Global Environment Research Coordination System

# Integrative observational study of oxygen and isotopes of carbon dioxide in the atmosphere to investigate the climate responses of the global carbon cycle
## （Abstract of the Final Report）

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## 1. Introduction

Mixing ratios of atmospheric carbon dioxide ($CO_2$) observed around the world still showed a steady increase and $CO_2$ emissions from fossil fuel burning have been increasing at global scale. The Paris Agreement, adopted in 2015 COP21, aims to balance the anthropogenic greenhouse gas emissions and the natural sinks in the second half of this century to maintain the increase in global temperatures well below 2ºC. To achieve this goal, it is crucially important to understand the future changes in the natural sink strengths because about half of the anthropogenic $CO_2$ emissions have been taken up by the natural sinks: land biosphere and the ocean. However, the responses of the natural sinks to the expected future global warming are still very uncertain.

Observing the changes in atmospheric $O_2$ concentration and carbon isotopic compositions of atmospheric $CO_2$, including stable carbon isotope ($^{13}C$) and radioactive carbon isotope ($^{14}C$), is useful to investigate the global carbon cycles. Nevertheless, the observations of these species are significantly limited in comparison with those of the atmospheric $CO_2$ because of the difficulty in the measurements.

## 2. Research Objectives

The objective of this research is to investigate the response of the carbon sink strength of the land biosphere and the ocean to the climate variability. To achieve the goal, extended observations of the atmospheric $O_2$, $CO_2$ and $CO_2$ isotopes are conducted in the Asia Pacific region. The atmospheric $O_2$ observations can be also used to constrain the air-sea gas exchanges. These estimated variations in the carbon sinks are examined for the long-term trends and the relationship to the climate variability such as the ENSO-cycle. In addition, the atmospheric $^{14}CO_2$ are measured to investigate the influences of the fossil fuel-derived $CO_2$ emissions on the carbon cycle. To improve our understanding of the air-sea $CO_2$ exchanges and the contributions of ocean circulation and ocean biological production to the exchange, $^{13}C$ and $^{14}C$ of dissolved inorganic carbon in the surface seawater are also conducted.

## 3. Research Methods

The air samples were collected in glass or stainless-steel flasks to analyze the $O_2$ concentrations and carbon isotopes ($^{13}C$ and $^{14}C$) on several fixed sites located in the Asia-Pacific

region and onboard cargo ships bound for the United States (New Century 2), Australia/New Zealand (Trans Future 5), and Southeast Asia (Trans Harmony) (Fig. 1). We also collected polluted air samples at HAT and COI using remotely controlled air sampling systems (event sampling systems) to investigate the relationship between $CO_2$ emissions from continental Asia and their isotopic signals. As for the atmospheric $O_2$, in-situ observations were conducted at HAT, COI, and onboard Trans Future 5 and New Century 2[1] (Fig. 1).

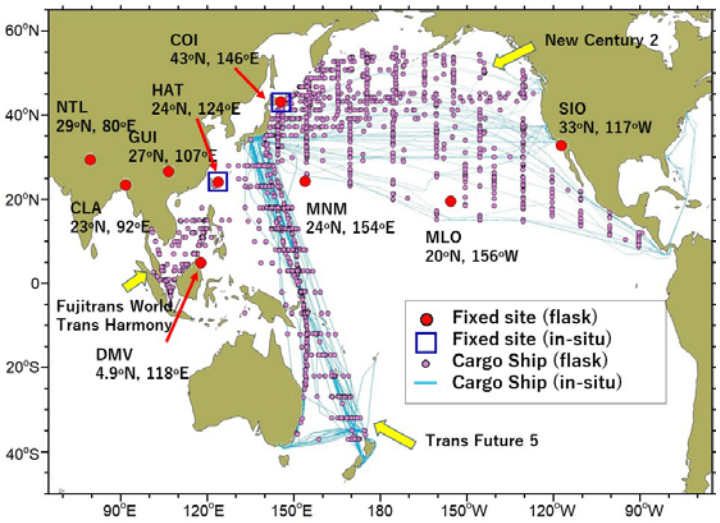


**Fig. 1.** Positions where flask samples were collected and in-situ $O_2$ measurements were carried out.

The $O_2$ and $CO_2$ concentrations of the flask samples were measured by a gas chromatograph equipped with a thermal conductivity detector (GC/TCD)[2] and a nondispersive infrared analyzer (NDIR), respectively. Then, $CO_2$ gases in the residual air samples were extracted for the analysis of the isotope ratios. The $^{13}C$ were measured by an Isotope Ratio-monitoring Mass Spectrometer (MAT 252, 253), and $\Delta^{14}CO_2$ were measured by CAMS (Compact Carbon Accelerator Mass Spectrometry; NEC 1.5SDH 500kV) performed by NIES.

Surface seawater samples were collected from a pumping line for $pCO_2$ analyzer into glass bottles (150~250ml). The dissolved $CO_2$ in the seawater sample was extracted and the isotope ratios ($^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios) were analyzed. Dissolved $O_2$ in seawater was continuously measured by an optical oxygen sensor (OPTODE).

## 4. Results and Discussions

(1) The global carbon budget was estimated based on the change in the observed atmospheric $O_2$ and $CO_2$. For example, the oceanic and land biotic sinks for the 18-year period (2000-2017) based on the observations at HAT and COI were 2.5±0.6 PgC $yr^{-1}$ and 1.6±0.8 PgC $yr^{-1}$, respectively.

Calculating the carbon budgets for the pentad periods consecutively, we examined the changing trend of the ocean and land sinks during a 14-year period (2001-2014), which are plotted in Fig. 2 together with the estimated sinks from GCP. The pentad ocean sinks showed an overall increasing trend for the entire period (2001-2014) In contrast, the pentad land sinks showed an increasing trend for 2001-2009 and a decreasing trend for 2009-2014. Enhancement of the ocean and land carbon uptakes in the 2000s was reported also by previous studies. In addition, the recent decreasing trend of the land uptake was found to be

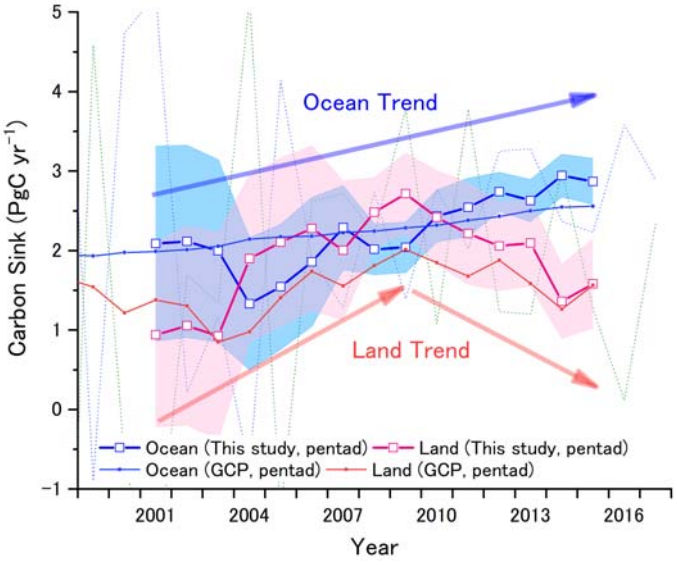


**Fig. 2.** Pentad averages of the global oceanic and land carbon sinks. Blue and red open squares represent the ocean and land sinks of this study. Blue and orange lines represent the ocean and land sink estimates from GCP

partially related to the global carbon cycle variation associated with the strong El Niño event in 2015 to 2016.

(2) Using carbon isotope ratio and oxygen isotope ratio of $CO_2$ collected over the Pacific Ocean and at several Asian sites, we determined global $CO_2$ budget and regional $CO_2$ sink/source characteristics were studied. We compared our long-term variation of $CO_2$ budget over a period of 1995-2018 based on the carbon isotope data with those based on process-based models from GCP (Fig.3). Our study showed long-term increase in the ocean $CO_2$ uptake. The increasing rate was a little faster than the model results, especially after 2007 our study showed much larger ocean sink. However, the recent three years oceanic sink did not increase but decrease a little. Such tendency was also reproduced by the model calculations.

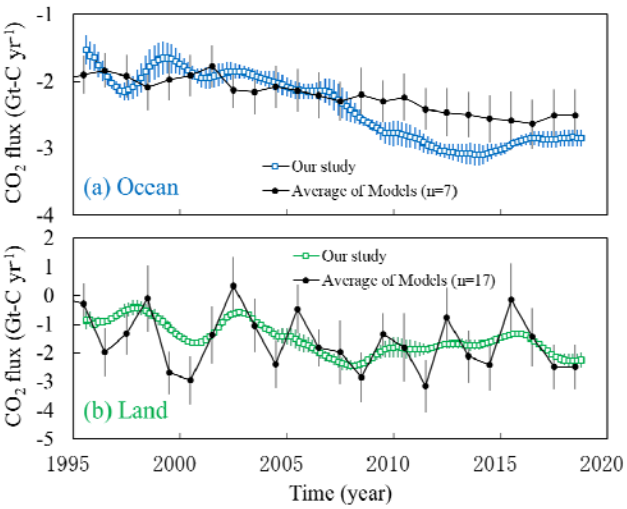


**Fig. 3**. Comparison between our observation and model calculation in ocean (a) and land (b) sink for atmospheric $CO_2$

In the case of land biosphere sink, both our observation and model calculation through the GCP were almost identical. As shown in the oxygen observation, land sink increases until 2008, then decreased a little until 2015. Yearly variation in land sink was related to global temperature, because land biosphere was influenced by climate. In 2015, global temperature was very high, while temperature during 2000-2008 was relatively low. Land sink decreased a lot in 2015, but after that land sink increased again for the next 3 years. Generally speaking, land sink is still increasing.

Furthermore, we studied $CO_2$ sink and source relation at several Asian sites using the relationship between $CO_2$ and delta $^{13}C$. We found that Indian sites were strongly influenced by crops cultivation and combustion of the crop residue over the plain. In China case we found that some contribution of $CO_2$ originates from cement production.

C isotope ratio and O isotope ratio in $CO_2$ were useful to identify its origin and evaluate budget. As for O isotope ratio, it was not enough information to evaluate its variation but it seemed to have some relation with El Niño event.

(3) We continued air sampling for radiocarbon measurements at HAT (routine sampling and Asian outflow (high-$CO_2$) sampling), COI, and MNM and on VOS. The $\Delta^{14}C$ values at HAT and COI from 2004 to 2012 were analyzed using CAMS at Paleo Labo and $\Delta^{14}C$ values after 2012 were analyzed using NIES-CAMS. We found larger decreasing trends in $\Delta^{14}C$ at HAT rather than at COI. The average level of $\Delta^{14}C$ in 2016 was lower at HAT by 5 permil than at COI, although there was almost no difference in averaged $\Delta^{14}C$ at both stations before 2012. We also observed significantly high $\Delta^{14}C$ event

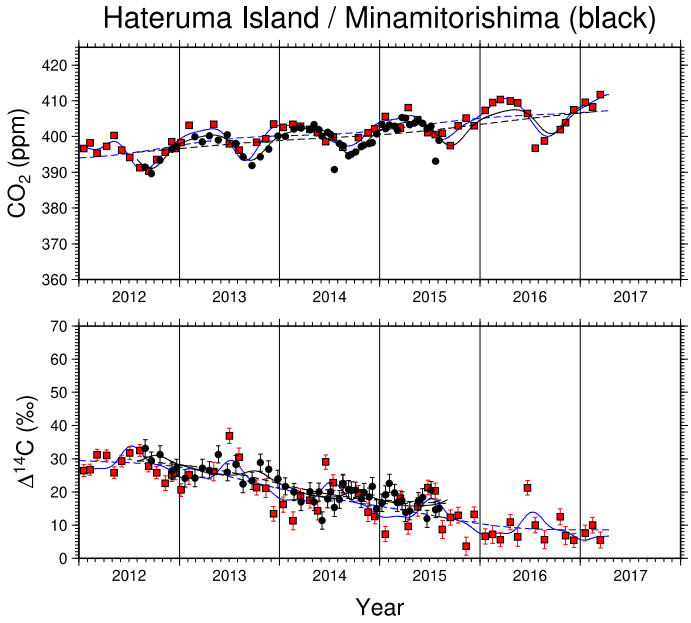


**Fig. 4**. $CO_2$ concentrations and$\Delta^{14}C$ observed at MNM (black) and HAT (red).

in summer at HAT. We found significant differences in $\Delta^{14}C$ levels between HAT and MNM: $\Delta^{14}C$ values at HAT were lower than at MNM except for in summer (Fig. 4). The differences might indicate seasonal cycle and interannual variations of $CO_2$ emissions from East Asia.

We analyzed $\Delta^{14}C$ of 6 high-$CO_2$ events due to Asian outflow observed at HAT and fossil fuel burning-derived $CO_2$ component ($C_{ff}$) was calculated as, $C_{ff} = C_{obs}(\Delta^{14}C_{bg}-\Delta^{14}C_{obs})/(\Delta^{14}C_{bg}+1000)$, where $C_{obs}$ is the observed $CO_2$ mixing ratio (ppm), $\Delta^{14}C_{bg}$ and $\Delta^{14}C_{obs}$ is the background and observed $\Delta^{14}C$ (‰), respectively. The results show differences in the $C_{ff}/d[CO_2]$ ratio: The $C_{ff}/d[CO_2]$ ratio was lower for the air from China (70% in average) than the other events (85% in average). This is consistent with our previous results: larger $CO_2$ emissions from biosphere over China in winter might be included in high-$CO_2$ events. Event sampling at COI showed that $CO_2$ emitted from forests had significantly higher $^{14}C$ values than the atmosphere, thus $^{14}C$ showed unique traceability for isotopic net movement between C pools in the forest area.

(4) Surface radiocarbon ($\Delta^{14}C$) in the North Pacific has been monitored using a commercial volunteer observation ship since the early 2000s. Here we discussed the temporal and spatial variations in $\Delta^{14}C$ in the summer surface water when the surface ocean is vertically-stratified over the 13 year period (2004-2016). The long-term $\Delta^{14}C$ decreasing trend after the late 1970s in the subtropical region has continued to the present and the rate of decrease of the Kuroshio and Kuroshio Extension, North Pacific and California current areas is calculated to be -3.3, -5.2 and -3.3 ‰/yr, respectively. After 2012 the $\Delta^{14}C$ of the Kuroshio and Kuroshio Extension area, however, has remained at an approximately constant value of around 50‰. The result may indicate that subtropical surface $\Delta^{14}C$ in the western North Pacific has reached an equilibrium with atmospheric $\Delta^{14}CO_2$. The $\Delta^{14}C$ in the subarctic region is markedly lower than values in the subtropical region and it seems that the decreasing tendency of surface $\Delta^{14}C$ has changed to an increasing tendency after 2010. The results may indicate that bomb-produced $^{14}C$, which has accumulated below the mixed layer in the past few decades, has been entrained into the surface layer by deep convection.

## References

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