CHANGES IN THE ATMOSPHERIC OXYGEN/NITROGEN RATIO DETERMINED FROM THE NIES FLASK-SAMPLING NETWORK

Y. Tohjima, H. Mukai, Y. Nojiri, T. Machida, and H. Yamagishi

National Institute for Environmental Studies, Tsukuba 305-8506, Japan;tohjima@nies.go.jp, lnmukaih@nies.go.jp, nojiri@nies.go.jp, tmachida@nies.go.jp, yamagishi.hiroaki@nies.go.jp

ABSTRACT
We present measurements of atmospheric O_2/N_2 ratio and CO_2 mole fractions from flask samples collected at Hateruma Island and Cape Ochi-Ishi, and onboard cargo ships between Japan and the United States, and Japan and Australia (or New Zealand). Average changes in the O_2 and CO_2 for the 6-year period from 1998 to 2004 are –23.3 ± 0.3 ppm and 10.4 ± 0.1 ppm, respectively. Assuming that the ocean is neither a source nor a sink for the atmospheric O_2, we estimate the CO_2 uptake by the terrestrial biosphere and the ocean to be 1.1 ± 0.6 PgC yr^{-1} and 2.0 ± 0.5 PgC yr^{-1}, respectively.

INTRODUCTION
Observation of the long-term change in atmospheric O_2 concentration, combined with CO_2 observation, can be used to constrain the global carbon budgets because atmospheric O_2 change is determined from O_2 consumption by fossil fuel burning, O_2 release from terrestrial biosphere associated with the CO_2 uptake, and oceanic O_2 flux. In the initial phase of the O_2 study, the terrestrial CO_2 uptake was simply calculated from the difference between the observed atmospheric O_2 decrease and the O_2 consumption by burning because the net oceanic O_2 flux was considered approximately zero [e.g. *Keeling et al.*, 1992, 1996; *Bender et al*., 1996; *Battle et al*., 2000]. Although recent studies have suggested that net oceanic O_2 flux is not zero and has significant interannual variation [e.g. *Plattner et al*, 2002], which induce the uncertainties in the budget estimations, the atmospheric O_2 measurements are still important tool to study global carbon cycle. Here we show the records of O_2/N_2 and CO_2 measurements for air samples collected from NIES flask sampling network, and discuss the CO_2 budget during 6-year period from 1998 to 2004.

EXPERIMENT
We have been collecting air samples at Hateruma Island (HAT: 24°3´N, 123°49´E) since July 1997 and at Cape Ochi-ishi (COI: 43°10´N, 145°30´E) since December 1998 [*Tohjima et al*., 2003]. We also started the flask sampling on board cargo ships sailing between Japan and United State and between Japan and Australia (or New Zealand) in December 2001 [*Tohjima et al.*, submitted to GRL]. The collected air samples are sent back to our laboratory, and the O_2/N_2 ratios are measured by gas chromatograph equipped with thermal conductivity detector [*Tohjima*, 2000] and the CO_2 mole fractions are measured by NDIR. The precision (one sigma rms) of the O_2/N_2 and CO_2 measurements is 5 per meg and 0.05 ppm, respectively [*Tohjima et al*, 2003]. Our O_2/N_2 reference scale is related to more than ten high-pressure cylinders; the drift of the O_2/N_2 ratio for each cylinder against the reference scale is less than ±1 per meg yr^{-1}, which corresponds to an error in CO_2 flux of ± 0.4 PgC yr^{-1}.

RESULTS AND DISCUSSION
Observed O_2/N_2 ratio and CO_2 mole fractions are shown in Figure 1 together with smooth-curve fits. Shipboard data are binned into 10-degree latitudinal bands (40°S-30°S, 30°S-20°S, 40°N-50°N). These smooth-curve fits to the data are computed by adopting the least square fitting technique and the digital filtering technique. From the smooth curve fits we calculate the annual mean (from January 1 to December 31) of O_2/N_2 ratios and CO_2 mole fractions. Then we calculate interannual changes of O_2/N_2 and CO_2 for individual time series. The observation at Hateruma, the longest record of our observation, allows us to evaluate 6-year change (1998-2004). Average changes for HAT and COI are calculated by integrating the average interannual changes for the overlapping 5-year period (1999-2004) and the interannual change of HAT between 1998 and 1999. In the same way, we calculate the average change for HAT, COI and shipboard data.

Figure 2 shows the relationship between changes in the O_2/N_2 and CO_2 calculated from HAT, COI and shipboard data. Each solid circle represents the annual average relative to the annual average at HAT in 1998. The average changes in the observed O_2/N_2 and CO_2 during the 6-year period (1998-2004) are –111 ± 2 per meg (–23.3 ± 0.3 ppm) and 10.4 ± 0.1 ppm, respectively. Note that the 6-year changes based on only HAT data and the average from

HAT and COI data agree with the above changes within the uncertainties. The broken line indicates the effects of the fossil fuel combustion and cement manufacturing to the atmospheric O_2/N_2 and CO_2 during the 6-year period. The figures of the fossil carbon emission are taken from *Marland et al*. [2005] and the O_2:C exchange ratios for the individual fossil fuel types are taken from *Keeling* [1988]. We assume that the fossil carbon emission in 2003 and 2004 is 7.0 GtC yr^{-1} including 0.2 GtC yr^{-1} from cement manufacturing, which is the same figure in 2002. After all, average fossil carbon emission for the 6-year period is 6.8 PgC yr^{-1}. The partitioning of the fossil carbon uptake between terrestrial biosphere and ocean is graphically shown in Figure 2, where the horizontal arrow indicates oceanic uptake of 2.0±0.5 GtC yr^{-1} and the arrow with a slope of –1.1 mol/mol, which is the O_2:C exchange ratio for photosynthesis and respiration, indicates terrestrial uptake of 1.1±0.6 GtC yr^{-1}. In this calculation, we assume that the ocean is neither a source nor sink for the atmospheric O_2. Recent studies suggested that the ocean is currently a significant net source of atmospheric O_2. Therefore, our estimates of the terrestrial and oceanic uptakes shown above may correspond to the upper and lower limits of the uptakes, respectively.

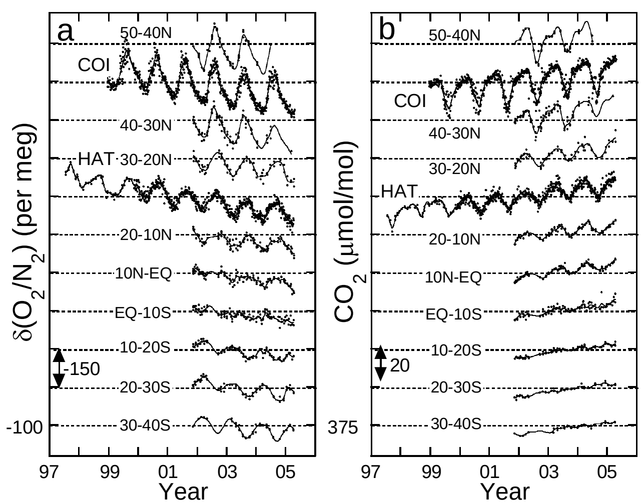

Fig. 1. Time series of observed (a) CO_2 mole fraction and (b) O_2/N_2 ratio. Shipboard data are binned into 10-degree latitude bands. The horizontal lines correspond to –100 per meg for O_2/N_2 and 375 ppm for CO_2. Solid lines indicate the smooth-curve fits.

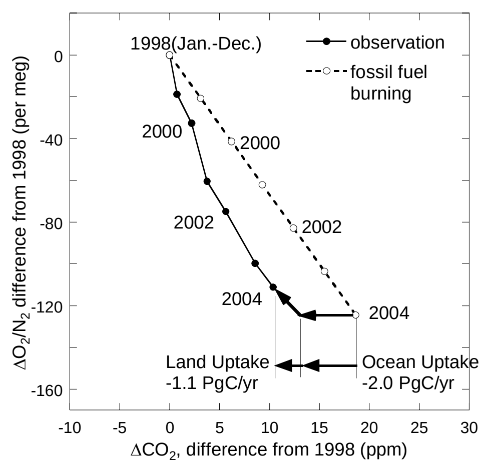

Fig. 2. Relationship between changes in the atmospheric CO_2 and O_2/N_2 from HAT, COI, and shipboard data. The broken line indicates the effect of the fossil fuel combustion to the atmospheric O_2/N_2 and CO_2. The solid arrows represent the partitioning of fossil CO_2 uptake between the terrestrial biosphere and the ocean.

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