

## 2.2. CARBON DIOXIDE

### 2.2.1. IN SITU CARBON DIOXIDE MEASUREMENTS

The mixing ratio of atmospheric CO<sub>2</sub> was measured with a continuously operating non-dispersive infrared analyzer (NDIR) at each of the four CMDL observatories during 1998 and 1999, as in previous years. Monthly and annual mean CO<sub>2</sub> concentrations are given in Table 2.2. These values are provisional, pending final calibrations of station standards. Preliminary monthly average CO<sub>2</sub> mixing ratios, selected for background conditions for the entire record through 1999, are plotted versus time for the four observatories (Figure 2.1.)

A new data acquisition system was installed at the Samoa Observatory, American Samoa (SMO) in July of 1998. This system uses an Intel CPU-based Unix workstation for controlling the CO<sub>2</sub> NDIR measurements. This system replaced the Control and Monitoring System (CAMS) data acquisition unit that experienced frequent failures.

At the Mauna Loa Observatory, Hawaii (MLO) in November 1998, the continuous CO<sub>2</sub>, CH<sub>4</sub>, and CO systems were moved into the Network for the Detection of Stratospheric Change (NDSC) building. The computer used for controlling the data acquisition was upgraded to an Intel CPU-based Unix workstation. The CO<sub>2</sub> analytical system was upgraded using a new design (Figure 2.2). These design upgrades were installed

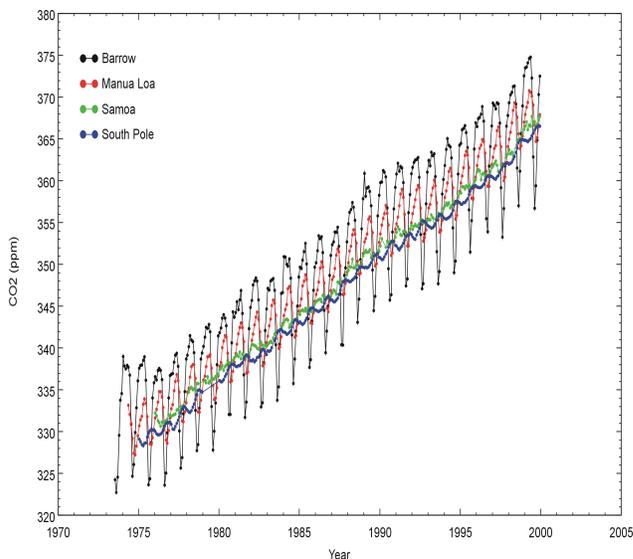


Fig. 2.1. Preliminary selected monthly mean CO<sub>2</sub> mole fractions in dry air expressed in ppm ( $\mu\text{mol/mol}$ ) at the four CMDL observatories.

TABLE 2.2. Provisional 1998 and 1999 Monthly and Annual Mean CO<sub>2</sub> Mole Fractions From Continuous Analyzer Data ( $\mu\text{mol mol}^{-1}$ , Relative to Dry Air WMO Mole Fraction Scale)

Month	BRW	MLO	SMO	SPO
<i>1998</i>				
Jan.	369.32	364.99	363.72	361.98
Feb.	370.29	365.80	363.25	362.10
March	370.59	366.95	363.44	362.26
April	371.27	368.44	363.04	362.58
May	371.33	369.32	—	362.90
June	369.18	368.79	—	363.39
July	361.53	367.59	364.83	363.92
Aug.	357.04	365.63	364.89	364.56
Sept.	361.14	363.84	364.98	364.86
Oct.	365.65	364.19	365.14	364.91
Nov.	368.96	365.36	365.72	364.93
Dec.	372.56	367.01	366.15	364.88
Year	367.40	366.49	364.52	363.61
<i>1999</i>				
Jan.	373.52	367.93	366.55	364.86
Feb.	373.62	368.80	367.05	364.78
March	374.10	369.38	366.11	364.69
April	374.63	370.77	366.68	364.86
May	374.81	370.59	366.52	365.06
June	372.28	370.12	367.70	365.38
July	362.85	369.07	367.03	365.70
Aug.	356.71	366.65	367.08	366.09
Sept.	359.40	364.70	366.54	366.35
Oct.	364.86	365.17	366.80	366.48
Nov.	370.34	66.50	367.33	366.60
Dec.	372.50	367.89	367.69	366.52
Year	369.14	368.13	366.92	365.61

at the South Pole Observatory, Antarctica (SPO) in December of 1998, and the same changes are planned for the Barrow Observatory, Alaska (BRW) and SMO in 2000.

This design involved new modular hardware to ensure each module in the CO<sub>2</sub> system can be replaced easily in case of failure. Three new rack-mountable boxes were installed and are shown in Figure 2.2 as dashed lines. The first contains the hardware for controlling the ambient air sample flow rates and pressure from the intake lines and pumps. This box is shared with the CH<sub>4</sub> and CO analysis systems. The second box controls the flow rate and elects the sample or standard gas that flows to the CO<sub>2</sub> analyzer. The third box is used for filling flasks from the ambient air sample lines.

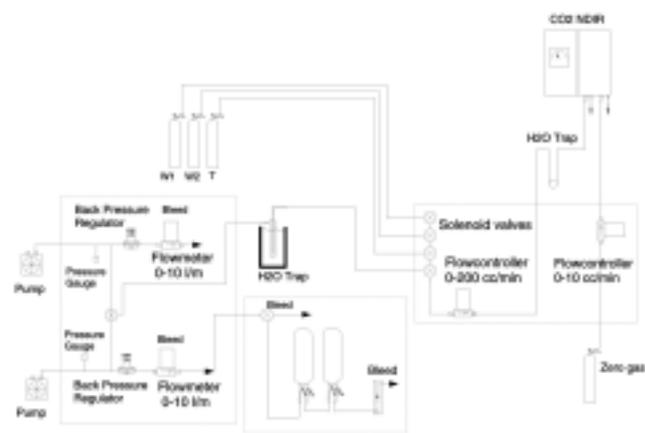


Fig. 2.2. System schematic for continuous measurement of CO<sub>2</sub>.

Several changes occurred in the way the CO<sub>2</sub> system operated after the upgrade. The four CO<sub>2</sub> station standards were removed. These gases were used to calibrate the two working tanks at weekly intervals in order to check for any drift in mixing ratio for the working tanks. Results of calibrations over many years show that the aluminum cylinders used for containing the CO<sub>2</sub> standard gases were stable. Results from these calibrations did not yield enough information to justify the extra effort to prepare, maintain, and analyze the results for the station standards. In place of the weekly calibrations using the station standards, a daily 1-hr long "Target" calibration was introduced using a separate Target standard gas. These daily calibrations can be used to track any changes in working gas mixing ratios and possibly any changes in the behavior of the CO<sub>2</sub> analyzer.

The tubing used for carrying the gases within the system was changed to 1.6 mm (1/16 in.) OD stainless steel. This tubing is much easier to handle than the previous 3.2 mm (1/8 in.) OD stainless steel and is the same type of tubing used for the CH<sub>4</sub> and CO chromatographic systems. Mass flow controllers are now used for controlling the flow rate, instead of a mechanical pressure controller previously used. This provides much more stable flow rates to the analyzer and increased precision since the CO<sub>2</sub> analyzer is sensitive to flow rate changes.

### 2.2.2. FLASK SAMPLE CARBON DIOXIDE MEASUREMENTS

Because the sources and sinks of carbon cycle gases (CO<sub>2</sub>, CH<sub>4</sub>, and CO) are highly variable over space and time, the CMDL global cooperative air sampling network (Figure 2.3) provides greater geographic coverage to complement the high-frequency in situ measurements at the four observatories. Air samples are collected approximately weekly at 48 land-based sites and aboard commercial ships. The samples are measured at CMDL for CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>, N<sub>2</sub>O, and SF<sub>6</sub>, and at INSTAAR for <sup>13</sup>C and <sup>18</sup>O of CO<sub>2</sub>. In 1998, 7800 samples were analyzed, and in 1999, 7500 samples were analyzed. Samples from seven sites are measured for <sup>13</sup>C of CH<sub>4</sub> at INSTAAR (section 2.3.3), and samples from three sites are measured for <sup>17</sup>O/<sup>16</sup>O of CO<sub>2</sub> at the University of California, San Diego. The isotopic and mixing ratio measurements are used to calculate sources and sinks by numerical inverse techniques or to constrain source/sink estimates obtained from process models.

After several years of intermittent sampling because of logistical problems, weekly sampling resumed at Christmas Island (CHR) with a new sample collector in November 1998. Sampling on the island of Kaashidhoo, Republic of Maldives,

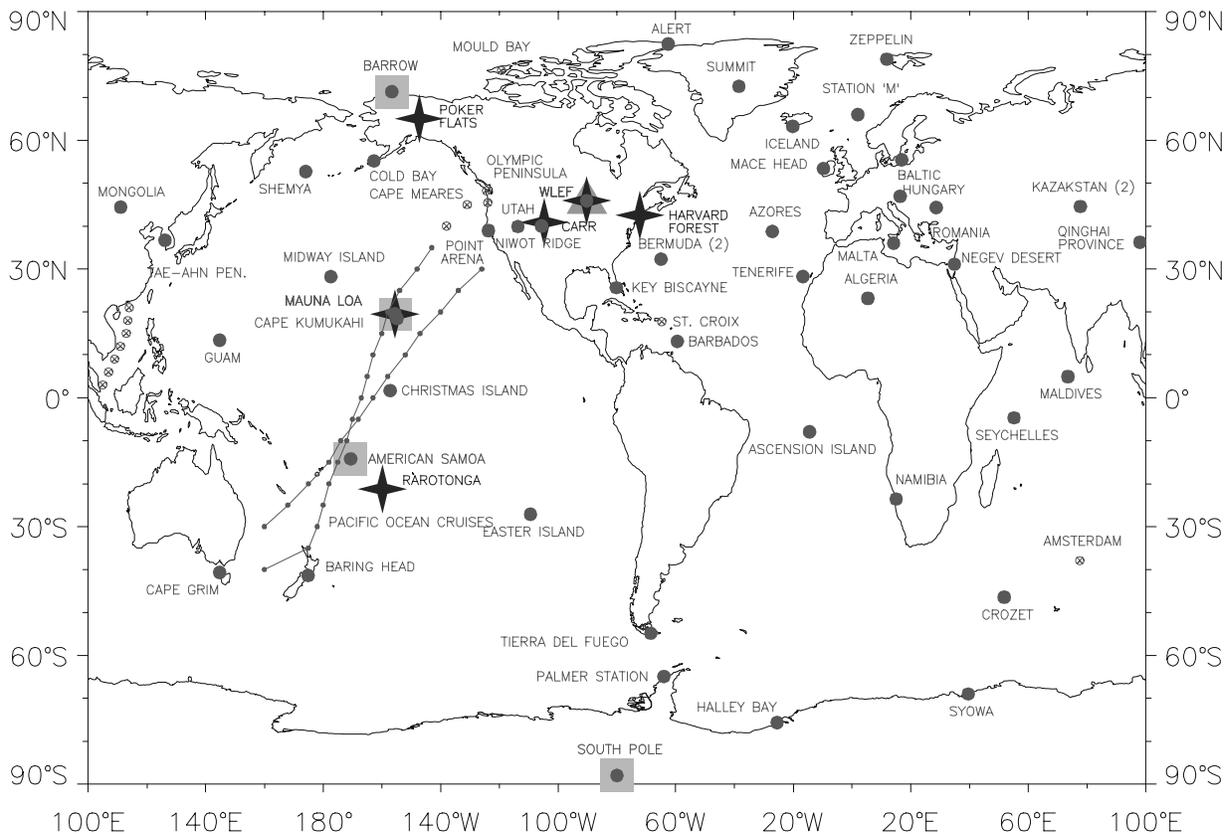


Fig. 2.3. Locations of the Carbon Cycle Greenhouse Gases Group measurement programs including the baseline observatories (squares), cooperative global air sampling network (circles), discontinued sites of same (open circles with cross), aircraft vertical profiles (stars), and the very tall tower site (triangle).

began in March 1998. Samples are collected at the Kaashidhoo Climate Observatory (KCO) in cooperation with the Maldivian Ministry of Home and Environmental Affairs and the Scripps Institution of Oceanography (SIO). The Kaashidhoo Climate Observatory was established as part of the Indian Ocean Experiment (INDOEX) project. It is hoped that sampling will continue at KCO, although no samples have been received since July 1999. Sampling at Point Arena, California, began in January 1999, thanks to the cooperation of the lighthouse keeper. This site replaces Cape Meares, Oregon, that was discontinued in March 1998. Since October 1999 monthly samples are collected at Baring Head, New Zealand. The samples are part of an intercomparison project with the National Institute for Water and Atmospheric Research (NIWA) (New Zealand). One member of each flask pair is analyzed at both NIWA and CMDL to evaluate the agreement of the two laboratories' analytical methods. Flask sampling at the tall tower site in Grifton, North Carolina (ITN) ended in June 1999 when the tower measurement program was terminated. In October 1998 the sampling program in the South China Sea (SCS) was interrupted when the M/V *Frontier Express* came off the Singapore-Hong Kong route. Sampling will resume if a suitable replacement ship can be found. The three-letter codes for two sites were changed to make them consistent with WMO conventions. The code for Mace Head, Ireland, is now MHD (formerly MHT) and the code for the site in Qinghai Province, China (formerly QPC) is now WLG (Waliguan Observatory).

The 1998 and 1999 annual mean CO<sub>2</sub> mixing ratios calculated from smooth curves fit to the data for 48 sites active during 1998-1999 are given in Table 2.3. Annual means for the shipboard data are given in Tables 2.4 and 2.5.

The globally averaged CO<sub>2</sub> mixing ratios and the long-term trend [Thoning *et al.*, 1989] calculated from the global air sampling network data for 1979 through 1999 are plotted as smooth curves in Figure 2.4a. The global CO<sub>2</sub> growth rate as a function of time is calculated by taking the derivative of the trend curve (Figure 2.4b). The average CO<sub>2</sub> growth rate for 1979-1999 is 1.5 ppm yr<sup>-1</sup>. The CO<sub>2</sub> growth rate varied from 0.5 ppm yr<sup>-1</sup> in 1982 and 1992 to 3.5 ppm yr<sup>-1</sup> in 1998, and there is no significant overall trend in the growth rate over this period. The CO<sub>2</sub> growth rate as a function of latitude and time is shown in Figure 2.5. In this figure it is apparent that much of the interannual variability of the growth rate arises from coherent variations on hemispheric to global scales. In some cases the growth rate variations originate in the equatorial region and then propagate toward higher latitudes in both hemispheres. Also, the highs and lows tend to be more extreme at mid- and high-northern latitudes. The growth rate anomaly that began in 1997 and peaked at record high values in early 1998 is unusual in that it appears nearly simultaneously and nearly as intensely throughout both hemispheres.

The CO<sub>2</sub> and δ<sup>13</sup>C data were combined with a two-dimensional atmospheric transport model [Tans *et al.*, 1989] to calculate the CO<sub>2</sub> sources and sinks underlying the growth rate variations. The model results for 1990-1999 are summarized in Table 2.6. The 1990-1997 average sources and sinks are shown with one sigma standard deviations to indicate the interannual variability during that period of time. In 1998 the net global CO<sub>2</sub> sink was only 0.5 Gt C compared with an average of 3.4 Gt C during the previous 8 years. Marked decreases in both the net oceanic and net terrestrial biospheric sinks contributed to this change that resulted in an atmospheric increase of 6.2 Gt C. In

TABLE 2.3. 1998-1999 Annual Mean CO<sub>2</sub> Mole Fractions From Network Sites

Code	Station	1998	1999
ALT	Alert, N.W.T., Canada	367.2	368.9
ASC	Ascension Island	365.0	366.3
ASK	Assekrem, Algeria	366.6	368.2
AZR	Terceira Island, Azores	365.6	368.8
BAL	Baltic Sea	369.8	371.0
BME	Bermuda (east coast)	366.9	368.7
BMW	Bermuda (west coast)	366.3	368.5
BRW	Barrow, Alaska	367.4	369.8
BSC	Black Sea, Constanta, Romania	372.2	376.4
CBA	Cold Bay, Alaska	369.3	371.2
CGO	Cape Grim, Tasmania	363.7	365.5
CHR	Christmas Island, Kiribati	[ ]	368.3
CRZ	Crozet Island	363.6	[ ]
EIC	Easter Island, Chile	363.3	365.0
GMI	Guam, Mariana Islands	366.7	367.9
GOZ	Gozo Island, Malta	[ ]	[ ]
HBA	Halley Bay, Antarctica	363.4	365.5
HUN	Hegyatsal, Hungary	369.3	370.8
ICE	Vestmanaeyjar, Iceland	366.9	368.5
ITN	WITN, Grifton, North Carolina	370.3	[ ]
IZO	Izana Observatory, Tenerife	367.1	368.5
KCO	Kaashidhoo, Maldives	366.1	[ ]
KEY	Key Biscayne, Florida	367.7	369.3
KUM	Cape Kumukahi, Hawaii	366.9	368.3
KZD	Plateau Assy, Kazakstan	369.4	371.0
KZM	Sary Taukum, Kazakstan	365.6	368.0
LEF	WLEF, Park Falls, Wisconsin	367.9	370.1
MHD	Mace Head, Ireland	366.3	368.4
MID	Midway Island	366.6	368.2
MLO	Mauna Loa, Hawaii	366.6	368.3
NMB	Bobabeb, Namibia	[ ]	366.5
NWR	Niwot Ridge, Colorado	366.5	368.4
PSA	Palmer Station, Antarctica	363.7	365.7
PTA	Point Arena, California	[ ]	370.8
RPB	Ragged Point, Barbados	366.3	367.6
SEY	Mahe Island, Seychelles	365.4	366.7
SHM	Shemya Island, Alaska	367.1	368.8
SMO	American Samoa	364.6	366.9
SPO	South Pole, Antarctica	363.8	365.6
STM	Ocean Station M	366.7	368.7
SYO	Syowa Station, Antarctica	364.5	365.7
TAP	Tae-ahn Peninsula, South Korea	370.6	373.1
TDF	Tierra del Fuego, Argentina	363.6	365.6
UTA	Wendover, Utah	366.9	369.1
UUM	Ulaan Uul, Mongolia	367.5	368.7
WIS	Sede Boker, Negev Desert, Israel	367.9	369.3
WLG	Mt. Waliguan, China	365.7	368.1
ZEP	Ny-Alesund, Svalbard	367.2	370.1

The square brackets indicate insufficient data to calculate the annual mean.

The 1999 annual means are provisional.

1999 the oceanic sink was still only a third of the decadal average while the terrestrial sink rebounded strongly, leading to a near-average atmospheric increase. The two-dimensional model results also indicate that the 1998 growth rate anomaly was driven predominantly by variations in the tropical zone, defined from 17°S to 17°N in our model, including a large increase in the terrestrial source during late 1997.

TABLE 2.4. 1998-1999 Annual Mean CO<sub>2</sub> Mixing Ratios From Pacific Ocean Cruises

Latitude	CO <sub>2</sub> (ppm)	
	1998	1999
30°N	366.7	370.0
25°N	367.5	370.1
20°N	367.0	369.3
15°N	367.3	368.6
10°N	366.9	369.5
5°N	367.0	368.7
Equator	366.8	368.7
5°S	365.9	368.1
10°S	365.1	367.6
15°S	364.5	367.3
20°S	364.5	366.6
25°S	364.1	366.3
30°S	364.0	365.9
35°S	364.2	366.2

TABLE 2.5. 1998 Annual Mean CO<sub>2</sub> Mole Fractions From South China Sea

Latitude	CO <sub>2</sub> (ppm)
	1998
21°N	369.2
18°N	368.0
15°N	367.6
12°N	367.4
9°N	367.0
6°N	367.5
3°N	367.9

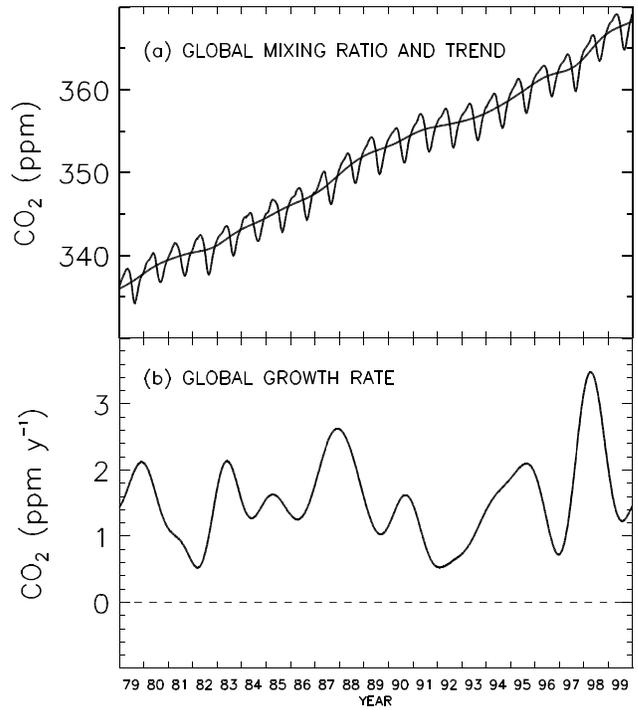


Fig. 2.4. (a) Globally averaged CO<sub>2</sub> mixing ratio and long term trend for 1979 through 1999 based on measurements from remote marine boundary layer sites in the global air sampling network. (b) The time variation of the global CO<sub>2</sub> growth rate calculated as the derivative of the trend curve in (a).

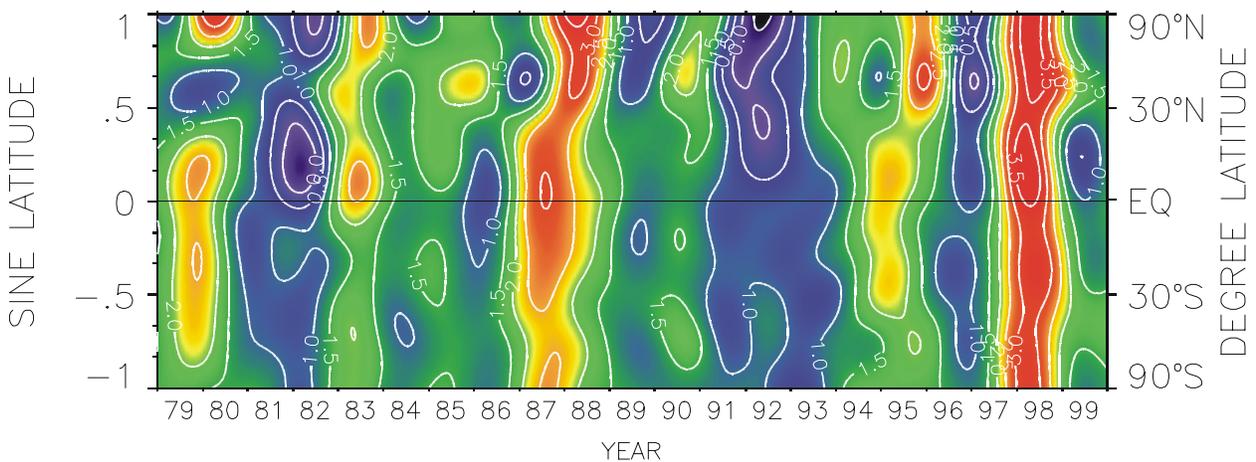


Fig. 2.5. CO<sub>2</sub> growth rate as a function of latitude and time based on marine boundary layer sites. Yellow, orange, and red indicate high growth rates (red is >3.5 ppm yr<sup>-1</sup>). Purple and black (black is <0.0 ppm yr<sup>-1</sup>) represent low growth rates. The transition between blue and green is the average CO<sub>2</sub> growth rate of ~1.5 ppm yr<sup>-1</sup>.

TABLE 2.6. Annual CO<sub>2</sub> Source and Sink Strength From a Two-Dimensional Atmospheric Transport Model

	Gt C = 10 <sup>15</sup> g		
	1990-1997	1998	1999
Fossil fuels	6.3 (0.2)	6.7	6.8
Atmospheric increase	2.9 (0.9)	6.2	3.1
Oceanic uptake	-2.0 (0.7)	-0.6	-0.7
Terrestrial biospheric uptake	-1.4 (0.9)	0.1	-3.1

Numbers in parentheses denote interannual variations (1  $\sigma$ ).

### 2.2.3. CARBON DIOXIDE STANDARDS AND REFERENCE GAS CALIBRATIONS

The 15 primary WMO standards, ranging in CO<sub>2</sub> mixing ratio from approximately 250 to 520  $\mu\text{mol mol}^{-1}$ , were calibrated at regular yearly intervals by the CMDL manometric system [Zhao *et al.*, 1997]. From September 1996 through December 1999 there were a total of 172 individual manometric determinations of the CO<sub>2</sub> mole fractions (Table 2.7). For comparison the CO<sub>2</sub> mole fractions were measured by SIO infrared absorption relative to the WMO X93 mole fraction scale (Table 2.7). The mean precision of the manometric measurement (standard deviation) is 0.13  $\mu\text{mol mol}^{-1}$ . The concentrations analyzed by SIO and CMDL in the atmospheric CO<sub>2</sub> concentration range of 300 to 400  $\mu\text{mol mol}^{-1}$  are in good agreement; therefore, the switch from SIO to CMDL for the maintenance of the WMO Mole Fraction Scale does not result in a large shift of the scale. The function of the primary standards is to provide continuity to the WMO scale as well as a quality-control check on the performance of the manometric system. The assigned values of the primaries are ultimately determined through the manometric analyses repeated at yearly intervals. The column in Table 2.7 labeled "Old scale" contains the concentration assignments of the WMO primary cylinders until the fall of 1999. They are based

on both CMDL manometric measurements and on the SIO infrared determinations but biased toward the larger number of SIO data. After the last round of CMDL manometric measurements that finished in January 2000, the values of the WMO primaries were reassigned and are now completely based on the CMDL manometric measurements. The average shift of the WMO Mole Fraction scale in the range of 350-400 ppm is +0.06 ppm (last column of Table 2.7, not using cylinder no.103).

Because we want to maximize the useful life span of the primaries, the primary calibration scale is transferred by way of NDIR measurements approximately twice a year to a set of secondary standards (not using no. 103). The secondaries, which typically have a useful lifespan of 3-4 years, are in turn used to calibrate all other cylinders in which each cylinder is always compared to a set of four bracketing secondaries. Therefore, the user will see a gradual shift of the calibration scale over a 3-yr period of about +0.06 ppm. During 1998 about 432 cylinders were assigned a value on the WMO Mole Fraction Scale in this way. The reproducibility, in the range between 250 and 520  $\mu\text{mol mol}^{-1}$ , has generally been better than 0.1  $\mu\text{mol mol}^{-1}$ . In the range of 325-425 ppm the reproducibility (one sigma) has been 0.014 ppm [Kitzis and Zhao, 1999].

On request, calibrations can be performed with the manometric system well outside of the range of atmospheric CO<sub>2</sub> values. Because there is some demand for calibrations well above 520  $\mu\text{mol mol}^{-1}$ , new primary CO<sub>2</sub> standards were created at the high end of the range at approximately 600, 700, 1000, 1500, 2000, 2500, and 3000  $\mu\text{mol mol}^{-1}$ . This will allow CMDL to perform CO<sub>2</sub> calibrations using the comparative infrared absorption technique rather than the time consuming manometric determinations.

Cylinders prepared by CMDL with a specified CO<sub>2</sub> concentration undergo the following procedures at the clean air pumping station at high elevation (3475 m) on Niwot Ridge, Colorado (NWR), 30 km east of Boulder, Colorado.

**New or Recently Hydrottested Cylinders:** (1) Cylinder is vented and then pressurized twice with dry natural air to about 20 atm (300 psi) and vented again. (2) Cylinder is filled to about

TABLE 2.7. Summary of Manometric Measurements of the WMO Primary CO<sub>2</sub> Standards Expressed as  $\mu\text{mol mol}^{-1}$  in Dry Air (ppm)

Cylinder Serial Number	N*	CMDL		SIO		Old Scale (ppm)	Difference (mano-old) (ppm)
		(ppm)	( $\pm$ )	(ppm)	( $\pm$ )		
110	9	246.66	0.11	246.65	0.25	246.64	0.02
102	13	304.40	0.11	304.38	0.09	304.38	0.02
111	14	324.01	0.13	324.01	0.08	324.00	0.01
130	9	337.27	0.11	337.26	0.08	337.27	0.00
121	11	349.39	0.11	349.34	0.11	349.34	0.05
103	15	353.37	0.08	353.17	0.11	353.22	0.15
139	11	360.91	0.06	360.81	0.15	360.83	0.08
105	10	369.40	0.12	369.33	0.17	369.33	0.07
136	7	381.32	0.15	381.25	0.18	381.27	0.05
146	11	389.52	0.15	389.51	0.20	389.51	0.01
101	13	396.35	0.17	396.24	0.20	396.24	0.11
106	9	412.08	0.15	411.96	0.24	411.96	0.08
123	11	423.09	0.18	422.91	0.30	423.03	0.06
107	16	453.18	0.18	452.79	0.43	452.92	0.26
132	13	521.35	0.17	521.00	0.83	521.08	0.27

\*Number of CMDL manometric calibrations for each cylinder

34 atm (510 psi) with dry natural air and stored for several weeks. (3) Before the final fill the cylinder is first vented and then spiked with either 10% or zero CO<sub>2</sub> in air, depending on the desired final mixing ratio. (4) Final cylinder is filled with ambient and dried natural air to 135 atm (2000 psi) during which the ambient CO<sub>2</sub> mixing ratio is monitored. (5) When water vapor content of the filled cylinder is measured, it must be less than 5 ppm, and it is usually less than 1 ppm. Drying is accomplished with magnesium perchlorate, Mg(ClO<sub>4</sub>)<sub>2</sub>. The pump is a Rix oil-less diving compressor.

**Previously Used Cylinders:** Steps 1 and 2 are replaced by venting and one fill with dry natural air to a pressure of 20 atm. Other trace gases, such as CH<sub>4</sub> and CO, can be targeted to specified values in the same cylinders.

#### **2.2.4. MEASUREMENTS OF STABLE ISOTOPES OF ATMOSPHERIC CO<sub>2</sub>**

Since 1989 the Stable Isotope Laboratory at INSTAAR has measured the stable isotopic composition of CO<sub>2</sub> from weekly flask samples of air obtained from the CMDL network of sites. A selection of only six sites and two ships in 1990 began the measurement effort that has grown to include approximately 45 stationary sites in the CMDL program as well as all of the shipboard samples. During 1999 over 11,000 isotopic analyses of δ<sup>13</sup>C and δ<sup>18</sup>O were made at INSTAAR that included 7500 flasks and 3200 tank air standards used for calibration. Combined with the CO<sub>2</sub> mole fraction measurements made by CMDL, the isotopic measurements offer a unique tool to investigate the sources and sinks of global carbon inferred from the spatial distribution of CO<sub>2</sub>. The tracking of large scale sources and sinks is an important part of the basis for our understanding of the carbon cycle and is one of the key tools necessary for making credible predictions about the future CO<sub>2</sub> loading of the atmosphere.

The degree to which isotopic measurements made on atmospheric samples are useful is limited by the precision of the mass spectrometer used. For example a change of just 0.02‰ in δ<sup>13</sup>C globally translates into a shift of 1.0 × 10<sup>9</sup> metric tons of carbon between an oceanic or terrestrial source to the atmosphere. Hence the measurements need to be of the highest precision attainable. In 1990 the program began making measurements with a VG SIRA Series 2 mass spectrometer. This instrument and extraction system produced an overall reproducibility of 0.03‰ for δ<sup>13</sup>C and 0.05‰ for δ<sup>18</sup>O (1σ of nine replicates). A Micromass Optima mass spectrometer was purchased and tested in 1996, fitted with a custom manifold and extraction system, and has been used since late 1996 exclusively for making flask measurements. The overall reproducibility for the Optima system is (1σ for replicate analyses) ±0.012‰ δ<sup>13</sup>C and ±0.031‰ for δ<sup>18</sup>O. The Optima system incorporates an automated 40-port custom manifold and a sample extraction system using all stainless steel parts and is based on the methods that were proven on the SIRA instrument.

The increased capacity attained with the 40-port manifold allowed us to make over 45,360 separate analyses on flasks and reference gases since the instrument was brought on-line in 1996. Instrument down time experienced during 1999 is calculated to be 2%. The combined effect of improved precision, increased capacity, and decreased down time, has resulted in more high-quality isotopic measurements that help characterize the present day carbon cycle.

#### **Addition of Aircraft Samples**

Very few changes or improvements were necessary to the mass spectrometer, sample preparation system, or protocols used in analysis during the last year. However, a few small hardware and software modifications were made to allow aircraft sampling kits to be analyzed for δ<sup>13</sup>C and δ<sup>18</sup>O of CO<sub>2</sub>. Protocols identical to normal flask measurements are used with the exception that longer pump times are added to evacuate the longer manifold connections to the aircraft suitcases. Tank air from the Niwot Ridge site was used to fill and test the aircraft kits, and results indicated a reproducibility slightly less than that of normal flasks. However, on repeated analyses of the same 20 aircraft flasks of tank air, the mean δ<sup>13</sup>C values remained stable (-0.05‰ change) while the mean δ<sup>18</sup>O values drifted (-0.38‰ change), showing what appear to be signs of moisture in the flasks from previous samples. These effects increase until the water in the flask has equilibrated with the CO<sub>2</sub>. These preliminary tests indicate that care should be taken to keep the aircraft sample flasks dry initially and to use some type of air drying system, particularly when sampling at lower altitudes. Thus far, over 400 aircraft flasks have been analyzed, and plans continue to allow for increased capacity to analyze these types of samples.

#### **Data Quality Checks**

The measurement protocol that began in late 1996 calls for three aliquots of air from a standard cylinder in the middle of every 40-flask run on the mass spectrometer. This additional cylinder, called the "quality control tank," provided an independent check on the performance of the entire system, all the way from the manifold, through the extraction system, to the ionization in the source of the mass spectrometer, and the final data reduction and corrections for N<sub>2</sub>O and <sup>17</sup>O made in software. In this manner, the day-to-day quality of data produced can be monitored before each run and steps to correct problems can be taken immediately. Figure 2.6 shows the standard deviation (1σ) for the δ<sup>13</sup>C value measured on three aliquots of air from a quality control tank measured at midpoint during each analysis run plotted as a 10-point running mean. The average standard deviation during the entire period (November 1998 to May 2000) is 0.010‰ and is usually less than 0.015‰. The unusually high values (>0.02‰) around run number 470 may be because of contamination from a reference gas regulator and a change in capillaries. The dramatic improvement (mean = 0.0061‰) after run number 720 resulted from a cleaning and rebuilding of the mass spectrometer source. The more transient fluctuations in between these periods are likely the result of water contamination in the manifold originating from flasks that contain moist air.

The same information is shown in Figure 2.7 for δ<sup>18</sup>O in the quality control tank. The average standard deviation is 0.044‰. The standard deviation of δ<sup>18</sup>O displays a similar but lagged response to the source rebuild relative to the δ<sup>13</sup>C record. This may be due to the extra time required to remove contaminants (including water) from the system following the rebuild.

Two other key tools in data quality checks have been the circulation of the so-called "Classic" standards with three other laboratories and the flask InterComparison Program (ICP). INSTAAR has and will continue to participate in these programs. The Classic standards are five tanks of air with a wide range of greenhouse gas constituents, including isotopic compositions of CO<sub>2</sub> that range over several permil. Regulators

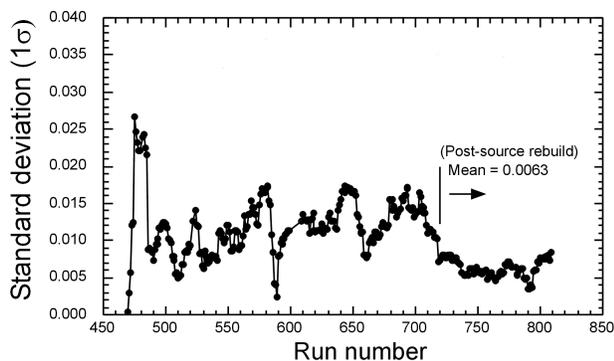


Fig. 2.6. Ten-point running mean of the standard deviation of the quality control tank  $\delta^{13}\text{C}$  as a function of run number. The data cover the period from November 1998 to May 2000.

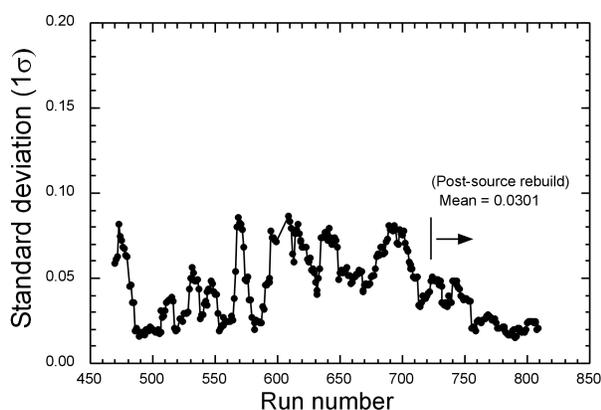


Fig. 2.7. Ten-point running mean of the standard deviation of the quality control tank  $\delta^{18}\text{O}$  as a function of run number. The data cover the period from November 1998 to May 2000.

are shipped with the tanks to ensure similar circumstances for measurement by the four different laboratories. This program is an important intercomparison tool, but one circuit among four laboratories takes many months to complete. The ICP protocol, where two or more laboratories sample the same air in flasks that go to both laboratories for analysis, provides a method for ongoing frequent comparison that has a higher chance of illuminating discrepancies between laboratories. However, the ICP measurements cannot be repeated, and thus the results carry larger error bars. Such programs are essential to the success of global integration of isotopic data.

#### Sampling Humid Air

In samples collected at humid, tropical locations without drying, the  $^{18}\text{O}/^{16}\text{O}$  measurements are highly variable and consistently more depleted in  $^{18}\text{O}$  because of the exchange of oxygen atoms between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules on the walls of

the flasks. Systematic tests at INSTAAR [Gemery *et al.*, 1996] showed that the exchange takes place during storage in the flasks when the relative humidity of the air sample is above 50%. There is also some dependence on the physical characteristics of each flask. The problem with wet air can be seen in the percentage of flask pairs that are considered similar enough to be retained in the data set. In order for a value to be retained, flask pair difference must be less than 0.09‰ for  $\delta^{13}\text{C}$  analyses and 0.15‰ for  $\delta^{18}\text{O}$  analyses. The average percentage of flask pairs that have been retained at 45 (fixed) stations is 93.4% for  $\delta^{13}\text{C}$  and only 69.7% for  $\delta^{18}\text{O}$  analyses. The reason for the lower success rate in  $\delta^{18}\text{O}$  pair agreement is closely tied to the moisture problem as seen in the low pair agreements at sites with high humidity (for example, see Figure 2.8).

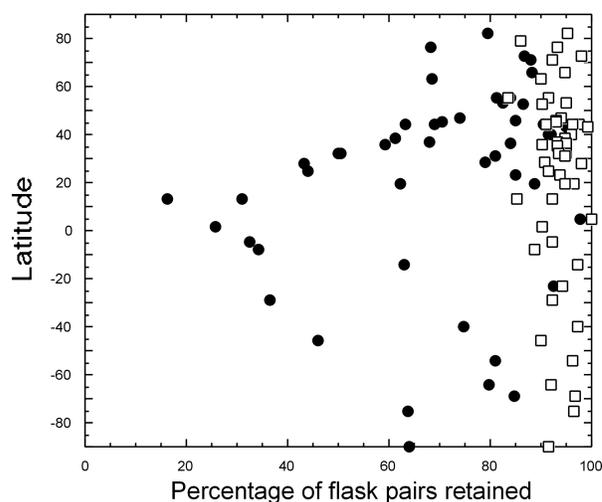


Fig. 2.8.  $\delta^{18}\text{O}$  (filled circle) and  $\delta^{13}\text{C}$  (open square) pair agreement in flask samples from the CMDL flask sampling network, plotted by latitude.

Field testing of a new prototype air sampling apparatus began at SMO in September 1994 and at Cape Kumukahi, Hawaii (KUM) in May 1995. The new Air Kitzis sampler (AIRKIT) differs from the older Martin and Kitzis Sampler (MAKS) in two important ways: (1) it has a thermoelectrically cooled condenser to remove water vapor from the air stream, and (2) it has a microprocessor to control the sampling process so that collecting the sample is more automated and less subject to operator error. The effect of drying the air sample is most dramatic for the measurement of  $^{18}\text{O}/^{16}\text{O}$  in  $\text{CO}_2$  (Figure 2.9). While large improvements in the reproducibility were gained when shifting analyses from the SIRA to the OPTIMA mass spectrometer, future improvements are expected for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  as more flask samples in the network are dried and wet air issues are overcome.

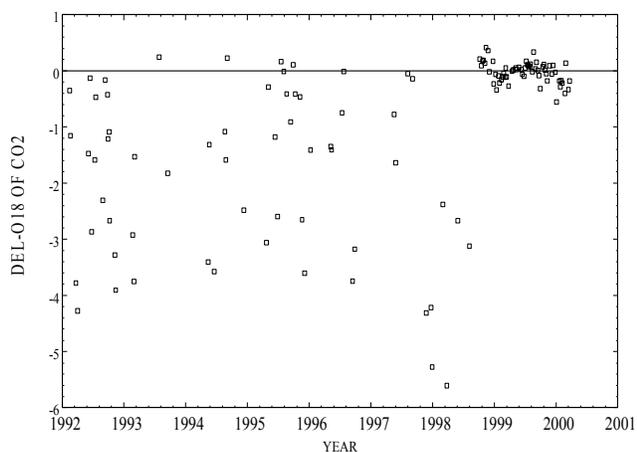


Fig. 2.9.  $\delta^{18}\text{O}$  values of atmospheric  $\text{CO}_2$  from Seychelles (Mahe Island,  $4^\circ40'\text{S}$ ,  $55^\circ10'\text{E}$ ). Note the switch to collecting dried air in September 1998.

#### Seasonality and Temporal Trends in Isotopes of $\text{CO}_2$

A sample of the isotope data is given in Figure 2.10, which shows time series of the  $\text{CO}_2$  mole fraction,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  at Barrow, Alaska, from 1990 through 2000. The striking anticorrelation between the seasonal cycles of mixing ratio and  $\delta^{13}\text{C}$ , reflects the strong influence of the annual cycle of photosynthesis and respiration imposed on the atmosphere by the terrestrial biosphere in the northern hemisphere. Whereas the mixing ratio shows an increasing long-term trend because of the use of fossil fuels, the trend of  $\delta^{13}\text{C}$  is to lighter values reflecting the depletion in  $\delta^{13}\text{C}$  of fossil fuel relative to the atmosphere.

The seasonal cycle of  $\delta^{18}\text{O}$  lags behind  $\text{CO}_2$  and  $\delta^{13}\text{C}$ , and while its interannual variability shows no steady trend, the  $^{18}\text{O}/^{16}\text{O}$  ratio appears somewhat unstable from year to year, most likely because of the large isotopic exchanges of oxygen between  $\text{CO}_2$  and different reservoirs of water in plant leaves and in soils.

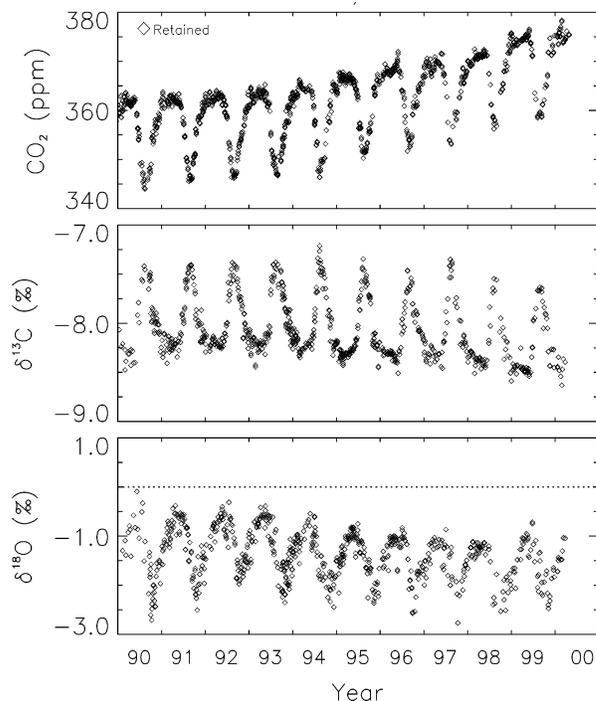


Fig. 2.10. Isotopic and concentration data for carbon dioxide at Point Barrow, Alaska.