Analysis of global CO_2 budget by observation of oxygen concentration and isotopic composition of carbon dioxide in the atmosphere (Abstract of the Interim Report)

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Total Budget for FY2001-FY2003 106,000,000Yen (**FY2003;** 37,855,000Yen)

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1. Introduction

Carbon dioxide is a major greenhouse gas in the atmosphere. Anthropogenic CO_2 has been emitted to the atmosphere for over 200years. Average growth rate of CO_2 in the atmosphere is reported to be about 1.5ppm/y, suggesting that half of emitted CO_2 is absorbed by ocean and land ecosystem. However, in 1998 high growth rate (over 3ppm/y) was recorded in everywhere in the world. This high growth rate was associated with high temperature tendency in the world, due to El Nino event. Because anthropogenic emission of CO_2 is considerably constant, natural sink variation is considered to be a major cause of such a large variation of growth rate of CO_2 in the atmosphere. Such variation of CO_2 budget can affect growth rate of CO_2 over the time and the concentration in the future. Therefore, scientific study on CO_2 cycle on the earth is important.

2. Research Objective

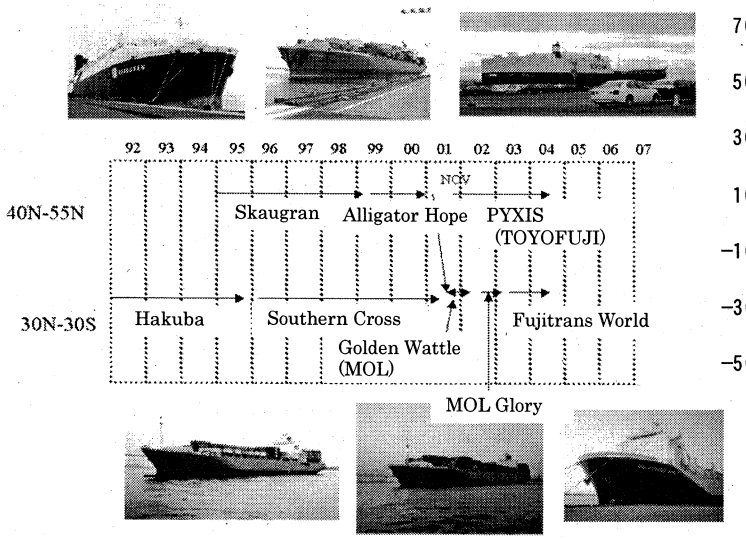
In order to clarify the mechanism of the variation of CO_2 budget in the atmosphere, oxygen concentration in the atmosphere and carbon isotope ratio of CO_2 were used in this work. Because oxygen is mainly produced by land plants, observation of oxygen production will allow us to estimate the amount of photosynthesis on the land. In this work, air samples were collected over the Pacific to observe a latitudinal average of oxygen, carbon dioxide concentration and isotope composition of CO_2.

A new glass-bottle sampler for this purpose was produced to install it on the commercial cargo ships, which are operated over the Pacific (e.g. between Australia and Japan, U.S.A.-Japan). In addition, two monitoring stations by NIES/Center for Global Environmental Research (CGER) were used to collect air sample frequently to make a time-series of oxygen and CO_2 isotope ratio around Japan.

3. Experimental

(1)Air sampling

Sampling was done over the Pacific by using two routes; Japan-Australia and Japan-USA. Figure 1 shows the ships we used for sampling in each period. We had to change the ships several times, because of the change of the ship route. Now, for the USA line, Pyxis (Toyo Fuji Kaiun) was used to collect air samples. Transworld (Fujitrans Co.) was used to sample air along the routes to New Zealand Sampling sites were shown in Fig.1, including two monitoring stations (Hateruma Island and Cape Ochi-ishi). Sampling method



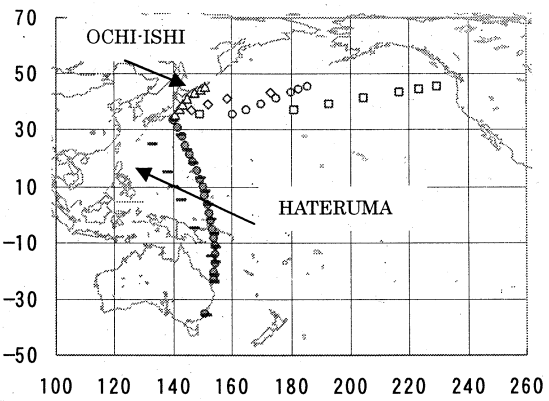


Fig.1 Sampling ships and sites over the Pacific and two monitoring sites

was about the same as written in previous report. At the monitoring station, sampling was done about twice a week.

(2) Bottle analysis and in-situ measurement

Oxygen analysis was firstly done for Glass bottle sample by using GC-TCD method developed by Tohjima[1]. Then CO_2 concentration was measured by NDIR method, followed by CO_2 extraction in a vacuum line. Isotope ratio for CO_2 was measured by Isotope Mass spectrometry (MAT252). In Hateruma, we installed GC system for oxygen in-situ measurement.

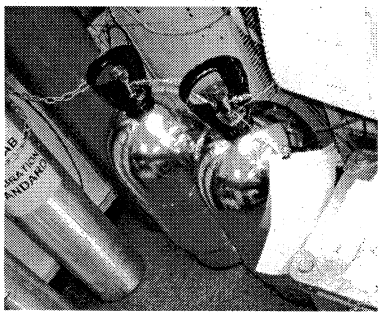


Fig.2 Stainless steel container (ESSEX Co)

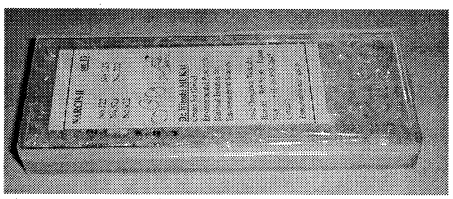


Fig.3 NARCIS-II sample

(3) Reference air sample for inter-comparison

Air was compressed in aluminum high-pressure cylinder. Part of the air was transfered from the cylinder to stainless steel 35L container (Fig.2). Isotope values and CO_2 concentration were measured after decanting.

(4) International isotope measurement comparison

CO_2 reference samples (NARCIS-I and II) were produced in this work for inter-comparison. There were distributed to the related laboratories in the world. NARCIS-I had similar isotope values to those of atmospheric CO_2, while NARCIS-II had similar values to NBS-19-CO_2. Some other CO_2 standards (from CIO and NIST) and air samples (from TACOS, CSIRO and NOAA) were used to compare the measurement of isotope ratios.

4. Results

(1) Oxygen latitudinal variation

The period of the record of O_2/N_2 ratios observed from air samples collected on board the cargo ships is still short to discuss precisely the decreasing trends. However, we observed clearly the latitudinal differences in the seasonal cycles and the annual averages of the O_2/N_2 ratios. The O_2/N_2 ratios increase in spring and summer and decrease in autumn and winter, in both hemispheres except the equatorial region (10°N-10°S). In Northern Hemisphere, the seasonal cycle of the O_2/N_2 was inversely related to that of CO_2, while in Southern Hemisphere there is less seasonal cycle of the CO_2. Seasonality in the atmospheric O_2/N_2 ratio in Southern Hemisphere can be attributed mainly to seasonality in oceanic O_2 flux.

Fig. 4 shows latitudinal distribution of averaged APO (Atmospheric Potential Oxygen) during the period from 2002 to 2003. Note that the observed data were grouped into latitudinal bins with 10-degree width from 50°N to 40°S and that the annual averages for the latitudinal bins were calculated from the fitting curves. The APO is a new tracer defined by $APO = \delta(O_2/N_2) + 1.1/0.2095 \cdot [CO_2]$[2], and the changes reflects mainly air-sea O_2 exchange. Therefore, global distribution of APO can be used to validate global ocean carbon cycle models through the oceanic O_2 fluxes[2,3]. In Fig. 3, model-simulated APO distribution from Gruber et al., (2001)[3] along cruise route is also depicted. The observed APO distribution agrees well with the simulation, especially in the northern hemisphere, suggesting the validity of the model study by Gruber et al. (2001).

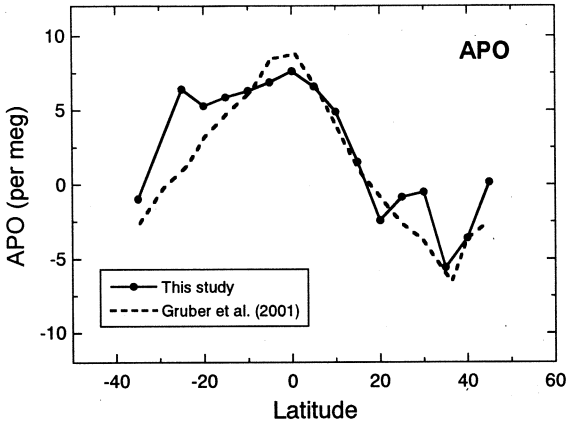


Fig. 4. Latitudinal distribution of the observed APO in this study and model-simulated APO by Gruber et al. (2001).

(2) Oxygen time series variation at Hateruma and Ochi-ishi

The O_2/N_2 ratios observed at Hateruma and Ochi-ishi are shown in Fig. 5. The average rates of decrease in the O_2/N_2 ratio were 20.6 $\pm$0.4 per meg yr^{-1} over 6.5 year period (1997.5-2003) for Hateruma and 20.1$\pm$0.6 per meg yr^{-1} over 5 year period (1999-2003) for Ochi-ishi.

We estimated average emission rate of fossil carbon of 6.4 GtC yr^{-1} (5.33 x 10^{14} mol yr^{-1}) for the period from 1998 to 2003. Since the stoichiometric ratio of O_2 to C for burning the current composition of fossil fuels is 1.45 [4], the rate of O_2 consumption from the burning of fossil fuels is calculated to be 7.72 x 10^{14} mol yr^{-1} for 1998–2003. We averaged the rates of decrease in the O_2/N_2 ratio observed at Hateruma and Ochi-ishi, and used the average of 20.4$\pm$0.8 per meg yr^{-1} as a global value for 1998–2003. This average rate of decrease in O_2/N_2 is equivalent to a rate of loss of atmospheric O_2 of (7.55$\pm$0.3) x 10^{14} mol yr^{-1}. If the ocean is neither a source nor a sink for O_2 for a period longer than the seasonal timescales, the land biota must emit O_2 to the atmosphere at a rate of (0.17 $\pm$0.4) x 10^{14} mol yr^{-1} to balance the O_2 budgets. This value is equivalent to the land CO_2 uptake of 0.2 $\pm$ 0.6 GtC yr^{-1}. Taking into account the average rate of increase in CO_2 at Hateruma and Ochi-ishi of 1.92$\pm$0.08 ppm yr^{-1} (4.1$\pm$0.2 GtC yr^{-1}) during the same period and CO_2 emission from cement production of 0.2 GtC yr^{-1}, we calculate the oceanic CO_2 uptake to be 2.3$\pm$0.8 GtC yr^{-1}. It should be noted that recent studies indicated that the ocean is currently a significant net source of atmospheric O_2[5,6,7], which would result in an overestimate of land CO_2 uptake. For example, Bopp et al.[6] estimated that the overestimate in land CO_2 uptake is about 0.5 GtC yr^{-1}.

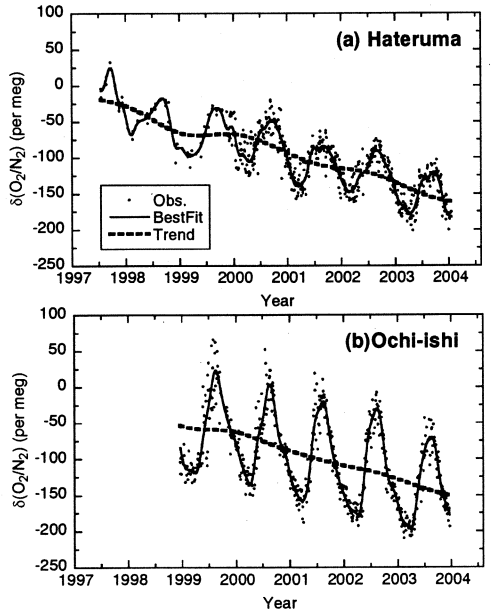


Fig.5. O_2/N_2 ratio at Hateruma and Ochi-ishi

The temporal variations of the instantaneous rates of changes in the CO_2 mixing ratio

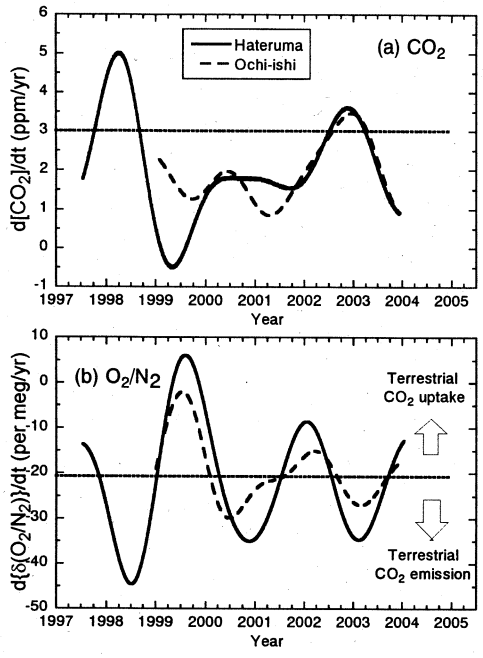


Fig. 6. The temporal variations of the instantaneous rates of changes in the (a) CO_2 mixing ratio and (b) O_2/N_2 ratios observed at Hateruma and Ochi-ishi.

and O_2/N_2 ratios, which are derivative of the long-term trends, are shown in Fig. 6. The rate of decrease in O_2/N_2 was rapid at Hateruma in 1998, and slower at both sites in 1999. The rate of growth of CO_2 was also rapid in 1998 and slower in 1999 at both sites. This relative change in the land uptake agrees qualitatively with the estimate based on the measurements of $\delta^{13}CO_2$. However, the quantitative changes in the land uptake deduced from the mass balance of atmospheric O_2 are significantly large. One of the explanations—as also reported by Battle et al. [8]—is that the imbalance in the annual air–sea exchange of O_2, which is closely related to the oceanic production and ventilation processes, produces significant interannual changes in the net oceanic O_2 flux.

(3) Isotopic signature for CO_2 variation

Carbon isotope ratio and CO_2 growth rate during 1995-2004 were studied precisely. Growth rate and isotope change pattern were illustrated in Fig.7. In 1998 and 2002, high growth rate and

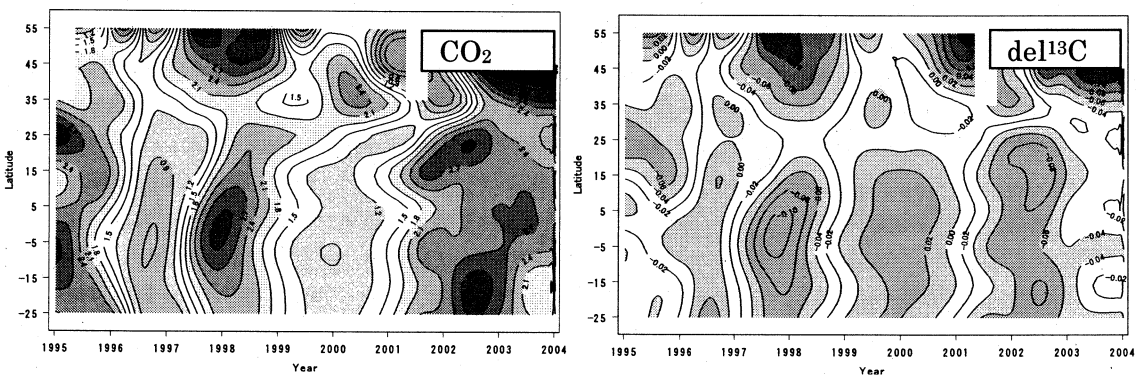


Fig.7 Latitudinal CO_2 growth rate and carbon isotope ratio change with time

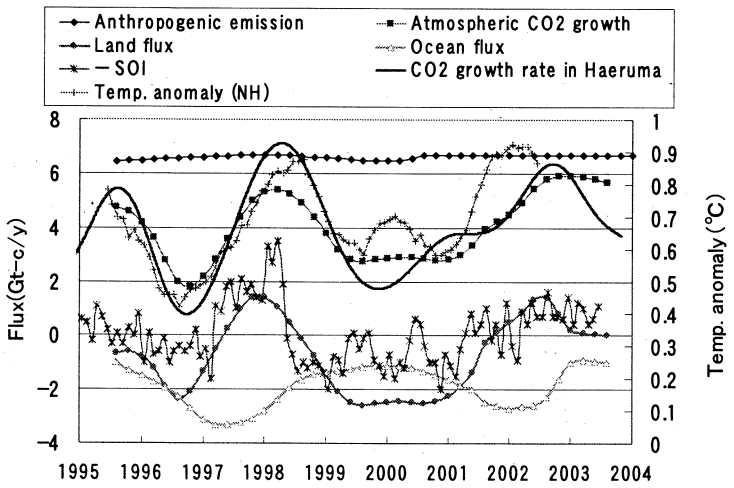


Fig.8 Estimated CO_2 flux by land and ocean calculated by using carbon isotope ratio

change rate in isotope ratio were seen at the same time, suggesting land ecosystem did not observed CO_2 so much.

Estimation of global flux was tried under certain condition. Figure 8 showed the large variation of land flux, while ocean flux only fluctuated in a small range of 1Gt. SOI and temperature anomaly well correlated with land flux change, suggesting higher temperature affect biosphere badly. On average, isotopic ratio observation showed that 0.5Gt-C was absorbed

by the land ecosystem and 1.8Gt-C was absorbed by the ocean. This estimation was considerably close to that from oxygen observation.

(4) Isotope data comparison and reference air

Pure CO_2 and air samples were measured by five institutes (NIES, NOAA, CSIRO, UHEI-IUP, CIO-RUG). For pure CO_2, good agreements were obtained, however, air samples showed large variations. Especially, the lab using air standard showed different behavior about the difference between pure CO_2 and atmospheric CO_2, suggesting that lab scale used in each case may affect the reported value.

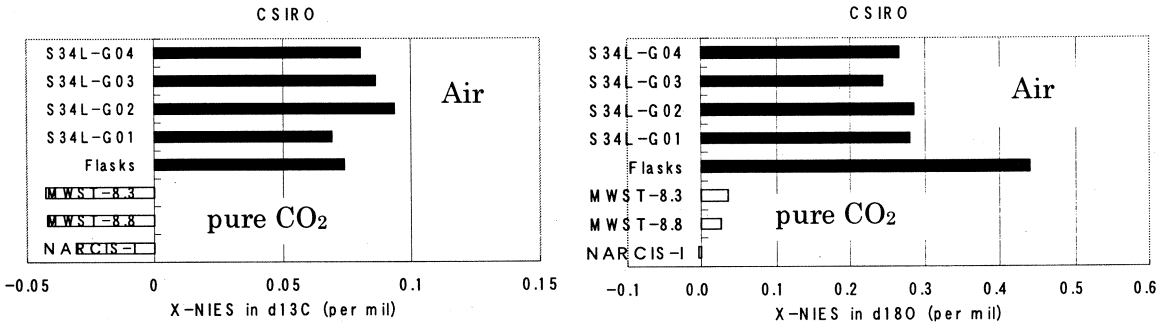


Fig.9 Comparison of isotope measurements with CSIRO

5. Conclusion

Air samples have been taken over the Pacific since 2002. Oxygen concentration measured along the cruise showed a different seasonal variation from CO_2. In the Southern Hemisphere oxygen concentration had a fairy large seasonal variation, while CO_2 did not have seasonal variation. This was due to the oceanic primary production. APO observed showed a good agreement with the oceanic model.

Long record of O_2/N_2 at Hateruma and Ochi-ishi showed recent small land ecosystem absorption of carbon dioxide of about 0.2Gt. Carbon isotope ratio observation showed that land ecosystem could be a source in El Nino year such as 1998 and 2002-2003. Recent temperature anomaly may be related to the decreasing of land sink rate. As a result, average atmospheric CO_2 increase rate went up to about 1.9 ppm/year during 1995-2004. Thus, analysis of time series of both oxygen and isotopic composition of CO_2 could give a good explanation to temporal budget change of CO_2 in the atmosphere.

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