

Carbon monoxide (CO) cycling in the Fram Strait, Arctic Ocean

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Abstract

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Abstract

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Plain Language Summary

Carbon monoxide (CO) is a gas that affects the atmosphere in a similar way as a greenhouse gas. It is released from the ocean into the atmosphere. Because of that, it contributes to regional warming in areas like the Arctic. However, not much is known about the main drivers of the CO production and consumption processes in this area. Therefore, we conducted experiments in the Fram Strait in August/September 2019 with surface water from four different locations and investigated the effects of potential environmental changes such as acidification. The water samples were exposed to light, darkness and acidified conditions for 48hrs. Acidification had no influence, but we identified two environmental factors that may enhance CO production and consumption: High amounts of organic material that absorbs UV light, and low concentrations of

nitrate, which is an essential nutrient fueling biological productivity in the ocean. CO consumption and production may increase in the future, but more research is required to assess if one or the other term will dominate. Our results will contribute to modelling studies to improve predictions on the magnitude of Arctic CO release and its potential role in Arctic warming.

1 Introduction

Carbon monoxide (CO) is an atmospheric trace gas which plays an important role for the radiative budget and oxidative capacity of the Earth's atmosphere (Forster et al., 2021).

Being ubiquitously supersaturated in the surface layer, the ocean is a source of CO to the atmosphere (Conte et al., 2019). The global oceanic emissions of CO are a minor source contributing only ~1% to the natural and anthropogenic sources of atmospheric CO. However, CO has a comparably short atmospheric lifetime (~ 2 months). Thus, its oceanic emissions can contribute significantly to the atmospheric budget, particularly in remote areas like the Arctic Ocean being usually only marginally affected by direct anthropogenic CO emissions. The few studies on CO in the Arctic Ocean report elevated and highly variable CO concentrations compared to other ocean basins (Tran et al., 2013). The highest CO concentrations were observed within bottom sea ice, suggesting production by ice algae (Song et al., 2011; Xie & Gosselin, 2005).

Oceanic CO is mainly produced photochemically via the reaction of UV-light with colored dissolved organic matter (CDOM) and particulate organic matter (POM) (Song & Xie, 2017; Stubbins et al., 2006). There is also evidence for biological CO production by phytoplankton (Gros et al., 2009; McLeod et al., 2021; Tran et al., 2013) and for thermal (dark) CO production from (C)DOM (Zhang et al., 2008). Tran et al. (2013) suggested that *Phaeocystis sp.*, dinoflagellates and, to a lesser extent, diatoms are the major biological CO producers in the Fram Strait. However, the CO production by algae lacks research on the physiological mechanisms and their interdependencies with biogeochemical parameters (Campen et al., 2021). Beside the emissions to the atmosphere, microbial consumption of CO is a major loss process in the ocean (Bates et al., 1995; Conrad et al., 1982; Xie et al., 2005).

Ongoing environmental changes in the Arctic Ocean such as the loss of sea ice, changing light penetration in the upper ocean, ocean acidification and altered nutrient and organic material supply

(e.g. Thackeray and Hall (2019); Hopwood et al. (2018); Stedmon et al. (2011); Terhaar et al. (2020)), might affect CO production and consumption pathways as well as its emissions to the atmosphere from this region (Campen et al., 2021). The distribution and magnitude of coastal nutrient fluxes is predicted to change (e.g. Hopwood et al. (2018)) due to increasing freshwater inputs via ice melting, which could lead to increased stratification, in turn limiting nutrient remineralisation (Lannuzel et al., 2020). However, between 2012 and 2018 chlorophyll *a* concentration in Arctic Ocean surface waters increased 16 times faster than before, suggesting an additional input of nutrients that could even sustain an increase in primary production (Ardyna & Arrigo, 2020) and with it CO precursors. Furthermore, light availability and penetration at the ocean surface is projected to increase due to loss of ice and decreasing albedo (Castellani et al., 2022; Pistone et al., 2014), potentially enhancing CO production in open surface waters and under-ice water during the melting season. Due to the increase of atmospheric carbon dioxide (CO₂), the pH in the surface ocean is decreasing (Canadell et al., 2021) and it was projected that the pH of the Arctic Ocean surface waters could significantly decrease by the end of this century (Terhaar et al., 2020). Decreasing pH (i.e. ocean acidification, OA) will alter biogeochemical cycles (Doney et al., 2009). OA is likely to influence the CDOM pool which, in turn, would alter CO production processes (Hopkins et al., 2020). However, to our knowledge, no studies on the effect of OA on CO cycling in the ocean have been published (see Hopkins et al. (2020)).

Yet, the magnitude at which these environmental changes will affect CO production and emissions from the Arctic Ocean is highly uncertain due to limited observations and lack of process understanding. This study aims to elucidate the impact of ocean acidification, light changes and multiple environmental parameters on CO consumption and production rates by means of in-situ incubations conducted in the Fram Strait in 2019.

2 Materials and Methods

2.1 Study area

The study was conducted during the cruise JR18007 with RSS James Clark Ross to the Fram Strait from 4 August to 6 September 2019. The Fram Strait, located between the west coast of Svalbard and the east coast of Greenland, is characterized by the inflow of Atlantic water via the West Spitzbergen Current (WSC) in the east and Arctic water outflow via the East Greenland Current

(EGC) in the west (e.g. Rudels et al. (2015)). Four incubation experiments were conducted at stations NT6A, Ice2, D7 and D5 (see Fig. 1). The stations NT6A, Ice2 and D5 were located at the shelf break. Ice 2 and D5 were also in proximity to the ice edge and D7 was located in the open ocean region of the Fram Strait. The EGC affected Ice2 as indicated by its lower salinities and colder water temperatures, whereas D7 and D5 were influenced by warmer and more saline Atlantic waters of the WSC (see Table S1 in the Supplement).

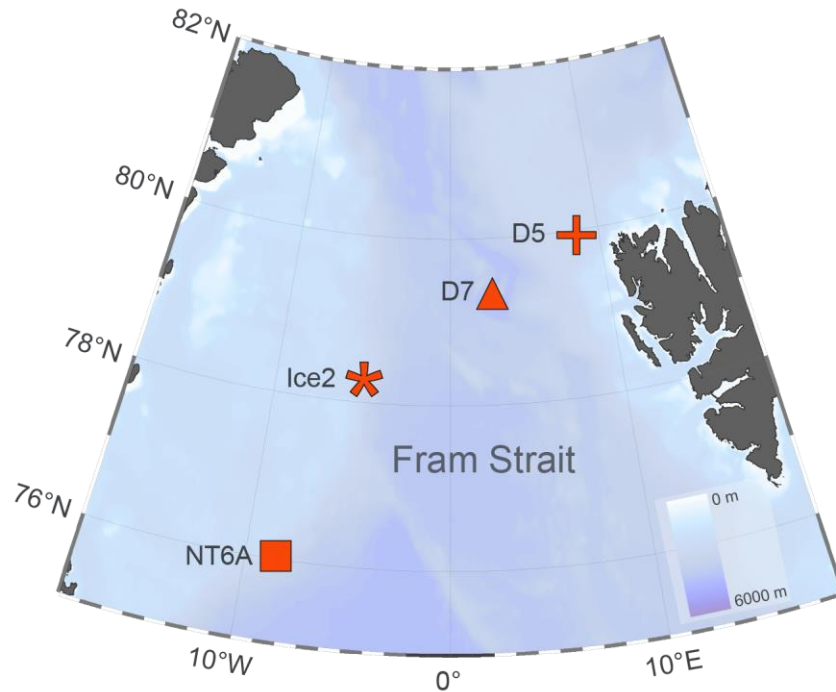


Fig. 1 Map showing the locations where incubation experiments were performed (stations NT6A, Ice2, D7 and D5).

2.2 Experimental set-up

For the incubation experiments, seawater from 5 m water depth was drawn from Niskin bottles attached to a 12-bottle hydrocast-CTD/rosette and subsequently incubated in the experimental enclosures for up to 48h. In total, eighteen 3.5 L light-transmitting incubation bottles (DURAN®, borosilicate glass, GL 45, DWK Life Sciences, Germany) were filled with seawater. Lids (GL 45) had PTFE-coated septa to easily press out the bulk water and close the bottles gas tightly. To characterize the setting of the upper water a vertical profile down to 100 m was performed before the start of the incubations. CO concentrations and ancillary measurements (see S2) from 5 m water depth served as sampling time 0 (t_0) of the incubations.

Bubble-free seawater samples for the determination of dissolved CO were taken in triplicates in 100 mL glass vials (both from Niskin bottles and incubation bottles) with a Tygon® tubing to avoid CO contamination by silicone rubber (Xie et al., 2002). The vials were immediately sealed and stored between 0 and 6 °C in the dark to suppress further CO production in the light. CDOM was sampled in brown glass vials of 500 mL with a screwed cap. Inorganic nitrate samples were drawn into 10 mL polyethylene tubes, which were pre-rinsed three times with sample water, and stored at -80° C until analysis at the GEOMAR's nutrient laboratory after the cruise. CDOM samples were stored in the dark and below 5 °C until filtration (for method details see S2).

The pH in each experiment was manipulated to represent three different atmospheric CO₂ mole fractions: 405.43 +/- 0.05 (Dlugokencky & Thoning, 2021), 670 and 936 ppm CO₂ for the treatments named ambient, pH1 and pH2, respectively. To this end, the pH in pH1 and pH2, were adjusted by -0.14 and -0.3, respectively, to approximate the IPCC's representative concentration pathway (RCP) 4.5 (moderate change) and RCP 8.5 (extreme change) relative to the ambient carbonate chemistry of the seawater at the time of the sampling. To manipulate the carbonate system, NaHCO₃ and HCl were added (Riebesell et al., 2011) and immediately checked for the resulting total alkalinity (TA) and dissolved inorganic (DIC) concentrations. Values of *p*CO₂ and pH_T (total scale) were calculated with the software CO2sys (Lewis & Wallace, 1998). Immediately after pH manipulation, bottles were gas tightly closed and incubated.

Light incubators had transparent Plexiglas sidewalls (GS 2458 UV transmitting) and no lid, so that the full natural sunlight spectrum could penetrate the enclosed incubation bottles from the sides and above (self-manufactured according to experimental needs, Fig. S3.1 in the supplements). While these incubators were placed on deck to allow natural sunlight penetration, black and covered water chambers served as dark incubators to exclude any light. All incubators were continuously flushed with ambient seawater to keep bottles at ambient temperature. Light and temperature were monitored continuously in each incubator (HOBO pendant® temperature/light, onset, USA). Oxygen saturation was monitored (in %) to make sure that the incubations did not become anoxic (O2xyDot®, OxySense, USA). CO concentrations were determined at the beginning of the incubation (*t*₀), after 12 h (*t*₁₂), 24 h (*t*₂₄) and 48 h (*t*₄₈) of incubation (Fig. S3.1).

2.3 CO measurements

Dissolved CO concentrations were determined by the headspace method as described by Xie et al. (2002). We established a headspace by injecting 15 mL CO-free synthetic air (purified via MicroTorr series, 906 media, SAES group, USA). The samples were then equilibrated for eight minutes. (Law et al., 2002; Xiaolan et al., 2010). A 5 mL subsample from the equilibrated headspace was injected with a gastight syringe into the sample loop of a CO analyser (ta3000 AMETEK, USA). Every sixth sample injection was followed by the injection of a standard gas mixture of 113.9 ppb CO in synthetic air (DEUSTE Gas Solutions, Germany) which was calibrated against a certified standard gas (250.5 ppb CO, calibrated against the NOAA 2004 scale at the Max Plank Institute for Biogeochemistry Jena, Germany).

Measured CO mole fractions from the headspace were corrected for the drift of the detector with the standard gas measurements and corrected for water vapour (Wiesenburg & Guinasso, 1979). The final dissolved CO concentrations were calculated based on Stubbins et al. (2006) with the solubility coefficients from Wiesenburg and Guinasso (1979).

For each of the CO concentration triplicates we calculated the arithmetic mean and estimated the standard error according to (David, 1951). The overall mean error for the measurements of dissolved CO was $\pm 0.025 \text{ nmol L}^{-1}$ ($\pm 17.4 \%$).

2.4 CO consumption and production rates

Net CO consumption (CR_{CO}) and production rates (PR_{CO}) were calculated as the slope of the linear regression line through all sampling times for each (dark/light) experiment and each pH (dark/light) treatment via a simple regression analysis. Gross production rates of CO (GP_{CO}) were calculated as the difference between PR_{CO} and CR_{CO} in order to demask the effect of microbial CO consumption.

Single CO gross production rates ($\text{singleGP}_{\text{CO}}$) were calculated between two sampling times (0 – 12 h, 0 – 24 h, 0 – 48 h) for each treatment and for each experiment, respectively to increase data points when possible. To check whether the consumption rates follow a first order loss they were plotted against the initial CO concentrations at t_0 , $[\text{CO}]_{t_0}$, of each incubation. All incubations showed a first order loss (Fig. S3.2) and the consumption rate constant (k_{CO}) for each experiment was thus determined as the slope of the linear regression.

3 Results and Discussion

3.1 CO concentration development during dark and light incubations

Fig. 2 gives an overview on how the CO concentrations ($[CO]$) developed over the incubation duration of 48 hours: In all dark incubations, except for pH2 at NT6A, CO concentrations decreased with time (i.e. over 48h). This was most likely resulted from microbial consumption of CO which is the dominating CO consumption process in Arctic waters (e.g. Xie et al. (2009); Xie et al. (2005)).

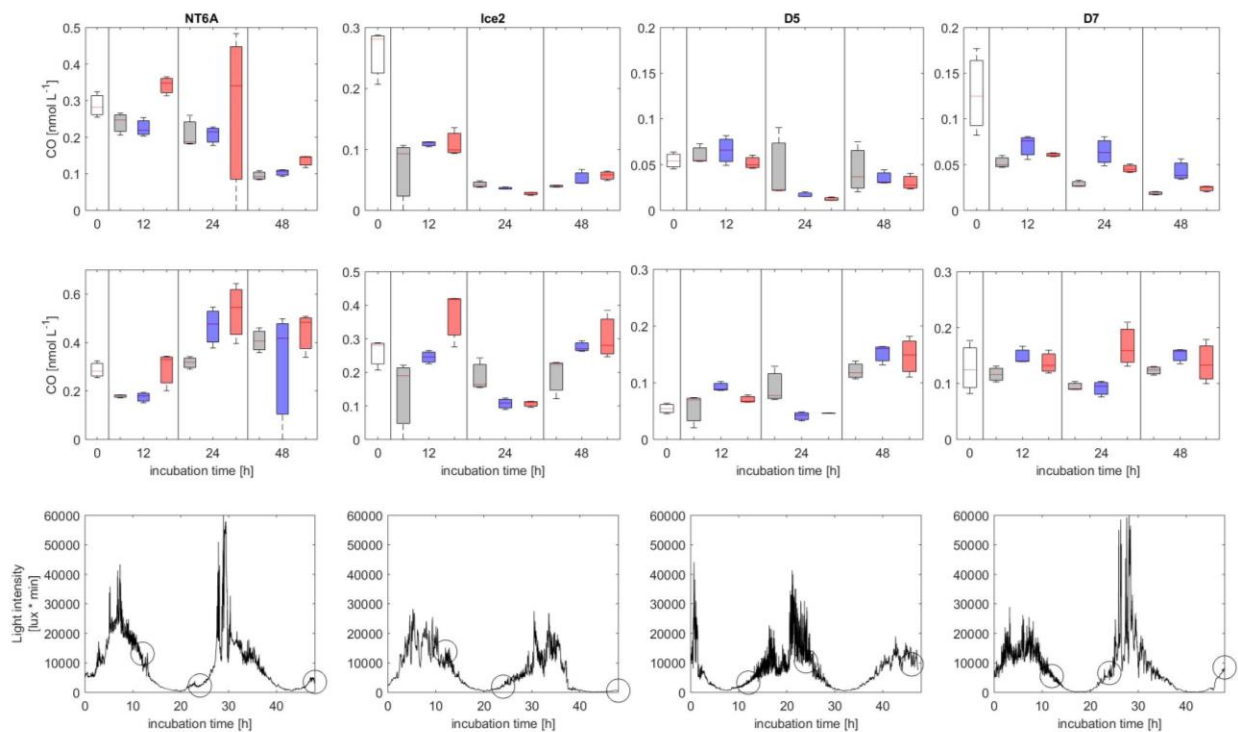


Fig. 2 Development of CO concentration (nmol L⁻¹) over 48 hours of incubations a) in the dark and b) in natural sunlight. c) shows the respective light intensities in the light treatments at each station (light intensities in the dark treatment were zero). Circles indicate the timing of sampling events in dark and light treatments.

white = initial concentration, grey = ambient, blue = pH1, red = pH2. The station names are indicated on the top. Please note that the scales of the y axes are varying between stations according to their CO maximum concentrations.

NT6A was an exception: pH2 showed an increase in $[CO]$ in the dark after 12 and 24 h of 0.54 (+/- 7.9%) and 0.122 nmol L⁻¹ (+/- 24.6 %) respectively. This increase could hint towards ongoing thermal CO production (Zhang et al., 2008).

The low initial CO concentrations (Table 1) are in line with the observation that CO surface concentrations can show a pronounced seasonal variability in Arctic waters. For example, Xie et al. (2009) reported considerably lower CO concentrations for September/October 2003 (0.17 – 1.34 nmol L⁻¹) than for June 2004 (0.98 – 13 nmol L⁻¹) from the Amundsen Gulf in the Beaufort Sea.

All light treatments showed a diurnal pattern of light intensity, though light was never completely absent because the incubations were performed in the Arctic summer. CO concentrations in the light incubations showed no uniform trend with time. Only during the incubations NT6A and D5 a significant increase of CO concentrations over 48h was observed. However, this is net production which includes microbial CO consumption. Since there was no obvious relationship between the timing of the sampling, [CO] and preceding light intensities (Fig. 2), this indicates that photochemical CO production did not exceed CO consumption. We speculate that if there was photochemical CO production it was directly consumed by bacteria. Alternatively, biological CO production by phytoplankton (Gros et al., 2009; Tran et al., 2013) or bacterioplankton and/or thermal production might have been dominant at NT6A and D5 (Zhang et al., 2008).

Table 1: Initial CO concentrations and CO consumption rate constants (k_{CO}) of the four incubation experiments conducted at different pH levels. Data are given as mean +/- estimate of standard deviation (for the initial CO concentrations) and as the slope of the linear regression +/- error of the slope (for k_{CO}).

Station	Initial CO conc. nmol L ⁻¹	k_{CO} , amb hr ⁻¹	k_{CO} , pH1 hr ⁻¹	k_{CO} , pH2 hr ⁻¹
NT6A	0.28 +/- 0.035	-0.023 +/- 0.004	-0.021 +/- 0.003	-0.016 +/- 0.012
Ice2	0.25 +/- 0.041	-0.038 +/- 0.015	-0.035 +/- 0.018	-0.034 +/- 0.023
D5	0.05 +/- 0.009	-0.006 +/- 0.003	-0.014 +/- 0.019	-0.016 +/- 0.021
D7	0.13 +/- 0.049	-0.038 +/- 0.0095	-0.021 +/- 0.005	-0.033 +/- 0.005

The k_{CO} computed from our experiments (Table 1) are comparable to previously published findings from Arctic waters: Xie et al. (2005) reported first order consumption rates constants k_{CO}

of $-0.040 \pm -0.012 \text{ hr}^{-1}$ and $-0.020 \pm -0.0060 \text{ hr}^{-1}$ in the coastal and offshore Beaufort Sea, respectively. (Please note that the k_{CO} were given as positive values in Xie et al. (2005)). In general, a lower pH did not affect the CO concentrations neither in the dark incubations nor in the light incubations, since the CO concentrations in the pH manipulated treatments did not differ significantly from the ambient treatments (as indicated by the error bars in Fig 2). Accordingly, pH affected neither k_{CO} nor GP_{CO} significantly (Fig. S3.3).

3.2 Effect of environmental variability on CO consumption and production

The effects of CDOM absorption, nitrate and Chl *a* concentrations and water mass properties on the variability of k_{CO} and GP_{CO} are shown in Fig. 3.

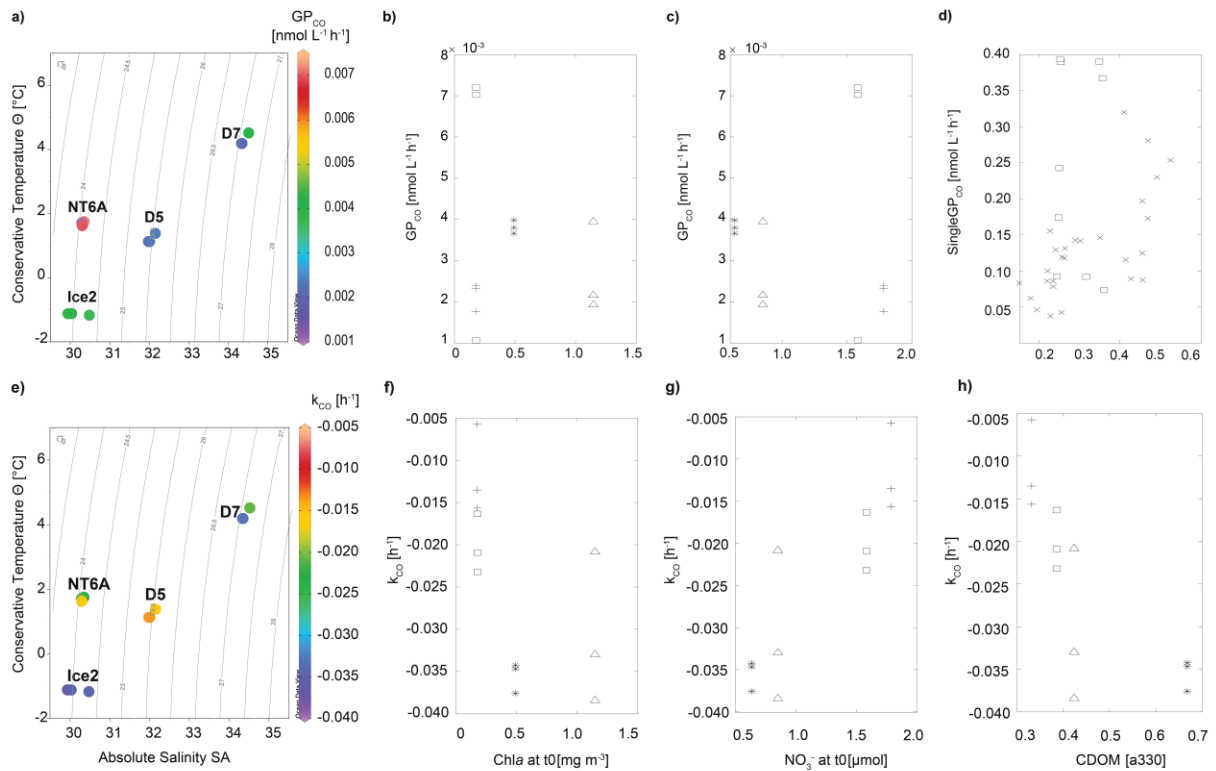


Fig. 3 Top row: Relationship between GP_{CO} and a) temperature/salinity incl. density, b) Chl *a*, c) NO_3^- at t_0 and d) relationship between single GP_{CO} and CDOM absorption (330 nm) at each sampling time.

Bottom row: Relationship between k_{CO} and e) temperature/salinity incl. density, f) Chl *a*, g) NO_3^- and h) CDOM absorption (330 nm) at t_0 . $\square$ = NT6A, * = Ice2, + = D5, Δ = D7, x = CDOM values at single sampling times of all stations excl. NT6A.

3.2.1 Water mass properties

It is obvious that the stations Ice2 and D7 had contrasting hydrographic settings: While Ice2 was located close to the ice edge and had a low water temperature and low salinity at t_0 , D7 was located in the open Fram Strait with a high water temperature and a higher salinity at t_0 (Fig. 3a). Therefore, Ice2 was most probably affected by freshwater input from ice melting and polar waters carried by EGC. D5 had a lower salinity compared to D7 and was also (at least partly) affected by freshwater from ice melting. NT6A had a low salinity which was comparable to Ice2 but the water temperature at t_0 was much higher compared to Ice2. Moreover, station NT6A had a steep halocline in about 10 m, whereas Ice2 was well mixed in the upper layer (see depth profiles in Supplements). Therefore, NT6A also being the southernmost station during our study had an apparently different hydrographic setting in comparison to the other three stations. When ignoring the data from NT6A, GP_{CO} showed a statistically significant correlation ($R^2 = 0.58$, $p < 0.05$) with increasing density. This implies, that surface waters in the Fram Strait with a higher fraction of freshwater (i.e. lower density), such as fresh meltwater or polar water characteristic for the EGC in the west Fram Strait, potentially lead to higher CO production rates GP_{CO}. There was no significant relationship for k_{CO} with density, which indicates that besides meltwater and polar waters additional factors must be affecting k_{CO} .

3.2.2 CDOM

CDOM is an important driver for CO photoproduction in the Arctic Ocean (e.g. Song and Xie (2017); Stubbins et al. (2006); Xie and Gosselin (2005)). However, CDOM absorption significantly correlated with singleGP_{CO} when the data from NT6A were excluded ($R^2 = 0.45$, $p < 0.05$, Fig. 3c).

CDOM absorption at t_0 was significantly correlated with k_{CO} ($R^2 = 0.57$, $p < 0.05$, Fig. 3g). Given that photochemical production from CDOM is a CO source, this is most likely an indirect correlation: High CDOM absorption induces photochemical CO production which, in turn, results in higher CO consumption (i.e. a lower k_{CO}), since k_{CO} depends on the initial CO concentration.

3.2.3 Chl *a*

Neither between Chl *a* and GP_{CO} (Fig. 3b) nor between Chl *a* and k_{CO} a significant relationship was found (Fig. 3f).

This is in contrast to Xie et al. [2005] who reported a negative correlation between Chl *a* and k_{CO} (please note again that Xie et al. [2005] reported k_{CO} as positive values). This implies that Chl *a*/ k_{CO} relationships seems not to be uniform within the Arctic realm, pointing to regional differences, possibly caused by the complex interplay between different water masses (Cherkasheva et al., 2014; Rudels et al., 2015).

The combination of relatively higher Chl *a* concentrations at t_0 with lower nitrate concentrations at Ice2 and D7 could explain the higher CO consumption rates at the two stations: nitrate might be depleted by the present phytoplankton community so that microbes seem to use the produced CO as an supplementary energy source (Cordero et al., 2019; Moran & Miller, 2007).

3.2.4 Nitrate

The effect of nitrate concentrations at t_0 on CO production rates was less obvious. There was a negative trend (albeit statistically not significant at the 95% significance level) of GP_{CO} with NO_3^- concentrations only when excluding the data from NT6A (Fig. 3c). Nitrate concentrations may indirectly influence GP_{CO} rates. Enhanced GP_{CO} rates at low NO_3^- concentrations may point to stress-related CO production during increasing nitrogen limitation.

k_{CO} rates were positively correlated with nitrate concentrations at t_0 ($R^2 = 0.78$, $p < 0.05$, Fig. 3f). This correlation could result from CO consumption by microbes as a supplement energy source when easily accessible nutrients like nitrate are depleted (Cordero et al., 2019).

4 Conclusions

In order to decipher the cycling of CO in the surface waters of the Fram Strait, we measured CO production and consumption rates in various incubation experiments at four sites in the Fram Strait in August/September 2019. Our results show that lower pH (representing future scenarios of ocean acidification) did not affect CO gross production (GP_{CO}) and consumption (k_{CO}) rates. We observed a tight coupling of CO production and consumption. Hence, the produced CO is not necessarily emitted to the atmosphere as the dissolved CO seems to be rapidly consumed before its atmospheric release. We conclude, therefore, that CO consumption mainly drives dissolved CO concentrations and hence seems to act as filter for the subsequent atmospheric CO emissions from the Fram Strait. This is line with the suggestion that microbial processes control the exchange of CO across the ocean-atmosphere interface (Moran and Miller, 2007). High rates of both CO production and CO consumption are favoured by a combination of high CDOM and low NO_3^-

concentrations. This points to a photochemical production of CO from CDOM which, in turn, is consumed rapidly by microbes preferably under oligotrophic conditions (i.e. increasing nitrate limitation). In the Arctic Ocean/Fram Strait, these conditions can be found both at ice edges as well as in the open ocean where a supply of nutrients via melting and/or mixing is followed by stratification (Cherkasheva et al., 2014). We identified both CDOM and nitrate as key drivers of CO cycling. This has the implication that predicted changes in terrestrial-derived and marine CDOM (e.g. Lannuzel et al., 2020), as well as dissolved nitrate inputs (Tuerena et al., 2022) will likely affect future CO production and consumption in the Fram Strait. Both trends might lead to higher CO gross production as well as higher CO consumption. It is yet uncertain whether both terms will balance each other out (as observed in our study) or whether one process will become dominant. The question if and under which conditions k_{CO} would stagnate should be addressed in future research, since in that situation CO would actually be emitted. Performing further multifactorial experiments including i.e. UV light intensity and bacterial community data could help to elucidate the explanatory power of the different environmental factors on both CO production and consumption. This would facilitate a better incorporation of both terms into models and would improve both CO emission estimates for the Arctic realm, and the assessment of how atmospheric CO emissions will affect the radiative budget and oxidative capacity of the Arctic atmosphere.

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Author's Declaration

The authors declare no conflict of interests.

Open Research

Data Availability Statement

The data will be archived at the BODC database (<https://www.bodc.ac.uk/data/all-data.html>) by the time of publication.

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Carbon monoxide (CO) cycling in the Fram Strait, Arctic Ocean

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Supporting information

Table S1

Water mass characterization after Fofonoff and Millard Jr (1983) and Rudels et al. (2005). PML: Polar Mixed Layer, PSW: Polar Surface Water, AAW: Arctic Atlantic Water, AIW: Arctic Intermediate Water

Station	depth (m)	Density σ_t (g L ⁻¹)-1000	Salinity	Temp., °C	water mass	water/origin	remarks
NT6A	5	24.12	30.04	1.36	PSWw - Warm Surface Water	North_Atlantic	
NT6A	31	27.49	34.41	2.49	PSWw - Warm Surface Water	North_Atlantic	
NT6A	100	27.88	34.97	2.87	AW & RAW - Atlantic Water & Recirculating Atlantic Water	North_Atlantic	
Ice2	5	24.83	29.02	-1.05	PSW - Polar Surface Water	Arctic	Ice edge,
Ice2	35	27.24	33.91	-1.15	PSW - Polar Surface Water	Arctic	shelf
Ice2	75	27.55	34.35	-0.42	PSW - Polar Surface Water	Arctic	break
Ice2	102	27.69	34.59	0.74	AAW - Arctic Atlantic Water	Arctic	
D5	5	25.61	32.00	1.37	PSWw - Warm Surface Water	North_Atlantic	Sea ice
D5	10	26.56	33.44	3.82	PSWw - Warm Surface Water	North_Atlantic	melting
D5	25	27.39	34.86	6.41	PSWw - Warm Surface Water	North_Atlantic	on
D5	40	27.56	34.73	4.15	PSWw - Warm Surface Water	North_Atlantic	warmer
D5	75	27.67	34.93	4.56	PSWw - Warm Surface Water	North_Atlantic	(Atlantic)
D5	110	27.72	34.99	4.52	AW & RAW - Atlantic Water & Recirculating Atlantic Water	North_Atlantic	water
D7	5	27.22	34.78	5.68	PSWw - Warm Surface Water	North_Atlantic	Open
D7	10	27.41	34.79	5.70	PSWw - Warm Surface Water	North_Atlantic	ocean
D7	100	27.78	34.99	3.98	AW & RAW - Atlantic Water & Recirculating Atlantic Water	North_Atlantic	

S2 Methods

S2.1 Ancillary measurements

The spectral absorption coefficient of CDOM at 330 nm (a_{330}) was determined for the seawater samples in 5 m from the CTD/rosette cast preceding the incubation experiments ($= t_0$) and from the individual experimental units at each timepoint (t_{12} , t_{24} , t_{48}) during the incubations. Each CDOM sample was filtered through a sterile, sample-washed 0.2 μ m membrane (GWSP, Millipore) into pre-combusted, sterile brown glass vials. CDOM absorption was measured according to the procedure as described in Lennartz et al. (2019) and the mean error of the method was 8%. We used purified MilliQ water as the reference. A Seabird SBE9plus sensor package (<https://www.bodc.ac.uk/data/documents/nodb/pdf/03plusbrochurejan07.pdf>) including an oxygen optode, a fluorescence sensor (Chl a) and a sensor for photosynthetic active radiation (PAR). All sensors were attached to the CTD/rosette. Vertical profiles recorded during lowering the CTD/rosette were considered here only.

Inorganic dissolved nutrients including nitrate were analysed using a Technicon segmented 4-channel flow colorimetric autoanalyser (Bran & Luebbe AAIII, SEAL Analytical). The analytical methods applied are described in Grasshoff et al. (1999). The detection limit was 2 nmol l⁻¹ during the cruise. The precision of the method was 8%, and of the colorimetric autoanalytical techniques was > 5% (Woodward and Rees, 2001).

S2.2 Note on statistical analysis

Simple regression test was chosen because multiple regression test had too low explanatory power due to the small number of experimental replicates.

S3 Figures

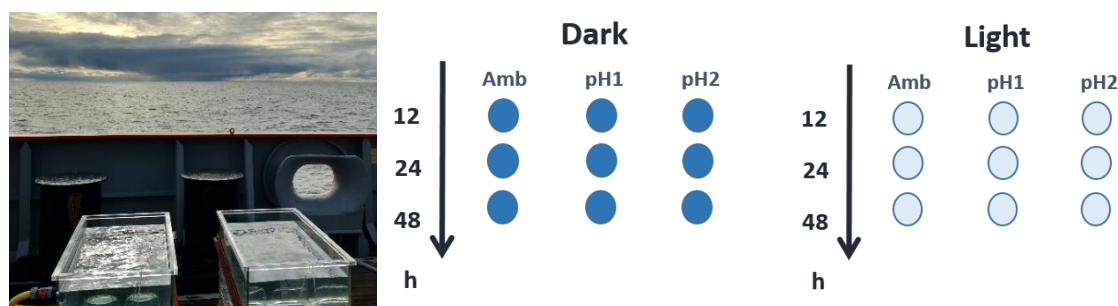


Fig. S3.1 Experimental set up of incubations. Left: The incubator tanks, which were, installed on-deck, supplied with natural seawater and made of natural sunlight-transmitting material, so that natural conditions of the surface ocean were mimicked. Right: Incubations were performed over a total of 48 hours in darkened and light tanks. Each dot represents one experimental unit referring to one treatment and sampling timepoint and was discarded after sampling (gases, CDOM, pH) was done. Samples were taken after 12, 24 and 48 hours. The pH in each experiment was manipulated to two lowered pCO₂ (pH) levels pH1: 670 ppm and pH2: 936 ppm CO₂ in comparison to the ambient pH (amb) as a control.

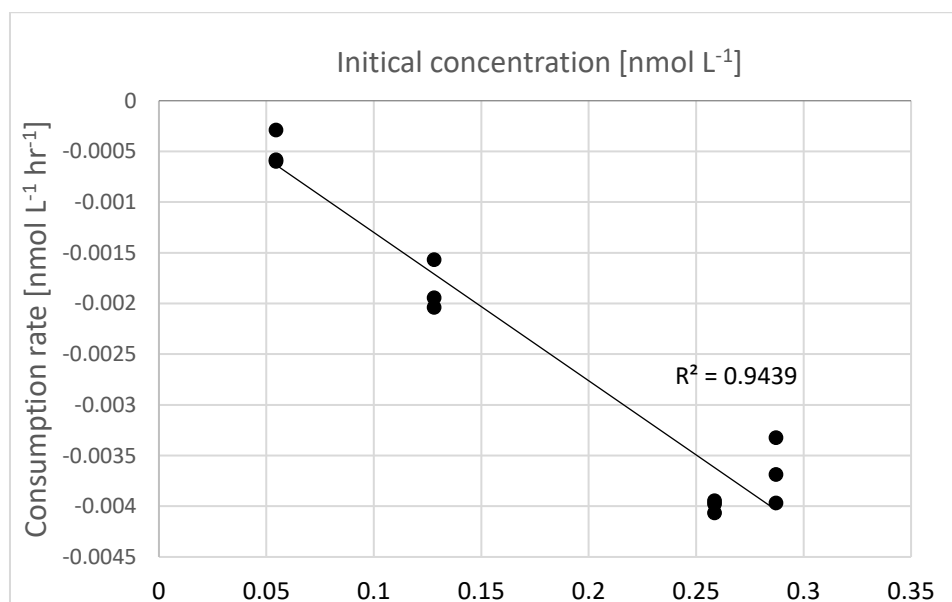


Fig. S3.2 Initial concentrations plotted against overall consumption rates per experiment. All consumption rates depend on the initial CO concentration (i.e. first order loss). R² = 0.94 with $p < 0.05$.

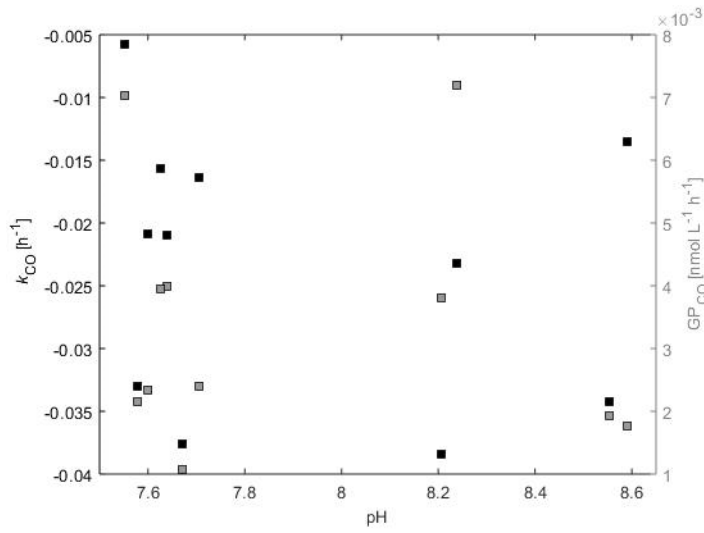


Fig S3.3 pH vs. k_{CO} and GP_{CO} .

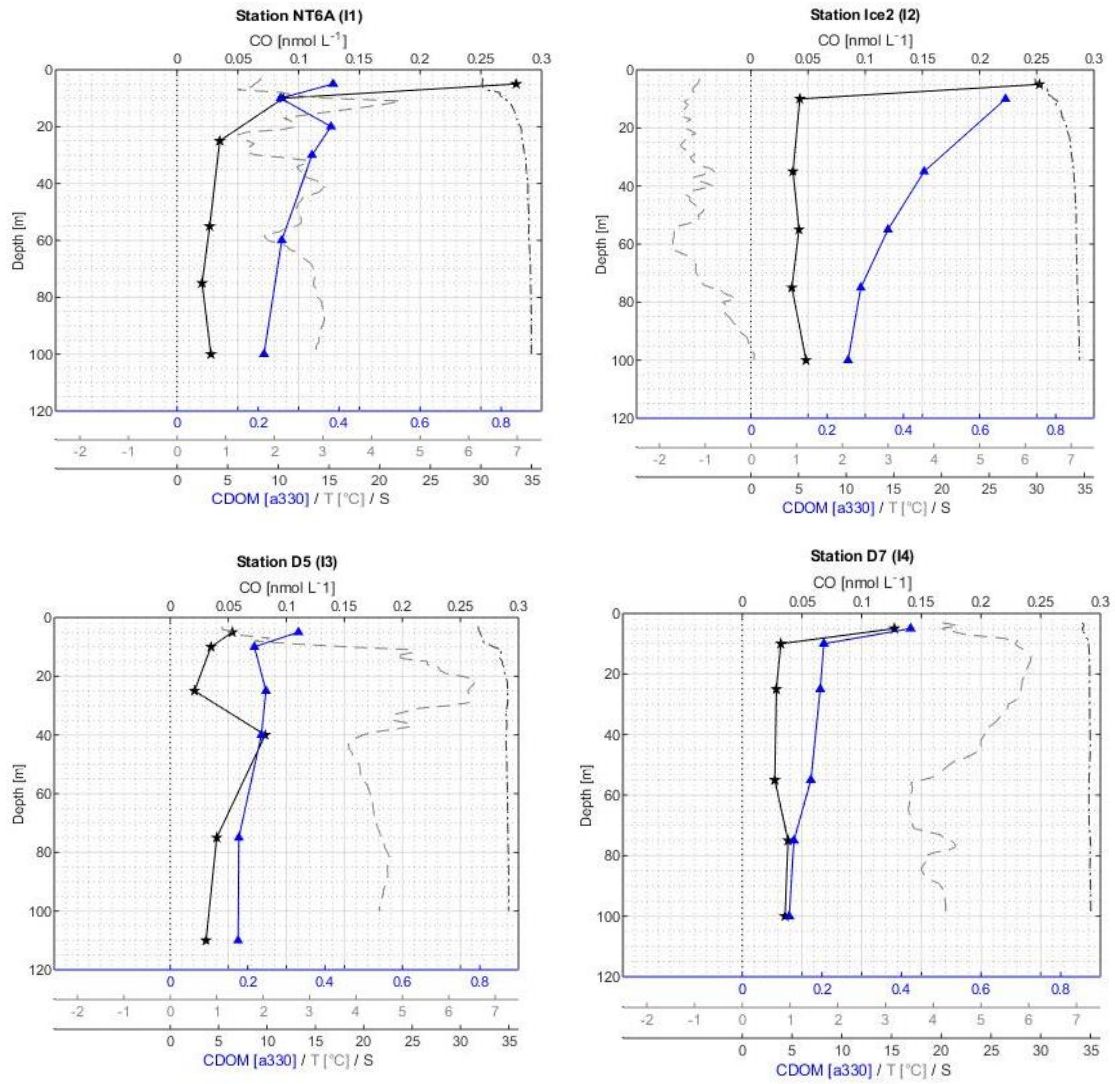


Fig. S3.4 Vertical profiles of dissolved CO concentration, salinity, temperature and CDOM at t_0 at each incubation location

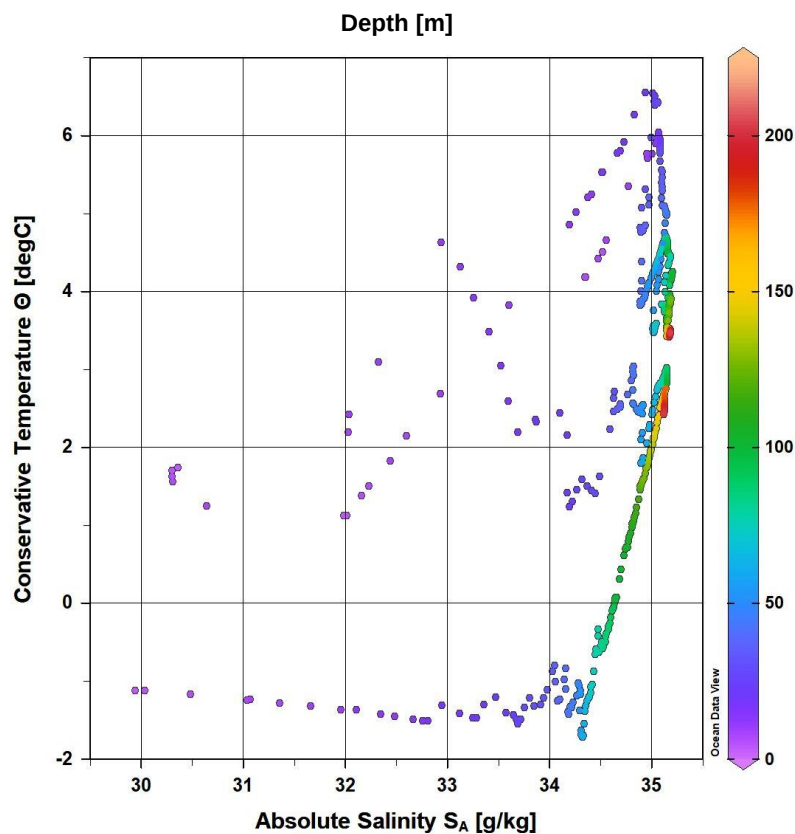


Fig S3.5 T/S distribution per depth at the incubation stations

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