



*Supplement of*

**Significant role of physical transport in the marine carbon monoxide (CO) cycle: observations in the East Sea (Sea of Japan), the western North Pacific, and the Bering Sea in summer**

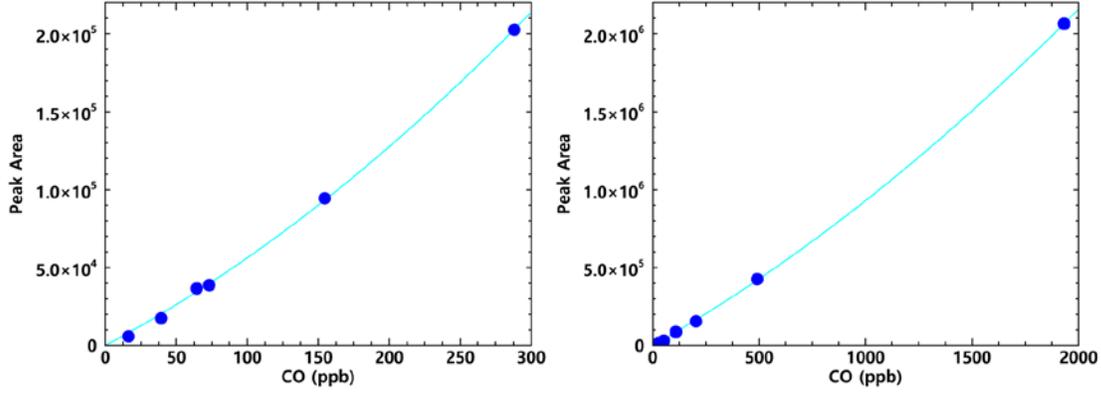
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## **Introduction**

This supporting information includes the following: (1) Example calibration curves for NOAA-GMD/WMO 2004 standard gases and Swiss Empa standard gases. These curves were used to scale the CO concentrations of commercial calibration gases (Figure S1). (2) Details on the calculation of the photochemical production of carbon monoxide (S1). (3) The derivation of the CO Schmidt number (S2). (4) An exploration of potential factors contributing to the difference in CO concentrations between the underway and discrete sampling methods (Figure S6). (5) Vertical profiles of physical properties in the water column at the hydrographic stations visited during the SHIPPO expedition (Figure S8).



**Figure S1.** Calibration curves using (a) NOAA-GMD/WMO 2004 standard gases and (b) Empa standard gases.

### S1. Photochemical Production of CO

The photochemical production rate ( $J$ ) of CO was calculated by Eq. (4) from the main text, which is reproduced here with the exception including the definition of the maximum depth at the bottom of the mixed layer (MLD) at the given station and the wavelength range between 290 and 800 nm.

$$J = \int_{z=0}^{z=\text{MLD}} \int_{\lambda=290}^{\lambda=800} I_0(\lambda, 0^-) e^{-k_d(\lambda)z} \times a_c(\lambda, z) \times \phi_{\text{CO}}(\lambda) d\lambda dz \quad (4)$$

The irradiance beneath the air-sea interface, denoted as  $I_0(\lambda, 0^-)$ , was calculated using equations (5) to (8) from the text. As shown in Figure S2a, wavelength-resolved irradiance over the air-sea interface ( $I(\lambda, 0^+)$ ) was calculated using the TUV model. Subsequently, the fractions of direct and diffuse spectral incident irradiance were computed using the Bird and Hulstrom model (Bird and Hulstrom, 1981), implemented in the Solrad program (Pelletier, 2008). These values were used to determine the albedo on the air-sea interface ( $A$ ) (Figure S3a) and the irradiance under the air-sea interface,  $I(\lambda, 0^-)$  (Figure S3b).

The diffuse attenuation coefficient ( $k_d(\lambda, z)$ ) was computed by Eq. (S1) from Sikorski and Zika (1993):

$$k_d(\lambda, z) = c \left( 1 - \frac{\gamma}{\left( \gamma + (1 - \gamma)(1 - \nu_0 + \nu_1/R) \right)} \right) \mu_0^{-1} \quad (\text{S1})$$

, where the beam attenuation coefficient,  $c$ , represents the sum of absorption coefficients by seawater ( $a_w$ ), *chl-a* ( $a_f$ ), CDOM ( $a_c$ ), and non-algal particles ( $a_n$ ), scattering

coefficients of seawater ( $b_w$ ) and all particles ( $b$ ), and Raman scattering coefficient of seawater ( $b_r$ ):

$$c = a_w + a_f + a_c + a_n + 0.5b_w + b_p + b_r \quad (\text{S2})$$

The other parameters in Eq. (S2) are referred to in equations (20) to (25) in Sikorski and Zika (1993). We assumed a direct forward scattering ( $\gamma$ ) of 95.09 % based on Sikorski and Zika (1993). The wavelength-resolved absorption and scattering coefficients described above were plotted in Figure S2b.

To calculate the photon energy absorbed by seawater and particles in the water column, the water depth was discretized with constant thickness of 1 m, and the total irradiance absorbed was integrated along the depth as follows:

$$\Delta I_0(\lambda, z_i) = I_0(\lambda, 0) \left\{ e^{-k_d(z_i - \Delta z/2)} - e^{-k_d(z_i + \Delta z/2)} \right\} \quad (\text{S3})$$

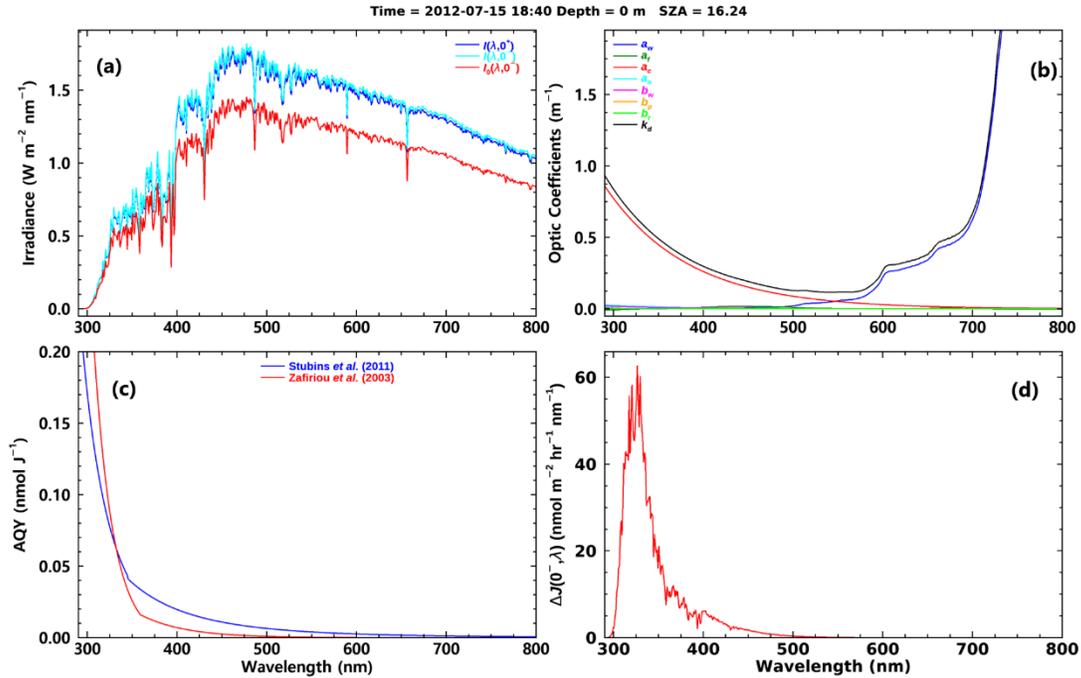
The photon energy absorbed by CDOM alone can be approximated as follows:

$$\Delta I_c(\lambda, z_i) \cong \Delta I_0(\lambda, z_i) \times \frac{a_c(\lambda)}{k_d(\lambda, z_i)} \quad (\text{S4})$$

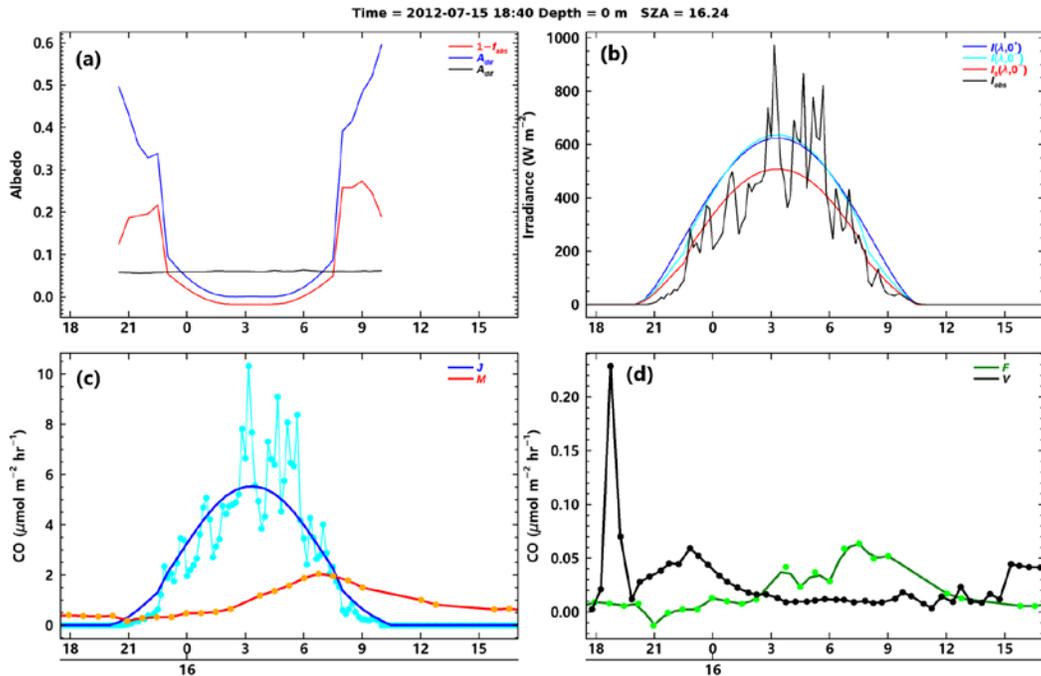
The photochemical CO production rate in the given depth range can be obtained by multiplying the apparent quantum yield of CO (Figure S2c) by the amount of photon energy absorbed by CDOM in Eq. (S5):

$$\Delta J(\lambda, z_i) = \Delta I_c(\lambda, z_i) \times \phi_{\text{CO}}(\lambda) \quad (\text{S5})$$

The value of  $J$  was determined by integrating  $\Delta J(\lambda, z_i)$  with respect to wavelength and depth on the given date (Figure S2d and Figure 3c).



**Figure S2.** Wavelength-resolved irradiance (a), absorption, scattering, and attenuation coefficients (b), apparent quantum yield (AQY) (c), and photon energy absorbed by CDOM in the surface layer of the ocean (d) at Station 1 in the East Sea (Sea of Japan) on July 16, 2012, when the solar zenith angle was at its lowest. Various parameters in the figure are represented by color codes and indices.



**Figure S3.** Diel variations of total albedo accounting for direct and diffuse lights (a), modelled and observed irradiance (b), photochemical production ( $J$ ) and microbial consumption ( $M$ ) (c), and air-sea CO exchange ( $F$ ) and turbulence eddy diffusive flux at the bottom of the surface mixed layer (d) at Station 1 in the East Sea (Sea of Japan) on July 16, 2012. Color codes correspond to the parameters displayed in each panel, indicated by their respective indices.

## S2. Derivation of $Sc$ for CO

The Schmidt number ( $Sc$ ) is dimensionless and is defined as the ratio of momentum diffusivity to mass diffusivity. The former is expressed with the kinematic diffusivity, which is the ratio of the dynamic diffusivity to the density of the solution. There are several parameterizations available for dynamic diffusivity and density of freshwater and seawater. For our calculations, we adopted the formulations provided by Korson et al. (1969) and Millero (1974) for dynamic viscosity and by Millero and Poisson (1981) for density. Recently Sharqawy et al. (2010) compiled existing parameterizations for use in the chemical engineering. The deviations between these parameterizations were found to be less than 0.1 % for density, while dynamic viscosity varied up to 1.2% at the freezing point of seawater at salinity 35, which may be attributed to the parameterization of the unmeasured values.

The diffusion coefficient for CO was initially measured by Wise and Houghton (1968), which was used by Bates et al. (1995) to calculate the Schmidt number of CO. Conrad et al. (1982) used the value of diffusion coefficient of CO,  $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , which was measured at 20°C in freshwater by Wise and Houghton (1968). Several parameterizations for gas diffusivity have been provided in literature. Among them, parameterizations by Wilke and Chang (1955), Hayduk and Laudie (1974), and Hayduk and Minhas (1982) are often used (e.g., Johnson (2010); Blomquist et al. (2012)). We adopted parameterization by Wise and Houghton (1968) since they used their own experimental results to derive diffusion coefficient. However, we adjusted their values to account for differences in temperature scale, water vapor pressure, and salt effect. In calculating diffusion coefficients ( $D$ ) using the Eyring equation (S6), we made several modifications. Firstly, we adjusted the temperature to the ITS 90 scale and converted it to the absolute Kelvin temperature of 273.15. Secondly, we accounted for water vapor pressure using the formulation by Ambrose and Lawrenson (1972):

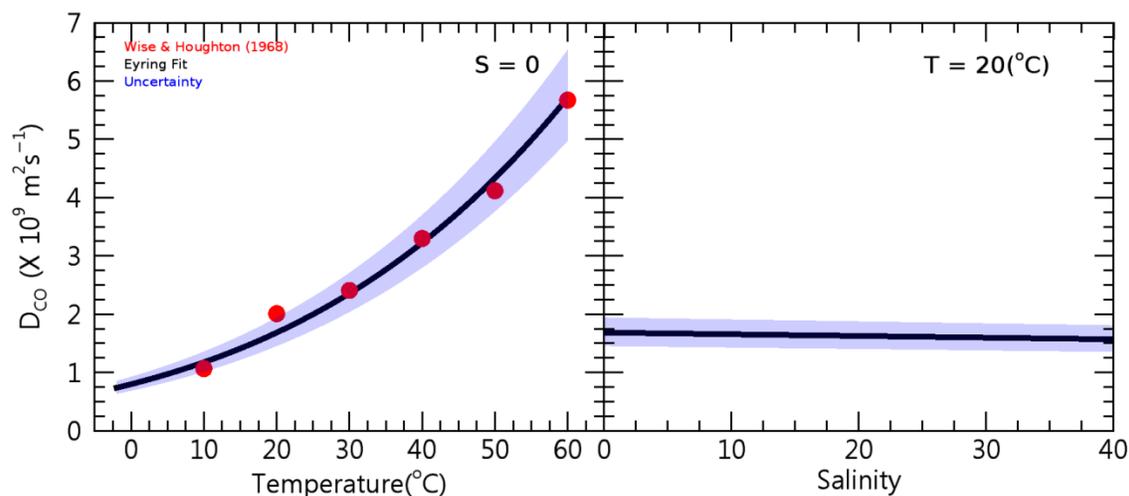
$$D = B \times \exp(-\Delta E_a / RT) \quad (\text{S6})$$

, where  $B$  represents pre-exponential constant,  $\Delta E_a$  activation energy,  $R$  gas constant, and  $T$  Kelvin temperature. However, Eq. (S6) does not account for the “salt effect”, which can lower diffusivity by up to 8% depending on the gas (e.g., King and Saltzman (1995)). Following experiments conducted by Jähne et al. (1987), we applied the salt effect linearly

in our parameterization, assuming a 6% reduction at salinity 35 compared to freshwater. Finally, we refitted the diffusion coefficients using the Levenberg-Marquardt method to determine  $B$  and  $\Delta E_a$ . The results are compared in Table S1 and depicted in Figure S4.

**Table S1.** Comparison of the coefficients of the Eyring equation

	Wise and Houghton (1968)	This study
Pre-exponent, $B$ ( $\times 10^5 \text{ m}^2 \text{ s}^{-1}$ )	4.07( $\pm 0.50$ )	4.47( $\pm 0.32$ )
$\Delta E_a$ ( $\text{kJ mol}^{-1}$ )	24.518( $\pm 0.042$ )	24.831( $\pm 0.182$ )



**Figure S4.** Diffusion coefficients of CO measured by Wise and Houghton (1968) (red solid circle) and the Eyring fitting (black solid line) to the data against temperature for fresh water (left) and fitting against salinity at  $20^{\circ}\text{C}$ . Blue shade represents uncertainties of the given diffusion coefficients.

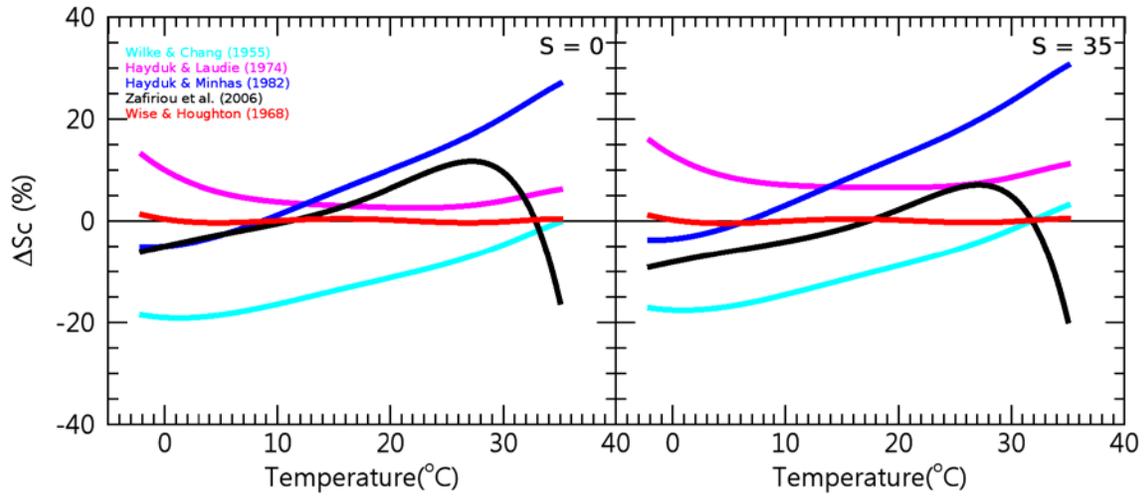
For deriving a parameterization of the CO Schmidt number, we used a 4th-order polynomial function of temperature in Celsius ( $t$ ) and salinity ( $S$ ) as follows:

$$Sc = A_0 + A_1 t + A_2 t^2 + A_3 t^3 + A_4 t^4 + S(B_0 + B_1 t + B_2 t^2 + B_3 t^3 + B_4 t^4) \quad (\text{S7})$$

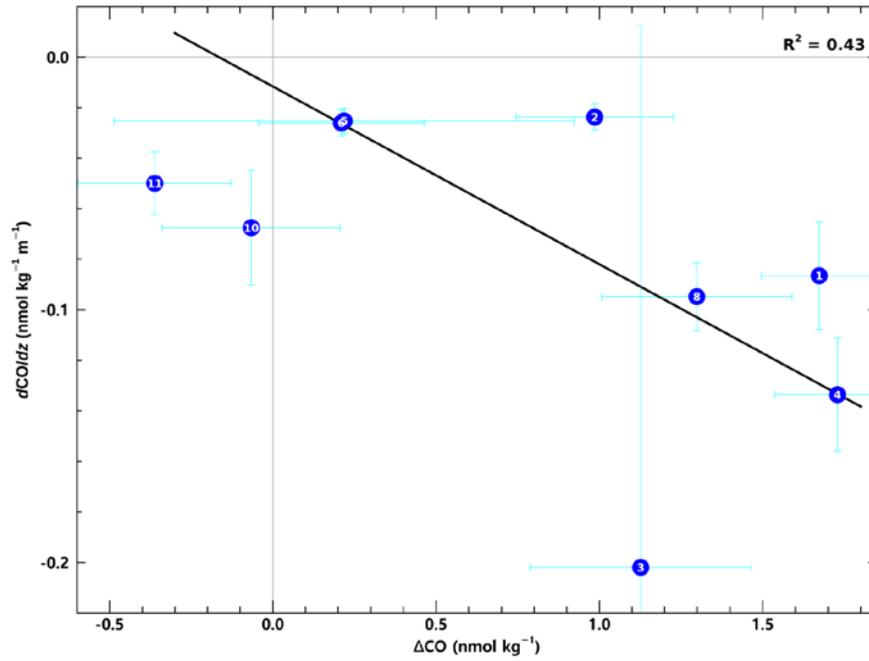
The coefficients  $A_i$ 's and  $B_i$ 's are listed in Table S2. The fitting process was restricted to the temperature range of  $-2^{\circ}\text{C}$  to  $38^{\circ}\text{C}$  and salinity values from 0 to 35. Deviations from this parameterization for measurements by Wise and Houghton (1968) and for other parameterizations are illustrated in Figure S5 for both fresh water and seawater at salinity 35.

**Table S2.** Polynomial coefficients in Equation S7

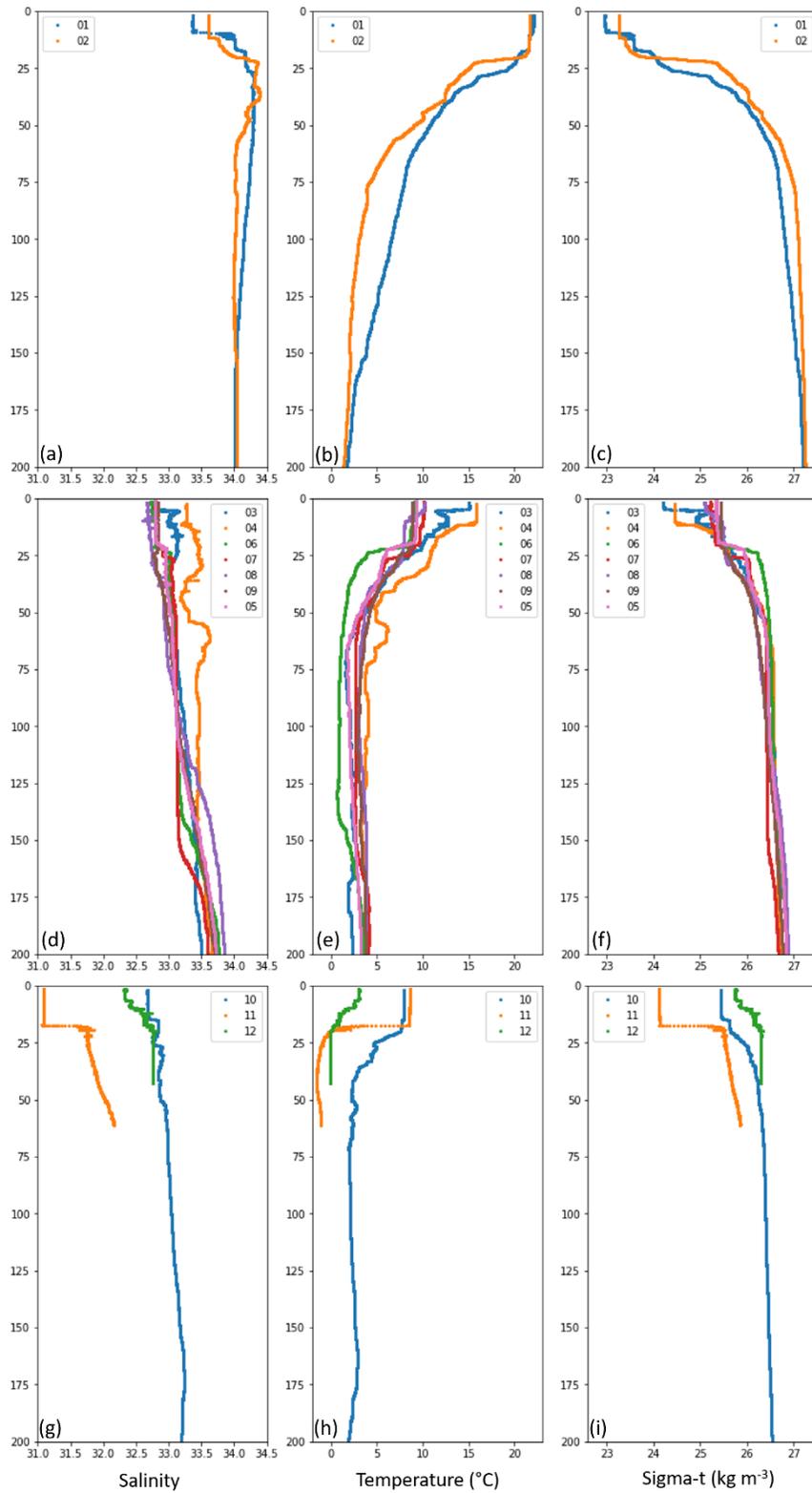
	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
Coeff.	2237.12	-159.444	5.70687	-0.01092382	0.00086435
	B <sub>0</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>
Coeff.	5.68820	-0.34916	0.011238	-0.00020114	1.5289E-06



**Figure S5.** Deviations from the Schmidt number described in Eq. (S7) and Table S2. Various  $Sc$  parameterizations in literature are indexed with matching the color of curves in the left panel.



**Figure S6.** Scatterplot of the vertical gradient of the CO profile at the stations versus the difference in CO concentrations between discrete and underway measurements at the depth of 7 m. Station numbers are shown in symbol. The scatter plot roughly indicates that the steep vertical gradient could be one of the causes for large  $\Delta CO$ .



**Figure S7.** Vertical profiles of seawater salinity, temperature, and density ( $\sigma_t$ ) at stations in ES (a–c), NP (d–f), and BS (g–i). Corresponding profiles to the parameter at Station 12 are added in panels of (g) to (i).

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