

# Decadal-scale increases of anthropogenic CO<sub>2</sub> in Antarctic Bottom Water of the Indian sector of the Southern Ocean

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The Southern Ocean is regarded as one of the most important sinks for global carbon budget, because it is estimated that approx. 40% of ocean uptake of anthropogenic CO<sub>2</sub> (hereafter abbreviated as antCO<sub>2</sub>) occurs in the Southern Ocean. In the ocean, it is known that Sub-Antarctic Mode Water and Antarctic Intermediate Water, both of which are Southern Ocean-origin, play a large role in absorbing antCO<sub>2</sub> and transporting it northward. However, for role of Antarctic Bottom Water (AABW) in accumulating and absorbing antCO<sub>2</sub>, it is still an open question. In the 1980' s, it was said that that accumulation and uptake of antCO<sub>2</sub> in AABW is small (Chen, 1982; Poisson and Chen, 1988), because existence of sea ices effectively blocks air-sea exchange of CO<sub>2</sub>, and because signals of antCO<sub>2</sub> are diluted by mixing with water (e.g., Circumpolar Deep Water) of no or little contamination of antCO<sub>2</sub>. Recent studies reveal that AABW is also contaminated significantly by antCO<sub>2</sub>, although it is not so high (Rios et al., 2012; Pardo et al., 2014). Furthermore, influences of ocean climate changes such as warming, desalination, acidification, etc. on ocean uptake of antCO<sub>2</sub> remain unclear.

To elucidate how large AABW, defined as neutral density of  $\sigma^n \geq 28.27 \text{ kg m}^{-3}$ , takes up antCO<sub>2</sub>, we examined decadal-scale increases of antCO<sub>2</sub> ( $\Delta \text{antCO}_2$ ) along a zonal section at nominal 62°S ranging from 30°E to 160°E in the Indian sector of the Southern Ocean. For the purpose, we used high-quality data for CO<sub>2</sub>-system and related properties collected about 17 years apart in 1994/1995 and 2012/2013. These data were obtained under international observation programs such as World Ocean Circulation Experiment and Global Ship-based Hydrographic Investigations Program. From depth - longitude section of  $\Delta \text{antCO}_2$ , it was found that there was a clear contrast of distributions of  $\Delta \text{antCO}_2$  in AABW between the eastern and western sides of the Kerguelen Plateau. That is, higher increases of  $> 5 \text{ mmol kg}^{-1}$  were found in the eastern side, while lower increases or even decreases were found in the western side. In the eastern side, in contrast to previous studies, increases of antCO<sub>2</sub> were largest ( $> 9.0 \text{ mmol kg}^{-1}$ ) in the bottom water, i.e., AABW. The higher increases were especially conspicuous east of 110° E. Significant increases of anthCO<sub>2</sub> in bottom and deep waters were detected through the section, although they became gradually reduced in magnitude and depth range westward from 110°E. Vertical distributions of  $\Delta \text{antCO}_2$  showed significant positive correlations with decadal-scale changes in CFC-12 and with distributions of SF<sub>6</sub>, both of which can be used as a proxy of ocean circulation and ventilation, meaning that the distributions were mainly controlled by physical processes. Comparison of  $\Delta \text{antCO}_2$  between calculation methods with and without total alkalinity presented differences of  $\Delta \text{antCO}_2$  west of 50°E (the latter was smaller than the former). This may be related to decreases in production of particulate inorganic carbons in the Southern Ocean (Freeman and Lovenduski, 2015). The highest storage rate of antCO<sub>2</sub> was estimated to be  $1.1 \pm 0.6 \text{ mol m}^{-2} \text{ a}^{-1}$  at longitudes 130°–160°E, which is a value integrated from surface to bottom layers of statistically-significant  $\Delta \text{antCO}_2$ . With this condition of integration, we believe that the value is conservative. West of the Kerguelen Plateau, the storage rate was  $0.2 \pm 0.1 \text{ mol m}^{-2} \text{ a}^{-1}$  at most. The contrast is due probably to differences of formation regions of AABW; west of 80°E (Kerguelen Plateau), the AABW consists mostly of Weddell Sea-origin water, while east of it, the AABW consists of both the Adélie coast- and Ross Sea-origin waters.

The above results highlight that processes for uptake and accumulation of antCO<sub>2</sub> by the bottom water work well in the Indian sector of the Southern Ocean, at least, in the eastern part of it.

Keywords: Anthropogenic CO<sub>2</sub>, Antarctic Bottom Water (AABW), Southern Ocean

## Underway measurements of surface $p\text{CO}_2$ and total alkalinity in Kuroshio-Oyashio transition region

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We made measurements of surface partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) and total alkalinity (TA) in Kuroshio-Oyashio transition region off the eastern Japan in June 2016. Surface TA was measured every 15 minutes. Spatial resolution of TA was 6 km in case of cruising at 12 knot.

Surface TA (open circle in Figure 1) showed fine spatial variation which can not be captured by the interpolation of the bottle sampling and measurement of TA (open square in Figure 1) at CTD station which located every 2 degrees in longitude. The estimation of TA by Lee *et al.* [2006] (gray dot in Figure 1) overestimated the measurement by up to  $30 \mu\text{mol/kg}$ .

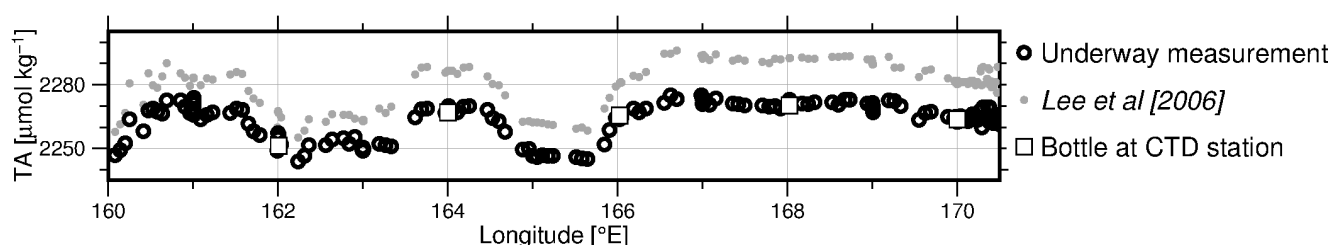
We calculated surface DIC from TA and  $p\text{CO}_2$  obtained by the underway measurements. Calculated DIC was in good agreement with the measured DIC taken from nearby CTD station. Difference and standard deviation between calculated and measured value were  $0.8$  and  $5.4 \mu\text{mol/kg}$  respectively ( $N = 38$ ).

Underway measurement of  $p\text{CO}_2$  and TA can reproduce other carbonate parameters such as DIC and pH accurately. This method is beneficial to understand carbon cycling in coastal region and Kuroshio-Oyashio transition region where spatial variation of TA is large.

The variation of TA by precipitation and evaporation can be excluded by salinity normalization.

Normalized alkalinity to Salinity = 35 ( $\text{NTA}_{35}$ ) has a large meridional gradient in the western North Pacific.  $\text{NTA}_{35}$  in the subtropical region and subarctic gyre were about  $2300$  and  $2370 \mu\text{mol/kg}$  respectively [Takatani *et al.* 2014]. In our observation,  $\text{NTA}_{35}$  also showed large zonal variation and ranged  $2310$ - $2355 \mu\text{mol/kg}$  along  $41^\circ\text{N}$  and  $2300$ - $2325 \mu\text{mol/kg}$  along  $37.5^\circ\text{N}$ . These dynamic spatial variation of  $\text{NTA}_{35}$  was attributable to the complicated distribution of Kuroshio and Oyashio water.  $p\text{CO}_2$  was concave against  $\text{NTA}_{35}$  and the smallest around  $\text{NTA}_{35} = 2320 \mu\text{mol/kg}$ . Below this  $\text{NTA}_{35}$ ,  $p\text{CO}_2$  increased thermodynamically due to temperature rise. On the other hand, nutrients was significantly high above this  $\text{NTA}_{35}$ . This indicated that  $p\text{CO}_2$  was high because the DIC supplied to the surface by the winter mixing had not been substantially reduced by biological production.

Keywords: Kuroshio-Oyashio transition region, Total alkalinity,  $p\text{CO}_2$



**Figure 1** Zonal variation of surface total alkalinity along  $41^\circ\text{N}$  in June 2016.

## Estimation of the increase in the anthropogenic carbon dioxide column inventory in the 137°E section by the eMLR method

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The ocean absorbs approximately 30% of the carbon dioxide (CO<sub>2</sub>) released into the atmosphere by human activities such as fossil fuel combustion and land-use changes, and is mitigating the progress of global warming. The western North Pacific subtropical zone is considered as one of the strong sinks of the anthropogenic CO<sub>2</sub> in the world oceans. It is important to evaluate the change in its column inventory in this area for the better understanding the global carbon cycle change, thereby better projection of the global warming. Japan Meteorological Agency has been carried out the atmospheric and oceanic CO<sub>2</sub> measurement along its repeat line at 137°E every year since early 1980s. The WOCE/GO-SHIP' s precise measurements with high-resolution and full water-column samplings have been made in the years 1994, 2010 and 2016. In this study, we evaluated the changes in the column inventory of the anthropogenic CO<sub>2</sub> in the 137°E section based on the biogeochemical data collected in these cruises using the eMLR method (Friis et al. 2005). In our eMLR analysis, we used the relationship between salinity-normalized preformed DIC (nDIC\*) and chemical tracer NO (Broecker, 1974).

$$\text{nDIC}^* = \{\text{DIC} - 117/170 \cdot (\text{O}_2^{\text{sat}} - \text{O}_2)\} \cdot 35/S,$$

$$\text{NO} = \text{O}_2 + 170/16 \cdot \text{NO}_3^- \text{ (Anderson and Sarmiento, 1994).}$$

NO is preformed oxygen concentration calculated using nitrate concentration. It is a quasi-conservative tracer that does not change with biological activity in the same water mass.

nDIC\* and NO are linearly correlated to each other below the winter mixed layer in the subtropical zone between 19°N and 34°N:

$$\text{nDIC}^* = a + b \cdot \text{NO}.$$

In the tropics to the south of 18°N, their relationships show non-linearity due to the north-south fluctuation of the North Equatorial Current and mixing with the water mass from the Southern Ocean. We then calculated the differences in nDIC\* among three cruises in 1994, 2010 and 2016 in the subtropics between 19°N and 34°N using the difference in the slope *b* in the above equation, and integrated over the water column above  $\sigma_\theta = 27.3$  to estimate the column inventory of anthropogenic CO<sub>2</sub>. The rates of increase in the anthropogenic CO<sub>2</sub> inventory were 0.83, 0.67 and 0.62 mol/m<sup>2</sup>/year (preliminary) at 30°N, 25°N and 20°N, respectively, for 22 years between 1994 and 2016, and 1.84, 1.57 and 1.44 mol/m<sup>2</sup>/year (preliminary) at 30°N, 25°N and 20°N, respectively, for 6 years between 2010 and 2016 (Fig. 1). The higher rate in the northern subtropics is attributable to the deeper ventilation (Fig. 2). It is also higher for the period from 2010 to 2016 than that from 1994 to 2016. We will also study in the different water masses such as those in the tropical zone and above the bottom of winter mixed layer where the relationship between nDIC\* and NO shows non-linearity.

Keywords: anthropogenic CO<sub>2</sub>, 137°E section, column inventory

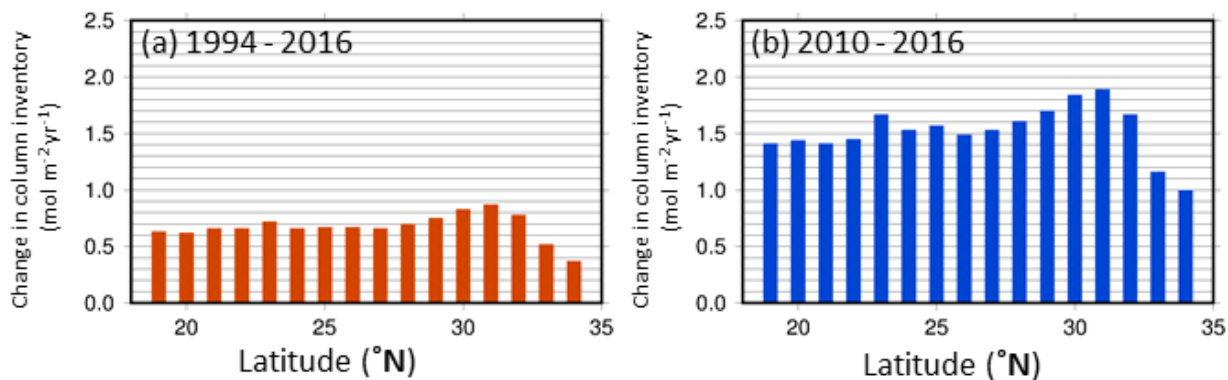


Fig. 1 Column inventory rates of anthropogenic CO<sub>2</sub> along 137E between (a) 1994 and 2016 and (b) 2010 and 2016.

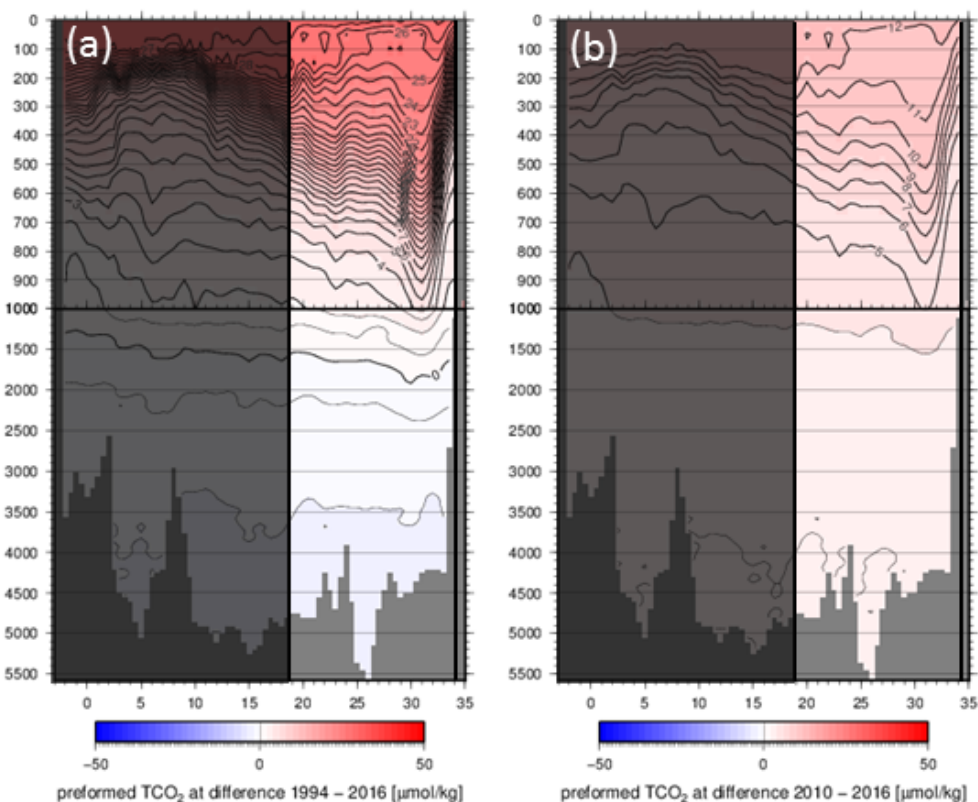


Fig. 2 Sections of anthropogenic CO<sub>2</sub> changes between (a) 1994 and 2016 and (b) 2010 and 2016. Gray colorings indicate areas outside the subtropical gyre.

## Lead spreading through sub-surface water over the North Pacific

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The international research programme GEOTRACES is revealing global distributions of trace elements in the ocean (<http://www.geotraces.org>). We have been studying the distributions of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using our chelating resin extraction-ICP-MS method (Minami et al., 2015) as a part of Japan GEOTRACES. This presentation reports our novel results from the North Pacific.

Seawater samples were collected during R/V Hakuho Maru cruises of KH-05-2 (along 160°W), KH-11-7 (along 165°E), and KH-12-4 (along 47°N) using a clean sampling system. The vertical profiles of dissolved Al, Mn, Co, Ni, Cu, and Cd were quite similar between cross-over stations of KH-05-2 and KH-12-4. However, a sub-surface maximum of dissolved Pb significantly decreased from 2005 to 2012. The decrease is consistent with the decrease of Pb in sub-surface water in the North Atlantic (Lee et al., 2011). On the ocean section along 160°W, the sub-surface Pb maximum was observed to the north of 10°N with a core at ~35°N and ~200 m depth. On an isopycnic surface of  $\sigma_0 = 26.00$ , the sub-surface Pb maximum decreased from 165°E to 130°W. In addition, both the dissolved Pb and Co showed scavenged profiles with a strong correlation >300 m depth for all stations. Although the concentrations of Co were high in surface waters near continents, those of Pb were high in surface waters beneath westerlies.

It is widely recognized that the sub-surface Pb maximum is caused by anthropogenic sources and the decrease in the Atlantic is due to the phase-out of leaded gasoline in the United States and Europe (Lee et al., 2011). Our data suggest that the decrease is slower in the Pacific. It is very likely that anthropogenic lead is majorly caused by coal burning in China, carried to the North Pacific by westerlies, dissolved in mixing layers, and spreaded through sub-surface water over the North Pacific by current systems.

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Minami, T., Konagaya, W., Zheng, L., Takano, S., Sasaki, M., Murata, R., Nakaguchi, Y. and Sohrin, Y. (2015) An off-line automated preconcentration system with ethylenediaminetriacetate chelating resin for the determination of trace metals in seawater by high-resolution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 854, 183-190.

Keywords: lead, GEOTRACES, North Pacific

## Speciation of inorganic iodine in bottom water of the Funka Bay, Hokkaido

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Dissolved iodine is typically present as inorganic compounds, iodate ( $\text{IO}_3^-$ ) and iodide ( $\text{I}^-$ ), in seawater at concentrations approximately 500 nmol/L. In oxic seawater,  $\text{IO}_3^-$  (400 - 500 nmol/l) is more stable than  $\text{I}^-$  (< 100 nmol/L). In hypoxic seawater,  $\text{IO}_3^-$  is reduced to  $\text{I}^-$  by abiotic chemical reaction. Reduction of  $\text{IO}_3^-$  in oxic surface seawater is believed to be relevant to nitrate reductase activity in phytoplankton cell and nitrate reducing bacteria (e.g. Tsunogai and Sase, 1969). Recent studies have proposed large variety of abiotic / biological  $\text{I}^-$  oxidation processes in seawater.

In this study, the objective was to investigate the temporal variation of iodine speciation in high productive coastal environment in subarctic area. Ship observations were conducted in Funka Bay, Hokkaido, in February, March, April, May, July, August, October, December of 2016. Seawater samples were vertically collected by CTD-observation system and Van-Dorn water sampler in the basin area of the Bay. The sampling depths were 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 75, 80, 85, 90 m. Nutrients ( $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_2$ ) were analyzed by colorimetric method, and  $\text{I}^-$  was analyzed by voltammetry (CSV). Total inorganic iodine was determined by the CSV analysis of  $\text{I}^-$  after the ascorbic reduction of  $\text{IO}_3^-$  (Total I:  $\text{T-I} = \text{I}^- + \text{IO}_3^-$ ).

The total column concentrations of T-I (560 - 580 nmol/L), which were averaged from the surface to the bottom water concentrations, had not distinct maximum or minimum throughout the year. On the other side, in the bottom water (90m),  $\text{I}^-$  concentrations increased from May (108 nmol/L) to July (150 nmol/L), and  $\text{IO}_3^-$  concentrations drastically decreased from May (432 nmol/L) to July (188 nmol/L). The  $\text{N}^*$  value ( $= \text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+ - 16 \cdot \text{PO}_4^{3-}$ ), which is used as an indicator of denitrification in seawater, was decreased from April (-6  $\mu\text{mol/L}$ ) to May (-12  $\mu\text{mol/L}$ ) and July (-14  $\mu\text{mol/L}$ ), implying that denitrification occurred in the bottom sediment. We considered that the decrease of  $\text{IO}_3^-$  concentration from May to July was resulted from the  $\text{IO}_3^-$  reduction in bottom sediment accompanied by nitrate reduction (denitrification).

Keywords: denitrification, coastal water, redox

# Relationship between dissolved zinc and silicate in the western North Pacific from subarctic to subtropical regions

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## Introduction

Zinc (Zn) is an essential trace nutrient for marine microorganisms and one of key parameters in international GEOTRACES project. Recent studies have revealed basin-scale distributions of dissolved Zn and the relationship between dissolved Zn and silicate (Roshan and Wu, 2015; Wyatt et al., 2014). In the subarctic North Pacific, the relationship between dissolved Zn and silicate is very different from that in other open oceans. The decoupling of dissolved Zn and silicate occurs in the subarctic North Pacific intermediate water (sigma-theta: 26.6–27.5), whereas in both shallow and deep waters generally similar trends to those of the subtropical North Pacific were observed (Kim et al., submitted). In this study, we will present the extensive zonal section full depth transect data of dissolved Zn across the subarctic and subtropical western North Pacific to investigate the influences of the subarctic North Pacific intermediate water by using relationship between dissolved Zn and silicate.

## Methods

Seawater samples were collected in the western North Pacific during the R/V Hakuho-maru KH-12-3 cruise (from July to August 2012), by using acid-cleaned Teflon-coated X-Niskin samplers deployed on CTD-CMS. Zn in seawater was determined with cathodic stripping voltammetry (CSV) with ammonium 1-pyrrolidinedithiocarbamate (APDC) after UV-digestion (Kim et al., 2015).

## Result and Discussion

The section distributions of dissolved Zn in the western North Pacific are similar to those of silicate. However, the relationships between dissolved Zn and silicate clearly indicate a decoupling of dissolved Zn and silicate in subarctic regions. Based on the relationship between dissolved Zn and silicate in the eastern subtropical North Pacific (Bruland, 1980; Conway and John, 2015), we calculated Zn\* as follows.

$$\text{Zn}^* = [\text{Zn}] - 0.052 \times [\text{silicate}] + 0.305$$

High Zn\* values were observed in the intermediate water masses from subarctic to subtropical regions. Therefore, Zn\* could be a very useful tracer to investigate the influence of the subarctic North Pacific intermediate water on the entire western North Pacific.

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Keywords: Zinc, Trace metal, North Pacific