REPORT OF THE EIGHTTH WMO MEETING OF EXPERTS ON CARBON DIOXIDE CONCENTRATION AND ISOTOPIC MEASUREMENT TECHNIQUES
(Edited by Thomas Conway)
(BOULDER, CO, 6-11 July 1995)
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# TABLE OF CONTENTS

1. OPENING OF THE MEETING .................................................................................. 1

2. INTERCOMPARISON OF FLASK AND IN SITU CO₂ PROGRAMMES
   AT ALERT, NORTHWEST TERRITORIES ......................................................... 1
   2.1 Conditions for Study ................................................................................. 2
   2.2 Procedure ................................................................................................. 3

3. RECENT CO₂ CALIBRATION PROBLEMS: AES/SIO/CMDL ......................... 3

4. STANDARDS ..................................................................................................... 5
   4.1 CMDL CO₂ Standards .............................................................................. 5
   4.2 SIO CO₂ Standards .................................................................................. 9
   4.3 Stable Isotopes in Carbon Dioxide ............................................................ 9

5. STRATOSPHERIC CO₂ MEASUREMENTS AND INSTRUMENTATION ............. 10

6. EXTENSION AND INTEGRATION OF ATMOSPHERIC CO₂ DATA INTO A GLOBALLY
   CONSISTENT MEASUREMENT RECORD ...................................................... 11

7. NEW AND DEVELOPING MEASUREMENT TECHNIQUES ............................... 20

8. A PLAN FOR GREATLY EXPANDED AIR SAMPLING THROUGH AUTOMATION .... 20

9. DATA REPORTING .......................................................................................... 20
   9.1 CDIAC Data Management Policies and Activities ...................................... 20
   9.2 The World Data Center for Greenhouse Gases (WDCGG) ....................... 21

10. PARTICIPATION IN THE INTERNATIONAL GLOBAL ATMOSPHERIC CHEMISTRY
    (IGAC) PROGRAMME .................................................................................. 24

11. GAW UPDATE ............................................................................................... 24

12. CLOSURE OF THE MEETING ....................................................................... 27

Annexes

1. List of participants ......................................................................................... 29
2. Previous meetings of the WMO experts in CO₂ measurement ....................... 33
3. Meeting programme ....................................................................................... 35
4. CO₂ measurement sites .................................................................................. 37
5. Laboratory reports
   5.1 Canada ...................................................................................................... 42
   5.2 China ......................................................................................................... 58
   5.3 France ........................................................................................................ 63
   5.4 Germany ..................................................................................................... 71
   5.5 Hungary ...................................................................................................... 75
   5.6 Italy .............................................................................................................. 78
   5.7 Japan ........................................................................................................... 81
   5.8 Korea .......................................................................................................... 86
   5.9 Sweden ....................................................................................................... 90
   5.10 USA ......................................................................................................... 97
6. WMO CO₂ measurement manual ................................................................. 103
7. Cylinder preparation for CMDL natural air standards .................................... 105
1. OPENING OF THE MEETING

The meeting was opened in Boulder, Colorado, by Dr. Pieter Tans (U.S.), who organized the meeting and agreed to act as chairman. Dr. Tans noted with regret the absence of Dr. Neil Trivett of Canada due to illness and expressed the participants' hope for a speedy and complete recovery. Several participants new to the World Meteorological Organization (WMO) CO₂ Experts Meetings were welcomed and introduced: Dr. Kristie Boering (Harvard University, U.S.); Dr. Kim Holmen (Stockholm University, Sweden); Dr. Laszlo Haszpra (Hungarian Meteorological Service, Hungary); Dr. Hidekazu Matsueda (Meteorological Research Institute, Japan); Dr. Hisayuki Inoue (Meteorological Research Institute, Japan); and Mr. Kazuto Suda (Japan Climatic Data Center). Dr. Tans was also pleased to state that three representatives from the International Global Atmospheric Chemistry (IGAC) component of the International Geosphere-Biosphere Programme (IGBP), including its chairman, Dr. Ron Prinn, would be attending the second day of the meeting.

The chairman encouraged the participants to continue the open exchange of data and ideas that has characterized this series of meetings. To this end, the agenda of the meeting included ample time for discussion as well as prepared talks.

2. INTERCOMPARISON OF FLASK AND IN SITU CO₂ PROGRAMMES AT ALERT, NORTHWEST TERRITORIES

Mr. Worthy, Atmospheric Environment Service (AES), Canada, presented findings of an intercomparison of flask and in situ carbon dioxide programs at Alert, Northwest Territories. AES currently maintains an in situ CO₂ programme and three separate CO₂ flask sampling programmes at Alert. Carbon dioxide flask programs are also maintained at Alert by four cooperating agencies. Table 1 provides a detailed summary of the AES and independent CO₂ flask programs. Table 2 provides a summary of the intercomparison results. The Commonwealth Scientific and Industrial Research Organization (CSIRO) was not included in this study because samples are collected using AES flasks, and Main Geophysical Observatory (MGO) programme was not included because there were not enough data to perform adequate analysis.

<table>
<thead>
<tr>
<th>Agency</th>
<th>Sampling History</th>
<th>Flask Type</th>
<th>Sampling Protocol</th>
</tr>
</thead>
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<tr>
<td>Atmospheric Environment Service (AES), Canada</td>
<td>1975 - present (weekly sample)</td>
<td>2-L greased stopcock</td>
<td>Evacuated grab sample</td>
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<td>1992 - present (weekly sample)</td>
<td>2-L single-valve Viton O-rings</td>
<td>Evacuated grab sample</td>
</tr>
<tr>
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<td>1993 - present (weekly sample)</td>
<td>2-L double-valve Buna-n O-rings</td>
<td>Pressurized flush method</td>
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<tr>
<td>Commonwealth Scientific and Industrial Research Organ. (CSIRO), Australia</td>
<td>1988 - 1993 (monthly sample)</td>
<td>5-L double-valve Teflon O-rings</td>
<td>Pressurized flush method</td>
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<td>1993 - present (monthly sample)</td>
<td>AES 2-L single-valve, Viton O-rings</td>
<td>Repeated pressurizing and venting</td>
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<td>National Oceanic and Atmospheric Admin. (NOAA), United States</td>
<td>1985 - 1992 (weekly sample)</td>
<td>0.5-L double-valve greased stopcocks</td>
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<td>1992 - present (weekly sample)</td>
<td>3-L double-valve Teflon O-rings</td>
<td>Pressurized flush method</td>
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<td>Scripps Institution of Oceanography (SIO), United States</td>
<td>1984 - present (weekly sample)</td>
<td>5-L greased stopcock</td>
<td>Evacuated grab sample</td>
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<tr>
<td>Main Geophysical Observatory (MGO) Russian Federation</td>
<td>1992 - present (bi-weekly sample)</td>
<td>2-L stainless steel single valve</td>
<td>Evacuated grab sample</td>
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</table>
Table 2. Intercomparison of Alert CO₂ In Situ and Flask Programmes

<table>
<thead>
<tr>
<th>Program</th>
<th>Number of data points</th>
<th>(Flask - in situ average (ppm))</th>
<th>(Flask - in situ median (ppm))</th>
<th>(Flask - in situ IQR* (ppm))</th>
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</thead>
<tbody>
<tr>
<td>AES greased stopcock</td>
<td>156</td>
<td>0.62 ± 0.82</td>
<td>0.52</td>
<td>0.64</td>
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<td>AES single valve O-ring</td>
<td>64</td>
<td>0.38 ± 0.30</td>
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<td>AES double valve O-ring</td>
<td>33</td>
<td>0.13 ± 0.23</td>
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<td>SIO greased stopcock</td>
<td>122</td>
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<td>0.28</td>
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<tr>
<td>NOAA_combined</td>
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<td>0.26 ± 0.32</td>
<td>0.25</td>
<td>0.40</td>
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<td>NOAA_greased</td>
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<td>0.40 ± 0.31</td>
<td>0.40</td>
<td>0.26</td>
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<td>NOAA_Teflon</td>
<td>57</td>
<td>0.05 ± 0.19</td>
<td>0.06</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*IQR: Interquartile region

Statistical significance tests on the preceding results indicate that the AES evacuated greased stopcock flask data set is not significantly different from the evacuated single valve O-ring flask data set. Both data sets, however, are significantly different from the AES pressurized double valve flask data set. The two National Oceanic and Atmospheric Administration (NOAA) flask data sets (greased stopcock and Teflon O-ring) were also found to be significantly different from one another. More detailed results are given in the station report (Annex A5.1).

The above results are evidence of the difficulties that exist within individual laboratories when it comes to merging data sets from different flask types. Merging data sets from cooperating agencies is even more difficult. There is an urgent need for studies relating the measurements from various independent CO₂ programs so that data sets can be merged in a consistent fashion. Some of the issues that need to be addressed are:

- Laboratory scale differences
- Storage and moisture effects in different flask types
- Field sampling procedures
- Sampling under variable field conditions

AES is proposing an extensive CO₂ interflask comparison between cooperating agencies. The outline of the proposal is presented in the following pages.

**Proposed Outline for Interflask Comparison Between Cooperating Agencies**

AES is proposing an extensive interflask comparison between cooperating agencies to address the issues listed previously. In order to remove the effects of laboratory scale differences, a single laboratory should perform the analyses. All agencies with CO₂ flask programs are invited to submit flasks for the intercomparison. AES is willing to perform the analyses and coordinate and document the study. The study would consist of filling flasks from each agency in our laboratory with calibration gas and performing storage tests. Following the storage tests, the flasks would be sent to the Alert, Canada, site for sampling. Sampling would be carried out during stable ambient conditions (April) and during variable ambient conditions (January). Once sampled, flasks would then be returned to AES for analysis. For quality control purposes, the same flasks should be used throughout the whole study.

2.1 Conditions for Study

- AES will provide the reference calibration standard gas to be used in the comparison.
- Each laboratory will provide 16 flasks and flask connectors if necessary. The study will be carried out as quickly as possible so as not to result in a shortage of flasks at the stations.
2.2 Procedure

Part I

- AES will fill 16 flasks of each type with a known reference calibration standard gas and analyze them immediately.

- The flasks will then be refilled for storage tests at 2 weeks, 4 weeks, 8 weeks and 16 weeks (four flasks of each type will be analyzed at each interval).

Part II

- Sixteen flasks of each type will be sampled consecutively at Alert during the month of April (ambient concentrations are most stable in Alert at this time).

- The flasks will be returned to the AES laboratory and analyzed with as little delay as possible.

Part III

- Sixteen flasks of each type will be sampled in Alert during the month of January (ambient concentrations are most variable in Alert at this time).

- Four flasks of each type will be sampled consecutively, twice a week, for 2 weeks.

- The flasks will be returned to the AES laboratory and analyzed with as little delay as possible.

NOTE: PRIOR TO SAMPLING FOR PARTS II AND III, THE FLASKS WILL BE RETURNED TO THE ORIGINATING LABORATORY FOR USUAL PRESAMPLE PREPARATION.

3. RECENT CO₂ CALIBRATION PROBLEMS: AES/SIO/CMDL

Mr. Doug Worthy, on behalf of Dr. Neil Trivett of the Atmospheric Environment Service, reported some discrepancies in the concentrations assigned to the Canadian National Standards provided by the Central CO₂ Laboratory/Scripps Institution of Oceanography (CCL/SIO) and the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL). Since the inception of the new continuous CO₂ measurement program in Canada in 1986, there has been very close cooperation and intercalibration between these three laboratories. In 1986 Canada purchased nine 50-L aluminum tanks from the CCL spanning concentrations from 310 to 390 ppm in 10 ppm steps. After filling, the concentrations were evaluated periodically over a 5-month period to assess stability. These tanks form the backbone of the Canadian calibration system. The calibration data for these nine tanks are given in Table 3.

Due to some difficulties at the CCL in 1989, the Canadian tanks were sent to CDML to be checked for drift. CMDL had just had their main suite of calibration gases recalibrated by the CCL; so this was thought to be a satisfactory substitute. In general, some drift was apparent at the high and low ends of the scale. In 1991 the tanks were sent to the CCL for recalibration as required by the WMO protocol. There seemed to be a large variability in the assigned concentrations by the CCL and the apparent drift noted at the high and low ends of the scale in 1989 apparently reversed directions. This caused serious concern in our program that our tanks were unstable and that CMDL concentrations seemed to be too low. The tanks were sent again to CMDL in 1993 for reevaluation. As in 1989, the CMDL tanks had just been calibrated by the CCL. Over this period CMDL indicated that their main suite of tanks had drifted very little and the drifts were easily quantified. The 1993 calibrations of our tanks were consistent with those by CMDL in 1989 but were becoming more inconsistent with the CCL numbers. Furthermore, the variability in CMDL numbers was much smaller than the CCL numbers.

In 1995 Canada purchased 18 new tanks from the CCL to form a new set of national standards. These tanks were used to check the concentrations of the original nine national standards. The drift pattern for the original tanks appeared to become even more inconsistent with what might be expected. Because of this, CMDL agreed to quickly reevaluate our original nine tanks before this meeting. The calibration of our original nine tanks against the new national standards was done internally and then checked by CMDL a few months later. It was evident that there was a serious discrepancy between the CCL and the CMDL scales in spite of the fact that the CMDL tanks are calibrated by the CCL. The CMDL
calibrations seemed to be quite consistent with each other (Table 3) whereas the CCL numbers were not. It should be noted that the numbers reported in Table 3 are all supposed to be on the 1993 CCL scale. Since we were unable to account for this discrepancy, this left Canada with a serious problem to determine the correct scale for the original national standards.

Mr. Worthy further reported to the meeting that the extent of intercalibration between these three programs is unique in the CO₂ community. It reflects the ease of shipping within the North American continent and the good relations between the programs. However, it does raise some concerns for all the international programs and emphasizes the importance of the interlaboratory calibrations. The WMO round-robin intercalibration suites do not have enough tanks or a wide enough concentration range to quantify such problems.

Mr. Moss of the CCL recommended that the Canadian tanks be returned to the CCL for another calibration and review of the calibration procedures and history for the Canadian tanks.

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### 4. STANDARDS

#### 4.1 CMDL CO₂ Standards

**Manometric Standards at CMDL**

A schematic diagram of the system is given in Figure 1. Air from a cylinder to be analyzed is dried at -70°C and flows at a flow rate of 600 cc min⁻¹ through a 6-L volume while its CO₂ content is measured. When the CO₂ mixing ratio is steady, the flow is stopped and the temperature and pressure of the 6-L volume are measured after they have come to equilibrium. The 6-L volume is isolated. The air from that volume is then slowly, via a servo valve, led through two liquid N₂ cold traps, freezing out CO₂, N₂O, and residual water while the pressure in the cold traps is maintained at 3 torr. Upon completion of the extraction, which takes about 30 minutes, the extract is dried with a dry ice-alcohol mixture, and the remaining CO₂ (and N₂O) is transferred to the small 10-ml volume by placing liquid N₂ around it. Upon closure of the valve, the 10-ml volume is thawed, and the temperature and pressure are continuously measured while equilibrium is reached. Because the volume ratio of the small and large volumes is known accurately, the molar ratio of CO₂ (together with N₂O) in the original air sample can be calculated with the virial equation of state, taking real gas compressibility into account.

The volume ratio is determined regularly in a fully automated way via successive expansions of dry air. Air is admitted into the 10-ml volume. After its temperature and pressure have attained equilibrium, the gas is expanded into the part of the evacuated manifold closed off by the valves numbered 204, 206, and 209 (Figure 1). The Glass Expansion (GE) valves are glass with a glass piston and Viton O-ring. Valve 208 remains open from here on. After regaining temperature and pressure equilibrium, the volume ratio between the 10-ml volume and 10-ml plus the manifold is determined from the pressure drop. The pressure is then restored and the procedure repeated by expanding, through opening valve 209, from the 10-ml plus the manifold into the volume closed off by valve 202. The next step is an expansion by opening valve 202, and the final step is an expansion from the sum of all volumes thus far into the 6-L volume by opening valve 206. The final volume ratio between the 10-ml and the 6-L volume is obtained by multiplying the volume ratios of the four separate expansions. Since the entire procedure is automated, it is repeated about ten times overnight. The reproducibility of volume ratio determinations on different days is shown in Figure 2. When the average is calculated separately for each day, the standard deviation of those averages is about one part in five thousand.
Figure 1. MANOMETRIC CO2 CALIBRATION SYSTEM
The primary manometer is a hollow fused silica spiral. The use of any metal in the primary system is not suitable, because it causes the adsorption of a measurable fraction of CO₂ on the walls of the system. The spiral manometer is regularly calibrated with a dead-weight tester. The latter consists of a very precisely machined piston sinking into a very precisely machined cylindrical bore. Air escapes between the cylinder wall and the piston while it slowly sinks. Since the sinking piston is "air-lubricated," the pressure underneath the piston is determined by the weight of the piston, local gravity, and the area of the piston until the piston stops. Different pressures are generated by placing additional weights on top of the piston. While the piston sinks, the pressure that is generated can be applied to any pressure sensors to be calibrated.

The temperature of the oven is uniform and controlled to an accuracy of 0.01 K. The temperature sensors are platinum resistance thermometers. The dashed line (Figure 1) encloses all components of the system that are inside the oven.

**Status of the Manometric System**

The reproducibility of repeated determinations of the CO₂ mole fraction in dry air is shown in Figure 3. The standard deviation is less than 0.1 ppm. A number of tests still need to be performed before absolute values can be assigned. The volume ratio determinations will also be done in a different way by comparisons with independently determined small and large volumes. In addition, four-step volume ratio determinations will be done with two manometers of different design connected in parallel. Extractions of CO₂ from CO₂-free N₂ cylinders ("blanks") will be performed. The dead-weight tester has recently been recalibrated at the factory. Furthermore, a series of comparisons will be done with independent gravimetric standards made in CMDL. The "final" absolute values of the CO₂ mol fraction as determined by CMDL will be compared with the current WMO scale as anchored by the manometric measurements at the Scripps Institution of Oceanography.
Figure 3. The reproducibility of repeated determinations of the CO₂ mole fraction in dry air.
4.2 SIO CO$_2$ Standards (*No material submitted.*)

4.3 Stable Isotopes in Carbon Dioxide

Discussion of stable isotope observations on CO$_2$ and methodologies again covered a significant part of the meeting. Links between the groups participating in the Coordinated Research Programme of IAEA on "Isotope variations of carbon dioxide and other trace gases in the atmosphere" (in the following referred to as IAEA-CRP) and WMO experts on "Carbon dioxide concentration and isotopic measurement techniques" have been intensified in the past 2 years. Since many of the laboratories with atmospheric CO$_2$ monitoring programs are also involved in stable isotope measurements, a joint WMO-IAEA meeting of both groups was suggested.

**Techniques and Standardization**

A detailed list of recommendations concerning air sampling and analysis techniques as well as data reduction and mass spectrometer correction factors for high precision $\delta^{13}$C measurements in atmospheric CO$_2$ was given in WMO report. This topic was not discussed again at the present meeting. A major problem for the laboratories involved in these measurements remains the urgent need for whole air standards for isotopes in atmospheric CO$_2$. This reference material is still not available.

As a first step toward a coordinated intercalibration between the laboratories with global observational programmes, and as part of the IAEA-CRP, R. Francey and C. Allison, CSIRO, Division of Atmospheric Research [see also Allison et al., 1994] are now preparing two sets of five high-pressure cylinders in the $\delta^{13}$C range of -6 to -11% and $\delta^{18}$O at about 0% with a CO$_2$ concentration variation of about -0.05% per ppmv. It was also decided to vary the N$_2$O concentrations between each set of cylinders. Three cylinders from each set will be circulated to each selected laboratory. It was suggested at the IAEA meeting in Vienna, November 1994, that only three or four laboratories shall be selected for the first round-robin intercomparison to speed up the procedure. All nonselected but interested laboratories will have to intercompare separately with one of the participating laboratories with respect to whole air standards. In addition, all laboratories participating in the WMO CO$_2$ concentration round-robin are encouraged to analyze stable isotope ratios in CO$_2$ as well as additional trace gas concentrations such as CH$_4$, CO, and N$_2$O in those samples.

NOAA CMDL, which now officially has taken over the task of the WMO Central CO$_2$ Laboratory, has offered to provide informative isotope ratio numbers on their secondary CO$_2$ standards prepared for the CO$_2$ community. On a long-term perspective, NOAA CMDL is also interested in assuming the task of the "Central CO$_2$ Isotope Laboratory" (CCIL).

It has again been strongly recommended that whole air with known N$_2$O concentrations as well as pure CO$_2$ gas standards are used routinely for isotope analyses of atmospheric CO$_2$. This is not only required for regular quality control of the CO$_2$ extraction line but also to recognize possible changes in mass spectrometer performance. Systematic shifts in whole air standards with respect to pure CO$_2$ gas have been observed by Wahlen [1994] and reported by C.D. Keeling at this meeting. These shifts may possibly be explained by changing ion source chemistry among nitrogen/oxygen compounds (N$_2$O, NO$_2$, etc.) due to aging of the filament.

**References**


5. STRATOSPHERIC CO₂ MEASUREMENTS AND INSTRUMENTATION - Kristle A. Boering, Bruce C. Daube, Jr., and Steven C. Wofsy

Measurement Description: The fast-response CO₂ instrument measures CO₂ concentrations in situ using the light source, gas cells, and solid-state detector from a modified nondispersive infrared CO₂ analyzer (Li-Cor, Inc., Lincoln, Nebraska); these components are stabilized along the detection axis, vibrationally-isolated, and housed in a temperature-controlled pressure vessel. Stratospheric air enters a forward-facing inlet and is compressed by a Teflon diaphragm pump. The CO₂ mixing ratio of air flowing through the sample gas cell is determined by measuring absorption at 4.26 μm relative to a reference gas of known concentration. In-flight calibrations are performed by replacing the air sample with reference gas every 10 minutes, with a low-span and high-span gas (that bracket concentrations of stratospheric CO₂) every 20 minutes, and with a long-term "surveillance" standard every 2 hours. The long-term standard is used sparingly and serves as a check of the flight-to-flight accuracy and precision of the measurements, augmented by ground-based calibrations before and after flights. Sample and reference gas pressures and temperatures are controlled to 320 ± 0.2 torr and 36.5 ± 0.2°C, respectively. Flow through the sample cell is maintained at 200 sccm, corresponding to a flush time of about 1.5 seconds. The instrument bandpass is 10 Hz and data are acquired at 4 Hz; reported data are generally median-filtered into 2-second intervals from the 4 Hz data. Measurements begin on ascent at 225 mbar (11 km) and end on descent at 290 mbar (9.5 km), often providing data for the upper troposphere. Interference from water vapor due to absorption and pressure-broadening is negligible for sampling conditions; dilution by H₂O corresponds to <0.03 ppmv (equivalent CO₂) for H₂O <85 ppmv.

Since its completion in November 1992, the ER-2 instrument has measured CO₂ on the SPADE and ASHOE/MAESA payloads, totaling 395 flight hours in 62 flights. The stratospheric measurements of CO₂ to date, in conjunction with simultaneous measurements of other species on the ER-2 (such as N₂O and H₂O), have allowed us to observe the seasonal, annual, and interannual changes in tropospheric CO₂ propagate into the lower stratosphere, providing qualitative and quantitative estimates of transport rates into and within the lower stratosphere. The amplitude of the seasonal variation of stratospheric CO₂ just above the tropopause is 2 to 3 ppm and is in phase with the Northern Hemisphere tropospheric cycle (although delayed by about 1 month). These variations are attenuated with altitude and at high latitudes, but seasonal changes are observable to 19 km at midlatitudes. Data spanning latitudes from 60°N to 70°S in March and April 1994 and October and November 1994 revealed that the seasonal variation of CO₂ in the lower stratosphere is the same in both hemispheres and that there is no mean north-south CO₂ gradient, providing further evidence that air enters the stratosphere mainly in the tropics from a nearly homogeneous source. Reliable comparisons with CO₂ measurements from the surface and the middle and upper troposphere are crucial to our studies in the stratosphere.

Accuracy: ±0.1 ppm; precision: ±0.05 ppm; response time: 2 seconds; weight: 115 pounds; power: 450 W max, 300 W typical.

Supplemental reading:


6. EXTENSION AND INTEGRATION OF ATMOSPHERIC CO₂ DATA INTO A GLOBALLY CONSISTENT MEASUREMENT RECORD - Ken Masarie and Pieter Tans

Atmospheric transport models are widely used to constrain sources and sinks of carbon dioxide by requiring that the modeled spatial and temporal patterns are consistent with the observations. Serious obstacles to this approach are the sparsity of sampling sites and the lack of temporal continuity among observations from different locations. Consequently, there is the potential for models to misinterpret these spatial and temporal gaps resulting in derived source/sink scenarios that are unduly influenced by the sampling distribution. Data extension and integration as described by Masarie and Tans [1995] are intended to address this issue by reducing possible biases resulting from the poor spatial and temporal coverage. The methods were developed using measurements from the CMDL cooperative air sampling network, but more recently measurement records from other laboratories have been extended and integrated into a global CO₂ database with careful attention to both methodology and calibration.

Data extension attempts to transfer knowledge gained during a limited period of measurements beyond the period itself. At Alert, NWT Canada (ALT), for example, CMDL began making measurements in 1985. We can approximate the features in the ALT record such as an average seasonal cycle, trend, and changes in the trend with a smooth curve fitted to the data. Also from this 10-year record, we can learn how ALT, on average, differs from other marine boundary layer (MBL) sites from the CMDL network that are nearby in latitude. Together, these two pieces of information can be used to extrapolate the ALT record beyond the actual measurements (ref. see Masarie and Tans [1995] for details). The resulting extended record at ALT (Figure 4a) contains smoothed values during the measurement record and derived extrapolated values prior to 1985 (no interpolated values were necessary). The Atmospheric Environment Service (AES) CO₂ program in Canada has maintained a sampling program at ALT since 1975. This independent sampling program provides an opportunity to compare CMDL smoothed and extrapolated values with smoothed values derived from the AES measurement record (Figure 4b). Figure 4c shows the calculated differences of the AES smoothed record minus the CMDL extended record for the period 1979-1992. The mean difference of AES smoothed values minus CMDL smoothed values from mid-1985 to late 1992 was (0.1 ± 0.7) ppm. The mean difference of AES smoothed values minus CMDL extrapolated values for the period 1979 to mid-1985 was (0.5 ± 0.9) ppm.

Several sampling sites have long uninterrupted records. At Cold Bay, Alaska (CBA), for example, the extended record for 1979 to 1994 has no interpolated or extrapolated values Figure 5a. As an exercise we excluded portions of the CBA record and reconstructed the record. The reconstructed extended record was then compared with the actual record. First, we excluded all data prior to January 1987. The resulting extended record produced extrapolated mixing ratios from 1979 through 1986 (Figure 5b). The mean difference of extrapolated values minus smoothed values for the 8-year period was (0.01 ± 0.93) ppm (Figure 5d). Second, we assumed sampling at CBA was discontinued in January 1987. The resulting extended data set contained extrapolated values from 1987 through 1993 (Figure 5c). The mean difference of extrapolated values minus smoothed values was -(0.02 ± 0.87) ppm (Figure 5d). This exercise has been repeated for several other long measurement records including the Schauinsland, Germany (SCH), and Mt. Cimone, Italy (MTC), in situ data sets. Figure 6 shows the reconstruction of the Schauinsland data kindly provided by Dr. Ingeborg Levin and Ms. Karin Uhse of Umweltbundesamt. The mean difference of extrapolated values minus smoothed values for the 8-year period 1979-1986 was (0.00 ± 1.73) ppm, and for 1987-1994 was -(0.07 ± 1.66) ppm (Figure 6d). Similarly, the reconstructed records for the Italian Meteorological Service site at Mt. Cimone are shown in Figure 7. The mean difference of extrapolated values minus smoothed values for 1979-1986 was (0.46 ± 1.28) ppm and for 1987-1994 was -(0.45 ± 1.13) ppm (Figure 7d).

A difference climatology as described by Masarie and Tans is a unique signature that highlights differences between measurements at an individual site and measurements at marine boundary layer sites nearby in latitude. To better understand the information contained in the difference climatology, we have begun looking more closely at the components that make up the difference. A difference record is constructed from the smooth curve fitted to individual site data minus the MBL latitude reference construct at the latitude of the site. The difference climatology is described by a function that approximates the average seasonal pattern and offset from zero of the difference record. The average seasonal cycle pattern described by the difference climatology is a linear combination of the seasonal cycle described by the latitude reference and the seasonal cycle of the smooth curve. In Figure 8 we examine the components that compose the average seasonal cycle pattern described by the difference climatology. The average seasonal cycle at SCH combined with the offset component of the difference climatology is shown as the solid curve, the detrended average seasonal cycle of the MBL reference constructed for the latitude of SCH is shown as the dashed curve, and the average seasonal pattern of the difference
climatology (e.g., the difference of the above two curves) is shown as the dashed-dotted curve. The amplitude, phasing, and shape of the average seasonal cycle of the latitude reference construct is representative of large well-mixed air masses sampled at marine boundary layer sites nearby in latitude to SCH. In contrast the average seasonal cycle at SCH defined by the smooth curve, reflects the station's proximity to regional sources and sinks. For example, the onset of the summer drawdown at SCH begins earlier than the drawdown of the MBL construct, perhaps signalling changes in regional fossil fuel consumption. The broadening of the trough in the summer at SCH is probably due to the interaction of regional photosynthetic uptake and respiration. Similar Figures (9 and 10) are shown for the Japan Meteorological Agency site at Ryori and the CMDL cooperative site at Ulaan Uul, Mongolia. We are hopeful that a more complete analysis using this technique will lead to (1) an improved method for selecting the MBL sites used in the data extension procedure, and (2) a better understanding of the impact regional sources and sinks have on measurement records.

Using the data extension techniques described by Masarie and Tans (1995), CMDL data, and data contributed by many other measurement programs, CMDL is compiling a global CO$_2$ database. The global database is comprised of a set of text files. For each measurement record there are two files. The first file contains the extended measurement record and has been formatted so that potential users can easily exclude extrapolated and interpolated portions of the record if they so desire. The second file contains the suggested relative weights for the measurements (based on the density of the data, the "scatter" in the data, and the length of the measurement period) and for the extrapolated and interpolated values. The emerging database is a cooperative effort by the many international groups making high-quality CO$_2$ measurements and should be acknowledged in the literature as such. Database documentation will encourage proper recognition by including a list of participating investigators and programs. It is likely that the list of investigators will be large and cumbersome to reference; at the recommendation of the participants of the CO$_2$ expert meeting, an acronym or phrase should be associated with the list so that in some instances only the acronym need be referenced. We propose that the phrase "Cooperative Atmospheric Data Integration Project - Carbon Dioxide" (CADIP-CO$_2$) be used to reference the global database and its contributors. In the literature we suggest authors cite the database as [CADIP-CO$_2$, 1996] and in the list of references as:

\[
\text{CADIP-CO$_2$: Cooperative Atmospheric Data Integration Project - Carbon Dioxide.}
\]
\[
\text{CD-ROM, NOAA/CMDL, Boulder, Colorado. [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/CADIP], 1996.}
\]

This complies with the recommended reference styles of both the American Geophysical Union and the American Meteorological Society. The complete global CO$_2$ database and documentation will be made available upon request to any data contributor. A subset of the database excluding the latest few years will be made available to the scientific community via the NOAA/CMDL FTP file server, Carbon Dioxide Information Analysis Centre (CDIAC), and WMO.

Reference

Figure 4. Comparison of CMDL smoothed and extrapolated values with AES smoothed data from independent sampling programs at ALT [82°27'N, 62°31'W]. (a) Extended CMDL record at ALT containing smoothed (solid circles) and extrapolated values (pluses); (b) Smoothed values from the AES flask sampling program at ALT for 1979 to late-1992; (c) Differences of AES smoothed values (panel b) from CMDL extended record (panel a). CMDL sampling at ALT began in June 1985 as indicated by the vertical dotted line.
Figure 5. Reconstruction of a portion of the CMDL flask sampling record at CBA [55°12'N, 162°43'W]. (a) The CBA record; (b) Reconstruction of the CBA record assuming the measurements begin in 1987. Smoothed values (closed circles) and extrapolated values (pluses) are plotted; (c) Reconstruction of the CBA record assuming the measurements end in 1987. Smoothed values (closed circles) and extrapolated values (pluses) are plotted; (d) Differences of extrapolated values (panels b and c) minus smoothed values (panel a). The vertical dotted line separates the two scenarios.
Figure 6. Same as Figure 5 but for the Umweltbundesamt in situ program at Schaulinsland, Germany [47°55'N, 7°55'E].
Figure 7. Same as Figure 5 but for the Italian Meteorological Service in situ program at Mt. Cimone, Italy [44°11'N, 10°42'E].
Figure 9. Same as Figure 8 but for Japan Meteorological Agency in situ program at Ryori, Japan [38°02'N, 141°50'E].
Figure 10. Same as Figure 8 but for the CMDL flask sampling site at Ulaan Uul, Mongolia [44°27'N, 111°06'E].
7. **NEW AND DEVELOPING MEASUREMENT TECHNIQUES** *(No material submitted.)*

8. **A PLAN FOR GREATLY EXPANDED AIR SAMPLING THROUGH AUTOMATION**

Dr. Pieter Tans presented a plan to expand the present air sampling and analysis capabilities by an order of magnitude at modest cost. (A version of the plan will be published in *Global Change Biology*). The reasoning is as follows. There are still several alternative possible explanations for the observed low growth rate during 1992-1993 of CO₂, during 1992 of CH₄, and the decrease in CO during that same time. Likewise, earlier "anomalies" in growth rates have not been explained. Presently the atmosphere is being undersampled so desperately that the chances are very slim for us to determine convincingly which of the many hypotheses advanced as explanations may be true. On the other hand, the magnitude of the global interannual variability in the net uptake of CO₂ by natural systems is so large that the variations can be expected to be coherent over very large regions, something like the scale of a continent. The largest problem in characterizing the current operation of the global carbon cycle is how to scale up from flux measurements on small spatial and/or temporal scales to the globe. Measurements on intermediate scales are almost completely missing.

The plan could be characterized as "minimized brute force" sampling over a limited area, e.g., of the North American continent. We know from experience that air samples from the continental boundary layer are very hard to interpret (except from desert areas), and the plan proposes flask sampling from inexpensive aircraft to obtain weekly or twice-weekly vertical profiles of the mixing ratios at about 50 sites. The observed high-frequency variations of the mixing ratios at existing sites are studied to estimate the temporal and spatial sampling frequency required in order to attain a certain level of precision for monthly means. The precision level should be sufficient to enable an assessment of monthly mean carbon fluxes on a spatial scale of a million km² and how these fluxes respond to variations of environmental forcing.

No new technology needs to be developed. The plan is based on the expanded use of existing "suitcase" sampling units with multiple sampling flasks (currently 20). The technology has been developed by Doug Guenther of CMDL and has been used successfully on Cessna aircraft for several years. The same units have been supplied to both CSIRO and the National Institute of Water and Atmospheric Research (NIWA) as well. The sampling event can be triggered either by pressure, time, or position via Ground Positional Satellite (GPS). The analysis is completely automated. The suitcase is handled as a unit; the individual flasks are never removed from the unit. Obviously, the same technology could be introduced into a part of the current surface sampling network as well.

9. **DATA REPORTING**

9.1 **CDIAC Data Management Policies and Activities - Tom Boden**

At this meeting, participants discussed and clarified several procedures adopted in 1990 at the Sixth WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, held at Lake Arrowhead, California, for the submission and distribution of data to the WMO World Data Centre for Greenhouse Gases (WDCGG) and Carbon Dioxide Information Analysis Centre (CDIAC). The procedures, topics considered, and the resolutions were as follows:

- According to a previous recommendation, data are to be submitted no less than once a year and ideally no later than 1 year after the end of a calendar year. This schedule has not always been met due to the complexities of the measurements and the data processing requirements; however, the 1995 participants recommended that this schedule continue to be the target deadline for data submission.

- At previous meetings, participants agreed that data of the highest resolution are to be submitted to the data centers from each site, along with summary statistics such as (selected) daily and monthly means. It was also agreed that isotopic data, if available, should be submitted along with meteorological data. Many groups are only sending monthly and annual summary statistics to the WDCGG and CDIAC. Meteorological and isotopic data are essential to better understanding the atmospheric CO₂ mixing ratio records and global carbon cycle. After some discussion, all groups were urged to send the data centers high-resolution data, the accompanying meteorological, and the isotopic records.

- A question was raised about where groups send their data (i.e., to the WDCGG, CDIAC, or both). Responses varied. Some groups send their data only to CDIAC believing CDIAC passes along data to the WDCGG after conducting preliminary quality assurance checks. CDIAC does transfer
data to the WDCGG but often not until the data are checked and fully documented. Similarly, WDCGG typically does not send data to CDIAC until their CD-ROM sets are completed. Participants agreed that groups should send data to both centers in whatever format is convenient for the measurement group. In addition, the participants urged greater communication between WDCGG and CDIAC, and it was suggested that CDIAC staff provide brief reports on their WWW home page to indicate the status of data sets being processed by the center. Issues of data center collaboration will be further addressed at a WMO-sponsored meeting in Asheville, North Carolina, in December 1995.

(4) According to previous recommendations, the WDCGG and CDIAC would provide "an annual listing of available data including the names of the providers of each data set, as well as a list of data requesters." CDIAC asked for a clarification of this recommendation, and after discussion it was decided the data centers did not have to provide such lists. As a service, however, WDCGG and CDIAC will continue to periodically provide measurement groups with a list of the individual data requestors.

(5) CDIAC asked what forms of data documentation the measurement groups would prefer to have available. For example, would they prefer published hard copy data documents and/or machine-readable descriptive files, each containing all the information previously agreed as necessary to fully document atmospheric CO₂ mixing ratios and atmospheric CO₂-related measurements. Responses varied, so it was agreed that CDIAC would try to accommodate the preferences of each measurement group. Summary statistics will continue to be published in the WMO WDCGG Data Report series and in the CDIAC Trends series.

The question was asked whether CDIAC would continue the time series compiled by G. Marland and CDIAC that offers global, regional, and national CO₂ emission estimates from fossil fuel burning and cement production on an annual basis. T. Boden views this as a core project for CDIAC and assured the participants that the work would continue as long as G. Marland has interest in the work. T. Boden described recent developments in the CO₂ emissions database, including: (1) Efforts to extend the global CO₂ emission record back to 1751 through the use of energy data published by Etemad et al. (1991); (2) Completion and availability of a 1° × 1° gridded CO₂ emission database. A 1° × 1° gridded population database was used to distribute the national CO₂ emission estimates within grid cells; (3) Efforts to compile regional δ¹³C signatures on a decadal scale from 1950-1990 using energy data published by the United Nations; (4) Results from detailed reviews of the carbon coefficients used in the Marland and Rotty (1984) methodology for solid, liquid, and gas fuels; (5) Plans to review and benefit from CO₂ emission inventories compiled by signatory countries of the United Nations Framework Convention on Climate Change; (6) Efforts to quantify national emissions of CO₂ from fuels used for non-energy purposes (e.g., asphalt); and (7) Plans to conduct detailed comparisons of the two major energy statistics databases used in CO₂ emission calculations, namely, the United Nations Energy Statistics Database and the World Energy Statistics and Balances Database compiled by the International Energy Agency’s Organization for Economic Cooperation and Development.

References


9.2 The World Data Centre for Greenhouse Gases (WDCGG) - Kazuto Suda

In the framework of the Global Atmosphere Watch (GAW) program, WMO established the World Data Centre for Greenhouse Gases (WDCGG) at the Japan Meteorological Agency (JMA) in Tokyo in October 1990. Its major functions are to collect data of the concentrations on greenhouse gases and other related gases except ozone from all parts of the world, to manage and develop a global database, to disseminate the data and analyzed results by publications and other means, and to exchange information with relevant organizations and institutes.
The functions of the WDCGG are as follows:

- Collection of data on the concentrations of greenhouse gases, such as carbon dioxide (CO₂), chlorofluorocarbons (CFCs), methane (CH₄), nitrous oxide (N₂O) and other related gases (carbon monoxide (CO), nitrogen oxides (NOₓ), sulfur dioxide (SO₂), etc.).
- Quality control of the collected data. Questionable data are sent back to the originators for confirmation or revision.
- Management of a database for the collected data.
- Processing and analysis of the collected data.
- Periodical publication of the Data Report, Data Catalog, and Data Summary.
- Distribution of the collected data on appropriate media, especially on electromagnetic media including a floppy diskette and CD-ROM.
- Information exchange with observation stations and related institutes.
- Coordination on international intercomparison of equipment for greenhouse gas measurement.

Data Collection, Processing, and Distribution

The WDCGG collects data of greenhouse gases and other related gases as well as station reports describing the method of measurement, circumstances of the site, and observation programs. The collected data of hourly, daily, monthly, and event values are processed into a database after quality control with statistical methods.

Table 4 lists the number of stations that submitted their station reports (upper part) and observation data of greenhouse gases (lower part). The station reports contain information on the date of commencement of the observation, a short description of the circumstances of the station, the instruments used for measurement and the procedures for calibration and data selection, which are all essential for using the observation data.

In order to reject the questionable data from the database, quality control is applied to all the submitted data. The quality control process includes extraction of deficient data by applying a statistical procession to the data. After the quality control, the questionable data are sent back to the original authors for confirmation. The revised data are restored in the database on the WDCGG.

The WDCGG distributes the collected data in printed media and on floppy diskettes. In addition, the WDCGG is preparing for the distribution of the data via Internet for the availability of the users by the end of 1995.
Table 4. Number of Stations Reporting Data as of May 1995

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</table>

The regions mentioned previously are designated by WMO: I-Africa; II-Asia, III-South America; IV-North America, V-Southwest Pacific; VI-Europe; Ant.-Antarctica; Ship-shipboard observations; and Air-airborne observations.

*The total number of countries and territories reporting data without duplicating the ones that makes observation in more than one region.

†A considerable number of stations belong to the NOAA CMDL observation network.

Publications

The collected data are arranged into the Data Report and published every 6 months. The daily, monthly, and annual data are listed in the report with some basic information including the names of the station and the authority that implements the observation, the calibration scale, the observation interval and the instrument. The Data Report was published in October 1992, October 1993, March 1994, and October 1994 and was distributed to the members of WMO, the contributors of the data and other relevant institutions. The Data Reports are available on floppy diskettes or other appropriate electromagnetic media as well as on CD-ROM.

The Data Catalog contains information on the observation stations including the location, circumstances, observation programs, and the instrument used for measurement. The first issue of the Data Catalog was published in December 1993.

The Data Summary covers the analysis and assessment of the concentrations of greenhouse gases including their global and regional distributions and trends. The first issue of the Data Summary was published in 1995.

The WDCGG CD-ROM contains the daily, monthly, and annual data of the concentrations of greenhouse gases that are distributed by the Data Report. A sample issue of the WDCGG CD-ROM was published in March 1994 and the first issue was published in 1995.

Analysis of Global Distribution of Greenhouse Gases

The WDCGG makes analyses of the past and present conditions of greenhouse gases based on the data collected from all parts of the world.
Figure 11 demonstrates the concentrations of CO₂ averaged over latitudinal zones of 20 degrees for 1983-1993. For all latitudinal zones, the concentrations increase with time. In the Northern Hemisphere, seasonalities are seen on the variations, with the amplitude being larger toward the northermmost latitudinal zone. In the Southern Hemisphere, the seasonal variation is smaller than in the Northern Hemisphere. The concentrations are highest in the northermmost latitudinal zones.

Figure 12 shows the increase rates of the concentrations of CO₂ in different latitudinal zones. It reveals that the increase rates were highest in 1987 or 1988 in all latitudes and that they were very high, particularly, in high latitudes in the Northern Hemisphere.

From these results, the following points might be concluded:

- The concentrations of CO₂ are highest in the middle and high latitudes of the Northern Hemisphere, where the industries are very active.
- The seasonal variation of the concentrations is conspicuous in the middle latitudes of the Northern Hemisphere where the difference in concentration is as much as 10-15 ppmv.
- The Northern Hemisphere is a major source of anthropogenic CO₂ from such activities as the consumption of fossil fuels and, at the same time, a major sink of CO₂ through biological processes on land.
- The concentrations of CO₂ in the Southern Hemisphere increase as if they follow the concentrations in the Northern Hemisphere. This suggests that CO₂ is transported from the Northern Hemisphere to the Southern Hemisphere and that the general atmospheric circulation can play an important role in this transportation.

10. PARTICIPATION IN THE INTERNATIONAL GLOBAL ATMOSPHERIC CHEMISTRY (IGAC) PROGRAMME

Three representatives from IGAC attended the meeting: Dr. Ron Prinn (Chairman, IGAC Scientific Steering Committee), Dr. Alex Pszenny (IGAC Core Project Officer), and Dr. Elliott Atlas (GLOCHEM Convener). The structure, goals, and strategies of IGAC, and the participation of the CO₂ experts group in IGAC were reviewed. The limited activity to date of the CO₂ research community within IGAC was acknowledged, but there was general agreement that carbon cycle research should continue to be an IGAC activity.

There was a consensus that the carbon cycle activity within IGAC should be broad and include not only atmospheric measurements, but should include or have strong linkages to biologists, ecologists, flux measurements, oceanographers, and modelers. The coordinating committee for this activity should definitely include representatives from these fields. In addition, the scope of measurements should be broadened to include CO and CH₄, and possibly N₂O, SF₆, ²²²Rn, etc.

At the same time, it was strongly felt that meetings of CO₂ experts, under WMO auspices, should continue independently from IGAC. These meetings are highly focused on measurements, measurement techniques and calibration issues, and have been extremely valuable to the international CO₂ measurement community. Since most of the laboratories measuring CO₂ are now measuring CH₄ and CO as well, future experts meetings will probably include these species.

In order to succeed, the IGAC carbon cycle activity needs enthusiastic leadership, goals, plans, and an implementation strategy. Several of the CO₂ experts expressed an interest in establishing a committee to formulate a revitalized activity plan. It was agreed that areas of carbon cycle research other than atmospheric measurements (e.g., biology, ecology, and modeling) need to be represented on this committee. It was not clear how to select committee members from outside the CO₂ experts group.

Subsequent to this meeting, Drs. Neil Trivett and Philippe Ciais agreed to be the convenors of the carbon cycle IGAC activity.

11. GAW UPDATE

Dr. John M. Miller, Chief of the WMO Environment Division, joined meeting in the latter half of the proceedings. He extended the best wishes of the WMO Secretary-General, Prof. G.O.P. Obasi, to the group. Dr. Miller gave a brief update of the GAW programme to the group that included the following.
Figure 12: Latitudinal growth rate for CO2
The issues of climate warming, stratospheric ozone depletion, chemical changes in the atmosphere, and transboundary pollution are likely to be with us for a long time: the causes will persist over the coming decade and more. Social awareness and demands for remedial and preventive actions will continue to increase.

The United Nations Conference on Environment and Development (UNCED-92) recognized that an essential condition to attain sustainable development was the ability to monitor and predict both the short and long-term evolution of the Earth's atmospheric environment and impacts on the total climate system. The GAW, established by Cg-XI as a major priority programme to monitor and assess the changing chemical composition and related physical characteristics of the atmosphere is a key contribution by WMO to the environmental issue in the post-UNCED period.

Some of the most important long-term objectives of GAW can be described as follows:

- To develop a functional observing system and provide reliable, spatially representative, long-term monitoring at regional and global background levels: partially with real-time capabilities for use in response to environmental emergencies.

- To contribute to the evaluation and application of atmospheric composition information and to facilitate the worldwide exchange of scientific information;

- To provide scientific researchers, modellers, policy makers and compliance officials with the needed information to address issues of atmospheric change in order to document, detect and understand such changes;

- To serve as an early warning and forecasting system for the composition of the atmosphere and for impacts on climate. UV-B radiation, the ozone layer, the integrated oxidation rates of the atmosphere and terrestrial and marine ecosystems;

- To engage the national weather services as WMO members in environmental issues by contributing to the development and enhancement of their scientific and technical capabilities in cooperation with specialized research institutions;

- To facilitate the training of monitoring station personnel and the transfer of technology in measurement techniques, data analysis and applications.

From its other programme, WMO has a long tradition of building operational observing networks that include an exchange of data and products in the framework of a worldwide community. GAW, as a contributing component of the Global Climate Observing System (GCOS) must deal with a wide variety of global issues different from all classical meteorological elements. Observations of chemical composition require a more sophisticated level of measuring techniques and quality awareness.

The scientific links between climate and atmospheric composition and the status of the current atmospheric change issues and future requirements for atmospheric composition measurements are important. The greatest influence of atmospheric chemistry on climate is associated with the ozone changes in the troposphere and the stratosphere. Atmospheric ozone changes will induce significant perturbation in the vertical composition and temperature profile of the atmosphere; they will also directly influence the UV-B radiation reaching the earth's surface. The roles of the major greenhouse gases, aerosols, ozone precursor gases and major atmospheric processes can be defined, as well as the influence of greenhouse gases and aerosols on atmospheric chemistry.

As a consequence of these new challenges, there must be a substantial collaboration between WMO, its technical commissions, international organizations and programmes - particularly its International Global Atmospheric Chemistry Programme (IGAC/IGPB) - as well as a large number of IAMAP activities on atmospheric chemistry and climate. The GAW also must consider the different perspectives and prerequisites of both highly industrialized and developing countries, by organization of appropriate training and dissemination of technical knowledge.

12. CLOSURE OF THE MEETING
LIST OF PARTICIPANTS

WMO Meeting of Experts on CO\textsubscript{2} Concentration and Isotopic Measurement Techniques
Boulder, Colorado, July 6-11, 1995

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PREVIOUS MEETINGS OF THE WMO EXPERTS IN CO₂ MEASUREMENT

The first meeting of the Experts on Carbon Dioxide Measurement was held in La Jolla, California, and sponsored by the World Meteorological Organization (WMO). WMO has sponsored all subsequent meetings, including the seventh in Rome. These meetings have provided a quasi-regular communication between all national CO₂ monitoring programmes, which has ensured that CO₂ is monitored with the best current techniques available, that advantage is taken of new methodologies as they become available, and that all programmes are intercalibrated by accepted international standards.

The following is a list of meetings in this series:

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<tr>
<th>LOCATION</th>
<th>DATE</th>
<th>PUBLICATION</th>
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<tr>
<td>1. La Jolla, California</td>
<td>March 3-7, 1975</td>
<td>4*</td>
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<tr>
<td>2. Geneva, Switzerland</td>
<td>September 8-11, 1981</td>
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<tr>
<td>3. Lake Arrowhead, California</td>
<td>November 4-8, 1985</td>
<td>39†</td>
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<td>4. Gaithersburg, Maryland</td>
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<td>5. Hilo, Hawaii</td>
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<td>6. Lake Arrowhead, California</td>
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<td>7. Rome Italy</td>
<td>September 7-10, 1993</td>
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<tr>
<td>8. Boulder, Colorado</td>
<td>July 6-11, 1995</td>
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* Number of reports in the WMO Executive Panel-I/Document 5, 13.3.1975.
† Number of reports in the WMO Environmental Pollution and Research Programme/GAW Report Series.
MEETING PROGRAMME

Agenda for WMO Meeting of Experts on CO₂ Concentration and Isotopic Measurement Techniques

Thursday, July 6

Morning session
09:00-12:00
Opening of meeting (David Hofmann)
Selection of chairman, rapporteurs
Reports of national programs (recent CO₂, isotopes, auxiliary measurements)

Thursday, July 6

Afternoon session
13:00-17:00
Reports of national programs (recent CO₂, isotopes, auxiliary measurements)

Friday, July 7

Morning session
08:30-12:00
Reports on status of WMO primary manometric calibrations scale (Scripps, CMDL)
Recent calibration problems experienced by several participants (Canada, Italy, others?)
Future of WMO calibration scale (Tans)
Isotopic calibrations, intercomparisons (Levin)

Friday, July 7

Afternoon session
13:00-17:00
Finalize recommended protocol for CO2 background measurement (Trivett’s document)

Monday, July 10

Morning session
08:30-12:00
A global carbon observing system (Tans)
New GAW stations (Miller)
Creation of a global database (Masarie)

Monday, July 10

Afternoon session
13:00-17:00
New developments in measurement and sampling techniques (Steele)
Drafting of WMO report of this meeting

Tuesday, July 11

Morning session
08:30-13:00
Participation in IGAC
Interaction with IPCC
Data centers, data distribution, archival (WDCGG, CDIAC)

Tuesday, July 11

Afternoon session
13:00-17:00
Unfinished items of the above list
Discussion and approval of WMO report of this meeting
Closure of meeting
### CO₂ MEASUREMENT SITES

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Abbreviations

AES Atmospheric Environment Service, Toronto, Canada
AWI Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany
BAS British Antarctic Survey, Great Britain
BBS Bermuda Biological Station
CFR Centre des Faibles Radioactivités, Gif sur Yvette, France
CMS Chinese Meteorological Administration
CNR Consiglio Nazionale delle Ricerche, Roma, Italy
CSIRO Commonwealth Scientific and Industrial Research Organization, Division of Atmospheric Research, Aspendale, Australia
ECN Netherlands Energy Research Foundation, Petten, The Netherlands
ENEA New Technologies, Energy and Environment Agency, Italy
ENEL/CRTN Italian Electric Energy Company
FAU Fraunhofer Institute für Atmosphärische Umweltforschung Garmisch Partenkirchen, Germany
GAW Global Atmosphere Watch
KMRI Korean Meteorological Research Institute, Korea
KNMI Royal Netherlands Meteorological Institute, The Netherlands
KNUE Korea National University of Education, Korea
IAP Institute for Atmospheric Physics, Budapest, Hungary
IMS Italian Meteorological Service, Roma, Italy
INM Instituto Nacional de Meteorologia, Madrid, Spain
ISC International Science Consultants, Ringwood, United Kingdom
IUP-HD Institute für Umweltphysik, University of Heidelberg, Germany
JMA Japan Meteorological Agency, Tokyo, Japan
MGO Main Geophysical Observatory, St. Petersburg, Russia
MISU/NILU Department of Meteorology, Stockholm University/Norwegian Institute for Air Research
NIPR National Institute of Polar Research, Japan
NIWA National Institute of Water and Atmospheric Research, New Zealand
NMI Norwegian Meteorological Institute, Norway
NOAA National Oceanic and Atmospheric Administration, USA
NSF National Science Foundation, USA
OUBA Österreichisches Umweltbundesamt, Wien, Austria
SIO Scripps Institution of Oceanography, La Jolla, California, USA
SNU Seoul National University, Korea
TU Tohoku University, Sendai, Japan
UBA Umweltbundesamt, Berlin, Germany
UCB University of Colorado, Boulder, USA
UCG University College of Galway, Ireland
UU State University Utrecht, Utrecht, The Netherlands
WIS Weizmann Institute of Science, Israel
LABORATORY REPORTS

Annex 5.1:       Canada
Annex 5.2:       China
Annex 5.3:       France
Annex 5.4:       Germany
Annex 5.5:       Hungary
Annex 5.6:       Italy
Annex 5.7:       Japan
Annex 5.8:       Korea
Annex 5.9:       Sweden
Annex 5.10:      USA
ANNEX 5.1: CANADA

AN EVALUATION OF CO₂ FLASK MEASUREMENT PROGRAMS AT ALERT, N.W.T.

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Environment Canada, Atmospheric Environment Service, Toronto, Canada

Introduction

As part of the mandate of the WMO GAW program, in situ and flask measurement programs have been established globally to monitor carbon dioxide and other trace gases such as CH₄, N₂O, and CO₂. Since in situ programs are costly and labor intensive to maintain, a number of agencies maintain flask sampling networks that provide good geographic coverage at a reduced cost. The type of flask and sampling protocol used by each agency varies. There is an urgent need for studies relating the measurements from various independent flask programs. This would enable data sets used in determining the global carbon cycle budget to be merged in a consistent fashion. The Canadian site Alert, which has an in situ CO₂ program maintained by the Atmospheric Environment Service (AES) and CO₂ flask programs maintained by five cooperating agencies, is suitable for such a study. The flask types and sampling protocols used by the cooperating agencies are given in Table 1. A proposal for an extensive interflask comparison is outlined in the main body of this report.

The Canadian CO₂ program started as a flask sampling program in 1969 at Ocean Station Papa (50°N, 130°W). It was a joint effort between C.D. Keeling of the Scripps Institution of Oceanography (SIO) and C.S. Wong of the Institute for Ocean Sciences (IOS). At that time, the two agencies also began a CO₂ intercalibration program. In 1975, AES added two new stations to the program, Alert (82°28'N, 62°30'W) and Sable Island (43°56'N, 60°01'W). In 1978, SIO established a third station at Cape St. James (51°56'N, 131°01'W). This station replaced Ocean Station Papa in 1982. Sampling continued at this site until August 1992 when the weather station was closed as part of a rationalization of the surface observing program. In 1981, the partnership between SIO and IOS ended, and AES and IOS became jointly responsible for the Canadian CO₂ program. Prior to 1988, flasks were analyzed by C.S. Wong of the Marine Carbon Research Centre at IOS. In early 1988, AES took over the analysis of the flasks.

Since 1975, flask samples have been collected at the Canadian baseline sites using evacuated 2-L greased stopcock flasks. This type of flask and the associated sampling protocol presents problems. The grease in the stopcock hardened in cold temperatures making the flask very difficult to open. The evacuated technique is subject to contamination from the operator and from leakage through the greased stopcock when the flask is under vacuum. To improve flask sampling, AES designed a single-valved 2-L flask with Viton O-ring seals. The flask is robust for sampling and the valves are easily opened even in extreme arctic conditions. The stopcock withstands pressurizing which increases the sample volume. These flasks were added to the program in 1989. To further improve sampling, a 2-L double-valved flask with Buna-n O-ring seals was designed and added to the program in April 1992. The double-valve design allows complete flushing of the flask prior to sampling. Flasks can also be pressurized. Samples are conveniently taken indoors, and the sample air is cryogenically or chemically dried, eliminating storage effects resulting from moisture. For a direct comparison, all three flask types are sampled at Alert on a weekly basis.

Using the two new flask designs has greatly improved sampling results in the AES flask network. AES plans to replace the greased flasks with the new flask types. Before merging the data sets, however, a thorough interflask comparison must be carried out so as not to introduce a bias in the historical CO₂ time series. In the following study, the three AES flask programs were evaluated relative to the AES in situ nondispersive infrared (NDIR) program. The independent flask programs of NOAA and SIO were also evaluated relative to both the AES in situ and flask programs. The results from the Commonwealth Scientific and Industrial Research Organization (CSIRO) flask program were not included in this study because the samples are collected using AES flasks; and the Main Geophysical Observatory (MGO), St. Petersburg, flask results were not included because there were not enough data to perform adequate analysis.
Table 1. CO₂ Flask Sampling Programs at Alert, Northwest Territories

<table>
<thead>
<tr>
<th>Agency</th>
<th>Sampling History</th>
<th>Flask Type</th>
<th>Sampling Protocol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Environment Service (AES), Canada</td>
<td>1975 - present (weekly sample)</td>
<td>2-L greased stopcock</td>
<td>Evacuated grab sample</td>
</tr>
<tr>
<td></td>
<td>1992 - present (weekly sample)</td>
<td>2-L single-valve, Viton O-rings</td>
<td>Evacuated grab sample</td>
</tr>
<tr>
<td></td>
<td>1993 - present (weekly sample)</td>
<td>2-L double-valve, Buna-n O-rings</td>
<td>Pressurized flush method</td>
</tr>
<tr>
<td>Commonwealth Scientific &amp; Industrial Research Organ. (CSIRO), Australia</td>
<td>1988 - 1993 (monthly sample)</td>
<td>5-L double-valve, Teflon O-rings</td>
<td>Pressurized flush method</td>
</tr>
<tr>
<td></td>
<td>1993 - present (monthly sample)</td>
<td>AES 2-L single-valve, Viton O-rings</td>
<td>Repeated pressurizing and venting</td>
</tr>
<tr>
<td></td>
<td>1985-1992 (weekly sample)</td>
<td>500-mL double-valve, greased stopcocks</td>
<td>Pressurized flush method</td>
</tr>
<tr>
<td>National Oceanic and Atmospheric Admin. (NOAA), United States</td>
<td>1992 - present (weekly sample)</td>
<td>2.5-L double-valve, Teflon O-rings</td>
<td>Pressurized flush method</td>
</tr>
<tr>
<td></td>
<td>1984 - present (weekly sample)</td>
<td>5-L greased stopcock</td>
<td>Evacuated grab sample</td>
</tr>
<tr>
<td>Scripps Institution of Oceanography (SIO), United States</td>
<td>1992 - present (bi-weekly sample)</td>
<td>2-L stainless steel single valve</td>
<td>Evacuated grab sample</td>
</tr>
<tr>
<td>Main Geophysical Observatory (MGO), Russian Federation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data Analysis

Six-hour averages (ending at 6, 12, 18, and 24 GMT) and the corresponding standard deviations were calculated from the daily 5-minute NDIR CO₂ concentration averages. Six-hour averages were selected for the evaluation to ensure that the flask sampling periods for all flask programs were covered. Flask sampling generally takes an afternoon to complete. The NDIR data were flagged for any irregularities (i.e., a vehicle at the site or adjustments to the analyzer). A median analysis was performed on the standard deviation values of the 6-hour NDIR averages to identify any outliers; the resulting frequency distribution is given in Figure 1. From the median analysis of the 6-hour standard deviations, the upper cutoff value for the outliers was 0.55 ppm. This is the upper quartile plus 1.5 times the interquartile range. Six-hour averages with standard deviations greater than this were deleted. The resulting data set containing the "baseline" 6-hour NDIR values was then compared to the CO₂ concentration values for the flask programs. In each case, the 6-hour NDIR averages were subtracted from the corresponding flask-pair averages. The frequency distributions for the differences between the three AES data sets and the NDIR are given in Figures 2a, 2b, and 2c, and the differences between the NOAA and SIO data sets from the AES NDIR are given in Figures 3a and 3b.

The NOAA Alert CO₂ flask data set consists of flask samples taken using pressurized 500-mL greased stopcock flasks (NOAA_G) up to May 1992 and flask samples taken using pressurized 2.5-L Teflon O-ring flasks (NOAA_T) from May 1992 to present. For this reason, the NOAA data set was subsequently separated into two data sets according to flask type. The same procedure of subtracting the AES NDIR value from the flask value was applied to both NOAA data sets. The frequency distributions of the results of this analysis are given in Figures 4a and 4b. A summary of the above results is presented in Table 2.
6-Hourly NDIR Standard Deviations
For Continuous Alert CO2 Measurements

Data Points
196

Average
0.37 +/- 0.72

Median
0.12, IQR 0.19
Alert CO2 Intercomparison
AES [Greased Flask - NDIR (6 Hr)]

Data Points
156

Average
0.62 +/- 0.82

Median
0.52, IQR 0.64
Alert CO2 Intercomparison
AES [Evac. O-Ring Flask - NDIR (6 Hr)]

Data Points
64

Average
0.38 +/- 0.30

Median
0.29, IQR 0.35
Alert CO2 Intercomparison
AES [Pressurized Flask - NDIR (6 Hr)]

Data Points
33

Average
0.13 +/- 0.23

Median
0.11, IQR 0.29
Figure 3(a)

SIO Flask - AES NDIR (6 Hr Avg)

Data Points: 122
Average: 0.35 +/- 0.48
Median: 0.29, IQR 0.28
Figure 3(b)

NOAA Flask - AES NDIR (6 Hr Avg)

Data Points
140

Average
0.26 +/- 0.32

Median
0.25, IQR 0.40
NOAA_G Flask - AES NDIR (6 Hr Avg)

Data Points
83

Average
0.40 +/- 0.31

Median
0.40, IQR 0.26
Figure 4(b)

NOAA_T Flask - AES NDIR (6 Hr Avg)

Data Points
57

Average
0.05 +/- 0.19

Median
0.06, IQR 0.20
Table 2. Intercomparison of Alert CO₂ In situ and Flask Programs

<table>
<thead>
<tr>
<th>Program</th>
<th>Number of Data Points</th>
<th>(Flask - In situ) Average (ppm)</th>
<th>Median (ppm) (Flask - In situ)</th>
<th>IQR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES greased stopcock</td>
<td>156</td>
<td>0.62 ± 0.82</td>
<td>0.52</td>
<td>0.64</td>
</tr>
<tr>
<td>AES single valve O-ring</td>
<td>64</td>
<td>0.38 ± 0.30</td>
<td>0.29</td>
<td>0.35</td>
</tr>
<tr>
<td>AES double valve O-ring</td>
<td>33</td>
<td>0.13 ± 0.23</td>
<td>0.11</td>
<td>0.29</td>
</tr>
<tr>
<td>SIO greased stopcock</td>
<td>122</td>
<td>0.35 ± 0.48</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>NOAA_Combined</td>
<td>140</td>
<td>0.26 ± 0.32</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>NOAA_Greased</td>
<td>83</td>
<td>0.40 ± 0.31</td>
<td>0.40</td>
<td>0.26</td>
</tr>
<tr>
<td>NOAA_Teflon</td>
<td>57</td>
<td>0.05 ± 0.19</td>
<td>0.06</td>
<td>0.20</td>
</tr>
</tbody>
</table>

As an independent check, the same analysis was carried out on the two NOAA data sets substituting the SIO flask values for the AES in situ values (i.e., NOAA flask - SIO flask). This analysis was also performed for the AES evacuated 2-L greased stopcock flask. The frequency distributions of the results for NOAA are given in Figures 5a and 5b and those for AES are given in Figure 6. The results are summarized in Table 3.

Table 3. Intercomparison of AES and NOAA Flask Programs to SIO Flask Program

<table>
<thead>
<tr>
<th>Program</th>
<th>Number of Data Points</th>
<th>(Flask - SIO) Average (ppm)</th>
<th>Median (ppm) (Flask - SIO)</th>
<th>IQR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES greased stopcock</td>
<td>164</td>
<td>0.30 ± 0.89</td>
<td>0.26</td>
<td>0.53</td>
</tr>
<tr>
<td>NOAA greased</td>
<td>75</td>
<td>0.13 ± 0.25</td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>NOAA Teflon</td>
<td>81</td>
<td>-0.30 ± 0.21</td>
<td>-0.27</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Statistical significance tests were carried out on the flask-AES NDIR results for the three AES and two NOAA flask data sets: the 2-L evacuated greased stopcock flasks [AES-G(156)], the 2-L evacuated Viton O-ring flasks [AES-O(64)], the 2-L pressurized double-valved Buna-n O-ring flasks [AES-P(33)], the 500-mL greased stopcock flasks [NOAA_G(83)], and the 3-L Teflon O-ring flasks [NOAA_T(57)]. (Note: The number inside the brackets denotes the number of data points in each data set.) Student t-tests were performed to determine whether the data sets are significantly different from one another relative to their mean values. The results for the AES flask programs are summarized in Table 4. At the 95% confidence limit (cl) determined using the student's t-test formula,

\[ t_d = \frac{\bar{x}_1 - \bar{x}_2 - (\mu_1 - \mu_2)}{\sqrt{\frac{N_1 s_1^2 + N_2 s_2^2}{N_1 + N_2 - 2} \left( \frac{1}{N_1} + \frac{1}{N_2} \right)}}^{1/2} \]

AES-G(156) was significantly different from AES-P(33), but was not significantly different from AES-O(64). AES-O(64) was significantly different from AES-P(33) and NOAA_G was significantly different from NOAA_T.
Figure 5(a)

NOAA_G Flask - SIO Flask

Data Points
75

Average
0.13 +/- 0.25

Median
0.12, IQR 0.26
Figure 5(b)  

NOAA_T Flask - SIO Flask

Data Points: 81
Average: -0.30 ± 0.21
Median: -0.27, IQR 0.22

Percentage

50 40 30 20 10 0

Difference (ppm)

< -1 -0.75 -0.25 0 0.25 0.75 1.25 1.75 2 2.5 3 3.7
Figure 6

AES-G Flask - SIO Flask

Data Points
164

Average
0.30 +/- 0.89

Median
0.26, IQR 0.53
Table 4. T-Test Results for Alert AES CO₂ Flask Programs

<table>
<thead>
<tr>
<th></th>
<th>AES-G(156)</th>
<th>AES-O(64)</th>
<th>AES-P(33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES-G(156)</td>
<td></td>
<td>NSD</td>
<td>SD</td>
</tr>
<tr>
<td>AES-O(64)</td>
<td>NSD</td>
<td></td>
<td>SD</td>
</tr>
<tr>
<td>AES-P(33)</td>
<td>SD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SD = Significantly Different
NSD = Not Significantly Different

The greased stopcock flask results show a high degree of variability. To test if the variability is a result of operator technique, the AES-G(156) data set was broken into subsets according to operator. The average, standard deviation and median were calculated for these subsets and are given in Table 5. The calculations were only performed for subsets with more than 10 data points. The data subsets were tested for significance against the AES-G(156) data set. The averages of the subsets vary from 0.15 to 1.31 ppm. T-test results at the 95% CI indicate that three of the four data sets are not significantly different from the AES-G(156) data set.

Table 5. Analysis Results of AES Greased Stopcock Flask Data For Individual Operators

<table>
<thead>
<tr>
<th>Operator</th>
<th>Number of Data Points</th>
<th>Average (ppm)</th>
<th>Standard (ppm)</th>
<th>Median (ppm)</th>
<th>T-Test vs. AES-G(156)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Flask-BND6)</td>
<td>(Flask BND6)</td>
<td>(Flask BND6)</td>
<td></td>
</tr>
<tr>
<td>V. Chorney</td>
<td>71</td>
<td>0.48</td>
<td>0.61</td>
<td>0.32</td>
<td>NSD</td>
</tr>
<tr>
<td>P. Chornik</td>
<td>13</td>
<td>0.15</td>
<td>1.21</td>
<td>0.38</td>
<td>NSD</td>
</tr>
<tr>
<td>M. Marsel</td>
<td>16</td>
<td>0.90</td>
<td>0.51</td>
<td>0.87</td>
<td>NSD</td>
</tr>
<tr>
<td>L. Oatway</td>
<td>17</td>
<td>1.31</td>
<td>1.17</td>
<td>0.76</td>
<td>SD</td>
</tr>
</tbody>
</table>

Discussion

The results of the analysis in which the AES NDIR concentrations are compared to the corresponding flask pair averages of the three AES flask programs (Figures 2a, 2b, and 2c) show similar results. In each case, the median and average value of the results are greater than zero, and the median value is lower than the average value. This indicates that the frequency distributions are not normally distributed but are skewed towards higher values. It is not possible to conclusively determine from this analysis why the AES flask values are higher than the NDIR values, nor is it possible to determine if the NOAA and SIO differences relative to the AES NDIR are due to scale differences.

Evaluating the three AES programs (which are on the same scale as the NDIR measurements), the evacuated greased stopcock flasks (Figure 2a) show the largest range of flask-NDIR differences and the largest number of positive outliers. The pressurized double-valve Buna-n O-ring flasks produce results closest to the NDIR measurements with the lowest variability. The findings are similar for the SIO and NOAA analyses, although conclusions can only be based on data distributions and not on absolute differences because of possible laboratory scale discrepancies. The results for the SIO evacuated greased stopcock flasks show high variability, although the results are less variable than the AES evacuated greased stopcock flasks. The NOAA pressurized Teflon O-ring flasks show low variability and flask-AES NDIR differences significantly lower than for the NOAA pressurized greased stopcock flasks. There are a number of possible explanations for these findings:

- Evacuated flasks are more easily contaminated
- Small volume flasks are more subject to contamination or storage problems
- Flushing flasks improves sampling results
- Drying air reduces storage problems in O-ring flasks
- Sampling from a manifold or line reduces possible operator contamination
The differences between the flask and the NDIR values could be a result of actual concentration differences between the air sampled with flasks and the NDIR analyzer. The flask sampling interval for an evacuated grab sample is only about 20 seconds and approximately 5 minutes for a pressurized sample. This could be a problem when comparing to six-hour NDIR averages. If the differences were related to this problem, however, one would expect to see an equal distribution of differences about zero.

T-test results (Table 4) show that the two AES evacuated flask data sets are not significantly different although both are significantly different from the AES pressurized flask data set. These results suggest that the two evacuated flask data sets can be merged; however, further studies are necessary before the pressurized data set can be successfully merged with either data set. The two pressurized NOAA flask types (greased stopcock and Teflon O-ring) also produce results that are internally inconsistent relative to the AES NDIR program (Figures 4a and 4b) and relative to the SIO flask program (Figures 5a and 5b). There is a 0.35 ppm difference between the two different NOAA flask types relative to the AES NDIR and a 0.43 ppm difference relative to the SIO flask program. T-test results show the two NOAA data sets, NOAA_G and NOAA_T are significantly different from one another. Again, this illustrates the difficulty of merging data sets collected using two different flask types.

Conclusion

Alert CO₂ flask measurements from five different flask programs were compared to in situ nondispersive infrared measurements of CO₂. Three were AES flask measurement programs and the other two were programs from independent agencies (NOAA and SIO). At this time, it is unclear whether the differences of the NOAA and SIO data sets relative to the NDIR measurements are related to laboratory scale differences. The results from all the flask programs are higher relative to the NDIR measurement program. It is not clear which factors (sampling protocol, contamination, storage, and humidity, etc.) are responsible for the positive differences relative to the NDIR. An evaluation of the AES flask measurement programs clearly shows that the AES evacuated greased stopcock flasks are subject to the most sampling problems, and the AES pressurized double-valve flasks are subject to the fewest problems. The NOAA and SIO flasks cannot be evaluated definitively because of laboratory scale discrepancies. A previous CO₂ standards intercomparison between AES and NOAA indicates that the scale difference between the two laboratories is between 0.1 - 0.2 ppm. This being the case, the results from the pressurized NOAA Teflon O-ring flasks would be comparable to those of the pressurized AES flasks. Further studies relating the measurements from different flask types must be undertaken before data sets from different flask types can be merged successfully within individual laboratories and between cooperating agencies. An extensive interflask and interlaboratory comparison, as outlined in the main body of this report, would provide such necessary data.
ANNEX 5.2: CHINA
REPORT OF NATIONAL CO₂ PROGRAMS
CHINESE CARBON DIOXIDE MONITORING

Wen Yupu, Chinese Academy of Meteorological Sciences
Zhang Xiaochun, Chinese GAW Baseline Observatory

Introduction

Routine atmospheric CO₂ concentration measurements in China have been performed since November 1994 at Mt. Waliguan, a new permanent station of the WMO GAW network. Various standard gases are calibrated by NOAA CMDL. Before then, temporary observations of CO₂ were made at Mt. Waliguan with a Siemens Ultramat-3 NDIR analyzer as part of the feasibility study of the baseline station. NOAA CMDL has had a flask sampling program at Mt. Waliguan since 1991.

In Situ Measurements

The Chinese GAW Baseline Observatory (CGAWBO) is located on Mt. Waliguan, Qinghai Province, China (36.28°N, 100.9°E; 3810 m asl). The plateau is covered with thin grass.

Measurement Instrument and Technique

Continuous CO₂ concentration measurements are made at CGAWBO using a Li-Cor 6251 NDIR and calibration gases provided by WMO. The sampled air is dried using a water trap at -52°C. The air intake is 80 m above the ground. The flow rate of the air sample is about 100 cc min⁻¹, and the zero gas flow rate is about 10 cc min⁻¹. Daily concentrations are calculated on the basis of hourly mean values. The raw data collected at Mt. Waliguan are stored on floppy disks. The data disks are returned to Beijing for further data processing.

Calibration Procedure

The working standards (W1 and W2) and the target gas are calibrated once a week using five station standards. The Li-Cor is calibrated with W1 and W2, respectively, once an hour in order to correct for the NDIR drift. The target gas is measured once a day as the air sample for quality control. The station standard gases are sent to the CAMS (Beijing) for calibrations with the tertiary standard gases twice per year. All of the standards were prepared and calibrated by NOAA CMDL.

The in situ calibrations show that the Li-Cor has a very linear output. The correlation coefficients were all above 0.999. Its repeatability and precision meet the requirements for background monitoring of CO₂.

Data Selection Method

The raw daily data are selected based on hourly mean values. The hourly mean values with standard deviations above 0.3 ppm are removed. Individual abnormal hourly mean values with smaller standard deviations are also removed. The retained data constitute about 90% of the total data (Figure 1).
Preliminary Results of CO₂ Concentration Measurements

The data show the annual difference of CO₂ concentration at Mt. Waliguan between 1992 and 1993 to be about 0.8 ppmv per year. However, the annual growth rate of CO₂ at Mt. Waliguan accelerates suddenly in 1994 to more than 2 ppmv per year. The summary of the results of routine CO₂ measurements at Mt. Waliguan from November 1994 is shown in Figure 2. According to the polynomial curve fit, the daily mean value maximum is about 364.7 ppm and occurred in late April or early May 1995. Selected monthly mean values are shown in Figure 3. The previous data (1991-1994) also gave the same result. The phase of the CO₂ curve is advanced a few weeks compared with MLO. Since November 1994, the routine data have been submitted to WDCGG.

Acknowledgments

The Chinese CO₂ monitoring program is supported by WMO. We express our thanks to them. We thank Kirk Thoning, Pieter Tans, Conglong Zhao, and Duane Kitizis of NOAA CMDL for providing technical assistance for the Li-Cor NDIR system of CGAWBO. We also thank J. Peterson, B. Mendonca, and T. Conway for their helpful suggestions on the programme.
Figure 2

Selected Hourly Averages of CO2 Conc.
Nov. 1994—May 1995 (CGAWBO)

Selected by:
W2 > W1 x 6
CO2 S.D. < 0.3 ppm
ANNEX 5.3: FRANCE

REPORT OF CENTRE DES FAIBLES RADIOACTIVITES

A. Gaudry, P. Ciais, V. Kazan, and P. Monfray
Laboratoire de Modelisation du Climat et de l'Environnement (France)

Centre des Faibles Radioactivités-Laboratoire de Modelisation du Climat et de l'Environnement (CFR-LMCE) maintains two continuous atmospheric CO₂ monitoring stations: (1.) Amsterdam Island, Indian Ocean (37° 46'S, 77° 31'E) and (2.) Mace Head Station, Ireland (53° 20'N, 09° 54'W), in cooperation with University College of Galway (Ireland) and International Science Consultants (United Kingdom).

Amsterdam Island

Atmospheric CO₂ has been recorded at Amsterdam Island since 1980. The long-term trend and the rate of increase of CO₂ appear in Figures 1 and 2, respectively. A slowing down of the rate of increase was observed in 1990-1992, possibly in response to sinks operating in the Northern Hemisphere (NH). An enhanced NH uptake may have been caused by the cooling following the eruption of Mt. Pinatubo volcano in June 1991. In 1994-1995 the growth rate is again close to 1.5 to 1.6 ppm year⁻¹ as in the 1980s.

Mace Head Station

Atmospheric CO₂ has been continuously monitored at Mace Head station since July 1992. Background conditions correspond to wind directions between 200° and 300° and wind velocities higher than 4 ms⁻¹. Additionally, we delete discontinuous data that sometimes correspond to air masses under local influence.

Concentrations are expressed in the 1993 WMO mole fraction scale in air.

Figure 3A shows the observed CO₂ variations for background conditions. Figure 3B plots the smoothed seasonal cycle obtained by filtering out the variability of the CO₂ signal on time scales shorter than 80 days. The average rate of increase derived from this record is close to 1.8 ppm year⁻¹.

The peak-to-peak amplitude of the smoothed curve is 14.9 ppm with a minimum in August and a maximum in April.

Figure 3C plots the short-term variations (residuals) obtained by subtracting the smooth curve in Figure 3B from the original data in Figure 3A. These variations are linked to fast advection of air masses from source or sink regions of the Northern Hemisphere. Their magnitude ranges from -6 to +8 ppm.

NOAA CMDL maintains a separate flask sampling program at Mace Head. This provides the opportunity to compare the CO₂ data of both laboratories. For each comparison, CFR data are hourly mean concentrations.

By taking all data available, the average difference between NOAA data and CFR data (NOAA-CFR) is -0.32 ppm with a large standard deviation of 1.37 ppm. By taking only samples corresponding to the background conditions as defined by CFR, the results are significantly improved (Figure 4). Then the average difference is 0.03 ppm with a standard deviation of 0.37 ppm (53 values). This tends to show that some flasks reflect a greater concentration variability when they are sampled out of background conditions.
Carbon Isotope Monitoring at Mace Head Station

Carbon isotopes have been measured at CFR-LMCE since 1993. The first flask samples were collected at Mac000e Head station on May 1993 and the results appear in Figure 5. The flasks collected by NOAA CMDL and measured at the Institute for Arctic and Alpine Research, University of Colorado, Boulder (INSTAAR), for isotopes are also shown in Figure 5. Figure 6 shows the differences observed between the CFR-LMCE δ¹³C data, the INSTAAR δ¹³C data, and a smoothed curve calculated from the INSTAAR data. By selecting only the δ¹³C data from both programs corresponding to background conditions, the average difference is -0.03 per mil with a standard deviation (1σ) of 0.07 per mil. It is not yet possible to assess whether or not there is a significant discrepancy between the isotopic scales used in both laboratories.

Future Development

In 1996 CFR plans to establish a flask sampling program to measure CO₂ and its stable isotopes in the Southern Hemisphere. Flask samples will be collected at Amsterdam Island onboard the ship servicing the French Austral stations located in the South Indian Ocean and the subantarctic area and at a new site which will be either La Reunion or Tromelin Island in the Western Indian Ocean.

In the Northern Hemisphere, flask samples will be collected onboard a ship making regular crossings between Le Havre and Panama.

The 3-D model of atmospheric transport of the Max Planck Institut für Meteorologie of Hamburg, version TM2Z, will be used to model CO₂ and its isotopes as well as the O₂/N₂ ratio.
Figure 1. The long-term trend of CO$_2$ at Amsterdam Island

Atmospheric CO2 at Amsterdam Island (38°S, 77°E)
Figure 2. The CO₂ growth rate at Amsterdam Island
Figure 3. Atmospheric CO₂ measurements at Mace Head, Ireland: (a) daily averaged CO₂ value; (b) smoothed CO₂ seasonal cycle obtained by filtering out variability on time scales shorter than 80 days; (c) residuals obtained by subtracting the smoothed curve (3b) from the data (3a).
FIGURE 4
CFR-NOAA (background conditions)

Figure 4. Comparison of CFR and NOAA measurements during background conditions at Mace Head. The symbols represent the CFR hourly average minus the NOAA flask value.
Figure 5. Measurements of $\delta^{13}$C at Mace Head, Ireland. Open circles represent measurements made by INSTAAR on CMDL flasks. Filled circles represent CFR LMCE measurements.
Figure 6. Residuals obtained by subtracting a smoothed curve calculated for the CMDL INSTAAR $\delta^{13}C$ from CMDL INSTAAR data (open circles) and from the CFR LMCE data (filled circles).
ANNEX 5.4: GERMANY

CONTINUOUS CO₂ CONCENTRATION AND ISOTOPE OBSERVATIONAL PROGRAMS IN GERMANY AND SUPPORTING TRANSPORT TRACER MEASUREMENTS (⁸⁵ KRYPTON AND SF₆)

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Introduction

This report summarizes German observational activities associated with the WMO-GAW program, and relevant for the understanding of the global atmospheric carbon dioxide cycle. It concerns measurement programs conducted by the following institutions: (1) Umweltbundesamt (UBA, Berlin), continuous CO₂ concentration measurements in Germany; (2) Institut für Atmosphaerische Radioaktivitaet (IAR-BIS, Freiburg), global atmospheric ⁸⁵Krypton network, (3) Institut für Umweltphysik (University of Heidelberg), global ¹⁴CO₂ network, concentration and stable isotope measurements of CO₂ on flask samples as well as global SF₆ network.

CO₂ Concentration and Stable Isotope Analyses

Continuous atmospheric CO₂ concentration measurements have been conducted in Germany by the Umweltbundesamt since 1972 [Levin et al., 1995]. Meanwhile, the essentially regional German network has been extended to eight sites (Figure 1). For a brief description of the instrumentation used at the individual UBA sites see Levin [1993]. A description of the GC measurement technique used at the Schaunsland station is given by Schmidt et al. [1996]. Since 1995, the UBA CO₂ network in Germany has been supplemented by continuous GC measurements from Heidelberg as well as weekly flask sampling for CO₂ concentration and biweekly sampling for stable isotope analyses at Schaunsland and at the German Antarctic station Neumayer (since 1994).

![Map of the continuous CO₂ monitoring sites run by the German Umweltbundesamt; the network is supplemented by continuous measurements in Heidelberg and by flask sampling at Jungfraujoch (Switzerland, Alps).](image)

Figure 1. Map of the continuous CO₂ monitoring sites run by the German Umweltbundesamt; the network is supplemented by continuous measurements in Heidelberg and by flask sampling at Jungfraujoch (Switzerland, Alps).
Global Network of $^{14}$CO$_2$ Observations

Our global network of quasi-continuous observations of $^{14}$CO$_2$ in the background atmosphere, which was established with international cooperation from the institutions running the background stations, was continued through the end of 1995. Table 1 shows the locations and site characteristics of the individual stations covering the globe from 82°N (Alert) to 71°S (Neumayer).

<table>
<thead>
<tr>
<th>Station</th>
<th>$^{14}$CO$_2$ Start</th>
<th>$^{85}$Kr Start</th>
<th>SF$_6$ Start</th>
<th>Position</th>
<th>Station Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>1987</td>
<td>1991</td>
<td>1993</td>
<td>83°N 62°W</td>
<td>Background</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>1986</td>
<td>1990</td>
<td>1996</td>
<td>47°N 8°E</td>
<td>Continental - background</td>
</tr>
<tr>
<td>Sonnblick</td>
<td>1990</td>
<td>-</td>
<td>-</td>
<td>47°N 13°E</td>
<td>Continental - background</td>
</tr>
<tr>
<td>Izana</td>
<td>1984</td>
<td>1987</td>
<td>1991</td>
<td>28°N 16°W</td>
<td>Background</td>
</tr>
<tr>
<td>Miami</td>
<td>-</td>
<td>1981</td>
<td>-</td>
<td>25°N 80°W</td>
<td>Regional - maritime</td>
</tr>
<tr>
<td>Llano del Hato</td>
<td>1991</td>
<td>-</td>
<td>-</td>
<td>8°N 71°W</td>
<td>Continental - background</td>
</tr>
<tr>
<td>Cape Point</td>
<td>-</td>
<td>1985</td>
<td>-</td>
<td>34°S 18°E</td>
<td>Background</td>
</tr>
<tr>
<td>Cape Grim</td>
<td>1987</td>
<td>1987</td>
<td>1978</td>
<td>41°S 145°E</td>
<td>Background</td>
</tr>
<tr>
<td>Macquarie Isl.</td>
<td>1992</td>
<td>-</td>
<td>-</td>
<td>54°S 159°E</td>
<td>Background</td>
</tr>
<tr>
<td>Neumayer</td>
<td>1983</td>
<td>1983</td>
<td>1986</td>
<td>71°S 8°W</td>
<td>Background</td>
</tr>
</tbody>
</table>

The general features of the distributions and temporal changes of $^{14}$C in atmospheric carbon dioxide have been reported in detail elsewhere [Levin et al., 1992, 1995]. Until now, our global data set of $^{14}$CO$_2$ observations has been used to verify global models of atmospheric CO$_2$ (compartment models of the global CO$_2$ cycle as well as 2-D atmospheric transport models [Hessheimer, 1990; Hessheimer et al., 1994]). A particularly important finding from a simple compartment model of the global carbon cycle is a serious imbalance of bomb $^{14}$C in all reservoirs exchanging carbon with the atmosphere [Hessheimer et al., 1994]. The most plausible adjustment of the CO$_2$ exchange parameters between the carbon reservoirs leads to a smaller uptake of anthropogenic CO$_2$ by the oceans than previously believed.

With our current understanding of the global CO$_2$ sources and sinks, the observed seasonal variations of $^{14}$CO$_2$ in the Northern Hemisphere cannot be explained quantitatively. Particularly unclear to date is the role of the different biospheric reservoirs with different $^{14}$C ages, respectively, different isotopic disequilibrium relative to the atmosphere, on the observed seasonality.

The general features of the observed mean meridional profile are qualitatively explained by our 2-D model estimates (Figure 2). The $^{14}$CO$_2$ level at the Southern Hemispheric sites, which is mainly determined by equilibration with $^{14}$C depleted surface ocean water in the circum-antarctic regions, cannot fully be reproduced by our model.

Atmospheric $^{85}$Krypton and SF$_6$ Observations

The global atmospheric observations of $^{85}$Krypton showed a slowdown of the increase rates at the beginning of the 1990s in both hemispheres that could be qualitatively explained by reduced $^{85}$Krypton emissions from reprocessing plants of the Former Soviet Union. In very recent years $^{85}$Krypton is again increasing at rates as observed in the 1980s [Weiss et al., 1992]. Within the Southern Hemisphere, we observe a significant concentration difference between 41°S and 71°S that can only be explained by a yet unidentified $^{85}$Krypton source in the Southern Hemisphere. These current developments in the global distribution and trend of atmospheric $^{85}$Krypton put limitations on this radioactive noble gas as tracer to validate global atmospheric circulation models. A new tracer suitable for this purpose has been measured recently, namely the inert trace gas SF$_6$ [Maias et al., 1994; Maias et al., 1998]. Since the very first measurements in 1970, the purely anthropogenic greenhouse gas SF$_6$ has increased by two orders of magnitude to a global value of about 3.3 ppt by the end of 1994. The observations can be best fitted by a quadratic curve with a recent increase rate of 6.9% per year (Figure 3). A significant north-south gradient of about 0.3 ppt is observed due to the anthropogenic origin of this
trace gas and its release to the atmosphere mainly through leakages of high voltage electrical switchings. With these characteristics and a more dense measurement network in the future, this new trace gas is a perfect tracer to validate atmospheric transport models [Levin and Hesshaimer, 1996].

Figure 2. Meridional distribution of $^{14}$CO$_2$ in the atmosphere, comparison of observations and estimates from our 2-D model [Hesshalmer and Levin, unpublished].

Figure 3. SF$_6$ observations at background stations in the Northern and the Southern Hemisphere [from Maiss et al., 1996] - comparison with model estimates [Levin and Hesshaimer, 1996].
Acknowledgments

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References

ANNEX 5.5: HUNGARY

CARBON DIOXIDE CONCENTRATION MEASUREMENTS IN HUNGARY

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Carbon dioxide concentration measurements in Hungary were started in June 1981, when a Siemens Ultramat 3 CO₂ analyzer was put into operation at the K-pusza regional background air pollution monitoring station (46°58'N, 19°33'E, 125 m asl). The station is located on the Hungarian Great Plain in the middle of the Carpathian Basin as far from pollution sources as possible in the highly industrialized, densely populated region of Central Europe. The station is operated by the Institute for Atmospheric Physics, which is part of the Hungarian Meteorological Service. To avoid the effect of the growing forest around the station, the station was moved approximately 500 m northwest to a larger clearing in October 1993.

Because the station is located at a low elevation region covered by vegetation typical of the temperate region of Europe, significant diurnal and seasonal concentration variations can be observed at the station. Nevertheless, the global fluctuation in the growth rate of the atmospheric carbon dioxide concentration can also be recognized even at such a site (Figure 1). Since the big depression in 1992 and 1993, the concentration has been growing again at a rate that is similar to that in the past (Figure 2). However, the concentration is still lower than in 1991 when it was at its maximum since the beginning of the measurements.

Since we have only one instrument, parallel comparison measurements at the old and the new site could not be made. However, after slightly over a year of operation, we have started to compare the data measured at the old and at the new site. The wintertime difference is negligible, and the standard deviation of the half-hour average concentration data is slightly smaller at the new site than at the old one. The summer daytime concentration increased by 4 ppm on an average in spite of the decrease in the annual average concentration from 1991 (chosen as the reference year) to 1994. At the same time the nighttime average concentration decreased significantly as the extremely high concentration values (above 500 ppm in some cases) disappeared. These extremely high concentrations were observed at the old site during calm nights when occasional CO₂-rich puffs reached the station from the nearby forest. Those nights were also always characterized by high concentration fluctuations. The difference between two consecutive half-hour averages might be as big as 100 ppm. On an annual basis, the concentration range decreased due to the better mixing conditions (Figure 3).

The question is how homogenous are the data from 1981 considering the annual averages and the long-term trend. The atmospheric CO₂ growth rate reached its minimum at the beginning of 1992, while the concentration reached its minimum approximately 1 year later. Both occurred before the station moves. After the change of the measuring site, we could not see any break in either the growth rate or the concentration. Therefore, we hope the data series can still be considered homogenous.

In cooperation with CMDL, we established a flask sampling site in Hungary in 1993 for their global cooperative flask sampling network. The site was chosen in such a way that it should also be suitable for vertical concentration profile measurements. The new site is located in a plain region of Western Hungary (Hegyhátsáll, 46°57'N, 16°39'E, 248 m asl) in an open region covered by fields and scattered forest. The inlet tube was mounted at 96-m height (344 m asl) on a TV transmission tower operated by Antenna Hungária Corporation. The first sample was taken on March 2, 1993. The data (CO₂, CH₄, CO, and ¹³C/¹²C) are available from NOAA under code HUN.

In October 1994, as a joint project with the CMDL Carbon Cycle Group, we also started the vertical concentration profile measurements, continuously monitoring the CO₂ concentration at four height levels from 10 m to 113 m. Here we use a Li-Cor Model 6251 analyzer. The standards are provided by CMDL. The continuous vertical concentration profile measurements and the flask sampling at the same site, as well as the measurements at K-pusza, will give us possibilities for several studies and comparisons. At the moment there are not enough data for detailed and reliable statistical analyses.
Figure 1. Growth rate of atmospheric CO₂ concentration at K-puszta, Hungary.

Figure 2. Atmospheric CO₂ concentration at K-puszta, Hungary.
Figure 3. Frequency distribution of the 30-minute average CO$_2$ concentration values measured at "old" K-puszta (1991) and at the new site (1994).

Figure 4. Average diurnal CO$_2$ concentration variations at Hegyhátsál at different elevations.

Climatologically the region of Hegyhátsál is not as calm as that of K-puszta; otherwise there is not much difference between the two sites. The diurnal concentration variation is also high at Hegyhátsál and depends on the elevation (Figure 4). Therefore, in the region of active vegetation the sampling height and the sampling time may be critical and they should be taken into account when comparing the data from different sites.
ANNEX 5.6: ITALY

A NEW CO₂ CONTINUOUS MONITORING STATION IN ANTARCTICA:
JUBANY (South Shetland)

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Tiziano Colombo, Italian Meteorological Service

Station Operation

The Italian National Research Programme in Antarctica (PNRA) and the Argentine National Department for Antarctica (DNA) agreed on the activation of a program based on the atmospheric carbon dioxide continuous measurements at the existing Jubany station, South Shetland Islands, which border on the Archipelago at the northern edge of the Antarctic peninsula. The station is placed along the shore of Potter Bay on King George Island, latitude 62°14′S, longitude 58°40′W, 15 m asl (Figure 1). The bay is surrounded by permanent glaciers, and snow covers the ground from April to November. The sea surface of the bay is frozen only during 2-3 months each winter. The soil is volcanic and the only vegetation is represented by sparse patches of moss and lichens. The meteorological conditions are characterized by a high percentage of cloud cover and a very high wind speed. A complete description of the station and technical details on the CO₂ laboratory are given in Ciattaglia et al. [1995].

Figure 1. Map of Antarctic continent showing the stations where cooperative programs of PNRA are running.
The measuring system is based on a Siemens Ultramat 5E analyzer whose scale is calibrated by reference to a set of eight station standards (CO$_2$ in air) by means of two working standards (zero and span). The station standard cylinders were determined in Italy by reference to the national standard scale made of another set of eight cylinders. The concentration of these standards was recently assigned by Scripps according to X93 absolute determination.

All of the devices used at Jubany station are based on the experience developed in Italy at Mt Cimone first and then at the CNR-ENEA Laboratory in Rome. The overall precision of the measurement should be on the order of 0.1 ppm. The station operation started on February 15, 1994, and at this time is continuously running under the control of DNA personnel. The PNRA contribution, after the initial installation phase consists mainly of data quality control and also of periodic visits (two per year) in order to supply spare parts, reference gases, and recalibration of station standards versus national primary standards.

Overview of First Year of Data

The CO$_2$ concentration data are expressed as hourly data and are based on 1-minute means. Data collected from February 15, 1994, to January 30, 1995, show well-defined features. First, there is a very limited variability within the hour. A criterion based on standard deviation (<0.5 ppm) is applied in order to select data, and the results are that approximately 85% of the hourly data meet this criterion. A second characteristic is the day-to-day variations on the order of 1 ppm, mostly related to synoptic circulation patterns of air masses. Finally, the seasonal behaviour of the measured concentrations shows a very limited oscillation: approximately 4 ppm difference between the February-March minimum and the August-September maximum. The day-night oscillation is very small; perhaps only during February and March an S shape (~0.3 ppm) in the 24-hour record appears if a polynomial smoothing is applied to the hourly data selected as indicated below.

First, the data selection is based on the standard deviation <0.5 ppm within the hour. This means that only hourly means not exceeding such a limit and calculated on 60 1-minute values are accepted. Second, a wind-related criterion is applied, i.e., values obtained when local wind is within a defined sector (corresponding to a possible influence of the base) and having speed of <10 kts are rejected. The amount of hourly values left after both selection phases is ~80%. This means that the site has good characteristics of remoteness and can represent the CO$_2$ background concentration for the Antarctic peninsula area quite well.

Figure 2 represents the mean daily concentrations for the first year. Day-to-day variations (<1 ppm) can be easily associated with the origin of air masses. The only forested area (~1000 km north) is represented by Tierra del Fuego and can be used to explain oscillations of this order of magnitude. During the initial period until Julian day 200, the anomalous upward shift (~0.5 ppm) indicated in the graph by the horizontal line is probably due to the use of a temporary station standard set of cylinders whose concentration was not as stable as it ought to be. Now the problem has been overcome; nevertheless the well-known problems related to the stability of the scale are continuously taken into account in order to obtain the data comparability that is fundamental for the WMO GAW program.
Figure 2. First year of CO$_2$ daily averages measured at Jubany stations.

Figure 3. Representation of diurnal behaviour of CO$_2$ concentrations with time (months).

Figure 3 shows the diurnal behaviour (1-, 2-, ... 24-hourly concentrations) during the 12 months of the year. As can be seen, the surface does not display any season-related features, thus confirming what was said above, i.e., the local scattered vegetation has no influence on the CO$_2$ measured at Jubany.

All of the selected hourly data were transmitted to WDCGG Tokyo and to CDIAC together with the standard meteorological information.

Reference
ANNEX 5.7: JAPAN

CONTRIBUTION OF THE JAPAN METEOROLOGICAL AGENCY
TO THE WMO GAW PROGRAMME AND ASSOCIATED ACTIVITIES

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Introduction

The Japan Meteorological Agency (JMA) is a leading organization in Japan in the observation and research of the climate system. JMA, as a governmental organization in charge of the scientific aspect of climate issues, has been providing relevant authorities and the general public with scientific information and advice on climate issues. Currently JMA carries out the following activities that are relevant to the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) and associated activities.

1. OPERATION OBSERVATION AND MONITORING OF GHGs (Figure 1)

![Map of JMA's operational observation network of greenhouse gases and other related gases. Solid circles: two GAW stations; solid lines: observation by the RV Ryofu Maru; dashed line: observation by scheduled flights.]

Figure 1. JMA’s operational observation network of greenhouse gases and other related gases. Solid circles: two GAW stations; solid lines: observation by the RV Ryofu Maru; dashed line: observation by scheduled flights.

1.1 Two GAW stations

JMA initiated operational observation of atmospheric CO₂ concentration in January 1987 at "Ryori" (39°02'N, 141°50'E) located in the northern part of Honshu (the mainland of Japan). The station is categorized as a regional station of the GAW programme. As of June 1995, CO₂, CH₄, CO, O₃ (surface), CFCs (CFC-11, 12, 113), N₂O, CCl₄, CH₃CCl₃, and turbidity are monitored at Ryori. The annual mean atmospheric concentration of CO₂ at Ryori in 1994 was 361.6 ppmv, which was 2.3 ppmv higher than in the previous year.

In March 1993, JMA established the second observation station at "Minamitorishima" (24°18'N, 153°58'E), an isolated island in the western North Pacific, as a global station of GAW. This station monitors CO₂, CH₄, CO, O₃ (total and surface) and turbidity as of June 1995. The annual mean atmospheric concentration of CO₂ at Minamitorishima in 1994 was 359.5 ppmv.
Figure 2a shows monthly mean background concentrations of atmospheric CO$_2$ at the above two stations. Figure 2b shows annual increase rates of the concentrations.

![Graphs showing CO$_2$ concentrations and increase rates.]

Figure 2. (a) Monthly mean concentrations of atmospheric CO$_2$ at Ryori and Minamitorishima. (b) Annual increase rates of the concentrations of atmospheric CO$_2$ at Ryori and Minamitorishima (differences from the value in the same month in the previous year as well as their 13-month running means).

1.2 Shipboard observation

To understand the role of the ocean as sources and sinks of atmospheric CO$_2$, JMA initiated operational monitoring of the concentrations of CO$_2$ both in the surface water and in the air over the western North Pacific in 1989 using the Ryofu Maru. Total inorganic carbonates, alkalinity and dissolved organic carbon in seawater from the subsurface to deep layers are also measured to evaluate the quantities transported into deep oceans. Together with CO$_2$, JMA also conducts the monitoring of CFCs, N$_2$O and CH$_4$ in the same ocean.

For 1996, the observations will be conducted along the 165°E meridional line in place of the 155°E meridional line by the renewed Ryofu Maru.

Figure 3 shows the pCO$_2$ difference ($\Delta$CO$_2$) between the surface seawater and the air along the 137°E and 155°E meridional lines in January and February and June and July 1993. It is revealed that in winter, pCO$_2$ in surface seawater is about 70 $\mu$ atm lower than in air in the areas between 20 and 30°N, while in summer it is about 50 $\mu$ atm higher in the areas around 25°N.
1.3 Airborne observation

The Meteorological Research Institute of JMA, in cooperation with the Ministry of Transport and the JAL Foundation, has been carrying out a project to observe CO$_2$ and CH$_4$ in the upper troposphere between 9- and 13-km altitude using scheduled flights of the Japan Airlines on a route between Tokyo, Japan, and Cairns, Australia, since April 1993. (The route has been changed to between Tokyo and Sydney since July 1994.) During a flight, air is sampled into flasks every 30 minutes (at an interval of about 3°40' in latitude) over the Pacific Ocean. Figure 4 shows the result of the observation made from April 1993 through April 1994. It demonstrates that from winter to spring in the Northern Hemisphere the CO$_2$ concentration increases considerably from south to north, while from summer to autumn CO$_2$ decreases slightly. In the north this suggests that the seasonal variation in CO$_2$ concentration at the surface due to the vegetation (photosynthesis and respiration) greatly affects the variation in the upper troposphere. Another point is that in low latitudes of the Southern Hemisphere (5-10°S) the highest concentrations were observed in December when the concentrations should be lower. This might be attributed to the southward transport in the upper atmosphere of a high concentration of CO$_2$ that originated in the Northern Hemisphere.

Figure 3. \( \Delta p\text{CO}_2 \) along the 137°E and 155°E meridional lines in January and February and June and July 1993

Figure 4. Latitudinal distribution of CO$_2$ concentrations observed by scheduled flights between Japan and Australia from April 1993 to April 1994
2. RESEARCH ACTIVITIES

The Meteorological Research Institute (MRI) of JMA has been carrying out a wide range of research on climate change through observation, process study, and modeling of the climate system. With regard to the observation of GHGs, MRI, sponsored by the Science and Technology Agency of Japan, carries out the following studies:

2.1 Shipboard programme

The mixing ratio of atmospheric CO₂ and CO₂ equilibrated with surface seawater
TCO₂ measurements in surface seawater and/or deep water
¹⁴C/¹²C measurements of TCO₂ (New Zealand and Netherlands)
The mixing ratio of CH₄ and CO in surface seawater and overlying air

2.2 Aircraft program

The mixing ratio of atmospheric CO₂, CH₄, and CO (9-13 km above the surface, twice a month).
The mixing ratio of atmospheric CO₂, CH₄, and CO (4-5 km above the surface, once a year).

2.3 Experimental field and tower program

Continuous measurements of the mixing ratio of atmospheric CO₂ and CH₄.

3. THE WORLD DATA CENTRE FOR GREENHOUSE GASES (WDCGG)

3.1 Function of the WDCGG

In the framework of the GAW program, WMO established the World Data Centre for Greenhouse Gases (WDCGG) at JMA in Tokyo in October 1990. Its major functions are to collect data of the concentrations of greenhouse gases and other related gases except ozone from all parts of the world, to manage and develop a global database, to disseminate the data and analyzed results by publications and other means and to exchange information with relevant organizations and institutes.

3.2 Data collection and distribution

As of May 1995, 149 stations (including ships and aircraft) in 50 countries submitted data of the concentrations of greenhouse gases. WDCGG welcomes contributions from relevant institutions all over the world.

The WDCGG distributes the collected data in printed media and on floppy diskettes as mentioned below. In addition, the WDCGG is preparing for the distribution of the data via Internet so that the ftp server can be available to the users by the end of 1995.

3.3 Publications

Data Report

The collected data are published every 6 months as Data Report. The daily, monthly and annual data are listed in the report with some basic information including the names of the station and the authority that implements the observation, the calibration scale, the observation interval, and the instrument.

A Data Report was published in October 1992, October 1993, March 1994, and October 1994 and was distributed to the members of WMO, the contributors of the data, and other relevant institutions. The data in the Data Reports are available on floppy diskettes or other appropriate electromagnetic media as well as on CD-ROM as described below.
Data Catalog

The Data Catalog contains information on the observation stations including the location, circumstances, observation programs, and the instrument used for measurement. The first issue of the Data Catalog was published in December 1993.

Data Summary

The Data Summary covers the analysis and assessment of the concentrations of greenhouse gases, including their global/regional distributions and trends. The first issue of the Data Summary will be published in 1995.

WDCGG CD-ROM

The WDCGG CD-ROM contains the daily, monthly and annual data of the concentrations of greenhouse gases that are distributed by the Data Report. A sample issue of the WDCGG CD-ROM was published in March 1994 and the first issue was published in 1995.

4. QUALITY ASSURANCE/SCIENCE ACTIVITY CENTERS (QA/SAC)

WMO plans to establish three Quality Assurance/Science Activity Centers (QA/SACs), one each in Germany, the United States, and Japan to deliver quality-assured data to the GAW data centers. JMA will serve as the QA/SAC for WMO Regions II and V (Asia and South West Pacific). The activities of the QA/SAC are scheduled to start in October 1995.
ANNEX 5.8: KOREA

THE CO₂ MEASUREMENT PROGRAMME IN KOREA

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The monitoring of atmospheric CO₂ in Korea has been carried out since 1990 at Kosan (33°17.4'N, 126°9.9'E, 72 m above sea level), Cheju Island, with weekly flask sampling. The concentrations of CO₂ have been measured in collaboration with Prof. C. D. Keeling at the Scripps Institution of Oceanography.

Figure 1a shows the results obtained at the station, presenting a strong seasonal variation of ~16 ppm. This variation appears to be due to the change in air mass arriving at the station: oceanic air mass with lower concentrations of CO₂ associated with southerly wind during the summer season and the continental one with higher concentrations associated with northwesterly wind during fall through spring times. The trend of CO₂ concentration is also shown in Figure 1b; those at Mauna Loa and La Jolla stations are also shown for comparison.

Figure 1. (a) The concentration of CO₂ in the air at Kosan station since summer 1990 obtained from flask samples. (b) The trend for CO₂ concentration during August 1990 to June 1994 at Kosan station.
Other greenhouse gases such as CFC-12, CFC-11 and N₂O were also measured for the same air samples used for CO₂ determination since early 1994. A simple manifold was constructed to transfer air samples left in the flask with subatmospheric pressure into the injection loop of the GC system as shown in Figure 2. The sample was transferred from the flask into the pre-evacuated injection loop by a pressure gradient made in the manifold side (Figures 2a and 2b). The sample in the injection loop was pressurized to ambient pressure by introducing the ambient air from the back (Figure 2c) and then injected into the GC for the measurement. The 52 cc isolation coil was introduced in the manifold to prevent any contamination of the sample in the injection loop by the back-flushed ambient air.

Figure 2. A schematic diagram of the interface manifold constructed for the analysis of CFC-12, CFC-11, and N₂O from flask samples (a, b, c).
The CFC-12, CFC-11, and N₂O concentrations of the air at Kosan station were very comparable to those of these gases estimated in clean background air at midlatitudes in the Northern Hemisphere; CFC-12 (530 pptv), CFC-11 (272 pptv), and N₂O (313 ppbv).

A pilot station at Seoul National University, in the southern suburbs of Seoul, has also been in operation since 1990 in order to carry out research for developing and improving measurement systems in Korea. A continuous measurement of CO₂ and other climate gases in the ambient air has continued since fall 1994. An example of CO₂ concentration variations in fall 1994 is shown in Figure 3 as a box diagram.

![Box Diagram](image)

Figure 3. A box diagram for concentrations of CO₂ observed at SNU station (September 1994-December 1994).

The newest CO₂ research started in recent years in Korea is the measurement pCO₂ at the air-sea interface over seas around Korea. The flux measurements and process studies at the ocean-land (biosphere)-air interface for greenhouse gases will be emphasized and be further expanded in the future. Figure 4 shows the initial result of the ΔpCO₂ (pCO₂ (surface water) - pCO₂ (air)) distribution obtained in summer 1994 and winter 1995 over the East Sea (Japan Sea).
Figure 4. Distribution of $\Delta pCO_2$ ($pCO_2$ (surface sea water) - $pCO_2$ (marine atmosphere)) of the surface sea waters in the East Sea in July 1994 and March 1995.
ANNEX 5.9: SWEDEN

CARBON DIOXIDE MONITORING ON ZEPPELINFJELLET (78°54' N, 11°53' E)

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This report provides a brief summary of the monitoring of climatically active species by the Department of Meteorology at Stockholm University (MiSU) at the monitoring site on Zeppelinfjellet mountain near Ny-Ålesund (78°54' N, 11°53' E) on Spitsbergen (Figure 1). A short presentation of the site and some results from the monitoring of carbon dioxide (CO₂) during 1989 through 1995 is given. The Zeppelin station monitoring site (474 m above sea level), utilized since March 1990, is excellent for background monitoring of CO₂ with minimal local contamination or other disturbance. Accuracy has continuously been increased and is approaching 0.1 ppm (v). During 1994 there are valid data for 94% of the year. Less than 0.1% of the data in 1994 were lost due to local contamination; the remaining loss is due to technical disturbances.

Figure 1: The Arctic, including parts of Eurasia and North America. The insert shows Svalbard, where N is the location of Ny-Ålesund (78°55'N, 11°56'E), L is Longyearbyen (78°13'N, 15°35'E), B is Barentsburg (78°05'N, 14°15'E), and P is Pyramiden (78°39'N, 16°25'E). In this report the Norwegian nomenclature is used and the term "Svalbard" defines the whole group of islands situated between 74°N and 81°N and longitudes 10°E to 35°E; the name "Spitsbergen" will be reserved for the largest island in the group. All large communities in Svalbard, including Ny-Ålesund, lie on Spitsbergen.
For January 1989 through April 1995 we observed an annual linear increase of atmospheric CO$_2$ of 0.69 ppm(v) and a seasonal amplitude of 16.2 ppm(v) at Ny-Ålesund. During the summer and fall of 1994, a dramatic recovery of the CO$_2$ trend towards increase rates of 2-3 ppm(v) year$^{-1}$ occurred from the anomalous low rate measured during 1993. There is mounting evidence that these variations in atmospheric increase rates are caused by changes in the terrestrial biosphere that, in turn, probably are due to climatological variations.

The Zeppelin station is operated by the Norwegian Polar Institute. The scientific mentor institution is the Norwegian Institute For Air Research (NILU), which collaborates closely with MISU regarding climatically active species. A suite of atmospheric parameters are measured by the participating parties. For further information regarding the NILU activities [Braathen and Hov, 1988 and Braathen et al., 1990]. The MISU measurements [Heintzenberg et al., 1991a, b; 1992; Holmén et al., 1995a, b] include carbon dioxide, two particle counters operating in different size ranges (5-1000 nm and 10-1000 nm radius), a nephelometer measuring the light (550 nm) scattering coefficient of particles, as well as instruments for selected meteorological data. As a complement to these measurements, MISU is also running a filter sampling program that yields information about the concentrations of major ions and soot in the particles. A discussion of the aerosol data from ZeppelinInfellet is given in Heintzenberg and Leck [1994].

During the early 1980s, measurements of atmospheric CO$_2$ were intermittently performed on Svalbard by means of flask sampling [Heintzenberg et al., 1991b]. Continuous measurements with a UNOR 4N instrument have been made since October 1988. During an initial period, the continuous measurements were performed at "Gruvbåden" (G in Figure 2) in the fjord valley near Ny-Ålesund, but in March 1990 the instrumentation was moved to the Zeppelin baseline station (Z in Figure 2).

NY-ÅLESUND

Ny-Ålesund, a former mining settlement, now primarily a research-dedicated community with its 20-200 (winter-summer) inhabitants, is located on the northern shore of Brøggerhalvøya facing Kongsfjorden. The peninsula Brøggerhalvøya lies on northwestern Spitsbergen about 100 km northwest of the Norwegian and Russian townships Longyearbyen, Barentsburg, and Pyramiden (Figure 1) where some coal mining is still going on and where most of the human population of Svalbard lives. The three communities have between one and two thousand inhabitants each.

Kongsfjorden is generally ice covered from January to mid-May, while the waters just west of Spitsbergen often are devoid of ice for most of the year [Vinje, 1982], due to the influence of the warm Norwegian Current, which has a branch (West Spitsbergen Current) flowing north following the west coast of Spitsbergen. Farther west near Greenland, and east and north of Svalbard, the ice conditions are severe and the ice may persist well into summer.

The annual mean temperature in the village of Ny-Ålesund is -6.2 C, the warmest month being July ($T_{mean} = 5.0$ C), and the coldest February ($T_{mean} = -14.6$ C). The mean yearly precipitation is about 400 mm. The snow around Ny-Ålesund starts to melt in May, and large portions of the low-level ground are snow free from late June until October-November. The winds in the village of Ny-Ålesund are relatively moderate, especially during summer. The annual frequency of wind-force 5 Beaufort or less (i.e., less than 11 ms$^{-1}$) is 96%. On an annual average, only 10 days have a wind-force of 8 or more (i.e., more than 17 ms$^{-1}$); these days are usually found during winter (December to March). Because of the drainage winds from the glaciers inland, the direction is most often from southeast (26% of the time) to east (14%) throughout the year. Due to the channelling effect of the mountains bordering the fjord-valley, the third most common sector is from northwest (9%). This and other relevant meteorological information is found in the report by Hansen-Bauer et al. [1990].
The first measurements of atmospheric CO₂ near Ny-Ålesund were executed during 1981 and 1982 in the actual village [Heintzenberg et al., 1983]. As the air-samples collected were subject to local contamination, it was decided that another site had to be chosen for the planned baseline station in the area. About 1.5 km southwest of the village was a suitable building equipped with the necessary electricity, etc. This new site "Gruvbådet" was used as the location of the monitoring station from October 25, 1988, until March 15, 1990. Here, the incidence of locally produced contamination as lower; however, some contamination still occurred.

Local sources of contamination in Ny-Ålesund include the oil burning power plant (P in Figure 2); about 20 cars running on the less than 10 km of roads available in the community; numerous snowmobiles (the number is, however, limited by the size of the winter population, usually fewer than 30 persons) running all over the low-lying area during the snow cover season (December through May), and occasionally ships that visit the fjord or call at the dock (D in Figure 2). The number of cruise ships visiting Ny-Ålesund in summer is steadily increasing. During June to September 1993, more than 100 vessels visited Ny-Ålesund. In the village there is also a small area for trash disposal (T in Figure 2) that is incinerated 5 to 10 times a month and might be smoldering several days afterwards. On the airstrip (A in Figure 2) small planes land and take off once a week during winter and two to four times a week during summer. There are also two helicopter landing facilities in the village (H in Figure 2) that are used during May and June when the airstrip is unusable or otherwise required due to weather conditions or special transportation needs.

THE ZEPPELIN STATION

At Zeppelinfjellet, local contamination is reduced to a minimum. Only privileged scientists and technicians have access to the station, which is reached by a dedicated cable way. The station is situated on a mountain ridge with steep rocky slopes and glaciers on all sides; there is no vegetation near the site. The station is usually manned by one or two persons during a few hours per day and left unattended for the rest of the time. With light winds, the visits to the station can sometimes be recorded by the CO₂ analyzer, and episodes of truly local contamination are easily observed in the record and these data are rejected. Contamination from the village of Ny-Ålesund is sporadically noticed, for example, when a persistent inversion in the valley breaks up.

The current CO₂ instrumentation is shown in Figure 3. The setup was operational at the Gruvbådet location until March 1990 when it was moved to Zeppelinfjellet. A revision is ongoing and an entirely new system is expected to become operational during the fall and winter of 1995.

Figure 4 is a plot of our data from January 1, 1989, through April 28, 1995. The data are plotted for the median reading during the 30 minutes following each calibration (every 3 hours). A harmonic function (described below) fitted through the entire data-set is also shown.

During winter (November-March) there is always a high degree of variability, most often towards higher CO₂ values. We attribute this to long-range transport of pollutants from eastern Europe [Lejenäs and Holmén, 1996]. In spring and summer (May-August) we see similar excursions but now towards lower CO₂ values. During these periods the air depleted in CO₂ has often spent some time over the waters of the northern North Atlantic prior to arrival at Ny-Ålesund [Engardt et al., 1996]. These waters are then highly undersaturated in CO₂ with respect to the atmosphere, following the initial phytoplankton bloom in early summer [Takahashi et al., 1993]. We believe that we see traces of intense oceanic uptake of CO₂ in our atmospheric data during the spring months.
Figure 2. Ny-Ålesund with surroundings. Elevations are in meters. The dotted line from V (the valley cableway station) to Z (Zeppelin station) shows the route of the dedicated cableway. For explanations of the other letters see the text. The dashed line marks the extent of the Vestre Lovénbreen glacier.
Figure 3. Schematic view of the MISU CO2 analyzing system. P1 is a 1.1 kW Siemens fan. P5 is a Gast MOA pump. P5 is placed in a pump-room; the lines from the stack through P5 to the service unit are a total of ca. 15 m of Decabon tubing. All tubing is steel except for air-intake and reference gas lines, which are Decabon. MFC are Brooks 5850E mass flow controllers. Flows are monitored with Brooks 5810N mass flow meters. L, M, H, and R are low, medium, high, and reference gas cylinders, respectively. C (at the top of the stack) is a cyclone that separates out particles larger than one micrometer. Dashed lines indicate electrical connections. The service unit houses a Nafion drying system. Data are stored as 1-minute averages in the data logger.
The highest daily-mean mixing ratios each year occur during the pollution episodes in January to April. Minimum CO$_2$ was reached in late August to early September during the 4 years for which we have accurate summer data. The difference between maximum and minimum daily-mean mixing ratio during a specific year is more than 20 ppm(v).

Figure 4. The CO$_2$ data from Ny-Ålesund during 1989 through February 1995. The data are plotted for every third hour based on the median value during the 30 minutes following a calibration. A harmonic function fitted through the entire data set is also shown. The data shown here and discussed in the text are tied to the provisional X93 scale by a set of six cylinders calibrated at NOAA CMDL in Boulder, Colorado, during the last 3 months of 1993.

In order to calculate an annual increase and a seasonal amplitude of CO$_2$ at Ny-Ålesund, the full data series (January 1, 1989 to April 28, 1995) was fitted to a linearly increasing harmonic function. The fitting proceeded as follows: First, consecutive 10-day means of CO$_2$ mixing ratios were calculated by omitting the lowest and highest 5% of data in each 10-day period. Next, these mean values where fitted by minimizing the square of the residuals, with appropriate attention being paid to the uncertainty of each data point (in this case the standard deviation around the 10-day mean mixing ratio) as described by Press et al. [1987]. The harmonic function which the data was fitted to reads:

$$q = q_0 + q_1 t + \sum (a_k \sin 2\pi kt + b_k \cos 2\pi kt)$$

Where $q$ is mixing ratio of CO$_2$, $t$ is time, $q_0$, $q_1$, $a_k$, and $b_k$ are the coefficients to be fitted. The sum is taken for $k = 1$ to 4, $q_1$ is the mean annual increase of CO$_2$ and the sum of harmonics defines the mean amplitude for the period that has been fitted.
This procedure yields a linear increase of atmospheric CO₂ at Ny-Ålesund of 0.69 ppm(v) year⁻¹ as well as seasonal amplitude (after subtracting the annual trend) of 16.2 ppm(v), for January 1989 through February 1995.

Acknowledgments

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References


ANNEX 5-10: USA

THE CO₂ MEASUREMENT PROGRAMME OF NOAA CMDL, U.S.A.

Reference Standards and Calibration Techniques

The transfer of calibrations from secondary to tertiary to working gases by infrared analysis continued as described in the report from the Seventh Meeting of Experts. The details have also been presented by Komhyr et al. (1985) and Thoning et al. (1987). The CMDL manometric system for absolute CO₂ mixing ratio measurements is described in Section 4.1 of this report.

In Situ and Flask Measurements

In situ measurements of atmospheric CO₂ continued at the four CMDL baseline observatories: Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and South Pole. These programmes have been described by Peterson et al. (1986); Komhyr et al. (1989); Thoning et al. (1989); Waterman et al. (1989); and Gillette et al. (1987). Instrument control and data acquisition equipment will be upgraded at Mauna Loa during 1995 and Barrow during 1996. The modifications will enable monitoring of instrument performance and access to data from Boulder via the Internet.

The CMDL Air Sampling Network and the CO₂ measurement results through 1992 have been presented by Conway et al. (1994). The apparatus used since December 1988 to measure the CO₂ mixing ratios in flask air samples was described by Thoning et al. (1995). The air sampling network currently consists of 45 fixed sites and three shipboard programmes. In addition to CO₂, most samples are also measured for CH₄, CO and H₂ mixing ratios, and the isotopic ratios $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O in CO₂. Samples from a subset of sites are being measured for N₂O and SF₆ as well.

At all the fixed sites samples are now collected in pairs of 2.5-L flasks equipped with two Teflon O-ring stopcocks by flushing and pressurizing with a battery powered air sampler (MAKS). For the shipboard programmes, air samples continue to be collected by opening evacuated flasks. Prototypes of a new air sampler (AIRKIT) have been successfully tested at Samoa and Cape Kumukahi. The AIRKIT includes a thermoelectric cooler to condense water vapor from the sample air stream at a temperature of ~5°C. Drying the sample is necessary to obtain reliable $^{18}$O/$^{16}$O measurements from humid tropical locations. The AIRKIT also contains a microcontroller and solenoid valves so that sample collection is more highly automated and less susceptible to operator error.

A comparison of flask and in situ measurements at the four CMDL baseline observatories is shown in Figure 1. The symbols represent the difference between flask pair averages and the corresponding in situ hourly averages. At all four sites there is an offset between the flask and in situ data starting in late 1993. The sense of the offset is that the flask averages are lower than the in situ hourly averages. The cause of this offset is not yet known, but it does not appear to be due to problems with standards or instrument calibration. In December 1995 we will perform careful comparisons at Mauna Loa between the in situ system and flask samples collected at the site. When the source of the offset is identified and quantified, a correction will be applied to the affected data.

Measurements of Carbon Dioxide on Very Tall Towers

As part of the CMDL effort to expand the carbon dioxide monitoring network into continental interiors we have started continuous measurements on two very tall TV transmitter towers in the United States, located in eastern North Carolina (WITN, 35°N latitude) and northern Wisconsin (WLEF, 45°N latitude). Our approach is to continuously monitor CO₂ and other tracers, and meteorological parameters at several heights on the towers to examine sources of variance in the CO₂ mixing ratios in the boundary layer over the continent. The main sources of variance are surface fluxes including atmosphere/biosphere exchange and anthropogenic activity (which we examine through correlations between various tracers such as CO and the CFCs), the dynamics of the planetary boundary layer, and transport.
Figure 2 shows CO₂ mixing ratios during a typical 3-day period in summer at the NC tower site. During the daytime the boundary layer is well mixed, and mixing ratios are similar at all three levels. There is a gradient of around 2 ppm between 51 m and 496 m, which reflects net photosynthetic uptake of CO₂. At night an inversion forms and CO₂ builds up to very high levels at 51 m. The 123-m level can be within or above the stable layer. There is a pulse of high CO₂ at 496 m in the morning when convection begins. The mixing ratio at 496 m in the afternoon is very constant for about 2-3 hours. This puts a lower limit on the horizontal scale of variability of 30-50 km, given typical wind speeds.

The 24-hour average CO₂ mixing ratios at each of the three levels on the North Carolina tower for each day during our 3 years of observations are shown in Figure 3. The big pluses are monthly statistics of the data, and the smoothed curves are generated using our standard smoothing algorithms. For measurements at 51 m the seasonal cycle is completely obscured. This is because the large buildup beneath the nocturnal inversion in summer compensates for the regional and hemispheric seasonal drawdown. At 123 m the seasonal cycle begins to emerge, and at 496 m it is quite evident and the magnitude is around 15 ppm. The 24-hour average mixing ratios are higher at 51 m than 496 m, and the levels are closer in winter than in summer.

We have done 1-D calculations to estimate the full vertical profile for CO₂ in the afternoon convective boundary layer at the NC tower site. Given a reasonable range of guesses at the surface flux, the convective layer depth, and mixing velocities we conclude that the mixing ratio at 496 m should be within a few tenths of a ppm of the mean for the whole convective layer. Given this, a comparison of the afternoon mixing ratios at the tower with our flask data from Bermuda (Figure 4), which is at about the same latitude, gives a measure of the daily drawdown or increase in CO₂ in the boundary layer due to terrestrial biology and anthropogenic emissions. It is not surprising that the seasonal cycle of afternoon values at the tower is larger than at Bermuda and that the phase at the tower is ahead of Bermuda. This data should be very useful to constrain regional and global model calculations of CO₂ exchange on the North American continent. The results for the first 2 years of observations at the North Carolina tower are published in Bakwin et al. (1995)

References


Figure 1

South Pole

Samoa

Mauna Loa

Barrow
WITN Tower Daily Averages

Figure 3
Because N. Trivett, the author of a draft WMO CO₂ measurement manual, was unable to attend this meeting, the discussion of the manual was limited to mostly general comments. The meeting participants were encouraged to send detailed comments directly to Dr. Trivett, who would then circulate a revised draft.

The meeting participants were very supportive of the draft manual. It was agreed that a very specific and detailed manual would be most useful. At the same time, it was felt that the manual should include a statement explaining that the recommended procedures would undoubtedly change as a result of increased knowledge and technological advances.

K. Holmén suggested that a discussion of in situ CO₂ data processing be included in the manual. This would include calculating CO₂ mixing ratios from raw data and subsequent data editing and data selection procedures. Since there are currently no agreed-upon data processing methods, NOAA/CMDL offered to include its methods, as an example, in an appendix to the manual.

The representatives from WMO and CDIAC both expressed interest in supporting the production of this manual.
ANNEX 7: CYLINDER PREPARATION FOR CMDL NATURAL AIR STANDARDS

The procedure that follows is used at NOAA/CMDL to fill high-pressure cylinders for use as measurement standards.

A. **New or hydrotested cylinder**
   1. Vent cylinder to ambient pressure.
   2. Fill the cylinder to ~300 psig with dry natural air and then vent to ambient. Repeat this step.
   3. Fill the cylinder to ~500 psig with dry natural air and store for 1-2 weeks.
   4. Vent to ambient pressure.
   5. Spike the cylinder with the appropriate amount of 10% or 0% CO₂-in-air.
   6. Fill the cylinder to >2000 psig with ambient air.
      a. The ambient CO₂ is monitored by NDIR during filling.
      b. The water vapor content of the filled cylinder is measured and must be <5 ppm. It is usually <1 ppm.

B. **Previously used cylinder**
   1. Fill to ~300 psig with dry natural air and then vent to ambient pressure.
   2. Spike as appropriate, then fill to >2000 psig with ambient air.
   3. Measure H₂O (<5 ppm).
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116. GAW Guide


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