Insights into carbonate environmental conditions in the Chukchi Sea

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Abstract

Healthy Arctic marine ecosystems are essential to the food security and sovereignty, culture, and wellbeing of Indigenous Peoples in the Arctic. At the same time, Arctic marine ecosystems are highly susceptible to impacts of climate change and ocean acidification. While increasing ocean and air temperatures and melting sea ice act as direct stressors on the ecosystem, they also indirectly enhance ocean acidification, accelerating the associated changes in the inorganic carbon system. Yet, much is to be learned about the current state and variability of the inorganic carbon system in remote, high-latitude oceans. Here, we present time-series (2016-2020) of pH and the partial pressure of carbon dioxide (pCO$_2$) from the northeast Chukchi Sea continental shelf. The Chukchi Ecosystem Observatory includes a suite of subsurface year-round moorings sited amid a biological hotspot that is characterized by high primary productivity and a rich benthic food web that in turn supports coastal Iñupiat, whales, ice seals, walrus (*Odobenus rosmarus*), and Arctic cod (*Boreogadus saida*). Our observations suggest that near-bottom waters (33 m depth, 13 m above the seafloor) are a high carbon dioxide and low pH and aragonite saturation state (Ω_{arag}) environment in summer and fall, when organic material from the highly productive summer remineralizes. During this time, Ω_{arag} can be as low as 0.4. In winter, when the site was covered by sea ice, pH was < 8 and Ω_{arag} remained undersaturated under the sea ice. There were only two short seasonal periods with relatively higher pH and Ω_{arag}, which we term ocean acidification relaxation events. In spring, high primary production from sea ice algae and phytoplankton blooms led to spikes in pH (pH > 8) and aragonite oversaturation. In late fall, strong wind-driven mixing events that delivered low CO$_2$ surface water to the shelf also led to events with elevated pH and Ω_{arag}. Given the recent observations of high rates of ocean acidification, and sudden and dramatic shift of the physical, biogeochemical, and ecosystem

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40 conditions in the Chukchi Sea, it is possible that the observed extreme conditions at the Chukchi

41 Ecosystem Observatory are deviating from carbonate conditions to which many species are

42 adapted.

44 **1. Introduction**

45   The quickly changing Arctic Ocean has climatic, societal, and geopolitical implications for

46 the peoples of the Arctic and beyond (Huntington et al., 2022). Arctic Indigenous Peoples are at

47 the forefront of this change and their food security, food sovereignty, culture, and ways of life

48 depend on healthy Arctic marine ecosystems (ICC, 2015). The Arctic is warming at a rate that is

49 up to four times that of the rest of the globe (Serreze and Barry, 2011; Serreze and Francis, 2006;

50 Rantanen et al., 2022). This phenomenon, called Arctic Amplification, is observed in air and sea

51 temperatures, has accelerated in recent years, and is expected to continue in the future (Rantanen

52 et al., 2022; Shu et al., 2022). Warming exerts a toll on sea ice extent, ice thickness, and the

53 duration of seasonal sea ice cover: ice is forming later in fall and retreating earlier in spring,

54 thereby increasing the length of the open water period (Stroeve et al., 2011; Serreze et al., 2016;

55 Wood et al., 2015; Stroeve et al., 2014). The lowest Arctic wide minimum sea ice extents were

56 recorded during the last 16 years of the 44 year-long satellite time-series (National Snow and Ice

57 Data Center, DiGirolamo et al. (2022)).

58   At the same time, the Arctic Ocean is vulnerable to ocean acidification. Although oceanic

59 uptake of anthropogenic carbon dioxide (CO_2) increases oceanic CO_2 and decreases pH and

60 calcium carbonate ($CaCO_3$) saturation states of calcite (Ω_{calc}) and aragonite (Ω_{arag}) globally,

61 climate induced changes to riverine input, temperature, sea ice, and circulation are accelerating

62 the rate of ocean acidification in the Arctic Ocean like nowhere else in the world (Woosley and

64   Millero, 2020; Qi et al., 2022a; Yamamoto-Kawai et al., 2009; Orr et al., 2022; Semiletov et al.,

65   2016; Qi et al., 2017). Recent observational studies propose that freshening of the Arctic Ocean

66   due to increased riverine input may play an even greater role in acidifying the Arctic Ocean than

67   the uptake of anthropogenic CO_2 (Woosley and Millero, 2020; Semiletov et al., 2016). In

68   addition, the cold Arctic waters have naturally low concentrations of carbonate ions (CO_3^{2-}) and

69   are therefore closer to aragonite undersaturation ($\Omega_{arag} < 1$) than more temperate waters (Orr,

70   2011; Sarmiento and Gruber, 2006), which leads to the chemical dissolution of free aragonitic

71    $CaCO_3$ structures (Bednaršek et al., 2021). Because of the naturally low concentrations of CO_3^{2-},

72   such high latitude waters have a lower capacity to take up anthropogenic CO_2 and buffer these

73   changes (Orr, 2011). As a result, concentrations of hydrogen ions (H^+) increase and pH decreases

74   faster in the Arctic than in the tropics, for example.

75   In the Pacific Arctic, the Chukchi shelf waters have warmed by 0.45 $^{\circ}$C decade^{-1} since 1990,

76   triple the rate since the beginning of the data record in 1922 (Danielson et al., 2020). Direct

77   observations of the inorganic carbon dynamics of the Chukchi Sea are mostly limited to June

78   through November because of the region's remoteness and accessibility during sea ice covered

79   months. Summertime profiles across the Chukchi Sea show steep vertical gradients in inorganic

80   carbon chemistry (Bates, 2015; Bates et al., 2009; Pipko et al., 2002; Mathis and Questel, 2013).

81   Surface waters have a low partial pressure of carbon dioxide (pCO$_2$) as a result of high primary

82   production after sea ice retreat, leading to aragonite supersaturated conditions, with $\Omega_{arag} > 2$

83   (Bates, 2015; Bates et al., 2009). In areas with sea ice melt or riverine freshwater influence, Ω_{arag}

84   tends to be lower and at times undersaturated (Bates et al., 2009; Yamamoto-Kawai et al., 2009).

85   At the same time, pCO$_2$ values near the seafloor are around 1000 μatm as a result of organic

86   matter remineralization, leading to summertime aragonite undersaturation (Mathis and Questel,

87 2013; Pipko et al., 2002; Bates, 2015). Between September and November, continuous

88 measurements from within a few meters of the surface suggest a mosaic of pCO$_2$ levels between

89 $\sim$ 200 to 600 µatm, likely due to patchy wind-induced mixing entraining high-CO$_2$ waters from

90 depth into the surface mixed layer (Hauri et al., 2013). Yamamoto-Kawai et al. (2016) used

91 mooring observations of S, T, and apparent oxygen utilization to estimate dissolved inorganic

92 carbon (DIC), total alkalinity (TA), and Ω_{arag} in bottom waters at their mooring site in the Hope

93 Valley in the southwestern Chukchi Sea to give first insights into year round variability of the

94 inorganic carbon system. They found slightly less intense aragonite undersaturation in spring and

95 winter compared to summer, with a net undersaturation duration of 7.5-8.5 months per year.

96   The Chukchi Ecosystem Observatory (CEO) is situated in a benthic hotspot (Figure 1) where

97 high primary production supports rich and interconnected benthic and pelagic food webs

98 (Grebmeier et al., 2015; Moore and Stabeno, 2015). The benthos is dominated by calcifying

99 bivalves, polychaetes, amphipods, sipunculids, echinoderms and crustaceans (Grebmeier et al.,

100 2015; Blanchard et al., 2013). Benthic foraging bearded seals (*Erignathus barbatus*), walrus

101 (*Odobenus rosmarus divergens*), gray whale (*Eschrichtius robustus*), and seabirds feed on these

102 calcifiers during the open water season (Kuletz et al., 2015; Jay et al., 2012; Moore et al., 2022).

103 The CEO site, located on the southern flank of Hanna Shoal, is a region of reduced stratification

104 (relative to other sides of the shoal) that likely alternately feels the effects of differing flow

105 regimes located to the west and to the east (Fang et al., 2020). Consequently, the site exhibits

106 relatively weaker currents (Tian et al., 2021) and so is conducive to deposition of sinking organic

107 matter that in turn feeds the local benthos (Grebmeier et al., 2015). Prolonged open-water

108 seasons during periods of high solar irradiance, in combination with an influx of new nutrients

109 and wind mixing, are likely enhancing primary and secondary production as well as advection of

110 zooplankton (Lewis et al., 2020; Arrigo and van Dijken, 2015; Wood et al., 2015). These

111 physical processes in turn fuel keystone consumers such as Arctic cod (*Boreogadus saida*) and

112 upper trophic level ringed seals (*Phoca hispida*), beluga (*Delphinapterus leucas*) and bowhead

113 whales (*Balaena mysticetus*) as well as predatory polar bears (*Ursus arctos*) and Indigenous

114 People who rely on the marine ecosystem for traditional and customary harvesting (Huntington

115 et al., 2020).

116   Perturbation of the seawater carbonate system associated with ocean acidification and

117 climate change can have significant physiological and ecological consequences for marine

118 species and ecosystems (Doney et al., 2020). All parameters of the carbonate system (pH, pCO$_2$,

119 Ω_{arag}, concentrations of HCO$_3^-$, CO$_3^{2-,}$ etc.) have the potential to affect the physiology of marine

120 organisms while a change in the saturation state (Ω) can lead to the dissolution of unprotected or

121 "free" CaCO$_3$ structures. Recent work has highlighted the importance of local adaptation to the

122 present environmental variability as a key factor driving species sensitivity to ocean acidification

123 (Vargas et al., 2017, 2022). As carbonate chemistry conditions vary enormously between

124 regions, marine organisms are naturally exposed to different selective pressures and can evolve

125 different strategies to cope with low pH or Ω, or high pCO$_2$. For example, the deep-sea mussel

126 *Bathymodiolus brevior* living around vents at 1600 m depths is capable of precipitating calcium

127 carbonate at pH ranging between 5.36 and 7.30 and highly undersaturated waters (Tunnicliffe et

128 al., 2009). The response to changes in the carbonate chemistry is also modulated by other

129 environmental drivers such as temperature or food availability (e.g. Thomsen et al., 2013;

130 Breitberg et al., 2015). Consequently, no absolute or single threshold is expected for ocean

131 acidification (e.g., Bednaršek et al., 2021) and a pre-requisite to assessing the impact on any

132 biota is the monitoring at a short temporal scale to characterize the present environmental niche.

133   When it comes to future impacts, the more intense and faster the changes associated with ocean

134   acidification, the more adverse associated biological impacts are expected (Vargas et al. 2017,

135   2022). As a result, it is anticipated that Arctic marine waters that are experiencing widespread

136   and rapid ocean acidification will potentially undergo severe negative ecosystem impacts

137   (AMAP 2018).

138   Here, we present satellite sea ice coverage data and four years of nearly continuous salinity,

139   temperature, and pCO$_2$ data, accompanied by pH, nitrate (NO$_3$), dissolved oxygen (O$_2$), and

140   chlorophyll fluorescence data for some of the time (Table 1, Figures 2 and 3). We developed an

141   empirical equation for estimating pH from moored pCO$_2$, temperature, and salinity and evaluated

142   it using discrete samples collected across the Chukchi Sea, Bering Sea, and Beaufort Sea. Our

143   timeseries allow us to assess the seasonal and interannual variability and controls of the

144   inorganic carbon system in the Chukchi Sea between 2016 and 2020 and characterize the

145   chemical conditions experienced by organisms. We discuss our observations in terms of

146   progressing acidification and implications to organisms in the Chukchi Sea region.

147

148   **2. Materials and Methods**

149   **2.1 The Chukchi Ecosystem Observatory (CEO)**

150   The Chukchi Sea is a shallow shelf sea with maximum depths < 50 m. It is largely a

151   unidirectional inflow shelf system with Pacific origin water entering the Chukchi Sea through the

152   Bering Strait and advecting north into the Arctic Ocean (Carmack and Wassmann, 2006). The

153   CEO (71°36' N, 161°30' W, Figure 1, Hauri et al., 2018) is located along the pathway of waters

154   flowing through Bering Strait (Fang et al., 2020) and thence from the west of Hanna Shoal

155   toward Barrow Canyon to the south, although the wind can also drive waters from the east over

156   the observatory site (Fang et al., 2020). From both shipboard and moored acoustic Doppler

157   current profiler records, the south side of Hanna Shoal mean flow is characterized by a weak

158   southward-directed current (Tian et al., 2021).

159   The observatory consists of oceanographic moorings that sample year-round, equipped with a

160   variety of sensors that measure sea ice cover and thickness (Sandy et al., 2022), light, currents,

161   waves, salinity, temperature, concentrations of dissolved oxygen, nitrate, and particulate matter,

162   pH, $p\mathrm{CO}_2$, chlorophyll fluorescence, zooplankton abundance and vertical migration (Lalande et

163   al., 2021, 2020), the presence of Arctic cod and zooplankton (Gonzalez et al., 2021), and the

164   vocalizations of marine mammals. During some years, the observatory included a third mooring,

165   an experimental "freeze-up detection mooring", which transmitted real-time data of conductivity

166   and temperature throughout the water column until sea ice formation. The primary moorings

167   stretch from the seafloor at 46 m to about 33 m depth, designed to avoid collisions with ice keels.

168   Pressure sensors at the top of the moorings show less than ± 1 m of excursion of the moored

169   sensor package from its deployment mean depth in any given year, indicating that mooring blow-

170   over or diving is not the cause of any observed large variability. Description of the CEO and lists

171   of sensors deployed at the site can be found in Danielson et al. (2017) and Hauri et al., (2018).

172   For this study we focus on the inorganic carbon system and its controlling mechanisms.

173

174   **2.2 $p\mathrm{CO}_2$**

175   We used a CONTROS HydroC CO_2 sensor (4H-Jena Engineering GmbH, Kiel, Germany) to

176   measure $p\mathrm{CO}_2$. The Contros HydroC CO_2 sensor was outfitted with a pump (SBE 5M, Sea-Bird

177   Electronics) that flushes ambient seawater against a thin semi permeable membrane, which

178   serves as equilibrator for dissolved CO_2 between the ambient seawater and the headspace of the

179   sensor. Technical details about the sensor and its performance are described in Fietzek et al.

180   (2014), who estimated sensor accuracy to be better than 1% with postprocessing.

181   A HydroC CO_2 sensor has been deployed at the CEO site since 2016. In all deployments,

182   except 2016, HydroC CO_2 sensors were post-calibrated. The lack of post-calibration in 2016 is

183   not expected to negatively affect data quality because a battery failure resulted in data returns

184   only over the first 3 months (August through November). Following a zero interval where the

185   gas was pumped through a soda lime cartridge to create a zero-signal reference with respect to

186   CO_2, and subsequent flush interval to allow CO_2 concentrations to return to ambient conditions,

187   measurements were taken in a burst fashion every 12 or 24 hours depending on deployment year

188   (Table 1). Average $p$$CO_2$ values are reported as the mean of the measure interval (Table 1) with

189   standard uncertainty (Equation 1) defined following best practices (Orr et al., 2018) and where

190   the random component is the standard deviation of the mean, and the systematic components

191   include sensor accuracy and estimated error of the regression during calibration.

192
$$u = \sqrt{u^2_{systematic} + u^2_{random}} \qquad (1)$$

193   More than 96% of the time, the relative uncertainty of the $p$$CO_2$ data met the weather data

194   quality goal, defined as 2.5% by the Global Ocean Acidification Observing Network (GOA-ON,

195   Newton et al., 2015).

196   HydroC CO_2 data were processed using Jupyter notebook scripts developed by 4H-Jena

197   Engineering GmbH using pre- and post-calibration coefficients interpolated with any change in

198   the zero-signal reference over the deployment (Fietzek et al., 2014). Further processing using in-

199   house MATLAB scripts included removal of outliers, calculation of the average $p$$CO_2$, and

200   calculation of uncertainty estimates for each measure interval.

201

202 **2.3 pH**

203   A SeapHOx sensor (Satlantic SeaFET™ V1 pH sensor integrated with Sea-Bird Electronics

204 SBE 37-SMP-ODO) was used to concurrently measure pH, salinity, temperature, pressure, and

205 oxygen (Martz et al., 2010). A SeapHOx was deployed at CEO in 2016, 2017, and 2018. No

206 SeapHOx was deployed in 2019 or 2020 due to supply chain delays and communication issues at

207 sea. Unfortunately, measured pH (pH_{SeaFET}) from the 2016 and 2018 SeapHOx deployments

208 were unusable due to high levels of noise in both the internal and external electrodes. In short,

209 we only have usable pH data between August 2017 and August 2018.

210   pH_{SeaFET} data were excluded during a 14-day conditioning period following deployment and

211 were processed with post-calibration corrected temperature and salinity from the SBE37

212 following Bresnahan et al. (2014) using voltage from the external electrode (V_{ext}), and pH_{Vext}

213 (pH calculated from the external electrode of the SeaFET) from an extended period of low

214 variability (18 February 2018). Despite the availability of discrete data from one calibration cast

215 (Cross et al., 2020b; Table 2), pH_{Vex} was used as the single calibration point (Bresnahan et al.,

216 2014) for a variety of reasons: 1) high variability of pH_{SeaFET} (0.0581 pH units) straddling a 12

217 hour window around the discrete sample collection time, 2) high temporal and spatial variability

218 often seen in the Chukchi Sea, and 3) the discrete pH sample was within the published SeaFET

219 accuracy of 0.05 (Table 2, Figure S1). pH_{SeaFET} values are reported as the mean of the measure

220 interval (Table 1) and standard uncertainty is calculated with Equation 1 with the standard

221 deviation of the average (random), and the SeaFET accuracy (systematic). Data handling and

222 processing were done using in-house MATLAB scripts. pH is reported in total scale and at *in*

223 *situ* temperature and depth for the entirety of this paper.

224

2.4 Nitrate

225

226   NO_3 measurements were from a Submersible Ultraviolet Nitrate Analyzer (SUNA) V2 by

227   Sea-Bird Scientific. The SUNA is an *in situ* ultraviolet spectrophotometer designed to measure

228   the concentration of nitrate ions in water. SUNA V2 data were processed using a publicly

229   available toolbox (Hennon et al., 2022; Irving, 2021) with QA/QC steps that included thermal

230   and salinity corrections (Sakamoto et al., 2009), assessment of spectra and outlier removal based

231   on spectral counts (Mordy et al., 2020), and concentration adjustments (absolute offset and linear

232   drift) based on pre-deployment and post-recovery reference measurements of zero concentration

233   (DI) water and a nitrate standard and, when available, nutrient samples taken from Niskin bottles

234   near the mooring site (e.g. Daniel et al., 2020).

235

2.5 CTD and Oxygen

236

237   Two CTDs were deployed on the CEO mooring near the HydroC CO_2 depth. The main

238   pumped Sea-Bird SeaCAT (SBE16) has been deployed on the CEO mooring around 33 m depth

239   since 2014. A pumped SBE43 oxygen sensor was deployed with the SBE16 during the 2015-

240   2016, 2017-2018, and 2019-2020 deployments but only data returns from the 2017-2018

241   deployment is discussed briefly in this manuscript (Figure S2).

242   The other pumped CTD was a Sea-Bird MicroCAT (SBE37-SMP-ODO), which was

243   integrated with an optical dissolved oxygen sensor (SBE63; Figure S2), and the SeaFET pH

244   sensor within the SeapHOx instrument. The SeapHOx was deployed in fall 2016, 2017, and

245   2018. The SBE37-SMP-ODO did not record any CTD or oxygen data during the 2016

246   deployment and only recorded CTD and oxygen data between August and November 3 in 2018

247   due to battery failure.

248   Processing of these data included temperature and conductivity correction using pre- and

249   post-calibration data following Sea-Bird Application Note 31 and oxygen correction using pre-

250   and post-calibration data following Sea-Bird Module 28. Oxygen was converted from ml/l to

251   μmol/kg following Bittig et al. (2018). Density and practical salinity were calculated using the

252   TEOS-10 GSW Oceanographic Toolbox (McDougall and Baker, 2011).

253   Differences between the two oxygen sensors (SBE43 and SBE63) of approximately 145 to

254   265 μmol/kg were observed over the 2017-2018 deployment, and both moored sensors had

255   varying offsets compared to nearby casts (Figure S2). Therefore, only relative oxygen values

256   from the freshly calibrated SBE63 are discussed in this paper.

257   The freeze-up detection mooring (Figure 6) consisted of four Sea-Bird SBE 37 inductive

258   modem CTD sensors that transmitted in real time hourly temperature, salinity, and pressure data

259   via the surface float from four subsurface depths (8, 20, 30, and 40 m; Hauri et al., 2018).

260

261   **2.6 Development of empirical relationship to estimate pH**

262   Empirical relationships for estimating water column pH have been developed for regions

263   spanning southern, tropical, temperate and Arctic biomes, using a variety of commonly measured

264   parameters (e.g., pH(S, T, NO_3, O_2, Si) Carter et al 2018; pH(O_2,T,S) Li et al., 2016; pH(θ,O_2)

265   Watanabe et al., 2020; pH(NO_3, T, S, P) and pH(O_2, T, S, P) Williams et al., 2016; pH(O_2, T)

266   Alin et al., 2012; pH(O_2, T) and pH(NO_3, T) Juranek et al., 2009). Given the tight coupling

267   between the concentration of H^+ and concentration of CO_2 solution, an empirical relationship for

268   estimating surface pH from $p$$CO_2$ was developed by the National Academies of Sciences,

269   Engineering and Medicine (2017) appendix F. Licker et al. (2019) used this empirical

270   relationship to calculate the global average surface ocean pH and found it represented the

271 relationship for surface water temperatures spanning 5°C to 45°C. Here, we take a similar

272 approach but extend it to water column pH in our cold region using temperature (T) and salinity

273 (S) as additional proxy parameters (Equation 2).

274 $$pH^{est} = \alpha_0 + \alpha_1 log\ (pCO_2) + \alpha_2 T + \alpha_3 S \qquad\qquad (2)$$

275 Where pH^{est} is the estimated value of water column pH, pCO_2 is from the HydroC, and T and S

276 are from the SBE16, and all α (α_0 = 10.4660, α_1= -0.4088, α_2 = 0.0013, α_3 = -0.0001) terms are

277 model-estimated coefficients determined using MATLAB's multiple linear regression algorithm

278 *regress.m* (Chatterjee and Hadi, 1986). After interpolating pH_{SeaFET} (Figure 4, red dots) to the

279 pCO_2 timestamp, the algorithm was trained over an arbitrarily chosen 180-day period

280 (15/9/2017-14/3/2018, Figure 4, dashed box). An uncertainty of 0.0525 for pH^{est} (Figure 3 and

281 Figure S1, gray shading) was determined with Equation 1, where the RMSE (the uncertainty in

282 the estimation) over the entire pH_{SeaFET} timeseries is the random component and the published

283 accuracy of the SeaFET is the systematic component (since the algorithm was trained with

284 pH_{SeaFET}). The algorithm cross-validation and evaluation are discussed in section 3.1. Unless

285 explicitly defined otherwise, observations of pH refer to pH^{est} for the remainder of this paper.

286

287 **2.7 Carbonate system calculations**

288   Moored data were collected at different sample intervals (Table 1) and were linearly

289 interpolated to the HydroC CO_2 timestamp to enable further calculations. TA, DIC, and Ω_{arag}

290 (Figure 11 a & b and Figure 3d) were calculated based on measured pCO_2, S, T, and pressure (P)

291 and algorithm-based pH (pH^{est}). Due to a lack of data, nutrient concentrations (Si, PO_4, NH_4,

292 H_2S) were assumed to be negligible in the CO2SYS calculations (e.g. deGrandpre et al., 2019;

293 Vergara-Jara et al., 2019; Islam et al., 2017). pH^{est} was used in lieu of pH_{SeaFET} to allow for

294 calculations over the whole pCO$_2$ record and due to erroneously large variability of DIC and TA

295 when pH$_{SeaFET}$ was used as an input parameter (Raimondi et al., 2019; Cullison-Gray et al.,

296 2011). The pH-pCO$_2$ input pair leads to large, calculated errors in DIC and TA (Raimondi et al.,

297 2019; Cullison-Gray et al., 2011) due to strong covariance between the two parameters (both

298 temperature and pressure dependent). Cullison-Gray et al. (2011) attributed unreasonably large

299 short-term variability in calculated TA and DIC to temporal or spatial measurement mismatches

300 between input pH and pCO$_2$ parameters and found that appropriate filtering alleviated noise

301 spikes. By using pH^{est}, which by the nature of its definition is well correlated to pCO$_2$, we are

302 eliminating some of these spurious noise spikes. We show Ω_{arag} calculated from pH$_{SeaFET}$-pCO$_2$

303 (Figure 3d, red line) because it is less sensitive to calculated errors as it accounts for a small

304 portion of the total CO$_2$ in seawater (Cullison-Gray et al., 2011).

305   All inorganic carbon parameters were calculated using CO2SYSv3 (Sharp et al., 2023; Lewis

306 and Wallace, 1998) with dissociation constants for carbonic acid of Lueker et al. (2000),

307 bisulfate of Dickson (1990), hydrofluoric acid of Perez and Fraga (1987), and the boron-to-

308 chlorinity ratio of Lee et al. (2010). Sulpis et al. (2020) found that the carbonic acid dissociation

309 constants of Lueker et al. (2000) may underestimate pCO$_2$ in cold regions (below ~8°C), and

310 therefore overestimate pH and CO$_3^{2-}$. However, we choose to use Lueker et al. (2000) because

311 they are recommended (Dickson et al., 2007; Woosley, 2021), continue to be the standard (Jiang

312 et al., 2021; Lauvset et al., 2021), and are commonly used at high latitudes (Duke et al., 2021;

313 Raimondi et al., 2019; Woosley et al., 2017). Furthermore, the difference between DIC

314 calculated from pH^{est} and pCO$_2$ and discrete samples interpolated to moored instrument depth

315 ranged from 266 to -195 μmol/kg using the K_1^* and K_2^* of Sulpis et al. (2020), compared to -38

316 to -7 μmol/kg using Lueker et al. (2000).

319

2.8 Sea ice concentration

Sea ice concentration at the observatory site was taken from the National Snow and Ice Data Center (NSIDC; DiGirolamo et al., 2022). Latitude and longitude coordinates were converted to NSIDC's EASE grid coordinate system (Brodzik and Knowles, 2002) and the 25-km gridded data were bilinearly interpolated to calculate sea ice concentration at the CEO site. Low sea ice is defined by < 15 % sea ice coverage per grid cell.

2.9 Estimation of model-based ocean acidification trend

Model results were obtained from historical simulations of five different global Earth System Models: 1) GFDL-CM4 (Silvers et al., 2018), 2) GFDL-ESM4 (Horowitz et al., 2018), 3) IPSL-CM6A-LR-INCA (Boucher et al., 2020), 4) CNRM-ESM2-1 (Seferian, 2019), and 5) Max Plank Earth System Model 1.2 (MPI-ESM1-2-LR, Wieners et al., 2019) that are part of the Coupled Model Intercomparison Project Phase 6 (CMIP6). Each simulation was used to calculate the annual trend of aragonite saturation state and pH at the closest depth and grid cell to the CEO mooring.

3. Results

In the following, we will evaluate the pH algorithm (section 3.1), analyze the large variability patterns (sections 3.2 and 3.3), and then take a closer look at the data from 2020 since the seasonal cycle was different in 2020 than in previous years (section 3.4).

3.1 pH algorithm

342   The algorithm estimated pH data from the CEO site reasonably well and within the weather

343   uncertainty goal as defined by Newton et al. (2015) most of the time. As a first step, pH^{est}

344   consistency was assessed through cross-validation (Figure 5) using the test dataset (outside the

345   training period, $r^2 = 0.9666$, RMSE = 0.166) and across the whole timeseries ($r^2 = 0.9598$, RMSE

346   = 0.0161, p<0.0001, Figure 5). Observed high frequency spikes in pH_{SeaFET} (Figure 4, red dots;

347   Figure 5d, red line) were not captured by the HydroC pCO_2 sensor (sampling frequency of 12 h)

348   and as a result, are not reproduced in the pH^{est} timeseries. Throughout the pH_{SeaFET} timeseries,

349   pH^{est} overestimates pH_{SeaFET} by a mean of 0.0008 and median of 0.0039. Since pH^{est} generally

350   overestimates pH_{SeaFET}, we assume that Ω_{arag} is also somewhat overestimated throughout this

351   manuscript. Discrete water samples were used as reference values to evaluate the algorithm at

352   the CEO site (Table 2) and were found to be within the pH^{est} uncertainty (Figure S1).

353   An independent verification of our algorithm was done using discrete data collected from the

354   Bering Sea to the Arctic Ocean on four research cruises in 2020, 2019, 2018, and 2017 (Figure

355   6d; Monacci et al., 2022; Cross et al., 2021; 2020a; 2020b), henceforth called the DBO dataset.

356   Samples collected from deeper than 500 m below the surface or flagged as questionable or bad

357   were excluded from this analysis. pH and pCO_2 were calculated from 1275 discrete samples

358   analyzed for TA, DIC, silicate, phosphate, and ammonium (except when silicate, phosphate, and

359   ammonium were assumed to be negligible for the 327 samples from cruise SKQ202014S;

360   Monacci et al., 2022) using CO2SYSv3 (Sharp et al., 2023; section 2.7 for details) and are

361   referred to as pH^{disc}_{calc} and $pCO_2^{disc}_{calc}$, respectively. pH^{disc}_{est} was based on discrete water samples

362   and calculated using Equation 2 and was fit to pH^{disc}_{calc} using a linear regression ($r^2 = 0.9975$,

363   RMSE = 0.0078, p-value < 0.0001; Figure 6 a – c). Mean and median differences between

364   pH^{disc}_{calc} and pH^{disc}_{est} were zero and 0.0022, respectively, with largest anomalies observed at

366 lower salinities (Figure 6c). Absolute differences between pH^{disc}_{est} and pH^{disc}_{cal} over the salinity

367 range observed at the CEO site (30.87 to 33.93) fall within the weather data quality goal

368 (Newton et al., 2015) 98.7% of the time with maximum absolute differences < 0.03. The

369 uncertainty of 0.0154 for pH^{disc}_{est} was determined using Equation 1, where the mean combined

370 standard uncertainty (u_c) for pH^{disc}_{calc} (0.0133; Orr et al., 2018) was the systmetic component,

371 and the regression RMSE was the random component.

372   Empirical relationships for estimating water column pH that rely on dissolved oxygen often

373 ignore surface waters to limit biases due to decoupling the stoichiometry of the O_2:CO_2

374 relationship due to air-sea gas exchange (e.g. Juranek et al., 2011; Alin et al., 2012; Li et al.,

375 2016). We see evidence of this bias in our algorithm at low salinity (Figure 6c) and low pCO_2

376 (not shown) when compared with the DBO dataset samples collected across the Arctic and from

377 the surface to 500 m, with pH^{disc}_{est} overestimating pH^{disc}_{calc} by a maximum of 0.049. If depth is

378 restricted to between 30 and 500 m when evaluating the algorithm with the DBO dataset,

379 algorithm performance improves ($r^2 = 0.9990$, RMSE = 0.0055, p-value < 0.0001; not shown)

380 and the maximum pH^{disc}_{est} overestimates pH^{disc}_{calc} by 0.022.

381

382 **3.2 Relaxation events**

383   The sub-surface waters at the CEO site comprise a high pCO_2, low pH, and low Ω_{arag}

384 environment, with mean values of $pCO_2^{mean} = 538 \pm 7$ µatm, $pH^{mean} = 7.91 \pm 0.05$, $\Omega_{arag}^{mean} =$

385 0.94 ± 0.23 across the full data record (Figure 3 b - d). In the following we will focus on spikes

386 of high pH and Ω_{arag} and low pCO_2 that occur in spring (May-June) and fall (September-

387 December); we define these spikes as relaxation events (see discussion for justification of term).

388   *Spring:* Springtime relaxation events at 33 m depth that exhibit relatively higher pH and

389   Ω_{arag} and lower pCO_2 compared to the overall mean, are likely consequences of photosynthetic

390   activity during sea ice break-up (Figures 2 and 3). In June of 2018 and 2019, near bottom pH and

391   Ω_{arag} spiked to > 8.17 and > 1.5, respectively, while pCO_2 dropped to < 286 µatm. Ω_{arag} remained

392   oversaturated and pH was greater than 8.0 for nearly all of June in 2018. In 2019, the relaxation

393   event was less sustained, with only four short (2-6 day-long) events of relatively higher pH and

394   Ω_{arag} > 1 in June. In both years, chlorophyll fluorescence spiked and either O_2 increased (in

395   2018) or NO_3 decreased (in 2019), which are signs of photosynthetic activity and primary

396   production.

397   *Fall:* The relaxation events in fall were characterized by large and sudden drops in pCO_2,

398   abrupt increases in pH and Ω_{arag}, and considerable interannual variability in their timing. Unlike

399   the relaxation events observed in spring, we attribute these fall relaxation events to wind-induced

400   physical mixing. To examine the controlling mechanisms causing these abrupt relaxation events

401   in fall, we will start with using water column salinity and temperature data from a freeze-up

402   detection buoy (Hauri et al., 2018) that was deployed in summer 2017 approximately 1 km away

403   from the biogeochemical mooring. The freeze-up detection mooring provided temperature and

404   salinity measurements every 7 meters throughout the water column from the time of its

405   deployment in mid-August until freeze-up. Data from the freeze-up detection mooring suggest

406   that warmer and fresher water from the upper water column gets periodically entrained down to

407   the location of the biogeochemical sensor package at 33 m depth, leading to enhanced variability

408   of density in August and September (Figure 7). Fluctuations of the pycnocline associated with

409   the passage of internal waves could also elevate signal variances. During this time pCO_2 often

410   decreased to or below atmospheric levels and pH sporadically reached values > 8. At the end of

413   September, a strong mixing event (with coincident strong surface winds) homogenized the water

414   column from the surface down to the location of the sensor package and caused a sudden

415   temperature increase from 0.4 °C to 3.9 °C (Figure 7c and 8a). At the same time, pCO$_2$ (Figure

416   7b and 8) decreased from 590 to 308 μatm. This suggests that warm and low CO$_2$ surface water

417   mixed with CO$_2$-rich subsurface water and led to a sustained relaxation period that subsequently

418   lasted until mid-November. Another mixing event further eroded the water column stratification

419   and replaced subsurface water with colder and fresher water (ice melt) from the surface at the

420   end of October. This second large mixing event did not lead to large changes in pCO$_2$, pH, and

421   Ω_{arag}.

422   Salinity and temperature records from the biogeochemical mooring at 33 m depth also

423   suggest fall season mixing events in all other years, when increases in temperature coincide with

424   decreases in pCO$_2$ (Figure 2b and c, 3a and 8). For example, two mixing events shaped the

425   carbonate chemistry evolution in fall 2018. pCO$_2$ decreased from 915 μatm to around 565 μatm

426   and Ω_{arag} increased to 0.9 as temperature increased and salinity decreased in early September

427   (Figures 2 and 8). pCO$_2$ then increased to 1160 μatm in late October, before decreasing to 385

428   μatm at the beginning of November, causing a spike in Ω_{arag} to 1.34. At the same time, salinity

429   decreased by 1 unit, suggesting a strong mixing event. Throughout November 2018, pCO$_2$

430   oscillated between 344 and 757 μatm and salinity between 31.01 and 32.97, hinting at additional

431   mixing.

432   Similarly, an early mixing event in 2019 decreased pCO$_2$ to 352 μatm at the beginning of

433   September. Short-term variability in pCO$_2$ with maximum levels of up to 855 μatm and

434   minimum values below 300 μatm, variable temperature and salinity, and sporadic aragonite

435   oversaturation events point to mixing through mid-September. At the end of October, a large

436 mixing event homogenized the water column, accompanied by a decline of salinity by >1 unit,

437 increase of temperature to 4 °C, and decrease of pCO_2 from 565 μatm to below 400 μatm. In a

438 similar fashion to 2018, this fall mixing event was followed by a month-long period of large

439 variability of pCO_2, salinity, pH, and Ω_{arag}, leading to short and sporadic aragonite oversaturation

440 events in November, and sustained oversaturation in December.

441

442 **3.3 Sustained periods of low pH and Ω_{arag}, and high pCO_2**

443 Waters at 33 m depth at the CEO site were most acidified during the sea ice free periods

444 until mixing events entrained surface waters to the sensor depth (section 3.2). pH and Ω_{arag}

445 started to gradually decrease from their maximum levels (Ω_{arag_max} = 1.65, pH$_{max}$ = 8.19) at the

446 beginning of June in 2018 to their annual low at the beginning of November (Ω_{arag_min} = 0.47,

447 pH$_{min}$ = 7.58, Figure 3 d and c). In November, the waters were also undersaturated with regards

448 to calcite (not shown) and pCO_2 peaked at 1159 μatm (Figure 3b). Dissolved oxygen decreased

449 by about 400 μmol kg^{-1} between July and October, when the sensor stopped working properly.

450 The decrease of dissolved oxygen suggests remineralization of organic material. The decrease of

451 pH, Ω_{arag}, O_2 and increase of pCO_2 was briefly interrupted by a strong mixing event in

452 September, which entrained warmer, fresher, and CO_2-poorer water down to 33 m depth (section

453 3.2, Figure 8). The 2019 observations paint a similar picture of remineralization during the

454 summer months, as the pCO_2 increase and pH and Ω_{arag} decreases were accompanied by an NO_3

455 increase (Figure 2d and 3b-d).

456 pCO_2 steadily increased and pH and Ω_{arag} decreased during the sea ice covered periods

457 (Figures 8). pH was < 8 and Ω_{arag} remained undersaturated under the sea ice. At the same time,

458 NO_3 slowly increased and O_2 decreased, which points to slow organic matter remineralization

459 (Figure 9). Short-term variability in pCO_2, especially in January of all three observed years, was

460 also reflected in salinity, O_2 and NO_3 (Figure 9) and could be attributed to advection, as the CEO

461 site is adjacent to contrasting regimes of flow and hydrographic properties (Fang et al., 2020).

462

463 **3.4 Spring and summer of 2020 were different**

464 The seasonal cycle in 2020 strongly contrasted with the previous observed years. pCO_2

465 gradually increased by roughly 200 µatm throughout the sea ice covered months to 650 µatm

466 when sea ice started to retreat at the beginning of July. By the end of July, pCO_2 doubled and

467 increased to 1389 µatm, which is the highest pCO_2 level recorded in this timeseries. The peak of

468 pCO_2 was accompanied by an increase in salinity of 0.5 while temperature did not change,

469 suggesting the influence of advection. At the beginning of August, pCO_2 dropped to 536 µatm

470 and then oscillated around 600 µatm through much of August before returning to around 900

471 µatm for the next month. Similarly, pH decreased to 7.5 at the end of July and then oscillated

472 around 7.85, while Ω_{arag} dropped to 0.37, and oscillated around 0.85. The steep drop and

473 oscillation of pCO_2 was reflected in NO_3, suggesting that primary production and

474 remineralization played a role. When pCO_2 and NO_3 decreased at the beginning of August,

475 temperature simultaneously increased by 0.7 °C and salinity decreased by 0.12, suggesting that

476 entrainment of shallower water masses may have played a role too. Comprehensive analyses of

477 the factors that resulted in the 2020 differing conditions are beyond the scope of this paper, but

478 deserve attention in a future effort.

479

480 **4. Discussion**

481   CEO data provide new insights into the synoptic, seasonal and interannual variability of

482   the inorganic carbon system in a time when ocean acidification and climate change have already

483   started to transform this area. The observations suggest that the CEO site is a high-CO_2 and low-

484   pH and low-Ω_{arag} environment most of the time, except during sea ice break-up when the effects

485   of photosynthetic activity remove CO_2 from the system, and later in fall, when strong storm

486   events entrain low $p$$CO_2$ surface waters to the seafloor. Lowest pH and $CaCO_3$ saturation states

487   and highest $p$$CO_2$ occur in summer through late fall when organic matter remineralization

488   dominates the carbonate system balance. During this time, Ω_{arag} can fall below 0.5 and even Ω_{calc}

489   becomes sporadically undersaturated ($\Omega_{calc} < 1$).

490

4.1 pH algorithm

492   Deploying oceanographic equipment in remote Arctic locations is challenging. The data

493   return from the SeapHOx sensors was disappointingly minimal, despite annual servicing and

494   calibration by the manufacturer. Our new pH algorithm is therefore even more important as it

495   fills pH data gaps in the CEO timeseries and can be applied with confidence from the Bering to

496   the western Beaufort seas (Figure 6). While another successful year of moored pH data return at

497   the CEO site is needed to fully evaluate our algorithm throughout the year, comparison with

498   single discrete water samples nearby the CEO site and the DBO dataset (section 3.1, Table 2,

499   Figures 6 and S1) suggest that our algorithm-derived pH meets the weather quality uncertainty

500   goal of ± 0.02 (Newton et al., 2015) much of the time.

501   The combination of our new algorithm with recent progress in monitoring $p$$CO_2$ with

502   Seagliders (Hayes et al., 2022) will further increase our ability to study the inorganic carbon

503   dynamics at times and locations when shipboard or mooring based measurements may not be

504   practical. Additional assessment is needed to determine to what degree the algorithm needs

505   adjustments beyond the region evaluated in this work.

506

507   **4.2 Uncertainty**

508   Inherent spatial and temporal variability of the inorganic carbon parameters in the

509   Chukchi Sea make the use of discrete water samples for evaluating sensor-based measurements

510   difficult. Historic continuous surface measurements from the area suggest that surface pCO_2 can

511   be as low < 250 µatm in early fall (Hauri et al., 2013), at a time of year when subsurface pCO_2

512   reaches its max of >800 µatm at the CEO site. This suggests a steep pCO_2 gradient of > 17 µatm

513   per meter. High-resolution pH data from the 2017/2018 deployment suggests high temporal

514   variability as well, further complicating the collection of discrete water samples to adequately

515   evaluate the sensors. The HydroC's zeroing function, in addition to our pre- and post-calibration

516   routines that factor into the post-processing of the data, gives us confidence in the accuracy of

517   the pCO_2 data, and further confidence in pH derived from pCO_2.

518   The pH^{est} uncertainty of 0.0525 is likely a conservative estimate based on our validation

519   of pH^{est} (section 3.1, Table 2). Consequently, propagated uncertainties in the calculated

520   parameters are high. As discussed in section 2.7, the pH-pCO_2 input pair exacerbates these larger

521   uncertainties. Mean TA(pH^{est},pCO_2), DIC(pH^{est},pCO_2), and Ω_{arag}(pH^{est},pCO_2), ± u_c (Orr et al.,

522   2018) are 2173 ± 281 µmol kg^{-1}, 2111 ± 263 µmol kg^{-1}, and 0.94 ± 0.23, respectively, when

523   input uncertainties are the standard uncertainty (Equation 1). When the input uncertainty for

524   pH^{est} is only the RMSE of 0.0161 (section 3.1), uncertainties decrease to ± 98 µmol kg^{-1}, ± 93

525   µmol kg^{-1}, and ± 0.09, respectively. When input uncertainties are only the random component of

526   the input parameters (i.e. standard deviation for pH$_{SeaFET}$ and pCO_2 and instrument precision for

527 T and S), $TA(pH_{SeaFET}, pCO_2)$, $DIC(pH_{SeaFET}, pCO_2)$, and $\Omega_{arag}(pH_{SeaFET}, pCO_2)$ u_c drops to $\pm$ 38

528 μmol kg^{-1}, $\pm$ 37 μmol kg^{-1}, and $\pm$ 0.06, respectively. Given the above uncertainties and that we

529 do not see significant biofouling at the CEO site, we believe that short term variability can be

530 discussed with confidence with this dataset. In other words, wiggles in the data represent real

531 events, despite the high uncertainty in the precise value of the calculated parameters.

532

533 **4.3 Subsurface biogeochemical drivers of pH, Ω_{arag}, and pCO_2**

534   Inorganic carbon chemistry can be influenced by advection and vertical entrainment of

535 different water masses, temperature, salinity, biogeochemistry, and conservative mixing with TA

536 and DIC freshwater endmembers. Here, we followed Rheuban et al. (2019) and separated the

537 drivers of the observed large pH, Ω_{arag}, and pCO_2 variability to provide additional insights into

538 our timeseries (Figure 10) using CO2SYS by altering input parameters temperature, salinity, TA,

539 and DIC. Anomalies (black) relative to the reference values $pH(T_0, S_0, DIC_0, TA_0)$, $\Omega_{arag}(T_0, S_0,$

540 $DIC_0, TA_0)$, and $pCO_2(T_0, S_0, DIC_0, TA_0)$, were calculated using a linear Taylor series

541 decomposition, adding up the thermodynamic effects of temperature and salinity, and the

542 perturbations due to biogeochemistry, and conservative mixing with freshwater DIC and TA

543 endmembers (Rheuban et al., 2019). Reference values T_0, S_0, DIC_0, and TA_0, are the mean of the

544 CEO timeseries. Freshwater from sea ice melt and meteoric sources (precipitation and rivers)

545 may influence the CEO site. TA and DIC concentrations of 450 μmol kg^{-1} and 400 μmol kg^{-1},

546 respectively, have been measured in Arctic sea ice (Rysgaard et al., 2007). Riverine input along

547 the Gulf of Alaska tends to have lower TA (366 μmol kg^{-1}) and DIC (397 μmol kg^{-1})

548 concentrations (Stackpoole et al., 2016, 2017) than rivers draining into the Bering, Chukchi, and

549 Beaufort Seas (TA = 1860 μmol kg^{-1}, DIC = 2010 μmol kg^{-1}, Holmes et al., 2021) all of which

Deleted: .

551 can influence the CEO site to some extent (Asahara et al., 2012; Jung et al., 2021). In this Taylor

552 decomposition we used sea ice TA and DIC endmembers (Rysgaard et al., 2007) but want to

553 emphasize that using Arctic river endmembers did not meaningfully change the results (not

554 shown). Figure 10 shows the effects of biogeochemical processes, temperature, salinity, and

555 conservative mixing with TA and DIC freshwater endmembers on pH, Ω_{arag}, and $p\mathrm{CO}_2$. The

556 effects of salinity (turquoise) and conservative mixing with TA and DIC freshwater endmembers

557 (green) are negligible for pH, Ω_{arag}, and $p\mathrm{CO}_2$. Temperature varied between -1.7 °C during the

558 sea ice covered months and up to 4 °C in late fall, when wind events mixed the whole water

559 column and entrained warm and low $p\mathrm{CO}_2$ surface waters to the instrument depth at 33 m (see

560 section 3.2 for a more in-depth discussion of these mixing events). During this time, the increase

561 in temperature counteracted the effect of biogeochemistry slightly and increased $p\mathrm{CO}_2$ and

562 decreased pH (Figure 10 a,c). Temperature did not affect Ω_{arag}.

563   Biogeochemistry (photosynthesis, respiration, calcification, dissolution) is the most

564 important driver of the inorganic carbon dynamics at 33 m depth at the CEO site. The springtime

565 relaxation events in 2018 and 2019 with relatively higher pH and Ω_{arag}, and lower $p\mathrm{CO}_2$, were

566 mainly driven by biogeochemistry (Figure 10, magenta). During these events O_2 increased and

567 NO_3 decreased, suggesting photosynthetic activity (Figure 2d, e and 3a). Near bottom

568 photosynthetic activity by phytoplankton or sea ice algae has been observed at different locations

569 across the Chukchi Sea (Arrigo et al., 2017; Ouyang et al., 2022; Stabeno et al., 2020; Koch et

570 al., 2020). Sediment trap data from a CEO deployment prior to the start of this $p\mathrm{CO}_2$ and pH

571 time-series suggest that export of the exclusively sympagic sea ice algae *Nitzschia frigida* peaked

572 in May and June, during snow and ice melt events (Lalande et al., 2020), further supporting the

573 hypothesis that sea ice algae contributed to the CO_2 draw down. Interestingly, TA also increased

575 significantly during these events in 2018 and 2019, which cannot be solely attributed to organic

576 matter production. Specifically, TA increased by 23 umol kg^{-1} in 2019 (Figure 11a). However,

577 with an observed NO$_3$ decrease of 7.6 umol kg^{-1}, we would expect an increase of TA by 7.6 umol

578 kg^{-1}. This is assuming that NO$_3$ is the primary source of nitrogen during organic matter

579 formation, and that assimilation of 1 umol of NO$_3$ leads to an increase of TA of 1 umol (Wolf-

580 Gladrow et al., 2007). The TA increase of 23 umol kg^{-1} is therefore larger than expected from

581 organic matter formation alone and is likely due to CaCO$_3$ mineral dissolution. While direct

582 evidence is missing, the strong TA increase suggests that CaCO$_3$ mineral dissolution during sea

583 ice break up also plays an important role at the CEO site. As observed in other Arctic areas, it is

584 possible that ikaite crystals that were trapped in the ice matrix dissolved in the water column

585 when sea ice melted (Rysgaard et al., 2012, 2007).

586

587 **4.4 Progression of ocean acidification in the Chukchi Sea**

588   Organisms living at the CEO site may have always been exposed to large seasonal

589 variability and low pH and Ω_{arag} (high pCO$_2$), but the combined and cumulative effects of

590 climate change and ocean acidification have rapidly made these conditions more extreme and

591 longer lasting. Ocean acidification serves as a gradual environmental press by increasing the

592 system's mean and extreme pCO$_2$ and decreasing mean and extreme pH and Ω_{arag}. Climate

593 induced changes to other important controls of the inorganic carbon system, such as sea ice,

594 riverine input, temperature, and circulation can act as sudden pulses and further modulate the

595 inorganic carbon system to a less predictable degree and cause extreme events (Woosley and

596 Millero, 2020; Orr et al., 2022; Hauri et al., 2021; Qi et al., 2017). Huntington et al. (2020)

597 describe a sudden and dramatic shift of the physical, biogeochemical and ecosystem conditions

---

620   in the Chukchi and Northern Bering seas in 2017. For example, satellite data for the CEO site

621   illustrate that the longest open water seasons on record occurred between 2017 and 2020. Before

622   2017, the open water season was on average 81 ($\pm$ 40) days long (i.e., below 15 %

623   concentration), of which 60 ($\pm$ 44) days were ice free, whereas between 2017 and 2020, the low

624   sea ice period was 157 ($\pm$ 30) days long, of which 152 ($\pm$ 24) days were ice free (Figure 12). Sea

625   ice decline and increased nutrient influx has also promoted increased phytoplankton primary

626   production in the area (Lewis et al., 2020; Arrigo and van Dijken, 2015; Payne et al., 2021).

627   Since our inorganic carbon timeseries started after the "dramatic shift" that was observed in the

628   Chukchi Sea in 2017 (Huntington et al., 2020) and given the uncertainty in model output in this

629   region, we can only speculate about how the changes in sea ice, temperature and biological

630   production may have affected seasonal variability and extremes of the inorganic carbon

631   chemistry at the CEO site. However, since the summertime low pH and Ω_{arag} and high pCO$_2$ are

632   tightly coupled to the length of the ice-free period and intensity of organic matter production, it

633   is possible that the observed summertime period of extreme conditions may have been

634   previously unexperienced at this site. We therefore think it is justified to call the spikes of pH

635   and Ω_{arag} "ocean acidification relaxation events", since the long-lasting summertime period of

636   extremely low pH and Ω_{arag} may be a new pattern.

637

638   **4.5 Relevance for ecosystem**

639   Marine organisms are exposed to a wide range of naturally fluctuating environmental

640   conditions such as temperature, salinity, carbonate chemistry and food concentrations that

641   together constitute their ecological niche. As evolution works toward adaptation, the tolerance

642   range of species and ecosystems to such parameters varies between locations and is often closely

643 related to niche status (Vargas et al., 2022). Stress can be defined as a condition evoked in an

644 organism by one or more environmental and biological factors that bring the organism near or

645 over the limits of its ecological niche (after Van Straalen, 2003). The consequence of the

646 exposure to a stressor will depend on organismal sensitivity, stress intensity (how much it

647 deviates from present conditions) and stress duration. In a synthesis of the global literature on the

648 biological impacts of ocean acidification, Vargas et al. (2017, 2022) showed that the extreme of

649 the present range of variability of carbonate chemistry is a good predictor of species sensitivity.

650 In other words, larger deviations from present extreme high pCO$_2$ or extreme low pH, would be

651 expected to exert more negative biological impacts. Organismal stress and niche boundaries have

652 implications for the definition and understanding of controls and future ocean acidification

653 conditions in experiments aimed at evaluating future biological impacts.

654   Our data provide insights on conditions that affect and determine local species'

655 ecological niches, and a necessary key is to evaluate or re-evaluate their sensitivity to present and

656 future carbonate chemistry conditions, particularly for the sessile benthic calcifiers that constitute

657 prey for mobile and upper trophic level taxa. For example, an experimental study on three

658 common Arctic bivalve species (*Macoma calcarean, Astarte montagui* and *Astarte borealis*)

659 collected in the CEO concluded that these species were generally resilient to decreasing pH

660 (Goethel et al., 2017). However, only two pH were compared (a "control" (pH of 8.1) and an

661 "acidified" treatment (pH of 7.8) and our results show that organisms are already experiencing

662 more extreme conditions today than have been experimentally manipulated. While these data

663 provide insights on these species' plasticity to present pH conditions, they cannot be used to infer

664 sensitivity to future ocean acidification or extremes of current conditions. Based on the local

665 adaptation hypothesis (Vargas et al. 2017, 2022), stress and associated negative effect on species

666   fitness can be expected when pH deviates from the extreme of the present range of variability

667   (pH<7.5) as shown in other regions (e.g. echinoderms: Dorey et al., (2013); crustaceans: Thor

668   and Dupont, (2015); bivalves: Ventura et al., (2016)).

669   At the CEO, our results show sustained periods of remarkably low pH (e.g., 7.5; summer

670   to fall, winter). Higher pH values are observed in spring and late fall. While we are lacking the

671   local biological data to sufficiently evaluate past and future ecosystem changes, a high rate of

672   ocean acidification as observed in the Chukchi Sea (Qi et al., 2022b, a), associated with potential

673   temperature-induced shifts in the carbonate chemistry cycle (e.g. Orr et al. 2022), have the

674   potential to impact species and ecosystems. Exposure to low pH increases organismal energy

675   requirements for maintenance (e.g. acid-base regulation: Stumpp et al., 2012, compensatory

676   calcification: Ventura et al., 2016). Organisms can cope with increased energy costs using a

677   variety of strategies, ranging from individual physiological to behavioral responses, depending

678   on trophic level, mobility, and other ecological factors. For example, they can use available

679   stored energy to compensate for increased costs or they can decrease their metabolism to limit

680   costs (AMAP 2018). At the CEO, the low pH period observed during the summer and fall is

681   associated with elevated temperature and an elevated food supply for herbivores (Lalande et al.,

682   2020). The high availability of food may then foster compensation for the higher energetic costs

683   associated with exposure to low pH. However, a longer period of low pH as suggested by our

684   data could lead to a mismatch between the low pH and food availability, with cascading negative

685   consequences for the ecosystem (Kroeker et al., 2021). In winter, the low pH conditions are

686   associated with low temperature, no light, and low food level concentrations. These conditions

687   are likely to keep metabolisms low and limit the negative effects of exposure to low pH

688   (Gianguzza et al., 2014). As food availability is limited by the absence of light, this strategy may

689   be compromised by an increase in temperature that could also lead to increased metabolism.

690   Additional work is needed to understand impacts of acidification conditions and variability on

691   the marine biota of the Chukchi Sea, including field and laboratory experiments that evaluate

692   biological response under realistic scenarios. The characterization of the environmental

693   conditions at the CEO, including the variability in time, can be used to design single and multiple

694   stressor experiments (carbonate chemistry, temperature, salinity, food, oxygen; Boyd et al.

695   2018).

696   Indigenous communities are at the forefront of the changing Arctic, including changes in

697   accessibility, availability, and condition of traditional marine foods (Buschman and Sudlovenick,

698   2022; Hauser et al., 2021). Several marine species are critical to the food and cultural security of

699   coastal Inupiat who have thrived in Arctic Alaska for millenia. While it is not possible to resolve

700   the consequences of the seasonal and interannual variations in carbonate chemistry documented

701   in this manuscript without a proper sensitivity evaluation, the seasonally low pH conditions have

702   the potential to impact organisms like bivalves in a foraging hotspot for walrus (Jay et al., 2012;

703   Kuletz et al., 2015). Walrus, as well as their bivalve stomach contents, are important nutritional,

704   spiritual, and cultural components, raising concerns for food security in the context of ecosystem

705   shifts associated with the variability and multiplicity of climate impacts within the region (ICC,

706   2015).

707

708   **5. Concluding Thoughts**

709   The Chukchi Sea is undergoing a rapid environmental transformation with potentially

710   far-reaching consequences across the ecosystem. While we are lacking a long-term time-series,

711   we used this dataset to investigate the drivers of extreme pH, Ω_{arag}, and $p\mathrm{CO}_2$ and document

712   conditions that could affect the ecological niches of organisms, including a fast rate of ocean

713   acidification, elongated sea ice free periods, increased primary productivity and elevated

714   temperature. While a combination of experimental and monitoring approaches is needed for an

715   understanding of the ecological consequences of these changes, our results also highlight the

716   urgency to mitigate CO_2 emissions and simultaneously support Indigenous-led conservation

717   measures to safeguard an ecosystem in transition. Indigenous People in the Arctic have

718   established strategies to monitor, adapt to, and conserve the ecosystems upon which they depend.

719   Ethical and equitable engagement of Indigenous Knowledge and the communities at the forefront

720   of climate impacts can help guide research and conservation action by centering local priorities

721   and traditional practices, thereby supporting self-determination and sovereignty (Buschman and

722   Sudlovenick, 2022).

723

724   **Data availability**

725   The inorganic carbon data used in this manuscript are publicly available (Hauri and

726   Irving, 2023a; Hauri and Irving, 2023b).

727

728   **Author contributions**

729   CH and BI managed and serviced the HydroC CO_2 and SeapHOx sensors, analyzed and

730   published the data, and wrote the manuscript. SD and Peter Shipton carried out the CEO mooring

731   deployments and recoveries and managed and serviced the CTD and NO_3 sensors. RP, DH, SD,

732   and SLD contributed to the manuscript.

733

734   **Competing interests**

735   The authors have no competing interests.

736

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Tables

Table 1. Chukchi Ecosystem Observatory location and instrument sampling frequency. Sensor

type and parameter measured (italicized) shown in top row. Values in parenthesis indicate the

number of measurements averaged over the measurement interval window.

Deployment	Latitude	Longitude	SUNA *NO₃*	HydroC CO_2 *pCO₂*	SBE16 *CTD+*	SBE37 *CTD*	SeaFET *pH*	SBE63 *O₂*
2016-2017	71°35'58.5600"N	161°31'06.2400"W	1 h	12 h (300/5 min)*	1 h	-	-	-
2017-2018	71°35'58.9200"N	161°31'08.0400"W	1 h	12 h (5/5 min)	2 h	2 h	2 h (30/5 min)	2 h
2018-2019	71°35'59.6400"N	161°31'41.1600"W	1 h	24 h (5/5 min)	1 h	2 h*	-	2 h*
2019-2020	71°35'58.9200"N	161°31'39.0000"W	1 h	12 h (5/5 min)	2 h	-	-	-

* indicates the sensor did not return data over the whole year due to battery failure

CTD+ indicates ancillary data was available with the SBE16 file (e.g., chlorophyll fluorescence)

Table 2. Evaluation of pH$_{SeaFET}$ and pH^{est} using reference pH from nearby discrete samples

(pH$^{disc}_{calc}$). Uncertainty, u$_c$, is the propagated combined standard uncertainty from *errors.m* (Orr

et al., 2018). pH$_{SeaFET}$ and pH^{est} were interpolated to the discrete timestamp. Figure S1 for

visualization of reference values.

Date	Cruise	Cast No.	Distance (km)	pH$^{disc}_{calc}$ ± u$_c$	Anomaly (pH^{est}-pH$^{disc}_{calc}$)	Anomaly (pH$_{SeaFET}$-pH$^{disc}_{calc}$)	Source

2017-09-10	HLY1702	127	0.52	8.0123±0.0166	-0.0450*	-0.0354	Cross et al., 2020a
2019-08-11	HLY1901	39	3.75	7.6423±0.012	0.0079*	-	Cross et al., 2021
2019-08-19	OS1901	33	0.27	7.7367±0.0145	-0.0200	-	unpublished

* indicates pH$^{disc}_{calc}$ was interpolated to mooring depth

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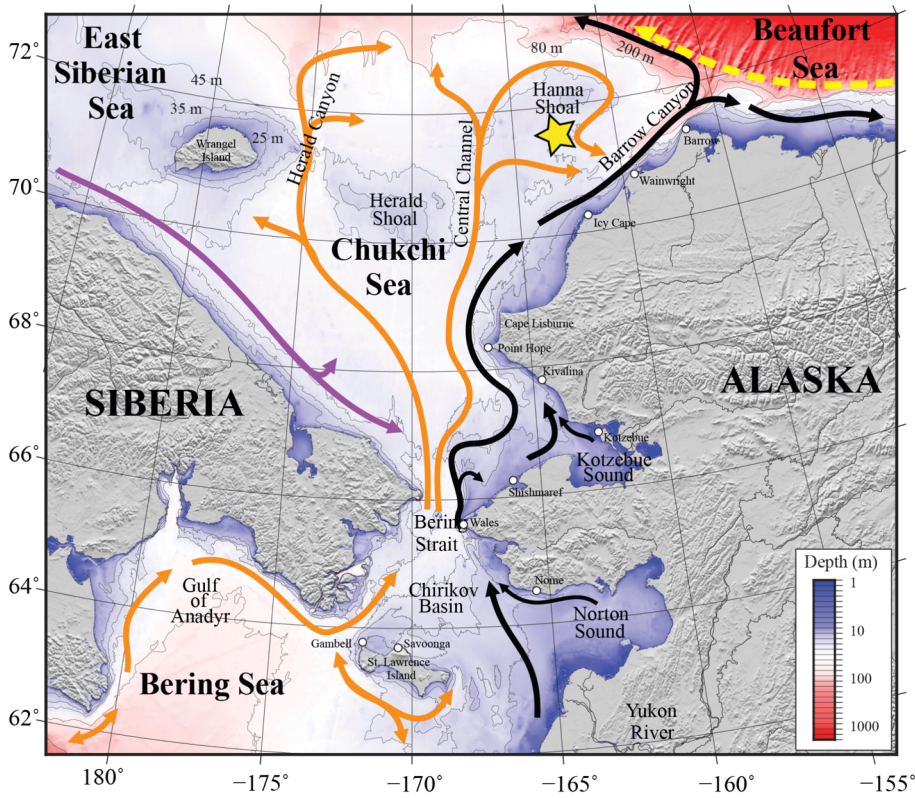
Figures

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1459 **Figure 1. Map of the study area.** Bathymetry of the Chukchi, northern Bering, East Siberian

1460 and eastern Beaufort seas is shown in color. The Chukchi Ecosystem Observatory (CEO)

1461 location near Hanna Shoal is marked with a yellow star. General circulation patterns are shown

1462 with arrows: black – Alaskan Coastal Water and Alaskan Coastal Current, dividing into the

1463 Shelf-break Jet (right) and Chukchi Slope Current (left, Corlett and Pickart, (2017)); orange –

1464 Anadyr, Bering, and Chukchi Seawater; purple – Siberian Coastal Current; yellow – Beaufort

1465 Gyre boundary current. Figure is from Hauri et al. (2018).

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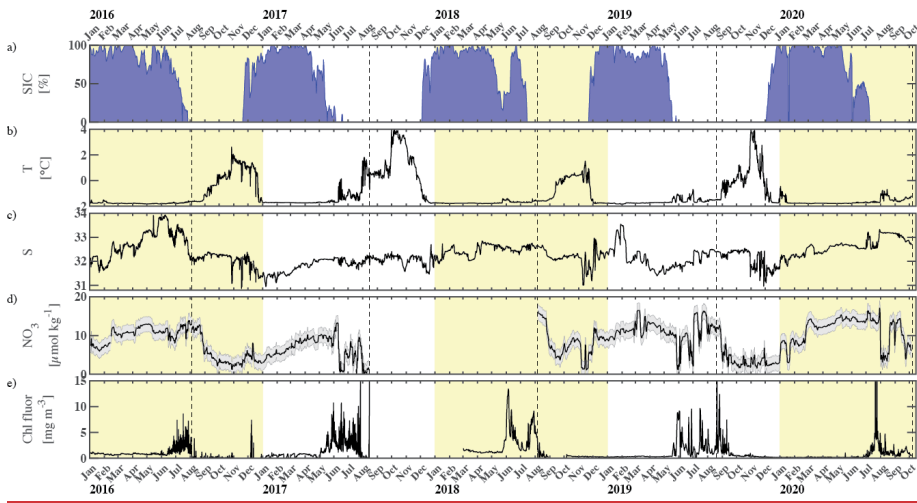
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1469 **Figure 2. Chukchi Ecosystem Observatory timeseries from 2016 through 2020.** a) sea ice

1470 concentration (blue shading to highlight coverage, %; DiGirolamo et al., 2022), b) temperature

1471 (°C), c) salinity, d) NO$_3$ with uncertainty envelope (μmol kg^{-1}), and e) chlorophyll fluorescence

1472 (mg m^{-3}). Years are indicated by alternating yellow and white background shading. The vertical

1473 dotted gray lines indicate the mooring turn around timing.
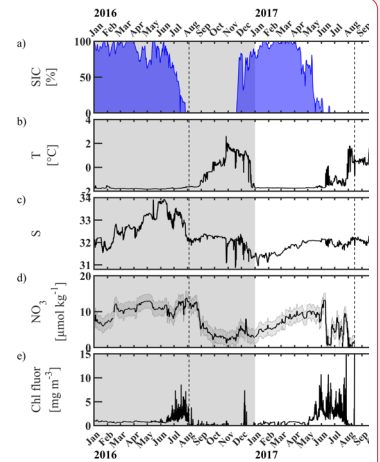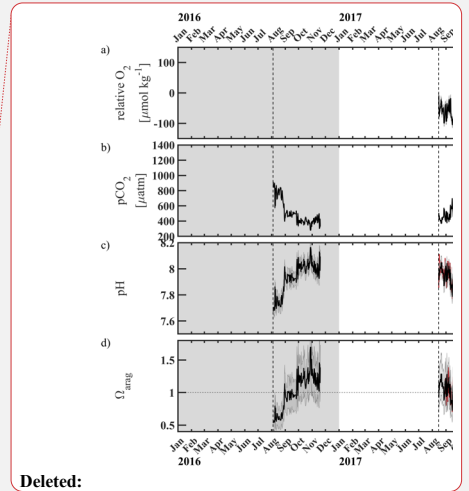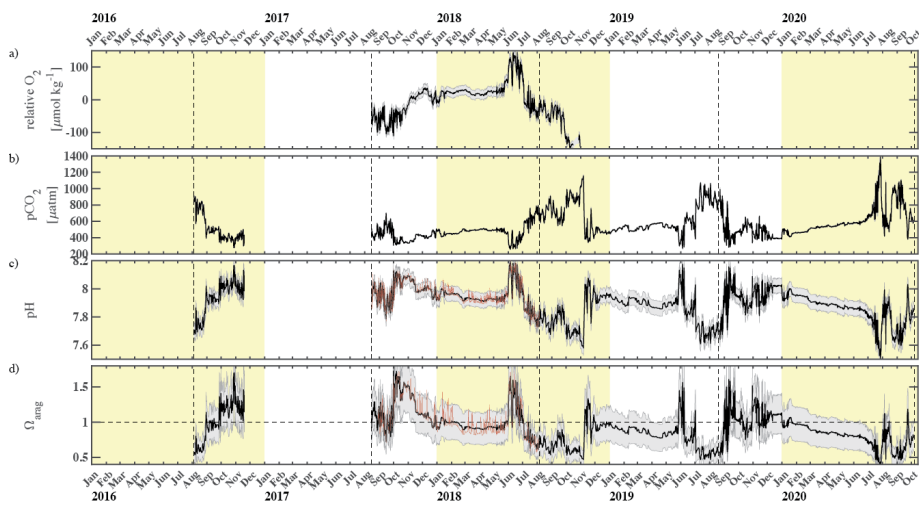
Figure 3. Chukchi Ecosystem Observatory timeseries from 2016 through 2020, part 2. a)

relative dissolved oxygen with uncertainty envelope (relative to the mean; μmol kg^{-1}), b) pCO$_2$

with uncertainty envelope (μatm; Hauri and Irving, 2023a), c) pH with uncertainty envelope

(pH^{est} in black, pH$_{SeaFET}$ in red; Hauri and Irving 2023b), and d) aragonite saturation state with

uncertainty envelope ($\Omega_{arag}(p$CO$_2$, pH^{est}) in black; $\Omega_{arag}(p$CO$_2$, pH$_{SeaFET}$) in red). Years are

indicated by alternating yellow and white backgrounds. The vertical dotted gray lines indicate

the mooring turn around timing.

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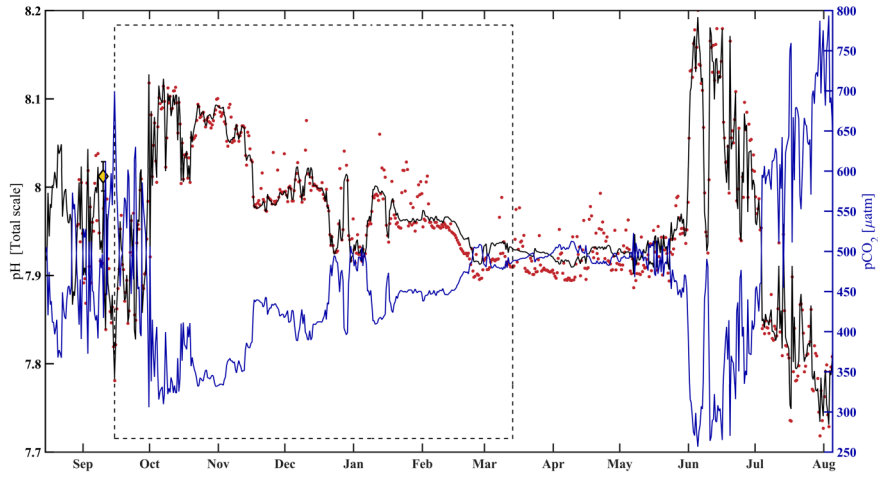
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Figure 4. HydroC pCO$_2$ and pH highlighting mirrored trend from mid-August 2017 to

beginning of August 2018. Measured pH (pH$_{SeaFET}$, red dots) is interpolated onto the HydroC

pCO$_2$ timestamp (blue), and pH^{est} is shown as the solid black line. The dashed box shows the

period over which pH^{est} was trained. The yellow faced diamond with error bars show reference

pH$^{disc}_{calc}$ ± u$_c$ (Table 2; Cross et al., 2020a; Orr et al., 2018).

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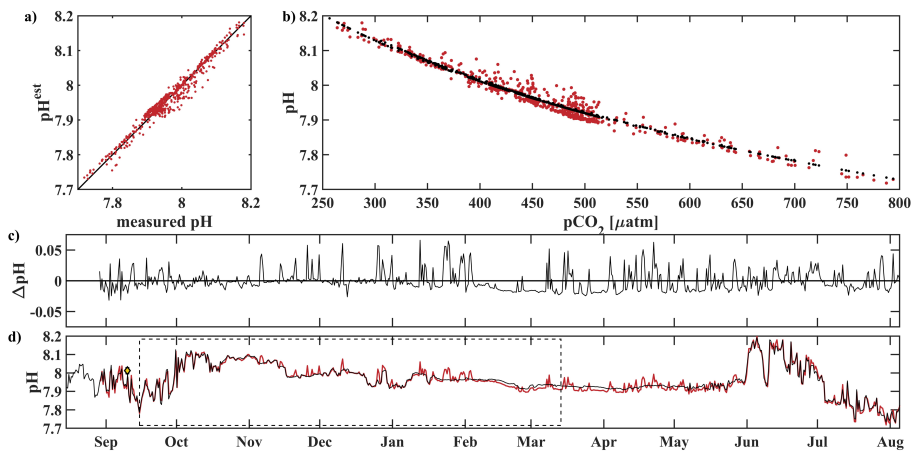
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1497 **Figure 5**. **Performance of the pH algorithm.** (a) pH_{SeaFET} vs pH^{est} with black line highlighting

1498 1:1 ratio, (b) pCO_2 vs pH_{SeaFET} (red) and pCO_2 vs pH^{est} (black), (c) residual pH ($pH_{SeaFET} -$

1499 pH^{est}), and (d) pH_{SeaFET} (red) and pH^{est} (black) vs. time, with dashed box highlighting the period

1500 over which pH^{est} was trained (15 September - 14 March 2017), and the yellow faced diamond

1501 with error bars showing reference $pH^{disc}_{calc} \pm u_c$ (Table 2; Cross et al., 2020).

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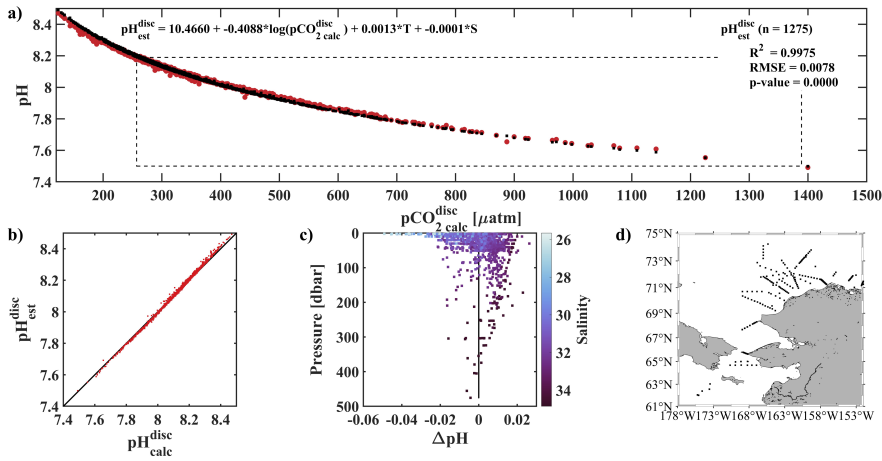
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1507 **Figure 6. Evaluation of the pH algorithm.** pH^{est} evaluation with pH^{disc}_{calc} from discrete

1508 samples collected during 4 cruises in the fall or early winter (August - November) of 2017-2020

1509 and pH^{disc}_{est} from our linear regression model (Equation 2). (a) $pCO_2^{disc}{}_{calc}$(TA, DIC) vs pH (red

1510 pH^{disc}_{calc} and black pH^{disc}_{est}) with dashed black box showing the range of pH and pCO_2 observed

1511 at the CEO at 33 m depth, (b) pH^{disc}_{calc} vs pH^{disc}_{est} with black 1:1 ratio, (c) residual pH (pH^{disc}_{calc} -

1512 pH^{disc}_{est}) vs depth with color shading by salinity and black vertical line at 0, and (d) map showing

1513 the locations of the 1275 discrete water samples used for evaluation (Monacci et al., 2022; Cross

1514 et al., 2021; 2020a; 2020b).

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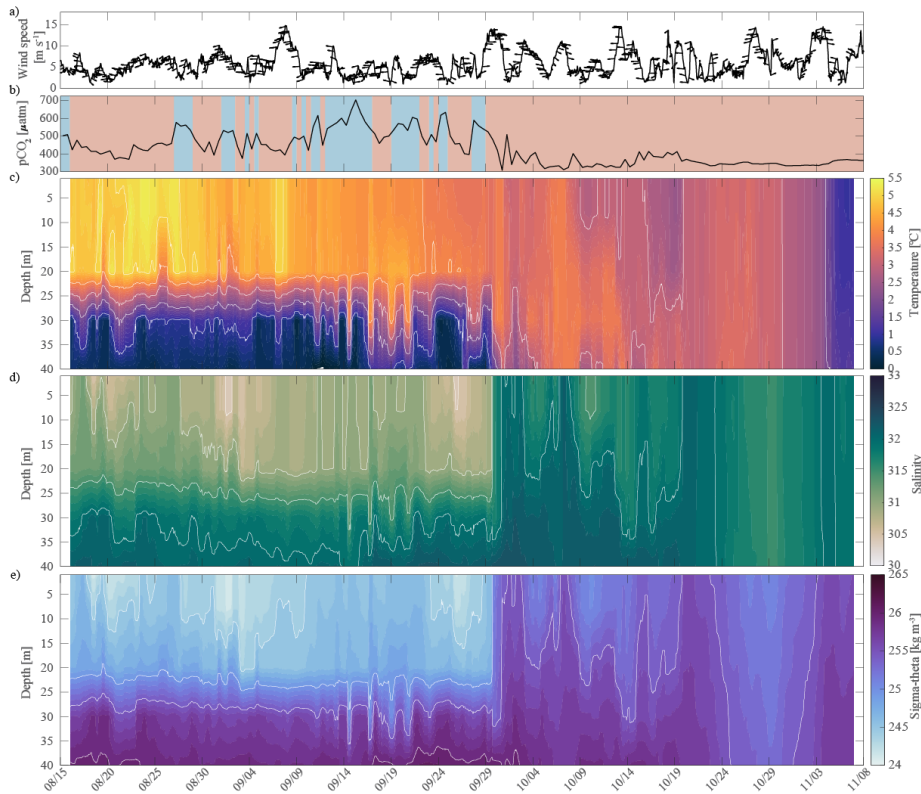
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Figure 7. Water column structure from late summer 2017 to freeze up. Profiles of a) wind

speed and direction (arrows pointing downwind) from the NOAA-operated Wiley Post-Will

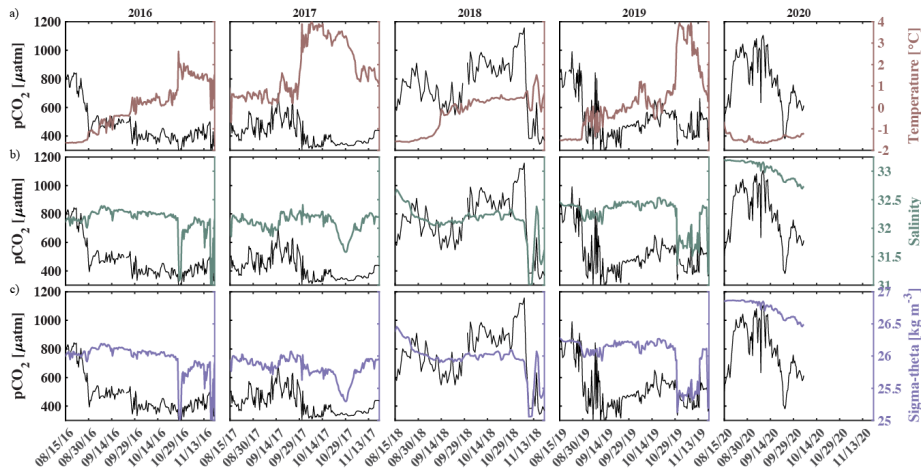
Rogers Memorial Airport, b) $p\text{CO}_2$ (µatm) with blue background indicating the water was

undersaturated regarding aragonite (Ω_{arag} < 1) and red shading indicating aragonite

oversaturation (Ω_{arag} >= 1), c) temperature (°C), d) salinity, and e) sigma-theta (kg m^{-3}).

Temperature (c) and salinity (d) were measured at 8, 20, 30, and 40 m by the Chukchi Ecosystem

Observatory freeze-up detection mooring deployed in fall 2017. Density was calculated with the

TEOS-10 GSW Oceanographic Toolbox (McDougall and Baker, 2011).

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1527 **Figure 8. Impact of water column mixing on *p*CO₂.** Timeseries of *p*CO₂ (black, left axis) and

1528 a) temperature (maroon, right axis), b) salinity (green, right axis), and c) density (purple, right

1529 axis) for 15 August to 1 December in 2016 -2020 measured at ~33m septh at the Chukchi Sea

1530 Ecosystem Observatory.

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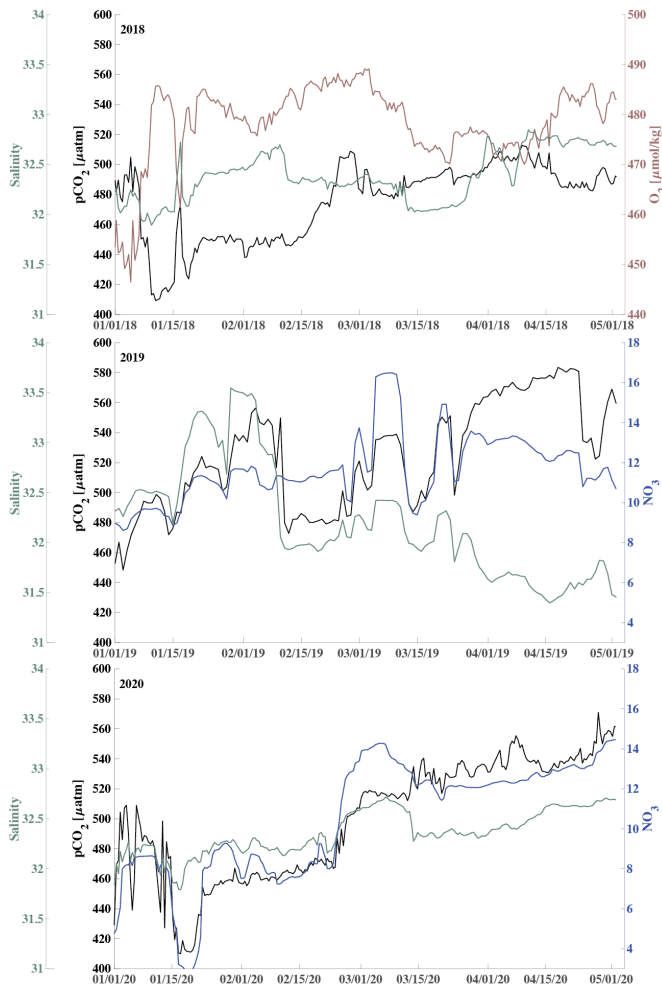
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Figure 9. Respiration under the sea ice. Timeseries of pCO$_2$ (black) and salinity (green, left

axis), and oxygen (O$_2$, μmol kg^{-1}, maroon, top) and nitrate (NO$_3$, μmol kg^{-1}, blue, middle and

bottom) concentration (right axis during January through April for 2018 (top), 2019 (middle) and

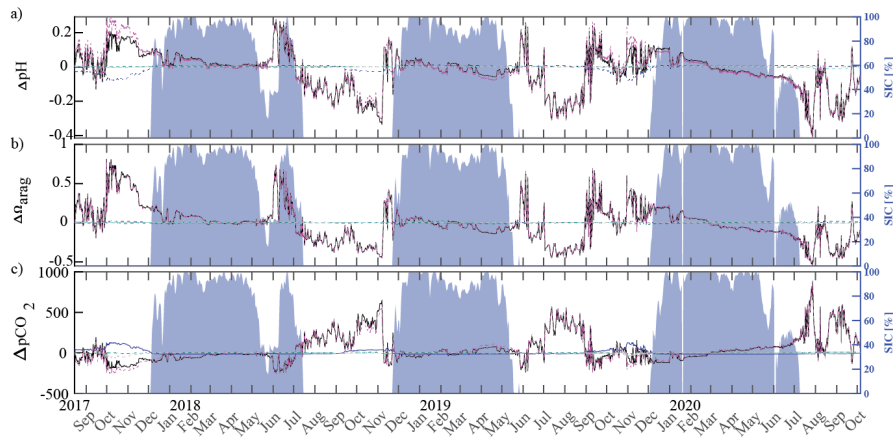
2020 (bottom).

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Figure 10. Drivers of the inorganic carbon system. Component timeseries of the linear Taylor

decomposition of a) pH, b) Ω_{arag}, and c) $p\mathrm{CO}_2$. Contributions of changes in salinity (red),

temperature (blue), biogeochemistry (pink), and freshwater mixing (green) to changes (black,

relative to the mean of the timeseries) in pH, Ω_{arag}, and $p\mathrm{CO}_2$ were computed following Rheuban

et al. (2019). The grey dotted line illustrates an estimated residual term. Sea ice concentration

(blue shading, %; DiGirolamo et al., 2022) is shown on the right axes.

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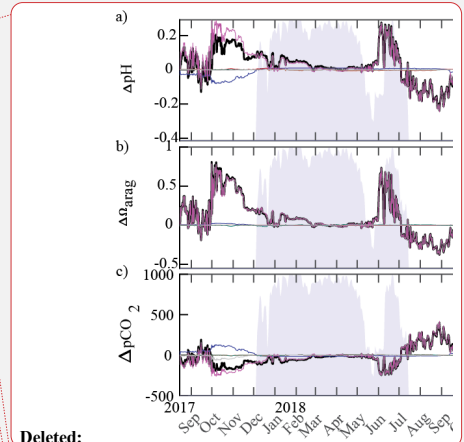
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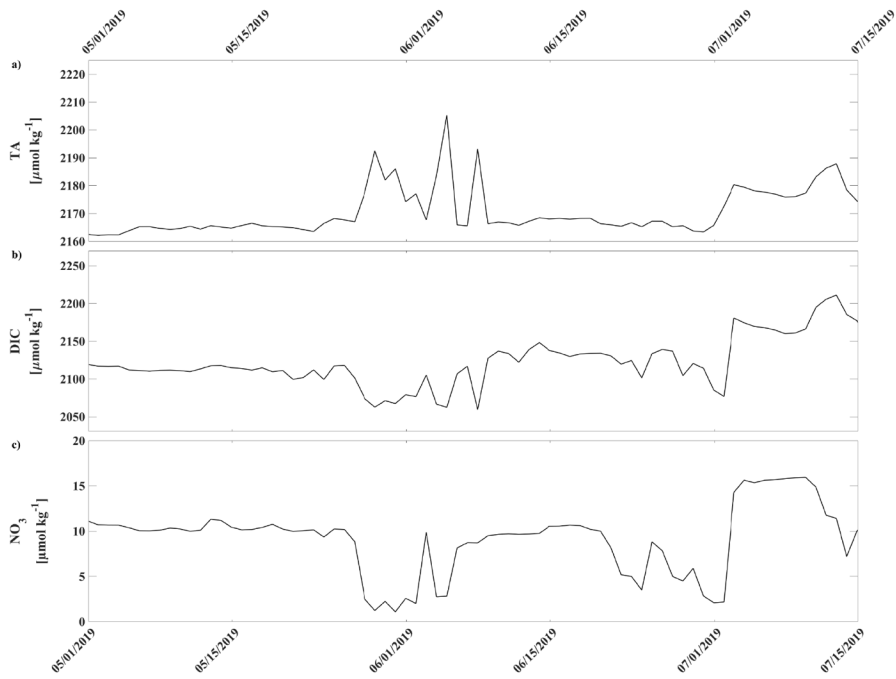
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Figure 11. Spring 2019 relaxation event. Timeseries of a) total alkalinity (TA, μmol kg^{-1}), b)

dissolved inorganic carbon (DIC, μmol kg^{-1}), and c) nitrate (NO$_3$, μmol kg^{-1}) from May 1st, 2019

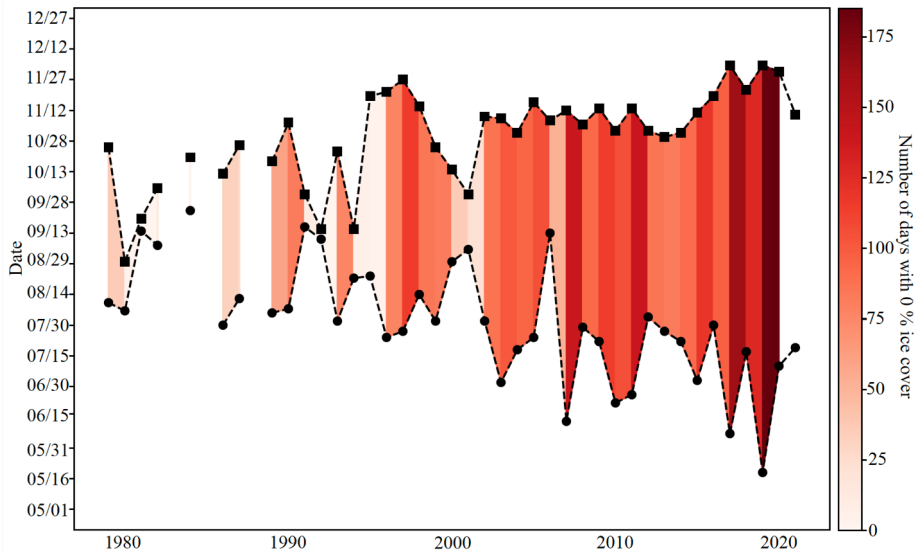
through July 15th, 2019.

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Figure 12. Low sea ice period at the Chukchi Sea Observatory. Timeseries of start (circle) and end (square) of low sea ice (< 15 % per grid cell) period from 1982-2021. Shades of red illustrate number of days with 0 % sea ice cover. The satellite sea ice cover at the observatory site was taken from the NSIDC (DiGirolamo et al., 2022).

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