Observation of oxygen and isotope ratio of carbon dioxide in the background atmosphere for the detection of long-term change in CO_2 sink of ocean and terrestrial ecosystem (Abstract of the Final Report)

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1. Introduction

Anthropogenic CO_2 emission has been increased rapidly in recent years. Especially, economic growth rate of Asian countries became very high and CO_2 emission from these countries occupied the large portion of the world-wide emission. Increase rate of atmospheric CO_2 concentration was also increasing up to 2 ppm/y in average. According to the budget calculation of CO_2 in the atmosphere, it was found that about 60% of anthropogenic CO_2 emission is remained in the atmosphere, and the rest dissolves in sea water or is taken up by terrestrial ecosystem.

However, the increase rate varied largely from year to year. Especially large increase rates were often recorded with El Nino period. Such high increase rate at El Nino events may be explained by the reduction of sink of land ecosystem caused by relatively high temperature at that time. On the other hand, oceanic sink is considered to be enhanced by the El Nino event because of the reduction of source strength around equatorial region.

Such natural carbon cycle will be affected by the climatic change (temperature, precipitation, wind velocity etc.) in the future and may reduce solubility of the CO_2 in the surface sea water and terrestrial CO_2 uptake. By model calculations, it is estimated that absorption of CO_2 by the ocean will reduce by approximately 25%. Some models projected that sink flux by terrestrial ecosystem would decrease after the year of 2050.

Global CO_2 budgets have recently been studied by observing oxygen and a carbon isotope ratio of CO_2 in the atmosphere. Because net oxygen production is mainly made by terrestrial ecosystem, observation of oxygen declining rate provides the first order estimation of net photosynthesis rate, considering oxygen consumption rate by the fuel combustion. On the other hand, carbon isotope ratio in the atmosphere can be used to estimate ocean and land sink fractions, because the isotopic fractionation effects is larger when CO_2 is absorbed by the terrestrial biosphere than that when ocean absorbs CO_2.

2. Research Objective

In order to find the variations and trends of terrestrial and oceanic sink flux of CO_2, long-range observations of atmospheric oxygen, CO_2 concentration and isotopes on global scale are necessary. In this study, oceanic background air is periodically sampled at various latitudes from 30S to 50N by using commercial cargo ships which are operated between Japan and New Zealand, and Japan and the US. "*SKAUBRYN*" from Seaboard International

Shipping Co. Ltd operated between Japan and Canada is used to take samples at higher latitude (around 55N).

Air sampling from 30S to 55N will be continued for a long time to detect the trend of flux change affected by the climatic feedback. Also two background monitoring sites (Hateruma and Ochi-ishi) in Japan are used as high frequency monitoring sites. We also prepare the standard oxygen gas mixture and isotope reference materials to make correct scales for precise analysis.

3. Experimental

(1)Air sampling

Sampling was conducted over the Pacific by using three routes; Japan-Australia, Japan-USA and Japan-Canada. Figure 1 shows sampling sites. Although Transworld (Fujitrans Co.) had been used to sample air along the routes to New Zealand, it was changed to Transfuture in November 2005. Two monitoring sites (Hateruma (HAT) and Cape Ochi-ishi (COI)) were also shown in Fig.1. At the monitoring station, sampling was done about twice a week.

(2) Bottle analysis and in-situ measurement

Oxygen was analyzed for glass bottle sample by using GC-TCD method developed by Tohjima[3]. Then CO_2 concentration was measured by NDIR method, followed by CO_2 extraction in a vacuum line to analyze isotope ratios. Isotope ratio for CO_2 was measured by Isotope Mass spectrometry (MAT 252). We installed GC system for oxygen in-situ measurement in both Hateruma and Ochi-ishi.

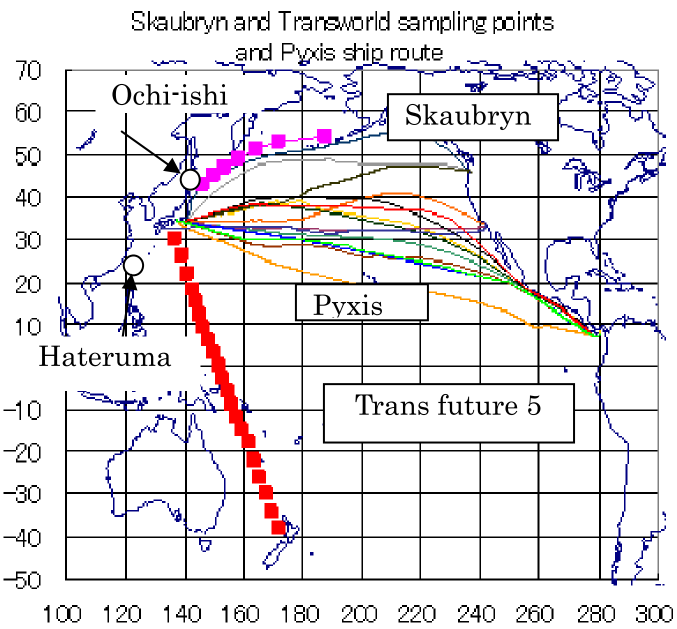


Fig1. Sampling sites for "Transfuture" and "Skaubryn". (Only Ship routes of Pyxis are shown.)

4. Results

(1) Estimation of global carbon budgets from the O_2/N_2 measurements based on the flask sampling from HAT, COI and cargo ships

The global oceanic and land biotic sinks of fossil fuel CO_2 have been evaluated from the changes in the atmospheric O_2/N_2 ratio and CO_2 concentration. For this evaluation, we have used the observations from HAT, COI, and cargo ships sailing between Japan and Oceania[1,2,3,4]. The time series of the atmospheric CO_2 mole fraction, O_2/N_2 ratio, and AOP

(Atmospheric Potential Oxygen[5]; APO=O_2+1.1×CO_2) are shown in Fig. 1. To calculate global carbon budgets, we have used a conventional method based on the changes in the O_2/N_2 and CO_2 developed by Keeling and Shurze (1992)[6] (O_2 method) and a new method based on the changes in APO and CO_2 developed by Manning and Keeling (2006)[7] (APO method). In the APO method, we have used the global atmospheric CO_2 observation from the NOAA/ESRL GMD network together with our APO data. In addition, we have adopted the ocean outgassing correction of 0.48 Pg C yr^{-1} in our estimation. The carbon budgets have been evaluated for the three periods: the 10-year period between 1998.5 and 2008.5 (period-I), the 9-year period between 1999.5 and 2008.5 (period-II), and 6-year period between 2002.5 and 2008.5 (period-III). Note that in this estimation we have used shipboard data collected in the western Pacific region between 40°S and 30°N.

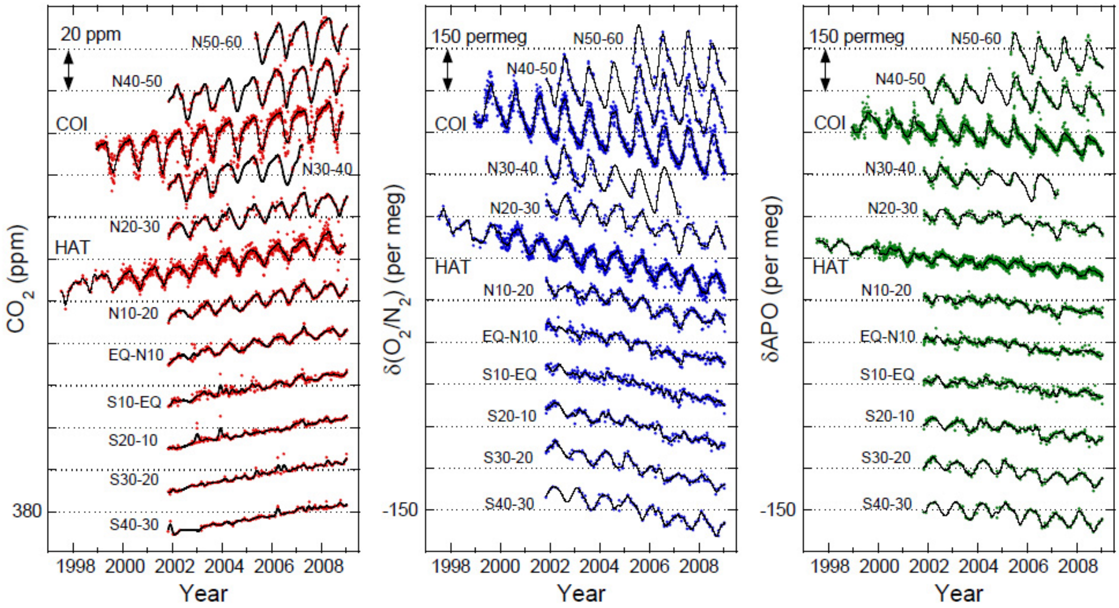


Fig. 1. Time series of observed (left) CO_2 mole fraction (top), (middle) O_2/N_2 ratio and (right) APO from the flask samples collected at HAT, COI and cargo ships sailing between Japan and Oceania and between Japan and the West Coast. Solid lines indicate the smooth-curve fits.

The estimated carbon sinks by using O_2 and APO methods for the above three periods are summarized in Table 1. The oceanic and land biotic sinks for the period-I based on the data from HAT are 2.4(2.4) Pg C yr^{-1} and 1.0(0.9) Pg C yr^{-1}, respectively, where the values in the parentheses are obtained by the APO method. The oceanic and land biotic sinks for the period-II based on the combined data from HAT and COI are 2.4(2.3) Pg C yr^{-1} and 0.9(1.2) Pg C yr^{-1}, respectively, and those for the period-III based on the combined data from HAT, COI, and cargo ships are 1.9(1.9) Pg C yr^{-1} and 1.4(1.6) Pg C yr^{-1}, respectively. Figure 2 graphically explain how to partition the fossil carbon uptake between ocean and terrestrial biosphere. In the figure, the changes in the atmospheric CO_2 and O_2/N_2 from the year of 1999.5, which is placed on the origin (ΔCO_2=0 ppm and $\Delta(\delta(O_2/N_2))$=0 per meg), to the year of 2008.5. The broken arrow indicates the hypothetical changes in CO_2 and O_2/N_2 caused by the fossil fuel consumption and cement manufacturing, and the squares represent the observed CO_2 and O_2/N_2 changes from HAT and COI. The arrow 'Z', which is parallel to the Y-axis, represents the ocean outgassing correction. When these two end points are connected by the two vectors which represent oceanic uptake with the slope of 0 and land biotic uptakes with the slope of -1.1 mol/mol, the length of the vectors on the X-axis correspond to the oceanic and land biotic CO_2 uptakes.

Table 1. Global oceanic and land biotic CO_2 sinks based on the O_2 method and APO method.

Time period	Sampling Location	ΔAPO or $\Delta O_2/N_2$ (per meg yr^{-1})	ΔCO_2[a] (ppm yr^{-1})	F[b] (Pg C yr^{-1})	α_F[c] (mol mol^{-1})	Ocean sink[d,e] (Pg C yr^{-1})	Land sink[d,e] (Pg C yr^{-1})
O_2 approach		$\Delta O_2/N_2$	NIES				
1998.5-2008.5	HAT	-19.65	1.90	7.42	1.387	2.41	0.96
1999.5-2008.5	HAT	-19.87	2.04	7.51	1.386	2.19	0.98
1999.5-2008.5	COI	-20.23	1.96	7.51	1.386	2.50	0.83
1999.5-2008.5	HAT,COI	-20.05	2.00	7.51	1.386	2.35	0.90
2002.5-2008.5	HAT	-20.68	2.23	7.86	1.382	2.06	1.06
2002.5-2008.5	COI	-20.24	2.14	7.86	1.382	2.07	1.23
2002.5-2008.5	Ship(40°S-30°N)	-18.49	1.99	7.86	1.382	1.68	1.94
2002.5-2008.5	HAT,COI,Ship	-19.80	2.12	7.86	1.382	1.94	1.41
APO approach		ΔAPO	NOAA/ESRL				
1998.5-2008.5	HAT	-9.58	1.94	7.42	1.387	2.38	0.92
1999.5-2008.5	HAT	-9.05	1.92	7.51	1.386	2.15	1.28
1999.5-2008.5	COI	-9.63	1.92	7.51	1.386	2.38	1.04
1999.5-2008.5	HAT,COI	-9.34	1.92	7.51	1.386	2.26	1.16
2002.5-2008.5	HAT	-8.79	2.07	7.86	1.382	1.98	1.46
2002.5-2008.5	COI	-8.85	2.07	7.86	1.382	2.01	1.43
2002.5-2008.5	Ship(40°S-3°0N)	-8.01	2.07	7.86	1.382	1.67	1.78
2002.5-2008.5	HAT,COI,Ship	-8.55	2.07	7.86	1.382	1.89	1.56

[a] CO_2 data from the NIES stations and the NOAA/CMDL network are used for O_2 and APO approaches, respectively.
[b] Based on global CO_2 production data from fossil fuel burning and cement manufacturing (Marland et al., 2007) and some extrapolated data.
[c] Calculated from CO_2 production figures by fossil fuel types (Marland et al., 2007) and the O_2:C molar combustion ratios for individual fuel types (Keeling, 1988).
[d] The value of 0.48 Pg C yr^{-1} is used for Z_{eff}.
[e] The estimated uncertainties for the oceanic and land sinks are ±0.7 and ±0.9 Pg C y^{r-1}, respectively.

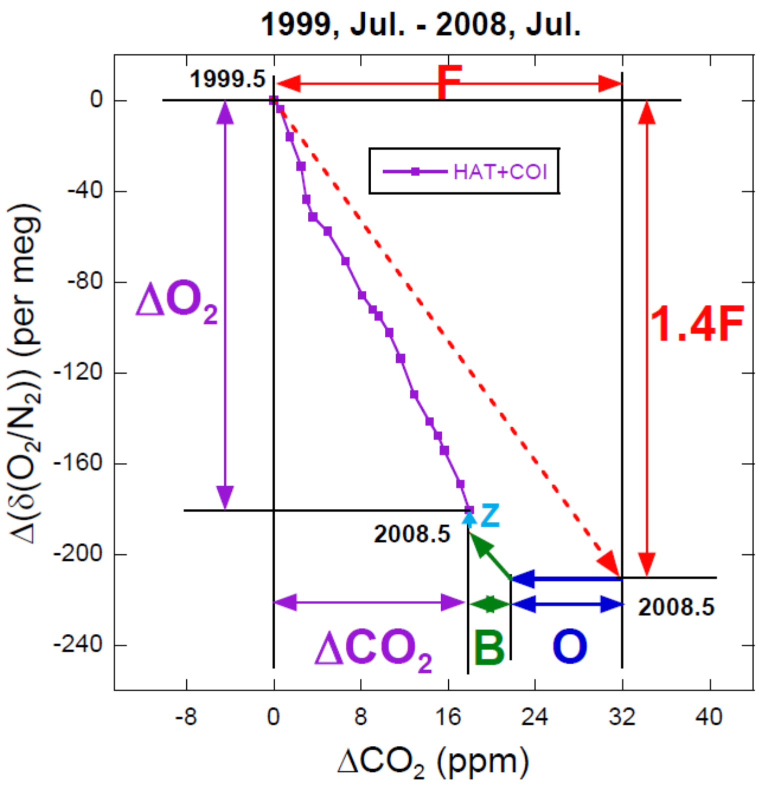


Fig. 2. Schematic figure explaining how to partition the fossil CO_2 sequestration between ocean and land biosphere. The changes in the CO_2 concentration and the O_2/N_2 ratio between the year of 1999.5 (origin) and the year of 2008.5 are plotted. The broken arrow represents the hypothetical changes in the CO_2 and O_2/N_2 ratio caused by the fossil fuel combustion and cement manufacturing. The observed changes based on the data from HAT and COI are plotted as the squares symbols. The arrow 'Z' represents the ocean outgassing correction, the arrow 'O' the oceanic sink, and the arrow 'B' the land biotic sink.

When the estimated sinks are compared between the O_2 and APO methods, the differences in the land biotic sinks are larger than those in the oceanic sinks. These results indicate that the carbon budgets estimation based on the O_2/N_2 measurements can give us more robust oceanic sink than the land biotic sink. In fact, the uncertainties in the estimation of the oceanic and land biotic sinks are ±0.7 Pg C yr^{-1} and ±0.9 Pg C yr^{-1}, respectively[4)]. The dominant sources of error are the uncertainties in the oceanic outgassing correction (~±0.4 Pg C yr^{-1}), the stability in the O_2/N_2 scale (~±0.4 Pg C yr^{-1}), and in the case of the land biotic sink, fossil fuel emissions (~±0.5 Pg C yr^{-1}). We should make more effort to reduce these uncertainties in future.

(2) Variation of APO

We have been carrying out in-situ monitoring of atmospheric O_2/N_2 ratio at Cape Ochi-ishi (COI; 43° 10'N, 145° 30'E) in the northern part of Japan since March 2005 by using a modified gas chromatography/thermal conductivity detector (GC/TCD) [6)]. APO shows large variability from April to early July 2005, suggesting that air-sea O_2 flux from algal bloom significantly affect the observations at COI.

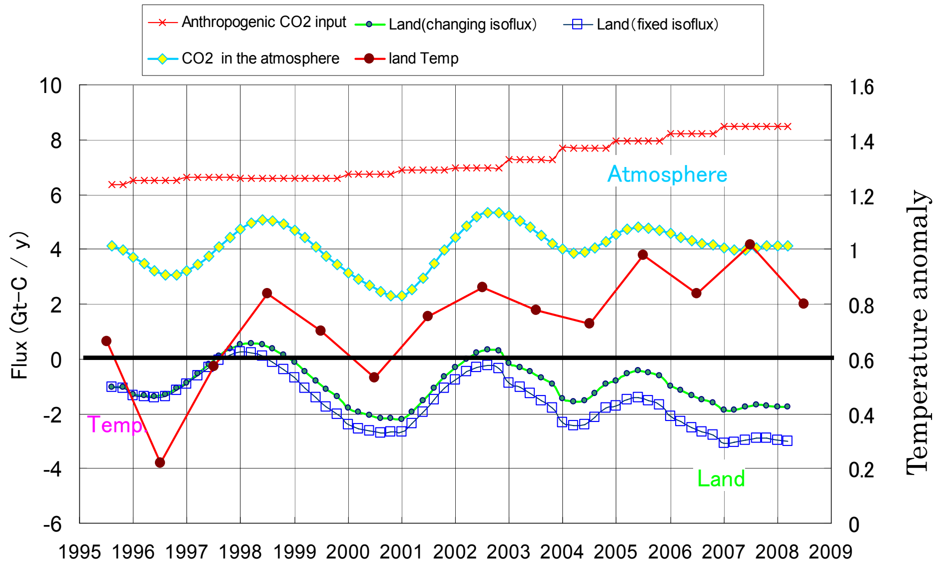
Seasonal variation of APO in air sample collected over the Pacific showed large difference in each latitude. High latitudinal bands showed higher seasonal amplitude in APO, suggesting higher algal primary production in such latitude. To evaluate oceanic oxygen flux, we need to understand such local characteristics on influence to flux estimation.

(3) Evaluation of budget of CO_2 by isotope analysis

By recent report it was estimated that emission of CO_2 exceeded 8 Gt-C in early 2005. In this work, we newly developed the way of calculation of isotope flux changing along with time, atmospheric CO_2 concentration and isotope value. Figure 3 shows atmospheric CO_2 accumulation and sink amounts of both ocean and terrestrial ecosystem in both cases in which a isoflux value is fixed and the isoflux changes with time. If we used newly developed "changing" isoflux, unrealistic oceanic sink fluctuation in El Nino year was greatly reduced. Oceanic sink level looked to gradually increase in ten years. However, "fixed" isoflux calculation indicated that ocean sink trend was rather stable although it had a large annual variation. Such a stable oceanic sink trend may be strange, because during 10 years, concentration of CO_2 increased by 20 ppm, which is corresponding about 20% of the difference between 380 and 280ppm, which is the value before the industrial revolution. Therefore, oceanic sink must increase a little bit at least. So, real oceanic flux must exist between both cases.

On the other hand, land sink had a large variation with peaks in 1998, 2002 and 2005. These peaks were well correlated with temperature anomaly in terrestrial area. Global temperature gradually increased for a recent decade, however, average sink level increase a little. Fixed isoflux calculation showed rapid increase of terrestrial sink flux, suggesting that real terrestrial sink seemed to increase for this observation period.

Terrestrial sink must negatively respond to temperature. However, recent temperature increase did not affected to the flux of terrestrial sink so actively. Especially terrestrial sink was considerably large even in relatively hot year such as 2007-2008. The reason is not clear why terrestrial sink became large until higher average temperature level. One explanation is related to the increase of CO_2 concentration during 10 years. However, calculated response factor of concentration increase to sink flux seemed to be unrealistic (i.e. too large). Terrestrial photosynthesis is variable and easily affected by climatic condition. Therefore, we need more case studies to clear the reason. It may suggest that northern terrestrial biosphere respond toward more-uptake sense. At the same time, fluctuation of number of forest fire may affect apparent terrestrial sink flux.



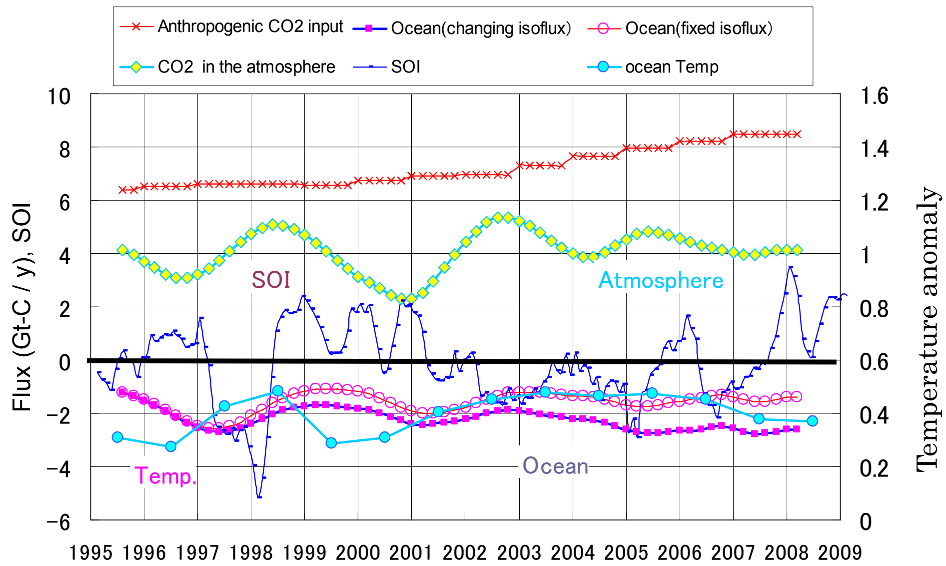


Fig3. CO_2 global budget estimated by carbon isotope ratio

(4) Radiocarbon trend in atmospheric CO_2

During 1960-1970 radiocarbon was produced by nuclear bomb test and introduced into lower stratosphere, subsequently reentered to troposphere. Radiocarbon was converted to $^{14}CO_2$ and mixed with ordinal CO_2 molecular and introduced into carbon cycle in nature. Atmospheric radio carbon $\Delta^{14}C$ decreased by supplying of oceanic CO_2 which has low $\Delta^{14}C$ during CO_2 exchange process between atmosphere and ocean.

Observed $\Delta^{14}C$ trends in 5 latitudes were shown in Fig. 4. Equatorial data showed larger variation than other data, while 44N data showed linear decreasing trend. It seemed that they had some inter-annual variation corresponding to gross CO_2 exchange between atmosphere and some reservoirs, such as soil organic matter, ocean, and plant.

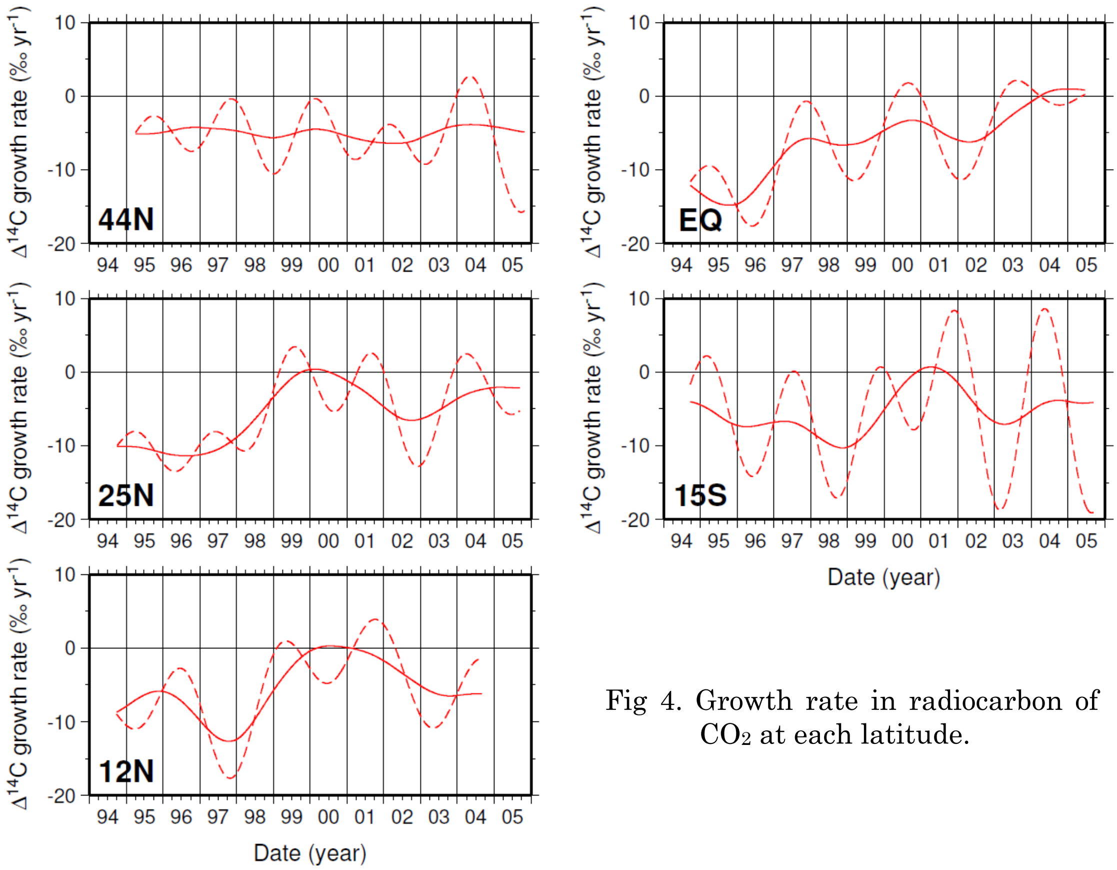


Fig 4. Growth rate in radiocarbon of CO_2 at each latitude.

5. Conclusion

CO_2 budget during 1999-2008 was estimated using both O_2/N_2 and APO. Their estimation showed that oceanic sink during that period would be about 2.3 Pg-C/y and terrestrial sink would be 0.9 Pg-C/y. Such estimation was fairly consistent with the estimation from isotopic calculation, which was about 2.2 Pg-C and 0.9 Pg-C.

A newly developed calculation way of isotope flux from isotopic disequlibrium between atmosphere and land, and atmosphere and ocean was very effective to reduce unrealistic fluctuation of ocean sink. Isotopic budget calculation revealed that land sinks seemed to have large variation while oceanic sink was fairly stable over the time with a relative increase of recent years. It was also found that terrestrial sink may increase relatively.

CO_2 increase seemed to apparently act as an accelerator for increase of sink fluxes for both terrestrial biosphere and ocean. However, limited observation period must affect such apparent conclusion. To evaluate longer response of climatic condition to trend of the terrestrial fluxes, we need more case studies.

Oxygen data obtained over the Pacific showed the regional characteristics. For eastern region of the Pacific different seasonal variations from those in western region in O_2/N_2 were observed.

Radiocarbon trend was analyzed and found to have inter-annual variation. Especially, equatorial data included a large variation, which was not the same as that of stable carbon isotope ratio.

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