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Gas exchange coefficients in seawater: Use of stable isotopes of oxygen

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The accurate estimation of transfer of trace gases across air-water interface is a necessity to understand the flows and biogeochemical cycles of materials at the earth surface. Transfer of a gas at the air-water interface depends on its exchange coefficient and the difference in its abundance between the media. A variety of parameterizations are proposed to calculate gas exchange coefficients (k) using surface film, surface renewal, and boundary-layer models based on results obtained from tracer experiments employing radon, SF_6, natural and bomb-produced ^{14}C. Several empirical equations are developed for k as a function of wind speed using linear, quadratic and cubic relationships. Different parameterizations led to k values that vary by a factor of 2 or more. Further, the results obtained from these have large uncertainties (~30%) with proportional errors in the fluxes estimated. We developed a novel method to estimate k using the three stable isotopes (16, 17 and 18) of oxygen dissolved in seawater. Due to different fractionation mechanisms in the stratosphere (mass-independent) and at the earth surface (mass-dependent processes such as photosynthesis, respiration, air-sea exchange etc.) the $\delta^{17}O$-$\delta^{18}O$ relationship of atmospheric O_2 is different from that at the surface of the earth. This difference, $^{17}\Delta$ anomaly, of dissolved oxygen in the surface mixed layer is controlled by balance between gross oxygen production (GOP, due to photosynthesis) and its influx from the atmosphere. The former increases the anomaly whereas the latter reduces. Therefore, it is possible to estimate transfer velocity of oxygen using average mixed layer $^{17}\Delta$ anomaly of dissolved oxygen and GOP.

We estimated transfer velocity of oxygen in the Sagami Bay, central Japan, using $^{17}\Delta$ anomaly measured during spring and summer seasons, at 2 hour intervals for two days during each season. The GOP was measured using Fast Repetition Rate Fluorometer (FRRF). The transfer velocities derived from $\Delta^{17}O$ anomalies showed consistent differences with that of Wanninkhof (1992) model estimates. The anomaly based transfer velocity is higher at lower wind speeds and vice versa; possibly because the anomaly in the mixed layer represents a signal averaged over the residence time of oxygen (~one week in case of Sagami Bay) and, therefore, transfer velocity is also averaged over time that differs from Wanninkhof model derived instantaneous piston velocity. This study suggests that weekly to monthly (based on the residence time of dissolved oxygen in the mixed layer) averaged transfer velocity, with reduced errors, can be derived using $\Delta^{17}O$ anomaly that better represent natural transfer coefficients, vertically integrated over time, in the surface ocean than that from instantaneous experiments.