Readout
HORIBA Technical Reports

English Edition November 1997 ■ No.1

Monitoring and Measuring Systems for Background Air Pollution

Yasuhiko Joo, Fumio Watanabe, Masamichi Aono
Hajime Mikasa

(Pages*23*–*28*)

株式会社 堀場製作所

Special Feature Article

Monitoring and Measuring Systems for Background Air Pollution

Yasuhiko Joo
Fumio Watanabe
Masamichi Aono
Hajime Mikasa

1. Introduction

At the United Nations Conference on Environment and Development (UNCED), the Earth Summit, held in Rio de Janeiro, Brazil in 1992, "Agenda 21" was adopted as a concrete plan of action on the environment for the 21st century, and the "Framework Convention on Climate Change" was signed. The Japan Meteorological Agency has been pursuing several projects as part of its contribution to this international effort. In addition to participating in the Background Air Pollution Monitoring Network (BAPMoN) promoted by the World Meteorological Organization (WMO), the Agency is enhancing and expanding the Global Atmosphere Watch (GAW) program, and has opened three new environmental monitoring posts: the Ryori Regional Station (Iwate Prefecture), the Minamitorishima Global Station (Metropolitan Tokyo), and the Yonagunijima Regional Station (Okinawa Prefecture). In addition, monitoring data continues to be collected to accurately assess future climate variation, and preserve the global environment. The accurate background measurement of greenhouse gases requires the ability to detect minute changes in concentrations over long periods of time (for example, a change of 350 ppmv in carbon dixide (CO_2) levels, approximately 0.4% per year, or a 1.7 ppmv change in levels of methane (CH_4), about 1% per year), as well as systematic measurement techniques. This paper introduces the current status of background air pollution monitoring and monitoring equipment for greenhouse gases used by the Japan Meteorological Agency.

2. Current Status of WMO Background Air Pollution Monitoring Network[1)]

In 1967, the Organization for Economic Cooperation and Development (OECD) advocated the monitoring of background air pollution and, towards this end, called for the establishment of a monitoring network overseen by the WMO. This led to the start of the BAPMoN in July 1970 with 15 monitoring stations in 11 countries. The purpose of BAPMoN is to "obtain global and regional background concentration levels (pollution conditions not affected by urban pollution and other high-concentration pollution sources) of atmospheric constituents, their variability and their long-term changes, from which the influence of human activities on the composition of the atmosphere can be judged". The monitoring network has been gradually expanded, but has been unable to live up to expectations due to varying conditions in the WMO member countries. This situation led to the formulation of the Agenda 21 action plan mentioned above. The WMO maintains two major monitoring networks, the BAPMoN and the Global Ozone Observing System (GO_3OS). GO_3OS, in particular, was developed to better understand circulation in the stratosphere, and heat balance. However, since individual environmental problems are all closely interconnected, adequately addressing the global problem of the environment requires build a monitoring network based on new conceptions that combine and develop existing notions of environmental monitoring. The GAW program was established in 1989 for just this purpose. In 1992, the GAW program adopted technical regulations for the purpose of "obtaining necessary data and other information from regions all over the world about the chemical composition and the related physical characteristics of the background atmosphere for better understanding atmospheric behavior and the interaction among the atmosphere, the oceans and the biosphere, and forecasting of the future global system." The monitoring stations belonging to the GAW are divided into the two categories shown in **Table 1**. As of December 1993, these monitoring stations consisted of 14 global stations and 382 regional stations. The WMO estimates that

Table 1 Functions and Site Conditions for GAW Monitoring Stations

Monitoring Station	Global Stations	Regional Stations
Role	Clarifying long-term changes in atmospheric components on a global scale affecting the weather and climate. Quite strict conditions are required.	Clarifying long-term changes in atmospheric components caused by industrial activities, land use, energy use, use of forest resources, and other changes in human activity at representative sites from continental regions starting of 500,000 km^2.
Site Conditions	A remote location where prominent changes in land use are not expected to arise in the next 20 to 30 years within an appropriate distance (30 to 50 km) in all directions from the monitoring station. To be free from the effects of regional sources of pollution for 60% of the total time throughout the year.	A location where the monitoring data to be collected will represent the characteristics of the region. To be free from the major effects of local pollution sources such as roads, burning, industry, and expanded agricultural activities.

Table 2 WMO GAW World Data Centers

Target	Country	Agency
Greenhouse gases	Japan	Meteorological Agency (Observation Department, Environmental Weather Section)
Atmospheric turbidity	United States	Oceanic Atmosphere Agency (National Climate Data Center)
Chemical composition of precipitation and dry deposition	United States	Oceanic Atmosphere Agency (National Climate Data Center)
Ozone (not including ground ozone)	Canada	Atmosphere and Environment Agency(World Ozone Data Centre)
Ground ozone	Norway	National Atmospheric Laboratory

for every major climatic zone and biome to be adequately covered, between 30 to 40 global stations will be required worldwide. Table 1 shows the functions and site conditions of the GAW monitoring stations. The background values measured at these monitoring stations are sent to data centers located all over the world (see **Table 2**). This data is then supplied to such people as researchers, observers, and policy makers in the form of printed reports or on computer floppy disks.

3. The Japan Meteorological Agency's Background Air Pollution Monitoring Network[1)]

The foundation of BAPMoN by the WMO marked the beginning of the Japan Meteorological Agency's involvement in establishing monitoring stations for background air pollution. From 1973 to 1975, the Meteorological Rocket Observation Station located in Ryori, Iwate Prefecture, was outfitted with monitoring facilities, and in January 1976 began monitoring atmospheric turbidity, the chemical composition of precipitation and dry deposition, and the surface weather. This was Japan's only WMO background air pollution regional station at the time. As awareness of global warming increased worldwide, however, in January 1987 the Japan Meteorological Agency started monitoring the atmospheric concentration of carbon dioxide, the most prevalent of the greenhouse gases. In 1990, monitoring also began for the atmospheric concentration of freon, and in 1991 methane and carbon monoxide were added. However, WMO requirements call for the establishment of one regional station for every 500,000-km^2 area of the earth's surface. If the surrounding sea area is included, then Japan was required to establish four to five monitoring stations. To cover these unmonitored areas in the GAW network, a global station was established in the northwest Pacific about 2,000 km south-southeast of Tokyo in January 1993. The Minamitorishima Meteorological Observing Station is located in the town of Ogasawara on Minamitorishima Island in the southeastern-most part of the Japanese archipelago, and is Japan's first global station. The monitoring of atmospheric carbon dioxide concentrations began there in March 1993, and measurements of the atmospheric concentration of methane, carbon monoxide, and other substances started in 1994. In January 1997, the Agency opened a regional station, this time in the far west of Japan. The Yonagunijima Island Regional Station is located on Yonagunijima Island in the Okinawa chain, some 1,900 km southwest from Tokyo. The background air monitoring items and measurement systems used by the Japan Meteorological Agency at these two stations are shown in **Table 3**.

Table 3 Background Air Pollution Monitoring Items and Measurement Systems

Target	Analyzer and Principle
Atmospheric turbidity	Sun photometer
Chemical composition of precipitation and dry deposition	pH meter, atomic absorption spectrophotometer
Trace components in the atmosphere	
Carbon dioxide	Non-dispersive infrared analyzer
Ground ozone	UV absorption method
Total Ozone	Brewer spectrophotometer
Methane	Non-dispersive infrared analyzer
Carbon monoxide	Non-dispersive infrared analyzer
Freon	Gas chromatography (ECD)

4. Procedures for Monitoring Greenhouse Gases [1)]

4.1 Monitoring Greenhouse Gases

The greenhouse effect is caused by the absorption of infrared light by greenhouse gases in the atmosphere. For this reason, the concentration of these gases are measured using infrared gas analyzers. However, because the background monitoring of greenhouse gases requires the ability to detect minute changes in the atmospheric concentration over long periods of time (for example, a change of 350 ppmv in CO_2 levels, approximately 0.4% per year, or a 1.7 ppmv change in levels of CH_4, about 1% per year), not only accurate monitoring equipment, but also special techniques for the entire monitoring system are needed.[2)] Common methods for the measurement and characteristics of the greenhouse gases today are shown in **Table 4**.

4.2 Monitoring Carbon Dioxide Concentration

Figure 1 shows the Japan Meteorological Agency's Minamitorishima Meteorological Observing Station, while **Figure 2** is a schematic diagram of the monitoring equipment for atmospheric carbon dioxide concentration. Minamitorishima Island is isolated in the ocean far from other land masses, and has high humidity year-round. Because of these conditions, the monitoring equipment used at the station incorporates improvements to the dehumidifier and filter to prevent sea salt particles from entering the equipment. The monitoring equipment consists of the Horiba differential-type non-dispersive infrared analyzer, a sample preconditioning unit, a control computer, and a calibrator. This system is capable of performing several automatic operations, as described in the next page.

Table 4 Common Measurement Methods and Characteristics of Greenhouse Gases

Greenhouse Gas	Reason for Monitoring	Measuring method/principle
Carbon dioxide	An important greenhouse gas as being the largest portion of greenhouse gases except for water vapor. Approximately 56% of greenhouse gases for over the past 10 years. Generated from the burning of fossil fuels, respiration by living things, and volcanic eruptions, among others. Consumed by the photosynthetic activity of plants	Differential-type NDIR to offer improved minimum detection sensitivity. Four high-precision standard gases are used to perform measurements while calibrating every two hours to compensate for drift and fluctuations in atmospheric pressure. The sample gas is dehumidified to less than -50°C so that the effects of interference and changes in partial pressure of the moisture can be disregarded.
Methane	An important greenhouse gas Approximately 15% of greenhouse gases for over the past 10 years. Generated from the decomposition of organic matter in the absence of oxygen in marshes and paddy fields, intestinal fermentation in animals, natural gas and coal excavation, and transportation processes, among others	• Gas chromatograph and FID (flame ionization detector) • Selective combustion method (Catalytic oxidation of NMHC) and Cross-flow modulation system NDIR
Freon	Cited for causing damage to the ozone layer, freon is an important greenhouse gas. Remains in the atmosphere from roughly 20 to 30 years up to several hundred years. Has a tremendous impact on the greenhouse effect with even low concentration, at approximately several hundred ppt (For each molecule of freon 13, there are over 10,000 molecules of CO_2)	Sample concentrator, Gas chromatography, and ECD (electron capture detector)

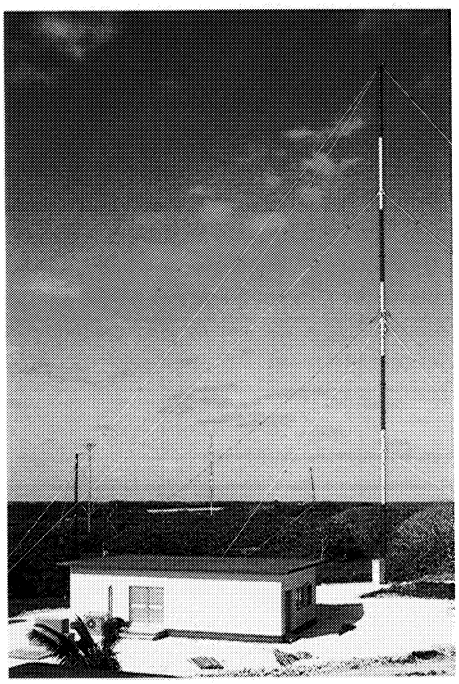

Figure 1 Minamitorishima Global Station

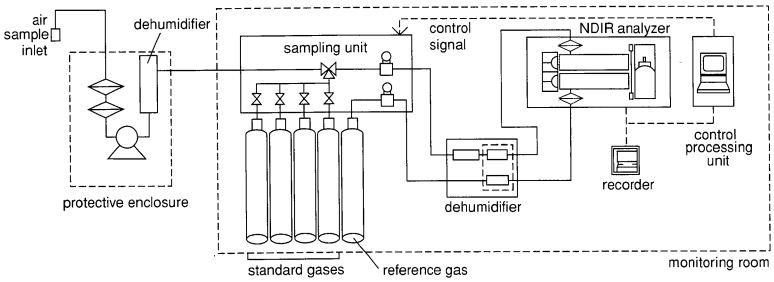

Figure 2 Schmatic Diagram of Carbon Dioxido Monitoring Equipment

(1) Preconditioning unit

To minimize the influence of vegetation on the atmospheric samples, samples are taken from an inlet mounted on a tower 20 meters above ground level. Air is drawn in using a suction pump, and dust particles are removed by a two-layer filter consisting of 40μm and 5μm mesh. Next, the air is cooled to approximately 6°C by a primary dehumidifier, and is then supplied to the monitoring unit. Inside this unit, secondary and tertiary dehumidifiers dehumidify the air to a dew-point temperature of -65°C or less so that moisture is completely removed. (This procedure eliminates the possibility of concentration errors in the carbon dioxide due to changes in partial pressure of the water vapor, as well as errors due to interference by the analyzer.)

(2) Analyzer

The differential-type non-dispersive infrared analyzer used at the station is designed so that the reference gas flows into the reference cell without closing off the zero gas. The analyzer expands the sensitivity by detecting the difference between the sample gas and the reference gas (for example, changes as small as 300 to 350 ppm can be detected).

(3) Data processor

The relational expression (calibration curve) between the carbon dioxide concentration and the measured value (output voltage value) of the analyzer is found by introducing in succession for six minute periods four monitoring standard gases having known concentrations. The air is then measured for 96 minutes . This 120-minute monitoring cycle is repeated automatically. The output voltage value of the analyzer is read every second and the average value for each 30-second interval is stored on a floppy disk. Finally, a calibration curve for every two hours is calculated based on the stored data, and then

the two adjacent calibration curves are divided into proportional time segments to find the atmospheric carbon dioxide concentration. Finally, the concentration data are found based on the average value and the divided calibration curves.

(4) Calibration

The WMO authorizes certain standard gases (known as "primary standard gases") for use in the measurement of greenhouse gases. These gases have been calibrated by the Scripps Institution of Oceanography (SIO) in the United States (now the Climate Monitoring and Diagnostics Laboratory), one of the WMO's Central Carbon Dioxide Laboratories (CCL). However, primary standard gases are extremely expensive and take considerable time to obtain, and for this reason the Agency acquires standard gases from other sources, and tests them against primary standard gases to assure their accuracy. These "secondary standard gases" are in turn used to calibrate the standard gases actually used for the measurement (known as "working standard gases" or "tertiary standard gases"). All of these standard gases are calibrated using the carbon dioxide standard gases calibration system installed at the Japan Meteorological Agency's headquarters. This calibration system is comprised of the Horiba differential-type non-dispersive infrared analyzer (comparative distribution type), a standard gases switching unit, a control computer, and other components. It achieves a measurement deviation of 0.05 ppmv or less against the WMO standard gases.

4.3 Monitoring Concentrations of Methane and Carbon Monoxide

The GC-FID method has conventionally been used for the measurement of methane. However, several problems still remained, such as low response speed due to non-continuous measurement, lack of sample causing an inadequate average data, and complicated maintenance process. This led HORIBA to develop a system integrating the selective combustion method into a cross-modulation non-dispersive infrared analyzer. This system is currently being used by the Japan Meteorological Agency.[3] **Figure 3** is a schematic diagram of the methane and carbon monoxide concentration monitoring equipment used at the Agency.

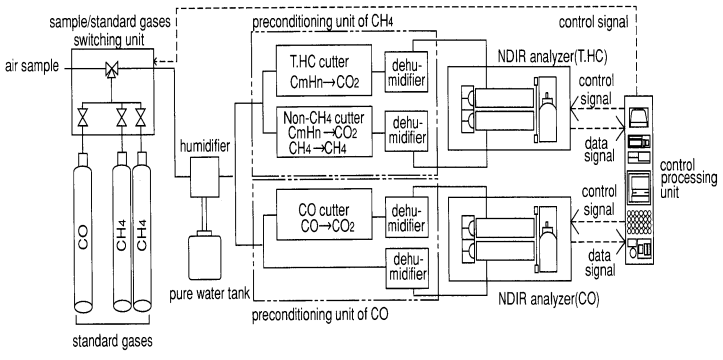

Figure 3 Schematic Diagram of Methane and Carbon Monoxide Monitoring Equipment

(1) Methane analyzer

A cross-flow modulation non-dispersive infrared gas analyzer with a differential quantity system is used to measure the difference in concentration between the sample gas and an ambient gas (reference gas) with methane removed. This analyzer combines the applications of the non-dispersive infrared analyzer with those of preconditioned sample gases. After the sample gas is humidified, non-methane carbons (NMC) are used to remove the non-methane hydrocarbons (NMHC) through oxidation.

Next, the sample gas is dehumidified through thermoelectric refrigeration to a dew-point temperature of 2.5°C, and is then supplied to the analyzer at a fixed flow rate. Once analyzed, the gas is humidified again, and catalysts (CAT) are used to remove total hydrocarbons (THC) through oxidation. The gas is then once again dehumidified through thermoelectric refrigeration, and is supplied as a reference gas to the analyzer at a fixed flow rate.

When NMHC are removed, roughly 10% of methane is lost. However overall methane loss is kept to a minimum by only removing 50% of the ethane (C_2H_6), through a process conducted at a temperature designed to maintain methane levels. Even with 50% of the ethane remaining, the nearly 100% removal of NMHC besides ethane combined with the selectivity of the non-dispersive infrared analyzer allows interference resulting from the remaining ethane to be ignored. Other interfering components (such as moisture, for instance) can also be held to minimal levels. This is achieved by dehumidifying a reference gas with the same components as the non-methane gas as the sample gas to the same temperature as the sample gas, and then performing differential measurement. An interference compensation detector is then used .

(2) Carbon monoxide analyzer

The configuration of the CO analyzer is nearly identical to the methane analyzer. However, the sample gas does not pass through catalysts, and the reference gas has the CO removed through oxidation with catalysts before being supplied to the analyzer.

(3) Data processor and calibration

The concentrations of the two standard gases for methane and the working standard gas for CO are successively measured, and then the concentrations of atmospheric methane and CO are measured for a fixed period. Continuous measurement is achieved by automatically repeating this nine-hour measurement cycle. The output voltage of the analyzer is read every second and the average value for each 30-second interval is stored on a floppy disk. A calibration curve for every nine hours is calculated based on the stored data, and then the two adjacent calibration curves are divided into proportional time segments to find the methane and carbon monoxide concentrations in the atmosphere. The working

standard gases are determined by Japan Chemical Inspection and Testing Institute (CITI). Finally, the concentration data are found based on the average value and the divided calibration curves. This monitoring system guarantees a measurement accuracy of 2ppbv or less for methane, and 5 ppbv or less for carbon monoxide against the CITI standard gases.

4.4 Selection of Background Data

Raw data is checked at the monitoring stations for missing data and other basic errors, and is then sent on floppy disk to the Japan Meteorological Agency's headquarters each month. These data are sent together with surface weather data, inspection records for the monitoring equipment, and information about the environment surrounding the monitoring station. The raw data are analyzed together with this accompanying information to identify the background air pollution data. In order to select the background data, the data affected by pollution caused by human activity and vegetation near the monitoring station and other local factors must be eliminated. The procedure used for selecting background data is described below:

(1) Clearly erroneous data from defective instruments discovered during regular inspections are eliminated, and the hourly data are calculated based on the arithmetic average of mean values taken every 30 seconds for one hour.

(2) Hourly data calculated from less than 60 mean values are eliminated.

(3) Hourly data whose standard deviation exceeds a certain threshold value (A) are eliminated.

(4) Hourly data for which the difference between the preceding and following hourly data exceeds a certain threshold value (B) are eliminated.

(5) The remaining hourly data are used as the background data.

(6) Daily mean data are calculated based on the hourly data selected as the background data.

(7) Monthly mean data are calculated based on the hourly data selected as the background data. The annual mean concentration is taken as the arithmetic average of the monthly mean data for one year.

The threshold values A and B are determined by examining past monitoring values for each monitoring element and station. With CO_2, for instance, threshold value A is 0.6 ppmv at Ryori and 0.3 ppmv at Minamitorishima, while threshold value B is 0.3 ppmv at both stations. These concentration data are corrected whenever the primary standard gases are replaced (generally, once every three years) based on the variation between the old standard gases and the standard gases being replaced.

4.5. Results of Meteorological Agency Monitoring

Figure 4 shows the annual change in atmospheric carbon dioxide concentration (provisional values) measured by the Agency. At Ryori, the annual mean concentration was 350.7

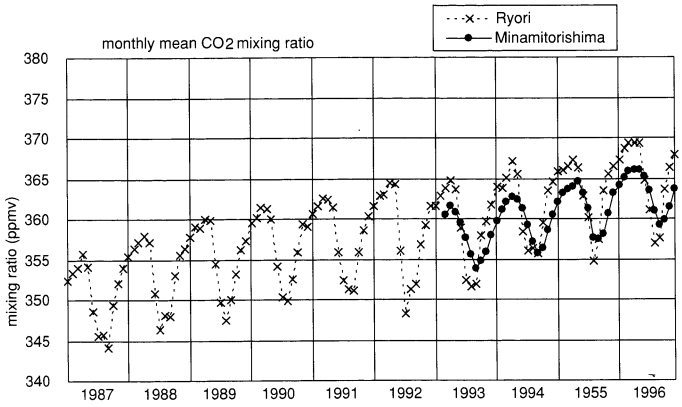

Figure 4 Annual Change in Atmospheric Carbon

ppmv when monitoring started in 1987. This rose to 365.2 ppmv in 1996, giving a growth rate of approximately 1.6 ppmv (0.4% per year). The monthly mean figures reveal that highest concentrations occur around March and April due to the effects of terrestrial biospheric activity.

The lowest values appear in July and August. When seasonal variation is expressed by the difference between the highest mean concentration for a single month and the lowest mean concentration for a single month, this difference is about 13 ppmv, roughly the same for other monitoring stations at mid-latitude locations in the northern hemisphere.

At Minamitorishima the annual mean concentration was 357.8 ppmv (this figure is actually the average for the ten-month period from March to December) when monitoring started in 1993. This value increased to 363.4 ppmv in 1996. The concentration at Minamitorishima was about 2 ppmv less than Ryori. This is consistent with the view that in the northern hemisphere, the concentration of carbon dioxide decreases at lower latitudes. The highest monthly mean concentration is found in April and May, and the lowest appears in September. The average amplitude of seasonal varition is approximately 8 ppmv, smaller than at Ryori. The amount of seasonal variation recorded at Minamitorishima is nearly the same (about 6 ppmv) as that measured at Mauna Loa in Hawaii. Thus, the difference

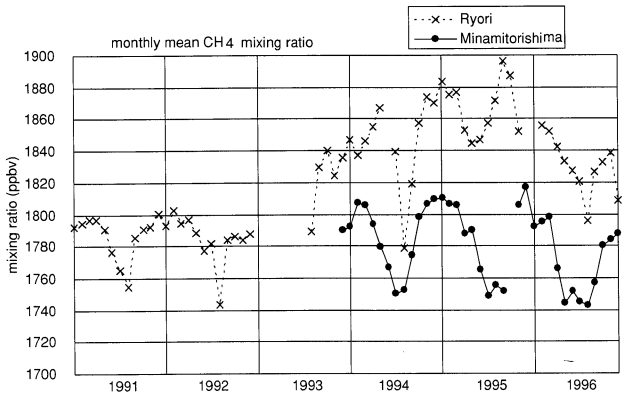

Figure 5 Annual Change in Atmospheric Methane Concentration

between the seasonal variation here and at Ryori is due to the latter's more northerly latitude and the stronger influence of plant activity because of proximity to the Asian continent. **Figure 5** shows the annual change in atmospheric methane concentration (provisional values). As with values for CO_2, the season variation for methane at both Ryori and Minamitorishima was low in the summer and high in the winter. The amplitude of seasonal variation at Ryori is about 50 to 100 ppbv per year, indicating considerable variation from year to year, while it is 60 to 70 ppbv at Minamitorishima.

Figure 6 shows the annual change in atmospheric CO concentration (provisional values). There is a clear seasonal variation in CO concentration at both Ryori and Minamitorishima, with low values in the summer and high values in the winter. The amplitude of seasonal variation is about 110 ppbv at Ryori, and 100 ppbv at Minamitorishima.

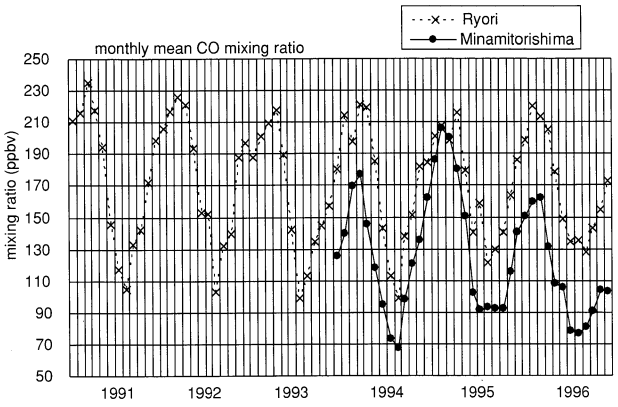

Figure 6 Annual Change in Atmospheric Carbon Monoxide Concentration

Conclusion

This paper explored the background monitoring of air pollution for greenhouse gases. To understand the global climate system, a comprehensive monitoring system is needed that encompasses not only the atmosphere, but also the oceans which cover 70% of the earth's surface, snow and ice cover, and the biosphere. In the years to come, the Japan Meteorological Agency will continue to support and expand the various networks for monitoring global environmental change, and to supply information to the global scientific community. For its part, Horiba is committed to the continued development of cutting-edge environmental monitoring systems that make these activities possible.

References

1) Y. Joo, H. Miyamoto, S. Hayashi,"Summary Report on the Background Air Pollution Monitoring by the Japan Meterological Agency", Weather Service Bullefin, No. 61.4, p. 145-179 (1994).
2) WMO: International Operations Handbook for Measurements of Background Atmospheric Pollution (1988)
3) H. Mikasa, T. Imaki and others, "Measuring Instrument of ambient CH_4 concentration", JP-A, No. 4 003346(u)
4) WMO: Status of the WMO Global Atmosphere Watch Program, WMO/TD-No. 636 (1993)

Abbreviations

BAPMoN: Background Air Pollution Monitoring Network
CCL: Central Carbon Dioxide Laboratory
CMDL: Climate Monitoring and Diagnostics Laboratory
GAW: Global Atmosphere Watch
GO3OS: Global Ozone Observing System
OECD: Organization for Economic Cooperation and Development
SIO: Scripps Institution of Oceanography
UNCED: United Nations Conference on Environment and Development
UNEP: United Nations Environmental Program
WMO: World Meteorological Organization

Yasuhiko Joo
Analyst for Atmospheric Environment;
Atmospheric Environment Division,
Observations Department,
Japan Meteorological Agency

Fumio Watanabe
Senior Scientific Officer;
Atmospheric Environment Division,
Observations Department,
Japan Meteorological Agency

Masamichi Aono
Chief of Greenhouse Gases Monitoring Section;
Atmospheric Environment Division,
Observations Department,
Japan Meteorological Agency

Hajime Mikasa
Assistant Office Manager,
Technical Information Office,
Horiba, Ltd.