Global Environment Research Coordination System

# Long-term broad observation of atmospheric oxygen and isotopic composition of atmospheric CO<sub>2</sub> aimed at monitoring the influences of global warming on the Earth surface environments (Abstract of the Interim Report)

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## 1. Introduction

Annual average global temperature, showing clear increasing trend after 1980 with interannual variation, approached 1.5 °C above the pre-industrial level (1850-1900) in 2023. Such global warming induced by continued emissions of the anthropogenic greenhouse gases including carbon dioxide (CO<sub>2</sub>) might reduce the strength of the natural carbon sinks, which are ocean and land biosphere. For example, high soil temperatures enhance the decomposition of organic matters; high ocean surface temperatures strengthen ocean stratification, reducing ocean uptakes through the weakening of mixing. Since about half of the fossil fuel-derived CO<sub>2</sub> is taken up by the natural sinks at present, the reduction of the natural sink strengths would accelerate global warming. The Paris Agreement, adopted at COP21 in 2015, 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 2 °C, possibly 1.5 °C. To achieve this goal, it is crucially important to well project the future changes in the natural sink strengths. However, the responses of the natural sinks to the expected future global warming are still very uncertain.

### 2. Research Objectives

We aim to investigate the responses of the carbon sink strengths of the land biosphere and the ocean to climate change. To achieve this goal, long-term extended observations of the atmospheric oxygen ( $O_2$ ),  $CO_2$  and  $CO_2$  isotopes (stable carbon ( $^{13}C$ ), and radioactive carbon ( $^{14}C$ )) are conducted in the Asia Pacific region because they are sensitive to the carbon exchanges between reservoirs. The atmospheric  $O_2$  observations can also be used to constrain the air-sea gas exchanges. These estimated variations in the strength of the carbon sinks are examined for long-term trends and the relationship to the inter-annual variations in climate such as ENSO-cycle. In addition, the atmospheric  $^{14}CO_2$  are measured to elucidate 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, ocean circulation, and ocean biotic activity,  $^{13}C$  and  $^{14}C$  of dissolved inorganic carbon in the surface seawater are also conducted.

### 3. Research Methods

Air samples were collected in flasks to determine the  $CO_2$  and  $O_2$  concentrations and carbon isotopes (<sup>13</sup>C and <sup>14</sup>C) in the atmospheric  $CO_2$ . The air samplings were carried out at several fixed sites, located in the Asia Pacific region and onboard cargo ships bound respectively for the United States, Australia/New Zealand, or Southeast Asia (Fig. 1). Using remote-controlled air sampling systems (event sampling systems), we also collected rather polluted air samples at HAT and COI 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 also conducted at HAT, COI, and onboard carbo ships sailing across the Northern Pacific and the western Pacific (Fig. 1).

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)<sup>1)</sup> and a nondispersive infrared analyzer (NDIR), respectively. Then, the stable



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

isotope ratios ( ${}^{13}C/{}^{12}C$  and  ${}^{18}O/{}^{16}O$  ratios) and  $\Delta^{14}CO_2$  of the residual CO<sub>2</sub> gases were measured by an Isotope Ratio-monitoring Mass Spectrometer (MAT 253) and a CAMS (Compact Carbon Accelerator Mass Spectrometry), respectively.

Surface seawater samples were collected from a pumping line for pCO<sub>2</sub> analyzer into glass bottles (150-250 ml). The dissolved CO<sub>2</sub> in seawater sample was extracted and isotope ratios ( $^{13}C/^{12}C$  and  $^{14}C/^{12}C$  ratios) were analyzed.

#### 4. Results and Discussions

(1) The global carbon sinks by the ocean and the land biosphere were evaluated from the change in the atmospheric potential oxygen (APO =  $O_2 + 1.1 \times CO_2$ ) data, which were obtained from flask

samples collected at HAT, COI, MNM and onboard cargo ships sailing across the western Pacific between 40°S and  $30^{\circ}N^{2}$ . The oceanic and land sinks for the 23 years (2000-2022) were  $3.0\pm0.8$ PgC yr<sup>-1</sup> and  $1.3\pm1.0$  PgC yr<sup>-1</sup>, respectively (Fig. 2).

To examine temporal change in the estimate carbon sinks, we computed the carbon budgets for the pentad (5-year) periods consecutively and plotted in Fig. 4, where the ocean and land sinks estimated by the GCP3) were also shown for comparison. The pentad ocean sinks show an overall increasing trend for the entire period, while there is a possibility that the recent trend is stagnant. In contrast, the pentad land sinks appeared to show an increasing trend for 2000-2009, a decreasing trend for 2009-2014, and an increasing trend after 2014. These changes in the trend of the land carbon uptakes may be related to the climatic variations.



**Fig. 2.** Vector analysis for the global carbon budget for 2000-2022 based on the APO and  $CO_2$  changes calculated by the data from HAT, COI, MNM, and cargo ships. Purple circles represent observed changes in APO and  $CO_2$ . Red, blue, light blue and green arrows represent the changes caused by the fossil fuel combustions, ocean uptake, ocean outgassing effect and land uptake, respectively.



Fig. 3. CO<sub>2</sub> growth rate and temperature anomaly (a) and  $\delta^{13}$ C change rate (b) at each latitude band and two monitoring stations (Hateruma (HAT) and Ochi-ishi (COI)). Average data was shown in

(2) Isotope ratios of CO<sub>2</sub> such as  $\delta^{13}$ C and  $\delta^{18}$ O have been measured over the Pacific from 60°N to 30°S since 1995. Because the isotope data for the higher latitude (from 40°N to 60°N) was rather sporadic, we have just used data from 30°N to 30°S to obtain global trends of CO<sub>2</sub> concentration and  $\delta^{13}$ C. Temporal variations in the CO<sub>2</sub> growth rate and  $\delta^{13}$ C change rate are shown in Fig.3. Both variations are correlated to the temperature anomaly. High temperature anomalies appear to reduce terrestrial CO<sub>2</sub> uptake and promote an increase in atmospheric CO<sub>2</sub> concentrations.

Simultaneously solving budget equations of the atmospheric  $CO_2$  and  ${}^{13}CO_2$ , we estimated land and ocean  $CO_2$  fluxes, based on the anthropogenic  $CO_2$  emission from the GCP data<sup>3)</sup> during the observing period. The temporal changes in the estimated ocean and land fluxes (sink flux is expressed by minus value.) are shown in Fig. 4, together with those based on the APO changes in this study and those based on ocean and terrestrial models from GCP<sup>3)</sup>. GCP results were converted to 2-year running average from the original data. Land  $CO_2$  flux of GCP model in the figure was sum of land sink and land-use change emissions in Global\_Carbon\_Budget\_2023.



**Fig. 4.** Interannual variations of carbon flux at the ocean a) and the land b) estimated by observation of APO and carbon isotope ratio, together with estimation by GCP models.

Estimated ocean fluxes based on APO and <sup>13</sup>C indicate gradual increase from early 2000s to 2015. The ocean flux by GCP changes more steadily and weaker than our observation-based fluxes especially 2006-2015. After 2015 peak, our observation showed that ocean sink gradually decreased toward 2022. Because a large El Nino occurred in 2015, oceanic CO<sub>2</sub> uptake may become weak especially over the equatorial Pacific. In addition, CO<sub>2</sub> emission rate did not increase in recent years by the influence from COVID19 and our reduction efforts of anthropogenic CO<sub>2</sub> emission. Such change in CO<sub>2</sub> input to the atmosphere can affect oceanic sink because oceanic sink

is based on the difference of CO<sub>2</sub> concentration between the atmosphere and surface ocean.

We concluded that these estimates were reliable because two fully-independent analyses showed good agreement. Basically, variation of land sink was associated with temperature anomaly and recently we still observed stable sink, even though temperature itself suddenly increased after 2015. However, average land sink did not increase basically after 2010. As for the ocean, CO<sub>2</sub> sink increased until 2010 and after that became rather constant (about 3Gt). However, ocean sink apparently started to increase again in the last 2 years, despite that the uncertainty is still very high due to lack of data.

(3) We continued air sampling for radiocarbon measurements at HAT (routine and event sampling), COI, MNM and on VOS.  $\Delta^{14}$ C for high CO<sub>2</sub> concentration events collected from 2020 to 2022 in HAT (Fig. 5) shows the ratio of CO<sub>2</sub> emitted from fossil fuel to total CO2 increase was different for each event, with high fossil fuel CO<sub>2</sub> ratios for event #32 (89%), event #34 (91%), event #35 (93%) and event #36 (89%) and lower for event #33 (79%) and event #37 (79%) These maximum fossil fuel CO<sub>2</sub> ratios were observed when the CO<sub>2</sub> concentration increase was at its maximum, suggesting that the air with lower fossil fuel CO2 ratios was mixed before and after the maximum CO<sub>2</sub> increase. In total, we have archived  $\Delta^{14}$ C data for 36 high CO<sub>2</sub> events at HAT.

(4) Analysis of <sup>14</sup>C ( $\Delta^{14}$ C) in surface seawater of the western Pacific obtained from Jan. 2010 to Mar. 2020 has been completed. It was revealed that there was a tendency that the $\Delta^{14}$ C in the surface water obtained between



**Fig.5.** CO<sub>2</sub> concentrations,  $\Delta^{14}$ C, fossil fuel CO<sub>2</sub> estimated from  $\Delta^{14}$ C and ratio of fossil fuel CO<sub>2</sub> to CO<sub>2</sub> increase observed by event sampling at HAT.

10S and 30N decreased during El Nino period and increased during the normal period after 2010, when the  $\Delta^{14}$ C concentration gradient between atmosphere and ocean was reversed (ocean > atmosphere).

## References

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