

## Air–water exchange and vertical profiles of organic carbon in a subarctic fjord

Sergio Ruiz-Halpern,<sup>a,\*</sup> Mikael K. Sejr,<sup>b</sup> Carlos M. Duarte,<sup>a</sup> Dorte Krause-Jensen,<sup>b</sup> Tage Dalsgaard,<sup>b</sup> Jordi Dachs,<sup>c</sup> and Søren Rysgaard<sup>d</sup>

<sup>a</sup>Department of Global Change Research, Institut Mediterrani d'Estudis Avançats (IMEDEA), Consejo Superior de Investigaciones Científicas-Universitat Illes Balears (CSIC-UIB) I, Balears, Spain

<sup>b</sup>Department of Marine Ecology, National Environmental Research Institute (NERI), University of Aarhus, Silkeborg, Denmark

<sup>c</sup>Instituto de Diagnóstico Ambiental y Estudios del Agua (IDAEA), Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Cataluña, Spain

<sup>d</sup>Greenland Climate Research Centre, Greenland Institute of Natural Resources, Nuuk, Greenland

### Abstract

In this article, we examine the air–sea exchange of exchangeable organic carbon (OC) as well as the internal pools and sources within a subarctic fjord. Air–water fluxes of OC ranged from an uptake of  $22 \pm 10$  mmol C m<sup>-2</sup> d<sup>-1</sup> in winter to a release of  $2 \pm 8$  mmol C m<sup>-2</sup> d<sup>-1</sup> in the fall, sizable compared to that of CO<sub>2</sub> (average uptake of 136 mmol C m<sup>-2</sup> d<sup>-1</sup> for the fall and  $2.6 \pm 0.84$  mmol C m<sup>-2</sup> d<sup>-1</sup> in the winter). The water column profiles of exchangeable dissolved organic carbon (EDOC) followed closely those of dissolved organic carbon (DOC), and EDOC represented, on average, about one-third of DOC. The dynamic characteristic and active cycling of EDOC was evidenced by incubation experiments performed on each fjord compartment (sediment, water column, macroalgae) where sediments and macroalgae were found to be substantial sources and the water column acted as a strong sink of EDOC.

Volatile organic compounds (VOCs) are important sources of carbon to the atmosphere (Guenther et al. 1995; Schauer et al. 2002) but have been only partially quantified. As the largest biome on Earth, covering 71% of the Earth's surface, oceans play a double role as a sink for terrestrially produced VOCs and semivolatile organic compounds (SOCs) (anthropogenic and of biological origin) (Jaward et al. 2004; Sinha et al. 2007) and as a source of volatile and semivolatile compounds released at different steps of the carbon flow in marine food webs (Steinke et al. 2002) or as a product of photochemical reactions (Laternus 1996; Sinha et al. 2007). Marine-originated organic compounds are active in the atmosphere, affecting tropospheric ozone concentrations (Monson and Holland 2001) and cloud formation (Vallina and Simó 2007), thereby contributing to regulate the Earth's climate (Williams 2004). Yet analyses of VOC fluxes focused on individual compounds of particular interest (e.g., isoprene, DMS, halocarbons; Holmes et al. 2000; Gabric et al. 2001; Chuck et al. 2005) are dominant in the VOC literature (Williams et al. 2004; Sinha et al. 2007) but do not allow assessment of the quantitative importance of these compounds as a pool of carbon. In addition, SOCs also contribute to the overall flux of organic compounds in aquatic ecosystems (Dachs et al. 2005), especially when considering the fluxes of organic compounds from the atmosphere to the ocean (Jaward et al. 2004). As a result, the total flux of carbon associated with fluxes of VOC and SOC and their role in the carbon budget of marine ecosystems is still largely unresolved. The scarcity of data on the dynamics of dissolved volatile and semivolatile compounds within marine ecosystems is even greater (Laternus et al. 1998), as research efforts have focused on

a few individual compounds that are not necessarily representative of the total pool of volatile and semivolatile compounds in the oceans (Laternus 1996; Sinha et al. 2007) and the sources and sinks of volatile and semivolatile compounds within marine ecosystems remain largely unresolved.

A major reason for the present paucity of knowledge on marine VOC and SOC dynamics is methodological, as there were, until recently, no methods available to quantify total carbon concentrations associated with VOC and SOC in seawater. Previous attempts to quantify total organic carbon (TOC) in air (Roberts et al. 1998) did not suffice in themselves to estimate the exchange between air and water since it was measured directly in the atmosphere (*see* Methods for details). Indeed, because the conventional approach to measuring dissolved organic carbon (DOC) includes bubbling of the acidified sample to remove inorganic carbon before analysis in a TOC analyzer (Spyres et al. 2000), the DOC measurements represent, in fact, measurements of nonpurgeable DOC. The purgeable or exchangeable fraction, not included in conventional DOC analyses, was defined by Dachs et al. (2005) as exchangeable dissolved organic carbon (EDOC), as the approach to measuring this pool involves purging the water sample with a carrier gas free of OC. Whereas some companies manufacture purgeable OC modules for their OC analyzers (e.g., Shimadzu TOC-Vcsh), these instruments do not seem to yield adequate results, as recovery rates are very low in standard curves ( $47.78 \pm 2.37\%$  recovery rate for Toluene on the Shimadzu TOC-Vcsh). However, Dachs et al. (2005) developed a new approach based on the equilibration of EDOC between air and pure water by purging off EDOC from seawater samples and equilibrating in pure, carbon-free water to estimate total concentrations of EDOC in seawater. Similarly, equilibration of gas-phase organic

\* Corresponding author: sergio.ruiz@uib.es

carbon (GOC) in carbon-free water with that in air allows estimation of GOC concentrations in air indirectly by measuring their concentration equilibrated in water as  $\text{GOC } H'^{-1}$ , where  $H'$  is the dimensionless Henry's law constant. This approach allows estimation of the direction and magnitude of air–sea OC exchange (Dachs et al. 2005). Using this approach, Dachs et al. (2005) demonstrated high concentrations of EDOC in the subtropical northeastern Atlantic, representing 30–40% of the DOC pool (Dachs et al. 2005), and identified significant atmospheric inputs of gas-phase organic matter to the subtropical Atlantic. These results confirm that EDOC can be a significant component of the C pool and fluxes in marine ecosystems of global relevance (Jurado et al. 2008). Dachs et al. (2005) provided data for the subtropical Atlantic. However, cold marine environments are areas of potentially large EDOC-GOC fluxes for a variety of reasons: (1) Henry's law constants ( $H'$ ) are low at low temperatures, displacing exchangeable OC to the water phase (Staudinger and Roberts 2001); (2) arctic macroalgae have already been identified as a source of halogenated VOC and are abundant and widely distributed (Laternus 2001); and (3) the presence of seasonal ice cover reduces the area for exchange, reducing fluxes between water and air during the wintertime.

Here we examine the concentration, air–sea exchange, and internal inputs and sinks of EDOC and GOC in a subarctic fjord ecosystem (Kobbefjord, southwestern Greenland), a rather contrasting environment to the subtropical open-ocean region where OC pools and fluxes were first assessed (Dachs et al. 2005). We assess the size of the EDOC pool relative to those of nonpurgeable dissolved and particulate OC pools. We then identify possible biological sources and sinks of EDOC and GOC and compare the magnitude of air–sea exchange of  $\text{CO}_2$  and GOC for this ecosystem.

## Methods

Kobbefjord is a 17-km-long, 0.8–2.0-km-wide deep sill fjord in Nuuk, capital of Greenland (Fig. 1). The average depth is 44 m, and the maximum depth is 120 m (Mikkelsen et al. 2008). The study took place between September 2007, before the onset of the ice-covered period, and May 2008, once the ice had already disappeared. During this time, the fjord was sampled in three different seasons; autumn, from 10 to 22 September 2007; winter, from 12 to 29 February 2008; and spring, from 13 to 27 May 2008. Sea ice is present seasonally in the fjord, with high interannual variation and typically covers the innermost part of the fjord (Mikkelsen et al. 2008).

We gathered data on OC and  $\text{CO}_2$  pools in the water column and the atmosphere. One station, located near the deepest area of the fjord, was repeatedly sampled in each sampling period to resolve changes in DOC, POC, and EDOC along the water column. At this station, five depths (1, 10, 20, 40, 80 m) were sampled using a 12-liter Niskin bottle, following casts with a SeaBird 19plus conductivity temperature depth (CTD) probe fitted with a fluorescence probe to profile properties in the water column. On most sampling occasions the fluorescence maximum was cap-

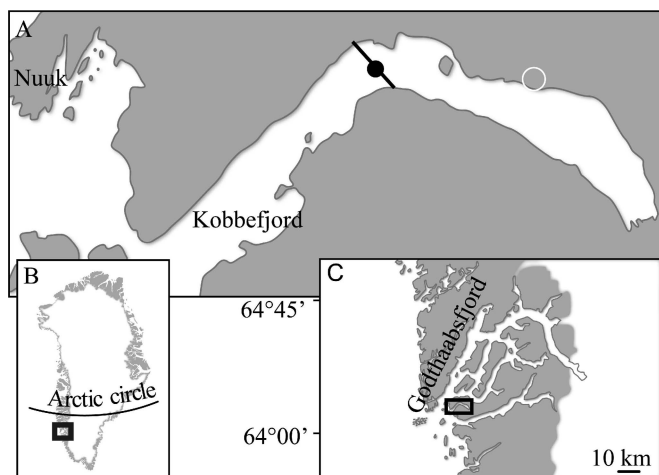


Fig. 1. (A) Map of Kobbefjord showing the maximum sea ice extent (black line) and the location of the sampling station (closed circle). (B) The location of the Godthaabsfjord system in Greenland and (C) details of the Godthaabsfjord system.

tured by the standard sampling depths, but on 11 September 2007, an additional sample was collected at 5-m depth to include the depth of the fluorescence maximum. Additional data from CTD casts performed through the year as part of a monitoring program were available to better characterize annual dynamics in the fjord.

In May 2008 we examined, using experimental incubations, the role of sediments, planktonic communities, and macroalgae, occupying the shallow margins of the fjord, in supporting EDOC fluxes. Six sediment cores (Plexiglas, 5.2-cm-diameter cylinders, containing 650 mL of overlying water) were taken at the fixed sampling station and incubated for 36 h at in situ temperature ( $2^{\circ}\text{C}$ ). Magnetic stirrers ensured sufficiently well-mixed overlying water. Two of the cores were sampled every 12 h to measure EDOC concentration in the waters overlying the sediment and establish the net flux of EDOC from the rate of change in EDOC concentration over time. In an attempt to identify possible autochthonous sources and sinks of EDOC to the fjord and calculate the net EDOC production or consumption by the pelagic community, water from 20-m depth, just below the depth of the chlorophyll maximum, was collected in three replicate, acid-cleaned 1-liter glass bottles and incubated for 48 h at in situ light and temperature conditions. EDOC concentration was extracted following the method described next at the beginning and end of the incubation. *Laminaria longicuris* (de la Pylaie 1824) is among the dominant macroalgae in the fjord and was hence used to examine EDOC release by macroalgae. Macroalgae from the shallow parts of the fjord were collected and incubated for 72 h in gastight plastic bags filled with seawater at in situ light and temperature conditions. Each of the three replicate bags contained 55.20, 60.70, and 55.70 g wet weight of macroalgal tissue and 1.04 liters of seawater, purged with high-purity nitrogen to remove EDOC before use. EDOC was measured at the beginning and end of the incubation period. A conversion factor of 0.1767 was used to obtain

dry weight (dry wt) from the wet-weight material (Wegeberg et al. 2006).

Water samples for determination of nonpurgeable DOC were filtered through precombusted fiberglass filters (Whatman GF/F) and frozen ( $-18^{\circ}\text{C}$ ) in precombusted and acid-washed 20-mL vials until analysis on a Shimadzu TOC-5000 analyzer (Shimadzu Corp.). Standards provided by Dennis A. Hansell and Wenhao Chen (University of Miami) of  $2\ \mu\text{mol L}^{-1}$  and  $45\ \mu\text{mol L}^{-1}$  TOC were used to assess the accuracy of the estimates. Samples for particulate organic carbon (POC) were measured on precombusted GF/F filters after filtration of 200–500 mL of seawater (volume depending on season). Filters were analyzed on an elemental analyzer (Robo-prep-CN, Europa Scientific).

Exchangeable OC exists both in gaseous phase in the atmosphere and dissolved in seawater. The fraction of exchangeable OC dissolved in seawater is operationally quantified as EDOC (Dachs et al. 2005), and that present in the air is not measured directly but equilibrated in ultrapure water and is referred to as GOC (gaseous OC), thus measuring  $\text{GOC } H'^{-1}$ . Samples for EDOC and GOC were collected and analyzed following the procedures described in Dachs et al. (2005). Samples for EDOC determination were collected by bubbling 1-liter seawater samples with high-purity  $\text{N}_2$  gas for 5–8 min, determined in laboratory experiments to suffice to reach equilibrium, to purge the volatile organic compounds, which were then trapped in 50 mL of ultrapure water free of carbon, preacidified with phosphoric acid to  $\text{pH} < 2$ . Subsamples from the ultrapure water trap containing the volatile compounds were then transferred to glass ampoules, precombusted at  $450^{\circ}\text{C}$  for 4.5 h, and OC was analyzed in duplicate by high-temperature catalytic oxidation on a Shimadzu TOC-5000A or TOC-V-csh, avoiding bubbling to prevent EDOC losses. Blanks were prepared in the field by bubbling the ultrapure water free of OC directly with high-purity  $\text{N}_2$  gas for 5–8 min and analyzed for OC as indicated previously. EDOC concentrations were calculated as the difference between carbon concentration in the samples and that in the blanks. The efficiency of EDOC extraction by this procedure ranges depending on the degree of volatility of the compounds and was assessed to be  $53 \pm 28\%$  and  $80 \pm 26\%$  for acetone and toluene, respectively (Dachs et al. 2005). These recovery efficiencies, however, cannot be used to properly assess accuracy, as there are no reference materials for the complex pool of compounds included in our measurements, likely involving hundreds of compounds. Duplicate EDOC and blank samples showed variability well above that for conventional DOC analyses, although duplicate analyses do not allow for statistical uncertainty to be properly estimated. We, therefore, pooled all the standardized duplicate estimates to examine the statistical distribution of the variability among duplicate pairs. This exercise, based on 227 duplicated estimates, indicated that the median and mean standard deviation of the GOC and EDOC estimates is  $5.2\ \mu\text{mol C L}^{-1}$  and  $6.3\ \mu\text{mol C L}^{-1}$ .

The total concentration of OC in the atmosphere at the sampling station (GOC) was determined indirectly (operationally as  $\text{GOC } H'^{-1}$ ) by equilibrating air and ultrapure

water for 30 min, determined experimentally to suffice to equilibrate the concentration in water, by bubbling prefiltered air (QMA filter, Whatmann) through 50 mL of acidified ( $\text{pH} < 2$  with  $\text{H}_3\text{PO}_4$ ) ultrapure carbon-free water upwind of the boat. Subsamples of this ultrapure water were immediately transferred into precombusted glass ampoules (at  $450^{\circ}\text{C}$  for 4.5 h), sealed, and analyzed in duplicate for OC as indicated previously. The TOC concentration in the water represents the concentration of gas-phase OC equilibrated in water and provides an operational estimate of  $\text{GOC } H'^{-1}$ , where  $H'$  is the dimensionless Henry's law constant. There are two main reasons to measure GOC using this procedure instead of directly measuring GOC in air: (1) that the concentration of GOC in air is likely to be very low, difficult to resolve with available instruments, and (2) that the ultimate reason to estimate GOC concentrations in air is to estimate the air–water flux, which depends on the differential between the GOC concentration in the air phase in equilibrium with the water (i.e.,  $\text{GOC } H'^{-1}$ ) and that in water (EDOC). Because the nature of the organic compounds making the atmospheric GOC pool in air is unknown and since Henry's law constants regulating the partitioning between the air and water phase are compound specific, the approach developed by Dachs et al. (2005) allows calculations of air–water diffusive OC fluxes by experimentally resolving  $\text{GOC } H'^{-1}$  directly, thereby avoiding error in the flux estimations derived from assumptions on  $H'$ .

Diffusive air–water exchange was estimated using the wind speed dependence of the mass transfer velocity ( $k600$ ) from instantaneous wind speeds ( $U10$ ,  $\text{m s}^{-1}$ ) following the equation  $k600 = 0.24 U10^2 + 0.061 U10$  (Nightingale et al. 2000). OC net diffusive fluxes ( $F_{\text{OC}}$ ) were estimated as the sum of gross volatilization ( $F_{\text{OC,VOL}} = k' \times \text{EDOC}$ ) and absorption ( $F_{\text{OC,AB}} = -k' \times \text{GOC } H'^{-1}$ ), where  $k'$  is the gas transfer velocity estimated from  $k600$  values and Schmidt numbers assuming an average molecular weight (MW) of GOC of  $120\ \text{g mol}^{-1}$  (Dachs et al. 2005). This arbitrary MW is chosen because it represents an intermediate value between volatile and semivolatile species, respectively (e.g., aromatics: benzene  $78\ \text{g mol}^{-1}$ , pyrene  $202\ \text{g mol}^{-1}$ ; aliphatic: butane  $58\ \text{g mol}^{-1}$ , heptadecane  $223\ \text{g mol}^{-1}$ ; polar: methanol  $32\ \text{g mol}^{-1}$ , dichlorophenol  $163\ \text{g mol}^{-1}$ ). Sensitivity analyses showed that estimates of  $k'$  are relatively insensitive to MW values, as a variability of 50–200% over the value of  $120\ \text{g mol}^{-1}$  assumed here led to a variability in  $k'$  of 23.11% and 18.77% over the mean value, respectively, which is relatively small in comparison with the uncertainties associated with the wind speed dependence of  $k'$  and other factors affecting  $k'$  (Calleja et al. 2009). Data on wind velocity and air temperature were obtained from local weather stations (Jensen and Rasch 2008, 2009), and appropriate solubility corrections were applied to estimate in situ air–water OC fluxes. By convention, we use negative fluxes to denote inputs from the atmosphere to the ocean and positive ones to denote volatilization to the atmosphere. The partial pressure of  $\text{CO}_2$  in the water ( $p\text{CO}_2$ ) was measured using a nondispersive infrared gas analyzer (Environmental Gas Monitor (EGM)-4, manufactured by pp systems) that measures

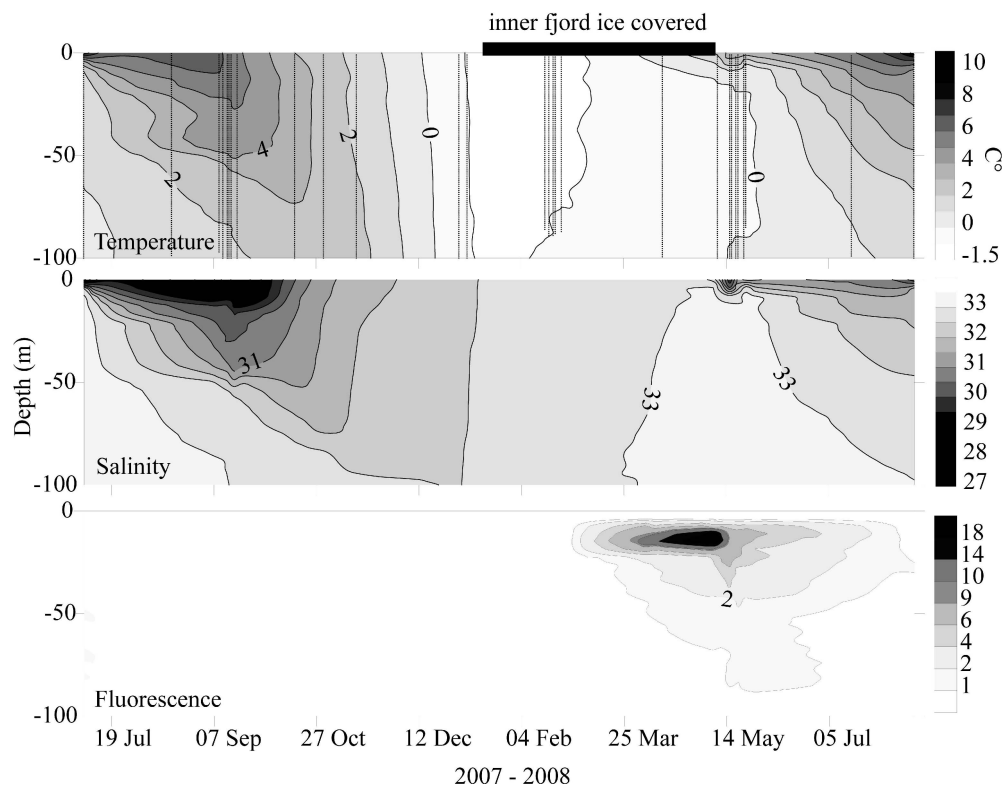


Fig. 2. (A) Temperature, (B) salinity, and (C) fluorescence distribution at the sampling station in Kobbefjord. Data obtained from regular CTD casts shown as vertical dotted lines on panel A. The duration of sea ice cover in the inner fjord is indicated by the black bar above panel A.

$p\text{CO}_2$  with a precision of  $\pm 10^{-6}$ . For atmospheric measurements, air is passed through a desiccation column (anhydrous calcium sulfate, Drierite) removing water vapor from the air in order to avoid interferences in  $\text{CO}_2$  measurements. For  $p\text{CO}_2$ , below-surface water was collected and passed through a gas exchange column (Mini-Module Membrane Contactor) and  $p\text{CO}_2$  measured as described previously. Measurements correspond, therefore, to those in dry air, as measured, and no efforts were made to correct this for the atmospheric moisture as proposed in Calleja et al. (2005). Details of this methodology have been described elsewhere (Calleja et al. 2005; Silva et al. 2008).  $\text{CO}_2$  exchange between air and water was estimated using short-term wind speed dependence (Wanninkhof and McGillis 1999).

## Results

The fjord started freezing on 05 January 2008, and the maximum ice extension was reached on 01 February 2008. The inner part was ice covered for almost 5 months (until 23 May 2008; Fig. 2), although some ice cover was retained at the land end of the fjord over much of the study. The water column at Kobbefjord remained well mixed, and plankton biomass was low throughout the ice-covered period. Following the ice melt in the spring, freshwater inputs progressively reduced salinity in the water column, concurrent with rising temperatures, and a fluorescence

peak corresponding to a spring phytoplankton bloom developed soon after the ice melt (Fig. 2).

DOC concentrations varied between a minimum of  $74 \mu\text{mol C L}^{-1}$  and a maximum of  $210 \mu\text{mol C L}^{-1}$ . EDOC at the permanent sampling station ranged from below the detection limit to a maximum of  $133 \mu\text{mol C L}^{-1}$  and was particularly high in February, when the fjord was partly ice covered (Fig. 3; Table 1). Integrated EDOC pools were highest in February 2008 and lowest in May 2009 (Table 1). EDOC and DOC concentrations followed parallel trends with depth. EDOC concentrations were, however, much lower than those of DOC (Fig. 3; Table 1), typically representing about a third of total OC ( $\text{TOC} = \text{DOC} + \text{EDOC} + \text{POC}$ ) but reaching values close to 50% in some instances (Table 1). POC represented a small fraction (on average  $0.53 \pm 0.03 \text{ mol m}^{-2} = 3.68\%$  of TOC), but spring values reached twice the level of fall and winter values (Table 1).

GOC concentration ranged from  $13 \mu\text{mol C L}^{-1}$  to  $79 \mu\text{mol C L}^{-1}$  and averaged  $42 \pm 5 \mu\text{mol C L}^{-1}$  along the study. GOC concentrations were closely correlated with those of EDOC ( $R^2 = 0.73$ ; Fig. 4), as expected from the dynamic equilibrium between these fractions, but GOC concentrations tended to exceed those of surface EDOC with GOC values exceeding EDOC concentrations in 10 out of the 14 paired samples collected by, on average,  $45 \pm 20\%$ . Seven out of the 14 paired samples were obtained at the permanent station, and the remainder were obtained

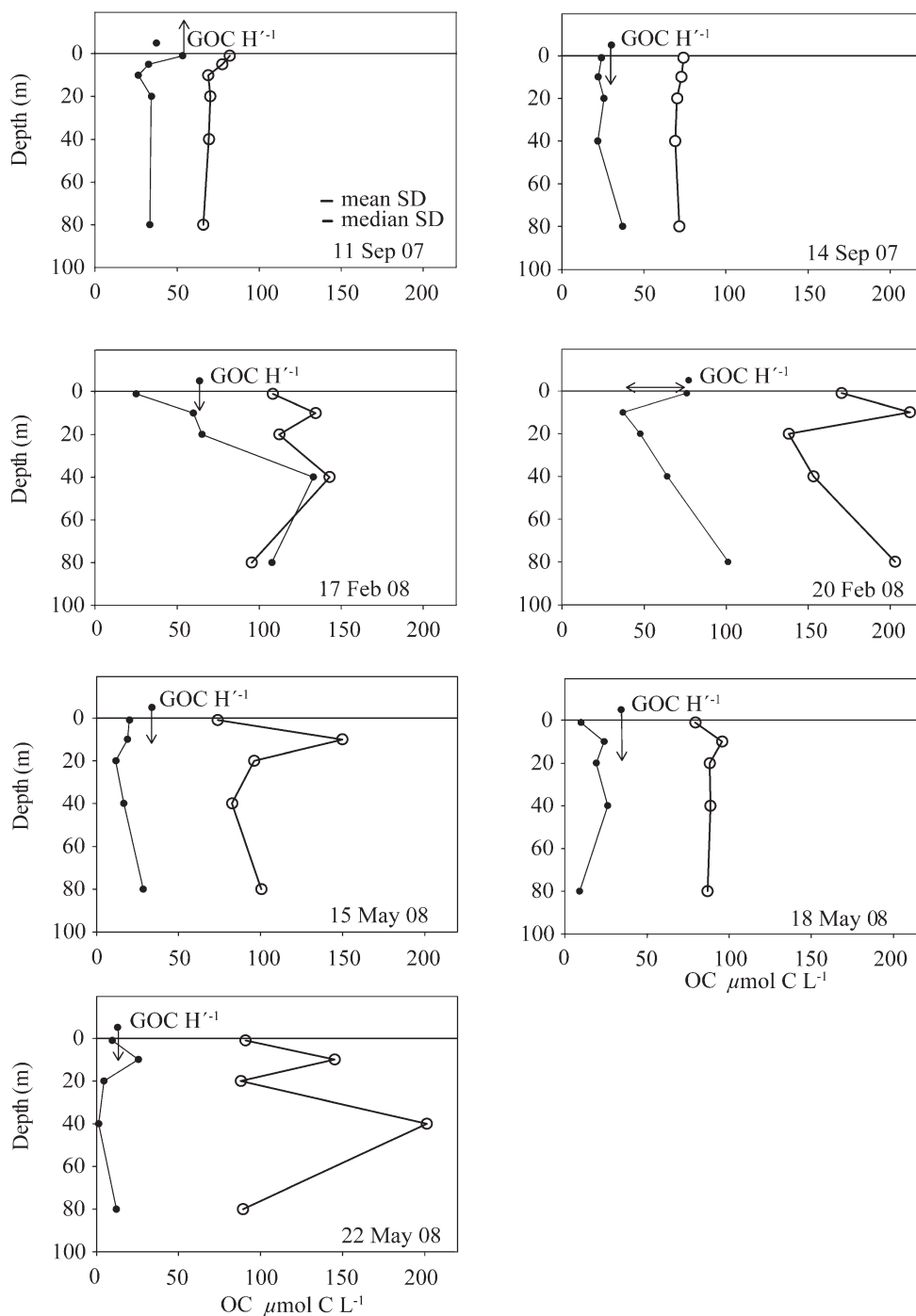


Fig. 3. Vertical profile of EDOC (closed circles), DOC (open circles), and GOC (large single dot) in  $\mu\text{mol C L}^{-1}$  at the sampling station in Kobbeffjord, Greenland. Arrows represent the direction of exchangeable OC flow between the atmosphere and the water (horizontal arrows indicate no significant net flux). Mean ( $6.3 \mu\text{mol C L}^{-1}$ ) and median  $5.2 \mu\text{mol C L}^{-1}$  standard deviations of replicate analysis are shown as scaled bars of the X axis in the first panel for reference.

from the synoptic survey throughout the whole fjord. The tendency for the equilibrium concentrations of atmospheric GOC to exceed OC concentrations in fjord surface waters (EDOC) indicates a prevalence of a net diffusive flux of GOC from the atmosphere to the fjord waters (Table 1). The diffusive flux of GOC from the atmosphere to the fjord

waters did not differ significantly from zero in the fall, as both influx and efflux were obtained in measurements conducted in the fall campaign (Table 1). A strong flux from the atmosphere to the water was detected in February. In May 2008 the transport of GOC was also directed from the atmosphere to the water but was much

Table 1. Inventory of air–sea fluxes of OC and CO<sub>2</sub> (positive values denote fluxes to the atmosphere, and negative values represent an inward flux into the water) and OC pools—EDOC, DOC, POC, and proportion of TOC accounted for by EDOC—in the water column of Kobbefjord (southwestern Greenland) at different dates along the study. When error estimates are not reported, only two values were estimated, and no standard error (SE) could be calculated.

Season	Date	Air–water exchange (mmol m <sup>-2</sup> d <sup>-1</sup> )		Water column OC pools (mol m <sup>-2</sup> )			
		OC	CO <sub>2</sub>	EDOC	DOC	POC	% EDOC
Fall	11 Sep 07	15.73		4.05	7.55	0.36	33.9
Fall	14 Sep 07	-1.37	-32.64				
Fall	18 Sep 07	-9.16	-240.50	3.25	7.82	0.35	28.4
	Mean±SE	1.73±7.35	-136.57	3.65	7.69	0.36	31.15
Winter	15 Feb 08	-37.66					
Winter	17 Feb 08	-42.33	-2.81	11.09	12.63	0.34	46.1
Winter	19 Feb 08	1.79	-1.07				
Winter	20 Feb 08	-0.73	-3.98	5.25	18.91	0.36	21.4
Winter	23 Feb 08	-30.82					
	Mean±SE	-21.95±10.47	-2.62±0.84	8.17	15.77	0.35	33.75
Spring	15 May 08	-4.54		2.40	10.82	0.81	17.1
Spring	16 May 08	-2.22	-1.63				
Spring	18 May 08	-3.18	-1.88	1.81	9.68	0.78	14.7
Spring	19 May 08	0.23	-4.61				
Spring	22 May 08	-2.41		1.03	13.74	0.72	6.7
Spring	23 May 08	-2.93					
	Mean±SE	-2.50±0.70	-2.71±0.95	1.75±0.40	11.41±1.21	0.77±0.03	12.84±3.16

smaller than that in winter (Table 1). CO<sub>2</sub> fluxes were always from the atmosphere into the water and were highly variable, spanning two orders of magnitude across measurements (Table 1).

Experiments to elucidate the role of various components of the fjord ecosystem as sinks or sources of EDOC were conducted in May 2008. Incubation of intact sediments led to an increase in EDOC concentration in the water column over time, indicative of a role of sediments as sources of

EDOC to the water column at a calculated average rate of 4.8 mmol C m<sup>-2</sup> d<sup>-1</sup>. The planktonic community appeared to act as a strong sink of EDOC, with a net decline in EDOC of 3.32 ± 0.64 μmol C L<sup>-1</sup> d<sup>-1</sup> derived from incubations of water collected at 20 m in May 2008. Incubations of macroalgal blades also showed these to release EDOC at an average rate of 0.44 ± 0.19 μmol C g dry wt<sup>-1</sup> d<sup>-1</sup>.

## Discussion

Our measurements indicate that EDOC is an important component of total OC in the water column of Kobbefjord, with EDOC representing, on average, 24 ± 5% of TOC concentrations and 37 ± 10% that of total (purgeable and nonpurgeable) DOC concentrations. This is comparable to the contribution of 30–40% of EDOC to DOC reported by Dachs et al. (2005) for the subtropical northeastern Atlantic and provides additional evidence that neglecting exchangeable OC leads to a significant underestimation of total DOC concentration in ecosystem carbon budgets, as the DOC concentrations reported in the literature refer to the nonpurgeable fraction. However, EDOC values were highly variable not only among seasons but also between dates in the same season.

The integrated EDOC pool was highest in the ice-covered period (February), when the ice cover prevented equilibration with the atmosphere over much of the fjord, compared to the open-water periods of the study (Fig. 4) and presumably also because of the significantly lower H' values at lower temperatures, thus favoring the retention of exchangeable OC in seawater. However, GOC concentrations (measured here as GOC H<sup>-1</sup>) in the atmosphere were also large in February, so that, despite the high EDOC concentration in seawater, the flux would still be from the

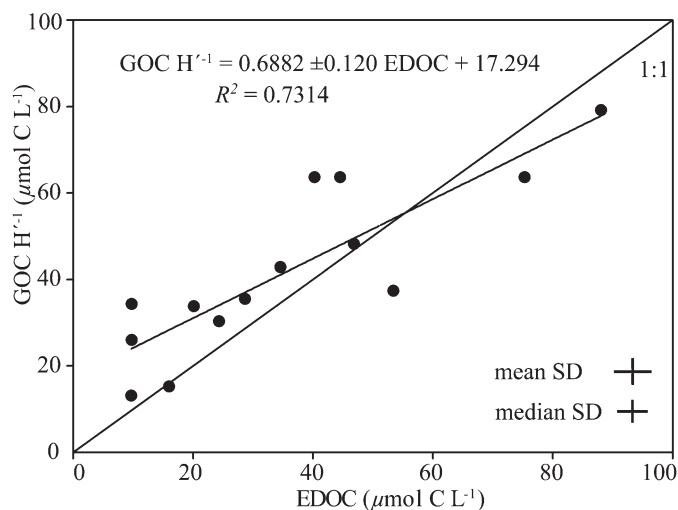


Fig. 4. The relationship between the equilibrium concentration of OC in the gaseous phase in the atmosphere (GOC) and the EDOC in surface water. The lines show the 1 : 1 line and the fitted least squares regression equation, shown in the figure ( $p < 0.0001$ ). Mean (6.3 μmol C L<sup>-1</sup>), and median 5.2 μmol C L<sup>-1</sup> standard deviations of replicate analysis are shown as scaled bars of the X and Y axes for reference.

atmosphere to the water column in the areas free of ice cover (Table 1), consistent with reports of enhanced deposition of semivolatile organic compounds at low temperatures due to low  $H'$  values (Satudinger and Roberts 2001). Elevated winter EDOC concentrations in seawater could be accounted for by low respiration rates and low temperature, together with low light and UV levels, thereby minimizing potential losses of EDOC. In addition, ice communities have been reported to release DOC (Thomas et al. 1995) and could also act as sources of EDOC to the fjord, although this possibility was not evaluated here. In any case, the large EDOC concentrations in winter are indicative of a prevalence of EDOC sources over losses and low temperatures displacing the air–water equilibrium toward the water.

Air–sea OC fluxes were generally lower than those reported by Dachs et al. (2005) for the subtropical Atlantic Ocean, except in winter, when potentially large fluxes over the ice-free regions of the fjord were comparable in magnitude to those reported by Dachs et al. (2005). The flux of OC was significant compared to that of  $\text{CO}_2$ , with a larger flux of  $\text{CO}_2$  into the fjord compared to that of exchangeable OC, except in May, when both fluxes were comparable in magnitude (Table 1). Whereas  $\text{CO}_2$  samples were relatively uniform within sampling periods, OC air–water fluxes changed greatly within sampling periods, including changes in the direction of the OC flux (Table 1).

The vertical profiles of EDOC presented (Fig. 3) suggest the dynamic cycling of EDOC in Kobbefjord, with active consumption and production processes taking place through the water column, as also evidenced by the incubation experiments performed. Kobbefjord acted as a sink for GOC, with an air–water flux of about  $3.12 \pm 1.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$ . This estimate should be considered an approximation, as it was calculated from three sampling campaigns, and better knowledge of year-round air–sea exchange would be necessary to improve the accuracy and precision of this estimate. The flux of GOC into the water column must be supported by a net consumption of EDOC in the ecosystem, maintaining the necessary EDOC deficit in the water column. Indeed, the experiments conducted in May point to a large consumption of EDOC in the water column, at a rate of  $3.32 \pm 0.64 \text{ mmol C m}^{-3} \text{ d}^{-1}$  at 20-m depth. This is consistent with the vertical profiles observed in May, which show a local minimum at this depth (Fig. 4). On the other hand, the maximum in EDOC concentration at 10-m depth (Fig. 4), the depth of maximum net primary production, suggests that the planktonic community acts as a source of EDOC to the ecosystem. In addition, four of the seven profiles showed an increase in EDOC concentration toward the deeper waters of the fjord (Fig. 4), suggesting the presence of a source of EDOC at depth. This suggestion was supported by the experiments conducted in May, which revealed the sediments to be a significant source of EDOC to the ecosystem, with an average input of  $4.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  to the overlying water column, about twice as high as that derived from the atmosphere in this period ( $2.5 \pm 0.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ; Table 1). The benthic EDOC flux is likely supported by the release of volatile and semivolatile compounds during the

decomposition of planktonic-derived POC, which would require, at sedimentation rates of  $39 \pm 3 \text{ mmol C m}^{-2} \text{ d}^{-1}$  estimated using sediment traps during this campaign, the release as EDOC of about 12% of the POC reaching the sediment. Finally, our experiments also identify the macroalgae in the shallow areas of the fjord as significant sources of EDOC to the ecosystem, consistent with previous reports—focused on individual compounds (Laternus 1996; Laternus et al. 1998)—that Arctic macroalgae are significant sources of VOCs. Although our results do not suffice to attempt a budget of EDOC for the ecosystem, which would require accounting for lateral exchanges as well, they do identify the atmosphere and benthic communities (bare sediments and macroalgal beds) as sources of EDOC. Our results also show that EDOC minima in the water column correspond to consumption of EDOC in the water column and suggest that deep chlorophyll maxima, associated with EDOC peaks, may be sources of EDOC to the water column.

In summary, the data presented here support the importance of VOCs and SOCs for the carbon budget of the subarctic fjord investigated. The results show that exchangeable DOC represents a large and dynamic carbon pool within the subarctic fjord studied, accounting for about one-quarter of total OC in the water column. The atmosphere and benthic compartments acted as sources of EDOC to the water column, which could be consumed in the water column. The mean GOC flux from the atmosphere to the water column of  $9 \pm 4 \text{ mmol C m}^{-2} \text{ d}^{-1}$  at Kobbefjord is well below the rates of 25 to  $31 \text{ mmol C m}^{-2} \text{ d}^{-1}$  reported by Dachs et al. (2005) for the subtropical northeastern Atlantic. However, GOC and EDOC pools and fluxes at Kobbefjord were sufficiently large as to be significant components of the carbon budget of this ecosystem. Our results for a subarctic fjord, therefore, add to those of Dachs et al. (2005) to show that VOCs and SOCs can be an important and dynamic component of the marine carbon pool. Yet this pool is grossly understudied and neglected from most accounts of carbon budgets in marine ecosystems. There is, therefore, a pressing need to characterize exchangeable OC concentration and dynamics as a step toward improving our understanding of carbon cycling in marine ecosystems.

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