

**Fluxes of C and nutrients to the Iceland Sea surface layer**

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# Fluxes of carbon and nutrients to the Iceland Sea surface layer and inferred primary productivity and stoichiometry

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Received: 29 September 2014 – Accepted: 9 October 2014 – Published: 6 November 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Fluxes of carbon and nutrients to the upper 100 m of the Iceland Sea are evaluated. The study utilises hydro-chemical data from the Iceland Sea time-series station (68.00° N, 12.67° W), for the years between 1993 and 2006. By comparing data of dissolved inorganic carbon (DIC) and nutrients in the surface layer (upper 100 m), and a sub-surface layer (100–200 m), we calculate monthly deficits in the surface, and use these to deduce the surface layer fluxes that affect the deficits: vertical mixing, horizontal advection, air–sea exchange, and biological activity. The deficits show a clear seasonality with a minimum in winter, when the mixed layer is at the deepest, and a maximum in early autumn, when biological uptake has removed much of the nutrients. The annual vertical fluxes of DIC and nitrate amounts to  $1.7 \pm 0.3$  and  $0.23 \pm 0.07 \text{ mol m}^{-2} \text{ yr}^{-1}$ , respectively, and the annual air–sea uptake of atmospheric  $\text{CO}_2$  is  $4.4 \pm 1.1 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The biologically driven changes in DIC during the year relates to net community production (NCP), and the net annual NCP corresponds to export production, and is here calculated to  $6.1 \pm 0.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ . The typical, median C : N ratio during the period of net community uptake is 11, and thus clearly higher than Redfield, but is varying during the season.

## 1 Introduction

Increasing our knowledge of the oceanic cycles of carbon and nutrients, and how they are linked, is crucial for improving ocean biogeochemical models and, thus, producing better projections of oceanic response and feedback to a changing climate. One important question is how the ocean carbon cycle may change as a result of increasing atmospheric  $\text{CO}_2$  from fossil fuel consumption.

The biological carbon pump, i.e., the biologically driven transport of carbon from the surface waters to the deep ocean, is a pathway that can sequester atmospheric  $\text{CO}_2$  for very long time (Falkowski et al., 1998; Sabine et al., 2004). With the present increase

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in atmospheric CO<sub>2</sub> the strength of the future biological carbon pump is very uncertain, and warrants further investigation (see, e.g., Passow and Carlson, 2012). To be able to reveal changes in the oceans we need repeated measurements and long-term time-series stations are highly valuable, for example the Hawaii Ocean Time-series (HOT) and the Bermuda Atlantic Time-series Study (BATS) (e.g., Church et al., 2013). In the Nordic Seas the time-series stations in the Norwegian Sea (Ocean Weather Station Mike) and the Iceland Sea, have greatly increased our knowledge of the carbon cycle in this region (e.g., Skjelvan et al., 2008; Ólafsson et al., 2009). In this paper we focus on the Iceland Sea, which is the shallowest of the main basins in the Nordic Seas. The Iceland Sea (Fig. 1) is most often defined as the waters delimited by Greenland in the west, the Denmark Strait and the continental shelf break south of Iceland to the south, by Jan Mayen and the Jan Mayen Fracture Zone to the north and by the Jan Mayen Ridge to the east (Pálsson et al., 2012). This is a complex hydrographical area with several water masses of very different origins (Swift and Aagaard, 1981). The surface currents are characterised by southwards flowing Polar Water and by northwards flowing Atlantic water. Along the western rim, the East Greenland Current (EGC) flows southward, carrying cold, low salinity water from the Arctic Ocean, as well as Atlantic-derived waters and locally formed water from the Greenland Sea (e.g., Rudels et al., 2005; Jónsson, 2007; Jeansson et al., 2008). In the south, the North Icelandic Irminger Current transports Atlantic Water northward through the Denmark Strait and then mostly eastwards along the northern shelf of Iceland. The East Icelandic Current carries a deflected part of the EGC southeastward, bringing a mixture of Polar and Atlantic water (e.g., Astthorsson et al., 2007). Thus waters both from the north and the south affect the area, and the variability of the Iceland Sea properties is connected to the varying strengths and properties of these different currents and water masses.

The biological carbon pump in the Nordic Seas has not been studied in great detail, and we need to improve our understanding of the driving processes. Until now there are only few estimates of the primary productivity in the relatively cold and low-salinity Arctic waters that dominate the upper water column of the Iceland Sea. Production

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estimates in this Arctic domain are in the range  $\sim 75\text{--}100\text{ gC m}^{-2}\text{ yr}^{-1}$ , based on data between 1958 and 1982 (Thordardottir, 1984; see Fig. 6 in Astthorsson et al., 2007) and  $179 \pm 36\text{ gC m}^{-2}\text{ yr}^{-1}$ , based on remote sensing (Zhai et al., 2012).

There are several production terms used in the literature, illustrating somewhat different fluxes. *New production*, as defined by Dugdale and Goering (1967), is the production that results from allochthonous (new) nitrate added to the surface layer by vertical or horizontal advection, or via air–sea exchange. This is different from *total production*, which also includes nitrogen regenerated within the surface layer. *Net community production* (NCP) is defined as net primary production minus community respiration (e.g., Platt et al., 1989). Estimates of NCP have traditionally been based on bottle  $\text{O}_2$  incubations (Gaarder and Gran, 1927), but are often based on oxygen budgets (e.g., Falck and Gade, 1999) or seasonal mixed-layer changes in oxygen or inorganic carbon, corrected for the air–sea fluxes (e.g., Körtzinger et al., 2008; Frigstad et al., 2014b), or  $\text{O}_2/\text{Ar}$  ratios (e.g., Reuer et al., 2007; Quay et al., 2012). *Export production* is the excess organic matter produced in the euphotic zone, on top of the production needed to sustain the productive system (Dugdale and Goering, 1967; Eppley and Peterson, 1979). Thus the export production cannot exceed the rate of added nutrients (i.e. new production), and these fluxes have been assumed to be equivalent on an annual average (Eppley and Peterson, 1979).

An issue under debate during the last decades, is the universal validity of the so-called Redfield ratio, describing the stoichiometry between carbon and nutrients in marine plankton, where the average C : N : P ratios are 106 : 16 : 1 (Redfield et al., 1963). Observations of deviations from this relationship are numerous (e.g., Takahashi et al., 1993; Anderson and Sarmiento, 1994; Daly et al., 1999; Körtzinger et al., 2001; Koeve, 2006; Tamelander et al., 2013; Frigstad et al., 2014a). It is common practise to use the traditional Redfield ratio to convert changes of nutrients into production of organic matter, both in observational and model studies, so any significant variability or deviations of these ratios could have a marked impact on estimated primary production.

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In this study we will use observational data of inorganic nutrients (nitrate, phosphate, and silicate) and inorganic carbon (total dissolved inorganic carbon (DIC) and  $p\text{CO}_2$ ) from the upper layers of the Iceland Sea to evaluate annual fluxes of carbon and nutrients into the surface layer, which we here define as the upper 100 m of the water column. From these fluxes we will estimate the long-term mean in primary production in the Iceland Sea, and the related stoichiometric relationships.

## 2 Data

The study utilises data from the Iceland Sea time series station, located at 68.00° N, 12.67° W (Fig. 1). Surface sampling of DIC and  $p\text{CO}_2$  started in 1983, and water column sampling for DIC and  $p\text{CO}_2$  started in 1991 and 1993, respectively (Ólafsson et al., 2010). Here we include data until 2006, and the data are available via the CARINA database (<http://cdiac.ornl.gov/oceans/CARINA/>).

Monthly long-term surface wind speed data are from the NCEP/NCAR reanalysis project (Kalnay et al., 1996), provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their web site at <http://www.esrl.noaa.gov/psd/>.

For the atmospheric  $\text{CO}_2$  near Iceland we use Globalview data from Vestmannaeyjar, south of Iceland, ICE\_01DO (GLOBALVIEW-CO2, 2011), and the barometric pressure are monthly means of sea level pressure (SLP) obtained from NOAA Fisheries Service, Environmental Research Division (<http://www.pfeg.noaa.gov/products/las.html>).

## 3 Methods

This study is based on the climatology (long-term means) of the hydrographical and chemical properties observed in the Iceland Sea. We calculated long-term monthly mean profiles by averaging all data for every month, for the chosen depths – every 10 m in the upper 300 m, every 50 m between 300 and 500 m, and then every 100 m

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from 500 down to the bottom (1900 m) – and further interpolated to the chosen depth intervals, using piecewise cubic Hermite interpolation.

The sampling frequency for the different months during the course of the time series sampling is shown in Table 1. Four months (January, April, July, and December) have been sampled less than three times, and for these months we choose to use calculated means based on the neighbour months.

The wintertime mixed layer in the Iceland Sea typically reaches down to 200 m at the end of the winter mixing (Ólafsson, 2003), which is supported by our calculated mean mixed layer depth (MLD) (Fig. 2). We tested several criteria for the MLD, based on either a difference in temperature ( $\Delta T = 0.2^\circ\text{C}$ ), or density ( $\Delta\sigma_\theta = 0.01, 0.03, 0.05,$  and  $0.125\text{ kg m}^{-3}$ ), all referenced to a near-surface value at 10 m (see, e.g., de Boyer Montégut et al., 2004), and choose the density difference criteria  $\Delta\sigma_\theta = 0.05\text{ kg m}^{-3}$ , agreeing with estimates of Ólafsson (2003) and Zhai et al. (2012). However, the seasonal drawdown in nutrients and DIC (see Fig. 3) is largely confined to the upper 100 m. Based on this we define the upper 100 m as the surface layer, and calculate the climatological fluxes in and out of this layer. The approach is described in detail below.

### 3.1 Calculation of deficits

We apply a box-model approach, which was developed for idealised annual plankton cycles (Evans and Parslow, 1985), and has been applied in, e.g., the Greenland and the Norwegian Seas (Anderson et al., 2000; Skjelvan et al., 2001; Falck and Anderson, 2005). Here we compute deficits (DEF) of nutrients and DIC in the surface layer relative to a defined sub-surface layer:

$$\text{DEF}_X = \int_{100}^0 ([X]_{\text{SSL}} - [X]_{\text{SL}}) dz \quad (1)$$

where  $X$  is the concentration of the constituent of interest (here nutrients and DIC), SSL is the sub-surface layer, and SL is the surface layer. Thus the deficit increases when

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there is a decrease in carbon or nutrients in the surface layer. While the surface layer is chosen to be the upper 100 m, the sub-surface layer is defined as the layer between 100 and 200 m, for which annual mean concentrations are calculated and applied in Eq. (1). Applying this on the monthly mean profiles, the deficits are calculated for every 10 m interval in the upper 100 m, relative to the mean concentration in the sub-surface layer, multiplied with 10, and summed up for each month (Anderson et al., 2000). As seen in Fig. 3 there is gradient in concentrations between the surface and sub-surface layer, for all months, resulting in a rather clear deficit also during periods of deepest mixing. This will have an effect on calculated vertical fluxes (see next section), but since we focus on the changes within the upper 100 m, we choose to subtract the minimum monthly deficit (i.e. the value for the month with the lowest deficit) from the calculated values all other months, for each constituent respectively. We thus get a “zero” deficit when it was at a minimum, and then compare all other months with that.

### 3.2 Flux calculations

The change in the deficit ( $\Delta DEF^X$ ) of constituent  $X$  are explained by the sum of the fluxes into and out of the surface layer; the vertical exchange with the deeper layers ( $F_{vert}$ ), the horizontal fluxes ( $F_{hor}$ ), the biological production ( $F_{bio}$ ), and the air–sea exchange ( $F_{atm}$ ):

$$\Delta DEF^X = F_{vert}^X + F_{hor}^X + F_{bio}^X + F_{atm}^X \quad (2)$$

Positive fluxes indicate a transport out of the surface layer. Regarding the time-series station as a very thin section the horizontal fluxes will balance, and  $F_{hor}$  could then be set to zero. We also assume no atmospheric input of nutrients, and thus  $F_{atm}$  is only of importance for the calculations of the DIC fluxes. The uncertainty in the different fluxes is estimated from error propagation of the SDs of the different terms in the flux calculations.

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The vertical flux to the surface layer can be calculated from Eq. (3) (Anderson et al., 2000; Skjelvan et al., 2001; Falck and Anderson, 2005):

$$F_{\text{vert}}^X = \frac{v_{\text{mix}}}{H} \text{DEF}^X \quad (3)$$

where  $v_{\text{mix}}$  is the vertical entrainment velocity, and  $H$  is the thickness of the surface layer. We estimate  $v_{\text{mix}}$  through changes in the calculated mixed layer depth (following, e.g., Skjelvan et al., 2001), and apply this for the periods with a deepening of the mixed layer, which is the period from September to March seen from the development of the MLD (Fig. 2). During the period from April to August there is a decrease in the MLD, and for this period we apply a background mixing through the base of the mixed layer of  $0.1 \text{ m d}^{-1}$  (Anderson et al., 2000; Skjelvan et al., 2001), which corresponds to a shallowing of  $3.0 \text{ m month}^{-1}$ . The applied entrainment velocities are shown in Table 1. We here define  $v_{\text{mix}}$  as negative to get a negative flux when directed into the surface layer.

The flux due to biological activity is given by Eq. (4):

$$F_{\text{bio}}^X = \Delta \text{DEF}^X - F_{\text{vert}}^X - F_{\text{atm}}^X \quad (4)$$

For the nutrients we assume a negligible atmospheric source, but when calculating the biological production from DIC,  $F_{\text{bio}}$  needs to be corrected for the air–sea flux (see below). The resulting fluxes are positive as long as the production is greater than the decay of organic matter, as is the case when there is a net biological uptake, removing DIC and nutrients from the surface layer.

The air–sea flux of carbon can be calculated from the difference in partial pressure of  $\text{CO}_2$  between seawater and air, the gas transfer velocity  $k$ , and the solubility of  $\text{CO}_2$  in seawater,  $K_0$ :

$$F_{\text{atm}} = kK_0 \Delta p\text{CO}_2 \quad (5)$$

where

$$\Delta p\text{CO}_2 = p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}} \quad (6)$$

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The solubility of CO<sub>2</sub> in the Iceland Sea surface water was calculated after Weiss (1974), using long-term monthly mean values of salinity and temperature in the upper 30 m. For the dependence of wind speed on the transfer velocity  $k$  we used the parameterisation of Sweeney et al. (2007) after Wanninkhof (1992):

$$k = 0.27u^2 \sqrt{\frac{660}{Sc}} \quad (7)$$

where  $u$  is the long-term surface wind speed (ms<sup>-1</sup>), and  $Sc$  is the Schmidt number. The transfer coefficient was then converted to mmonth<sup>-1</sup> by multiplying with (365.25/12) × (24/100).

To calculate the partial pressure of the atmosphere from the molar fractions obtained from GLOBALVIEW we used the formulation:

$$pCO_{2,atm} = XCO_2(P_b - P_w) \quad (8)$$

where  $P_b$  is the barometric pressure (in atmospheres), and  $P_w$  is the water vapour pressure calculated from temperature and salinity in the sea surface layer, according to Cooper et al. (1998). The partial CO<sub>2</sub> pressure in the sea surface is calculated from the long-term mean of the  $pCO_2$  data in the Iceland Sea time series, using the upper 30 m.

## 4 Results

The deficits of nutrients and DIC in the upper 100 m decrease from January to March (Fig. 4), as a result of the deepened mixed layer depth (Fig. 2). The increase in the deficits after March, related to biological production, continues until a maximum in September, after which the deficits decrease again. For silicate this is slightly different, with a minimum in February and a maximum in September, but then also a small deficit peak in May. The small decrease in deficit in silicate from May to June coincides

with a reduced rate of the deficit increase in phosphate and DIC. There is a significant uptake of nutrients from winter to late summer (Fig. 3), but the system, on average, never gets fully depleted. The calculated fluxes deduced from change in the deficits, related to vertical mixing, air–sea exchange, and biological production, are presented in the following and summarised in Table 2 and Fig. 5.

#### 4.1 Vertical fluxes

The calculated vertical fluxes add carbon and nutrients to the mixed layer all year around, even though the fluxes during the period of decreased, or shallow, MLD are small. The annual vertical fluxes of DIC and nutrients to the mixed layer was estimated to be  $1.7 \pm 0.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$ ,  $0.23 \pm 0.07 \text{ mol N m}^{-2} \text{ yr}^{-1}$ ,  $0.019 \pm 0.004 \text{ mol P m}^{-2} \text{ yr}^{-1}$ , and  $0.12 \pm 0.04 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ , for DIC, nitrate, phosphate, and silicate, respectively. The flux of DIC equals  $\sim 20 \text{ g C m}^{-2} \text{ yr}^{-1}$ , where the presented uncertainties are calculated from error propagation of the terms in Eq. (3). (See details in Sect. 6.2.)

#### 4.2 Air–sea flux of CO<sub>2</sub>

The air–sea flux is directed into the surface layer all year around, as the region is permanently undersaturated with respect to atmospheric CO<sub>2</sub> (Fig. 5). The calculated annual flux was  $4.4 \pm 1.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ , which is consistent with the estimate of Ólafsson et al. (2009) of  $4.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ . When converted, the calculated flux into the Iceland Sea is  $53 \text{ g C m}^{-2} \text{ yr}^{-1}$ .

#### 4.3 Biological production

The biologically related fluxes of carbon and nutrients all show a two-peak seasonality, with the first maximum in April–May, and a second, larger peak in September. The nutrients also show a negative flux in October, when there is still a net uptake of carbon.

The change in the deficit ( $\Delta\text{DEF}$ ) equals zero over the course of the year, and thus there is a balance between the calculated fluxes (Eq. 2). For the nutrients, with the

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assumption of negligible horizontal and air–sea fluxes, there is thus a balance between the net vertical fluxes and the net biological fluxes, and the latter amounts to  $0.23 \pm 0.18 \text{ mol N m}^{-2} \text{ yr}^{-1}$ ,  $0.019 \pm 0.011 \text{ mol P m}^{-2} \text{ yr}^{-1}$ , and  $0.12 \pm 0.14 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ , respectively (Table 2). Following the definition of new production (Dugdale and Goering, 1967), and our assumptions of negligible horizontal and air–sea flux of nitrate, the addition of nitrate from vertical mixing must equal new production. In the Iceland Sea this amounts to  $0.23 \pm 0.07 \text{ mol N m}^{-2} \text{ yr}^{-1}$ .

The biologically driven change in DIC, corrected for vertical flux and air–sea exchange, corresponds to NCP, with positive numbers illustrating net autotrophy, and negative values net heterotrophy. There is a very small or negative NCP in the first part of the year, but from March to October there is a net autotrophic production (Fig. 5). There is also a small positive NCP in December, but this could be due to the fact that we based the fluxes in December and January on deficits calculated for the months close in time, due to few data. This will not be discussed further.

The net annual NCP corresponds to the export production, when assuming steady state. In the Iceland Sea this sums up to  $6.1 \pm 0.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ , or  $73 \pm 11 \text{ g C m}^{-2} \text{ yr}^{-1}$ .

The seasonal drawdown of nitrate, corresponding to the period of net community uptake (i.e. increasing deficit; April to September; see Fig. 4), relates to the total production. This period shows positive biological fluxes, and the sum of these amounts to  $0.53 \pm 0.12 \text{ mol N m}^{-2} \text{ yr}^{-1}$ . The difference between the new and total production ( $0.30 \pm 0.14 \text{ mol N m}^{-2} \text{ yr}^{-1}$ ) gives the regenerated production, which represents 57 % of the total production. Thus we get an  $f$  ratio (i.e. the ratio between new and total production) of 0.43 in the Arctic domain of the Iceland Sea. Performing the same calculations for phosphate and silicate give a total production of  $0.036 \pm 0.013 \text{ mol P m}^{-2} \text{ yr}^{-1}$  and  $0.30 \pm 0.16 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ . The regenerated production amounts to approximately 47 and 60 %, respectively. The net uptake of silicate does, however, start one month earlier than for the other nutrients, but do also show a negative flux in June, when there is a net uptake of nitrate and phosphate (Fig. 5).

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## 4.4 Stoichiometry of the calculated fluxes

An evaluation of the stoichiometric relationships between carbon and nutrients show varying values during the year, as well as for the different fluxes (Table 3). Focusing on the carbon-to-nitrate ratio, and starting with the calculated monthly deficits, there is a rather high agreement in the seasonality between DIC and nitrate, and during the first part of the seasonal drawdown (April–May) the ratio of the deficits is close to 6.4, however, during the summer and autumn the ratio is either lower (June to August; 5.3–6.1) or higher (September to December; 7.1–8.6) (Fig. 6).

Evaluating the stoichiometry for the biological production is not straightforward since the flux of carbon and nitrate do not show the same direction for all months; as mentioned earlier there is a net biological production based on DIC from March to September, while the net biological production based on nitrate starts one month later (see Fig. 5). The change in deficits of DIC and nitrate (Fig. 4), however, both show a net uptake from April to September, so we will use this period to evaluate the biologically related stoichiometry. The C : N ratios of the monthly biological production (Fig. 7), during the period of seasonal drawdown of DIC and nitrate, differ between the early and the late part of the season, with C : N ratios of  $\sim 10$  in April and May, and  $\sim 12$  between July and September, while the value in July is below 6.

## 5 Discussion

### 5.1 Primary production in the central Iceland Sea

The main aim of this study is to investigate primary production and related stoichiometry in the central Iceland Sea. This domain is dominated by Arctic waters, and is the least productive of the waters around Iceland (e.g., Gudmundsson, 1998; Assthorsson et al., 2007), but could be representative of the whole Arctic domain in the Nordic Seas, with similar hydro-chemical properties.

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How realistic is our estimated annual net production (NCP) of  $73 \pm 36 \text{ g C m}^{-2} \text{ yr}^{-1}$  in the Iceland Sea? Gudfinnsson (2012) found, from his data of daily productivity, an average annual phytoplankton productivity of  $65 \text{ g C m}^{-2} \text{ yr}^{-1}$ , and Thordardottir (1984) presented an average annual primary production (1958–1982) in the Arctic domain, in the vicinity of the time series station, of  $75 \text{ g C m}^{-2} \text{ yr}^{-1}$ , based on measured  $^{14}\text{C}$  uptake at light saturation. A modelling study (Skogen et al., 2007) suggests a mean annual production in the Iceland Sea at  $70 \text{ g C m}^{-2} \text{ yr}^{-1}$ , with an  $f$  ratio of  $\sim 0.7$ . These estimates show a large agreement with the estimates in our study, giving more trust in our results, and the approach. The amount of new production differs clearly though, and it is possible that some of our assumptions underestimate this term. The uncertainty in the vertical flux is discussed more in Sect. 6.2.

From remote sensing data Zhai et al. (2012) gave a production estimate in the Arctic domain of  $179 \pm 36 \text{ g C m}^{-2} \text{ yr}^{-1}$ . This is more than twice as high as the estimates based on in situ data. This has also been seen in other comparisons between production estimates based on in situ and remote sensing data (see, e.g., Richardson et al., 2005; Körtzinger et al., 2008; Frigstad et al., 2014b).

The negative nutrient flux in October, when there is still a net uptake of carbon (Fig. 5), is similar to what have been observed in the Norwegian Sea (Falck and Anderson, 2005), which were explained largely by a build-up of dissolved organic matter (DOM), which is relatively low in nutrients. We will discuss this further below, in relation to the stoichiometry of the production.

## 5.2 Variable stoichiometry

The evaluation of the C:N ratios during seasonal drawdown (April to September) of DIC and nitrate (Fig. 7) showed a clear deviation from the Redfield C:N ratio of 6.6, except in June, when the production was lower. The consumption of carbon relative nitrate in excess of Redfield, a phenomena termed “carbon overconsumption” (Toggweiler, 1993), was higher during the late summer production (C:N ratio  $\sim 12$ ) com-

pared to the early production peak (C : N ratio  $\sim 10$ ). Similar increases in carbon over-consumption during the later part of the productive season have been described in several studies from different ocean regions, and have been explained by the build up of low-N DOM (e.g., Toggweiler, 1993; Williams, 1995; Kähler and Koeve, 2001; Körtzinger et al., 2001). Without any data of DOM in the central Iceland Sea we cannot find direct evidence supporting this mechanism in our study, but the similarity to the Atlantic-dominated Norwegian Sea (Falck and Anderson, 2005) suggest that this may be a general feature also in the Nordic Seas. This should be evaluated further in the future. Nonetheless, different mechanisms seem to affect the flux of carbon and nitrogen during the season, as shown for different regions (e.g., Banse, 1994; Kähler and Koeve, 2001; Frigstad et al., 2011).

As mentioned previously the different length of the season with a net nitrate-based production, and a net carbon-based production, makes it difficult to do a direct comparison between the estimates of new production and NCP. However, this illustrates the problem in converting new production into NCP, or export production, using the Redfield ratio. As discussed by Laws (1991) these terms may not be related, and would assume that nitrate and carbon are assimilated by autotrophs during new production, in the same ratio as carbon and nitrate are recycled by heterotrophs. If we, despite the mentioned problem, compare the total new production and NCP during the year, from the values in Table 2, we get a net C : N ratio of  $\sim 26.5$ . Thus, if we would convert the computed new production into export production, using the ratios of Redfield (6.6), or Takahashi et al. (7.3), we would underestimate the export production by more than 70 %, assuming our estimated export production is reasonable. This confirms the findings of, for example, Sambrotto et al. (1993), who found that the actual carbon production exceeds any estimate based on nitrogen consumption, converted by the Redfield C : N ratio, by 36–81 %. Furthermore, the C : N ratio have been observed to differ both between seasons (e.g., Körtzinger et al., 2001; Frigstad et al., 2011) and between regions (e.g., Koeve, 2006; Tamelander et al., 2013; Frigstad et al., 2014a), with values as high as  $\sim 15$ .

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The C : N ratio for the annual vertical fluxes (7.4) is also higher than Redfield, but agrees well with the estimated stoichiometry in the region by Takahashi et al. (1993). However, this value represent the relationship between measured properties in the surface waters over the year, which includes the net effect of air–sea exchange, biological activities, and mixing. Due to this Banse (1994) cautioned against using observed in-situ DIC : nitrate relationships to make statements about elemental ratios during biological production, and respiration, and recommended smaller closed, controllable systems to find mechanistic explanation to uptake ratios in upper layers.

### 5.3 Comparison to production estimates for other parts of the Nordic Seas

How representative of the Nordic Seas are our estimated production terms in the Iceland Sea? The average NCP in the Nordic Seas, based on an oxygen budget, have been estimated to  $\sim 36 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Falck and Gade, 1999). This is roughly half of the annual NCP we find in the central Iceland Sea. However, to evaluate regional differences we compare with estimates for the different basins in the area.

For the Greenland Sea, Richardson et al. (2005) estimated the annual primary production to 81 or  $70 \text{ g C m}^{-2} \text{ yr}^{-1}$  if excluding observations within the ice or at the ice edge. Anderson et al. (2000) estimated the annual new production, in the upper 150 m, of  $34 \text{ g C m}^{-2} \text{ yr}^{-1}$ , based on a box model similar to ours, and nitrate data (using a C : N ratio of 7.5). With an  $f$  ratio of 0.56 (Smith, 1993) this corresponds to a total production of  $61 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Richardson et al., 2005). The likely range of annual primary production in the Greenland Sea is in the range  $60\text{--}100 \text{ m}^{-2} \text{ yr}^{-1}$  (Richardson et al., 2005), which is in agreement with the range of estimates for the Iceland Sea.

In the Norwegian Sea the primary production has been estimated to  $80 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Rey, 2004) and that the new production is 60 % of that. It has also been pointed out that where zooplankton grazing is high as in the Norwegian Sea new production may be underestimated (Bathmann et al., 1990) and could be as high as 80 %. Results from a modelling study (Skogen et al., 2007) suggests a mean annual production in the Norwegian Sea at  $65 \text{ g C m}^{-2} \text{ yr}^{-1}$ , with an  $f$  ratio of  $\sim 0.75$ .

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Falck and Anderson (2005) used a box model approach similar to the present study, and for the Norwegian Sea, they assumed the export production to correspond to the vertical flux of nutrients to the surface layer (upper 100 m), which equalled  $0.23 \text{ Nm}^{-2} \text{ yr}^{-1}$ , or  $18 \text{ gCm}^{-2} \text{ yr}^{-1}$ ; when using the traditional Redfield C : N ratio (6.6).

5 Their new production estimate amounted to  $0.51 \text{ molNm}^{-2} \text{ yr}^{-1}$ , or  $41 \text{ gCm}^{-2} \text{ yr}^{-1}$ , using the same ratio. If equalling their vertical flux of nitrate with new production, and their total production with the sum of all positive biological fluxes during the year, we get an  $f$  ratio of 0.43 (the same as in the Iceland Sea). This is clearly lower than the earlier estimates mentioned above (Rey, 2004; Skogen et al., 2007).

10 Earlier estimates of new production in the Norwegian Sea ( $70^\circ \text{ N}$ ,  $0^\circ \text{ E}$ ) are in the range  $21\text{--}29 \text{ gCm}^{-2} \text{ yr}^{-1}$  (Bodungen et al., 1995). These values agree with estimates of NCP, based on oxygen fluxes in the Norwegian Sea, of  $\sim 24\text{--}32 \text{ gCm}^{-2} \text{ yr}^{-1}$  (Skjelvan et al., 2001). The new production estimate is in reasonable agreement with what we estimate for the Iceland Sea, but it is clear that previous NCP estimates based on oxygen budgets are significantly lower than what we get in the Iceland Sea. This could partly be due to the oxygen-to-carbon conversion applied, mostly based on the traditional Redfield ratio, but the only way to unravel real or artificial differences is to analyse the whole region with the same method. This should be pursued in the near future to investigate regional differences, but also to evaluate trends and changes in the system.

20 Nevertheless, the range of methods and approaches, both based on observations and models, and different assumptions, including ours, still seems to reach some consensus of annual primary production in the Nordic Seas of  $\sim 60\text{--}100 \text{ gCm}^{-2} \text{ yr}^{-1}$ . More work is needed to evaluate regional similarities and differences in stoichiometry and any temporal trends in primary production. Related to the last point is to understand the drivers of the variability in biological production, both natural and anthropogenic, and how the increasing levels of atmospheric  $\text{CO}_2$  will affect the biological carbon pump.

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## 6 Uncertainties

One obvious source of error is the fact that our approach only makes long-term averages for all months, so any trends in the observed properties will cause some uncertainty in the resulting values. With this mentioned we proceed to evaluate the uncertainty of the approach and the individual fluxes.

### 6.1 Deficit calculations

The uncertainties in the deficit calculations are related to the interannual variability in the observed concentrations in the surface layer and in the sub-surface reference concentrations, and the uncertainties arising from the averaging procedures of the monthly profiles. The uncertainty from using one single reference concentration for each constituent for the whole year is less than 8 % for any of the constituents (seen from the SD of the annual mean values), highest for silicate, so this error is negligible compared to the uncertainty in the different fluxes. The uncertainty in the monthly surface layer concentrations (seen from the average monthly SD) is, again, largest for silicate (values up to 40–50 %), but for nitrate and phosphate there is a maximum in late summer/early autumn, when the concentrations are at the lowest, of ~ 20–30 %. Due to the high concentrations of DIC the uncertainty in these numbers are insignificant. If we propagate the uncertainties in the surface concentrations and the reference concentrations and use this as the overall uncertainty in the monthly deficits we get the values depicted in Fig. 4, which are quite substantial for some of the months, with a relative error of up to 100 % at or just after the early peak in production, but lower (~ 20–60 %) during the later part of the year. The uncertainty in the values from the first part of the year, during the period of deepened mixed layer, is rather low in absolute sense, compared to later in the year, but due to the low deficits in this period the relative errors gets very large (see Fig. 4).

There is a potential error in assessing the production, and related terms, in the upper 100 m, when the MLD apparently reaches much deeper in winter. However, the verti-

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cal distribution of nutrients and DIC do show a homogeneous upper 100 m in winter, followed by a gradient, with some bends, down to stable concentration at depths below ~ 300 m. Profiles of salinity show the same feature, and thus different water masses are present. Deficits were also calculated for the upper 200 m (referenced to the mean between 100 and 200 m), and the upper 300 m (referenced to the mean between 300 and 400 m), but the resulting deficits were either largely unchanged, or smaller than for the upper 100 m. Since we here mainly want to evaluate the fluxes of importance for the production, and these seems to be confined to the upper 100 m, we expect this error to be minor compared to the uncertainty in the different fluxes.

## 6.2 Vertical flux

The uncertainty in the vertical fluxes could be significant. With the assumption that the air–sea fluxes, as well as the horizontal fluxes of nutrients could be neglected, the increase in nutrient concentration during periods of deepened mixed layer depths should equal the vertical fluxes. Since we estimate the vertical entrainment velocity from the observed changes in MLD, there is both an uncertainty related to the chosen method to calculate MLD, and the variability in the monthly MLD during the time series. The variability-driven uncertainty in the mean monthly MLD is on average ~ 30 % (Fig. 2). For nitrate this agrees with our calculated total uncertainty from error propagation, while the calculated uncertainty in the vertical flux of DIC and phosphate is ~ 20 %, and 37 % for silicate (see Table 2).

## 6.3 Air–sea exchange

From the propagation of the errors due to spread in the mean values of the  $p\text{CO}_2$  values for atmosphere and sea surface, and putting this error estimate in the flux calculation for each month, we get an annual uncertainty of  $1.1 \text{ mol m}^{-2}$ , which is 25 % of the estimated annual flux. This agrees with previous findings from the North Atlantic and

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the Nordic Seas (Körtzinger et al., 2001; Olsen et al., 2003). Körtzinger et al. (2008) have estimated a maximum error in calculated CO<sub>2</sub> fluxes of 40 %.

## 6.4 Biological production

Since the biological production is calculated as the residual of all other terms (Eq. 4) it also carries the uncertainty of each of these terms. Some of the uncertainty could be connected to interannual variability in the timing of the peak in the productive events, something that should be evaluated further in later studies. To estimate the uncertainty in the  $\Delta DEF$  term we use the relative error in the calculated deficits, and multiply these with the  $\Delta DEF$  values for each month, for each constituent. The relative error in the deficit for the months with “zero” (after our baseline subtraction; March for all species, except silicate, that has February) or very low deficits (in February for N and C) are either useless (infinite for zero deficit) or unrealistically large. For these months we instead use the uncertainty in MLD as the minimum error. For February this is  $\sim 50\%$ , and for March  $\sim 30\%$ . As seen in Table 2 the total estimated error in the biologically related fluxes are quite substantial for the nutrients, but only about 15 % for carbon.

## 7 Conclusions

The computed monthly fluxes of dissolved inorganic carbon, nitrate, phosphate and silicate in the Iceland Sea show similarities in the seasonality, but also a decoupling during the year, illustrating different mechanisms effecting the uptake and remineralisation of the different constituents. We estimate an Iceland Sea new production of  $0.23 \pm 0.07 \text{ mol N m}^{-2} \text{ yr}^{-1}$ , based on nitrate added to the surface layer via vertical mixing, and an annual net community production (NCP) of  $6.1 \pm 0.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$  (or  $73 \pm 11 \text{ g C m}^{-2} \text{ yr}^{-1}$ ). The presented NCP shows a high agreement with earlier estimates of primary production in the Iceland Sea, and to other parts of the Nordic Seas. The estimated C:N ratios during net biological uptake are in the range 10–12, and

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thus indicate that a conversion of the nitrate-based new production to carbon using traditional Redfield C : N would markedly underestimate the primary production in the Iceland Sea.

*Acknowledgements.* This research was supported from the European Union FP7 projects GreenSeas (265294), EURO-BASIN (264933), and, CarboChange (264879). Siv Lauvset is acknowledged for valuable help with netctd files.

This is publication AXXX from the Bjerknes Centre for Climate Research.

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**Table 1.** Monthly computed MLD (median values) and entrainment velocities ( $v_{\text{mix}}$ ). These are used when calculating the vertical fluxes. The values in bold are calculated from surrounding monthly data. See text for details.

Month	MLD Median (m)	$v_{\text{mix}}^{\text{a}}$ ( $\text{m month}^{-1}$ )	Number of sampled months <sup>b</sup>
1	<b>118</b>	<b>-29</b>	2
2	147	-29	16
3	168	-21	3
4	<b>116</b>	-3	1
5	65	-3	14
6	30	-3	8
7	<b>25</b>	-3	1
8	21	-3	16
9	32	-11	4
10	37	-5	4
11	59	-22	14
12	<b>89</b>	<b>-30</b>	2

<sup>a</sup>  $v_{\text{mix}}$  is defined as negative to get the resulting flux into the surface layer negative.

<sup>b</sup> This is the number of sampled months in the data set. For months sampled less than three times, averaged numbers have been used.

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**Table 2.** Summary of annual fluxes ( $\text{mol m}^{-2} \text{yr}^{-1}$ ) of carbon, nitrate, phosphate, and silicate to the surface layer (upper 100 m) of the Iceland Sea; vertical flux ( $F_{\text{vert}}$ ), air–sea flux ( $F_{\text{atm}}$ ), and biological production ( $F_{\text{bio}}$ ). Negative values indicate a flux into the surface layer. The horizontal fluxes are assumed to be balanced over the year, and thus set to zero.

	$F_{\text{vert}}$ ( $\text{mol m}^{-2} \text{yr}^{-1}$ )	$F_{\text{atm}}$ ( $\text{mol m}^{-2} \text{yr}^{-1}$ )	$F_{\text{bio}}$ ( $\text{mol m}^{-2} \text{yr}^{-1}$ )
Carbon	$-1.7 \pm 0.3$	$-4.4 \pm 1.1$	$6.1 \pm 0.9^{\text{a}}$
Nitrate	$-0.23 \pm 0.07$	–	$0.23 \pm 0.18^{\text{b}}$
Phosphate	$-0.019 \pm 0.004$	–	$0.019 \pm 0.011$
Silicate	$-0.12 \pm 0.04$	–	$0.12 \pm 0.14$

<sup>a</sup> Corresponds to NCP.

<sup>b</sup> Corresponds to new production.

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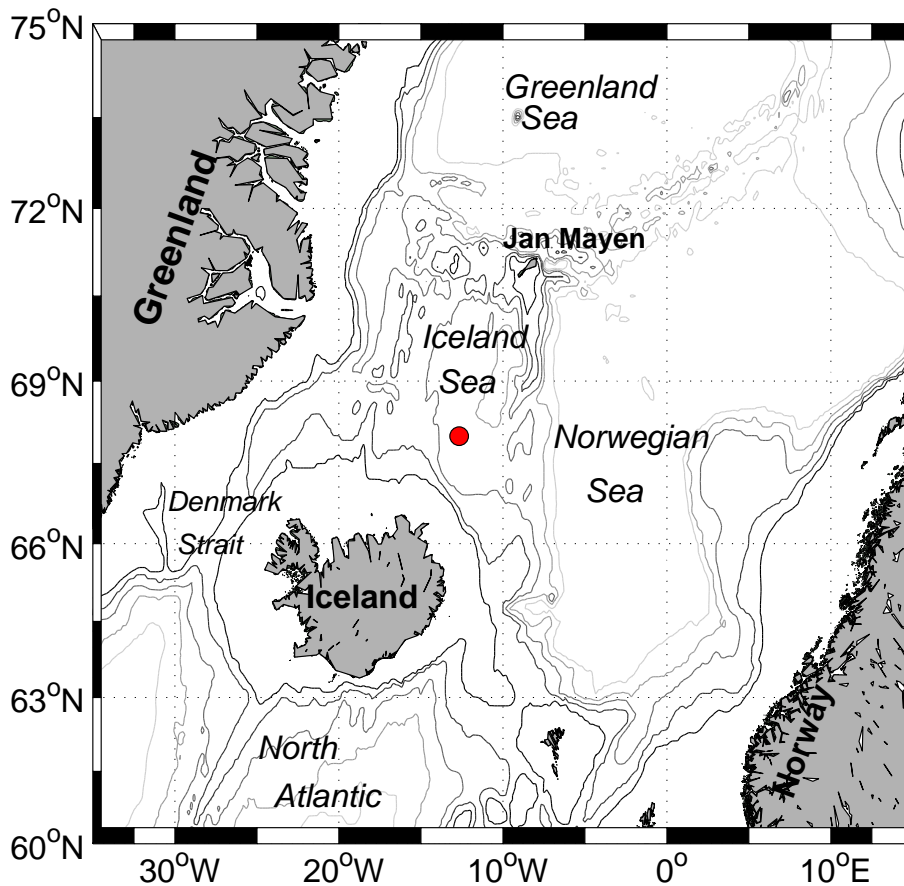


**Table 3.** Stoichiometric (median) ratios of computed monthly vertical fluxes and of biological production during the period of seasonal drawdown (net community uptake).

	Vertical flux <sup>a</sup> (all year)	Net uptake <sup>a</sup> (Apr–Sep)
N : P	14.8	14.9
C : N	6.41	11.0
C : P	98.9	154
C : Si	13.8	17.8 <sup>b</sup>
N : Si	2.02	1.49 <sup>b</sup>
Si : P	7.57	9.67 <sup>b</sup>

<sup>a</sup> We use the median of the monthly values since some months show large deviations.

<sup>b</sup> Since the biologically related flux of silicate is negative in June these numbers are only based on April–May, and July–September.



**Figure 1.** Map of the Nordic Seas region. The red filled circle marks the position of the time-series station.

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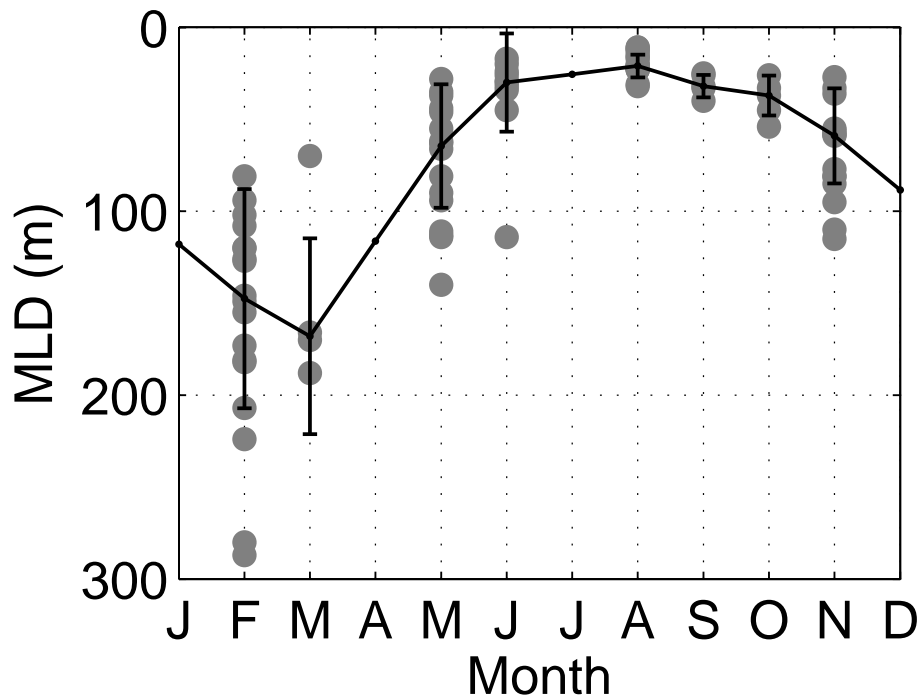
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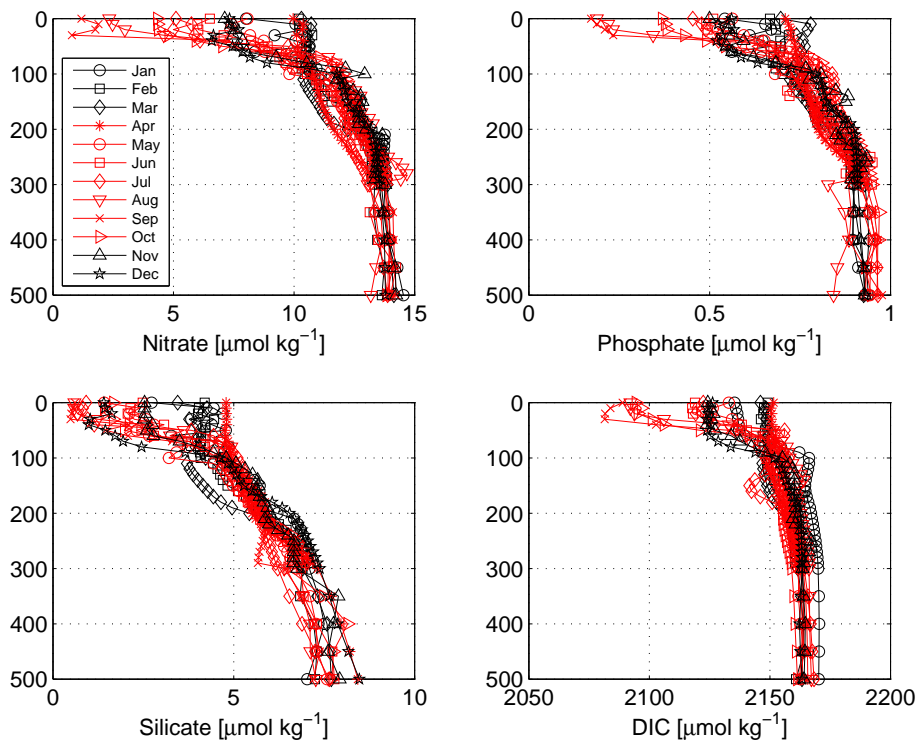


**Figure 2.** Calculated mixed layer depth (MLD) at the Iceland Sea time-series station, using the density difference criteria of  $\Delta\sigma_\theta$   $0.05\text{ kg m}^{-3}$ . The grey dots show the MLD for each year, and the line is the median of the values for each month, and the error bars show the SD. The values for the months without shown data are calculated.

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**Figure 3.** Mean monthly concentration profiles (upper 500 m) in the Iceland Sea, of nitrate (upper left), phosphate (upper right), silicate (lower left), and DIC (lower right). The black profiles indicate months with an increase in MLD and the red profiles depict months with a decreased or very shallow (< 40 m) MLD (see Fig. 2).

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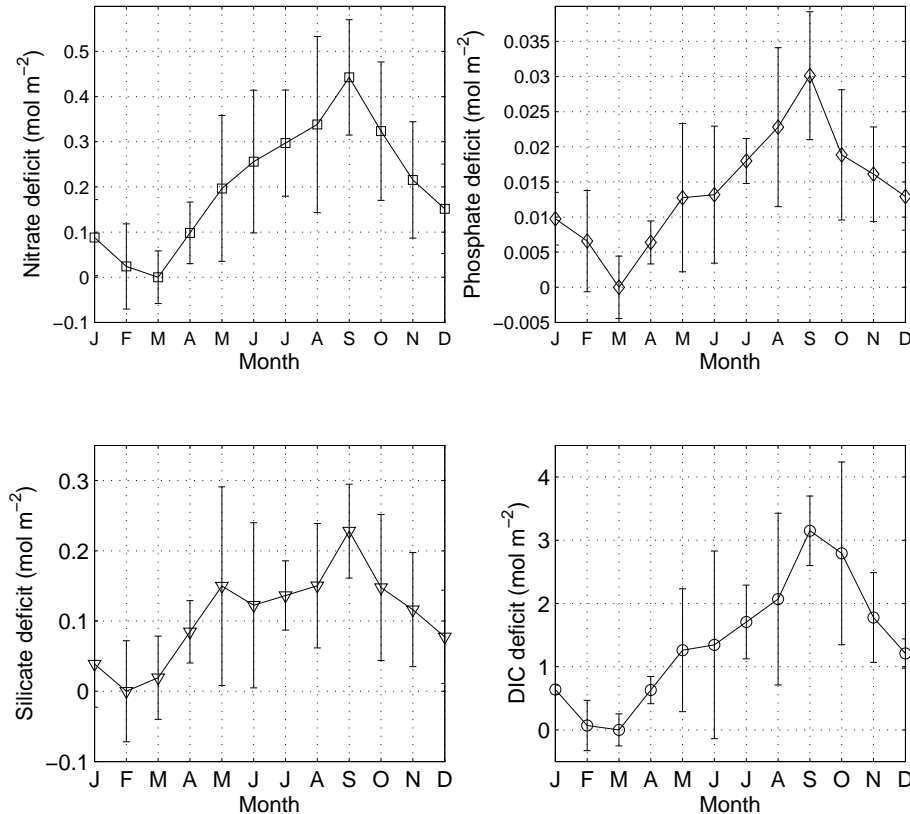
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**Figure 4.** Calculated monthly-mean deficits of nitrate, phosphate, silicate, and carbon, in the upper 100 m in the Iceland Sea. For the calculations we used mean monthly values for the 100–200 m depth range as reference. The error bars show the propagated error (uncertainty) from the SD of the respective reference concentrations and the average monthly SD in the surface layer. As for the MLD calculations, the months sampled less than three times in the time series have been calculated, based on the adjacent months. See text for details.

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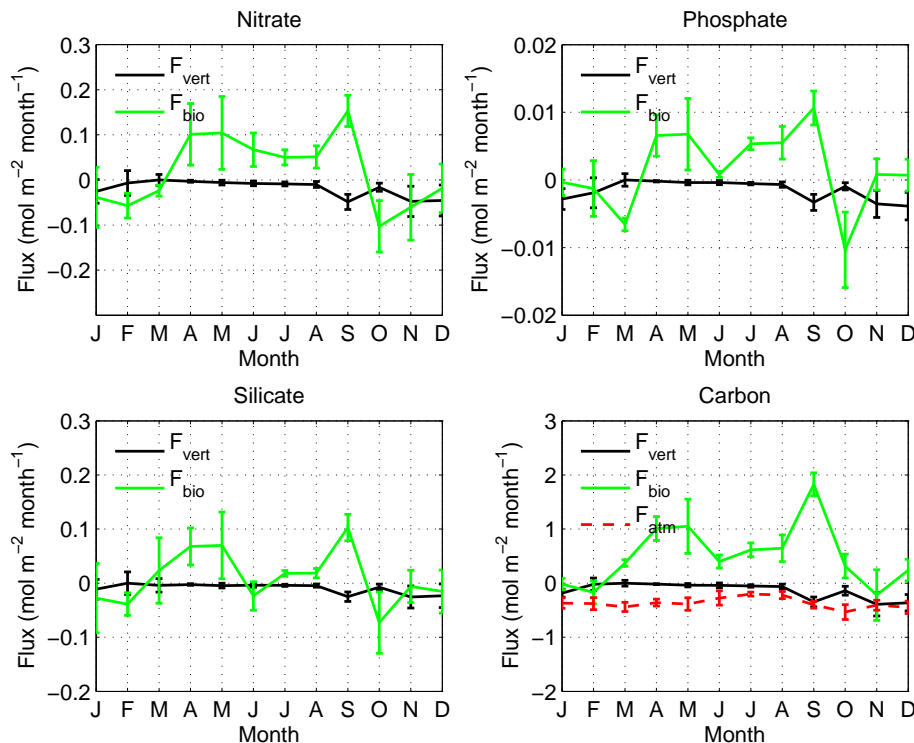
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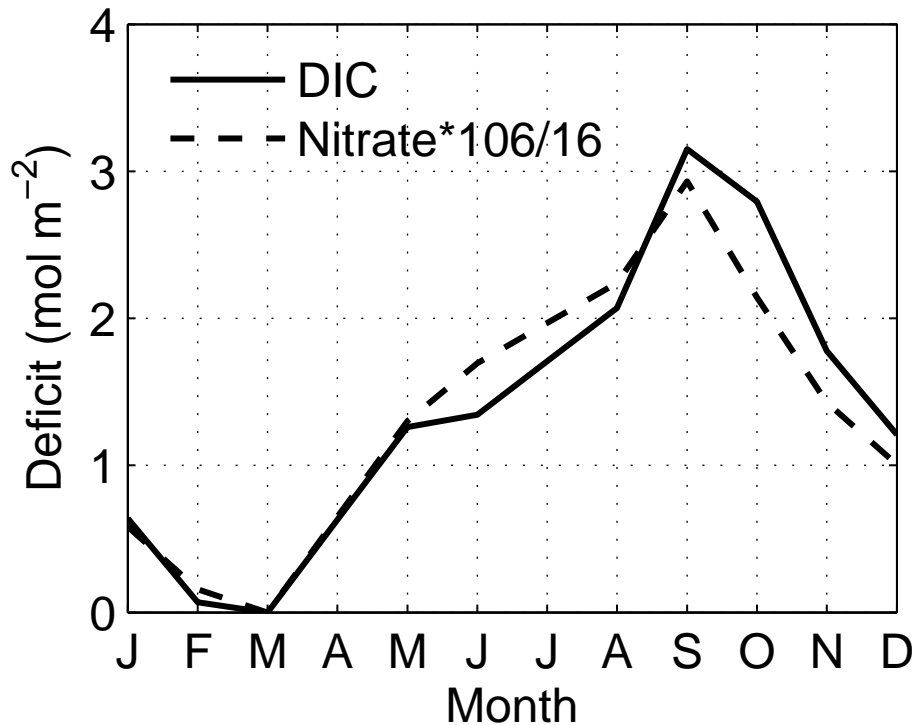


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**Figure 5.** Calculated seasonal fluxes to the upper 100 m in the Iceland Sea, for nitrate, phosphate, silicate and DIC. All fluxes are in  $\text{mol m}^{-2} \text{ month}^{-1}$ . The figures show the vertical flux ( $F_{\text{vert}}$ ; solid black line), the biological production ( $F_{\text{bio}}$ ; green solid line), and the air–sea flux of  $\text{CO}_2$  ( $F_{\text{atm}}$ ; red dashed line for carbon). The error bars show the propagated errors (see Sect. 6). Note that the scale on the y axis is different for all constituents.



**Figure 6.** Comparison of calculated monthly-mean deficits of DIC and nitrate in the upper 100 m in the Iceland Sea (see Fig. 4). The nitrate deficits are multiplied with the Redfield C : N ratio of 6.6.

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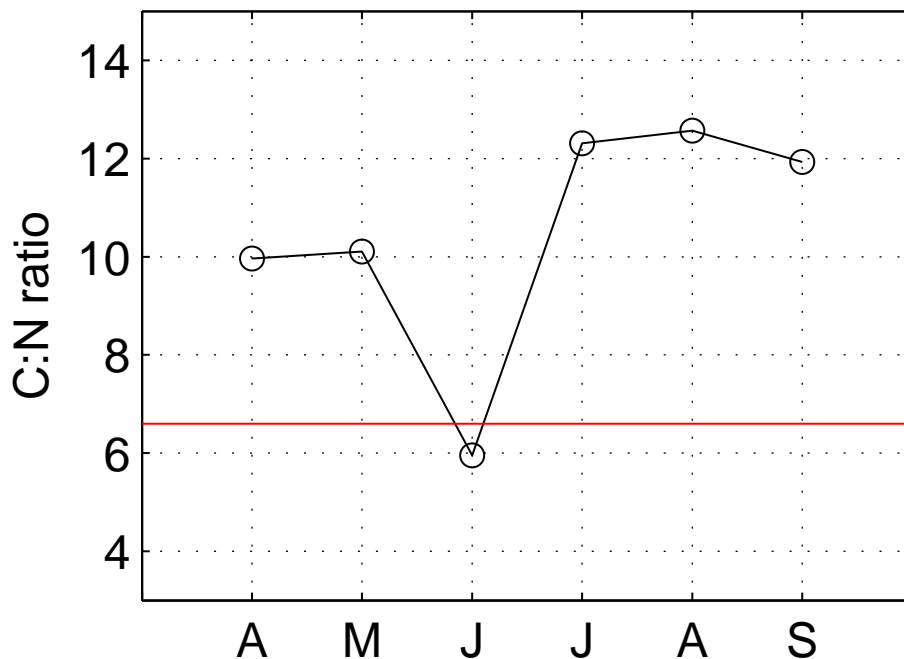
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**Figure 7.** Average monthly C : N ratios for biological production (see Fig. 5) during the period of seasonal drawdown (April–September) of DIC and nitrate in the Iceland Sea. The red line shows the Redfield C : N ratio of 6.6.

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