

# IN SITU MEASUREMENTS OF THE ClO/HCl RATIO: HETEROGENEOUS PROCESSING ON SULFATE AEROSOLS AND POLAR STRATOSPHERIC CLOUDS

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**Abstract.** Simultaneous in situ measurements of stratospheric ClO and HCl have been made for the first time. From numerous flights of the ER-2 aircraft covering latitudes 24-90°N from October 1991 through March 1992, a detailed study of the partitioning of reactive to reservoir chlorine identifies the ClO/HCl ratio as a key indicator of heterogeneous processing both outside and within the Arctic polar vortex. For ClO mixing ratios below about 120 pptv, remarkably constant ClO/HCl values of about 15% characterize the lower stratosphere. The observed values are significantly higher than those derived from a 2-D model using either gas phase photochemistry alone (2%), or including heterogeneous sulfate chemistry (5-10%). During the Arctic early spring, after inorganic chlorine conversion of HCl into reactive chlorine has taken place, the vortex edge is poorly defined by ClO levels. Loss of HCl and its slow recovery following low-temperature polar heterogeneous chemistry distinguishes HCl as a new and unique dynamical tracer of PSC-processed air, long after PSC's have disappeared and ClO has recovered to its lower levels.

## Introduction

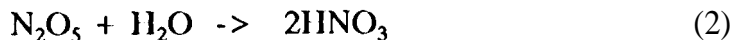
Polar ozone loss is initiated by the heterogeneous conversion on polar stratospheric clouds (PSC's) of inorganic chlorine from its reservoirs HCl and ClONO<sub>2</sub> to labile forms [see reviews by Solomon, 1990; and by Webster et al., 1993; and references therein]:



Following the return of sunlight, ozone loss results from the maintenance of high ClO levels which drive O<sub>3</sub> recombination through ClO + ClO and ClO + BrO

catalytic cycles [Anderson et al., 1991; Brune et al., 1991].

In the absence of heterogeneous chemistry, stratospheric ozone loss is determined principally by the  $\text{NO}_2 + \text{O}$  catalytic cycle, with an increasing contribution from the  $\text{ClO} + \text{O}$  cycle at higher altitudes. However, in the lower stratosphere, in-situ measurements of  $\text{NO}/\text{NO}_y$  [Fahey et al., 1993], and of  $\text{ClO}$  [Avallone et al., 1993] have shown that models using only gas phase chemistry poorly fit observations, and produce better agreement when the heterogeneous reaction on sulfate aerosol [Cadle et al., 1975]



is included. This reaction serves to directly decrease  $\text{NO}_x$ , and increase  $\text{HNO}_3$ . The gas phase photochemistry is then responsible for producing increased  $\text{OH}$  from  $\text{HNO}_3$  photolysis, and increasing  $\text{ClO}$  abundances at the expense of the inorganic chlorine reservoirs. Predicted additional reduction in  $\text{HCl}$  from reaction 7 is small, while increases in  $\text{ClO}$  are expected to be significant. The effect on the gas-phase catalytic cycles controlling ozone loss below 25 km is to remove the dominance of  $\text{NO}_x$  control [Fahey, 1993], and increase the role of both  $\text{HO}_x$  and  $\text{Cl}_y$  chemistry [McElroy et al., 1992].

The atmospheric chlorine loading of about 3.5 ppbv is currently increasing about 3% per year and is predicted to diminish by only about 10% over the next 20 years [WMO, 1991; McFarland and Kaye, 1992] as surface emissions are phased down. With the inorganic chlorine budget therefore conserved on shorter timescales, the ratio of midday  $\text{ClO}$  to  $\text{HCl}$ , the longest-lived chlorine reservoir, is expected to be a key indicator of heterogeneous processing on sulfate aerosol surfaces.

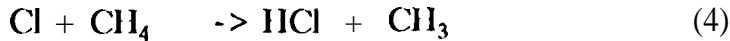
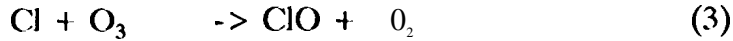
The reactive and reservoir gases of the lower stratosphere often show dramatic and characteristic changes during or following PSC processing within the polar vortices. Because recovery times for reservoir gases such as  $\text{HCl}$  and  $\text{HNO}_3$  may be long, the opportunity exists for using low reservoir abundances to identify polar air masses which have found their way to mid-latitudes during springtime break-up of the polar vortex. Specifically, low  $\text{HCl}$  (with a calculated recovery time of about 90 days [ref ]) would be associated with vortex air whose inorganic chlorine has been processed by PSC's [Webster et al., 1993], and low  $\text{NO}_y$  (with even longer recovery times) with vortex air which had been denitrified.

In this paper, we report the first in-situ measurements of  $\text{ClO}$  and  $\text{HCl}$  in the stratosphere, and compare the behavior of the  $\text{ClO}/\text{HCl}$  ratio with models incorporating heterogeneous chemistry, both outside and within the

polar vortex over a wide latitude range (24-90 °N).

#### The ClO/ICl ratio

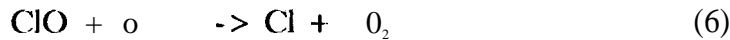
As emphasized by DeMore [1991], most of the atomic chlorine which appears in the stratosphere from whatever source reacts either with  $O_3$  or with  $CH_4$ :



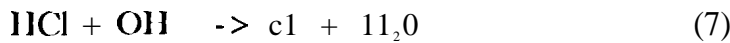
The second reaction is in fact the principal source of stratospheric HCl, and determines the IICl recovery rate following its loss from the PSC chemistry of reaction 1. In this case the source of Cl is from reaction of ClO with NO either already present (if removal of  $NO_x$  small), or produced from  $HNO_3$  photolysis in the recovery of the polar vortex:



In the upper stratosphere where atomic oxygen is more abundant, the reaction



completes the catalytic cycle with reaction (3) to produce  $O + O_3$  net loss. The principal loss of IICl occurs through reaction with OH (and PSC conversion in polar winter):



With the radicals Cl, ClO, and OH exhibiting strong diurnal variation, not expected in the long-lived reservoir IICl, the ClO/HCl is meaningful only away from large solar zenith angles. Under conditions of photochemical equilibrium, where the rates of ClO production and loss are balanced, the ClO/HCl ratio is approximated by [Brasseur and Solomon, 1986]:

$$\begin{aligned} \frac{[ClO]}{[HCl]} &= \frac{k_3[O_3]}{k_4[CH_4]} \times \frac{k_7[OH]}{k_6[O] + k_5[NO]} \\ &= \frac{k_7[OH]}{k_4[CH_4]} \cdot \frac{[ClO]}{[Cl]} \end{aligned} \quad (8)$$

where a small contribution from the reaction of Cl with  $HO_x$  reservoirs such as  $HO_2$  is neglected. To a first approximation, the ClO/HCl ratio therefore depends

linearly on the ratio  $k_3/k_4$ , whose value is about 900 at 200 K, as measured by DeMore [1991].

Photolysis of the additional  $\text{HNO}_3$  produced from the heterogeneous  $\text{N}_2\text{O}_5$  hydrolysis of reaction 2 should increase O11 abundance while removing  $\text{NO}_x$ . Because the  $\text{ClO}/\text{HCl}$  ratio is directly proportional to the O11 abundance, it is therefore expected to increase over gas phase values when sulfate aerosol chemistry is occurring.

The largest values of the  $\text{ClO}/\text{HCl}$  ratio are expected to be observed in sunlit air parcels which have recently experienced PSC chemical processing, since substantial repartitioning of inorganic chlorine results, with high  $\text{ClO}$  levels being associated with large  $\text{HCl}$  losses [Webster et al., 1993].

### The $\text{HCl}$ and $\text{ClO}$ instruments

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument is a scanning tunable diode laser spectrometer capable of measuring  $\text{HCl}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NO}_2$ , and  $\text{HNO}_3$  simultaneously using high-resolution laser absorption in the 3-8  $\mu\text{m}$  wavelength region [Webster et al., 1993b; May and Webster, 1993]. This new addition to the ER-2 payload for polar studies, was configured to measure  $\text{HCl}$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  for the 1991/2 Airborne Arctic Stratospheric Expedition (AASE-II) mission out of Moffett Field, California, Fairbanks, Alaska, and Bangor, Maine.

The  $\text{ClO}$  measurements were made by another instrument on the same ER-2 aircraft using the technique of atomic resonance fluorescence detection of  $\text{Cl}$  atoms resulting from chemical conversion of  $\text{ClO}$  by injected  $\text{NO}$ , as described elsewhere [Brune et al., 1991]. Uncertainties in measured  $\text{ClO}$  and  $\text{HCl}$  are typically about 15% each, but for  $\text{HCl}$  can vary from flight to flight. For low  $\text{HCl}$ , uncertainties are about 25%, with a minimum detectable amount of about 0.04 ppbv.

In flights typically 6-7 hours long, the ER-2 aircraft attains a maximum pressure altitude of about 50 mbar, covering a latitude range of about 23°N. Northerly and southerly flights from the three mission locations allowed latitudes spanning 22°N to 90°N to be reached.

### Results

#### *ClO/HCl ratio outside the vortex*

Figure 1 shows measurements of  $\text{ClO}$  and  $\text{HCl}$  for several flights from October 1991 through March 1992, covering latitudes spanning 26-90°N, and pressure altitudes of  $\geq 50$  mbar. The data included are limited to  $\text{ClO}$  mixing ratios of 100 pptv and below, and to solar zenith

angles  $\leq 80^\circ$ . What is immediately apparent is the remarkable constancy of the ClO vs. HCl relationship from flight to flight, over a wide latitude and seasonal range. A linear fit to the data produces the identity:

$$\text{ClO (ppbv)} = 0.2 * \text{HCl(ppbv)} - 0.045. \quad (9)$$

For comparison, model predictions of the ClO/HCl ratio for gas phase only, and including the heterogeneous reaction 2 for two levels of sulfate aerosol surface area, are also plotted. The observed values of ClO/HCl are significantly higher than those derived from the 2-D model using either gas phase photochemistry alone (2%), or including heterogeneous sulfate chemistry (5-10%).

Remote sensing submillimeter heterodyne measurements of ClO and HCl were recently reported by Stachnik et al. [1992] for the middle stratosphere (25-40 km) where ClO/HCl ratios significantly less than model predictions were observed. These authors concluded that the ClO/Cl ratio was unlikely to be the source of the observed discrepancy, and identified the lower uncertainty bound for the  $\text{O}(\text{I}) + \text{HCl}$  reaction 7 of 30% below the mean value [DeMore et al., 1992], in combination with unusually high  $\text{Cl}_2$  (not measured) amounts.

Recent measurements of ClO [Avalone et al., 1993, this issue] from 15 to 30 km in March 1991 clearly show ClO values increased by 15% at 32 km, and nearly 90% at 22 km compared with earlier balloon measurements of 1986 [Brune et al., 1988]. Although the addition of the  $\text{N}_2\text{O}_5$  heterogeneous hydrolysis of reaction 2 produced better agreement of their modeled ClO profile with the measurements, below 20 km the observed ClO remained higher than the model prediction. These authors concluded that the abundance of  $\text{ClONO}_2$  was greater than model predictions, as indicated by the earlier measurements of HCl [Webster et al., 1993], but could not rule out the possibility that PSC-processed air was being sampled.

Models including the heterogeneous sulfate chemistry of reaction 2 also systematically overestimate the abundance of HCl in the lower stratosphere, compared to direct in-situ measurements which imply that higher amounts of  $\text{ClONO}_2$  or another temporary chlorine reservoir exist [Webster et al., 1992]. We believe that the inability of models to duplicate the observed ClO/HCl values results from both an underestimation of ClO and an overestimation of HCl amounts.

#### *Heterogeneous conversion on PSC's*

Large increases in the ClO/HCl ratio were observed following inorganic chlorine conversion on PSC's, as

shown in Fig. 2 for flights on December 12, 1991, shortly after PSC formation began [see Newman et al., 1993], and on February 13, 1992, during the vortex recovery period. In a flight of January 20, 1992, deep into the vortex, where large HCl losses of up to 1 ppbv were observed [Webster et al., 1993] with high ClO values of up to 1.4 ppbv [Toohey et al., 1993], ClO/HCl ratios as high as 35 were calculated. During the early sunlit period following PSC conversion, high ClO levels are accompanied by loss of HCl equal to  $1/2(\text{ClO} + 2\text{Cl}_2\text{O}_2)$ , an HCl loss is not observed without ClO production (see [Webster et al., 1993]).

Even during the large perturbations to the inorganic chlorine partitioning following PSC chemical conversion, the ClO vs. HCl relationship is approximately held for ClO values below about 100 pptv, as shown in Fig. 2. That is, air parcels containing 100 pptv or less ClO are apparently not involved in PSC conversion. While it is tempting to identify a minimum ClO threshold for PSC conversion, the invariance in the ClO vs. HCl relationship probably simply reflects the homogeneity of the ClO vs. pressure altitude profile, identifying air parcels with  $\leq 100$  pptv ClO with temperatures always above that for PSC formation. However, some of these air parcels do in fact get quite cold, and the above observations therefore argue against the occurrence of significant chlorine conversion at temperatures above Type I PSC formation.

Flights like that of February 17, 1992 shown in Fig. 3 are very important for sampling air within and outside the Arctic vortex, in which three types of air were encountered: that showing no PSC processing (high HCl, low ClO); that showing recent chemical conversion (low HCl, high ClO); and that showing chemical recovery (low HCl still, but low, recovered, ClO). All three air types are evident in the data of Fig. 3. Large losses in HCl (negative values of  $\Delta\text{HCl}$ ), of up to 0.9 ppbv, coincide with the transition across the vortex edge, defined by the maximum zonal wind speed. Loss of HCl is calculated from the difference in the measured amount with that expected from its observed identity with the dynamical tracer  $\text{N}_2\text{O}$ , given by Webster et al. [1993]:

$$\text{HCl}(\text{ppbv}) = 1.56 - 0.0046 * \text{N}_2\text{O}(\text{ppbv}) \quad (10)$$

established (for  $\text{N}_2\text{O}$  mixing ratios  $>100$  ppbv) from numerous flights outside the chemically-perturbed vortex region.

Once vortex chemical recovery has set in, high ClO is a poor tracer of the chemically perturbed region. While the ClO/HCl ratio exhibits sharp gradients entering this region, HCl itself, with its longer recovery times, is clearly

the best tracer of PSC-processed air. As a dynamical tracer, HCl plays a role complimentary to that of NO<sub>y</sub>, which serves as a diagnostic tracer for vortex denitrification [Fahey et al., 1990].

#### *CIO, HCl across the vortex boundary*

Figure 4 shows the behavior of CIO,  $\Delta$ HCl, and CIO/HCl with latitude, using data from two flights, with the vortex edge marked. For the February 13 flight,  $\Delta$ HCl and CIO/HCl show sharp gradients at the vortex edge, the large HCl losses from 56-70°N being the signature of air which has earlier experienced PSC chlorine conversion. CIO increases markedly only deeper in the vortex near 63°N latitude, and shows only a gradual monotonic increase over the vortex edge at lower latitudes. Stratospheric air encountered at latitudes from 56-63°N is identified with air which had earlier seen PSC processing (low HCl), but has now partially recovered.

Not only is CIO a poor tracer of the chemically-processed vortex edge, but the behavior of  $\Delta$ HCl and CIO/HCl with latitude illustrate that caution must be exercised in identifying the observed gradual increase in CIO across the maximum wind boundary with material transfer in and out of the vortex. In fact, CIO/HCl shows little if any increase outside the vortex edge, meaning that vortex containment is effective even during recovery periods in mid-February.

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Fig. 1. Measurements of ClO vs. HCl for flights of Oct. 14, 1991, Feb. 13, 1992, and March 15 and 22, 1992, covering latitudes spanning 26-90°N. The data included

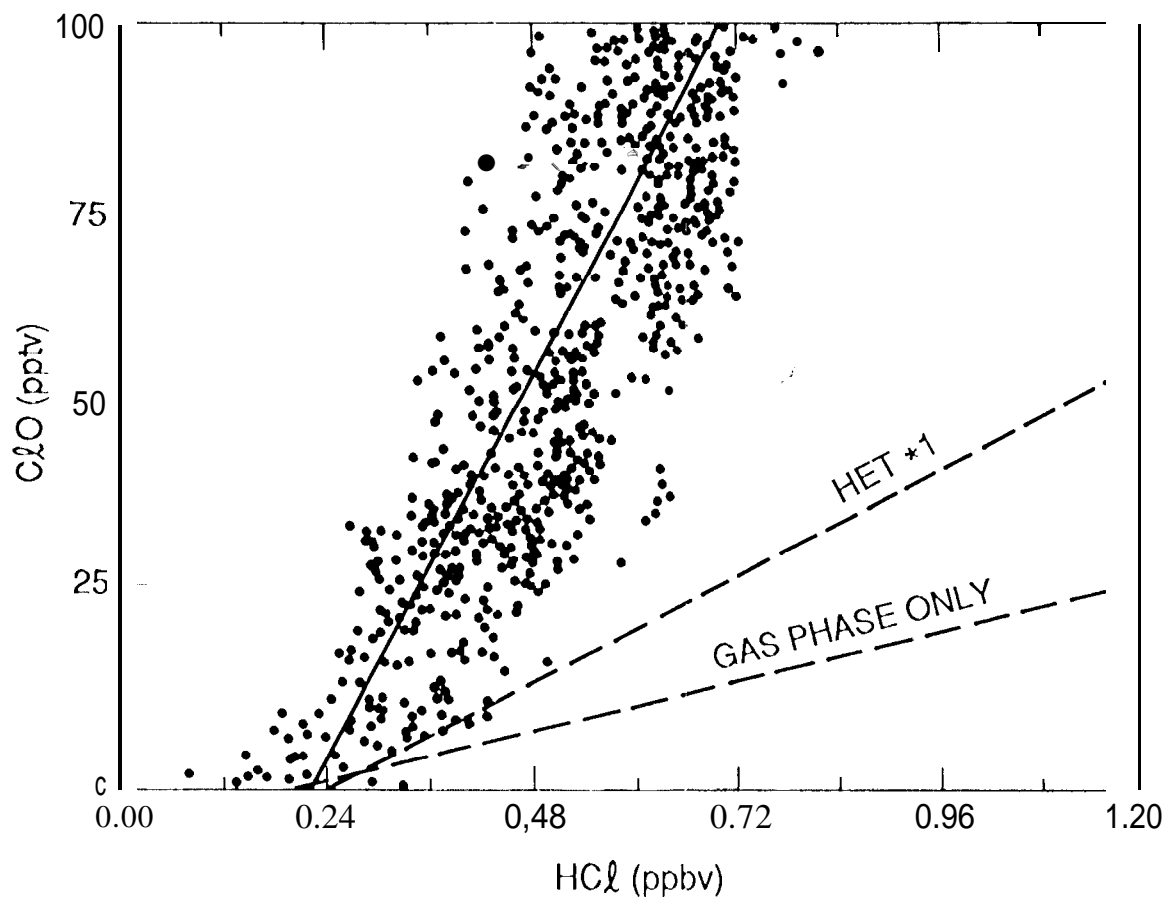
are limited to ClO mixing ratios of  $\leq 100$  pptv, and to solar zenith angles  $\leq 80^\circ$ . Also plotted are model predictions of the ClO/HCl ratio for gas phase only ( ), and including heterogeneous chemistry ( ).

Fig. 2. ClO vs. HCl for two flights penetrating Arctic vortex air, the one of Dec. 12, 1991 during the early period of PSC formation and inorganic chlorine conversion, and the second of Feb. 13, 1992 during the vortex recovery period after which significant conversion had taken place. The line on each plot represents the relationship of Eq. 9 in the text.

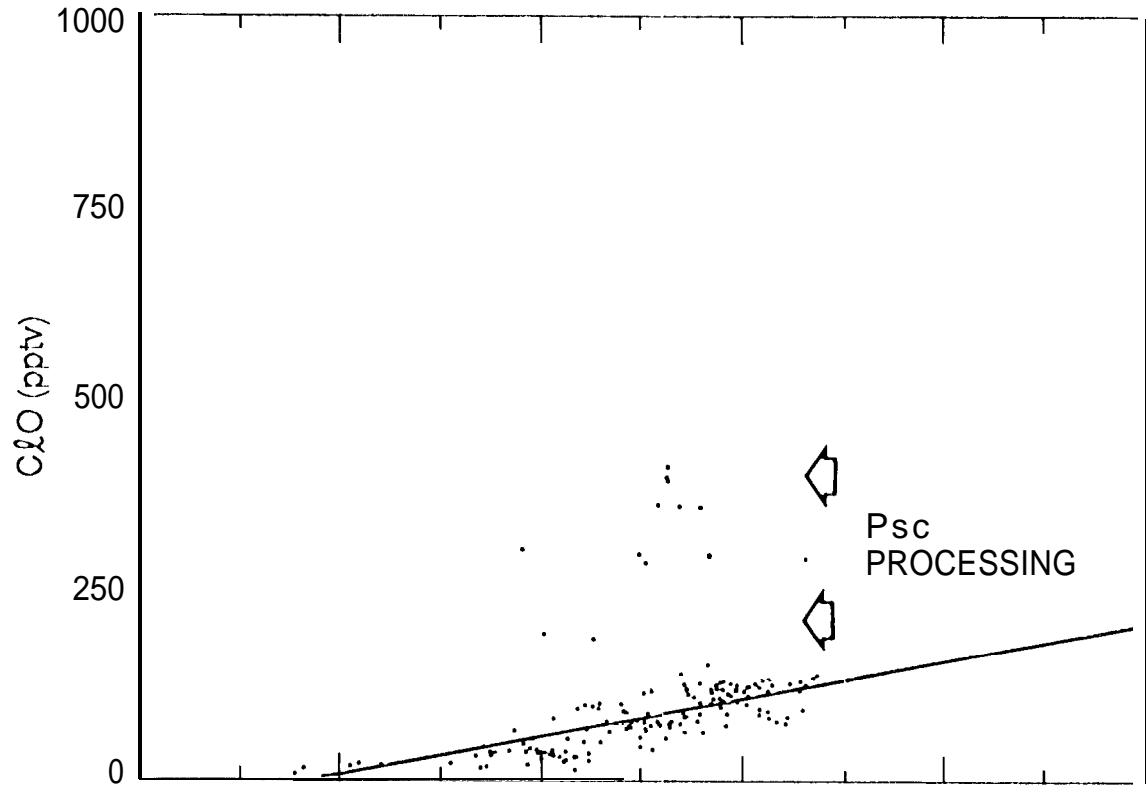
Fig. 3. Recorded data of measured ClO and HCl along the flight track of Feb. 17, 1992, with calculated  $\Delta$ HCl from Eq. 10 of the text, and the measured ClO/HCl ratio. Broken lines mark the vortex edge as defined by the maximum in the mean zonal wind.

Fig. 4. The variation in ClO, HCl, and ClO/HCl as a function of latitude, illustrated by data from two flights from Bangor, Maine: a flight south on March 22, 1992, and a flight north on Feb. 13, 1992. The two traces for each parameter correspond to the inbound- and outbound- legs for the March 22 flight, while the Feb. 13 data for ClO and ClO/HCl ratio are vertical axis scale expansions. The broken line marks the vortex edge as defined by the maximum in the mean zonal wind.

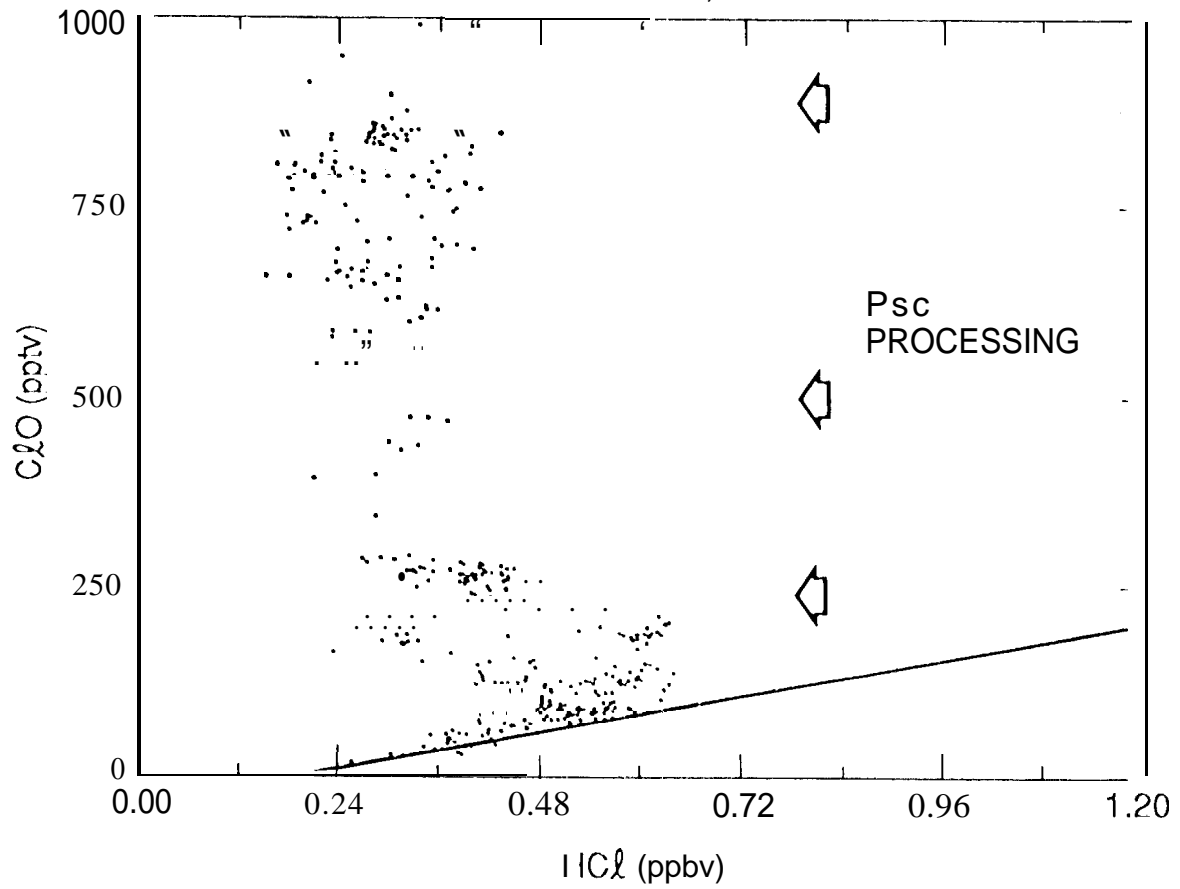
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DECEMBER 12, 1991



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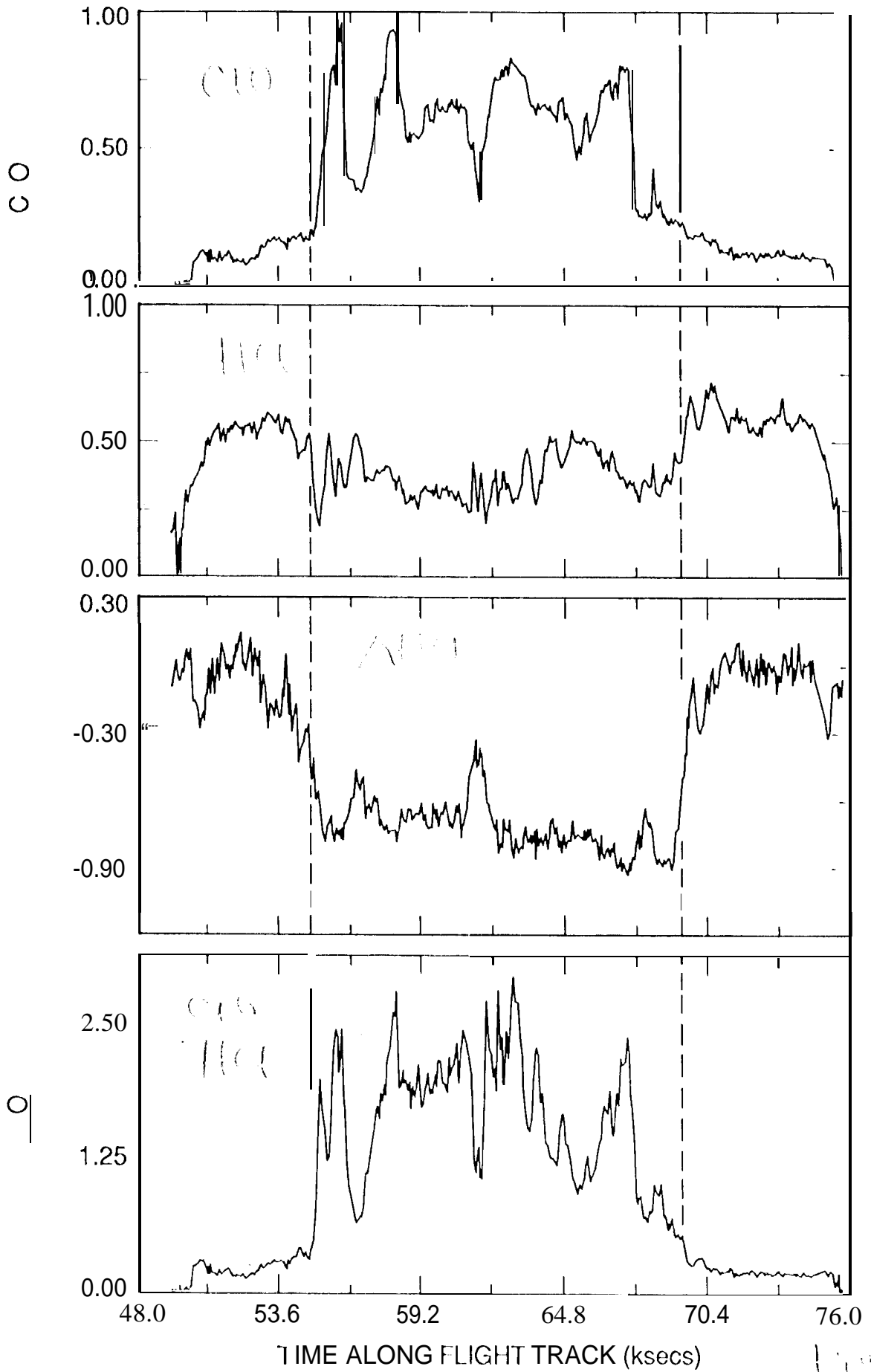


Figure 8

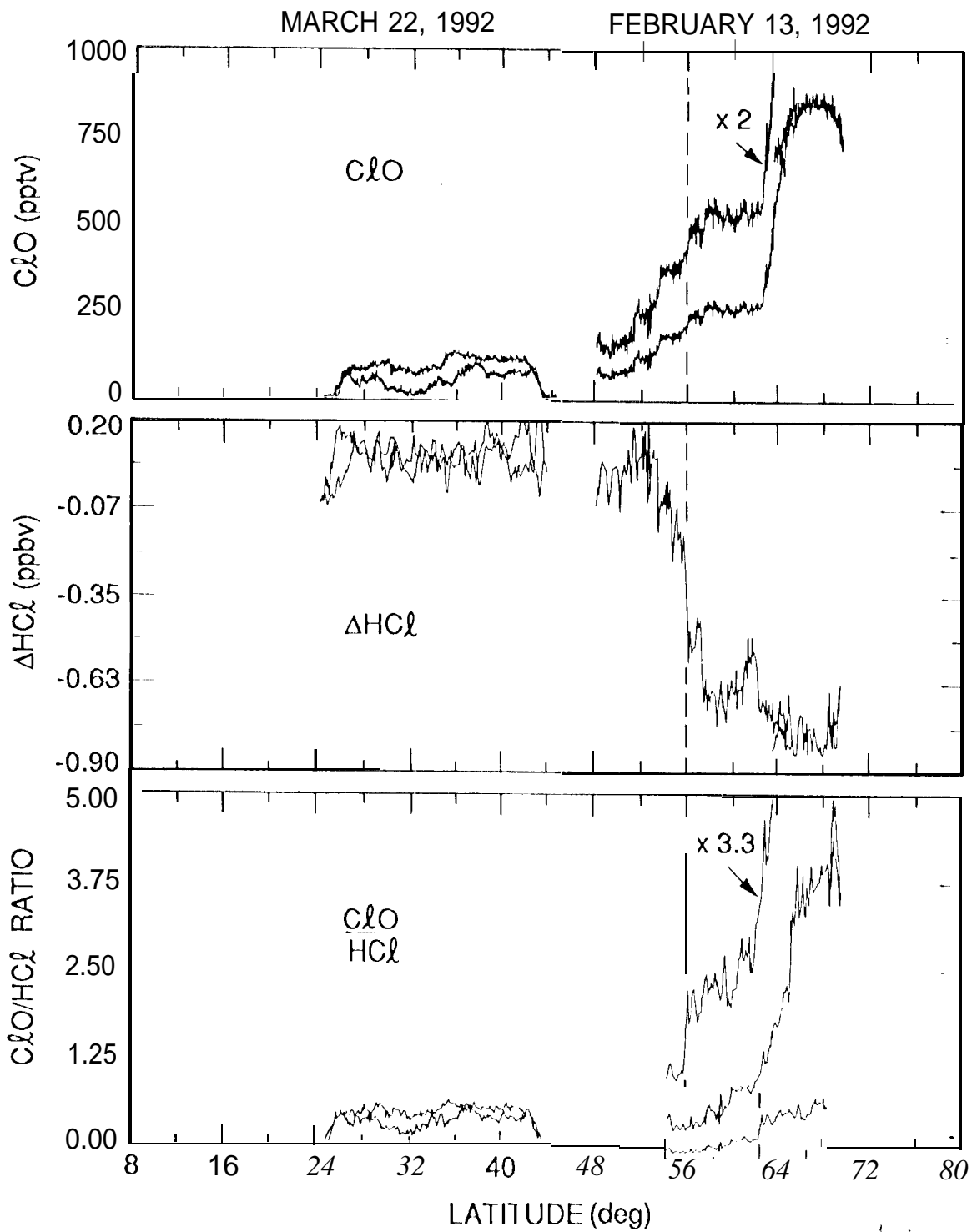


Fig 4