

## QBO and QTO of atmospheric trace elements nitrous oxide and chlorofluorocarbons: An update

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**सार** – वर्ष 1978 से 2001 के दौरान विभिन्न स्थानों में N<sub>2</sub>O (नाइट्रस ऑक्साइड) और CFC (क्लोरोफ्लोरोकार्बन) सांद्रणों (मासिक मान) के विप्लेखन से मौसम संबंधी परिवर्तिताओं का पता चला है। जब 12 माह के गतिमान औसत (12 एम.) के आधार पर इनकी गणना की गई और 3 वर्षों के गतिमान औसत (37 एम.) को 12 एम. से घटाया गया, तब प्राप्त हुए शेष (12 एम. – 37 एम.) से क्यू. बी. ओ. (अर्ध-द्विवार्षिक दोलन, 2 से 3 वर्ष) और क्यू. टी. ओ. (अर्ध-त्रैवार्षिक दोलन, 3 से 4 वर्ष) क्षेत्रों में चरम अंतराल वाले दोलनों का पता चला है। उच्च उत्तरी अक्षांशों में क्यू. बी. ओ. समतापमंडलीय निम्न अक्षांशीय पवनों के क्यू. बी. ओ. के लगभग समान रहे और अक्षांशों में क्यू. टी. ओ. एनसो (एल निनो/दक्षिणी दोलन) के समान रहे।

**ABSTRACT.** An analysis of N<sub>2</sub>O (nitrous oxide) and CFC (chlorofluorocarbon) concentrations (monthly values) at various locations during 1978-2001 indicated seasonal variations. When these were minimized by calculating 12-month running means (12m) and 3-year running means (37m) were subtracted from 12m, the residues (12m-37m) showed oscillations with peak spacings in the QBO (quasi-biennial oscillation, 2-3 year) and in the QTO (quasi-triennial oscillation, 3-4 year) regions. The QBO at high northern latitudes roughly resembled the QBO of stratospheric low latitude winds and the QTO at low latitudes resembled the QTO of ENSO (El Niño/Southern oscillation).

**Key words** – QBO, QTO, ENSO, Chlorofluorocarbon.

### 1. Introduction

The Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA), Air Resources Laboratory, Boulder, Colorado, has been making meticulous measurements of several trace elements such as CO<sub>2</sub> (carbon dioxide), CO (carbon monoxide), CH<sub>4</sub> (methane), O<sub>3</sub> (ozone), N<sub>2</sub>O (nitrous oxide) and CFC (chlorofluorocarbons) since 1977, with continuous monitoring network at Barrow, Alaska; Mauna Loa, Hawaii; Cape Matatula, American Samoa and South pole, Antarctica, and an air sampling network and flask sampling program at several dozens of other locations. Details of the instruments, measurement techniques, calibrations, updating with corrected data etc. are given in the various CMDL Summary reports (latest report No. 26, 2001). Another group has been conducting the Atmospheric Lifetime Experiment (ALE) program since 1978 (Prinn *et al.*, 1983; Rasmussen and Lovelock, 1983), followed by the Global Atmospheric Gases Experiment (GAGE) program, and later, AGAGE, where measurements are made of CFCs and N<sub>2</sub>O at five

locations, Ireland (first at Adrigole, then at Mace Head); U.S. West Coast (first at Cape Mears, then at Trinidad Head); Ragged Point, Barbados; Cape Matatula, American Samoa; Cape Grim, Tasmania (history and results are presented in Prinn *et al.*, 1990, 2000). In earlier communications (Kane, 1994, 2000a,b, 2002), it was shown that the time series of these elements showed interannual variations, roughly in the QBO (Quasi-biennial, 2-3 years) and/or QTO (Quasi-triennial, 3-4 years) ranges. However, for some elements, the data available were only annual means and for only a few (about 6) years. In the present communication, the data for CFCs and N<sub>2</sub>O are examined for longer intervals.

For N<sub>2</sub>O (nitrous oxide), Montzka *et al.* (1992) reported a growth rate of ~0.6 ppb/yr during 1977-1985, which increased to ~1.1 ppb/yr during 1988-1991. Since 1991, the growth rate of N<sub>2</sub>O decreased to ~0.5 ppb/yr and the annual values leveled off in 1993 (Thompson *et al.*, 1994). Using 10 years of ALE/GAGE N<sub>2</sub>O data (1978-1988), Prinn *et al.* (1990) estimated trends in the northern and southern hemispheres. They concluded that the major trends and latitudinal distributions were

consistent with the hypothesis that stratospheric photodissociation is the major atmospheric sink for  $N_2O$ ; but the  $N_2O$  increases were not caused solely by increases in anthropogenic  $N_2O$  emissions (fossil fuel combustion etc.) but were probably due to a combination of a growing tropical source (land disturbance) and a growing northern mid-latitude source (fertilizer use and fossil fuel combustion). They also conducted a multiple regression analysis which included cycle (annual, quasi-biennial) terms and concluded that a statistically significant QBO was evident at Barbados and Tasmania but otherwise, both annual and quasi-biennial oscillations were weak or insignificant at all sites. Recently, Elkins *et al.* (2003) summarized the up-to-date situation as follows: Two significant anthropogenic sources of  $N_2O$  are the production of fertilizers and removal of animal and human waste. Considering the expected increase in both, the  $N_2O$  level which was ~300 ppb in 1977 and ~315 ppb in 2000, is expected to be ~450 ppb by the end of the present century. Regarding  $N_2O$  of marine origin,  $N_2O$  is produced by nitrifying and denitrifying bacteria and the denitrifying typically occurs most intensely during coastal upwelling zones on the eastern boundary of the Pacific Ocean. Hence, during El Niños (warm water temperature anomalies in equatorial Pacific) when the upwelling is decreased, fluxes of oceanic  $N_2O$  to the atmosphere are expected to decrease. Also, El Niños change global atmospheric circulations creating significant dry periods in the tropical productive forests. The dry conditions result in less production of  $N_2O$  by bacteria and hence, low fluxes of  $N_2O$  in the tropics during El Niño. Elkins *et al.* (2003) mention that such a decrease in growth rate of  $N_2O$  was observed by them during the giant El Niño of 1997-1998.

For CFCs (chlorofluorocarbons, notably CFC-11), there had been a rapid increase from 1978 (start of observations) to about the early to middle of 1990s, (from 170 ppt to 270 ppt, about 60% increase at Barrow, Alaska), after which the growth rates of all major CFCs have been declining, with the exception of CFC-12 ( $CCl_2F_2$ ) (Cunnold *et al.*, 1997; Dutton *et al.*, 2003). Earlier, Elkins *et al.* (1993, 1994) presented the NOAA data for global and hemispheric monthly means of CFC-11 and 12 for 1977-1992 and discussed the characteristics of their growth rates, particularly the decrease of the growth rates, as also their relationship with ENSO events. They also mentioned that there was a good correlation between the maximum of easterly winds of the equatorial stratosphere and the drop in the southern hemisphere growth rates for both CFCs. Cunnold *et al.* (1994) used an independent data set (ALE/GAGE) of both CFC and fitted an annual cycle and a 29-month (2.4 years) oscillation and estimated their amplitudes for the period 1978-1991. Earlier, Prinn *et al.* (1992) had noted a QBO in another

CFC (methyl chloroform). QBO and ENSO effects have been reported earlier for stratospheric ozone also (Zerefos *et al.*, 1992). Prinn *et al.* (2001) have presented evidence of substantial variations of atmospheric hydroxyl radicals in the past two decades.

In recent years, a QBO has been considered as well established in some trace elements. Hamilton and Fan (2000) noted a QBO (Quasi-Biennial Oscillation) in long-lived greenhouse gases and examined the role of dynamical QBO of stratospheric low latitude winds in modulating STE (Stratosphere-Troposphere Exchange) in such a manner as to produce such a QBO, particularly in methane, while Georgetta and Bengtsson (1999) examined the same effect in water vapor.

In the present communication, variations on intermediate time scales are reported for data of more than 20 years, mainly with a view to compare with the quasi-biennial oscillation (QBO) known to exist in stratospheric low latitude zonal winds (Reed *et al.*, 1961; Veyard and Ebdon, 1961) and the quasi-biennial and quasi-triennial oscillations (QBO, QTO) in ENSO (El Niño/Southern Oscillation, Rasmusson *et al.*, 1990).

## 2. Data

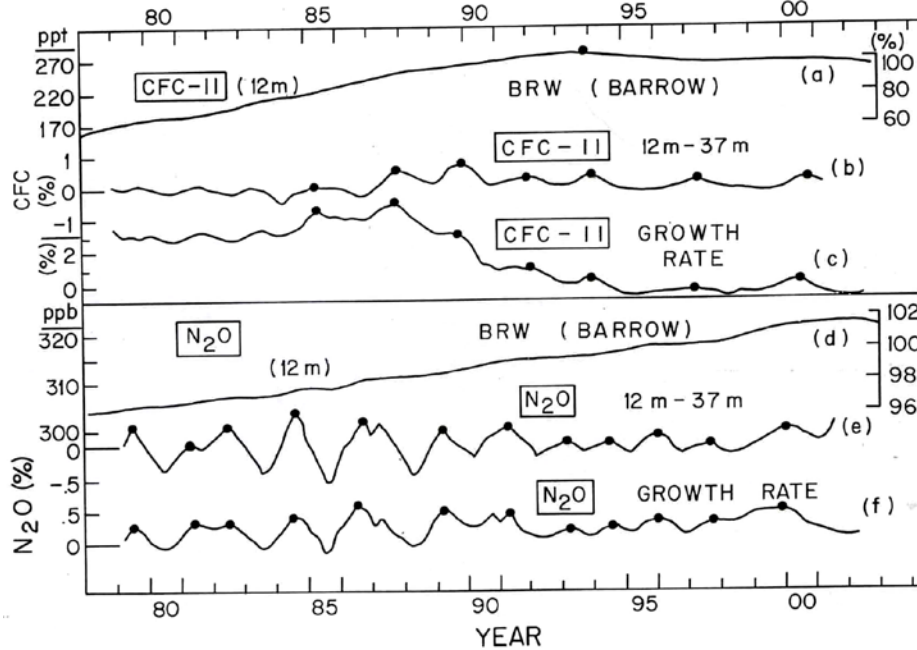
The data used are monthly values of  $N_2O$  and CFC-11 and CFC-12, from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) and available at their website <ftp://ftp.cmdl.noaa.gov/hats/>, and from the Atmospheric Lifetime Experiment (ALE/GAGE/ALEGAGE), available at the Carbon Dioxide Information Analysis Center (CDIAC) website [http://cdiac.esd.ornl.gov/ftp/ale\\_gage\\_Agage](http://cdiac.esd.ornl.gov/ftp/ale_gage_Agage). Not all CFC and  $N_2O$  data were suitable (continuous enough) for long-term studies. Only the following were used:

*CMDL data* - BRW Barrow, Alaska, USA (71° N); NWR Niwot Ridge, Colorado, USA (40° N); MLO Mauna Loa, Hawaii, USA (20° N); SMO Cape Matatula, American Samoa (14° S); SPO South Pole, Antarctica, USA (90° S).

*ALE/GAGE/ALEGAGE data* - MHD Mace Head, Ireland (53° N); RPB Ragged Point, Barbados (13° N); SMO Cape Matatula, American Samoa (14° S); CGO Cape Grim, Tasmania, Australia (41° S).

For ENSO (El Niño/Southern oscillation), data were obtained from the Climate Prediction Center NOAA website <http://www.cpc.ncep.noaa.gov/data/indices/>. Data

for 30 hPa wind were supplied privately by Dr. Naujokat of the Institute of Meteorology, Berlin University.



**Figs. 1(a-f).** Plots for 1978-2002 of CFC-11 at Barrow, (a) The 12-month running means (12m), (b) (12m-37m), (c) Growth Rate. (d,e,f), similar plots for  $N_2O$  at Barrow

### 3. Interannual variability

#### 3.1. Sample plots for Barrow, Alaska

In most of the parameters, there were a substantial seasonal variation. Since the purpose of the present study is to concentrate on interannual variations, the seasonal variation was suppressed by calculating 12-month running means. Fig. 1(a) shows a plot of the 12-running means (12m) of CFC-11 at Barrow ( $71^\circ N$ ). A large long-term trend is seen, with the values rising from  $\sim 155$  ppt in 1978 to  $\sim 278$  ppt in 1993-1994 and falling thereafter to  $\sim 263$  ppt in 2002. Superposed on this trend are small oscillations (not easily seen), which can be discerned if the long-term trend is removed. This was done by calculating 3-year (37 months, to get the centering correct) running means (37m) and subtracting these from the 12-month running means (12m). The residues (12m-37m) are shown in Fig. 1(b). Small oscillations (range less than 1%) are seen (peaks marked by dots). For studying interannual variability, a parameter often calculated is the "Growth Rate", defined as the level change in 12 months (ppt/year). Thus, the value for any month 'm' of any year 'y' is subtracted from the value of the same month 'm' of the next year (y+1) and these changes (gradient over 12 months) are calculated for successive months. It was noticed that these fluctuated considerably, rather erratically. Hence, their 12-month running means were calculated, which were fairly

smooth. Fig. 1(c) shows the plot of the 12-month running means of the Growth Rate. As can be seen, plots (b) and (c) show similar oscillations (peak positions tallying), indicating that our parameter (12m-37m) is almost the same as the Growth Rate, except that the Growth Rate has long-term variations, while (12m-37m) will be biased in favor of QBO (quasi-biennial oscillation, 2-3 years). The Growth Rate was more than 3% per year in early years but declined to almost zero by 1993-1994. Thus, the parameter (12m-37m) seems to be a better representation of short-term (1-3 year) variability. However, one loses data of about 18 months from each end. One can use 25m instead of 37m, but then the window will be still more restricted to periodicities near 2 years. Values averaged over larger than 37m would reduce the data length still more. We found 37m a reasonable compromise.

Figs. 1(d-f) show similar plots for  $N_2O$  at Barrow. Again, the plots (e) (12m-37m) and (f) Growth Rate match very well [better than the matching of (b) and (c)], mainly because the long-term variation of  $N_2O$  is much smaller (only  $\sim 6\%$  from 1978 to 2002) as compared to that of CFC-11 ( $\sim 40\%$ ). For further analysis, the parameter (12m-37m) is used.

#### 3.2. Plots for CFC-11 and CFC-12

Fig. 2 shows the plots for the parameter (12m-37m) The two top plots are for CFC-11 only, for CMDL BRW for CFC-11 (full line) and CFC-12 (crosses and dashes).

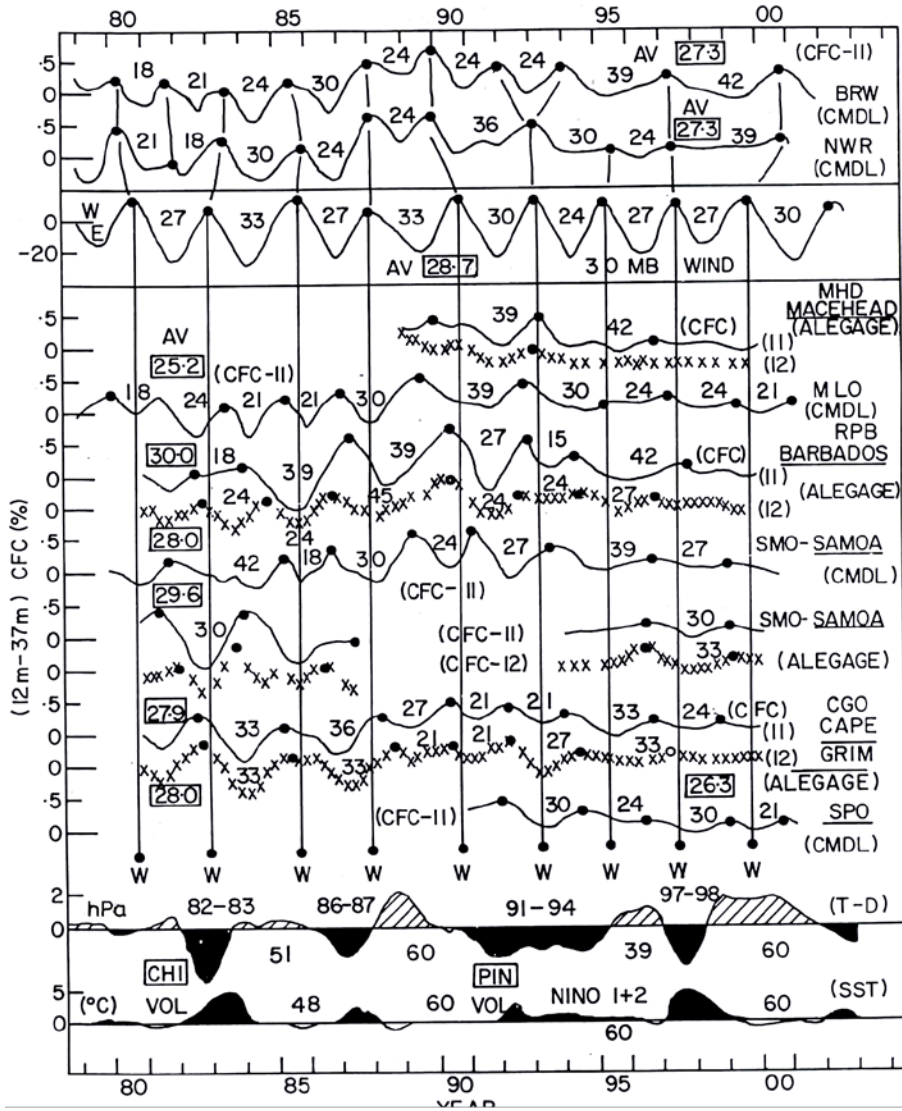


Fig. 2. The (12m-37m) of CFC-11 (full lines) and CFC-12 (crosses), at Barrow (BRW), Niwot Ridge (NWR), Mace Head (MHD), Mauna Loa (MLO), Barbados (RPB), Samoa (SMO), Cape Grim (CGO), South Pole (SPO). Peaks are marked by dots and numbers are spacings in months of successive peaks. Numbers in rectangles are average spacings, in months. The third plot is for 12m of 30 hPa low latitude zonal wind (positive, westerly; negative, easterly). The two bottom plots are for ENSO indices, namely, Southern Oscillation Index (SOI) obtained as Tahiti minus Darwin pressure difference (T-D), and Sea surface temperature (SST) in the Niño 1+2 region in eastern Pacific (~90°W). El Niños are shown black. Volcano eruptions (Chichon in 1981, Pinatubo in 1991) are indicated

(Barrow) and NWR (Niwot Ridge). Smooth oscillations are seen, with magnitudes of  $\sim \pm 0.5\%$ . The peaks are marked with dots. Most of these are obvious, but in some cases, some ambiguity may be involved. (For example, whether Niwot Ridge had 3 peaks in 1980, 1981-1982, 1983, or just two in 1980 and 1983. We have considered

three peaks. Later in 1989-1992, there was a very small peak in 1991, but we have ignored it, as it would give very small spacings, about 17 and 19, instead of total 36. Admittedly, there is some subjectivity involved). The peak spacings of successive peaks are indicated by numbers (in months) and are in a wide range 18-39 months. Peaks for

BRW and NWR are connected with (almost) vertical lines. Many of them tally well. The third plot is for 12m of

the zonal low latitude wind at 30 hPa (stratospheric) level and shows peaks in a spacing range of 24-33 months. The

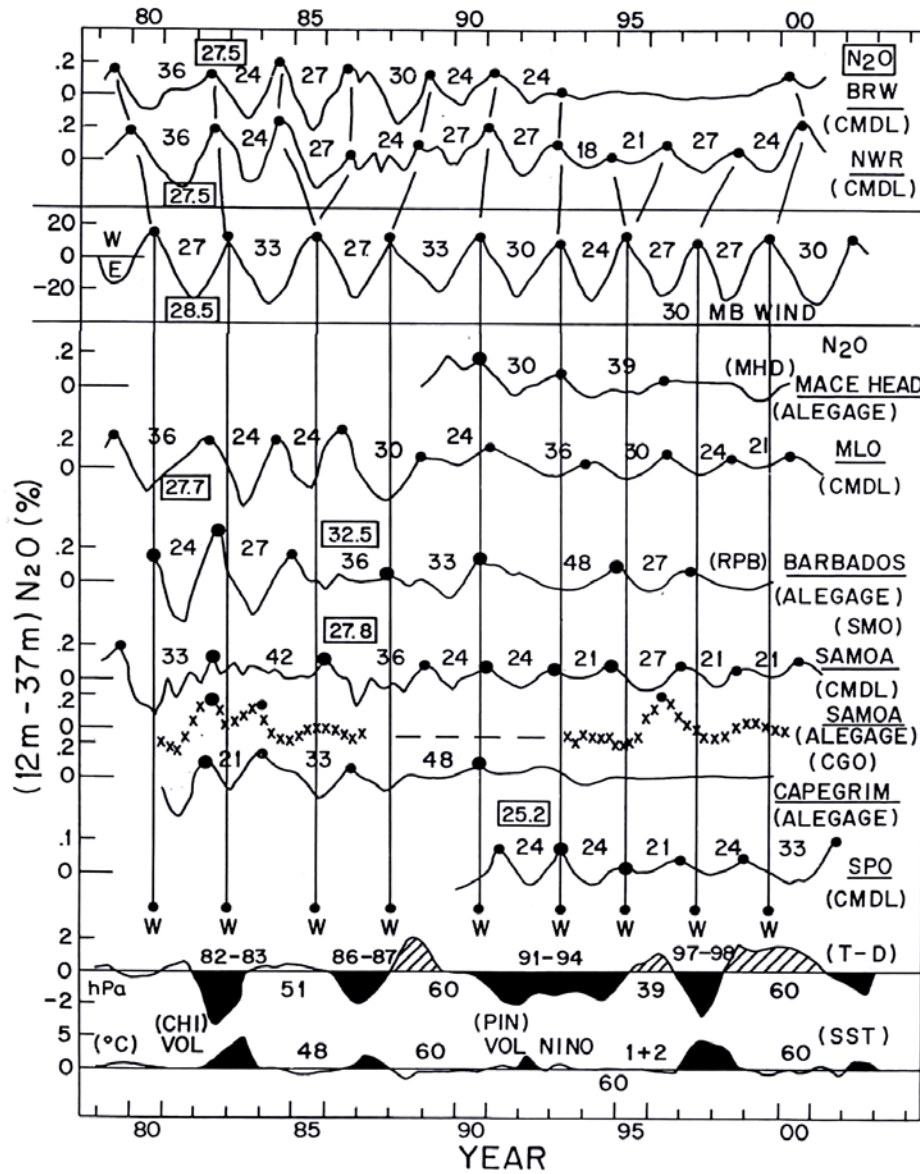


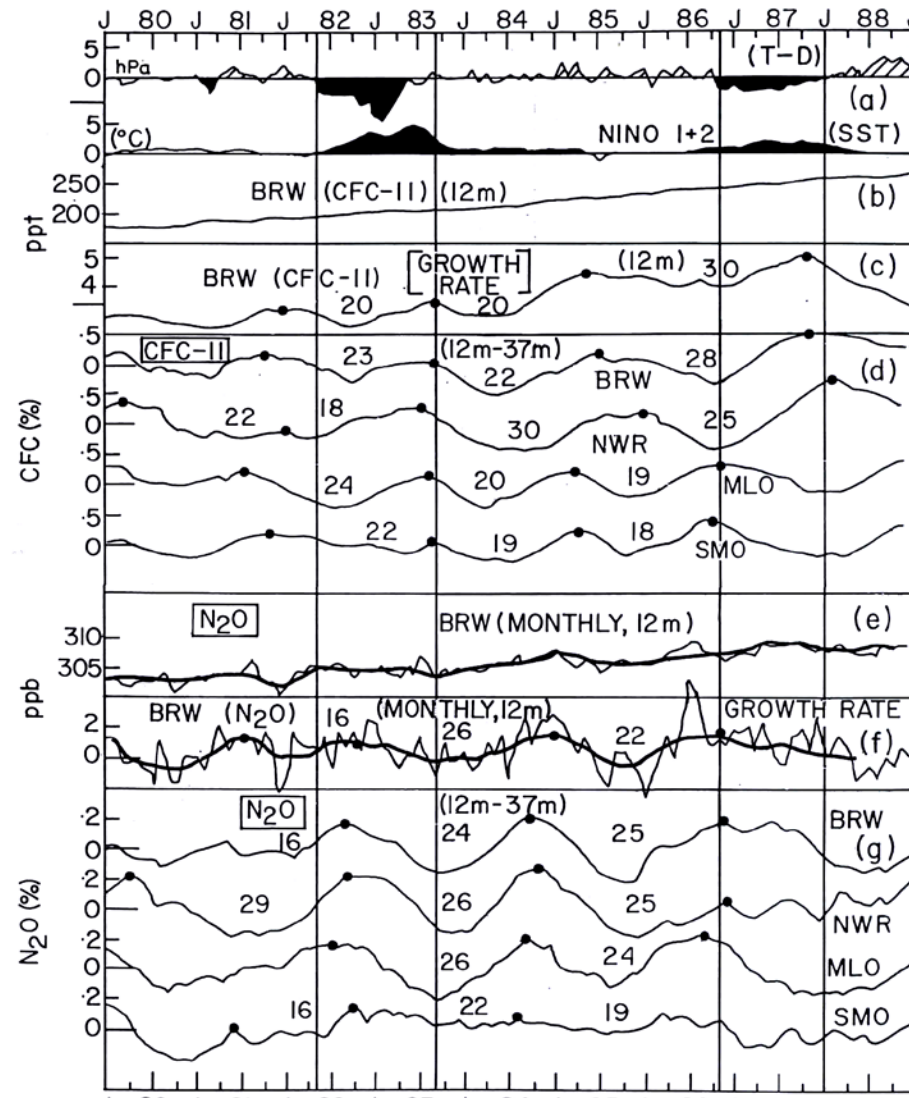
Fig. 3. Same as Fig. 2, for N<sub>2</sub>O at different locations

matching of wind peaks with CFC-11 peaks is not perfect. There are lags or leads of several months, but the average of nine successive spacings for CFC-11 at BRW and NWR is 27.3 months for each (numbers shown in rectangles), not very different from the 28.7 months of 30 hPa wind. The other plots are for CFC-11 (full lines) and CFC-12 (crosses and dashes) at other locations. The average spacings are: CMDL MLO (Mauna Loa), 25.2 months; ALEGAGE RPB (Barbados), CFC-11, 30.0 months, CFC-12, 28.0 months; CMDL SMO (Samoa),

29.6 months; ALEGAGE CGO (Cape Grim), 27.9 months; CMDL SPO (South Pole), 26.3 months, all near the 28.7 months of 30 hPa wind. Thus, a possible relationship between CFC variations and stratospheric winds is indicated. The bottom plot is for ENSO indices, namely the Southern Oscillation Index represented by Tahiti minus Darwin atmospheric pressure difference (T-D), and the SST (sea surface temperature) anomalies in Niño 1+2 region in the eastern Pacific (~90° W, near the Peru-Ecuador coast). The El Niño years are painted black.

The spacings between successive El Niño events are in the range 39-60 months, much larger than that of 30 hPa

winds and CFCs (~28 months). Two volcanic eruptions are also indicated, one (Chichon) in 1981 mixed up with



**Figs. 4(a-g).** Plots for 1980-1988 (El Niños of 1982-1983 and 1986-1987 are shown black). (a) 12m for ENSO indices (T-D) and SST, (b, c) CFC-11 12m and Growth Rate for Barrow (BRW), (d) CFC-11 (12m-37m) for BRW, NWR, MLO, SMO. (e,f)  $N_2O$  12m and Growth Rate for Barrow (BRW), (g)  $N_2O$  (12m-37m) for BRW, NWR, MLO, SMO

the strong El Niño of 1982-1983, and another in 1991 (Pinatubo) mixed up with the weak but extended El Niño of 1991-1994.

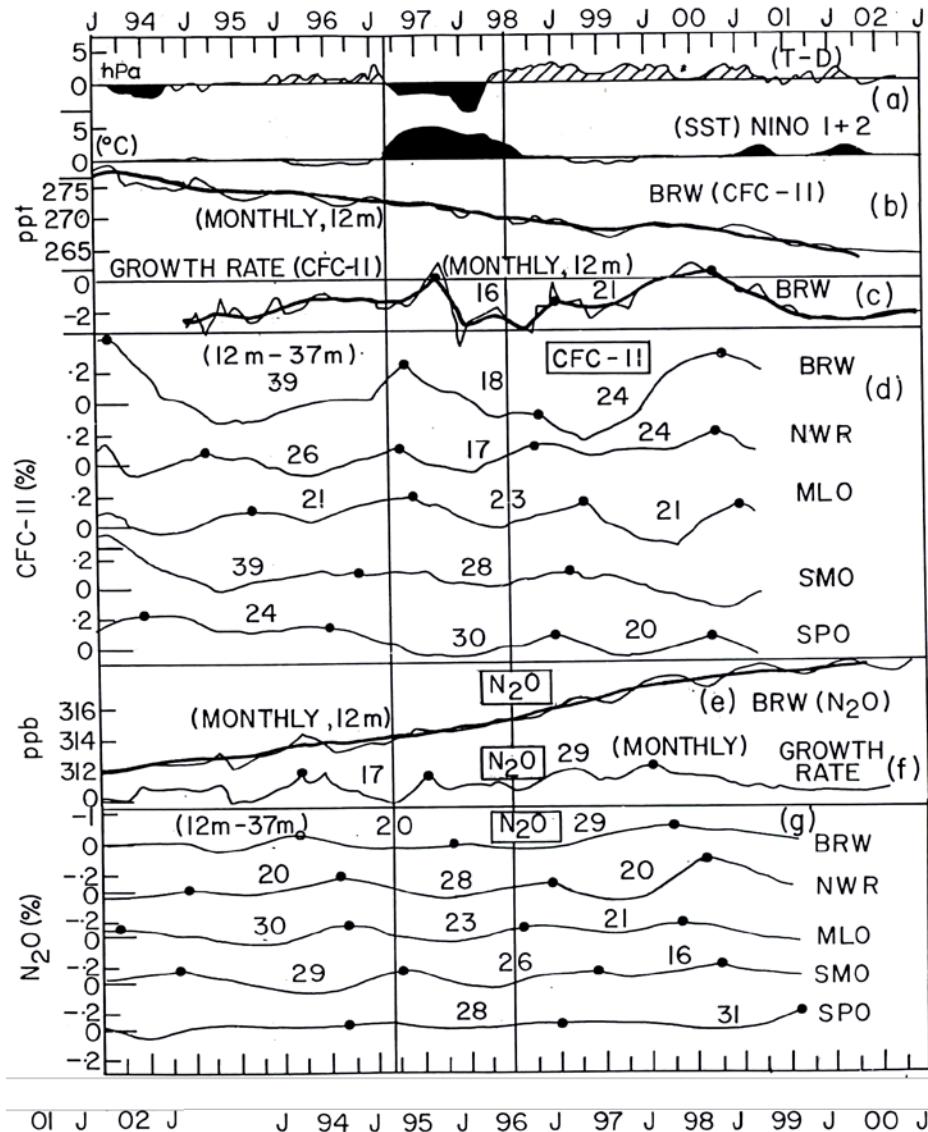
### 3.3. Plots for $N_2O$

Fig. 3 shows plots similar to those of Fig. 2 but for  $N_2O$  instead of CFC. In the two top plots for  $N_2O$  at BRW and NWR, there are prominent oscillations (magnitudes  $\sim \pm 0.2\%$ ) only during 1978-1992. During 1992-2000, there

are virtually no oscillations, while the third plot for 30 hPa wind shows oscillations throughout. For 1978-1992, BRW and NWR  $N_2O$  show average spacings of 27.5 months (shown in rectangles), almost the same as the 28.5 months of wind. In the other plots, the average spacings are: CMDL MLO (Mauna Loa), 27.7 months; ALEGAGE RPB (Barbados), 32.5 months; CMDL SMO (Samoa), 27.8 months; CMDL SPO (South Pole), 25.2 months (for 1991-2001 only), all much lesser than the spacings of 39-60 months of the ENSO indices plotted at the bottom

of Fig. 3, where two volcanic eruptions are also indicated, one (Chichon) in 1991 mixed up with the strong El Niño

of 1982-1983, and another in 1991 (Pinatubo) mixed up with the weak but extended El Niño of 1991-1994.



Figs. 5(a-g). Same as Fig. 4, for 1994-2002 (El Niño of 1997-1998 is shown black)

#### 4. Strong El Niño events

In the last 20 years, two giant El Niño events occurred, in 1982-1983 and 1997-1998. If El Niños have any influence on trace elements, these two events should show the effects prominently. Hence, detailed plots are examined as follows:

##### 4.1. The El Niño of 1982-1983

Fig. 4 shows a detailed plot of monthly values for 1980-1988. The two top plots in (a) are for ENSO indices

(T-D) and SST. The vertical lines enclosing black portions indicate the presence of the strong El Niño of 1982-1983 and the moderate El Niño of 1986-1987. The third plot (b) is for the 12-month running means (12m) of CFC-11 at BRW (Barrow, Alaska), which indicate a monotonic increase from ~175 ppt in 1980 to ~260 ppt in 1988 (~50% increase). (The seasonal variation or BRW was very small and the monthly values were almost the same as 12m). Plot (c) shows the 12m of the Growth Rate at Barrow, while plots (d) shows the parameter (12m-37m) for BRW, NWR, MLO, SMO. Peaks are marked with dots. For Barrow, the Growth Rate and (12m-37m) show

similar variations with almost identical peak locations. The peaks in (12m-37m) of NWR are roughly similar to those of BRW, but the peaks in MLO and SMO are different, indicating latitude differences. Nevertheless, the spacings are all in the range 19-30 months and the plots are smooth all through with no extra deviations or distortions in the El Niño intervals. Thus, El Niño effects are not obvious.

In the lower part of Fig. 4, the plots are for N<sub>2</sub>O. In (e) for Barrow, the monthly values (thin lines) and the superposed 12m (thick line) are shown and a small seasonal variation is indicated (eliminated in 12m). (f) shows the Growth Rate for Barrow (monthly values, thin lines; 12m, superposed thick line). Plots (g) show the (12m-37m) for BRW, NWR, MLO, SMO. The (12m-37m) of BRW and NWR are similar to those of the Growth Rate of BRW, but (12m-37m) of MLO and SMO are different, indicating latitude differences. However, the spacings are all in the range 16-29 months and the plots are smooth all through with no extra deviations or distortions in the El Niño intervals. Thus, El Niño effects are not obvious.

#### 4.2. The El Niño of 1997-1998

Fig. 5 shows a detailed plot of monthly values for 1994-2002. The two top plots in (a) are for ENSO indices (T-D) and SST. The vertical lines enclosing black portions indicate the presence of the strong El Niño in 1997-1998. The third plot (b) is for the monthly means (thin lines) and 12m (thick line) of CFC-11 at BRW (Barrow, Alaska), which indicate a monotonic decrease from ~278 ppt in 1994 to ~263 ppt in 2002 (~5% decrease in recent years). A small seasonal variation can be seen. Plot (c) shows the Growth Rate at Barrow (monthly means, thin lines; 12m, thick line). Plots (d) show the parameter (12m-37m) for BRW, NWR, MLO, SMO. Peaks are marked with dots. For Barrow, the Growth Rate (12m) and (12m-37m) show similar variations with almost identical peak locations. The peaks in (12m-37m) of NWR are roughly similar to those of BRW, but the peaks in MLO and SMO are different, indicating latitude differences. Nevertheless, the spacings are all in the range 18-39 months and the plots are smooth all through with no extra deviations or distortions in the El Niño intervals. Thus, El Niño effects are probably dubious.

In the lower part of Fig. 5, the plots are for N<sub>2</sub>O. In (e) for Barrow, the monthly values (thin lines) and the superposed 12m (thick line) are shown and a small seasonal variation is indicated (eliminated in 12m). (f) shows the Growth Rate for Barrow (monthly values only, as these are smooth enough and do not need 12m). Plots (g) show the (12m-37m) for BRW, NWR, MLO, SMO.

The (12m-37m) of BRW are similar to those of the Growth Rate of BRW, but (12m-37m) of NWR, MLO and SMO are different, indicating considerable latitude differences. However, the spacings are all in the range 16-31 months and the plots are smooth all through with no extra deviations or distortions in the El Niño intervals. Thus, El Niño effects are dubious.

## 5. Spectral analysis

So far, QBO characteristics were examined by visual inspection, which could be subjective. Also, average spacings imply only one periodicity, while there could be a mixture of more than one periodicities. To detect all periodicities rigorously, all the series (12m-37m) were subjected to a power spectrum analysis, using MEM (Maximum Entropy Method of Spectral Analysis, Burg, 1967; Urych and Bishop, 1975), which detects periodicities much more accurately than the conventional BT method (Blackman and Tukey, 1958). Similar to the parameter lag  $m$  in BT, MEM has a parameter called LPEF (Length of the Prediction Error Filter), which can be chosen. With low LPEF, only low periodicities are resolved. Larger LPEF resolve larger periodicities, even those approaching the data length, but the errors are larger and, low periodicities show peak-splitting. An LPEF of ~50% of the data length is generally adequate and was used in the present analysis.

MEM has a drawback *viz.*, the power estimates are not reliable (Kane and Trivedi, 1982). Hence, MEM was used only to identify the possible periodicities  $T_k$ , which were then used in the expression:

$$f(t) = A_0 + \sum_{k=1}^n [a_k \sin(2\pi t/T_k) + b_k \cos(2\pi t/T_k)] + E$$

$$= A_0 + \sum_{k=1}^n r_k \sin(2\pi t/T_k + \phi_k) + E \quad (1)$$

where  $f(t)$  is the observed series and  $E$  the error factor. A Multiple Regression Analysis (MRA, Bevington 1969) was then carried out to obtain the best estimates of  $A_0$ ,  $(a_k, b_k)$  and their standard errors, by a least-square fit. From these,  $r_k$  and their standard error  $\sigma$  (common for all  $r_k$  in this methodology) can be calculated and any  $r_k$  exceeding  $2\sigma$  would be significant at a 95% (a priori) confidence level.

Fig. 6 shows the results of MEM (amplitude *versus* periodicities in years, marked with numbers). The two top plots are for ENSO parameters (T-D) and SST (Niño



1+2). The periodicities of the two are not exactly alike, but both have two most prominent periodicities near

3.8 years (QTO) and 5 years, and two much smaller periodicities in the QBO region (~2.1 and ~2.5 years),

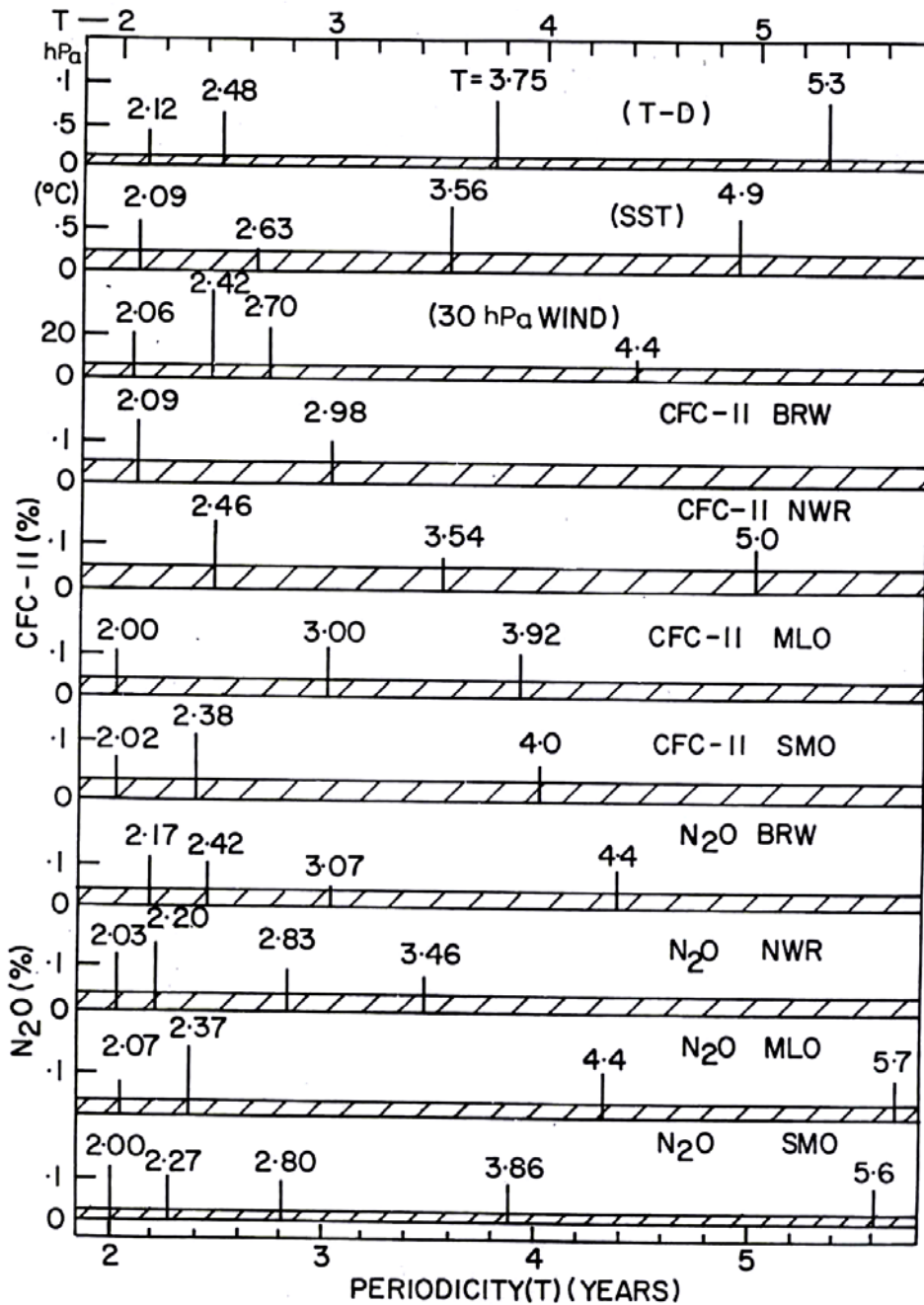


Fig. 6. Spectra (amplitudes versus periodicities detected by MESA) for ENSO indices (T-D) and SST, 30 hPa wind, CFC-11 at BRW, NWR, MLO, SMO, and N<sub>2</sub>O at BRW, NWR, MLO, SMO. Numbers indicate periodicities T, in years. The hatched portion is the 2σ limit and lines protruding above these are amplitudes significant at a confidence level exceeding 95%

which may be what Rasmussen *et al.* (1990) mentioned as a “biennial component”. The hatched portion represents the 2σ limit, and all the periodicities of (T-D) and

highly significant. (From an analysis of artificial samples as inputs, the errors in the values of the periodicities in the QBO, QTO region are estimated to be less than ±0.03

years, Kane and Trivedi, 1982). The third plot is for 30 hPa zonal wind. Here, the prominent periodicities are in the QBO region and there are three of them, 2.06, 2.42, and 2.70 years, the first two matching with (T-D) QBO (2.12 and 2.48 years). Thus, there is no unique QBO and hence, the spacings of 30 hPa wind shown in Fig. 2(c) and Fig. 3(c) vary in a wide range 24-33 months. Also, the stratospheric winds and (T-D) may be interrelated in the QBO region.

The next four plots in Fig. 6 are for CFC-11 at BRW, NWR, MLO and SMO. For high northern latitudes (BRW), the prominent periodicities are in the QBO region (2.09 and 2.98 years) but not exactly the same as those of the 30 hPa wind (2.06, 2.42, 2.70 years). For lower latitudes (NWR, particularly MLO and SMO), there are prominent periodicities in both QBO and QTO region, and these are similar to the ENSO periodicities. Thus, ENSO effects seem to be more prevalent at lower latitudes. The last four plots are for N<sub>2</sub>O at BRW, NWR, MLO and SMO. Here again, the same pattern is seen, namely a larger proportion of ENSO effects at lower latitudes. For BRW at high northern latitude, the QBO of BRW (2.17 and 2.42 years) matches well with wind QBO (2.06, 2.42 years) as well as with (T-D) QBO (2.12, 2.48 years). Thus, it is difficult to ascertain whether the QBO of CFC-11 and N<sub>2</sub>O at Burrow is related to the QBO of stratospheric wind only or QBO of ENSO only, or both.

Since the parameter (12m-37m) is biased in favor of a QBO, the other parameter usually used namely 'growth rate' was analyzed in a similar way. A comparison of the results of spectral analysis for (12m-37m) and the growth rate showed that the QBO periodicities were almost exactly the same for both, periodicities tallying within  $\pm 0.02$  and amplitudes within 5%. In the QTO region also, the periodicities tallied within  $\pm 0.02$ , but the amplitudes were ~15% higher in the growth rate. Thus, qualitatively, the above conclusions are fully valid and do not seem to depend on differences of methodology in obtaining (12m-37m) and the growth rate.

## 6. Possible mechanism

In the various CMDL summary reports, trace element values are plotted as time series, where the seasonal variations are the most predominant. Sometimes, the deseasoned values are also plotted (also, growth rates), which do show oscillations, but the major efforts have been mostly for studying relationships with natural disasters like forest fires, bio-mass burning, volcanic eruptions etc., while some attention has been paid to regular periodicities like QT (~3 years) and QQ (~4 years) (Dettinger and Ghil, 1998), where the QT was interpreted

as indicating relationship with eastern tropical Pacific SST (part of the ENSO phenomenon) and the QQ was interpreted as a terrestrial-ecosystem response to global QQ climate variations. The QBO received little attention as such and was considered as a contribution from the minor QBO of the ENSO phenomenon, which has a major QTO. Kane (1994) hinted that there was a QBO in some trace elements, which may be related to the QBO of stratospheric winds. Coughlin and Tung (2001) found a QBO in extra-tropical lower troposphere sea surface temperature. Earlier, stratospheric QBO signals were detected in O<sub>3</sub>, CH<sub>4</sub> and HF (Cordero *et al.*, 1997; Randel *et al.*, 1998; Tung and Yang, 1994). Recently, Giorgetta and Bengtsson (1999) argued as follows, "The tropical tropopause is considered to be the main region of upward transport of tropospheric air carrying water vapor and other tracers to the tropical stratosphere. The lower tropical stratosphere is also the region where the quasi-biennial oscillation (QBO) in the zonal wind is observed. The QBO is positioned in the region where the upward transport of tropospheric tracers to the overwork takes place. Hence, the QBO can in principle modulate these transports by its secondary meridional circulation", and they investigated this modulation by an analysis of General Circulation Model (GCM) experiments with an assimilated QBO. The experiments showed that firstly, the temperature signal of the QBO modifies the specific humidity in the air transported upward and secondly, the secondary meridional circulation modulates the velocity of the upward transport. Thus, the GCM successfully generated the QBO secondary meridional circulation and hence a QBO temperature signal. The interannual variability of the stratospheric equatorial humidity was marked by upward propagating anomalies emanating from the tropopause, on time scales of ENSO after strong El Niño or La Niña events, but varying on the stratospheric QBO time scales in between. Further, Hamilton and Fan (2000) explored the role of the stratospheric QBO in modulating the interannual variations of long-lived tropospheric constituents and showed that a dynamical QBO may modulate STE (Stratosphere-Troposphere Exchange) in such a manner as to produce a QBO in global-mean tropospheric tracer mixing ratio. They considered two possible effects. One (*transport mechanism*) involved the QBO modulation of the flux of air through the tropical tropopause into the stratosphere. The other (*ozone mechanism*) was related to the stratospheric wind QBO causing QBO modulation of the stratospheric ozone, which would cause a QBO in the UV radiation filtering downwards, which would pass on the QBO to the OH radical produced by UV photolysis of tropospheric ozone. Thus, trace elements having very strong chemical interaction with tropospheric OH radicals would pick up the OH QBO. The two trace elements having OH as a strong sink are CH<sub>4</sub> and C For methane,

Hamilton and Fan (2000) reported stratospheric QBO effects 'modest but not negligible'. Camp *et al.* (2001) compared the methane measurements at Cape Grim (40° S, 144° E) with TOMS+SBUV ozone data and concluded that at least a part of the methane QBO signal was responding to ozone forcing, with a lag of about 6 months. For CFCs and N<sub>2</sub>O, the analysis so far indicates a reasonable relationship for trace elements at high latitudes with 30 hPa wind, indicating that the *transport* mechanism of Hamilton and Fan (2000) operates successfully for high latitude troposphere. For low latitudes, the association seems to be more with ENSO. A clue could come through the QBO and QTO of atmospheric temperatures. A detailed analysis was presented in Kane and Buriti (1997), where temperature data from a 63-station radiosonde network for 1958-1992 (Angell, 1994) were grouped for seven climatic zones 90° N - 60° N, 60° N - 30° N, 30° N - 10° N, 10° N - 10° S, 10° S - 30° S, 30° S - 60° S, 60° S - 90° S, and for five altitude levels, namely, surface, 850-300 hPa, 300-100 hPa, 100-50 hPa and 100-30 hPa. A spectral analysis showed that in the temperatures in tropopause and lower stratosphere (100-30 hPa), there were strong QBOs at all latitudes, resembling those of stratospheric low latitude winds (~30 months). At lower and lower altitudes in the troposphere, the prominence of QTO was larger and larger, as compared to QBO, at all latitudes. At the surface, the QBO was negligible and mostly, QTO prevailed, except in high latitudes, particularly in the polar regions, where QBO was significant and larger than QTO. Thus, there was considerable latitude dependence, QTO predominant in low latitudes at all altitudes, while QBO was substantial in polar regions at all altitudes. In effect, ENSO QTO was more effective in low latitudes (all altitudes), while stratosphere QBO was more effective in high altitudes, and low altitude high latitudes. This pattern would certainly be reflected as ENSO effects on GC patterns, which would transmit the same to trace elements.

## 7. Conclusions and discussion

An analysis of N<sub>2</sub>O (nitrous oxide) and CFC (chlorofluorocarbon) concentrations (monthly values and their 12-month running means) at various locations during 1978-2001 indicated the following:

(i) A short-term variation was the seasonal variation (already known) in all parameters, but it is not studied here and was eliminated by calculating 12-month running averages (12m).

(ii) For Barrow, Alaska, a large long-term trend was seen in 12m of CFC-11, with the values rising from ~155

ppt in 1978 to ~278 ppb in 1993-1994 (~80% increase) and falling thereafter to ~263 in 2002. (Dutton *et al.*, 2003 mention that CFC-12 did not show a decrease after 1993). For N<sub>2</sub>O at Barrow, the long-term variation of N<sub>2</sub>O was much smaller (only ~6%), but the trend was monotonically upward from 1978 to 2002.

(iii) Superposed on these trends were small oscillations which could be discerned if the long-term trend is removed. The long-term trends were estimated by calculating 3-year (37 months, to get the centering correct) running means (37m) and these were subtracted from the 12-month running means (12m). The residues (12m-37m) showed small oscillations of magnitudes  $\sim\pm 0.5\%$  for CFC-11 and  $\sim\pm 0.2\%$  for N<sub>2</sub>O. The oscillations had successive peak spacings mostly in the QBO (quasi-biennial oscillations, 2-3 year) region, particularly for high northern latitudes. A few peaks were in the QTO (quasi-triennial oscillations, 3-4 year) range, particularly for low latitudes.

(iv) During the major El Niños of 1982-1983 and 1997-1998, the QBO patterns were maintained and no extra deviations or distortions were noticed, indicating that El Niño effects were probably small for CFCs and N<sub>2</sub>O.

(v) A spectral analysis of the (12m-37m) series indicated that the 30 hPa wind had predominant peaks only in the QBO region, a strong peak at 2.42 years, and minor but significant peaks at 2.06 and 2.70 years. In contrast, the ENSO indices, namely, Southern Oscillation Index Tahiti minus Darwin atmospheric pressure difference (T-D) and Pacific SST, had a major peak in the QTO region at ~3.6 years, a slightly smaller peak at ~5 years, and minor peaks in the QBO region. The CFC-11 and N<sub>2</sub>O at high latitudes had strong QBOs resembling those of 30 hPa wind, while at low latitudes, there were small QBOs almost resembling the 30 hPa QBO, but larger QTOs resembling the QTO of ENSO. Thus, trace elements at high and low latitudes had differing relationships with stratospheric winds and ENSO. Results for the parameter 'growth rate' were similar to those of (12m-37m), indicating that these results did not depend upon the differences in the methodology of obtaining these parameters.

(vi) These results indicate that the transport mechanism proposed by Hamilton and Fan (2000), namely, that a dynamical QBO may modulate STE (Stratosphere-Troposphere Exchange) in such a manner as to produce a QBO in global-mean tropospheric tracer mixing ratio is effective of CFC and N<sub>2</sub>O in high latitudes, while at low latitudes, the ENSO effects prevail.

QBO in the troposphere has attracted attention for several decades and its comparison with wind QBO has been a matter of great controversy. Yasunari (1985), Gutzler and Harrison (1987), Kawamura (1988) reported a tropospheric QBO. In addition to the ENSO mode (40-60 month period), the zonal wind in the troposphere has a component of transient east-west circulation with the QBO time scale, which shows a totally eastward propagation (Yasunari, 1989). Thus, there is some evidence that the stratospheric and tropospheric QBO are *coupled* and these are, in turn, coupled to the QBO of the equatorial eastern Pacific SST, suggesting a dynamical link between stratospheric QBO and the large scale coupled atmosphere/ocean system. However, Trenberth (1980) mentions that the QBO shown by troposphere ultra-long waves of the Southern Hemisphere does not match with stratospheric QBO. Meehl (1987) identified a *biennial* signal in the coupled ocean-atmosphere system in the tropical Indian and Pacific regions, which does not seem to be related to stratospheric QBO (Rasmusson *et al.*, 1990). In any case, the ENSO mode (40-60 months) present in SST seems to be an independent parameter. Gray *et al.* (1992) have hypothesized a mechanism by which stratospheric QBO influences ENSO variability while Geller and Zhang (1991) and Geller *et al.* (1997) illustrate a mechanism by which SST variations can modulate tropical wave activity and finally, the QBO of SST would tend to force a stratospheric zonal flow oscillation with the same period as the oceanic QBO. Ropelewski *et al.* (1992) feel that tropospheric QBO is mainly related to ENSO. If the ENSO and stratospheric winds have a connection in the QBO region, the argument whether the QBO of tropospheric parameters (including trace elements) is related to ENSO or stratospheric winds, becomes superfluous.

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