

B-7.5 Study on geochemical cycles of carbon dioxide by measurements of its isotope ratio and oxygen/nitrogen ratio in the atmosphere

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Total Budget for FY1996-FY2000 46,618,000 Yen (FY 2000; 15,963,000 Yen)

Abstract Estimation of carbon dioxide budget in the atmosphere is important issue to assess the future increase of CO₂. Growth rate of carbon dioxide was known to change every year. Such a variation may be related to CO₂ budget in nature. In this study, we focused on isotope ratio of carbon dioxide and oxygen concentration change associated with the CO₂ growth. These two parameters can give us useful information on the CO₂ budget in the atmosphere. To observe these parameters, bottle sampling of background air over the Pacific was carried out with two ships-of-opportunity and by using two monitoring stations (Hateruma Island and Cape Ochi-ishi). Carbon isotope ratio (1995-2000) showed latitudinal gradient and clear seasonal variation with a long-term change. Isotopic budget calculation showed that the CO₂ source flux from land biosphere increased in 1998 with a small increase of CO₂ sink flux by the ocean, followed by changing to ocean as a source in late 1998. Then land biosphere changed to sink in 1999. Gradually ocean became sink again in 2000.

The 3-year record (Jul.1997-Jun.2000) and 2-year record (Dec.1998-Nov.2000) of the O₂/N₂ ratios clearly showed seasonal variations, which inversely co-vary with variations in the CO₂ mixing ratio. The changing rates of CO₂ mixing ratio and O₂/N₂ ratio at Hateruma were 2.1±0.1 ppm/yr and -3.7±0.5 ppm/yr, respectively. Assuming that the CO₂ production rate by fossil fuel consumption during the same period is 6.6 GtC/yr, these observed CO₂ and O₂/N₂ trends correspond to the land biotic and oceanic uptakes of 1.5±1.0 GtC/yr and 0.9±1.1 GtC/yr, respectively.

Key words Carbon dioxide, Carbon isotope ratio, Oxygen concentration, Pacific ocean, bottle sampling, Hateruma

1. Introduction

CO₂ growth rate in the atmosphere has been found to correspond to about half of anthropogenic CO₂ input. Therefore it is believed that half of anthropogenic input is

absorbed by somewhere; land biosphere and/or ocean. It is important to estimate how much CO₂ is absorbed by both sinks and how they absorb CO₂. To estimate future CO₂ increase, we have to know the mechanism of the variation of sink strength.

Carbon isotope ratio is one of good tracers to estimate origin of the concentration change of CO₂, because there is difference in isotope fractionation factor between photosynthesis (ϵ_{ab}) and oceanic uptake (ϵ_{ao}).

$$dC/dt = C_F + C_{No} + C_{Nb} \text{ ----- (1)}$$

$$d\delta^{13}C_a/dt = C_F \times \delta_f + C_{No}(\delta_a + \epsilon_{ao}) + C_{Go}(\delta_o - \delta_a) + C_{Nb}(\delta_a + \epsilon_{ab}) + C_{Gb}(\delta_b - \delta_a) \text{ ----- (2)}$$

N: net flux, G: gross flux, o: ocean, b: biosphere, a: atmosphere, F: fossil, δ : $\delta^{13}C$, C: corresponding concentration of CO₂

Gross flux of CO₂ from ocean and biosphere, and disequilibria of isotope ratio to the atmospheric CO₂ are not fully evaluated, but by using two equations both fluxes from ocean and biosphere can be calculated.

Measurements of atmospheric O₂/N₂ ratio have also proven to be useful to quantify the oceanic and land biotic uptakes for anthropogenic CO₂. This is based on the fact that O₂ is closely connected with CO₂ by photosynthesis, respiration, and combustion and that O₂ is less soluble in seawater than CO₂.

$$d[O_2]/dt = -\alpha C_F + \beta C_b \text{ -----(3)}$$

α and β are conversion coefficients between O₂ and CO₂ at the combustion of fossil fuel and photosynthesis. In this case, oxygen concentration gives us biological flux of oxygen. Therefore, we can know the uptake amount of CO₂ by the biosphere.

In this study, both isotope analysis and oxygen concentration analysis were tried. Especially, new analytical method using GC-TCD system was developed. To get global average of sample, automatic bottle sampling system was made for both ship sampling over the Pacific and for two monitoring stations. By comparing both results provided by isotope analysis and oxygen analysis, CO₂ flux variation is discussed.

2. Method

2.1 Sampling

For Australia route, the sampling was conducted by Hakuba-Maru (NYK/Nihon Yusei Co.) from 1992 to 1995 and had changed to Southern Cross-Maru (Mitsui O.S.K. Lines, Ltd.) since 1996. For Canadian route, M/S Skaugran (Seaboard International Shipping Co.) was used till October in 1999, then switched to Aligator Hope (Mitsui O.S.K. Lines, Ltd.) Air was sampled (after dried) in 3L stainless steel tank with a pressure of 0.3 MPa.

For oxygen analysis, air samples have been manually collected at Hateruma in 1-L glass flasks since July 1997. Six flask samples were collected during monthly servicing visit; usually flask sampling was carried out over 2 days and three flasks were filled consecutively

at 1-hour intervals each day. At Ochi-ishi, automated flask sampling system using 2-L glass flasks was installed in December 1998. Air samples are drawn from intakes at the top of towers by diaphragm pumps and are passed through cold traps (-40°C). The sample flasks are flushed with the dried air for about 1 hour at a constant pressure of 0.2 MPa.

2.2 Analysis

CO₂ in the sample was extracted in the vacuum line and trapped in a glass tube. Isotope ratio of CO₂ was analyzed with isotope mass spectrometer (MAT252, ThermoQuest). Working standard was calibrated against NBS19. All data for isotope ratio was expressed as a deviation from VPDB-CO₂ in delta. O₂/N₂ ratios are measured by a gas chromatograph equipped with thermal conductivity detector (GC/TCD) (Tohjima, 2000). To improve the precision statistically, we repeated alternate analyses of sample and a reference gas 7 times for 1-L flask samples and 14 times for 2-L flask samples. The expected standard errors are about 7 per meg for 1-L and about 5 per meg for 2-L flasks.

Changes in the O₂ concentration are expressed in terms of the relative deviations of O₂/N₂ ratio from a reference gas according to

$$\delta(\text{O}_2/\text{N}_2) = [(\text{O}_2/\text{N}_2)_{\text{sample}}/(\text{O}_2/\text{N}_2)_{\text{reference}} - 1] \times 10^6. \quad (4)$$

3. Results

3.1 Isotope ratio

Latitudinal average of CO₂ and C isotope ratio were calculated in each 10° from 1995 to 2000. These latitudinal averages of trends were averaged, making global average trends of both CO₂ and isotope ratio. From the average trend, growth rate of CO₂ concentration and isotope change rate were shown in Fig.1.

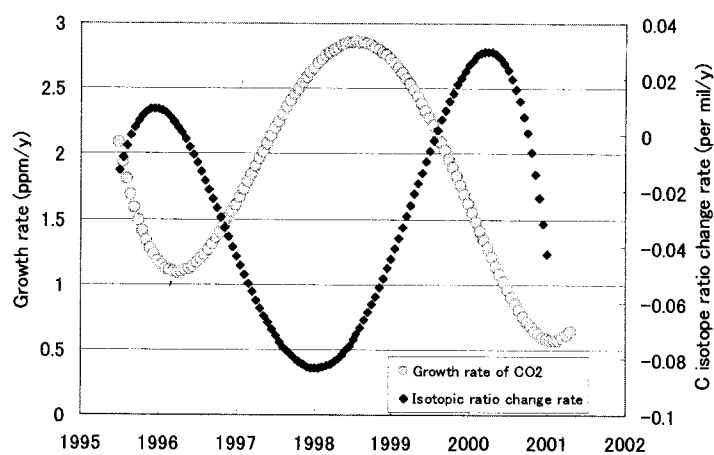


Fig.1 Average growth curve and isotope ratio change rate

This figure showed 1998 maximum in CO₂ growth rate, associated with rapid decreasing rate in delta 13C. This suggested that land biosphere became source in this period. At the same time, in 1998 oceanic uptake seemed to be weakened in accordance with La Nina phenomenon. Such variations of flux were calculated to correspond to 1-3 Gt-C/y, suggesting that large variation in CO₂ budget happened with climate change.

3.2 Oxygen

The O₂/N₂ ratios and CO₂ mixing ratios for the air samples in the flasks collected at Hateruma from July 1997 through June 2000 and Ochi-ishi from December 1998 through November 2000 are shown in Figure 1. Each symbol for Hateruma indicates average value for the flasks collected on the same day.

The observed O_2/N_2 ratios for both sites clearly showed seasonal cycles, which inversely co-vary with the CO_2 mixing ratios. In order to extract the average linear trend and average seasonal cycle in the time series, we fitted the data to a function composed of a linear polynomial and a series of 2 harmonics of the annual cycle. The peak-to-peak amplitudes of the average seasonal cycles of O_2/N_2 and CO_2 were 64 per meg and 7.1 ppm for Hateruma and 137 per meg and 14.4 ppm for Ochi-ishi.

The average decreasing rate determined by the above mentioned fitting procedure was 17.5 ± 2.4 per meg/yr ($=3.7 \pm 0.5$ ppm/yr) during the 3-year periods of this study. During the same period, the average increasing rate of CO_2 similarly calculated from the flask data is 2.1 ± 0.3 ppm/yr, which agrees well with that calculated from in situ data of 2.11 ± 0.06 ppm/yr. These observed CO_2 and O_2/N_2 trends at Hateruma correspond to the land biotic and oceanic uptakes of 1.5 ± 1.0 GtC/yr and 0.9 ± 1.1 GtC/yr, respectively. Most of the uncertainties are attributed to the uncertainty of the atmospheric O_2 decreasing rate, which can be reduced when the records of O_2 measurements are much more extended.

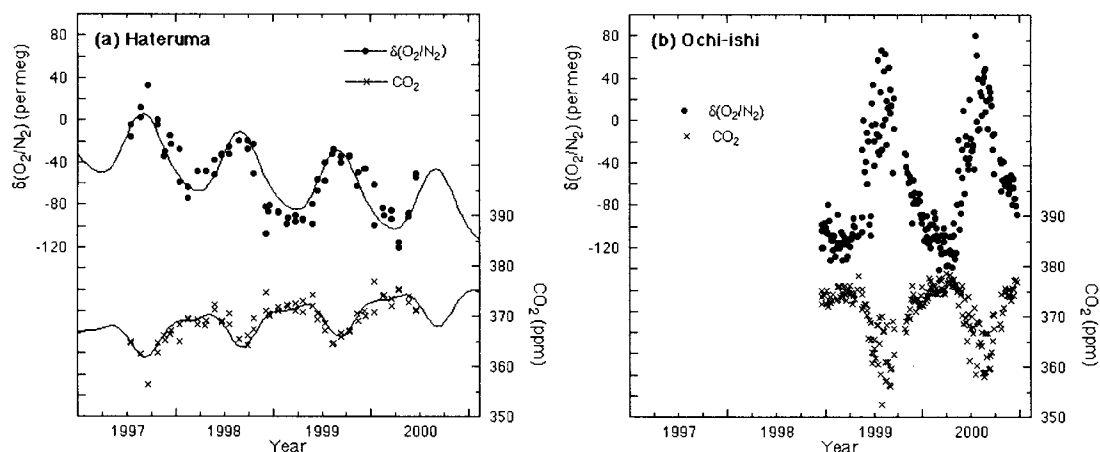


Fig.2 Oxygen concentration observed in two stations

4. Discussion

Because observation period and sites were limited for oxygen analysis, it was difficult to compare directly both results from isotopes and oxygen. However, in the same period, isotopic change rate was about -0.035 per mil, suggesting that about the same strength of sink for both land biosphere and ocean was expected. Such expectation was fairly consistent with the budget estimation by oxygen analysis at Hateruma.

5. References

Tohjima, Y., 2000. Method for measuring changes in the atmospheric O_2/N_2 ratio by a gas chromatograph equipped with a thermal conductivity detector, *J. Geophys. Res.* **105**, 14,575-14,584.