Supporting Information for

Limits on marine carbon dioxide removal potential set by coastal air-sea gas exchange rates

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Text S1: Mathematic details on the alkalinity addition simulation

Background discrete measurements for dissolved inorganic carbon (DIC), total alkalinity (TA), temperature and salinity were collected within Hvalfjörður in April 2024. Focussing on measurements within the surface layer (<10 m), these parameters were used to calculate partial pressure values of CO_2 using CO2SYS (version 01.05 - Lewis and Wallace, 1998). This resulted in the following parameter values at the sampling station located within the narrows close to the head of the fjord.

Mean TA (upper 10m): 2251.8 ± 50 µmol/kg

Mean DIC (upper 10m): 2045.9 ± 50 µmol/kg

Mean pCO_2 (upper 10m): 257.98 ± 30 µatm

Mean Temperature (upper 10m): 5.68 °C

Mean Salinity (upper 10m): 33.4161 PSU

In order to simulate an alkalinity addition to the local fjord water, we added 30 µmol/kg to all discrete TA measurements, which resulted in a decrease in the local pCO$_2$ to 223.2 ± 30 µatm at the location in the narrows.

Mean atmospheric CO_2 measurements from April 2024 in Iceland, being recorded as 428.6 ppm, were converted to partial pressure values at the sea surface using the following equation:

$$pCO_2 = xCO_2 * (p_{atm} - p_{H2O}),$$

with the water pressure being calculated as in Weiss & Price 1980.

$$ln(p_{H2O}) = 24.4543 - 67.4509 * (\frac{100}{Mean\ Temp + 273.15}) - 4.8489$$

$$* \, ln(\frac{Mean\,Temp + 273.15}{100}) - 0.000544 * Mean\,Salinity$$

and

$$p_{atm} = 1atm$$

This attend in atmospheric pCO$_2$ values above the sea surface of 424.8 µatm, which resulted in a thermodynamic concentration gradient of -166.8 µatm using the background pCO$_2$, and of -201.6 µatm when considering the pCO$_2$ value present in the surface water after the simulated alkalinity enhancement, respectively.

ΔpCO$_2$ = 258 – 424.8 = -166.8 µatm (background concentration)

ΔpCO$_2$ = 223.2 – 424.8 = -201.6 µatm (alkalinity enhancement)

Including the solubility for CO$_2$ in seawater, according to Weiss (1974), the flux was calculated using varying k$_{600}$ parameterization for different wind speeds.

$$F_{CO2} = k_{600} * K_0 * \Delta pCO_2$$

with

$$ln(K_0) = A1 + A2(\frac{100}{Mean\,Temp\ +\ 273.15}) + A3 * ln(\frac{Mean\,Temp\ +\ 273.15}{100})$$

$$+Mean\,Salinity[B1 + B2(\frac{Mean\,Temp + 273.15}{100}) + B3(\frac{Mean\,Temp + 273.15}{100})^2]$$

with

A1 = -58.0931; A2=90.5069; A3=22.2940; B1=0.027766; B2=-0.025888; B3=0.0050578

Text S2: Residence time analysis of water within Hvalfjörður

The surface water residence time within Hvalfjörður is based on the inventory analysis of SF_6 concentrations over time. It includes detailed investigation of the water volume within Hvalfjörður, based on bathymetry data provided from the Icelandic coast guard (see Fig. S2.1) and results from underway surface measurements of SF_6 throughout the experimental timeframe.

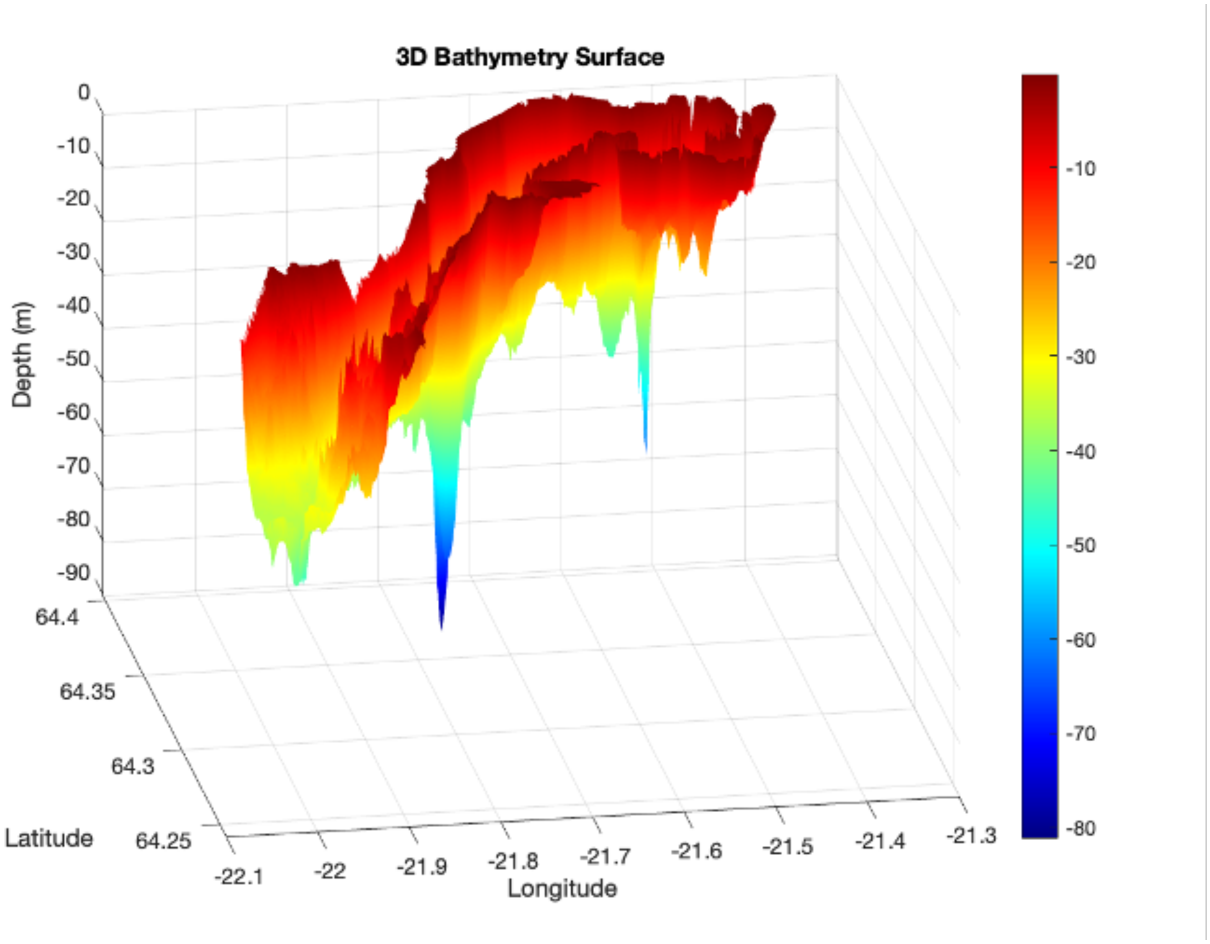

Fig. S2.1: Interpolated 3D bathymetry surface of Hvalfjörður from measurements provided by the Icelandic coast guard.

The volume of water within Hvalfjörður was computed to be approximately 3.08 km^3.

Interpolating the measured scattered surface water concentrations to cover the fjord surface area (see Fig. S2.2a) and estimating the vertical spread of the tracer throughout the water column from discrete water samples of SF_6 measured twice a day at various depths, the inventory of SF_6 (mols of SF_6) within Hvalfjörður each day was computed (see Fig. S2.2b and S2.2c). As the concentrations decrease towards the bottom of the fjord, mean depths were considered to represent a uniform distribution of surface water concentrations to calculate the moles of SF_6 present within the fjord.

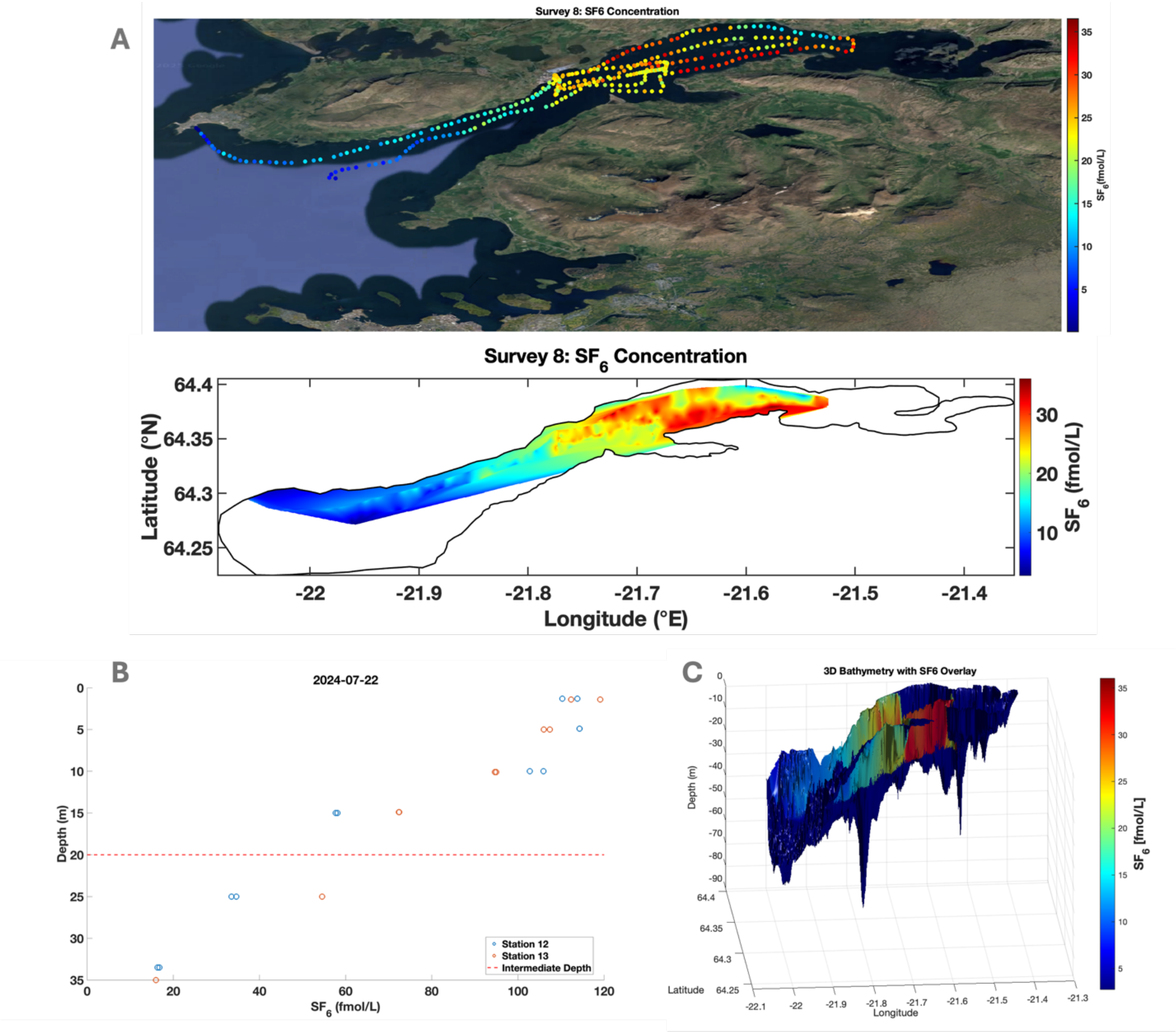

Fig. S2.2: (A) Example for survey 8 following the tracer injection showing the measured surface water concentrations during the survey (top panel) and the interpolation onto the fjords surface area (bottom panel). (B) Example of discrete measurements on July 22nd visualizing the decreasing concentration by depth. The red dotted line represents the mean depth that day, considered in the calculation of the SF_6 inventory within the fjord, representing the depth of an estimated uniform distribution of surface water concentrations. (C) 3D view on the SF_6 concentrations present within Hvalfjörður, calculated from the surface distribution and the mean depth determined from the discrete samples.

As this inventory decrease, based on the SF_6 concentration change over time, includes the flushing rate of water out of the fjord and the outgassing of SF_6 into the atmosphere over time, we analyzed the rate of the air-sea gas exchange portion to compute the residence time solely based on the flushing rate. Including the wind speeds and current velocities measured over the stretch of the experiment and considering two different parameterizations to calculate the gas flux resulted in a residence time of the fjord water being ~3.7/3.8 days based only on the flushing rate (see Fig. S2.3). Due to uncertainties in the calculation, caused by the interpolation of the scattered surface water measurements and estimated vertical distribution, the residence time is approximately 4 days. The outgassing factor was calculated once by using the gas transfer velocity from a coastal seagrass system to calculate the flux (Dobashi and Ho, 2023) and once based on the parameterization of k determined in this study. From the resulting inventory decrease, based only on the flushing rate, the mean residence time of water within the fjord was calculated from the exponential decay by analyzing the e-folding time.

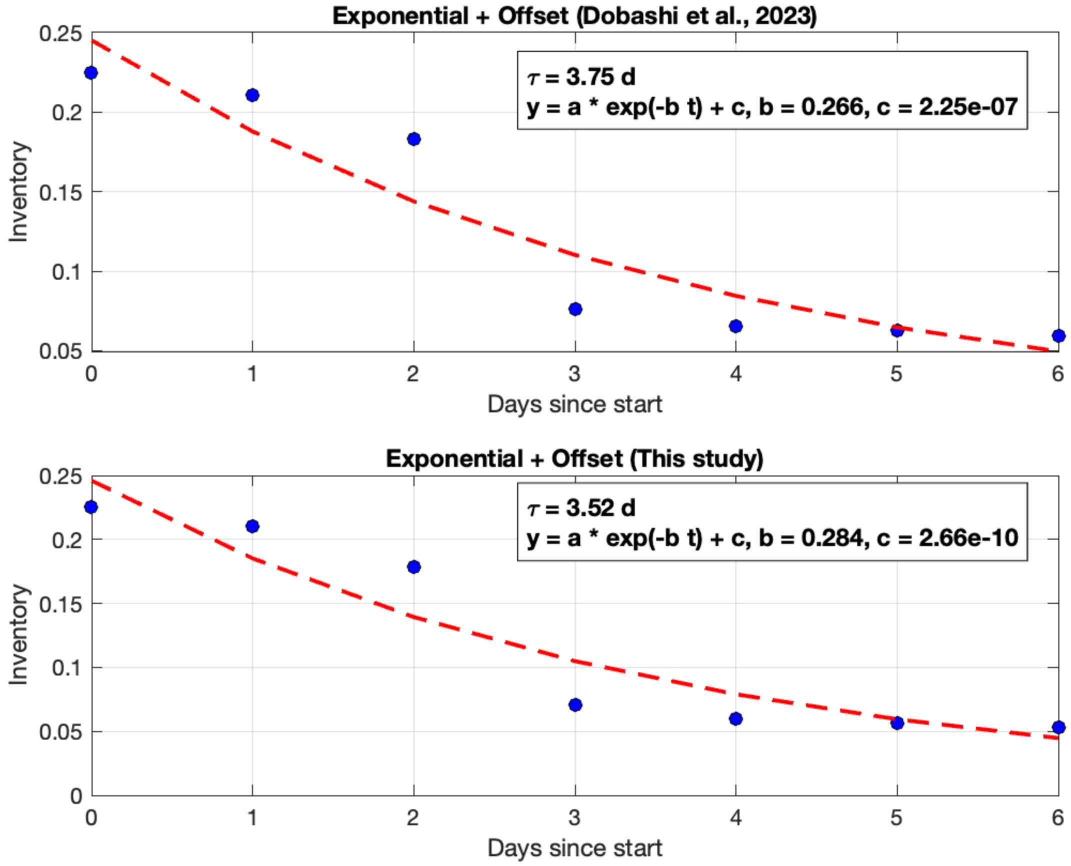

Fig. S2.3: Calculated inventories, solely based on the flushing rate after extracting the air-sea gas exchange using the parameterization from Dobashi et al., 2023 (upper panel) and the parameterization reported in this study (lower panel). The exponential decay over time is used to calculate the residence time, τ.

Text S3: One-box model description for Hvalfjörður

To evaluate the influence of *k* and varying subduction scenarios on the efficiency of alkalinity-driven CO_2 uptake in Hvalfjörður, we implemented a simplified one-box model (see Fig. S3.1). The model tracks the fraction of an artificially created surface water CO_2 disequilibrium that equilibrates with the atmosphere during a typical fjord residence cycle, accounting for carbonate-system buffering. Further, this is extrapolated over a one-year period to estimate the alkalinity addition (ΔTA) required to achieve a target CO_2 removal of 1 Gt CO_2 yr^{-1} under different *k* parameterizations used for the air-sea gas exchange rate and subduction scenarios once the water exits the fjord.

The one-box framework assumes a homogeneous surface mixed layer of depth *h* (5 m), exchanging CO_2 with the atmosphere according to a first-order process controlled by *k* (m s^{-1}). Because only a small fraction of total DIC exists as dissolved CO_2, the effective equilibration rate is reduced by carbonate buffering. The fraction of an initial air–sea CO_2 disequilibrium that equilibrates within a time *t* is expressed as:

$$f(t) = 1 - e^{-kBt/hR}$$

where *f(t)* represents the fraction of the CO_2 perturbation removed from the surface layer by air–sea gas exchange during the residence time *t*, *B* is the Revelle factor and *R* the ionization fraction of DIC. This formulation assumes constant *k* and *h* and neglects any temporal changes in surface water conditions over a single residence time cycle.

The model assumes a residence time of four days for surface water in Hvalfjörður, corresponding to the timescale over which approximately 67% of surface water is exchanged with offshore water. The total number of such exchange cycles per year is therefore *N* = 365 / 4 ≈ 91.25. The amount of CO_2 taken up per m^2 of surface area during one cycle (U_{cycle}) is given by:

$$U_{cycle} = h * \Delta C \ * f(t)$$

where ΔC_0 represents the initial CO_2 mole fraction difference between the atmosphere and the ocean (µmol m^{-3}), calculated from a simulated baseline perturbation in TA of 30 µmol kg^{-1} using CO_2SYS, causing a change in pCO_2 in the water.

To calculate the total annual uptake, the model sums in-fjord equilibration during each residence time cycle and offshore equilibration of exported water, taking into account the remaining time in the year available for each exported parcel to equilibrate, multiplying by the fjord surface area (A):

$$U_{fjord} = \sum_{c=1}^{N} (U_{in-fjord,c} + U_{offshore,c}) * A$$

For all exported surface water, offshore air-sea CO_2 exchange is calculated using the open ocean gas transfer velocity parameterization of Ho et al. (2006), independent of the parameterization applied within the fjord.

To explore the impact of varying subduction scenarios, the model accounts for the fraction of unequilibrated water that is exported from the fjord but does not re-equilibrate with the atmosphere. The effective fraction (f_{eff}) combines the in-fjord equilibration fraction *f(t)* with the exported fraction that remains at the surface:

$$f_{eff} = f(t) + 0.67 * (1 - f(t)) * (1 - subduction)$$

Here, “subduction” represents the proportion of exported water that is permanently removed from the surface without atmospheric contact.

If subduction = 1, all exported disequilibrium is lost to the subsurface and if subduction = 0, all exported water remains at the surface and can fully equilibrate offshore given sufficient time.

The varying subduction scenarios considered were:

(i) 100% of the water subducts immediately after leaving the fjord, where only in-fjord equilibration counts towards removal,

(ii) 50% of the water subducts and the other half is exported at the surface for further equilibration in the Atlantic, considering the time remaining in the year after each cycle, and

(iii) 0% subducts, where all fjord outflow remains in contact with the atmosphere offshore, allowing continued equilibration for the remainder of the year.

The alkalinity addition required to achieve a target global removal of 1 Gt CO_2 yr^{-1} (*M_target* = 2.272 × 10^{13} mol CO_2 yr^{-1}) is then derived by scaling the baseline alkalinity perturbation (ΔTA_0 = 30 µmol kg^{-1}) according to the modeled fjord uptake:

$$\Delta TA_{required} = \Delta\, TA_0 * \frac{M_{target}}{U_{fjord}}$$

This linear relationship assumes that CO_2 uptake scales proportionally with the imposed alkalinity perturbation, an approximation that holds for the small perturbations used here but might vary with higher perturbations.

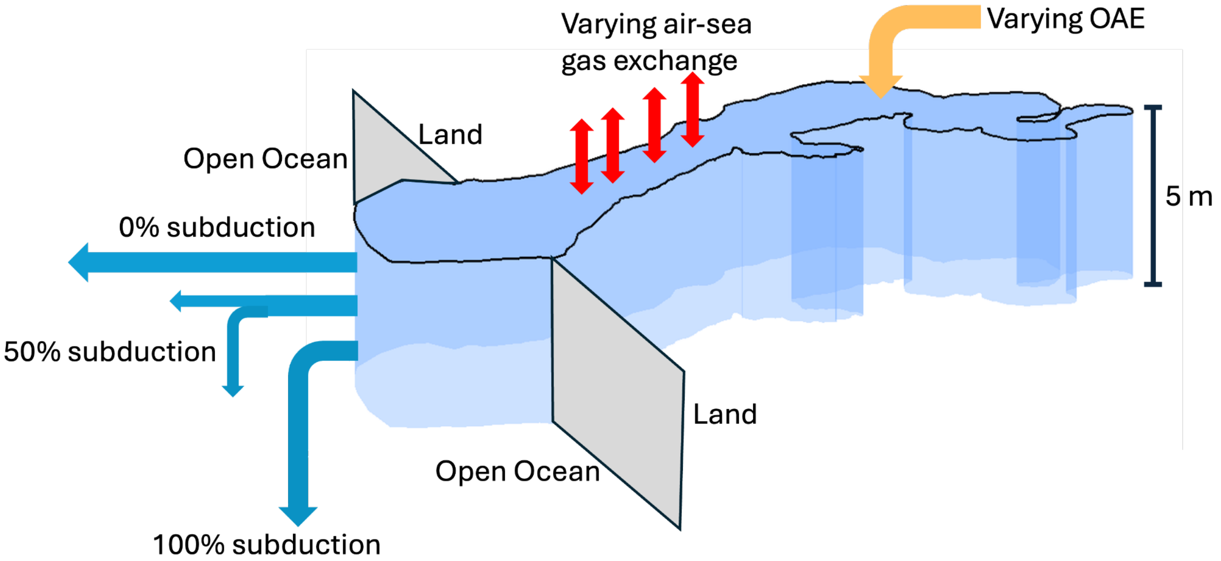

Fig. S3.1: Display of the implemented one-box model of Hvalfjörður, including a possible OAE and the different subduction scenarios, once the water enters the open ocean.

Text S4: One-box model example for Ho et al. (2006) with 100% subduction

The following example illustrates the one-box calculation for the *k* parameterization of Ho et al. (2006), assuming 100% subduction (i.e., exported water does not equilibrate offshore). This represents the lowest possible gas-exchange efficiency scenario for this given *k*.

<u>Relevant parameters for the calculation:</u>

Seawater density: ρ = 1026.2 kg m^{-3}

Mixed layer depth: h = 5 m

Fjord volume: V = 3.08 * 10^{9} m^{3}

Fjord surface area: A = V/h = 6.16 * 10^{8} m^{2}

Residence time: t = 4days = 345600 s

Exchange rate: 0.66 (66%)

Cycles per year: N = 365/4 = 91.25

Baseline alkalinity perturbation: ΔTA_0 = 30 μmol kg^{-1}

Corresponding mole fraction difference: ΔC_0 = -10.63 μmol kg^{-1}

Target CO_2 removal in one year: M_{target} = 2.272 * 10^{13} mol yr^{-1} = 2.272 * 10^{19} μmol yr^{-1}

k parameterization: $k = 0.266 * u_{10}^2$ (Ho et al., 2006)

Wind speed: u_{10} = 5 m s^{-1}

Schmidt number for CO_2 under baseline conditions (T = 5.68 °C & S = 33.4161 PSU):

Sc_{CO2} = 1472 (Dobashi and Ho, 2023)

Schmidt exponent: n = 0.5

Schmidt exponent: n = 0.5

Carbonate chemistry inputs: DIC = 2045.9 µmol/kg, TA = 2251.8 µmol/kg, pCO_2 = 257.98 µatm

Revelle factor: B = 11.9 (calculated from mean DIC, TA, T and S using CO2SYS)

Ionization fraction: R = 154 (computed from R = DIC / (K_0 * pCO_2))

Step 1 — Determine gas-transfer velocity (k)

The open-ocean parameterization from Ho et al. (2006) gives:

$$k_{600} = 0.266 * u_{10}^2 = 0.266 * 5^2 = 6.65\ cm\ h^{-1}$$

Converted to m s^{-1} and corrected for temperature via the Schmidt number:

$$k = \frac{6.65}{100*3600} * (\frac{Sc_{CO2}}{600})^{-1/2} = 1.18 * 10^{-5} m\ s^{-1}$$

Step 2 — Fraction equilibrated during residence time

$$f(t) = 1 - e^{-kBt/hR} = 1 - exp(-\frac{1.18 * 10^{-5} * 11.9 * 345600}{5 * 154}) = 0.0609$$

This means 6% of the surface disequilibrium equilibrates with the atmosphere during one 4-day cycle under the consideration of the open ocean parameterization for gas exchange from Ho et al. (2006).

Step 3 — Per-cycle CO_2 uptake per unit area

The volumetric CO_2 perturbation is:

$$\Delta C_{vol} = \Delta C_0 * \rho = 10.63 * 1026.2 = 10909\ \mu mol\ m^{-3}$$

$$U_{cycle} = h * \Delta C_{vol}\ * f(t) = 5\ m * 10909\ \mu mol\ m^{-3} * 0.0609 = 3319.9\ \mu mol\ m^{-2}$$

Step 5 — Total fjord uptake per year

$$U_{fjord} = \frac{365}{4} *\ A *\ U_{cycle} = \frac{365}{4} * (6.16\ *\ 10^{8}\ m^{2}) * 3319.9\ \mu mol\ m^{-2} = 1.87 * 10^{14} \mu mol\ yr^{-1}$$

Step 6 — Required alkalinity addition

$$\Delta TA_{required} = \Delta\ TA_0 * \frac{M_{target}}{U_{fjord}} = 30\ \mu mol\ kg^{-1} * \frac{2.272 * 10^{19} \mu mol\ yr^{-1}}{1.87 * 10^{14} \mu mol\ yr^{-1}} = 3.65\ *\ 10^{6}\ \mu mol\ kg^{-1}$$

Step 7 — Conversion to µmol m^{-3}

$$\Delta TA_{required,vol} = \Delta\ TA_{required} * \rho = 3.65\ * 10^{6}\ \mu mol\ kg^{-1} * 1026.2\ kg\ m^{-3}$$

$$= 3.75\ *\ 10^{9} \mu mol\ m^{-3}$$

Text S5: Details on Station selection for determining k_{600}

From a total of 19 Stations set up during the experiment to collect tracer samples at various depths, the first two served to gather background samples and were therefore not included in the estimation of *k*. Furthermore, until station 7 (approximately 48 h after the injection), the tracers were not yet well mixed throughout the mixed layer depth (MLD), as indicated by high variability in the measured $^3He/SF_6$ ratios within the tracer profiles. Consequently, Stations 3-6 were excluded from the determination of *k*. In addition, instrument malfunction would have led to a discard of the Stations 3 & 4 regardless.

As described in the main text, the MLD was determined from smoothed CTD profiles, best characterized using buoyancy anomalies (Stevens et al., 2011) and the selection of stations used for determining *k* was based on the following four criteria:

1) Clear stratification within density, temperature, and salinity profiles
2) Both tracers show a similar profile pattern, with decreasing or increasing concentrations with depth
3) Consistent or minimally varying $^3He/SF_6$ ratios within the determined MLD
4) A decrease in both tracer concentrations and the ratio compared to the previous station, ensuring that sampling occurred within the center of the patch.

All selected criteria were met at stations 7, 10, and 12. Stations 8, 15, 18, and 19 fulfilled all criteria except for the stratification; however, including them in the parameterization improved the results. Station 9 was excluded because the SF_6 tracer concentration of the samples included in the parameterization increased compared to Station 8, while ^3He decreased. The same applied to stations 14, 16, and 17, where both tracer concentrations and/or the ratio increased towards the following station. Finally, stations 11 and 13 were not included, as they neither improved the parameterization nor showed good stratification, had varying tracer profiles, and in terms of station 11, the ratio increased by a lot from station 10.

This resulted in stations 7, 8, 10, 12, 15, 18, and 19 being included in the parameterization of *k*.

Text S6: CTD data quality control

The temperature, conductivity, and pressure data from the upcast of each profile was used for analysis in this study, as the downcast did not allow sufficient time for the sensors to equilibrate. During the upcast, the CTD was periodically stopped for water sampling, resulting in flat plateaus in the profiles (see Fig. S6.1). To address this issue, the data were smoothed at increments of 0.15 m for each CTD station, spanning the shallowest to the deepest measurement at each station. The mean of all CTD measurements within a ±0.1 m range was then assigned to the corresponding depth value. Finally, the data were smoothed, as in Saito et al. (2007), using a seven-point median filter, followed by vertical smoothing with a three-point Hanning filter applied twenty times.

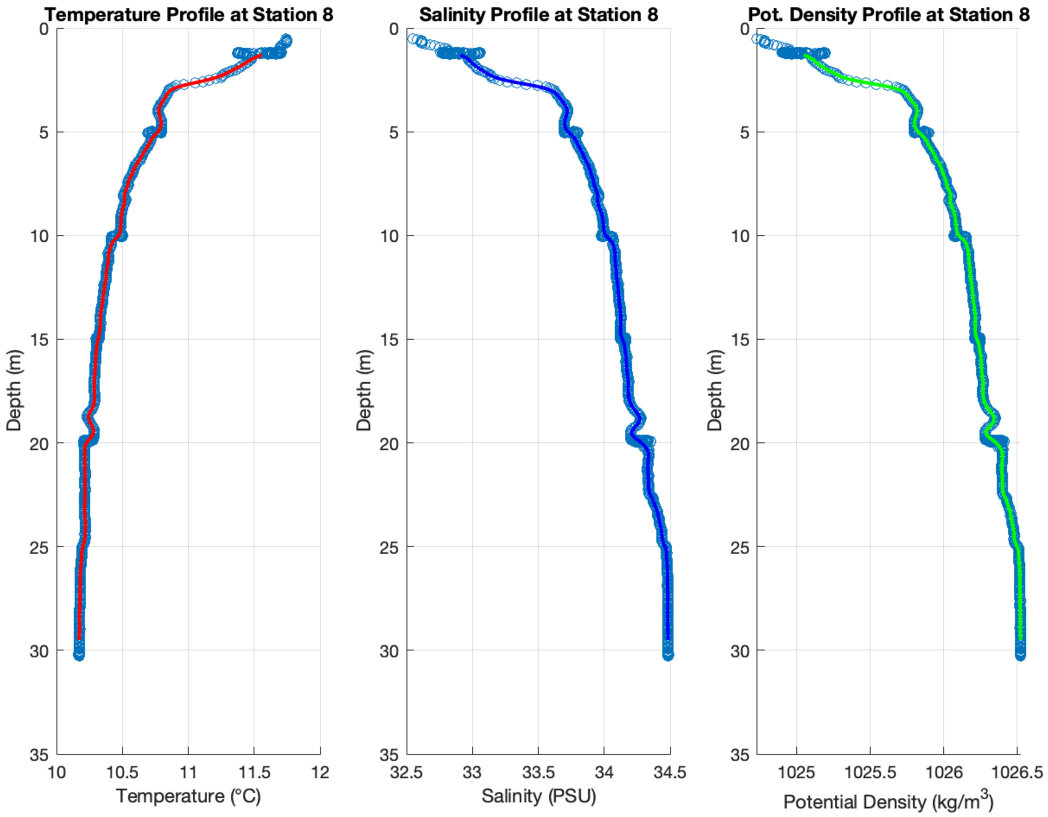

Fig. S6.1: Display of the raw CTD data points and smoothed data (solid lines), as an example at station 8.

Figures:

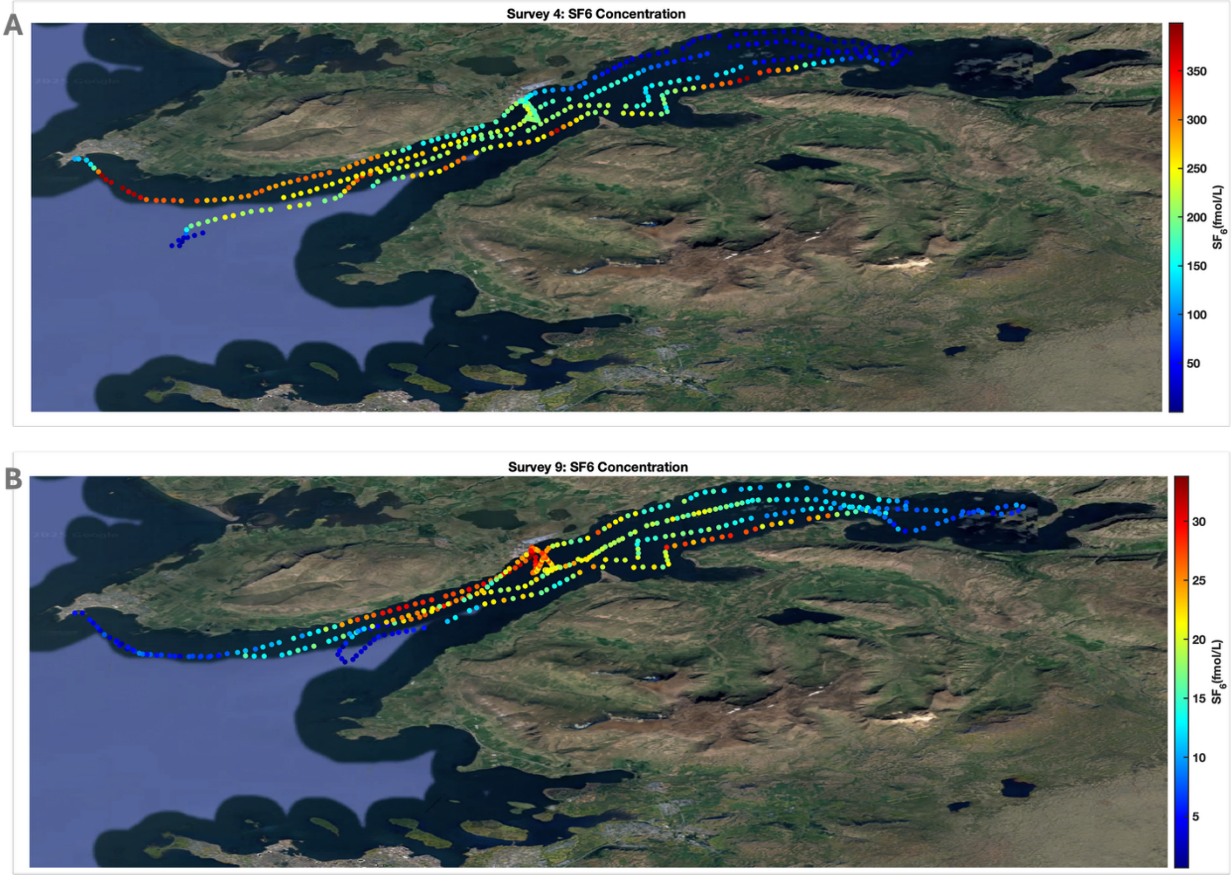

Fig. S7: Measured underway SF_6 tracer concentration after (A) 96h (Day 4) following the release and (B) after 216h (Day 9) following the release. The color represents concentration variability, with red dots indicating high concentrations and blue dots low concentrations, relative to the maximum concentration measured that day.

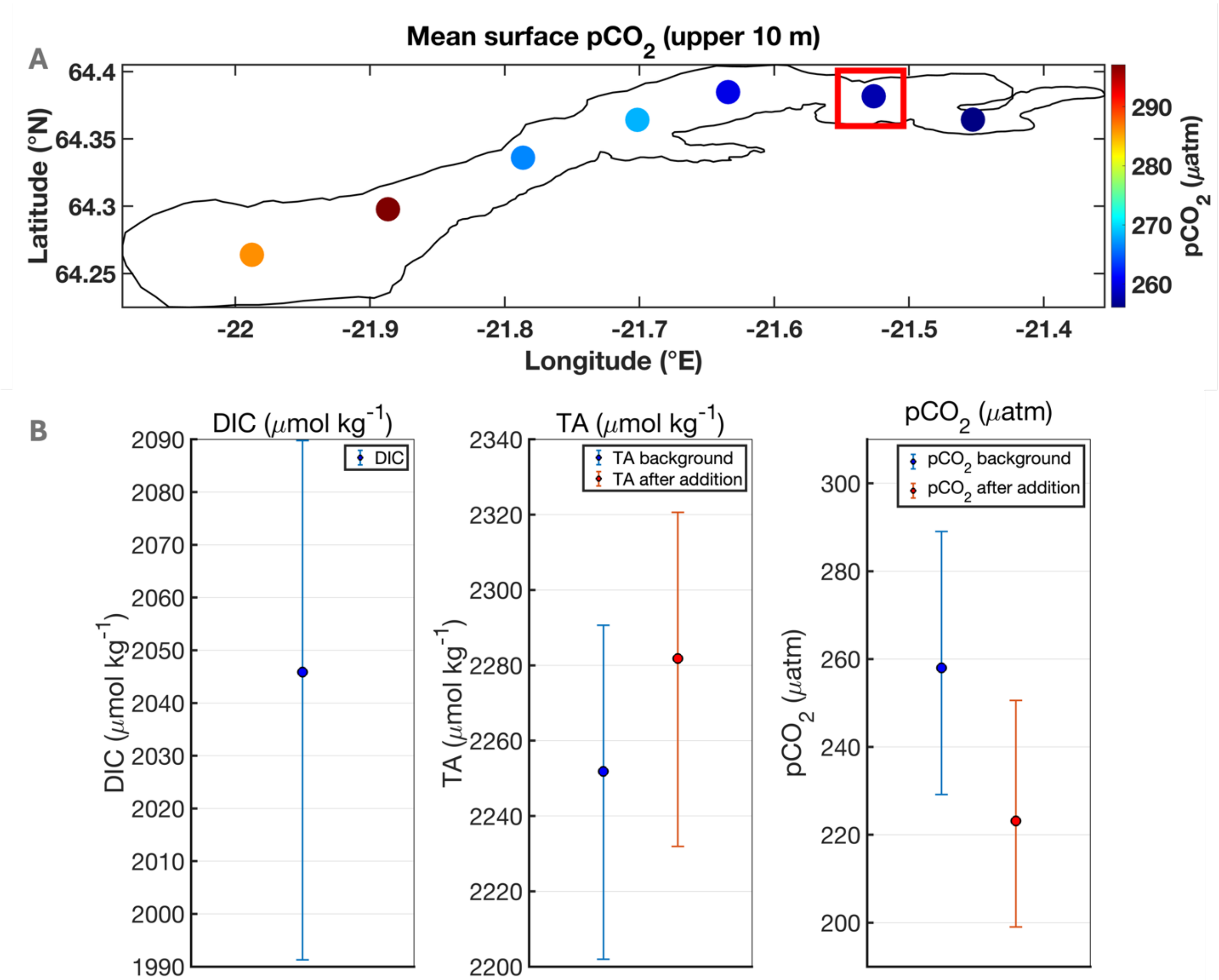

Fig. S8: (A) Calculated pCO_2 from DIC and TA samples collected in the upper 10 m within Hvalfjörður in April 2024. (B) Variability in DIC and TA measurements from the upper 10 m in April 2024 in the narrows of Hvalfjörður (red box in Figure A), shown in blue. The simulated TA addition of 30 µmol/kg is shown in red, along with the resulting pCO_2 values calculated using CO2SYS.

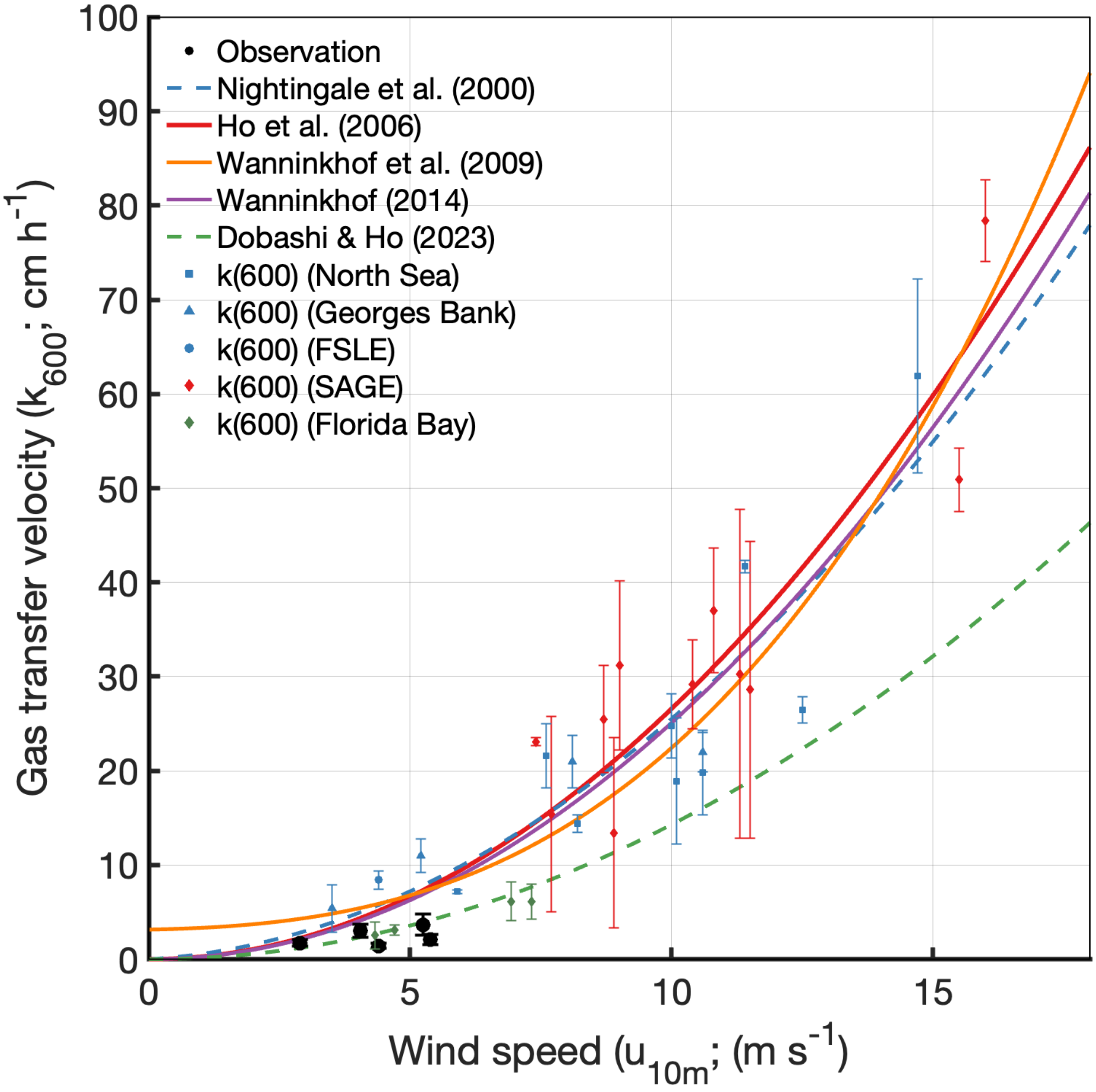

Fig. S9: Observed k_{600} values (cm h^{-1}) with correlating wind speeds at 10 m height (m s^{-1}). Published open-ocean parameterizations are shown in solid lines, and coastal parameterizations in dashed lines, with historic data points included in the corresponding parameterization in the same color.