



General Search Results--Full Record

Article 4 of 6



An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements

Novelli PC, Connors VS, Reichle HG, Anderson BE, Brenninkmeijer CAM, Brunke EG, Doddridge BG, Kirchhoff VWJH, Lam KS, Masarie KA, Matsuo T, Parrish DD, Scheel HE, Steele LP

JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES

103: (D15) 19285-19293 AUG 20 1998

Document type: Article **Language:** English **Cited References:** 26 **Times Cited:** 16

Abstract:

The Measurement of Air Pollution from Satellite (MAPS) instrument measures carbon monoxide (CO) in the middle troposphere from a space platform. In anticipation of the deployment of MAPS aboard the space shuttle Endeavor for two 10-day missions in 1994, plans were made to prepare a set of correlative measurements which would be used as part of the mission validation program. Eleven laboratories participated in the correlative measurement program by providing NASA with the results of their CO field programs during April and October 1994. Measurements of CO in the boundary layer, while not used in the MAPS validation, provide a picture of CO in the lower troposphere. Because measurements of CO made by different laboratories have been known to differ significantly, all correlative team members participated in an intercomparison of their measurements to define potential differences in techniques and calibration scales. While good agreement was found between some laboratories, there were differences between others. The use of similar analytical techniques and calibration scales did not always provide similar results. The results of the intercomparisons were used to normalize all ground-based measurements to the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory CO reference scale. These data provide an internally consistent picture of CO in the lower atmosphere during spring and fall 1994.

KeyWords Plus:

REFERENCE SCALE, CO

Addresses:

Novelli PC, NOAA, Climate Monitoring & Diagnost Lab, 325 Broadway, MS R-E-CG1, Boulder, CO 80303 USA.

NOAA, Climate Monitoring & Diagnost Lab, Boulder, CO 80303 USA.

NASA, Langley Res Ctr, Hampton, VA 23681 USA.

Natl Inst Water & Atmospher Res, Inst Geol & Nucl Sci, Lower Hutt, New Zealand.

CSIR, EMATEK, AIM, Stellenbosch, South Africa.

Univ Maryland, Dept Meteorol, College Pk, MD 20742 USA.

Inst Nacl Pesquisas Espaciais, Sao Paulo, Brazil.

Hong Kong Polytech Inst, Dept Civil & Struct Engn, Hong Kong, Hong Kong.

Univ Colorado, Cooperat Inst Res Environm Sci, Boulder, CO 80309 USA.

Japan Meteorol Agcy, Tokyo, Japan.

NOAA, Aeron Lab, Boulder, CO 80303 USA.

Fraunhofer Inst Atmosphar Umweltforsch, D-8100 Garmisch Partenkirchen, Germany.

CSIRO, Div Atmospher Res, Aspendale, Vic 3195, Australia.

Publisher:

AMER GEOPHYSICAL UNION, WASHINGTON

IDS Number:
112LE

ISSN:
0747-7309

Article 4 of 6



Copyright © 2001 Institute for Scientific Information

An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements

P.C. Novelli,¹ V.S. Connors,² H.G. Reichle, Jr.,^{2,3} B.E. Anderson,²
 C.A.M. Brenninkmeijer,^{4,5} E.G. Brunke,⁶ B.G. Doddridge,⁷ V.W.J.H. Kirchhoff,⁸
 K.S. Lam,⁹ K.A. Masarie,^{1,10} T. Matsuo,¹¹ D.D. Parrish,¹² H.E. Scheel,¹³ and
 L.P. Steele¹⁴

Abstract. The Measurement of Air Pollution from Satellite (MAPS) instrument measures carbon monoxide (CO) in the middle troposphere from a space platform. In anticipation of the deployment of MAPS aboard the space shuttle *Endeavor* for two 10-day missions in 1994, plans were made to prepare a set of correlative measurements which would be used as part of the mission validation program. Eleven laboratories participated in the correlative measurement program by providing NASA with the results of their CO field programs during April and October 1994. Measurements of CO in the boundary layer, while not used in the MAPS validation, provide a picture of CO in the lower troposphere. Because measurements of CO made by different laboratories have been known to differ significantly, all correlative team members participated in an intercomparison of their measurements to define potential differences in techniques and calibration scales. While good agreement was found between some laboratories, there were differences between others. The use of similar analytical techniques and calibration scales did not always provide similar results. The results of the intercomparisons were used to normalize all ground-based measurements to the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory CO reference scale. These data provide an internally consistent picture of CO in the lower atmosphere during spring and fall 1994.

Introduction

During the past 25 years, measurements of carbon monoxide (CO) in the atmosphere have been made by research groups around the world. These were used to describe the distributions of CO in the boundary layer and in the upper troposphere,

evaluate trends in atmospheric mixing ratios, and examine the role of CO in atmospheric chemical cycles [Seiler and Junge, 1970; Logan *et al.*, 1981; Novelli *et al.*, 1992, and references therein]. It has been reported, however, that measurements of CO made by different laboratories may differ by as much as 30%. These differences were believed due, in large part, to differences in the calibration gases used in the analysis [Weeks *et al.*, 1989; Kirchhoff and Marinho, 1990; Novelli *et al.*, 1991]. In the absence of experiments comparing CO measurements made by various groups, the combination of field data in an interpretable manner was limited, preventing the development of an accurate picture of global CO distributions. This knowledge is needed for a rigorous evaluation of the current understanding of the global CO cycle.

Our programs combine space-based measurements of CO [Connors *et al.*, 1996; Reichle *et al.*, this issue] with a set of intercalibrated ground-based measurements to provide a detailed picture of CO in the troposphere. These measurements can be used to examine the distributions of CO in the troposphere, examine its transport from source regions, and serve to validate models of its global budget.

Carbon monoxide mixing ratios in the middle troposphere have been examined for short periods of time using the Measurement of Air Pollution from Satellites (MAPS) instrument. MAPS measures CO from a space platform using gas filter correlation radiometry, with a maximum signal at approximately 400 mbar [Reichle *et al.*, 1986, 1990, this issue]. During previous flights of MAPS (in 1981 and 1984) the mission validation was attempted by comparing measurements of CO made from space to those made in the middle troposphere from

¹NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado.

²NASA Langley Research Center, Hampton, Virginia.

³Now at Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh.

⁴National Institute for Water and Atmospheric Research (NIWA), Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand.

⁵Now at Max Planck Institute for Chemistry, Mainz, Germany.

⁶ADM-EMATEK, CSIR, Stellenbosch, South Africa.

⁷Department of Meteorology, University of Maryland, College Park.

⁸Instituto Nacional de Pesquisas Espaciais (INPE), San Jose dos Campos, Sao Paulo, Brazil.

⁹Department of Civil and Structural Engineering, Hong Kong Polytechnic Institute, Hong Kong.

¹⁰Also at Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder.

¹¹Japan Meteorological Agency, Tokyo

¹²NOAA Aeronomy Laboratory, Boulder, Colorado.

¹³Fraunhofer Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen, Germany.

¹⁴Commonwealth Scientific and Industrial Research Organization (CSIRO), Division of Atmospheric Research, Aspendale, Australia.

Copyright 1998 by the American Geophysical Union.

Paper number 97JD00031.
 0148-0227/98/97JD-00031\$09.00

aircraft platforms. These correlative measurements were made by two laboratories using different methods and calibration scales. The effectiveness of the validation programs was limited by the sparsity of and inconsistencies in the correlative measurements. The latter were traced to differences in the calibration scales used by the participating laboratories (Reichle *et al.*, 1990).

Prior to the 1994 flights, a correlative measurement team was assembled that agreed to provide the MAPS team with the results of their field measurement programs during the periods of the 1994 missions. To maximize the usefulness of the correlative data, all team members agreed to participate in an intercomparison of CO measurements.

The correlative measurement team had four goals: (1) to compare CO measurements made by the different laboratories, (2) to use the intercomparison results to normalize measurements made in the boundary layer and the free troposphere to a common scale, (3) to use the internally consistent data set to create a detailed picture of CO distributions in the lower atmosphere, and (4) to provide CO mixing ratios measured in the middle troposphere for use in the MAPS validation program. The first three goals are addressed in this paper; the validation of the MAPS measurements is discussed by Reichle *et al.* [this issue].

Methods

Eleven laboratories participated in the intercomparison experiment. The principal investigators, their analytical methods and calibration schemes, and the locations of their field measurements are given in Table 1. The analytical methods in the intercomparison included gas chromatography followed by hot mercuric oxide reduction detection (GC-HgO) and gas filter correlation (GFC) radiometry. GC-HgO uses chromatography to separate chemical components of air. Reduced species (such as CO) then react with solid mercuric oxide to form elemental mercury, which is measured photometrically. Low detection limits (2 parts per billion (ppb) (1 ppb = 1 nmole mole⁻¹)) and high precision (1-2% on multiple analyses) can be achieved. Gas filter correlation is a nondispersive infrared technique that determines the absorption of radiation in the fundamental wavelength of CO (4.7 μm). The precision of any reported value improves with longer averaging time and ranges from 1 to 10% (Parrish *et al.*, 1994; World Meteorological Organization (WMO), 1995a). Detection limits depend on instrument configuration and range from 20 to 100 ppb.

Both techniques require the use of external standards with known CO content to quantify samples having unknown CO. The accuracy of both measurements reflects the sum of the accuracies of the analytical method and the reference gases. While GFC has a linear response over a wide range of CO concentrations, GC-HgO often exhibits nonlinear response over those found in the troposphere. Results from the GC-HgO technique are therefore sensitive to the calibration procedure used. Detailed descriptions of both methods can be found in the works of Crill *et al.* [1995] and WMO [1995a].

The intercomparison experiment was organized by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) as a round robin calibration of four CO-in-air mixtures. The standards were purchased from Scott-Marrin, Inc. (Riverside, California), with the following target (unanalyzed) trace gas concentrations: 500 ppb H₂, 1700 ppb CH₄, 350 ppm CO₂, and

either 50, 100, 150 or 200 ppb CO. The four standards are henceforth referred to by these nominal CO concentrations. The four calibration gases were expected to reflect the range of CO mixing ratios found in the troposphere during spring and summer, the seasons of the scheduled flights of MAPS. Each standard was shipped unmarked with a dedicated two-stage, brass, high-purity, high-pressure regulator for gas delivery (Scott Specialty Gases, Plumsteadville, Pennsylvania). Because there was only a limited supply of calibration gas available for the intercomparison, each laboratory was asked to use a minimum amount for their analysis. The discreet sampling of the GC-HgO method (which uses very small sample volumes) may have been better suited for this experiment than the GFC method (which benefits from longer sampling periods).

The experiment was conducted "blind"; only CMDL knew the nominal concentrations of the standards prior to their distribution. About halfway through the experiment, preliminary results from the first five laboratories were provided to their principal investigators. Upon completion of the round robin, results were provided to all participants. To check for drift in the standards during the experiment, CMDL calibrated the standards three times: at the beginning, in the middle, and at the conclusion of the experiment (Table 2). The precision on a CO value assigned to a cylinder by CMDL on the basis of calibrations made days or weeks apart typically ranges from ± 0.5 to 1%. Within this uncertainty no significant change in the CO content of the standards was detected by CMDL.

Intercomparison Results

The results of the intercomparison (Table 3) show that while there was generally good agreement between the laboratories, there were also some differences. Since two of the goals of the intercomparison were to define possible differences in measurements at various field sites and to subsequently normalize field data to a common scale using the results of the intercomparison, it was important that the laboratories use the same protocols in the laboratory which were used in the field. Each laboratory was asked to calibrate the standards using experimental protocols mimicking those used at their field sites. In many cases it was impractical to calibrate the standards at each field site. As a result, many laboratories made their measurements in their home laboratory. The intercomparison results were used assuming that measurements made at the home labs and the field sites were consistent. This is a fair assumption for the GC method but perhaps less so for GFC, where analysis times were limited by the experimental design. A long-term intercomparison of field measurements made by University of Maryland (UMd) and CMDL show somewhat better agreement than that of the laboratory experiment [Doddridge *et al.*, this issue]. This improvement reflects the longer averaging time used in the field GFC measurements.

In this paper we do not describe the differences between individual laboratories; the results of the experiment are presented in Table 3 for the reader to make those comparisons. In reviewing the results, it should be noted that institutions, which measure CO in consistently high or low CO environments, may not have optimized their instruments for the range of CO levels in the standards.

Next we comment on two general characteristics of the data set and provide possible explanations for systematic differences

Table 1. List of Participants, Their Methods, Standards, and Sites of Field Measurements

Identification*	Principal Investigator	Method/Standards†	Calibration‡	Sites	Reference
CMDL	P.C. Novelli	GC-HgO/CMDL	2	Niwot Ridge, Colorado Mauna Loa, Hawaii Pt. Barrow, Alaska NOAA/CMDL Cooperative Air Sampling Network	Novelli <i>et al.</i> [1992]
NASA-DC8	B.E. Anderson	GC-HgO/CMDL	1	North America aircraft flights	**
UMd	B.G. Doddridge	GFC/NIST	1,3	Mace Head, Ireland Heimaey, Iceland Ragged Point, Barbados Chesapeake Bay, aircraft	Doddridge <i>et al.</i> [1992]
IFU	H.E. Scheel	GC-HgO/IFU	2	Zugspitze, Germany	Cvitas and Kley [1994]
NIWA	C.A.B. Brenninkmeijer	GC-HgO/NIWA	2	Baring Head, New Zealand	Brenninkmeijer [1993]
CSIRO	L.P. Steele	GC-HgO/CMDL	2	Cape Grim, Tasmania Pt. Charles, Australia Cape Ferguson, Australia Mawson, Antarctica	**
CSIR	E.G. Brunke	GC-HgO/IFU	2	Cape Point, South Africa	Brunke <i>et al.</i> [1990]
NOAA-AL	D.D. Parrish	GFC/NIST	1,3	Sable Island, Canada	Parrish <i>et al.</i> [1994]
JMA	T. Matsuo	GFC/CITI	2	Kyori, Japan Misamisima, Japan	WMO [1995b]
HKP	K.S. Lam	GFC/NIST	1,3	Cape D'Aguilar, Hong Kong	Parrish <i>et al.</i> [1994]
INPE	V.W.J. Kirchhoff	GC-HgO/OGI, CMDL	1	Cuiaba, Brazil	Kirchhoff and Marinho [1990]

*Laboratories are listed in chronological order of their calibration of the standards. CMDL, National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory, United States; CSIR, Council for Scientific and Industrial Research, South Africa; CSIRO, Commonwealth Scientific and Industrial Research Organization, Australia; HKP, Hong Kong Polytechnic University, Hong Kong; IFU, Fraunhofer Institute for Atmospheric Environmental Research, Germany; INPE, Brazilian Institute for Space Research, Brazil; JMA, Japan Meteorological Agency, Japan; NASA, National Aeronautics and Space Administration, United States; NIWA, National Institute of Water and Atmospheric Research, New Zealand; NOAA-AL, NOAA Aeronomy Laboratory, United States; Umd, University of Maryland, College Park.

†Analytical method as defined in text.

‡Standard scale: CMDL, CMDL CO scale; NIST, National Institute of Science and Technology, United States; OGI, Oregon Graduate Institute; CITI, Chemical Inspection and Technology Institute; NIWA, (as above).

§Calibration procedure: 1 = one point calibration; 2 = multipoint calibration; 3 = standard dilution.

**Not provided.

between laboratories. First, it is clear that the choice of analytical method strongly influenced the results. The uncertainties associated with measurements made by gas filter correlation were greater than those determined by GC-HgO reduction detection. These differences are directly related to the precision of the analytical method [WMO, 1995a] and are most dramatic at low CO levels where the errors associated with the mean CO values determined by GFC were on the average five times those determined by GC-HgO. While the error of any particular mixing ratio determined by GFC is, in part, dependent on the averaging time of the signal, GC-HgO reduction consistently produced more precise results under the experimental conditions of the intercomparison.

Second, it was found that laboratories using similar methods and a common reference scale could have significant differences in the CO values they assigned the standards. CMDL, the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO), the Brazilian Institute for Space Research (Instituto Nacional de Pesquisas Espaciais (INPE)), and the National Aeronautics and Space Administration-DC8 (NASA) all used GC-HgO and standards referenced to the CMDL CO scale, but the mixing ratios reported for these standards differed by as much as 50%. CSIRO and NASA used standards obtained directly from CMDL. The relationship between the INPE standards and CMDL was less clearly defined. In the past, INPE used CO standards from the Oregon Graduate Center.

Table 2. Results of Multiple Calibrations of the Four MAPS Standards by CMDL, 1993 to 1995

Nominal CO	July 1993	July 1994	October 1995	Mean
50	51.5 (0.21)	51.9 (0.50)	51.1 (0.95)	51.5 (0.40)
100	97.1 (0.40)	98.2 (0.29)	97.6 (0.55)	97.6 (0.55)
150	147.7 (0.90)	148.1 (0.40)	147.4 (0.24)	147.7 (0.35)
200	197.4 (0.97)	198.3 (1.20)	198.4 (1.16)	198.0 (0.55)

All mixing ratios are expressed as parts per billion by mole fraction, referenced against the CMDL CO calibration scale. Values in parentheses are one standard deviation.

commercial sources, and NASA. For the calibration of the four MAPS standards, a reference gas reportedly tied to the CMDL scale was used. However, in light of the intercomparison results it is apparent that this reference was lower than its assigned CO value. The mixing ratios reported for the MAPS standards on the basis of recalibration of INPE working standards, using a standard obtained directly from CMDL (Table 3), suggest that the difference between laboratories was largely because of a problem with the reference gas used.

Differences also exist among the experimental results of UMD, NOAA Aeronomy Laboratory (AL), and Hong Kong Polytechnic University (HKP). These laboratories all use GFC as their analytical technique in combination with standards from the National Institute of Standards and Technology (NIST). Reported precisions for these laboratories range from 1 to 5% (referenced in Table 1). Nonetheless, the reported mean CO values were found to differ by 9 to 20 ppb (10-14%). The lowest NIST standard reference material available for CO is

approximately 10 ppm CO, about 50-200 times greater than typical CO in the lower troposphere. Therefore the procedure used to dilute and introduce the standards into the airstream and subsequently calibrate the samples affects the results.

It is apparent that the use of comparable methods and a common reference scale do not, a priori, guarantee similar results. Analytical procedures must also be considered. Many GC-HgO detectors reportedly exhibit nonlinear response over the range of atmospheric CO concentrations. Approaches to correct the nonlinearity may vary from group to group yielding slightly different results. Most commercially available GFCs required modifications to measure the low amounts (<100 ppb) of CO found in the atmosphere [Dickerson and Delany, 1988]. Small differences in these modifications as applied to a particular instrument could lead to the variation as observed in the intercomparison results.

Data Integration

The results of the intercomparisons were used to normalize the field measurements from each laboratory to the CMDL CO reference scale. The CMDL scale was chosen because (1) the origin and evaluations of this scale have been well documented in the literature; (2) it is in agreement (to within 1%) with the high concentration CO scale distributed by NIST; (3) it is thought to have an accuracy between 1 to 2% (although it is difficult to evaluate absolute accuracy, we base our estimate upon comparison to the NIST CO scale and others); and (4) it serves as the WMO primary calibration scale, and we anticipate it will be maintained in the future [Novelli et al., 1991, 1994; WMO, 1995a].

Table 3. Intercomparison Results

Laboratory	Cylinder Identification			
	CCI22042	CCI22056	CCI22045	CCI22041
CMDL*	51.5 (0.12)	97.1 (0.23)	147.7 (0.52)	197.4 (0.58)
UMd	59.0 (2.4)	101.9 (2.1)	151.8 (2.7)	199.5 (1.4)
NASA	56.4 (0.64)	101.2 (0.44)	151.1 (0.58)	197.8 (0.39)
IFU	51.9 (0.90)	96.9 (1.2)	149.0 (1.0)	200.4 (0.36)
NIWA†	56.1 (0.6)	102.7 (1.0)	154.1 (1.5)	204.5 (2.0)
CSIRO‡				
a	52.6 (0.12)	98.5 (0.17)	148.7 (0.28)	196.9 (0.35)
b	50.9	98.6	149.2	196.9
CSIR	53.3 (0.25)	99.5 (0.15)	152.7 (0.1)	203.4 (2.1)
CMDL‡	51.9 (0.29)	98.2 (0.17)	148.1 (0.23)	198.3 (0.69)
JMA	49.7 (2.0)	95.5 (4.2)	152.9 (2.7)	197.1 (1.8)
HKP	50 (2.5)	104.3 (9.8)	159 (4.6)	187 (2.1)
AL	54.5 (2.2)	101.0 (2.6)	155.9 (2.4)	207.2 (1.3)
INPE				
a	39.8	65.8	96.3	129.5
b	58.9	97.4	142.5	191.6
CMDL‡	51.1 (0.55)	97.6 (0.32)	147.4 (0.14)	198.4 (0.67)

CO mixing ratios are reported in parts per billion. Values in parentheses are the standard error of the mean of three to four calibrations.

*July 1993.

†Reported uncertainty as 1%

‡(a) Reported 1994. (b) revised 1996, no error reported.

§July 1994.

||No error reported, a, original values assigned the standards by INPE and used in the reprocessing of the April and October INPE field measurements at Cuiaba, Brazil; b, recalculated mixing ratios based upon comparison of the INPE working standard to a CO-in-air standard purchased from CMDL January 1996.

¶October 1995

CO CALIBRATION ADJUSTMENT

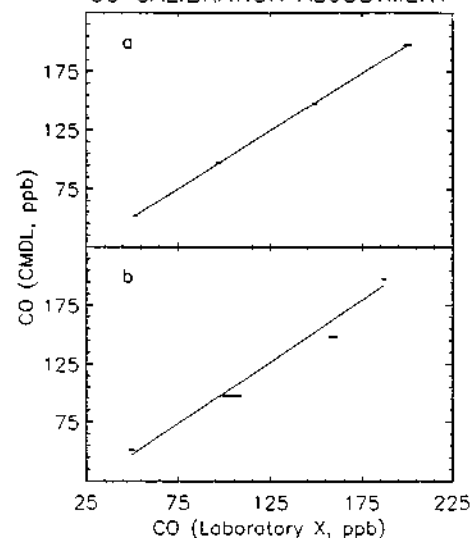


Figure 1. (a) Plot of the Fraunhofer Institute for Atmospheric Environmental Research, Germany (IFU), calibration results versus those of the Climate Monitoring and Diagnostics Laboratory (CMDL). Curve is the orthogonal second-order regression through the data. The curve coefficients and their standard deviation are also presented. (b) Plot of Hong Kong Polytechnic University (HKP) calibration results versus those of CMDL. The curve is the orthogonal linear regression through the data. Curve coefficients and their standard deviation are presented in Table 4.

The relationship between the results of each laboratory (Laboratory X) and CMDL was derived by plotting the assigned CO values against one another. The mixing ratios and standard errors assigned to the four standards were fit using a second-order orthogonal regression, and the curve coefficients and their

standard deviations were determined using computational routines developed by Boggs and Rogers [1990] (Figure 1, Table 4). These coefficients were then applied directly to the field data of Laboratory X; the resulting reprocessed mixing ratios were effectively equivalent to those calculated against the CMDL scale. The equations used to describe the relationship between Laboratory X and CMDL and then used to normalize the field data from each laboratory to the CMDL scale are presented in Table 4. The CO levels observed at Cape D'Agular, Hong Kong, were the greatest found at any of our sites and much higher than those used in the intercomparison experiment. Hence we found the reprocessed field measurements were quite sensitive to the function used to define the relationship between HKP and CMDL laboratory results. When a second-order polynomial was used to describe this relationship, the resulting normalized field measurements were extreme (often >3000 ppb relative to the CMDL scale). These high values resulted from the curvature of the function at concentrations above that of the highest standard (200 ppb). When normalized to the CMDL scale using a linear fit to the calibration results, the HKP field data, while still high, were more similar to those found at other regionally polluted sites (such as the Tae-ahn Peninsula, Korea).

The agreement between the different laboratories and CMDL was generally quite good, and the slope of their relationship neared unity with only small offsets. For most sites the conversion to the CMDL scale from the original data typically resulted in changes to the mixing ratios of less than 10%. The one exception was the data from Cuiaba, Brazil. The intercomparison indicated INPE had a nearly constant low offset of 30% relative to CMDL, a correction for which was applied to the field data. This offset was largely eliminated after INPE obtained a standard directly tied to the CMDL scale.

Reichle et al. [this issue] present CO mixing ratios determined from several aircraft flights (at altitudes of 7 to 10 km) made nearly coincident with MAPS overpasses. Comparisons of the aircraft and MAPS results indicated that CO mixing ratios determined from the MAPS instrument agreed with those made from the aircraft (normalized to the CMDL CO scale) to better than $\pm 10\%$. The middle troposphere CO mixing ratios from MAPS and all the reprocessed boundary layer CO mixing ratios provided by the correlative team are, therefore, also comparable to within 10%. These data provide a unique, intercalibrated, multidimensional data set that can be used to study the global

Table 4. Coefficients for Equations Describing the Relationship of Laboratory X and CMDL

Laboratory X	a ₀	a ₁	a ₂
CMDL	0.0000 ± 0.0000	1.0000 ± 0.0000	0.0000 ± 0.0000
CSIR	-2.3387 ± 1.6598	1.0251 ± 0.0375	-0.0002 ± 0.0002
CSIRO	4.7628 ± 0.4452	0.9001 ± 0.0100	0.0004 ± 0.0001
HKP*			
a	-4.2561 ± 10.6380	1.0679 ± 0.0725	
b	34.0831 ± 18.8250	0.1613 ± 0.4523	0.0038 ± 0.0199
IFU	-1.7795 ± 1.7194	1.0433 ± 0.0331	-0.0002 ± 0.0001
INPE	-24.5630 ± 0.4570	1.9932 ± 0.0137	-0.0021 ± 0.0001
JMA	10.9677 ± 8.9165	0.7759 ± 0.0195	0.0009 ± 0.0008
NASA-DC8	-4.145 ± 3.280	0.9799 ± 0.0583	0.0002 ± 0.0002
NIWA	-3.5360 ± 0.4075	0.9830 ± 0.0085	0.0000 ± 0.0004
NOAA-AL	-0.0833 ± 4.742	0.9494 ± 0.0830	0.0000 ± 0.0003
UMd	-10.8951 ± 3.4719	1.0726 ± 0.0591	-0.0002 ± 0.0002

*Coefficients presented for a, linear regression, and b, quadratic fit.

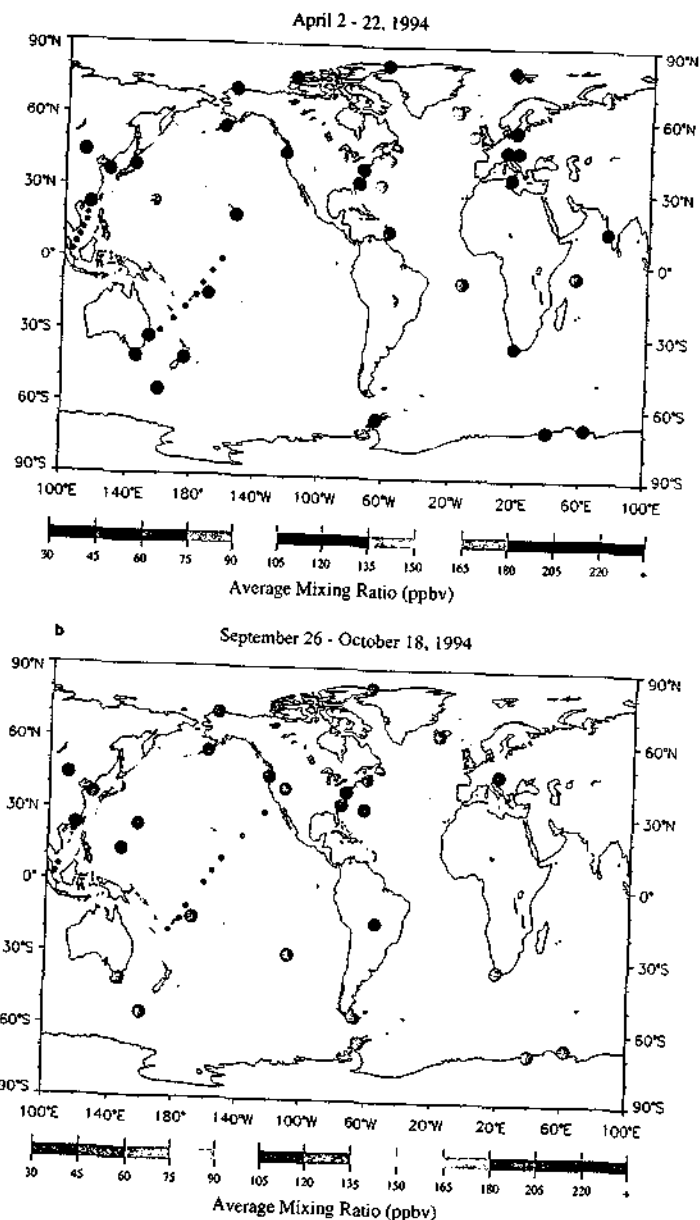


Plate 1. Boundary layer, mission-averaged CO mixing ratios provided by correlative team members. All mixing ratios have been normalized to the CMDL scale as described in the text. Large symbols indicate land sites, smaller symbols indicate shipboard sites. Correlative measurement sites located above the boundary layer (Mauna Loa, Hawaii; Niwot Ridge, Colorado; Zugspitze, Germany; and Tenerife, Canary Islands) are not represented. (a) April 2-22, 1994, (b) September 26 to October 18, 1994.

Table 5. Comparison of Flask and In Situ Mission-Averaged CO

Site*	April		October	
	Flask	In Situ	Flask	In Situ
CGO†	42.4 (1.9)	47.7 (1.5)	65.7 (1.3)	NA
BRW‡	183.3 (5.0)	182.5 (4.1)	128.8 (9.0)	125.4 (3.7)
MLO‡	121.3 (16.0)	NA	78.4 (7.8)	82.5 (6.5)
NWR‡	155.7 (8.2)	157.2 (23.3)	124.4 (12.6)	132.5 (50.6)
ICE§	174.4 (2.6)	170.2 (8.2)	124.9 (2.8)	133.4 (15.3)
RPB§	78.1 (8.0)	81.8 (8.0)	71.2 (1.0)	72.6 (12.4)
MHT§	169.9 (4.8)	160.7 (17.7)	137.1 (1.3)	128.7 (15.4)

CO mixing ratios in ppb. Values are the mission averages ± 1 standard deviation. NA, not available.

*April in situ, April 9-19, 1994; October in situ, September 30-October 11, 1994. All flask measurements were made by NOAA/CMDL, values represent average for April 2-22, 1994 (April), or September 26-October 18, 1994 (October). All CMDL results are referenced to NOAA/CMDL CO calibration scale. In situ measurements from laboratories other than CMDL were normalized to CMDL scale as described in the text.

†In situ measurements made by CSIRO at Cape Grim, Tasmania (CGO) based upon revised calibrations.

‡In situ measurements made by CMDL at Pt. Barrow, Alaska (BRW), Mauna Loa, Hawaii (MLO) and Niwot Ridge, Colorado (NWR).

§In situ measurements made by UMD at Heimaey Iceland (ICE), Ragged Point Barbados (RPB), and Mace Head, Ireland (MHT).

distribution of CO, its vertical and horizontal transport, and provide a constraint for model simulations of the global CO cycle. The complete correlative data set will be made available from the Carbon Dioxide Information Analysis Center, Oak Ridge, Tennessee.

Average CO mixing ratios measured in the boundary layer for periods corresponding to the April and October flights of MAPS are presented in Plate 1. As a whole, the sites were selected to represent regional scale air masses and not local environments. The measurements were made using instruments located in situ and by grab sampling techniques. Sites with in situ instruments provided hourly averaged CO mixing ratios. Less frequent measurements were made at sites where grab samples were collected. Many sites in Plate 1 were part of the CMDL cooperative air sampling network (Conway *et al.*, 1994), in which 2.5 L of air were collected about once per week in glass flasks and shipped to a central laboratory in Boulder, Colorado, for analysis. The CMDL sampling program, including the stability of the sample containers, calibration, and analytical techniques are described in detail by Novelli *et al.* (1991, 1992). The weekly flask results were combined to provide an average CO mixing ratio over the period of interest. At several locations in the southern hemisphere a single pair of flasks was collected by Commonwealth Scientific and Industrial Research Organization (CSIRO) during each mission (e.g., Cape Ferguson, Macquarie Island, and Point Charles, Australia; Mawson, Antarctica). Therefore the mixing ratios for these locations, as presented in Plate 1, represent a brief snapshot of CO at a specific time during the mission.

To examine how mission-averaged mixing ratios determined from three to four weekly flask samples compare to the continuous or quasi-continuous measurements made in situ, we compare the results from both approaches at seven sites (Table 5). Comparison of the CMDL flask sample results with the normalized in situ measurements of CMDL, CSIRO, and UMD indicate that the flask samples represented average conditions at these sites remarkably well during the MAPS flights. Often the grab samples and in situ mission-average CO values agreed to within a few ppb; all were within the standard deviation of the in situ mean. The locations where the mean values from flasks and in situ measurements had a greater absolute difference (Mace

Head, Niwot Ridge) were those that were occasionally impacted by strong local or regional anthropogenic CO sources. The larger standard deviations associated with the mean CO mixing ratios determined in situ illustrate that these sites were exposed to a wide range of CO levels during the MAPS flights.

In April, CO mixing ratios in the boundary layer typically approach their seasonal maximum in the northern hemisphere while beginning their recovery from the summer minimum in the southern hemisphere. In April 1994, CO levels in the background atmosphere were greatest (>180-185 ppb) in the high latitudes of the northern hemisphere and lowest (<40-45 ppb) in the high southern hemisphere. Extreme levels of CO (>250 ppb) were observed near cities (i.e., Hong Kong) and in regionally polluted areas such as eastern North America, Europe, and eastern Asia. High CO in these areas most likely reflects large surface emissions from the combustion of fossil fuels coupled with the near-seasonal minimum in the zonal scale destruction of CO by reaction with OH.

Mixing ratios in the southern hemisphere during April ranged from 75 ppb in the lower latitudes to about 40 ppb in the high southern hemisphere. One notable exception is Cuiaba in central Brazil. Higher CO at this location may reflect enhanced production of CO from the oxidation of nonmethane hydrocarbons emitted from the cerrado. Earlier measurements have clearly shown the tendency for higher CO mixing ratios in this area relative to those found in the marine boundary layer (Kirchhoff and Marinho, 1989). In April, across the Pacific Ocean (used to represent the unpolluted marine boundary layer (MBL)) there was a rather smooth transition from high CO in the high latitudes of the northern hemisphere to low CO mixing ratios in the south (180 to 40 ppb).

The distribution of CO in the boundary layer was much different in October. In the background MBL, CO levels were typically greater in the northern hemisphere compared with the south, but the difference between north and south was much smaller. This reflects the seasonal nature of the interhemispheric gradient, which reaches a maximum in April and a minimum in September. In regions affected by urbanization, elevated CO levels were again found, reflecting emissions from fossil fuel combustion and other industrial sources.

In October, enhanced CO was also measured in the tropics

over central Brazil, the tropical South Atlantic Ocean (Ascension Island), the southern South China Sea (SCS), and in northern Australia. In the southern hemisphere, September and October mark the height of the burning season, and astronaut photographs taken from the space shuttle show numerous fires over Brazil, Africa, and Australia during the period of the October flight [Reichle *et al.*, this issue]. The high CO levels found at Curitiba reflect widespread burning in Brazil. Ten-day isentropic back trajectories show that air reaching the southern part of the SCS was transported from the southeast over Indonesia, Kalimantan (formerly Borneo), and northern Australia. Burning is common in these regions [Hao *et al.*, 1990], and during this period, northern Australia experienced a severe drought that favored numerous wildfires. Thick smoke haze covered Singapore and the southern SCS during September and October 1994 [Singapore Meteorological Service, 1995]. These certainly contributed to the high CO levels measured in this area. The back trajectories also indicate air was transported southward over the Southeast Asian coast to the northern SCS. The high CO observed in the northern SCS may primarily reflect anthropogenic emissions from development to the north.

The distribution of CO in the boundary layer presented here clearly shows widespread pollution of the atmospheric boundary layer. In the northern hemisphere, emissions from urban centers in the midlatitudes lead to regional scale enhancements of CO. Relative to the April distributions of CO in October, mixing ratios in the southern tropics are elevated by nearly a factor of 2 by emissions from seasonal biomass burning.

Conclusion

The results of the intercomparisons conducted as part of the MAPS experiment indicate differences exist among CO measurements made by multiple laboratories. Before CO mixing ratios measured by different groups can be combined into a common data set, there is a clear need for intercomparison of the measurements. The intercomparison of standards, such as those made here, are one way to define differences in measurements. The intercomparison of field intercomparisons [Hoell *et al.*, 1985] and the long-term intercomparison of measurements at a background monitoring site [Doddridge *et al.*, 1994, this issue] are other ways to define differences in measurements.

The data presented here provide a unique picture of CO in the boundary layer. These data show the regional importance of two CO sources: fossil fuel burning in urbanized areas and CO emissions from regions under the influence of biomass burning. Novelli *et al.* [1995] use the internally consistent data set presented here in combination with the midtroposphere CO measurements by MAPS and the meteorology of the two missions to compare the distributions of CO near the surface with those in the midtroposphere in terms of the source, sinks, and transport of this gas.

Acknowledgments. The diligent efforts of all site personnel and sample takers were the basis of the data set presented here. Joyce Harris provided the South China Sea isentropic back trajectories. Funding from NASA, the NOAA Global Climatic Change Program and NSF (AEROCE) are gratefully acknowledged, as well as all other national and international programs that support the effort to define the distributions of CO in the troposphere.

References

- Boggs, P. T., and J. E. Rogers, Orthogonal distance regression, *Am. Meteorol. Climatol. Math.*, **112**, 183-194, 1990.
- Brenninkmeyer, C. A. M., Measurements of the abundance of ^{14}C in the atmosphere and the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric CO in New Zealand and Antarctica, *J. Geophys. Res.*, **98**, 10,595-10,614, 1993.
- Brunke, E. G., H. E. Scheel, and W. Seiler, Trends of tropospheric carbon monoxide, nitrous oxide, and methane as observed at Cape Point, South Africa, *Atmos. Environ.*, **24(A)**, 585-595, 1990.
- Connors, V. S., P. C. Novelli, and H. G. Reichle Jr., Space shuttle vees changing atmospheric carbon monoxide, *Environ. Sci. Technol.*, **77**, 466-467, 1996.
- Conway, T. J., P. P. Tans, L. S. Waterman, K. W. Thoning, D. R. Kuzis, K. A. Masarie, and N. Zhang, Evidence for interannual variability of the carbon cycle from the NOAA/CMDL global air sampling network, *J. Geophys. Res.*, **99**, 22,831-22,846, 1994.
- Crill, P. M., J. H. Butler, D. J. Cooper, and P. C. Novelli, Standard analytical methods for measuring trace gases in the environment, in *Biogenic Trace Gases: Measuring Emissions From Soil and Water*, edited by P. A. Matson and R. C. Harris, 394 pp., Blackwell Sci., Cambridge, Mass., 1995.
- Cvitas, T., and D. Kley (Eds.), The TOR Network. A Description of TOR Measurement Stations, *EUR Spec. Publ.*, **182** pp., Eur. Exp. on the Transp. of Environ. Relevant Trace Constituents in the Troposphere over Eur., Garmisch-Partenkirchen, Germany, 1994.
- Dickerson, R. R., and A. C. Delany, Modification of a commercial gas filter correlation CO detector for enhanced sensitivity, *J. Atmos. Oceanic Technol.*, **5**, 424-431, 1988.
- Doddridge, B. G., R. R. Dickerson, T. G. Spain, S. J. Oltmans, and P. C. Novelli, Measurements of carbon monoxide at Mace Head, Ireland, in *Ozone in the Troposphere and the Stratosphere, Proc. Quad. Ozone Symp., 1992*, edited by R. D. Hudson, pp. 134-137, NASA Conf. Publ. 3366, 1994.
- Doddridge, B. G., R. M. Morales, K. P. Rhoads, J. T. Merrill, P. C. Novelli, R. R. Dickerson, V. S. Connors, and H. G. Reichle Jr., Ground-based and airborne observations of carbon monoxide during NASA Measurements of Air Pollution From Satellites (MAPS) missions SRL-1 and SRL-2, *J. Geophys. Res.*, this issue.
- Hao, W. M., M. H. Liu, and P. J. Crutzen, Estimates of annual and regional release of CO₂ and other trace gases to the atmosphere from fires in the tropics based on the FAO statistics for the period 1975-1980, in *Fire in the Tropical Biota: Ecosystems Processes and Global Challenges*, edited by J. G. Goldmann, pp. 440-462, Springer-Verlag, New York, 1990.
- Hoell, J. M., Jr., G. L. Gregory, D. S. McDougal, G. W. Sachse, G. F. Hill, E. P. Condon, and R. A. Rasmussen, An intercomparison of carbon monoxide measurement techniques, *J. Geophys. Res.*, **90**, 12,880-12,889, 1985.
- Kirchhoff, V.W.J.H., and E.V.A. Marinho, A survey of continental concentrations of atmospheric CO in the Southern Hemisphere, *Atmos. Environ.*, **23**, 461-466, 1989.
- Kirchhoff, V.W.J.H., and E.V.A. Marinho, Surface carbon monoxide measurements in Amazonia, *J. Geophys. Res.*, **95**, 16,933-16,943, 1990.
- Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, **86**, 7210-7254, 1981.
- Novelli, P. C., J. W. Elkins, and L. P. Steele, The development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, *J. Geophys. Res.*, **96**, 13,109-13,121, 1991.
- Novelli, P. C., L. P. Steele, and P. P. Tans, Mixing ratios of carbon monoxide in the troposphere, *J. Geophys. Res.*, **97**, 20,731-20,750, 1992.
- Novelli, P. C., J. E. Collins Jr., R. C. Myers, G. W. Sachse, and H. E. Scheel, Reevaluation of the NOAA/CMDL carbon monoxide reference scale and comparison with reference gases used at NASA-Langley and the Fraunhofer Institute, *J. Geophys. Res.*, **99**, 12,833-12,839, 1994.
- Novelli, P. C., V. S. Connors, H. G. Reichle Jr., R. E. Newell, and Y. Zhu, Carbon monoxide in the boundary layer and in the middle troposphere during October 1994, *Environ. Sci. Technol.*, **77**, 1995.
- Parnish, D. D., J. S. Holloway, and F. C. Fehsenfeld, Routine, continuous measurement of carbon monoxide with parts per billion precision, *Environ. Sci. Technol.*, **28**, 1615-1618, 1994.
- Reichle, H. G., Jr., V. S. Connors, J. A. Holland, W. D. Hynes, H. A. Wallio, J. C. Casas, B. B. Gormsen, M. A. Saylor, and W. D. Hesketh, Middle and upper tropospheric carbon monoxide mixing ratios as measured by a satellite-borne remote sensor during November 1981, *J. Geophys. Res.*, **91**, 10,365-10,387, 1986.
- Reichle, H. G., Jr., V. S. Connors, J. A. Holland, R. T. Sherrill, H. A. Wallio, J. C. Casas, E. P. Condon, B. B. Gormsen, and W. Seiler, The distribution of middle tropospheric carbon monoxide during early October 1984, *J. Geophys. Res.*, **95**, 9845-9856, 1990.
- Reichle, H. G., Jr., et al., Space shuttle based global CO measurements during April and October 1994, MAPS instrument, data reduction, and data validation, *J. Geophys. Res.*, this issue.
- Seiler, W., and C. Junge, Carbon monoxide in the atmosphere, *J. Geophys. Res.*, **75**, 2217-2226, 1970.
- Singapore Meteorological Service (SMS), Smoke haze over Singapore, Malaysia, and Indonesia, *WMO Bull.*, **44**, 147-150, 1995.
- Weeks, J. A., I. E. Galbally, P. J. Fraser, and G. Mathews, Comparison of the carbon monoxide standards used at Cape Grim and Aspendale, in *Baseline Atmospheric Program 1987*, edited by B. W. Forgan and G. P. Ayers, pp. 21-25, Austr. Gov. Dep. Sci. and Technol., Canberra, Australia, 1989.
- World Meteorological Organization (WMO), Report of the WMO meeting of experts on global carbon monoxide measurements, *WMO Rep. 98*, 75 pp., edited by P. C. Novelli and R. M. Rosson, Geneva, 1995a.

World Meteorological Organization (WMO), *WDCGG Data Report 7*, 190 pp., J. Meteorol. Agency, Tokyo, 1995b.

B. E. Anderson and V. S. Connors, NASA Langley Research Center, Hampton, VA 23681.

C. A. M. Brenninkmeyer, Max-Planck Institute for Chemistry, Mainz, Germany.

E. G. Brunke, ARM-EMATEK, CSIR, Stellenbosch, South Africa.

B. G. Doddridge, Department of Meteorology, University of Maryland, College Park, MD 20742.

V. W. J. H. Kirchhoff, INPE, Sao Jose dos Campos, Sao Paulo, Brazil.

K. S. Lam, Department of Civil and Structural Engineering, Hong Kong Polytechnic Institute, Hong Kong.

T. Matsuo, Japan Meteorological Agency, Tokyo, Japan.

P. C. Novelli, and K. A. Masarie, NOAA Climate Monitoring and Diagnostics Laboratory, 325 Broadway, MS R/E/CG1, Boulder, CO 80303. (e-mail: pnovelli@cmdl.noaa.gov.)

D. D. Parnish, NOAA Aeronomy Laboratory, Boulder, CO 80303.

H. G. Reichle, Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27607.

H. E. Scheel, Fraunhofer Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen, Germany.

L. P. Steele, CSIRO, Division of Atmospheric Research, Aspendale, Australia.

(Received July 15, 1996; revised December 19, 1996; accepted December 19, 1996.)