APN/NIES Workshop on “Inter-calibration of Isotope Measurements for Atmospheric CO2” (APN 2000-19)

Project Leader:

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PREFACE

Workshop for inter-calibration of isotope ratio measurement for atmospheric CO2

Introduction

At the Fifth APN Inter-Governmental Meeting in Pakistan, Mr. Onogawa from the National Institute of Environmental Studies (NIES) in Japan proposed a workshop to plan a strategy for the inter-calibration of CO2 measurements. This workshop was funded and organised by NIES with support from APN.

Background

Atmospheric CO_2 is produced not only by human activities but also nature itself. Understanding of CO_2 fluxes from nature, such as land biota and oceans is essential to discuss/promote CO_2 reduction for the prevention of global warming. At the same time, CO_2 flux from nature is affected by global climatic events, such as El Nino Southern Oscillation (ENSO). The Asia Pacific region includes important areas such as the equatorial area of the Pacific and Southeast Asia, where ENSO causes dramatic annual CO_2 fluxes. For this reason some laboratories in this region have been carrying out CO_2 measurements over the Pacific Ocean.

CO_2 isotope ratio measurement is usually used to identify sources of CO_2. Several scientists in this region are carrying out such isotope ratio measurements of CO_2 by using monitoring stations, airplanes and ships. The National Institute for Environmental Studies (NIES) in Japan is also measuring latitudinal distribution of carbon and oxygen isotope ratios of CO_2 over the Pacific using two ships. However, inter-calibration among these measurement programmes has not been carried out sufficiently. A small difference in the scale between laboratories may cause a serious problem in calculation of CO_2 geographical flux. Current differences exceed the required levels, and therefore adjustment of their scales to one common scale is necessary to make the analysis more reliable.

Objectives

This workshop will provide a good opportunity to exchange information between regional communities and discuss the methodology for isotope measurement of atmospheric CO_2 in this region.

This workshop will involve comparison of isotope measurement methodologies from each laboratory and a discussion on the possibility of inter-calibration of CO_2 isotope measurement in the Asia-Pacific region. At the same time, The Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia is planning a world wide inter-calibration for CO_2 concentration and isotopes. They are now seeking a means to organise many institutes throughout the world. This workshop will also assist these efforts.

Agenda

Workshop on Inter-calibration of Isotope Measurements for Atmospheric CO_2

November 9-10, 2000
Tsukuba, Japan

Thursday, 9 November

09:30-10:00

Opening speech
Dr. Ryutaro YATSU (Director, APN Secretariat)

APN presentation
Mr. Martin RICE (Programme Manager, APN Secretariat)

Session A: Problems

Chair
Dr. Takakiyo NAKAZAWA (Tohoku University)

10:00-10:40 **The Role of Carbon Dioxide Isotope Measurements in Global Carbon Budgeting**
Dr. Roger FRANCEY (CSIRO)

10:40-11:10 **Flask Sampling for CO_2 Concentration – Advantages of Multiple Agency Sampling at a Given Site**
Dr. Neil TRIVETT (ESR)

11:10-11:50 **NIST-IAEA Metrological Standards for Isotope Ratio Measurements of Carbon Dioxide**
Dr. Michael VERKOUTEREN (NIST)

11:50-13:00 **Lunch**

Session B: Introduction by each laboratory

Chair
Dr. Hitoshi MUKAI (NIES)

13:00-13:40 **The CSIRO Atmospheric Research (GASLAB) Stable Isotope Measurement Program**
Dr. Colin ALLISON (CSIRO)

13:40-14:20 Isotope Measurements of Atmospheric Carbon Dioxide at Tohoku University, Japan
Dr. Takakiyo NAKAZAWA (Tohoku University)

14:20-15:00 Isotope Measurements in Greenhouse Gases at INSTAAR/NOAA
Dr. James WHITE (Univ. of Colorado)

15:00-1530 Measurements of CO_2 Stable Isotopes in the Absence of N_2O by the GC-IRMS Technique
Mr. Gordon BRAILSFORD (NIWA)

15:30-15:45 Break

Chair
Dr. Yoshiyuki TAKAHASHI (NIES)

15:45-16:15 Determination of Stable C and O Isotopes in Environmental Samples
Dr. Yetang HONG & Dr. Yiqiang ZENG (Inst. Geochemistry)

16:15-16:35 Stable Carbon and Oxygen Measurements of the Meteorological Research Institute: Past, Present and Future
Dr. Hisayuki YOSHIKAWA
(Meteorological Research Institute, Japan)

16:35-17:05 The Current Status of Isotopic Studies of CO_2 in Korea
Dr. Kyung-Ryul KIM (Seoul National University)

17:05-17:35 Carbon Isotopes: Current and Future Application at China Global Atmosphere Watch Baseline Observatory
Dr. Jie TANG & Dr. Lingxi ZHOU (Chinese Acad. Meteor. Sci.)

17:35-18:00 Carbon and Oxygen Isotope Analysis of Atmospheric CO_2 and Newly Prepared Reference CO_2 Gas in NIES
Dr. Hitoshi MUKAI (NIES)

18:00-20:00 Reception

Friday, 10 November

Session B: laboratory reports by Japanese geochemists

Chair
Dr. Yetang HONG (Inst. Geochemistry)

09:30-10:00 **Preparations of Standards for Carbon and Oxygen Isotopic Compositions of CO_2 at Center for Ecological Research, Kyoto University.**
Dr. Atsuko SUGIMOTO (Kyoto University)

10:00-10:30 **Reference Standards for the Determination of Carbon and Oxygen Isotopic Ratio of CO_2 at IHAS (Nagoya Univ) and IRCJS (Kyoto)**
Dr. Hiroyuki KITAGAWA (Nagoya University)

10:30-10:40 **Short Summary**
Dr. Hitoshi MUKAI (NIES)

Session C: inter-calibration

Chair
Dr. Atsuko SUGIMOTO (Kyoto University)

10:40-11:20 **What Have We Learnt about Inter-Calibration of Atmospheric CO_2 Stable Isotope Measurements?**
Dr. Colin ALLISON (CSIRO)

11:20-11:50 **Activity for ^{18}O Inter-Calibration for H_2O Inter-Laboratory Calibration of Isotopes and Isotopomers in non-CO_2 Greenhouse Gases including H_2O**
Dr. Naohiro YOSHIDA (Tokyo Institute of Technology)

11:50-13:00 **Lunch**

Chair
Dr. Toshinobu MACHIDA (NIES)

13:00-13:40 **Lessons from Our Trace Gas InterComParison activities**
Dr. Ken MASARIE (NOAA)

13:40-14:20 **GLOBALHUBS**
Dr. Roger FRANCEY (CSIRO)

14:20-14:50 **AEROCARB and European Inter-Comparison Programs, Situation and Perspectives**
Dr. Laurent JOURD'HEUIL (LSCE)

14:50-15:00 **Break**

Session D: Discussion

Chair
Dr. Neil TRIVETT (ESR) & Dr. Roger FRANCEY (CSIRO)

15:00-17:00	**Discussion for the future**
17:00	**Closing remarks**

ABSTRACTS

A-1

The Role of Carbon Dioxide Isotope Measurements in Global Carbon Budgeting

Roger FRANCEY

CSIRO Atmospheric Research, Aspendale, AUSTRALIA 3195

Keeling (1958) played the most influential role in introducing the stable carbon isotope ratio to determine the role of the terrestrial biosphere in determining atmospheric levels of CO_2. Monitoring of the atmospheric $\delta^{13}C$ by a number of groups at a small number of locations was underway by the early 1980's and data from 3 groups are regularly quoted (e.g. *Keeling et al.*, 1995; *Nakazawa et al.*, 1997; *Francey et al.*, 1995). By the early 1990's, Colorado University commenced measurements on flasks from the extensive NOAA/CMDL network of upward of 50 sites, providing comprehensive global coverage for the first time (*Trolier et al.*, 1996).

Until now, the role of atmospheric $\delta^{13}C$ measurements in clarifying the global carbon budget has not been as effective as originally envisaged. Two main reasons for this are calibration errors, both within and between laboratories, and uncertainties in isoflux corrections (variations in atmospheric $\delta^{13}C$ which are independent of net $\delta^{12}CO_2$ changes).

a) Calibration errors: Latest results from the IAEA CLASSIC confirm persisting intercalibration problems between the four major laboratories (*Allison, this conference*). Here, four long time-series of Southern Hemisphere $\delta^{13}C$ from 3 of the laboratories will be compared. These records are expected to be identical within quoted precisions, but large and varying differences are evident. Some of the causes for differences have now become apparent. The GLOBALHUBS strategy is designed to monitor differences between all laboratories measuring CO_2 isotopes, and to further clarify the causes for differences.

b) Isoflux uncertainty: A prime justification for using $\delta^{13}C$ has been to determine how much of the increasing anthropogenic CO_2 is removed by terrestrial compared to oceanic reservoirs. Because of the large cycling of atmospheric CO_2 in and out of the terrestrial and oceanic reservoirs (annual gross fluxes are 50-100 times the annual net fluxes), there is the potential for atmospheric $\delta^{13}C$ changes if the isotope equilibrium between atmosphere and surface reservoir is disturbed. This occurs on the century timescale due to fossil fuel emissions. Two methods of estimating the fossil fuel isoflux are described, which reconcile $\delta^{13}C$ estimates of oceanic and terrestrial uptake with independent estimates. The uncertainty in global partitioning due to fossil isoflux remains around ± 1 PgC yr^{-1}.

   The fossil fuel isoflux is not a limiting factor in attributing higher frequency (seasonal to decadal) variations to ocean or terrestrial forcing. However, at these higher frequencies, recent concerns have been raised about isoflux limitations to using $\delta^{13}C$, related to effective changes in terrestrial photosynthetic discrimination on both global and regional scales. Using long-term Cape Grim records, the maximum global isoflux contribution to interannual variability will be explored.

Measurement of atmospheric $\delta^{13}X$ are likely to continue, and to provide an increasingly valuable constraint on the atmospheric carbon budget, as past difficulties are carefully addressed. There are logistic advantages (e.g. compared to O_2/N_2 which also mainly reflects terrestrial CO_2 exchange, in sampling and analysis) and it is likely that the two methods will be complementary in addressing potential systematic biases in both signals. Second-order variations in $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2 carry information on terrestrial ecosystem responses which will increase in value as ecosystem models improve. Closely coordinated CO_2 and CO_2-tracer sampling may also emerge as a key requirement.

Keeling, C.D., 1958. The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. *Geochim. Cosmochim. Acta* 13, 322-34.
Keeling et al., 1995. Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. Nature 375, 666-670.
Nakazawa et al., 1997. Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region. J. Geophys. Res. 102, D1, 1271-1285.
Francey et al., 1995. Changes in the oceanic and terrestrial carbon uptake since 1982. Nature 373, 326-330, 1995.
Trolier et al., 1996. Monitoring the isotopic composition of atmospheric CO2: Measurements from the NOAA global sampling network. J. Geophys. Res. 101, D20, 25,897-25,916.

A-2

Flask Sampling for CO_2 Concentration - Advantages of Multiple Agency Sampling at a Given Site

Neil TRIVETT, Victoria HUDEC, and Douglas WORTHY
Environmental Systems Research, Burlington, ON, Canada
Meteorological Service of Canada, Downsview, ON

At the 10th World Meteorological Organization's (WMO) meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques, Stockholm, 23-26 August 1999, a proposal, which became known as "Global Hubs" was put forward to address some of the known problems associated with quality control of global trace gas measurements from both in-situ and grab samples, focussing on but exclusive to carbon dioxide and its respective isotopes.

The Canadian flask sampling started in 1975 with 2 litre flasks with greased stopcocks similar to those used by SIO on their 5 litre flasks and by NOAA on their 1/2 litre flasks. Because of the problems associated with opening the stopcocks in the very cold conditions in the high Arctic several new flask types were designed with single and double O-ring stopcocks. When the results from the various types of flasks are compared to the in-situ NDIR measurements, there are some obvious biases in the flask data record. Since NOAA, SIO, and CSIRO also collect flasks at Alert, it is possible to check the Canadian flask results against independent program measurements.

This presentation summarizes the internal consistency problems previously reports to WMO and presents some new evidence that with due care the bias between in-situ measurements and flask sample measurements of CO_2 can be minimized to a level (0.02 to 0.04 µmole per mole CO_2) similar to that achieved by 2 independent in-situ measurements (NDIR and GC).

A-3

NIST-IAEA Metrological Standards for Isotope Ratio Measurements of Carbon Dioxide

R. Michael VERKOUTEREN
Atmospheric Chemistry Group
National Institute of Standards and Technology

Quality assurance systems entail well-designed measurement methods, competent staff, adequate instrumentation, reliable reference materials (RMs), laboratory quality assurance procedures, and proficiency testing. The scope of this contribution is limited to the constitution of "reliable RMs" for $\delta^{13}C$ and $\delta^{18}O$ measurements, which include standard carbonates, waters, and CO_2 RMs. These RMs are used for purposes of instrument calibration and traceability to the accepted isotopic VPDB (and VSMOW) scales. In particular, RM8562, RM8563, and RM8564 are pure CO_2 materials of paleomarine, petroleum, and corn origins, respectively, and are useful for realization of the accepted scales. These RMs are packaged in 9-mm diameter glass breakseals containing about 400 micromoles of gas and are characterized for sample-to-sample isotopic heterogeneity and stability. These CO_2 isotope RMs are now distributed by the National Institute of Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA). $\delta^{13}C$ and $\delta^{18}O$ value assignments and uncertainties were determined by three complementary methods: 1) multilaboratory comparison exercises, 2) direct measurement and correction for cross-contamination effects, and 3) isotopic closure of delta measurements *between* RMs ($\Delta\delta^{45}CO_2$, $\Delta\delta^{46}CO_2$, and $\Delta\delta^{47}CO_2$).

An ongoing multilaboratory exercise was designed by the IAEA-Advisory Group to enable the consistent and precise assignment of $\delta^{13}C$ and $\delta^{18}O$ values across standard carbonates, waters, and the RMs 8562-8564. Mandatory chemical procedures were followed in each laboratory, and raw measurement data were processed at NIST to determine $\delta^{13}C$ and $\delta^{18}O$ values using accepted standard numerical procedures. Due to the combination of strict laboratory chemical processing and central data processing, observed standard deviations across laboratories decreased (i.e., improved) by factors of 2 to 3 over prior multilaboratory exercises. Preliminary results suggest that the current value assignments for most RMs should be modified slightly to more negative delta values. Continuing activities are attempting to improve the cross contamination correction to the measurement data, and final value assignments and uncertainties will be determined at the end of the current exercise.

While the aforementioned standard numerical procedures have been documented in previous IAEA TECDOCs, a more explicit and globally empirical approach to disseminating this information is needed in light of the substantial improvement in standardized results from central data processing. For this reason, NIST has established a Web-based interactive data processing system at

www.acg.nist.gov/outputs/algorithm.html

This Web-based system is designed to promote the proper usage of isotope RMs and improve the quality of reported data taken from measurement programs relevant across laboratories, industries, nations, and regional/global networks. Users may wish to validate their laboratory data systems, or specify the values of fundamental variables usually fixed in reduction algorithms in order to see the effect upon the calculations. By using this Website and the CO_2 RMs as part of a total quality assurance system, significant improvements may be realized in the combined standard uncertainties of $\delta^{13}C$ and $\delta^{18}O$ determinations.

B-1

The CSIRO Atmospheric Research (GASLAB) Stable Isotope Measurement Program

Colin ALLISON
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CSIRO Atmospheric Research has been involved in the measurement of the stable isotopes of atmospheric CO_2 for about twenty years. A brief history of the CSIRO stable isotope measurement program will be presented, including a description of the techniques used for the collection, extraction, analysis and data processing of samples.

B-2

Isotope Measurements of Atmospheric Carbon Dioxide at Tohoku University, Japan

Takakiyo NAKAZAWA

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Tohoku University, Sendai 980-8578, Japan

The isotopic ratios of atmospheric CO_2 provide us with valuable information about the global carbon cycle. In view of such an importance, we have measured $\delta^{13}C$ and $\delta^{18}O$ of CO_2 since 1984 for air samples collected using ground stations, aircraft, ships and scientific balloons. A brief description of the technical aspect of our measurements is as follows:

The air samples collected in glass or stainless steel flasks were first measured for the CO_2 concentration using a non-dispersive infrared analyzer and gravimetrically prepared standard gases. Then, CO_2 was extracted cryogenically from the remaining samples of typically 300-500 ml and sealed in a Pyrex glass tube with a diameter of 6 mm.

At the beginning of our measurement program, we used a Finnigan MAT δ-E for the mass spectrometer analysis, but the MAT δ-S mass spectrometer has been used since 1991. $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 were calculated from an ion current ratio of mass 45 to 44 and that of mass 46 to 44 using an ion correction scheme given by Mook and Grootes (1973). External precision for our $\delta^{13}C$ and $\delta^{18}O$ measurements were estimated to be 0.02 and 0.03 ‰ (one standard deviation), respectively.

To maintain consistency of the data for a long time, our standards were classified into three categories of primary, secondary and working standards. The primary standard was CO_2 gas produced by reacting NBS-18 (-5.029 ‰ for $\delta^{13}C$ and -23.035 ‰ for $\delta^{18}O$) with 100 % phosphoric acid at 25°C.

It was found that the $\delta^{13}C$ and $\delta^{18}O$ values of the standard gases stored in a variable volume of the mass spectrometer showed gradual positive shifts after their introduction. To compensate for the drifts in $\delta^{13}C$ and $\delta^{18}O$ values of the working standard gases, 'test samples' with known values of $\delta^{13}C$ and $\delta^{18}O$, which were extracted from a CO_2-in-air standard gas, were analyzed before and after sample analyses.

N_2O involved in air samples cannot be separated from CO_2 by the above-mentioned cryogenic extraction method. Since N_2O has the same mass as CO_2, the contribution of N_2O in CO_2 samples must be eliminated for precise determination of $\delta^{13}C$ of CO_2. Therefore, correction factors were determined experimentally after Mook and Van der Hoek (1983).

B-3

Isotope Measurements in Greenhouse Gases at INSTAAR/NOAA

James W.C. WHITE, Bruce VAUGHN, Mark DREIER, Candace EVANS
Stable Isotope Laboratory, University of Colorado, Boulder

Since 1989, the Stable Isotope Laboratory at INSTAAR , University of Colorado has been measuring the stable isotopic composition of atmospheric CO_2 from weekly flask samples of air obtained from the network of sites operated by the NOAA Carbon Cycle Group, at the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder, Colorado. Begun with a selection of six sites and two ships in 1990, the measurement effort has grown to include all 55 sites in the CMDL program. During calendar year 1999 over 11,000 isotopic analyses of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 were made at INSTAAR. This included 7,800 sample flasks and 3,200 air standards used for calibration. Currently the measurement precision is ±0.01 ‰ $\delta^{13}C$ and ±0.03 ‰ for $\delta^{18}O$.

Carbon and oxygen stable isotope ratios of atmospheric carbon dioxide, $\delta^{13}CO_2$ and $\delta C^{18}OO$, provide important, independent information about carbon sources and sinks. Combined with CO_2 mole fraction measurements, the $\delta^{13}CO_2$ measurements can be used to quantitatively separate gross fluxes between the atmosphere and the terrestrial biosphere from gross fluxes between the atmosphere and the ocean. $\delta C^{18}OO$ measurements are just beginning to be usefully exploited. As the two main mechanisms for controlling $\delta C^{18}OO$ on annual to decadal time scales are oxygen isotopic exchange with soil water and oxygen isotopic exchange with leaf water, this isotope can potentially be used to separate photosynthetic and respiratory fluxes for land plants. As the atmosphere integrates surface processes over space and time, CO_2 concentration measurements, combined with isotopic measurements, provide constraints for regional scale sources and sinks of atmospheric CO_2 on time scales of months and longer. In the future, atmospheric monitoring will also play a central role in verifying any international carbon emission agreements in much the same way that seismic monitoring was used to monitor compliance with nuclear test ban treaties.

The degree to which isotopic measurements made on atmospheric samples are useful is seriously constrained by the precision of the measurement. For example, a change of just 0.02 ‰ in $\delta^{13}C$ measured at one site could translate to an equivalent of 1.0×10^9 metric tons of carbon in models of surface fluxes. Such precision is challenging enough on a short term basis, but this precision is needed over decades if we are to use the data to study trends over longer periods of time. A high precision instrument is required along with diligent, frequent intercalibrations between laboratories .

We will describe the isotopic measurements made at the Stable Isotope Lab at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado. These include traditional dual inlet mass spectrometry, as well as the recently developed Gas Chromatography Isotope Ratio Mass Spectrometry (GC-IRMS). Our new program in $\delta^{13}C$ of CH_4 will also be discussed.

B-4

Measurements of CO_2 Stable Isotopes in the Absence of N_2O, by the GC-IRMS Technique

Gordon W. BRAILSFORD
National Institute of Water and Atmospheric Research
Wellington, New Zealand

The measurement of stable isotopes in atmospheric carbon dioxide are complicated due to the presence of nitrous oxide in air and the fact that both gases have isotopes of the same mass. Conventional high precision measurements of isotope ratios in CO_2 use corrections for the contribution made by the nitrous oxide to the measured value. A method has been developed that separates the carbon dioxide in the air sample from the nitrous oxide on a Porapak –Q chromatographic column, dries the sample and carries the eluting peaks on a stream of helium into an isotope ratio mass spectrometer. The chromatography allows the CO_2 and N_2O peaks to be clearly separated for all masses and the stable isotopic ratios of CO_2 are determined without interference from N_2O

We present data from our GC-IRMS system for CO_2 stable isotope ratios $\delta^{13}C$ and $\delta^{18}O$, the precision for these species is currently 0.02 ‰ and 0.04 ‰ respectively on whole air samples. The sample size used is 8 nmol CO_2 in the sample loop with 0.8 nmol of CO_2 reaching the Isotope Ratio Mass Spectrometer. Factors important in obtaining the precision are discussed and the limits of detection are examined.

This technique developed at NIWA has been intercompared with CSIRO using both flasks of air collected by each laboratory and using a tank of air that remains as a single filling measured many times by both methods. Data from these comparisons are used to verify the GC-IRMS technique.

B-5

Determination of Stable C and O Isotopes in Environmental Samples

Yiqiang ZENG, Yetang HONG, Yongxuan ZHU
State Key Laboratory of Environmental Geochemistry
Institute of Geochemistry, Chinese Academy of Sciences

The State Key Laboratory of Environmental Geochemistry, affiliated with the Institute of Geochemistry, Chinese Academy of Sciences, funded by the loan of World Bank in 1989, has opened formally to domestic and foreign scientists since 1995. The Laboratory consists of 25 permanent researchers, 20 visiting scholars, 8 technicians and about 40 graduate students.

Research on stable isotopes regarding environment is one of the main orientations in this laboratory. Concerning this field, following projects have been carried on up-to-now.

1. Investigation on transfer rules of soil organic carbon by $\delta^{13}C$ values.
2. Characteristics of soil CO_2 relating to atmospheric CO_2 budget in Guizhou karst area.
3. Peat C and O isotope evidence of climate change in China in past 6000 years.

Serving above projects, our lab constructed and developed applicable sampling and analyzing methods for measurement of stable C and O isotopes:

1. Measurement of soil organic C isotopes.
2. Measurement of C isotopes of soil CO_2 in karst area.
3. Measurement of C and O isotopes of cellulose in peat core.

Among those methods, procedure of preparation line for O isotope sample of peat core was firstly established in China, with which we successfully extracted cellulose from peat sediment samples and obtained a serial of O isotope data related to the climate change during the past 6000 years. The results also showed solar activity would be a relative factor to past climate change.

Concerned Main facilities in our laboratory:

1. Isotope ratio mass spectrometer (Finnigan MAT 252)
2. Element Analyzer (PE2400 II)
3. Gas Chromatography (HP6890)

B-6

Stable Carbon and Oxygen Measurements of the Meteorological Research Institute: Past, Present and Future

Hisayuki YOSHIKAWA INOUE and Hidekazu MATSUEDA
Geochemical Research Department, Meteorological Research Institute
Nagamine 1-1, Tsukuba, Ibaraki, 305-0052, Japan

At the meeting, I will talk about;

- Measurements of stable carbon and oxygen isotopes of atmospheric CO_2 over 1980s

- Measurements of stable carbon isotope of dissolved inorganic carbon in seawater samples

- Possibilities about carbon and oxygen isotope measurements of air samples collected by aircraft

B-7

The current status on isotopic studies of CO_2 in Korea

Mi-Kyung PARK and Kyung-Ryul KIM
SEES, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

In 1990, a program for monitoring the CO_2 concentration of clean background atmosphere in Korea was initiated with flask sampling at Kosan, Cheju Island. Evacuated 3-liter glass flasks were used for collecting air samples with a sampling rate of once per week on the average. Two samples were collected during each sampling event to check the sampling procedure: results from these two flasks were compared for the validity of the data. In 1992, measurement of the isotopic composition of CO_2 also started in conjunction with concentration measurement.

The concentration data show that there is a strong seasonal variability with lower concentrations in summer and higher values in early spring, in general. The amplitude of these seasonal variations is 17 ppm. The amplitude of the seasonal variations is larger in high altitude among marine stations. However, the value at Kosan is much higher than those of marine stations with a similar latitude of 12 ppm, reflecting continental influence at the Kosan station. Besides seasonal variability, the increasing trend of atmospheric CO_2 is clearly seen with an average rate of 1.5 ppm per year, which is comparable to typical values in mid-latitude in the Northern Hemisphere.

Carbon isotopic composition of CO_2 also shows patterns similar to those of the concentrations, such as seasonal variability and a trend. The trend of isotopic composition reflects the addition of carbon dioxide with lighter isotopic compositions compared to atmospheric CO_2. This effect is most clearly seen when plotting isotopic composition as a function of the inverse of its concentration. The end-member isotopic composition shows -25 ‰, which is very close to the carbon isotopic composition of CO_2 produced by fossil fuel combustion. However, the isotopic composition of CO_2 from other sources such as biomass burning is also close to -25 ‰, thus raising difficulties for the discerning of the causes of variability in CO_2 concentration at the site.

The measurement of C-14 isotopic composition will be a definite improvement in this regard, for C-14 composition from fossil fuel and biomass is clearly discernible. Research in this direction is under way at the moment. Results will be further discussed at the meeting.

B-8

Carbon Isotopes: The Current and Future Application at China Global Atmosphere Watch Baseline Observatory

Jie TANG, Lingxi ZHOU, Yupu WEN
Chinese Academy of Meteorological Sciences

1. The measurement program of CGAWBO

To respond the needs of global monitoring on atmospheric change, China Global Atmosphere Watch Baseline Observatory (CGAWBO) was established in 1994, which standing as the highest global baseline monitoring station in the world, making up the important gap of GAW network over the Eurasia continent. It has relatively comprehensive routine measurement program covering from greenhouse gases, ozone, reactive gases, solar radiation, black carbon aerosol, precipitation chemistry to meteorology.

2. The current routine measurement program for $\delta^{13}C$ in carbon dioxide

The routine measurement for $\delta^{13}C$ in carbon dioxide from 3-L flask sample is an important cooperative program with CMDL/NOAA, USA. Long record for $\delta^{13}C$ in carbon dioxide has been archived since 1991 and the work has been started since last year to make comprehensive interpretation on the CO_2 concentration data set together with the results of $\delta^{13}C$ in carbon dioxide. Preliminary analysis revealed a linear relationship between $\delta^{13}C$ and the CO_2 concentration with correlation coefficient of 0.88, and a mean decrease rate, with the magnitude of -0.02‰ /ppmv, of $\delta^{13}C$ with respect to the CO_2 concentration increase during 1992～1999. It suggests that the significance of the CO_2 exchange between the atmosphere and the terrestrial biosphere be obviously on the long time trend/seasonal cycles of the CO_2 concentration in such continental area.

3. The measurement of $\delta^{14}C$ in black carbon aerosol at CGAWBO

As an indicator of anthropogenic pollution, black carbon has been monitored since 1992 at CGAWBO. Data indicated a rapid increase of black carbon since 1994, which may attribute to the rapid change in energy consumption over China. In a national supported research project, samples collected in 2000 at CGAWBO will be analyzed by accelerator mass spectrometry (AMS) for $\delta^{14}C$ to characterize the contribution of biomass burning to the carbonaceous particles.

4. The future perspectives

As national flask sampling network for CO_2, including three regional GAW stations in addition to CGAWBO, is being built up recently. The network will serve as a platform for monitoring major greenhouse gases with a capability analyzing related carbon isotopes.

B-9

Carbon and Oxygen Isotope Analysis of Atmospheric CO_2 and Newly Prepared Reference CO_2 Gas in NIES

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NIES and CGER (Center for Global Environmental Research) are conducting several monitoring programs of greenhouse gases in Asia-Pacific region by using two monitoring stations, ship-of-opportunity and aircraft. Since 1995, we have measured both C and O isotope ratio for CO_2, which was collected automatically in glass or stainless steel bottles at these facilities. Sample air was pressurized up to 3 atm after drying. CO_2 in the sample air was extracted in the vacuum line, which was made of glass. About 0.35 ml of CO_2 was usually extracted from 1 liter of sample air. Recovery was always checked by measuring of extracted CO_2 volume. The extracted CO_2 was trapped in a glass tube.

Isotope analysis was done with MAT 252. During one year after we purchased the MAT 252, we often observed a small drift of measured value, despite that we had a very good balance (zero enrich). Such a small shift was very hard to trace and reproduce, because the reason of drift was almost unknown. However, it must be related to background, contamination from non-point sources, and linearity.

To avoid long-term drift of MASS measurement and to minimize the effect of linearity problem in measurement,

1) We used reference CO_2 having delta values similar to the air ,
2) Sample was often frozen back to the glass tube, to measure it again.

To correct daily drift by the fractionation of reference CO_2, reference CO_2 is measures as a sample at the end of measurement. To calculate $\delta^{13}C$ and $\delta^{18}O$, we use Craig correction. N_2O correction was also done based on the N_2O/CO_2 ratio.

Recently new reference CO_2 (NACIS: NIES Atmospheric CO2 Isotope ratio Standard) (over 1300 samples) was prepared to be used for the inter-calibration activity. The reference was adjusted to have isotope ratios similar to those of the actual air (NACIS tentative value $\delta^{13}C = -8.5$, $\delta^{18}O = -0.7$ vs VPDB-CO_2) by mixing of carbonate standard followed by sea water equilibrium procedure. Homogeneity of the sample was fairy good (S.D. $\delta^{13}C=0.003$, $\delta^{18}O=0.009$ (n=28)) enough to be used as inter-calibration sample. This NACIS has been distributed to 9 laboratories in Japan and 3 laboratories in other countries to check the basic scale of MASS spectrometer in each laboratory. Because inter-calibration test has not been done so far in Japan, the preliminary inter-calibration was first necessary.

As a next step, the CO_2 extraction procedure from sample air should be checked. In the near future, I would like to try to make reference air samples by using NACIS standard. If some modification to the value of $\delta^{13}C$ and $\delta^{18}O$ occurs during CO_2 extraction, we can detect the level of deviation and its direction (whether making it lighter or heavier).

B-10

Preparation of Standards for Carbon and Oxygen Isotopic Compositions of CO_2 at Center for Ecological Research, Kyoto University

Atsuko SUGIMOTO
Center for Ecological Research, Kyoto University

For the measurement of carbon and oxygen isotopic compositions of CO_2, reference CO_2 gas is necessary. In the standard method, $CaCO_3$ reaction with H_3PO_4 is made at 25˚C. For the measurement of oxygen isotopic composition, removal of water form the phosphoric acid is essential, because remaining water can exchange oxygen isotope with CO_2. In such low temperature as 25˚C, it is difficult to make 100% phosphoric acid, because melting point of pure H_3PO_4 is about 40˚C. It takes also time to complete reaction. It takes overnight until reaction is over usually.

In our laboratory, therefore, reaction of $CaCO_3$ with phosphoric acid is made at 50˚C. Produced CO_2 is extracted from the reaction system at the same time. This method can minimize the possibility of isotope exchange between CO_2 and water, and also air contamination during reaction. Reproducibility of d values is good for $\delta^{18}O$ too. But in some standard, produced CO_2 at 50˚C is slightly different from that at 25˚C. Procedure for standard preparation may be important for inter-calibration of d values of CO_2. In the case of carbonate, reaction temperature is not so important, when sample and standard is digested with phosphoric acid at the same temperature. However, in the case of CO_2 is fractionation factor can affect the $\delta^{18}O$ value.

Expression of oxygen isotope ratio of CO_2 is also problematic. There are three standards are currently used to express the $\delta^{18}O$: SMOW, PDB, and PDB-CO2. PDB-CO2 scale is extremely confusing. One common standard should be used. SMOW may be the best to express the $\delta^{18}O$, because we sometime need to think about the exchange of O isotope with water. If we use PDB-CO2, it is very difficult to compare the values, because fractionation factor, which is not yet fixed, is needed to draw down to PDB and SMOW scale.

B-11

Refererence Standards for the Determination of Carbon and Oxygen Isotopic Ratio of CO_2 at IHAS (Nagoya Univ) and IRCJS (Kyoto)

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(International Research Center for Japanese Studies (IRCJS), Kyoto)

The quality assurance measurement of isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) of atmospheric CO_2 as well as environmental samples depends on the availability of reliable homogeneous and stable local standard materials. Here the set of laboratory standard materials available at IHAS (from April, 2000) and IRCJS (to March 1999), and isotope-enriched CO_2 gas for determining the measurement parameters of mass spectrometers will be introduced.

We have used two types of pure CO_2 gas (one from a well, heavy in $\delta^{13}C$; Std1), the other offered from Japanese company, being light in $\delta^{13}C$; Std2). All the laboratory standard materials are calibrated by NBS19 as primary standard as well as NBS18 (carbonate), NBS20 (carbonate), NBS21 (graphite, only for $\delta^{13}C$) and GS17 (carbonate offered from Groningen University for inter-lab. comparison). Std1 and Std2 gases are used for the daily startup test of the mass spectrometry. Std1 is also used as the machine reference standard for $\delta^{13}C$ and $\delta^{18}O$ measurements of VG Optima mass spectrometers at IRCJS and MAT 251 mass spectrometers at IHAS.

In order to determine the cross contamination for the mass spectrometers, we have produced isotope-enriched CO_2 gas. Std1 1-L CO_2 gas is brought in equilibrium with 10 ml artificially (^{18}O and ^{17}O) enriched water (to about 2000 ‰). Then ^{13}C-enriched CO_2, produced from highly enriched sodium bicarbonate, is admixed. When we need to change the parameter settings of VG Optima and MAT 251 mass spectrometers, the enriched CO_2 gas (to +1000 ‰ for $\delta^{13}C$ and ca. +2000 ‰ for $\delta^{18}O$) as well as two laboratory standard materials have been measured. The enriched CO_2 gas is effective to determine the optimum parameters of mass spectrometers such as evacuating time before introducing the next sample and change over delay.

B-12

Short Summary

Hitoshi MUKAI

Sampling

Bottle	Glass	stainless steel
drying	necessary for ^{18}O	
Pressure		

Extraction

line	Glass	Stainless + glass
way	manual- glass ample	auto --- on line analysis
air volume	50 ml - 1000 ml	
pressure	e.g. 100 Pa, or flow rate control (NOAA)	

Mass spectrometer

Model	MAT 251, 252 delta-S delta-plus	PRISM OPTIMA
Backg. measurement	every time, delay e.g. 60sec	once a day
Integration delay	e.g. 50 sec	e.g. 15 sec
Integration	16 sec	20 sec
cycle	5	10

volume	not the same, variable volume	same for both ref. and sample
O17 correction	Craig or Santosa	Craig
	delta 45 ,46 equation (by, Allison, NIST)	
N2O correction	N_2O/CO_2 ratio, Ionization Efficiency	
reference	e.g. extracted CO_2 from Air , artificially adjusted CO_2 gas, others	
running STD	Standard air (NOAA, CSIRO, (Tohoku))	

Standards

standard	delta ^{13}C (vs VPDB)	delta ^{18}O (vs VPDB)	delta ^{18}O (vs VPDB-CO_2)
Air	e.g. -8	e.g. 10	e.g. 0
NBS-19	+1.95	-2.2	-12.32
CO2-NBS19	+1.95	8.03	-2.2
NBS-18	-5.04 -5.029	-23.05 (NIST) -23.035 (IAEA)	-32.96
CO2-NBS18	-5.04	-13.04	-23.05
RM8562(CO2)	-3.76	-8.45	-18.51
RM8563(CO2)	-41.56	-23.72	-33.63
RM8564(CO2)	-10.45	0.19	-9.96
GS19, GS20	-7.5, -8.61		-0.66, -1.43
NACIS (NIES)	-8.5	9.5	-0.7

C-1

What Have We Learnt about Intercalibration of Atmospheric CO_2 Stable Isotope Measurements?

Colin ALLISON
CSIRO Atmospheric Research, Aspendale, AUSTRALIA 3195

Results from the recently completed second circulation of the IAEA CLASSIC cylinders have confirmed the observations made during the first circulation. Namely, there are large, consistent differences between the measurement scales used in the four laboratories. The results from the two CLASSIC circulations and from other, complementary comparison exercises in which CSIRO is involved, will be presented. The significance of these exercises to the GLOBALHUBS strategy will be described.

C-2

Activity for ^{18}O Inter-Calibration for H_2O Inter-Laboratory Calibration of Isotopes and Isotopomers in Non-CO_2 Greenhouse Gases including H_2O

Naohiro YOSHIDA
Department of Environmental Science and Technology, Tokyo Institute of Technology

There have been important activities relating to the interlaboratory calibration of isotopes in water and trace gases recently.

One was the 2nd IAEA Interlaboratory Comparison for Stable Isotope Analyses of Precipitation. The IAEA Isotope Hydrology Laboratory organized in 1998/99 the 2nd interlaboratory comparison test for analytical laboratories engaged in routine analyses of hydrogen and oxygen stable isotope composition of water samples. This intercomparison exercise was carried out in the framework of the Analytical Quality Control Services (AQCS) programme of the International Atomic Energy Agency. The first interlaboratory comparison test of this kind carried out in 1995 was restricted to laboratories analyzing, on a regular basis, precipitation samples collected in the framework of the Global Network "Isotopes in Precipitation" (GNIP), jointly operated by IAEA and WMO (Araguás-Araguás and Rozanski, 1995). The 2nd test was open to all laboratories engaged in isotope analyses of water samples.

The other was IAEA-Advisory Group Meeting on Stable Isotope Ratio Measurements by GC/C/IRMS and Laser Spectroscopy, 20-23 September 1999, Vienna, Austria. In Sept., 1999, a meeting was held at the International Atomic Energy Agency on Stable Isotope Ratio Measurements by CF/IRMS and Laser Spectroscopy. A series of review papers was prepared and is presently under review for publication as an IAEA TECDOC. A short summary and the recommendations of the working groups on applications in biogeochemistry, in biology and medicine (labelled compounds), and in atmospheric and hydrological studies will soon be available on the homepage of the IAEA Isotope Hydrology Section:
http://www.iaea.org/programmes/ripc/ih/index.html.

The results of widely scattered interlab. comparison are briefly summarized. The importance of isotope ratio in precipitation for tracing carbon dioxide in terms of oxygen-18 and methane of deuterium is shown in the area of Siberia. A report from the atmospheric group of IAEA-AGM is summarized for trace gas interlab. comparison. Some activities toward the establishment of standards for isotopes and isotopomers of nitrous oxide will be reviewed in the forthcoming meeting; First International Symposium on Isotopomers (ISI 2001), 23-26 July, 2001 in Yokohama, Japan.
URL: http://nylab.chemenv.titech.ac.jp/ISI2001/isi2001.html

C-3

Lessons from Our Trace Gas InterComParison Activities

<u>Ken MASARIE and Pieter TANS</u>
NOAA CMDL Boulder CO, USA

Several laboratories have established ongoing InterComParison (ICP) programs to document long-term differences among independent data sets. The success of these programs depends on the use of advanced data management strategies as well as a high degree of cooperation among participating labs. NOAA CMDL has ongoing ICP experiments with AES (Canada), CSIRO (Australia), NIWA (New Zealand), and CMDL/HATS (U.S.A.); and has proposed ICP experiments with NIES (Japan) and LSCE (France). While each ICP experiment is unique and carefully designed to ensure success, success has been limited. A host of logistical problems have plagued the existing and proposed ICP activities including the transport of samples between countries, the timely and automatic exchange of data, the frequency of ICP samples, the additional demands on personnel and equipment, and the level of commitment by participating labs. Where logistical problems have been overcome, independently identifying the causes of observed measurement differences has been exceedingly difficult. In cases where the traceability of the calibration has not been actively maintained, we have no reliable way to assess the relative merits of the conflicting data sets.

A concerted international strategy to assess and improve the comparability of long-term measurements of CO_2 and the stable isotopes of CO_2 is long overdue. However, a global strategy will be even more susceptible to the problems common to the smaller ICP experiments. As a global strategy emerges, we must keep at the forefront the reasons why existing ICP activities have not realized their full potential.

C-4

GLOBALHUBS

Roger FRANCEY

CSIRO Atmospheric Research, Aspendale, AUSTRALIA 3195

GLOBALHUBS is an intercomparison strategy for greenhouse gas measurements arising from the CSIRO-NOAA attempts, over 8 years, to merge data from our respective networks. It also builds on the NOAA experience of conducting the WMO-endorsed round-robin comparisons of CO_2 measurement, and similar role played by CSIRO for the IAEA CLASSIC comparisons of CO_2 isotope measurements. It is designed to routinely link with the NOAA developed GLOBALVIEW data integration (and possibly other global databases), involving input from the current ~20 international laboratories, with capacity to accommodate more. It is a proposal that has received strong endorsement from both WMO and IAEA “measurement expert” meetings involving the majority of laboratories involved in the measurement of greenhouse gas levels in the background atmosphere.

The objective is “greatly improved inter-laboratory comparability for measurement of long-lived atmospheric trace gas species, resulting in improved derivation of source/sink fluxes from spatial and temporal atmospheric composition changes”.

The GLOBALHUBS proposal incorporates four main elements, it:

1. maintains constant comparison between four geographically distributed “HUB” Laboratories (e.g. in USA, Europe, Asia and Australia).
2. equips each HUB with hardware and software to provide regular low-cost, well-characterized air to regional laboratories for the purpose of quality control through ongoing intercomparisons, and
3. routinely and promptly (via the web) incorporates the laboratory results into the GLOBALVIEW global integration of measurements (results are also available to other international databases).
4. Develops and/or improves links to primary standards for all species of interest, in at least one HUB laboratory.

The current status and prospects for implementation of GLOBALUBS will be discussed.

C-5

AEROCARB and European Intercomparison Programs, Situation and Perspectives

Laurent JOURD’HEUIL, Philippe CIAIS
LSCE

The European Commission (Research DG) under its programme Energy, Environment and Sustainable Development (Key Action on Global Change, Climate and Biodiversity) accepted the funding of a cluster (CARBOEUROPE) of projects aiming to upgrade the existing monitoring networks and develop tools to quantify the terrestrial biosphere carbon balance from the ecosystem scale to the continental scale both in Europe and in some specific areas of the globe (Siberia and Amazon).

The **AEROCARB** project (*funded March 2000; duration 36 months*) is the atmospheric observation component of the CARBOEUROPE cluster. The project is based on a synergy of atmospheric measurements, mesoscale atmospheric transport models, surface emission data, and diagnostic models of land ecosystems carbon exchange. It will be a first attempt to develop an unified **European network of atmospheric CO_2 and related tracers concentration measurements**. The observational strategy of the science plan is oriented towards the acquisition of three complementary type of atmospheric measurements. The first set of observations will be regular CO_2 concentration vertical soundings over the interior of the European continent, that will help to better retrieve the continental fluxes in models. The second set of observations will be regular O_2 and $^{13}CO_2$ concentration in air samples to separate in the European CO_2 concentration signal the contribution of the ocean fluxes. The third set of observations will be regular $^{14}CO_2$ and CO measurements, that will separate the fossil sources contribution. The remaining part of the CO_2 concentration signal will be interpreted as the effect of net exchange between terrestrial ecosystems and the atmosphere.

Finally, uncertainties will be assessed in the inverted fluxes pertaining to the a priori information injected in the inversions, as well as to the atmospheric transport fields. The final deliverable of the project will be a top-down quantitative estimate of the European carbon balance, where fossil and terrestrial components will be constrained separately. Interaction with stakeholders will be strongest at this stage of the project, with the publication of a summary report and the establishment of a web-site with the inversion results.

The suite of projects of the CARBOEUROPE cluster represent a complex multi-scale and multi-disciplinary framework of investigation which needs a specific infrastructure to facilitate calibration and real-time accessibility of observations, and to report recommendations for an operational monitoring of the carbon balance of European ecosystems towards the external end-users: stake holders, negotiators and European policy makers.

The objective of the **TACOS-INFRASTRUCTURE** project (*proposed september 2000 for a 36 months duration*) is to establish this infrastructure for monitoring the carbon balance of European ecosystems based on existing research projects. This will lay off the foundation for a fully operational observing system for the terrestrial sources and sink of CO_2 over Europe, in light of the Kyoto Protocol.

The road towards the objective above is paved with the **improvement of calibrations for the existing European network of atmospheric CO_2 stations**, and with the implementation of an online data-transmission system for flux tower measurements. The flux towers and the atmospheric stations networks will be integrated within a synergetic approach where tall towers will become atmospheric monitoring sites for use in transport models.

Atmospheric CO_2 and related tracers measurements, presently being carried out through scattered national and EU funded programmes by different laboratories, will be integrated into a unified dataset. Based on the overall GLOBALHUBS strategy developed by Dr. R. J. Francey at CSIRO-DAR, a **“European HUB” laboratory** will be set up, with the ultimate goal to take responsibility for Europe for the distribution of well characterised air standards in high pressure cylinders. In the mean time, at the international level, a dynamic monitoring of calibration activities is expected to be jointly established between the European “HUB” and three other CO_2 “HUB” laboratories that may operate in Australia, USA, and Asia. At the European level, the intercomparability of CO_2 measurements will be monitored further between four main institutes (LSCE-France, Univ. Heidelberg-Germany, Centrum Isotope Research-Netherlands, MPG-Jena-Germany) which operate or will soon operate air sampling networks.

Quality controlled atmospheric CO_2 concentration and CO_2 flux data, meteo and additional ecological data will be archived to a data centre accessible via the Web. We have identified as major end users of the TACOS-INFRASTRUCTURE data a large scientific community world-wide in the field of atmospheric sciences, ecology and forestry as well as stakeholders and policy makers involved in the Post-Kyoto decision process related to the sequestration of carbon in the land biosphere.

Summary

APN/NIES Workshop on Inter-calibration of Isotope Ratio Measurement for Atmospheric CO2
9-10 November 2000, Tsukuba, Japan

Thursday, 9 November

Opening addresses: Dr. Hitoshi Mukai of NIES gave a brief welcome and thanked participants for attending the workshop. Dr. RyutaroYatsu, APN Director, also expressed his thanks to all participants for attending and for Dr. Mukai for organising the workshop. Yatsu gave a brief outline of his hopes for the workshop and wished them success in their efforts. Mr. Martin Rice, APN Porgramme Manager, then gave a presentation about the APN. Finally, Dr. Mukai introduced the objectives of the workshop and the agenda.

Session A: Problems

Chair: Dr. Nakazawa

A-1: Francey (CSIRO), The Role of Carbon Dioxide Isotope Measurements in Global Carbon Budgeting. Main purpose is to distinguish between terrestrial and oceanic fluxes of CO2. Francey focused on the difficulties of using carbon 13, the problems with calibration and isoflux, and solutions such as GLOBALHUBS. He discussed global atmospheric budgeting and his concern at scientists' lack of standardization. Talked about problems of isofluxes and then gave a vector diagram on carbon 12 & 13 global budgeting. Talked about Oxygen and Nitrogen changes in Cape Grim (1976-98) using archive tanks (achievement of better equilibrium results), and about extracting bubbles of air from ice cores (one thousand years). Outlined box diffusion model. Francey also discussed the need to consider problems when planning experiments and the disagreement of ocean-based estimates. Hence why Carbon 13 was left out of IPCC Report. We need to explain these problems if we are to address Carbon 13. Need for calibration! Outlined Carbon 13 CSIRO program and discussed comparisons of Southern Hemisphere Carbon 13 records from Scripps (Keeling), NOAA (White) and CSIRO (Francey & Allison) using extractions of air samples. Suggested that Cape Grim could be used as a standard for Global Carbon Budget. Measurement of Carbon 13 is likely to continue, and to provide an increasingly valuable constraint on the atmospheric carbon budget, as past difficulties are carefully addressed.

A-2: Trivett (ESR), Flask sampling for CO_2 concentration – advantages of multiple agency sampling at a given site. Outlined the history of Canadian flask sampling (which started in 1975) and discussed work submitted to WMO by Meteorological Service of Canada. Talked mainly about concentration measurements. Introduced Global Atmospheric Watch's Global Network and Alert Flask Measurements and other programs. Discussed the deviations of AES greased stopcock flasks from AES in-situ carbon dioxide caused by heating the flasks during evacuation. Technology for collection using containers has got much better. For example, pressurized O-Ring

Flasks. In summary, the internal consistency problems previously reported to WMO and emphasised that with due care the basis between in-situ measurements and flask sampling measurements of CO2 can be minimized to a similar level (0.02 micromole per mole CO2) to that achieved by two independent in-situ measurements (NDIR & GC). However, we need to look at the whole picture, i.e. sampling extraction in the field and analysis in the lab.

A-3: Verkouteren (NIST), NIST-IAEA Metrological Standards for Istope Ratio Measurements of Carbon Dioxide. Verkouteren described the advantages of multiple agency sampling at a given site and briefly outlined role of NIST. What are standards? Verkouteren outlined what standards actually are, fundamental realization of SI, reference materials, data and methods. He then outlined the Isotope Metrology System and discussed the production of CO2 Isotope Reference Materials using gas circulation manifold and tubular 9mm break seals and the steps involved, such as CO2 ROMs inter-comparison from scientists throughout the world. A more explicit and globally empirically approach to disseminating information is needed in light of the substantial improvement in inter-laboratory reproducibility from central data processing. This resulted in the establishment of NIST web page interactive data processing system at: www.nist.gov/widps-co2

Dr. Nakazawa closed the morning session.

Session B – Introduction by each laboratory

Chair Mukai opened the session and introduced Dr. Allison from CSIRO.

B-1: Allison (CSIRO), The CSIRO Atmospheric Research (GASLAB) Stable Isotope Measurement Program. Allison explained that CSIRO Atmospheric Research has been involved in the measurement of the stable isotopes of atmospheric CO2 for about twenty years. He then gave a brief history of CSIRO stable isotope measurement program, including a description of the techniques used for the collection, extraction, analysis and data processing of samples. Allison concluded factors that are not considered important at the 0.01% level – N2/CO2 ionisation efficiency and constants, a and K, and working gas, etc. What factors are important? Air standards, as are consistent procedure, known or agreed standard composition, on going checking of air measurements and variation in the working gas effect.

B-2: Nakazawa (Tohoku University), Isotope Measurements of Atmospheric Carbon Dioxide at Tohoku University, Japan. Nakazawa talked about technical aspects of air sample measurements taken from ground stations, aircraft, ships and scientific balloons. Techniques such as air samples collected in glass or stainless steel flasks, Finnigan MAT carbon-E and MAT carbon-S mass spectrometer analysis

B-3: White (INSTAAR/NOAA), Isotope Measurements in Greenhouse Gases at the INSTAAR/NOAA. What do we measure? We measure isotopes of CO2 and C13 and O18, isotopes of CH4 and isotopes of water vapour. Then discussed rate of atmospheric CO2 increase (fossil fuel emissions), global fluxes, CO2 sources in major latitude zones.

Data quality control was covered – calibrate to V-PDB (water and carbonate), inter-calibrations with other labs and long-term standards (CO2 in air). Concerning long-term standards White discussed tanks of dried air filled at Niwot Ridge. Currently use 16, expanding to 24. Some tanks do drift however. Finished on CH4C13 measurements in the South Pole, Barrow and Mauna Loa. Talked about differences of collection with different flasks.

B-4: Brailsford (NIWA), Measurements of CO_2 Stable Isotopes in the Absence of N_2O by the GC-IRMS Technique. Discussed the Baring Head auto sampler system & CO2 system. But the main focus of the talk was on NIWA GC-IRMS system. Brailsford explained the process of separating CO2 & N2O, GC-IRMS isotope trace and source equilibration. Explained further that some calculations were made on the short noise limit of the system. Re-capped limiting factors, such as temperature (variations alter peak centre), pressure (influence of sample going into the open split), water impurities, timing & dilution at the open split. Compared dual inlet & GC-IRMS techniques (high vacuum/helium stream, single separation with multiple determinations/individual separation and determination, etc). Data readings of NIWA – CSIRO oscillator and Baring Head New Zealand CO2 isotopes were also illustrated.

Chair: Dr. Yoshiyuki TAKAHASHI (NIES)

B-5: Hong & Zeng (Inst. Geochemistry), Determination of Stable C and O Isotopes in Environmental Samples. Dr. Zeng thanked Dr. Mukai & APN. Introduced the institutes laboratories location and function, main facilities such as multi channel energy analysis system, element analyser, MAT 252 and computer facilities. Investigation of transfer rules of organic carbon by isotope C18, characteristics of soil CO2, Peat C & O isotope evidence of climate change in China over the past 6,000 years. Discussed sampling and oxidizing, sampling tubes to draw CO2 in soil, preparation line for isotope analysis. The most important research focuses on peat sediment in Hongyuan. Outlined mechanics and measurements of NACIS. Hong then discussed some work undertaken by Dr. Allison & White and the composition of C3 & C4 plants in peat. Hong introduced the geography of peat distribution in China, and showed photos of peat profiles (peat changing into mud, 6000 year timeline estimate) and sampling sites in North East China (dried Mar Lake) and peat samples in the laboratory. Displayed calibrated age diagram (a) which consists mainly of C3 plant and (b) described eight dry periods (climate proxy report). Outlined advantages of peat deposit as climate proxy record and global inter-calibration of peat isotopes as climate proxy indicator.

B-6: Yoshikawa (Meteorological Research Institute, Japan), Stable Carbon and Oxygen Measurements of the Meteorological Research Institute: Past, Present and Future. Yoshikawa gave list of papers related to stable isotope measurements. He also introduced paper on pCO2 and isotope C13 in the air and surface seawater in Western North Pacific. Why did we give up studies? No land base-line stations. Therefore, it was impossible to study seasonal variation. Second reason was quality control of isotope measurement, where the limited number of researchers didn't help. Currently studying global carbon cycle. Gave sample locations of aircraft measurements between

Japan and Australia as well as CO2 measurements taken from the meteorological tower (200m) in Tsukuba.

B-7: Kim (Seoul National University), The Current Status of Isotopic Studies of CO_2 in Korea. Gave current status of Korean sampling on Kosan, Cheju Island (collect 3 litre glass flask samples once a week). Difficulties with keeping up with standards. Kim has worked with the Korean Meteorological Agency to set up sample measurements in Korea for the past ten years. Discussed CO2 measurement process illustrating data diagrams.

B-8: Tang & Zhou (Chinese Acad. Meteor. Sci.), Carbon Isotopes: Current and Future Application at China Global Atmosphere Watch Baseline Observatory. Tang displayed a map of GAW stations and outline of CGAWBO (location & environment) and routine measurement program at CGAWBO and showed a photo of the CGAWBO facility. He also described the major research programs, which act as a platform for many national programs (China Ozone Research Program, etc). Measurements of CO2 and C13 at CGAWBO (in-situ CO2 measurement and flask sampling) and data quality assessment. Discussed measurement of black carbon at CGAWBO. Started manual Aethalometer in 1991 and Aethalometer AE-10 & 14 since 1994. Recordings at different sites around China. Tang noted different concentration levels at different sites. Highest levels in Southeast China, and increased levels since 1994 due to economic development in China. Talked about the future and the “basic work” project and national sampling network for greenhouse gases.

B-9: Mukai (NIES), Carbon and Oxygen Isotope Analysis of Atmospheric CO_2 and Newly Prepared Reference CO_2 Gas in NIES. Introduced NIES monitoring program (sampling & extraction). Sampling from Japan-Canada, Japan-Australia (“ship of opportunity”) and Japan (land stations). Plan to sample from Japan to Peru in future. Outlined methods of sampling, such as drying and the use of 3L stainless steel bottles (temperature & pressure). Regarding the stations in Northern & Southern Japan, they use similar techniques but with glass. Takes about one and a half hours. Displayed photos of flasks on board the ship and photos of the land stations in Japan and the sampling equipment. Highlighted CO2 concentration at Hateruma station using a diagram. Discussed differences between continuous sampling and bottled sampling. Previous problems with old mass spectrometers (OPTIMA etc). Use of MAT 252 makes good balance (.01 per mil to 0.02). There is however some drift. Outlined drift of the measurement values for various references. The cause of the drift is still unknown. Mukai then compared his data with University of Tohoku’s (Nakazawa) and NOAA. Japan has many mass spectrometers and geochemists but not so much inter-calibration. This lead to new reference CO2. This NACIS inter-comparison is now distributed to 10 Japanese institutes and universities and foreign country laboratories (China & USA).

Dr. Takahashi & Mukai closed the day’s session

Friday, 10 November

Dr. Hong opened today's session.

B-10: Sugimoto (Kyoto University), Preparations of Standards for Carbon and Oxygen Isotopic Compositions of CO_2 at Center for Ecological Research, Kyoto University. Dr Sugimoto's presented the interaction between biosphere and the environment. She talked about the IGBP, plants and water cycles in Siberian Taiga at Yukutsk. Introduced air sampling at tower site at Yukutsk, then the transfer of air into a glass bottle, water & CO2 extraction line, and the standard and ref. CO2 preparation (comparing CaCO3 - H3PO4 reaction at 25 degrees Celsius vs. fifty degrees – at fifty degrees the reaction is very rapid. Sugimoto prefers to prepare phosphoric acid at this temperature). She also explained her standards for calculating isotopes C13 & O18. Concluded that for inter-calibration we need more than two standards for scale and fixed fractionation factor.

B-11: Kitagawa (Nagoya University), Reference Standards for the Determination of Carbon and Oxygen Isotopic Ratio of CO_2 at IHAS (Nagoya Univ.) and IRCJS (Kyoto). Talked about laboratory standard materials and preparation of C13 and enriched CO2 gas for getting the optimum, parameters of the mass spectrometers using primary standard NBS 19. Discussed working reference CO2 and daily check, parameters for atmospheric CO2 isotope measurements (VG-Optima), routine measurement and the history of the primary standard and C13 & O18 assessments vs. NBS19. Kitagawa summarized C13 & O18 standards vs. PDB. In order to get reliable isotope data of CO2, there is a need for more detailed experiments for isotope measurement. This is now in progress.

B-12: Mukai (NIES), Short Summary (abstracts attached)**.** In this session, Mukai asked several participants to clarify points made during the previous presentations. For example, drifts of delta 18, pressure used at extraction, sampling (problems with stopcocks). Sampling methods depend on your goals, for example Francey said CSIRO uses small flasks for use on aircraft. White outlined NOAA methods. Mukai asked participants to discuss materials used for containers. Concerning the mass spectrometer Mukai asked participants knowledge of delay times. Collection methods were also touched upon (Allison method & NIST). Last point was NIST pure CO2 standard. Allison said don't use NBS18.Verkouteren clarified standards. White believes that you can't use any NBS standards to inter-calibrate well enough.

Chair Sugimoto opened Session C – Inter-Calibration

C-1: Allison (CSIRO), What Have We Learnt about Inter-Calibration of Atmospheric CO_2 Stable Isotope Measurements? Discussed IAEA Classic circulation of lab air standards for stable isotope inter-comparisons at CSIRO, INSTAAR/CMDL, Scripps, Tohoku University. Touched upon sharing of flask samples (Cape Grim) with other laboratories and institutes (INSTAAR, NIWA, etc.) Summarised offsets between CSIRO & INSTAAR observed in CLASSIC & ICP and checked differences by using measurement taken from a different site, in this case at the South Pole. Allison also mentioned CSIRO-NIWA oscillator. Concluded lessons learned, such as consistent offsets between labs over time, flask air programs suggest offsets can vary over time, oscillator is confirming variation in offset between CSIRO & NIWA flask measurements. Where do we go from here? Access causes of differences, centralized reporting of results and GLOBALHUBS. (see Francey's presentation).

C-2: Yoshida (Tokyo Institute of Technology), Activity for ^{18}O Inter-Calibration for H_2O Inter-Laboratory Calibration of Isotopes and Isotopomers in Non-CO_2 Greenhouse Gases including H_2O. Outlined important activities in this field such as the 2nd IAEA inter-lab comparison for stable isotope analysis of prescription, IAEA advisory group meeting on stable isotope ratio measurements by GC/C/IRMS and Laser Spectroscopy (briefly highlighted list of atmospheric species of interest required to meet scientific requirements) and IAEA and a short history of N2O standardisation.Yoshida also discussed work being undertaken in Russia and future results to be submitted to GBC (Siberia, Thailand & Japan). Explained what isotopomers are (a set of molecules isotopically substituted) and talked about work submitted to Nature. Introduced International Symposium on Isotopomers (ISI 2001) 23-26 July 2001, Yokohama, Japan. http://nylab.chemenv.titech.ac.jp/ISI2001/isi2001.html

Chair Machida opened the afternoon session.

C-3: Masarie (NOAA), Lessons from Our Trace Gas InterComParison activity. Discussed NOAA CMDL carbon cycle greenhouse gases measurement programs – Global View CO2 2000 Cooperative Atmospheric Data Integration Project. Whereby this project has objectives to improve the value of individual data sets by establishing comparables with other data sets. Essential components are cooperative spirit, ongoing, frequent, minimal burden to participating labs, maximize the opportunities and for success it needs to be highly automated and results have to be examined routinely. NOAA CMDL has ongoing ICP experiments with AES (Canada), CSIRO (Australia), NIWA (New Zealand) and CMDL/HATS (USA); and has proposed InterComParison (IPC) experiments with NIES (Japan) and LSCE (France). Masarie concluded that as a global strategy emerges, we must keep at the forefront the reasons why existing ICP activities have not realized their full potential. Critical challenge to this group is to establish a central inter-calibration unit.

C-4: Francey (CSIRO), GLOBALHUBS. A global strategy for improved global gas measurements. At this moment, GLOBALHUBS is only an idea, although it is gathering momentum. The concept is driven by a desire to improve precision and location of fluxes of greenhouse gases for the monitoring of composition differences in the global atmosphere. The approach is to achieve greater global coverage by reducing calibration errors. Francey outlined the map of uncertainty in CO2 sources and the need for us to do much better. He then focused on the CO2 measurement expert meeting, WMO, Geneva, 1981. Francey added that we still have not achieved levels. He then went on to state that present strategies are not working. Francey outlined the need to compliment what Masarie discussed in his presentation (Francey mentioned WMO round robins). He then went on to discuss problems with C13. Re-emphasised differences between reported C13 values (CLASSIC: 1st circulated) which is a challenge for us. Discussed CSIRO new technology. For example, LOWFLO CO2 Analyser and GLOBALHUBS and global quality control for long-lived trace gas measurements.

(GLOBALHUBS OHP enclosed – Francey stated that these are proposed details). Outlined need for patience, carbo Europe will be a good test. Francey finished with costs of $300,000+ to set up and annual operational costs of around $80,000. The HUB Manager will take up a lot of the costs. Aerocarb Europe has asked for similar amounts.

C-5: Jourd'Heuil (LSCE), AEROCARB and European Inter-Comparison Programs, Situation and Perspectives. Jourd'Heuil gave a brief introduction of AEROCARB which will be a first attempt to develop a unified European network of atmospheric CO2 and related tracer concentration measurements. The overall objective is to demonstrate the feasibility of estimating and monitoring the net carbon balance on decadal time scales by means of an integrated approach. This approach is based on a synergy of atmospheric measurements, mesoscale atmospheric transportation models, high-resolution data measurement, etc. Jourd'Heuil acknowledged the work of Francey and the concept of GLOBALHUBS. He then talked about Terrestrial and Atmospheric Carbon Observing System (TACOS) and the Global Quality Control for Long-Lived Trace Gas Measurements – Europe and HUB (35 stations worldwide).
Aerocarb: www.lsce.cnrs-gif.fr/aerocarb/index.htm.
Tacos: www.lsce.cnrs-gif.fr/tacos/index.htm.

Discussion for the future - Chairs Trivett & Francey
Trivett discussed problems of isotope measurements. Gave a history of the WMO & IAEA meeting in September last year. At the meeting Francey put forward the GLOBALHUBS concept, which received a positive response. This resulted in Trivett & Francey touring labs throughout the world introducing the concept and gauging interest for GLOBALHUBS. Overall they have received a positive response but face financial and administrative burdens. Trivett also issued reports. Looked at programs and agencies for money. Francey was invited to a planning meeting, where he put forward a proposal for funding. At the same time IGBP were having meetings about the carbon cycle. Put together a framework for research. Francey discussed atmospheric side at meeting in Portugal. Here it was accepted that there is a need for more stations at source sink sites. How to do this? Discussions continued. Obviously there is a need to address inter-compatibility (problems with FLUX, need to bring them on board). Things are beginning to get started in Europe, Australians are seeking money, NOAA has been helpful with equipment, Mukai & NIES was approached to sow the seeds of this issue in Asia. Francey stated that if you have questions about GLOBALHUBS please ask.

Opened to the floor

White need to calibrate to primary standards (some absolute ratio) who is responsible for this?
Francey can make progress with high precision but huge costs. Some levels may not sound important today but in the future they can be very important. Isotope measurements linkage with other organisations very important. Integrate learning of GLOBALHUB. First of all there is homework to be done in Europe & Asia. Setting up GLOBALHUBS will mean that information can be quickly propagated. To set up a regional hub we need to look at regional expertise and utilise them. Must not be

dominated by US or Australia. Give opportunities to everyone, this is a global problem, should not be content with just our labs (CSIRO, NOAA, etc.)

White IAEA, NIST or WMO need to deal with the standards. Need for big banner behind you

Francey suggests IAEA to work with NIST

Jourd'Heuil are we waiting for political decision? We must do it

Verkouteren as for NIST this is our mission, money is secondary, justification is important.

Francey this justification will be possible

Trivett talks about the integration document; this is intended to be distributed to funding agencies and government organisations that have a vested interest. Support by IGBP, IHDP and WCRP who agree that GLOBALHUBS are needed to get the data together. The document is not a prescription, it's a framework.

Francey importance of WMO & IAEA measurement experts meeting in Japan, September 2001. If things go quicker we may need a meeting before this. We hope to have a far more detailed proposal before the September meeting. Maybe time for this issue to go into a new gear. Personally I'm (Francey) just taking it as it comes. Possible APN funding for the Asia-Pacific region. Some of the ideas need to be tested in Europe. What do people feel about the formalisation of GLOBALHUBS?

Trivett reminded people of web page (under construction) could set up discussion group to exchange views

White definition of a hub?

Francey expertise that doesn't hold up the transit of containers, solves logistic problems and reports are done well. Doesn't have to be one lab.

White this is important

Francey if the region can cope with handling the containers, then any proposal should be accepted from any region. He also stated the need for quality control and infrastructure for learning

Trivett outlined the need for an oversight committee

Mukai not so difficult to circulate the cylinder, the problem is high frequency circulation. Relation between GLOBALHUBS and NOAA round robin – what is the connection?

Francey round robin would keep the four hubs together, if we can demonstrate that GLOBALHUBS can do better, then maybe round robins may get phased out by WMO/IAEA.

Brailsford what frequency of flask sampling is required to make a comparison?

Francey differs with species. Lab will pay a fee, this should cover HUB overheads. Review every two years to see how effective it is

Brailsford what is the limit of frequency? How would you integrate work already being undertaken.

Francey people must use GLOBALHUBS for current scientific issues - has to be science driven

Allison they are joint exercises, this determines the frequency.

Francey for example CO2 inversion modellers are now giving us advice on how often to take samples at the site

Masarie answers Brailsford's earlier question - GLOBALHUBS is a structure, it can go with current circulations and work together. Keep things going in addition with

GLOBALHUBS. Newly created inter-comparisons with customers throughout the world should be used in addition with GLOBALHUBS. Things will carry on, round robins will not go away overnight. GLOBALHUBS may not work, although he doesn't think so.

Francey each lab has to decide if they can afford to keep both things happening.

Trivett next CO2 meeting we need a better idea of how to go forward. A proposal out of Asia would be very nice on how to set it up. We have the foundations from this (APN/NIES) workshop. Take the next stage and set up a small group of participants from this meeting.

White world may not want to pay for GLOBALHUBS. There is political consideration but it is up to scientists to get things going. The system needs to be flexible, some group needs to get things started, and you can't rely on governments to do things. Francey's efforts (GLOBALHUBS) highlight this.

Trivett we have the technical capabilities driven by our scientific agenda. Although we still have to do more if we are to take the next step. We need to do things differently. GLOBALHUBS is a timely proposal.

Mukai when you say GLOBALHUB – is this a system of inter-comparison or organisationally orientated?

Francey GLOBALHUBS is a tool to merge data, we need to be able to do this to stay relevant – it's a scientific community response.

Trivett it's not something that is imposed, it's a suggestion. If we get the four hubs then we can integrate the data sets. We need to be able to put the data sets together, if we don't do that, then globally we will suffer.

Verkouteren how global does it have to be to answer some of the global questions

Francey increase coverage of CO2 sites by 30%. We may have to wait until satellites come, etc. GLOBALHUBS has real potential.

Verkouteren this is the next big step for us to answer these large global questions.

Francey displayed GLOBALHUBS quality control OHP, developing labs can get frequent checks at low costs. We need to establish this floating scale and how it can be linked to set standards. GLOBALHUBS is a quick tool for us to get information that we need.

Mukai we don't have so many customers in Asia

Francey should not be used as a calibration tool, just as a information tool for quick access. Every two years there will be a review process to improve.

Mukai like to hear comments from other Asia participants

Kim Japan might have a large number of customers. Start at some point in Japan. Let Japanese customers talk amongst themselves. Then Korea & China can act.

Francey you should also consider the data base (inter-compatibility flow).

Francey no current flow of information into global view

Masarie there is some, however, GLOBALHUBS would be of huge benefit to global view.

Jourd'Heuil this confirms aim of AEROCARB.

-**Trivett** closed the meeting-

Inter-calibration of Isotope Ratio Measurement for Atmospheric CO_2
(Tsukuba, Japan; November 9-10, 2000)

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