

Mechanisms of air-sea CO₂ exchange in the central Baltic Sea

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Abstract Air-sea gas exchange regulates the cycling of climate-relevant gases such as carbon dioxide (CO₂), yet significant uncertainties remain in its quantification. The gas transfer velocity (K), a key parameter for estimating CO₂ flux, is usually expressed as a function of wind speed (U_{10N}). This approach overlooks the role of fetch and surfactants, which can substantially affect K . However, no field study has systematically quantified their combined effects under fetch-limited and surfactant-abundant ocean conditions. To fill this research gap, we conducted air-sea gas exchange studies during a cruise in the central Baltic Sea, a system with high surfactant levels and a short fetch. We report independent determinations of K using eddy covariance (EC) and dual-tracer (³He/SF₆) techniques, together with direct measurements of natural surfactants and modelled wave parameters. Both methods yield consistent results; however, EC-based CO₂ transfer velocities are, on average, 33% lower than those reported in previous EC studies in the open ocean. Sea-state-dependent parameterisations indicate that limited fetch reduces K by 8%, while elevated surfactant concentrations may have contributed to the additional 25% reduction. We developed an updated parameterisation that includes wind stress, sea state, and surfactants. When applied to climatological forcing, it yields a 40% stronger seasonal cycle (greater oceanic uptake during summer and enhanced outgassing during winter) of CO₂ flux in the Baltic Sea than obtained with the conventional U_{10N} -based parameterisation. These findings highlight the need to move beyond

29 U_{10N} in parameterising K and estimating regional fluxes, especially when evaluating the potential
30 of marine carbon dioxide removal (mCDR) in coastal seas.

31 **Short summary** Air-sea gas exchange regulates the Earth’s climate. However, the description of
32 the kinetic exchange process only uses wind speed, neglecting other drivers. In this study, we
33 investigate how fetch and natural surfactants modulate air-sea carbon dioxide exchange.
34 Measurements from the central Baltic Sea show that limited fetch and elevated surfactants
35 significantly suppress this exchange. A new parameterisation is provided, improving regional
36 carbon budgets and evaluations of climate solutions.

37

38 1. Introduction

39 The ocean is a major sink of carbon dioxide (CO_2) emitted by human activities, substantially
40 mitigating climate change (Friedlingstein et al., 2025). Beyond its natural carbon uptake capacity,
41 marine-based carbon dioxide removal (mCDR) has emerged as a climate mitigation approach
42 under ongoing global warming (Doney et al., 2024). Accurate quantification of global ocean
43 carbon flux and the regional mCDR efficiency is essential for climate predictions. Air-sea CO_2
44 flux is often estimated using the bulk formula:

$$45 \quad F = K_{660} \left(\frac{Sc}{660} \right)^{-n} (\alpha_w f\text{CO}_{2w} - \alpha_i f\text{CO}_{2a}) \quad (1)$$

46 where F ($\text{mmol m}^{-2} \text{ day}^{-1}$) is the air-sea CO_2 flux, K_{660} (cm h^{-1}) is the gas transfer velocity
47 normalized to a Schmidt number (Sc) of 660, corresponding to CO_2 in seawater at 20°C . The value
48 of the exponent n is between $1/2$ and $2/3$ (Jähne et al., 1987), and is often assumed to be $1/2$ in the
49 ocean environment (Wanninkhof et al., 2009). CO_2 solubilities (e.g., $\text{mol L}^{-1} \text{ atm}^{-1}$) at the base of
50 the mass boundary layer and at the air-sea interface are α_w and α_i , respectively. CO_2 fugacity ($f\text{CO}_2$,
51 μatm) at these locations is $f\text{CO}_{2w}$ and $f\text{CO}_{2a}$. Sc and α depend on water temperature and salinity
52 (Wanninkhof, 2014; Weiss, 1974). Notably, if both the CO_2 flux and $f\text{CO}_2$ are known, K_{660} can be
53 derived.

54 Equation 1 highlights the central role of K_{660} as the kinetic forcing parameter in air-sea CO_2
55 exchange. K_{660} is directly driven by near-surface turbulence (Garbe et al., 2014). On a global scale,
56 wind forcing has a dominant effect on gas transfer velocity, and other factors, such as friction

57 velocity, waves, and bubbles, are strongly linked with wind speed (Wanninkhof et al., 2009). Thus,
58 the readily available 10-meter neutral wind speed (U_{10N}) is often used as the sole variable for
59 parameterising K_{660} (e.g., Ho et al., 2006; Nightingale et al., 2000; Wanninkhof, 2014). However,
60 wind is not the only factor driving gas exchange, as other factors not fully linked to wind speed
61 can substantially influence this exchange at regional scales, particularly in the coastal ocean
62 (Upstill-Goddard, 2006). Existing U_{10N} -based K_{660} formulations in the Baltic Sea yield
63 controversial results (e.g., Gutiérrez-Loza et al., 2022; Kuss et al., 2004), highlighting the lack of
64 mechanistic understanding of air-sea gas exchange.

65 Surfactants are surface-active compounds, molecules, or biomolecules. They are ubiquitous in the
66 ocean and often highly concentrated in coastal waters through biological production and terrestrial
67 inputs (Mustaffa et al., 2020; Sabbaghzadeh et al., 2017; Wurl et al., 2011), suppressing gas
68 exchange by damping surface turbulence and forming an additional diffusion barrier (McKenna
69 and McGillis, 2004; Pereira et al., 2016). In contrast, wave breaking enhances gas transfer,
70 especially for low-soluble gases, by introducing bubbles as an exchange pathway in addition to
71 the interfacial exchange route (Bell et al., 2017; Blomquist et al., 2017; Dong et al., 2025; Woolf,
72 1997). Wave breaking is strongly impacted by wind fetch (defined as the distance over which wind
73 acts on the water surface), because limited fetch suppresses wave breaking and bubble generation
74 (Fairall et al., 2006; Kunz and Jähne, 2018; Ocampo-Torres and Donelan, 1995; Prytherch and
75 Yelland, 2021; Woolf, 2005). Understanding how these mechanisms influence air-sea gas
76 exchange is essential for regional (coastal) carbon budgets and for developing robust monitoring,
77 reporting, and verification (MRV) frameworks to support mCDR strategies (e.g., Ho et al., 2023).

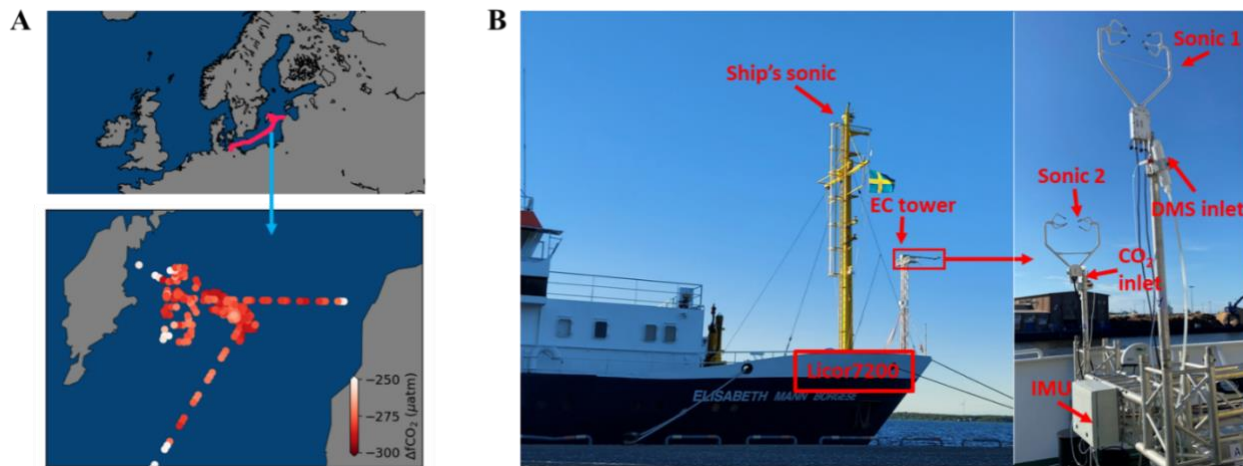
78 The Baltic Sea, with its high summer primary productivity (Schmidt and Schneider, 2011) and
79 limited fetch, provides an ideal natural laboratory for investigating the combined effects of
80 surfactants and fetch on air-sea gas exchange. We therefore conducted a comprehensive gas
81 exchange experiment in the central Baltic Sea to quantify the impact of factors additional to wind
82 speed on gas exchange.

83 **2. Methods**

84 **2.1 CenBASE cruise**

85 The Central Baltic Air-Sea Exchange Experiment (CenBASE; EMB 295) was conducted in
86 summer 2022, immediately after the phytoplankton bloom season, to capture strong air-sea gas
87 exchange signals (Parard et al., 2016; Bittig et al., 2024). The research cruise on the *R/V Elisabeth*
88 *Mann Borgese* (EMB) departed from Rostock, Germany, on 2 July and returned on 18 July, with
89 the primary study area located in the Gotland Basin (Fig. 1A).

90 Eddy covariance (EC) CO₂ flux observations (Section 2.2) and the ³He/SF₆ dual-tracer experiment
91 (see Appendix A1) were performed simultaneously to determine gas transfer velocities,
92 representing the second successful joint deployment of these two approaches after GasEx-98 (Ho
93 and Wanninkhof, 2016; McGillis et al., 2001). Surfactant samples were collected from both the
94 microlayer and underlying water (see Appendix A2). Wave parameters were extracted from the
95 ERA5 hourly reanalysis data product (0.5° × 0.5°) (Hersbach et al., 2020) based on the cruise
96 track's spatiotemporal coordinates. Additional measurements included *f*CO₂, sea surface
97 properties, and meteorological variables to support the analysis.



98
99 **Figure 1: CenBASE cruise tracks and the ship-based eddy covariance (EC) system.** Left panel: Cruise
100 tracks in the central Baltic Sea, color-coded by air-sea CO₂ fugacity differences (Δ*f*CO₂). Middle panel:
101 Research vessel EMB during the CenBASE cruise; a custom-built EC tower is mounted at the bow. Right
102 panel: Instruments mounted on top of the tower, including sonic anemometers, a motion sensor (IMU), and
103 the CO₂ inlet. Additional setup details are provided in Section 2.

104

105 2.2 Eddy covariance CO₂ flux measurements

106 The EC technique allows for direct measurements of air-sea CO₂ flux using the following equation:

$$107 \quad F = \rho \overline{w'c'} \quad (2)$$

108 where ρ is the mean molar density of dry air (in mole m⁻³), w is the vertical wind velocity (in m s⁻¹), and c is the dry air mole fraction of CO₂ (in ppm or $\mu\text{mol mol}^{-1}$). The primes denote the
109 fluctuations from the mean, and the overbar indicates time averaging. Due to the dynamic nature
110 of the marginal sea environment, a 10-minute averaging interval was chosen, shorter than the 20-
111 30 minutes typically used in the open ocean (e.g., Blomquist et al., 2017). The CO₂ transfer
112 velocity ($K_{660_CO_2}$) is derived by combining Equations 1 and 2. The EC momentum flux is similarly
113 calculated as $\rho \overline{w'u'}$, where u is the horizontal wind component. The friction velocity (u_*) is then
114 derived as the square root of the momentum flux magnitude.
115

116 Most components of the EC system were mounted on a custom-built tower at the bow of the ship
117 to minimize the flow distortion (Fig. 1B). The tower extended 5 m above the deck, reaching a
118 height of 14 m above mean sea level (MSL). A three-dimensional (3D) sonic anemometer
119 (CSAT3B, *Campbell Scientific*) was installed on the starboard arm to measure the wind
120 fluctuations, with a backup unit on the port side (CSAT3). An Inertial Measurement Unit (IMU,
121 *SBG Systems*), housed in a meteorological box at the top of the tower, recorded ship motion. The
122 IMU was positioned 66 cm from the starboard sonic and 173 cm aft of it. CO₂ fluctuations were
123 measured using a LI-7200 gas analyzer. The sampled air was dried with a Nafion dryer operating
124 in ‘reflux’ mode (Perma Pure LLC, 2024). Air was drawn from the port-side inlet through a ~10-
125 m Teflon tube (3/8" inner diameter) at a stable flow rate of $33.2 \pm 0.3 \text{ L min}^{-1}$, which results in
126 turbulent flow within the tube. The 20-Hz signal from the sonic anemometer, IMU, and LI-7200
127 was logged by a datalogger (CR6, *Campbell Scientific*).

128 Data processing and quality control procedures followed those described in Dong et al. (2021).
129 Briefly, motion corrections were applied to the wind (Edson et al., 1998; Miller et al., 2008) and
130 CO₂ signals (Miller et al., 2010) to remove contamination from ship motion. A nitrogen puff test
131 revealed a 0.3 s e-folding response time, which is used to correct the high-frequency attenuation
132 (Blomquist et al., 2014). The time delay (~2.5 s) between the inlet and the gas analyzer was
133 assessed via the maximum covariance method. Flow distortion was minimized by mounting the
134 EC tower arms beyond the ship's hull.

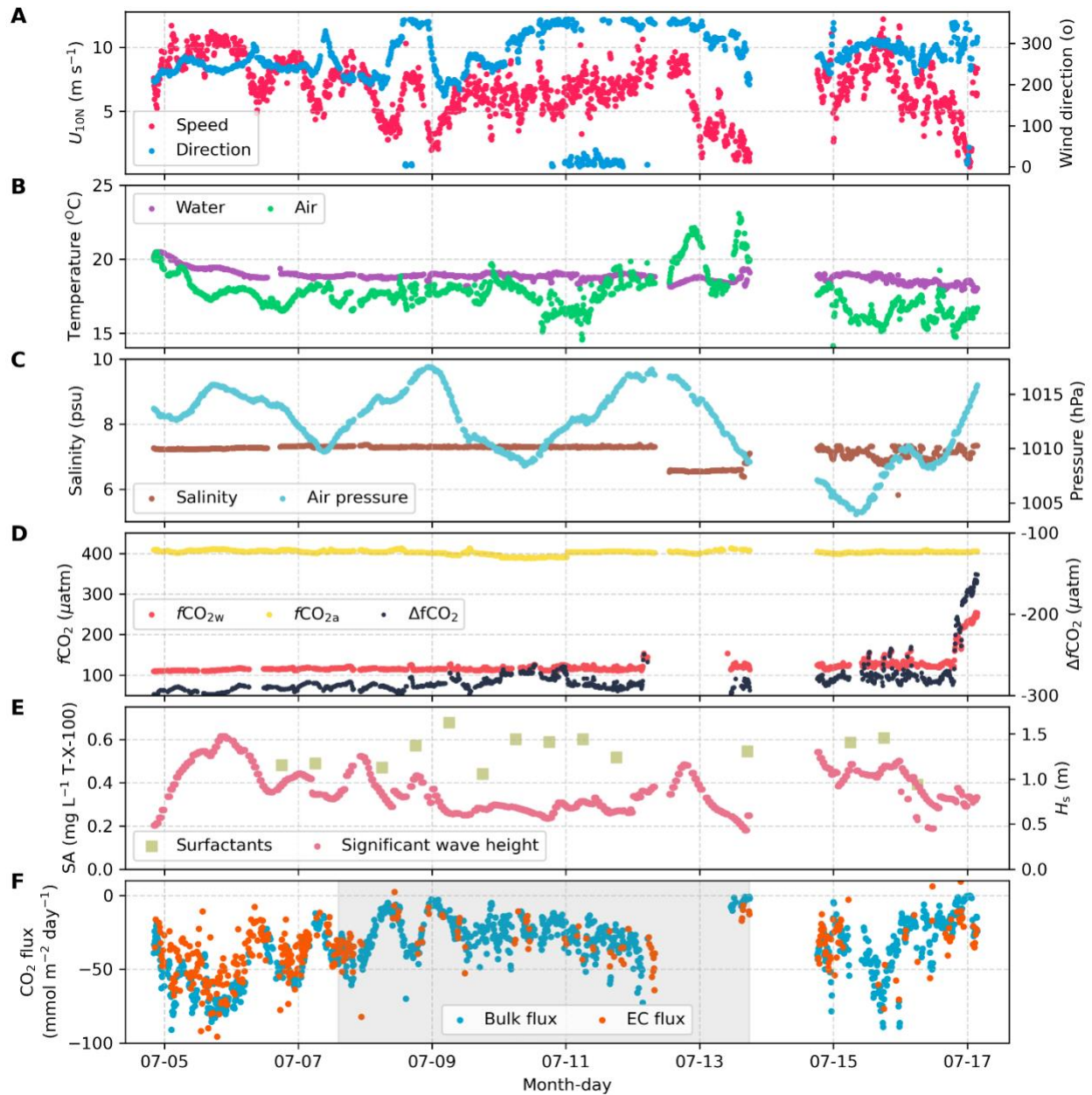
135 **2.3 Auxiliary observations**

136 The partial pressure of CO₂ in surface water was measured at 1-minute intervals using the Mobile
137 Equilibrator Sensor System (MESS) paired with two off-axis integrated cavity output laser
138 spectrometers (oa-ICOS, Los Gatos Instruments) (Sabbaghzadeh et al., 2021). Seawater was
139 continuously drawn from the ship's inlet at a depth of ~3.3 m. Atmospheric CO₂ was measured
140 daily using an air inlet mounted on the ship's foremast at 13.5 m above MSL. These air CO₂ data
141 are compared to the absolute CO₂ values measured by the EC gas analyzer (LI-7200, LI-COR, Inc.)
142 to generate the 10-min time series of atmospheric CO₂. Sensor calibration was performed almost
143 daily using standard gases from the Central Analytical Laboratories of the European Integrated
144 Carbon Observation System (ICOS RI). Mean wind measurements were obtained from a sonic
145 anemometer mounted 17 m above MSL on the ship's foremast to minimize flow distortion
146 (O'Sullivan et al., 2013). Residual distortion was corrected using the ERA5 reanalysis wind
147 product and nearby station records (see Appendix A3). Atmospheric pressure and temperature at
148 ~13.5 m MSL were recorded by the onboard weather station. Surface seawater temperature and
149 salinity were monitored by the ship's underway system and calibrated against CTD (conductivity,
150 temperature, and depth) casts. A spar buoy equipped with cameras and sensors for temperature,
151 salinity, and dissolved oxygen was deployed at several stations to characterize upper-ocean bubble
152 and water column dynamics.

153 In addition, EC air-sea CO₂ flux observations from previous open-ocean cruises (Yang et al., 2022)
154 are also used for comparison with the CenBASE results. Wave parameters were extracted from the
155 ERA5 analysis wave product according to these open-ocean EC cruise tracks (see Yang et al.,
156 2022) and the CenBASE cruise. The COARE model is used to estimate the bulk u_* (Edson et al.,
157 2013). For the open-ocean scenario, environmental variables from the corresponding cruises are
158 used as inputs to the COARE model (Yang et al., 2022). The environmental parameters observed
159 during the CenBASE cruise are used to estimate the Baltic Sea u_* in the COARE model.

160 **3. Results**

161 **3.1 Environmental variables and the CO₂ flux**



162

163 **Figure 2: Ten-minute averages of environmental variables and air-sea CO₂ flux.** A: Neutral 10-meter
 164 wind speed (U_{10N} , red) and wind direction (blue). B: Surface seawater temperature (purple) and air
 165 temperature (green). C: Seawater salinity (brown) and sea-level air pressure (light-blue). D: CO₂ fugacity
 166 in surface seawater (red) and atmosphere (yellow), and their difference ($\Delta f\text{CO}_2$, black). E: Surface
 167 microlayer surfactant activity (SA, light green squares) and significant wave height extracted from ERA5
 168 (H_s , red); F: Bulk CO₂ flux estimates (blue, based on K_{660} parameterisation from Ho et al., 2006) and EC
 169 CO₂ flux observations (orange). The dual-tracer tracing period is indicated by the light gray shading. Data
 170 are missing from 12-14 July due to a medical event and a temporary shortage of liquid nitrogen, which
 171 required the vessel to leave the primary study area.

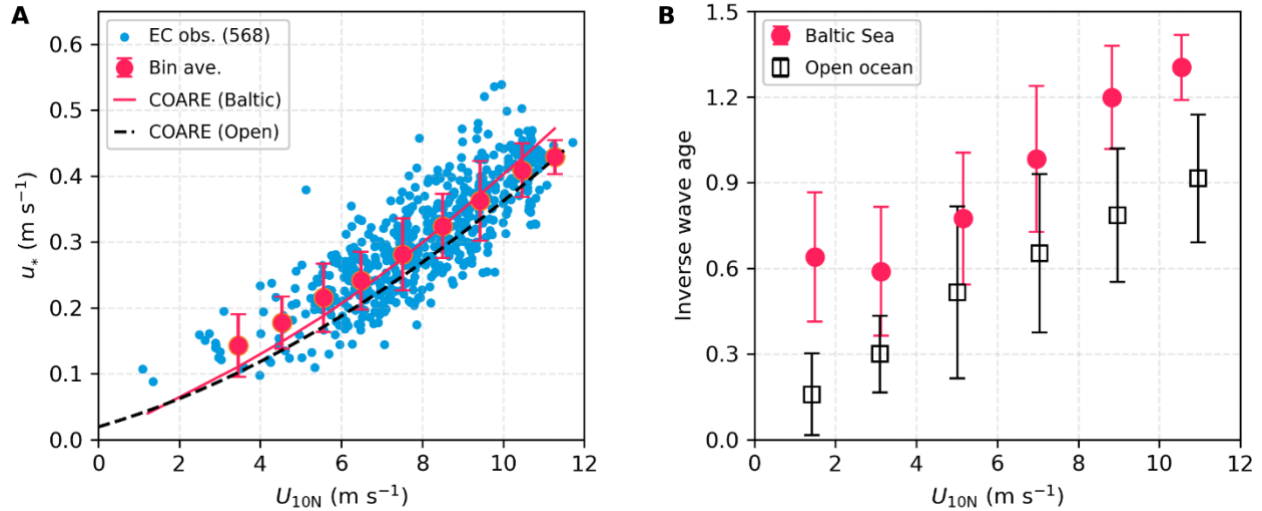
172 During CenBASE, winds predominantly originated from the west to north sector (Fig. 2A), with
173 an effective fetch of approximately 50-300 km in the main study area (Fig. A1, Appendix). The
174 wind speed ranged from 1 to 12 m s⁻¹ (Fig. 2A). Water depth across the central Baltic Sea study
175 site ranged from ~50 to 250 m. Surface water was generally warmer than the overlying air (Fig.
176 2B), resulting in an unstable boundary layer. Surface salinity remained consistent at approximately
177 7.3 throughout the study region (Fig. 2C). The cruise took place shortly after a summer
178 phytoplankton bloom, resulting in remarkably low sea surface *f*CO₂ (~120 μatm; Fig. 2D).
179 Atmospheric *f*CO₂ remained constant at ~403 μatm, creating a strong air-sea gradient ($\Delta f\text{CO}_2 \approx -$
180 280 μatm on average; Fig. 2D) that generated strong ocean CO₂ uptake signals.

181 Surface microlayer surfactant activity (SA), expressed as Triton-X-100 equivalents, was relatively
182 constant at 0.54 ± 0.08 mg L⁻¹ (Fig. 2E), significantly higher than typical open-ocean values (0.1-
183 0.2 mg L⁻¹; Mustaffa et al., 2020; Sabbaghzadeh et al., 2017). Modeled significant wave height
184 (H_s) remained below 1.5 m (Fig. 2E), lower than expected for comparable wind speeds in the open
185 ocean (Fig. A2). Bulk CO₂ fluxes estimated from the measured $\Delta f\text{CO}_2$ and an open-ocean dual-
186 tracer K_{660} parameterisation (Ho et al., 2006) were higher than observed EC fluxes under high
187 wind speeds and lower than observed EC fluxes under low wind speeds (Fig. 2F and Fig. A3).
188 During the tracer-tracking period (8-14 July), frequent ship heading changes reduced EC flux
189 quality, leading to most valid EC measurements being obtained from outside this period (Fig. 2F,
190 light-gray shading). Nevertheless, as both EC and dual-tracer were collected in the same study
191 area, the K from both methods can be reasonably considered simultaneous measurements.

192 **3.2 Friction velocity**

193 The friction velocity is a key parameter characterizing near-surface turbulence. Observed values
194 of u_* from EC momentum fluxes during CenBASE were 10% higher than modelled open ocean u_*
195 at the same wind speeds (Fig. 3A), likely reflecting fetch-related differences. The wave field in the
196 central Baltic Sea is much younger than in the open ocean, with wave age ~60% lower at the same
197 wind speed (Fig. 3B). The waves are shorter and steeper than in the open ocean (Fig. A2). This
198 wave field enhances sea surface roughness and elevates u_* relative to the open sea. u_* predicted by
199 the COARE3.6 model, when forced with observed environmental and extracted wave parameters
200 during CenBASE, broadly agrees with measurements (Fig. 3A). This suggests that the COARE
201 model remains applicable in fetch-limited marine environments when wave information is

202 included, despite being developed primarily from open-ocean observations (Edson et al., 2013).
 203 Given that u_* is an indicator of surface wind-induced turbulence, this elevated u_* is expected to
 204 enhance CO₂ transfer velocity (see Section 3.4).



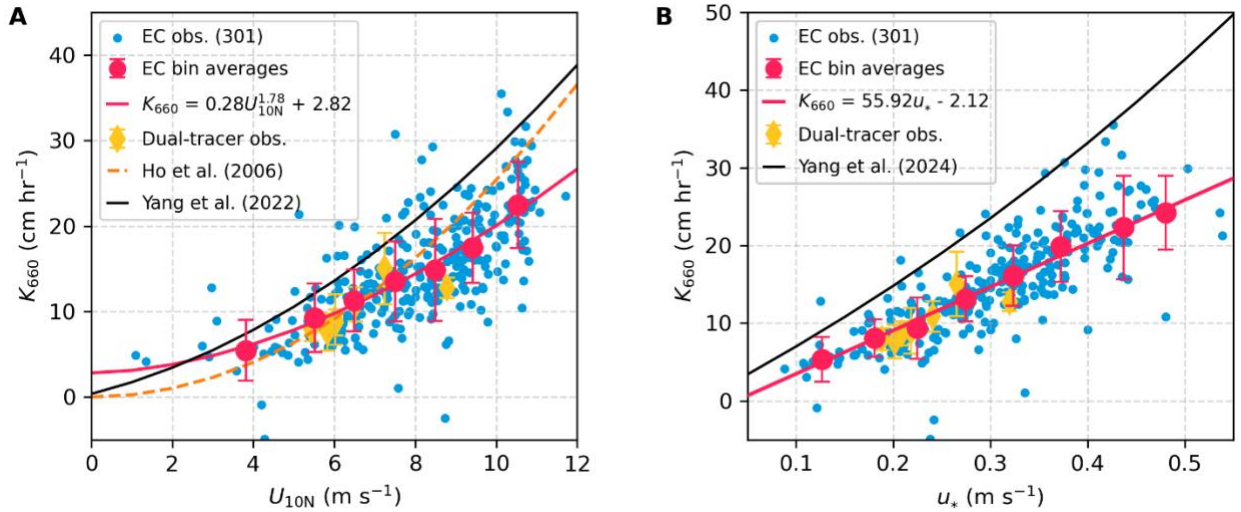
205
 206 **Figure 3: Friction velocity (u_*) and inverse wave age in the Baltic Sea (CenBASE) and open ocean. A:**
 207 u_* derived from EC air-sea momentum fluxes versus 10-meter neutral wind speed (U_{10N}). Blue dots: 10-
 208 min u_* observations during CenBASE (568 points), with red points corresponding to bin averages (per 1 m
 209 s⁻¹). Red line: u_* simulated by COARE3.6 using the Baltic Sea environmental data; Black-dashed line:
 210 COARE3.6 simulations in the open ocean. **B:** Inverse wave age (U_{10N}/C_p) in the Baltic Sea (red dots) and
 211 open ocean (black squares). Error bars denote ± 1 standard deviation (STD) of bin averages. The hourly
 212 wave parameters are shown in Fig. A2 of the Appendix.

213

214 3.3 Gas transfer velocities from EC and DT

215 The CO₂ transfer velocity ($K_{660_CO_2}$) was derived from EC air-sea CO₂ flux and ΔfCO_2 observations
 216 using Equation 1. After quality control, 301 valid 10-min $K_{660_CO_2}$ data points were retained (Fig.
 217 4). The large $|\Delta fCO_2|$ ($\sim 280 \mu\text{atm}$) ensured accurate $K_{660_CO_2}$ derivations, with hourly uncertainties
 218 of $\sim 20\%$ (Fig. A4), substantially lower than typical cruise-based uncertainties (e.g., $\sim 30\%$ during
 219 the HiWinGS cruise; Blomquist et al., 2017). The cool skin correction (reduces ΔfCO_2 by $\sim 2 \mu\text{atm}$;
 220 Woolf et al., 2016) is negligible relative to the observed ΔfCO_2 and was therefore ignored. K_{660}
 221 from the DT experiment is summarized in Appendix A1.

222 The EC dataset offers high temporal resolution (~ 10 min), enabling investigation of small-scale
 223 processes influencing gas exchange. The EC observations span a broad range of wind speeds (1 to
 224 12 m s^{-1} , Fig. 4A), providing a robust constraint of K_{660_CO2} under low-to-moderate wind conditions.
 225 In contrast, DT-derived K_{660} represents daily averages, in which short-term extremes (i.e., low and
 226 high wind conditions) are smoothed, resulting in seven observations concentrated at U_{10N} of 5-9
 227 m s^{-1} (Fig. 4A). Within this wind range, DT-and EC-derived K_{660} values are in good agreement,
 228 with the former on average being only slightly ($\sim 8\%$) lower than the latter (Fig. 4).



229 **Figure 4: Gas transfer velocity (K_{660_CO2}) in the central Baltic Sea during the CenBASE cruise. A:**
 230 **Relationships between K_{660} and U_{10N} . B: Relationships between K_{660} and observed u_* .** Blue dots in both
 231 panels represent 10-min K_{660_CO2} ($N = 301$), with red dots denoting bin averages ($1 \text{ m s}^{-1} U_{10N}$ bins or 0.05
 232 $\text{m s}^{-1} u_*$ bins) ± 1 STD. Red lines indicate the fit to the bins, with R^2 of 0.48 for the fit with U_{10N} and 0.59
 233 for the fit with u_* . Yellow diamonds show dual-tracer (DT) transfer velocities ($K_{660_3He/SF6}$) measured
 234 concurrently with EC (Dobashi et al., 2026). The orange line in panel A denotes the open ocean DT-based
 235 parameterisation from Ho et al. (2006). The black lines in panels A and B correspond to the open-ocean
 236 EC-based parameterisations of Yang et al. (2022; U_{10N} -dependent) and Yang et al. (2024; u_* and sea-state
 237 dependent), respectively.
 238

239
 240 DT-derived K_{660} values during CenBASE also generally agree with the open-ocean DT-based
 241 parameterisation of Ho et al. (2006) under equivalent wind speeds (orange dashed line in Fig. 4A),
 242 with the former on average being only $\sim 7\%$ lower than the latter. However, EC-derived K_{660_CO2}
 243 values deviate systematically from this open-ocean relationship (Ho et al., 2006), being higher at

244 low wind speeds (1-7 m s⁻¹, +12%) and lower at high wind speeds (7-12 m s⁻¹, -18%) (Fig. 4A).
 245 This divergence does not contradict the agreement between the DT-and EC-based K_{660}
 246 observations, as this agreement falls within the 5-9 m s⁻¹ range (where the DT data concentrate).
 247 Fitting K_{660_CO2} with U_{10N} reveals a weaker wind speed dependence than the open ocean DT-based
 248 parameterisation (Fig. 4A). It is worth noting that including a constant term in the K_{660_CO2} - U_{10N}
 249 fitting function (i.e., $K_{660_CO2} = aU_{10N}^b + c$, $R^2 = 0.48$) improves the fit compared to a purely
 250 power-law form (i.e., $K_{660_CO2} = aU_{10N}^b$, $R^2 = 0.42$) (Fig. A5), suggesting a non-zero CO₂
 251 exchange (~ 3 cm hr⁻¹) under calm conditions. This is unsurprising, since the chemical
 252 enhancement (Cole & Caraco, 1998; Fairall et al., 2022; Yang et al., 2022) and likely buoyancy
 253 flux sustain CO₂ transfer at low wind speeds (McGillis et al., 2004; Wanninkhof et al., 2009).

254 Notably, the DT data collected during CenBASE provide only limited constraints at wind speeds
 255 below 5 m s⁻¹ and above 9 m s⁻¹, and the K_{660} - U_{10N} relationship derived from these data is sensitive
 256 to the chosen functional form (Fig. A5). Moreover, the DT-based open-ocean K_{660} estimates are
 257 lower than the EC CO₂-based estimates across the wind speed range observed during CenBASE
 258 (Fig. 4A), likely reflecting differences in methodology. Because the CenBASE DT data have been
 259 interpreted in detail by Dobashi et al. (2026), and, more importantly, because the EC measurements
 260 resolve finer-scale processes and ensure methodological consistency, the subsequent section
 261 focuses on comparing EC CO₂ observations in the Baltic Sea with those in the open ocean.

262 3.4 Suppression of air-sea CO₂ exchange

263 The EC-derived K_{660_CO2} during CenBASE was generally lower than open-ocean EC CO₂ transfer
 264 velocities (Yang et al., 2022; 2024) (Figs. 4A and 4B), indicating a substantial suppression of CO₂
 265 exchange in the Baltic Sea. To explain this reduction, we partition the total gas transfer velocity
 266 (K_{660}) into interfacial (K_{i660}) and bubble-mediated (K_{b660}) components (i.e., $K_{660} = K_{i660} + K_{b660}$).
 267 K_{i660} is primarily driven by wind stress or u_* , whereas K_b depends on both the wind forcing and
 268 sea state. A machine-learning analysis of 15 open ocean datasets identified significant wave height
 269 (H_s , including both windsea and swell) as a key proxy for sea state that strongly affects K_{660_CO2}
 270 (Yang et al., 2024). Based on this analysis, Yang et al. (2024) express the K_{660} as (Fig. 4B, black
 271 line):

$$272 \quad K_{660} = K_{i660} + K_{b660} = 55u_* + 10u_*H_s \quad (3)$$

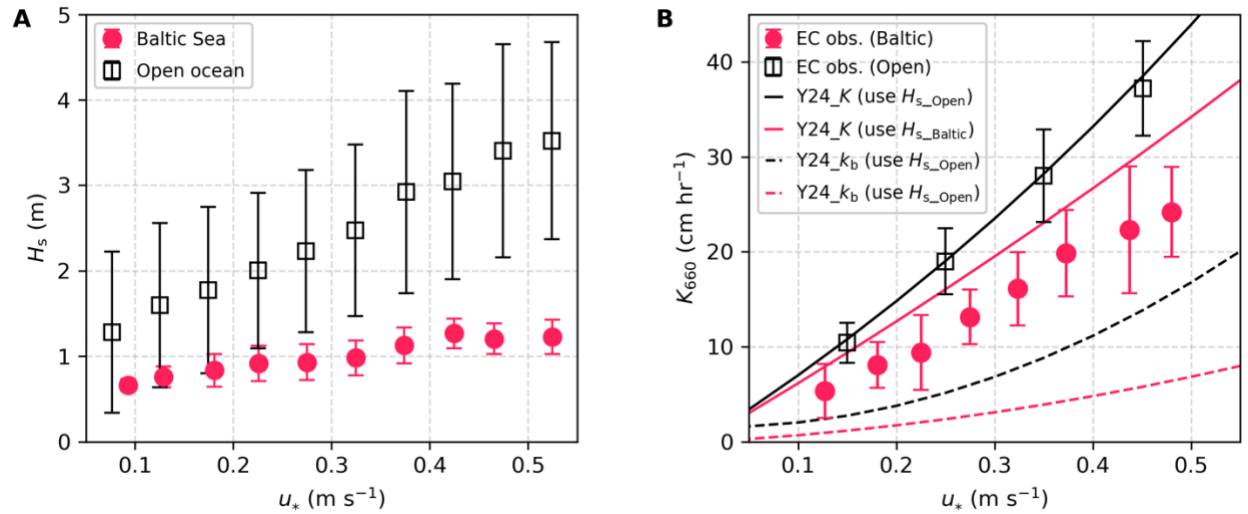
273 Because K_b depends on solubility, normalizing it using the Schmidt number (i.e., converting K_b to
274 K_{b660}) may not be strictly appropriate. However, the sensitivities of the CO₂ transfer velocity to $Sc^{-1/2}$
275 and α^{-1} are nearly identical (see Fig. A1 in Dong et al., 2025). Therefore, normalization using
276 either Sc or α produces almost the same gas transfer velocities. For simplicity and consistency, we
277 adopt the Sc -based normalization in this study.

278 The observed EC K_{660} during CenBASE averaged 14.9 cm hr⁻¹. To compare this value with open-
279 ocean conditions at equivalent wind speeds, we apply the wind-speed observations from the
280 CenBASE cruise (i.e., wind speed values shown in Fig. 4A) to Equation 3 to estimate open-ocean
281 K_{660} , yielding average values of $K_{i660} = 15.1$ cm hr⁻¹, $K_{b660} = 7.0$ cm hr⁻¹, and $K_{660} = 22.1$ cm hr⁻¹.
282 This means that the observed K_{660} during CenBASE was 33% (7.2 cm hr⁻¹) lower than the open-
283 ocean K_{660} estimate.

284 Equation 3 implies a linear dependence of K_{660_CO2} on u_* . Regression of the observed K_{660_CO2}
285 against u_* indeed yields an approximately linear relationship (Fig. 4B), consistent with prior
286 findings at low-to-moderate winds (Landwehr et al., 2018; Yang et al., 2022). Additionally, the
287 K_{660_CO2} - u_* fit ($R^2 = 0.59$) outperforms the K_{660_CO2} - U_{10N} fit ($R^2 = 0.48$), confirming that u_* better
288 captures variability in gas transfer velocity than U_{10N} (Jähne et al., 1987; Landwehr et al., 2018;
289 Yang et al., 2022). As shown in Fig. 3A, the observed u_* during CenBASE was ~10% higher than
290 open-ocean values under equivalent wind speeds, implying a ~10% enhancement in K_{660_CO2} due
291 to fetch-related increases in shear stress (Vickers and Mahrt, 1997). It is important to note that the
292 observed 33% reduction in K_{660_CO2} includes this enhancement, suggesting that CO₂ exchange was
293 suppressed even more, by ~43% (9.2 cm h⁻¹) relative to open-ocean conditions.

294 According to Equation 3, K_b is linearly dependent on H_s . Due to the limited fetch, the H_s during
295 CenBASE was 57% lower than in the open ocean at the equivalent u_* (Fig. 5A, Table 1), and this
296 reduction is expected to cause a comparable decrease in K_b . Using the extracted H_s values from
297 ERA5 for CenBASE, the parameterised K_{b660} decreases on average from 7.0 cm hr⁻¹ to 4.0 cm hr⁻¹,
298 corresponding to an 18% suppression on the total K_{660_CO2} (Fig. 5B; Table 1), explaining about
299 half of the observed suppression during CenBASE.

300



301

302 **Figure 5: Comparison of significant wave height (H_s) and $K_{660_CO_2}$ between the Baltic Sea and the**
 303 **open ocean. A:** H_s in the Baltic Sea during CenBASE (red dots) and in the open ocean (black squares),
 304 with error bars representing ± 1 STD. The data are extracted from ERA5 according to the EC cruise tracks
 305 (Yang et al., 2022) and the CenBASE cruise track. **B:** $K_{660_CO_2}$ observations in the Baltic Sea during
 306 CenBASE (red dots, the same as the red dots in Fig. 4B) and in the open ocean (black squares, Yang et al.,
 307 2022). The black and red solid lines correspond to the parameterised total CO_2 transfer velocity (i.e.,
 308 $K_{660_CO_2}$ from Equation 3; Yang et al., 2024) using the open ocean and the Baltic Sea H_s , respectively. The
 309 black and red dashed lines denote the parameterised bubble-mediated transfer component (K_{b660} ; Equation
 310 3) using the open ocean and the Baltic Sea H_s , respectively.

311

312 Surfactants inhibit both interfacial (e.g., Frew, 1997) and bubble-mediated gas exchange (e.g.,
 313 Woolf, 1993), and their concentrations in the Baltic Sea are substantially higher than in the open
 314 ocean. We assume that all residual suppression of $K_{660_CO_2}$ during CenBASE, which cannot be
 315 explained by fetch effects, is caused by surfactants. Under this assumption, the residual 25%
 316 suppression (i.e., 5.4 cm hr^{-1} ; Fig. 5B and Table 1) reflects the impact of elevated surfactant levels.
 317 This effect is not captured by the Yang et al. (2024) parameterisation, which is based primarily on
 318 open-ocean observations characterized by low surfactant concentrations (Wurl et al., 2011; Fig.
 319 A6).

320 The resulting suppression fraction (sf) is consistent in magnitude with previous field-based
 321 estimates (Fig. 6; Mustafa et al., 2020; Salter et al., 2011; Yang et al., 2021) within uncertainty
 322 (see Section 3.5). The constrained sf is generally smaller than laboratory-derived values (Fig. 6A),

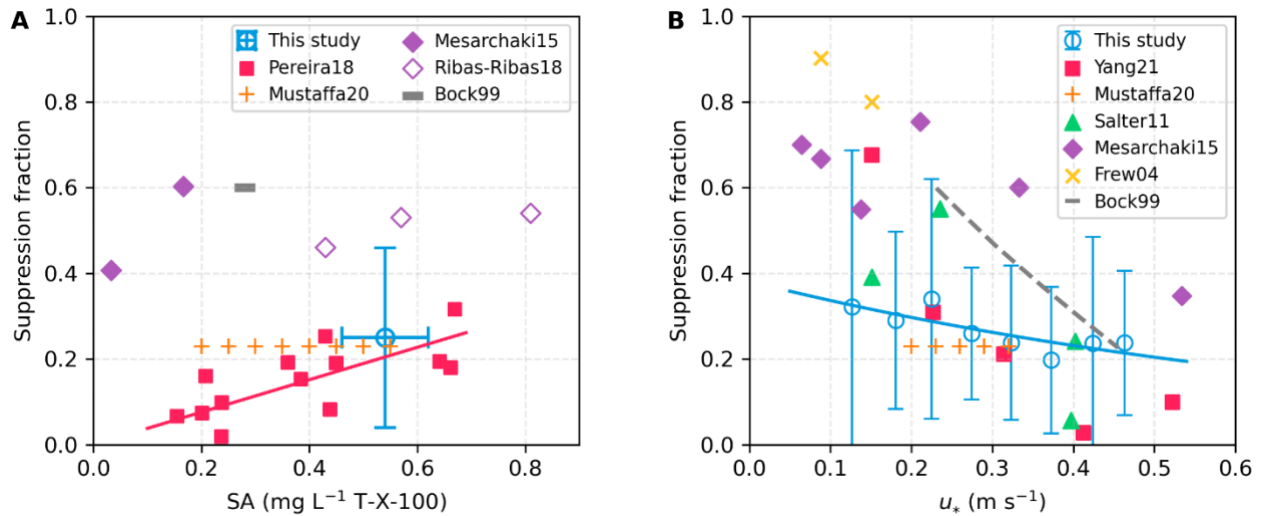
323 likely due to challenges in extrapolating laboratory conditions to the field. Notably, previous
 324 studies report conflicting relationships between sf and surfactant concentration. Some show
 325 increasing sf with increasing concentration (Mesarchaki et al., 2015; Pereira et al., 2018; Ribas-
 326 Ribas et al., 2018), whereas others identify a threshold concentration above which sf shows little
 327 change (Mustaffa et al., 2020; Schmidt and Schneider, 2011) (Fig. 6A). Because surfactant
 328 concentrations were nearly constant during CenBASE, we cannot assess this relationship here.

329 Several studies also show that sf decreases with wind speed (Fig. 6B; Bock et al., 1999; Mesarchaki
 330 et al., 2015; Salter et al., 2011; Yang et al., 2021), and the sf constrained here aligns well with
 331 these findings, especially those from field observations. Fitting sf as a function of u_* yields a
 332 correction factor (i.e., $1 - sf$) that can be applied to Equation 3 to account for surfactant effects,
 333 generating the updated parameterisation:

$$334 \quad K_{660} = (1 - 0.38e^{-1.25u_*})(55u_* + 10u_*H_s) \quad (4)$$

335 This parameterisation reflects conditions during CenBASE, where the surfactant concentration
 336 was relatively stable at $\sim 0.5 \text{ mg L}^{-1}$. If a SA concentration-dependent sf is needed, one option is
 337 the published linear relationship $sf = 0.32SA + 0.025$ (Pereira et al., 2018). However, this
 338 formulation maybe physically inconsistent because it predicts a non-zero suppression even when
 339 $SA = 0$, whereas sf should theoretically approach zero in surfactant-free conditions. To address this,
 340 we re-evaluated the same dataset used in the original study (Pereira et al., 2018) and fitted a
 341 proportional relationship that passes through the origin: $sf = 0.38SA$. The goodness-of-fit ($R^2 =$
 342 0.49) is only marginally lower than the original relationship (0.51 , Pereira et al., 2018), indicating
 343 that the proportional form captures the data nearly as well while remaining physically realistic. For
 344 the mean CenBASE surfactant concentration ($SA = 0.54 \text{ mg L}^{-1}$), this relationship yields $sf = 0.21$.
 345 Applying this SA-dependent suppression to the wind-dependent correction in Equation 4 results
 346 in the combined parameterisation:

$$347 \quad K_{660} = \frac{1-0.38SA}{0.79} (1 - 0.38e^{-1.25u_*})(55u_* + 10u_*H_s) \quad (5)$$



348

349 **Figure 6: Surfactant-induced suppression fraction on K_{660} (sf) from this study and previous work. A:**

350 sf as a function of surfactant concentration under low-moderate wind speeds. The blue circle shows the

351 mean constrained sf from this study; horizontal and vertical error bars denote the standard deviation of

352 observed SA and the associated uncertainty of the constrained sf . Red squares indicate sf from wave-tank

353 experiments with natural Atlantic seawater at wind speeds $<13 \text{ m s}^{-1}$ (Pereira et al., 2018), with the red line

354 showing the linear fit ($sf = 38 \times SA$). Orange pluses show sf constrained from field K_{660} observations using

355 the chamber technique with natural surfactant (Mustaffa et al., 2020). Diamonds (filled/unfilled) and the

356 grey dash represent wave-tank studies using artificial soluble surfactants (Mesarchaki et al., 2015; Ribas-

357 Ribas et al., 2018; Bock et al., 1999). **B:** sf as a function of u_* . Blue circles show sf constrained from the

358 residual suppression of observed K_{660_CO2} from this study, with error bars indicating uncertainties. The blue

359 line corresponds to the fit based on the blue circles ($0.38 \times e^{1.25u_*}$, $R^2 = 0.65$). Red squares represent values

360 derived from an EC-based CO_2 transfer velocity study (Yang et al., 2021). Orange pluses denote the

361 Mustaffa et al. (2020) dataset with surfactant concentrations of 0.2-0.6 mg L^{-1} . Green triangles show sf

362 inferred from EC-based DMS and DT exchange experiments in artificial insoluble surfactant patches (Salter

363 et al., 2011). Purple diamonds represent Mesarchaki et al. (2015), who used $\sim 0.2 \text{ mg L}^{-1}$ of artificial soluble

364 surfactant. Yellow crosses indicate sf derived from coastal heat transfer measurements (Frew et al., 2004).

365 The grey dashed line shows laboratory experiments with artificial soluble surfactants at $\sim 0.3 \text{ mg L}^{-1}$ (Bock

366 et al., 1999).

367

368

369 Previous studies have suggested that water-side convection may influence gas exchange in both

369 open-ocean (McGillis et al., 2004) and Baltic conditions (Rutgersson and Smedman, 2010). During

370 CenBASE, a small spar buoy recorded oxygen, temperature, and salinity at depths of 1.2 m and

371 2.9 m. Dissolved oxygen exhibited small-scale variability with similar patterns at both depths (Fig.
372 A7), indicating coherent near-surface structure over 5-20 m scales, likely driven by wind-induced
373 turbulence intermittently exposing surface patches to the atmosphere. In contrast, no
374 corresponding variability was observed in temperature or salinity (Fig. A7), suggesting that
375 convection played a negligible role in gas exchange under the observed conditions. This supports
376 our assumption that the deviation in K_{660_CO2} between the Baltic Sea and the open ocean can be
377 fully attributed to the combined effects of limited fetch and elevated surfactant levels.

378

379 **3.5 Uncertainty analysis**

380 The quantification results shown above are not free from uncertainty. First, we use the $K_b \propto u_* H_s$
381 relationship for the bubble component, which fits best with the EC-based K_{660_CO2} observations
382 (Yang et al., 2024). However, alternative formulations have been proposed, such as $K_b \propto$
383 $u_*^{1.67} H_s^{0.67}$ (Deike and Melville, 2018) and $K_b \propto u_*^{0.9} H_s^{0.9}$ (Brumer et al., 2017a; Fairall et al., 2022).
384 These different exponents indicate that the relative contributions of u_* and H_s to gas exchange may
385 vary slightly, introducing parameterisation uncertainty. Yang et al. (2024) reported that the R^2 for
386 the fit (i.e., Equation 3) is ~ 0.75 , indicating that $\sim 25\%$ of the variance in the observed K remains
387 unexplained by the parameterisation. We therefore assign a 25% uncertainty to the
388 parameterisation given in Equation 3. This uncertainty propagates through the suppression
389 estimates. For instance, the uncertainty in the u_* -related K enhancement estimate is approximately
390 0.6 cm hr^{-1} (i.e., $2.2 \text{ cm hr}^{-1} \times 25\%$). The suppression analysis uses H_s data derived from ERA5
391 reanalysis, which likely carries an uncertainty of about 30% in the Baltic Sea (Giudici et al., 2023).
392 Consequently, the uncertainty in the H_s -related suppression estimate is $\sim 1.6 \text{ cm hr}^{-1}$ (i.e.,
393 $\sqrt{(4.0 \times 25\%)^2 + (4.0 \times 30\%)^2} \text{ cm hr}^{-1}$). The uncertainty associated with the surfactant-related
394 suppression is substantially larger because it is not directly determined but inferred as a residual
395 after accounting for other components. Combining the propagated uncertainties from the
396 parameterised total K and from two fetch-induced suppression estimates yields an uncertainty of
397 5.8 cm hr^{-1} (i.e., $\sqrt{(22.1 \times 25\%)^2 + 0.6^2 + 1.6^2} \text{ cm hr}^{-1}$), corresponding to approximately 110%
398 of the estimated suppression value (Table 1).

400 Furthermore, it is worth noting that the two corrections in Equation 5 (i.e., the SA - sf correction and
 401 the u_* - SA correction) are implicitly assumed to be independent. However, potential interactions
 402 between u_* -dependent SA variation and the SA influence on sf may introduce additional uncertainty
 403 into Equation 5.

404 **Table 1.** Comparison of mean gas transfer velocities between measurements in the Baltic Sea and estimates
 405 using the open ocean parameterisation from Yang et al. (2024) under identical wind speed conditions
 406 (Equation 3). The percentages in parentheses in the K_i , K_b , and K columns indicate the relative difference
 407 between the Baltic Sea and the open ocean. The last column is the uncertainty assessment of the values in
 408 the K column with the values in parentheses representing the relative uncertainties. The positive (negative)
 409 sign represents the enhancement (suppression).

		K_{i660} (cm hr ⁻¹)	K_{b660} (cm hr ⁻¹)	K_{660} (cm hr ⁻¹)	Uncertainty (cm hr ⁻¹)	
Open ocean (model)		15.1	7.0	22.1	± 5.5 (± 25%)	
Impact factors (model)	Fetch	u_*	+1.5 (+10%)	+0.7 (+10%)	+2.2 (+10%)	± 0.6 (± 25%)
		H_s	0	-4.0 (-57%)	-4.0 (-18%)	± 1.6 (± 40%)
	Surfactants	Unsure	Unsure	-5.4 (-25%)	± 5.8 (± 107%)	
Baltic Sea (CenBASE, EC)		-	-	14.9 (-33%)	-	

410

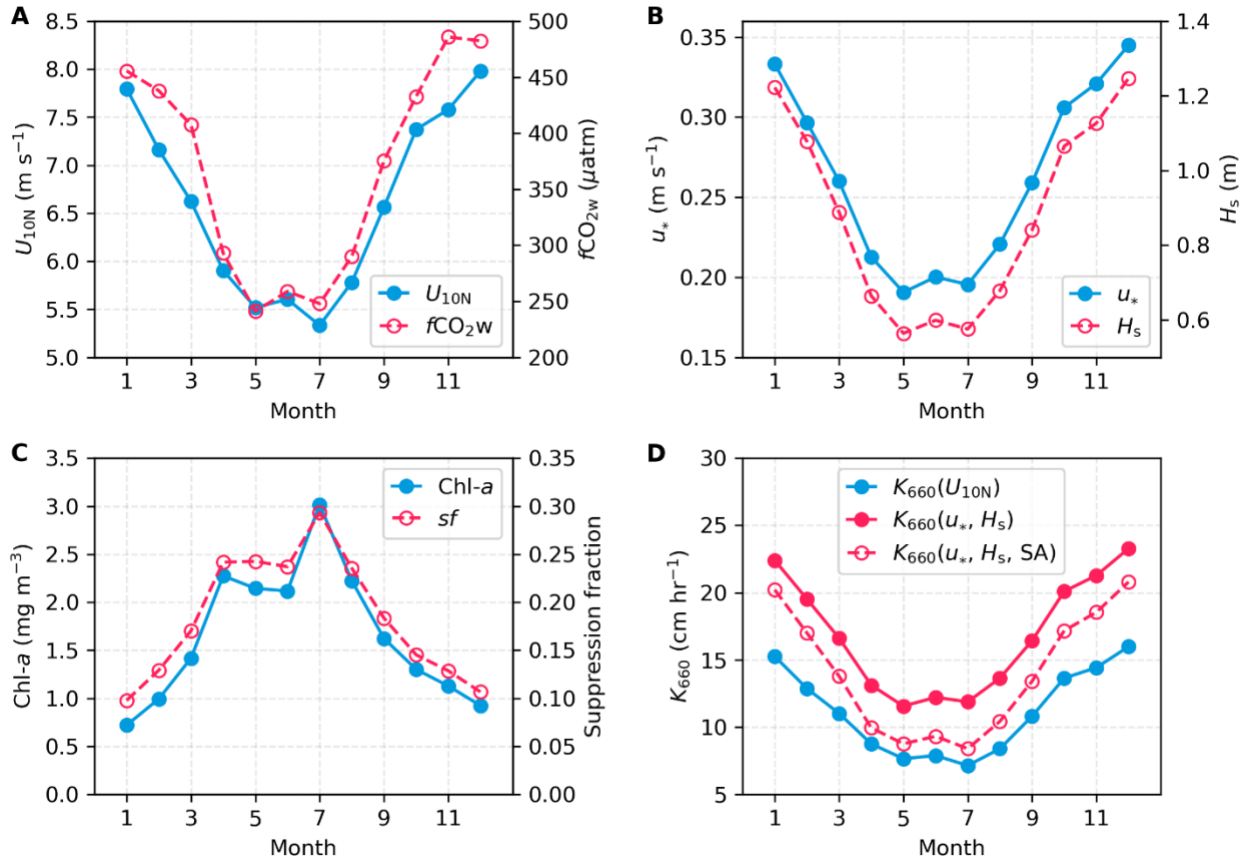
411 3.6 Implications for Baltic Sea CO₂ flux estimates

412 The CenBASE cruise took place during the summer bloom (July), when chlorophyll a (Chl- a) is
 413 high (Pitarch et al., 2016) and fCO_{2w} is strongly reduced by primary productivity (e.g., Parard et
 414 al., 2016; Bittig et al., 2024). To upscale these results, we adopt a fCO_{2w} product from Bittig et al.
 415 (2024) to examine how fetch and surfactants shape the climatological CO₂ flux of the Baltic Sea.
 416 This climatological fCO_{2w} product is derived by combining observations and model patterns. The
 417 fCO_{2w} indicates a CO₂ sink in summer and a source in winter (Fig. 7A). However, weaker summer
 418 winds and stronger winter winds suggest that the magnitudes of uptake and outgassing may be
 419 similar. Seasonal cycles of u_* and H_s closely follow wind speed (Fig. 7B), while Chl- a peaks during
 420 the spring-summer bloom and remains low in winter (Fig. 7C). We estimate monthly surfactant
 421 concentrations by scaling the July CenBASE value (0.54 mg L⁻¹) with monthly Chl- a
 422 concentrations following the idea of Wurl et al. (2011) and using the formula $0.54 \times \text{Chl-}a / \text{Chl-}$

423 a_{July} mg L⁻¹. Equation 5 is then used to compute the corresponding suppression of gas transfer,
424 $1 - \frac{1-0.38SA}{0.79}(1 - 0.38e^{-1.25u_*})$. The resulting sf reflects the seasonal Chl-*a* cycle and modulations
425 by u_* , yielding ~25% suppression in summer and ~10% in winter (Fig. 7C). However, surfactant
426 concentrations are not solely determined by Chl-*a*; for example, humic acids also act as surfactants
427 (e.g., Klavins & Purmalis, 2010), and the Baltic Sea is known for elevated humic acid levels due
428 to significant terrestrial inputs (Hammer et al., 2017). Therefore, estimating surfactant levels solely
429 from Chl-*a* has inherent limitations.

430 We estimate K_{660} using three parameterisation schemes: the conventional open ocean DT-based
431 U_{10N} formulation (Ho et al., 2006), the open ocean EC CO₂-based u_*-H_s formulation (Equation 3;
432 Yang et al., 2024), and the Baltic Sea EC CO₂-based u_*-H_s-SA formulation (Equation 5). Although
433 all these schemes reproduce similar seasonal patterns, their magnitudes differ (Fig. 7D), reflecting
434 sea state and surfactant effects as well as methodological differences. The u_*-H_s-SA
435 parameterisation yields lower values than the u_*-H_s scheme because it incorporates surfactant-
436 induced suppression from the surfactant. This suppression is especially strong in summer when
437 SA concentrations are highest, leading to the largest discrepancies between the estimated
438 climatological K_{660} from the u_*-H_s-SA and the u_*-H_s schemes. As shown in Section 3.4, K_{660} during
439 CenBASE has been reduced by 33%. Notably, this reduction is relative to open-ocean EC-based
440 estimates. However, compared with the open ocean DT-based U_{10N} formulation, however, this
441 reduction occurs only at wind speeds above ~7 m s⁻¹. At lower wind speeds, the EC-based K_{660}
442 observations during CenBASE exceed the DT-based estimates (Fig. 4A). Because climatological
443 Baltic Sea wind speeds are typically below 7 m s⁻¹ in Spring, Summer, and Autumn (Fig. 7A), the
444 u_*-H_s-SA parameterisation produces higher K_{660} than the U_{10N} formulation in these seasons. In
445 winter, despite higher wind speeds, the u_*-H_s-SA scheme still exceeds the U_{10N} -based estimates
446 due to modulation of the surfactants. The SA concentration in winter is estimated to be three times
447 lower than during the summer CenBASE cruise (Fig. 7C), resulting in much weaker suppression.

448 Overall, relative to the conventional U_{10N} formulation (Ho et al., 2006), the u_*-H_s-SA
449 parameterisation increases K_{660} in all seasons, enhancing both summer CO₂ uptake by ~10% and
450 winter outgassing by ~30%, and amplifying the seasonal cycle by ~40%. These opposing seasonal
451 effects are expected to largely compensate, resulting in only a modest change in the annual mean
452 CO₂ flux.



453

454 **Figure 7: Climatological seasonal variations of environmental variables and gas transfer velocities in**

455 **the Baltic Sea. A:** U_{10N} (blue) and fCO_{2w} (red; Bittig et al., 2024). **B:** u_* (blue) and H_s (red). U_{10N} , u_* , and

456 H_s are averaged from the ERA5 monthly reanalysis data product (Hersbach et al., 2020) for 1998-2018. **C:**

457 Surfactant concentrations scaled from monthly chlorophyll-*a* (Chl-*a*) (Pitarch et al., 2016) and surfactant-

458 induced suppression fraction of K_{660} based on the *SA*- and U_{10} -dependent parameterisation (Equation 5). **D:**

459 K_{660} estimated from different parameterisations: U_{10N} -based (blue; Ho et al., 2006), u_* - H_s -based (red solid;

460 Equation 3, Yang et al., 2024); u_* - H_s -*SA*-based (red dashed; Equation 5).

461

462

463 4 Discussion and conclusions

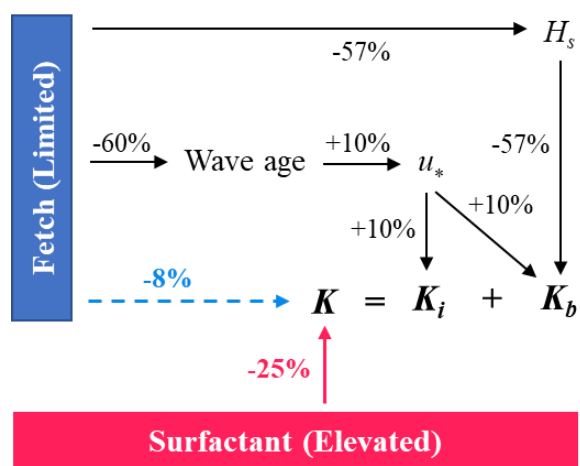
464 A robust understanding of air-sea gas exchange mechanisms is fundamental for accurately

465 quantifying CO_2 fluxes, which is essential for accurate carbon budgets and climate projections.

466 Most previous studies have focused on the open ocean, where K_{660} is typically parameterised as a

467 function of wind speed. In contrast, marginal seas such as the Baltic Sea exhibit more complex

468 dynamics due to limited fetch and abundant surfactants, which modulate the wind speed
 469 dependence of gas exchange. To investigate these processes, a dedicated experiment was
 470 conducted in the central Baltic Sea during the CenBASE cruise, employing two commonly used
 471 techniques: eddy covariance and dual-tracer methods. The K_{660} derived from both techniques
 472 agrees well, confirming the reliability of both methods for gas transfer velocity observations. The
 473 observed CO_2 transfer velocity shows a significant reduction compared to the open-ocean CO_2
 474 observations and parameterisations under comparable wind conditions (Yang et al., 2024; Fig. 4).
 475 This reduction can be attributed to three competing processes (summarized in Fig. 8): 1) a 10%
 476 enhancement from fetch-limited increases in friction velocity, 2) an 18% suppression from reduced
 477 significant wave height, and 3) a 25% suppression from elevated surfactant concentrations.
 478 Together, these effects explain the overall 33% reduction in CO_2 exchange during CenBASE
 479 relative to the EC-based open ocean $K_{660_CO_2}$.



480
 481 **Figure 8: Schematic illustrating how fetch and surfactants modulate the CO_2 transfer velocity (K) in**
 482 **the Baltic Sea relative to the open ocean.** Values denote the relative magnitude of enhancement (+) or
 483 suppression (-) for each process (Table 1). Black arrows and their associated values indicate the effect of
 484 fetch on individual gas exchange components, while the blue value on the dashed arrow shows the net fetch
 485 effect on total K . The red value and arrow represent the constrained surfactant-induced suppression of K .

486
 487 During CenBASE, fetch lengths ranged from 50-300 km, in contrast to more than 1000 km in the
 488 open ocean. The limited fetch exerts both enhancing and suppressing effects on gas exchange in
 489 the Baltic Sea (Fig. 8). Shorter fetch produces a younger wave field dominated by shorter and

490 steeper waves, increasing surface roughness and thereby enhancing u_* and K_{660} . At the same time,
491 limited fetch constrains wave development, leading to a ~60% reduction in H_s (Fig. 5A). As a key
492 proxy for wave-breaking intensity (Brumer et al., 2017; Deike, 2021; Zhao et al., 2003), reduction
493 in H_s diminishes wave breaking and consequently suppresses bubble-mediated gas transfer
494 (Dobashi & Ho, 2023; Fairall et al., 2006; Ocampo-Torres & Donelan, 1995; Woolf, 2005). These
495 findings emphasize the need to incorporate sea-state dependence into K_{660} parameterisations
496 (Brumer, 2017; Deike & Melville, 2018; Fairall et al., 2022; Yang et al., 2024). When direct wave
497 observations are unavailable, reanalysis products (e.g., ERA5; Hersbach et al., 2020) can serve as
498 a first-order estimate of wave conditions for K evaluation (Bessonova et al., 2025; Giudici et al.,
499 2023).

500 Although bubble effects are expected to be stronger for low-solubility tracers such as ^3He and SF_6
501 than for CO_2 , the EC CO_2 -derived and dual-tracer-derived K_{660} values agreed closely (Fig. 4A).
502 This is primarily because the bubble contribution to the total gas exchange during CenBASE was
503 relatively small due to the low wind regime (Fig. 5B). According to the widely used model (Woolf,
504 1997), bubble-mediated transfer contributes ~25% to total CO_2 exchange and ~35% to $^3\text{He}/\text{SF}_6$
505 exchange under wind speeds of 0-12 m s^{-1} . This difference corresponds to only ~1.5 cm hr^{-1} higher
506 K_{660} for dual tracers, which lies well within the measurement uncertainty and is therefore not
507 practically distinguishable. Moreover, the much lower salinity in the Baltic Sea further limits the
508 bubble-induced solubility dependence of K . Although the bubble size observations with the bubble
509 cameras on a spar buoy did not work during CenBASE, it is well established that bubbles coalesce
510 easily in fresh water (this is inhibited in salt water), so the initial bubble size distribution in fresher
511 water quickly evolves towards larger bubbles through coalescence (e.g., De Leeuw et al., 2011).
512 This coalescence effect has little influence on the gas transfer of moderately soluble gases such as
513 CO_2 but reduces K_b for very low-solubility gases (e.g., ^3He and SF_6) due to the reduction of bubble
514 surface area, thereby narrowing the difference in K_{b660} between CO_2 and $^3\text{He}/\text{SF}_6$. This also
515 indicates that the parameterisation of the bubble-mediated component derived from open-ocean
516 EC data (Yang et al., 2024) remains applicable to the Baltic Sea, despite differences in salinity and,
517 thereby, the bubble-size distribution.

518 The suppression of gas exchange by surfactants has been well documented in laboratory studies,
519 which report 10-65% reductions in K depending on surfactant concentration (Bock et al., 1999;

520 Frew et al., 1990; Goldman et al., 1988; Mesarchaki et al., 2015; Pereira et al., 2016; Pereira et al.,
521 2018; Ribas-Ribas et al., 2018; Schmidt & Schneider, 2011). Based on the empirical relationship
522 derived by Pereira et al. (2018) using laboratory data, the CenBASE microlayer surfactant
523 concentration ($0.54 \pm 0.08 \text{ mg L}^{-1}$) corresponds to an estimated $\sim 20\%$ reduction in K . Field studies
524 have reported similar magnitudes of suppression (24-55%) under artificial surfactant additions
525 (Brockmann et al., 1982; Salter et al., 2011). More recently, field chamber measurements indicate
526 $\sim 23\%$ suppression for natural surfactant levels exceeding 0.2 mg L^{-1} (Mustaffa et al., 2020), and
527 EC-based $K_{660_CO_2}$ observations have shown $\sim 30\%$ suppression at moderate winds ($\sim 7 \text{ m s}^{-1}$) under
528 likely high surfactant conditions (Yang et al., 2021). Thus, the 25% suppression estimated in this
529 study agrees well with previous laboratory and field results.

530 Our findings refine the mechanistic understanding of air-sea gas exchange and have important
531 implications for estimates of coastal CO_2 flux estimates. Using the u_*-H_s-SA parameterisation, both
532 summer uptake and winter outgassing of CO_2 in the Baltic Sea increase compared to a conventional
533 U_{10N} -based parameterisation, amplifying the seasonal cycle. Because many coastal regions exhibit
534 similarly short fetches and elevated surfactant concentrations (Fig. A6), the mechanism-based
535 parameterisation proposed here is expected to yield systematically different gas exchange
536 efficiencies than conventional wind-speed-based formulations. The mechanism-based K
537 parameterisation could alter coastal CO_2 flux estimates (e.g., Resplandy et al., 2024), influencing
538 annual means, long-term trends, seasonal cycles, and spatial patterns. An improved estimate of the
539 ocean CO_2 sink may also help reduce discrepancies between the data-based and model-based
540 global carbon budgets (Friedlingstein et al., 2025). The improvement in the estimate of K is
541 especially important for mCDR studies, which are often tested or developed in coastal
542 environments (e.g., Ho et al., 2023). Beyond CO_2 , the updated parameterisation may also apply to
543 other greenhouse gases, such as N_2O , which share the same interfacial exchange mechanism and
544 exhibit similar bubble-mediated behavior due to their comparable solubility. Application to DMS
545 is also possible, provided the bubble-mediated component is omitted.

546 Despite the advances from the CenBASE campaign, several uncertainties remain. The surfactant-
547 induced suppression was inferred from residual differences between Baltic Sea and open-ocean
548 $K_{660_CO_2}$ after correcting for fetch effects, and therefore carries considerable uncertainty even
549 though the magnitude is consistent with previous field constraints. We were unable to partition the

550 surfactant-induced suppression between interfacial and bubble-mediated pathways because
551 available evidence is insufficient to quantify their relative roles. Observations were limited to low-
552 to-moderate wind speeds ($<12 \text{ m s}^{-1}$), preventing evaluation of the surfactant effect under high
553 wind-speed conditions. Furthermore, surfactant concentrations were relatively uniform during
554 CenBASE, so suppression could not be assessed across natural SA concentration gradients. Given
555 the strong seasonal and spatial variability in biological production, the transferability of our
556 quantified suppression values beyond the CenBASE conditions is uncertain. Addressing these
557 limitations will require coordinated, multi-season observations across diverse fetch conditions,
558 surfactant regimes, and wind speeds. Such efforts are essential for building a generalizable
559 framework for gas exchange in marginal seas and for improving both regional CO_2 budgets and
560 assessment of emerging mCDR applications.

561

562 **Appendix**

563 **A1. Dual-tracer experiments**

564 The K was determined using the $^3\text{He}/\text{SF}_6$ dual tracer technique in addition to the eddy covariance
565 method. ^3He and SF_6 were injected into the surface ocean, and their concentrations were monitored
566 over time. Assuming that air-sea gas exchange is the only process affecting the $^3\text{He}/\text{SF}_6$ ratio, K
567 can be derived from the temporal change in their ratio (Nightingale et al., 2000). The two tracers,
568 ^3He and SF_6 , were injected with a molar ratio of 1:340 on 6 July 2022 at ~ 7 m depth for 40 minutes,
569 centered at 57.263°N , 20.147°E . The injected tracers were then tracked using an underway SF_6
570 analysis system (Ho et al., 2002), which continuously measures the SF_6 concentration at the water
571 surface, and the vessel-mounted acoustic Doppler current profiler (ADCP) (150 kHz Ocean
572 Surveyor, RD Instruments).

573 Near the center of the patch of injected tracers, water samples were taken using the CTD rosette
574 equipped with 13 5-L Niskin bottles. Discrete SF_6 samples were taken from the Niskin bottles
575 using 250-ml syringes. The SF_6 concentration was measured onboard the ship using a gas
576 chromatograph equipped with an electron capture detector (GC-ECD) in combination with a
577 purge-and-trap system (Bullister and Weiss, 1988; Gerke et al., 2024). About 40 ml of seawater
578 for discrete ^3He samples was collected in copper tubes placed in aluminum channels, with both
579 ends sealed by stainless steel clamps. The ^3He samples were sent to the laboratory at the Institute
580 of Environmental Physics at the University of Bremen after the cruise. There, ^3He was analyzed
581 using a helium isotope mass spectrometer (MAP 215-50) (Sültenfuß et al., 2009).

582 **A2. Surfactant sampling**

583 Surfactant samples from the SML were collected from a small workboat positioned ~ 500 m
584 upwind of the research vessel (Karnatz et al., 2025). The SML was sampled using the glass-plate
585 technique and transferred into amber borosilicate glass bottles (Cunliffe and Wurl, 2014; Harvey
586 and Burzell, 1972). When weather conditions were unfavorable, SML sampling was conducted
587 from the bow of the research vessel using a Garrett screen. For surfactant samples, 18 mL of SML
588 samples were transferred into acid-washed and pre-combusted (500°C , 8 h) 20 mL glass vials and
589 immediately frozen at -20°C . Surface activity was analyzed within one year of collection by

590 phase-sensitive alternating-current voltammetry using a 797 VA Computrace polarograph
591 (Metrohm, Switzerland), following Cosović & Vojvodić (1982).

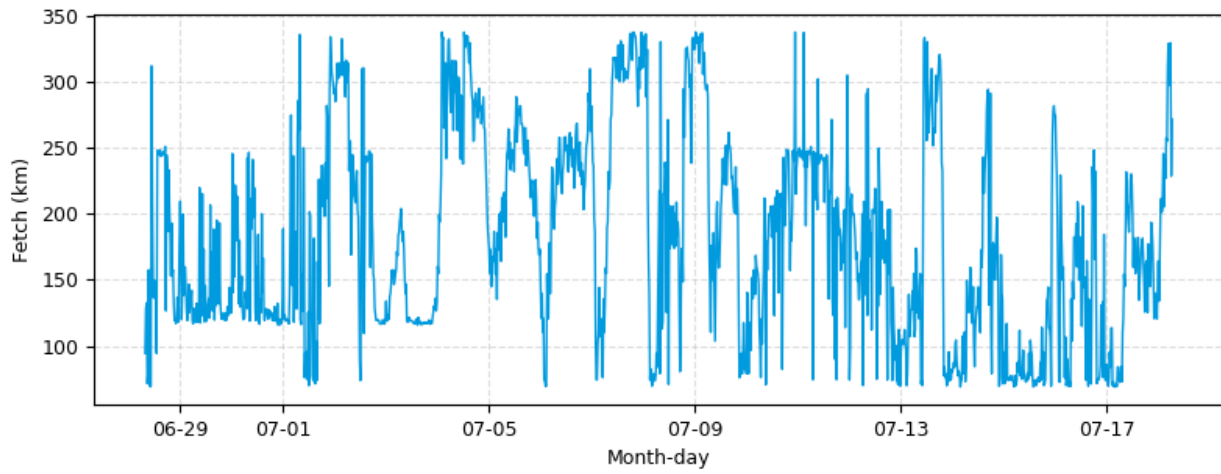
592 **A3. Wind speed distortion correction**

593 During CenBASE, wind speed was measured using two instruments: a 2D sonic anemometer
594 mounted on the ship's foremast (~17 m above MSL) and a 3D EC sonic anemometer on the front
595 tower (~14 m above MSL) (Fig. 1). The foremast measurements are expected to be less distorted
596 because of the higher position of the sensor (O'Sullivan et al., 2013) and are, therefore, used in
597 this study. Nevertheless, previous work shows that foremast-mounted anemometers can still be
598 biased when the wind is not bow-on (e.g., Landwehr et al., 2018). To address this, we follow
599 Landwehr et al. (2020) and use ERA5 reanalysis wind speeds, which are not affected by ship-
600 relative flow distortions, to correct the ship measurements.

601 Because ERA5 winds may contain regional biases, we first calibrate ERA5 using in situ
602 measurements from the Östergarnsholm station (Rutgersson et al., 2020). Winds from five
603 measurement heights (normalized to U_{10}) are highly consistent, supporting the robustness of the
604 station record (Fig. A8). We then compare station winds with ERA5 winds extracted at the station
605 location for the period March-December 2024. To avoid land contamination, only winds from the
606 open sector (80°-160°; Rutgersson et al., 2020) are used. ERA5 is slightly lower than the station
607 wind below 6 m s⁻¹ but higher at stronger winds (Fig. A8). Two linear regressions are applied to
608 ERA5 data, resulting in good agreement with the station winds (Fig. A8). Although the ERA5
609 wave data used in this study are simulated by a wave model forced with ERA5 winds, which may
610 contain minor biases, these are not expected to substantially affect the simulated wave fields
611 (Durrant et al., 2013).

612 The corrected ERA5 winds are then extracted at the CenBASE cruise location and time to serve
613 as a reference for correcting ship wind distortions. The ratio of ship to corrected ERA5 wind speed
614 as a function of relative wind direction shows the expected distortion pattern (Fig. A9; Moat et al.,
615 2006; B. Moat & Yelland, 2015). We fit this ratio using three functions according to the relative
616 wind direction: (1) quadratic for -30° to 45°, (2) linear for -90° to -30°, and (3) linear for 45° to
617 90° (Fig. A9). This fitted relationship is used to correct the ship's wind speed. After correction,
618 the ratio of ship to ERA5 wind speeds aligns closely with unity (Fig. A9).

619

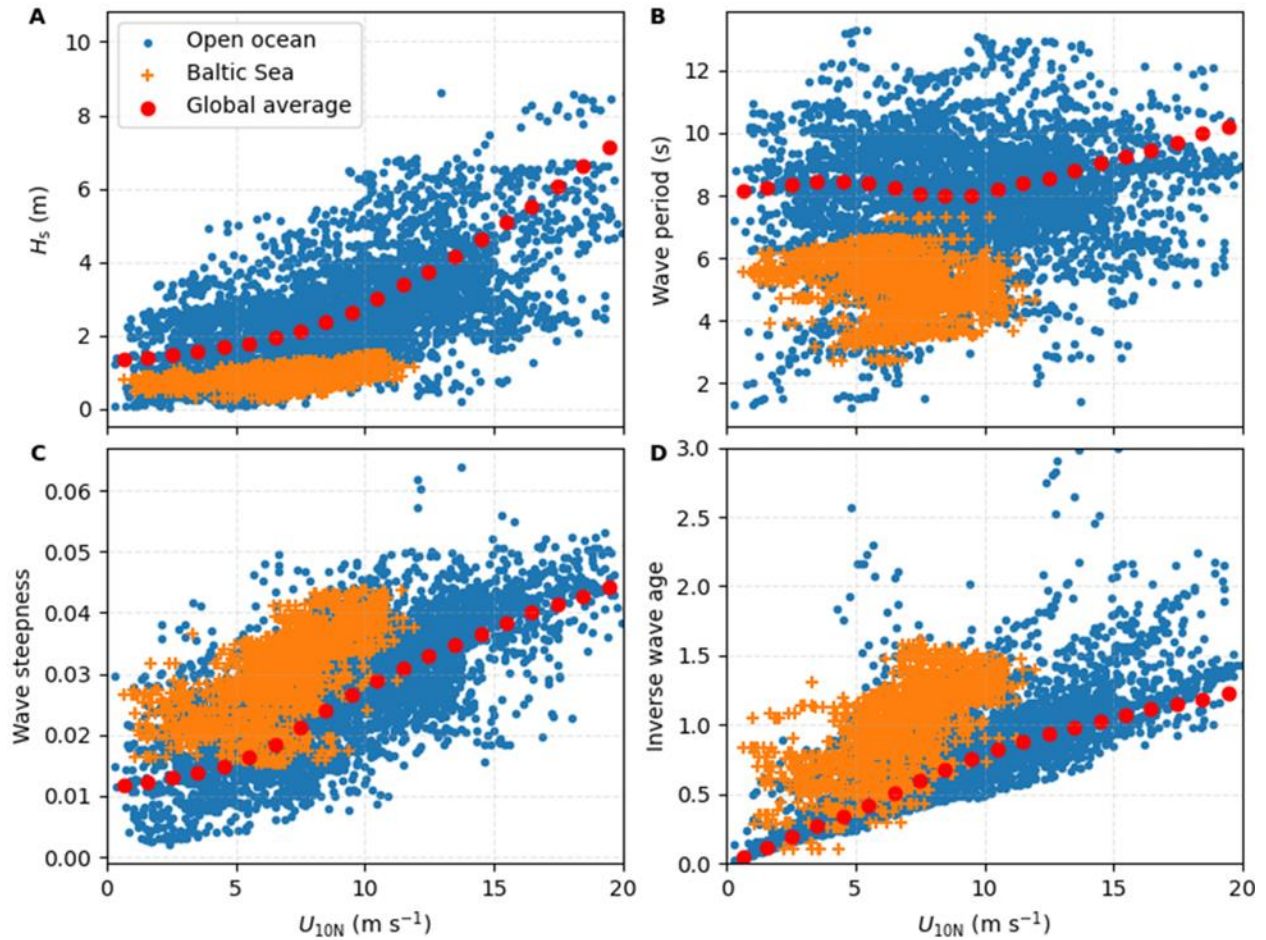


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621 **Figure A1: Fetch of the location according to the CenBASE cruise track.** It is estimated based on the
622 length to the land and the wind direction.

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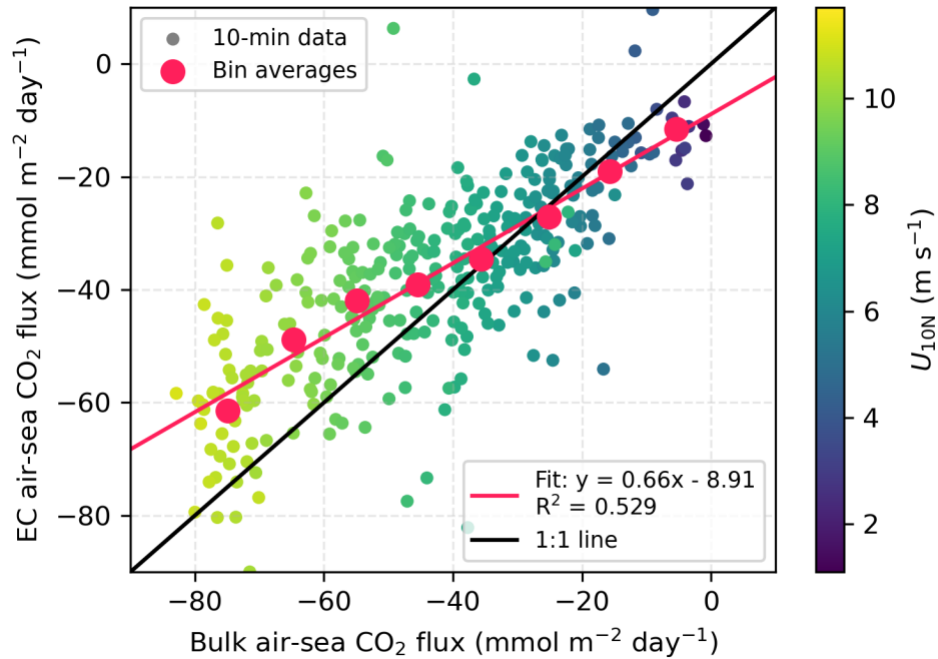


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626 **Figure A2: Wave properties versus wind speed.** Orange: Waves in the Baltic Sea during CenBASE; Blue:
 627 Waves in open ocean cruises with eddy covariance measurements (see Yang et al., 2022); and Red: Waves
 628 in the global ocean average. For the global ocean average, we use the year 2024 as an example and take the
 629 first day of each month at 00:00 to capture seasonal variability. **A:** Significant wave height; **B:** Wave period;
 630 **C:** Wave steepness; **D:** Inverse wave age. See section 2.3 of the Method for information on wave data
 631 extraction.

632

633



634

635 **Figure A3: Bulk air-sea CO₂ flux estimates versus EC air-sea CO₂ flux observations.** The Ho et al.
 636 (2006) parameterisation is used for the bulk flux estimate. The small dots are 10-minute flux data, and the
 637 large red dots represent the bin averages for every 10 mmol m⁻² day⁻¹ flux interval. The EC flux observations
 638 are lower in magnitude than the bulk flux estimates at wind speeds higher than ~7 m s⁻¹.

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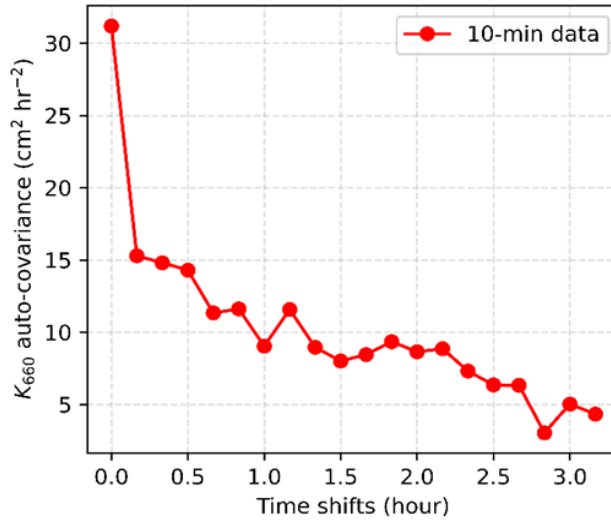
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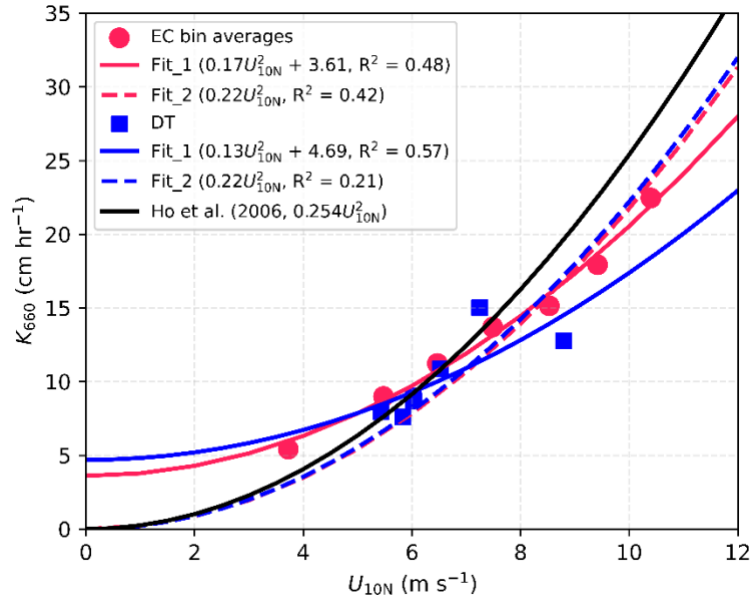
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646 **Figure A4: Auto-covariance of EC-derived CO₂ transfer velocities (K_{660}).** The 10-min K_{660} time series
 647 from 4-7 July, selected for its continuity (see Fig. 1F), was used for this analysis. The first point represents
 648 the variance of the K_{660} time series, while the second point shows the covariance between the original series
 649 and a version shifted by one point (i.e., 10-min). The decrease from the first to the second point indicates
 650 the random uncertainty in this K_{660} time series (~50%). This uncertainty can be further reduced to ~20% for
 651 a 1-hour average (i.e., $50\%/\sqrt{6}$).

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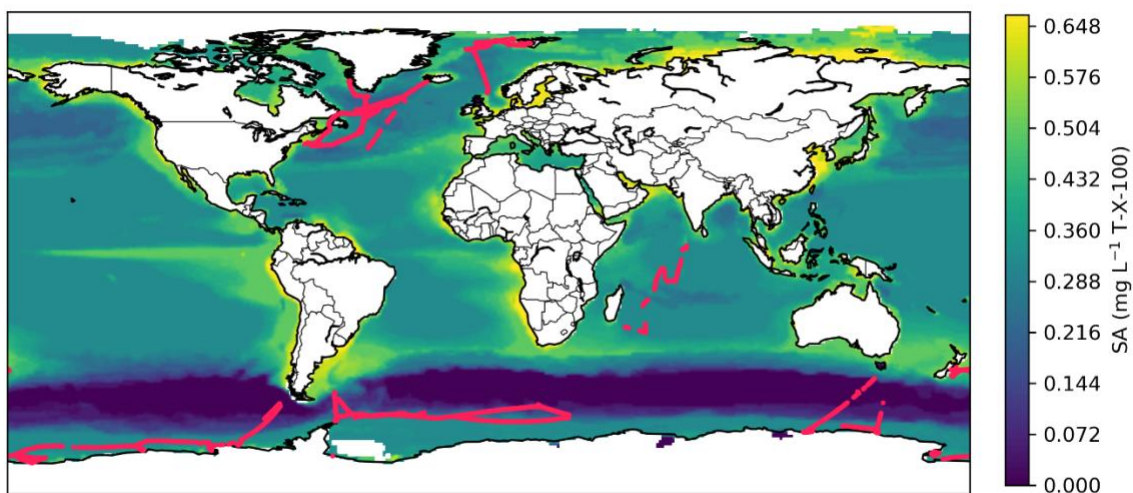
656 **Figure A5: Observed and parameterised gas transfer velocities (K_{660}).** Red dots show 10-min EC-
 657 derived bin averages (for each $1 \text{ m s}^{-1} U_{10N}$ bin), with red lines representing parameterisations fitted to these
 658 data. Blue squares denote DT-derived K_{660} values (timescale ~ 1 day), with blue lines showing
 659 corresponding parameterisations. Solid lines follow the fitting form $K_{660} = aU_{10N}^2 + b$, while dashed lines
 660 follow $K_{660} = aU_{10N}^2$.

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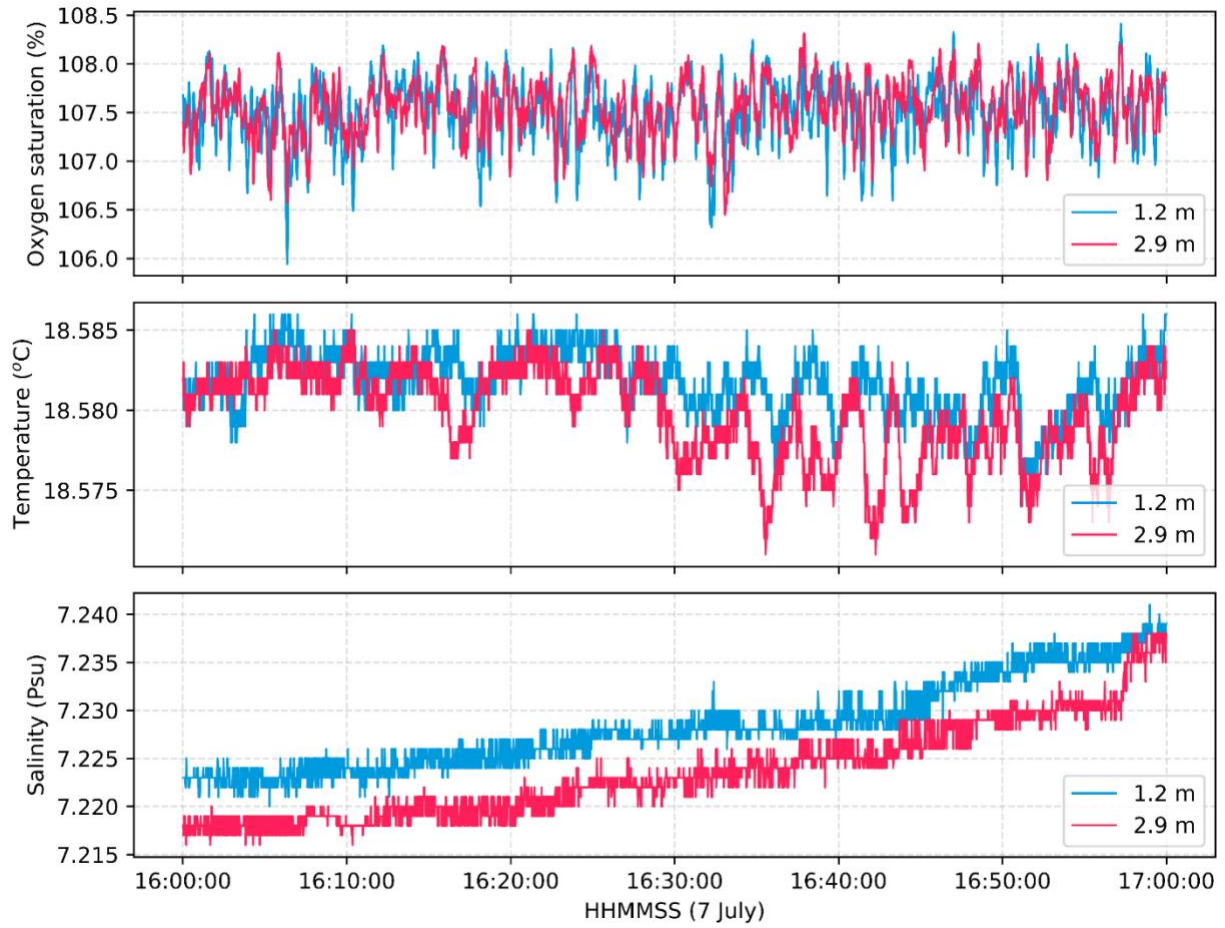
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 666 **Figure A6: Estimated surfactant distributions in the global ocean and the open ocean EC cruise**
 667 **tracks.** The surfactant concentration is estimated following Wurl et al (2011) shown here as an annual mean.
 668 Red lines indicate the EC cruises that were synthesized in Yang et al. (2022).

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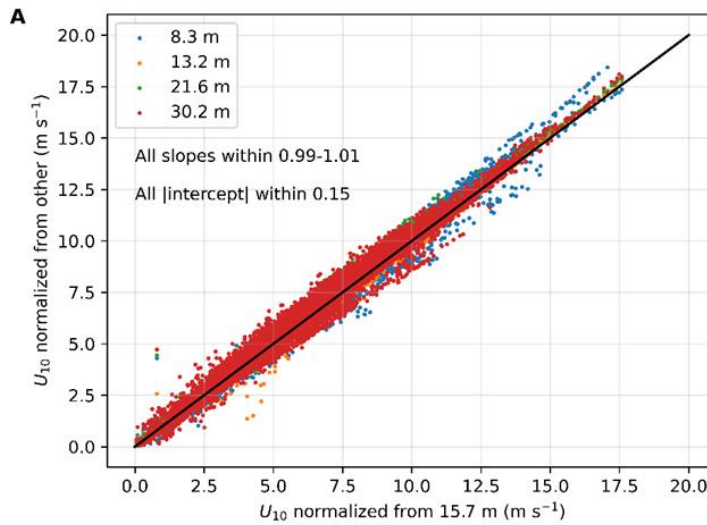
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671 **Figure A7: Representative dissolved oxygen, salinity and temperature data from the small spar buoy,**
 672 **showing the differences measured at 1.2m and 2.9m depth. The patterns shown here are typical of both**
 673 **day and night measurement periods.**

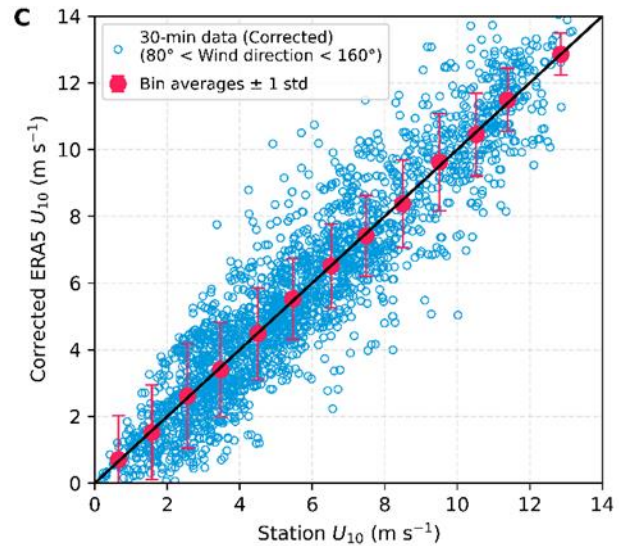
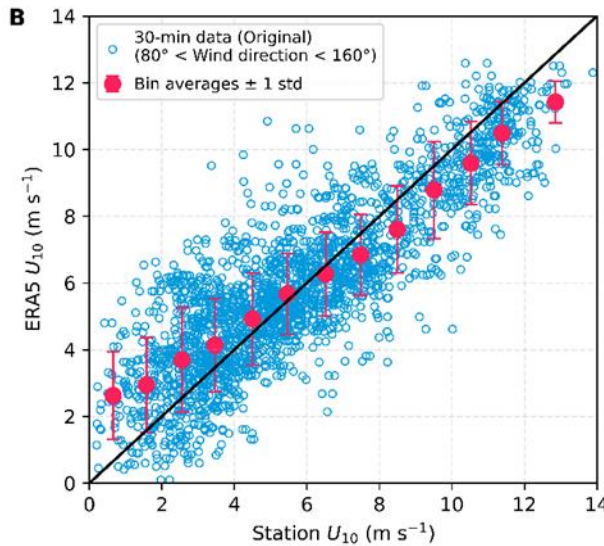
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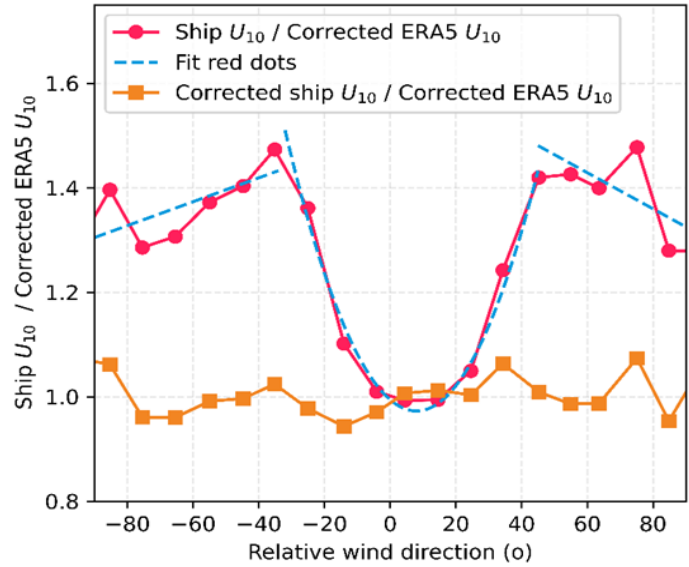
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679 **Figure A8: Correction of ERA5 wind speed using reference measurements from the Östergarnsholm**
 680 **station (restricted to the open sector, 80°-160°; Rutgeresson et al., 2020).** **A:** Comparison of the wind
 681 speed measurements from different heights at the Östergarnsholm station. All wind speeds were normalized
 682 to 10-meter height above MSL (U_{10}). **B:** Comparison of the station U_{10} measurements and the extracted
 683 ERA5 U_{10} at the location of the Östergarnsholm station. The red points are bin averages with error bars
 684 representing 1 standard deviation. The red points in panel B are fitted with two linear relationships: (1) $y =$
 685 $0.64x + 2.05$ for station $U_{10} < 7.5 \text{ m s}^{-1}$, and (2) $y = 0.88x + 0.28$ for station $U_{10} > 7.5 \text{ m s}^{-1}$ for correction.
 686 **C:** Comparison of the station and ERA5 U_{10} after the corrections using the relations in panel B.

687



688

689 **Figure A9: Ratio of ship wind speed to subsampled ERA5 wind speed before (red) and after**
 690 **correction (yellow) as a function of relative wind direction (RWD). ERA5 wind speeds were first**
 691 **calibrated against the Östergarnsholm station record (Fig. A8). The fitted relationships (blue) are: (1) $y =$**
 692 **$0.00036(\text{RWD} - 8)^2 + 0.97$ for -30° to 45° , (2) $y = 0.0023\text{RWD} + 1.51$ for -90° to -30° , and (3) $y = -$**
 693 **$0.0035\text{RWD} + 1.64$ for 45° to 90° .**

694

695

696 **Code and data availability**

697 The code that was used to produce the figures is available in the supplementary material. The
698 processed 10-min EC CO₂ fluxes, wind speeds, friction velocity, and gas transfer velocity can be
699 found in the supplementary material.

700 **Supplement link**

701 The link to the supplement will be included by Copernicus

702 **Author contributions**

703 CM, DH, AE, and GR designed the project. YD processed and analyzed the data in consultation
704 with CM, DH, and RD. CM collected the eddy covariance measurements; HCB collected the CO₂
705 fugacity data; and JK, AE, and BS collected the surfactant data. The dual-tracer data were provided
706 by RD and DH. HC collected the spar buoy measurements. YD prepared the first draft of the
707 manuscript, and all co-authors contributed to and approved the final version.

708 **Competing interests**

709 The authors declare that they have no conflict of interest.

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714 responsibility lies with the authors. Views expressed in the text are those of the authors and do not
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725 Data analysis and visualization were completed using Python. ChatGPT was used to carefully
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734

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