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Observations and Analysis of Atmospheric Hydroxyl

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Ground-based measurements of sunlight absorption at the OH P₁(1) resonance line at 308 nm have been made on a continuous basis at Fritz Peak, Colorado. The derived OH vertical column abundances show the persistence of a new seasonal regime which began in 1991. The fall minimum has been consistently depressed about 10-15% below the 1980-1990 average fall values. While the initial onset of depressed fall abundances occurred a few months after the Pinatubo eruption, there has been no fall OH recovery correlating with decreased amounts of volcanic aerosol found since spring 1993. The Colorado data also continues to exhibit an AM-PM asymmetry which varies seasonally, approximately in phase with local total ozone. These observations were presented at the Front Range AGU meeting in February 1996 and were published in Geophysical Research Letters in July 1996 (preprint enclosed). An update through the fall of 1996, when morning abundances were found to be extremely low, was presented at the Fall 1996 AGU meeting (abstract attached).

A PEPSIOS instrument of identical design is currently operational and has been used since April 1996 for OH column measurements at New Mexico Tech, Socorro, NM. Title for both instruments was transferred from Florida Atlantic University to New Mexico Tech in February of 1996. Comparative measurements from the two instruments for April-July 1996 indicate small differences in OH column abundances, with New Mexico (34°N) abundances about 10% above Colorado (40° N) values for comparable solar zenith angles. A more detailed comparison will require at least one full year of data from both locations.

New Mexico measurements were obtained on June 10, 1996, concurrently with a balloon launch of the NASA STRAT mission from Fort Sumner, New Mexico. We hope to make use of STRAT measurements H₂O, CH₄, and O₃ which are particularly relevant to OH photochemistry. Additional work at New Mexico Tech involves a comparison of P₁(1) and Q₁(3) absorption by the method of Doppler shift of solar limb spectra. These are being used to infer path weighted temperatures and for validations studies on the standard method of analysis using the single P₁(1) line. Results were presented at the Fall 1996 AGU meeting (abstract attached).

A graduate student in the Physics Department at New Mexico Tech has been supported since August 1996. The student is investigating column OH behavior using the NCAR 2-D model of the middle atmosphere. Graduate student support was not available until the start of the second year (Nov. 15, 1996), therefore funds have been transferred from the allocation for the research associate, who resigned from the project July 1, 1996.

We have undertaken computational studies of the OH $P_1(1)$ resonance line profile, testing for temperature variation effects on the lower state energy population and Doppler width. Effects of pressure broadening are also considered explicitly within a Voigt line-shape. The radiative transfer calculations include high resolution data from the Kitt Peak solar irradiance atlas. Our simulations demonstrate that the use of a 250 K temperature for OH column retrievals produces results that match the input column to within 5%, where the input OH profile is based on standard photochemical models. For OH vertical profiles radically different than standard models, for example with an enhanced contribution from the lower stratosphere, we find a relatively small impact on linewidth parameters due to temperature and pressure differences in the path weighted OH column. Resultant changes to the lower state energy population could be significant, however, leading to an overestimate of up to 10% in the retrieved column. These studies are obviously sensitive to the assumed OH vertical profile; our new results from simultaneous measurements of the $Q_1(3)$ and $P_1(1)$ lines will be valuable in this regard.

A manuscript describing the OH observations from Fritz Peak and Socorro was submitted to Geophysical Research Letters in December of 1997. A preprint of this manuscript is attached.

Measurements of Atmospheric OH by the Method of Doppler-shifted Solar Limb Spectra

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A new series of OH column measurements was initiated in April 1996, from Socorro, New Mexico (34 N, 107 W). These data include ultraviolet absorption spectra of atmospheric OH retrieved from observations of the east and west solar limb. The resulting Doppler shifts of solar spectra permit an unambiguous identification of absorption features by terrestrial OH. Relative intensities of spectral lines arising from distinct lower state rotational levels are used to obtain path-weighted temperatures of the OH column. Results for the OH column measurements and mean temperatures will be presented.

American Geophysical Union Abstract Form

Reference # 0000

Session 0.00

1. 1996 Fall Meeting
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A New Regime of Atmospheric OH Seasonal Behavior at Fritz Peak, Colorado, 1991-96

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The 18-year data base of OH column measurements at Fritz Peak, Colorado, is being extended through 1996. Of particular interest is the departure, beginning in fall 1991, of the normalized OH abundances from the average seasonal behavior of the 1980-1990 record. Fall abundances at low sun in 1991-1995 averaged about 15% below 1980-1990 values. Comparable data for 1996 will be presented. The significance and possible explanations of the changes in OH seasonal behavior will be discussed.

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Abstract Form**

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Continuing development in the regime of decreased atmospheric column OH at Fritz Peak

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Abstract

A new regime of reduced hydroxyl (OH) column abundances at Fritz Peak Observatory, first observed in the fall of 1991, continues to develop. Beginning in 1991, morning OH abundances in the fall season at Fritz Peak (40°N , 105°W) were found to be about 15% lower than the previous 1980-1990 average. Most recently, OH abundances for July 1997 were 30% below the corresponding 1980-1990 mean; these are the lowest values of column OH observed since 1980. Measurements for August-October 1997 indicate a continued regime of depressed (25%) OH abundances. The fall afternoon abundances were also low in 1997, yielding a PM-AM asymmetry of about 6% which is near the annual average for Fritz Peak. This is the first occasion since 1980 that the fall PM-AM difference of about 35% has not appeared. The winter season maximum of 15%, a persistent feature of the 1980-1990 measurement record, also failed to appear in 1996-97.

Introduction

The daytime photochemistry of atmospheric OH is driven primarily by solar ultraviolet radiation and the OH column abundance is therefore a strong function of solar zenith angle. Sources of odd-hydrogen ($\text{HO}_x = \text{OH} + \text{HO}_2 + \text{H}$) consist principally of H_2O and CH_4 . Much of the destruction is due to recombination of HO_x to form H_2O . Fast reactions with oxygen, nitrogen, and chlorine compounds also contribute to the loss and partitioning of HO_x . Odd-hydrogen thus has a relatively short lifetime and is not subject to transport. Consequently, the diurnal, seasonal, and long term behavior of atmospheric OH is responsive to the photochemistry and transport changes in free radical and source constituents. It has been called an indicator species for the photochemistry relating to stratospheric O_3 .

The ground-based column OH observations with PEPSIOS (PolyEtalon Pressure-Scanned Interferometric Optical Spectrometer) instruments have indeed shown considerable diurnal, seasonal, and long term variations, as well as geographic differences [Burnett and Burnett, 1996; Wood et al., 1994; Burnett et al., 1989, and references therein]. The limited success in interpretation of this data base suggests a need for refinements in descriptions of the combined action of the other free radicals and their interactions with OH [Burnett and Burnett, 1995]. This paper will concentrate on the continuing development of the change in column OH behavior at Fritz Peak, Colorado for 1991-1997.

Fritz Peak Data Base

The 20-year data base of column OH measurements at Fritz Peak (40°N , 105°W) is updated to fall 1997. The data generally shows the expected strong correlation with solar zenith angle, χ . When abundances are normalized to an average annual solar zenith angle dependence, we find additional systematic variations. The measurements from 1977 to 1980 demonstrated a 40% increase with high sun enhancement. The abundances from 1980 to 1990 were relatively stable with winter maximum, spring submaximum, and fall minimum. A diurnal asymmetry was found to vary seasonally, favoring PM abundances in fall and favoring AM abundances by a smaller amount in spring [Burnett et al., 1989, and references therein].

In fall 1991, OH abundances in the early morning were reduced substantially below the previous 10-year average. This anomalous seasonal regime per-

sisted through 1995 [Burnett and Burnett, 1996]. The timing of the change coincided with elevated volcanic aerosol over Fritz Peak from the eruption of Mount Pinatubo in June of 1991 [Langford et al., 1995]. However, reduced fall abundances have continued despite the abatement of volcanic aerosol beginning in spring of 1993 [Jager et al., 1995]. In Figure 1, the normalized abundances for AM, $\chi > 45^\circ$ is updated through fall of 1997. August to October early AM ($\sec\chi > 1.4$) normalized abundances for 1991-96 are about 10% below the corresponding 1980-1990 average. The 1997 August-October values have dropped an additional 15%. Winter abundances did not recover to the annual maximum in 1996-97 and the 1997 abundance decrease to 25% below the early morning 1980-1990 average occurred abruptly in July. The 1997 summer-fall early morning normalized abundances are the lowest values found for the entire data base, with the exception of the 1977-1979 period.

In Figure 2, the average solar zenith angle dependence of August-October abundances for 1996 and 1997 are shown, along with a curve of the averaged observations for August-October 1980-1990. Morning abundances in 1996 show a steep solar zenith angle increase towards midday to near the 1980-90 average in the afternoon. The resulting PM-AM asymmetry is similar to the fall diurnal behavior for all of the 1980-1990 observations at Fritz Peak. The average PM-AM difference in fall normalized abundances, excluding 2 hours around midday, has been about 35%. In 1997, the summer-fall midday and PM abundances remained near AM values and the PM-AM asymmetry was only about 6% for the first time since 1980. This is near the annual average value of the diurnal PM-AM difference. A small asymmetry of this sort may be expected due to the relatively slow odd-hydrogen recombination in the mesosphere.

Figure 3 shows the monthly average of normalized abundances of all data (AM and PM) for 1996 through October 1997 at Fritz Peak and at Socorro, NM (34°N , 107°W). Normalized abundances at Socorro (about 700 km south) remained 5 to 10% above 1980-96 Fritz Peak values until August 1997, when the signature of low morning abundances first began to appear. Colorado normalized abundances dropped abruptly in July to 0.7 of the 1980-1990 annual average and have remained near this level through October. New Mexico normalized abundances dropped more gradually in late summer, reaching 0.77 of the 1980-1990 Colorado average in September. Interestingly, both the recent decrease and the 1996 late

spring submaximum at New Mexico appear about 2 months later than at Colorado. The late spring submaximum is unclear at each location in 1997, in part due to the rapid changes in the baseline of overall abundances. The fall abundances for these locations are well below the fall values for all Colorado observations since 1977-79.

Discussion

The large number of individual spectral measurements (over 6,000 since 1990 at Fritz Peak) provide a clear indication of the average OH behavior with respect to solar zenith angle and season. The magnitude of the 1991-1997 OH abundance decreases from the 1980-1990 average are well in excess of experimental uncertainties. It should be noted that the PEPSIOS instrumentation, data acquisition, and analysis procedures have remained unchanged since initiation of measurements in 1977. It is extremely unlikely that the geographic differences and the seasonal and long term changes reported here can be attributed to experimental artifacts.

These continuing abundance changes for 1996-97 suggest a further, more general, development in the column OH observations since 1991 towards a fundamentally different photochemical situation. The extent to which this is a global change is unclear however. PEPSIOS column OH measurements for 1990-1995 at Lauder, New Zealand (45° S) gave no clear response to the Pinatubo aerosol. The New Zealand data also indicated larger abundances than for Colorado, and only a small PM-AM asymmetry with negligible seasonal variation [Wood *et al.*, 1994]. The possibility of a long term trend at that location is uncertain since this observation series ended in 1995. No other measurements, besides those from New Zealand or shown in Figures 1-3, have been taken with PEPSIOS instrumentation since 1991.

Column OH measurements from Tokyo (36° N) have been reported for 1992-1995 [Iwagami *et al.*, 1997]. These were made with instrumentation of lower spectral resolution and with analysis procedures different from the PEPSIOS data. The abundance values were approximately 65% of the Colorado 1980-1990 values with uncertainties of about 10%. These are consistent, within experimental error, with the most recent Colorado and New Mexico observations. These data suggest that the regime of reduced OH may have been established earlier at the Tokyo location than at Colorado. Tokyo observations were not

made prior to 1992 however.

Related Observations

Contributions to the OH column abundance are expected from the troposphere, stratosphere, and mesosphere. Model calculations predict maximum concentrations near 45 km, with about 60% of the total column between 35 km and 60 km. Observations of constituents relevant to OH concentrations in these regions are of interest for explanation of the recent changes in OH column abundances.

Troposphere

Observations of tropospheric OH made in Colorado in fall 1993 yielded average midday concentrations of $4 \times 10^6 \text{ cm}^{-3}$, with maximum concentrations during pollution episodes of $15 \times 10^6 \text{ cm}^{-3}$ [Mount *et al.*, 1997]. If the average OH concentration is taken to be representative of the vertical distribution of tropospheric OH at this location, the tropospheric contribution to the observed OH column for fall midday would be $0.3 - 0.5 \times 10^{13} \text{ cm}^{-2}$, or about 20% of the column changes reported here for midday. It therefore seems unlikely that tropospheric OH changes could have contributed more than a small fraction of the progressive OH column change.

Stratosphere

The abrupt onset of the OH abundance changes following the Pinatubo eruption, with its heterogeneous chemical effects on column NO₂, has been previously noted [Burnett and Burnett, 1996]. Northern midlatitude column NO₂ reached minimum values in January 1992 and recovered to near normal values in 1995. Measurements of midlatitude NO₂ generally exhibit a seasonal decrease from summer to winter; there is also an additional daytime increase in NO₂ due to the photolysis of N₂O₅ [Van Roozendael *et al.*, 1997, and references therein]. Column OH has also shown a seasonal summer-to-winter decrease and a fall diurnal increase. Model calculations which include these NO_x tendencies and use presently accepted photochemical reactions and recommended rates have not, as yet, reproduced the magnitude and time behavior of the column OH observations. In Figure 1, the seasonal decrease is seen to steepen beginning in 1991. In Figure 2, the 35% fall diurnal OH decrease, which has been a persistent feature of the measurements until 1997, dropped to the seasonal average of 6%. It

may be noted that NO concentrations play a sensitive role in the methane oxidation sequence. The partitioning of ClO_x ($\text{Cl} + \text{ClO}$) is highly dependent on NO; the Cl/ClO ratio is approximately proportional to NO/O_3 . Elevated Cl concentrations which might dominate the initial reactions in the methane oxidation sequence should become less effective in enhanced HO_x production as NO concentrations are decreased [Burnett and Burnett, 1995]. However, explanation of the continued development of the anomalous OH regime evidently requires consideration of a causal mechanism different from the apparent earlier heterogeneous NO_x reactions.

Other measurements from midlatitudes have shown small changes since 1991. Total ozone at Boulder during this time has shown no significant departure from its gradual 0.5 % yr^{-1} decrease since 1980 [Dobson Total Ozone date courtesy of CMDL/NOAA]. Measurements of total ozone from Socorro, initiated in June 1997, also show no unusual behavior. We have investigated zonally averaged data near 40°N from the Halogen Occultation Experiment [Russell *et al.*, 1993]. Data up to July 1997 indicate no significant recent changes in stratospheric H_2O , CH_4 , or O_3 . Results at 1 mb (near the stratopause) indicate a gradual 10% increase in H_2O and about a 20% decrease in CH_4 since 1992. The seasonality and magnitudes of these trends are not consistent with the OH column changes.

Recent meteorological conditions in the Arctic winter have been more conducive to ozone loss than in most previous winters since 1978-79 [Zurek *et al.*, 1996]. Unusually low total ozone and enhanced ClO were observed in February-March 1997 [Newman *et al.*, 1997; Santee *et al.*, 1997]. Meridional transport of this polar-processed air could result in altered mid-latitude photochemistry. However, the photochemical time scales necessary for this air to recover to normal midlatitude values would need to be at least several months to account for the observed OH effects.

Mesosphere

Measurements from the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) in November 1994 yielded mesospheric OH concentrations which were somewhat less than theoretical predictions [Conway *et al.*, 1996; Summers *et al.*, 1996]. Also, microwave measurements of mesospheric HO_2 by Clancy *et al.* [1994] revealed concentrations which were 2 times larger than expected from model calculations using recommended reaction rates. Clancy *et al.*

suggested that the data are consistent with a reaction rate for $\text{HO}_2 + \text{O}$ which is 60 to 80% smaller than the currently assumed rate. Such a change in HO_x partitioning would also predict decreased mesospheric OH values. A further consequence would be a smaller calculated destruction rate for mesospheric ozone, long considered a model-observation discrepancy.

The recent fall AM column OH abundances are about 10% below theory, a difference of about $0.8 \times 10^{13} \text{ cm}^{-2}$ at $\chi = 60^\circ$. A possible interpretation of this change might be the failure during this recent period of the 1980-1990 mechanism for enhanced OH. The latest abundance values might then be an upper limit for the remaining column. The theory-observation discrepancy would thus be reasonably consistent with the HO_2 and the OH mesospheric measurements. However, the failure to understand processes responsible for the enhancement in OH abundances observed during 1980-90 makes the above assumptions questionable.

Final results from the August 1997 MAHRSI campaign may provide a definitive answer concerning the altitude region responsible for the recent Colorado column OH changes. Normalized total column OH abundances for August 1997 were 21% below those for August 1994 and 30% below those for November 1994. Similar decreases in MAHRSI measurements of OH above 40 km between 1994 and 1997 would confirm a mesospheric change; absence of change in MAHRSI measurements would imply a stratospheric location for the OH column decrease.

Summary

The circumstances of the apparent 1991 OH response to Pinatubo aerosol and the current increased Arctic heterogeneous chemistry each suggest some relation with the recent OH phenomena. However, the absence of verification/correlation with large changes in other constituents in observations at the Colorado midlatitude location do not permit further progress in explanation. The magnitude and continuing development of the OH behavior indicate an important midlatitude atmospheric change which has not been reported in other observations nor predicted by current models.

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Observatory has also been a major support factor and is greatly appreciated.

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Figure 1. Column OH monthly normalized abundances, 1990-1997, for AM, $\chi > 45^\circ$ at Fritz Peak Observatory, Colorado. Normalization is with respect to the annual average AM solar zenith angle dependence for 1980-1990. Error bars are standard error of the mean. The solid curve is the average seasonal behavior of similar data for 1980-1990.

Figure 2. Vertical column OH abundances at Fritz Peak for August-October, 1996 and 1997, plotted against secant of the solar zenith angle. Error bars are the standard error of the mean. The solid curve is the average of observations for August-October 1980-1990. The dotted curve shows model values using photochemistry with pre-1980 chlorine levels [Burnett and Burnett, 1995].

Figure 3. Monthly averaged column OH normalized abundances of all data for 1996 and 1997 at Fritz Peak Observatory, Colorado and for Socorro, New Mexico. Normalization is with respect to the annual average of AM and PM solar zenith angle dependence at Fritz Peak for 1980-1990. Error bars are the standard error of the mean.

FRITZ PEAK, CO₂, NORMALIZED OH ABUNDANCES
AM LOW SUN, SOLAR ZENITH ANGLE > 45°

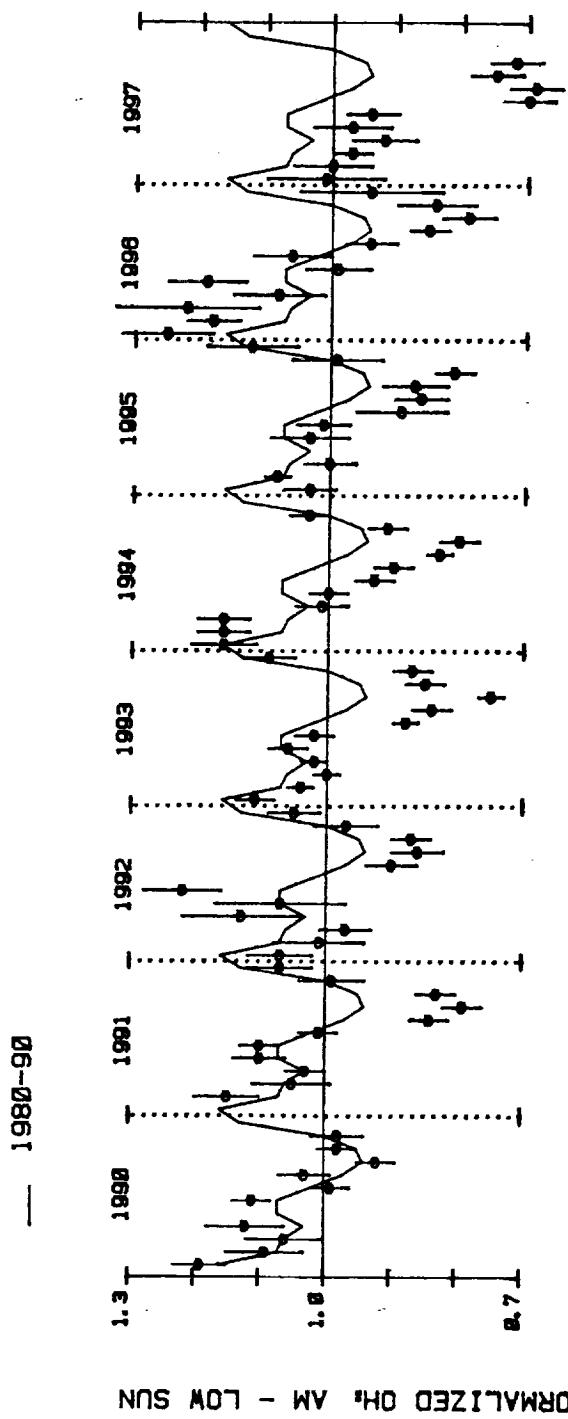
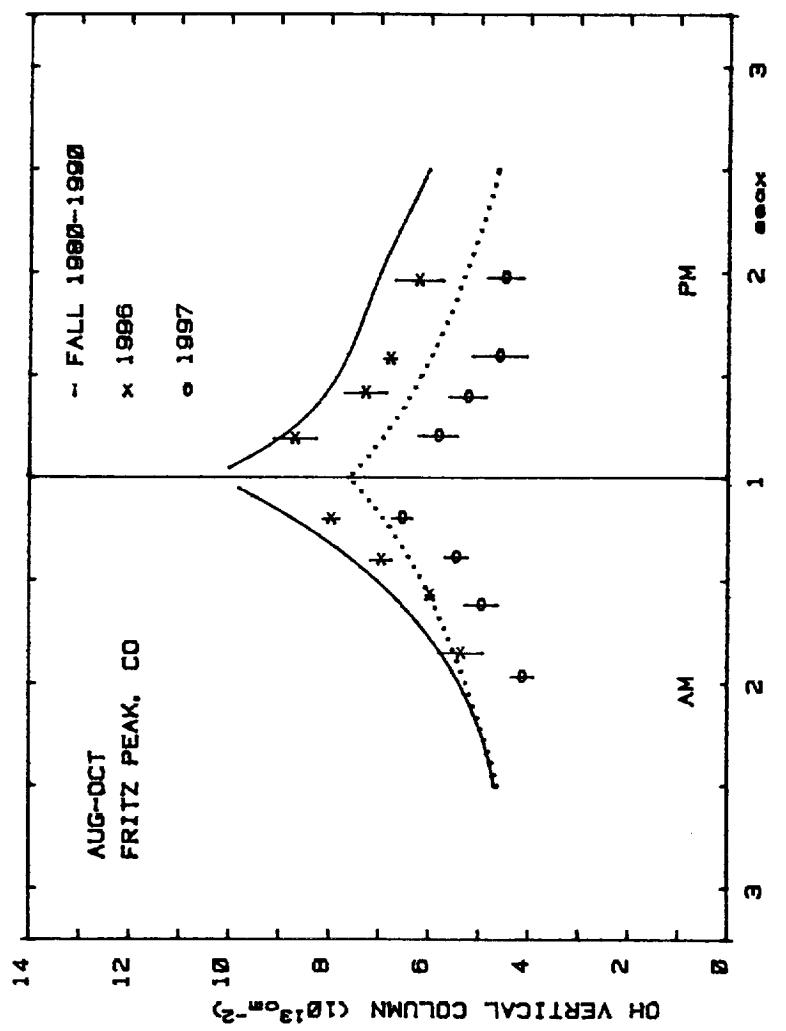


Figure 1



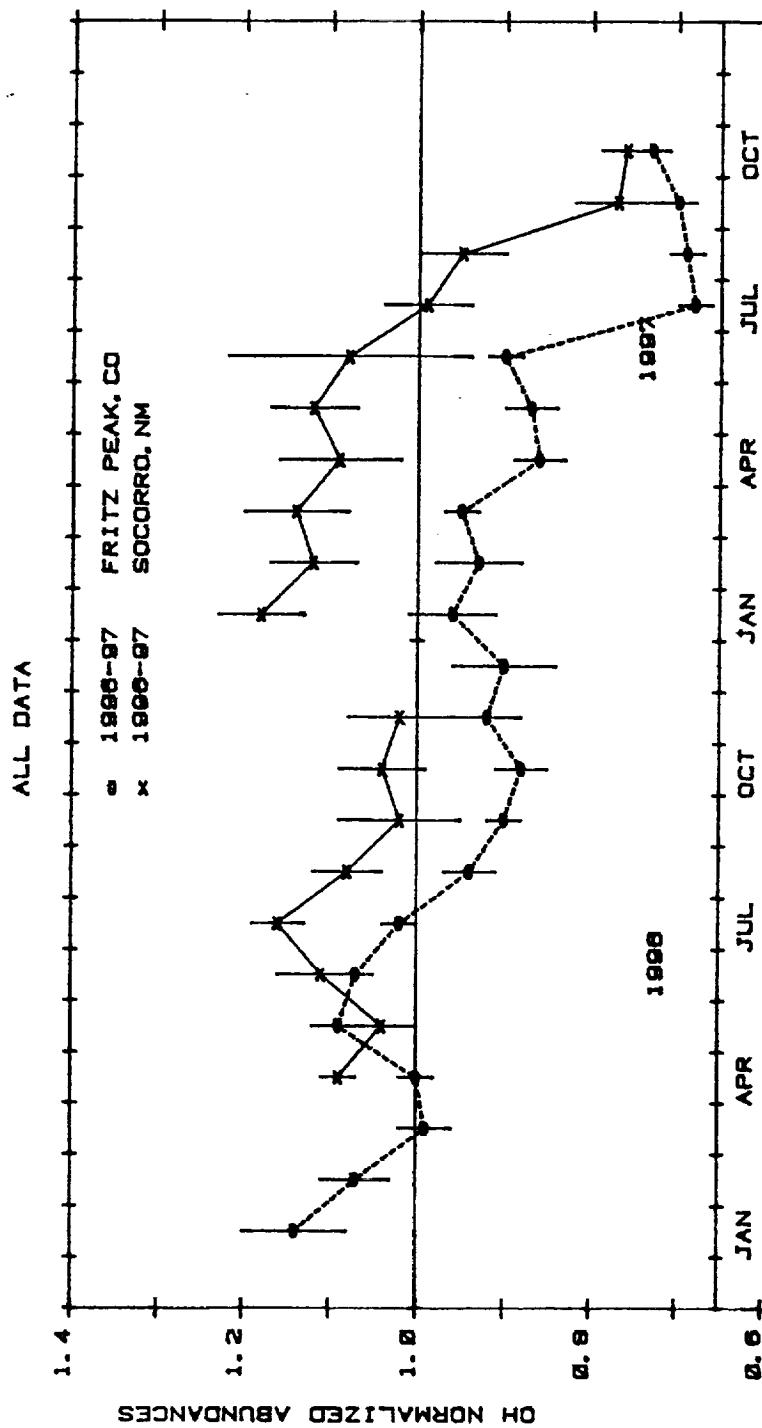


Figure 3