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Validation of CFC-12 measurements from the Improved Limb Atmospheric Spectrometer (ILAS) with the version 6.0 retrieval algorithm

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[1] Measurements of CFC-12 were made by the Improved Limb Atmospheric Spectrometer (ILAS) between 57°N and 72°N in the Northern Hemisphere and between 64°S and 89°S in the Southern Hemisphere. ILAS was launched on 17 August 1996 on board the Advanced Earth Observing Satellite (ADEOS). The ILAS validation balloon campaigns were carried out from Kiruna, Sweden (68°N, 21°E), in February and March 1997 and from Fairbanks, Alaska (65°N, 148°W), in April and May 1997. During these validation balloon campaigns, CFC-12 was measured with the in situ instruments ASTRID, BONBON, and SAKURA and the remote sensing spectrometers MIPAS-B, FIRS-2, and MkIV. ILAS version 6.0 CFC-12 profiles obtained at the nearest location to the validation balloon measurement are compared with these validation balloon measurements. The quality of ILAS CFC-12 data processed with the version 6.0 algorithm improved significantly compared to previous versions. Low relative differences between ILAS CFC-12 and the correlative measurements of about 10% were found between 13 and 20 km. The comparison of vertical profiles shows that ILAS CFC-12 data are useful below about 20–22 km inside the vortex and below about 25 km outside the vortex. However, at greater altitudes the relative percentage difference increases very strongly with increasing altitude. Further, correlations of CFC-12 with N_2O show a good agreement with the correlative measurements for N_2O values of $N_2O > 150$ ppbv. In summary, ILAS CFC-12 data are now suitable for scientific studies in the lower stratosphere. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 3360 Meteorology and Atmospheric Dynamics: Remote sensing; *KEYWORDS:* CFC-12, ILAS, validation

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1. Introduction

[2] Dichlorodifluoromethane, CF_2Cl_2 or CFC-12, has accumulated in the atmosphere owing to its use as a propellant gas in aerosol sprays, as a foaming agent, and as a refrigerant. Although emissions of CFC-12 have decreased substantially since the 1990s, mixing ratios of CFC-12 in the atmosphere continue to increase today because emissions are still greater than the small losses associated with its long atmospheric lifetime of around 100 years. However, the mixing ratios of CFC-12 are increasing at a much slower rate than in previous decades. Growth rates between 1997 and 2001 were between 2 and 3 pptv yr^{-1} [*World Meteorological Organization* (*WMO*), 2003]. Through UV photolysis of CFC-12 chlorine atoms are released in the stratosphere. The chlorine atoms eventually initiate an efficient catalytic chain reaction resulting in the net destruction of ozone, as first postulated by *Molina and Rowland* [1974] and *Crutzen* [1974]. Additionally, CFC-12 contributes to the anthropogenic greenhouse effect due to its

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Table 1. Error Analysis for the ILAS Version 6.0 CFC-12 Data, Part 1

Altitude, km	Internal,[a] pptv	External, pptv	Average,[b] pptv	Total Error,[c] pptv	Total Error,[d] %	Repeatability, %
10	190	30	530	190	35.1	2.5
15	100	40	400	110	27.2	7.6
20	150	40	240	150	63.4	7.7
25	170	80	220	190	87.9	14.1
30	250	80	110	260	234.9	88.2
35	460	10	40	460	1091.3	204.4

[a] Average of internal errors associated with all retrievals.

[b] Average of all retrieved CFC-12 mixing ratios.

[c] Root-sum square of internal and external errors.

[d] Total error (pptv) divided by average (pptv).

strong absorption characteristics in the 8–13 μm region [e.g., *Zhong et al.*, 1993]. CFC-12 is emitted at the surface of the Earth and has no significant sinks in the troposphere. It is mainly photolized in the middle to upper stratosphere. Thus CFC-12 is a long-lived atmospheric tracer gas [e.g., *Solomon and Garcia*, 1984], which may be useful for the understanding of atmospheric dynamics and for testing the accuracies of the transport codes of atmospheric models. As shown here, with the ILAS version 6.0 retrieval algorithm, the ILAS CFC-12 data are now significantly improved compared to previous versions and can be used for such studies. This paper presents the validation of ILAS CFC-12 data through comparisons with balloon measurements made during the ILAS validation balloon campaign. Additionally, we will compare correlations of N_2O with CFC-12 from ILAS with those obtained from the validation measurements.

2. ILAS Data

[3] The Improved Limb Atmospheric Spectrometer (ILAS) on board the Advanced Earth Observing Satellite (ADEOS) measured atmospheric species continuously from 1 November 1996 to 30 June 1997. ILAS is a solar occultation satellite sensor which measures the absorption of stratospheric species in the infrared region of solar radiation [*Sasano et al.*, 1999]. During the 8-month measuring period the latitudes of 57°–72°N and 64°–89°S were covered. Measurements were made about fourteen times per day in each hemisphere. Vertical profiles are obtained using an onion peeling method described by *Yokota et al.* [2002]. The retrieval altitude grid is 1 km in geometric altitude. The estimated time taken to measure a profile is less than 30 s and about 3–4 min if exoatmospheric measurements are included.

[4] The main differences between the version 5.20 and version 6.0 retrieval algorithms are the revised calculation of absorption coefficients, revised determination of the tangent height, updated molecular spectroscopic parameters, and revised initial values of climatological parameters like gas concentration, temperature, and pressure. Especially the revised calculation of absorption coefficients using "pseudo line" parameters led to an improvement of the CFC-12 data quality. CFC-12 absorptions at 850 to 950 cm^{-1} and 1050 to 1200 cm^{-1} are measured with the infrared spectrometer of ILAS.

[5] The error analysis for the ILAS CFC-12 measurements follows the method described in detail by *Yokota et al.* [2002] and *Sugita et al.* [2002]. The total errors are defined as the root sum of squares of the internal and external errors. The internal errors are evaluated for each measured CFC-12 value using the residuals of the spectral fitting. The external errors consist of the uncertainties in the temperature profiles used as input for gas retrieval and the approximations necessary for the nongaseous component correction [*Yokota et al.*, 2002]. These errors are shown in Table 1.

[6] Further, in Table 1 the repeatability of the measurements evaluated from the data obtained during a dynamically quiescent period (10 days at the end of March 1997 at latitudes between 87.0°S and 87.9°S) in the Southern Hemisphere is listed. The repeatability is defined as the standard deviation divided by the average mixing ratio for the quiescent period. The total errors are significantly larger than the repeatability for all altitudes, suggesting that the error analysis performed in version 6.0 ILAS retrieval algorithm still overestimates the internal errors as suggested by *Yokota et al.* [2002].

[7] Table 2 shows the systematic bias errors associated with the nongaseous component correction of the ILAS retrieval algorithm [*Yokota et al.*, 2002]. To evaluate the systematic errors caused by the simple linear interpolation between the window spectral elements, we simulated transmittance using infrared absorption spectra for sulfate aerosols (50 and 75 wt% H_2SO_4/H_2O binary solutions) and PSCs (nitric acid trihydrate (NAT), supercooled ternary solutions (STS) for four compositions, and ice) as the nongaseous component and a priori profiles as the gaseous component. Using these simulated transmittances, retrievals of the verti-

Table 2. Error Analysis for the ILAS Version 6.0 CFC-12 Data, Part 2[a]

Altitude, km	S(75),[b] pptv	S(50),[b] pptv	NAT, pptv	ICE, pptv	STS(5,37),[c] pptv	STS(33,15),[c] pptv	STS(47,3),[c] pptv	STS(60,0.5),[c] pptv
15	14	10	30	92	−1	25	30	32
20	30	23	66	202	−2	54	66	71
25	66	50	145	447	−4	121	147	157

[a] Systematic biases caused by the nongaseous component correction are listed for three selected altitudes. The error values for two selected aerosol extinction coefficients (AEC) at 780 nm are shown (AEC = 0.0005 km^{-1} for sulfate aerosols and AEC = 0.001 km^{-1} for PSC).

[b] S(75) and S(50) denote 75 and 50 wt% H_2SO_4/H_2O binary solutions, respectively.

[c] STS(5,37), STS(33,15), STS(47,3), and STS(60,0.5) denote 5, 33, 47, and 60 wt% H_2SO_4/37, 15, 3, and 0.5 wt% HNO_3/H_2O ternary solutions, respectively.

Table 3. List of the Balloon and ILAS Measurements in 1997 Used for the Comparison[a]

Balloon Instrument	Validation Date	Validation Time	Validation Latitude	Validation Longitude	Validation DPV_{edge}, %	ILAS Date	ILAS Time	ILAS Latitude	ILAS Longitude	ILAS DPV_{edge}, %	Difference Time	Difference Distance, km
ASTRID	10.02	11:15	67.94	27.45	15	10.02	13:13	68.44	34.96	20	−01:57	314
ASTRID	25.02	11:10	68.47	25.99	35	25.02	14:49	69.65	25.27	35	−03:39	135
BONBON	11.02	09.53	68.01	25.54	30	11.02	14:26	68.57	17.39	35	−04:33	341
SAKURA	22.02	09.30	67.89	21.10	35	22.02	14:30	69.48	27.04	35	−05:00	154
SAKURA	18.03	07:26	67.89	21.10	25	18.03	15:24	69.55	38.34	10	−07:58	601
MIPAS-B	24.03	19:42	69.60	30.10	30	24.03	16:03	69.11	34.49	30	03:38	180
FIRS-2	30.04	00:02	69.30	−148.91	−30	30.04	06:01	63.78	−149.12	−35	−05:59	614
MKIV	08.05	11:29	68.07	−147.35	−20	08.05	05:45	62.34	−141.92	−25	05:43	685

[a] The dates and times of the measurements are given in "DD.MM" and "hh:mm." The locations are given in latitude degrees north and longitude degrees east (+) and west (−) and the time difference in "hh:mm." For ASTRID, BONBON, FIRS-2, MkIV, and ILAS the averaged location of the vertical profile and the time at $t = 0$ is used. For MIPAS-B the averaged location and time and for SAKURA the time and location near 20 km was used. DPV_{edge} values are taken from *Kanzawa et al.* [2003, Figure 5] at 20 km ((+) inside the vortex, (−) outside the vortex), see text for definition.

cal profile of the gaseous concentration of CFC-12 were made after applying the linear interpolation method for the nongaseous contribution in the version 6.0 retrieval algorithm. Assuming typical air number densities at altitudes of 15, 20, and 25 km, the error for the retrieved CFC-12 mixing ratios ranged from 10 to 66 pptv for the two types of sulfate aerosol with a value of the aerosol extinction coefficient (AEC) at 780 nm of 0.0005 km^{-1}. Further, systematic biases for the several types of PSCs (AEC = 0.001 km^{-1}) are listed in Table 2. The largest errors are found for ice (e.g., 202 pptv in 20 km). This is due to the fact that the largest residuals of the aerosol extinction coefficient occur at wavelengths between 8.3 and 9.6 μm [*Yokota et al.*, 2002, Figure 5]. The absorption of CFC-12 mainly occurs in this wavelength region.

3. Balloon Data

[8] During the eight month period of continuous operation of ILAS, validation experiments were conducted in Kiruna, Sweden (68°N, 21°E), and Fairbanks, Alaska (65°N, 148°W), from February to May 1997. Note that all these measurements were conducted in the Northern Hemisphere. Balloon validation data (except ozone [*Sugita et al.*, 2002]) are not available for the Southern Hemisphere. Eight balloon flights were made using six different techniques for measuring CFC-12. While the measurements in Kiruna were made well inside the polar vortex, with one exception which was made close to the edge of the vortex, the measurements in Fairbanks were made outside the polar vortex [*Kanzawa et al.*, 2003]. The balloon measurements are listed in Table 3 and a short description is given below.

[9] The ASTRID instrument is a grab sampler [*Bauer et al.*, 1994] and measurements were performed in Kiruna on 10 and 25 February 1997 inside the polar vortex. However, though on 10 February the measurement was made inside the vortex at most altitudes, air close to the vortex edge was sampled between 17 and 20 km [*Kanzawa et al.*, 2003, Figure 5]. BONBON and SAKURA are cryogenic whole air samplers [*Schmidt et al.*, 1991; *Honda et al.*, 1996]. The measurements with BONBON and SAKURA were performed in Kiruna inside the vortex on 11 Feburary and on 22 February and 18 March, respectively. The MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding) and FIRS-2 (Far-Infrared Spectrometer) are limb emission sounding spectrometers [*Fischer and Oelhaf*, 1996; *Johnson et al.*, 1995; *Jucks et al.*, 1998; F. Friedl-Vallon et al., Design and characterization of the balloon-borne Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B2), submitted to *Applied Optics*, 2004]. Both spectrometers measure a large number of trace gases simultaneously under day and night conditions. The measurement of MIPAS-B was performed in Kiruna on 24 March 1997 inside the vortex [*Wetzel et al.*, 2002] while the measurement of FIRS-2 was performed in Fairbanks on 30 April 1997 outside the vortex. The MkIV is a solar occultation FTIR (Fourier transform infrared) spectrometer, which was designed and built at the Jet Propulsion Laboratory (JPL) in the early 1980s. The MkIV instrument allows the retrieval of over 30 different atmospheric gases [*Toon*, 1991]. The CFC-12 profile was measured on 8 May 1997 in Fairbanks, Alaska, outside the polar vortex.

4. Individual Comparison

[10] For the comparison of ILAS CFC-12 vertical profiles with the correlative measurements, the ILAS profile obtained at the location closest to the correlative measurement on the same UT day was determined. While the FIRS-2 and MkIV data are given on a 1-km altitude grid, the data of ASTRID, BONBON, SAKURA, and MIPAS-B, which are sampled at a lower altitude grid, are linearly interpolated onto this 1-km altitude grid. Figures 1a–1h show the comparisons for each profile, the relative percentage difference, and the relative PV percentage difference. The error bars for ILAS are the total errors. The total error is defined as the root-sum square of the internal and external errors [*Yokota et al.*, 2002]. One-sigma precision error bars were plotted for the MIPAS-B, FIRS-2 and MkIV vertical profiles. We do not draw error bars for the in situ measurement instruments ASTRID, BONBON, and SAKURA, but we give information about the accuracy and precision of these instruments in the figure captions [*Kanzawa et al.*, 2003]. The relative percentage difference between ILAS and the correlative balloon measurement is defined as

$$\begin{aligned} \mathrm{D} = {} & [\mu(\mathrm{ILAS}) - \mu(\mathrm{Validation})] \\ & /\{[\mu(\mathrm{ILAS}) + \mu(\mathrm{Validation})]/2\} * 100, \end{aligned} \tag{1}$$

in percent (%) for each 1-km altitude grid, where μ denotes the mixing ratio of CFC-12 for ILAS and validation balloon

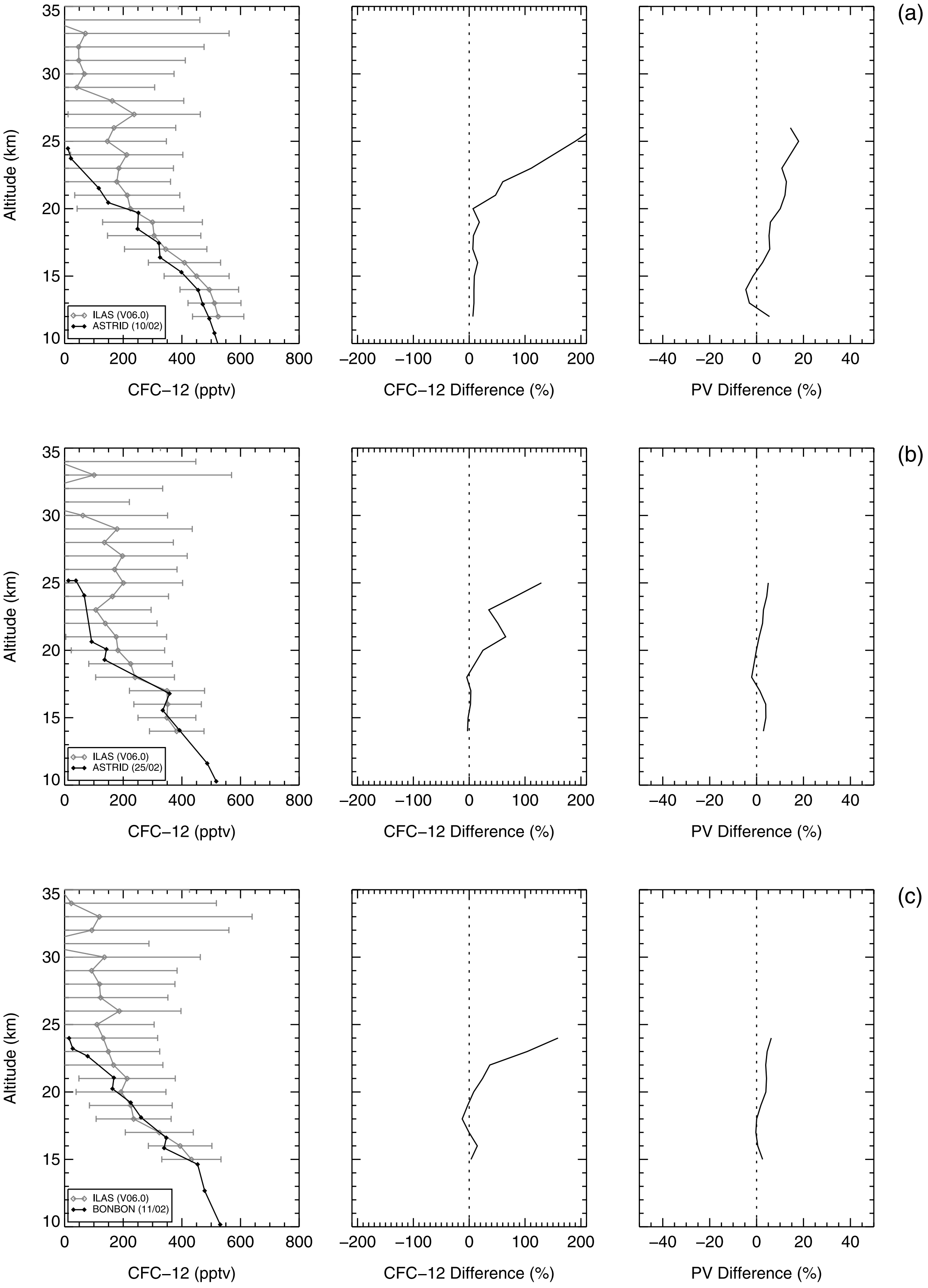

Figure 1. Comparison of vertical profiles of CFC-12 mixing ratios for eight ILAS validation flights. The left panel shows the ILAS version 6.0 vertical profile (shaded) versus the balloon validation measurement (in black), the middle panel shows the relative percentage difference, and the right panel shows the relative PV difference. The error bars of ILAS are total errors. (a and b) ASTRID (precision, 5.0 pptv or 2.0%; accuracy, 2.0%). (c) BONBON (precision, 5.0 pptv or 2.0%; accuracy, 2.0%). (d and e) SAKURA (precision, 2.5%; accuracy, 2.0%). (f) MIPAS-B (one-sigma precision). (g) FIRS-2 (one-sigma precision). (h) MkIV (one-sigma precision).

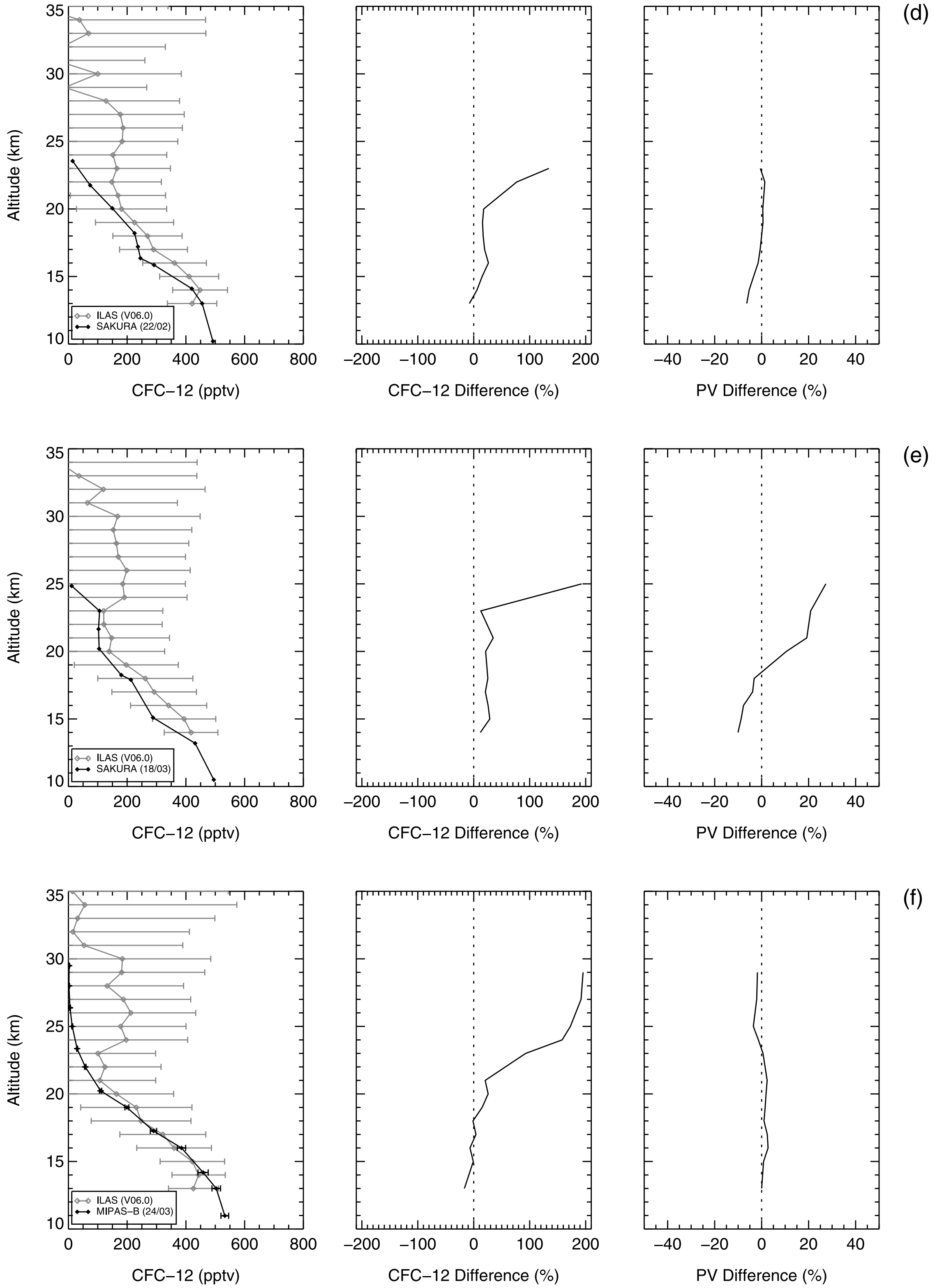

Figure 1. (continued)

measurement. As an index of the difference in air masses sampled, the relative PV difference is defined as

$$DPV = [PV(X) - PV(Y)]/PV(Y) * 100, \qquad (2)$$

in percent (%) for each 1-km altitude grid, where PV(X) and PV(Y) denote the PV values at the time and locations X and Y, whereby X specifies the time and location of the ILAS measurement and Y the time and location of the validation measurement [*Kanzawa et al.*, 2002, 2003]. The PV was derived from UKMO meteorological analyses. Further, as an index of the relative position of the ILAS and the correlative balloon measurements with respect to the polar

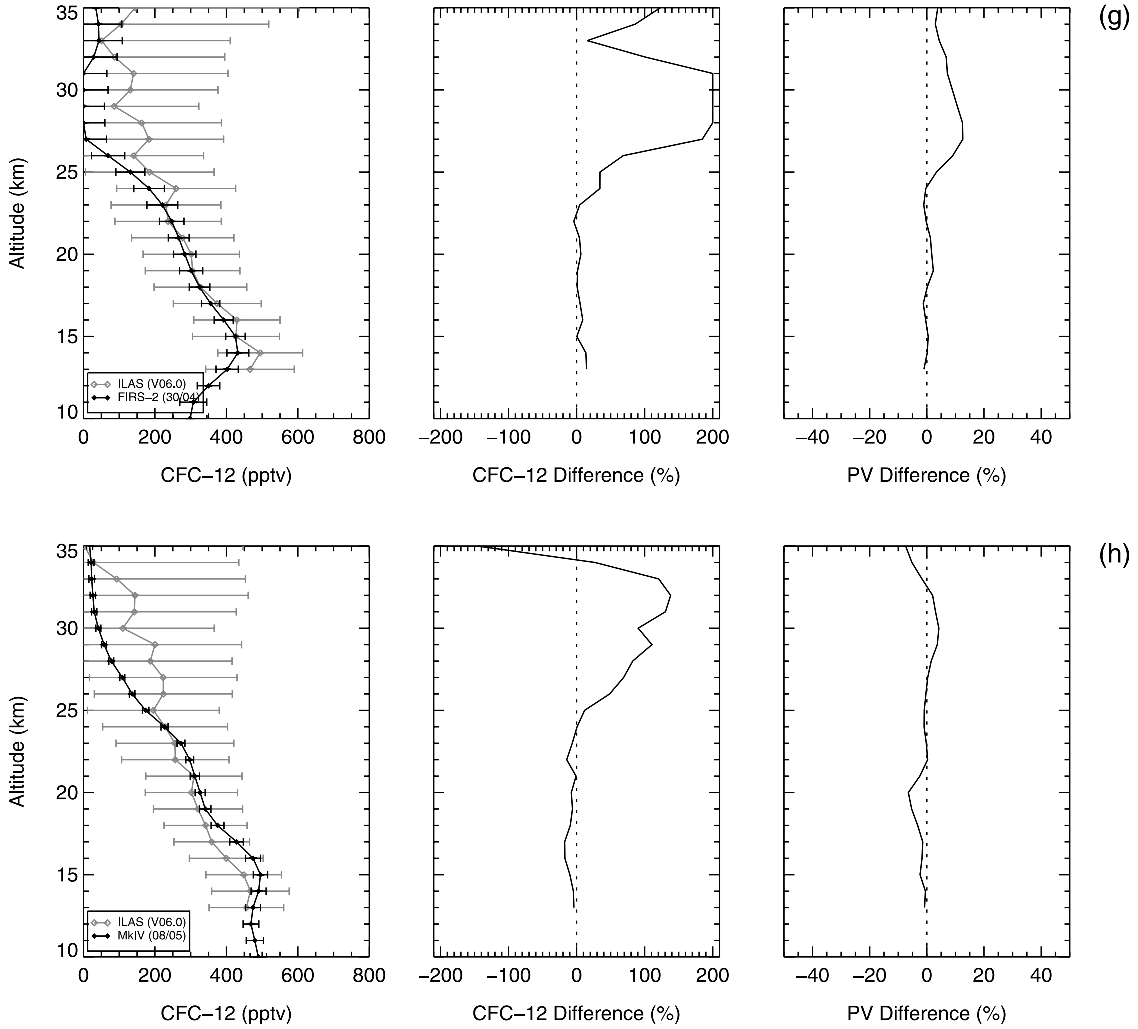

Figure 1. (continued)

vortex edge approximate values of DPV_{edge} at 20 km are given in Table 3. These values were taken from *Kanzawa et al.* [2003, Figure 5]. DPV_{edge} is defined as in equation (2), but here X specifies the PV at the time and location of the validation and ILAS measurement, respectively, and Y the PV at the polar vortex edge.

[11] Figures 1a and 1b show the results of the comparison with ASTRID on 10 and 25 February 1997. The balloon profiles were obtained very close to the ILAS measurement location at a distance of 314 km and 135 km, respectively, and with a time difference of 01.57 hours and −03.39 hours, respectively. On 10 February at altitudes between 12 and 20 km the relative percentage difference is less than +20%. From 20 to 25 km the relative percentage difference increases with altitude up to +200% at 25 km. Very low relative differences were found on 25 February at altitudes of 14–18 km (less than ±5%). Above 18 km the relative difference increases up to +130% at 25 km with a slight decrease of relative difference between 21 and 23 km from +70 to +40%. The relative PV difference on 10 February was less than +20% at the altitude range of 13–26 km. On 25 February the relative PV differences were very low, around ±5% at all altitudes.

[12] The validation balloon measurement with BONBON was performed on 11 February 1997 (Figure 1c). The corresponding ILAS profile was measured very close to the BONBON measurement at a distance of 341 km with a time difference of −04.33 hours. Very low relative percentage differences of −10% to +20% can be found from 15 to 20 km. Above 20 km the relative percentage difference increases with different slopes up to +40% at 22 km and up to +160% at 24 km. The relative PV difference was less than +5%.

[13] Measurements of CFC-12 with SAKURA were performed on 22 February and 18 March 1997 (Figures 1d and 1e). On 22 February the distance to the nearest ILAS profile was very small (only 154 km), but on 18 March the distance was rather large (601 km). The time difference between ILAS and SAKURA for these two measurements was −05.00 hours and 07.58 hours, respectively. The comparison shows low relative percentage differences at lower altitudes. On 22 February relative percentage differences of less than +20% were found between 13 and 20 km. Up to 23 km the relative percentage difference increases up to +140%. A similar behavior can be found for the comparison on 18 March. Up to 23 km the relative percentage difference is very low (less than +30%), but increases very strongly with altitude up to +200% at 25 km. The relative PV difference on 22 February was very low around −5% at altitudes of 13 to 17 km and below 1% at

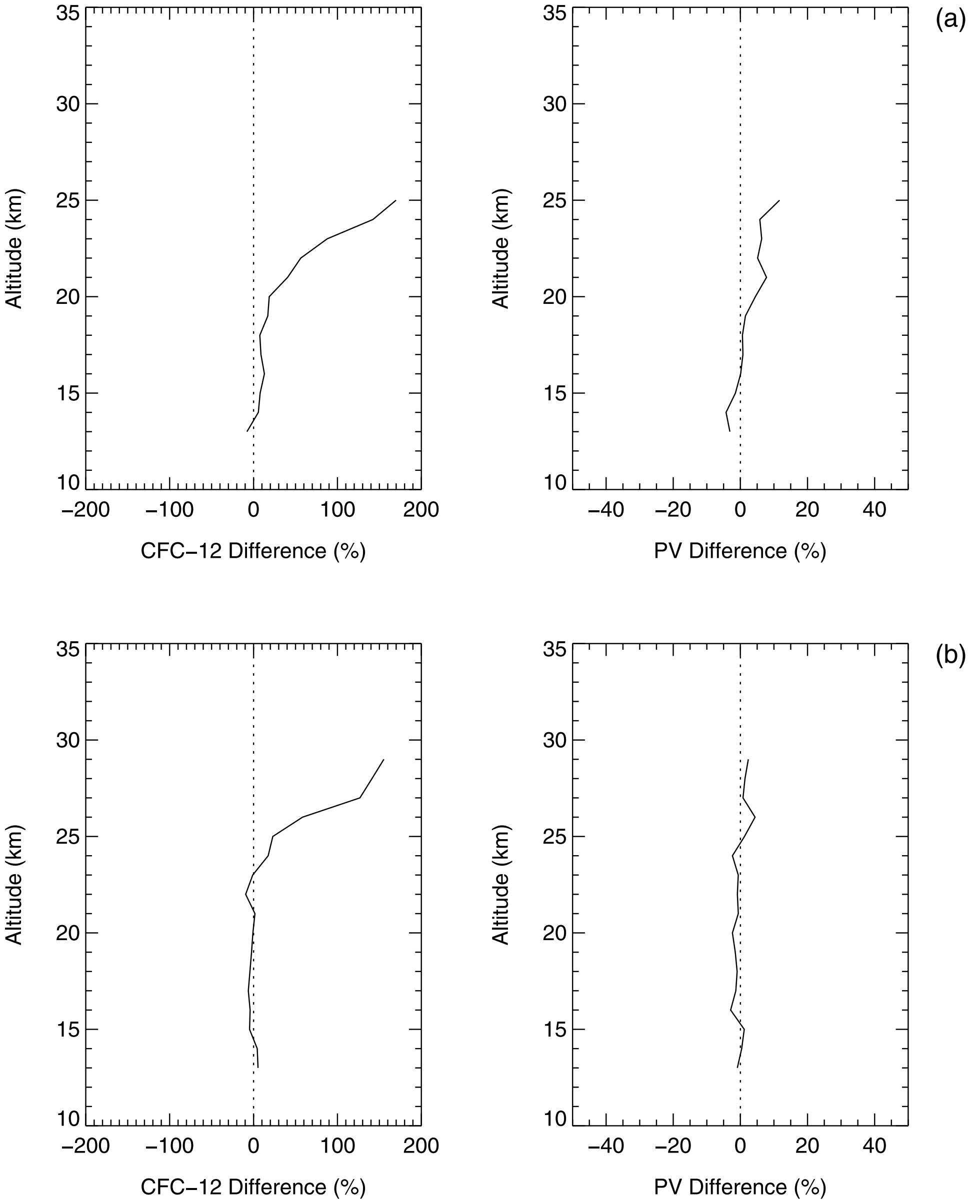

Figure 2. CFC-12 difference and PV difference for measurements (a) inside (Kiruna) and (b) outside (Fairbanks) the vortex. The relative percentage differences derived from the six comparisons of ILAS with balloon measurements inside the vortex and the two comparisons of ILAS with balloon measurements outside the vortex were averaged.

altitudes of 18 to 23 km. Both measurements were made inside the polar vortex. On 18 March the PV differences are very large with values of −10% to +30%. This is likely due to the great distance between the ILAS and SAKURA measurement showing that the measurements were performed at different locations with respect to the center of the polar vortex.

[14] The measurement with MIPAS-B was performed on 24 March 1997 inside the polar vortex (Figure 1f). The distance to the corresponding ILAS profile was very small being 180 km. The time difference between ILAS and MIPAS-B was 03:38 hours. As for the comparisons with ASTRID, BONBON, and SAKURA up to 20 km, the relative differences of MIPAS-B were low (less than −15% and +20%). Above 20 km the relative percentage difference increases up to 190% in 29 km.

[15] The comparison with the measurements of the FIRS-2 spectrometer, one of the two measurements performed in Fairbanks, Alaska, constitutes one of the two comparisons outside the polar vortex (Figure 1g). With the FIRS-2 instrument, CFC-12 was measured up to 35 km on 30 April 1997. The time difference between FIRS-2 and ILAS was −05:59 hours. Very low relative percentage differences were found though the distance to ILAS was rather large being 614 km. The relative percentage differences were less than −10% up to 23 km and less than 30% up to 25 km. Above 25 km, very large relative percentage differences of about ±200% were found.

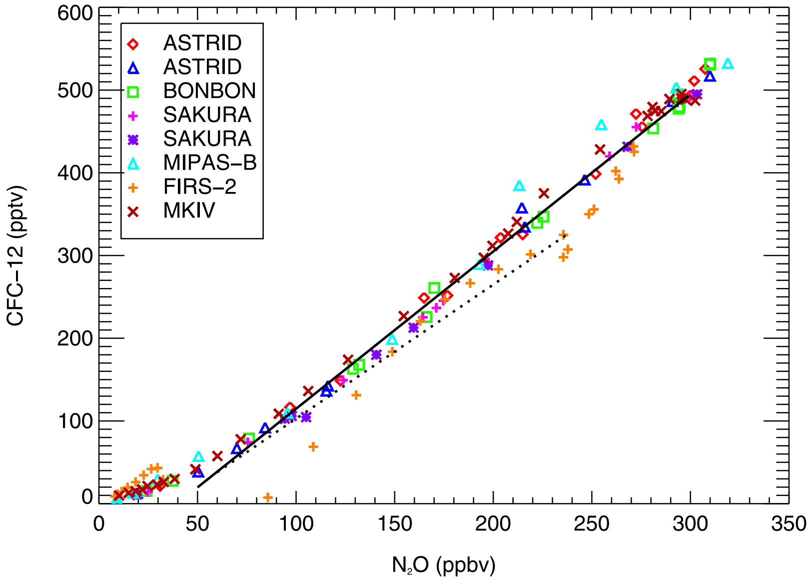

Figure 3. Correlation of CFC-12 and N_2O measured by the eight balloon flights used for the comparison in Figure 1. A linear fit through the balloon data was estimated yielding CFC-12 (pptv) = −75.4 + 1.90 ∗ N_2O (ppbv) (solid line). This fit is valid for 50 ppbv < N_2O < 300 ppbv. Additionally, a linear fit reported by *Müller et al.* [2001] for the winter 1991/92 is shown (dotted line). This linear fit is given by CFC-12 (pptv) = −59.2 + 1.62 ∗ N_2O (ppbv) for 60 ppbv < N_2O < 240 ppbv.

[16] The measurement with the MkIV spectrometer constitutes the second comparison performed in Fairbanks, Alaska. With the MkIV spectrometer, CFC-12 was measured up to 35 km on 8 May 1997, outside the polar vortex (Figure 1h). The time difference between MkIV and ILAS was 05:43 hours. As for the comparison with FIRS-2, low relative differences of less than −20% were found at altitudes between 13 and 25 km though the distance to ILAS was also rather large being 685 km. Above 25 km, very large relative percentage differences of about ±140% were found.

[17] Though the measurements of FIRS-2 and MkIV were both made at the furthest distance from ILAS of all comparisons, the best agreement between ILAS and balloon was found for these two validation measurements for altitudes up to 25 km. The low PV differences of less than 10% between ILAS and FIRS-2 and between −5% to +5% between ILAS and MkIV indicate that these measurements were performed in similar air masses. Both the balloon and the ILAS measurements were made in an air mass which was not strongly influenced by polar vortex air.

[18] The ILAS CFC-12 values were systematically larger than those obtained from the balloon measurements at altitudes where CFC-12 mixing ratios were low (Figure 1). However, the estimated total errors of the ILAS CFC-12 measurements were large (Table 1). Low values of CFC-12 mixing ratios occur inside the polar vortex at altitudes above 20 km and are caused by diabatic descent [e.g., *Bauer et al.*, 1994]. Because the measurements of the FIRS-2 and MkIV spectrometer were performed outside the vortex such low CFC-12 mixing ratios occur at greater altitudes leading in general to a better agreement with the ILAS measurements. Therefore large differences between ILAS and the correlative measurements of ASTRID, BONBON, SAKURA, and MIPAS-B, which were performed inside the vortex, occur above about 20 km altitude while great differences between ILAS and the correlative measurements of FIRS-2 and MkIV, which were performed outside the vortex, occur above about 25 km altitude (Figure 2).

[19] To summarize the eight comparisons, the relative percentage differences were averaged over all comparisons inside the vortex (Figure 2a) and outside the vortex (Figure 2b). Inside the vortex total differences of around +10% to +20% can be found at altitudes of 13 to 20 km. At altitudes above 20 km the relative percentage difference increases with increasing altitude up to +170% at 25 km. Outside the vortex total differences of around −10 to +20% can be found at altitudes up to 25 km. Above 25 km the relative percentage difference increases up to +160% in 29 km. The relative PV percentage differences are low for all altitudes ranging around ±5% inside the vortex and −1% and +5% outside the vortex. In general, the ILAS values are greater than the balloon measurements except for MkIV where the ILAS values were lower. Though the relative percentage differences for CFC-12 above 20 km are rather large compared to the other validation studies made for species such as O_3, N_2O or CH_4 [*Sugita et al.*, 2002; *Kanzawa et al.*, 2003] the balloon profiles for all comparisons lie within the reported error bars of ILAS.

5. N_2O–CFC-12 Correlations

[20] Throughout the stratosphere compact relations are expected between tracers for which quasi-horizontal mixing along isentropes is fast compared to their chemical lifetimes. Furthermore, if the chemical lifetime of both tracers is long compared to the time-scale of vertical advection the relation between both tracers is linear [*Plumb and Ko*, 1992]. The relationship between the long-lived tracers N_2O and CFC-12 is conserved throughout the winter as shown, e.g., for the

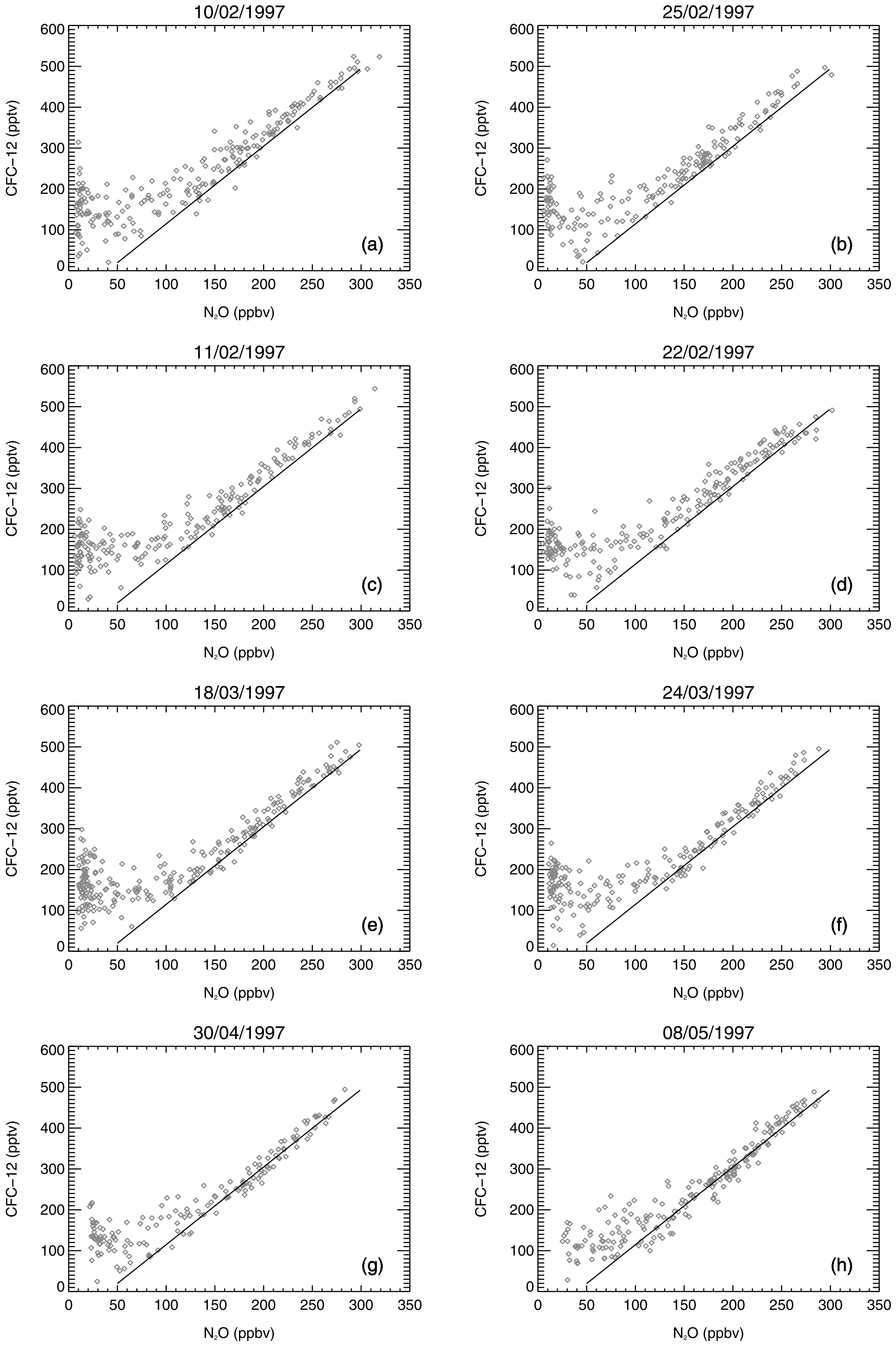

Figure 4. Correlations of CFC-12 and N_2O measured by ILAS for the dates when the validation measurements were performed are compared to the linear fit (black solid line) deduced from the balloon measurements (equation (3)). The complete set of Northern Hemisphere ILAS profiles measured at each particular day (14 profiles) are shown (diamonds).

Arctic winter 1991/1992 by *Müller et al.* [2001]. Likewise in the CLAES (Cryogenic Limb Array Etalon Spectrometer) data a linear relationship of CFC-12 and N_2O was observed for N_2O mixing ratios >100 ppbv for the southern spring of 1992 and 1993 [*Nightingale et al.*, 1996].

[21] From all the balloon measurements conducted in 1997 for the validation of CFC-12 measured by ILAS a linear fit was calculated from the correlations with N_2O. In the calculation of the fit was the FIRS-2 data restricted to the altitude range of 13 to 26 km. At greater altitudes (low N_2O) the FIRS-2 measurements are affected by a poor signal-to-noise ratio while at lower altitudes (high N_2O) the data are strongly variable due to the fact that during the FIRS-2 measurement on 30 April an atmospheric fold was sampled. Figure 3 shows all N_2O−CFC-12 balloon correlations and the resulting fit. For N_2O values between 50 to 300 ppbv the linear fit yields

$$\text{CFC-12} = -75.4 + 1.90 * N_2O, \tag{3}$$

with CFC-12 mixing ratios in pptv and N_2O mixing ratios in ppbv. Additionally, the linear fit reported by *Müller et al.* [2001] for the winter 1991/92 from balloon-borne measurements in the Arctic is shown. Comparing the linear fit for 1991/1992 to the one deduced from the 1997 balloon data the well-established increase in CFC-12 mixing ratios in the stratosphere over this time period [*Engel et al.*, 1998, 2002] is noticeable.

[22] Correlations of ILAS CFC-12 and N_2O mixing ratios for all days when balloon measurements were performed show a linear relationship, which is in agreement with the linear fit deduced from the balloon measurements (Figure 4). The ILAS data, while showing a similar behavior in principle, scatter around this fit. Because the CFC-12/N_2O correlation is conserved throughout the winter [*Müller et al.*, 2001] scatterplots of the ILAS CFC-12/N_2O relation of individual days or averages over long time periods (e.g., a month) are very similar. We have chosen to present the data for individual days for better readability of the figures. Validation studies have shown that the uncertainty of N_2O is less than 10% at 10–30 km altitude [*Kanzawa et al.*, 2003]. Therefore, as in the comparison of vertical profiles, a positive bias of ILAS CFC-12 is found. That is, in general, the ILAS CFC-12 mixing ratios are greater than the CFC-12 mixing ratios of the correlative balloon measurements. For N_2O values lower than $\approx$125–150 ppbv the ILAS CFC-12 data veers away strongly from the linear fit estimated from the correlative data. Therefore correlations of CFC-12 and N_2O from ILAS measurements should only be considered in the data range of 125 ppbv < N_2O < 300 ppbv.

[23] Since the ILAS CFC-12/N_2O correlations for N_2O values of 125 < N_2O < 300 ppbv of April and May (Figures 4g and 4h) agree better with the fit estimated from the balloon measurements than the ILAS CFC-12/N_2O correlation of February and March (Figures 4a–4d), there may be a slight seasonal dependence in the ILAS CFC-12 data, as found in the ILAS CH_4 data [*Kanzawa et al.*, 2003]. The cause of this issue is still under investigation.

[24] A linear fit from the ILAS data was estimated using the CFC-12/N_2O correlations of the 8 days of measurements described above (not shown). For N_2O values between 150 and 300 ppbv the linear fit yields CFC-12 = −51.80 + 1.88 * N_2O with CFC-12 mixing ratios in pptv and N_2O mixing ratios in ppbv.

6. Conclusions

[25] We validated ILAS version 6.0 CFC-12 data and showed that due to the improvement of the retrieval algorithm compared to previous versions the ILAS CFC-12 data product is now suitable for scientific studies. We considered eight correlative measurements obtained with six different measuring instruments. At altitudes between 13 and 20 km the relative percentage differences were rather low, but they start to increase with increasing altitude up to +120% at 25 km. Both the balloon and ILAS measurements were performed in similar air masses as suggested by the low PV differences. The only exception is the comparison with SAKURA on 18 March 1997. Due to the large distance to ILAS of 601 km large differences in the relative PV differences were found, suggesting that the measurements were made in different air masses. Though the largest distances to ILAS were found for the comparisons with the FIRS-2 and MkIV spectrometers (614 km and 685 km) both measurements were made in similar air masses outside the polar vortex as suggested by the low relative PV differences. Compared to validation studies of other trace gases measured by ILAS, the relative percentage difference between ILAS measurements and correlative measurements of CFC-12 are greater in this study. However, they lie within the ILAS error bars.

[26] Additionally, we presented correlations of CFC-12 and N_2O. As for the comparison of vertical profiles, the greatest differences in the correlations of CFC-12 versus N_2O was found for low CFC-12 values (less than about 200 pptv) and low N_2O values (less than 150 ppbv) where the data veer away from the linear fit deduced from the correlative balloon measurements. The positive bias of the ILAS CFC-12 data is also seen in the correlations. However, the correlations show that the ILAS data are in good agreement with the linear fit for CFC-12 values between 150 ppbv < N_2O < 300 ppbv. Correlations of CFC-12 and N_2O for N_2O values lower than 125 ppbv should not be considered because of the strong deviations from the linear fit deduced from the balloon measurements.

[27] The analysis of the agreement of ILAS CFC-12 measurements with the correlative measurements, both in terms of vertical profiles and of CFC-12/N_2O correlations, indicates that ILAS CFC-12 measurements become problematic (positive bias with large errors exceeding 100%) for low CFC-12 values (less than $\approx$200 pptv). This is reflected in the large relative differences between ILAS CFC-12 and CFC-12 from the correlative measurements at altitudes above 20–22 km inside the vortex and above about 25 km outside the vortex. In summary, we conclude that ILAS CFC-12 data retrieved with the version 6 algorithm are reliable within the reported error bars and are thus suitable for scientific studies for altitudes below about 20–22 km inside the polar vortex and below about 25 km outside the polar vortex.

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References

Bauer, R., A. Engel, H. Franken, E. Klein, G. Kulessa, C. Schiller, and U. Schmidt (1994), Monitoring the vertical structure of the Arctic polar vortex over northern Scandinavia during EASOE: Regular N_2O profile observations, *Geophys. Res. Lett.*, *21*, 1211–1214.

Crutzen, P. J. (1974), Estimates of possible future ozone reductions from continued use of fluro-chloro-methanes (CF_2Cl_2, $CFCl_3$), *Geophys. Res. Lett.*, *1*, 205–208.

Engel, A., U. Schmidt, and D. S. McKenna (1998), Stratospheric trends of CFC-12 over the past two decades: Recent observational evidence of declining growth rates, *Geophys. Res. Lett.*, *25*, 3319–3322.

Engel, A., M. Strunk, M. Müller, H.-P. Haase, C. Poss, I. Levin, and U. Schmidt (2002), Temporal development of total chlorine in the high-latitude stratosphere based on reference distributions of mean age derived from CO_2 and SF_6, *J. Geophys. Res.*, *107*(D12), 4136, doi:10.1029/2001JD000584.

Fischer, H., and H. Oelhaf (1996), Remote sensing of vertical profiles of atmospheric trace constituents with MIPAS limb-emission spectrometers, *Appl. Opt.*, *35*, 2787–2796.

Honda, H., S. Aoki, T. Nakazawa, S. Morimoto, and N. Yajima (1996), Cryogenic air sampling system for measurements of the concentrations of stratospheric trace gases and their isotopic ratios over Antarctica, *J. Geomagn. Geoelectr.*, *48*, 1145–1155.

Johnson, D. G., K. W. Jucks, W. A. Traub, and K. V. Chance (1995), Smithsonian stratospheric far-infrared spectrometer and data reduction system, *J. Geophys. Res.*, *100*, 2091–3106.

Jucks, K. W., D. G. Johnson, K. V. Chance, W. A. Traub, J. J. Margitan, G. B. Osterman, R. J. Salawitch, and Y. Sasano (1998), Observations of OH, HO_2, H_2O, and O_3 in the upper stratosphere: Implications for HO_x photochemistry, *Geophys. Res. Lett.*, *25*, 3935–3938.

Kanzawa, H., et al. (2002), Validation and data characteristics of water vapor profiles observed by the Improved Limb Atmospheric Spectrometer (ILAS) and processed with the version 5. 20 algorithm, *J. Geophys. Res.*, *107*(D24), 8217, doi:10.1029/2001JD000881. (Correction, *J. Geophys. Res.*, *108*(D4), 8218, doi:10.1029/2003JD001601, 2003.)

Kanzawa, H., et al. (2003), Validation and data characteristics of nitrous oxide and methane profiles observed by the Improved Limb Atmospheric Spectrometer (ILAS) and processed with the Version 5.20 algorithm, *J. Geophys. Res.*, *108*(D16), 8003, doi:10.1029/2002JD002458.

Molina, M. J., and F. S. Rowland (1974), Stratospheric sink for chlorofluoromethanes: Chlorine atom catalysed destruction of ozone, *Nature*, *249*, 810–812.

Müller, R., U. Schmidt, A. Engel, D. McKenna, and M. Proffitt (2001), The O_3/N_2O relationship from balloon-borne observations as a measure of Arctic ozone loss in 1991–1992, *Q. J. R. Meteorol. Soc.*, *127*, 1389–1412.

Nightingale, R., et al. (1996), Global CF_2Cl_2 measurements by UARS cryogenic limb array etalon spectrometer: Validation by correlative data and a model, *J. Geophys. Res.*, *101*, 9711–9736.

Plumb, R. A., and M. K. W. Ko (1992), Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10,145–10,156.

Sasano, Y., M. Suzuki, T. Yokota, and H. Kanzawa (1999), Improved Limb Atmospheric Spectrometer (ILAS) for stratospheric ozone layer measurements by solar occultation technique, *Geophys. Res. Lett.*, *26*, 197–200.

Schmidt, U., R. Bauer, A. Khedim, E. Klein, G. Kulessa, and C. Schiller (1991), Profile observations of long-lived trace gases in the Arctic vortex, *Geophys. Res. Lett.*, *18*(4), 767–770.

Solomon, S., and R. R. Garcia (1984), On the distribution of long-lived tracers and chlorine species in the middle atmosphere, *J. Geophys. Res.*, *89*, 1633–1644.

Sugita, T., et al. (2002), Validation of ozone measurements from Improved Limb Atmospheric Spectrometer (ILAS), *J. Geophys. Res.*, *107*(D24), 8212, doi:10.1029/2001JD000602.

Toon, G. C. (1991), JPL Mark IV interferometer, *Opt. Photonics News*, *2*, 19–21.

Wetzel, G., et al. (2002), NO_y partitioning and budget and its correlation with N_2O in the Arctic vortex and in summer midlatitudes in 1997, *J. Geophys. Res.*, *107*(D16), 4280, doi:10.1029/2001JD000916.

World Meteorological Organization (WMO) (2003), *Scientific Assessment of Ozone Depletion: 2002*, *Rep. 47*, Geneva.

Yokota, T., et al. (2002), Improved Limb Atmospheric Spectrometer (ILAS) data retrieval algorithm for version 5.20 gas profile products, *J. Geophys. Res.*, *107*(D24), 8216, doi:10.1029/2001JD000628.

Zhong, W., J. D. Haighand, and J. A. Pyle (1993), Greenhouse gases in the stratosphere, *J. Geophys. Res.*, *98*, 2995–3004.

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