

**Onboard
measurement system
of atmospheric
carbon monoxide**

H. Nara et al.

Onboard measurement system of atmospheric carbon monoxide over the Pacific Ocean by voluntary observing ships

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Abstract

Long-term monitoring of carbon monoxide (CO) mixing ratios in the atmosphere over the Pacific Ocean is being carried out on commercial cargo vessels participating in the National Institute for Environmental Studies Voluntary Observing Ships program. The program provides a regular platform for measurement of atmospheric CO along four cruising routes: from Japan to Oceania, from Japan to the United States, from Japan to Canada, and from Japan to Southeast Asia. Flask samples are collected during every cruise for subsequent analysis in the laboratory, and in 2005, continuous shipboard CO measurements were initiated on three of the routes. Here, we describe the system we developed for onboard measurement of CO mixing ratios with a commercially available gas filter correlation CO analyzer. The fully automated system measures CO in ambient air, and the detector sensitivity and background signals are calibrated by referencing the measurements to a CO-in-air standard gas (~1 ppmv) and to CO-free air scrubbed with a catalyst, respectively. We examined the artificial production of CO in the high-pressure working gas standards (CO balanced with purified air at ppmv levels) during storage by referencing the measurements to CO standard gases maintained as our primary scale before and after use on the ships. The onboard performance of the continuous CO measurement system was evaluated by comparing its data with data from laboratory analyses of flask samples using gas chromatography with a reduction gas detector. The reasonably good consistency between the two independent measurement methods demonstrated the good performance of both methods over the course of 3–5 yr. The continuous measurement system was more useful than the flask sampling method for regionally polluted air masses, which were often encountered on Southeast Asian cruises.

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Atmospheric carbon monoxide (CO) is an important trace gas in the tropospheric photochemistry. Because most of the hydroxyl (OH) radicals in the troposphere are consumed by reaction with CO, CO influences the distribution of other reduced trace gases such as methane by changing the oxidation capacity of the atmosphere (Logan et al., 1981). Although CO is naturally produced by oxidation of hydrocarbons, anthropogenic sources including fossil fuel combustion and biomass burning account for a large portion of CO emissions. The atmospheric distribution of CO is determined mainly by the locations of emission sources and by subsequent long-range transport of air masses containing CO, because of its relatively long lifetime. These two factors result in complexity in the temporal and spatial variations of CO on a global scale (Novelli et al., 1998a). Therefore, additional observational evidence is needed for a better understanding of the factors affecting temporal and spatial variations of CO and its effect on the oxidation capacity of the atmosphere.

To improve our understanding concerning global distributions of CO, investigators have made stationary, shipboard, airborne, and satellite observations of CO during the past decades. For example, Novelli et al. (1998a, 2003) used a global air-sampling network of 49 surface stations established by the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory's Global Monitoring Division (GMD) to capture the global distribution of CO and long-term trends in CO mixing ratios in the lower troposphere. Several observation programs made atmospheric observation using civil aircraft over a wide area in upper troposphere and lower stratosphere along the flight routes. Nedelec et al. (2003) reported aircraft observations of CO made starting in 1997 as a part of the Measurements of Ozone, Water Vapour, Carbon Monoxide and Nitrogen Oxides by In-Service Airbus Aircraft (MOZAIC) program, customizing a commercially available infrared analyzer to obtain continuous, high-precision measurements. Brenninkmeijer et al. (1999) started Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) program in

AMTD

4, 4505–4537, 2011

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1997. The aircrafts partitioning CARIBIC program loaded airfreight container equipped with automated in situ measurement instruments and sampling devices for observing more than 60 different trace gases and aerosol properties, and CO was continuously measured by a vacuum ultraviolet spectrometer (Brenninkmeijer et al., 2007).

5 Satellite observation can provide global pictures of CO distributions on a monthly or even daily basis. On the basis of Measurements of Pollution in the Troposphere (MOPITT) observations, Yurganov et al. (2005) reported an increase in the total column abundance of CO in the summer and autumn of 2002 and 2003 over boreal regions in the Northern Hemisphere. Tanimoto et al. (2008a) diagnosed consistency between
10 MOPITT observations and emission estimates of CO from East Asia for the period from 2000 to 2006. Observations made by the Atmospheric Infrared Sounder (AIRS) demonstrated its ability to track long-range transport of CO from emission sources (Yurganov et al., 2008; Tanimoto et al., 2009a). However, determination of absolute CO mixing ratios by means of satellites is challenging, and information on the vertical
15 profiles and structures is often limited (Warner et al., 2007; Yurganov et al., 2008). Thus satellite observations of CO still need to be supported and validated by in situ observations.

Uncertainties in global CO distributions remain large because past observations tended to be sporadic and localized. Moreover, interannual variations and long-term
20 trends of CO are often ambiguous owing to difficulties in measuring CO precisely and accurately. For example, most ground-based measurements of CO have been made by means of gas chromatography with reduced gas detection (GC/RGD), gas filter correlation (GFC)/nondispersive infrared absorption analysis, or a vacuum ultraviolet resonance fluorescence VURF (e.g., Parrish et al., 1994; Gerbig et al., 1996, 1999; Novelli et al., 1998b; Tanimoto et al., 2000, 2009b; Takegawa et al., 2001; Nedelec et al., 2003; Sawa et al., 2007). The resulting data often show differences originating from
25 differences between the measurement techniques and calibration scales (Novelli et al., 1991, 1998a; Tanimoto et al., 2007; Ou-Yang et al., 2009; Zellweger et al., 2009). Novelli et al. (1998b) compared data obtained by eleven laboratories as a part of program

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for validation of the Measurement of Air Pollution from Satellites (MAPS) instrument and found significant differences among several laboratories, even among laboratories using similar methods and a common standard gas. Maintenance of CO gas standards is often plagued by drift of the CO mixing ratios in high-pressure gas cylinders, particularly at ppbv levels (Novelli et al., 1991, 1994, 2003). Although the drift rate of CO mixing ratios is only a few ppbv per year (compared to the few tens to hundreds of ppbv CO at which the standards are prepared), the drift substantially affects derivation of long-term trends and interannual variability of CO (Zander et al., 1989; Brunke et al., 1990; Novelli et al., 2003; Zellweger et al., 2009). Furthermore, the drift substantially affects the calibration scales maintained for long-term atmospheric monitoring programs. For these reasons, obtaining accurate measurements of CO is still a challenge, which highlights the need for rigorous control of the accuracy and precision of CO instrumentation and calibration scales.

In March 1992, the National Institute for Environmental Studies (NIES) began observing atmospheric CO by means of flask sampling followed by laboratory analysis. In November 2005, NIES started continuous observations of CO, to better understand CO distributions over the Pacific Ocean and to examine the possible influences of rapidly increasing human activity in this region. Here we present a new system for continuously measuring CO, together with quality assessment and quality control results for CO data obtained over a period of years.

2 NIES Voluntary Observing Ships program for long-term atmospheric monitoring

Since 1992, NIES has been operating a long-term program for monitoring trace gases of atmospheric importance in the background air over the Pacific Ocean. The NIES Voluntary Observing Ships (NIES VOS) program makes use of commercial cargo vessels because they operate regularly over fixed routes for long periods and sail over a wide area between various ports. This program allows systematic and continuous

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measurements of trace gases, providing long-term datasets for background air over the Pacific region, spanning wide latitudinal zones in both the Northern and Southern Hemispheres. Figure 1 shows current spatial coverage of atmospheric observations operated in the NIES VOS program. In collaboration with maritime shipping companies, present observations have been made onboard motor vessels (M/V) *Fujitrans World* (FTW; owned by Kagoshima Shipping Co., Japan), *Pyxis* (PX; owned by Toyofuji Shipping Co., Japan), *Skaubryn* (SKB; owned by Seaboard International Shipping Co., Canada), and *Trans Future 5* (TF5; owned by Toyofuji Shipping Co., Japan) since September 2007, November 2001, June 2007, and November 2005, respectively. These ships sail between Japan and Southeast Asian countries (Southeast Asia route, 4-week interval), between Japan and the United States (North America route, 9-week interval), between Japan and Canada (North America route, 8-week interval), and between Japan and Australia and New Zealand (Oceania route, 6-week interval), respectively.

2.1 Setup for atmospheric observations

We set up a laboratory in a room in the cabin of each ship, and installed an observation system customized for atmospheric monitoring. The system is robust because it runs in automatic mode under the relatively severe conditions on a ship during cruises (e.g., conditions created by vibration from the ship's engine and sea swell). Moreover, for the ship's safety, the instruments do not require the use dangerous substances, including gases. Our observation system consists of a continuous measurement system, a flask sampling system, and a data management system. These are described in more detail in the following sections. Electric power is supplied by the ship's generator through a transformer equipped with an automatic voltage regulator and an uninterruptible power supply to provide rectified electric current, because the voltage of the ship-generated electric power fluctuates. A constant voltage and constant frequency unit is used for the continuous measurement system.

2.2 Continuous measurement system

Mixing ratios of CO₂ and O₃ are continuously monitored with commercially available analyzers. Ambient air is drawn from an intake on the top deck of the ship so that contamination originating from the ship's exhaust can be avoided or, at least, minimized.

5 For O₃ measurement, air samples are collected through Teflon tubing to prevent O₃ loss on the inner surface of stainless steel tubing. Air samples are passed through a Teflon filter and a glass water trap to remove dust and condensed water before being directed to the measurement systems. The details of the configuration of the CO₂ and O₃ measurement systems are similar to those reported in previous publications
10 (Watanabe et al., 2005; Chierici et al., 2006; Nara et al., 2011).

2.3 Flask sampling system

Flask samples of air are collected with an automatic air sampler unit (SU701, Kimoto Electric Co., Osaka, Japan) for later laboratory analysis (Fig. 2). The sampling system consists of air sampling equipment, a cryogenic dryer, a metal bellows pump, a solenoid valve unit, an air compressor, and a controlling device. The air sampling
15 equipment consists of seven sampling flasks (2.5-L Pyrex or 3.3-L electro-polished stainless steel flasks) equipped with two air-actuated stopcocks and sealed with Viton O-rings (for glass flasks) or Ni-Co alloy diaphragms (for stainless steel flasks). These flasks are housed in an aluminum case to prevent physical damage and to avoid sunlight, which might photodegrade gas species (e.g., Novelli et al., 1992). The metal
20 bellows pump (MB-151, Metal Bellows Corp., MA, USA) and the solenoid valve unit are computer-controlled by means of the system control device. The solenoid valve unit controls the supply of compressed air to operate the air-actuated stopcocks. The system control device is linked to a GPS system, to which the latitude and longitude
25 of the sampling locations (Fig. 1) are predesignated. As is the case for the continuous measurement system, ambient air is taken from the air intake on the top deck of the ship. Air samples are drawn by means of the metal bellows pump through stainless

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

steel tubing at a flow rate of 5 STP L min⁻¹. After the sampled air is dehumidified by passage through a cryogenic dehumidifier kept at about -48 °C, the air is introduced into a glass or stainless steel sampling flask. The flask is rinsed by sample air for the first 15 min (glass) or 5 min (stainless steel) and subsequently pressurized by sample air up to 1.6 and 2.5 kgf cm⁻² for collection, respectively. The line pressure and the operating records are logged to confirm completion of each sampling and to check the operating conditions after the voyage during maintenance access.

When the ship is berthed at its Japanese port, the air sampling equipment is removed from the ship and taken to NIES for analysis. Mixing ratios of CO as well as CO₂, CH₄, N₂O, H₂, and SF₆ in the glass flasks are determined by means of the procedure of Machida et al. (2008). For CO quantification, a GC/RGD instrument (RGD-2, Trace Analytical, Menlo Park, CA, USA; or Peak Performer, Peak Laboratories, Mountain View, CA, USA) is used (typical analytical precision 0.3 ppbv). The mixing ratios of hydrochlorofluorocarbons, perfluorocarbons, methyl chloride, methyl bromide, methyl iodide, tetrachloroethylene, trichloroethylene, chloroform, dimethyl sulfide, isoprene, *n*-pentane, and benzene in the stainless steel flasks are determined by GC coupled with mass spectrometry (Li et al., 1999).

2.4 Data management system

The data management system consists of a data server and a display client. All the instruments in the atmospheric observation room are linked with one another via a local area network. The data server reads data from the individual instruments and integrates the data after synchronizing them to UTC obtained from the GPS. These integrated files are then stored on the data server as 10-s- and 1-min-averaged data. The display client simultaneously displays ship tracks and temporal variations for selected species on a 24-h scale. The display client is set to print the displayed data once a day as a daily report. The ship's crew inspects the atmospheric observation system daily to make sure that it is operational. The printed daily report and a completed checklist

are sent from the ship to NIES by e-mail. If any abnormal condition is found in the daily report or the checklist, we contact the ship crew to shut down the instrument for the ship's safety, if necessary.

3 Continuous CO measurement system

5 Along three of the four currently operating VOS routes, continuous monitoring of CO in air was initiated on the M/V TF5 in November 2005, and monitoring began on the M/V SKB and the FTW in June and September 2007, respectively (Fig. 1). We use a commercially available GFC/nondispersive infrared CO analyzer (Model 48C or 48i, Thermo Electron Inc., Franklin, MA, USA) equipped with a sample dryer unit (SDU) and a calibration control unit (CCU) customized for use onboard the ships. The GFC
10 detector operates on the principle that CO absorbs infrared radiation at a wavelength of 4.6 μm . Some other trace gases also absorb at this wavelength, such as water vapor (H_2O) and CO_2 , and these gases can interfere with CO quantification at ppbv levels (Dickerson and Delaney, 1988; Fried et al., 1991). Although CO_2 also absorbs in the
15 infrared, H_2O has a greater effect on CO quantification because there is a large amount of H_2O in the atmosphere. Dickerson and Delany (1988) reported that interference by H_2O can be reduced by drying the air samples. Nedelec et al. (2003) estimated the H_2O interference to be about 6 ppbv CO per hPa H_2O for their GFC system. Because we used dry CO-in-air gas standards to calibrate the GFC sensitivity, H_2O removal from
20 the sample air was required in order to eliminate H_2O interference expected for humid air samples collected from marine air masses over the ocean.

In addition to H_2O interference, drift of background signals generates uncertainty in the CO determination. Because substantial background drift occurs in response to changes in ambient temperature over short periods (from minutes to an hour), the
25 changes in the signal intensity have to be corrected for if CO is to be precisely quantified. To overcome these analytical difficulties on the ships, we use a sample dryer unit and an automatic calibration unit for the continuous CO measurements. Here we

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



describe in detail the design and performance of the continuous CO measurement system, including the quantification method and quality assurance and quality control measures.

3.1 Sample dryer unit

5 The CO measurement system is shown schematically in Fig. 3. The SDU (500 mm depth × 300 mm wide × 500 mm high; mass 20 kg) consists of an oil-less diaphragm pump, an electric cooler, a peristaltic tubing pump, and a Nafion Perma Pure dryer. Teflon tubing (1/4 inch) is used for all the plumbing to prevent CO losses to the inner surface of the tubing. The diaphragm pump (MOA-P108, GAST Manufacturing Inc.,
10 Benton Harbor, MI, USA) draws ambient air from the air intake and subsequently feeds the air to the electric cooler (thermoelectric dehumidifier, DH-109, Komatsu Electronics Inc., Kanagawa, Japan) at a flow rate of 4.5 l min^{-1} to dehumidify the air to a dew point of $1\text{--}3^\circ\text{C}$. The condensed water in the cooler is drained by the peristaltic tubing pump (PB series 7017, Masterflex, Barrington, IL, USA) at a flow rate of 4.8 ml min^{-1} .
15 The dried air stream is further dehumidified by passage through the Nafion Perma Pure dryer (PD-50T-24MKR, Japan Controls Co., Tokyo, Japan) with the help of the pressure difference between the sample and purge gases. A countercurrent as a purge gas for the dryer is generated by partial diversion of the main sample flow: the sample stream (4.5 l min^{-1}) is split into a 1.5 l min^{-1} main sample flow and a 3.0 l min^{-1} purge gas flow
20 by means of a pressure regulating valve to optimize the drying capacity. The two-step drying procedure provides a 1.5 l min^{-1} dry airstream at a dew point below -30°C .

3.2 Calibration control unit

The CCU is 430 mm depth × 482.6 mm wide × 132.5 mm high and has a mass of 15 kg (Fig. 3). Its main components are solenoid valves, pressure regulating valves, two
25 mass flow controllers, and a CO scrubber. The sample gas, standard gas, and nitrogen gas are connected to the CCU, and the gas pressures are adjusted to approximately

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Onboard
measurement system
of atmospheric
carbon monoxide**H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

0.05 MPa by back-pressure and forward-pressure regulating valves. Operation of each three-way solenoid valve is controlled by an electric time relay switch (Daily Time Switch, H5L-A, Omron, Tokyo, Japan). The dry sample stream from the SDU is introduced to the CCU, and by switching the solenoid valves, the gas stream can be directed either to the GFC directly or to the GFC through the CO scrubber. The flow rates of these gas streams are kept at 800 ml min^{-1} by a mass flow controller (Thermal Mass Flow Controller 3660, Kofloc, Tokyo); the air stream is introduced to the GFC, and the excess 700 ml min^{-1} of sample stream is exhausted to the outside. Injection of nitrogen gas is controlled with a manually operated two-way solenoid valve. The nitrogen gas is used to purge the optical cell of the GFC to prevent absorption of particles and polar substances onto the cell surface, and the nitrogen gas is introduced into the GFC at a flow rate of 40 ml min^{-1} , which is adjusted by means of another mass flow controller.

CO-free gas (zero-air) is produced inside the CCU by passage of the sample air stream through the CO scrubber. We used SOFNOCAT 514 (Molecular Products, Thaxted, Essex, UK), a hydrophilic CO oxidizing agent, to scrub CO from ambient air without altering the humidity. Nedelec et al. (2003) used SOFNOCAT to produce zero-air in their CO measurement system installed onboard MOZAIC aircraft and determined the CO removal rate during long-term operation. We calculated the rate of CO removal by SOFNOCAT in the experiments carried out onboard the ships by comparing the GFC signal intensities of zero-air generated through SOFNOCAT with those of synthetic air, which is free of CO (Japan Fine Products, Kanagawa, Japan). No substantial deterioration in CO removal capacity was found beyond the analytical precision of the GFC while the air temperature and humidity were varied between 7.6 and 30.1°C and between 48.5 and 84% , respectively. In addition, our periodic checks during maintenance of the observation instruments demonstrated that the CO removal capacity of SOFNOCAT remained constant for at least 1 yr of continuous usage on the ship.

3.3 GFC detection unit

Before the GFC was installed on the ships, its analytical performance was evaluated. The analytical precision and detection limit of the GFC were evaluated with six high-pressure cylinders containing CO balanced with purified air at known mixing ratios (49.25, 95.98, 195.48, 300.01, 508.25, and 1121.50 ppbv), which were calibrated against the NIES 09 CO scale. From replicate measurement of these gases for 10 min, the analytical precision was determined to be 10 ppbv ($\pm 1\sigma$) for different CO levels, indicating no dependency on the CO mixing ratio within the range examined here. The detection limit was determined by analysis of CO-free air for 20 min. The variability of the baseline CO signals for 20 min corresponded to 6 ppbv ($\pm 1\sigma$), and the resulting detection limit was determined to be 18 ppbv (3σ of the measurement). The linearity of the GFC response was tested with a VURF CO analyzer (Ultra-fast carbon monoxide analyzer, Aero-Laser GmbH, Garmisch-Partenkirchen, Germany), which has an excellent linear response to CO mixing ratios over a wide range (Gerbig et al., 1996; Gerbig et al., 1999). The GFC signal intensity is plotted against the CO mixing ratios determined by the VURF instrument in Fig. 4. Least-squares fitting gave a determination coefficient (R^2) of 0.99 for CO mixing ratios ranging from 49 to 1122 ppbv. The residual of the GFC signals from the fitting line at each mixing ratio was well distributed within the typical analytical precision, demonstrating the good linearity of the GFC response.

3.4 CO quantification

In our CO measurement system, sample air and zero-air are introduced into the GFC alternately on a 1-h cycle: sample air for 40 min followed by zero-air for 20 min to correct for background drift during ambient air measurement. For correction of the day-to-day variability in the GFC sensitivity, standard gas is injected to the GFC for 10 min once a day. The CO mixing ratios are calculated from the mean signal intensity of the sample gas for 40 min with reference to the mean signal intensity of the standard gas after correction for the background drift of the GFC. The background drift during

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Onboard
measurement system
of atmospheric
carbon monoxide**H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

sample and standard gas injection is estimated by linear interpolation between two averaged signal intensities for zero-air, which is injected before and after measurements of sample or standard gas. The net signal intensities are calculated by subtracting the interpolated background signals from the average signal intensity of sample and standard gas. To eliminate possible contamination from the ship's exhaust, we evaluated CO data against empirical criteria established from CO₂ measurements. When CO₂ data are processed, 10-min averages and standard deviations are calculated from 10-s data. When the mean CO₂ values exceed 3 σ , corresponding CO data are judged as indicating contamination. Along the Southeast Asia route, the CO data are evaluated on the basis of CO₂ and O₃ data because local emission sources, including biomass burning, are common, resulting in high temporal variability.

We used a CO standard gas balanced with purified air at a mixing ratio of approximately 1.1 ppmv as a reference gas for CO quantification by GFC. Novelli et al. (2003) reported that gas standards drift to higher CO values in high-pressure cylinders over time. Tanimoto et al. (2007) reported the possibility of artificial CO production on the metal surface inside the cylinders of air-balanced CO standards, whereas this effect is negligible for N₂-balanced CO standards. For this reason, the use of a N₂-balanced CO standard gas is preferable, but GFC measurements require air-balanced CO standard gases owing to the changes in GFC sensitivity in the presence of O₂. To overcome these problems, we use CO standard gases balanced with air at the ppmv level to minimize CO increases, because the rate of CO increase is typically on the order of several ppbv per year (Novelli et al., 1994). In our study, we referenced all the CO mixing ratios to the NIES 09 CO scale. In 1996 NIES established a scale for CO measurements by preparing four CO-in-air gravimetric gas standards in 9.4-L high-pressure aluminum cylinders (NIES 96 scale; CO mole fractions: ca. 50, 150, 250, and 350 ppbv). The NIES 96 scale was in use from 1996 to 2008. In 2008, the NIES CO scale was changed to reference ppmv-level gas standards (NIES 09 scale) to minimize the effects of the artificial CO increases described above. The NIES 09 CO scale consists of four air-balanced CO standard gases in 9.4-L high-pressure aluminum cylinders prepared

**Onboard
measurement system
of atmospheric
carbon monoxide**H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

gravimetrically at 2030, 3028, 4027, and 5032 ppbv. These gas standards are quantified by a VURF instrument. The background signals are determined with CO-free air (zero-air) produced by passing purified air (<5 ppbv CO) through SOFNOCAT 514. The NIES CO scales are periodically examined by means of rigorous calibration with gravimetrically prepared standard gases and through international comparisons with scales from other laboratories. For example, the NIES 09 CO scale was compared to the WMO-2004 scale maintained by the NOAA/Earth System Research Laboratory's Global Monitoring Division in a round-robin intercomparison project in 2002–2007, and the scale was assessed in the Cucumber CarboEurope intercomparison experiment in 2008. These intercomparisons indicated that the NIES 09 CO scale is higher than the WMO-2004 scale by 10–11 ppbv at the 150 ppbv level and by 12–13 ppbv at the 310–330 ppbv level (Katsumata et al., 2011).

We determine the CO increase in the standard gases used to quantify the CO mixing ratios by means of continuous measurements and flask analysis. The evolution of CO relative to the original CO mole fraction in our CO standard gases is shown in Fig. 5. Although the CO mole fraction in all standard gases increases over time, the impact of the CO increase for continuous measurements (ppmv-level) is clearly minimal. In contrast, the standard gases prepared at ppbv-level show substantial CO increases. The rates of CO increase in these standard gases are high, ranging from 8 to 19 ppbv y⁻¹, whereas those reported by NOAA are only 1–2 ppbv y⁻¹ (Novelli et al., 1994). These results suggest that high-frequency calibration of CO-in-air standard gases at the ppbv-level will be required in order to sustain primary calibration scales of CO in individual laboratories.

4 Quality assurance and quality control of CO monitoring

4.1 Comparison of continuous and flask measurements

Ambient CO mixing ratios observed continuously on the ships in various regions over the Pacific Ocean are shown in Fig. 6, along with ratios determined by GC/RGD analysis of flask samples. In general, continuous measurements and flask analysis data agreed reasonably well. The continuous measurements along the TF5 and SKB routes revealed smooth and homogeneous variations of CO, which are typical for the clean atmosphere in remote regions; in contrast, short-term variations were captured near ports in the Northern Hemisphere. In general accordance with the distribution feature of observed CO, the flask analyses present climatological features of CO along these routes.

Along the Southeast Asia route, the continuous measurements clearly captured the high variability of CO due to regional pollution, and the flask analyses missed many elevated peaks. These results suggest that the continuous measurements by GFC are more useful than flask analyses particularly along the Southeast Asia route, despite the fact that the analytical precision of GFC is poorer than that of GC/RGD.

4.2 Consistency of continuous and flask analyses

The CO mixing ratios obtained by continuous measurement and by flask analyses were scrutinized to evaluate the consistency and robustness of both the measurement techniques and the gas standards. The flask samples were collected and analyzed between November 2005 and June 2010 for TF5, between July 2007 and March 2010 for SKB, and between September 2007 and May 2010 for FTW. After screening for contamination from the ships, the numbers of flask samples used for the comparison were 723, 96, and 115 in total for TF5, SKB, and FTW, respectively.

Scatter plots of continuous measurement data versus flask analysis data for the three shipping routes are shown in Fig. 7. The observed CO mixing ratios ranged from 41

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to 364 ppbv for all three routes. The continuous measurements and the flask analysis data were highly correlated (the determination coefficients were ~ 0.97 for all the VOS ships). The slopes of the plots calculated by least-squares fitting were very close to 1 (0.98–1.01), and the intercepts were close to zero (–3.8 to 2.6). Although a few outliers were observed in each dataset, they likely originated from a mismatch between the averaging time for the continuous measurements (40 min) and the discrete and instantaneous sampling time for the flasks. The excellent linear relationships between the two CO datasets did not depend significantly on the mixing ratios, demonstrating that there was no significant degradation of CO in the flask samples during storage after collection.

The temporal variations and relative frequency distributions of the differences between the two datasets are shown in Fig. 8. The differences showed Gaussian distributions, and 87, 93, and 80 % of the TF5, SKB, and FTW data fell within the range of typical GFC analytical precision (± 10 ppbv). The average values were close to zero (–1.8 to 2.7 ppbv), and the standard deviations were less than 10 ppbv (5.3–7.5 ppbv). The long-term trends of the differences during the past 3–5 yr were neither systematic nor substantial for any of the TF5, SKB, and FTW data, beyond the GFC analytical precision of ± 10 ppbv. For TF5 data, differences seemed to increase slightly during the latter half of 2008, remain constant until early 2010, and then drop back to close to zero. Such temporal variations may reflect minor issues in either the continuous measurements or the flask analysis data, warranting further study. Nevertheless, the differences over the last 5 years were well within the typical GFC analytical precision. These results demonstrate the internal consistency between the two different techniques with different gas standards.

5 Preliminary results of continuous CO measurements

The CO distributions in different seasons from March 2008 to February 2009 are presented in Fig. 9 for the combined data for all three VOS observations. Along the TF5

**Onboard
measurement system
of atmospheric
carbon monoxide**H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

route, enhancements of CO were observed in the northern mid-latitude region, particularly during the boreal winter (Figs. 6 and 9d), due likely to continental outflow from East Asia driven by a Siberian high-pressure system. Except in the mid-latitude region in the Northern Hemisphere, CO mixing ratios were generally lower than those observed along the other routes, and the ratios showed a smooth southward decreasing gradient. We attribute this north-to-south gradient mainly to the localization of the CO sources in the Northern Hemisphere. The north-to-south gradient was larger in the boreal winter than in the boreal summer (Fig. 9b), reflecting typical CO seasonality (maximum in winter and minimum in summer) in each hemisphere. The observed CO distributions along the TF5 route were consistent with previous observations at remote sites (e.g., Novelli et al., 2003), suggesting that TF5 captured typical background CO mixing ratios in both hemispheres over the Pacific Ocean.

Along the SKB route, the CO mixing ratios showed a longitudinally homogeneous distribution in the northern North Pacific between 160 and 230° E. A seasonal maximum and minimum were observed in the boreal spring (Fig. 9a) and boreal summer, respectively. A small longitudinal gradient, decreasing from west to east, was observed in the CO distribution during all four seasons (see Fig. 6 as an example of the longitudinal gradient in the boreal winter). The maximum longitudinal gradient was observed in the boreal spring, which coincided with the maximum mixing ratios. This result suggests that the CO mixing ratios along the SKB route were perturbed by Eurasian continental emission sources in the boreal spring. Tanimoto et al. (2008b) reported springtime CO enhancement at Rishiri Island in northern Japan due to biomass burning in eastern Siberia. Biomass burning may contribute to the CO maximum in the boreal spring.

In contrast to the CO distributions along the TF5 and SKB routes, the CO distribution along the FTW route showed large temporal and spatial variations. The overall CO mixing ratios along this route were markedly higher than along the other two routes, showing a maximum in December–February (Fig. 9d) and a minimum in June–August (Fig. 9b). Systematic atmospheric observation has not been performed in Southeast

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Asia, and our observation reveals several important features of the CO distribution, especially during the northern winter. We describe four distinct periods (Fig. 6). In period 1, a prominent CO enhancement was observed when the ship sailed in the coastal region of China. During the northern winter, atmospheric circulation in the Asian region is driven by Asian monsoon circulation: air masses that pass over the East Asia region travel to the East/South China Sea, whereas the region is covered during the northern summer season by clean maritime air from the Pacific. The CO enhancement was most likely due to the prevailing continental outflow, which efficiently picked up anthropogenic emissions from the surface and transported CO from East Asia to the East/South China Sea. In periods 2 and 4, the CO mixing ratios increased when the ship sailed in the coastal area of Indochina. Several previous studies reported that biomass burning activity becomes high during the dry season in Indochina (December–April; Pochanart et al., 2003; Kondo et al., 2004). Our backward trajectory analysis indicated that the ship captured air masses that passed over Indochina within a day, suggesting that biomass burning affected the CO distribution. In period 3, the CO mixing ratios increased when the ship sailed in the Strait of Malacca. A variety of ships constantly sail in the strait, and therefore CO emissions from ships have a large impact in this region. As is not clear in Fig. 9, CO enhancement is often observed during the late dry season in Indonesia (September–November) around the southern part of the South China Sea, owing to the extensive biomass burning associated with agricultural activity in Borneo (Nara et al., 2011). Thus, the FTW route captured several important polluted outflows containing high CO mixing ratios.

6 Summary and conclusions

Atmospheric CO mixing ratios were continuously measured over the Pacific Ocean on commercial cargo vessels participating in the NIES VOS program. For onboard CO measurements, an in situ CO measurement system was developed employing a commercially available GFC instrument combined with a customized sample dryer unit

**Onboard
measurement system
of atmospheric
carbon monoxide**H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

and a calibration control unit. The excellent linearity of the GFC data, verified by means of a VURF instrument, allowed the use of ppmv-level CO-in-air gas standards. Use of the gas standards onboard the ships minimized the influence of drift in background signals and the sensitivity of the GFC instruments. The standard gases were also calibrated against the NIES 09 CO scale before and after use to correct for artificial CO increases in the working gas standards used on the ships. Comparison between the NIES 09 CO scale and the WMO-2004 scale indicated that the former was higher than the latter by 10–11 ppbv at the 150-ppbv level and by 12–13 ppbv at the 310–330-ppbv level.

The CO mixing ratio data obtained by continuous measurement were compared with data obtained by flask sampling and subsequent laboratory GC/RGD analysis. The continuous CO data provided a more detailed picture of the CO distribution than did the flask sampling data, although the latter captured the general features of the CO distribution. In Southeast Asia, the flask analyses provided only marginal information on CO distribution, owing to the large spatial and temporal variations of CO. These results clearly suggest the need for continuous measurements with high time resolution. Statistical analysis showed good consistency between the two datasets obtained with the two measurement techniques, demonstrating that the continuous measurement data had no systematic errors and biases relative to the flask sampling data for any of the three ships.

The CO observations by the three VOS ships revealed characteristic features of the CO distributions in the three regions. Along the Oceania route observed by TF5, a latitudinal gradient from north to south was observed, reflecting the fact that the majority of CO emission sources are located in the Northern Hemisphere. Along the North Pacific route of SKB, longitudinal distributions were relatively uniform with a slight west-to-east gradient in all seasons, likely due to substantial impacts from emission sources on the Eurasian continent. In contrast, data from the Southeast Asia route of FTW showed large spatial and temporal variations, due likely to the transport of polluted air masses of continental origin. Overall, these results suggest that the NIES

VOS program is a useful platform for studying the global distribution of CO, contributing to better understanding of the global CO budget.

Acknowledgements. We appreciate Toyofuji Shipping Co. for their generous cooperation with the NIES VOS program. We thank Y. Terao for valuable discussions and K. Katsumata for assistance in maintaining and calibrating the CO standard gas. We also thank S. Kariya, T. Yamada, and T. Nojiri of the Global Environmental Forum for their assistance with the observations. This work was conducted with financial support of Global Environment Research Account for National Institutes provided by the Ministry of the Environment of Japan.

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- 30

**Onboard
measurement system
of atmospheric
carbon monoxide**

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Onboard
measurement system
of atmospheric
carbon monoxide**

H. Nara et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Onboard
measurement system
of atmospheric
carbon monoxide**

H. Nara et al.

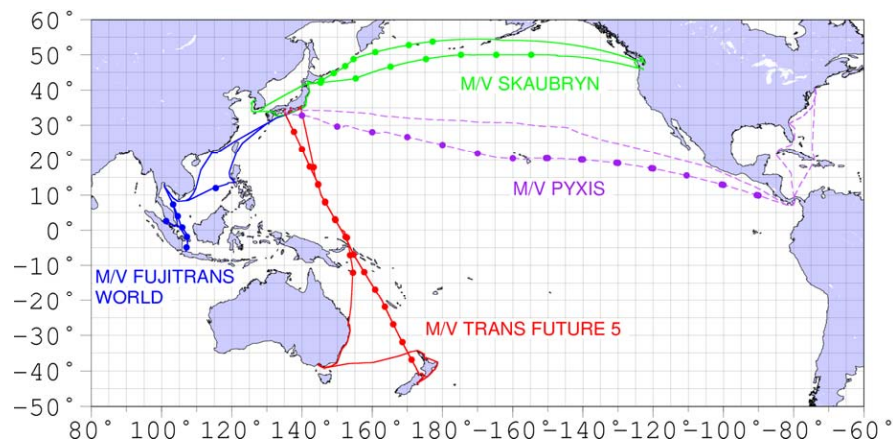


Fig. 1. Current geographical coverage of atmospheric monitoring in the NIES VOS program: blue, *Fujitrans World*; purple, *Pyxis*; green, *Skaubryn*; red, *Trans Future 5*. For atmospheric CO, both continuous measurement and flask sampling followed by GC/RGD analysis are being conducted along the three routes indicated by solid lines, whereas only flask sampling is conducted along the route indicated by the dashed lines. Dots denote flask sampling points.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

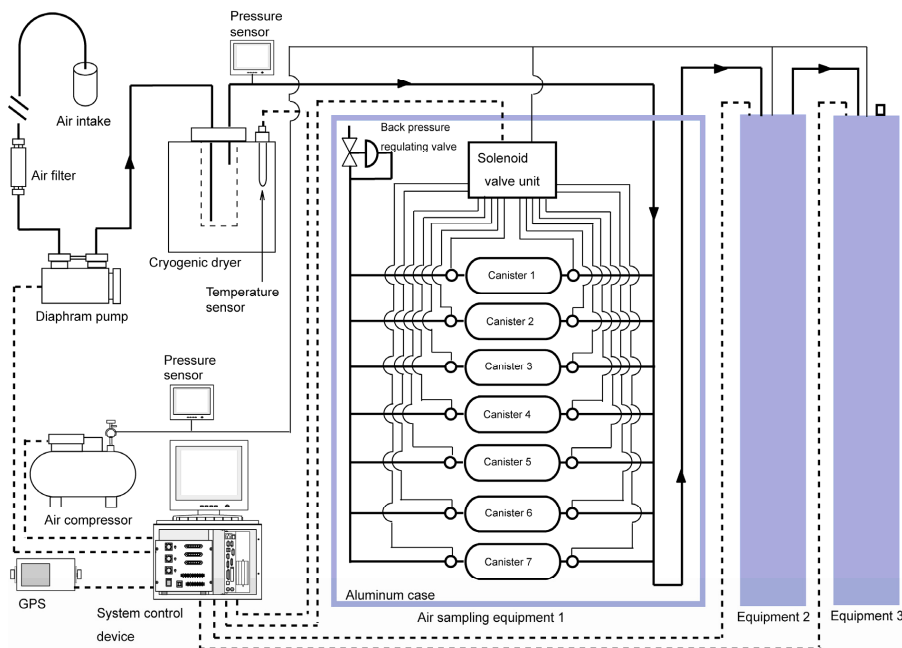


Fig. 2. Schematic diagram of a flask sampling system for the NIES VOS program. Thick and thin solid lines denote lines for sample and compressed air respectively. Thick dashed lines denote the electric wiring that connects the system control device with discrete components of the system.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

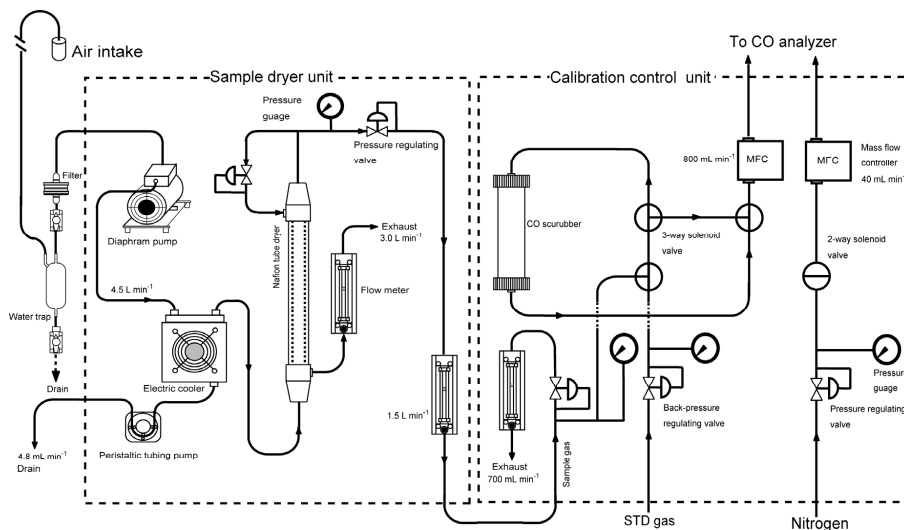


Fig. 3. Schematic diagram of the continuous CO measurement system, including a sample dryer and a calibration control unit.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

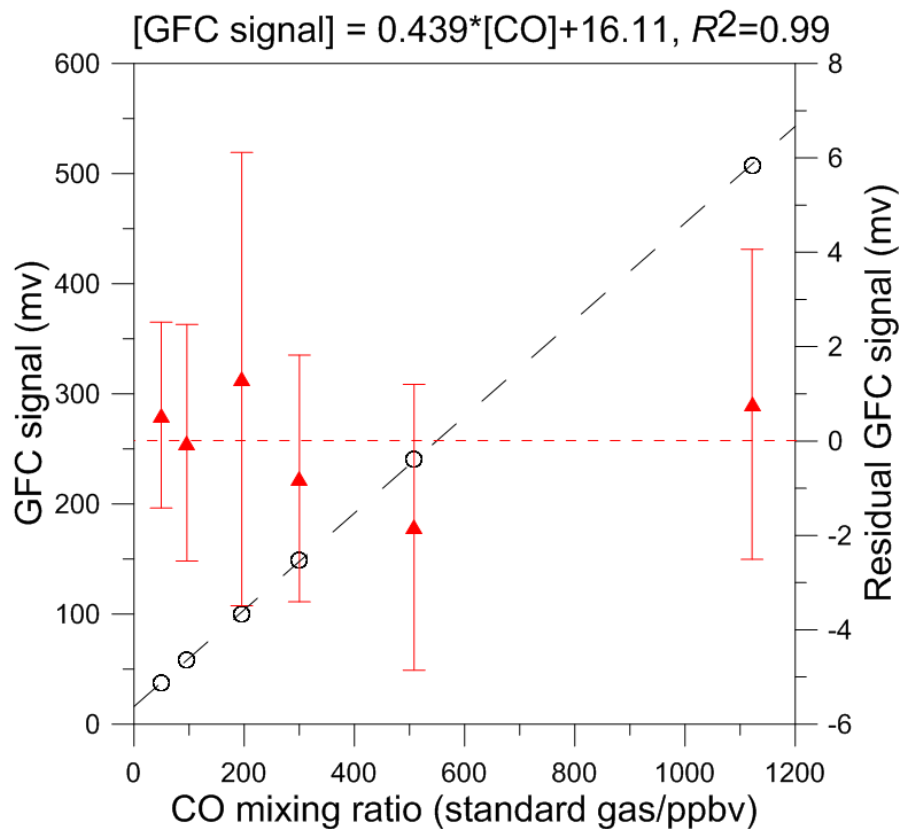


Fig. 4. Linear response of GFC signals versus CO mixing ratios in the NIES 09 CO scale (open circles) determined by VURF. Averages of the GFC signal residual from the fitting line at each CO mixing ratio are also plotted (triangles) with 1σ values as vertical bars.

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

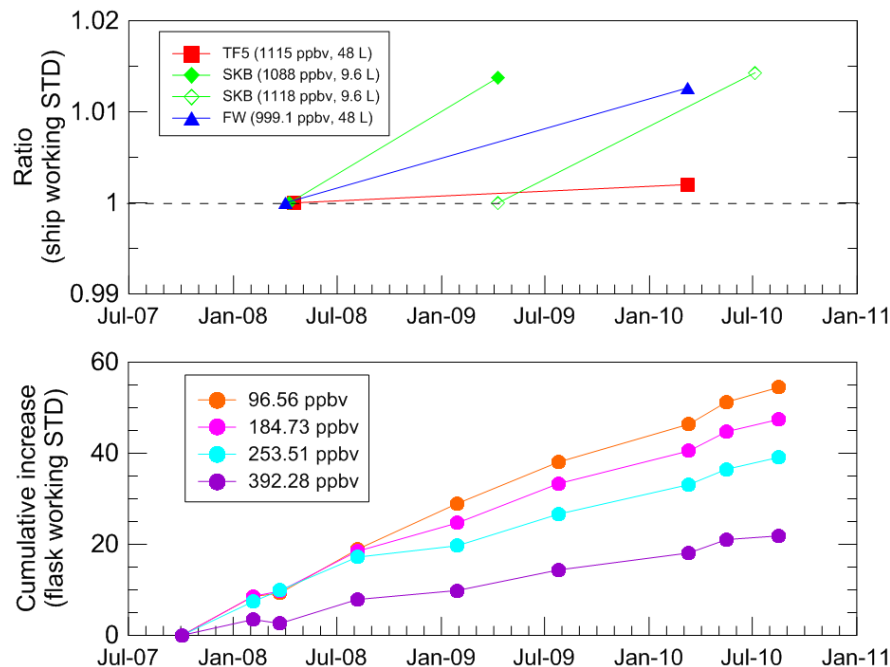


Fig. 5. Calibration history of CO gas standards used for continuous onboard CO measurement (upper) and flask analysis (lower). Note that onboard CO standard gases were calibrated before and after use, whereas the standards for flask analysis were calibrated periodically.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

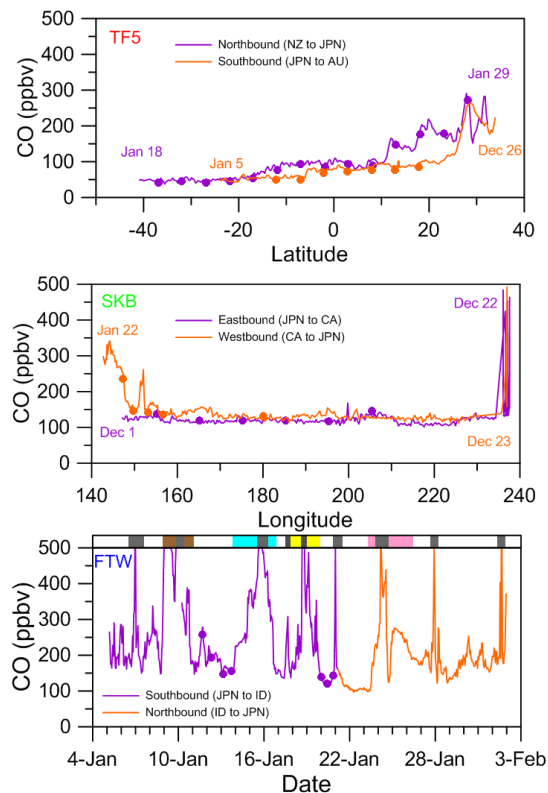


Fig. 6. Variations of CO mixing ratio observed by the three ships from December 2008 to January 2009 as a function of latitude (TF5), longitude (SKB), and date (FTW): continuous data (lines) and flask analysis data (solid circles). Four distinct CO increase periods are indicated by color coding across the top of the bottom panel: period 1, brown; period 2, cyan; period 3, yellow; period 4, pink. Gray denotes the ship's berthing at each port. For more details, see Sect. 5.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Onboard
measurement system
of atmospheric
carbon monoxide**

H. Nara et al.

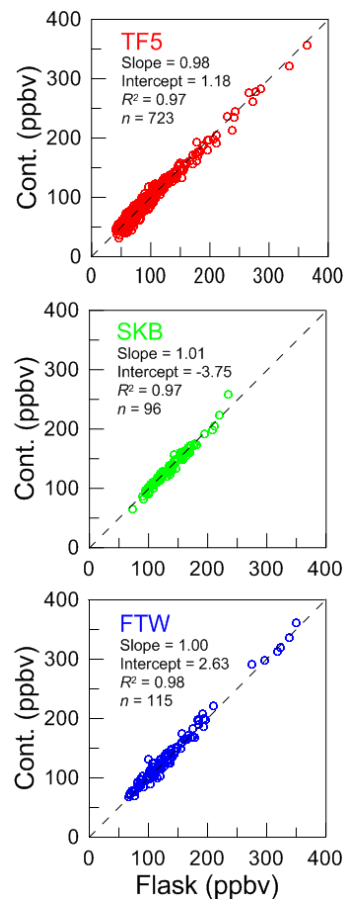


Fig. 7. Scatter plots of CO mixing ratios obtained by continuous (cont.) measurements against ratios obtained by flask analyses (flask) for TF5, SKB, and FTW. The dashed lines indicate the 1:1 correspondence lines.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

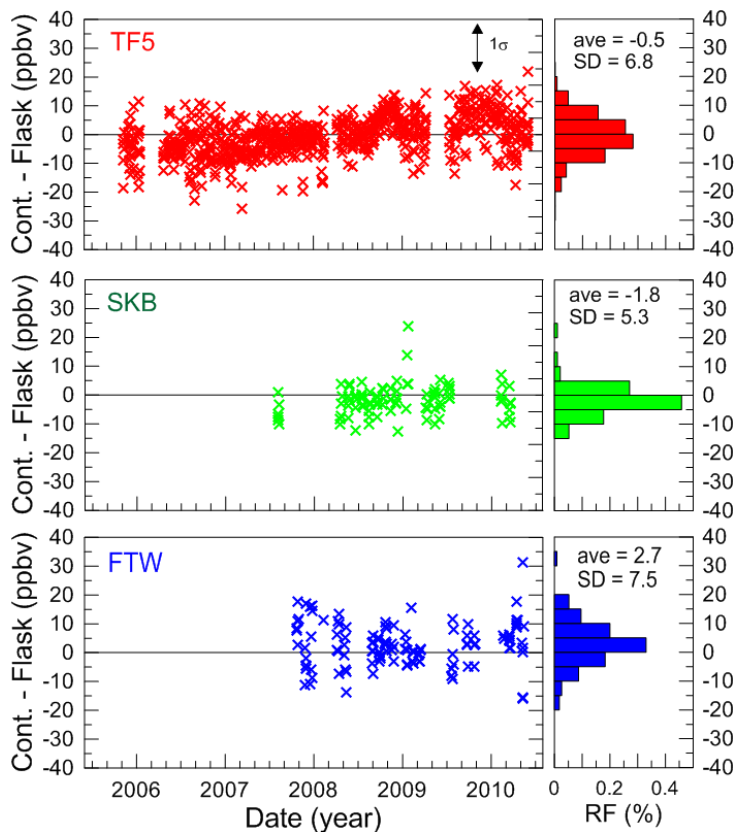


Fig. 8. Temporal variations (left) and relative frequency (RF) distributions (right) of the differences between continuous (cont.) measurements and flask analysis measurements for TF5, SKB, and FTW. The typical analytical precision of continuous measurements by GFC (1σ) is illustrated by a doubled-headed arrow (left). The averages and standard deviations (SD) are also indicated (right). Each bin is 5 ppbv.

Onboard measurement system of atmospheric carbon monoxide

H. Nara et al.

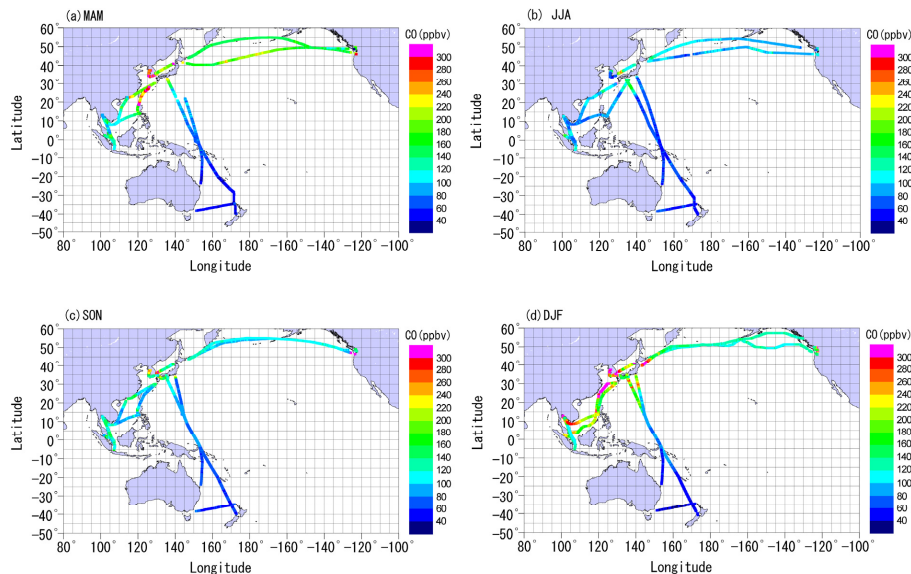


Fig. 9. Distribution of CO mixing ratios observed by three ships from March 2008 to February 2009: **(a)** March, April, and May (MAM), **(b)** June, July, and August (JJA), **(c)** September, October, and November (SON), **(d)** December, January, and February (DJF).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)