Formulation of disequilibrium for estimating the oceanic anthropogenic CO_2 over the Southern Ocean

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【Introduction】

The ocean is estimated to absorb approximately a quarter of the anthropogenic CO_2 released by human activity [Le Quere et al., 2015]. The ocean is thought to mitigate the effect of global warming. The Southern Ocean (SO) is expected to absorb 40% of the ocean uptake of anthropogenic CO_2 [Khatiwala et al., 2013]. Unfortunately, there are few observational data of carbonate materials (dissolved inorganic carbon (DIC), total alkalinity (TA), pH) for estimating the oceanic anthropogenic CO_2 due to severe weather conditions. It is difficult to grasp the detailed spatiotemporal dynamics of the oceanic anthropogenic CO_2 with high resolution.

On the other hand, in order to estimate the anthropogenic CO_2, we must consider that two-step dissociation occurs when CO_2 dissolves in the ocean. It takes six months for CO_2 to reach the equilibrium in the surface mixed layer, which is about twenty times that of oxygen. Therefore, CO_2 is generally in a disequilibrium state at the air-sea interface [Sarmiento and Gruber, 2006]. To calculate the anthropogenic CO_2 in the seawater, the disequilibrium (DIC_{diseq}) by the air-sea gas exchange is required. Additionaly, we need to correct the effects of biological activities as remineralization and $CaCO_3$ dissolution (Eq. 1);

$$DIC_{anth} = DIC_{obs} - DIC_{pi\text{-}sat} - DIC_{diseq} - DIC_{soft} - DIC_{carb} \qquad \text{(Eq. 1)}$$

where the subscript, anth, obs, pi-sat, soft and carb mean the anthropogenic amount, the observational amount, the saturated amount in the pre-industrial era, the amount by remineralization of organic matter and the amount derived from $CaCO_3$ dissolution, respectively.

In previous studies, the chemical tracers must be used to estimate the DIC_{diseq} [e.g., Gruber et al., 1996] while the measurement for the chemical tracers is awkward. Since the chemical tracers data are less than the basic hydrological data in the SO, it is difficult to estimate the anthropogenic CO_2 over the entire SO. In this study, we attempted to estimate the DIC_{diseq} over the SO south of 30 °S without using the chemical tracers.

【Method and Data】

We assumed that CO_2 exchange at the air-sea interface is vertically constant within the surface mixed layer (MLD) of the ocean. In order to estimate the DIC_{diseq}, we modified Eq. 1 to calculate the $DIC_{MLD,diseq}$ in the MLD (Eq. 2) [Li et al., 2019];

$$DIC_{MLD,diseq} = DIC_{MLD,obs} - DIC_{MLD,sat} - DIC_{MLD,soft} - DIC_{MLD,carb} \qquad \text{(Eq. 2)}$$

where the subscript, MLD means the value in the surface mixed layer. $DIC_{MLD,sat}$ is the current saturated DIC that can be calculated from the chemical equilibrium of seawater CO_2 and atmospheric pCO_2. $DIC_{MLD,soft}$ and $DIC_{MLD,carb}$ can be obtained from the stoichiometric ratios of nitrogen, oxygen and carbon.

Using the GLODAP v2 data set such as temperature (T), salinity (S), dissolved oxygen (DO), apparent oxygen ultilization (AOU), TA, and DIC in the MLD in the SO south of 30 °S, we calculated the DIC_{diseq}. Based on the obtained $DIC_{MLD,diseq}$, we attempted to obtain the parameterization for the DIC_{diseq} with T, S and AOU.

【Results and Disscusion】

We obtained the equation of DIC_{diseq} as follow:

$$DIC_{diseq} \ (\mu mol \ kg^{-1}) = -203.5 + 0.8244 \cdot T + 5.547 \cdot S - 0.5170 \cdot AOU \qquad \text{(Eq. 3)}$$

$$(R^2 = 0.66, \ RMSE = 8.0 \ \mu mol \ kg^{-1}, \ n = 6,759)$$

Eq. 3 can allow us to obtain the DIC_{diseq} from the surface to the bottom in the SO south of 30 °S. Furthermore, we will depict the detailed spatiotemporal changes in the anthropogenic CO_2 over the SO by applying Eq. 3 to the 466 Argo profiling floats during 2003-2019.