HYDROCHLORIC ACID AND THE CHLORINE BUDGET OF THE LOWER STRATOSPHERE

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Abstract. Content rations of HCl measured in the lower stratosphere in 1993 by the ALIAS instrument on the ER-2 aircraft reveal that only 40% of inorganic chlorine (Cl_y, inferred from in situ measurements of organic chlorinated source gases) is present as HCl, significantly lower than model predictions. Although the sum of measured HCl, ClO, and $ClONO_2$, the latter inferred from measurements of ClO and NO_2, equals Cl_y to within the uncertain y of measurement, it is systematically less than Cl_y by 30-50%. This discrepancy suggests that concentrations of $ClONO_2$ may exceed those of HCl near 20 km altitude, consistent with a slower photolysis rate for $ClONO_2$ than calculated using recommended cross sections. Comparison of profiles of HC1 measured during 1992 and 1993 at mid-latitudes by balloon (BLISS and MARKIV), space shuttle (ATMOS), and satellite (HALOE) instruments with the aircraft data reveal an apparent pressure dependence to the HCl to Cl_y ratio, consistent with a factor of 3-10 reduction in the photolysis rate for C.10NO_2 at ER-2 altitudes. However, the. diurnal variation of ClO is well-simulated by models using the recommended photolysis rate, and simultaneous measurements of $ClONO_2$ and HCl at mid-latitudes by ATMOS and MARKIV report $HCl/(HCl + ClONO_2)$ ratios $\geq$ 50%. Preliminary measurements by ALIAS in the southern hemisphere report HCl/Cl_y values of about 75%. It is unclear to what extent elevated aerosol surface area, uncertainties in the estimation of Cl_y or in the photolysis rates, or missing react ive pathways cent ribute to our inability to balance the budget of inorganic chlorine using the aircraft measurements.

introduction

Our understanding of chlorine-catalyzed ozone destruction is built upon the concept of transport of industrially-pro. duced organic chlorine compounds into the stratosphere [Prather et al. 1990] and photochemical conversion into inorganic forms. Normally, for the mid-latitude lower stratosphere, hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$) are the dominant (reservoir) gases. Chlorine monoxide (ClO) and chlorine atoms (Cl), which catalyze loss of ozone, typically constitute less than 10% of the total inorganic chlorine [Brune et al., 1990]. However, concentrat ions of C1O may be elevated as the result of heterogeneous reactions on volcanic aerosols [Avallone et al., 1993; Fahey et al., 1993], or enhanced dramatically by heterogeneous conversion of HCl and $ClONO_2$ on polar stratospheric cloud (PSC) particles [Webster et al,, 1993]. The amount

of C1O produced by heterogeneous reaction of HCl and C1ONO, depends initially on the relative amounts of HCl and $ClONO_2$ present, since the reaction will halt when the less abundant species is depleted. Therefore knowledge of the initial concentrations of HCl and $ClONO_2$ is important in predicting ozone loss from industrially produced compounds.

Since its first measurement in 1975 [Fanner et al., 1976], HCl has been measured in the stratosphere by ground-based, balloon, aircraft, shuttle, and satellite remote sensing techniques. However, in situ measurements of HCl have been few in number and limited primarily to altitudes ≥ 25 km [May and Webster, 1989].

The in situ measurements

We present data obtained from NASA's ER-2 aircraft during the 1993 Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) out of Moffett Field, California. These data are the first extensive in situ measurements of HCl at altitudes below 20 km, covering a latitude range of 15-60°N. Concentrations of numerous other gases relating to chlorine chemistry were measured, including C1O [Stimpfle et al. 1994], NO_2 [Jaeglé et al., 1994], the dynamical tracers N_2O, CH_4, and meteorological parameters such as temperature and pressure (see Table 1).

The ALIAS instrument is a scanning tunable diode laser spectrometer which uses high-resolution laser absorption in the 3-8 μm wavelength region [Webster et al., 1994] to directly measure HC1, NO_2, CH_4, and N_2O. Extensive calibration and testing of the intake and sampling system (fast flow at 16 1/s), including post-flight analysis of the inlet residue, has revealed no systematic instrument or sampling error that could be greater than 10%. The fidelity of the measurement of HC1 in the multi-pass cell is checked by the simultaneous recording of strong CH_4 lines close to the R(I) HCl absorption line at 2926 cm^{-1} [Webster et al., 1994]; the CH_4 concentrations derived from these lines are cross-checked with those measured in another, independent channel devoted to measurements of CH_4 and N_2O.

HCl observations and model predictions

A tight anti-correlation is exhibited between HC1 and the dynamical tracer N_2O for data obtained on east-west flights near 340N on May 6 and 7, 1993, as shown in Fig. 1. Measured values of HCl are about 50% lower than concentrations calculated using reaction rates and absorption cross sections from DeMore et al, [1992], allowing for the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ [Salawitch et al., 1994] (Fig. 1). The model predicts HCl should constitute 70% of C}, whereas the data" suggest HCl/Cl, is about 40%, We note that data obtained on May 11 and May 12 1993, although through similar air masses with near-constant N_2O values of 245 ppbv, show HC1 values about 30 % higher and lower, respectively, than those of May 6 and 7. However, these two flights do not sample air with N_2O values below 240 ppbv, and therefore do not change the HC1

vs. N_2O fit for SPADE flights at the lower N_20 values in which the discrepancy with the model is most evident.

Figure 2 compares ALIAS measurements of HCl and N_2O with shuttle, balloon, and satellite data taken between August 1992 to May 1993, over similar latitude ranges near 34°N, except the ATMOS data which is ftom 32-50%. When plotted against the dynamical tracer N_2O (Fig. 2A), the ALIAS HCl measurements of HCl appear lower than satellite (HALOE [Russell et al. 1993]), space shuttle (ATMOS [Gunson et al. 1993]), balloon (MARKIV) [Toon et al. 1992], and recent balloon in situ (BLISS) [May and Webster, 1989] measurements, especially at smaller N_2O values. However, when all the HCl vs. N_2O data are binned according to three pressure ranges (Figs. 2A and 213), an apparent pressure-dependence to the HCl/Cl_y partitioning is revealed for the data set as a whole. While BLISS and HALOE do show a pressure dependence in their individual data sets, this is not evident for the ATMOS and MARKIV data sets, nor indeed the AI .IAS data set itself over the. small range of pressure sampled.

The apparent disagreement between the individual data sets seen in Fig. 2A may result from the difficulty in comparing HCl measured at different altitudes (pressures), even for similar concentrations of N_2O. Indeed, the ER-2 aircraft, while it may encounter N_2O amounts as low as 50 ppbv (Bangor, Maine, Feb. 17, 1992, during vortex descent), never flies above 20 km, i.e. at pressures < SO mbar. Remote sensing measurements have. the opposite problem: their limited ability to retrieve data below 20 km in the presence of Pinatubo aerosol restricts HCl vs. N_2O data sets to higher altitudes, although including high levels of N_2O normally associated with lower altitudes.

As a means of normalizing the various measurements of HCl to study vertical profiles for comparison with models, we plot HCl/Cl_y as a function of pressure, as shownin Fig. 2B. The model results [Salawitch et al., 1994] for HCl/Cl_y are sensitive to the amount of ozone, showing differences in April/May bet ween the northern and southern hemispheres. The lifetime of HCl is about 30 days at 20 km; since the atmosphere does not have strong latitudinal gradients in the HCl/Cl_y ratio, a steady-state model constrained by measured ozone is suitable for this analysis. In general, the model predicts that HCl/Cl_y should reach a minimum near 27 km altitude (see Fig. 2B), the region where the mixing ratio of $ClONO_2$ reaches a maximum. For the mid-latitudes in May, a minimum in HCl/Cl_y of 40% is predicted in the north, and 60% in the south, These two curves are plotted in Fig. 2B to show the range of model redactions. The ALIAS data, while lower than the model and both the MARKIV and ATMOSdata, lie in the 15-20 km altitude region where the HCl/Cl_y fraction is changing rapidly, and all data sets show significant spread. All the northern latitude data. sets except that of MARKIV show the altitude of the HCl/Cl_y minimum significantly lower than that of the model. Most of the data points above 25 km lie at HCl/Cl_y values higher than the model.

Chlorine partitioning in the lower atmosphere

The partitioning of inorganic chlorine between reactive and reservoir forms depends on the temperature, altitude, and latitude history of an air parcel (characterized by its specific N_2O mixing-ratio). Our understanding of chlorine partitioning is tested by comparing estimates of Cl_y inferred from correlations of organic source gases and N_2O obtained during AASE-II [Woodbridge et al. 1994] to the sum of measured concentrations of HCl, ClO, and $ClONO_2$*, the latter representing chlorine nitrate inferred from in situ measurements of ClO and NO_2 (see Table 1). For high sun elevat ions, where the photolysis lifetimes are short compared to atmospheric transport, a steady-state approximation yields [Kawa et al., 1993]:

$$[ClONO_2]^* \simeq k[ClO][NO_2][M]/J_{ClONO2} \qquad [1]$$

where J_{ClONO2} is the photodissociation coefficient for $ClONO_2$ (J = 1/photolysis lifetime), k the rate constant for the reaction ClO + NO_2 + M → $ClONO_2$ + M.

Figure 3 shows that the sum of measured HCl and ClO with $ClONO_2$* is 50-70% of Cl_y. Similar results were found for the few other SPADE flights for which simultaneous HCl, ClO, and NO_2 measurements were available. For the May 7, 1993 flight, the aircraft flew at constant pressure-altitude, repeatedly in and out of two air masses characterized by different levels of N_2O. For air with an N_2O mixing ratio of about 120 ppbv, relatively high amounts of ClO and NO_2 minimize the uncertainties in calculating $ClONO_2$* using Eq. (1): for these air masses, the sum HCl + ClO + ClONO," is 2.0 ± 0.9 ppbv, compared with Cl_y = 3.0 ± 0.6 ppbv. Although the budget can be made to balance witbin these absolute uncertainties, the sum systematically falls short of Cl_y in all flights studied.

Based on our analysis, 30-50% of Cl_y cannot be accounted for, a serious discrepancy in our understanding of the partitioning of inorganic chlorine in the lower stratosphere. This shortfall does not exhibit strong correlation with N_2O, temperature, particle surface area, solar zenith angle, or latitude.

The budget shortfall was also evident in results from the 1991 /2 AASE-II aircraft campaign, in which HCl/Cl_y values of about 35-50% were reported from the ALIAS measurements. These same HC1 measurements produced a balanced stoichiometric ratio of 1:2 for the HC1 loss vs. ClO + $2Cl_2O_2$ production, consistent with expectations based on the HCl + $ClONO_2$ reaction being responsible. [Webster et al., 1993].

Recently, Sander et al. (private communication, 1994) have discovered that the photodissociation cross-section for $ClONO_2$ exhibits a pressure dependence, becoming smaller at higher pressures (=50 mbar). Slower photolysis of $ClONO_2$ would lead to significantly more $ClONO_2$ and less HCl than previously thought possible. We have calculated the value of J_{ClONO2} needed to balance production and loss of $ClONO_2$ (J_{ClONO2}*), by assuming the actual concentration of $ClONO_2$ is the difference between Cl_y and measured HCl. For aircraft data obtained on May 7 and 14, 1993, we have

compared J_{ClONO2}* to J_{ClONO2} calculated using a radiative transfer model and recommended cross-sections [DeMore et al., 1992]. By comparing calculations of steady-state values with results from a time-dependent photochemical model, a correction term is included at the higher solar zenith angles where the steady-state approximate ion breaks down. For these flights, values of J_{ClONO2}* required to balance the $ClONO_2$ budget are typically 3-10 times smaller than calculated values.

Observations of HCl during SPADE suggest that concentrations of $C10N0_2$ exceed concentrations of HCl in the lower stratosphere, consistent with a pressure-dependent photolysis rate for $C10NC)_2$. Although direct observations of $C10N0_2$ and HCl in the MARKIV data set are able to accommodate a reduction of J_{ClONO2} by a factor 2, both the ATMOS and MARKIV data sets are in general well-represented by models using standard chemistry and J_{ClONO2} values. In addition, the measured variation of ClO with solar zenith angle [Stimpfle et al., 1994] is simulated accurately by a model using values of J_{ClONO2} based on recommended cross sections [Salawitch et al,, 1994],

Recent measurements of HCl by AI JAS in the. southern hemisphere (winter of 1994) show HCl/Cl_y values close to 75%, significantly higher than the values presented here. This apparent interhemispheric difference is difficult to relate m changes in J_{ClONO2} alone, and alternat ive explanat ions may have to be sought.

Simultaneous measurements of OH and HO_2 from the. ER-2 aircraft [Wennberg et al., 1994] rule. out the. possibility y of higher OH abundances creating greater HCl loss than expected. The extent to which elevated aerosol surface areas following the volcanic erupt ion of Mt. Pinatubo are responsible for loss or repartitioning of inorganic chlorine is unclear, but may hold the key to understanding the aircraft data showing a relative increase in HCl/Cl_y at southern latitudes in 1994 compared to that in northern latitudes in 1991 through 1994. The ATMOS Spacelab 3 measurements of HCl and $ClONO_2$, made in 1985 when aerosol surface area was close to non-volcanic background levels, agree well with model predictions.

Resolution of the discrepancies between individual HCl/Cl_y measurements and between model and measurements may involve: errors in estimating J_{ClONO2} or in estimating Cl_y; the presence of an unknown pathway linking HCl and $ClONO_2$, perhaps linked to the presence. of enhanced volcanic aerosol following the eruption of Mt. Pinatubo; unidentified instrument artifacts; incomplete spectroscopic information used in the retrievals of $C10N0_2$ for remote. sensing instruments; or chemical processes occurring in the lower stratosphere unaccounted for by current models. In situ measurements of $ClONO_2$ to accuracies better than about 30% are needed for direct comparison with those of HC1.

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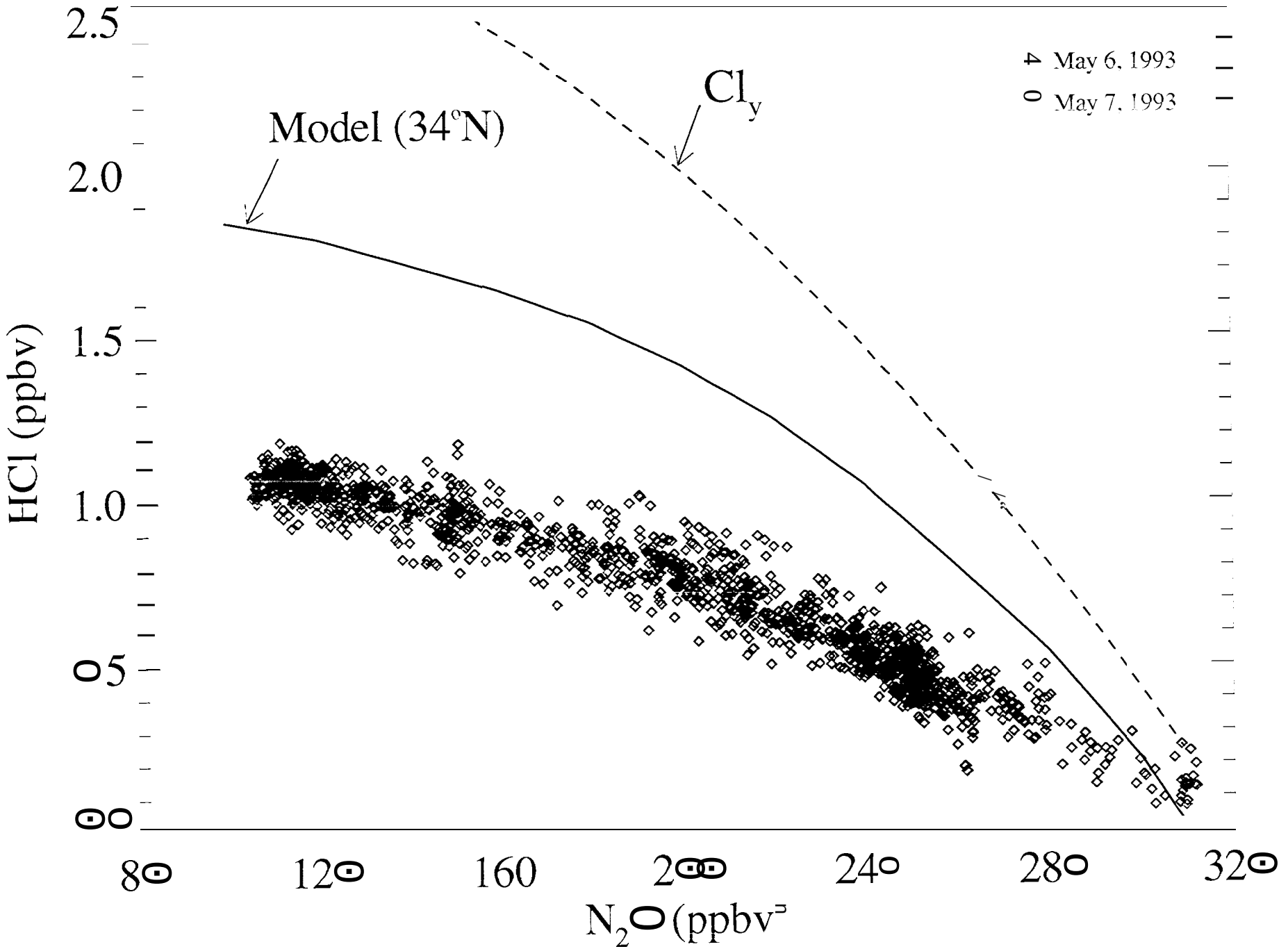
Figure 1. ALIAS in situ measurements of HCl (diamonds), Cl, inferred from in-situ measurements of organic chlorine [Woodbridge et al., 1994], and model results [Salawitch et al,, 1994] as a function of N_20 for aircraft flights of May 6 and 7, 1993.

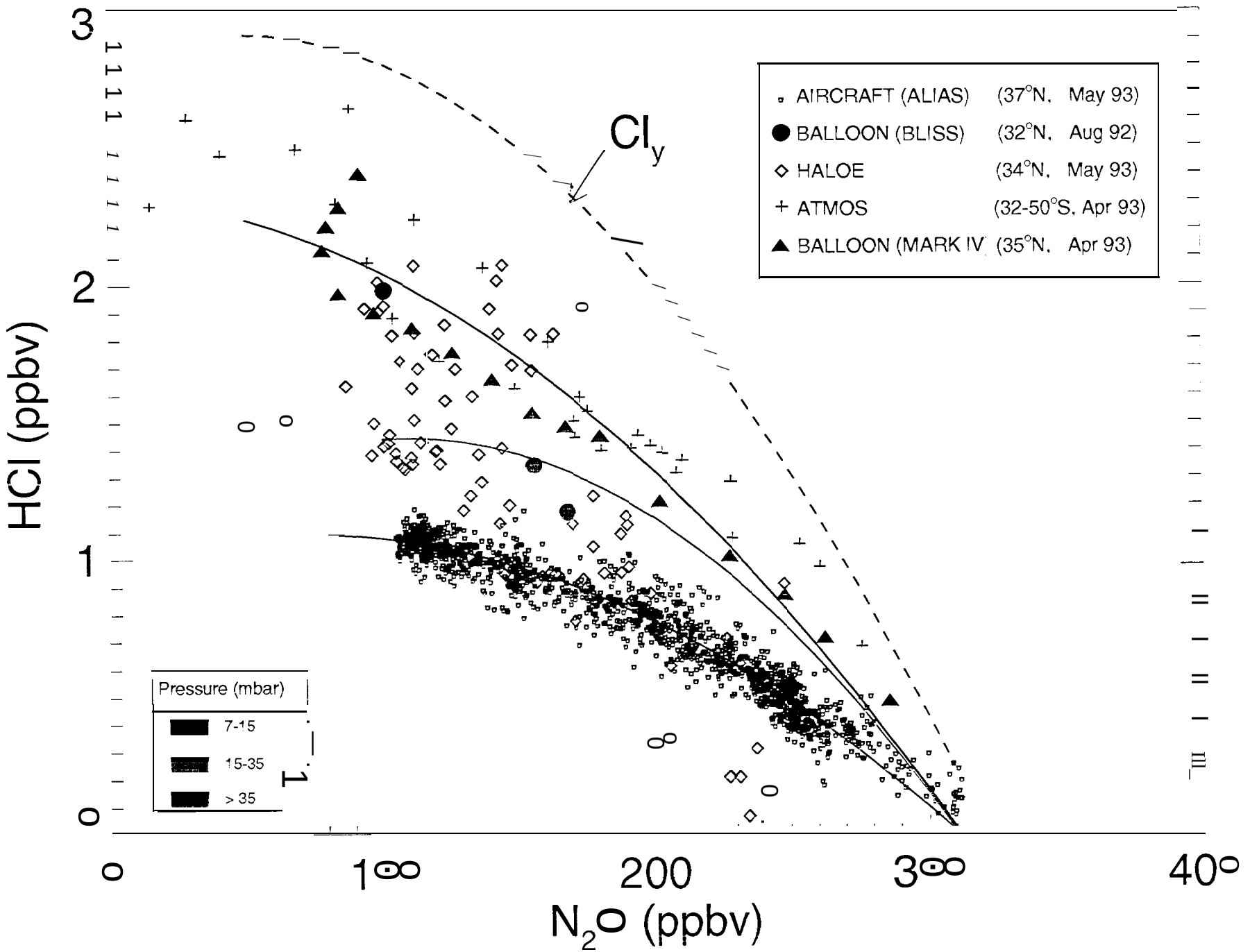
Figure 2. Comparison between different measurements of (A) HCl vs. N_20, and (B) HCl/Cl_y vs. pressure with model predictions. Uncertainties for each measurement range from 10 to 25%. Measurements of CH_4 from BLISS and from H ALOE are converted to equivalent N_2O values according to the correlation $N_2O(ppbv) = (CH_4(ppbv) - 336.8)/4.78$ established from ALIAS N_2O and CH_4 data from several flights. The lines in (A) are the fits to the HCl vs. N_2O data, producing the relationships (in ppbv): HCl = 2.31 - $9.3x10^{-5}(N_2O)$ - $2.4x10^{-5}(N_2O)^2$ for 7 to 15 mbar; HCl = 0.75 -1 1. $1x10^{-2}(N_2O)$ - $4.3x10^{5}(N_2O)^2$ for 15 to 35 mbar; HCl = 1.00 + $2.6x10^{-3}(N_2O)$ - $1.9x10^{-5}(N_2O)^2$ for pressures ≥ 35 mbar. Model results in (B) for north and south mid-latitudes are coast rained by ATMOS observations obtained at 30"N in May 1985 [McElroy et al., 1992] and at 32 to 50°S in April 1993, assuming a 5 % yield of HC1 from the reaction of C1O -t OH. Data points in (B) are restricted to points with N_2O levels < 290 ppbv.

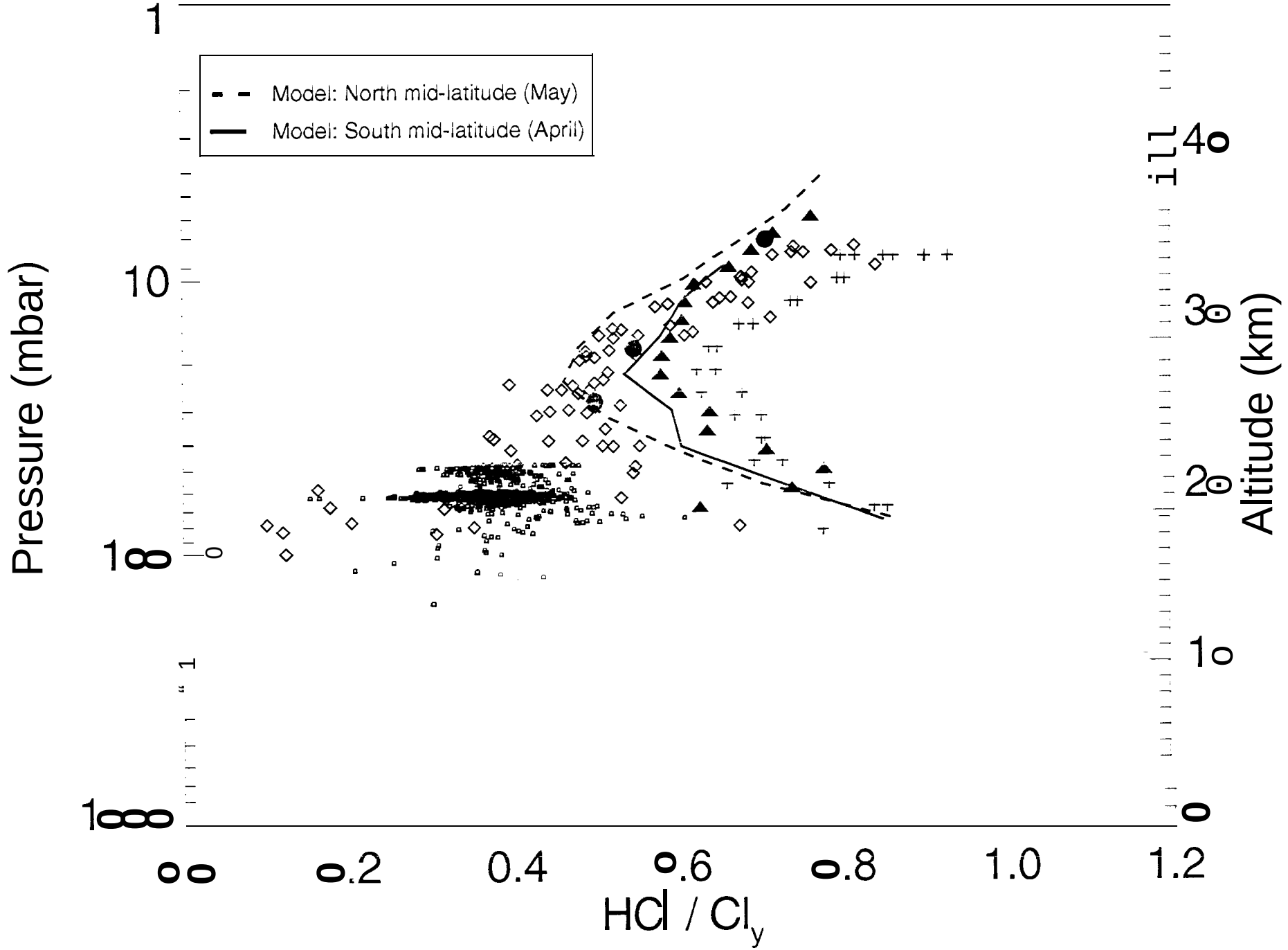
Figure **3.** Measured mixing-ratios for ClO, NO_2, HCl, and the inferred mixing-ratios of $ClONO_2$ for May 7, 1993, compared with Cl_y* using J_{ClONO2} calculated using recommended cross sections. The pressure range is about 50 to 70 mbar, with > 90% of observations obtained at pressures > 53 mbar. Latitude is constant at 37°N; SZA ranges from 310 to 81°. Between 85 and 90 ksecs, where N_2O changes from 200 to 110 ppbv, NO, is changing from 290 to 400 pptv, and C1O from about 20 to 4S pptv.

Table 1. Aircraft (ER-2) measurements

Species	Technique	Accuracy (~ 1 u)
N_2O	JR Absorption (ALIAS)	10%
HCl	ALIAS	15%
NO,	ALIAS	15%
ClO	resonance fluorescence	15%
Pressure	MMS	0.5 mbar
Temperature	MMS	0.3 K
$C10N0_2$,	inferred from ClO, NO_2	80%
Cl_y	inferred from CFC's	20%
Modelled J- values		30%


2.5
2.0
1.5
1.0
0.5
0.0
HCl (ppbv)
Model (34°N)
Cl$_y$
May 6, 1993
May 7, 1993
1:1
80
120
160
200
240
280
320
N$_2$O (ppbv)


AIRCRAFT (ALIAS) (37°N, May 93)
BALLOON (BLISS) (32°N, Aug 92)
HALOE (34°N, May 93)
ATMOS (32-50°S, Apr 93)
BALLOON (MARK IV) (35°N, Apr 93)
Cl_y
Pressure (mbar)
7-15
15-35
> 35
HCl (ppbv)
N_2O (ppbv)
0
1
2
3
200
400


Model: North mid-latitude (May)
Model: South mid-latitude (April)
Pressure (mbar)
Altitude (km)
HCl / Cl$_y$
1
10
100
0
20
40
0.2
0.4
0.6
0.8
1.0
1.2

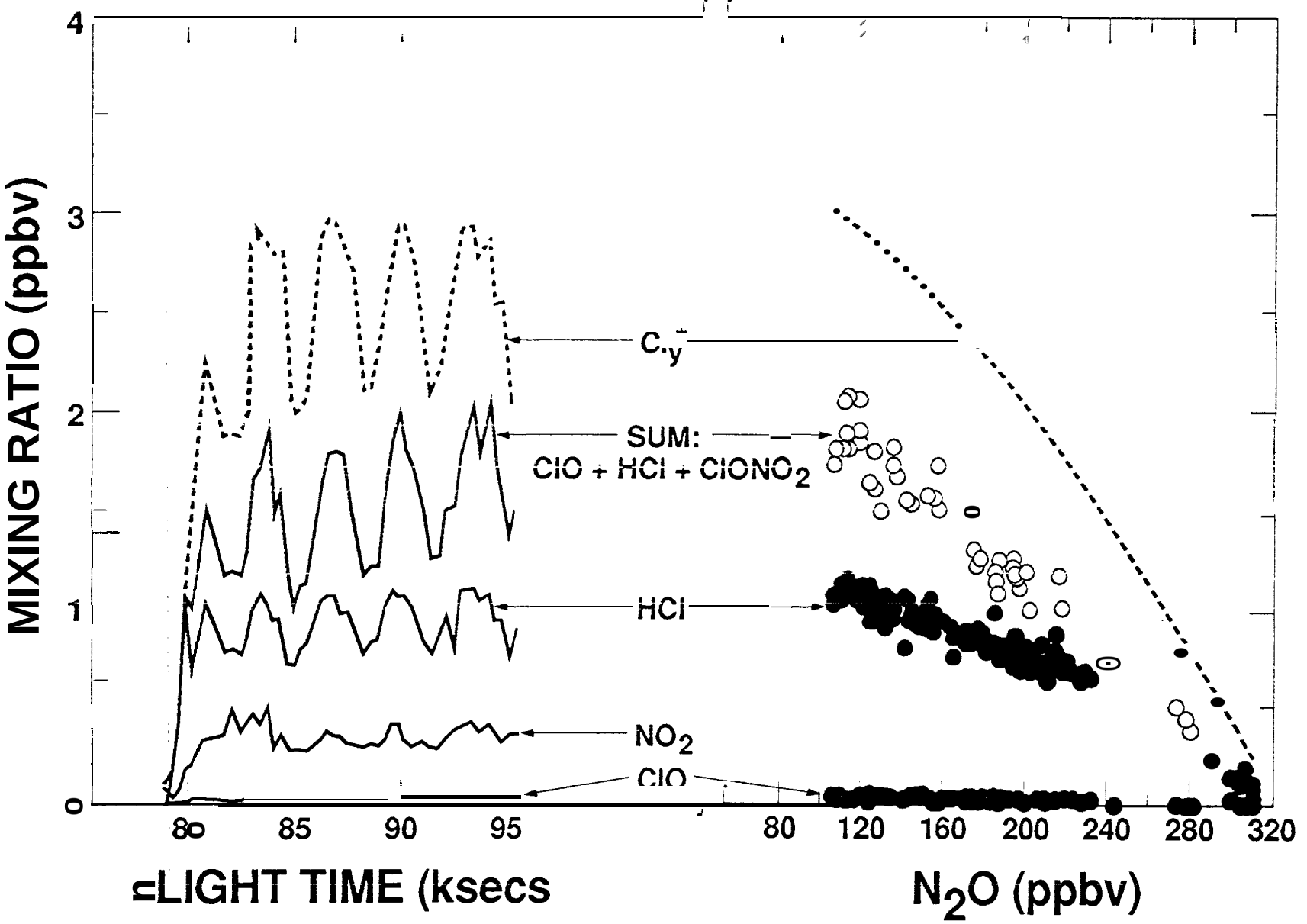

MIXING RATIO (ppbv)
4
3
2
1
0
C_y
SUM:
ClO + HCl + ClONO$_2$
HCl
NO$_2$
ClO
80
85
90
95
LIGHT TIME (ksecs
80
120
160
200
240
280
320
N$_2$O (ppbv)

Figure 3