

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Abstract. We have compared volume mixing ratio profiles of N2O, ClF-11, Cl-C-12, CC14, SF6, and HCl measured for the mid-latitude stratosphere by the ATMOS Fourier transform spectrometer during the ATLAS-3 Space Shuttle mission of Nov 1994 with in situ measurements acquired aboard the NASA I:R-2 aircraft during the same time period. Consistency is demonstrated between the space-borne and in situ correlations of [Cl-C-11] and [SF6] with [N2O] at all altitudes and of [ClW-12] with [N2O] for [N2O] < 250 ppb. ATMOS measurements of [Cl-C-12] are 10% lower than in situ data near the tropopause, and ATMOS observations of [CC14] are uniformly 15-20% higher. ATMOS and in situ observations of [HCl] vs [N2O] agree to within 10% for [HCl] > 1 ppb, but ATMOS measurements of [I-ICl] exceed in situ observations for smaller [I-ICl]. The sum [ClONO2]+[I-ICl] observed by ATMOS is consistent with the levels of inorganic chlorine inferred from in situ measurements of chlorine source gases. Photochemical model simulations of ATMOS observations of [ClONO2] and [I-ICl] are improved by allowing a minor channel of the reaction ClO+OH to produce IICl.
Introduction

The ATMOS (Atmospheric Trace MOlecule Spectroscopy) Fourier transform spectrometer uses solar occultation measurements to derive volume mixing ratio (VMR) profiles of more than 30 constituents in the earth's atmosphere [Gunson et al., 1996]. During the ATMOS/ATLAS-3 Space Shuttle mission of November 1994, a coincidence was obtained at mid-latitudes with measurements from the final two flights of the NASA Earth Reconnaissance aircraft (ER-2) during the ASHOE/MAIISA campaign. In a companion paper [Chang et al., 1996], good agreement is demonstrated between ATMOS and ER-2 measurements of [N2O], and correlations of long-lived tracers [O3],[NOy],[NO2], and [ClI4] with [N2O]. This paper examines correlations of [ClICl1],[ClICl12],[ClICl13],[ClICl14],[ClICl15], and [ClI1Cl] with [N2O] measured by the two platforms, and compares ATMOS measurements of inorganic chlorine with photochemical model simulations.

Twelve ATMOS occultations, occurring between 4 Nov and 9 Nov 1994, are near-coincident with the mid-latitude (30-510 N) portions of ER-2 flights on 2 Nov and 4 Nov, into or out of Moffett Field, CA (37° N). Chang et al., [1996] discuss the coincidence criteria more fully. Although these data arc differentiated with respect to observed temperature (the colder of the ATMOS and ER-2 data form a good temperature coincidence and are denoted "cold;" the remainder arc classified as "warm"), no difference associated with variations in temperature is observed in the level of agreement of correlations of long-lived tracers measured from ATMOS and the ER-2 [Chang et al., 1996]. Measurements of halogenated gases are examined here as correlations vs the long-lived tracer [N2O] to account for the dynamical histories of the sampled air masses. All ER-2 correlations use the data for [N2O] obtained by ATLAS (Airborne, ‘J’unable Laser Absorption Spectrometer) [Loewenstein et al., 1989], which, for the flight segments considered here, are largely within 1% of [N2O] measured by ACATS-IV (Airborne Chromatograph for Atmospheric Trace Species) [Elkins et al., 1995]. The comparisons are based on Version 2 ATMOS data.

Halogen Source Gases

ATMOS measures VMRs of CFC-11 (CCl3F), CFC-12 (CCl2F2), CCl1F2, CCl13Cl, and CCl4, which together constitute ~80% of total tropospheric organic chlorine [Zander et al., 1996]. The ACATS-IV gas chromatography on the ER-2 measures ClIC11, CFC-12, CFC-113 (CCl2F-CFC12), CCl3CCl3, CCl4, and halon-211 (CBrClF2), which also comprise ~80% of tropospheric chlorine. 130th ATMOS and ACATS-IV measure the
long-lived tracer SF$_6$. These gases are measured by ACATS-IV with precisions and accuracies of better than 1% and 2% respectively, at intervals of 3 min for all halogenated gases, except SF$_6$ which is measured every 6 min. ACATS-IV is calibrated on the ground against the same standards that are used in the NOAA/CMDL network of tropospheric measuring stations [Elkins et al., 1993], and in flight by running a sample of air with mixing ratios near stratospheric levels once every 4 ambient samples or 15-30 min.

Except for [1 ICI], the species measured by ATMOS examined in this paper are retrieved using transitions at wavenumbers less than 1000 cm$^{-1}$, accessible with either Filter 9 (625-2450 cm$^{-1}$) or Filter 12 (625-1400 cm$^{-1}$). At wavenumbers < 1000 cm$^{-1}$, spectra from Filter 9 exhibit degraded signal-to-noise-ratios (SNR) compared with Filter 12 due to the shape and width of the optical bandpass functions. This effect is evident in the large variability in VMRS of species which are retrieved by fitting a single, spectral window at low wavenumbers, such as CFC-11, CFC-12, CCl$_4$, CClON2, and SF$_6$. This problem was especially severe during ATLAS-3, due to lowered instrumental gain settings. Retrievals of halogenated gases obtained using Filter 9 are thus not considered in the present paper. The majority of other gases retrieved in Filter 9 are based on fitting features at higher wavenumbers or an ensemble of spectral windows and are relatively unaffected by these difficulties.

Figure 1a shows correlations of [CFC-11] with [N$_2$O]. ATMOS measures [CFC-11] with an estimated precision of better than 5% (reported precisions, meant to reflect random errors in the measurement, are calculated during the retrieval process from considerations such as residual errors in the fitting of spectra) and systematic uncertainty of 1190, based on combining uncertainties in the spectroscopic band intensities with uncertainties related to the tangent pressure assignment [Gunson et al., 1996]. The altitude range of the comparison extends from the tropopause to $\sim$30 km ([N$_2$O]=100 ppb). The agreement between ATMOS and IIR-2 measurements of [CFC-11] is excellent, even in the region near the tropopause where the accuracy of the space-based measurements might be expected to be diminished.

Correlations of [CFC-12] with [N$_2$O] are shown in Fig. 1b. ATMOS measures [CFC-12] with an estimated precision of better than 5% and a systematic uncertainty of 9% [Gunson et al., 1996]. The ATMOS [CFC-12] measurements are consistent with IIR-2 data for [N$_2$O] < 250 ppb, but the observations deviate at higher [N$_2$O], with the ATMOS data being 10% low just above the tropopause. The bulk of the mid-latitude (25-49° N)
correlations of [CFC-12] vs [N2O] measured during AT1, AS-3 (not shown) exhibit a sharp transition in [CIC-12] from ~450 ppt to known tropospheric values, for [N2O] ~310 ppb. As this behavior is not exhibited by other long-lived tracers measured by ATMOS, a temperature-dependent bias is suspected in the version 2 retrievals of [CFC-12].

Figure 1c shows [CCl4] vs [N2O]. ATMOS measures [CCl4] with an estimated precision of 5-10% and a systematic uncertainty of 20% [Gunson et al., 1996]. The ATMOS values in Fig. 1c are uniformly 15-20% higher than the in situ data. CCl4 is retrieved by fitting the ν3, ν1+ν4 bandhead centered at 796 cm⁻¹ [Brown et al., 1996], using the temperature-dependent absorption cross sections and band intensities of Orlando et al. [1992]. The measured integrated band intensities for these transitions vary considerably in the literature [Pugh and Rae, 1976], and an error in the value adopted in the ATMOS retrievals could be responsible for the deviation. Figure 1d shows comparisons of [SlF6]. ATMOS measures [SlF6] with an estimated precision of 5-10% and a systematic uncertainty of 11% [Gunson et al, 1996]. The ATMOS and in situ data are consistent within their combined uncertainties, and can be used to provide an accurate estimate of the age of stratospheric air.

Inorganic Chlorine

The coincidence between ATMOS and ER-2 measurements in Nov 1994 provides a test of our understanding of partitioning of inorganic chlorine (Cl₃) at mid-latitudes. ATMOS measures [HCl] and [ClON02], which are the dominant forms of Cl₃ in the lower stratosphere for air unaffected by polar stratospheric clouds (1%). In situ instruments aboard the ER-2 observe [HCl] and [ClO], the latter being the reactive form of Cl₃ that regulates photochemical loss of ozone. Although ATMOS does not observe [HCl] and [ClONO₂] in the same occultations, constituents such as [O₃] and [N2O] measured in multiple optical filters provide a framework for combining these observations.

Measured correlations of [HCl] vs [N2O] arc shown in Fig. 2a. ATMOS measures [HCl] in filter 3 with an estimated precision of better than 5% and a systematic uncertainty of 5% [Gunson et al., 1996]. The Al JAS (Aircraft Laser infrared Absorption Spectrometer) diode laser instrument provides in situ measurements of [HCl] using transitions in the same spectral band used by ATMOS [Webster et al., 1995]. For the Nov 1994 flights, Al JAS reports [HCl] at 6 minute intervals with a precision of 0.07 ppb (5% at 1.5 ppb, increasing to 20% at 0.35 ppb) and an accuracy of 5%. For [HCl] > 1 ppb, the ATMOS observations are ~10% higher than the ER-2 data, but the measurements agree within their combined uncertainties. For [HCl] < 1 ppb, the ATMOS measurements are higher on average by
-40%, although the upper range of variability of the ER-2 data nearly overlap the space-based observations.

Stratospheric [I CI] observed by ALIAS at a given [N₂O] during Nov 1994 is ~60% higher than measured by ALIAS in May 1993, where mid-latitude [I CI]/[Cl_y] ratios of 0.4 were reported for the N11, compared to model results of ~0.7 [Webster, 1994]. The deviation of [I CI] observed by ALIAS from model expectations appears correlated with sulfate aerosol loading [Webster et al., 1995], which peaked in 1992 following the 1991 eruption of Mount Pinatubo. Although ATMOS made observations of [I CI] in March 1992, only limited data were obtained below 25 km at latitudes, because the sun tracker performed poorly where the aerosol loading was dense. However, ATMOS observations in March 1992 at other latitudes and in April 1993 showed no readily discernible aerosol effect on [I CI] or [ClONO₂] [e.g., Rinsland et al., 1994].

The correlation of [ClONO₂] vs [N₂O] measured by ATMOS is plotted in Fig. 2b. ATMOS detects [ClONO₂] with an estimated precision of 10-20% and a systematic uncertainty of 20% [Gunson et al., 1996]. Peak [ClONO₂] of 0.9 ppb occurs at ~26 km altitude ([N₂O] ~ 120 ppb), leading to a maximum of ~0.5 for the [ClONO₂]/[I CI] ratio. Although in situ measurements of [ClONO₂] have never been made, [ClONO₂] inferred from simultaneous measurements of [ClO], [NO], and [NO₂] in previous ER-2 missions are in broad agreement with both theory and ATMOS observations at aircraft altitudes [Stimpfle et al., 1994; Salawitch et al., 1994].

Figure 2c shows ATMOS measurements of [I CI]+[ClONO₂] vs [N₂O] compared with an estimate of total inorganic chlorine [Cl] derived from subtracting total organic, chlorine measured from the ER-2 during the 1992 AS1311 aircraft campaign from the total organic chlorine loading measured in the troposphere, corrected for the age of stratospheric air [Woodbridge et al., 1995]. The [Cl] relation shown in Fig. 2c has been increased by 6.7% relative to the published relation to account for changes in stratospheric chlorine [Zander et al., 1996]. The sum [I CI]+[ClONO₂] is determined by adding to each ATMOS measurement of [I CI] a value of [ClONO₂] interpolated from an average of the four filter 12 profiles. For air unprocessed by PSCs at altitudes below 24 km ([N₂O] > 140 ppb), [I CI]+[ClONO₂] is expected to equal total [Cl_y] to within several percent. Assuming the destruction of organic source gases with increasing altitude is balanced by the formation of inorganic chlorine, the consistency of [I CI]+[ClONO₂] measured by ATMOS and the inferred [Cl_y] of Woodbridge et al. [1995] provides strong corroborative
evidence for the ability of ATMOS to accurately measure the major components of Cl systems. Zander et al. [1996] demonstrate that total inorganic chlorine measured by ATMOS (supplemented by remote-sensing observations of [ClO] and [ClOCI]) balances with total organic chlorine measured by ATMOS (supplemented by balloon-borne in situ measurements of [ClFC113] and [Cl3CCl3]) over the altitude range 16 to 50 km, resulting in a constant value for the sum of inorganic and organic chlorine.

A constrained photochemical model [Salawitch et al., 1994] is used to test our understanding of partitioning within the inorganic chlorine family. For each constituent, the model solves for the variation of concentration with time that results in no net production (or loss) over a 24 hr period, for local solar conditions. Photolysis rates are calculated using profiles of ozone and temperature measured by ATMOS and a surface albedo of 0.24, and include effects of Rayleigh scattering [Minschwaner et al., 1993]. The model is constrained by ATMOS measurements of [O3], [NOy], [HCl] + [ClONO2], [112.0], [Cl 14], [C2H6], and [CO], supplemented with correlations of [Br/ vs [N2O], [I2] vs pressure, and aerosol surface area profiles from the SAGE II satellite-borne instrument [G. K. Yue and L. W. Thomason, private communication, 1996]. Approximately 200 reactions, including those describing heterogeneous chemistry, are included.

The model is constrained to match the sum of [Cl] and [ClONO2] as defined by the ATMOS data, but not their ratio. In the middle stratosphere, the [ClONO2]/[HCl] ratio is sensitive to the yield of HCl from the reaction ClO + O1 [e.g., Michelsen et al., 1996]. DeMore et al. [1994], based on a review of the kinetic literature, note the yield of HCl from this reaction is uncertain between limits of 0 and 14%. The models considered here utilize two sets of kinetic parameters: the first uses reaction rate constants and photolytic cross sections from the JP, 1994 compilation [DeMore et al., 1994] and a 0% HCl yield from ClO + O1; the second ("Model C" of Michelsen et al., [1996]) incorporates modified rate constants for reactions Cl + Cl14 and O1 + Cl based on a reexamination of the kinetic literature, a revised quantum yield of O1D from photolysis of O3 [Michelsen et al., 1994], and a 7% yield of HCl from the reaction ClO + O1. Differences in the partitioning of [ClONO2] and [HCl] predicted by the two models are on balance due to production of HCl from ClO + O1; the sensitivity of model results to each kinetic parameter is discussed in Michelsen et al. [1996].
Model results for [HCl] and [ClONO₂] at local sunset arc compared with ATMOS observations in Figs. 2a and b. For [N₂O] > 200 ppb, both models predict similar levels of [HCl] and are consistent with the partitioning of [ClONO₂] and [HCl] observed by ATMOS. At lower levels of [N₂O], the model allowing for production of HCl from ClO+O1 results in better agreement with the ATMOS data. Figure 2d shows a comparison of modeled [ClO], calculated subject to constraints imposed by the ATMOS data but corresponding to mid-afternoon solar conditions sampled by the ER-2, with coincident observations of [ClO], which is measured on the ER-2 with a 2σ accuracy of 30% [Stimpfle et al., 1994]. Although both models overestimate [ClO] for [N₂O] < 240 ppb, data for [ClO] agree more closely with the model which allows for production of HCl from ClO+O1.

A detailed analysis of ATMOS measurements combined with either MAS (Millimeter-wave Atmospheric Sounder) or MLS (Microwave Limb Sounder) observations of [ClO] over a wide range of latitudes and altitudes during Nov 1994 show that observed levels of [ClO] and [ClONO₂] relative to [HCl] are overpredicted by models, unless they allow for an additional source of HCl besides the reactions of Cl with hydrocarbons and HO₂ [Michelsen et al., 1996; Rinsland et al., 1996]. ATMOS measurements of chlorine partitioning inside the Antarctic vortex during ATLAS-3, which revealed [HCl] ~ [Clg] and [ClONO₂] << [HCl] for air with severely depleted levels of [O₃] and [NOₓ], are likewise consistent with theory, testing a different photochemical regime (very low [O₃], and high [Cl]/[ClO] ratios) than the mid-latitude observations [Rinsland et al., 1996]. Overall, broad agreement is obtained between theory and ATMOS, MAS and MLS observations of inorganic chlorine gases, provided that production of HCl from ClO+O1 is considered. The decade-long record of ATMOS observations of organic chlorine allows distributions and trends to be quantified for gases that are both precursors of ozone destroying radicals and significant contributors to greenhouse warming [Zander et al., 1996].

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Figure Captions

Figure 1: Correlations of [CHCl, CFC-12, [CCl4], and [SF6] vs [N2O] measured by ATMOS and instruments aboard the ER-2, differentiated with respect to temperature as in Chang et al. [1996]. Measurements of [CHCl, CFC-12, [CCl4], and [SF6] are made on the ER-2 by ACATS-IV [Elkins et al., 1995]; [N2O] is measured by ATLAS [Loewenstein et al., 1989]. ATMOS error bars reflect estimated precision; systematic uncertainties are discussed in the text.

Figure 2: Correlations of [HCl], [ClONO2], inferred [Cl2], and [ClO] vs [N2O] measured by ATMOS and instruments aboard the ER-2, and derived from model calculations. Measurements of [HCl] are made on the ER-2 by ATLAS [Webster et al., 1994]; [ClO] is measured by resonance fluorescence of Cl [Stimpfle et al., 1994]; and [N2O] is measured by ATLAS [Loewenstein et al., 1989]. Model results for [ClO] are shown for SZA of 65°, rather than sunset. J. A. 94 [DeMore et al., 1994] assumes 0% HCl yield on O1+ClO; Model C is as described in Michelsen et al., 1996. Dashes in third panel (c) represent uncertainty in [Cl2] of Woodbridge et al., 1995.