Evaluation of standards and methods for continuous measurements of carbon monoxide at ground-based sites in Asia

by

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Abstract

An international exercise to directly assess the consistency of standards and methods for measuring carbon monoxide (CO) was conducted as part of the East Asian Regional Experiment 2005 (EAREX 2005) in the framework of the Atmospheric Brown Clouds (ABC) project. Four groups representing Japan, Korea, Hong Kong, and Taiwan made comparisons at the Gosan super-site on Jeju Island, Korea, in March 2005, by setting up individual instruments with gas standards which are commonly used in ground-based monitoring programs in Asia. Intensive comparisons between two Japanese groups showed that a non-dispersive infrared absorption (NDIR) instrument agreed fairly well with a gas chromatograph / reduction gas detector (GC/RGD) with 1-h time resolution, confirming that NDIR methods are useful for monitoring, in particular, large temporal variations of CO in ambient air. Although international comparison of ambient measurements by NDIR indicated general agreement, comparison of gas standards revealed difficulties in preparing accurate and stable standard gases for monitoring CO at ambient levels.

1. Introduction

Carbon monoxide (CO) is an important trace gas in the troposphere, playing a key role in regulating oxidizing capacity of the atmosphere through reactions with the principal oxidizing agent, hydroxyl radical (OH). Owing to

its relatively long atmospheric lifetime (i.e., 1–2 months), CO can be used as a tracer for combustion sources, and it has often been measured with ozone (O₃) and other chemical species to help interpretation of their variability. Measurements of CO also help to validate transport schemes in chemistry transport models and to improve bottom-up estimates in emissions inventories of air pollutants. In particular, continuous measurements of CO in continental outflow plumes were used to quantify net O₃ formation (e.g., Parrish *et al.*, 1998; Kajii *et al.*, 1998) and

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emission ratios of carbon dioxide, elemental carbon, oxides of nitrogen, and halocarbons from anthropogenic sources based on correlations of these species against CO (e.g., Suntharalingam *et al.*, 2004; Palmer *et al.*, 2006; Matsumoto *et al.*, 2003; Takegawa *et al.*, 2004; Koike *et al.*, 2003; Yokouchi *et al.*, 2006; Wang *et al.*, 2002; Wang *et al.*, 2004). Therefore, improvement of accuracy, which includes trueness and precision, of CO measurements is a key factor in providing better constraints from in situ observations.

The East Asian Regional Experiment 2005 (EAREX 2005) experiment was conducted as part of the Atmospheric Brown Clouds (ABC) project, an international initiative supported by the United Nations Environmental Program, with the main focus on intercomparison of key chemical species and physical parameters that play an important role in climate change driven by short-lived air pollutants (Nakajima *et al.*, 2007). These factors broadly included gaseous species and aerosols, and radiatively important physical parameters. An activity to improve the capability of measuring gaseous chemical species was organized, and measurement and calibration techniques for two major gaseous species, O₃ and CO, were intercompared. The overall strategies and detailed results for O₃ are described elsewhere (Tanimoto *et al.*, 2007).

Measurements of CO made by different laboratories have been known to differ significantly (e.g., Novelli *et al.*, 1998). These differences reflect the accuracy of the analytical methods and the differences in calibration gas scales. The gas chromatograph / reduction gas detector (GC/RGD) is widely used to detect CO in ambient air at remote sites, as it is highly sensitive and selective to reduced species, including CO and H₂. However, this technique requires the frequent and careful maintenances and several standard gases at ambient levels to check and compensate for non-linear responses of HgO (Novelli *et al.*, 1998). The NDIR method is also broadly used to measure CO for air-quality monitoring because of its good linear response, wide dynamic range, and relatively high time resolution. However, the sensitivity of NDIR to CO is moderately affected by water vapor, and background levels are affected by temperature drifts (Parrish *et al.*, 1994). Accurate detection of CO at low mixing ratios by NDIR often suffers from these factors, and hence the detection limit and precision are, in principle, not as good as those of GC/RGD. On the other hand, NDIR has the advantage of a linear response, and needs only a single standard gas at levels higher than ambient. These two methods are complementary to each other.

The past intercomparison programs reported the differences in CO standard scales (e.g., Novelli *et al.*, 1998). Drift in the standard cylinders was identified as one of the limiting factors concerning scale stability. Preparing and keeping standard CO mixtures at low mixing ratios is still difficult because of positive artifacts during storage, likely

as a result of the oxidation of organics onto the internal metal surface of the cylinders (Novelli *et al.*, 1998). Furthermore, instrument limitations, such as non-linearity of GC/RGD, made the scale difficult to maintain, and reported data sometimes need revisions (Novelli *et al.*, 2003). The interconsistency of the CO scales in the World Meteorological Organization Global Atmospheric Watch program (WMO/GAW) has not yet been fully established (WMO, 2006). Beside WMO/GAW scale, gravimetric standards are widely used to calibrate CO instruments especially in national networks. However, the experiments comparing CO measurements made by various groups were limited, especially in Asia.

Worldwide networks based on flask samplings and laboratory analysis by GC/RGD are run by the WMO (http://www.wmo.ch/web/arep/gaw/gaw_home.html) and the US National Oceanic and Atmospheric Administration (NOAA) (<http://www.cmdl.noaa.gov/>) for the baseline monitoring of greenhouse gases and other trace species. NDIR instruments are more often used in air quality monitoring communities than in these networks, since this method has lower sensitivity but higher time resolution, and hence is suitable for tracking pollution episodes. For example, continuous measurements with NDIR in the Northern Hemisphere detected the enhancement in CO due to continental outflow from anthropogenic sources (e.g., Parrish *et al.*, 1998) and boreal forest fires (e.g., Tanimoto *et al.*, 2000; Jaffe *et al.*, 2004). NDIR methods are partly used at regional monitoring sites, where ambient CO mixing ratios vary greatly owing to polluted air masses. In fact, the Ryori, Yonagunijima, and Minamitorishima sites, operated by the Japan Meteorological Agency (JMA) as part of the WMO/GAW program, use an NDIR-based monitoring system (JMA, 2005). Sawa *et al.* (2007) analyzed the mechanisms of transport of widespread pollution events seen in CO data obtained at these stations.

In this paper, we describe experiments to intercompare the methods and standards for ambient measurements of CO. The objectives of this study were to examine the capability and characteristics of NDIR-based measurement systems, to identify technical issues related to instruments and gas standards, and to evaluate the consistency of CO data among individual groups. These activities will enhance the comparability of ambient CO data collected in multiple monitoring networks.

2. Experimental Settings

Standard gases and ambient data were compared in two activities: (1) ABC international (on-site) comparison at Gosan station, Korea (33°17'N, 126°10'E), where agreement of independent NDIR instruments was evaluated; and (2) ABC local (off-site) comparison at Tsukuba station, Japan (36°03'N, 140°08'E), where an NDIR technique was

evaluated with reference to a GC/RGD method.

2.1 International comparison

Table 1 lists all groups participating in the Gosan intercomparison, with a brief description of their instrument packages. Four groups from Korea, Hong Kong, Taiwan, and Japan participated. HKPU acted as a pilot laboratory for CO, and intensively compared gas standards from individual groups. Participating laboratories brought their CO monitors and laboratory standard gases. The instruments from Japan, Korea, and Hong Kong were based on the NDIR technique, but were all built by different manufacturers. Individual participants used independent standard gases and calibration procedures (span and zero). The Japanese group used gravimetrically prepared standard gases and calibrated the instrument daily by direct injection. Measurement cycles consisted of 40-min ambient measurement periods and 20-min zeroing periods each hour. Instruments were zeroed by passing sample air through a catalyst (Molecular Products, Sofnocat 514). The Korean group used a gravimetric gas standard and injected it into the instrument every 3 to 7 days after dynamic dilution based on mass-flow controllers with zero-air supplied by a zero-air generator (TEI, model 111). During the first week of the experiment, instrumental zeroing was tested twice a day with the same zero-air, but the zeroing frequency was increased to every hour afterward. The Hong Kong group

used a manometric gas standard manufactured by Scott-Marrin Cylinder (USA), which was traceable to the US National Institute of Standards and Technology (NIST). They calibrated the instrument daily by injecting the standard gas after dynamic dilution with zero-air supplied by a zero-air generator, as did the Korean group. The instrument was zeroed every 2 h by introducing zero-air. The sample air was not dehumidified for these three instruments. The Taiwanese group used a GC/RGD instrument. However, since the instrumental status was preliminary and the absolute mixing ratios were not reported, on account of the lack of an independent standard gas, their data are not discussed here.

Each group set up and operated its measurement system as it normally did in its own studies. Since the Korean group had already set its instrument package at Gosan with a large-flow sampling inlet/manifold, the Japanese and Taiwanese groups shared this sampling system. The Hong Kong group used its own sampling system. The sampling inlets for each group were close to each other to ensure that the same air masses were sampled by each group. A 25-mm (OD) Teflon and/or glass inlet/manifold with sampling ports for 6-mm tubing mounted on the container were used for sampling of ambient air. Ambient measurements were made during the intensive observation period (IOP), 4–30 March 2005. Standard gases were compared during the pre-IOP.

Table 1 List of participating groups in the EAREX 2005 international comparisons.

Country/region	Organization	Participant	Method	Instrument	Span Cal.	Zero Cal.
Japan	NIES	H. Tanimoto*	NDIR	Horiba, APMA-360	Gravimetric standards (direct injection)	Through catalyst (Sofnocat)
	MRI	Y. Sawa, H. Matsueda, A. Wada				
	NIAES	S. Yonemura				
Korea	SNU	K.-R. Kim	NDIR-GFC	TEI, 48C	Gravimetric standards (dynamic dilution)	From zero-air supply (TEI, 111)
	HUFS	G. Lee*, J.-Y. Jung				
	KU	M. Lee				
Hong Kong	HKPU	T. Wang*, S. Poon, A. Wong	NDIR-GFC	API, 300	Manometric standards (dynamic dilution)	From zero-air supply (TEI, 111)
Taiwan	NCU	N.-H. Lin, J.-L. Wang, C.-F. Ou-Yang	GC/RGD	Trace Analytical, RGD-ta3000R	Pressurized ambient air	NA
	EPA	C.-F. Wu				

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NDIR, non-dispersive infrared absorption; GFC, gas filter correlation; GC/RGD, gas chromatograph/reduction gas detector; TEI, Thermo Environment Instruments; API, Advanced Pollution Instruments

Table 2 Comparison of the several NIES CO standard gases with the MRI primary scale.

Cylinder ID	Matrix gas	Date for preparation (dd/mm/yyyy)	NIES scale CO (ppbv)	MRI scale CO (ppbv)	Difference (ppbv)
CPB-29547	Synthetic air	26/01/2004	100.0	113.8 ± 3.7	+13.8
CPB-29549	Synthetic air	26/01/2004	499.0	507.0 ± 3.8	+7.1
CPB-29550	Synthetic air	26/01/2004	999.0	1006.4 ± 3.5	+6.5
CPB-03029	Synthetic air	03/08/2003	1802.0	1810.3 ± 4.7	+8.3

2.2 Local comparison

Off-site comparisons between NIES and MRI were held after the on-site comparisons, in Tsukuba, Japan, where the performance of NDIR and GC/RGD at ambient levels was directly compared. The MRI GC/RGD instrument (Yanaco, TRA-1) has been operated on a meteorological tower at the MRI campus on a routine basis since 2001. Air samples were injected into the GC every 5 min after dehumidification through a combination of an electronic cooler unit and an $\text{Mg}(\text{ClO}_4)_2$ trap. The sampling height was sequentially altered among 1.5, 25, and 200 m above the ground level (agl). The MRI GC/RGD was calibrated by four CO standard gases: three standards balanced with nitrogen (122, 494, 803 ppbv) and one balanced with air (253 ppbv). These four standards were injected into the GC every 3 h. Ambient CO mixing ratios were calculated with second-order polynomial calibration curves. Hourly data at 1.5 m were calculated from four discrete measurements normally, or three measurements when standard gases were injected into the GC. Although GC/RGD gives a non-linear response, it was found to be significant only at the mixing ratios above 3 ppmv for this instrumental setup (Sawa, 2005). The detection limit of the MRI GC/RGD instrument is ~3 ppbv, and the precision is estimated to be 2 ppbv at typical mixing ratio of 150 ppbv. For the NIES NDIR instrument, air samples were continuously taken at 1.5 m agl. The instrumental set-up was basically the same as deployed at Gosan. Briefly, span calibration was done typically every week using standard gas containing 1.0 ppmv CO in air (Taiyo Toyo Sanso). The detection limit of the hourly CO measurements is ~15 ppbv, based on 3σ

(standard deviation) of baseline fluctuation. The overall uncertainty of the hourly average CO data at a typical mixing ratio of 150 ppbv is estimated to be $\pm 10\%$, including contributions from the precision, flow controllers, and calibration gas. The consistency of standard gases from these two groups was also evaluated.

3. Results and Discussion

3.1 Consistency of Gas Standards

First, we examined the consistency of CO standard gases between NIES and MRI. Four standard gases used at NIES were measured with an analytical system at the MRI laboratory and referenced to the MRI primary scale. A detailed description of the MRI primary scale will be published elsewhere, although some of the MRI standards and their analytical methods are already reported (Matsueda *et al.*, 1999; Sawa *et al.*, 1999; Sawa, 2005). Briefly, five standard gases were gravimetrically prepared in the range of 50 to 3000 ppbv in either 10-L or 48-L aluminum cylinders by Taiyo Toyo Sanso (Japan), and were used as the primary standards at MRI. All standards were balanced with high-purity nitrogen to minimize possible initial contamination from a diluent gas. Using a methanizer, CO was converted to CH_4 , and then the mixing ratios of CH_4 were determined by gas chromatograph/flame ionization detector (GC/FID) with a measurement uncertainty of about 3 ppbv (1σ). Our measurements of the five primary standards by GC/FID were internally consistent within ± 2 ppbv. In addition, all of these standards were confirmed to be stable without a drift of CO content during the past

Table 3 Stability of the Japanese CO standard gases for the EAREX 2005 campaign.

Cylinder ID	Matrix gas	Date of calibration (dd/mm/yyyy)	Gravimetric scale CO (ppbv)	MRI scale CO (ppbv)	Difference (ppbv)
CPB-03048	Synthetic air	01/02/2005	1000.0	1006.9 ± 2.5	+6.7
		14/06/2005		1013.6 ± 3.3	
CPB-23397	Nitrogen	01/02/2005	1028.0	1012.3 ± 3.0	-1.1
		14/06/2005		1011.2 ± 3.0	

Table 4 Comparison of the CO standard gases from Japan, Korea, and Hong Kong.

Country/region	Cylinder ID	Matrix gas	Each scale (ppmv)	Hong Kong scale CO (ppmv)	Difference (%)
Japan	CPB-03048	Air	1.010*	1.203 ± 0.031	−16.0%
Japan	CPB-23397	N ₂	1.012*	1.153 ± 0.018	−12.2%
Korea	YA-000188	N ₂	7.500	7.532 ± 0.047	−0.4%
Hong Kong	LL-41986	N ₂	153.8	—	—

* Average between pre- and post-calibrations.

several years.

Table 2 compares the NIES CO standard gases used in this study with the MRI primary standards at the mixing ratios of 100, 500, 1000, and 1800 ppbv. All standard gases from NIES were gravimetrically prepared in 10-L aluminum cylinders by Taiyo Toyo Sanso (Japan), and these standards were measured at MRI during 8–10 March 2004. These gases tested here are all laboratory-level reference standards used by the NIES Atmospheric Chemistry Group, and are not scaled to the NIES primary scale, because that scale is currently not available at ppmv levels (T. Machida, personal communication, 2007). The discrepancies in the four comparisons ranged from 7 to 14 ppbv beyond the measurement uncertainty, independent of the gravimetrically assigned CO mixing ratios. This suggests that air-balanced standards have positive biases in the initial mixing ratios, likely due to either contamination from synthetic air balance or artificial production of CO on the metal surface in the gas cylinders. Although the relative impact of this offset was less than 1% at 1 ppmv, it could be as large as >10% at 100 ppbv, even if standard gases were still fresh.

Table 3 describes the Japanese CO standards used in the international comparison at Gosan. These standard gases were gravimetrically prepared and then referenced to the MRI primary scale. We prepared two sets of standards to check the influence of base gas on the initial CO mixing ratios and its stability during the intercomparison. Two standard gases were prepared at ~1 ppmv in 10-L aluminum cylinders at Japan Fine Products (Japan) on 24 January 2005, and compared with the MRI primary scale before and after the international comparison at Gosan. The initial mixing ratios gravimetrically assigned were 1000.0 and 1028.0 ppbv for those balanced with synthetic air and nitrogen, respectively. The calibration results against the MRI primary scale showed slight but significant differences from the gravimetrically assigned mixing ratios before the intercomparison. More importantly, the post-calibration done by MRI in June 2005 showed a significant increase in the CO mixing ratios for the standard balanced with air beyond the measurement uncertainty. However, the nitrogen-balanced standard showed no significant difference between pre- and post-calibrations, indicating

good stability of CO content in nitrogen. This is likely due to the production of CO in the cylinders during storage, as suggested by several previous reports (e.g., Novelli *et al.*, 1998). However, the increase in the CO mixing ratios in the air-balanced standard at 1 ppmv was only +0.67% during the course of 4 months, and was far less than the precision of the NIES NDIR instruments.

Table 4 summarizes the international comparison of standard gases from three groups representing Japan, Korea, and Hong Kong. Since the standard gas from Taiwan was pressurized ambient air and was not referenced to any standard gas prepared by either gravimetric or manometric methods, and long-term stability was not certified, we did not discuss it in the official results. The standard gases from Korea and Hong Kong were balanced with nitrogen, but were prepared at different mixing ratios. The Korean and Hong Kong standards were dynamically diluted to the ambient levels, and the Japanese standards were directly introduced. Measurements were made using the Hong Kong NDIR instrument, and were referenced to its standard. The standards from Korea and Hong Kong were in excellent agreement, within 1%. In contrast, both standards from Japan differed greatly from those from Hong Kong,

Fig. 1 Temporal variations in CO measured by (a) the NIES NDIR instrument and the MRI GC/RGD instrument in Tsukuba from April to June 2005, and (b) three NDIR instruments from Japan, Korea, and Hong Kong at Gosan in March 2005. Ambient data are hourly means. The NIES data are referenced to the MRI primary scale, and the others are based on individual calibration scales. Time is expressed in local time (UTC+9).

disagreeing by more than 10%. Although this large disagreement between Japan and Hong Kong may be partly due to uncertainty resulting from the dynamic dilution processes, the difference is larger than we expected, and the reasons are unresolved. The 4% difference between the two standards from Japan might partly be due to a carrier gas effect on infrared absorption, similar to that reported for carbon dioxide measurements (e.g., Inoue *et al.*, 1999). Overall, more intercomparison experiments are needed to identify possible factors responsible for the differences in the primary standard scales in each group.

3.2 Consistency of Ambient Measurements

Figure 1a shows temporal variations in CO measured by the NIES NDIR instrument and the MRI GC/RGD instrument at the MRI campus in Tsukuba from late April to mid-June 2005. Tsukuba is located about 50 km from Tokyo, and hence is considered to be in the suburbs of the mega-city. The NIES NDIR instrument was calibrated by the standard gas balanced with air (as described in Tables 3 and 4), and thus the NIES ambient data were referenced to the MRI primary scale. During approximately 2 months in spring, the ambient data apparently showed day-to-day pollution episodes (e.g., days 117, 128, 135, 141, 144, 152–154, 160), likely due to transport from Tokyo or local sources. The data also showed relatively low and stable mixing ratios at 150 to 200 ppbv which continued for several days (e.g., days 131–135, 149–151). The two methods tracked the largely varying mixing ratios in both polluted and relatively clean air masses. Figure 1b shows temporal variations of CO measured by three NDIR instruments from Japan, Korea, and Hong Kong at Gosan in March 2005. Data are based on

individual calibration scales. Gosan is located at the southwestern tip of Jeju Island, and the Gosan station is considered to be a remote monitoring site, which is often affected by continental outflow from the Asian continent. In contrast to Tsukuba, temporal variability was relatively smooth at Gosan. Ambient mixing ratios ranged from 120 to 1000 ppbv for the whole period, depending on the air mass types. All three instruments followed the CO mixing ratios, from relatively clean air masses (e.g., days 68–69, 78, 84) to heavily polluted air masses (e.g., days 70, 74, 77, 80, 82). All measurements captured the most serious pollution events in a quantitative manner. For example, in the pollution event around day 77, the maximum mixing ratios reported by Japan, Korea, and Hong Kong were 1034, 1012, and 1059 ppbv, respectively. The agreement was within 5% at 1000 ppbv. However, shorter-term variability was often different from instrument to instrument, although all three instruments captured synoptic-scale transport of CO very well. The temporal variations observed by the Japanese group showed smooth curves, while those by the Korean group showed high variability and sometimes biases. The behavior of the data of the Hong Kong group was between those of Japan and Korea. There were visible discrepancies among the three data sets, in particular during low and stable mixing-ratio periods.

Figure 2 shows scatter plots of the ambient data measured by the NIES NDIR against those by the MRI GC/RGD in Tsukuba. Although several points are distant, both data sets clearly show tight correlation in the range

Fig. 2 Scatter plots of the ambient data measured by the NIES NDIR against those by the MRI GC/RGD in Fig. 1(a) (black circles). Dependence of the differences in the two methods on the CO mixing ratios is also shown (gray pluses). The dashed line shows 1:1 correspondence.

Fig. 3 Relative fraction of the differences in ambient mixing ratios of (a) NIES – MRI, (b) Korea – Japan, and (c) Hong Kong – Japan. The NIES data in (a) are referenced to the MRI primary scale. The other data are based on individual calibration scales. Each bin is 10 ppbv. Arrows and numbers indicate arithmetic means.

from 140 to 940 ppbv. The least linear square fit shows a slope of 0.96 and a negligible intercept with a correlation coefficient (R^2) of 0.96. Some data stray from the 1:1 correspondence line above 500 ppbv. This is likely due to the differences in sampling frequency between NDIR (i.e., continuous) and GC/RGD (i.e., 4 samples in an hour) at high mixing ratios, where short-term variability is also large. These small biases affect the overall slope, but excluding the data above 500 ppbv provides a slope of 0.99, demonstrating that data provided by the NIES NDIR and the MRI GC/RGD instruments are closely correlated with negligible biases in slope and intercept at ambient levels.

Figure 3 shows the relative fractions of the differences in ambient mixing ratios measured in Tsukuba and at Gosan. The histogram of the difference between the NIES NDIR and the MRI GC/RGD in ambient data in Tsukuba shows a sharp shape in distribution. Sixty percent of all data cover the range of ± 10 ppbv, and 84% cover ± 20 ppbv, with a calculated mean of -1.2 ppbv. In contrast, the histograms of the difference between the Korean and Hong Kong NDIR instruments from the Japanese NDIR instrument in ambient data at Gosan show a broader shape in distribution. The Japanese NDIR data were used as a reference since they were found to agree well with those observed by the MRI GC/RGD method. This is partly because all instruments are based on the NDIR method, which is less precise than GC/RGD. In addition, short-term variability in the NDIR measurements contributed to the broad distribution. Only 33% of the Korean data covered ± 20 ppbv; 53% of the Hong Kong data covered ± 20 ppbv, and 85% covered ± 40 ppbv. The mean difference, calculated to be $+3.3$ ppbv in the Hong Kong data, is in the range of uncertainty of the measurements, but the mean of $+22.1$ ppbv in the Korean data is greater than the uncertainty. The results of this field intercomparison suggested that the accuracies of observed CO values reflect the sum of the accuracies of the analytical method and the reference gases. In addition, the use of similar analytical techniques did not always provide similar results.

4. Summary and Future Tasks

Four international groups using different sampling systems and measurement procedures participated in the direct assessment of the standards and methods for continuous measurement of CO at ground-based stations in Asia. A series of comparisons revealed that preparation of accurate and stable CO standard gases is still challenging in the range from ppbv to ppmv. Significant differences were found between the standard gases with different balance gases (i.e., nitrogen or air), likely due to artificial CO formation at initial production or during storage. Inconsistency of the calibration scales among different institutions was found to be substantial, and this requires

future improvement. The evaluation of hourly ambient measurements in Tsukuba suggested that both NDIR and GC/RGD instruments function reasonably well in the range of mixing ratios from 100 to 1000 ppbv. Although all three NDIR instruments well captured synoptic-scale transport of CO from continental sources, precision at relatively low mixing ratios should be improved if they are used for long-term baseline monitoring. These efforts were the first step in ensuring comparability of ongoing measurements and in establishing a collaborative monitoring network in Asia. Further exercise requires round-robin-type intercomparison to ensure traceability for gas standards. Comparisons with the baseline monitoring communities such as WMO and NOAA and with air pollution groups are also needed. Collaboration with Chinese and Indian groups is highly required.

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List of Acronyms

EPA, Environmental Protection Administration (Taiwan)
GAW, Global Atmospheric Watch
HKPU, Hong Kong Polytechnic University (Hong Kong)
HUFS, Hankuk University of Foreign Studies (Korea)
JMA, Japan Meteorological Agency (Japan)
KU, Korea University (Korea)

MRI, Meteorological Research Institute (Japan)
 NCU, National Central University (Taiwan)
 NIAES, National Institute for Agro-Environmental Studies
 (Japan)
 NIES, National Institute for Environmental Studies (Japan)
 NOAA, National Oceanic and Atmospheric Administration
 (USA)
 SNU, Seoul National University (Korea)
 WMO, World Meteorological Organization

References

- Inoue, H.Y., M. Ishii, H. Matsueda, S. Saito, T. Midorikawa and K. Nemoto, 1999: MRI measurements of partial pressure of CO₂ in surface waters of the Pacific during 1968 to 1970: re-evaluation and comparison of data with those of the 1980s and 1990s. *Tellus*, **51B**, 830-848.
- Jaffe, D., I. Bertsch, L. Jaeglé, P. Novelli, J. S. Reid, H. Tanimoto, R. Vingarzan and D.L. Westphal, 2004: Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. *Geophys. Res. Lett.*, **31**, L16106, doi:10.1029/2004GL020093.
- Japan Meteorological Agency (JMA), 2005: Annual Report on Atmospheric and Marine Environment Monitoring. No. 5 (CD-ROM).
- Kajii, Y., K. Someno, H. Tanimoto, J. Hirokawa, H. Akimoto, T. Katsuno and J. Kawara, 1998: Evidence for the seasonal variation of photochemical activity of tropospheric ozone: Continuous observation of ozone and CO at Haplo, Japan. *Geophys. Res. Lett.*, **25**, 3505-3508.
- Koike, M., Y. Kondo, K. Kita, N. Takegawa, Y. Masui, Y. Miyazaki, M.W. Ko, A.J. Weinheimer, F. Flocke, R.J. Weber, D.C. Thornton, G.W. Sachse, S.A. Vay, D.R. Blake, D.G. Streets, F.L. Eisele, S.T. Sandholm, H.B. Singh, and R.W. Talbot, 2003: Export of anthropogenic reactive nitrogen and sulfur compounds from the East Asia region in spring. *J. Geophys. Res.*, **108**, Art. No. 8789.
- Matsueda, H., H.Y. Inoue, M. Ishii and Y. Tsutsumi, 1999: Large injection of carbon monoxide into the upper troposphere due to intense biomass burning in 1997. *J. Geophys. Res.*, **104**, 26867-26879.
- Matsumoto, K., Y. Uyama, T. Hayano, H. Tanimoto, I. Uno and M. Uematsu, 2003: Chemical properties and outflow patterns of anthropogenic and dust particles on Rishiri Island during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia). *J. Geophys. Res.*, **108**, 8666, doi:10.1029/2003JD003426.
- Nakajima, T., S.-C. Yoon, V. Ramanathan, G.-Y. Shi, T. Takemura, A. Higurashi, T. Takamura, K. Aoki, B.J. Sohn, H. Tsuruta, N. Sugimoto, A. Shimizu, H. Tanimoto, Y. Sawa, N.-H. Lin, C.-T. Lee, D. Goto, M. Yamano and N. Schutgens, 2007: Overview of the ABC EAREX 2005 regional experiment and a study of the aerosol direct radiative forcing in the East Asia, *J. Geophys. Res.*, submitted.
- Novelli, P.C., V.S. Connors, H.G. Reichle, B.E. Anderson, C.A.M. Brenninkmeijer, E.G. Brunke, B.G. Doddridge, V.W.J.H. Kirchhoff, K.S. Lam, K.A. Masarie, T. Matsuo, D.D. Parrish, H.E. Scheel and L.P. Steele, 1998: An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements. *J. Geophys. Res.*, **103**, 19285-19293.
- Novelli, P.C., K.A. Masarie, P.M. Lang, B.D. Hall, R.C. Myers and J.W. Elkins, 2003: Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires. *J. Geophys. Res.*, **108**, Art. No. 4464.
- Palmer, P.I., P. Suntharalingham, D. B. A. Jones, D. J. Jacob, D. G. Streets, Q. Fu, S. Vay and G. W. Sachse, 2006: Using CO₂-CO correlations to improve inverse analyses of carbon fluxes. *J. Geophys. Res.*, **111**, D12318, doi:10.1029/2005JD006697.
- Parrish, D.D., J.S. Holloway and F.C. Fehsenfeld, 1994: Routine, continuous measurement of carbon monoxide with parts per billion precision. *Environ. Sci. Technol.*, **28**, 1615-1618.
- Parrish, D.D., M. Trainer, J.S. Holloway, J.E. Yee, M.S. Warshawsky, F.C. Fehsenfeld, G.L. Forbe and J.L. Moody, 1998: Relationships between ozone and carbon monoxide at surface sites in the North Atlantic region. *J. Geophys. Res.*, **103**, 13357-13376.
- Sawa, Y., 2005: A study of variations and transport of carbon monoxide in the free troposphere over the western Pacific. Ph.D. thesis, 184 p., Tohoku Univ., Sendai, Japan.
- Sawa, Y., H. Matsueda, Y. Tsutsumi, J.B. Jensen, H.Y. Inoue and Y. Makino, 1999: Tropospheric carbon monoxide and hydrogen measurements over Kalimantan in Indonesia and northern Australia during October, 1997. *Geophys. Res. Lett.*, **26**, 1389-1392.
- Sawa, Y., H. Tanimoto, S. Yonemura, H. Matsueda, A. Wada, S. Taguchi, T. Hayasaka, H. Tsuruta, Y. Tohjima, H. Mukai, N. Kikuchi, S. Katagiri and K. Tsuboi, 2007: Widespread pollution events of carbon monoxide observed over the western North Pacific during the EAREX 2005 campaign. *J. Geophys. Res.*, doi:10.1029/2006jd008055, in press.
- Suntharalingam, P., D. J. Jacob, P. I. Palmer, J. A. Logan, R. M. Yantosca, Y. Xiao, M. J. Evans, D. Streets, S. A. Vay and G. Sachse, 2004: Improved quantification of Chinese carbon fluxes using CO₂/CO correlations in Asian outflow. *J. Geophys. Res.*, **109**, D18S18.
- Takegawa, N., Y. Kondo, M. Koike, G. Chen, T. Machida, T. Watai, D.R. Blake, D.G. Streets, J.H. Woo, G.R. Carmichael, K. Kita, Y. Miyazaki, T. Shirai, J.B. Liley and T. Ogawa, 2004: Removal of NO_x and NO_y in Asian outflow plumes: Aircraft measurements over the western Pacific in January 2002. *J. Geophys. Res.*, **109**, Art. No. D23S04.
- Tanimoto, H., Y. Kajii, J. Hirokawa, H. Akimoto and N.P. Minko, 2000: The atmospheric impact of boreal forest fires in far eastern Siberia on the seasonal variation of carbon monoxide: Observations at Rishiri, a northern remote island in Japan. *Geophys. Res. Lett.*, **27**, 4073-4076.
- Tanimoto, H., H. Mukai, Y. Sawa, H. Matsueda, S. Yonemura, T. Wang, S. Poon, A. Wong, G. Lee, J.Y. Jung, K.R. Kim, M.H. Lee, N.H. Lin, J.L. Wang, C.F. Ou-Yang, C.F. Wu, H. Akimoto, P. Pochanart, K. Tsuboi, H. Doi, C. Zellweger and J. Klausen, 2007: Direct assessment of international consistency of standards for ground-level ozone: Strategy and implementation toward metrological traceability network in Asia. *J. Environ. Monit.*, doi:10.1039/b701230f.
- Wang, T., T.F. Cheung, Y.S. Li, X.M. Yu and D.R. Blake, 2002: Emission characteristics of CO, NO_x, SO₂ and indications of biomass burning observed at a rural site in eastern China. *J. Geophys. Res.*, **107**, Art. No. 4157.
- Wang, T., C.H. Wong, T.F. Cheung, D.R. Blake, R. Arimoto, K. Baumann, J. Tang, G.A. Ding, X.M. Yu, Y.S. Li, D.G. Streets and I.J. Simpson, 2004: Relationships of trace gases and aerosols and the emission characteristics at Lin'an, a rural site

- in eastern China, during spring 2001. *J. Geophys. Res.*, **109**, Art. No. D19S05.
- WMO, 2006: Joint WMO-GAW/ACCENT workshop on the global tropospheric carbon monoxide observation system, quality assurance and applications, edited by Jörg Klausen, Proc. Joint WMO-GAW/ACCENT workshop on the global tropospheric carbon monoxide observation system, quality assurance and applications, Dubendorf, Switzerland, 24-26 October 2005, Empa Dubendorf, pp. 1-36.
- Yokouchi, Y., S. Taguchi, T. Saito, Y. Tohjima, H. Tanimoto and H. Mukai, 2006: High frequency measurements of HFCs at a remote site in east Asia and their implications for Chinese emissions. *Geophys. Res. Lett.*, **33**, L21814, doi:10.1029/2006GL026403.

アジアの地上観測サイトにおける一酸化炭素の連続測定のための 標準ガスと測定手法の評価

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ABC 国際プロジェクトの枠組みのもとで開催された EAREX 2005 キャンペーンの一環として、大気中一酸化炭素のための測定手法と標準物質の整合性を直接比較する国際相互比較実験が行われた。2005 年 3 月に日本、韓国、香港、台湾の 4 グループが、各自の連続測定器と標準ガスを済州島の Gosan 観測所に持ち寄って、国際比較を行った。これらは、これまでアジアにおける大気モニタリングに用いられてきた手法である。日本のグループから持ち込んだ手法である国立環境研究所の NDIR 測定器は、一時間の時間分解能で気象研究所の GC/RGD 法と良い一致を示した。このことから、NDIR 法は大きな濃度変動を示す状況下で大気中一酸化炭素濃度を連続的にモニターするために有用であることが確かめられた。国際相互比較における 3 台の NDIR 装置による実大気測定結果は概して良い一致を示したが、標準ガスの比較からは、大気レベルにおいて精度・確度ともに高い一酸化炭素の標準ガスを調整し維持することの困難さが指摘された。