Supporting Information for

**Significant contribution of physical transport in Marine Carbon Monoxide Cycles — Observations in the East Sea (Sea of Japan), the Western North Pacific, and the Bering Sea in summer**

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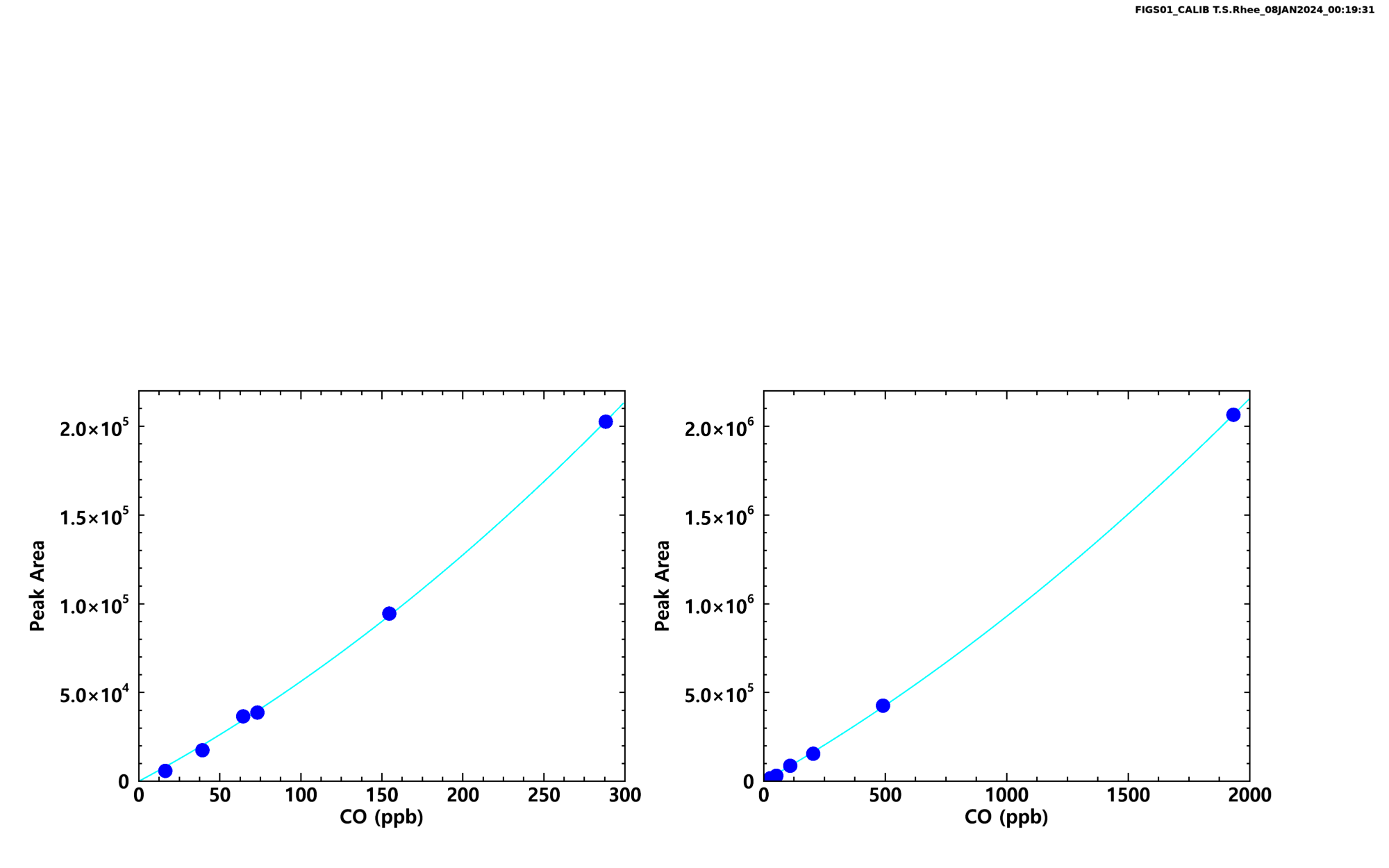
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**Introduction**

This supporting information includes (1) example calibration curves for NOAA-GMD/WMO 2004 standard gases and Swiss Empa standard gases, which 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 (Text S1), (3) the derivation of the CO Schmidt number (Text S2), (4) a potential factor contributing to the CO concentration difference between the underway and discrete sampling methods (Figure S6), and (5) vertical profiles of physical properties in the water column at the hydrographic stations visited during the SHIPPO expedition (Figure S7).

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



Text S1. Photochemical Production of CO

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

|  |  |  |
| --- | --- | --- |
|  |  | (4) |

The irradiance beneath the air-sea interface, *I*0(*λ*,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*(λ,0+)) was calculated using TUV model. Then, 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), and were used to determine the albedo on the air-sea interface (*A*) (Figure S3a) and the irradiance under the air-sea interface, *I*(λ,0-) (Figure S3b).

Diffuse attenuation coefficient () was computed by Eq. (S1) from Sikorski and Zika (1993):

|  |  |  |
| --- | --- | --- |
|  |  | (S1) |

, where beam attenuation coefficient, *c*, represents the sum of absorption coefficients by seawater (*aw*), *chl-a* (*af*), CDOM (*ac*), and non-algal particles (*an*), scattering coefficients of seawater (*bw*) and all particles (*b*), and Raman scattering coefficient of seawater (*br*):

|  |  |  |
| --- | --- | --- |
|  |  | (S2) |

Other parameters in Eq. (S2) are referred to the equations (20) to (25) in Sikorski and Zika (1993). Finally, the direct forward scattering, *γ*, was assumed to be 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, *i.e*. 1 m, and the total irradiance absorbed was integrated along the depth as follows:

|  |  |  |
| --- | --- | --- |
|  |  | (S3) |

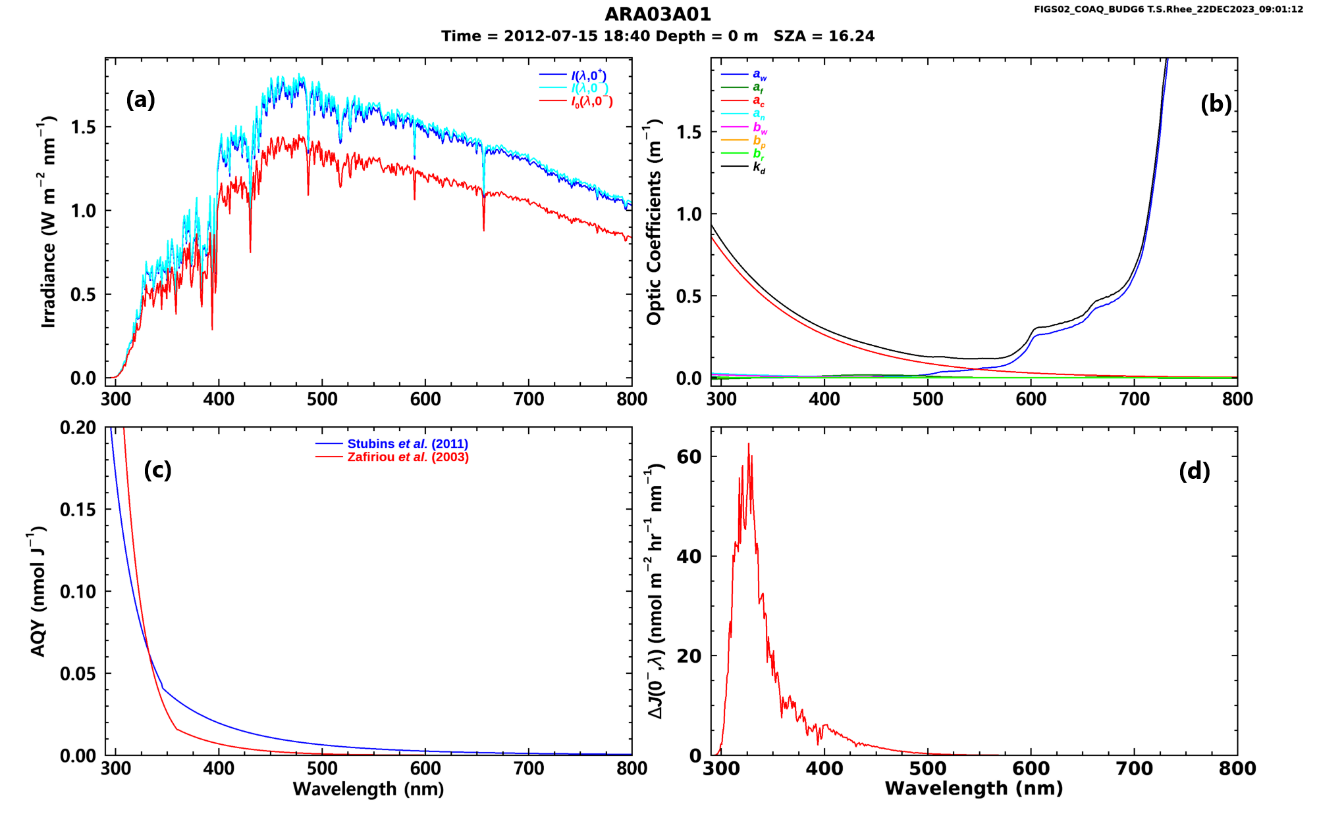
The photon energy absorbed by CDOM alone can be approximated as follows:

|  |  |  |
| --- | --- | --- |
|  |  | (S4) |

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

|  |  |  |
| --- | --- | --- |
|  |  | (S5) |

*J* was determined by integrating with respect to wavelength and depth on the given date (Figure S2d and Figure 3c).



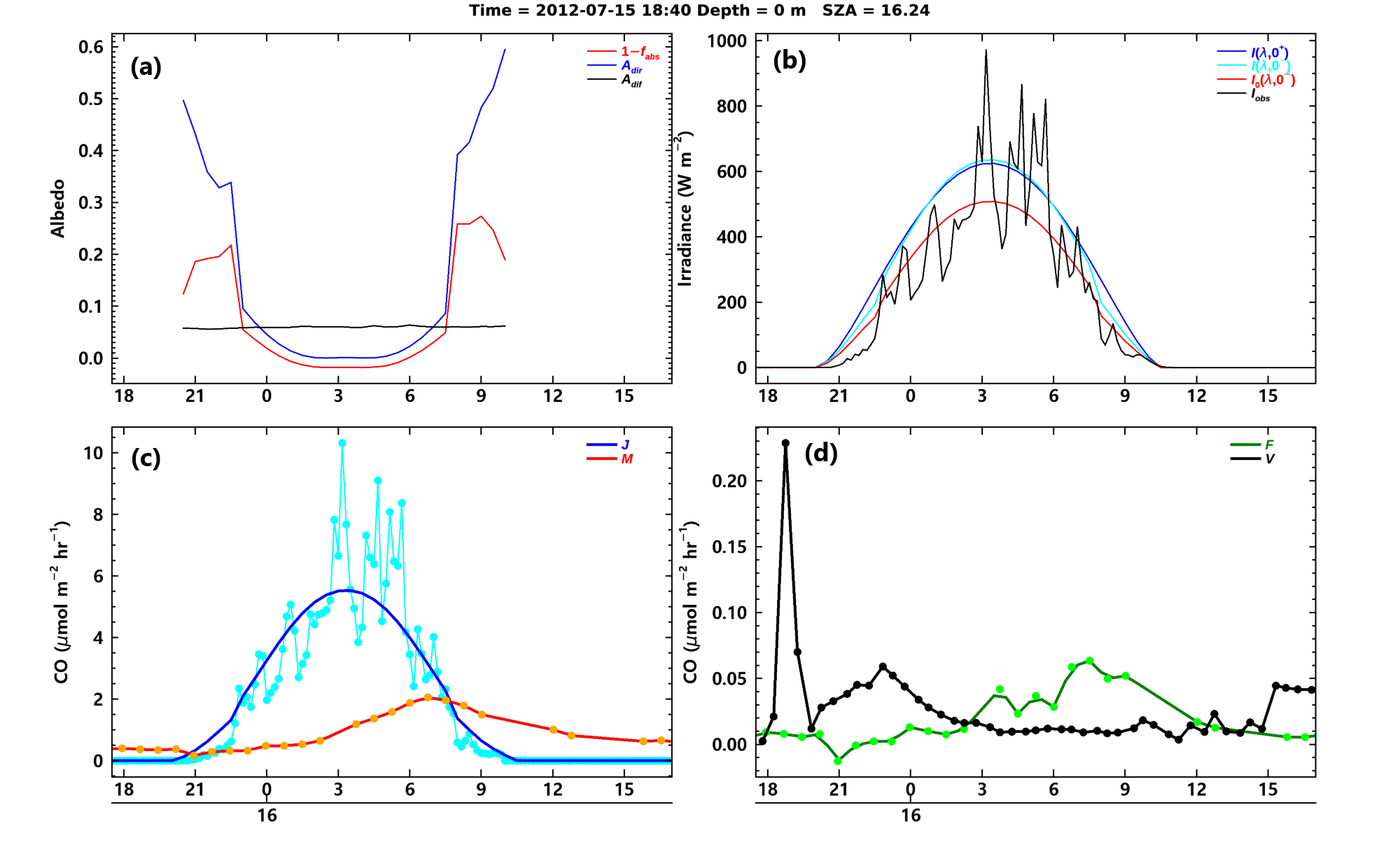


Figure S3. Diel variations of total albedo accounting for direct and diffuse lights (a), modelled and observed irradiance (b), photochemical production (*J*) and microbial consumption (*M*) (c), and air-sea CO exchange (*F*) and turbulence eddy diffusive flux at the bottom of the surface mixed layer (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.

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.

Text 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. While there are several parameterizations available for dynamic diffusivity and density of freshwater and seawater, we have adopted the formulations provided by Korson et al. (1969) and Millero (1974) for the calculation of dynamic viscosity and by Millero and Poisson (1981) for the 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.

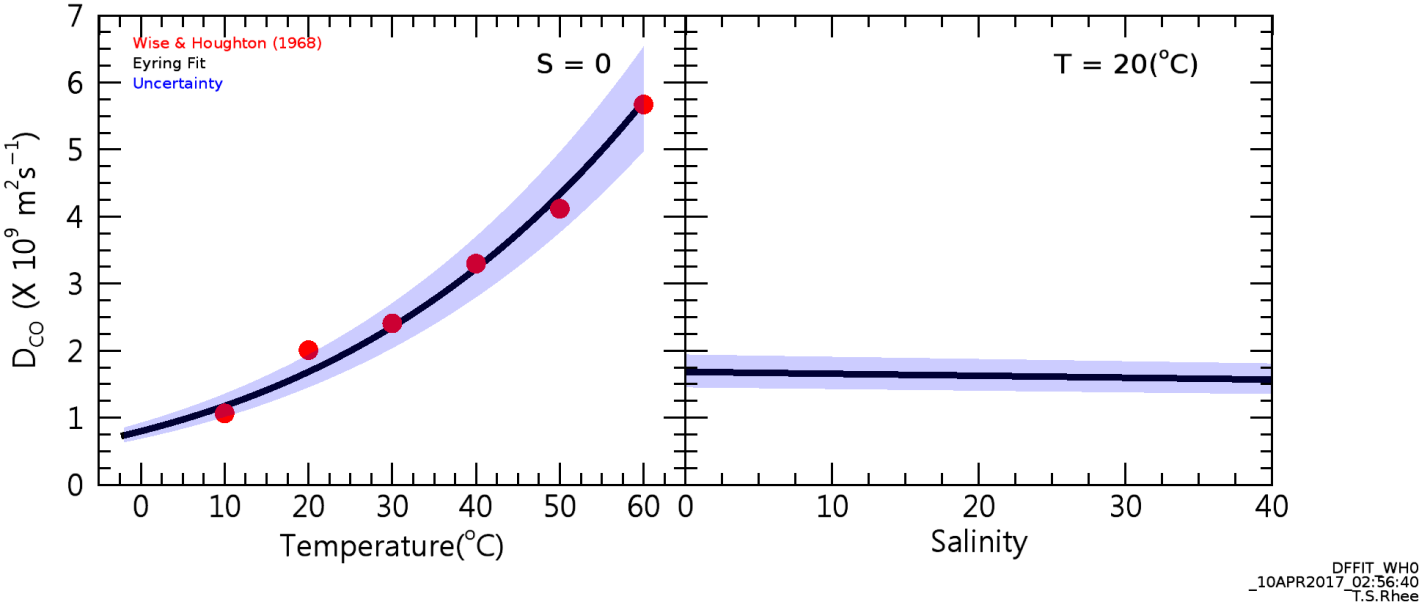
The diffusion coefficient for CO was initially measured by Wise and Houghton (1968), which was used by Bates et al. (1995) for calculating the Schmidt number of CO. Conrad et al. (1982) used the value of diffusion coefficient of CO, 2.3x10-9 m2 s-1, which was measured at 20°C in freshwater by Wise and 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. When calculating diffusion coefficients (*D*) using the Erying equation (S6), we modified the temperature to the ITS 90 scale, the absolute Kelvin temperature of 273.15, and the water vapor pressure using the formulation by Ambrose and Lawrenson (1972):

|  |  |
| --- | --- |
| *D* = *B*×exp(-Δ*Ea*/*RT*) | (S6) |

, where *B* represents pre-exponential constant, Δ*Ea* 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 Δ*Ea*. 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* (x105 m2 s-1) | 4.07(±0.50) | 4.47(±0.32) |
| Δ*Ea* (kJ mol-1) | 24.518(±0.042) | 24.831(±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°C. Blue shade represents uncertainties of the given diffusion coefficients.

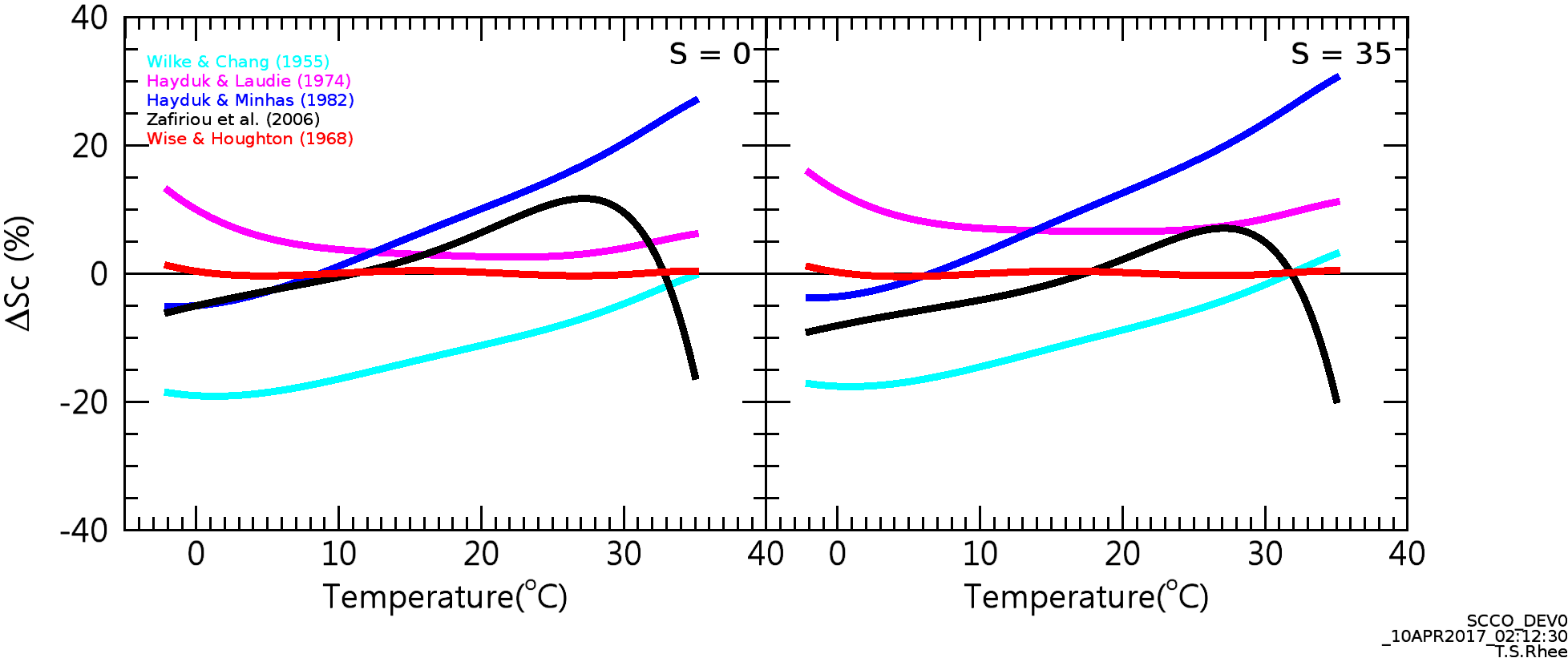
To derive a parameterization of the CO Schmidt number we applied a 4th-order polynomial function of temperature in Celsius (*t*) and salinity (*S*) as follows:

|  |  |
| --- | --- |
| *Sc* = A0 + A1 *t* + A2 *t*2 + A3 *t*3 + A4 *t*4 + S(B0 + B1 *t* + B2 *t*2 + B3 *t*3 + B4 *t*4) | (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°C to 38°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

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | A0 | A1 | A2 | A3 | A4 |
| Coeff. | 2237.12 | -159.444 | 5.70687 | -0.01092382 | 0.00086435 |
|  | B0 | B1 | B2 | B3 | B4 |
| 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.

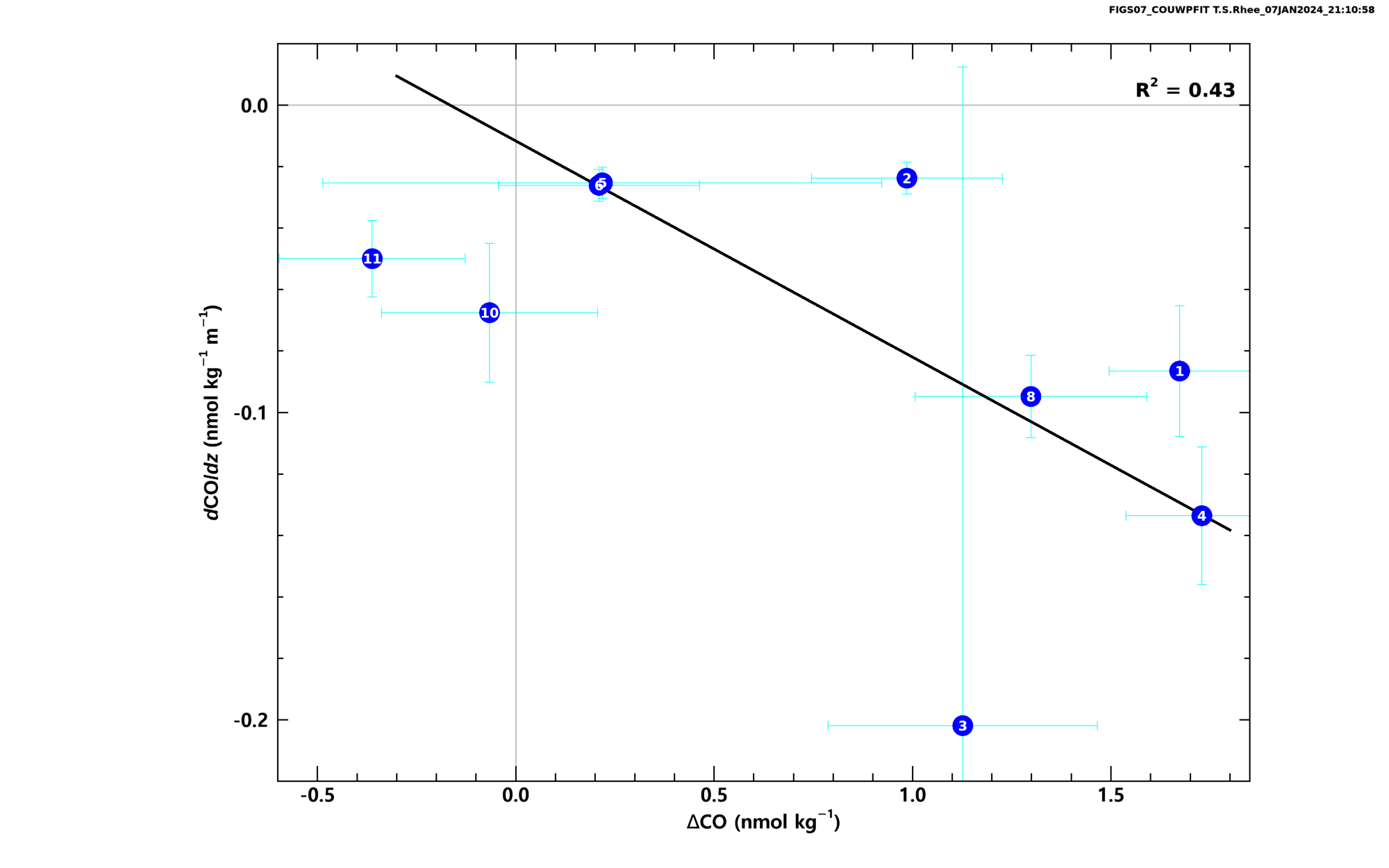


Figure S6. Scatterplot of the vertical gradient of the CO profile at the stations versus the difference in CO concentrations between discrete and underway measurements at the depth of 7 m. Station numbers are shown in symbol. The scatter plot roughly indicates that the steep vertical gradient could be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



**Figure S7**. Vertical profiles of seawater salinity, temperature, and density (σt) 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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