LONG-TERM OBSERVATION OF CO_2 CONCENTRATION AND ITS ISOTOPE RATIO OVER THE WESTERN PACIFIC

H. Mukai[1], Y. Nojiri[2], Y. Tohjima[3], T. Machida[4], Y. Shibata[5] and H. Kitagawa[6]

[1]*Center for Global Environmental Research, National Institute for Environmental Studies, Tsukuba, Ibaraki, 305-8506 Japan; lnmukaih@nies.go.jp*

[2]*Climate Change Research Project, NIES, Tsukuba, Ibaraki, 305-8506 Japan; nojiri@nies.go.jp*

[3]*Atmospheric Division, NIES, Tsukuba, Ibaraki, 305-8506 Japan; tohjima@nies.go.jp*

[4]*Atmospheric Division, NIES, Tsukuba, Ibaraki, 305-8506 Japan; tmachida@nies.go.jp*

[5]*Chemistry Division, NIES, Tsukuba, Ibaraki, 305-8506 Japan; yshibata@nies.go.jp*

[6]*Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya City, 464-8601, Japan; hiroyuki.kitagawa@nagoya-u.jp*

ABSTRACT
Air was collected systematically from 1995 to 2005 over the Pacific from 30S to 55N in latitude by ships-of-opportunity to monitor global trend of CO_2 concentration and its variation in the atmosphere. The monitoring results showed that three El Niño events during 10 years mostly affected regional and temporal variation of CO_2 growth rate and its budget. Variation of carbon isotope ratio showed that the CO_2 flux from terrestrial biosphere seemed to rapidly increase at that time, correlated with global temperature anomaly. Oxygen isotope ratio had increasing trend in this period, similar to the variation of temperature. Atmospheric $^{14}CO_2$ variation also seemed to be influenced by El Niño event.

INTRODUCTION
Atmospheric CO_2 concentration is increasing gradually by anthropogenic CO_2 input. For better understanding of CO_2 budget in the atmosphere, isotopic signatures of CO_2 are often observed in addition to its concentration. Global CO_2 budget can be discussed based on the difference of fractionation factors in the individual sink processes (i.e. absorption by ocean and photosynthesis). Although environmental conditions can affect the degree of isotopic discrimination, photosynthesis by C3 plant can be most affective to the temporal change (e.g. daily and seasonal) in carbon isotope ratio. Oxygen isotope ratio of CO_2 is not conservative parameter, but can be changed through exchange reaction with oxygen of water. Especially it is related to gross primarily production and soil respiration. On the other hand, because radiogenic carbon is not emitted by fossil fuel, ^{14}C can be a good tracer of CO_2 cycle.

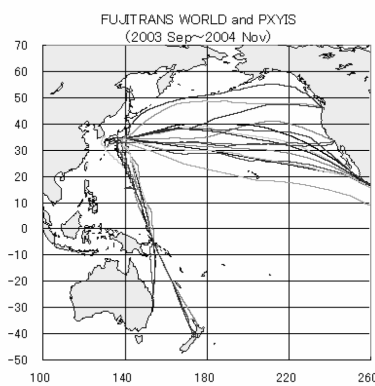

Fig.1 Recent ship routes for sampling

EXPERIMENTAL
Oceanic background air has been collected over the Pacific since 1995 by using commercial cargo ships. We used two main ship routes for the sampling; JPN – Australia - New Zealand (southern route) and JPN - Canada - USA (northern route). We could gain kind cooperation from following ships; as the southern route, HAKUBA-MARU (Nihon Yusei) (1995), SOUTHERN CROSS (MOL) (96-2000), GOLDEN WATTLE (MOL) (2001), GLORY (MOL) (2002), and FUJITRANS WORLD (Kagoshima Senpaku) (2003-2005); as the northern route, SKAUGRAN (Seaboad Int. Shipping Co) (1994-1999), ALLIGATOR HOPE (MOL) (1999-2000), PYXIS (Toyofuji) (2001-2005) and SKAUBRYN (Seaboad). Air inlet was usually placed on a small mast at the bow of the ship. Air was drawn through the stainless steal tube from the air inlet by a metal bellows pump and compressed in the 3L stainless steel canister up to 2.5 atm after

removing moisture. Sampling was done automatically about at least every 3 degree in latitude. GHGs concentrations in the canister were measured by usual methods. CO_2 was extracted for further isotopic analysis. Isotope ratios were measured by usual dual inlet method (MAT252). ^{14}C was measured by accelerator mass spectrometry in NIES.

RESULTS AND DISCUSSION

For recent 10 years (1995-2005), 18-20 ppm increase in concentration was observed in all sampling latitudes. Observed CO_2 growth rate was relatively higher than that of longer average (1.6 ppm/y) from 1985 to 2001 [WDCGG]. High CO_2 growth rate over 3 ppm/y was observed in tropical area in 2002 following the case at the last El Nino in 1998. In addition to the increase of anthropogenic emission from 5.4Gt/y to about 7 Gt/y through 20 years period, El Niño events associated with relatively high global temperature seemed to affect rapid CO_2 growth increase.

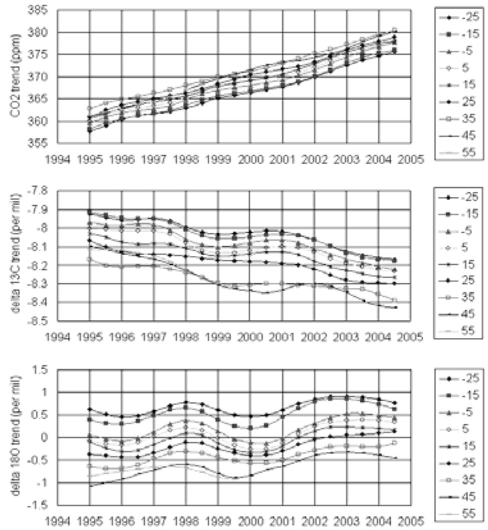

Fig.2 Latitudinal average trends for CO_2, $\delta^{13}C$ and $\delta^{18}O$.

Decreasing rate of carbon isotope ratio was about 0.025 per mil/y during observed period with a large decreasing rate of 0.08 per mil/y at El Niño year. To estimate the global budget of CO_2, atmospheric volume weighted average was calculated. By using simple global flux equation by *Francey et al.* [1995], oceanic and terrestrial net CO_2 fluxes were roughly estimated. In three El Niño years of '95, '97/'98 and 2002, terrestrial sink was found to be very small or even a small source (1 Gt/y), causing high CO_2 growth rate about 3 ppm/y. On the other hand, in La Niña year of 2000, terrestrial sink was large (2 Gt/y). Oceanic sink was fairy stable at about 2 Gt/y with a small increase (around 1 Gt/y) at El Niño period and small decrease in La Nina period. (In 2002 El Niño year, change of oceanic sink was much smaller than that in '97 El Niño). Such apparent fluctuation of oceanic sink may be partly explained by the variation of isotopic discrimination by photosynthesis and /or contribution of C4 plants [*Randerson et al.*, 2002].

Oxygen isotope ratio had a weak increase trend during the observed period, which was a little different tendency from previously analyzed trend during 1993-1998 by Ishizawa et al. [2002]. It also had a local maximum in El Niño year, when the CO_2 growth rate became high. Such variation may be correlated with temperature. Because equilibrium in $\delta^{18}O$ of CO_2 with water will give a negative effect against temperature increase, other factors such as increase of $\delta^{18}O$ of water in the soil and plant by dry condition and/or rapid decrease of gross primarily production may be related to the $\delta^{18}O$ increase.

Data of $\Delta^{14}C$ at 15S and 25N had a systematical gap (about 5 permil) and both values continued to decrease with a decay time of 16 y. In El Niño year ^{14}C seemed to show weak positive anomaly. It may suggest the possibility of showing rapid flux of CO_2 from terrestrial biosphere.

REFERENCES

Francey, R. J., P. P. Tans, C. E. Allison, I. G. Enting, J. W. C. White and M. Trolier (1995), Changes in oceanic and terrestrial carbon uptake since 1982, *Nature* 373, 326-330.

Ishizawa M., T. Nakazawa and K. Higuchi (2002), A multi-box model study of the role of the biospheric metabolism in the recent decline of $\delta^{18}O$ in atmospheric CO_2, *Tellus* 54B, 307-324.

Randerson, J. T., G. J. Collatz, J. E. Fessenden, A. D. Still, J. A. Berry, I. Y. Fung, N. Suits and A.S. Denning (2002), A possible global covariance between terrestrial gross primary production and ^{13}C discrimination: Consequences for the atmospheric ^{13}C budget and its response to ENSO, *Global Biogeochem. Cycles* 16 (4), 1136, doi:10.1029/2001GB001845.